XVII International School-Seminar "Spectroscopy of molecules and crystals"

ABSTRACTS

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Preface

The Book contains abstracts of papers presented to 17 International School-Seminar "Spectroscopy of Molecules and Crystals" (17ISSSMC). The School was founded by Professor Galyna Puchkovska and is held biannually starting from 1973. Topics of the School cover recent advances in theoretical and experimental spectroscopy of: crystalline solids, nanosystems, liquid crystals and amorphous materials, liquids, gases, polymers and biological systems, surface and thin films, intermolecular interaction. Computer simulation, nonlinear optical phenomena, new spectroscopic methods, and applications are considered too.

Abstracts are published in the authors' version.

The Book of Abstracts is recommended for publications by the Academic Council of Faculty of Physics of National Taras Shevchenko University of Kyiv.

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0.1 Molecules

"Filming" atomic motions during chemical reactions by time-resolved X-ray diffraction

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A time-resolved x-ray diffraction study is presented to visualize atomic motions during recombination of laser-dissociated iodine molecules in solution. The reaction is triggered optically by an intense laser pulse, and molecular motions are probed by a time-delayed x-ray pulse. The experimental set-up is described first, emphasizing technical difficulties of this kind of experiments. A statistical theory of time-resolved x-ray diffraction is also presented. Information about variations of molecular geometry may be reached by varying the time delay between the pump and probe pulses. Proceeding in this way, motions of the iodine atoms can be followed in real time. It is shown that these motions are strongly correlated with those of the solvent molecules. The solvent thus plays an active role, and is not only an inert medium hosting the reaction. Thermal expansion of the liquid due to the laser heating is observed too. One concludes that, hundred years after the basic Roentgens discovery, filming of atomic motions in liquids by x-rays became possible.

Vibrational Spectra and Structure of the Liquid Methanol

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Using Raman spectroscopy and computer simulation the structure changes occurring in such partly ordered systems as liquid crystals, alcohols and glassforming materials were investigated in the temperature region 150 - 340 K. It was found that in liquid crystals these structure changes are connected with thermal prehistory of samples, with the rate of their cooling and heating. In such liquid crystals as some ether isomers two possible explanations of the nature of mesomorphic transitions exist: molecular conformations and dimerization. In the case of alcohols the measurements, the modeling calculations, their comparison with the spectra of clusters registered during the cooling of methanol clusters on large argon clusters[1] and with the results of femtosecond experiments[2] have shown that in liquid methanol dynamical 3-4-molecular cluster structure exists. At that the time of hydrogen bond dissociation in the clusters determines the time of the dephasing of intramolecular vibrations and the width of vibrational bands in the spectra.

- [1] F. Huisken, M. Slemmer J. Chem. Phys. <u>98</u>(10), 1993.
- [2] K. J. Gaffney, P. H. Davis, I. R. Piletic et al. J. Phys. Chem. <u>106</u>(50), 2002.

Green Function Method and Raman Spectroscopy

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This report focuses on one among many theoretical problems in resonant Raman spectroscopy. That is the problem of the increase of the Raman effect tensor towards infinity when the incident light frequency approximates to an absorption band. There are many approaches to the theoretical consideration of the Raman effect. One of them consists in the following. The hamiltonian of a system, which includes an electromagnetic radiation field and the charged particles has three summands. The first one describes movement of electrons and nuclei, the second - the electromagnetic field, the third - the interaction between field and matter. The vector potential A is chosen usually in Coulomb calibration and it is necessary to take into account the instant interaction between the charged particles.

Raman scattering is a second order effect with respect to an operator of interaction between the electromagnetic field and the matter. This operator is considered as a small perturbation and the corresponding quantum transition is realised through the intermediate states. For the correct usage of the method of small perturbation the fulfilment of following equations is necessary:

$$|E_0 - E_i| \gg V_{0i}, |E_i - E_f| \gg V_{if}$$
 (1)

where E_0 is the energy of initial state, E_i - intermediate, V_i - final, V_{if} - the interaction operator matrix elements between the initial and intermediate states, - between the intermediate and final.

As it is well known, when the frequency of incident light approximates to the absorption band, the energy of intermediate state approximates to the initial state energy. Then the expression for Raman scattering tensor - value, which determines the scattering light intensity, goes to infinity and the corresponding expression gets senseless and so called virtual transitions become real and resonance scattering is considered as a competitor to luminescence. The expression (1) gets invalid and the method of small perturbations can not be used.

Weiskopf and Wigner [1] had improved the small perturbations method applying to the resonance scattering. The formula, which was obtained by these authors is used for Raman scattering description.

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In our paper we are going to consider the Raman effect using quite a different method. We shall use Green functions method and polariton description of electromagnetic waves in crystals. The polaritons are normal vibrations, which represent a mixture of electromagnetic field vibrations and the electronic exitations. The elementary act of Raman scattering consists in the transformation of one polariton (electromagnetic wave in crystal) into another polariton and phonon. If the latter belongs to the optical branch - this will be Raman scattering, if the phonon belongs to the acoustical branch - this will be Mandelstam-Brillouin scattering. Here the Stokes component of Raman and Brillouin scattering is described. An anti-Stokes component is described by transition of the polariton and the phonon into another polariton of larger energy.

Let us consider the situation, when it is possible not to take into account the extinction of polaritons. Group velocity depends on frequency according to the formula $\nu_0 \approx (\omega_0 - \omega_\mu)^2$, and the index of refraction $n \approx (\omega_0 - \omega_\mu)^{1/2}$, where $\omega_\mu = E_\mu/\hbar$ and ω_0 – primary radiation frequency. Taking into account the considerations mentioned above we have got for intensity of scattering light

$$I = S(\omega_0 - \omega_\mu)^{-3/2}$$
(2)

This result is obtained in the situation, when extinction is neglected.

But if extinction is taken into account v_0 and n are finite values and any difficulties in describing resonant Raman scattering are absent.

It is necessary to note, that the refraction index n, group velocity v_0 and resonant Raman scattering intensity can be measured independently and formula (2) can be compared to experiment.

[1] Weisskopf V., Wigner E. Zs. f. Phys. 1930; 63: 54.

Theory of Hyperraman and Scattering Light on Light

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The non-linear effects can be classified to the number of quasi-particles which participate in an elementary act. Raman scattering process is characterized by participation of three quasi-particles. They are two photons and one phonon. Hyperraman scattering covers the participation of four quasi-particles. They are two photons of primary radiation, one photon of resulted radiation and one phonon. The energies of the mentioned quasi-particles are connected with the law of energy conservation: $\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3 + \hbar\omega_4$, where ω_1 and ω_2 are the frequencies of primary radiation, ω_3 is the scattering radiation, ω_4 are the frequencies of phonon, \hbar is the constant of Plank.

The consideration is presented within the theory of polyaritons which represent themselves the so-called "hybrids" of electromagnetic waves and electronic or vibration states.

As it was mentioned in literature, (see for example [1]) the contribution into the nonlinear effects causes a great deal of mechanisms. They are:

- 1. the interaction of the cross-photons field with the crystal charges;
- 2. the interaction of Coulon exitations;
- 3. the kinematicn interaction.

The mentioned above mechanisms happen to be to some extent actual being observed in different spectrum intervals. The contributions they cause can be divided using the polarization measurements as well as by measuring the frequency dependence for the primary and scattering radiation.

The Green function method can be applied to the Raman scattering. The given report presents the application of this method and the method of small perturbations to Hyperraman scattering. The mentioned above techniques can be considered as the effects of higher order and allow to study some properties of effect.

At the definite conditions Hyperraman scattering causes the photons of scattering the light on light when two photons with the frequencies ω_1 and ω_2 are transformed into two another photons ω_3 and ω_4 . As in the case of Hiperraman effect, there is the connection between these frequencies: $\hbar\omega_1 + \hbar\omega_2 = \hbar\omega_3 + \hbar\omega_4$. It is caused by the law of energy conservation. The dependence of mentioned above effects on crystal symmetry, experiment geometry, electromagnetic radiation value and vibration mode type of Hiperraman scattering.

The given report presents some practical recommendations concerning the experiments of observations the mentioned effects.

 P.A.Korotkov, L.N.Ovander, N.S.Tue. Raman-effect in the molecular crystals, Edition ZITI, Zhitomir, Ukraine, 2000, p. 226. (in Russian)http:www.ziet.zhitomir.ua/ua/faculty/fim/Kaf_phis.html

Molecular modelling and studies of specific intermolecular interactions in 4-pentyl-4'-cyanobiphenyl-titanium dioxide systems by vibrational spectroscopy

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Investigation of two-component systems based on TiO₂ crystalline powders, as-prepared and placed into 4-pentyl-4'-cyanobiphenyl (5CB) has been carried out by vibrational spectroscopy methods (experiment and theory). Vibrational spectra of pure TiO₂ powders, 5CB, and also heterogeneous systems TiO₂-5CB have been analyzed. Vibrational spectra samples have been measured at room temperature in a region of 4000-400 cm^{-1} .

Calculation of the energy, mechanical, electrooptical parameters, dipol moment, computer simulation of the structure and vibrational spectra of free molecule 5CB were performed with the program GAUSSIAN 03 package [1] for Windows.

For finding - out the mechanism of molecular interactions between 5CB molecules and TiO2 surface the theoretical modelling of the vibrational spectrums of 5CB with consideration of a hydrogen bounding effect. Molecules 5CB about the surface of TiO2 form hydrogen bonds with \equiv Ti-OH, through C \equiv N group.

 B. James, Foresman and Aleen Frisch Exploring Chemistry with electronic structure methods. Second Edition, Gaussian Inc., Pittsburgh PA, 1996, p. 302.

Temperature shifts of electronic spectra of large aromatic molecules in the gas phase: On the nature of diffusion band origins

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Temperature shifts of $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ phenanthrene and $S_1 \leftarrow S_0$ fluorene spectra are measured. The results with data for anthracene are treated according to the Mirumyants and Demchuk model [1, 2] which gives the linear dependence of spectral bands frequencies on temperature:

$$\nu = AT + B$$

The A and B values for the most longwave diffuse spectral bands are listed below with their uncertainties and correlation coefficients. The values of B differ from frequencies of quasilinear 0,0 bands, ν_0 , measured in supersonic jets or in a very long cell (for anthracene) at ambient conditions. The differences $\Omega = B - \nu_0$ correspond to antisymmetric out-of-plane molecular core vibrations.

