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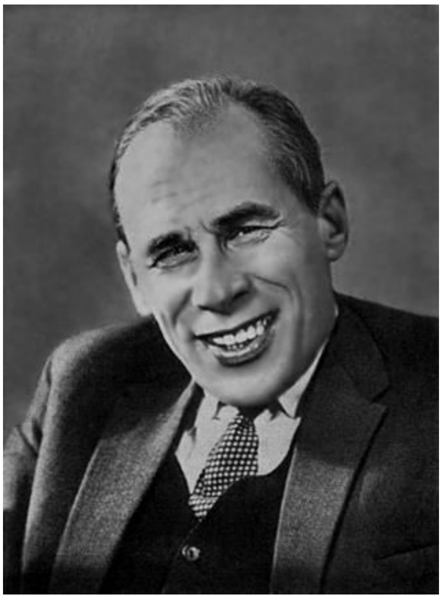

The name of Academician Vladislav Voevodsky is known throughout the world to researchers working in chemical physics. His effort and talent were responsible for many key advances in the investigation of gas chain branched reactions, reactions of hydrocarbon cracking, and heterogeneous reactions of radicals and atoms.

Academician Voevodsky was one of the first to realize the potential of magnetic resonance technique in studying free radicals and other paramagnetic particles. He and his colleagues developed the EPR technique into a powerful experimental method for investigating chemical reactions, founding a new field of science, chemical radiospectroscopy. This work, in turn, led to a breakthrough in the study of many fundamental chemical phenomena, including were free-radical mechanisms of chemical reactions, electron delocalization and transfer, elementary acts in solid and liquid matter radiolysis, mechanisms of photochemical and photobiological processes, and heterogeneous catalysis.

Academician Voevodsky was one of the founders of the Institute of Chemical Kinetics and Combustion, Novosibirsk, Russia and of the Department of Natural Sciences of Novosibirsk State University. For many years he was the Dean of the Department. He raised and inspired a community of scientists known worldwide who continue to work in chemical physics today. His students had a major impact on the development of chemical kinetics and chemical physics, a field of science, which describes physics and chemistry of elementary chemical reactions.

The conference in Academician Voevodsky's honor brings together scientists studying elementary chemical processes from all over the world.

Voevodsky Prize

In the memory of Academician V.V. Voevodsky and in connection with his 80th anniversary the V.V. Voevodsky Institute of Chemical Kinetics and Combustion of the Siberian Branch of the Russian Academy of Sciences and the International Tomography Center established in 1997 the Voevodsky Prize, which is awarded once in two years. The Prize is awarded to Russian and foreign scientists, in turn, for outstanding contributions to investigation of the kinetics and mechanisms of chemical reactions, composition and properties of active intermediates, elementary acts in photo- and radiation chemistry using radiospectroscopy techniques.

Awarding of the Voevodsky Prize is based on a competition. Candidates are nominated by scientific institutes or by individual scientists. The final decision is made by an Award Committee, consisting of 7 members. Members of the Committee are selected by the Scientific Council of the Institute of Chemical Kinetics and Combustion and are renewed each five years. The Voevodsky Prize is presented either at the session of the Scientific Council of the Institute of Chemical Kinetics and Combustion or during the conference dedicated to the memory of V.V. Voevodsky. An Awardee must participate in these meetings and deliver a lecture on his scientific work.

Laureates of the Voevodsky Prize

Academician Anatoly Leonidovich Buchachenko, “For outstanding contribution to the investigation of mechanisms of chemical reactions, structure and properties of free radicals by radiospectroscopic methods”, 1997.

Professor Arnold Hoff, “For outstanding contribution to the investigation of primary photochemical processes of energy conversion in photosynthesis by radiospectroscopic methods”, 1999.

Professor Lev Alexandrovich Blumenfeld, “For outstanding contribution to the investigation of structure and properties of paramagnetic intermediates in biological systems”, 2001.

Professor Leonid Borisovich Volodarsky, “For outstanding contribution to the chemistry of stable nitroxide radicals, which opened wide field for EPR applications”, 2002.

Professor Klaus Möbius, “For outstanding contribution to the investigation of paramagnetic intermediates of chemical and biochemical processes with application of advanced EPR methods”, 2004.

Academician Yuri Dmitrievich Tsvetkov, “For outstanding contribution to the development of radiospectroscopic methods, investigation of structure and properties of free radicals and of spin-labeled biological systems”, 2006.

Professor Gertz Il’ich Likhtenshtein, “For for achievements in biological studies with help of EPR spectroscopy”, 2007.

Academician Yuri Nikolaevich Molin, “For outstanding contribution to the development of spin chemistry and of methods of paramagnetic species detection based on quantum coherence”, 2009.

Professor Robert Kaptein, “For outstanding contributon to the theory and practice of chemically induced nuclear polarization and the development of novel applications of nuclear magnetic resonance in structural biology”, 2012.

Academician Kev Minullinovich Salikhov, “For outstanding contributon to the development of theoretical foundations of spin chemistry and chemical radiospectroscopy”, 2014.

Professor Jack Freed, “For outstanding contribution to the theory and practice of chemical radiospectroscopy based on innovation of new pulsed ESR methods”, 2017.

Academician Renad Zinnurovich Sagdeev “For outstanding contribution to spin chemistry development and research of molecular magnets”, 2017.

Invited Lectures

Distance measurements in nucleic acids using advanced SDSL with nitroxide and trityl radicals

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Pulsed dipolar (PD) EPR spectroscopy is a powerful technique allowing for distance measurements between spin labels in the range of 2.5-10.0 nm. Until recently, PD EPR experiments were limited to cryogenic temperatures. Recently, application of spin labels with long electron spin dephasing time at room temperature such as triarylmethyl radicals and nitroxides with bulky substituents at a position close to radical centers enabled measurements at room temperature by PD EPR. The features of PD EPR at ambient temperatures, in particular, requirements on electron spin phase memory time, ways of immobilization of biomolecules, the influence of a linker between the spin probe and biomolecule, and future opportunities will be reviewed [1-8].

Recently, we developed a promising approach to SDSL of RNAs, which is based on the complementary-addressed reaction between the target RNA residue and a derivative of oligodeoxyribonucleotide [9]. We apply this approach to SDSL of Hepatitis C Virus (HCV) RNA Internal Ribosome Entry Site (IRES) consisting of up to 350 nucleotides and having a complicated spatial structure, and thereby for the first time clearly demonstrate the SDSL of long structured RNA [10]. The results of our last work demonstrate that DEER/PELDOR spectroscopy can be successfully applied for intramolecular distance measurements in multicomponent supramolecular complexes, in particular in sophisticated molecular machineries of cell-ribosomes, including IRES-elements of some viruses and for estimation of their influence on the coupling with ribosomes and corresponding conformations transitions.

This work is supported by Russian Scientific Foundation № 14-14-00922.

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Dynamic Nuclear Polarization coupled with rapid dissolution: From technology to new science

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The so-called “dissolution Dynamic Nuclear Polarization” (D-DNP) method is based on the combination of DNP at low temperatures (typically 1.2 K in our laboratory) and high fields (6.7 or 9.4 T in our case) using frozen glassy samples that contain stable radicals such as TEMPO with ESR transitions that can be saturated by microwave irradiation. Once the nuclear polarization has built up to appropriate levels, the samples can be melted rapidly by injecting a hot solvent, and transferred as quickly as possible to an NMR or MRI system for detection. In the last 5 years, our group at EPFL in Lausanne, and more recently our team in Paris, endeavored to achieve the highest possible polarizations (as much as 90% for protons and 60% for carbon-13 are possible) in the shortest possible time (typically 20 to 60 minutes). Cross-polarization in the manner of Hartmann and Hahn has proven to be particularly efficient for carbon-13, nitrogen-15, phosphorus-31, and deuterium, and should also be applicable to yttrium-89, silicon-29 and many other nuclei. Since the efficiency of cross-polarization critically depends on the relaxation time in the rotating frame of the spin-locked proton magnetization, and since the latter can be significantly extended if the electron spins are predominantly in their ground state, it has turned out that gating the microwave irradiation off prior to cross-polarization greatly improves the efficiency of cross-polarization. After dissolution, the hyperpolarization tends to decay through spin-lattice relaxation, unless it is transferred to some sort of long-lived state. We have recently discovered by serendipity that systems containing two or three magnetically equivalent deuterium nuclei, which usually suffer from rapid spin-lattice relaxation rates, can have surprisingly long-lived states that correspond to imbalances of populations in spin states belonging to different irreducible representations of the symmetry groups.

From reactivity of solids to high-pressure crystallography and back: Response of molecular crystals to mechanical stress

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The contribution gives a survey of the research that started at the Institute of Chemical Kinetics and Combustion and has been then carried out through over several decades at other institutions in various collaborations. Any reaction in a crystal is accompanied by generating stress. The manifestations of this stress are elastic and plastic strain and fragmentation. As a reaction proceeds, the mechanical stress that arises in the crystal can have a significant influence on the subsequent transformation. This phenomenon is termed as feed-back, which can be either positive, or negative. One can introduce the concept of "chemical pressure", to describe the reaction in the crystal which is stressed by the reaction itself. In selected cases the mechanism of the reaction in relation to the mechanical response of crystals can be studied in detail. We illustrate this, using selected examples of reactions in molecular crystals. The effects of "chemical pressure" can be compared with those of strain imposed by hydrostatic compression. Modern high-pressure crystallography makes it possible to follow even subtle changes in molecular geometry and intermolecular interactions. We discuss structural distortion induced by high pressure and structural transformations, in a comparison with strain and structural transformations accompanying chemical reactions in the same crystal. Eventually, we consider the chemical reactions induced by irradiation or heating if occurring in the hydrostatically compressed crystals.

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New horizons for applying the method of Time-Resolved Magnetic Field Effects in recombination fluorescence of spin-correlated radical ion pairs

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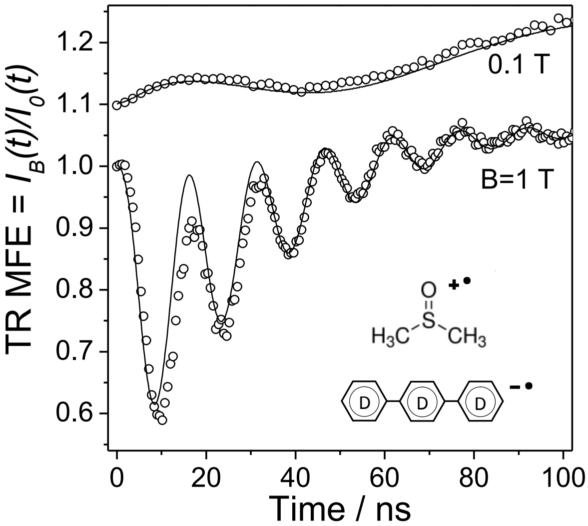
In organic media, the primary chemical effect of ionizing irradiation is the generation of radical ion pairs (RIPs), for which the spin state of two unpaired electron spins in the RIP's partners is typically singlet. The spin state of RIPs ensemble oscillate between singlet and triplet ones due to magnetic interactions of the electron spins, which results in the non-statistical yield of the singlet electronically excited states of the RIPs' recombination products.



Ratios of fluorescence intensity decays at high (indicated in the graph), and low, B < 0.05 mT, magnetic fields, $I_B(t)/I_0(t)$, for 1 mM of perdeuterated *p*-terphenyl in dimethyl sulfoxide ($\varepsilon = 47$). Smooth lines are fits to the experiments for $\Delta g = 0.0047$ and negligible hyperfine couplings in the recombining radical ions (shown in the graph).

This spin evolution can be visualized using the magnetic field dependence of the radiation-induced recombination fluorescence intensity decay from the irradiated solutions of a luminophore. Analysis of the time-resolved magnetic field effect (TR MFE) allows determining the magnetic resonance parameters of the recombining radical ions on the nanosecond time scale. Previously, this approach was applied to study short-lived organic radical ions in irradiated weakly polar liquids.

However, recent studies showed that the spin correlation effects in the irreversible RIP recombination can be observed also in doped polymers and highly polar liquids, as demonstrated in the figure with an example of the observation of the primary radical cation in liquid DMSO. The novel results obtained using the TR MFE method in a series of previously unexplored media are presented, and some perspectives of studies of short-lived species carrying both electric charge and unpaired electron spin in irradiated organic liquids as well as doped polymers are discussed.

Energy transduction: What cytochrome *bc*$_1$ tells us

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The cytochrome *bc*$_1$ protein complex is an essential component of many organisms. It transports electrons as part of the mitochondrial electron transport chain and transduces, or converts, some of the energy of the electrons into chemical energy for the cell to use. It also is the interface where pairs of electrons transported by ubiquinol are passed to cytochrome *c*, which can carry only single electrons. The cytochrome *bc*$_1$ complex uses several strategies to ensure that energy transduction is carried out with good efficiency while preventing the escape of any electrons. Pulsed EPR spectroscopy has been important in determining the sequence of reactions, the chemical intermediates, and the energetic landscape of the electron transport/transduction process. Rapid freeze-quenching of intermediates states has been combined with pulsed EPR methods, such as HYSCORE, ESEEM and ENDOR, to identify key intermediates. EPR relaxation measurements on these intermediates reveal their location in the protein complex.

The cytochrome *bc*$_1$ complex achieves its high efficiency and stability by several strategies, including the recycling of unused electrons, the use of the use of insulating barriers, and by performing the crucial reactions in a series of tightly-coupled steps.

I06

Basic processes of spin dynamics in disordered solids and magnetic resonance and relaxation of polarized beta-active nuclei

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A review is presented on theoretical and experimental studies of the basic processes of spin dynamics in disordered media carried out in the Institute for Experimental and Theoretical Physics.

Experimental investigations were based on the beta-NMR spectroscopy (magnetic resonance and relaxation of polarized beta-active nuclei) [1, 2]. Unique possibilities of the method for studies of condensed media are discussed shortly as well.

Theoretical studies were fulfilled basing on the general principles of nonequilibrium statistical mechanics together with concentration expansions and numerical simulations [3, 4].

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I07

Modern ESR at ACERT and applications in biophysics

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I will describe recent developments at our Cornell-ACERT research center.

Over the years we have developed the theory of slow motional ESR, and we have provided many experimental studies based on it. In recent years we have applied it for a new methodology to study the initial step in viral attack of a cell for many types of viruses. In a current study we have shown that the same transmembrane protein (HAP2) mediates the fusion of sperm and egg cells, and does the same for viral attacks of cells for virus types such as Dengue and Zika [1]. This raises the question: What came first – the virus or the egg?

The method of Pulse Dipolar Spectroscopy (PDS-ESR) that ACERT helped to pioneer has gained widespread use. We have been studying the complex mechanism of bacterial chemotaxis signaling; it involves a sensor that senses food or poison in its path, and its signal is then sent a distance of over 200 Å by receptor proteins to the active protein units which then signal the flagellum motor, telling it whether to move forward or away. Our extensive PDS studies [2] have elucidated key details of all these steps in the signaling chain.

We have pioneered Fourier transform Two-Dimensional Electron-Electron Double Resonance to study room-temperature dynamics in fluids and proteins. In recent work at 95 GHz with 1.2 kW pulses [3], we have studied the exchange of a spin probe between aqueous and lipid membrane phases. We see 2D cross-peaks emerge between the signals from the two phases. The rate of exchange was quantitatively measured in the microsecond range, which is a range not readily available by other techniques. But this is the range of protein conformational changes, and we are adapting the method to this objective.

Finally, I address how to proceed when one's experiments, after much struggle, do not provide adequate SNR. We have developed a new denoising method, based on wavelet transforms, that enables one to improve the SNR by about two orders of magnitude while preserving the fidelity of the signal. Examples of retrieving signals from noisy ESR spectra will be shown [4].

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I08

Are the current theories of electron transfer applicable to reactions in ionic liquids? A dynamic ESR study

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Ionic liquids (ILs) are molten salts of mainly organic cations and inorganic or organic anions, liquid at room temperature. They are of interest, not only from scientific point of view but also for chemical industrial productions. Environmental friendly industrial productions based on so-called "Green Chemistry" principles mainly use ionic liquids as solvent to avoid classical toxic organic solvents. But, only a few reports exist on ESR-spectroscopic investigations using ionic liquids as solvents. We would like to report on dynamic ESR-measurements using the ionic liquids: 1-butyl-3-methylimidazolium hexafluorophosphate, 1-butyl-3-imidazolium fluoroborate and 1-ethyl-imidazolium ethylsulfate.

At our lab a high-pressure system for use in electron spin resonance (ESR) spectroscopy was constructed. The apparatus allows the application of pressures of up to 100 MPa to solutions and with several key solvent properties (viscosity, dielectric constant, relaxation times, refractive index) being pressure dependent, reaction kinetics may be probed *via* pressure variations.

Some electron-self exchange reactions of organic redox couples have been measured by ESR-linebroadening: $MV^{+\bullet}/MV^{++}$ methylviologene, $TCNE^{-\bullet}/TCNE$ tetracyanoethylene, $TCNQ^{-\bullet}/TCNQ$ tetracyanoquinionedimethane, $TMPPD^{+\bullet}/TMPPD$ tetramethyl-*p*-phenylene-diamine, $TEMPO^{\bullet}/TEMPO^{+}$, $COT^{\bullet}/COT$ cyclooctatetraene and $TTF^{+\bullet}/TTF$ tetrathiofulvalene have been measured in various organic solvents and in different ILs. From ESR-line-broadening experiments rate constants corrected for diffusion vary between $8.2 \cdot 10^{7}\ M^{-1} \cdot s^{-1}$ and $1.2 \cdot 10^{9}\ M^{-1} \cdot s^{-1}$, depending on the ionic liquid used. The activation energies range from $\Delta G^{*} = 27.4 - 42.1$ kJ/mol [1-5]. These results will be compared with measurements obtained in different common classical organic solvents. The solvent dependent outer-sphere reorganization energy is discussed in the sense of Marcus-Theory. Parts of this theory are not applicable to electron transfer reactions in ionic liquids [6]. Similar results are obtained from heterogeneous electrochemical measurements of electron transfer rates in ILs.

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β-Amyloid, terahertz microwaves, and the magic angle

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This presentation will selectively cover two closely related topics that employ magic angle spinning (MAS) NMR, dynamic nuclear polarization (DNP), or both.

First, we discuss dynamic nuclear polarization (DNP) experiments that utilize terahertz microwaves (~150-600 GHz) generated by gyrotron microwave sources together with paramagnetic polarizing agents to enhance the sensitivity of MAS NMR experiments. Specifically, we irradiate electron-nuclear transitions that transfer the large electron polarization to nuclear spins *via* the Overhauser, cross and solid effects. In addition, we have recently initiated time domain DNP in order to circumvent the field dependence of CW DNP. We show that spin locking the electrons and matching the NOVEL condition, $\omega_{0I} = \omega_{1S}$ (the nuclear Larmor frequency and the electron Rabi frequency, respectively) serves as an effective approach to time domain DNP. Furthermore, the spin lock can be modulated with ramps and chirps to increase the efficiency of the polarization transfer.

Second, we describe recent MAS experiments aimed at producing high resolution structures of amyloid fibrils. Many peptides and proteins form amyloids whose structures are of considerable pathological as well as functional importance. We have developed a suite of MAS NMR experiments including a new NNC experiment that permits determination of atomic resolution structures of fibrils. We demonstrate the methodology with a description of the atomic resolution structure of fibrils of monomorphic Aβ_{42}, the toxic species associated with Alzheimer's disease.

Magnetic field effects on radical pair recombination: Unexpected consequences of chemical reactivity

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In a variety of animals, magnetoreception is hypothesized to rely on truly quantum effects reigning in spin correlated radical pairs formed transiently by photo-induced electron transfer reactions in the flavor-protein cryptochrome. It is puzzling that in many respects the compass performance in animals surpasses the predictions of model calculations [1], suggesting the presence of a powerful, yet unknown, amplification process. This prompted us to seek quantum and classical amplification mechanisms.

Here, we report on three effects that, in our recent studies of radical pair recombination in flavin-based systems, resulted in large magnetic field effects (MFE).

The primary magnetic field effect on flavin photoreactions can be amplified chemically by slow radical termination reactions under conditions of continuous photoexcitation. The nature and origin of the amplification are revealed by studies of the intermolecular flavin–tryptophan and flavin–ascorbic acid photocycles and the closely related intramolecular flavin–tryptophan radical pair in cryptochrome. Amplification factors of up to 5.6 were observed for magnetic fields weaker than 1 mT [2].

In the photoreaction of flavin mononucleotide with ascorbic acid, at low pH two chemically distinct radical pair complexes are evidenced by concentration dependent studies of the MFE. These complexed species give rise to exponential recombination kinetics and a surprising surge in the amplitude of the low-field effect. On the contrary, at pH 7, the effect is in close agreement with model calculations based on a Green's function approach [3].

Based on model calculations, we propose a new mechanism of magnetoreception in cryptochromes that features a spin-selective electron transfer reactions with a paramagnetic scavenger (Zeno effect). The new scheme offers clear and important benefits such as a greatly enhance sensitivity to a 50 μT magnetic fields and magnetosensitivity for radicals that are more than 2 nm apart. We also show that the effect does not only pertain to anisotropic MFEs, but can boost the isotropic low-field effect [4, 5].

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Thermodynamic and transport data for the systems polymer/dense gases

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Applying supercritical fluids for particle formation may overcome the drawbacks of conventional particle size reduction processes. Powders and composites with special characteristics can be produced. The bases for design of polymer micronisation processes are fundamental thermodynamic data and transport data for the system polymer/dense gas. An overview of methods for investigation of the thermodynamic properties of the binary systems containing polymer and gas will be presented.

Behavior of polyethylene glycols with different molar masses (ranging from 1,000 g/mol to 100,000 g/mol and other polymers in the binary systems with different gasses (CO_2, SF_6, propane, argon, xenon) will be presented. The external balance method was developed for determination of the solubility of gas into substrates which are soluble in gas. Densities and viscosities of gas saturated solutions of polyethylene glycols were measured by new methods developed by the authors. Capillary rise method adapted to the measurement conditions and sample properties was applied to investigate the interfacial tension.

The obtained fundamental data were used to determine process parameters for micronistaion of polymers with PGSSTM (Particles from Gas Saturated Solutions) process co invented by author of this manuscript (USP 6,056,791) for the formation and formulation of fine particles. In PGSS™ process the substance or the mixture of substances to be powdered must be converted into a spray-able form by liquefaction/dissolution. This can be achieved by melting or/and dissolving of the substance or mixture of substances in a liquid solvent, or by dispersing solids or liquids in a melt or solution, and saturation of the melt/solution/dispersion with the gas. Thus, viscosity and surface tension is lowered to such extent that low and high viscous fluids can be sprayed in a nozzle forming fine droplets. In this way, fine particles are obtained, where the morphology, particle size, particle size distribution and crystallinity (various polymorphs) can be adjusted with operating process parameters.

The presentation gives an extended overview of fundamental data for binary systems of polymers with different sub-and supercritical fluids and processing of polymers for production of novel polymeric materials with special properties.

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Influence of polarity and ionic strength on intramolecular spin exchange in nitroxide biradicals

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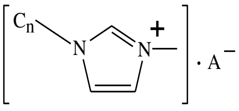
Short nitroxide biradicals of similar composition: $(H_5C_6)O{=}P(OR_6)_2$ (**1**), $H_5C_6\text{-}P(OR_6)_2$ (**2**) and $O{=}S(OR_6)_2$ (**3**), where OR_6 is 1-oxyl-2,2,6,6-tetramethyl-4-oxypiperidine, were studied by EPR spectroscopy [1-3]. Influence of temperature, solvent nature and the ionic strength was characterized by changes in the isotropic ^{14}N hyperfine splitting (hfs) constant a and values of intramolecular electron spin exchange (IESE) integral |J|, and compared with the data obtained from DFT calculations. Thermodynamic parameters of the conformational rearrangements were also calculated. Molecular solvents of different polarity from toluene to water were used. The ionic strength in aqueous solutions was changed with addition of various concentrations of LiCl. The obtained results are compared with those obtained for the biradicals dissolved in several ionic liquids (ILs):



ILs

Here C_n are ethyl, 1-butyl, 1-octyl, and A^- are BF_4^-, PF_6^-, and Cl^-. Viscosities of ILs are taken from the literature.

Structural and dynamic properties of biradicals, and also differences in the behavior in molecular solvents, ILs, "salty" aqueous solutions, and in the IESE mechanism for these solvents will be discussed in the paper.

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Parahydrogen-based signal enhancement in NMR and MRI

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Nuclear magnetic resonance, and particularly its spatially resolved modality (MRI), often suffer from insufficient sensitivity. Consequently, major research efforts are currently directed at the development of nuclear spin hyperpolarization (HP) techniques that are capable of boosting NMR sensitivity by several orders of magnitude, with significant progress achieved in this field during the last decade or so. Among such HP techniques, parahydrogen-induced polarization (PHIP), including its variants such as SABRE, is arguably the simplest and technically least demanding one. Since the first unambiguous demonstration of PHIP in 1987 and until 2007, observation of PHIP effects was associated exclusively with homogeneous processes in solution, such as H_2 activation and catalytic hydrogenation of unsaturated compounds by dissolved transition metal complexes. However, during the past decade PHIP effects in liquid and gas phase hydrogenations of alkenes and alkynes have been also demonstrated with numerous heterogeneous hydrogenation catalysts, and further extension to other catalyst types is clearly feasible. Representative recent examples of such studies will be discussed.

The ability to produce and observe PHIP effects in heterogeneous catalytic processes significantly expands the range of potential applications of PHIP-derived signal enhancement in NMR and MRI. There are currently two main directions in this research field. One of them encompasses mechanistic studies of heterogeneous catalytic transformations of industrial importance which involve H_2 as one of the key reactants. In addition to heterogeneous hydrogenations, PHIP effects were recently demonstrated, for instance, in catalytic oligomerization and desulfurization processes. Utilization of signal enhancement in MRI can also provide new valuable knowledge about the dynamic processes in operating reactors. All this can be very useful for catalytic and chemical engineering applications of magnetic resonance.

Another major direction in this field is the production of HP molecular markers for biomedical studies. Unlike homogeneous catalysts, the heterogeneous ones can be easily filtered out after the reaction, potentially providing biocompatible hyperpolarized samples. Examples of liquid and gas phase hydrogenations of unsaturated compounds with parahydrogen to produce catalyst-free hyperpolarized substances for potential in vivo use and to prolong hyperpolarization lifetime will be described.

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Creating a multitude of entangled nuclear spin qubits in hyperpolarized molecular solids

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The generation and retrieval of entanglement among several quantum bits (qubits) is an important challenge in quantum information science. Up to now, quantum entanglement has been realized in a variety of physical solids including quantum dots, ion traps, superconductors and optically polarized point defects in diamond and silicon carbide. In this talk, we introduce photo-excited molecular solids as novel quantum systems in which questions related to entanglement can be explored. The story begins about 40 years ago when huge nuclear spin polarization has been detected in organic triplet states at level anti-crossing (LAC) conditions [1-3]. So far, however, the quantum interaction responsible for the nuclear hyperpolarization was not identified.

Model system of the present study is triplet pentacene in a *p*-terphenyl crystal at LAC conditions. First, a laser pulse generates the triplet state and initiates entanglement between an electron spin and 14 hyperfine coupled proton spins. This gives rise to huge oscillatory electron and nuclear spin polarization. Then, a resonant high-power microwave (mw) pulse disentangles the electron spin from the nuclear spins. As a result, robust entanglement is formed among 14 proton spins. This gives rise to quantum oscillations [4] in the nuclear spin polarization in the form of frequency combs. Thus, at triplet LAC conditions, a multitude of entangled nuclear spin qubits is created by a single mw pulse. The total spin of these qubits depends on the type and number of hyperfine coupled nuclei which can be tailored at will. Using a rigid host crystal, one is able to extend the decoherence time T_{2N} of the nuclear spin qubits from the microsecond to the millisecond range. Because of the huge polarization, generated at LAC, these molecular solids are capable of forming genuine multipartite entanglement at ambient conditions. This makes them attractive alternatives to conventional physical solids for which great effort is required to build a sufficiently large qubit device.

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Self-diffusion of aromatic chiral molecules in external magnetic fields. ^{1}H NMR

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The action of external magnetic fields on matter is a topical problem in various fields of physics, chemistry, biology, and medicine. The mechanisms underlying the observed responses to such action remain unclear and debatable. In particular, many human diseases are known to be caused by blood hyperviscosity, which can be reduced by the applied external magnetic field. The reduction of viscosity is related to the increased mobility of individual particles arranged along magnetic field lines. However, in some cases, a magnetic field can, on the contrary, retard the mobility, because the induced magnetic moments increase the scattering cross-section of a diffusing particle.

In the present work the mobility of aromatic chiral molecules 1-phenylethanol and 1-phenyl-1-propanol in liquids was studied by ^{1}H NMR spectroscopy as a function of the strength of external magnetic field, temperature, and concentration of enantiomers. The activation parameters were found to depend on the applied field. This effect is caused by the induced magnetic moments in aromatic molecules. The use of ultrahigh magnetic fields seems to be promising for investigation of intermolecular interactions of chiral molecules [1, 2].

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Reactions in non-thermal plasma, chlorofluorocarbon destruction, and atmospheric chemistry

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In the presentation, the mechanisms of chemical transformations in non-thermal plasmas (such as generated in the streamers of corona discharges, dielectric barrier discharges, *etc.*) are reviewed. In such discharges plasma is in highly non-equilibrium state. Translational temperature of electrons is much higher than the translational temperature of heavy neutral molecules and ions. In addition, vibrational temperature of ions and molecules could be also substantially larger than the translational temperature. This difference in temperatures (30,000 – 100,000 K for translational temperature of electrons and 300 – 500 K for molecular species) leads to the specificity of the chemical transformation driven by such plasmas.

Current chemical models of the chemistry of the atmosphere include only homogeneous and heterogeneous processes initiated by the primary photochemical reactions. However, relatively recently discovered novel electrical discharges in the upper atmosphere (generically dubbed as Transient Luminous Events (TLEs)), might have direct impact on the atmospheric chemistry.

The analysis of numerous laboratory studies on the destruction of different chemical compounds in non-thermal plasmas reveal the major mechanism of their reactions in low mixing ratio air mixtures. It appears that the physical nature of the TLEs (such as “red sprites”, “elves”, and “blue jets”), properly adjusted to much lower pressures, is similar to the physics of the streamers in corona and dielectric barrier discharges observed in the laboratory conditions at ambient pressures and temperatures.

The results of the laboratory studies on the chlorofluorocarbon destruction as well as on the ozone production together with the estimates of the global frequency of the TLEs indicate that these novel electrical discharges might contribute significantly to the chemical models of the atmosphere.

Multielectron and optimum distance electron transfer processes in biology. 47 years of history

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The concept of multielectron (four) electron mechanisms was first suggested by Likhtenshtein and Shilov in 1970 [1] and then developed and applied to such "heavy" enzymatic and chemical reactions as reduction of molecular nitrogen and water splitting in mild conditions [2]. On the basis of thermodynamic grounds and kinetic considerations, it was predicted that only four electronic processes with formation of the derivatives of N_2H_4 and free O_2 are thermodynamically available for the N_2 reduction and O_2 oxidation, respectively, at ambient biological conditions. These predictions were entirely fulfilled. In the photosynthesis and photochemistry, the main problem for the conversion of the light energy to chemical one is retention of the energy of photo separated charges for a further use. It was proposed [3] that the only way to prevent the fast charges recombination and, therefore, a waste of the energy is constructing a system of intermediate acceptors separated by nonconductive bridge of 6-8 Å composed of non-saturated chemical bonds (hopping mechanism). This conclusion was supported first by a model of the photosynthetic reaction center build up on the basis of using ESR and other methods [4], and later by X-ray analysis. To estimate the values of the rate constant of electron transfer (k_{ET}) and the exchange integral (I_{SE}) in donor – acceptor pairs an approach based on an analogy between superexchange processes, such as electron transfer and triplet-triplet energy transfer and spin-exchange, was developed [5]. The estimated values of k_{ET} and I_{SE} appeared to be in good agreement with the corresponding experimental data. The suggested equations can be used for calculation of k_{ET} and I_{SE} in systems of interest.

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A novel technique for conversion of spin pair singlet state into observable spin hyperpolarization by means of adiabatic switching of spin-locking magnetic field

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A new method has been proposed allowing one to convert initial multiplet spin order into polarization of almost any desired kind. It is based on hyper-polarizing a system of scalar coupled spins in the presence of a strong RF-field, which is subsequently slowly (adiabatically) reduced to zero. The method allows one to convert multiplet polarization into net hyper-polarization without any loss. The correct choice of the frequency of the RF field makes it possible to change the sign of the integral polarization. For instance, our technique can be applied to the case of ParaHydrogen Induced Polarization (PHIP), which gives very strong hyper-polarization resulting in NMR enhancements of up to 10,000; in contrast, the original polarization is purely of the multiplet kind. We showed theoretically and experimentally that PHIP can be fully converted into net spin order by properly setting the RF-field frequency.

We suggest using this approach also to convert initial multiplet electron spin order into net electron polarization. It is based on hyper-polarizing a system of dipole-dipole coupled electron spins in initial singlet state in the presence of a strong MW-field, which is subsequently slowly (adiabatically) reduced to zero. Such the system can serve as photoinduced charge separated radical pair in photovoltaic cells. The spectrum resulting from adiabatic switching of the strong MW field and its difference with Pake doublet will be analyzed for the radical pair which appears in singlet state of two electron spins. The effect of setting the MW-field frequency will be investigated.

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The development and application of ESR *in situ* for studying the catalytic processes at elevated temperatures and pressures including supercritical fluids

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The considerable growth of the level of chemical technologies during last decades made it economically feasible to realize certain catalytic processes at elevated temperatures and pressures. Nowadays a lot of chemical reactions de facto take place under sub- or supercritical (SC) conditions in so-called supercritical fluids (SCF). SCF have a unique combination of properties: the density, heat capacity and dissolving power in SC condition approximates those observed in the liquids, while the diffusion and viscosity are between the corresponding values for the gaseous and liquid state, that often provides unusual behavior of SCF which is beneficial for catalytic processes [1-2].

The numbers of methods that can be effectively applied to study the processes taking place in SC media at the atomic and molecular scale are rather limited. In this respect ESR is a unique tool to investigate the mobility of the paramagnetic particles and dynamics of their local environment in SCF. The precise analysis of ESR spectra of paramagnetic ions and spin probes provides the data on rotation dynamics of the paramagnetic particles and clusters as well as on the spin exchange rate between the radicals in SCF *in situ* and paramagnetic ions clusterization stage that can be seen from the exchange narrowing of the absorption ESR lines directly during the clusterization process [3-4]. The development of original approach for the precise simulation of ESR spectra of the slowly rotating paramagnetic particles (clusters) showed that the correlation between their size and characteristic rotational time (that can be determined *in situ* while incomplete averaging of anisotropic hyperfine interaction is observed) can serve as a unique tool for quantitative estimation of particle size distribution in multicomponent hydrocarbon systems. Among various applications it allows one to investigate directly the stability of crude oils, as well as the aggregation/disaggregation processes of asphaltenes (the heaviest oil fraction) at elevated temperatures/pressures that often determines the efficiency of the extraction and processing of heavy oils [5-6].

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Photomodulated chromogenic systems on the basis of photochromic spiropyrans

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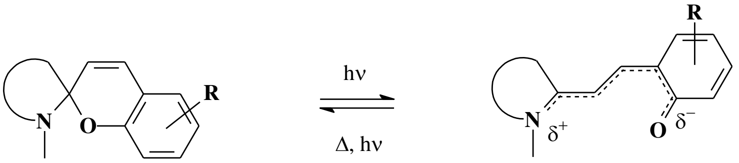
Photomodulated chromogenic systems including the photochromic core are promising candidates for the use in different areas of molecular electronics and photonics as molecular switches [1]. Among the photochromic compounds a special position belongs to the spiropyrans. Spiropyrans have high photocoloration quantum yields and exhibit a wide variety of spectral and kinetic characteristics [2].



A **B**

Modulation of a chromogenic properties based on photochromic compounds can be attained in several ways. The rearrangement $\mathbf{A} \rightleftharpoons \mathbf{B}$ itself affects the ability of a molecule to change chromogenic properties. In the case of spiropyrans, cyclic (**A**) and merocyanine (**B**) isomers have significant differences in chromogenic properties in particular such as absorption, fluorescence, ionophoric properties. Under these conditions, chromogenic properties of a photochromic spiropyrans can be modulated by switching back and forth between the cyclic and merocyanine isomeric forms.

Another approach to the photomodulated chromogenic systems is based on labeling a photochromic spiropyran molecule with a chromogenic unit, whose target properties can be modulated by the photonduced changes in the structure of the photochromic core.

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Quantum bits in ^{29}Si enriched crystals

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All-silicon quantum computing is the strategic idea of the nearest steps in information technologies. In purified silicon crystals with low isotope concentration, long coherency time of nuclear spins ^{29}Si (up to 1 min at room temperature), as well as compatibility of silicon q-bits with modern electronics, attract efforts of many scientific groups to creation of nanoareas on the Si:B surface convenient to be explored as q-bits [1, 2]. Theoretical basis of spin processing of quantum information [1], as well as specific schemes of quantum registers containing ^{29}Si chains or layers [2, 3], are well developed. A brief review of these methods and experimental contribution of our group will be proposed.

Particularly, we have found few unexpected effects provided by magnetic isotope in silicon crystals. First of them is the effect of external magnetic field [4] and/or hyperfine magnetic field of Si nucleus on the oxidation of silicon surface [5]. Hyperfine magnetic field increases oxidation up to 2 times [5]. These data provide a possibility to fix the image of the q-bit by AFM detected oxidized nano areas of the Si surface [4]. Another significant result is the redistribution of the ^{28}Si, ^{29}Si, ^{30}Si isotopes and ^{29}Si^{16}O complexes in subsurface layers under a plastic deformation of Si crystals. The redistributions are selective, *i.e.,* ^{29}Si and ^{29}Si^{16}O concentrations became rather different to the ones corresponding to ^{28}Si, ^{30}Si and ^{29}Si^{16}O, respectively, under plastic deformation. This redistribution can be explored for selection of isotope atoms and isotope distribution control by local stresses under nanoindentation. Thus, a mechanical technique of the q-bit formation was proposed.

Measurements of the HR NMR and ESR signals in the studied samples provided direct information about their nuclear and electron spin subsystems. Analysis of the Pake doublet and its temperature dependence reveals Korringa temperature dependence indicating a strong contribution of the heavy and light holes to nuclear spin relaxation. Systematical study of the spin dynamics in heave isotope enriched crystals Si:B and Si:P will be presented. Mathematical treatment of the obtained results and consideration of the logic gates corresponding to NMR transitions are proposed.

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EPR investigations of external influences (light, pressure, temperature and atmospheric components) on the magnetic properties of transition metal compounds

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This report is devoted to the study of various external influences on the magnetic properties of transition metals complexes. External factors affecting the magnetic properties of compounds are light, temperature, pressure, and atmospheric components like oxygen and water vapor. The investigation of the unusual properties of copper and nickel polymer compounds is presented. The reasons of the appearance of unusual properties are the admixture of water in the solution during crystallization and the subsequent action of pulsed uniaxial pressure. Water molecules being an effective ligand randomly break the periodicity of the polymer structure. Applied pulse pressure leads to the closure of polymer chains through an oxygen bridge producing a random distribution of ferromagnetic and antiferromagnetic interactions. In the EPR spectra, this leads to the appearance of nonresonance absorption and ferromagnetic resonance spectra. A similar effect of water vapor is observed in polymerization processes of $(tBu)_4PcAlCl$ and $(tBu)_4PcGaCl$.

The effect of oxygen on the photolysis of rhodium complexes with nitroxyl ligands $Rh(L)_2Cl_3{\cdot}3H_2O$ and $Rh_2(L)_3Cl_6{\cdot}6H_2O$ (L is 4-phenacetylidene-2,2,5,5-tetramethyl-imidazolidine-1-oxyl) in ethanol solutions was studied. It is shown that in the absence of oxygen a photoexcitation within the absorption band of the rhodium complex leads to the formation of hydroxylamines. In the presence of oxygen in the solution, oxygen effectively quenches the excitation of rhodium complexes and does not allow the formation of hydroxylamines. At the same time, the oxygen molecules in the triplet state interact with hydroxylamines to form peroxide states and nitroxyl radicals.

The formation of paramagnetic states was observed as a result of the charge transfer between tantalum complexes $Ta\{C_6H_2(CH_3)_2O_2\}_3^-\{(CH_3)_2NH_2\}^+$ and molecular oxygen. A dynamic effect of changing the position of the unpaired electron between three bidentate ligands was detected at room temperature. The dynamic process consists in breaking one bond of the bidentate ligand with equal probability for all three ligands. In this case, the unpaired electron is localized on the one of the carbons of the aromatic ring, and in the EPR spectra HFS from one hydrogen atom with $A(H) = 1.94$ mT is observed. As the temperature decreases, both wings of the bidentate ligands are closed on the tantalum ion and this leads to the localization of unpaired electron on oxygen containing fragment of the ligand. HFS from the hydrogen disappears and a new EPR spectrum appears with an anisotropic g-factor ($g_1 = g_2 = 2.010$, $g_3 = 1.999$). This process is characterized by activation energy $E = 1$ kcal/mol.

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Electronic structure and magnetic properties of half fluorinated graphene

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The structure and composition of graphite fluorides are determined by the synthetic conditions, namely, crystallinity and particle size of graphite, reaction temperature, and fluorinating agent, and two stoichiometric compounds with CF and C_2F composition are known. A layer of the graphite fluoride CF consists of trans-linked cyclohexane chairs in which sp^3-hybridised carbons combine with fluorine atoms by covalent bonds. Incorporation of two kinds of carbon atoms, linked with fluorine atoms and bare carbon, into graphite fluoride C_2F could give the various structures within a C_2F composition. Here, from the comparison of the experimental NEXAFS spectrum of graphite fluoride C_2F produced at room temperature and theoretical spectra plotted for three different models we show that the more preferable fluorine pattern is the formation of zigzag-like CF chains. The models were calculated within density functional theory at the B3LYP/6-31G level. CK-edge NEXAFS spectrum was simulated using the so-called (Z+1)-approach, where a fictitious Z+1 compound with an additional proton in its atomic nucleus is introduced instead of the real Z compound containing a core level hole. The applicability of this approach to the graphite fluorides was previously tested for the CF compound. Recent measurements revealed magnetic properties for the fluorinated graphite fluorides, and the results will be discussed.

Photochemistry of dithiolate Cu(II) and Ni(II) complexes

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The dithiolate complexes of transition metals are widely used in chemistry, however, the photochemistry of these compounds has been little studied. They show high photochemical activity in the presence of electron acceptors such as halogen-containing molecules. The report will demonstrate the results of study of fast photoprocesses for the dithiolate Ni(II) and Cu(II) complexes in CCl_4 and $CHCl_3$ solutions using femto- and nanosecond laser photolysis [1-3]. The information on the nature, optical spectra, reactions and kinetic parameters of particles participating in photochemistry of dithiolate complexes will be reported. For the photochemistry of dithiocarbamate $Cu(S_2CNEt_2)_2$ complex in chloroform the quantum-chemical calculations (DFT, TD-DFT and PCM methods) of the structure and optical spectra of transient species arising in the chain of photochemical transformations will be presented.

The dithiolate NiL_2 complexes in the presence of disulfides are photochromic systems whose operation is determined by the reversible coordination of S-radicals with the nickel ion. The weak chemical activity of S-radicals leads to the absence of side reactions and determines a large number of cycles of photochromic transformations. For NiL_2 – disulfide systems the data on spectra, reactions, and kinetics of unusual intermediates will be presented.

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The role of weak non-covalent interactions in drug delivery: NMR and EPR study

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Modern advances in nanotechnology and supramolecular chemistry have now allowed to come close to solving a number of problems of medicine. In particular, it concerns the use of nanoscale aggregates to increase the bioavailability of drug compounds and their targeted delivery. According to expert's opinion, the use of nanotechnology in the field of medicine can bring the most significant results in the near future. Use of natural oligosaccharides and polysaccharides as complexants for delivery of drug compounds significantly increases their therapeutic activity and storage stability, and also reduces the side effects. Application of modern physical methods allows obtaining unique information about the structure, dynamics, and physicochemical properties of supramolecular inclusion complexes of the drugs. The report will presents some examples illustrating the possibilities of NMR and EPR techniques to study the role of weak non-covalent interaction in supramolecular aggregates (inclusion complexes, micelles and liposomes) used as drug delivery systems (DDS), as well as examples of application of these techniques for elucidation of the mechanisms of increasing the bioavailability of drug compounds in the complexes. Various NMR techniques, such as saturation transfer, NMR relaxation measurements (both T_1 and T_2), are sensitive to the overall molecular motion of organic molecule in solution, which is very different for free and bound ligands. These simple approaches can be used to elucidate the structure and stability of various drug delivery systems, and to measure the influence of various DDS on the physical and functional properties of cell membranes. Interesting and practically important results were obtained using the natural polysaccharide arabinogalactan and oligosaccharide glycyrrhizin as the DDS with a wide range of drug compounds. In particular, it was demonstrated that (a) Complexation increases by tens or hundreds times the solubility of poorly soluble drugs and their activity; (b) Complexation significantly increases the stability of "guest" compounds including oxidative stability and photostability; (c) Some DDS have an impact on the permeability of cell membranes.

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How good is the generalized Langevin equation to describe the dynamics of photo-induced electron transfer in fluid solution?

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The dynamics of unimolecular photo-triggered reactions can be strongly affected by the surrounding medium, for which a large number of theoretical descriptions have been used in the past. An accurate description of these reactions requires knowing the potential energy surface and the friction felt by the reactants. Most of these theories start from the Langevin equation to derive the dynamics, but there are few examples comparing it with experiments [1].

Here we explore the applicability of a Generalized Langevin Equation (GLE) with an arbitrary potential and a non-markovian friction [2]. To this end we have performed broadband fluorescence measurements [3] with sub-picosecond time resolution of a covalently linked organic electron donor-acceptor system in solvents of changing viscosity and dielectric permittivity. The free energy surface (FES) of the reaction is established using stationary electronic spectroscopy, while the dynamics of a non-reacting reference provide the calibrating tool for the non-markovian friction over the FES. In addition, the simpler and computationally faster Generalized Smoluchowski Equation (GSE) is also applied for comparison [4].

While both approaches reproduce the measurements in most of the solvents reasonably well, the GSE shows larger discrepancies whenever the dynamics become slow. At long times some differences arise from the intrinsic shortcomings of the solvatochromic model and at short times from the excess excitation energy.

The here applied method can be used to predict the dynamics of any other reacting system, given the FES parameters and solvent dynamics are provided. Thus no fitting parameters enter the simulations, within the applicability limits found for the model in this work.

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Minor interactions with major consequences in chemical reactions

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V.V. Voevodsky was looking for some manifestations of relatively small interactions in chemical kinetics and catalysis. Unfortunately, he left us too early and the spin chemistry appeared later.

In my talk I am going to present shortly the following items:

- Steps in development of spin chemistry
- Basic theoretical results in spin chemistry
- Hyperpolarization of spins in a course of chemical reactions
- Perspectives: from spin chemistry to quantum biology!?

The magic of trehalose: Coupling between matrix properties and protein function

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Some organisms can survive complete dehydration and high temperatures adapting to an *anhydrobiotic* state in which the intracellular medium contains large amounts of disaccharides, particularly trehalose and sucrose. Trehalose is most effective also in protecting isolated *in vitro* biostructures.

In an attempt to clarify the molecular mechanisms of disaccharide bioprotection, we compared the structure and dynamics of sucrose and trehalose matrices at different hydration levels by means of high-field W-band EPR and FTIR spectroscopies [1]. The hydration state of the samples was characterized by FTIR spectroscopy, the structural organization was probed by EPR using a nitroxide radical dissolved in the respective matrices. Analysis of the EPR spectra showed that structure and dynamics of the dehydrated matrix as well as their evolution upon re-hydration differ substantially between trehalose and sucrose. The molecular model of the matrices provides an explanation for the different protein-matrix dynamical coupling observed in dried ternary sucrose and trehalose matrices, and accounts for the superior efficacy of trehalose as a bioprotectant.

Furthermore, for bacterial photosynthetic reaction centers [2] it is shown that at low water content the protein-matrix coupling is modulated by the sugar/protein molar ratio in sucrose matrices only. This effect is suggested to be related to the preference of sucrose, rather than trehalose, as bioprotective disaccharide in some anhydrobiotic organisms [3].

Additionally, we report on results of a multiresonance high-field EPR investigation of water exchangeability between protein and trehalose matrix which give a new inside into the mechanism of trehalose bioprotective efficiency [4].

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I29

Ionic transport in orientationally disordered phases

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Orientational disorder is typical for many high-temperature phases of ionic salts with non-spherical cations or anions. The orientationally disordered phases (ODP) have relatively high free volume that favors to local dynamic processes in the crystal lattice, including the ionic migration. Up to date there are many experimental data on structural and thermodynamic properties of ODPs, however, transport properties of such phases have not been studied in detail.

In this report we present a comprehensive analysis of ionic conductivity data, obtained in different systems:

- in a series of alkali nitrates, perchlorates and nitrtites, with different type of crystal structure, where the relationships between crystallographic parameters and ionic conductivity were revealed;
- in ODPs of rubidium nitrate where the mechanism of ionic transport was investigated using MD computer simulation and it was found that the ionic conductivity is limited by the point defects formation and ion migration is closely related to the anionic reorientation;
- in solid solutions $RbNO_3 - RbNO_2$ where the influence of ionic substitution on structural, thermodynamic and transport properties of ODPs was studied;
- in high-temperature ODPs of substituted ammonium organic salts with a strong orientational disorder of aliphatic groups;
- in composite and nanocomposite systems where orientationally disordered amorphous phases may be stabilized due to the interface interaction between ionic salt and nanodispersed additive.

In all cases, orientational disordering leads to a considerable increase in ionic conductivity due to the decrease in both the point defects enthalpy and the ion migration energy. It should be noted that in contrasts to ordinary ionic salts with close-packed ionic structures, in ODPs large-sized ions, like Rb^+, Cs^+ or BF_4^-, may be more mobile than ions with smaller size. Therefore, ODPs may be regarded as promising basic materials for development of solid electrolytes for solid-state electrochemical devices.

Nuclear spin hyperpolarization at variable magnetic field

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While Nuclear Magnetic Resonance is a highly informative method, well-established both in spectroscopy and imaging, it suffers from its intrinsically low sensitivity that often limits its applicability. Reason is the weak interaction between the nuclear magnetic moment and the external field, with energies of only the 10^{-6} part of optical photons. Moreover, it is much smaller than the thermal energy kT at ambient conditions with the consequence, that at Boltzmann equilibrium all spin energy levels are nearly equally populated. The relative population difference, also termed spin polarization P, is usually only 10^{-4} or smaller. As the NMR signal is proportional to P, it is advantageous to work off thermal equilibrium and devise techniques for high levels of P, called hyperpolarization. Popular methods are DNP, OP NMR, PHIP and CIDNP. They rely on different mechanisms, but all have in common that their efficiency varies with the magnetic field strength. The use of field variation is twofold; it is applied for optimization of the hyperpolarization level, but also for analysis of the complex hyperpolarization process giving information on the transient species involved and their reaction pathways. Characteristic features in the field dependence are often related to avoided crossings (LACs) of the spin levels, the position of which can be used to determine magnetic interactions parameters.

Since hyperpolarization is of transient nature it must be utilized before it returns to the equilibrium value driven by spin-lattice relaxation. Thus, for optimum use information on the relaxation behavior and its field dependence (relaxation dispersion) is important. Of particular interest in this context are long-lived spin states, *i.e.,* spin configurations that are immune to major relaxation mechanisms. Prominent examples are singlet states.

Our contribution will focus on magnetic field variation in the range below 10^{-4} T, where coupling between different nuclear spin species is operative in polarization transfer. New instrumentation with precise field settings down to 10 nT combined with high resolution NMR observation at 9.4 T as well as applications in hyperpolarization and relaxation will be discussed.

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Dinitrosyl iron complexes with thiol-containing ligands represent a 'working form' of nitric oxide: EPR and physiological evidence

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The present work is an overview of experimental data obtained in our EPR and physiological studies designed to investigate the generation of mono- and binuclear forms of dinitrosyl iron complexes (M- and B-DNIC, $[(RS^-)_2Fe^+(NO^+)_2]$ and $[(RS^-)_2Fe^+{}_2(NO^+)_4]$, respectively), with special reference to their biological activities as nitric oxide (NO) and NO^+ donors in animal cells and tissues.

Previous studies [1, 2] have shown that the concentration of paramagnetic (EPR-detectable) M-DNIC, whose EPR signal has the following values of the g-factor: $g_\perp = 2.04$, $g_{||} = 2.014$, $g_{aver.} = 2.03$ (the so-called 2.03 signal) and is largely detected in cultured animal cells, exceeds by at least one order of magnitude that of other NO species including S-nitrosothiols and organic nitrites and nitrates [1]. In animal as well as in plant tissues, NO predominantly initiates the synthesis of diamagnetic (EPR-silent) B-DNIC in amounts commensurate to the total concentration of NO in biological objects [2, 3]. Treatment of thus generated B-DNIC with diethyldithiocarbamate (DETC) or N-acetyl-L-cysteine (NAC) capable of accepting the Fe^{2+}-mononitrosyl group in the Fe^{2+}-dinitrosyl $[Fe^+(NO^+)_2]$ fragment of DNIC or the whole Fe^{2+}-dinitrosyl fragment yields EPR-detectable mononitrosyl iron complexes with DETC (MNIC-DETC) or M-DNIC with NAC (M-DNIC-NAC), respectively. The intensities of their EPR signals characteristic of MNIC-DETC with $g_\perp = 2.035$ and $g_{||} = 2.02$ or of M-DNIC-NAC with $g_{aver.} = 2.03$ reflect the concentration of B-DNIC in body organs and tissues [3].

M- and B-DNIC with thiol-containing ligands synthesized by chemical routes have diverse effects on human and animal organisms including cultured cells and isolated organs where they mimic miscellaneous biological activities of NO and NO^+ [2]. Moreover, these complexes produce potent vasodilating and, as a consequence, hypotensive effects, *e.g.,* they suppress platelet aggregation, increase the elasticity of red blood cells, accelerate skin wound healing, and so on. In addition to their regulatory effect on biological objects, DNIC capable of releasing NO in high doses manifest a strong cytotoxic activity similar to that of NO [2]. Our studies established a remarkable ability of B-DNIC with glutathione to suppress, completely and selectively, the growth of non-malignant endometrial tumors in rats with experimental endometriosis [2]. Similar results were obtained in [4] and our most recent in-depth study [5] into DNIC effects on malignant tumors.

By virtue of their high biological activity, which mimics diverse biological effects of NO, and the unique capability to accumulate in animal tissues in amounts commensurate to the total concentration of NO, DNIC with thiol-containing ligands have every reason to be regarded as a 'working form' of NO, one of the most universal regulators of biological processes occurring in virtually all representatives of the animal world. Binding of NO to DNIC increases its stability and provokes its accumulation (predominantly, in the form of protein-bound DNIC) and further transfer to its biological targets in the form of low-molecular DNIC [2].

The total body of experimental data strongly suggest that NO can effectively determine biological activities of other low-molecular compounds, such as hydrogen sulfide and ozone. Hydrogen sulfide or, more specifically, its ionic forms, initiate the conversion of DNIC with thiol-containing ligands into DNIC with persulfide ligands, which, in its turn, increases the stability of appropriate DNIC and thus controls their biological activity [6]. It is conjectured that ozone, whose strongly pronounced prooxidant activity is now well-established, can initiate the synthesis of inducible NO synthase and thus increase the total concentration of NO in body organs and tissues.

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EPR spectroscopy for study of solid catalytic materials

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EPR spectroscopy is a convenient and informative tool for investigation of paramagnetic and non paramagnetic active sites on the surface of oxide catalysts and intermediates of chemical reactions taking place on their surface. In some cases this method makes it possible to follow evolution of materials during the formation of active catalysts. Experimental methods and the most interesting results obtained at Boreskov Institute of Catalysis during investigation of different types of catalytic systems will be presented in this report. This will include the following results and methods:

1. Investigation of the formation mechanism and reactions with participation of ion-radical intermediates formed during catalytic and photocatalytic processes on the surface of oxide materials.

2. Application of radical cations and radical anions of adsorbed compounds as spin probes for investigation of various active sites on the surface of oxide catalysts. Correlation with catalytic activity.

3. Characterization of active sites in Oxide@C core-shell structures. Detailed investigation of the active site evolution during phase transformations in Al_2O_3 and Al_2O_3@C systems.

4. Application of ferromagnetic resonance for investigation of Ni evolution during the formation of catalysts for synthesis of carbon nanofibers.

5. Investigation of the formation and destruction of localized electrons in C12A7:e and C12A7:e@C electrides. The influence of size effects on the electron dynamics in these systems.

The concentration of active sites on the surface of catalysts is usually low. Therefore, EPR in many cases can yield information about active sites of catalytic systems that cannot be studied by other physicochemical or spectroscopic methods.

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Molecular alignment and mobility in partially ordered media as determined by EPR of nitroxide spin probes

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Numerical simulation of EPR spectra of nitroxide probes introduced in the medium is used for determination of structural and dynamic properties of organized soft media. New approaches for a more detailed and informative description of EPR spectra in the course of determination of the desirable characteristics are discussed.

The mutual positions of probe molecules can be determined from angular dependence of the dipole-dipole broadening of EPR spectra. The estimation of probe-to-probe distance and probe molecular orientation enable to reveal the detailed molecular organization of the partially ordered medium.

The molecular rotation mobility in ordered media is commonly determined by the numerical simulation of spectra shape using the stochastic Liouville equation with Brownian rotation diffusion mechanism. The non-Brownian rotations, such as librations and rotational jumps, should be taken into account for correct simulations of spectra in the case of small nitroxide molecules. The possibility to estimate the rotation anisotropy is analyzed.

The description of orientational order by the mean field potential is demonstrated to be an oversimplification as the identical local potential are not valid to all points of the macroscopic sample. The new method for numerical simulation of EPR spectra of ordered media is suggested: the local potential is used for description of local molecular orientation and rotation, but independent model-free distribution of local directors describes the macroscopic molecular orientation. High rank order parameters, which describe the real shape of molecular orientation distribution function, can be determined by joint numerical simulation of EPR spectra recorded for different orientation of the sample relative to magnetic field of spectrometer.

The discussed methods are illustrated by the experimental data for ordered nematic and smectic liquid crystals, liquid crystalline polymers and membranes of graphite oxide. The experimental angular, as well as temperature and concentration, dependences of EPR spectra for a series of nitroxide radicals are simulated and analyzed. The number of evaluated parameters and unambiguity of the results of least-squire minimization are discussed.

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Recent progress in RIDME spectroscopy with paramagnetic metal centers

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Relaxation Induced Dipolar Modulation Enhancement (RIDME) is a pulse EPR technique for measuring electron-electron magnetic dipolar interaction. This technique was first proposed in Novosibirsk [1] and has direct relation to the Novosibirsk ‘scientific school’ of EPR spectroscopy founded by academician V.V. Voevodsky. Further developments [2-6] made RIDME technique attractive for measuring nanometer-range distances between paramagnetic centers with broad EPR spectra. In particular, our group was actively developing RIDME-based distance determination methodology over the last three years. In this presentation, we will give a general overview of the RIDME technique and present our recent results on measuring and analyzing RIDME dipolar evolution data in model compounds with high-spin paramagnetic centers. Special attention will be paid to the treatment of dipolar frequency overtones appearing in the RIDME experiments with such centers. We will discuss some important features of the dipolar modulation build-up during the mixing block of the RIDME experiment, dependence of the RIDME signal on temperature, mixing time, detection position and spin-spin distance, phase cycling issues, treatment of the hyperfine interaction artefacts, as well as the problem of background correction.

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Competition of singlet and triplet recombination of radical pairs in photoreactions of 3,3′,4,4′-tetracarboxy benzophenone and biologically important molecules

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Photoinduced electron transfer serves as a versatile method for generating elusive radicals of biologically important molecules. It is of great importance to use a well characterized water soluble organic triplet photosensitizer that efficiently reacts with the compounds of interest. In our work, 3,3′,4,4′-tetracarboxy benzophenone (TCBP) was chosen because of its high intersystem crossing quantum yield and high reactivity of the excited triplet state with the additional advantage of good solubility in aqueous solution over a wide pH range. However, when using TCBP as a photosensitizer, we detected a rather unusual CIDNP kinetic behavior for the protons of the species participating in the photoreaction For all amino acid residues of tyrosine, histidine and tryptophan [1] as well as for purine nucleotides [2] studied so far the polarization formed in the reaction of free diffusive collision of radical pairs (so called F-pairs) was much lower in comparison with the standard case of triplet precursor and recombination from the singlet state of radical pairs which is typical for other triplet sensitizers. The kinetic evolution of CIDNP for the protons of TCBP was completely different from that of all sensitizers studied earlier. This unusual CIDNP kinetic behavior was explained by the presence of a triplet recombination channel of the radical pairs along with the singlet one that contributes to nuclear polarization. It leads to the formation of the amino acid residue or nucleotide in its ground state and TCBP in a triplet state of low energy. This low-lying triplet of TCBP is characterized by its relatively long lifetime of 1 ms or longer. Taking into account such a triplet recombination channel allowed us to obtain excellent coincidence of experimental and simulated CIDNP kinetics. In the simulation we utilized the analytical solutions obtained for the ratio between CIDNP formed upon geminate and bulk recombination of radical pairs with singlet and triplet competitive channel of recombination [3]. Thus, the triplet back electron transfer is a key factor that governs the kinetic behavior of CIDNP at the photoreaction between TCBP and biologically relevant molecules in aqueous solutions.

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Influence of the excitation light intensity on the rate of fluorescence quenching reactions

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Chemical reactions in solution develop at rates that depend on a number of factors: temperature, pressure, electric and magnetic fields, driving force and solvent characteristics such as the refractive index, the dielectric constant and the viscosity. However, for photoinduced reactions it has never been explored experimentally if the rate of the bimolecular reactions depends itself on the intensity of the triggering light. The present work attempts to elucidate this question.

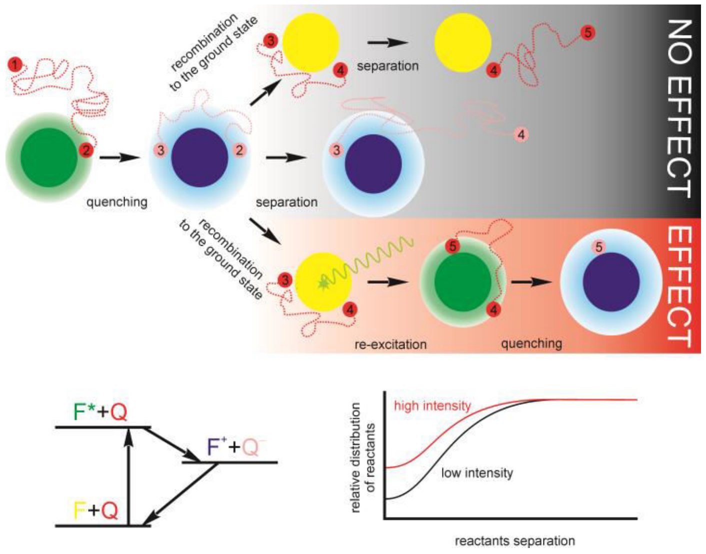

Figure 1. The effect of multiple excitation events on the same pair of reactants is illustrated sequentially from left to right with three different possibilities: upper part no effect is observed on increasing the excitation intensity of after a second pulse because either there is no absorption of a second photon before the reactants separate, or because there is no recombination back to the ground state. In the lower part of the panel an effect is observed because the recombination is fast enough and a second photon is absorbed. In the lower panel a simplified reaction scheme is shown, and the fluorophore-quencher pair distribution function changes under CW excitation on increasing the light intensity.

More precisely, the effect of multiple light excitation events on bimolecular photo-induced electron transfer reactions in liquid solution is studied experimentally. It is found that the decay of fluorescence can be up to 25% faster if a second photon is absorbed after a first cycle of quenching and recombination. A theoretical model is presented which ascribes this effect to the enrichment of the concentration of quenchers in the immediate vicinity of fluorophores that have been previously excited. In figure 1 a simplified picture of the effect and the model is presented. Despite its simplicity, the model delivers a qualitative agreement with the observed experimental trends. The original theory by Burshtein and Igoshin was created for continuous light excitation though [1]. A qualitative extrapolation from the here presented pulse experiments to the continuous excitation conditions lead us to conclude that in the latter the order of magnitude of the increase of the quenching efficiency upon increasing the light intensity of excitation, must also be on the order of tens of percent. These results mean that indeed the rate constant for photo-induced bimolecular reactions depends also on the intensity of the excitation light [2].

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Helpful discussions with Dr Arnulf Rosspeintner from the University of Geneva and Professors Konstantin Ivanov and Nikita Lukzen from the International Tomography Center of the Russian Academy of Sciences in Novosibirsk are also cherished.

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NMR Crystallography as a new tool for characterization of active sites of solid catalysts

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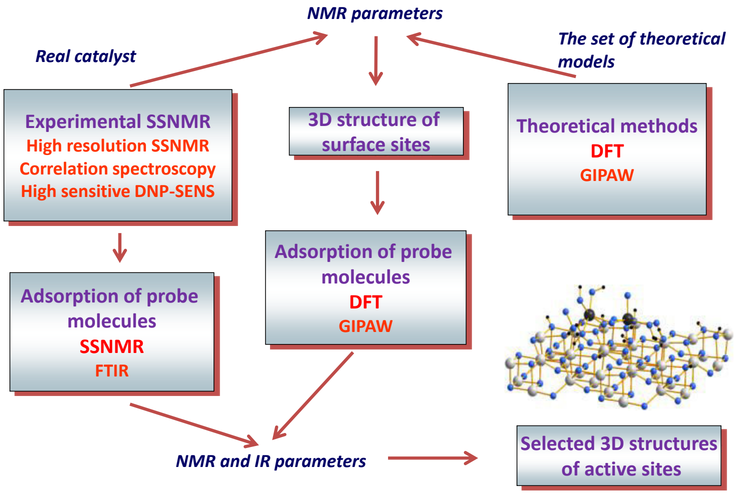
NMR Crystallography merges state-of-the-art multinuclear Solid-State NMR with DFT computations. This method became a powerful tool for structure determination in biochemistry and in material science. As for catalysts, NMR crystallography has great potential since it could serve not only for characterization of the structure of surface sites, but also for characterization of their catalytic activity. In this work we are going to demonstrate different steps of this multistage investigation on the example of supported oxide catalysts. The first step of this study is to verify NMR crystallography approach to the systems under study on the example of individual compounds (not shown in the figure). After this it is possible to start the next step which consists of identifying NMR parameters of real catalysts by experimental SSNMR (see scheme). On the basis of the obtained values of these parameters several sets of models may be proposed. For these models NMR parameters are calculated by DFT. When a good matching between experimental and calculated NMR parameters is achieved a conclusion is drawn that the 3D structure of surface sites is identified.



Next step is connected with adsorption of test molecules (H_2O, CO_2, CH_3OH, *etc.*) on the real catalysts (experimental part) and on the model surface sites (theoretical part). At this stage it is reasonable to use additional experimental techniques (for example FTIR). In the case of good agreement between experimantal and theoretical parameters it is possible to select 3D structures of active sites.

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Precise analysis of time resolved MARY in photo excitation of Flavin Adenine Dinucleotide

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Magnetic field effects (MFEs) on the photochemical reaction of flavin containing system have been getting a great attention from interests in the magnetoreception of blue light receptor proteins [1] for animal navigation. Recently, the microscope based detection of MFEs was developed targeting the flavin containing biological systems [2-3]. In them, the photo-induced intramolecular electron transfer reaction of FAD [4] was used to test the equipment without analysis of the MARY (MFE on reaction yield) spectra. Recently, we observed the $B_{1/2}$ (half width of half maximum of the MARY spectra) shift of cw-MARY (continuous wave: *i.e.,* not time resolved MFE measurement) depending on the quencher (free tryptophan) concentration. Since the quencher concentration would change the lifetime of triplet and radical pair state, these results imply the time evolution of MARY without external quencher. Therefore, the time resolved measurements are awaited.

Here we present the newly developed time resolved MFEs in the laser flash photolysis using the very stable diode pumped pulse laser. This provides the time resolved MFE spectrum (2D-MARY) with very high S/N ratio as shown in figure 1. The time evolution of the $B_{1/2}$ value was simulated by the stochastic Liouville equation in the model containing the interconversion between radical pair and triplet excited states [4]. The calculation nicely fitted the experimental results with very fast spin dephasing in the radical pair states.

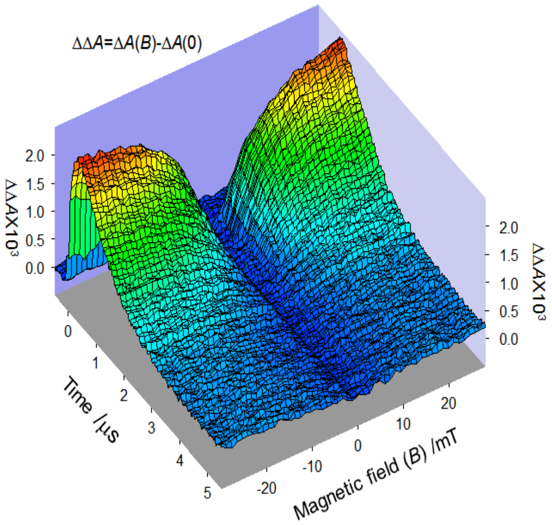

Figure 1. Time resolved MFE spectrum (2D-MARY)

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I39

Persistent radical effect: From fundamental chemistry to nitroxide mediated polymerization and material sciences

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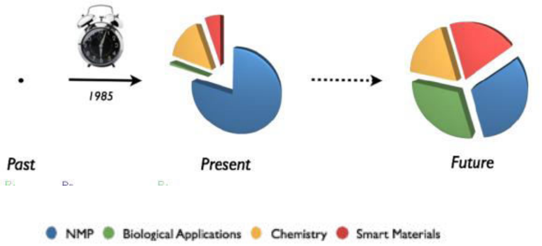
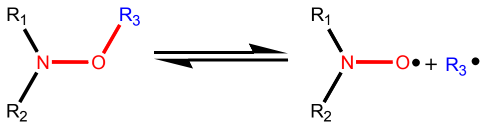
Radical reactivity of alkoxyamines has been discovered in 1974 in Moscow [1]. In 1985 in Australia, Rizzardo and colleagues [2, 3] promoted their application as initiator/controller in Nitroxide Mediated Polymerization, the first Controlled Radical Polymerization technique. Kinetics for the decomposition of alkoxyamines are controlled by the Persistent Radical Effect [4]. For the next 20 years, C-ON bond homolysis, the key reaction, for the applicNation of alkoxyamines has been thoroughly investigated [5] leading to the development of 5 variants of NMP. Two of these variants – Spin Labeled-NMP (SL-NMP) [6] and “click”-NMP [7] – have been developed in the Vorozhtsov Institute. This talk covers the kinetics, the fundamental aspects, and the most recent applications of this chemistry.





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I40

Mechanism of ultrafast electron transfer in Photosystem I: Femtosecond spectroscopy upon excitation of reaction center chlorophylls in the far-red edge of the Q_Y band

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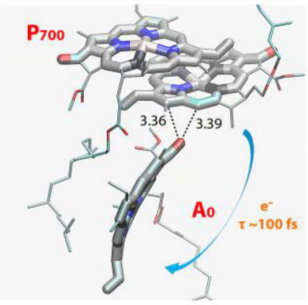

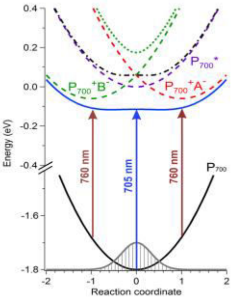

The ultrafast primary charge separation in Photosystem I (PS I) from cyanobacteria *Synechocystis sp. PCC 6803* excited by femtosecond pulses centered at 720 and 760 nm was studied by pump-to-probe laser spectroscopy. The red edge of PS I absorption spectrum follows the exponential decline consistent with the empirical Urbach rule: Absorbance(ν) ~ exp[(h·(ν-ν_0)/E_U], where the Urbach energy E_U is equal to the thermal energy (24 meV). The cutoff of short wavelength spectral components of 760 nm pulse allows direct excitation of reaction center chlorophyll molecules without apparent involvement of the light-harvesting antenna pigments. The transient spectrum manifests the features of the primary ion-radical pair P700$^+$A0$^-$ at time delay <180 fs, followed by formation of the secondary pair P700$^+$A1$^-$ with a characteristic time of 26 ps. The obtained data are rationalized in the framework of the adiabatic three-state model that includes the chlorophyll dimer P700 as the primary electron donor, and two symmetrically arranged nearest chlorophyll molecules of the primary acceptor A0. A strong electronic coupling between P700 and A0 is governed by a specific arrangement of chlorophylls. Excitation in the maximum of P700 absorption band generates electronic states with the highest contribution from excited state P700*, whereas excitation in the far-red edge of P700 band predominantly generates charge transfer state P700$^+$A0$^-$ in both branches of redox-cofactors. The model accounts for the ultrafast formation of P700$^+$A0$^-$ and the exponential decline of PS I absorption in accordance with the Urbach rule.

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I41

NMR studies of yeast telomerase

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The elongation of single-stranded DNA repeats at the 3’-ends of chromosomes by telomerase is a key process in maintaining genome integrity in eukaryotes. Abnormal activation of telomerase leads to uncontrolled cell division, whereas its down-regulation is attributed to ageing and several pathologies related to early cell death. Telomerase function is based on the dynamic interactions of its catalytic subunit (TERT) with nucleic acids — telomerase RNA, telomeric DNA and the DNA/RNA heteroduplex. Here, we present NMR structure of the N-terminal (TEN) domain of TERT from the thermotolerant yeast *Hansenula polymorpha* (hpTEN, figure 1a) and demonstrate the structural conservation of the core motif in evolutionarily divergent organisms. Using the NMR titration experiments, we identify the TEN residues (figure 1b) that are potentially involved in interactions with the telomerase RNA and in the recognition of the ‘fork’ at the distal end of the DNA product/RNA template heteroduplex. We propose that the TEN domain is involved in restricting the size of the heteroduplex during telomere repeat synthesis, thus assisting in TERT biological function.

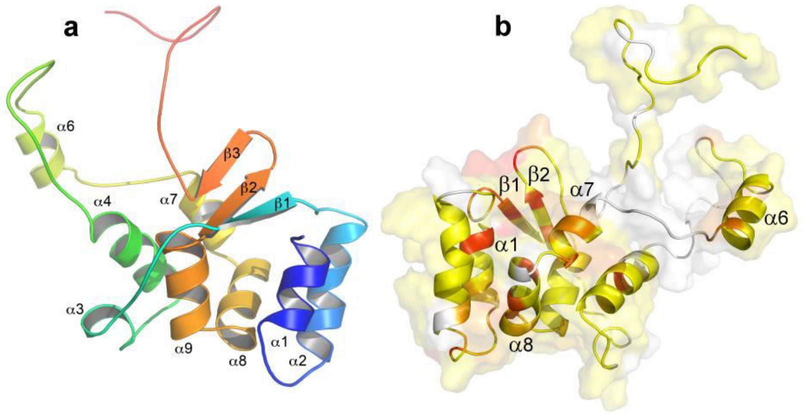

Figure 1. Structure of hpTEN. (a) Representative NMR conformer; (b) location of the hpTEN domain residues that are most affected by interactions with DNA/RNA ‘fork’.

NMR studies were supported by the Russian Science Foundation (Grant No 14-14-00598).

Oral Presentations

Level anti-crossing spectra of nitrogen-vacancy centers in diamond detected by using modulation of the external magnetic field

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The NV center in diamond is a widely known defect of the diamond lattice consisting of a nitrogen atom and a vacancy located in adjacent lattice sites. The negatively charged nitrogen-vacancy center (NV^- center) in diamond is of great interest due to its unique properties. The NV^- centers are promising systems for numerous applications, in particular, for quantum information processing and nanoscale magnetometry.

We report a study of the magnetic field dependence of the fluorescence of diamond single crystals containing NV^- centers. In such spectra, when the sample is oriented precisely, numerous sharp lines are found, which correspond to Level Anti-Crossings (LACs) in coupled spins systems comprising an NV^- center. For sensitive detection of such LAC-lines we use lock-in detection to measure the photoluminescence intensity [1]. This experimental technique allows us to obtain new LAC lines [1, 2]. Additionally, a remarkably strong dependence of the LAC-lines on the modulation frequency is found. Specifically, upon decrease of the modulation frequency from 12 kHz to 17 Hz the amplitude of the LAC-lines increases by approximately two orders of magnitude [3].

Theoretical modeling of such LAC-spectra enables characterization of paramagnetic defect centers and determination of their magnetic resonance parameters, such as zero-field splitting and hyperfine coupling constants. The outlined method thus enables sensitive detection of paramagnetic impurities in diamond crystals.

This work was supported by the Russian Foundation for Basic Research (Grant No 16-03-00672).