Molecule	A	σ_A	B	σ_B	ρ	ν_0	Ω
Anthracene	- 0.9689	0.146	27959	79	0.999	27688	271
$S_1 \leftarrow S_0$							
Phenanthrene	-1.175	0.038	35654	18	0.999	35384	270
$S_2 \leftarrow S_0$							
Phenanthrene	-1,30365	0,097	29588	49	0,997	29333	355
$S_1 \leftarrow S_0$							
Fluorene $S_1 \leftarrow$	-1.0436	0,1623	33990	83	0.998	33782	208
S_0							

The conclusion that the origin of vibronic sequences of diffusive bands in the gas phase spectrum is not the broadened ν_0 band but is $\nu_0 + \Omega$ band was made. Studies of liquid solutions show that the same situation exists in the liquid phase.

- [1] Mirumyants S.O. and Demchuk Yu.S., Optika i spektr. 56, 241-246, 1984.
- [2] Demchuk Yu.S., Optika i spektr. 93, 222-227, 2002.

Electro-optical parameters of the spectrally active molecules, determined from the solvent influence on the electronic spectra

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The dipole moments and the polarizabilities in the electronic states involved in the electronic bands appearance are determined by using theories regarding the solvent influence on the wavenumbers in the maximum of the electronic bands.

Multiparameter regressions were used in order to express the contribution of the intermolecular interactions to the spectral shifts as function of the solvent macroscopic parameters (electric permittivity and refractive index).The coefficients that multiply the solvent functions in the spectral shifts expressions are used to determine the dipole moments in the excited states and the dipole moment of the transition for some cycloimmonium ylids.

The polarizabilities in the excited state involved in the electronic transition were also estimated from the non-polar solvents influence on the visible electronic bands of some molecules characterized by a high symmetry. The anthracene derivatives were considered for this study.

Takehiro Abe model for a pure simple liquid permitted us to estimate the dipole moments and polarizabilities of some molecules that can be approximated by spheres and that have a small dipole moment when they are solved in simple liquids. This model has been applied to some anthracene and nitrophenole derivatives.

The values of the dipole moments and polarizabilities obtained by using different models are discussed taking into consideration the limits of the used theories in which the electro-optical parameters are expressed as functions of the solvent macroscopic parameters and of the spectral shifts induced by the solvents.

Theoretical analysis of Raman and resonance Raman spectra of guanine

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The simplest bases of nucleic acids are the important objects to apply theoretical methods of Raman and resonance Raman spectroscopy. In this study classical approach was used to get the relative line intensities in the Raman spectra of guanine and its deuterated-substituted analogues. To describe the intensity distribution in the resonance Raman spectra (RRS) of guanine, in contrast, the quantum-mechanical method was used. Satisfactory agreement between theoretical and experimental data was achieved in both cases and the comparable analysis of vibration mode activity was made. The influence of hydrogen bonds on Raman spectra was also discussed. It was shown that guanine exists in different tautomeric forms (G-N9H and G-N7H) in aqueous solutions with different pH-factors.

Our calculations gave an opportunity to correct the interpretation of some lines in spectra of deuterated-substituted guanine as well as to confirm the validity of obtained set of force constants and electrooptical parameters. The study of intermolecular interactions by modeling of the force field allowed us to determine the H-bonds N7...HN14 and O12...HN1 in polycrystalline state. The analysis of the force and electrooptical parameters showed the presence of H-bonds in the alkaline medium and the joining of H(D) to N7 atom. It has been estimated that there are two tautomeric forms of guanine in aqueous solution. The G-N9H is preferable in neutral aqueous solution and in medium with pH<0 and the G-N7H - in the medium with pH=11.

Monte Carlo Simulation of Molecular Rotational Diffusion

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Observation of the molecular rotational diffusion in solution can be used to estimate various molecular properties as shape, structure, orientation, energy transfer parameters. The measurement of time resolved fluorescence anisotropy is a technique that can be used to investigate molecular rotation diffusion.

Theory for the interpretation of the time resolved fluorescence aniso-tropy decay affected by molecular rotational diffusion was offered by Bel-ford (M. Ehrenberg, R. Rigler, 1972). In the Belfords model fluorophores absorption and emission dipoles have well-defined orientations with respect to the axes of the molecule. However, this formalism could hardly be adapted to complex molecular systems, for example, porphyrine polymers, molecular stacks, and other self-organized and partly-ordered molecular aggregates.

An alternative and often-successful approach to retrieving molecular characteristics from the time resolved fluorescence anisotropy decay is the Monte Carlo simulation method (S. Harvey, H. Cheung, 1972). The rotational motion of a diameter of a rigid sphere with an arbitrarily chosen orientation at zero time can be described by a master equation analogous to the Ficks second law. For the description of hydrodynamic properties of a complex molecule, it is often convenient to approximate its shape by a smooth and symmetrical geometrical figure. For example, ellipsoids of revolution, which are three-dimensional bodies, generated by rotating an ellipse around one of its characteristic axes. Ellipsoids have three principal axes, each of which associated with a characteristic rotational diffusion coefficient.

A large population of identical molecules, each with its own internal coordinates and orientations of the moments of absorption and emission, is generated with a random number generator, which is further used for the simulation of Brownian rotation. The simulation of excitation considers the probability of photon absorption. This value is proportional to square of the cosine of the azimuthal angle of the absorption dipole and independent of the polar angle of the absorption dipole. Brownian rotation is simulated by series of small rotations around all molecular axes while fluorophor stays is exited. The magnitude of each rotational step is determinate by the rotational diffusion coefficient. After emission the anisotropy decay is computing using coordinates of the emission dipole at the laboratory coordinate system. Our proposed model, based the Monte Carlo simulation, could potentially be applied to analysis of timeresolved fluorescence anisotropy decay of complex molecules. As input the program requires: fluorescence lifetime of molecule, rotational diffusion coefficients, orientation of molecular axes of symmetry and orientation of the absorption and emission dipoles.

Conception of nonlinear wave's interaction in physics and spectroscopy of the condenced media

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The basic laws of nonlinear resonant interaction of waves were investigated in series of author's works. The new phenomena were established: 1) the existence of coherent superpositions of waves with several frequencies matching with the characteristics of energy states of quantum media; 2) nonlinear quasisynchronism, that determine the spatial accumulation of nonlinear effects in extensive media; 3) nonlinear concentration of energy on the definite frequencies; 4) resonant interfocusing and defocusing of wave; 5) parametric light generation with narrow lines structure of spectra. The knowledge of universal conformities with laws of nonlinear wave interactions opens a new stage in the development of solid-state physics, for which all excitations are collective. The received results allow to study more deep the processes of excitation dinamic in condensed media and correctly to interpret the spectral data. In particular, the phenomena induced dispersion and nonlinear quasi-synchronism allows to explain displacement of spectral band in the party from a resonance or phase matching, that is shown at two-photon absorption and stimulated scattering of light, and also at four-photon mixture of waves. Detection of collective (wave) properties of excitation in liquids and presence at them of such characteristic as the wave vector, opens new ways in the development of biophysics and in study of the molecular physics phenomena. The forming of coherent superpositions of waves explains the essential weakening of absorption of waves, that is fundamental for microwave radiation in alive organisms and existence of the Chinese meridians. For the first time is shown, that many anomalies of water media have a nonlinear-optical nature. For example, the maximum of speed of a sound in water at 75° C and maximum heat conductivity about 135° C are connected with the generation of the second harmonic of longitudinal acoustic (LA) waves $\sim 120 \ cm^{-1}$ and excitation of longitudinal optical (L) waves $\sim 270 \ cm^{-1}$.

Phase transitions (PT) of melting and boiling, and polymorphous transformations of structure of solids also have a nonlinear-wave nature. It is established the phonon discreteness behaviour of heats of PT for molecular, covalent and ionic crystals and also for metals. The essence of the new approach is, that of thermal excitation low-frequency grating and intermolecular modes to reduce generation high-frequency resonant excitation, resulting to PT. For example, melting of the ice is caused by excitation of summary tone TO and L modes of net of hydrogen bonds, melting of silicon is connected with the excitation of overtone $8\nu_o$ of the known grating mode $\nu = 520 \text{ cm}^{-1}$, and melting of CsBr – with overtone $27\nu_o$. Temperature determines only initial level of thermal excitation of interactive waves, and the heats of transitions are determined by

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frequencies of the effectively generated high-frequency waves. The higher nonlinearity of medium is, the smaller is temperature PT and more is their heat. Only this theory allows to explain the reduce of melting temperatures of crystallohydrate and many alloys by many hundreds degrees, despite of increasing of the bonding energy. This theory allows also to understand the essential reduce of the freezing temperatures of liquid mixtures and electrolyte solutions, despite of the strong intermolecular interaction, for example H_2O and H_2SO_4 . The fluctuation phenomena frequently observed and discussed in physics are also a direct consequence of nonlinearity of occurring processes. The phenomenon of nonlinear concentration of energy thermal excitation allows to explain the high speeds of diffusion processes in the condensed media. The basic properties of liquids are caused by the collective nature of elementary excitation and their nonlinear interaction.

Mass-spectroscopy of dissociative ionization of polyatomic molecules: production of ionized fragments

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Molecules containing a large number of atoms (in many cases — up to several dozens) attract much attention of researchers due to their specific role in various technological areas. Among them of special interest are the processes of plasma etching, biological applications, laser and fusion problems etc. The diversity of processes involving such complex molecules requires variety of methods of their investigation. Among them the mass spectroscopic studies of polyatomic molecules and their constituents occupy one of the leading places. Of special interest are the processes resulting in the molecule fragmentation under the influence of ionizing radiation (i.e. gamma-quanta, high-energy photons, charged particles), where mass spectroscopy is one of the most powerful and reliable tools of research.

Electron interactions with polyatomic molecules are being a subject of extensive studies within last few decades (see, e.g. [1]). Electrons incident on the molecule cause dramatic changes in the molecular structure, resulting in bond break and formation of a series of molecular, atomic and ionic fragments. The lower is the energy of electrons the more fine effects could be revealed when studying the products of molecule dissociation.

Here we report on a critical survey of our recent studies on electron-impact ionization and dissociative ionization of polyatomic molecules performed by using a mass spectroscopic technique. The circle of molecules under study was rather wide ranging from simplest ones (e.g., atmospheric gases, water) to complex organic species (benzene, pyridine, dimethylformamide, etc.) including their deuterated analogs, and several halogen-containing molecules (freons, sulfur hexafluoride). The main emphasis was drawn to the investigation of the near-threshold behavior of ionization cross sections and, in particular, to the determination of the appearance potentials for different ionic fragments produced by electron impact.

The experimental apparatus included a high-vacuum chamber, electron and molecular beam sources and a quadrupole mass analyzer with the relevant PC-based digital data acquisition and processing system. The details of the experimental technique could be found elsewhere [2]. It should be noted that the incident electron energy spread was $\pm 0.5\,$ eV allowing the appearance potentials to be determined with the same accuracy. A least-square method-based fitting algorithm was applied to determine the absolute values of the appearance potentials.