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Quantum theory of spin-dependent biological magnetosensitivity

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The problem of the “primary magnetoceceptor” in living organisms ranging from bacteria cells to human body is the main one for magnetobiology and magnetomedicine. Absence of any specialized organs forces the search for physical and chemical mechanisms at the intracellular level. The proposed mechanisms should include physical, chemical, enzymatic, and physiological stages together with the experimental confirmations and the theoretical background.

Intracell enzymatic reactions that are accompanied by the electron transfer or displacement are proposed as the most possible mechanism of biological magnetosensitivity. A rigorous quantum theory is proposed based on the spin density matrix formalism. The theory predicts magnetic field dependencies of enzymatic reactions in low magnetic fields less or comparable to the Earth’s magnetic field or hyperfine interaction constants. The key magnetosensitive stage is assumed to be singlet-triplet conversion of ion-radical pairs in active sites of enzymes producing vital substances.

Magnetic fields H were shown to be able to change rate constants $k_p(H)$ of enzymatic reactions; magnetic field dependencies are described as

$$\frac{k_p(H)}{k_1} = 1 - \frac{k_{-1}}{k} \cdot \rho_{SS}(H),$$

where $\rho_{SS}(H)$ is the fraction of the singlet ion-radical pairs, k_1 is the rate constant of the direct electron transfer, k_{-1} is the rate constant of the backward electron transfer, and k is the rate constant of ion-radical transformation into enzymatic reaction products. The matrix element $\rho_{SS}(H)$ can be found as the steady state solution of the Liouville equation.

Magnetic field dependencies $k_p(H)$ were calculated for the Δg- and HFI-mechanisms of spin conversion, which qualitatively match the experimentally obtained dependencies.

O03

Zero-area optical pulses – how it can be used in chemical kinetics

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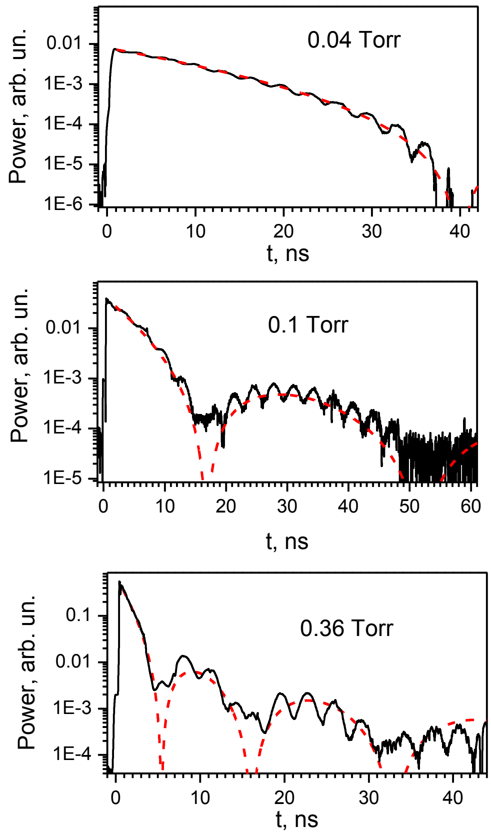
The propagation of short light pulses in resonant and optically dense media is accompanied by numerous remarkable effects. The most striking effect is the self-induced transparency (2-π pulses). For relatively weak pulses, a similar effect is the formation of zero-area pulses (0-π pulses). Propagation of such pulses is associated with several stages in which energy is transferred from electromagnetic radiation to the medium and back from the medium to the electromagnetic radiation. The direction of the energy transfer is controlled by the phase of the electromagnetic wave. In contrast to the 2-π pulses, the shape of a 0-π pulse is continuously changing during the pulse propagation in the medium.



We observed formation of such optical pulses in experiments with Novosibirsk Free Electron Laser in various molecular gases. The laser operates in the far infrared region that corresponds to the rotation spectra of the molecules. The figure shows examples of the observed 0-π pulses in gaseous HCN.

One of the main difficulties encountered in the measurements of the rate constants of free radicals (especially in the radical-radical reactions) is the necessity of reliable determination of the absolute concentrations of free radicals. Further advances in the solution of this problem could be achieved *via* development of novel experimental techniques of free radical detection which allow determination of the absolute concentrations of free radicals without calibrations.

The analysis of the shape of the 0-π pulses allows determination of the integral absorption coefficient of the absorbing medium, $\int \alpha(v)dv$, which is insensitive to the broadening of the absorption line. Moreover, determination of the integral absorption does not require measurements of the absolute radiation intensity in the absence of the absorption. This method is proposed for the direct determination of the absolute concentrations of free radicals and allows avoiding ambiguities associated with the impact of different factors on the linewidth of the absorption line. Experiments with the hydroxyl radical (OH), one of the most important oxidizing species in combustion and the atmosphere, are in progress.

Following the kinetics of solid state photochemical reaction by measurement of macroscopic mechanical response in crystals

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Photochemical reactions can cause macroscopic mechanical effects when occurring in crystals. The deformation is the external manifestation of internal change of molecular conformation and intermolecular interactions caused by the reaction. It can be considered as a mechanical response to the reaction. The magnitude of the response can be quite large in the case of needle shaped crystals with thickness compared to the irradiation penetration depth. The reaction non-uniformity due to light absorption leads to a remarkable crystal bending. For single-crystal-to-single-crystal transformations, provided that certain conditions are fulfilled, the magnitude of the response, like the curvature of bending crystal, can be a measure of the transformation degree.

Reversible NO_2-ONO linkage photoisomerization was studied in thin needle-like crystals of $[Co(NH_3)_5NO_2]\,Cl\,NO_3$. Measurement of the crystal elongation and curvature changing in the course of the reaction allowed high-precision determination of the kinetic parameters of the quantitative model of the reaction. Temperature dependencies of the quantum yield of the photoisomerization and of the reverse thermo-isomerization reaction, as well as the compositional (nitro/nitrito) dependencies of the quantum yield and of the light penetration depth, have been found. We illustrate how the kinetic constants and their temperature dependencies can be found with high precision for the direct photochemical and for the reverse thermal transformations. We also show the possibility to detect the feed-back phenomenon and to characterize it quantitatively.

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O05

The influence of the “cage effect” on the mechanism of reversible bimolecular multistage chemical reaction in solutions

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Manifestations of the “cage effect” at the encounters of reactants are theoretically treated on the example of multistage reactions in liquid solutions including bimolecular exchange reversible reactions as elementary stages. It is shown that consistent consideration of quasi-stationary kinetics of multistage reactions (possible only in the framework of the Encounter Theory) for reactions proceeding near reactants contact in the framework of one-site model can be made on the basis of the concepts of a “cage complex” (quasi-stationary concentrations method). Though mathematically such a consideration is more complicated, it is more clear from the standpoint of chemical notions. It is established that the presence of the “cage effect” leads to some important effects not inherent in reactions in gases or those in solutions proceeding in the kinetic regime, such as the appearance of new transition channels of reactant transformation that cannot be caused by elementary event of chemical conversion for the given mechanism of reaction. This results in that, for example, rate constant values of multistage reaction determined by standard kinetic equations of formal chemical kinetics from experimentally measured kinetics can differ substantially from the real values of these constants.

Also, manifestations of the “cage” effect at the encounters of reactants have been theoretically treated for multistage reactions proceeding from different active sites in liquid solutions. By the site of a given channel (any group of two reacting particles) we imply a definite relative position of the pair reactants (or their molecular groups) of the channel at which the reaction occurs. It is shown that for reactions occurring near the contact of reactants a consistent consideration of quasi-stationary kinetics of such multistage reactions (possible in the framework of the Encounter Theory only) can be made on the basis of chemical concepts of the “cage complex”, just as in the case of one-site model. However the scheme of the “cage complex” is now more complicated and includes additional transition between states of the “cage complex” determined solely by reactants motion (including rotation). Exactly as in one-site model, the presence of the “cage” effect gives rise to new channels of reactant transformation that cannot result from elementary event of chemical conversion for the given reaction mechanism. Besides, the multisite model demonstrates new (as compared to one-site model) features of multistage reaction course.

EPR study of MOF-based functional systems

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Metal-organic frameworks (MOFs) represent relatively new type of porous media with tunable structural properties. They find numerous applications in different fields of chemistry and materials science, including gas storage and catalysis. The opportunity to design functional centers with high precision and flexibility opens lots of new perspectives. In particular, photocatalysis using MOF-based systems appears highly promising. Of particular significance is the development of visible light-driven systems catalyzing water splitting and generating hydrogen for green energy applications. MOFs represent versatile scaffolds for introducing light-absorbing groups and redox-active metals, where photoinduced electron transfer can create charge-separation states with tunable properties acting as active catalytic sites.

Since long, Electron Paramagnetic Resonance (EPR) was actively used in studies of electron transfer reactions and charge separation states. Recently we applied EPR to investigate magnetic and structural properties of promising photocatalytic systems based on NH_2-MIL-125 and NH_2-UiO-66 frameworks with various metals embedded [1, 2]. Combined study using continuous wave (CW) EPR, pulse EPR and time-resolved EPR allowed conclusions on efficiency of electron transfer reactions in studied MOF-based systems, on structural and magnetic peculiarities of active catalytic centers, and on the mechanisms of their catalytic activity.

Investigation of guest-host interactions in MOFs is highly important for selective gas adsorption and storage, as well as for designing new stimuli-responsive materials. The post-synthetic adsorption of nitroxide spin probes allows studying structural dynamics of MOFs and radical-MOF interactions using CW and pulse EPR, as was exemplified with MIL-53(Al) [3, 4]. We also applied this approach to investigate adsorption of several gases in another perspective framework ZIF-8.

We anticipate that the amount of EPR applications to functional MOFs will grow in the coming years, and the present work highlights several new and promising directions in this emerging field.

This work was supported by the Russian Science Foundation (No 14-13-00826).

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Investigations of quantum correlations and decoherence of quantum states with magnetometry and methods of magnetic resonance

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The development of new technologies is intimately related to the use of such physical resources as materials, various types of interactions, and energy sources. In the 20th century, this list of technologically important resources was augmented with information, which came into great demand since the invention of computers, processing complex information outside human brain. Quantum effects should be taken into account due to the miniaturization of microprocessors, and the time when logic elements in microchips will be made of a few atoms seems not to be far. New quantum technologies develop intensively. As a result, quantum computers will be created, new methods of quantum cryptography will be developed, quantum teleportation will find practical applications, quantum metrology will create a new generation of scientific devices.

Quantum correlations depending on measurements are responsible for formidable advantages of quantum devices over their classical analogues. Investigations of quantum correlations are based on their measures: entanglement and quantum discord. We found a connection of these measures with physical parameters observed in experiments. In particular, we found a connection of entanglement and quantum discord with the magnetic susceptibility [1]. As a result, using the temperature dependence of the magnetic susceptibility for nitrosyl iron complexes (NIC), we obtained the temperature dependencies of entanglement and quantum discord. The critical temperatures of the emergence of entangled states for the different NICs were determined. We also showed that quantum discord can be significant even without any entanglement, *i.e.,* at high temperatures. This means that, in principle, quantum technologies can work at sufficiently high temperatures.

We also investigated decoherence of quantum states with methods of multiple quantum (MQ) NMR. The point is that MQ NMR not only creates multi-qubit coherent states, but also allows the investigation of their relaxation under the action of a correlated spin reservoir. We suggested that decoherence can be described by the relaxation of MQ NMR coherences in MQ NMR experiments. The theory of the relaxation of MQ NMR coherences in 1D-systems was developed [2]. The dependence of the relaxation (decoherence) times on the number of correlated spins was found.

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Role of the electron-phonon interaction in single semiconductor quantum dot blinking

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Two decades have passed since the first observation of long-term fluorescence intensity fluctuations (blinking) of single colloidal CdSe quantum dots (QDs) with a ZnS shell. Despite the enormous efforts (see for example [1]), the molecular mechanism of these fluctuations, showing a wide spectrum of characteristic timescales from hundreds of microseconds to hours, remains a mystery. While a number of models have been proposed to explain the phenomenon, all of these are rooted in two fundamental microscopic mechanisms, namely Efros/Rosen charging mechanism [2] and alternative mechanism of Frantsuzov and Marcus [3].

In order to distinguish the effects of the charging, Dan Oron's group conducted a series of experiments on designed colloidal quantum dots, incorporating a highly emissive CdSe core, which can be linked (or not linked) by a tunneling barrier to an engineered hole trap composed of PbS [4]. The experiments show the coexistence of two principally different types of fluorescence intensity fluctuations. We present a new physical model of the phenomenon combining two molecular mechanisms. In the absence of the inorganic trap fluorescence intensity fluctuations are caused by variations of the electron-phonon interaction value. When the hole trap is attached to the quantum dot the second type of fluctuations, based on the charging/neutralization mechanism, appears. The model quantitatively reproduces the properties of the single quantum dot long-correlated fluorescence intensity fluctuations including the intensity distribution and power spectral density.

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Study on spectral characteristics of laser ignition of fossil coals. Comparison with ignition of benzene in model porous matrices

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We first began the basic studies of ignition of fossil coals under the irradiation of pulsed laser generated by yttrium-aluminum garnet crystal, operated in free-mode generation [1-4]. Depending on the degree of metamorphism, fossil coals represent a carbon hydrocarbon skeleton, as well as high-boiling and low-boiling hydrocarbons intercalated and adsorbed in a porous carbon matrix. In the experiments on laser ignition a series of processes proceed: heating of the coal matrix, diffusion and desorption of hydrocarbons, burning of hydrocarbon molecules on the surface, desorption of light hydrocarbons and burning them in gas phase, and finally burning of coke residue. In the interpretation of experimental data, we take into account the composition of hydrocarbons and minerals, *e.g.,* coal ash, as well as detailed analysis of the composition of products of combustion. For a better understanding of the complex processes to be studied it is needed to highlight and study the features of laser ignition of hydrocarbons in porous matrices.

To accomplish this, we have begun a series of model experiments on laser ignition of hydrocarbons in a well characterized porous material γ-Al_2O_3 with registration of intermediate and final products. Porous matrix was impregnated with benzene and irradiated by pulsed laser: wavelength – 1064 nm, pulse duration – 120 μs [1-4].

Using the electron-optical method (spectrophotochronograph on the basis of a streak-camera and polychromator) the spectra of luminescence of γ-Al_2O_3, saturated with benzene were obtained. Visually a flame was observed, and combustion is accompanied by rich emission of soot, the radiative properties of the combustion products consisting of a mixture of gases plus soot particles need detailed study. It is shown that the registered radiation spectra have a complicated nature – against the background of the broadband spectrum there are distinctly allocated lines, presumably CO lines of the Herzberg system (466 nm, 497 nm, 531 nm), which corresponds to ($C^1\Sigma \rightarrow A^1\Pi$) transition, and fourth positive system ($A^1\Pi \rightarrow X^1\Sigma$) [5], characteristic of CO recombining with oxygen [6].

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Parahydrogen allows ultra-sensitive indirect NMR detection of catalytic hydrogen complexes

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The ^{1}H NMR signal of dissolved molecular hydrogen enriched in parahydrogen (p-H_2) exhibits in the presence of an organometallic hydrogenation catalyst a perplexing, partially negative line shape (PNL). It results from a strongly enhanced two-spin order connected to the population of the T_0 level of orthohydrogen (o-H_2). This two-spin order is made visible by a slow asymmetric exchange process between free hydrogen and a transient catalyst-hydrogen complex. By Only Parahydrogen Spectroscopy (OPSY) it is possible to selectively detect the two-spin order and suppress the signal from the thermal o-H_2. The intensity of the PNL can be strongly affected by long narrow-band radio frequency (RF) irradiation. When the RF-frequency is in resonance with the chemical shift values of the hydrogen bound to the elusive catalyst or of the free hydrogen, a strong intensity reduction of the PNL is observed. Numerical simulations of the experiments performed at 500 MHz and 700 MHz proton frequency show that the indirect detection has at least three orders of magnitude higher sensitivity than the normal NMR experiment. A theoretical model, including reversible binding and S-T_0 evolution, is developed, which reproduces the NMR line-shape, the nutation angle dependence and the dependence on the frequency of the irradiation field of the PNL and permits the determination of the proton chemical shift values and the sign of the scalar coupling in the transient NMR invisible complex where singlet-triplet conversion take place. Our method enables sensitive detection of organometallic complexes with H_2, which are otherwise invisible for NMR.

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Penetration of nifedipine molecule through DOPC lipid bilayer in the presence of glycyrrhizic acid

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Glyzyrrhizic acid (GA) is known to have medicinal properties by itself. However, it is able to support transportation of other drug molecules through the membrane. Such a drug molecule is nifedipine, as it is hydrophobic and quite small. It was shown that nifedipine molecule forms stable associates with GA [1]. Modern molecular dynamics simulation provides instruments to calculate Gibbs free energy profile of a penetration process. We used the umbrella sampling approach realized in GROMACS package for calculation of the potential of mean force (PMF) of a drug molecule penetration through a lipid bilayer. Thirty five independent umbrella-windows spaced in 0.2 nm, each 50 ns long, were used for calculation. PMF was calculated for nifedipine in pure DOPC lipid bilayer and in the DOPC with GA dissolved. It was shown that potential barrier for small nifedipine molecule is significantly lower than for GA calculated earlier [2]. However, GA has little impact on the barrier of nifedipine transition through the lipid tails layer, as GA is predominantly located near lipid heads of one of the lipid half-layers [2]. PMF profile provides important information about potential barriers inside bilayer and sheds light on the mechanism of permeation process.

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Analytical solution of the nonstationary problem of filtration combustion of gases

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A particular analytical solution of the nonstationary problem of filtration combustion of gases (FCG) makes it possible to elucidate the trends in the structure and characteristics of FCG waves with varying parameters of the problem, and is also a prerequisite for numerical methods of solving the problem. The impossibility of finding analytic solutions of nonstationary FCG problems in quadrature formulas forces researchers to resort to numerical solutions. However, bringing the model system to an equivalent system, one can find an analytical solution in quadratures, which was done by the authors of the paper. In this case, we consider the two-temperature mathematical model of the FCG, known in the scientific literature, in a moving coordinate system:

$$\begin{aligned}
&\rho_1 c_p \frac{\partial T_1}{\partial \tau} - \rho_1 c_p U \frac{\partial T_1}{\partial \xi} + \rho_1 c_p \upsilon_1 \frac{\partial T_1}{\partial \xi} = -\alpha (T_1 - T_2) + \rho_1 Q J \ , \\
&\rho_2 c_2 \frac{\partial T_2}{\partial \tau} - \rho_2 c_2 U \frac{\partial T_2}{\partial \xi} = \alpha_2 \lambda_2 \frac{\partial^2 T_2}{\partial \xi^2} + \alpha (T_1 - T_2) \ , \qquad \alpha = \frac{12 \alpha_2 \lambda_1}{d^2} , \\
&\rho_1 \frac{\partial \eta}{\partial \tau} - \rho_1 U \frac{\partial \eta}{\partial \xi} + \rho_1 \upsilon_1 \frac{\partial \eta}{\partial \xi} = -\rho_1 J, \ \ J = \eta k_0 \exp\left(-\frac{E}{R T_1} \right).,
\end{aligned} \tag{1}$$

with initial and boundary conditions:

$$\begin{aligned}
&\tau = 0: \ T_1 = T_0, \ \ T_2 = T_0, \ \ \eta = \eta_0, \\
&\xi = 0: \ T_1 = T_{1*}, \ \ T_2 = T_{2*}, \ \ \eta = \eta_*, \\
&\xi = \infty: \ \frac{\partial T_1}{\partial \xi} = 0; \ \frac{\partial T_2}{\partial \xi} = 0; \ \ \eta = \eta_0.
\end{aligned} \tag{2}$$

The system (1) is considered under the assumption $\rho_1 \approx \rho_{10}$, $\upsilon_1 \approx \upsilon_{10}$ and is reduced to an equivalent system, by summing the first and third equations in place of the first equation (1) and by summing all the equations in place of the third equation (1). The second equation (1) remains unchanged. The analytical solution of the transformed system (1) has the form:

$$
\begin{aligned}
&\frac{T_1}{T_e} = 1 + \frac{\beta(u_0 - 1)}{2\gamma_2 a\sqrt{\pi\bar{\tau}}} \exp\left(-\frac{\bar{\xi}^2}{4a^2\bar{\tau}}\right)\cdot\left[1 + \left(\frac{1}{\alpha'}\right)\left(\frac{\bar{\xi}^2}{4a^2\bar{\tau}^2} - \frac{1}{2\bar{\tau}}\right)\cdot\left(\varphi - \frac{\chi_2}{a^2}\right) + \frac{\varphi\bar{\xi}}{2a^2\bar{\tau}\alpha' u_0}\right] \\
&\frac{T_2}{T_e} = 1 + \frac{\beta(u_0 - 1)}{2\gamma_2 a\sqrt{\pi\bar{\tau}}}\cdot\exp\left(-\frac{\bar{\xi}^2}{4a^2\bar{\tau}}\right), \qquad T_e = T_0 + \frac{Q\eta_0}{c_p\left(1 - \varphi/(u_0 - 1)\right)}, \\
&n = \gamma_1\beta\left(1 - \frac{T_1}{T_e}\right) + \frac{1}{2a\sqrt{\pi\bar{\tau}}}\exp\left(-\frac{\bar{\xi}^2}{4a^2\bar{\tau}}\right),
\end{aligned}
\tag{3}
$$

where $\beta = \dfrac{RT_e}{E}$, $\gamma_1 = \dfrac{c_p T_e \beta}{Q\eta_0}$, $\gamma_2 = \gamma_1\varphi$, $\varphi = \dfrac{\rho_2 c_2}{\rho_{10} c_p}$, $\alpha' = \dfrac{\alpha}{\rho_{10} c_p k_0 \exp(-1/\beta)}$,

$$
u_0 = \frac{\upsilon_{10}}{U}, a = \sqrt{\frac{\chi_2(u_0 - 1)}{\varphi u_0}}, \chi_2 = \frac{\alpha_2\lambda_2}{\rho_{10} c_p k_0 \exp(-1/\beta) L^2}, \ L = \frac{\upsilon_{10}}{k_0 \exp(-1/\beta)}\ .
$$

O13

Combustion chemical kinetics of biodiesel surrogates

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Declining worldwide supplies of conventional petroleum-based hydrocarbon fuels for industrial and transportation applications are leading the world to developing alternative sources for these fuels. Global climate change concern has also motivated considerable interest in providing renewable energy sources that offer the potential of zero net CO_2 emissions. One very promising solution to these challenges is the use of biodiesel, which is typically produced through the conversion of biolipids with methanol (or ethanol), yielding fatty acid methyl (or ethyl) esters as biodiesel and glycerol as a by-product. Over the recent years, the use of biodiesel fuels has been constantly growing, mostly as components of mixtures with conventional petroleum-based diesel fuels. Understanding combustion chemical kinetics of biodiesel components (methyl and ethyl esters of fatty acids) and their blends with hydrocarbons could facilitate significantly the prediction of combustion characteristics of such fuels (including PAH and soot formation). The use of surrogates instead of the real biodiesels plays a key role in this endeavor. Experimental data on spatial distribution of concentrations of different species in flames (*i.e.,* flame structure) in various conditions provide principal information on chemistry and mechanism of combustion of a particular fuel. Many efforts have been undertaken by the authors of this work to extend the experimental database on structure of flames of methyl and ethyl esters using flame sampling molecular beam mass spectrometry with electron ionization and vacuum ultraviolet photoionization, a powerful tool for detecting short-living intermediates in flames. In this work the main experimental results on the structure of flames fueled by methyl (methyl pentanoate, methyl hexanoate, methyl decanoate) and ethyl (ethyl butanoate, ethyl valerate) esters recently obtained by the authors are presented. Available chemical kinetic models for combustion of these esters are validated against new experimental data. Performances and deficiencies of the models in predicting the data are discussed. An up-to-date view on detailed combustion kinetics of methyl and ethyl esters is given.

EPR of germanium-vacancy defect in diamond: Experiment and DFT calculation

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Optically active centers in diamond have been extensively studied because they can find different applications in quantum information processing. In 2015, a new color center in germanium-doped diamond was detected. Similarly to the optically active SiV$^-$ center, a negatively charged state of the germanium-vacancy center was observed in photoluminescence spectra. Quantum nanophotonics platforms have recently been created based on the germanium-vacancy color center.

Electron paramagnetic resonance spectroscopy is a powerful tool used to determine the local structure of paramagnetic centers. Thus, germanium-doped diamond crystals were studied by EPR. A new paramagnetic center was detected in high-pressure high-temperature diamonds synthesized in Mg-Ge-C system. This center has an axial symmetry along the <111> direction and is characterized by the following spin-Hamiltonian parameters: $S = 1$, $g_{\|} = 2.0025$, $g_{\perp} = 2.0027$, $D = 80.3$ mT, $E = 0$. Additional growth experiments were performed using germanium enriched with the ^{73}Ge isotope ($I = 9/2$). The hyperfine structure of one ^{73}Ge atom was detected with the isotropic constant $A \approx 1.64$ mT. The new spectrum was attributed to the neutral germanium-vacancy defect since the new paramagnetic center had the same symmetry and spin state as the SiV^0 paramagnetic center. The large value of the zero-field splitting parameter D was suggested to be a result of the spin-orbit interaction. Indeed, Ge has a significantly larger spin-orbit coupling constant than Si (λ(Ge) = 940 cm^{-1}, λ(Si) = 149 cm^{-1}), giving a significantly larger D (D(SiV^0) = 35.7 mT, D(GeV^0) = 80.3 mT).

The calculations performed within the DFT cluster method confirmed the assignment of the experimental EPR spectrum to the paramagnetic GeV^0 ($S = 1$) defect. There is a good agreement between the experimentally obtained and calculated spin-Hamiltonian parameters. The zero-field splitting tensor was analyzed for the GeV^0 center, and it was shown that the spin-orbit coupling interaction actually gave the dominant contribution to the total D parameter.

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O15

EPR studying of codon-anticodon interaction of mRNA with tRNAs in human ribosome

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mRNAs form complicated supramolecular complexes with ribosomes and their small subunits (80S and 40S subunits for mammals), which are responsible for the protein synthesis in the cells of all organisms. Recently, we demonstrated that DEER/PELDOR can be fruitfully applied for measurements of intramolecular/intermolecular distances in such multicomponent supramolecular machineries and for evaluating dynamic properties of ligands bound to these machineries [1].

In this work a mRNA analog – oligiribonucleotide UGUGUUCGACA, with nitroxide labels attached at C5 5'atom of U- residue and C8 3' atom of A residue, was used to study complexes of human ribosomes and codon-anticodon interaction with tRNA using DEER. Model 80S ribosomal complex with mRNAs were assembled with participation of tRNAPhe that targets UUC triplet (coding for Phe) into P site of ribosome. The distances between spin labels were measured in 5 model complexes of mRNAs analog with 80S ribosomes, where tRNA was located at A site and/or at E-site.

The measurement of intramolecular distances in mRNA allowed to establish the fundamental differences between the mRNA conformations fixed in the mRNA-binding site of the human ribosome by codon-anticodon interaction with tRNA in the P site and mRNA associated with the ribosome in the absence of tRNA. The data confirmed the cooperative character of the coupling between molecules of tRNA at A-, P- and E-sites of ribosome and allowed to make conclusion concerning the absence of codon-anticodon interaction in the E-site of ribosome.

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Structure and spin-dependent recombination of charge-separated state in polymer/fullerene composites

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The key process in organic solar cell operation is charge separation under light illumination. When the active layer (typically, a blend of fullerene and conductive polymer) absorbs light, an exciton is formed. It diffuses through the material until it decays to the ground state or reaches the donor-acceptor interface where the electron is transferred from polymer to fullerene. Thus a charge-separated (CS) state is formed. The understanding of charge separation mechanism at organic donor/acceptor interface still remains a challenge. To address this problem structure and recombination of the CS state were studied by Q-band pulse EPR spectroscopy (Electron Spin Echo, ESE).

Laser-flash induced echo-detected EPR spectra of the composites of different conjugated polymers with fullerene PC60BM were measured and analyzed. The spectral shape is characteristic for singlet-born spin-correlated radical pair, with some admixture of Emission/Absorption spin polarization [1]. It was found that ESE intensity in the middle and at the edges of the spectrum depends differently on microwave intensity. This is caused by relatively strong magnetic interaction (combination of exchange and dipolar interactions) between the spins of the positive and negative polarons constituting CS state, which brings the radical pair away from weak spin coupling limit. From this dependence the strength of exchange interaction of 5 MHz was estimated for P3HT/PC60BM composite. It should be noted that interspin distance distribution is broad for CS state in polymer/fullerene composites [2], and the above value corresponds to its lower edge. The feature caused by strong magnetic coupling within CS state dominates the flash-induced EPR spectrum for poorly-performing composites MEH-PPV/PC60BM and RRa-P3HT/PC60BM. It is less pronounced for average efficiency composite P3HT/PC60BM and almost disappears for highly efficient composites PTB7/PC60BM and PCDTBT/PC60BM. Thus, the relative amplitude of the „anomalous" EPR feature the can be used as a figure of merit for OPV material.

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Spin effects and chiral drugs stereoselectivity

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A model reaction, the photo-induced donor-acceptor interaction in linked systems - dyads, has been used to study the comparative reactivity of a well-known anti-inflammatory drug, (S)-naproxen (NPX) and its (R)-isomer, since it is well known that S and R NPX are very different in their medical properties. (R)- or (S)-NPX in these dyads are linked to (S)-N-methylpyrrolidine (Pyr) using a linear or cyclic amino acid bridge (AA or CyAA), or tryptophan. The donor-acceptor interaction is reminiscent of the binding (partial charge transfer, CT) and electron transfer (ET) stages involved in the extensively studied inhibition of the cyclooxygenase enzymes (COXs) by the NPX enantiomers. Besides that, both optical isomers undergo oxidative metabolism by enzymes from P450 family, which also includes ET stages.

The scheme proposed for the excitation quenching of (R)- and (S)-NPX excited state in these dyads is based on the joint analysis of the chemically induced nuclear polarization (CIDNP) and fluorescence data. The rate constants of the individual steps in the suggested scheme and the fluorescence quantum yields of the NPX local excited states and exciplexes show stereoselectivity [1]. The ^{1}H CIDNP effects in this system appear in the back electron transfer stage in the biradical-zwitterion, which is formed *via* photoinduced ET in dyads [1,2]. A difference between CIDNP effects of two dyads diastereomers in electron transfer ET process also has been demonstrated. For the first time CIDNP phenomenon has been used to study the difference in the properties of chiral short-lived paramagnetic particles. There are diastereomers of “naproxen-tryptophan”, and “naproxen - CyAA - CyAA CyAA N-methyl pyrrolidine. It has been shown that the observed CIDNP enhancement coefficient of R,S diastereomers twice exceeds those for the SS analogue. A comparison of the experimental ratio of CIDNP coefficients of R,S and S,S diastereomers with those calculated in the frame of radical pair theory let us associate the difference with that of magnetic resonance parameters of the R,S and S,S BZ. This result allows one to expect also some difference in the distribution of electron densities in the diastereomers. The latter may be one of reasons for the abovementioned differences in the R and S NPX reactivity.

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O18

Physical chemical properties of matter at extreme conditions

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The equation of state (EOS) is the fundamental property of matter defining its individual properties. EOS governs the system of gas dynamic equations and defines significantly the accuracy and reliability of the results of numerical modeling. In practice, it is required for numerical modeling of numerous processes arising under conditions of extreme energy densities. In this report we shall give examples of different EOS, discuss the progress in experimental study of material properties at high pressure, high temperature, and in theoretical methods as well.

In spite of a significant progress achieved in the construction of EOS, the range of applicability of each theory is local and, rigorously speaking, none of them allows to provide for a correct theoretical calculation of thermodynamic properties of matter on the entire phase plane from the cold crystal to liquid and hot plasmas. Wide-range multi-phase EOS for metals of most practical interest will be reported, as well as results of numerical modeling of processes at extreme conditions. This EOS fully assigns the free energy thermodynamic potential for metals over the entire phase diagram region of practical interest. It accounts for solid, liquid, plasma states, as well as two-phase regions of melting and evaporation. To construct EOS, the following information at high pressures, high temperatures was used: measurements of isothermal compressibility in diamond anvil cells, data on sound velocity and density in liquid metals at atmospheric pressure, electrical explosion of conductors measurements, registration of shock compressibility for solid and porous samples in incident and reflected shock waves, impedance measurements of a shock compressibility under condition of an underground nuclear explosion, data on isentropic expansion of shocked metals, calculations by Debay-Huckel and Thomas-Fermi models, evaluations of the critical point. More simple caloric EOS developed for plastics, alloys, rocks, minerals, composites are also presented, and the comparison with available at extreme conditions experimental and theoretical information is given.

Examples of numerical modeling of processes at extreme conditions with the use of real EOS of matter are given along with discussion of EOS importance in different domains of the phase diagram.

Coherence transfer processes in EPR spectroscopy of free radicals in liquids: The role of forbidden transitions

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The Redfield approach [1] to description of relaxation of free radicals in liquid state prescribes to ignore the coupling of evolutions of coherences by relaxation if these have different transition frequencies (the so-called Redfield kite). This drastically simplifies description of the system spin dynamics but sometimes omits its important features [2]. A brief theoretical analysis of the coupling of allowed transitions coherences by paramagnetic relaxation in liquids was presented in [3], it was shown to shift the involved EPR lines to each other and add broadening to them. Spectral changes caused by allowed transitions coherence transfer due to radical collisions in solution were comprehensively studied in [4]. In glassy solids relaxation induced coherence transfer may cause appearance of a narrow pattern in the EPR spectrum of a triplet molecule [5].

In this contribution the coupling of forbidden and allowed transitions by relaxation processes is taken into account. A model system of a radical having coupled electron and nuclear spins ($S = I = 1/2$) is analyzed. The forbidden transitions do not manifest in EPR spectrum themselves, but coupling of these with the allowed ones by relaxation leads to admixture to the signal observed as a dispersion-like low intensity line proportional to the coherence transfer rate. Resonance frequencies of the two new lines are split by approximately double nuclear Zeeman frequency having the same center as the two allowed lines.

This work was supported by: the National Science Foundation (Grant 1416238) and the Russian Foundation for Basic Research (Grant 14-03-93180).

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A global view on the structure of solutions

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The structure of solutions is an important object of research in physical chemistry. For more than a century, the concepts of the structure of solutions have been developed on the basis of experimental data. Now, the computer simulation is an important tool for study of solutions.

To have a concept of the structure of solutions on microlevel based on the data of macroscopic experiments, one has to come up with theoretical models. Now we know the coordinates of the atoms, and the problem of studying the structure of a solution is reduced to processing a file of a molecular-dynamic trajectory. Such work requires its own specific methods and approaches. However, what is important is that having a solution *in silico*, you can raise new questions about the structure of solutions, going beyond the capabilities of experiments and traditional paradigms. In particular, it is possible to consider the solvation shell in a new way and to carry out its description on a quantitative level. One can proceed to describe the associates in solution, and also characterize the location of the dissolved molecules as a whole, to characterize the structure on *global* level. Thus, now one can proceed to problems that usually do not arise, or are discussed only on a qualitative level, since data on this are difficult to obtain from macroscopic experiments.

We have generated a set of molecular dynamics models of aqueous solutions of some osmolyte molecules at different concentration, and performed investigation of their global structure by Voronoi-Delaunay method and cluster analysis of the solutes. It was shown, in particular, that the molecules of TMAO are distributed in the solutions as the random spheres at the corresponding concentration. On the other hand, urea and TBA molecules demonstrate a very different behavior [1, 2]. This analysis gives new information for understanding physical-chemical properties of solutions.

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O21

X-ray generated exciplexes of diphenylacetylenes with -CF_3 or -OMe substituent group

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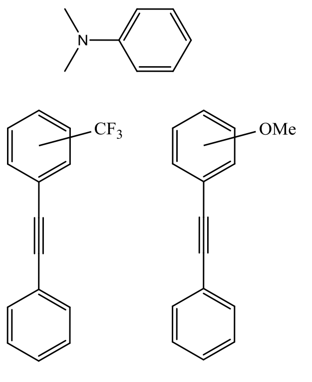
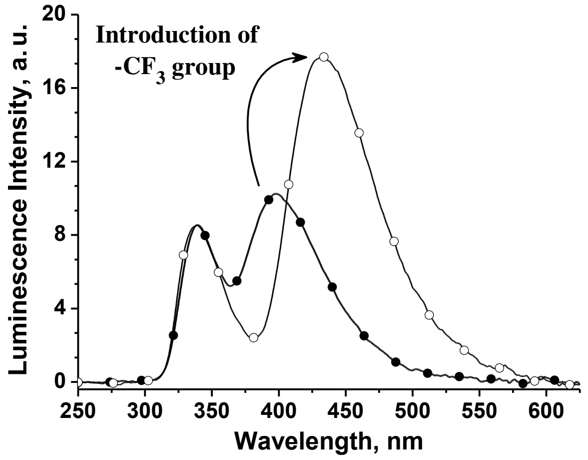
This work reports the investigation of six synthesized diphenylacetylenes (DPAs) with systematically varied position of donor (-OMe) or acceptor (-CF_3) substituent group and unsubstituted DPA. DPAs under study were found to have different luminescence properties, namely luminescence lifetimes vary from less than 200 ps to 0.96 ns, and quantum yields vary from 0.005 to 0.45. Nevertheless, all of the substituted DPAs efficiently form exciplexes with *N,N*-dimethylaniline under X-ray irradiation of *n*-dodecane solution *via* radical ion pair recombination. The exciplex lifetime and the position of exciplex emission band depend strongly on the nature of the substituent group. For instance, the acceptor groups shift exciplex emission bathochromically, compared to unsubstituted DPA, whereas the donor groups shift it hypsochromically. The shifting of the exciplex emission is found to correlate with electron affinity of corresponded substituted DPA. Electron affinities are obtained by means of quantum chemical calculations at CAM-B3LYP level of theory and 6-31+G(d,p) basis set.





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Parity violation energy difference between rotosymmetric isomers of DABCO molecule

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Electroweak interaction being a natural source of parity symmetry violation, constantly attracts research attention as a potential cause of homochirality in biological systems, even though the corresponding energy differences between chiral isomers are extremely small. Back in 1991, A. Salam proposed a hypothesis that the subtle energy difference together with a type of Bose condensation phenomenon may allow for a second-order phase transition, when the less stable D-enantiomers tunnel into the more stable L-enantiomers below some critical temperature [1], which was expected to be observed in chiral amino acid crystals. Although extensive studies over the next fifteen years could not clearly prove that any of phase transitions observed in amino acid crystals were actually the “Salam phase transition”, these works gave rise to another wave of computational and experimental research interest in parity violation effects, not only in biologically relevant systems, but also in other types of chemical systems with heavier elements. Recently, one of the phase transitions in a metal-organic framework $[Zn_2(C_8H_4O_4)_2{\cdot}C_6H_{12}N_2]$ at 60 K was suspected to be the “Salam phase transition” [2, 3]. In this work, we calculate the effect of parity violating interactions on the energy of electronic system of DABCO ($C_6H_{12}N_2$) molecule and $[Zn_2(C_6H_{12}N_2)]^{4+}$ cation for further analysis of the suspicious phase transition in $[Zn_2(C_8H_4O_4)_2{\cdot}C_6H_{12}N_2]$.

Geometries of ($C_6H_{12}N_2$) molecule and $[Zn_2(C_6H_{12}N_2)]^{4+}$ cation were optimized in GAUSSIAN09 at M11/def2qzvp level of theory. Calculations of parity violating energy terms at various levels were performed in DIRAC program suit. The results show that the presence of Zn^{2+} cations strongly enhances the parity violation energy. We also compare results obtained using four-component Dirac-Coulomb Hamiltonian and exact two-component (X2C) Hamiltonian.

The work was supported by the Russian Science Foundation (Grant 16-12-10016).

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Indirect NMR detection of reversible protonation of guanosyl radical in neutral aqueous solution

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Basic DNA photochemistry has been the subject of numerous investigations, in model systems as well as in isolated and cellular DNA. It is well known that UV light can interact with DNA either by direct absorption, or *via* photosensitization by endogenous or exogenous chromophores present in drugs, cosmetic agents, metabolites, *etc*. Guanine is the main target of one-electron oxidation reactions, as it has the lowest oxidation potential among all DNA components. Upon one-electron oxidation, guanine is converted into a cation radical ($G^{\bullet+}$). The guanine cation radical can deprotonate to form the neutral guanine radical $G(-H)^{\bullet}$, and these two radicals are involved in the subsequent processes of pathological DNA damage.

Recently Choi *et al.* [1] using time-resolved resonance Raman spectroscopy combined with pulse radiolysis have proposed a new guanine cation radical species $(G^{\bullet+})'$ that results from protonation at the N7 position of the neutral guanine radical $G(-H)^{\bullet}$. This work caused the debates, namely Sevilla *et al.* [2] challenged the interpretation of results of Choi *et al.* and noted that authors did not show strong evidence for the formation of $(G^{\bullet+})'$, since their DFT calculation failed to reproduce the experimental results. From our side, we support the hypothesis proposed by Choi *et al.* and provide evidences for the new guanine cation radical specie $(G^{\bullet+})'$ formation. Our CIDNP kinetic data, obtained in the photoreaction of guanosine-5′-monophosphate (GMP) with photosensitizer 3,3′,4,4′-tetracarboxy benzophenone (TCBP) in neutral aqueous solution, demonstrate the inversion of CIDNP sign for both TCBP and GMP on microsecond timescale. The independence of CIDNP kinetics on the addition of acetate (proton acceptor), and acceleration of CIDNP sign change upon addition of phosphate (proton donor) suggested that the radical transformation responsible for the observed CIDNP kinetics is the protonation of neutral guanosyl radical at the N7 position with the formation of cation radical $(G^{\bullet+})'$. From the analysis of pH-dependent CIDNP kinetics, protonation and deprotonation rate constant were determined, which allowed to estimate pK_a of cation radical $(G^{\bullet+})'$ at 8.2 in D_2O (8.0 in H_2O). Obtained CIDNP data allows also to estimate the g-factor of protonated at N7 guanosyl cation radical as being nearly equal to that of protonated at N1 guanosyl cation radical.

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Novel thieno[3,4-*b*]pyrazines for organic optoelectronics

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Theoretical treatment of pulsed Overhauser DNP

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DNP is a powerful method to create non-thermal polarization of nuclear spins, thereby enhancing their NMR signals. The DNP effect is due to transfer of the electron spin polarization to nuclear spins in the presence of MW-pumping; the NMR enhancement is proportional to the ratio of the magnetogyric ratios of electron γ_e and nucleus γ_n. In the case of Overhauser-type DNP (DNP in liquids) the NMR signal enhancement is

$$\varepsilon = 1 + \xi \cdot f \cdot s \cdot \frac{\gamma_e}{\gamma_n} \tag{1}$$

with ξ, f and s being the coupling factor, leakage factor and saturation factor, respectively. It is well-known that MW-pumping required for reaching maximal s values can cause substantial heating of the sample. For this reason, using pulsed techniques of pumping instead of cw-pumping is of great interest.

Here Overhauser-type DNP formed by a periodic sequence of EPR-pulses is discussed. Earlier [1] the case of a single ideal pulse per period was discussed and an elegant general expression for the NMR enhancement has been obtained. The expression for the enhancement was shown to be similar to that known for cw-pumping with the saturation factor re-defined as the deviation of the electron spin magnetization from its equilibrium value averaged over the cycle of the pulse sequence.

In this work a general theoretical approach to pulsed Overhauser-type DNP is presented. Our theory can treat pulsed irradiation of EPR transitions for an arbitrary periodic pulse sequence. The NMR enhancement is analyzed in detail as a function of the EPR-pulse length for ideal pulses and pulses with a finite rise-time. Both inhomogeneously broadened and multicomponent spectra are discussed. The dependence of the NMR enhancement on Heisenberg exchange rate is discussed. It is shown that one can achieve the maximal theoretically allowed NMR enhancement for pulsed pumping even when the duty cycle of pumping is low. The dependence of the DNP effect on the duty cycle, electron spin relaxation times, pulse shape and rise time has been studied in detail. Experimental low-field DNP data are in good agreement with this theoretical approach.

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Quantum chemical study of magnetic coupling in “breathing crystals” $Cu(hfac)_2L^R$

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Family of “breathing crystals” is the polymer-chain complexes of $Cu(hfac)_2$ (hfac is hexafluoroacetylacetonate) with nitronyl nitroxide radicals (L^R) [1]. The polymer chains consist of one-, two- or three-spin clusters. The “breathing crystals” experience simultaneous magnetic and Jahn-Teller type structural phase transitions with a change of total cluster spin and a drastic change of bond lengths (*ca.* 10-12%).

In the present work the intra-cluster magnetic coupling constants for several compounds of the ”breathing crystal” family have been calculated both by band structure methods GGA+U and hybrid DFT for the isolated exchange clusters. The calculation results confirm changing the sign of the magnetic coupling constant under the structural phase transition in the corresponding compounds. For some compounds the theoretical treatment also revealed a significant exchange between the radicals of the neighboring polymer chains in a wide temperature range. For some compounds the magnetostructural transition is smooth, and a satisfactory agreement with the experiment can be reached only when one considers the system being in one of two geometrical configurations corresponding to the low-temperature or high-temperature phases. This assumption was confirmed by the broadening of the diffraction peaks in the transition region and was earlier used in communication [2].

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Mechanistic study of micropollutants photooxidation by Fe(III) species and humic substances

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Photochemical processes are playing an important role in global cycles of organic nutrients in environment. For example, photosynthesis is one of the most known and important photochemical events which support existence of the life on Earth. A less known but no less important process is photodegradation, which in opposition to photosynthesis leads to transformation of organic carbon to inorganic one.

Humic substances (HS, including humic and fulvic acids) and Fe(III) complexes are naturally photoactive components, which are widely present in surface waters. Both classes are able to generate reactive oxygen species (ROS) under solar irradiation, which can react with dissolved organic pollutants initiating their degradation. That is why much attention is paid nowadays to investigation of HS and Fe(III) complexes photochemistry and to development of approaches to water treatment based on generation of ROS (so-called Advances Oxidation Processes, AOP).

This talk exhibits several examples of a mechanistic study of UV photooxidation of several classes of wide-spread micropollutants (including arsenic species, herbicides and bisphenols) by Fe(III) species and humic substances. Main information was obtained by combination of steady-state and flash photolysis methods with ICP-AES, ICP-AES-HG and LC MS techniques. Main attention was paid to:

(i) identification of active short-lived transient species (including ROS, triplet states and organic radicals)

(ii) nature of final photoproducts

(iii) quantum yields of photoreactions

(iv) construction of whole mechanisms of photodegradation of target compounds

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O28

The impact of oxygen encounter complexes on photophysics of molecular oxygen in gas and liquid phases

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The photoabsorption of “isolated” oxygen molecules is very weak within the whole UV-IR spectral region where all electronic transitions of ground state O_2 molecule are spin and/or orbital symmetry forbidden. But the interaction of oxygen molecules with molecular environment provides a strong enhancement of UV-absorption by oxygen and other molecules. This drastic effect is governed by encounter complexes X-O_2 and takes place when molecules collide in the gas or liquid phase. Collision-induced absorption of oxygen encounter complexes also dramatically changes oxygen photochemistry causing new photochemical processes such as formation of singlet oxygen species $O_2\,(^1\Delta_g)$ which play important role in nature. Recently we found out a new process of singlet oxygen $O_2\,(^1\Delta_g)$ formation that was unknown before [1]. Singlet oxygen molecules were detected by their IR-luminescence centered at 1.27 μm after UV-excitation of various gas mixtures by laser radiation. We have established that this new photochemical process proceeds *via* UV-excitation of X-O_2 complexes and measured the $O_2\,(^1\Delta_g)$ quantum yield spectral dependence for the first time. Relying on the obtained data we made estimations of the role of this new process in the Earth atmosphere. The first experiments on singlet oxygen formation form X-O_2 complexes in liquid were made.

We suggest the probable mechanism to consist of two processes responsible for singlet oxygen formation. One results from collision-induced absorption of O_2 giving rise to excited triplet oxygen molecules $X\text{–}O_2 + h\nu \rightarrow X + O_2\,(A'\,^3\Delta_u)$ with their further annihilation in collisions with the ground state O_2 molecules giving rise to singlet oxygen. Another process consisting of a simultaneous change of the X-O_2 complex’s both partner spins $^3(^1X\text{–}^3O_2) + h\nu \rightarrow {}^3(^3X\text{–}^1O_2) \rightarrow {}^3X + {}^1O_2$ is the one of peculiar interest. We suppose that this process results in $O_2\,(^1\Delta_g)$ formation in widespread wavelength region depending on oxygen collisional partner X in any oxygen-containing media.

The authors gratefully acknowledge the financial support of this work by the Russian Foundation for Basic Research (Grants 15-03-03204, 16-33-00060, 16-33-60092).

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Principle of detailed balance in the luminescence of complicated systems

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It is well-known that if the photoluminescence spectrum and the quantum yield of a certain luminophore are independent of the excitation wavelength (*i.e.,* Vavilov's law is applicable), then the absorption $\varepsilon(\lambda)$ and fluorescence $F(\lambda)$ spectra of this substance are linked with the black-body spectrum $P(\lambda, T)$ by the so-called Kennard–Stepanov relation [1-3]: $F(\lambda) \sim P(\lambda, T)\cdot\varepsilon(\lambda)$, where T is the absolute temperature. Moreover, Kennard proposed a hypothesis that every photoluminescent matter must satisfy the more general relation, which may be called the principle of detailed balance for luminescence (PDBL):

$$P(\lambda_1, T)\cdot F(\lambda_1, \lambda_2) = P(\lambda_2, T)\cdot F(\lambda_2, \lambda_1),$$

where $F(\lambda_{\mathrm{ex}}, \lambda_{\mathrm{em}})$ is the luminescence intensity at wavelength λ_{em} as a result of being irradiated by some unit photon flux at wavelength λ_{ex}. This principle leads to the Kennard–Stepanov relation provided that Vavilov's law is obeyed. However, the PDBL still lacks a solid theoretical justification and an experimental verification.

Here we give a general thermodynamic proof of the PDBL for photoluminescence of an arbitrary body in thermal equilibrium and extend it into the time-domain:

$$[1 + n(\lambda_1)]\cdot P(\lambda_1, T)\cdot F(\lambda_1, \lambda_2, t) = [1 + n(\lambda_2)]\cdot P(\lambda_2, T)\cdot F(\lambda_2, \lambda_1, t),$$

where $n(\lambda)$ is the Bose–Einstein occupation number and $F(\lambda_{\mathrm{ex}}, \lambda_{\mathrm{em}}, t)$ is the rate of emission from the body at wavelength λ_{em} at time t as a result of arrival of a photon at the body at wavelength λ_{ex} at zero time. It follows from this equation that the photoluminescence decay kinetics is invariant under the interchange of the excitation and emission wavelengths.

The PDBL has been tested experimentally for the solution of InP/ZnS core-shell colloidal nanocrystals [4]. For this system, neither the Vavilov's law nor the Kennard–Stepanov relation is valid, but it turned out that the excitation-emission matrix indeed obeys the symmetry relationship with the functional form implied by the PDBL.

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O30

Photoinduced reactions of eye lens chromophores with proteins under anaerobic conditions

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The irradiation of near-visible UV range, 320-400 nm (UV-A), is considered as one of the main causes of the oxidative stress formation in healthy tissues. The oxidative stress, a prevalence of pro- over anti-oxidants, is the major factor for the development of various diseases, including skin cancer and cataracts. Under UV-A radiation, the photoexcited chromophores of tissues can react with proteins and lipids leading to their oxidation and the formation of other irreversible modifications. Currently, the mechanisms and products of these reactions are poorly studied.

The main goal of the present work is the study of UV-A-induced processes in living tissues using the chromophores and proteins of the human eye lens as a model system. The investigation of these photoinduced reactions is also important for understanding the molecular mechanisms of age-related changes within the eye lens tissue and the development of cataracts. A key feature of the present work is the use of anaerobic conditions as the most relevant to the eye lens, which is characterized by extremely low level of molecular oxygen, less than 2 μM.

Under UV-A radiation, the majority of the eye lens chromophores react with aromatic amino acid residues of proteins (tryptophan and tyrosine) *via* electron transfer to a chromophore. The major decay channel of the forming radicals is back electron transfer with the restoration of the parent molecules. The reactions between a chromophore and amino acid radicals mainly occur *via* oxygen atom subtraction from the chromophore to the amino acid radical. Subsequent radical reactions result in the formation of dimeric forms of chromophore and protein oligomers with high molecular weight. These photochemical reactions can be inhibited by natural antioxidants of the eye lens, ascorbate and glutathione. Ascorbate, an effective quencher of triplet states, prevents the formation of radicals, whereas glutathione, an effective scavenger of radicals, inhibits the radical reactions. Thus, the obtained results support an important role of UV-A induced reactions in the formation of oxidative stress in living tissues and demonstrate an effective way to inhibit them.

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O31

The influence of preliminary mechanical activation of silicon and niobium powders on thermal explosion

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One of the self-propagating high-temperature synthesis (SHS) parameters is the heating rate, leading to thermal explosion. A thermal explosion (TE) is used for the synthesis in low-energy systems, in which it is impossible to implement SHS without any pre-preparation [1]. Mechanical activation (MA) is widely used to facilitate SHS reactions in low-caloric systems such as Nb–Si mixtures. Niobium silicides find their application in aerospace engineering due to their heat resistance (above 1700°C) and relatively large strength/density ratio. These materials are operative at temperatures 200°C higher than other alloys.

In this work we studied the influence of joint MA on the synthesis of niobium silicides by TE. We found the duration of MA, after which TE becomes possible, critical and maximum temperatures for the TE, and the composition of the synthesized product. We also found the conditions for obtaining a single-phase product.

Commercially available powders of Nb ($d < 80$ μm) and Si powders ($d < 100$ μm) were used in our experiments. The Nb–Si mixtures containing 62.3 wt % Nb and 37.7 wt % Si ($NbSi_2$ stoichiometry) were activated in a water-cooled planetary mill (60 *g*, steel vial and steel balls 5 mm in diameter, mill/ball ratio 1:20). MA time was varied between 1 and 30 min (under Ar). The activated mixtures were pelleted and then heated with a constant rate under Ar in a constant volume set

It was established that TE can be carried out only after preliminary MA from 2 to 28 min. There is a general decrease in the maximum and increase in the critical temperature of the reaction with increasing time of MA. After MA for 2 and 4 min TE occurs in the presence of a liquid phase, at other MA times, the reaction occurs in solid-phase mode. Multiphase and single-phase ($NbSi_2$) products may be formed after TE. A single-phase product formed after 2 and after 14 min of MA.

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Modulation of chromenes fluorescence *via* photochromic reaction and solvent polarity

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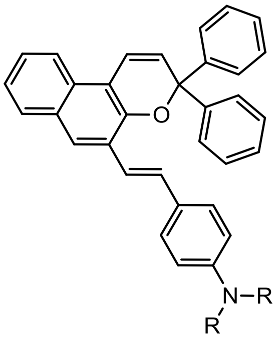
Fluorescent switches at the molecular level had attracted considerable interest during recent years, because they afford promising electronic devices and controllable fluorescent labelling of biomolecules. The photochemical transformations associated with photochromic compounds can be exploited to switch the emission of complementary fluorophores under the influence of optical stimuli. In current work we studied both photochromic and fluorescent properties of several chromenes (see scheme). It was found that coloured forms of these compounds are not fluorescent because of the efficient intramolecular energy transfer.



In the course of the preliminary experiments we found that fluorescence efficiency and position of emission band depend on the solvent polarity. The more polar solvent, the higher is fluorescence quantum yield and the more red-shifted is fluorescence band. It is well known that such behavior indicates the formation of a so-called internal charge transfer (ICT) state. ICT state is stable in polar solvents, on the other hand, in non-polar ones it is characterized by low stability and short lifetime. Time-resolved experiments in pico- and nanosecond time-domains in different solvents revealed a competition between photochemical and ICT channels of energy relaxation after excitation.

Metabolomic profiling of biological tissues by NMR spectroscopy

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The role of metabolomics in the study of human pathogeneses and in the development of new approaches to the medical diagnostics rapidly increases during the last decades. One of the most powerful methods in metabolomics is high-resolution nuclear magnetic resonance spectroscopy (NMR), which allows to identify and quantify a number of components in complex mixtures, that enables a detailed study of physiological processes occurring in biological tissues and fluids. The concentrations of tens of metabolites in a sample can be measured directly in a single experimental run.

In this report we present the results of the application of metabolomics to the eye research. ^{1}H 700 MHz NMR spectroscopy was used for the metabolomic profiling of ocular tissues and biofluids of animals (rat, rabbit) and humans. The concentrations of a wide range of metabolites were measured in cornea, lens, aqueous humor, vitreous humor and blood serum. The comparison of the quantitative metabolomic composition of the eye tissues and blood serum from healthy donor and patients with cataract and keratoconus will be present. The analysis of post-mortem metabolomic changes in biological fluids opens the way to develop new methods for the estimation of post-mortem interval (PMI), and may also help in the analysis of disease-induced metabolomic changes in human tissues when the postoperational samples are compared to the post-mortem samples from healthy donors.

This work was supported by RFBR (Project 17-03-00656, 16-33-00669), and the Grant of the President of RF (Project MK-1515.2017.3)

O34

Radical cations of small heterocycles at low temperatures: Patterns in phototransformations

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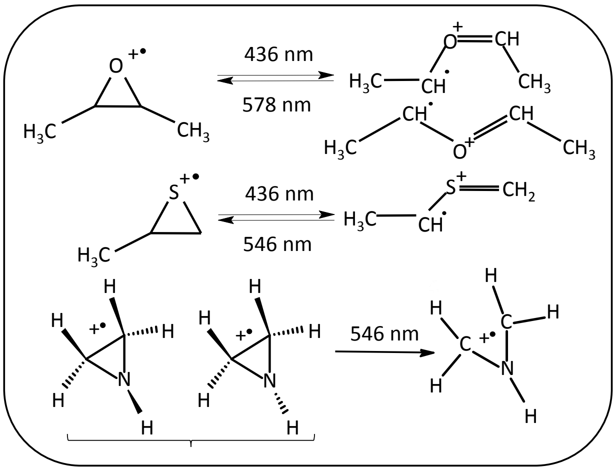
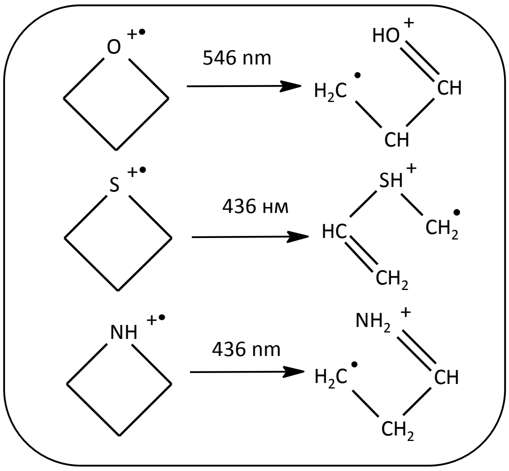
Several representatives in a series of radical cations originating from three- and four-membered heterocycles containing oxygen, sulfur and nitrogen were studied regarding their photochemical behavior in low-temperature freonic matrices by the means of EPR and UV/Vis spectroscopy and with references to DFT calculations for geometries and magnetic resonance parameters.





These radical cations can be viewed as convenient model compounds in the studies of reactivity for heterocyclic intermediates: on one hand, reliable quantum chemical techniques are readily available for them; on the other hand, their transformations are not as varied as those for larger heterocycles. Several types of pathways have been discovered for the mentioned species, some of them quite unusual: they include reversible photocyclization for methyloxirane, methylthiirane and 2,3-dimethyloxirane radical cations; C–N bond cleavage with the formation of two stabilized rotamers for azetidine radical cations; formation of one ring-open form from two ring-closed isomers of aziridine radical cation of comparable statistical significance; and lack of any photochemical activity for tetramethyloxirane radical cations.

Implications are drawn to connect several crucial parameters defining radical cations (charge and spin distribution, molecular symmetry and conformation) to the availability of different pathways and the choices between the possible photoproducts.

This work has been performed with financial support granted by the Russian Foundation for Basic Research (Project 16-03-00029).

The role of the level anti-crossings of the spin energy levels for the formation of hyperpolarization in the solid state

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Nuclear spin hyperpolarization is often used for enhancing weak NMR signals. There are several hyperpolarization methods known named Dynamical Nuclear Polarization (DNP), Chemically Induced Dynamic Nuclear Polarization (CIDNP), Optical Nuclear Polarization (ONP), Para-Hydrogen Induced Polarization (PHIP), *etc.* Presently, there is a growing interest to spin hyperpolarization in solid state, because many chemical and biochemical processes take place in the solid state. As far as theoretical treatment of hyperpolarization in solids is concerned, the main problem is the presence of anisotropic interactions rendering the spin dynamics very complex. While the mechanisms of polarization formation in liquids are well established and understood, detailed analysis of solid-state polarization mechanisms still remains challenging. Recently we have shown that a theoretical approach based on Level Crossings (LC) and Level Anti-Crossings (LAC) is an efficient tool to reveal the complex spin dynamics in the case of CIDNP. In solids all features in the field dependence of CIDNP come from the LACs, because anisotropic interactions result in perturbations which turn LCs into LACs. We have interpreted known CIDNP mechanisms in terms of the LAC concept. This consideration allows one to find analytical expressions for the magnetic field range, where different CIDNP mechanisms are operative; furthermore, the LAC description gives a clear way to determine CIDNP sign rules. We also propose to analyze triplet-state ONP in molecular crystals in terms of level crossing phenomena as well, namely, to attribute features in the ONP magnetic field dependence to LACs in a radical pair. Like in the CIDNP case, anisotropic interactions play a significant role in ONP formation. Using this method we have analyzed the orientation dependence of ONP and derived analytical formulas for the positions of LAC-derived features in the field dependence of polarization. Kinetics of ONP in the presence of mw-irradiation was also analyzed using the “fictitious spin” description of the electronic triplet state.

This work has been supported by the Russian Science Foundation (Grant No 15-13-20035) and the Russian Foundation for Basic Research (Grants No 17-03-00932 and 16-33-00590).

The dynamics of spin label surroundings probed by ^{2}H Electron Spin Echo Envelope Modulation spectroscopy

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Electron Spin Echo Envelope Modulation (ESEEM) spectroscopy is a widely used tool for studying the structure of paramagnetic centers. For ^{2}H nuclei, the ESEEM pattern is determined by anisotropic electron-nuclei hyperfine interactions (HFI) and nuclear quadrupolar interaction (NQI). For the electron-nuclear distance larger than 0.4 – 0.8 nm, the NQI dominates.

The ESEEM lineshape temperature dependence is expected to reflect the motions of deuterated molecules (or of their segments). This was verified for model systems – nitroxide methyl group rotation and stochastic librations of solvent molecules in the surrounding of spin probes in glass [1, 2].

Biological hydration water is important not only for the self-associations and keeping structure of biomolecules, but is also significant for their mobility. Hydration water is also known as a plasticizer, and aspects of correlation in dynamical transition for biomolecules and hydration water are heavily discussed nowadays. In model biological membranes the dynamical transition from restricted to isotropic motions of water molecules was observed below 200 K. The temperature of this transition slightly depends on acyl phospholipid chain saturation and correlates with dynamical transition in the membrane core, observed by Raman and EPR spectroscopies [3].

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[3] N.V. Surovtsev *et al.,* J. Phys. Chem. B, 2012, 116, P.8139-8144.

Relaxation-induced coherence transfer within triplet states and origin of the narrow line in the EPR spectrum of triplet C_{70}

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EPR spectroscopy of photoexcited triplet species is rather important to obtain zero-field splitting parameters and information about molecular motions. In most experiments the EPR spectrum of photoexcited triplet states consists of a broad component and a narrow line. The broad component originates from unpaired electrons forming a triplet state and exhibiting a zero-field splitting interaction. The narrow EPR line superimposes the broad component near its center region. In literature this narrow line was tentatively attributed to photoinduced radicals with $S = 1/2$, however, this was not proved in general.

In the present work X-band light-induced continuous wave EPR (LEPR) spectra of triplet fullerene C_{70}, $^3C_{70}$, in glassy decalin and o-terphenyl (OTP) were obtained in the temperature range between 50 and 130 K (for decalin) as well as between 77 and 200 K (for OTP). The LEPR spectra consisted of broad and narrow EPR lines [1].

The observed LEPR lineshapes of $^3C_{70}$ could be attributed to the result of relaxation-induced coherence transfer between two single-quantum resonance transitions. When the molecular orientation is such that both EPR-allowed transitions between the triplet sublevels have similar transition frequencies, the two coherences may collapse, providing a narrow line feature in the center of the spectrum. This effect may be simulated as jumps of the EPR lines within the LEPR spectrum of $^3C_{70}$ between symmetrical LEPR positions [1].

The obtained temperature behavior of the narrow LEPR line intensity of $^3C_{70}$ is in agreement with the pronounced Orbach-Aminov temperature dependence of spin-lattice relaxation of $^3C_{70}$, which was directly investigated by the electron spin echo inversion recovery technique [2].

This work was supported by the Russian Foundation for Basic Research, grants 15-43-543220 and 15-03-07682.

[1] M.N. Uvarov *et al.,* Appl. Magn. Res., 2016, 47, P.781.
[2] M.N. Uvarov *et al.,* J. Chem. Phys., 2015, 143, 244314.

Optical properties of magnetoactive compounds based on copper(II) ions and stable nitroxide radicals

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Development of functional stimuli-responsive molecular materials is a hot topic in modern science. Up to date, a large number of compounds exhibiting spin crossover (SCO) or valence tautomerism and sensitive to various external stimuli (temperature, pressure, light, *etc.*) has been developed. More important, Light-Induced Excited Spin State Trapping (LIESST) phenomenon has been found, which involves (i) photoswitching between two spin states of the system and (ii) metastability of the photoinduced (high-spin) state at cryogenic temperatures.

SCO-like and LIESST-like phenomena were found in a relatively new family of polymer-chain compounds $Cu(hfac)_2L^R$ based on copper(II) ions and stable nitroxide radicals. The spin state of the whole copper(II)-nitroxide cluster can change depending on temperature, applied pressure, or irradiation with light. It is remarkable that, despite the principal differences between SCO compounds and copper(II)-nitroxide based molecular magnets, the manifestations of thermal transitions and LIESST-like phenomena are quite similar. However, contrary to the SCO compounds, optical properties of $Cu(hfac)_2L^R$ are significantly less understood.

In this work we report the first detailed experimental and theoretical study on the UV/VIS–near-IR absorption spectra of $Cu(hfac)_2L^R$ compounds, with the primary focus on their electronic structure and its temperature dependence upon magnetostructural transitions. Three representative compounds $Cu(hfac)_2L^{Me}$, $Cu(hfac)_2L^{Et\text{-}CP}$ and $Cu(hfac)_2L^{Pr}$ showing either abrupt (former two) or gradual (latter one) magnetostructural transition were selected. Registration of the spectra in a very broad range (200 – 2500 nm or 50000 – 4000 cm^{-1}) allowed to detect a number of transitions from high-energy π-π* to low-energy d-d types. The assignment of these transitions was confirmed by quantum chemical calculations. The data obtained are of high importance for the following optimization of the forward and backward switching of $Cu(hfac)_2L^R$ compounds by light in order to control their spin states.

This work was supported by FASO Russia (Project 0333-2016-0001) and RFBR (No 15-03-07640 and 17-33-80025).

Detection of hyperfine structure in the OD ESR spectra of radical ions in polymer matrices

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Organic polymer materials are actively used in recent years to create new devices for electronics, optoelectronics, photovoltaics, spintronics. In this connection, much attention is paid to the study of transport and recombination of charged particles in polymer matrices containing additives of charge acceptors. One of methods for studying such particles is Optically Detected Electron Spin Resonance (OD ESR) of radical pairs. It uses the recombination luminescence of spin-correlated radical ion pairs for the indirect detection of electron spin resonance. OD ESR is orders of magnitude more sensitive than conventional ESR, and it has found successful application for the studies of liquid nonpolar solutions in radiation chemistry. In recent years, one of the variants of the method, PLDMR (Photoluminescent Detected Magnetic Resonance) has been successfully used in the study of the recombination of photogenerated charge pairs in organic semiconductor polymers. Unfortunately, its informativity in the study of polymers is limited by the need to use very low temperatures, while the greatest interest is the study of processes in the operating range of electronic devices, that is, at room temperatures.

Until now, in polymer systems, none of the variants of optical detection of ESR managed to achieve conditions that allow observing the hyperfine structure of the spectrum of radical ions arising upon irradiation. At the same time, the resolution of the hyperfine structure would significantly increase the informativeness of the method. In this case, as shown by numerous experiments in liquid solutions, it becomes possible to reliably identify the recombination partners, and, observing the changes in the hyperfine spectral components when the experimental conditions change, to obtain information on the dynamics and mechanisms of charge recombination.

In this paper we report the first observation of the resolved hyperfine structure in the ESR spectra of charge pairs recombining in a solid polymer matrix at room temperature.

The effects of ammonia crystallization on ZSM-5 zeolite structural transformation and ESR spectra of copper ammines

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In the presence of adsorbed ammonia molecules a morphological transformation of orthorhombic phase to monoclinic is characteristic for structure of ZSM-5 zeolite. By XRD and ESR spectroscopy in the mode of heating/cooling it is shown that the temperature of change of the copper electronic state from the associated complexes with the orbital ordering of Cu^{2+} ions ($g_{\|}^{ex} = 2.24$, $g_{\perp}^{ex} = 2.05$) to the isolated ions $[Cu(NH_3)_4]^{2+}$ ($g_{\|} = 2.24$, $g_{\perp} = 2.06$, $A_{\|} = 180$ G) correlates with the temperature of phase transformation of orthorhombic phase of zeolite to monoclinic (figure). The observed effect of change of the electronic state of copper-ammonia complexes is explained by an increase in the size of zeolite channel from 0.53x0.56 nm to 0.58x0.59 nm. It is caused by crystallization of $NH_3{\cdot}nH_2O$ in zeolite channels. The temperature of the mentioned changes depends on the ammonia content in the Cu-ZSM-5 sample, but it does not depend on the chemical nature of copper salts (acetate, nitrate, chloride, *etc.*). This temperature varies from 190 to 220 K.

Correlations between structure of the copper-ammonia complexes (which were varied by change of NH_4OH/Cu^{2+} ratio and pH of the copper-ammonia solutions) and temperature of phase transition of orthorhombic zeolite phase to monoclinic are revealed.

We propose that structural transition of zeolite can be used for identification of the associated copper ions and their location in zeolite micropores.

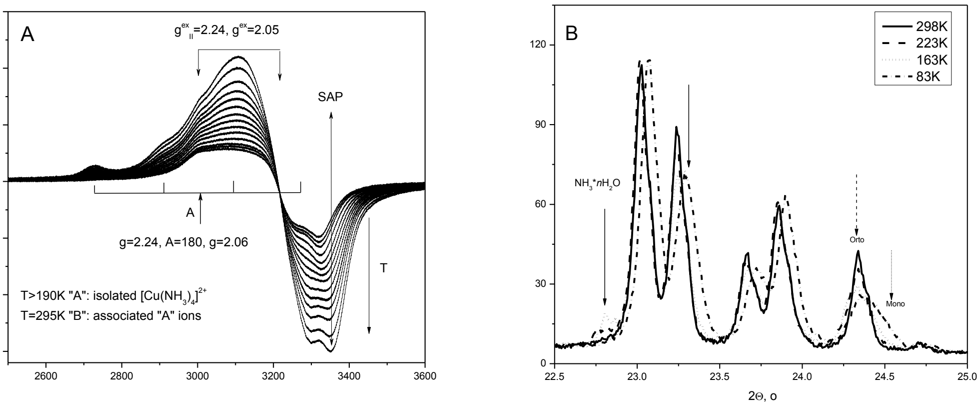

Figure. ESR spectra (A) and X-ray pattern (B) registered at 83 – 298 K (Bruker EMX-Micro 6/1 EPR spectrometer and Bruker ADVANCE X-ray diffractometer, Kemerovo) for 2%Cu-ZSM-5 sample with the associated $[Cu(NH_3)_4]^{2+}$ ions. The sample was synthesized by hydrolytic polycondensation.

X-ray diffraction studies for understanding mechanical effects on solid-state transformations

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Solid-state transformations including chemical reactions and phase transitions are accompanied by generation and relaxation of mechanical stresses and strain. These phenomena are of utmost importance for process kinetics and spatial propagation. Single-crystal to single-crystal transformations are of special interest since they make it possible to follow structural strain by single-crystal X-ray diffraction and optical microscopy. Many of these reactions are accompanied by various photo- and thermomechanical effects, including bending, twisting, curling, jumping of crystals. These effects are closely related to the anisotropy of mechanical properties, which can be followed particularly well by studying the crystal structure under high pressure or low temperature. Combining photo- / thermo- crystallography with high-pressure research can have a synergetic effect when elucidating the mechanisms of the effects.

In this contribution we discuss the experimental results obtained for several classes of compounds showing photomechanical and thermomechanical effects: Co(III) complexes with general composition $[Co(NH_3)_5NO_2]XY$ (where X, Y = Cl^-, Br^-, I^-, NO_3^-) undergoing UV or visible light-induced photoisomerization to give $[Co(NH_3)_5ONO]XY$ as products; a series of rare-earth element hydrated oxalates $(REE)_2(C_2O_4)_3\cdot 10H_2O$ (REE = Sm, Y) undergoing dehydration to $(REE)_2(C_2O_4)_3\cdot 6H_2O$ with crystal shape change on slight heating with pronounced thermomechanical effects; organic molecular crystals undergoing phase transitions on changing temperature accompanied with significant mechanical response of the crystal (*e.g.*, 1,2,4,5-tetrabromobenzene). Crystal structures have been studied by single-crystal diffraction on irradiation, at variable temperatures and high pressures *in situ*. The data on structural changes (anisotropic strain, ordering / disordering, structural phase transitions and chemical reactions) under different conditions have been compared.

The work was supported by a grant from RFBR (16-33-60093 mol_a_dk).

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From mechanism of mechanochemical reactions to design of nanomaterials

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The mechanism of ultrafast mechanochemical synthesis (MS) of complex oxides [1] was determined in sophisticated case “double black box” by a classic approach – quantitative study of “kinetics” in a wide class of similar systems $MeO + MO_3 = MeMO_4$ and structure investigations of crystal products. The threshold character of MS phenomenon for ultrafast formation of nanocrystals with $T_m \leq 3000$ K at room T was demonstrated in the dependence of effective temperature T^* in contact reaction zone on the yield in kg/MJ units. The main factors influencing the yield were established: enthalpy of reaction, molecular mass of reagents and difference in Mohs hardness. MS in the contact of solids during mechanical loading/unloading is described by common equation for primary act $A + B \leftrightarrow (D)^* \rightarrow AB_x$, where $(D)^*$ is intermediate dynamic state in the form of rollers. Ultrafast MS in a limited number of nonstoichiometric oxides by diffusionless mass transfer is accompanied by a giant content of vacancies in crystal products (free volume ~10%) and e^- emission. MS was observed practically only in a mineral structure types. This fact was used to synthesize dozens of new compounds. The effects of the model were verified in independent experiments by direct determination of density and observation of very strong ferromagnetic resonance in a number of treated by single impacts powders of nonmagnetic insulators (TiO_2, NaF, NH_4I, *etc.*). Giant electron mechanoemission under loading of solids was used for development of a new class of engineering Electro-mass-classifier (EMC). Its principle of operation is based on the generation of charged aerosols (*gas-dusty plasma*) with its separation in internal electric fields. A combination of high energy mills and EMC provides unique possibilities for nanopowder design technologies. Development of multilevel nanocomposites with adjusted architecture for oxygen membranes will be demonstrated for realization of alternative green energy with practically unlimited resources – low ranked carbon fuels.

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Kinetics of reversible photochemical processes by NMR under photostationary and nonstationary conditions: State of the art and prospects of application for therapy

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Various experimental NMR techniques have been used for studying both irreversible and reversible photochemical processes (RPCP). In the report modern NMR-based methods of studying the kinetics, determination of the quantum yields and mechanisms of RPCP reactions are surveyed. A detailed consideration of the peculiar features of the experimental techniques, based on NMR lineshape analysis and double resonance NMR (the spin saturation transfer and the transfer of inversion of fractional nuclear spin population), used for the determination of the effective rate constants and of quantum yields of RPCP processes, will be presented. Modern NMR methods are applicable to studies of the kinetics and mechanisms of reversible photochemical processes in solutions characterized by the effective rate constants for the photoprocesses varying between 10^{-3} and 10^{2} s^{-1}. It is for example illustrated by a calculated time-dependent NMR line shape under nonstationary conditions presented in the figure They offer unique possibilities for studying the kinetics of RPCP processes immediately under photostationary conditions and analyzing the interconversions of molecular forms in degenerate systems (*e.g.*, photoisomerization of enantiomers). NMR studies of RPCP are aimed at solving problems in biophysics (design of photosensors, *etc.*). They can also help us understand the mechanisms of cyclic chemical reactions in living organisms that involve absorption of light (*e.g.*, sensing of light information or photodynamic therapy) and be useful in dose evaluation and location of X-ray irradiated regions.