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We have measured the appearance potentials for almost all of ionic fragments produced by electron incidence on the complex molecules under study. The comparison of our data with those quoted from the electronic NIST database [3] (if available) shows that for the most of the fragments the agreement with the reference data is fairly good within the limits of experimental error. At the same time, a number of data have been obtained by us for the first time.

More detailed information and discussion of results will be presented at the Conference.

- Christophorou L.G., Electron-Molecule Interactions and Their Applications. V. 12, Academic Press, Orlando (1983),
- [2] Snegursky A.V. and Zavilopulo A.N., Nucl. Instr. Meth.B. 126, 301 (1997).
- [3] NIST Database, http://webbook.nist.gov.

Spectroscopic study of imidazo- and triazolophenazine deriviatives

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Heterocyclic dyes are often used as a suitable model system and as a sensitive element in different devices for detecting slight environmental changes or as an intercalative fluorescent probe upon studies of nucleic acids. All these advantages permit wide range applications - from medicine to nanomaterial science. Imidazo- and triazolophenazine derivatives can be successfully used in all these fields.

Effects of side substitutients on vibrational spectra (Raman and IR absorption spectroscopy) of imidazophenazine as well on the electronic ones (visible absorption and fluorescent spectroscopy) have been studied. The observed vibrational spectra were analyzed using harmonic frequencies, IR intensities and Raman activities calculated at the DFT(B3LYP)/ $6-31++G^{**}$ level of theory. Based on this analysis, assignments of the spectral bands were performed. Total atomic charge distributions for all the studied phenazine derivitives were also calculated. As nitrogen atoms of phenazole, imidazole and triazole rings possess lone electronic pairs, they can be acceptors of protons. Visible absorption and fluorescent spectra of imidazo- and triazolophenazine derivitives were investigated in aqueous buffered solutions over the wide pH range from 0 to 12. A possibility of using these dyes as sensors for some pH is discussed.

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Inelastic neutron scattering (INS) studies of torsion CH_3 vibrations in methyl derivatives

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The results of spectroscopic studies in low frequency region of various methylderivatives and their charge transfer complexes are reviewed. Inelastic neutron scattering technique was chosen as most suitable method in studies of low frequency modes related to CH₃ torsional vibrations. Among various compounds tetramethylbenzene (durene) tetramethylpyra-zine (TMP) tetramethylbenzoquinone (TMBQ) and hexamethylbenzene were distingnished. As electron acceptors in change transfer complexes chloranilic acids (CLA) tetracyanoquinodimethane (TCNQ), tetracyano-ethylenes (TCNE) and tetracyanobenzene (TCNB) were used. In addition to INS as well as IR and Raman spectra the structure of complexes, the tunneling splitting and quasielastic neutron scattering were analyzed. The role of unconventional hydrogen bonds and charge transfer interaction are discussed.

Monte Carlo Simulation of Energy Transfer Processes

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Methods of the fluorescence spectroscopy, especially ones based on spectroscopic tracking of the energy transfer (ET), are widely used to study the structure and inner processes in different matters, such as molecular crystals, thin molecular layers and complex biomolecular systems [1]. Often the complexity of molecular systems makes difficult the interpretation of experimental data. The existing theoretical models for ET processes describe rather a limited set of molecular systems and their fluorescent properties. Another a powerful alternative approach to analyse photophysical processes in the experimental systems is a Monte Carlo simulation modelling [2]. This method allows to estimate the physical parameters of the investigated system.

The standard simulation models of electronic excitation energy transfer mainly deal with a single ET mechanism either dipole-dipole ET [3] or exchange ET [4]. Whereas in experimental systems several ET mechanisms, like non-radiative multipole, exchange, and radiative, can compete simultaneously. Columnar liquid crystals, porphirin thin films and zeolite crystals with high density of molecular packing are such systems [5] - [7]. Therefore the development of a universal simulation model, which might include several different energy transfer mechanisms, is of high importance.

This work is aimed on the development of the simulation model for electron excitation energy transfer implementing several mechanisms. The developed simulation model imitates ET in a three-dimensional molecular structure in which the dipole-dipole, exchange and radiative ET mechanisms occur. The simulation is performed in two stages:

- 1. On the first stage the spatial structure of the studied system is generated. The outcome are the coordinates of fluorescent molecules. To avoid border effects the periodic boundary conditions are used.
- 2. On the second stage the energy transfer processes is simulated using the Monte Carlo method. The original algorithm was taken from [1] and it has been modified by including exchange and radiative energy transfer pathway. The results of our simulation are in a good agreement with published data.
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The absorption profiles of molecular liquids in the overtone region and the fundamental bands intensities of the greenhouse gases.

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Precise data on the intensities of strong fundamental absorption bands of greenhouse gases are important for reliable remote sensing of the atmosphere. It's not easy to obtain accurate values in the gas phase due to very low concentrations needed, as a rule, for such measurements. A new approach was developed being based on the analysis of absorption profiles of the overtone and combined bands in the spectra of these substances in the liquid phase, close to melting point. It was shown earlier that the profiles might be quantitatively described when the interaction of the transition dipole moments is taken into account in the framework of the cell model of a liquid. Now the experiments were carried out with molecular liquids SF₆, CF₄, SiF₄, NF₃, CHF₃, CClF₃, CBrF₃, OCS, N₂O and CO₂ with intensities of fundamental bands of 1000-400 km/mole. IR spectrophotometer Brucker IFS28 at 1 cm^{-1} resolution was used for spectral measurements within 7000-1000 $\rm cm^{-1}$ interval. The condensation of the gases was performed in low temperature optical cells with path length 93 mkm and 2.02 cm respectively. The measurements were carried out within 90-225 K. The evaluated from the analysis of these spectral data fundamental absorption bands intensities are coincide within 5-10% with the most reliable literature ones.

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Raman spectra of acetonitrile CN vibrations in aqueous and other solutions. Experimental and non-empirical calculation results.

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Nonempirical quantum-chemical calculations show the possibility of dimmer formation in pure acetonitrile and in its solutions with water and formic acid. Therefore the low-frequency asymmetry of CN vibrations band in Raman spectra of liquid acetonitrile can be related to existence of dimmers. In neutral solvent within concentrations 1.0 - 0.1 mole fr. the CN vibrations band is conserved, however in aqueous solutions and in solutions with formic acid in this concentration region other type of asymmetry appears: firstly, with dilution of acetonitrile there appears a high-frequency asymmetry and band broadens, further at concentrations lesser than 0.5 mole fr. again appears a low-frequency asymmetry. These features of CN band behavior are connected in this work with existence of the acetonitrile-proton donor solvent aggregates. On existence of the aggregates in solution of acetonitrile-water indicates also such fact as appearance of maxima frequency difference for CN band in parallel and perpendicular polarized components of the band and the change of this difference with concentration of acetonitrile.

Spectroscopy of aromatic hydrocarbons of automobile petrol

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Development of spectroscopic methods for testing of light oil products provides a possibility to reveal very small amount of light oil products by a nondestructive monitoring.

In this work electron absorption and luminescence spectra of different types of automobile petrol with octane numbers 76 (trade mark is A76) and 92 (trade mark is A92) and its hexane solutions were investigated. Samples for investigation were obtained from the same oil refinery. Electron absorption spectra were measured at liquid state of petrol at room temperature. Luminescent properties were investigated at RT, 77 and 4.2 K temperatures of samples.

Obtained luminescence spectra can be considered as composition of three main wide bands in the 360 - 425, 425 - 475, and 475 - 550 nm spectral regions. There were distinctive changes in the emission spectra when temperature of the samples decreases up to 77 K and 4.2 K. Sample are frozen at these temperatures and are in solid (glasslike) state. There was essential improvement of the quasi linear structure of the spectral bands in frozen state of petrol.

Luminescence characteristics such as spectral distribution, shape, number and intensity of spectral details depend on petrol content in solutions. Concentration dependences of luminescence intensities of both wide luminescence bands of liquid solutions at room temperature and peak intensities of luminescence lines of quasi linear spectra of frozen solutions were constructed.

Linear spectra of the frozen petrol and their solutions are considered as a superposition of the emission spectra of the various polycyclic aromatic hydrocarbons (PAHs) in petrol composition. These components respond in a different way on the decreasing of temperature and transition from liquid to frozen state. Obtained quasilinear spectra have been compared with literature data on luminescence both of many individual PAHs and their mixtures in various solutions and this comparison was resulted in establishment of some PAHs which responsible for luminescence of petrol.

Obtained results confirm made before conclusions about necessity to increase selectivity and sensitivity of luminescence methods. We suppose the choice of the conditions of luminescence measurements will provide effective detection of the certain PAHs and, therefore, it can allow determination of small quantity of petrol. Data obtained for hexane solutions of petrol are interesting for environment monitoring and forensic examination because they show possibility to operate with very small quantities of the investigated substances. In the work the perspectives of practical using described above experimental results are modeled on an example of examination of small pine-tree pieces wetted by the automobile petrol.

Nonlinear fundamental frequency shifts of molecular oscillations in Raman and IR spectra

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The discrepancy between fundamental frequency values observed in IR and Raman spectra has been studied. It was supposed that this effect results from competition between the resonance and the dissipative relaxation of vibration excitations. Nonlinear interaction of exciting, and Stokes and Anti-Stokes waves was analyzed. IR and Raman spectra of some dipolar liquids were recorded and the comparative analysis of isotropic, anisotropic Raman, and IR band contours was carried out. It was found that difference between IR and Raman frequencies decreases in the process of dilution in inert solvents.

The modeling of the benzophenone vibrational spectra and intermolecular interaction peculiarities in near-surface layer of benzophenone-titanium dioxide system

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Vibrational spectra of benzophenone (BP), and of heterogenic bicomponent systems on the basis of polycrystals consisting of titanium dioxide (TiO_2) nanoparticles embedded in benzophenone were measured.

The modeling of the structure and vibrational spectra of the considered compounds by method of fragments (LEV-100 program complex) and B3LYP/6-31G(d) (Gaussian'03 software) was carried out. The structures of benzophenone free molecule and vibrational spectra of it were calculated. An estimation of the specific intermolecular interaction magnitude and of its influence on benzophenone vibrational spectrum in BP-TiO₂ bicomponent mixture was made.

It was found that hydrogen bond is basic mechanism of the intermolecular interaction between TiO_2 nanoparticles crystal surface and benzophenone. The hydrogen bond is formed at the proton sharing between oxygen atom of carbonyl group of benzophenone which is near the surface of TiO_2 nanoparticles and hydroxyl group of Ti-OH which is TiO_2 hydrate fragment. The energy of H-bond is 7 kcal/mole.

The H-bond formation is substantially transforms pure benzophenone spectrum in O-H and C=O valence bonds regions. It stimulates to the forming of layers with certain orientation of adsorbent (benzophenone) molecules.