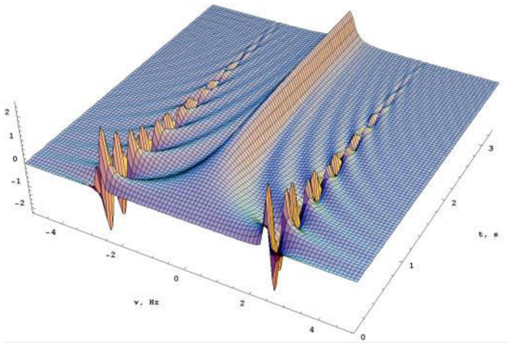

Figure. Time-dependent NMR line shape for two-site exchange in a system with equal population ($T_1 = T_2 = 7$ s, $\Delta\nu = 5$ Hz) under the conditions of the rate constant *k* of RPCP abruptly increased at zero time from 0 s^{-1} to 100 s^{-1}.

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O44

Comparative study of optical properties and X-ray induced luminescence of octahedral molybdenum and tungsten cluster complexes

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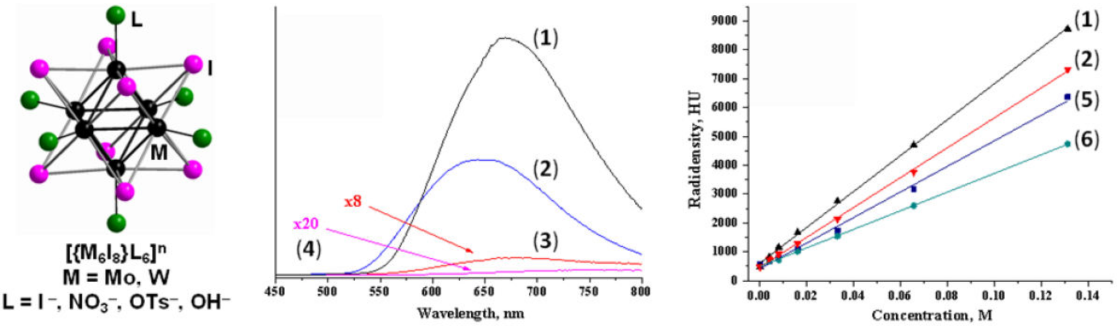
The bioimaging agents prone to X-ray excited optical luminescence are currently being developed in the context of photodynamic therapy (PDT) – medically approved cancer treatment technique based on the photoexcitation of a sensitizer. In the case of PDT, X-ray excitation may solve a major drawback of the conventional PDT technique, namely its inability to treat tumors deep under the skin due to the strong absorption of the excitation UV/Vis light by biological tissue.

Octahedral metal cluster complexes have high potential for biomedical applications. In order to evaluate, the benefit of these moieties for combined CT/X-ray luminescence computed tomography, this work compares the photoluminescence, radiodensity and X-ray induced luminescence properties of octahedral tungsten complexes: $(Bu_4N)_2[\{W_6I_8\}I_6]$ (**1**) and new complexes $(Bu_4N)_2[\{W_6I_8\}(NO_3)_6]$ (**2**), $(Bu_4N)_2[\{W_6I_8\}(OTs)_6]$ (OTs^-: *p*-toluenesulfonate) (**3**) and $[\{W_6I_8\}(OH)_4(H_2O)_2]{\cdot}6H_2O$ (**4**) with those of the corresponding molybdenum analogues: $(Bu_4N)_2[\{Mo_6I_8\}I_6]$ (**5**), $(Bu_4N)_2[\{Mo_6I_8\}(NO_3)_6]$ (**6**), $(Bu_4N)_2[\{Mo_6I_8\}(OTs)_6]$ (**7**), $[\{Mo_6I_8\}(OH)_4(H_2O)_2]{\cdot}2H_2O$ (**8**).



(a) (b) (c)

The general structure of cluster anions in compounds **1**-**8** (a); corrected and normalized X-ray induced luminescence spectra for tungsten complexes (b); the dependence of radiodensity of **1**, **2**, **5** and **6** in DMSO solution in Hounsfield unit scale *vs.* concentration (c).

Tailoring rotational dynamics by a rational design of the octacarboxylate linkers in Cu-based Metal-Organic Frameworks

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Metal-organic frameworks (MOFs) are an emerging class of porous, multifunctional materials showing great potential in a wide range of applications. Given their metal-organic hybrid nature, MOFs have an exceptionally high degree of structural diversity and tailorability. Thus, not only is the on-demand design of materials that incorporate pores of precise shapes and dimensions achievable, but also the inner surface of these materials becomes a platform for incorporating desirable functionality for target applications. For instance, the dynamics of molecular rotors (*e.g.,* phenyl rings) within MOF materials is one of the key property to their functionalization as they form part of the internal pore surface and are thus highly sensitive to the presence of guest molecules and play an important role into mediating the guest-host interactions. In a reversed perspective, the MOFs with mobile fragments in their framework might be as well regarded as an ordered array of stochastic molecular rotator accessible to various external stimuli, *i.e.,* temperature, guest chemical nature and concentration, *etc.* These intrinsic molecular rotations might influence various functional properties of the array, such as frequency dependent dielectric properties or luminescence properties. Hence it is essential to develop a rational way to control the rotational dynamics in ordered solid. One of the most interesting (and challenging!) solution is the rational design of the framework structure. In this regard, the MOFs offer a unique platform to probe the influence of altering the ligand structure on the molecular dynamics and rotational freedom within the resultant framework.

In this work we report the modulation of porosity in a series of isoreticular octacarboxylate Cu-based MOFs. By varying the length and nature of the heteropolyaromatic cores of the linkers, we have selectively extended the length of metal-organic cages ongoing from MFM-180 to MFM-185 along one direction, effectively avoiding framework interpenetration and changing the electronic and steric forces affecting the linkers phenylene fragments rotation. We also report the temperature-dependent ^{2}H NMR studies of selectively deuterated MFM-18i-d16 (i = 0, 1, 3, 5) to define the rotational and flipping modes of the phenyl groups within these structures in the solid state and confirm that for the first time, a rational synthetic design has allowed control of the torsional dynamics of linkers in MOF solids [1].

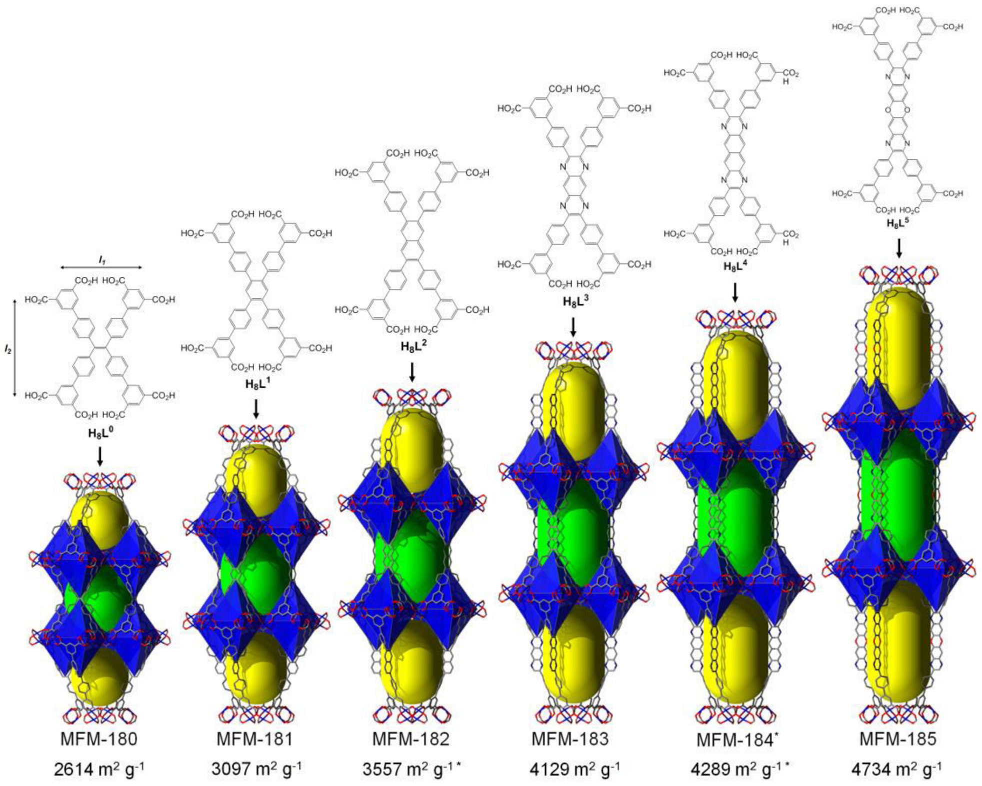

Figure 1. Chemical structures for the octacarboxylate linkers H_8L^0 to H_8L^5 used for the synthesis of MFM-180 to MFM-185, representation of the cage assembly in MFM-180, MFM-181, MFM-182, MFM-183, MFM-184 (*predicted structure) and MFM-185, and corresponding BET surface areas (*computed).

[1] F. Moreau *et al.,* Proc. Natl. Acad. Sci. U.S.A., 2017, 114, P.3056-3061.

Stable dialkyl halonium ions (R_2Hal^+) and their chemical properties

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Halonium ions (R_2Hal^+) are reactive intermediates in electrophilic chemistry and are effective methylating and protonating agents for a variety of compounds. Chloronium cations (figure) in their salts $(C_nH_{2n+1})_2Cl^+[CHB_{11}Cl_{11}^-]$, with n = 1 to 3 and exceptionally stable carborane anions, are stable at ambient and elevated temperatures. Their temperature decomposition decreases with the increasing n from 1 (*ca.* 150 °C) to 3 (*ca.* 80 °C) because of increasing ionicity of C−Cl bonds in the $C{-}Cl^+{-}C$ bridge. At room temperature, the salts of cations with n ≥ 4 are unstable and decompose. Interaction of these cations with chloroalkanes has been studied. It was shown indirectly that unstable salt of fluoronium ions $(CH_3)_2F^+(CHB_{11}F_{11}^-)$ must exist at low temperatures. The proposed $(CH_3)_2F^+$ cation is much more reactive than the corresponding chloronium, showing at room temperature chemical properties expected of $(CH_3)_2Cl^+$ at elevated temperatures.

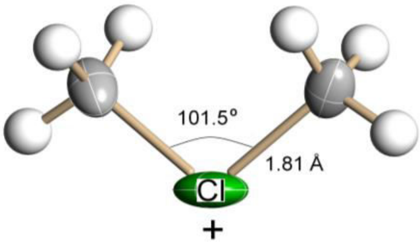

Figure. Dimethyl chloronium cation in its salt with $CHB_{11}Cl_{11}^-$ anion

Poster Presentations

An alternative membrane-modifying mechanism of the antimicrobial peptides action

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A serious problem in current-day medicine is bacterial multidrug resistance. Peptides of fungi origin present a new promising class of antimicrobial drugs which disrupt bacterial membranes. Membrane-peptide interactions are actively studied by different techniques, but molecular mechanisms of peptide antimicrobial action are still under debating.

The antimicrobial activity of Alamethicin (Alm) and Thichogin GA IV (Tri) peptides is usually explained by formation of pores or ion channels in the membrane, which appear above some threshold peptide concentration. However, membrane-perturbation effects for antimicrobial peptides were observed also below the critical concentration, at very low peptide concentration, which assumes the existence of an additional mechanism of their action [1, 2]. The nature of this mechanism is still unclear.

In this work, Alm and Tri action on the spatial distribution of spin labeled stearic acids in the membranes was studied. Fatty acids are essential intermediates in membrane homeostasis. Pulse EPR methods were used for studying weak electron-electron (*e-e*) dipole-dipole interactions, employing the effects of the so-called “instantaneous spectral diffusion” in electron spin echo (ESE) decay, and electron-nuclei (*e-n*) dipole-dipole interactions, employing the effects of ESE envelope modulation (ESEEM). The *e-e* interactions are sensitive to the nanoscale spin label local concentration, while *e-n* interactions are informative about the proximity of the deuterated Tri to the spin label.

Both peptides were found to strongly influence the surface distribution of the stearic acid, acting as nucleation molecules that capture stearic acids around themselves. Such an effect can take place for other lipid-like molecules in the membrane as well. As the peptide-lipid interactions can compete with the protein-lipid interactions, the functioning of these supramolecular complexes can be violated by this capturing mechanism.

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Action of ionizing irradiation on carbon nanotubes

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We studied the influence of ionizing irradiation on the properties of various samples containing carbon nanotubes. The samples with carbon nanotubes were aqueous suspensions, powders, films, and rubber pieces. The samples were irradiated by electrons with energy of 3 MeV. The dose was from 10 to 300 kGy. Then mechanical properties, conductivity, Raman and EPR spectra of the samples were measured.

A reduction of sample conductivity at increasing the irradiation dose and Raman spectra transformations indicate the generation of topological defects in carbon nanotubes under irradiation. The mechanical properties of different samples change in a variety of ways depending on their chemical composition.

NMR investigation of iron(II) sulfate complex with 4-amino-1,2,4-triazole possessing spin crossover

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Compounds having bistability property, which means an ability to exist in two states with long enough life time, attract much attention of researchers. The compounds referred to are complexes of metals with electronic configuration d^3-d^7 possessing spin crossover (SCO) – spin multiplicity change under external conditions, *i.e.,* temperature, pressure or certain wave length light irradiation. SCO can appear only at a certain value of ligand field strength and definite ratio of splitting parameter between low (Δ_{LS}) and high (Δ_{HS}) spin forms of complex and the value of spin pairing energy. Most frequently SCO is observed in complexes of iron(II) and iron(III) with nitrogen containing ligands having FeN_6 coordination site (node).

In the present report for experimental investigation of SCO in water solution we used Nuclear Magnetic Resonance (NMR). The study was carried out on the example of Fe(II) complex with 4-amino-1,2,4-triazole (NH_2trz) of composition $Fe(NH_2trz)_3SO_4 \cdot H_2O$. This compound, as it was shown by method of static magnetic susceptibility for solid phase, possesses a sharp thermally induced SCO $^1A_1 \Leftrightarrow {}^5T_2$ with hysteresis at $\mu_{eff}(T)$ curve [1]. The forward transition when heating is observed at 346 K, and backward when cooling – at 319 K. In the current study, a solution was prepared with concentration of the complex of $1.5 \cdot 10^{-3}$ mol/L in D_2O, which was investigated in the temperature range 280 – 365 K. The weighed portion of complex was dissolved in heavy water when mixing at a magnetic stirrer. It was experimentally shown that, when heating in the temperature range 342 – 347 K, a dramatic change in NMR spectra is observed in contrast to the spectra at low temperatures. Particularly, “broadening” of signals corresponding to the protons of 4-amino-1,2,4-triazole in the complex was found. This spectral change is possibly due to the SCO effect. Thereby, for the investigation of thermo-inductive SCO, NMR can be applied together with various other methods.

The work was supported by the Russian Foundation for Basic Research (Grants No 14-03-90006 Bel_a and No 14-03-00386-a). The authors are grateful for the financial support.

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P04

Radical anion dimers of decafluorobiphenyl and 4-aminononafluorobiphenyl. Two more to a small family

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Two examples are only known in literature for the arene radical anion dimers (RADs) $[2Ar]^{-\bullet}$ detected in liquid solutions [1]. Both examples refer to radical anions (RAs) of polyfluorinated arenes, namely octafluoronaphthalene and 1,2,4,5-tetrafluorobenzene.

Recently, radical anion (RA) of 4-aminononafluorobiphenyl [2] have been detected in alkane solutions by the techniques of optically detected EPR (OD EPR). Further investigations showed that the spectrum changes observed with temperature or concentration variation can be realized by assuming RAD formation. Some features of the curves of time-resolved magnetic field effect (TR MFE) obtained for decafluorobiphenyl solution in isooctane possibly indicate the RAD formation as well.

Using density functional theory we have analyzed the possibility of the RAD formation and considered electronic and geometric possible structure for all the RADs mentioned above. Theoretical interpretation of hfc parameters measured experimentally was made.

According to the calculation results, in the case of the RADs not having substitutes other than fluorine, the unpaired electron density is equally distributed at both aromatic fragments. Due to the spin density delocalization the out-of-plane distortions known for fluorinated arene RAs diminish. The dimer structures are stabilized by interaction of two π-systems. In the case of the RADs of 4-aminononafluorobiphenyl analogous structures are unfavorable in energy, and the most stable ones are H-bonding dimers formed by RA and its neutral precursor. The unpaired electron transfer between the two fragments results in hfc averaging.

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Sorption enthalpy of oxygen and argon in glassy poly(ethyl methacrylate)

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The solubility of oxygen and argon in glassy poly(ethyl methacrylate) ($T_g = 63^{\circ}C$) was studied in the temperature range 175 K to 273 K. It is shown that the sorption isotherms of these gases coincide in the entire range of temperatures studied. It can be shown that the change in the enthalpy of 1 mole of gas molecules during the transition from the gas phase to the polymer under equilibrium conditions (hereinafter enthalpy of dissolution) is equal to:

$$\left(\frac{\partial H_s}{\partial N_s}\right)_T - \left(\frac{\partial H_g}{\partial N_g}\right)_T = -kT^2\left(\frac{\partial \ln P}{\partial T}\right)_{N_s} \qquad (1)$$

where H_s and H_g are enthalpy of gas molecules in the polymer and in the gas phase, N_s and N_g – the amounts of gas in these phases, T – temperature, P – equilibrium gas pressure, k is the Boltzmann constant. The coincidence of the isotherms of sorption of oxygen and argon means that the dissolution enthalpies of these gases are very close in the entire investigated temperature range. The enthalpy of dissolution depends on the interaction energy of gas molecules with polymer molecules, the size of the solute molecules and the types of motions in which the gas molecules in the polymer participate. The sizes of the oxygen and argon molecules are very close. The collision diameters of these molecules are ≈ 3.5 Å. The interaction between oxygen molecules or argon atoms with polymer molecules is realized by the London dispersion forces. Lennard-Jones temperatures characterize the magnitudes of this interaction. These values are for oxygen and argon are close (107 K and 93 K). The boiling points of oxygen and argon (90 K and 87 K) are also close. Therefore, there is no reason to believe that the energies of the interaction of argon and oxygen with the polymer molecules differ markedly. However, argon is a monatomic molecule, and oxygen is a diatomic molecule. Thus, the coincidence of sorption isotherms for argon and oxygen suggests that the contribution of rotational motion to the enthalpy for diatomic molecules is the same in the gas phase and in polymer. The oxygen molecules rotate in polymer matrix and in gas identically.

Kinetics of spin crossover with thermal hysteresis

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Spin crossover or spin transition is a switching between the low spin state (LS) and the high spin state (HS). Strongly cooperative spin crossover behavior leading to wide thermal hysteresis loops is a necessary prerequisite for practical applications of spin crossover complexes. Thermal hysteresis is a kinetic phenomenon and kinetic studies of the LS → HS and the HS → LS transformations within thermal hysteresis loop are of importance for understanding the spin transition mechanism and for estimating the lifetimes of the spin states. Despite numerous studies of the HS → LS relaxation of the light induced excited HS states, kinetic studies near the temperatures of heating and cooling branches of thermal hysteresis are scarce.

Recently we performed the first kinetic studies of the LS → HS transition within thermal hysteresis. These experiments were performed on the anhydrous complex $[FeL^1_2](BF_4)_2$ ($\mathbf{1}^{\mathbf{A}}$, L^1 = 4-(3,5-dimethyl-1*H*-pyrazol-1-yl)-2-(pyridin-2-yl)-6-methylpyrimidine). The hysteresis loop width for the $\mathbf{1}^{\mathbf{A/LS}} \leftrightarrow \mathbf{1}^{\mathbf{A/HS}}$ spin transition depends on water and ethanol content in sealed ampoules and varies from *ca.* 30 K up to 145 K. The kinetics of the $\mathbf{1}^{\mathbf{A/LS}} \rightarrow \mathbf{1}^{\mathbf{A/HS}}$ transition is sigmoidal, which is indicative of strong cooperative interactions. The activation energy for the spin transition is very high (hundreds of $kJ\cdot mol^{-1}$). Kinetics of the $\mathbf{1}^{\mathbf{A/HS}} \rightarrow \mathbf{1}^{\mathbf{A/LS}}$ transition can be either sigmoidal or exponential depending on water and ethanol content in the ampoule: high water and ethanol concentrations lead to sigmoidal kinetics.

Being a kinetic phenomenon, the thermal hysteresis is scan rate dependent. We demonstrated for the first time that scan rate magnetic studies of the LS → HS spin transition represent a powerful method for monitoring spin crossover kinetics and estimating activation energy. This method of estimating the activation energy of spin crossover can be used for studying complexes showing more or less reproducible cooperative spin crossover behavior at a certain scan rate and at the same time demonstrating detectable scan rate dependency of spin crossover curves.

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Reinvestigation of spin crossover in prototypical iron(II) complex with 4-amino-1,2,4-triazole

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The spin crossover phenomenon is a switching between the low spin state (LS) and the high spin state (HS). For practical applications it is desirable to synthesize spin crossover complexes showing wide hysteresis. One of the most exciting examples of such complexes is the 1D polynuclear complex $Fe(ATrz)_3(NO_3)_2{\cdot}H_2O$ (ATrz = 4-amino-1,2,4-triazole) [1]. Magnetic properties of $Fe(ATrz)_3(NO_3)_2{\cdot}H_2O$ were reinvestigated to gain an insight into the impact of water molecules on the spin transition [2]. Variations in the outerspheric water molecule content in the complex induce dramatic changes in its spin crossover regimes. Under vacuum the complex loses water molecules and shows a wide (*ca.* 30 K) and reproducible hysteresis loop, $T_c\uparrow$ = 337 – 345 K, $T_c\downarrow$ = 316 – 313 K. In sealed ampoules the complex $Fe(ATrz)_3(NO_3)_2{\cdot}H_2O$ shows a narrow hysteresis (*ca.* 1 – 4 K), $T_c\uparrow$ = 326 – 329 K, $T_c\downarrow$ = 326 – 324 K. After adsorption of water the complex $Fe(ATrz)_3(NO_3)_2{\cdot}nH_2O$ (n = 1.25 – 1.6) demonstrates a narrow two-step spin transition. For the system $Fe(ATrz)_3(NO_3)_2{\cdot}nH_2O$ (n = 3.6 – 16.6) wide hysteresis (*ca.* 5 – 20 K) re-appears near room temperature ($T_c\uparrow$ = 319 – 321 K, $T_c\downarrow$ = 300 – 315 K). Kinetics of the LS → HS and the HS → LS spin transitions within hysteresis loop have been studied for the first time for 1D polynuclear iron(II)-triazole complexes [2]. For anhydrous complex and for the complex containing *ca.* one water molecule per formula unit, kinetics appeared to be decelerating (non-cooperative). However, kinetics and cooperativity appeared to be strongly sensitive to the presence of extra-amounts of water in the system: high water content switches the decelerating HS → LS kinetics to sigmoidal (cooperative). Thus, the presence or absence of water molecules can affect cooperative interactions between iron(II) centers in 1D polynuclear iron(II) complexes with 1,2,4-triazoles.

This work was financially supported by Russian Foundation for Basic Research (Project No 15–03–05374a).

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Modelling of the femtosecond intramolecular dynamics in the high-lying electronic states of molecular iodine

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Molecular iodine I_2 is a benchmarking molecule for the studies of the photophysics of molecular Rydberg and ion-pair (IP) states. Recently a progress in the experimental study of intramolecular dynamics in high-lying electronic states of I_2 has been achieved with the use of femtosecond pump-probe technique in combination with the velocity map imaging of the photofragments [1]. This approach allowed the authors to investigate the propagation of wavepackets in the excited Rydberg and the ion-pair states of I_2. In a pumping step, I_2 molecules were excited by UV radiation in a two-photon process in the Rydberg states. Probing radiation provided electron photodetachment from the wavepacket in the excited state giving rise to a pair $I + I^+$. Measured Total Kinetic Energy Release (TKER) for observed photodissociation channels corresponds to the kinetic energy of intramolecular motion in the excited state at the moment of the electron photodetachment by the probing radiation. The variation of delay time between the pumping and the probing pulses provides information about the propagation of the wavepacket in time.

The important role of the ion-pair states in the predissociation dynamics of excited I_2 has been established. The interpretation of experimentally measured data has been provided with the use of the results of intramolecular dynamics simulation in the IP states within classical approach. In the current work the results of the dynamics simulation within the classical and quantum approaches are presented and compared. Within the classical approach the Newton laws of motion were used for the calculation of reduced mass motion in the ion-pair states. Within the quantum approach the exponential split operator method [2] has been used for a numerical solution of time dependent Schrödinger equation for wavepackets. Matlab and Wolfram Mathematica programs have been used to perform all calculations. The comparison of the experimental data with the results of the modelling allows us to make conclusions on the features of the intramolecular dynamics in the excited states of I_2.

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Modelling of the femtosecond dynamics of the photoinduced desolvation of rubidium atoms from helium nanodroplets

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Recently a progress in the experimental study of femtosecond dynamics of photoexcited and photoionized rubidium (Rb) atoms attached to helium nanodroplets (HeN) has been achieved with the use of femtosecond pump-probe technique in combination with the velocity map imaging of the photofragments [1]. This approach allowed the authors to investigate the dynamics of solvation and desolvation due to propagation of wavepackets in the different electronic states of Rb-HeN complex. In a pumping step, Rb-HeN complex was excited by VIS or IR radiation to the repulsive states. Measured Total Kinetic Energy Release (TKER) of Rb^+ after probe pulse for observed photodissociation channels corresponds to the kinetic energy of intramolecular motion in the intermediate state at the moment of the electron photodetachment by the probing radiation. The variation of delay time between the pumping and the probing pulses provides information about the propagation of the wavepacket in time.

Previously the simulation of this dynamics was carried out within classical approach [2]. Authors have simulated classically the system, but it did not have good correspondence with the experimental data. In the current work the model of the desorption has been changed and the results of the quantum dynamics simulation are presented and compared with experimental results. Within the quantum approach the exponential split operator method [3] has been used for a numerical solution of time dependent Schrödinger equation for wavepackets. Matlab and Wolfram Mathematica programs have been used to perform all calculations. The suggested approach allows us to get much better agreement between the results of simulation and experimental data on the femtosecond dynamics of photoinduced Rb atoms desolvation from helium nanodroplets.

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Free radicals in the atmospheric photonucleation of aromatic aldehydes

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Atmospheric concentrations of short-lived free radicals generated in the photolysis of biogenic aldehydes are much below detection limits, even if special concentrating measures are taken. However, the participation of free radicals may be indirectly assessed by measuring the concentrations of stable products known to be formed in free radical stages. These stages are of key importance for photonucleation because they define whether a gas-phase route or gas-to-particle conversion will be the dominating mechanism. Aromatic aldehydes were shown to be efficient aerosol-generating species contributing substantially into the nanometer-sized (breathable) fraction of atmospheric organic aerosol. To reveal the free radical stages of photonucleation, most common atmospheric aromatic aldehydes (benzaldehyde, salicylaldehyde, anisaldehyde, and furfural) were photolyzed under laboratory conditions in a flow set-up. Spin trapping from the gas phase was carried out to reveal the primary radical species generated in the photolysis of these aldehydes. To identify spin adducts, the expected free radicals were generated using independent methods to measure the hyperfine splitting constants of their adducts. The formyl radical was detected as the primary product for all studies aldehydes. Spin traps used in the studies were substituted dihydropyrazine-1,4-dioxide compounds with conjugated and isolated double bonds in the pyrazine cycle. The spin adducts formed by the compound with isolated double bonds had unusually long lifetimes (up to 45 minutes), which provided additional possibility to carry our chromatographic identification as a supplement to EPR measurements. Free radicals composed of one, two, and three aromatic cycles bound in chain were successfully detected. The spin trap with conjugated double bonds allowed us to distinguish (relying on hyperfine splitting constants) between initial photolytically generated aromatic radicals and the products of their interaction with oxygen. Thus, the evidence of a competition between polymerization and photooxidation mechanisms in the photonucleation of aromatic aldehydes was obtained. The roles of atmospheric free radicals OH and HO_2 generated in natural atmospheric processes were also studied. In general, OH was found to act as a promoter of the gas-phase route, while HO_2 contributes into aerosol by rendering additional oxygen atoms to form peroxy products readily undergoing gas-to-particle conversion. Thus, free radicals participating in the atmospheric photonucleation of aromatic aldehydes were identified, which helped us to establish the mechanism of gas-to-particle conversion.

P11

Mechanism of CH-cyclization of 1-alkynylanthraquinones into thienoanthraquinones with the participation of Na_2S

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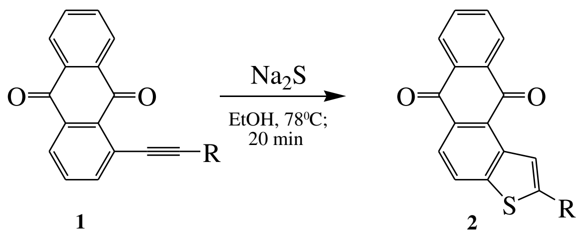
The process of CH-cyclization (Scheme) [1, 2], proceeding with the substitution of aromatic hydrogen atom aided by a nucleophilic reagent (Na_2S), implies the detachment of hydrogen in the form of hydride ion. However, this particle is known to be the most unfavorable one for detachment from the viewpoint of energy. Nevertheless, this reaction proceeds with the same rate as the similar cyclization with the substitution of chlorine atom [1]. As a result of the studies of the mechanism of this reaction, we established the following:



1 R = Alk, Ar

2

Scheme

1. Cyclization is initiated not by sodium sulfide but by the secondary product of its transformation – S^o_2 molecule.

2. The formation of S^o_2 occurs *in situ* during the side reversible reduction of substrate **1** by sodium sulfide. 1-Alkynyl-9,10-anthrahydroquinone withdrawal from the equilibrium as a result of the side cyclization to the hydroxyl group promotes the accumulation of S^o_2 in the reaction medium.

3. As a result of the interaction of S^o_2 with substrate **1,** with the participation of H_2O molecule, a cationic intermediate is formed; in which cyclization itself proceeds into thienoanthraquinone **2** with the release of H_2O and S^o. Thus, the elementary act of cycle formation occurs as electrophilic displacement of hydrogen atom in the form of proton.

4. Non-triviality of this CH-cyclizaiton mechanism also involves the fact that S^o released in the elementary act of cyclization undergoes a chain of interactions in the reaction medium to get transformed into S^o_2, thus initiating the next cyclization act. So, cyclization initiated by S^o_2 acquires the nature of a chain process.

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Effect of pH on sensitized photo-oxidation of thymine and thymidine in aqueous solution: CIDNP study

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At present, there is great interest in model studies of the processes of one-electron oxidation of DNA bases, since there are evidences that such processes occur in a living cell. The one-electron oxidation of DNA duplex results in the formation of a nucleobase cation radical that is subsequently consumed in chemical reactions that often lead to mutations. The electron transfer processes occur mainly involving guanine – the nucleic base with the lowest oxidation potential. However, there are evidences that in some cases in oligonucleotides that lack guanines, reactions occur also with the participation of other DNA bases, as well as thymine. While direct absorption of UV light leads mainly to the formation of pyrimidine dimers, an interaction of UV light with DNA bases in the presence of photosensitizers leads to the formation of short-lived nucleotide radicals, including thymine radicals. Further work is however required in order to establish the detailed mechanisms of photosensitized formation of the short-lived radical intermediate and its characterization at physiological conditions. In present work, we used TR CIDNP technique for studying the photoinduced oxidation of thymine, T, and its nucleoside thymidine, dT, in the expectation that the information obtained will provide a basis for understanding reactions associated with electron removal from this class of compounds in DNA. We chose two commonly used photosensitizers for the radical generation: 2,2′-dipyridyl (DP) and water-soluble derivative of benzophenone, namely 3,3′,4,4′-tetracarboxy benzophenone (TCBP). The pH-dependences of geminate CIDNP was explained in terms of reactants pK_a values. A complementary analysis of the pH-dependences of geminate CIDNP and CIDNP kinetics obtained for the reactions of T and dT with triplet-excited TCBP (DP) in wide pH range enabled us to get information on transient radical intermediates of T and dT, and to establish detailed mechanisms for the reactions studied.

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NMR study of Co nanoparticles encaged in carbon nanocapsules

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Nanosized materials are of interest as a three-dimensional analog of multilayered structures. Their properties depend on their size, shape, crystallographic structure and chemical composition. Encapsulation of materials inside carbon shells is of considerable interest because the encapsulated species are protected from degradation (oxidation or hydrolysis).

Our samples have been prepared with gas-phase synthesis method. Induction melting and evaporation proceed at the suspended state. Nanoparticles condense in Ar atmosphere containing hydrocarbons (methane or butane) [1].

^{59}Co NMR spectra of the nanoparticles of cobalt encapsulated in carbon shell have been obtained at the temperature range from 4 K to 300 K. We have shown the presence of metallic hcp and fcc Co structures, which are mentioned in several sources [2, 3]. Along with them an additional line is observed. It is probably connected with cobalt carbides (Co_3C, Co_2C) similarly to previous Mössbauer spectroscopy studies of Fe nanoparticles in carbon shell [1].

In the present study we discuss the redistribution of the relative volume of the two structural phases of cobalt in the nanocomposites as compared with metallic cobalt powder.

This work was performed in the framework of the State Program (Theme “Spin” № 01201463330) and was supported by the RFBR (Project № 16-02-00416).

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Study of physicochemical properties of insect internal environment with L-band EPR spectroscopy

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Magnetic resonance is a powerful tool for noninvasive investigation of biological objects. Application of soluble paramagnetic probes provides an opportunity for functional measurements of living objects. The purpose of this study was to apply EPR methods for determination of acidosis and oxygenation in hemolymph of living insects. Physicochemical parameters such as pH and oxygen concentration are of physiological importance and, particularly, could both demonstrate the living status and reflect the immune response of insects on invasion by pathogens.

These parameters were investigated in *Galleria mellonella* larvae using functional spin probes (pH and oxygen sensitive) using low-field EPR spectrometer (L-band, 1 GHz).

Parasitic invasion of larvae caused by entomopathogenic fungi *Metarhizium robertsii* resulted in reliable decrease of pH by 0.1-0.2 units. It is important to note that deep injection of fungi conidia in insect's haemocoel reliably resulted in greater acidosis than invasion through the cuticle.

The key stage of immune response of insects is melanization process which is oxygen consuming. EPR oxygen measurements were performed using a C-centered stable nitroxide, TAM. A significant decrease of oxygen concentration of 1.5-fold was detected in the immune response of larvae activated by treatment with standard immune activator, zymosan. This result indicates a significant acceleration of melanization during immune response.

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P15

Photochemistry of 2,3-diarylcyclopentenones: Photochromism and skeletal rearrangement

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2,3-Diarylcyclopent-2-en-1-ones (DCPs) represent a class of photochromic diarylethenes having unique abilities to the chemical modification of the cyclopentenone ring. Typically, DCPs demonstrate photochromic properties based on photocyclization (figure 1). Replacement of a thiophene ring to a benzene ring results in the lack of photochromism due to irreversible skeletal rearrangement (figure 2).

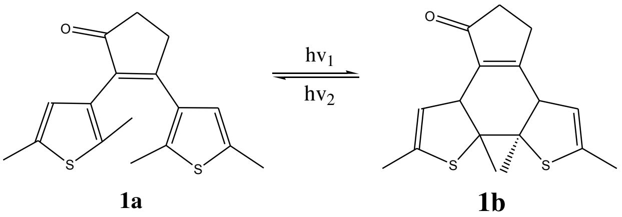

Figure 1. Photochromic transformations of a typical thiophene ring-containing DCP.
1a – initial (open) form, **1b** – photoinduced (closed) form.

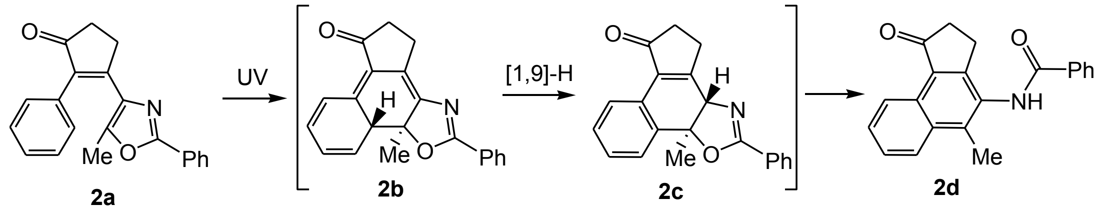

Figure 2. Skeletal rearrangement of a benzene ring-containing DCP. **2a** – initial compound, **2b**, **2c** – intermediates, **2d** – final product.

Mechanisms of structure-dependent photochemical reactions of DCPs were studied. Thiophene-containing DCPs (figure 1) demonstrate parallel reactions: (1) photocyclization, (2) triplet state formation, and (3) monomolecular side reaction leading to degradation. For the benzene-containing unsymmetrical DCPs (figure 2) two types of intermediates were recorded in the course of laser flash photolysis experiments and interpreted as the triplet state of the initial compound **2a** and intermediate **2b**.

Finally, mechanisms of diarylethene-like photochromic transformations and unusual skeletal rearrangement of the DCPs were established.

P16

Dynamical transition in proteins observed by spin-probe relaxation

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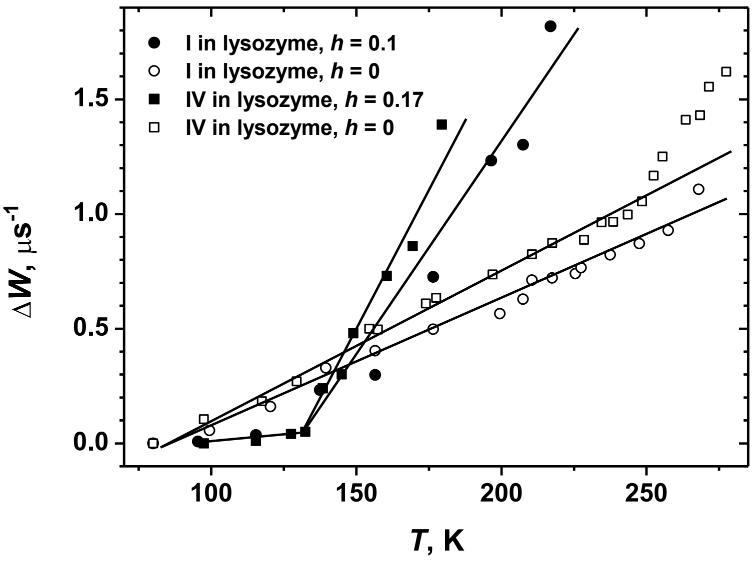
In glassy and biological media the phenomenon of low-temperature dynamical transition is well-known from neutron scattering experiments. These experiments allow deriving the mean squared displacement of hydrogen atoms. So, the dynamical transition manifests itself as high-amplitude motions of hydrogen atoms above some temperature. However, the nature of the molecule motions is unclear.