Incommensurate phase transitions in crystalline 4,4-dichlorobenzophenone

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In recent years considerable interest has been given to the study of the phase transition to an incommensurate phase, which is often called "incommensurate phase transition" [1]. Such transitions have been found in a group of molecular compounds, the molecular shape of which is similar in the sense that they all have two benzene rings. Example is 4,4-diclorobenzophenone (hereafter DCBP). It has high (HT) and low (LT) temperature monoclinic crystalline phases and an intermediate phase, which has incommensurate structure [2, 3].

Despite an extensive literature devoted to phase transitions in DCBP, some doubtful and ambiguous results for the DCBP, should be noted. Our interest in a study of incommensurate phase transition has been stimulated by the fact that DCBP has never been investigated with IR spectroscopy. However IR spectra in principle could throw additional light towards the understanding of the incommensurate phase.

In this paper we report the experimental results of the temperature evolution of the infrared spectra and thermal properties of DCBP with decreasing/increasing temperature. IR spectra were recorded on Bruker IFS-88 FTIR spectrometer over a broad frequency range (300-3600 cm⁻¹). Thermal properties were performed on a Perkin-Elmer DSC7.

It has been found that formation of the incommensurate phase on cooling from HT phase begins from 184 K, continuous to 161 K and accompanied by a small heat release. Heat release effect results in the LT phase formation. Upon heating from LT the formation of the incommensurate phase accompanied by a small heat absorption. It begins from 192 K and continuous up to 206 K, leading to HT phase formation. IR spectra exhibits only subtle changes in the spectrum of incommensurate phase in comparison with the IR spectra of HT and LT phases. The obtained IR and thermal results have been discussed in the light of the crystallographic studies [3].

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Vibrational spectra and structural-dynamic models of 2-biphenylmethanol

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In this work the structure of 2-biphenylmethanol (2BPM) in crystal and glassy states was investigated using the X-ray diffraction, vibrational spectroscopy and quantum chemistry methods.

The structure of the unit cell was determined using X-ray diffraction analysis at room temperature. IR absorption and Raman spectra of 2BPM at the wide range of temperatures (from liquid helium temperature up to 350 K) have been measured. Preliminary analysis of the experimental data points to the presence of the H-complexes of 2BPM in the sample, which are represented by tetramers in the case of crystal state.

The modeling of the structure and vibrational spectra of 2BPM by the method of fragments using LEV-100 program package and by the density functional method (B3LYP/6-31G(d)) using Gaussian03 software was carried out. The structural-dynamic models of free 2BPM molecule and of its different H-complexes are described: the energies, the geometries, the mechanical and electro-optical parameters and the vibrational (IR absorption and Raman) spectra were calculated. The possibility of using of fragment approach in quantum-mechanical modeling was discussed.

Full interpretation of the measured vibrational spectra of the crystal samples of 2BPM was given. A conclusion about 2BPM structure both in crystal and glassy state with taking into account of specific intermolecular interactions was made.

Intermolecular interaction and intramolecular coupling in alklcyanobiphenyl compounds

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Alkylcyanobiphenyl compounds with n=2-7 (n-number of carbon atoms in alkyl chain) which posses directly crystal (C) to nematic liquid crystal (nLC) transition were investigated by vibrational and electronic spectroscopy methods.

Vibrational spectra of investigated compounds in meso- and crystalline phase display some bands with different frequencies, intensities and broadening. Such redistribution of bands in vibrational spectra of 5CB, 6CB and 7CB in crystalline and liquid crystal phase can be explained by structural change of molecules and conformational mobility of molecules.

Absorption and emission electronic spectra of above molecules were investigated in diluted polar and nonpolar solvent as well in crystalline phase. Different shapes and brightness bands of emission spectra (FWHM) depending on the polarity of solvent were observed while for absorption spectra only batochromic shift was observed.

It is well know that biphenyl and its derivatives as alkylcyanobiphenyl compounds posses close lying S_1 and S_2 states which can interact by intramolecular coupling. Result of this behavior can be observed in fluorescence spectra.

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Theoretical analysis of two-component equilibrium of aromatic molecules in solution based on NMR data

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Stochastic cooperative (STOCH-C) and non-cooperative (STOCH-NC) models have been developed for NMR analysis of the hetero-association of aromatic compounds in solution, in order to take into account all physically-meaningful association reactions of molecules in which there are no limitations on the lengths of the aggregates and complexes. These algorithmical approaches are compared with previously published basic (BASE) [1] and generalized (GEN) [2] analytical statistical thermodynamical models of hetero-association of biologically-active aromatic molecules [1] using the same sets of published NMR data measured under the same solution conditions (0.1 phosphate buffer, pD=7.1, T=298K). It is shown that, within experimental errors, the BASE analytical model may be used to describe molecular systems characterized by relatively small contributions of hetero-association reactions, whereas the GEN model may be applied to hetero-association reactions of any aromatic compound with different selfassociation properties. The STOCH-C computational algorithm enabled the effect on hetero-association of the interactions of molecules with different cooperativity parameters of self-association to be estimated for the first time and it is proposed that the algorithm for the stochastic models has great potential for detailed investigation and understanding of the interactions of aromatic molecules in solution.

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Conformational analysis of 1-vinylimidazole and 1-vinyl-2-methylimidazole by 1H and 13C NMR spectroscopy and ab initio calculation

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Ab initio calculations of geometries for molecules of 1-vinylimidazole (1) and 1-vinyl- 2-methylimidazole (2) were carried out by Gaussian 98W program package with different basis sets (6-31G, 6-311(d,p)) and different methods: HF and B3LYP. The molecular energy potential of compounds (1) and (2) as a function of the rotational angle around bond N(1)- C(alpha) were obtained.

Two minima are located on the potential energy surface of compounds (1) corresponding to planar conformers with different spatial orientation of vinyl group: anti-C(2) (global minimum) and sin-C(2) (local minimum). The energy difference between the global minimum and local minimum is estimated as 0.48 - 0.84 Kcal/mol according to different methods. Partial populations for two conformers were evaluated as 0.8 (anti-) / 0.2 (sin-) from Boltzmann equation for relative population.

Three minima are located on the potential energy surface of compounds (2) corresponding to planar conformer with anti-arrangement vinyl group and 2-methyl group (global minimum) and two symmetrical minima (local minima) corresponding non-planar sin- orientation of vinyl group and 2-methyl group. Two local minima correspond to the torsion angle 30 degree complying to the location of vinyl group out of plane imidazole ring. The energy difference between the global minimum and local minima amounts 2.06 to 1.6 Kcal/mol according to different methods. Partial populations for tree conformers were evaluated as 0.97 (anti) / 0.03 (sin).

1H and 13C NMR shielding constants were computed via GIAO method for conformations corresponding to the states in global and local minima of energy. The value of chemical shifts were averaged by partial populations. The best correspondence with experimental data were achieved on method B3LYP with basis set 6-31G. NMR data confirm the results of calculation. Chemical shifts of C(betta) carbon of vinyl group indicate the well conjugation vinyl group with imidazole ring. Analysis 2D spectra NOESY show exiting (1) as mixing of two conformers with sin- and anti- arrangement of vinyl fragment. For compound (2) observe correlation only for anti-conformer. Planar structure of investigated molecules confirms observed long range spin coupling between protons of vinyl group and protons of imidazole ring.

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Conformation changes of actinocin derivatives by the Raman spectroscopy and H-metric.

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By method of Raman spectroscopy and -metric within the intervals of pH=3,5-7,0 was investigated of waters solutions of actinocin derivatives lateral chains derivates with different length are conducted (newly synthesized ligands - analogues of anticancerantibiotics). There were discovered changes of spectral parameters (frequencies and intensities) of the ligand solutions at the increase of acidity of environment.

The possible sites of protonization of the functional groups and alterations of the chromophore ring conformation are discussed. Analysis of obtained Raman spectra of the considered ligands and of the titration curves under different values pH permitted to make assignments of corresponding bands and to determine constants of protonization. The results of investigation may be useful to estimate of deposit of electrostatic co-operation at formation of complexes biologically active cations with the negatively charged matrices of nucleic acids.
Optical emission spectroscopy of air plasma in the blowing arc discharge

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Spectroscopic characterization of air plasma in electric discharges is of permanent interest because of various important applications [1]. In this work we report about the study of a specific case of the atmospheric pressure air plasma in the transverse blowing arc DC HV discharge [2].

In the experiments, a free jet of the compressed air ran from the nozzle across the gap between the opposite electrodes, ignited and formed a bright crescent-shaped arc as well as a highly reactive afterglow downstream. For diagnostics we applied a method of the optical emission spectroscopy (OES) using a rapid PC-operated lightguiding CCD-based UV-VIS-NIR spectrometer (spectral resolution ~0.3 nm) with the calibrate spectral lamps. Measurements were conducted in different sections of the plasma jet (spatial resolution ~0.1 mm) under variation of discharge parameters. Within the spectrum of wavelengths from 200 to 1100 nm all remarkable emissions were monitored, and all analytical atomic lines O, N, H and molecular bands of N₂, O₂, NO, OH, NH, CN were identified [3]. On this base, the curves of changes of selected emissions' intensity along the plasma jet were analyzed depending on the flow rate and discharge power.

From relative intensities of the copper CuI lines (product of the electrode emission) at 510.5, 515.3, 521.8, 578.2 nm and oxygen OI lines at 777.3, 844.6, 926.0 nm, using the Boltzmann plot, we determined the temperatures of electronic excitation of free atoms, T_{exc} . From the nitrogen 1st negative system $N_2^+(B^2\Sigma_u^+ - X^2\Sigma_g^+)$ bands (0,0) 391.4, (1,1) 388.4 nm, etc and 2nd positive system $N_2(C^3\Pi_u^+ - B^3\Pi_g^+)$ bands (0,0) 337.1, (0,1) 357.7, (0,2) 380.5 nm, etc (dominating components in the plasma-forming gas), we determined the excitation temperatures of vibrational states of molecules, T_V . The excitation temperature of rotational states, T_R , because of non-resolved rotational spectral structure, was estimated by the comparison of the measured spectra of the $N_2 2^+(0,0)$ 337.1 nm and (1,4) 399.8 nm bands and the corresponding synthetic V-R spectra calculated on the known spectral constants, using the Gaussian instrumental function. The electron density is deduced from the Stark broadening of the Balmer HI α line 656.3 nm.

We found that there is no LTE in the studied arc discharge during its space/time evolution, and effects of the strong non-izothermality have place when a usual two-temperature approach with T_e for electrons and T_g for heavy particles is not valid.

The measured/estimated characteristic temperatures are within a relation $T_e \sim T_{exc} > T_V > T_R \sim T_g$, where T_{exc} differences from T_V and T_R more than twice. This indicates a transitional regime of the arc discharge [4] when it is supported both by the thermal ionization (function of the gas temperature) and by the direct electron impact ionization (function of the electric field).