In this work, the low-temperature dynamical transition in lysozyme protein with different hydration level and with incorporated spin probes was studied by two-pulsed electron spin echo (ESE) technique. The obtained data were compared with neutron scattering data available for lysozyme in literature. This comparison allowed suggesting a new hypothesis on the nature of the dynamical transition. In particular, the sharp increase of the anisotropic relational rate (ΔW) above 130 K in hydrated lysozyme (see figure) may be related to the onset of glass transition in the hydration layer.

P17

Peculiarities of ZnTPP spin dynamics in C2-methylated Ionic Liquids studied by Time-Resolved EPR

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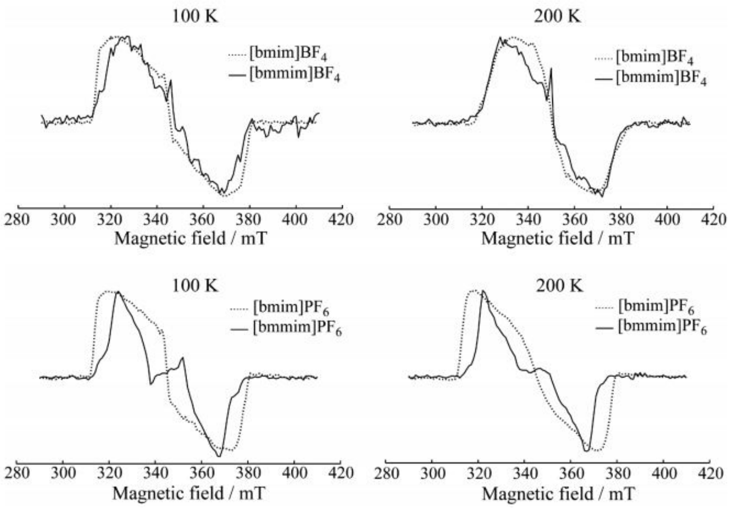
Unusual physical properties of ionic liquids (ILs) can be implemented in many different applications and are very sensitive to the structure of IL. In this work we investigate the spin dynamics of probe molecule Zn tetraphenylporphyrin (ZnTPP) dissolved in a series of ILs using time-resolved electron paramagnetic resonance (TR EPR). We compare the TR EPR characteristics in C2-methylated imidazolium-based ILs [bmmim]BF_4 and [bmmim]PF_6 and in their C2-protonated analogs [bmim]BF_4 and [bmim]PF_6 to assess the influence of C2-methylation. The corresponding TR EPR signatures are drastically different in the two types of ILs. The analysis of experimental data allows assumptions that the ZnTPP molecule is distorted in C2-methylated ILs, contrary to other organic media and C2-protonated analogs. The mobility of ZnTPP in C2-methylated ILs is smaller compared to that in C2-protonated analogs, implying different microenvironment formed around dissolved ZnTPP [1].



This work was supported by the Russian Science Foundation (No 14-13-00826).

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The structure of TMAO and TBA water solutions

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The molecules of trimethylamine-N-oxide (TMAO) and tert-butyl alcohol (TBA) are very similar. Both of them contain the same hydrophobic parts formed by three methyl groups, and their hydrophilic moieties differ slightly. Despite this fact, solutions of TBA and TMAO have different properties, which is related to the structure of TMAO and TBA solutions.

We study molecular dynamics models of TMAO and TBA solutions at different concentrations, and compare their structure with systems of random hard spheres, which represent "an ideal solution" (a random spatial distribution of particles). All-atom molecular dynamics simulation was performed in Gromacs 5.0.7 package. Force fields were from [1] for TBA, from [2] for TMAO. For water, TIP4P_2005 model was used.

TBA-TBA radial distribution functions and their local mole fraction show a tendency of the TBA molecules to contact each other even at very low concentrations (0.5 mole percent). The probability of such contacts is much higher than for random spheres at the corresponding density. It can be related with the enthalpic effect (hydrogen bond formation between TBA molecules) and hydrophobic interaction. On the contrary, the probability of contacts between TMAO molecules in solution is much less, like in the system of random spheres. We calculated also the variance of the Voronoi volume distributions for TMAO molecules in solution and for random spheres. The coincidence between TMAO solutions and the random spheres was obtained for all studied concentrations (up to 10 mole percent). On the contrary, the variance of the Voronoi volume distributions for TBA solutions is always larger than for random spheres. It reveals an inhomogeneity in the spatial distribution of TBA in solution, which is absent in TMAO solution. We also carried out a cluster analysis of the systems of solute molecules and random spheres. It was shown that the cluster characteristics for TMAO solutions are the same as for random spheres. The solutions of TBA are also different, which relates to the association process.

Thus, we can see that TMAO spatial distribution in solution is essentially random, as for random spheres. On the contrary, the spatial distribution of TBA molecules in solution deviates from random. This fact can clarify the differences in the observable behavior of solutions of these molecules.

Financial support from grants RFFI (No 15-03-03329), is gratefully acknowledged.

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Some practical aspects of registering signal with long relaxation times in Magnetic Resonance Sounding

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Magnetic resonance sounding (MRS) is a method to detect groundwater located at a depth of up to 100 m based on the registration of NMR signal from aquifers in the earth magnetic field [1]. This method is being actively developed in the last couple of decades partly due to commercial availability of MRS instruments [2]. Since the decay of MRS signal depends on pore sizes among other reasons, certain works study the effect of pore sizes on the relaxation times of MRS signal [3]. As the body of experimental data grows, the method is expanded and improved. Thus, the work [4] demonstrates the possibility of registering MRS signals with very short relaxation times (about 10 ms). This will likely enable a broader application of surface NMR to include the vadose zone, saturated silts and clays, and formations with high magnetic mineral content.

Short relaxation times of groundwater signal are partly due to small sizes of pores, in which the water may reside. Of particular interest is also the other limiting case, when pore sizes may be in the millimeter range and more, and MRS signal relaxation times may reach about 1000 ms. Although in practice MRS signals with such long relaxation times may be not that common, they have their own features that we shall discuss in this presentation.

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Lipid-mediated clusters of spin-labeled molecules in model membranes and their dissolving in presence of lipid rafts

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The clustering of molecules is an important feature of plasma membrane organization. It is challenging to develop methods for quantifying membrane heterogeneities because of their transient nature and small size. Here, we obtained evidence that transient membrane heterogeneities can be frozen at cryogenic temperatures, which allows the application of solid-state experimental techniques sensitive to the nanoscale distance range. We employed the pulsed version of electron paramagnetic resonance (EPR) spectroscopy, the electron spin echo (ESE) technique, for spin-labeled molecules in multilamellar lipid bilayers. ESE decays were refined for pure contribution of spin-spin magnetic dipole-dipolar interaction between the labels; these interactions manifest themselves at a nanometer distance range. The bilayers were prepared from different types of saturated and unsaturated lipids and cholesterol (Chol); in all the cases, a small amount of spin-labeled compounds 5-doxyl-stearic-acid (5-DSA) or 3β-doxyl–5α-cholestane (DChl) was added. The found local concentration of 5-DSA and DChl molecules was much higher than the mean concentration in the bilayer, evidencing the formation of lipid-mediated clusters of these molecules. Two-dimensional 5-DSA molecule clusters were found, whereas flat DChl molecules were found to be clustered into stacked one-dimensional structures. These clusters disappeared when the Chol content was varied between the boundaries known for lipid raft formation at room temperatures. The room temperature EPR evidenced entrapping of DChl molecules in the rafts. The obtained data provide further insights into the lipid rafts functioning.

P21

Metabolomic profiling of human blood plasma and aqueous humor

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The optical elements of the eye – cornea, lens, and vitreous humor – are avascular tissues, and their nutrition and waste removal are provided by aqueous humor (AH). The AH production occurs through the active secretion and passive diffusion/ultrafiltration of the blood plasma. The comparison of the metabolomic profiles of AH and plasma is important for understanding the mechanisms of biochemical processes and metabolite transport taking place in vivo in ocular tissues.

The quantitative metabolomic profiling was carried out with the use of two independent methods – high frequency ^{1}H NMR spectroscopy and HPLC with high-resolution ESI-MS detection. To obtain qualitative NMR spectra, the samples must be purified from proteins and lipids. Therefore, the first part of the work was the evaluation of the effectiveness of various methods of purification of blood serum from proteins and lipids for metabolomic profiling by ^{1}H NMR. It has been shown that the most effective methods of sample preparation are the extractions with methyl and ethyl alcohols followed by the sample purification from lipids. A single extraction allows to extract about 85% of metabolites from the serum sample.

The second part of the work was the determination of concentrations of a wide range of the most abundant metabolites in the human AH and blood serum and their comparative analysis. A quantitative metabolomic profile of the human aqueous humor (71 metabolites) was obtained for the first time. A comparative analysis of the metabolomic compositions of aqueous humor and blood serum show that the concentrations of the most metabolites are similar in aqueous humor and blood serum with the exception of ascorbate, whose level in AH is two orders of magnitude higher than in serum.

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The mobility of the framework linker in MIL-53 (Al) in the presence of different xylene isomers

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The separation of xylene isomers is an important process in chemical industry. The standard separation procedure can be performed by the thermal or cryogenic distillation processes, which are very energy consuming. One of the promising ways to improve this industrial process is the exploitation of microporous media that perform as a molecular sieve.

Metal-organic frameworks (MOFs), being highly tunable, versatile compounds with high internal surface area, offer a unique platform for creation of new highly efficient sorbents and molecular sieves. Several MOFs are known to have high selectivity of xylene separation. An important example is MIL-53 (Al) that has demonstrated *o-*/*p-*xylene separation factor as high as 3.5 in 298-343 K temperature range. In order to use the full potential of MOF as a tunable platform we need to uncover the molecular mechanism behind the selectivity.

Several research groups have approached this problem by combining X-ray diffraction analysis and Grand Canonical Monte Carlo computational technique, and have come to the conclusion that the separation selectivity is caused by different guest-host interaction [1-2]. They defined the preferable position of xylene in the channels of the framework and the way it interacts with it.

In present work we decided to study the rotational dynamics of xylene in MIL-53 in order to shed some light on the separation mechanism. The mobility of the phenylene fragments of MIL-53 (Al) linkers was monitored in 298-573 K temperature range. At temperatures above 420 K the linker dynamics was studied by the analysis of the spectra lineshape arising from the solid echo pulse sequence [3]. It turned out that there is no difference in linker mobility in this temperature range. To study slower dynamics at lower temperatures we have applied spin alignment technique. It has shown that temperature evolution of the linkers rotation rate constant below 400 K stopped following the Arrhenius law and was nonmonotonic [4].

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Many-particle aspects in the theory of association-dissociation reaction

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Investigation of migration dependent reactions in condensed matter leads to the necessity of going outside the limits of the applicability of the kinetic law of mass action. At small densities of reactants this is realized using non-Markovian binary kinetic equations that take into account both initial correlations of reactants and long-term ones formed in the course of the reaction. However, unlike the law of mass action, qualitative intuitive considerations are insufficient for the derivation of kinetic equations in the framework of the non-Markovian theory. More rigorous mathematical derivation is required based on many-particle treatment of the reaction system.

Traditionally the many-particle problem for the description of migration dependent reactions is formulated on the basis of the Waite concepts. In the context of these notions dilute solution is considered as gas of reactants put in neutral solvent matter. Reactivity is described by elementary rate, and translational mobility with allowance for force interaction between reactants – by the Markovian process.

For example, for association-dissociation reaction the reaction system kinetics in the thermodynamic limit is defined by an infinite-dimensional vector of the mean point density that obeys a series of connected equations equivalent to the Liouville equation. However, for arbitrary initial conditions, this series has no hierarchy property (it is impossible to recover the density of a lower order from the mean point density of a higher one) which is inherent in the classical BBGKY series of the many-particle theory of physical kinetics. Additional analysis allowed us to formulate physical requirements necessary for the obtained series to be the basis for derivation of kinetic non-Markovian equations, *i.e.,* for it to play the role of hierarchy of reduced distribution functions (RDF) of physical kinetics.

Note that the main derivations of the presented many-particle consideration have already been used by the authors without due substantiation in setting up non-Markovian binary kinetic equations for both irreversible and reversible reactions for specific cases taking place when additional simplifying physical assumptions are used.

Exciplex formation in non-polar solutions

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Experimental investigation of non-polar solutions of certain donor-acceptor systems revealed a difference in the spectra of their luminescence generated by optical and X-irradiation. An increase in the quantum yield of exciplex luminescence relative to the quantum yield of intrinsic luminescence of the excited molecule was detected experimentally under X-irradiation as compared to the case with optical excitation of the same sample. This indicates that in the given case the mechanism of exciplex formation substantially differs from exciplex production mechanism under optical excitation. It has been suggested that the main distinction is a multistage character of exciplex generation due to recombinations of radiation generated radical ion pairs.

To verify this assumption, in this work we experimentally investigated exciplex generation under optical and X-irradiation for a deliberately chosen model system, a mixture of anthracene (energy donor under optical excitation, electron acceptor under X-irradiation, intrinsic luminophore) and *N,N*-dimethylaniline (DMA, energy acceptor under optical excitation, electron donor under X-irradiation) in non-polar solution, performing the comparative experiments on the same samples in identical conditions, and theoretically calculated and compared exciplex generation efficiencies under optical and X-irradiation for varied mixture composition on the basis of two schemes.

Exciplex formation under optical excitation was described conventionally using a simple scheme that assumes optical excitation of the anthracene molecule that is subsequently deactivated by spontaneous radiation or forms exciplex with DMA emitting in a different wavelength range. Exciplex generation under X-irradiation was described on the basis of a multistage scheme including both geminate and bulk channels. These calculations explain the experimentally observed change in the ratio of the quantum yields of excited electron acceptor and exciplex, and the corresponding change in exciplex generation efficiency under X-irradiation as compared to the case of optical excitation.

Photoaccumulating systems based on thin films of TiO_2-MoO_3-V_2O_5 oxides

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The thin-film photocatalysts TiO_2/MoO_3 and $TiO_2/MoO_3:V_2O_5$ obtained through the combination of sol-gel and sintering techniques were investigated using reactions of photooxidation of probing dyes, EPR spectroscopy with *in situ* UV irradiation, scanning electron microscopy, X-ray diffraction analysis and photoluminescent detection of peroxo species [1]. It has been shown that due to accumulation of charges produced under UV illumination these photocatalysts retain oxidation activity and ability for self-sterilization in the dark for a long time after termination of illumination.

Several types of paramagnetic centers (PCs) were detected and characterized by EPR, and peculiarities of changes of PCs concentration as a function of the UV-light illumination time and in the dark afterwards allowed authors to describe the most probable detailed mechanism of the photocatalytic processes and "dark" processes after stopping the illumination. We hope that this understanding will drive us to the creation of new optimized and effective photocatalytic and antibacterial systems.

Our investigations have demonstrated that in the case of thin-film $TiO_2/MoO_3:V_2O_5$ photocatalyst a system of photoelectron-trapping centers, which are characterized by different lifetime in contact with molecular oxygen, is formed. This allows generating the peroxo compounds performing with high efficiency, which is sufficient for providing the possibility for self-cleaning (sterilization) of the photocatalyst surface during long time after finishing the UV-light exposition.

This work was supported by Russian Foundation for Basic Research (Project No 16-53-00136-Bel-a) and by the Basic Research Foundation of Belarus (Project No X16P-074).

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A new method for robust filtering of hyperpolarized multiplet spin order

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The PHIP (Para-Hydrogen Induced Polarization) method increases the sensitivity of NMR enabling new applications, for example, in NMR studies of catalytic hydrogenation processes. Amplification of the signal in the PHIP method comes from the non-equilibrium population of the nuclear spin states in the para-hydrogen molecule. Signal enhancement factors of the order of 10^2-10^5 are feasible, which significantly extends the application range of NMR spectroscopy in chemistry, biology and medicine.

PHIP signals at high magnetic field have an anti-phase character: individual lines in NMR multiplets are enhanced, but the total NMR intensity is zero. At low spectral resolution (*e.g.*, in MRI) the anti-phase lines cancel each other and the signal-to-noise ratio decreases dramatically. Furthermore, for using PHIP in MRI with the aim to increase image contrast, it is necessary to separate hyperpolarized signals from thermally polarized signals, *e.g.,* of the solvent or tissues.

There are NMR pulse sequences known, which enable selective detection of PHIP signals: OPSY (Only Parahydrogen SpectroscopY) [1] suppresses background signals and leaves only anti-phase lines in the spectrum, whereas an "out-of-phase" echo based sequence [2] suppresses the background signals and transforms the multiplet polarization of nuclei into net polarization. However, both sequences do not allow one to obtain a spectrum completely free of distortions and unwanted signals.

The aim of this work is to develop a robust filter for detecting only multiplet nuclear spin hyperpolarization. To solve this problem, we modify the OPSY and "out-of-phase" echo sequences. The developed filter efficiently converts the "anti-phase" PHIP spectrum into an "in-phase" spectrum (1) in minimal time and (2) completely suppressing the signal from thermally polarized nuclei.

The proposed method of PHIP detection can be used in studies of catalytic hydrogenation by NMR, as well as for increasing the image contrast in MRI.

This work has been supported by the Russian Foundation for Basic Research (Project No 16-33-00679).

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Influence of coal dust particles sizes on laser ignition threshold

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The ignition of low-rank coals under the influence of neodymium laser (wavelength 1.06 μm, pulse duration 120 μs) was studied [1-4]. The laser influence simultaneously stimulates coal matrix heating, diffusion and desorption of hydrocarbon volatiles, combustion of heavy hydrocarbons at the particles' surface, desorption of light hydrocarbons and their combustion in the gas phase, and, finally, the combustion of the coke residue. We distinguished three types of ignition thresholds on the analysis of glow kinetics. The first threshold corresponds to particles' heating, the second one to volatiles' ignition, and the third one to the coke residue combustion.

The purpose of this work is to study the effect of coal particles' size on the ignition thresholds of previously studied coals used in the works [1, 2]. The particle sizes in the range (100 μm – 0.14 μm) are used. Gas coal and lignite were used. The coal compositions are similar to those described in [1, 2]. Coals were ground in a ball mill. The finest coal dust fraction of ≤ 100 μm in size was selected. The fraction has a wide size distribution. The separation of smaller fractions was carried out by the sedimentation method. As in [1, 2], the samples of coals were placed in a copper container with a diameter of 5 mm and a depth of 2 mm. The first harmonic ($\lambda = 1064$ nm) of a pulsed yttrium-aluminum garnet crystal laser operating in the free-running mode was used as an ignition source. The pulse duration was 120 microseconds.

It was found that, when the particle sizes decrease in the range (100-1) μm, all three ignition thresholds decrease monotonically. With a further decrease in size, the ignition thresholds increase. This result can be associated with an increase in the relative fraction of the ash component relative to the coke residue with decreasing particle sizes $d < 1$ μm. Thus, the critical dimensions having the smallest ignition thresholds have particles of ~ 1 μm in size.

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Photophysical processes for Eu^{3+} complexes with a chiral ligand containing 1,10-phenanthroline and (–)-menthol

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Luminescent compounds of Eu^{3+} ion are promising as materials for OLEDs and biosensors [1, 2]. In this work the photophysical processes for Eu^{3+} complexes with a chiral ligand containing 1,10-phenanthroline and (–)-menthol fragments (the structure of **L** ligand is shown in figure 1) are determined. In the solid state, the $Eu(L)_2(NO_3)_3$ complex exhibits a bright red luminescence with a quantum yield of 0.87. The luminescence kinetics at wavelength of 615 nm (the $^5D_0 \rightarrow {}^7F_2$ transition) has an initial arising front with a time of 1.2 μs followed by a nonexponential decay with three exponentials times. The arising of red luminescence (1.2 μs) is associated with energy transfer from the triplet level of the ligand to the Eu^{3+} ion.

In acetonitrile the $Eu(L)_2(NO_3)_3$ complex dissociates, and there are simultaneously three particles in the solution: the free **L** ligand, complexes with one ($EuL(NO_3)_3$) and two ($Eu(L)_2(NO_3)_3$) ligands in the first coordination sphere. All three compounds have nonoverlapping luminescence spectra (figure 1). The **L** ligand luminescence (370 nm) decays with a time of 2.5 ns (in free state), and this time for $EuL(NO_3)_3$ complex (485 nm) increases to 38 ns. The $Eu(L)_2(NO_3)_3$ complex in solution exhibits a characteristic red *f-f* luminescence. The poster will present photophysical parameters for all three compounds.

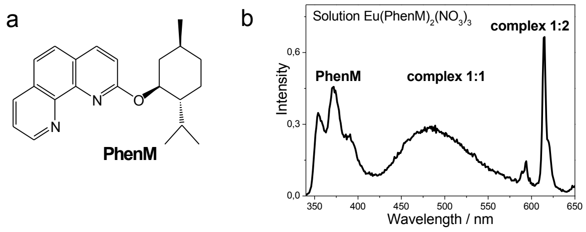

Figure 1. The structure of **L** ligand (a) and the luminescence spectrum upon dissolution of the $Eu(L)_2(NO_3)_3$ complex in CH_3CN (b).

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Study of the mechanism of sodium 2,3-disulfanylpropane-1-sulfonate (unithiol) soft oxidation by mass spectrometry with electrospray ionization

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At present time life sciences place greater focus on the study of the effect of weak physical factors, especially electromagnetic fields, on the processes occurring in the molecular systems of living organisms. Because of extremely low intensities of these factors, manifested, however, in the pronounced macroscopic reactions of living systems, biological tests are commonly used for their registration. Actually, instead of biological tests, in this case biochemical processes can be used for studying molecular systems.

As a chemical test of the effect of external physical factors on living systems, V.V. Sokolovsky proposed to use the soft oxidation of unithiol (sodium 2,3-dimercaptopropane-1-sulfonate $C_3S_3O_3H_7Na$) [1]. The unithiol test is based on determination of the nonspecific resistance of the organism according to the rate of the metabolic reaction of the thiol-disulfide transformation in human, and it was realized by amperometric titration. It was assumed that the dimensional proximity of the two SH groups facilitates the formation of an intramolecular disulfide bond during oxidation under soft conditions and, thus, allows to simulate the functional center of proteins responsible for their redox transformations.

In order to justify the validity of the unithiol test, the mass spectrometric study of the oxidation reaction of unithiol by hydrogen peroxide was carried out by a high-resolution mass spectrometer MX-5310 (Institute for Analytical Instrumentation RAS, Russia) with electrospray ionization using the modified procedure described in [2]. As the result, first of all, it was detected that in aqueous solutions unithiol self-associates $(C_3S_3O_3H_7Na)_n$, $n = 1 - 10$. Moreover, the molecules in the associates mainly form a disulfide bond between each other, and the intramolecular oxidation products of unithiol are present in small amounts.

Second, it was found that the fraction of the molecules in associates, which form a disulfide bond between themselves, increases with the growth of hydrogen peroxide concentration in the reaction mixture. However, with n increasing the change in the intensities of the analytic signals of unithiol associates ceases to be a decreasing tendency, which may indicate interconversion of associates.

Thus, the realization of the unithiol test by mass-spectrometry with electrospray ionization revealed new elementary reactions occurring during thiol-disulfide transformation. It opens up new possibilities for interpreting the influence of weak physical factors on living systems.

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Investigation of the energy profile of helix unwinding in DNA by means of atomic force spectroscopy

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DNA molecules play important roles in a variety of biological processes in living organisms. Many processes, including transcription and replication, proceed with the formation and denaturation of a double helix. Investigation of the energy profile of complexation reactions is a key to understand the mechanisms of such processes.

It was shown that an external force exerted on a complex causes a decrease in the height of energy barrier separating bound and unbound states of biomolecules. In turn, this causes a decrease in the lifetime of biomolecular complex and an increase in the probability of its denaturation. At a certain value of the force, the barrier vanishes, and intermolecular chemical bonds break. The strength of the complex is a function of the loading rate experienced by chemical bonds at the moment of rupture. The bond rupture force, plotted as a logarithm of the loading rate, can provide information about the height and position of the energy barrier along reaction coordinate.

We studied the energy profile of the rupture of a model DNA complex formed by complementary oligonucleotides by means of atomic force spectroscopy. One of them was covalently immobilized on the surface of the solid substrate, and the second one on the tip of AFM probe. Approaching and retraction between the probe and the substrate lead to the formation and denaturation of the double-stranded DNA complex. The height of the peak observed in a force-distance curve reflects the bond rupture force. By varying the probe retraction velocity, different rates of DNA complex loading were achieved. The measured dependence of the force vs. logarithm of loading rate has two linear regions with different slopes. This indicates the existence of two energy barriers in the model system under study. The positions of the barriers along the dissociation pathway, lifetime and dissociation constants of the DNA complex were estimated.

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Trehalose as immobilizer of biopolymers for room temperature pulsed dipolar EPR spectroscopy

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Pulsed Electron Paramagnetic Resonance (EPR) is among the best techniques for nanoscale distance measurements in biomolecules, including large biological complexes. Most of the pulsed EPR experiments are carried out at cryogenic temperature in order (1) to immobilize biological system with the aim to prevent averaging of anisotropic dipolar interaction between spins by rotational diffusion, and (2) to reach long phase memory time (T_m) of the spin labels. The latest trend in this field is EPR measurements at room temperature using immobilizers such as sepharose, modified silica gels (Nucleosil) and trehalose. Among all of these immobilizers trehalose is the most universal and can be used for both proteins and nucleic acids.

Therefore in this work we investigated relaxation properties of nitroxide and triarylmethyl (TAM) radicals in glassy trehalose in order to optimize the design of spin labels and to select parameters for EPR spectroscopy. We studied nitroxides with different substituents adjacent to the NO-moiety. In all cases T_m was close to 700 ns and did not essentially depend on the structure of substituents [1]. At the same time, for TAM radicals the room temperature T_m for Finland trityl is nearly independent on the radical deuteration, and is sensitive to deuteration of water and/or trehalose (T_m can exceed 2.8 μs).

There are many reports on the use of trehalose for successful storage of proteins, however, similar application of trehalose to nucleic acids and their complexes has not been addressed so far. In this work we provide the first demonstration of room-temperature EPR distance measurements in nucleic acids using trehalose as the immobilizing media. We propose an approach that keeps structural conformation and unity of immobilized double-stranded DNA [2].

This work was supported by Russian Science Foundation (Grant 14-14-00922).

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Spin probe study of $CO_2/O_2/N_2$ gas sorption in ZIF-8

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Metal organic frameworks (MOFs) are recently developed materials with astonishing adsorption characteristics. MOFs are simple for synthesis, so a variety of forms has been created, and now physical properties of this material have to be studied by modern methods. One of the promising applications for MOFs is a gas storage. So gas adsorption at MOFs is the topic of the actual research.

Due to the exceptional thermal (up to 500°C) and chemical stability, the zeolitic imidazolate frameworks (ZIFs) subgroup of MOFs was chosen for the research of gas adsorption. One of the most popular and chemically studied ZIFs is ZIF-8. It has a cubic lattice structure and sodalite (SOD) topology with 11.6 Å and 3.4 Å diameter cavities. Small pore apertures of ZIF-8 are expected to separate branched alkanes from linear. Recently ZIF-8 membranes were shown to be able to split up gas mixtures, such as H_2/CH_4, CO_2/CH_4, C_2/C_3, ethylene/ethane, propylene/propane, H_2/propane.

Electronic paramagnetic resonance (EPR) method is well used for MOFs research. As metal organic frameworks have no EPR signal, TEMPO probe molecules are used to scan the structure of the frame by a continuous wave (CW) and pulsed EPR methods through molecular mobility inside the frame.

In this work we conducted EPR experiments with TEMPO probe. CW EPR technique was applied for TEMPO@ZIF-8 system filled with different gases ($CO_2/O_2/N_2$). Line shape analysis was made to demonstrate that the high quantity of adsorbed gas inside the frame tends to increase the rotational correlation time of the system. Molecular dynamic (MD) and TGA were made as supporting methods.

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Estimation of the molar absorption coefficient of copper salicylate within the spectral range 300-350 nm

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Additional absorption has been detected in absorption spectra within the range 300 – 350 nm after addition of copper sulfate $CuSO_4{\cdot}5H_2O$ to a solution of sodium salicylate NaHSal (pH = 7.8). The additional maximum absorption was observed at 320 nm. Assuming that the additional absorption depends on the formation of copper salicylate CuSal, we have determined the molar absorption coefficient ε_{CuSal} of this complex to be $(3.8 \pm 0.02){\cdot}10^3\ M^{-1}{\cdot}cm^{-1}$. This value is almost the same as the coefficient of molar absorption for monoanion $HSal^-$ $\varepsilon_{HSal^-} = (3.6 \pm 0.04){\cdot}10^3\ M^{-1}{\cdot}cm^{-1}$, and 2.5 times to much as order of magnitude higher than $\varepsilon_{Fe^{3+}HSal^-} = (1.55 \pm 0.05){\cdot}10^3\ M^{-1}{\cdot}cm^{-1}$ for iron salicylate. The difference in ε_{CuSal} and $\varepsilon_{Fe^{3+}HSal^-}$ is explained by the difference in the initial electron states of the Cu^{2+} and Fe^{3+} ions that have the d_9 and d_5 configurations, respectively.

The effect of recrystallization of aqueous solutions of metal sulfates on the acid-base balance

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A comparative study of pH values in recrystallized aqueous solutions of manganese, copper, and iron sulfates and the calculated values for the pH levels of similar solutions obtained directly from solid salts has been performed for the first time. The trend for the positive deviation of the pH_{rec} values from the pH_{calc} values has been established. The positive deviation was the strongest in the case of iron sulfate solutions. The sample of the recrystallized aqueous solution (recrystallized water) consisted of water obtained by melting of the initial aqueous solution after freezing of 60% of the solution (by volume). Four hypotheses were proposed to explain the positive deviation of pH_{rec} from pH_{calc}: (1) low CO_2 concentration; (2) more efficient adsorption of anions on the freezing front compared to that of cations; (3) mechanochemical and radiation chemical processes that occur upon the melting of ice; and (4) Fe^{2+}-catalyzed decomposition of hydrogen peroxide formed in the recrystallized solution. Analysis of the putative causes showed that the fourth hypothesis provided the most adequate explanation of the difference between pH_{rec} and pH_{calc}. The formation of hydrogen peroxide in recrystallized water is proposed to occur due to the recombination of OH radicals formed during the radiation chemical processes.

Photochromism of diarylethenes in solutions and polymer matrices

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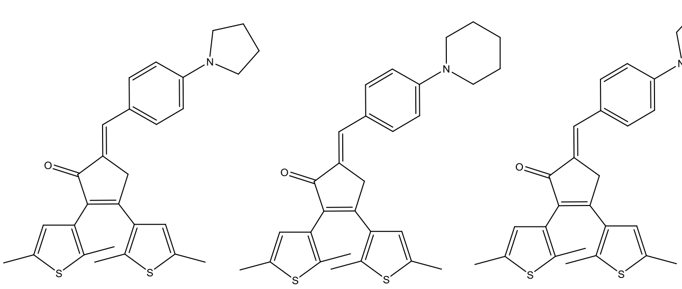
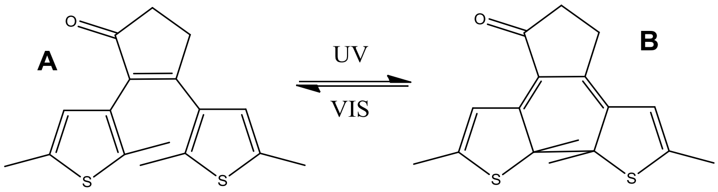
Fluorescent photochromic materials draw strong interest for their possible application in organic photonics such as optical logic systems, optical memory, visualizing sensors, as well as characterization of polymers and biological systems.

In current work both photochromic and fluorescent properties of several diarylethenes were investigated (see scheme 1).



Scheme 1. Diarylethenes substituted by dimethylaniline derivatives that were studied.

Spectral and photochromic parameters of investigated compounds have been measured in four solvents at room temperature. Quantum yields of photochromic transformation A ↔ B (scheme 2) $\phi_{A\to B}$ and $\phi_{B\to A}$, as well as extinction coefficients of closed-ring isomer, were determined by kinetic methods.



Scheme 2. Typical reaction of photochromic transformation of diarylethenes.

It was found that the photocyclization reaction quantum yield of all compounds decreases with the increase of solvent polarity. In addition, the solvent polarity is revealed to significantly affect fluorescence. Increasing the value of the dielectric constant was found to result in a strong shift of the emission band position from 450 nm (*n*-hexane) to 550 nm (DMSO and ethanol) for all three compounds. The intense emission of the compounds became weak and hardly detectible in *n*-hexane.

Stereoselectivity of photo-CIDNP in chiral systems

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Stereoselectivity of the photoinduced electron transfer has been investigated with the model compounds (R/S)-naproxen (NPX) linked to (S)-*N*-methylpyrrolidine (Pyr) or tryptophan.

Based on chemically induced nuclear polarization (CIDNP) and fluorescence data, the scheme of excitation quenching of NPX excited state in the dyads has been proposed, including the intramolecular electron transfer, biradical zwitterion, exciplex, and back electron transfer.

Photo-CIDNP experiments have been performed with individual diastereomers and with their mixture. The experiments show that the effect for R,S-diastereomer is twice bigger than for S,S-analog. A theoretical modeling of the effect allows to conclude that electron-nuclear hyperfine interaction is responsible for the difference in the CIDNP effects in these diactereomers.

Also, as it has been shown in the experiments with diastereomers mixture, the ratio of the CIDNP values is dependent on concentrations. X-Ray data at room temperature indicate the possibility of forming bonds joining diastereomers. In particular, it has been demonstrated that molecules in both (R,S)- and (S,S)- dyads are linked by N-H…O hydrogen bonds. So, it has been assumed that the effect is caused by dimerization of the dyads and difference in the efficiency of electron transfer processes in the homo- and hetero-dimers.

The mathematical model allows us to describe the experimental dependence of the effective CIDNP on dyad concentration. It has pointed to participation of excited diastereomers dimer in electron transfer process and can be considered as one of the first experimental examples of the simplest autocatalytic systems that were predicted in the F. Frank's theory of the origin of chiral compounds.

Influence of an outer-sphere anion on the crystal structure of photosensitive complexes $[Co(NH_3)_5NO_2]XNO_3$, (X = Cl, Br, I)

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In the 1980s, it was observed that crystals of $[Co(NH_3)_5NO_2]XY$ complexes under the photo-isomerization of $[Co(NH_3)_5NO_2]XY \rightleftarrows [Co(NH_3)_5ONO]XY$ relax with significant mechanical responses (figure 1).

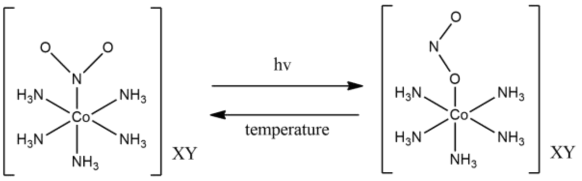

Figure 2. Photo-isomerization of Co(III) complexes

This phenomenon has received a name - the photomechanical effect, and in the English-speaking literature – the photosalient effect. This phenomenon is very interesting, because it helps us study in detail the mechanisms of photoconversion in such crystals, as well as the phenomenon of feedback. Besides, photo-isomerization in Co(III) complexes is single crystal-to-single crystal, that's why it can be studied by X-ray diffraction method. In addition, applications of the photomechanical effect are possible in various areas: from medicine to instrument engineering.

In this work, a crystal structure analysis of the known complex of $[Co(NH_3)_5NO_2]ClNO_3$ and the newly obtained complexes $[Co(NH_3)_5NO_2]BrNO_3$ and $[Co(NH_3)_5NO_2]INO_3$ was carried out. The crystal structure of $[Co(NH_3)_5NO_2]ClNO_3$ and $[Co(NH_3)_5NO_2]BrNO_3$ are the same, but differ from $[Co(NH_3)_5NO_2]INO_3$, despite the same symmetry group (Pnma). The calculation of the voids around the nitro group in the crystals of these complexes shows us that the activation energy of the photoisomerization reaction decreases in the $ClNO_3$, $BrNO_3$, and INO_3 series.

Assessments of the presence of hydrogen bonds formed by the nitro groups of these complexes were made. On the basis of hypothesis that the photomechanical effect depends on hydrogen bonds at nitro-groups inner-sphere cations, it was predicted that the mechanical responses weakened in $[Co(NH_3)_5NO_2]BrNO_3$, as compared with $[Co(NH_3)_5NO_2]ClNO_3$, and the effect was absent in $[Co(NH_3)_5NO_2]INO_3$.

The possibility to operate the homogeneous propane pyrolysis by CO_2-laser radiation

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The propane pyrolysis is one of the main processes to produce light olefins. The process takes place at the temperatures above 750°C. This leads to a rapid deterioration of reactors and formation of undesirable compounds like coke and heavy hydrocarbons.

The propane pyrolysis was studied in the presence of CO_2-laser radiation in order to raise process efficiency. Ethylene is one of the main products of the reaction. Absorbing the radiation with wavelength 10.6 μm it turns into an excited state and then relaxes. Thus a gas mixture is heated. In this case a high-temperature zone is formed on the reactor axis and the process is homogeneous. However the main part of energy for the endothermic pyrolysis process can be introduced into the reactor through the reactor walls. The experiments were carried out using the modeling reactor with laminar flow in order to demonstrate the possibility of the process control by radiation.

In the absence of radiation the conversion is monotonically increasing with the walls' temperature. The threshold of the pyrolysis process was found at 590°C. In the presence of laser radiation the threshold of reaction is decreased down to 560°C and the propane conversion is significantly increased. The focusing of the radiation from 12 mm to 3 mm results in sharply rising conversion. The increase of the conversion in the presence of radiation can be explained by an increase in temperature on the axis of the reactor. But it is due not only to thermal effect. The process of pyrolysis is described by a radical-chain mechanism. The chemically active radicals are important participants in the process. A previously developed kinetic scheme shows that the radicals appearing at the beginning of the chain are $C_2H_5\bullet$ and $CH_3\bullet$, the radicals responsible for chain propagation are $n\text{-}C_3H_7\bullet$, $H\bullet$, $iso\text{-}C_3H_7\bullet$ and at the chain termination the acting radicals are $CH_3\bullet$ and $iso\text{-}C_3H_7\bullet$. The numbers of radicals formed in the high-temperature zone is excessive in comparison with the main volume of the reactor. These radicals diffuse into the bulk of the reactor and start the reactions in the entire volume. By focusing the beam the intensity increases from 27 W/cm^2 to 425 W/cm^2. Accordingly the temperature on the axis and the number of generated radicals also increase in this area and in the low temperature zone.

Thus, the use of the laser provides an increase in the conversion. It is possible to operate the propane pyrolysis by the laser radiation at relatively low temperatures. The laser radiation also can be an "initiator" which only generates reactive radicals and the remaining necessary energy comes from the walls.

Primary photochemical processes for hexacloroosmate(IV) in aqueous solutions

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Potential applications of photochemistry of the noble metal complexes are photocatalysis and oxygen-free photodynamic therapy of malignant tumors. In many cases, the information concerning their photochemical properties is not complete. Mechanisms were put forward based on the results of the stationary experiments; these mechanisms should be verified by application of modern time-resolved methods.

In this work, photochemistry of the $OsCl_6^{2-}$ complex was studied by means of stationary photolysis, nanosecond laser flash photolysis and ultrafast kinetic spectroscopy (with a 100 fs time resolution) in aqueous solutions. The only process is photoaquation (1), which is fully completed within 100 ps. Quantum yield of photoaquation is wavelength-dependent.

$$Os^{IV}Cl_6^{2-} + H_2O \xrightarrow{h\nu} Os^{IV}Cl_5(OH)^{2-} + Cl^- + H^+ \qquad (1)$$

Based on the experimental data, two possible reaction mechanisms were proposed (electronic and vibrational excitation are depicted as * and “hot”). The difference between these mechanisms is in the nature of the Os(IV) intermediates.

Mechanism 1

$$Os^{IV}Cl_6^{2-}({}^3T_{1g}) \xrightarrow{h\nu} {}^3(LMCT)_{hot}$$

$${}^3(LMCT)_{hot} \rightarrow Os^{IV}Cl_6^{2-}({}^1T_{2g}{}^*)_{hot}$$

$$Os^{IV}Cl_6^{2-}({}^1T_{2g}{}^*)_{hot} \rightarrow Os^{IV}Cl_6^{2-}({}^1T_{2g}{}^*)$$

$$Os^{IV}Cl_6^{2-}({}^1T_{2g}{}^*) \rightarrow Os^{IV}Cl_6^{2-}({}^3T_{1g})$$

$$Os^{IV}Cl_6^{2-}({}^1T_{2g}{}^*) \xrightarrow{H_2O} Os^{IV}Cl_5(H_2O)^{2-} + Cl^-$$

Mechanism 2

$${}^3(LMCT)_{hot} \rightarrow \{Os^{IV}Cl_5^-...Cl^-\}_{hot}^{cage}$$

$${}^3\{Os^{IV}Cl_5^-...Cl^-\}_{hot} \rightarrow \{Os^{IV}Cl_5^-...Cl^-\}$$

$${}^3\{Os^{IV}Cl_5^-...Cl^-\} \rightarrow Os^{IV}Cl_6^{2-}({}^3T_{1g})$$

$${}^3\{Os^{IV}Cl_5^-...Cl^-\} \xrightarrow{H_2O} Os^{IV}Cl_5(H_2O)^- + Cl^-$$

The financial support of the Russian Science Foundation (Grant 15-13-10012) is gratefully acknowledged.

Collective vortex-like patterns of the diffusive motion in liquid argon. Computer modeling

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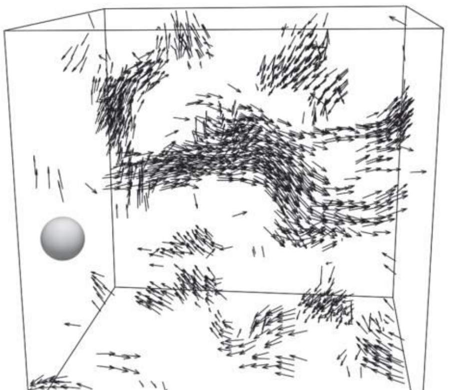
Displacements of molecules in liquids are inevitably collective. In dense liquids there is no such an empty space that a single molecule could move. Therefore, a single molecule can move only together with other molecules as a part of a group. In this work, we propose a method to visualize collective movements of atoms in the molecular dynamics model of liquid argon (50 000 atoms in a box with periodic boundary conditions, Lennard-Jones potential with the conventional parameters, reduced temperature, density, and pressure $T^* = 0.85$, $\rho^* = 0.84$, and $P^* = 0.85$). First, we calculate the displacements of all the particles over quite a long time interval Δt. Then, we consider atoms within a sphere of a given radius R_0 and calculate the vector $\Delta\mathbf{R}$ of the average displacement of these atoms. The more correlated these movements, the larger is $\Delta\mathbf{R}$. Thus, the quantity ΔR is a measure of correlation of movements within the sphere. We arrange the sphere centers in points of a lattice dividing each edge of the model box into 30 pieces. Thus, there are $30\times30\times30 = 27000$ points, and to each of them we attach the vector of average displacement of particles located within the sphere centered at this point. Such a procedure allows one to consider the relative positions of the vectors $\Delta\mathbf{R}$ throughout the model space; *i.e.,* it enables one to construct a field of vectors of average displacements of atoms.

Figure presents a typical visualization of average displacements of particles (here $R_0 = 0.85$ nm, $\Delta t = 100$ ps). We see that the clusters of comoving particles form long winding flows that look like a part of a vortex. Clusters extend over long distances, much longer than atom diameter. The vortex-like patterns change noticeably in 20-30 ps. These structures can be detected when observing atom displacements over long time intervals, on the order of hundreds of picoseconds, and over long distances, about tens of nanometers. Obviously, there is a hierarchy of structures in the liquid: clusters observed at $\Delta t \sim 10$ ps and $\Delta t > 100$ ps are absolutely different.



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Spin trapping studies of conformation changes in albumin induced by the terahertz radiation: Interaction with NO

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Conformational rearrangements caused by the THz radiation in albumin inevitably affect the transport properties of the protein and thus have biological consequences. We showed in our previous studies that THz irradiation of the film samples of bovine serum albumin (BSA) causes changes of oxygen adsorption on the active sites of BSA molecule. In the present work we studied the changes of adsorption and reactivity of BSA towards NO – one of the most essential biological mediators involved in many physiological and pathologic processes. NO is a unique secondary messenger in cells. It is paramagnetic and interacts with the paramagnetic sites in BSA. NO is known to form stable complexes with albumin.

NO was obtained through the interaction of sodium nitrite with $FeCl_3$ in the presence of HCl. THz-irradiated and non-irradiated BSA film preparations were transferred into aqueous solutions, and NO was bubbled in the solutions through a capillary. The interaction of NO with BSA was followed by means of spin trapping with 1,2,2,5,5-pentamethyl-3-imidazoline-3-oxide (PMIO). This spin trap has an amine nitrogen atom and thus it can be protonated. Spin adducts of both types – protonated and non-protonated, differing in hyperfine splitting constants, – can be observed within pH 3 to 6.5. It was discovered that the interaction with the THz-irradiated BSA samples involves more efficient oxidation of NO into NO_2 than the interaction with non-irradiated preparations. The presence of NO_2 causes local decrease in pH, which is exhibited in EPR spectra as an increase in the ratio of the signal intensities of the protonated to non-protonated spin adducts. So, the complex of NO with irradiated BSA turns out to be weaker than that with non-irradiated BSA. Experiments with decreased oxygen concentration (after oxygen removal from solution) showed that even in this case NO is oxidized at a higher rate and to a higher extent in the solutions with irradiated BSA than in the solutions with non-irradiated BSA. Possible reason for accelerated NO oxidation may be conformation changes induced by the THz radiation In particular, preliminary semi-empirical simulations suggest that the proline fragment of BSA may be the structural unit responsible for the change in the reactivity of BSA towards NO.

Photochromic properties of a 2,3-diarylcyclopentenone

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Organic photochromic compounds have attractive properties for the application to optical memories, switches and non-linear optical medium [1]. One of prospective classes of organic photochromes are diarylethenes, having such advantages as absence of dark reactions, high quantum yields, rather high photostability, and preservation of a photochromism in solid state, which is a great scarcity among organic photochromes. Photochromism of diarylethenes is caused by transitions between two isomers called open and closed forms (figure 1). Recently synthesized 2,3-diarylcyclopentenones [2] have unique abilities to the chemical modification of the cyclopentenone ring.

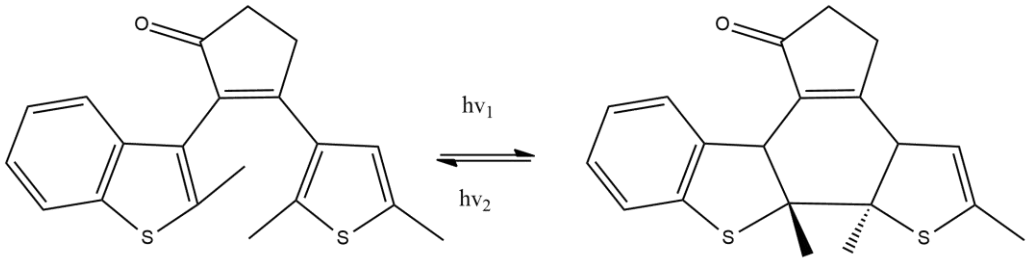

Figure 1. Photochromism of 2,3-bis-(2,5-dimethyltiophen-3-yl-cyclopent-2-en-1-on) (DMTC).

Primary photochemical properties of DMTC (figure 1) were studied by means of stationary and nanosecond laser flash photolysis (LFP). Quantum yields of direct and inverse reactions and molar absorption coefficient of the closed form in CH_3CN were determined to be 0.17, 0.042 and 7500 $M^{-1}cm^{-1}$. In the LFP experiments the formation of the triplet state of the open form was recorded, which was shown to be parallel reaction to the ring closure. Spectral and kinetic parameters of the triplet state are determined. Prolonged irradiation of DMTC results in photodegradation.

Finally, mechanisms of diarylethene-like photochromic transformations and unusual skeletal rearrangement of the DCPs were established.

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Free radical diallyl disulfide rearrangement in the KOH/DMSO system

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Svetlana V. Amosova, Boris A. Trofimov

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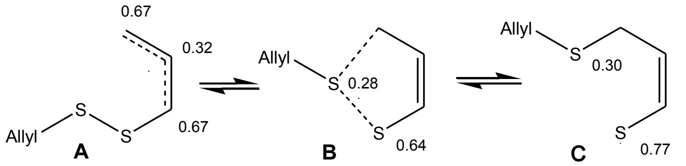
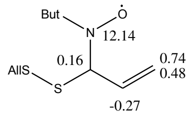
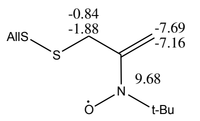
Diallyl disulfide (**1**) is known as a natural phytoncide contained in onions and garlic, and causes their useful properties. Under the influence of some reagents, **1** is able to rearrange *via* S-centered radicals (**C**), forming propene-1,3-dithiol derivatives. Reduction of yields of final products in the presence of typical inhibitors of radical processes stimulated the use of EPR methods in the spin trapping technique (MNP, ND, PBN) and quantum chemistry (DFT) to study the rearrangement reaction **1** in the overbased DMSO/KOH medium. Indeed, in the EPR spectra, the signals of spin adducts with radicals All-SS-C$^{\bullet}$H-CH=CH$_2$ (α-radical) and All-SS-CH$_2$-C$^{\bullet}$=CH$_2$ (β-radical is a rearranged α-radical), formed due to the oxidation of anions of **1**, were detected. To estimate the probability of formation of free radicals during the rearrangement of **1** and the stability of their spin adducts, quantum-chemical calculations were performed by the ub3lyp/aug-cc-pvdz method, which showed that the total energy of the α-radical (A) is significantly lower than the β- (27.8 kcal/M) and γ- (94.3 kcal/M) radicals. The distribution of the spin density in **A** was 0.7, 0.3, 0.7 on the α, β and γ atoms of the allyl fragment, which indicates a delocalization of the radical center and, accordingly, spin adducts can be expected to form in all three positions. DFT calculated HFS constants in α-, β- and γ- spin adducts agree with experimental data.

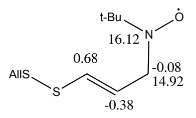




α-adduct



β-adduct



γ-adduct

Contrary to expectations, spin adducts of **C** are not observed due to lower thermodynamic stability. The calculated values of the equilibrium constants indicate that under the conditions of thermodynamic equilibrium the concentrations of **A** and **C** radicals will be close, and the relative stability of the latter will become the determining factor for the formation of a particular spin adduct. The results obtained allowed us to establish a radical mechanism for the rearrangement of **1** with the participation of S-containing C-centered radicals in the presence and in the absence of an alkylating reagent.

EPR spin probe approach for MOF investigation

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Electron paramagnetic resonance is a spectroscopic technique for the study of unpaired electronic spins. It has been successfully applied to many areas of science, including MOFs. For instance, EPR spectroscopy enabled investigation of photocatalysis in MOFs occurring due to electron transfer inside the framework, and structural transitions driven by temperature or pressure in flexible MOFs using spin probe detection, determination of parameters relevant for quantum computing, and magnetic properties of these systems. However, despite an extensive range of applications, this area of research is not well developed, partly because of the difficulties arising during sample preparation. To apply the technique one need to incorporate EPR-active species into the structure.

Recently we have shown that post-synthetic adsorption of stable nitroxide radicals, followed by EPR detection, is a powerful approach for studying the breathing behavior and guest-host interactions in structurally-flexible MOFs [1]. The huge advantage of the new approach is the ability to use negligible amounts of guest molecules to probe the MOF’s interior, without altering the framework structure. For example, by embedding three derivatives of TEMPO (4-oxo-TEMPO, 4-hydroxo-TEMPO, 4-acetamido-TEMPO) in the MIL-53(Al) framework, we could monitor structural “breathing” of this MOF with temperature in order to gain deeper understanding of the underlying guest-host interactions [2]. Different substituents in piperidine ring led to different mobility and reactivity of the corresponding nitroxides. The obtained EPR data and Molecular Dynamics (MD) calculations showed that the efficiency of nitroxide radical reaction with μ2-hydroxo group of MIL-53(Al) strongly correlates with the character of its molecular motion, and the reversibility of this reaction upon structural “breathing” is a general phenomenon. These findings have been applied for further investigation of μ2-hydroxo group activity in other MOFs.

CW and Pulse EPR techniques were applied for nitroxide radical@MOF system. Molecular dynamic calculations were made for qualitative explanation of experimental results.

We are grateful to the RSF (№ 14-13-00826) and the RF President's Grant (MK 3272.2017.3) for financial support.

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Manipulation of quantum dots using optical trap

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Colloidal quantum dots are fluorescent semiconductor particles with sizes of several nanometers. Due to their optical properties, including the dependence of fluorescence spectra on size, they are often used in various studies as fluorescent probes. In addition, quantum dots are considered as objects for photovoltaics and semiconductor nanodevices. The ability to control the position of single quantum dot allows to study the individual properties of these particles, as well as their influence on each other. A modern tool to manipulate the position of micro and nanoparticles is optical traps. The particles are trapped by a well-focused laser beam. Studies using optical traps of nanodiamonds, quantum dots, single DNA molecules attached to polystyrene microspheres are known.

We created an optical trap according to the scheme of an inverted microscope. To form optical trap, a 1064 nm continuum-wave laser beam is focused by a microscope objective. The quantum dots of ZnCdSeS with a peak of fluorescence at 530 nm were trapped from dodecane solution in a microfluidic cuvette. The size of quantum dots according to the manufacturer's (PlasmaChem) data is less than 10 nm. To observe fluorescence of the trapped dots, they were excited by a defocused 405 nm laser beam. The image was recorded by a CCD camera. During the experiment an increase of fluorescence intensity was observed, which is apparently due to an uncontrolled increase of the number of quantum dots in the optical trap. The position of the trapped quantum dots relative to the cuvette can be changed in three dimensions, moving the cuvette relative to the microscope objective.

Thus, we have a tool to manipulate nanoparticles. In addition to quantum dots, we manipulated polystyrene microspheres and micro-diamonds of about 1 μm in size using our optical trap.

AIMD of radicals in frozen solutions and its relation to Overhauser-DNP in insulating solids

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We have investigated the modulation of the electron-nuclei hyperfine interactions due to the vibrational modes of a radical [1]. This coupling embodies a magnetic relaxation pathway that facilitates electron polarization transfer to the nuclei and thus signal enhancement in NMR (NMR hyperpolarization). Using *ab initio* molecular dynamics simulations, we have examined the mechanism and time evolution of the enhancement: which particular motional modes facilitate single quantum and double quantum transitions and how the polarization is transferred to bulk solvent as well as the magnitude of this effect.

We shed light on the origin of the recently discovered Overhauser effect – mediated dynamic nuclear polarization in insulating solids containing the BDPA radical [2], an effect that was otherwise traditionally confined to metals or liquids. Our findings reveal one possibility why the particular class which the BDPA radical represents exhibit this effect, thus facilitating the rational design of new radicals that facilitate Overhauser effect enhancement in insulating solids.

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Generating long-lived order in multi-spin systems by adiabatically ramped RF-fields

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Long-lived spin state is an important new concept in the field of Nuclear Magnetic Resonance (NMR). These states are used to store spin hyperpolarization, to study slow transport, to investigate slow molecular dynamics, *etc.* Long-lived singlet states are quite known in spin pairs where the dipole-dipole interaction, typically, the main cause of relaxation, cannot drive singlet-triplet transitions. One of the methods of generating such states in spin pairs is given by slow (adiabatic) switching of a radiofrequency field.

Potentially, long-lived states can exist in systems with more than two coupled spins. For example, it is of interest to study long-lived states in systems containing two spin pairs. In such systems there are two possible kinds of long-lived states: singlet state of each particular spin pair and singlet-singlet state of the two pairs. It is intriguing to develop methods for generating such long-lived states and to perform their comparative analysis, *i.e.,* to assess their lifetimes and their dependence on the molecular structure.

In this work we propose methods for generating long-lived states in four-spin and five-spin systems by adiabatically ramped RF-field. To analyze spin order conversion pathways, we performed correlation of spin states at zero RF-field and at high RF-field; we also determined suitable offsets of the RF-field from the center of the NMR for transferring the population of the T_+T_+ state (most populated at equilibrium conditions) to the singlet-singlet state due to adiabatic switching of the RF-field. We have also determined the maximum NMR signal of a four-level system remaining after applying the RF-on and RF-off switches. Numerical modeling was run to obtain the optimal parameters for improving the efficiency of generating singlet-singlet states. Last but not least, we performed experiments for generating all possible long-lived states in four-spin and five-spin systems. Such experiments revealed the abovementioned kinds of long-lived states; their lifetimes were measured and analyzed.

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Extending the lifetime of hyperpolarized propane gas through reversible dissolution

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Parahydrogen Induced Polarization (PHIP) is a promising method of NMR signal amplification that can be applied in MRI studies for such sciences as catalysis and medicine. However, the wide use of gases hyperpolarized by the PHIP method is limited by their short relaxation times (0.6 s for propane in 7.4 T). Therefore, the investigation of preserving polarization for a long period of time is of great scientific and practical interest. In this paper, the possibility of increasing the lifetime of a hyperpolarized gas (propane) by dissolving in deuterated organic solvents (acetone, methanol) was demonstrated.

It was found that the relaxation time gains 50-fold increase because of the relaxation mechanism alteration: in the liquid phase the dipole-dipole relaxation mechanism predominates, while in the gas phase the spin-rotation relaxation is the main mechanism. The measured hyperpolarization lifetime of propane (T_{HP}) was 35 seconds, while the T_1 time of propane in acetone was found to be 38.7 and 33.3 seconds for CH_2 and CH_3 groups, respectively. It is important that T_{HP} highly depends on the concentration of O_2, which being paramagnetic creates an effective relaxation channel for the hyperpolarization.

Afterwards, MRI images were obtained in the XY and XZ planes for a 10 mm NMR tube with hyperpolarized propane dissolved in deuterated acetone. The total time of the experiment was 1.7 seconds, FLASH MRI pulse sequence was used and the echo time (TE) was 14.8 milliseconds. The key result of the studies conducted is that the hyperpolarized gas was successfully extracted from the solvent back into the gas phase with preserving hyperpolarization level as it was in the solvent phase. Thereafter, ^{1}H NMR spectra of gas phase hyperpolarized propane retrieved from the solvent were obtained.

UV-degradation of some bisphenols and their complexes with β-cyclodextrin

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Bisphenols (BPs) are widely used in production of polycarbonate plastics, epoxy resins, adhesives, coatings for drink packages and food cans. As a consequence BPs have been widely detected in the environment and food products. However, many (*e.g.,* well-known bisphenol A) of them belong to endocrine-disrupting chemicals (EDCs) and were reported to possess acute toxicity and estrogenic activity. Conventional treatment techniques are not effective enough for removal of the majority of EDCs, while photochemical and photocatalytic processes have proved themselves as perspective methods for water purification and disinfection from these compounds.

In this work aqueous photochemistry of three bisphenols (4,4'-hydroxyphenylmethane (BPF), 4,4'-hydroxyphenylethane (BPE) and 4,4-bis(4-hydroxyphenyl)valeric acid (DPA)) and their complexes with β-cyclodextrin was studied by means of stationary (XeBr excimer lamp, 282 nm) and laser flash photolysis (6 ns, Nd:YAG laser, 266 nm). Main attention was paid to determination of primary photochemical processes, nature, spectral and kinetic properties of excited states and primary intermediates and their further transformation products.

For all studied systems the main primary photochemical process was observed to be photoinization with formation of phenoxyl radical – hydrated electron pair. In present work quantum yields of primary intermediates formation and BPs photodegradation, rate constants of intermediates disappearance and their spectral properties were determined. Also, on the basis of all obtained data, a scheme of BPs transformation in aqueous solutions was proposed.

For all studied compounds inclusion of BPs in cyclodextrin cavity leads to great increase of photodegradation quantum yields but does not substantially affects photolysis mechanism.

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The NMR and MD study of glycyrrhizin membrane-modifying activity

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Glycyrrhizic acid (glycyrrhizin, GA) is a natural oligosaccharide contained in liquorice root. Due to its amphiphilic properties GA can form supramolecular complexes with a wide range of hydrophobic drugs resulting in increase of drug solubility, stability and bioavailability. It is suggested that bioavailability enhancement may be caused not only by the increase of the drug solubility, but also by the GA influence on the properties of lipid membranes. In the present work we have tried to clarify the mechanism of GA action on drugs bioavailability by studying the mechanism of GA influence on the properties of lipid membrane.

In the NMR experiments unilamellar liposomes were used as a model. We have studied the GA influence on the mobility of lipid molecules using nuclear magnetic resonance (NMR) relaxation technique with shift-reagents addition. The relaxation times are sensitive to the mobility of groups of protons, so, using NMR one can obtain data on the mobility of different functional groups of molecule and make assumptions about GA localization in membrane. We have also studied the phase transitions in lipid membrane by means of NMR. To confirm the results of NMR study, the molecular dynamics (MD) simulations of GA interaction with lipid bilayer were carried out.

We have established that GA interaction with liposome leads to changes in lipid mobility and phase transition temperature. It could mean that GA is able to integrate into lipid bilayer. NMR and MD results point that GA is integrated only in the external half-layer. Also the joint action of GA and cholesterol results in the formation of rigid structures and pores in the bilayer.

This study sheds some light on the mechanism of the drugs bioavailability enhancement in the presence of glycyrrhizin. Since it is believed that a change in the phase state of the lipid bilayer can lead to the formation of channels in the membrane, these results contribute to an understanding of the mechanism of GA action as a drug delivery agent, as well as the mechanism of its own biological activity.

Photochromic materials based on metal-organic coordination polymers

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Relevance of this work is caused by the problem to create solid photochromic materials demonstrating both high quantum yields of photocoloration/photobleaching and improved resistance to photodegradation. Materials of this type are prospective for applications in molecular electronics. The goal of this study was to create the supramolecular adducts of organic photochroms and metal-organic coordination polymers and to evaluate their photochemical characteristics. We have synthesized the photochromic adducts of the metal-organic framework (MOF) with the composition $[Zn_4(dmf)(ur)_2(ndc)_4]\cdot 5DMF\cdot H_2O$, where ndc^{2-} = 2,6-naphthalenedicarboxylate, ur = urotropin, dmf = *N,N*-dimethylformamide (further – MOF-1) with *trans*-stilbene and 2,3-bis-(2,5-dimethylthiophen-3-yl-cyclopent-2-en-1-one), further referred to as DMTC, belonging to diarylethenes (which are among a few classes of organic photochroms retaining high photochemical activity in the solid state).

Adduct of MOF-1 with *trans*-stilbene [1] demonstrates *cis-trans* isomerization characteristic for stilbenes. Quantum yields were an order of magnitude higher than for polycrystalline *trans*-stilbene and comparable with the typical values for solutions. No side reactions characteristic for solutions were observed. Adduct of MOF-1 with DMTC [2] has demonstrated the reversible photocyclization typical for diarylethenes. Quantum yield for the adduct was 40% higher than for solid DMTC. Both the parent photochrom and its adduct are prone to photodegradation caused by monomolecular side reaction.

In general, the performed study has demonstrated the prospects of the chosen approach to the creation of new solid photochromic materials.

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Nuclear long-lived state in ^{15}N-enriched azobenzenes

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The molecule of azobenzene (AB) has recently drawn much attention because it can be photo-switched between its *cis* and *trans* forms. There have been many proposals to exploit this property, *e.g.,* for solar energy storage or biomolecular applications. Recently it was found that nuclear spins of the *cis* form can be efficiently hyperpolarized. For conservation of this non-thermal polarization the relaxation behavior has to be characterized in detail. Here we present results on ^{15}N relaxation and its dependence on the external magnetic field. Field cycling experiments using a shuttling device were performed in the range from 10^{-6} T to 16.4 T. The relaxation dispersion for *trans*-AB (figure 1a) is shown in figure 1c. The strong decrease of T_1 for fields above 1 T is ascribed to the growing importance of chemical shift anisotropy. Slower relaxation at high field can be obtained when long lived spin states (LLS) are exploited. These states of singlet symmetry are immune to dipolar relaxation, but can be accessed only by special pulse sequences. The optimization of such sequences for a system of 12 coupled spins-½ will be discussed. In figure 1b this longevity is demonstrated; while T_1 at 16.4 T is 4 s, T_{LLS} is found to be longer than 2 min. Our measurements are useful for understanding the complicated relaxation processes of the LLS in multi-spin systems. The discovered longevity also opens the potential implementation of ^{15}N-enriched azobenezene for NMR measurements of slow molecular diffusion.

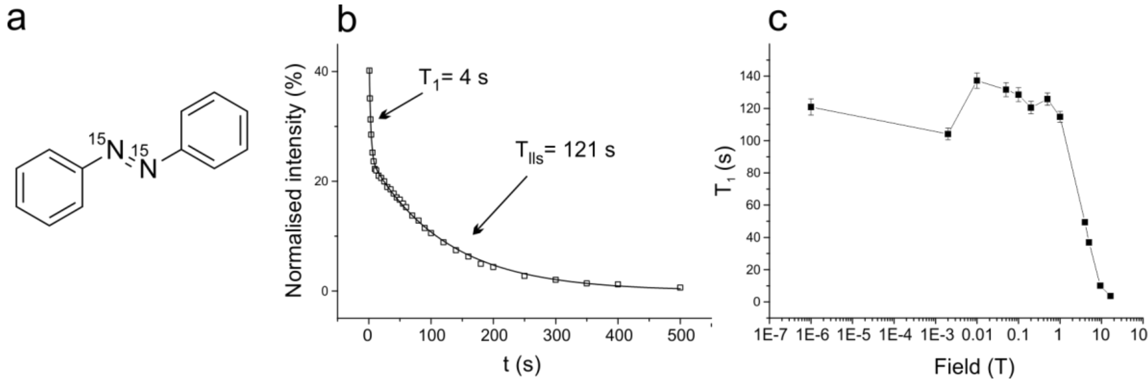

Figure 1. Study of ^{15}N nuclear relaxation in azobenzene. (a) Molecule of *trans*-azobenzene. (b) T_{LLS} measurement of ^{15}N at 16.4 T. (c) Dependence of T_1 on the magnetic field.

Investigation of glycyrrhizic acid influence on a lipid bilayer

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Glycyrrhizic acid (GA) enhances the action of several drugs. The mechanism of this enhancement is supposed to be connected with impact of GA on the permeability of membranes, particularly, with the formation of additional voids. Using all-atom molecular dynamic simulations we study the influence of GA on model lipid bilayers.

First of all, the ability of GA to penetrate into lipid bilayer from surrounding water was shown. The GA molecule that is situated inside the bilayer diffuses between lipid tails but predominantly localizes near the lipid heads. Using Voronoi-Delaunay method we were looking for additional voids in the bilayer that can appear due to a GA molecule. Empty spheres inscribed between atoms of the system were calculated. We observed that GA does not induce the appearance of large voids. Lipid tails form the homogeneous environment around the GA molecule. Thus, the supposition that GA enhances the permeability of lipid bilayers by creating additional voids does not find confirmation.

The clustering of several GA molecules inside lipid bilayers was studied. As it was shown before, GA molecules form stable associates in water. Formation of such associates is caused by hydrophobic interactions, *i.e.,* due to existence of water hydrogen bonds network. In disordered non-polar environment (liquid heptane, DOPC bilayer), as we revealed, stable GA associates do not appear, because hydrogen bonds between GA molecules are not strong enough to hold the molecules near each other. Stable GA associates appear if lipid tails in the bilayer are more ordered. Such GA associates constrict the bilayer forming hydrogen bonds with lipid heads of both layers. At the same time, such GA associates induce an additional increase of lipid order in the bilayer, which was shown on the example of DPPC bilayer at different temperatures.

EPR spectroscopy for gas adsorption study in Metal-Organic Frameworks

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Adsorptive separation and gas storage are very important for present and future industry. Nowadays zeolites are used for separation purposes. With an ever increasing need for a more efficient, energy-saving, and environmentally benign procedures, new adsorbents must be found. Metal-organic frameworks (MOFs), constructed by metal-containing nodes connected by organic ligands, should become this new type of porous materials. They are promising candidates for gas storage and separation due to their large surface areas, adjustable pore sizes and controllable properties, as well as acceptable thermal stability. Therefore a lot of new structures are synthesized annually. The claimed application requires detailed knowledge about pore properties and the behavior of guest molecules confined in such systems. This has stimulated intense research using in situ X-ray diffraction, calorimetry, Fourier transform infrared spectroscopy, neutron scattering, NMR, EPR and MD simulations.

In this work we are attempting to use electron paramagnetic resonance (EPR) methods for investigation of gas adsorption in MOF materials. Recently EPR spectroscopy was shown to be very promise for MOF systems making it possible to obtain important and unique information. But for its application one needs to incorporate EPR-active species into the MOF structure. Here we demonstrate two different approaches, EPR spin probe method and MOF structure doping with EPR active metal ions.

In particular, the spin probe approach was employed for ZIF-8 framework that demonstrates good sorption properties for carbon dioxide and unusual guest-dependent open-gate phenomena [1]. Acceleration of probe molecule was demonstrated under CO_2 adsorption. All results obtained by EPR spectroscopy were supported by molecular dynamics. Pulse (HYSCORE and ENDOR) methods were used for Cu^{2+} doped $[Zn_{2-x}Cu_x(1,4\text{-bdc})_2(dabco)]$ framework. In this study we determine the preferential site of methane sorption, which can be helpful for molecular design of new system for CH_4 storage.

We are grateful to the RSF (№ 14-13-00826) and the RF President's Grant (MK 3272.2017.3) for financial support.

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Mechanochemical synthesis of titanium nitride in an energy-intensive mill

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A mechanochemical synthesis of inorganic substances under an active gaseous atmosphere is a promising method to produce superfine powders containing a significant amount of gaseous components.

This paper investigates the thermal explosion in the Ti – N system (titanium powder is ground in the energy-intensive mill) by using the experimental methods and a mathematical model in the macroscopic approximation to develop an understanding of the mechanism of mechanochemical synthesis.

The Ti powder with particle size less than 100 microns was ground and mechanically activated in a planetary mill (M-3) under the atmosphere of nitrogen at a pressure of $4{\cdot}10^5$ Pa in the drum of the mill. It was seen that due to grinding, the Ti particle size decreased and reached 28 microns after MA for 1 min, and then increased and reached 48 microns after 5 min of MA due to the agglomeration of particles. A further increase in the MA time leads to the fact that the Ti particles are again ground and after MA from 10 to 20 minutes, the titanium particle size was slightly changed and was about 20 microns. The nitrogen pressure in the chamber also remains practically constant during MA up to 19 min. At the same time, when the MA time reaches 20 min, there is a sharp decrease in the nitrogen pressure, which indicates the beginning of an intense chemical reaction accompanied by the gas absorption during the synthesis of titanium nitride. At this moment, a small peaking of the temperature (up to 10°C) is observed on the surfaces of the mill wall, which is apparently caused by the heat release of the reaction during the formation of the final product.

The mechanochemical synthesis of titanium nitride was experimentally studied in the energy-intensive mill to develop a mathematical model of this process in the macroscopic approximation. The mechanical activation was found to intensify the chemical conversion in the Ti – N system. The kinetic constants of the grinding and activation of titanium powder particles under the nitrogen atmosphere were determined using the experimental data and the developed mathematical model.

Non-covalent associates of statins with novel drug-delivery system – glycyrrhizic acid

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Statins, inhibitors of 3-HMG-CoA reductase, are the most effective drugs decreasing LDL-Cholesterol and mortality of atherosclerosis and ischemic heart disease. However, for most statins, an effective therapeutic daily dose causes undesirable side effects. Therefore, it is so important to search for "new, improved" statins. Currently, the most effective and promising method is the use of supramolecular complexes for delivery of drugs and reduction of side effects. Since the choice of the complexant is a very important task, we turned to the natural compound glycyrrhizic acid (GA) – a natural triterpene saponin extracted from licorice roots and known for its biological activity and the ability to form various self-associates in solution. It was found that, besides increasing the solubility and reducing the minimum of therapeutic doses of drugs in the presence of GA, glycyrrhizic acid leads to the emergence of new therapeutic properties. The latter indicates that GA self-associates can participate in a specific interaction of statins with a corresponding enzyme or receptor. In this regard, it is important to know the mechanism of GA aggregation and their structural features. The available information on this issue is incomplete and often contradictory: complexes of different composition, micelles and gels are described for different media. The present study is devoted to NMR investigation of GA self-association and its association with statins in solution at various pH and concentrations. The use of various NMR techniques allows to demonstrate the processes of micelle formation and gelation in water/methanol mixtures at low pH. It was shown that NMR chemical shifts of the protons of GA triterpene moiety are sensitive to the nearest environment under GA aggregation (micelle formation). Dependences of NMR chemical shifts on concentration of GA show that micelles are formed by hydrophobic interaction between the triterpene moieties of GA molecules. The proximity of critical gelation concentration and critical micelle concentration at the same pH shows that gel is produced from micelles. Formation of inclusion complexes of some statins (atorvastatin, simvastatin and rosuvastatin) with GA self-associates in water-alcohol mixtures was also demonstrated.

Photophysics and photochemistry of mixed diazide Pt^{IV} complexes

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Pt^{IV} complexes are tested as prodrugs for anticancer photodynamic therapy, which can be provided in the absence of dissolved oxygen. The mechanism of action is based on photoreduction of Pt^{IV} to Pt^{II} complexes inhibiting DNA transcription and replication similar to cisplatin. The therapeutic effect of diazide Pt^{IV} complexes *cis,trans,cis*-[Pt^{IV}(N$_3$)$_2$(OH)$_2$(NH$_3$)$_2$] (**1**) and *trans,trans,trans*-[Pt^{IV}(N$_3$)$_2$(OH)$_2$(NH$_3$)$_2$] (**2**) is close to that of cisplatin [1].

In this work primary photochemical processes were studied for aqueous solutions of **1** and **2** by means of steady-state photolysis, nanosecond laser flash photolysis and ultrafast kinetic spectroscopy (time resolution ~100 fs). The process was shown to be multistage. The first stage is the photosubstitution of an azide ligand to a water molecule. This process was found to be a chain reaction with the concentration-dependent quantum yield. In the laser flash photolysis experiments the formation of two sequentially occurring Pt^{III} intermediates were recorded. Disproportionation of Pt^{III} intermediates leads to the formation of final Pt^{II} products, providing the therapeutic effect of the initial compounds.

In the experiments on ultrafast kinetic spectroscopy we observed the formation of intermediate absorption, most likely belonging to the lowest electron-excited state of the initial complex. These species were transformed to the Pt^{III} intermediates recorded in the nanosecond time domain, the characteristic time of these processes was about 10 ps. Therefore, primary photochemical processes for **1** and **2** were examined in the wide time region, from absorption of light quanta to formation of final products.

The financial support of the Russian Science Foundation (Grant № 15-13-10012) is gratefully acknowledged.

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Magnetic-resonance sounding of pore-space microstructure

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The magnetic-resonance sounding (MRS) [1, 2] of medium to coarse-grained sand aquifer has resulted in the following relaxation times: $T_2^* = 60$ ms (by free-induction decay), $T_2 = 220$ ms (by spin-echo), and $T_1 = 700$ ms (by inversion-recovery) (figure 1).

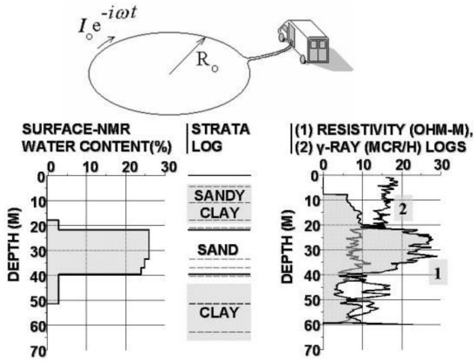

Figure 1 Scheme of MRS of medium to coarse-grained sand aquifer stratified by drilling data.

The solution of the Bloch-Torrey equations for the relaxation times is as follows [3]:

$$1/T_1 = 1/T_{1\text{bulk}} + \rho_1 \cdot S/V$$

$$1/T_2 = 1/T_{2\text{bulk}} + \rho_2 \cdot S/V + (\gamma \cdot G \cdot t)^2 \cdot D/12$$

$$1/T^*_2 = 1/T^*_{2\text{bulk}} + \rho_2 \cdot S/V + (\gamma \cdot G \cdot t)^2 \cdot D/3 + \gamma \cdot G \cdot a,$$

where S/V is the surface-to-volume ratio of pores, a is a core grain radius, γ is the gyromagnetic ratio of protons, t is time. With regard to the longitudinal and transverse relaxation times for free water $T_{1\text{bulk}} = 1.4$ s and $T_{2\text{bulk}} = 1$ s measured from the ice surface of Novosibirsk reservoir, the core grain size $a = 2.5 \cdot 10^{-2}$ cm determined using drilling data, and diffusion coefficient of water $D = 1.3 \cdot 10^{-5}$ cm^2/s at 277 K, the surface relaxivities $\rho_1 = 7 \cdot 10^{-3}$ cm/s, $\rho_2 = 3.5 \cdot 10^{-2}$ cm/s, and the local field gradient $G = 2 \cdot 10^{-2}$ Gauss/cm have been determined [4, 5].