Another character effect is the nonlinear rise of the emissions ("ignition") downstream the arc resulted from the kinetic non-equilibrium in the dynamically moving plasma. All characteristic temperatures varied very much, and the level of non-izothermality is not permanent along the arc. It depends not only on the arc current but also on the airflow that is blowing the arc plasma column, providing convective heat transfer. A highest value $T_{exc} \sim 1.2$ eV is measured in the center of the arc. In the afterglow, T_{exc} decreases while T_V and T_R keeps longer. Then increasing the arc current, the value T_{exc} becomes larger. At a lager flow rate, the gradient T_{exc} becomes smaller. Despite of high pressure, the air plasma in the blowing arc remains ionizationally non-equilibrium with the overheated electron component due to the effective energy carry-over. According to estimation in comparison with a hypothetic case of the LTE Saha's law, a degree of nonequilibrium is as high as $\sim 10^2 - 10^3$.

We conclude that even small variations in the blowing arc plasma conditions due to their spatial/temporal instability, decomposition, contamination, etc can produce large visual changes in the spectral emission which is functionally related with the temperatures and concentrations of plasma components, so the OES could serve as a powerful tool for diagnostics of nonequilibrium air plasma.

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Cross-sections of atom-atom collisions calculated within TDDFT

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Introduction. Atom-atom collisions are an efficient method for investigating and changing properties of solid. Researches in this field have been performed since the early 60-s, when Firsov and Lindhard had developed their theories, in which elastic and inelastic energy losses taken into account independently. Obtained results agree with experiments with an error about 30%. Now plenty of investigations are aimed to modify nanoobjects by particle beams. Theoretical [1] and experimental [2] studies have shown that in this case correlations between nuclear scattering and electronic stopping became important. In this article an *ab-initio* studies of above cross-sections were performed in framework of time-dependent density functional theory (TDDFT) [3].

Model and equations. Let the system consists of N_i nuclei and N_e electrons. Nuclei are treated classically by coordinates $\vec{R}_A(t)$ and momentums $\vec{P}_A(t)$. Electrons are treated within quantum mechanics by density $\rho(\vec{r},t) = \sum_{j=1}^{N_e} |\psi^j(\vec{r},t)|^2$, where $\psi^j(\vec{r},t)$ are single-particle wave functions satisfied the Kohn-Sham equations [3]. They can be presented as $\psi^j(\vec{r},t) = \sum_{\alpha} a^j_{\alpha}(t)\varphi_{\alpha}$,

where $\{\varphi_{\alpha} (\vec{r} - \vec{R}_{A_{\alpha}})\}\$ is a basis-set, $a_{\alpha}^{j}(t)$ are expansion coefficients, and A_{α} denotes an atom on which the orbital φ_{α} is centred. The system of coupled equations, which describe self-consistently and simultaneously the dynamics of classical and quantum subsystems, are derived:

$$\dot{a}^{j}_{\alpha}(t) = -\sum_{\beta\gamma} S^{-1}_{\alpha\beta} \left(iH_{\beta\gamma} + B_{\beta\gamma} \right) a^{j}_{\gamma}, \tag{1}$$

$$M_A \ddot{\vec{R}}_A = -\frac{\partial}{\partial \vec{R}_A} \sum_{B=1}^{N_i} \frac{Z_A Z_B}{\left|\vec{R}_A - \vec{R}_B\right|} + \sum_{j=1}^{N_e} \sum_{\alpha\beta} a_\alpha^{j*} \left(-\frac{\partial H_{\alpha\beta}}{\partial \vec{R}_A} + \vec{D}_{\alpha\beta}^A\right), \quad (2)$$

where $\vec{D}_{\alpha\beta}^{A} = \left\langle \varphi_{\alpha} \middle| \frac{\partial}{\partial \vec{R}_{A}} (V_{eff} - V) \middle| \varphi_{\beta} \right\rangle + \sum_{\gamma\delta} \left(\vec{B}_{\alpha\gamma}^{A+} S_{\gamma\delta}^{-1} H_{\delta\beta} + H_{\alpha\gamma} S_{\gamma\delta}^{-1} \vec{B}_{\delta\beta}^{A} \right)$ + $i \left[\vec{C}_{\alpha\beta}^{A+} - \vec{C}_{\alpha\beta}^{A} + \sum_{\gamma\delta} \left(B_{\alpha\gamma}^{+} S_{\gamma\delta}^{-1} \vec{B}_{\delta\beta}^{A} - \vec{B}_{\alpha\gamma}^{A+} S_{\gamma\delta}^{-1} B_{\delta\beta} \right) \right], S_{\alpha\beta} = \langle \varphi_{\alpha} | \varphi_{\beta} \rangle,$ $H_{\alpha\beta} = \left\langle \varphi_{\alpha} \middle| \hat{t} + V_{eff} \middle| \varphi_{\beta} \right\rangle, \vec{B}_{\alpha\beta}^{A} = \left\langle \varphi_{\alpha} \middle| \frac{\partial}{\partial \vec{R}_{A}} \varphi_{\beta} \right\rangle,$ $\vec{C}_{\alpha\beta}^{A} = \dot{\vec{R}}_{B} \left\langle \frac{\partial}{\partial \vec{R}_{B}} \varphi_{\alpha} \middle| \frac{\partial}{\partial \vec{R}_{A}} \varphi_{\beta} \right\rangle, B_{\alpha\beta} = \dot{\vec{R}}_{A} \vec{B}_{\alpha\beta}^{A}, \hat{t} - \text{single-electron kinetic energy}$ - 39 - operator, effective potential V_{eff} is determined as

$$V_{eff}(\vec{r},\vec{R},t) = -\sum_{A=1}^{N_i} \frac{Z_A}{\left|\vec{R}_A - \vec{r}\right|} + \int \frac{\rho(\vec{r}',t)}{\left|\vec{r}' - \vec{r}\right|} d^3r' + V_{xc}(\rho),$$
(3)

exchange-correlation potential $V_{xc}(\rho)$ we taken in LDA approximation [3].

Results and discussions. The differential cross-section $d\sigma$ and total cross-section σ of elastic (subindex n), inelastic (e) and summarized (t) scattering of protons on hydrogen and helium atoms were calculated. The obtained results clearly reveal that nuclear scattering and electronic stopping are not independent, that is: $d\sigma_t = d\sigma_n d\sigma_e + d\sigma_{cor}$, where the former describes correlation of these processes. This quantity becomes essential in energy range $E_p \approx (1 \div 10) E_I$ where E_I is atom ionization energy. The calculations show that this effect arises due to difference between incoming and outcoming branches of the ion trajectory. This takes place because the electronic subsystem is excited and it changes the interaction potential on the outcoming branch.

Conclusions. The obtained results indicate that correlation between nuclear scattering and electronic stopping can influence essentially on energy losses of ions in low energy range. In case of nanoclusters it can finally lead to equilibrium states which different from predictions within conventional approaches.

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New aspects of the formation intensity ${}^{3}A_{2} \leftarrow X^{1}A_{1}$ transition and study of fine structure ${}^{3}A2$ term in molecule of ozone

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The singlet-triplet transitions in the ozone molecule have been the subject of much interest during last decade for both experimentalists and theoreticans. The triplet states of ozone are connected with the kinetics of formation and dissociation processes $O_2 + O \rightleftharpoons O_3$, and are therefore important for the photochemistry of the atmosphere. In our investigations, we paid special attention to the role of the lowest triplet excited states in the absorption spectrum of ozone, as well as to the analysis of the nature of the fine structure lowest triplet ${}^{3}A_{2}$ state. We calculated the fine magnetic structure of this term taking into account the contributions from the spin-orbit and spin-spin coupling by the method of multiconfiguration self-consistent field (MC-SCF) using the program DALTON. On the basis of the calculations performed, we can predict a large contribution from the spin-orbit coupling to the energies of the zero-field splitting of the ${}^{3}A_{2}$ state. The spin-orbit coupling with the ground $X^{1}A_{1}$ state is shown to make the main contribution to the zero-field splitting of the ${}^{3}A_{2}$ term. The calculated parameters D and E agree well with experiment. In our previously investigations the possibility of assignment of a weak absorption in the near IR region, termed the Wulf band, to the spin-forbidden singlet-triplet (S-T) transition ${}^{3}A_{2} \leftarrow X^{1}A_{1}$, caused by spin-orbit coupling, was studied on the basis of quantum-chemical calculations [1, 2]. From experimental analysis [3, 4] of the vibrational-rotational strcture of the Wulf band with the use of an ultrahigh resolution found the first spectrocopic evidence in favout ${}^{3}A_{2} \leftarrow X^{1}A_{1}$ assignment earlier proposed in the theoretical works. In this study we want to compare the MC-SCF results for the ${}^{3}A_{2} \leftarrow X^{1}A_{1}$ transition intensity in ozone absorption with the recently developed density functional theory (DFT). We used the ccpVTZ,6-311G** and 6-311++G(3df,3pd) basis sets in both types of calculations of the S-T transition probability. The results of the MC-SCF method strongly depend on the basis set chosen. DFT slightly underestimates the transition energy, which is a common aspect of the method. However, the relative intensities for the S-T transition to different moment to the T^{y} spin-sublevel. This becomes to 0.0039 au in DFT calculations. We find the DFT dipole transition moment values to be close to 0.0047 au. One should note that the measured cross-sections of the least-broadened rotational lines from high-resolution spectroscopy provide a similar transition moment value. Thus the DFT results seem very reasonable. The ratio $M_y(T^y)/M_z(T^z)$ is equal to 0.37 using the cc-pVTZ basis set, although an analysis of rotational lines indicates that this ratio is close to 10. Again the DFT ratio $M_y(T^y)/M_z(T^z) = 11.7$ (6-311 G^{*} is in good agreement with experimental data. Thus complicatesd S-T spectra is well reproduced in the DFT approach and despite the fact that the DFT method is based on the single-determinant density, it gives quite good geometry of the first excited triplet state of this biradical species. The MC-SCF and DFT quadratic response calculations showwed that the most intense among lowest S-T transitions is the ${}^{3}A_{2} \leftarrow X^{1}A_{1}$ transition (f=6*10-7). Therefore the results of performed caculations confirms that the ${}^{3}A_{2}$ triplet state as it determines the largest part of the Wulf band intensity

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The ν_1 band shape of the H₂O...HCl, H₂O...HF and its deuterium isotopomers in the gas phase: experiment and anharmonic ab initio calculation

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The present work is motivated both by fundamental questions concerning the mechanisms of the v(HHal) vibration-rotation band formation in the B...HHal complexes in the gas phase and by practical questions regarding the role of B...HHal aerosol complexes in atmospheric chemistry. Note that the calculations and experiments necessary to study these issues are near the limits of our technical ability. In this work, we examine four systems in considerable detail: $_2O...HF$, $D_2O...DF$, $_2O...DF$, and $_2O...HCl$ complexes.

The spectra of ${}_{2}O/HF$ and $D_{2}O/DF$ mixtures at 293 K in cells 20 and 1200 cm long were recorded in the range 4200-1500 cm⁻¹ at a resolution of 1.0-0.02 cm⁻¹ with Bruker IFS-28, Bruker IFS-113v, and Bruker IFS-120 HR Fourier spectrometers. The measurements were made at a total pressure of the mixture $p(X_{2}O + XF) < 20$ -25 Torr, where X=H, D. With the use the contour consist of the sum of Lorentzian and Doppler curves, free molecules H₂O, HDO and D₂O absorption bands were estimated and in result of the division of bands, the $\nu_1(HF)$ and $\nu_1(DF)$ absorption bands contours for the light and heavy complexes were defined. The ν_1 band of the H₂O...HF complex has an asymmetric form characteristic of B...HHal complexes with a distinct low-frequency head and an extended high-frequency wing. Due to a smaller increase in the rotational constant upon $\nu_1(DF)$ excitation, the structure of the D₂O...DF and ₂O...DF complexes is less pronounced than in the case of lighter complex.

One difficulty, from the experimental point of view, is that the infrared spectra of such species are extremely anharmonic. Of course, it is exactly this high degree of anharmonicity that makes the spectra so interesting. Thus it is highly desirable to improve the accuracy of theoretical prediction of the infrared spectra in order to facilitate experimental study. Such situation requires computing the anharmonic vibrational spectra of B...HHal complexes using ab initio potential energy and dipole moment surfaces.

We have developed an algorithm for anharmonic spectrum calculations based on consistent variational multidimensional anharmonic calculations of the vibrational energy levels, the frequencies and intensities of the considered transitions, and the rotational constants. This method can provide reasonably accurate anharmonic vibrational frequencies. In the present study, we applied this method to obtain infrared spectra of 20...HF, D20...DF, 20...DF, and 20...HCl hydrogen-bonded complexes.

The theoretical spectra were obtained by summing the parallel rovibrational bands of the fundamental and hot transitions. The nonempirical spectrum of

 $H_2O...HF$ reproduces rather well the positions of the maxima and the ratio of their intensities in the low-frequency region and correctly describes the intensity decrease in the high-frequency wing of the band. Note that the results of this calculation showed that the $\nu_6(B_2)$ mode (libration of the water molecule) essentially differs from the other intermolecular modes: its potential has a barrier whose height increases with elongation (excitation) of hydrogen halide. As a result the frequency of hot transition (1,1) $(v_1=0, v_6(B_2)=1)$ is lower than that of the fundamental transition. This regularity is unusual for H-bonded complexes and changes the interpretation of spectral features of the band shape of complexes. Therefore, the central, most intense, peak is associated with the transition from the ground state, while the lowest-frequency peak with the P branch head of transition from the $v_6(B_2) = 1$ state. This description is in contradiction with the commonly adopted assignment, which leads to a new frequency value of the ν_1 fundamental transition of 3633.8 cm⁻¹, instead of 3608 cm^{-1} . Similar calculations of H₂O...DF predict a value of 2689 cm^{-1} for the $\nu_1(DF)$ stretch and a less structured band shape. Note that this estimate is obtained with allowance for the influence of all five intermolecular vibrations on the $\nu_1(DF)$ mode.

With the anharmonic frequency values calculated by us for the isolated molecules HF and DF, we obtain values of -331.8 and -229.4 cm⁻¹ for the ν_1 (HF) and ν_1 (DF) frequency shifts on formation of the H₂O...HF and H₂O...DF complexes. In this study the dipole moment surfaces of complexes were calculated in the MP2 approximation with the BSSE correction taken into account. The dipole moment averaged over the vibrational ground state of H₂O...HF is 4.204 D, which is only 3 percent higher than the experimental result. The quality of our calculations is demonstrated by the fact that the values of ν_1 (HF)/ ν_1 (DF) = 1.3633 and 1.3561 obtained by us, respectively, for the isolated molecules and their complexes with water are very close to the corresponding values 1.3654 and 1.3562 derived from the experimental studies in argon matrices.

A similar quantum-chemical calculation of the complex $H_2O...HCl$ and the variational solution of 1D and 2D anharmonic problems showed that in this complex the $v_1 = 1$ 0 hot transition frequency from the $v_6(B_2) = 1$ state should also be lower than the fundamental transition frequency. Using the calculated values of the rotational constant for the initial and final states, the gas-phase absorption spectrum of $H_2O...HCl$ at 25 K was computed. The band shape is controlled by the values of rotational constants B" and B' and temperature. In the theoretical spectrum the ratio of the peak heights of R and P branches is 0.78, the spacing between the maxima is 4.4 cm⁻¹, and the width of the whole band at half maximum is 8.0 cm⁻¹. This spectrum is in good agreement with the results of recent low-temperature experiments.

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Registration of the vibronic structure of dyes under multiple scattering and gain conditions

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The laser dye vapours and solutions are known to be characterised by nonstructural wide luminescence spectrum conditioned by homogeneous and inhomogeneous broadening and overlapping of large amount of the vibronic bands. The feature of the spectrum badly complicates the investigation of the energy levels structure of the dye molecules. The structure sometimes becomes apparent at helium temperatures under monochromatic excitation about an electron transition [1] and under the lasing in the non-dispersed cavity, that can be assigned to the method of intracavity spectroscopy (ICS). The main drawback of the method is appearance of the cavity mode structure in the lasing spectra (LS) that complicates the spectra identification. That is why it is apropos to develop the method being analogous to the ICS but free of the mentioned drawback.

We investigated the method of the implicit structure registration of laser dyes luminescence spectra by analyses of the amplified luminescence spectra. The idea of the method is to cover the laser dye solution of definite concentration with coating made of highly effective diffusive reflector. In the case of the solid dye solution such coating can be made by applying a dense layer of finedispersed particles (Al_2O_3, CeO_2) to the sample surface itself. Just the small part of the sample surface is free of coating to pump the radiation. To avoid any mirror reflection from the sample sides they were initially frosted. In such coating the proper conditions for multiple radiation pass through the sample are hold as it is in the ICS method but non-resonant feature of the reflection does not lead to modes formation. Thus the gain band is continuos. The method is conceptually the non-resonant multiple amplification (NRMA) one where the insignificant against a background structure reveals itself due to multiple radiation amplification.

We investigated a number of dyes of various molecules structure: polymethyne dyes 920, 923 and astroflocsin, pyrromethene 597, rhodamine 6G in the solid polyurethane acrylate solution (PUA). To compare both approach lasing spectra of the dyes were also investigated in the Fabry-Perot resonator where mode formation is actual.

The proposed method is found out to allow factually the laser dye luminescence spectra structure observation: the NRMA spectra of the 920 and 923 dyes having the simplest structure clearly reveal linear structure against the wide continuous background. The distance between spectral bands of the structure is about ~ 1nm. The band intensity decreases monotonically as either the pump intensity decreases or temperature grows. Under low pump intensities and temperature T > 50K bands are invisible against the wide background. The relative band intensities depend on the dye and its concentration. The band wavelengths in the NRMA spectra are close to the bands in the lasing spectra of these dyes. The rest of the investigated dyes reveal linear structure in the lasing spectra only.

Hence the spectra obtained by proposed NRMA method reveal the individual features of the dye thus the method can be used for the dye molecule structure investigation. For astroflocsin the spectrum it is occurs to be fundamentally different. Under the high amplification there are two relatively narrow unstructured bands to locate 25nm apart. However widely known laser dye R6G did not reveal thin bands in the spectrum. Its spectrum is narrower than 4nm and broaden under the amplification reduction.

The observed by the NRMA method fine structure was shown to be conditioned by spectral structure of dye molecule and did not caused by any external spectrum modulation.

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Light rays focusing and their intensity increasing in inhomogeneous medium near the critical point

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The trajectories of light rays propagation in inhomogeneous system under gravity near the critical point have been experimentally investigated in the work by light scattering and refractometry technique. Change of their divergence angle at different heights has been taken into account [1, 2].

It has been shown that they focused by inhomogeneous medium under these conditions. It occurs increase of their intensity.

These data also shows that the essential increasing of the beam intensity $I_{pass}(z \approx 0)$ is observed near the level of the critical isochore z = 0 when the system approaching to the critical temperature. This result can be explained by the same physical processes, which occurs when the powerful laser beams interacts with the liquid medium far from the critical point [3, 4], which leads to their self focusing.

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Depolarized light scattering in inhomogenous systems under gravity near the critical point

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The polarized and depolarized light scattering in inhomogeneous n-pentane and cyclopentane under gravity near the critical temperatures have been experimentally studied.

The altitude and temperature dependences of the polarized and depolarized components of the scattered light have been measured for the five wavelengths of light in the visible range, $\lambda_1 = 633$ nm; $\lambda_2 = 579$ nm, $\lambda_3 = 546.1$ nm, $\lambda_4 = 436$ nm, and $\lambda_5 = 405$ nm.

The obtained results showed that the altitude dependences of the depolarization factor $\Delta(z)$ have qualitatively different characters for different λ . For $\lambda_1 = 633$ nm, the factor Δ grows when going from the level with critical isochore; for $\lambda_3 = 546.1$ nm, the factor Δ is almost independent of the altitude z; for $\lambda_5 = 405$ nm, the depolarization factor decreases with z increasing. Such behavior of the depolarization factor near the critical point in an optically inhomogeneous environment has been revealed experimentally for the first time and cannot be explained by assuming the presence of only the secondary light scattering.

On the basis of the obtained results, it has been shown that the depolarized light scattering in such inhomogeneous systems consists of the depolarized secondary [1],[2] and depolarized primary [3],[4] light scattering, the latter being caused by the tensor character of fluctuations of the dielectric permittivity of the medium in the vicinity of the critical point.

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The complexation of chalcone 4,4' - alkylamino derivatives with Mg^{2+} , Ca^{2+} and Ba^{2+} ions.

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Chalcones are compounds using as models for charge transfer investigations under organic ligands complexation.

In presented work we have studied the complexation of following monodentant and bidentant chalcones: 4-(dimethylamino)-chalcone, 4-(dime-thylamino)-4'-aminochalcone, 4-(N-monoaza-15-crown-5)chalcone and 4-(N-monoaza-15-crown-5)-4'-aminochalcone.

 Mg^{2+} , Ca^{2+} and Ba^{2+} ions were used as complexing agents since they have no absorption bands in the ligand absorption region.