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Dual effect of nitric oxide on the enzyme-mediated melanization

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Melanization is the process of formation of natural polymer melanin, which is widespread in living organisms. The browning of fruit and root shears, the dark color of animal skin and hair are caused mostly by melanin formation. The most important function of this process is the protective activity. The key enzyme of the melanization process is phenoloxidase (PO). In invertebrates, the melanization underlies the immune response. The particular mechanisms of triggering and regulation of this process was actively studied, but many aspects are still unclear.

Phenoloxidase belongs to oxygenases; it catalyzes the initial steps of melanization, namely, the hydroxylation of monophenols and oxidation of ortho-diphenols by molecular oxygen into the corresponding ortho-quinones. Then these quinones undergo a spontaneous intramolecular cyclization to yield indoles that polymerize subsequently into melanin through a cascade of reactions. The active site of PO contains a coupled binuclear copper. Some investigations report that NO manifests a high affinity for copper-containing enzymes and proteins.

The aim of our work was to understand how interaction of NO with PO affects its enzyme activity and melanization rate.

The study has demonstrated a dual effect of nitric oxide on the rate of phenoloxidase-mediated 3-(3,4-dihydroxyphenyl)-L-alanine (DOPA, substrate of PO) oxidation and melanization. NO generated by a donor at low rates proportionally increased PO-mediated DOPA oxidation. A competitive PO inhibitor, phenylthiourea, resulted in significant inhibition of NO-mediated DOPA oxidation. Analysis using fluorescent and EPR methods demonstrated that the effect of NO on DOPA oxidation is explained by oxidation of NO to NO_2 at the active site of PO followed by oxidation of DOPA by NO_2. On the contrary, a bolus addition of NO gas solution to PO resulted in a significant decrease in the observed PO activity. In conclusion, the results of the study suggest that NO may have a significant regulatory role on melanization process in invertebrates, as well as in humans, and results in protective or damaging effects.

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Quantum chemical calculations of the optical spectra of intermediates: Photochemical reactions of nickel and copper dithiolate complexes

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The modern development of computer technology makes it possible to apply computational methods in various fields of chemistry. Quantum chemical calculations are often used to confirm experimental data in the scientific articles. The determination of the exact geometry and physicochemical properties of short-lived particles, for which X-ray diffraction analysis is not applicable, is of great interest. This problem is especially important for determining the mechanism of photochemical transformations of various particles, for example, dithiolate complexes of transition metals. In literature one can find investigations devoted to the determination of the mechanism for the appearance of intermediates in the photochemistry of these complexes [1, 2] by the method of pulsed photolysis, but the exact structure of these intermediate particles remains unknown. The conducted studies of the spectral and kinetic characteristics of the active intermediate particles formed in the photochemical transformations of complexes of this class, as well as quantum chemical calculations of their characteristics, will verify the proposed mechanisms.

The aim of this work is to determine the geometry and calculate the electronic absorption spectrum for dithiolate complexes of some transition metals, intermediates, and final products of their photochemical reactions.

All quantum chemical calculations for the dithiocarbamate complex $Cu^{II}(Et_2NCS_2)_2$, dithiophosphinate complex $Ni^{II}(i\text{-}Bu_2PS_2)_2$ and several intermediates appearing in the photochemistry of these complexes were carried out in the Gaussian 09 program. The calculation of the exact geometry was carried out using the DFT method. The effect of solvent was taken into account according to the PCM model. The resulting geometry was used to calculate the electronic spectrum by the TD-DFT method. The calculations were carried out in the approximations of the exchange functionals B3LYP and UB3LYP, PBE and UPBE, using different wave function bases.

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Mechanisms of aromatic amino acid modifications in anaerobic photolysis sensitized by kynurenic acid

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During the lifespan of an individual, eye lens proteins (crystallins) accumulate numerous post-translational modifications, which eventually lead to the loss of water solubility and aggregation of proteins, *i.e.,* to the development of cataract. Recent studies have shown that one of the sources of protein modifications is UV-A light (315 – 400 nm) induced radical reactions of intrinsic chromophores of the eye lens with tryptophan (Trp) and tyrosine (Tyr) residues. Earlier we have shown that these radical reactions lead to the oxidation of Trp residues and aggregation of the main eye lens protein, α-crystallin. However mechanisms of these reactions are currently not clear. The aim of the work is to shed light on mechanisms of protein modifications in UV-A induced radical reactions using simple objects, single Trp and Tyr amino acids (AA), and kynurenic acid (KNA) as the most effective photosensitizer of the human eye lens.

The study was carried out with steady-state and time-resolved optical spectroscopy, high-performance liquid chromatography and mass spectrometry. The concentrations of radicals and molecular oxygen in solution are the main factors that strongly influence the photolysis. To study direct reactions between KNA and AA radicals and to minimize the influence of O_2 we performed steady-state photolysis with the pulsed laser radiation.

Our results have shown that $KNA^•$ and $AA^•$ radicals, formed in the quenching reaction of ^TKNA by AA, react in following reactions: 1) the back electron transfer with the formation of initial reagents; 2) the transfer of oxygen atom from carbonyl or carboxyl groups of KNA to AA with the formation of deoxygenated products of KNA; 3) the dimerization of AA *via* radical recombination; 4) the oxidation of $KNA^•$ radical in the reaction with O_2 and subsequent electron transfer from the formed superoxide $O_2^{-•}$ to $AA^•$ radical with restoration of the initial reagents; 5) the cross-linking of the radicals KNA and AA with the production of KNA-AA conjugates.

The reaction (1) is the major pathway of radical cross-termination reactions. The main products of all studied reactions are dimers of AA of different structures. Higher decomposition of reagents in the case of Trp as compared with Tyr indicates a more efficient back electron transfer in the Tyr/KNA pair. The charge on the amino group of AA backbone reduces the AA photodecomposition that speaks in favor of higher susceptibility for photoinduced damage of AA being inside polypeptide chain of protein.

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Study of singlet oxygen O_2 ($^1\Delta_g$) formation *via* photoexcitation of contact complexes X-O_2 (X = TiO_2, WO_3 and all trans-retinal)

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In recent studies [1, 2] it was found that local environment plays an important role in molecular oxygen O_2 photochemistry and photophysics. Molecular oxygen UV absorption is dramatically enhanced and new channels of generation of reactive oxygen species, such as singlet oxygen O_2 ($^1\Delta_g$), appear due to interaction with its local environment. It occurs in weakly bounded complexes X-O_2, where X is a molecule-partner. Such complexes are formed during molecular collision in gas (encounter complexes) or in liquid (contact complexes).

Singlet oxygen plays an important role in different natural photoprocesses due to its high reactivity. In addition, singlet oxygen is used in many applications, such as photodynamic therapy or bacterial disease treatment. For these reasons, a new method of singlet oxygen generation is an important goal. In previous studies carried out in molecular beams [1] and in gas phase [2] it was suggested that generation of O_2 ($^1\Delta_g$) might occur under UV-VIS photoexcitation in any environment containing O_2 in dependence to molecule-partner's properties.

In this study, we focus on investigation of photoprocesses of molecular oxygen in contact complexes X-O_2 (X = TiO_2, WO_3 and all trans-retinal), in particular, generation of singlet oxygen due to complexes' photoexcitation. The selected complexes X-O_2 are in interests of photocatalysis and photobiology. Water and organic solutions were used as solvents. We registered absorption spectra of solutions without oxygen and under high oxygen pressure. Depending on solution, photoexcitation was at 355-532 nm. We attribute the registered luminescence near 1.27 μm to generation of singlet oxygen O_2 ($^1\Delta_g$). In this study, the process of singlet oxygen generation is discussed.

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The Alamethicin self-assembling in membrane at low concentrations by EPR spectroscopy

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In the post-antibiotical era, the membrane-modifying peptides become perspective medical drugs for treating bacterial infections. The mechanism of peptide antimicrobial action is normally supposed to be related to channel formation in the membrane that results in the ion disbalance across the membrane. However, the channel formation occurs only at high peptide/lipid ratio, higher than ~ 0.5-1 mol. %. It was supposed that at lower concentrations peptides can also provide membrane-modifying properties [1, 2]. However, the details of these peptide membrane-modifying properties at low concentrations are weakly studied.

In this work, Alamethicin F50/5 (Alm) spin labeled analogs were studied in a model biological membrane at the peptide/lipid ratios of 0.067-1 mol. %. It was found that Alm self-associates in dimers ($n = 2$) even at the lowest concentration studied, 0.067 mol. %. The peptide concentration increase up to 0.5 mol. % results in increase of the mean number of molecules in cluster, to the mean value of $n = 3.75$, with the dispersion $\delta n \sim 1.5$. So these data point at distribution of Alm clusters. The concentration of onset from planar to transmembrane peptide orientation was found. The distance distribution between spin labels in peptide is described in terms of multi-spin interactions [3].

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Pulse and CW EPR study of triarylmethyl radicals in glassy trehalose

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Trehalose has been recently advanced as efficient immobilizer of biomolecules for room-temperature EPR structural studies, including pulsed dipolar EPR spectroscopy (PDS) allowing nanoscale distance measurements. Immobilization is necessary to prevent the averaging of dipolar coupling by rotational diffusion, which is usually achieved by freezing at cryogenic temperatures. Another crucial parameter for PDS is electron spin relaxation (namely, phase memory time T_m) that has to be slow enough providing then accessibility to longer distances. Recently triarylmethyl (TAM) spin labels attached to DNA in trehalose have manifested the longest T_m at room temperature compared to previously used spin labels and immobilizers [1]. Moreover, DNAs have preserved native conformation in trehalose. Thus, the combination of TAM spin labels and trehalose allows effective structural studies in biologically ambient conditions.

In this work, we studied relaxation properties and mobility of TAM radicals in glassy trehalose, namely Finland trityl (H36 and D36 forms) and OX63D, in order to define the optimal structure of TAM spin labels. As far as relaxation is highly contributed to by protons, we studied the dependence of T_m on deuteration of radical and matrix and on water content in samples. We found that D36 form of Finland trityl in deuterated at hydroxyl groups trehalose exhibits the longest T_m of 2.8 μs. In addition, to reveal the mechanism of relaxation we investigated the temperature dependence of T_m at X- and Q-band frequencies. Based on the obtained data we determined the mechanism as librational motion.

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EPR study of light-induced metastable states in two-spin $Cu(hfac)_2L^R$ compounds

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Molecular magnets $Cu(hfac)_2L^R$, where hfac is hexofluoroacetylacetonate and L^R is nitronyl-nitroxide radical, undergo thermo- and light-induced phase transitions. Within the transition, the magnetic moment changes, along with the geometry and character of exchange interaction in spin clusters. Similarity of magnetic effects in $Cu(hfac)_2L^R$ to classical spin-crossover caused a significant scientific interest to these systems. Namely, some of them experience LIESST effect at cryogenic temperatures. Previously mostly $Cu(hfac)_2L^R$ with three-spin exchange clusters were studied. In 2015 we obtained first results proving photo-switching in polymeric compounds containing two-spin exchange clusters [1]. Therefore, the purpose of the present work was to establish relationships between structures of two- and three-spin compounds and their magnetic properties.

Method of Electron Paramagnetic Resonance spectroscopy was used due to high sensitivity to the magneto-structural transitions in $Cu(hfac)_2L^R$. We studied two different two-spin systems with different structure and magnetic moment behavior and one three-spin system for comparison. We found significant difference in relaxation parameters of two-spin systems from self-decelerating relaxation of three-spin systems [2]. Namely, two-spin compounds feature extremely high stability of photoinduced states in the temperature range 5 – 20 K, with relaxation time up to 200 hours. We showed that the origin of long relaxation is not the cooperativity effect, but a high energy barrier between light-induced and ground states. In its turn, the high energy barrier is caused by stronger structural distortion of two-spin exchange cluster. Namely, the difference in Cu-O distance within exchange spin cluster between light-induced and ground states is greater for two-spin systems than for the three-spin analogues.

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Impact of the active site amino acid residues on the lesion recognition by human 8-oxoguanine DNA glycosylase 1

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Attack of the reactive oxygen species, produced in routine cellular metabolism or under action of environmental factors, on DNA results in numerous oxidative base modifications, with 8-oxoguanine being the most common of them. In the subsequent replication this lesion could be misread by a DNA polymerase, at first creating an oxoG:A mispair and then resulting in a G:C to T:A transversion. In humans, the first step of the repair pathway, the excision of the oxidized base, is performed by human 8-oxoguanine DNA glycosylase 1 (hOGG1). Several key amino acids have been identified as necessary for both the lesion recognition and glycosylase activity of the enzyme, though the specific roles for some of them are still not exactly clear. In X-ray crystal structures of the protein-DNA complex the cytosine base is engaged by Asn-149, Arg154, Arg204 and Tyr203 amino acid residues, while the 8-oxoguanine is reverted out of the DNA helix into the enzyme active site with the Gly-42 residue being likely responsible for discrimination between the undamaged and damaged DNA base, and Lys-249 and Asp268 serving as catalytic residues.

In order to investigate the role of specific residues on the structure of recognition complex for oxidized and native DNA, molecular dynamics simulations were performed for both unbound protein and protein-DNA complex based on existing crystal structures of hOGG1 with K249Q, D268A, G42S, R154A, R204A and Y203A substitutions introduced. Together with the data from previous stopped-flow kinetic experiments, the results of molecular dynamics allow to better understand the impact of specific amino acids on processing of both damaged and intact DNA, showing both the effects of active site residues Lys-249, Asp268 and Gly-42, as well the Arg154, Arg204 and Tyr203 residues interacting with the opposite DNA strand.

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Magnetic properties of Co^{II} with large ZFS: Experimental and computational study

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Transition metal ions (TMIs) are very important not only in chemistry and biology, where they play a crucial role in many processes, but also in physics where they are considered as key units for perspective data storage devices based on single-molecule magnets (SMMs). The ability of SMM to store the magnetization is caused by spin-reversal barrier, which originates from the zero field splitting (ZFS) of the system. Small and moderate values of ZFS (up to 20 cm^{-1}) can be measured experimentally with required accuracy, while for the very large ZFS (up to 200 cm^{-1}) such techniques are quite complicated or give only an estimation of ZFS. In turn, Frequency-Domain Fourier-Transformed THz-EPR spectroscopy covers the required frequency range and thus is a choice technique for investigation of ZFS in TMIs.

In this work we present a thorough study of six high-spin Co^{II} complexes with the ZFS ranging from ~ 50 cm^{-1} to 175 cm^{-1}. FD-FT THz-EPR data were complemented with X-band spectra and magnetic susceptibility measurements. This broad experimental ground was used to test the validity of the different magnetic models (effective spin 1/2, spin 3/2, Lines model, total angular momentum J) and to determine the magnetic resonance parameters within these models. The performed quantum chemical calculations were benchmarked by comparison to the experimental results and that allowed further insight on the examined magnetic models. The spin 3/2 model was confirmed as the most relevant for the majority of the studied Co^{II} complexes.

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The influence of magnetic dilution on the magnitude of zero-field splitting in a cobalt(II) complex

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In recent years the usage of magnetically diluted samples has become a valuable and widespread technique in the field of molecular magnetism. When a paramagnetic compound is randomly distributed in a matrix of its diamagnetic analogue it is possible to reveal intrinsic molecular-based magnetic properties and distinguish them from those of intermolecular origin. It is crucial since the most appealing potential applications of single-molecule magnets (SMM), such as data storage and quantum computing, imply the ability of manipulation of individual molecules, as well as partial or even complete suppression of intermolecular interactions.

Such investigations of magnetic properties as a function of the dilution mostly rely on the assumption that the introduction of a diamagnetic matrix does not influence intramolecular SMM's characteristics, one of the most fundamental of which is zero-field splitting (ZFS). In order to probe this assumption it is necessary to measure ZFS for both concentrated and diluted samples. One of the most widespread and suitable techniques for such purposes is electron paramagnetic resonance (EPR) spectroscopy. However, when ZFS exceeds quantum energy of the standard EPR spectrometers precise experimental determination of this parameter becomes quite a challenging task because of the lack of appropriate sources of THz-radiation, as well as high enough magnetic fields.

In this work we present a FD-FT THz-EPR [1] study of the Co^{II} complex $[Co(piv)_2(2\text{-}NH_2\text{-}Py)_2]$ along with its magnetically diluted analogues described by the general formula $[Co_xZn_{(1-x)}(piv)_2(2\text{-}NH_2\text{-}Py)_2]$. This technique allowed the first example of direct observation of very large ZFS in diluted systems up to 10% of cobalt content. We report a drastic decrease of ZFS from ~75 cm^{-1} to ~50 cm^{-1} in the range of $x = 0.5 \div 0.25$. X-ray analysis revealed that such a significant and unexpected effect arises from abrupt changes in bond lengths between the central atom and coordinating ligand atoms in the same range of Co^{II} concentration.

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Investigation of the formation of CnEm dimers in water by the molecular dynamics method

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CnEm molecules (alkyl polyethylene glycol ether) have a hydrophobic chain of *n* methyl groups and a hydrophilic part of *m* ethylene glycol units. In an aqueous solution, they show different properties of self-association, depending on the values of *n* and *m*. The use of such molecules helps study the initial stage of association of amphiphilic molecules in solution, and to clarify the contributions of the hydrophobic and hydrophilic parts in this process. In this presentation, we further investigate the effect on the association of temperature and of the addition of a hydrophobic molecule.

The behavior of two identical CnEm molecules placed in a model box has been studied by the molecular dynamics method. The molecules C6E3, C6E6, C12E3 and C12E6 were considered. Solutions were studied at 300 K and 360 K, both in pure water and with the addition of one molecule of cholesterol. Because of diffusion, the molecules can converge, forming an associate (dimer). However, it is not stable, and the molecules diverge again.

Different approaches are considered for establishing the emerging of associates and their quantitative description. More stable pairs arise when the molecule has a large hydrophobic part ($n = 12$). Increasing the temperature promotes the association. The molecules in the associate are in contact predominantly with hydrophobic parts, and the hydrophilic parts are oriented arbitrary. All of this says that the main driving force for association of the molecules is the hydrophobic interaction. Adding a molecule of cholesterol stabilizes the existing associates. Moreover, associates of molecules with a small hydrophobic part ($n = 6$) become visible.

Quenching of kynurenic acid in triplet state by biological compounds

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Human lenses contain natural metabolites, called UV-filters because of their ability to absorb UV-light in the 300-400 nm spectral region. The main UV-filters are kynurenine and its derivatives. Under physiological conditions, these compounds can undergo decomposition, causing the accumulation of photochemically active products. The reactions of these products with the lens proteins lead to the protein modifications and aggregation, and, as a result, to the cataract development. One of the decay products is kynurenic acid (KNA). Photoexcitation of KNA results in the formation of the triplet state (^{T}KNA) with high quantum yield (about 80%). The molecules in the triplet state can react with amino acids, antioxidants and proteins of the lens. The ability of biological compounds to quench the excited molecules depends on the properties of acid-base forms of the quencher and the excited molecule.

The equilibrium between protonated and deprotonated forms of the ^{T}KNA molecule was investigated using laser flash photolysis measurements. The electronic spectra of the triplet ^{T}KNA in protonated and deprotonated forms have been obtained, the rate constants of the ^{T}KNA quenching by oxygen, tryptophan, tyrosine, cysteine and ascorbate at different pH's have been measured, and the quenching mechanisms have been established. It was found that the most efficient ^{T}KNA quenchers are oxygen, tryptophan and ascorbate: they quench ^{T}KNA with almost diffusion-controlled rate constants, which practically do not depend on the solution pH. The rate constants of the ^{T}KNA quenching by tyrosine and cysteine are noticeably lower, and their values significantly change with the protonation of the initial reagents.

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Influence of substituents on the lappaconitine derivatives photophysics and reactivity

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Lappaconitine is a diterpeniod alkaloid that possesses a wide range of biological activities, including antiarrhythmic, anti-inflammatory, antioxidative, anticancer, immunoregulatory activity, *etc.* Lappaconitine consists of a donor fragment – the *N*-acetyl anthranilic acid residue (AA), and an acceptor fragment – a diterpene that largely determines their reactivity (figure 1).

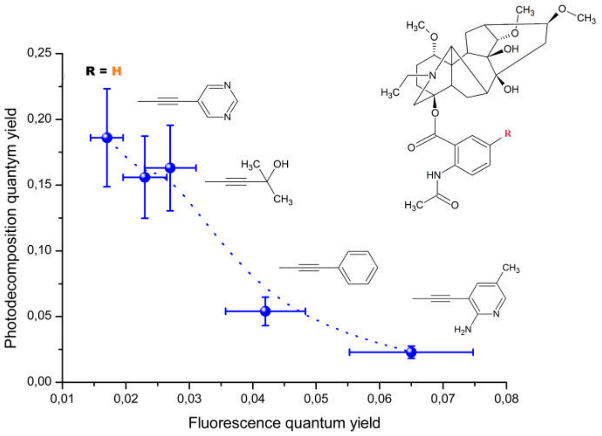

Figure 1. Correlation of fluorescence and photodecomposition quantum yields.

Data obtained in previous studies using methods of spin chemistry indicated that photodegradation of lappaconitine and its derivatives occurs from the triplet excited state. According to [1] photoreaction begins from reversible intramolecular electron transfer with subsequent cleavage of the ester bond. Since anthranilic fragment is a chromophore in these molecules, as well as a potential electron acceptor in redox processes, it can be expected that substituents will have a significant impact on the efficiency of the intramolecular ET. In order to verify the hypothesis about direct connection between lappaconitines reactivity (photostability) and photophysical properties we examined fluorescence and photodecomposition quantum yields of lappaconitine derivatives.

Actually, as expected, a relatively high quantum yield of fluorescence is typical for photostable AA derivatives, in particular, the methyl ester of AA. All systems under study demonstrated a decrease of photodecomposition quantum yield versus lappaconitine. It can be suggested that the introduction of substituents into lappaconitine decreases the photocleavage. Therefore, the insertion of substituents in lappaconitine molecule might be the way to improve their photostability.

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Generation of Ti and W atoms and their oxides in the molecular beam

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The study of the nature of photophysical and photochemical processes proceeding in the photocatalytic oxidation with participation of the complexes of oxygen with photocatalysts titanium dioxide and tungsten trioxide are of great interest. The most powerful techniques for the study of elementary photoinduced processes are used in the conditions of molecular beam. In this work titanium and tungsten oxides were generated directly in the molecular beam, since in common conditions they are not volatile. The oxides were prepared by two methods: with photodecomposition of volatile compounds and by ablation. Volatile hexacarbonyl tungsten $W(CO)_6$ and titanium isopropoxide $Ti(OC_3H_7)_4$ were used in the first method, and Ti and W foil, TiO crystal and pressed TiO_2 and WO_3 were used in ablation. For photoexcitation of precursor substances and photoionization of the formed photoproducts the radiation of solid-state Nd:YAG laser at the wavelengths of 266 and 532 nm was used. Photoproducts were detected with the time-of-flight mass-spectrometry. In figure 1 an example of the mass-spectrum of the photofragments is presented.

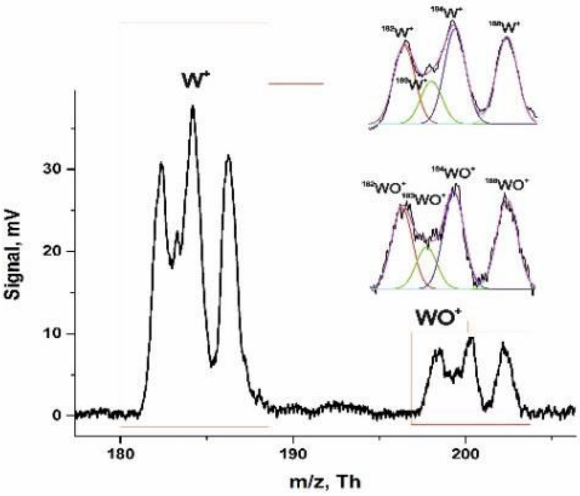

Figure 1. Mass spectrum of the tungsten hexacarbonyl photofragments. On the right inset the deconvolution of mass-peaks of tungsten atoms and their oxide into isotopic contributions is shown.

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P73

Solvent-free synthesis of metal sulfides by thiourea decomposition and probing the surrounding by DNP SENS NMR spectroscopy

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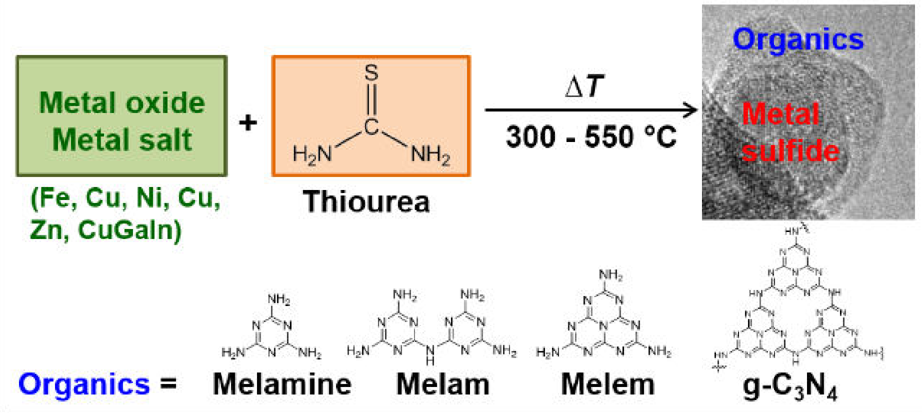
A simple solid-state solvent-free method of synthesis for a series of transition metal sulfides (MSs) using inexpensive thiourea as a reactive precursor at relatively low temperatures is presented. MSs were synthesized with single metals (Fe, Co, Ni, Cu, and Zn) and a prototype quaternary MS. The thermal decomposition of thiourea produced *in situ* carbon disulfide, which induced a reaction with the metal precursor to form MSs at low temperatures. The MS particles were surrounded by carbon nitride species that resulted from thermal decomposition of thiourea, which was confirmed by dynamic nuclear polarization (DNP) nuclear magnetic resonance spectroscopy. This synthesis protocol, owing to dynamic characteristics, involves the formation of a variety of organic polymeric complexes. The DNP NMR technique was effective for identifying the compositions and structures of the products, as well as their interactions with the MS.



Fullerenes C_{60} and PCBM as spin probes for investigation of inhomogeneities in ionic liquids

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Ionic liquids are becoming more popular nowadays due to their unique properties. They can be used as new "green" solvents or electrolytes. The PCBM is a buckyball's derivative. It is an excellent electron acceptor thus it is applied for production of organic solar cells and other flexible electronic devices.

The goal of the present work is the investigation of chemically induced electron spin polarization (CIDEP) dynamics of PCBM and C_{60} in different ionic liquids and other solvents. This knowledge is very important for application of fullerenes and ionic liquids. Experiments were done using an X-band time-resolved EPR spectrometer.

The TR EPR spectra of fullerenes C_{60} and PCBM dissolved in ionic liquids $[C_{10}mim]BF_4$, $[bmmim]PF_6$, $[bmim]BF_4$, toluene, ortho-terphenyl and THF were measured at 100 K. The influence of each solvent on the EPR spectrum line shape was noticed. The influence of triplet molecule's surrounding on the formation of its electron spin polarization was suggested. The temperature dependence of PCBM dissolved in $[C_{10}mim]BF_4$ was analyzed in the range from 90 K to 295 K. It was found that the decay shape of kinetic curve had bi-exponential nature that can be the evidence of the inhomogeneities' presence with different CIDEP relaxation time of dissolved fullerene. The decomposition procedure of EPR spectra lines into two components corresponding to each subensemble was applied (figure 1), and specific parameters of EPR spectra line shapes were calculated.

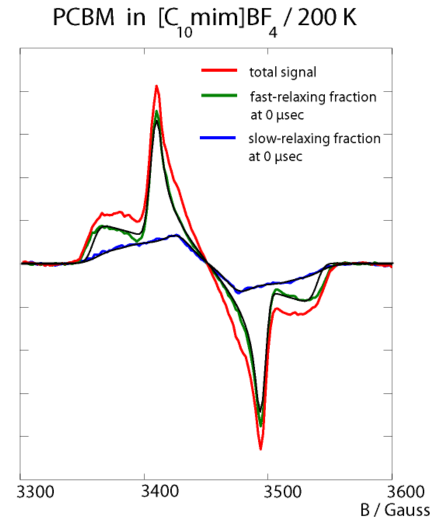

Figure 1. Decomposition of TR EPR spectrum of PCBM in $[C_{10}mim]BF_4$

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P75

Analytical solution of the PELDOR inverse problem using the integral Mellin transform

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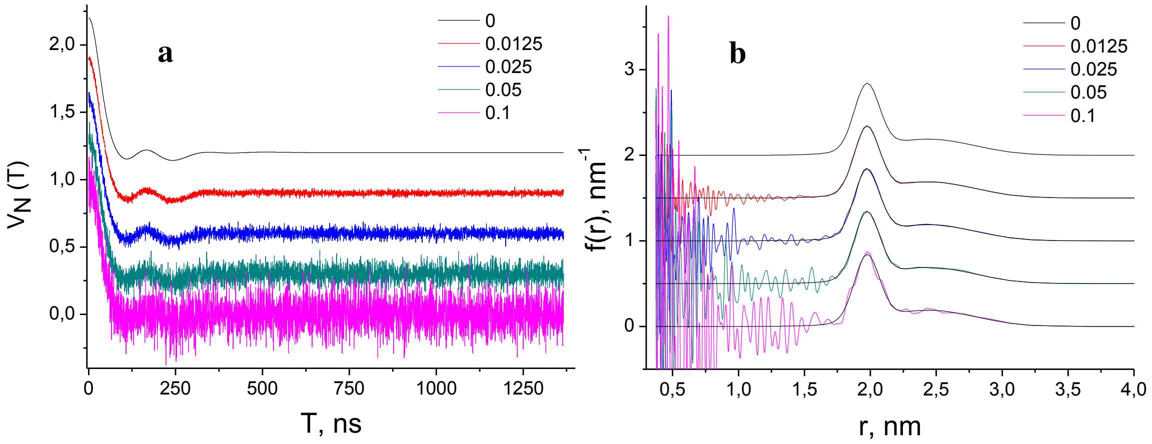
We describe a new approach to solving the inverse problem in pulsed double electron-electron resonance (PELDOR, also known as DEER) spectroscopy to obtain the distance distribution function between two radicals from time-domain PELDOR data. The approach is based on exact analytical solutions of the Fredholm integral equations of the first kind using integral Mellin transforms to provide the distance distribution function directly.



The figure demonstrates the quality of distance distribution recovery by the algorithm suggested: dependence of the reconstructed curve on noise level in input data. **a** – normalized PELDOR curves V(T) with different levels of Gaussian noise (0, 0.0125, 0.025, 0.05 and 0.1%); **b** – distance distributions f(r) obtained from this V(T).

This work was supported by the Russian Science Foundation project 15-15-00021.

P76

DMSO action on hydrogen atom abstraction reaction from Zn^{II}(3,5-di-*iso*-propylsalicylate)$_2$ by *tert*-butylperoxyl radicals

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In recent years special interest is given to metalloelement chelates and their interaction with different radicals. This is due to the fact that superoxide dismutase enzyme antiradical ability, which regulates amount of radicals in animal and human body, contains transition metal ions, including Zn^{2+}.

In this study rate constants for hydrogen atom abstraction reaction from Zn^{II}(3,5-di-*iso*-propylsalicylate)$_2$, $Zn^{II}(DIPS)_2$, by the *tert*-butyl peroxyl radicals ($ROO^{\bullet}$) were measured by kinetic EPR method. Experiments were carried out in heptane (figs. 1, 2), with different concentrations of dimethyl sulfoxide (DMSO).

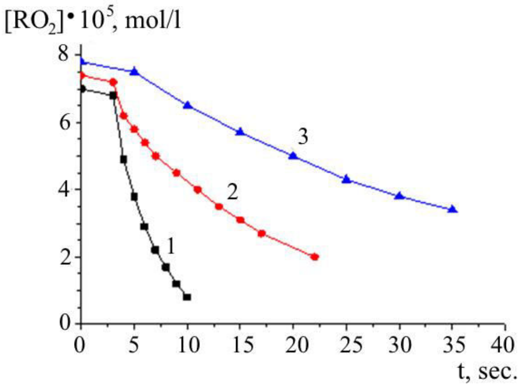

Figure 1. Kinetic curves of $Zn^{II}(DIPS)_2$ interaction with *tert*-butyl peroxyl radicals, t = -32°C
1 - [DMSO] = 0, $[Zn^{II}(DIPS)_2]_0 = 3.5 \cdot 10^{-2}$ mol/l,
2 - $[DMSO]/[Zn^{II}(DIPS)_2]_0 = 0.695$,
3 - $[DMSO]/[Zn^{II}(DIPS)_2]_0 = 1.39$.

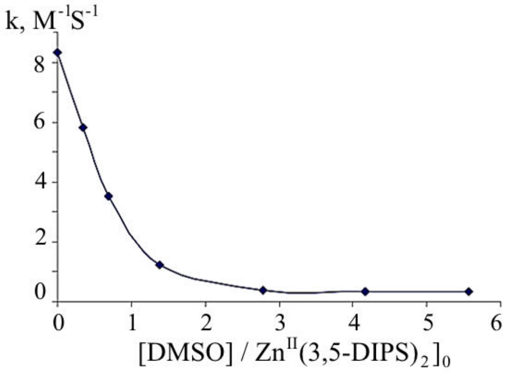

Figure 2. Rate constants dependence from $[DMSO]/[Zn^{II}(DIPS)_2]_0$ for $Zn^{II}(DIPS)_2$ + DMSO system and $ROO^{\bullet}$ radicals reaction.

From the obtained data it is obvious that DMSO at molar equivalent quantities does not directly impede the reaction center of radical scavenging, but acts indirectly by bonding axially to the zinc atom, which changes the coordination geometry in such a way as to increase intramolecular hydrogen bonding within the coordinated ligand and thus diminish the fraction of salicylic OH groups available to transfer a hydrogen atom. As a result, H-atom donating reactivity of $Zn^{II}(DIPS)_2$ decreases upon coordination of DMSO.

P77

Ultrafast exciton dynamics and photocatalytic activity of Ni-promoted CdS nanocrystals stabilized with polymeric shell

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The goals of the present work were: 1) to study the exciton dynamics of CdS nanocrystals (NCs) stabilized with oleic groups and functionalized with an amphiphilic copolymer in the femto-, picosecond time window; 2) to measure the photocatalytic activity of the same NCs with Ni cocatalysts in the reaction of H^+ reduction to hydrogen.

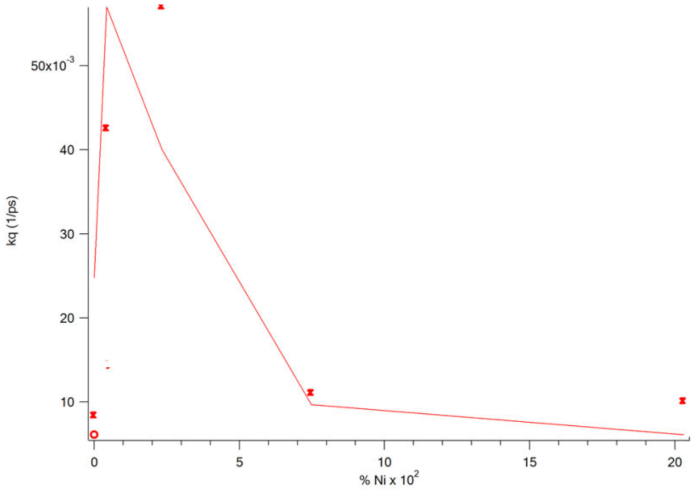

Figure 1. The exciton lifetime *vs* Ni concentration in CdS NCs.

Ni was deposited in these nanocrystals using pathways: (1) in the course of their synthesis by thermal decomposition of nickel(II) acetylacetonate ([Ni(acac)$_2$]), or (2) *via* photodeposition of Ni from $NiCl_2$ aqueous solution.

The dependence of the exciton lifetime as a function of the Ni concentration, the size of NCs, and the percentage of Cd was determined. The exciton lifetime depends on the Ni concentration not monotonically (figure 1). The minimal exciton lifetime was found for the Ni concertation corresponding to ~ 1 Ni ion per NC.

The similar non-monotoninc dependence was registered for the photocatalytic activity *vs* Ni ions concertation in NCs.

This work was supported by Russian Science Foundation grant 17-13-01506.

P78

Complete description of photo initiated Para-Hydrogen Induced Polarization

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Para-Hydrogen Induced Polarization (PHIP) is a modern, promising way to create hyperpolarization to overcome the inherent low sensitivity of NMR spectroscopy. PHIP exploits nonequilibrium population of para-hydrogen (or hydrogen in its singlet nuclei spin state). Usually in PHIP a hydrogenation reaction necessary for transferring the spin order to a substrate is running for several seconds, whereas in photo-initiated PHIP[1] (photo-PHIP) it is proceeding only for a few µs after initiation by a light flash.

This timing control of photo-PHIP allows us to fully describe the coherent nature of PHIP: we are able to detect zero-quantum coherences "in-phase" and "out-of-phase", as well as a "signal" from singlet spin order of para-hydrogen, and track their evolution caused by differences in chemical shift and J-couplings in the complex.

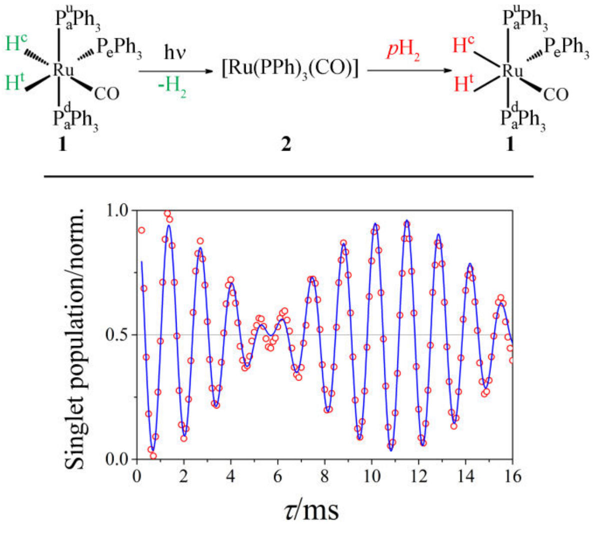

Figure. Photo-PHIP reaction (top) and singlet spin order evolution in 1.

Typically, the maximal polarization level in PHIP experiments is of the order of 10% while in photo-PHIP by using RF pulses up to 100% of total polarization is expected. Thus, the photo-PHIP method will allow one to optimize PHIP hyperpolarization conditions in order to increase the sensitivity of NMR and MRI. Investigation of evolution of zero-quantum coherences (or singlet spin order provides information about sign of J-couplings that is essential for characterizing of the complex structure.

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[1] O. Torres *et al.,* J. Am. Chem. Soc., 2014, 136, P.10124-10131.

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