Metal ions involving to first complexing site - the crown cycle leads to decrease of the charge transfer resulting in hypsochromic shift of absorption bands.

The second complexing site is carbonyl group. In this case complexation of metal ions leads to growth of electron-accepting properties of carbonyl group, to charge transfer increasing and to bathochromic shift of absorption bands.

The values of stability constants of first and second complexation stages have been determined. The correlation between electron-accepting ability (charge density), ion diameter and stability of the complexes have been considered.

Conclusions about influence of metal ion parameters on interfragmental charge transfer in the excited state have been made.

Acid-base properties in the excited state and fluorescent behavior of 3 thiazolylchromone derivatives

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Arylchromone derivatives are interesting models for excited state proton transfer investigations. 7-hydroxy-3-(1,3-thiazol-2-yl)-4H-chromen-4-one (3-thiazolylch-romones, 3-TC) are also perspective medicines and pharmaceutical preparations. The investigation of fluorescence properties of 3-TC in a large pH/H0 interval permit to reveal emitting forms suitable for qualitative analysis of these compounds.

3-thiazolylchromones contain two proton-accepting sites - oxygen atom of the carbonyl group and nitrogen atom of the thiazol cycle. Subsequently, it is possible to suppose the formation of four acid-base forms: neutral, thyazolium cation, benzopyrylium cation and dication. In the case of 7-hydroxy derivatives, the formation of anion, two neutral tautomer forms and cationic tautomer is possible, too.

In the presented work quantum chemical investigations of thermodynamic characteristics (enthalpies of formations, Gibbs energies) of 3-TC acid-base forms in the excited state, comparative analysis of their theoretical and experimental fluorescence spectra, as well as estimation of stability of the forms in different pH/H0 regions have been examined. It was found that only four emitting forms may be presented in 3-TC fluorescence spectra. These are thyazolium cation, dication (for all the 3-TC) and also anion and cationic phototautomer (for 7-hydroxy 3-TC).

Benzopyrylium cation and tautomeric form obtained by protonation of carbonyl group are thermodynamically unstable; neutral form and tautomeric form with protonated thyazolyl moiety possess the non-fluorescent excited state.

Mechanisms of emitting species formation were analyzed using Forster method and molecular dynamics. It was found that anion formation in acid media (till $pH \approx 1$) is due to photodissociation process, and cationic phototautomer forms from the thiazolium cation through the non-fluorescing neutral tautomeric form.

Photoluminescence of silver complexes in solutions of electrolytes

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In this work the energy structure of absorptive and radiative centres of water solutions of inorganic salts and acids, contained the silver ions as activator, is investigated. The absorption, luminescence and photoexcitation spectra of silver solutions in wide temperature range of 4 - 290 K are explored. It has been established, that at small silver ion concentrations the luminescent intensity is proportional to concentration of an activator.

The detection of luminescence of silver ions in the concentrated solutions of haloid and oxygen-containing salts and acids at low temperatures and the investigation of its spectral characteristics allow to develop the high-sensitivity luminescent techniques of test of silver ions in frozen vitreous solutions of salts and acids. The given luminescent analysis techniques take account of the structural individuality of determined ions of microimpurity and the quantum yield of radiation of Ag⁺ ions in explored solutions as well. The sensitivity of luminescent analysis of test of Ag⁺ ions makes $1.1 \cdot 10^{-9}$ g/ml (on photoexcitation spectra) and $\sim 10^{-8}$ g/ml (on luminescence spectra). The ultimate sensitivity of test of Ag⁺ ions in solutions by absorption technique makes $\sim 10^{-7}$ g/ml at T=290 K. It will be noted, that the sensitivity of conventional luminescent techniques of test of Ag⁺ ions at using of the organic solvents makes $\sim 10^{-6}$ g/ml.

The examination of impurity ions of Ag⁺ in different composition solutions allows to elucidate the energy structure of absorptive and radiative centres in solutions activated by silver, and supplements the conception about the mechanism of absorption and emission of light in composition-like phosphorus.

Excitation of noncoherent radiation in light-scattering heterophase medium with singlet oxygen molecules

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Non-equilibrium non-linear optical phenomena in heterophase media with microdroplets are of great interest and importance both for fundamentals and applications [1]. In this work we report on the specific case of a fine-dispersed gas- liquid system containing microdroplets of condensed oxygen O₂ and gas mixture of ground $O_2(X^3\Sigma_u^-)$ and electronically excited $O_2^*(a^1\Delta_g)$ molecules. It can be produced in a chemical singlet oxygen generator with the yield $Y_{\Delta}=0.6$ -0.9 at P=20-100 Torr and T=70-90 K [2]. O₂^{*} carry energy ≈ 0.98 eV, able to emit IR light at $\lambda = 1.27 \ \mu m \ (^1\Delta \rightarrow ^3\Sigma \text{ transition})$, and have a long lifetime $(\tau_q^R = 4 \times 10^3)$ s in g-phase, $\tau_l^R = 2$ s in l-phase). Due to extraordinary metastability against collisional quenching, O_2^* can transfer to long distances and diffuse to droplets. At the same time, each droplet surrounded by the diffusing O_2^* can act as an optical microcavity (open spherical dielectric waveguide). Due to a quasi-total internal reflection of incident photons propagating along the spherical boundary and excitation of oscillation of whispering-gallery-modes (WGM) localized near the interface, droplets provide an effective optical feedback and work as a high-Qresonator $(Q \ge 10^6 [3])$. Cavity quantum electrodynamics modifies the density of states, and O_2^* metastables confined within droplets may have an enhanced probability of radiation transitions (up to a few orders of magnitude higher than in a free space), so that spontaneous emission of O_2^* can be affected by the collective process of superluminescence [2]. In this case a quantum yield of O_2^* radiation increases dramatically (up to 0.98 [3]). The photon flux within droplets is limited only by the rate of diffusion and relaxation of O_2^* on the droplet surface. The out-of-droplet field decays exponentially, so that maximum of Htype WGM is inside the droplet, whereas maximum of E-type WGM lies near the droplet surface, just in the same area where a partial inversion population can be. The pathlength of trapped light can be as long as several meters. Selfexcitation of the light amplification by stimulated emission radiation induced by WGM in droplets can arise even in a weakly amplifying medium, if the spatially averaged round-trip optical gain exceeds the optical losses due to absorption and radiation leakage. The criterion is $\alpha\lambda/2\pi>1$, where $\alpha=\sigma\Delta N^*$ is a gain, σ is a cross-section of stimulated emission, ΔN^* is a density of inversion. The threshold ΔN^* corresponds to $Y_{\Delta}=0.02$. The self-excitation in the system of WGM can be fulfilled even in case when it is not a case for any single mode. It is remarkable, WGM is transmitted in that spectral region where optical decay is very small (<0.2 dB/km), and a time-averaged energy stored by WGM is restricted only by the optical damage limit (heating of droplets).

In fine-dispersed media the light propagation is accompanied by scattering. We consider a medium where the character size R, light scattering path Λ , and light wavelength λ are in relation: $\lambda \ll \Lambda \ll R$ ($\Lambda = 1/\pi_0^2 N_0$, a_0 is a droplet radius, N_0 is a droplet concentration). In this case a photon transport has a diffusion nature, and optical path grows as R^2/Λ . If such medium has a gain $\bar{\alpha}$ conditioned to criterion $\bar{\alpha}R^2/\Lambda > 1$ [4], it causes stimulated emission, only radiation is omnidirectional (non-coherent). In small volume $\delta V(\Lambda^3 \ll \delta V \ll R^3)$ the average density of photons of arbitrary polarization, direction and frequency is $\varphi_{\omega}(r,t)\rho_{\omega}\delta\omega$ ($\rho_{\omega}\equiv \omega^2/\pi^2c^3$, $\omega=2\pi c/\lambda$), coefficient of diffusion of photons is $D_p=c\Lambda/3$, and temporal increment of growth of photons is $\nu_{\omega}=-\omega\epsilon''$ ($\epsilon''\equiv\Im\epsilon$ is an average value of the imagine part of permittivity). The photon flux is described by transport equation (1):

$$\partial \varphi_{\omega} / \partial t = D_p \Delta \varphi_{\omega} + \nu_{\omega} \varphi_{\omega} + \Re_{\omega}; (D_p \partial \varphi_{\omega} / \partial r + S_{\omega} \varphi_{\omega})_{\Sigma} = 0$$

where \Re_{ω} is a rate of emission of photons, S_{ω} is a loss of photons at the surface Σ . Time-dependent spatial distribution of metastables $N_{g.l}^*(r,t)$ in g-, l-phases has become settled by kinetic equations (2):

$$\partial N_{g,l}^*/\partial t = D_{g,l} \Delta N_{g,l}^* - N_{g,l}^*/\tau_{g,l} + \Re_{g,l}^*; (J_{g,l}^* + D_{g,l} \partial N_{g,l}^*/\partial r)_n = 0$$

here $D_{g,l}$ is diffusion constants, $\tau_{g,l}$ is lifetimes $(\tau_g \gg \tau_l)$, \Re_g is a rate of excitation $(\Re_l=0)$, $J_{g,l}^*$ is flux of metastables to/from droplets. The conditions of the light generation and its angular distribution depend on the form of active volume and the size and density of droplets. In case of spherical volume of radius R we have two criteria that can be realized in practice:

A) In case of small droplets, $a_0 k \leq 1$ $(k \equiv 2\pi/\lambda)$, i.e. Raleigh light scattering, threshold condition is $1/R \leq (16/\sqrt{3})N_0(a_0k)^2 \sqrt{a_0\bar{\alpha}_0(\epsilon_0-1)}/(\epsilon_0+2)$, where ϵ_0 is a permittivity of *l*-phase, $\bar{\alpha}_0$ is a spatially averaged light gain in droplets. For $a_0=0.1 \ \mu m$ and $N_0=10^{13} \ cm^{-3}$ (volume content of *l*-phase is $\sim 10^{-3}$), a minimal value *R* needed for the light generation is 20-30 cm.

B) In case of large droplets, $a_0 k \gg 1$, i.e. Mie light scattering, threshold condition is $1/R \le \sqrt{3}N_0 a_0^2 \sqrt{a_0 \bar{\alpha}_0 \eta}$, where η is a factor of O_2^* heterogeneity. For $a_0=10 \ \mu m$, a value R=40-50 cm is compared with case (A) at density $N_0=10^6-10^7 \ cm^{-3}$.

One could show that spectrum of stimulated radiation due to light scattering in the regime of generation is narrowing to Lorentzian profile $(\Delta_{st} \ll \Delta_{sp})$. Intensity of radiation (if absorption is neglected) is $I_d =$

 $\nu_{\omega}\omega^4/2\pi^3 c^3$ [2]. Depending on conditions, it can exceed the intensity of luminescence in homogeneous gas (at the same O₂^{*} concentration) by factor $I_d/I_g=10^3$ and more. We may conclude that due to the strong optical feedback in the light-scattering fine-dispersed heterophase medium with condensed singlet oxygen molecules , it is possible a stimulated emission of non-coherent radiation with a high quantum efficiency.

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The dynamic symmetry of the model system of two molecules

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This work is devoted to research of dynamic symmetry for the model mechanical system of two identical spherical bodies concerning orthogonal transformations. The mechanical energy symmetry to action of the reflection operator of the state vector is considered. For the model mechanism of the momentum and angular momentum exchange between the hard rough spheres an explicit mathematical expression of the reflection operator is found.

Investigation of pH - mediated changes in absorption and fluorescence spectra of imidazophenazine

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The imidazo(4,5-d)phenazine (IPzn) is effectively used for derivatizations of 3' -terminus of antisence oligonucleotides to stabilize their hybridization with nucleic acids [1]. IPzn is a polar amphoteric compound; its properties depend strongly from acidity of solution.

Visible absorption and fluorescent spectra as well as the fluorescence polarization degree of IPzn were investigated in aqueous buffered solutions over the wide pH range of 0 - 12 at room temperature. At neutral pH imidazophenazine has two absorption bands attributed to different $\pi^* \rightarrow \pi$ transitions: an intense shortwave band with a maximum at 385 nm and a longwave broad shoulder extending to 490 nm. IPzn has a broad structureless fluorescence spectrum with a maximum at 562 nm.

Because of the presence of nitrogen atoms in hetero rings of IPzn, protonation occured in the acidic medium. It results in changes of extinction as well as of shape and position of absorption bands. Two cationic forms of IPzn are found. Also, at high pH values the appearance of the anionic form of imidazophenazine is observed. Deprotonation of IPzn chromophore results in the increase of extinction coefficient and appearance of corresponding absorption bands. The dependence of fluorescence intensity versus pH showed that only neutral form of dye fluoresces intensively. Its fluorescence polarization degree was found to be around 0.015 under excitation in the longwave absorption band. The anionic form has weak fluorescence with the polarisation degree of 0.03. The cationic forms are nonfluorescent. The causes of pH-mediated spectral changes are discussed.

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Estimation of basicity and first electronic transition wavelength in large arrays of polymethine dyes

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Purposeful synthesis of polymethine dyes (PMDs) calls for appropriate methods of estimating the basic properties of novel heterocyclic nuclei applicable as PMD end groups. Estimations of this kind imply the choice of theoretical (quantum chemical or empirical) parameters for a sufficient number of both known and newly obtained heterocyclic systems, and the establishment of quantitative correlations between these parameters and experimental PMD characteristics.

Of particular interest is the prediction of molecular properties using the simplest theoretical approaches which, in contrast to sophisticated quantum chemical methods, enable not only numerical but also analytical representation of the relationship between PMD integral characteristics and molecular constitution. Such approaches can be exemplified by a model invoked here, the long-chain approximation, which has been developed since the seventies as an analytical approximation of the Hueckel method in order to describe quasi-one-dimensional conjugated systems [1, 2, 3].

In the present work, effective topological parameters of the long-chain approximation (electron donor ability $U^{424} U^{43e}$ and effective length L) are calculated for a large array of polymethine dyes (about 100 carbocyanines with end nuclei belonging to 6 structural series) and correlated with experimental chemical and spectral dye characteristics (basicity thermodynamically determined by the negative logarithm of the conjugated acid dissociation constant $U^{440} U^{41a} \,$ and first electronic transition wavelength λ_{exp}). A stable correlation is established between the series $U^{424} U^{43e}$ and $U^{440} U^{41a} U^{430}$ (R = 0.96). The U^{424} U^{43e} -dependence of U^{440} U^{41a} U^{430} is found which has a general linear character on the whole basicity interval for the selected cyanine array and enables the prediction of the U^{440} U^{41a} U^{430} values for new dyes based on the U^{424} U^{43e} values of their end groups as well as the solution of the inverse problem. A moderate coefficient of the correlation between λ_{theor} calculated by L and λ_{exp} (0.84) suggests that the effective length of end nuclei is an appropriate quantity rather for finding trends in dye absorption maxima than for quantitative prognostication. Two ways of approximating the experimental values of dye absorption wavelengths are considered which involve homographic and linear functions of L.

The accuracy of λ_{exp} prediction can be improved using the corrected effective length values. The correction is derived from the coefficients of the linear correlation equation; it eliminates a systematic error of PMD absorption maximum determination which arises from the neglect of interelectronic repulsion in the long-chain approximation. As shown, the corrected effective length provides a significantly (by more than half an order) reduced deviation between experimental and calculated data. It is also helpful in a more precise estimation of other molecular properties involving the absorption region, e.g., linear and nonlinear polarizabilities. Thus, the effective length can point out the structure of end groups that provide a desired light absorption region for a PMD. Generally, the long-chain approximation appears as an instrument for the tentative estimation of molecular properties and selection of promising structures at the primary stage of PMD molecular design.

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Quantum effect of Atakhodzhaev in the vicinity of liquid-crystal transition

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Scattering of light and neutrons allow one to obtain information on the energy structure of self-coordinated field of substances in principal non-excited energy state, as well as to discuss structural-dynamic processes in condensed media.

According to existent ideas, the width of line of the central component of Rayleigh light scattering (RLS) in liquids depends on concentration of molecules, for which the dynamics of the mass centers and orientations is of random or Brownian character. Precipitous or fluctuation energy transition of Brownian molecules between two equilibrium orientation positions can be characterized as a re-orientation or relaxation time τ of particles. In molecular systems exponential dependence of τ on temperature is usually observed (i.e. the dependence of $lg\tau$ on 1/T is of linear character).

In work [1] authors observed that near the crystallization point there occurs an oscillation in the dependence $lg\tau$ on 1/T in paradichlorinebenzene. Quantization or oscillation of various properties of substances in the vicinity of liquid-crystal phase transition was descivered in [2]-[4]. However, this effect was discovered for the first time in [1], and that would be correct to name this phenomenon "the quantum effect of Atakhodzhaev".

Physical nature of the phenomenon can be explained by taking into account the field-substance interaction. In atomic-molecular systems as a result of the field-substance interaction and surrounding particles an oscillating wave function of response (WFR) of particles is formed on each single particle. Phase correlation among WFRs of particles leads to formation of the self-coordinated field in a set of particles. The energy structure of WFR of particles is identical to the energy structure of the self-coordinated field of the substance. That is why the WFR of particles is an internal order parameter, and it plays basic role in formation of macroscopic and mesoscopic properties of substances [5, 6]. The energy structure and number of induced wave harmonics in WFR depend on the energy of interaction with environment.

Realization of the phase coherency among the harmonics of WFR of particles leads to formation of the coherent cover or surface energy in a set of particles as a whole. As a result, the properties of integrity and continuity of the substance are formed. From this follows that formation of the surface energy in a system of interacting particles may be considered as a transition of the substance to condensed (particularly, in liquid) state.

The self-coordinated field of molecular liquids and amorphous substances is manifested as a low-frequency continuum with maximum $\nu_{max} \sim 10 cm^{-1}$ – $100cm^{-1}$ and half-width $\Delta \nu_{1/2} \sim \nu_{max}$. As a result of self-organization and selfcompression a formation of collectivized electrons (or conductivity electrons) occurs in atomic-molecular systems. Phase correlation among WFRs of collectivized electrons leads to formation of the self-coordinated field of electrons. In disordered substances the self-coordinated field of electrons is manifested as a broadband background in spectra of Raman scattering (RS) with maximum $\nu_{max} \approx (2-5)10^3 cm^{-1}$ [7].

Disturbance of the phase correlation in self-coordinated field of substances leads to appearance of Brownian particles and formation of the central component of RLS [5]. That is why the width of RLS line depends on concentration and dynamics of Brownian molecules in studied substances. With changing temperature a change of the energy structure of self-coordinated field of the substance, and, respectively, change of concentration and dynamics of Brownian particles take place. However, significant concentration of Brownian particles masks the quantum character of this process that leads to experimental linear dependence of $lg\tau$ on 1/T.

The surface energy or coherent cover of substances plays determining role in formation of their macroscopic and mesoscopic properties. The coherent cover provides self-organizing influence on the substance. With decreasing the temperature of liquid there occurs an increase of the phase coherency among harmonics of WFRs of molecules, which is accompanied by increase of rigidity of the liquid and increase of frequency of the self-coordinated field. Increase of self-compression in substance may lead to change of geometric parameters of molecular structure. With decreasing temperature in the vicinity of liquidcrystal phase transition a jump-like transition of a molecule from one type of the balanced energy structure to other occurs due to increase of the surface energy of the substance and coherent cover of WFRs of molecules. At this a jumplike change of the frequency of self-coordinated field and the surface energy of the substance occurs. In the process of this transition there occurs a transient weakening of the coherent properties o WFRs of molecules and, respectively, the frequency of WFRs of molecules.

As a result, change of concentration of Brownian molecules becomes possible. Jump-like change of the energy structure of the self-coordinated field of substance leads to quantum change of the concentration of Brownian particles that leads to quantum change or oscillation of the width of central component in RLS spectra. This process takes place within a narrow temperature interval. The quantum effects, which were discovered in [2]-[4] can be explained in terms of above-mentioned ideas.

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Spectra-structure correlations of phosphorusorganic compounds with various coordination number of heteroatom

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With the aim of explaining differences of force constants and revealing the nature of true and formally double bonds P=X (X=O,N,C) for normally- and hypervalent phosphorus P_{II} or P_{IV} compounds the frequences of the latter were established and the northally-coordinated analysis was carry out. It was shown that in most cases vibrational frequences v(P-X) are not characteristic and do not reflect the double bonding degree in the molecule. The value of the bond force constant obtained from quantum chemical calculating and refining by the solution of the reverse spectral task is a more accurate parameter.

Some examples of vibrational frequences and force constants of double bonds P=O and P=S simple oxy/thia halogenides of phosphorus are given below.

	v(P=O/S) cm ⁻¹	$K^{P=O/S}$ x10 ⁶ cm ⁻²		v(P=O/S) cm ⁻¹	$K^{P=O/S}$ x10 ⁶ cm ⁻²
F ₃ P=O	1410	17.6	FP=0	1292	16.5
$Cl_3P=O$	1308	17.1	ClP=0	1258	15.5
Me ₃ P=O	1161	13.7	HP=0	1188	13.8
$Cl_3P=S$	767	7.25	ClP=S	716	7.4

It is known that in phosphazo compounds degree of multiplicity of P=N bond can be estimated using vibrational spectra with v(P=N) frequency and $k_{p=n}$ force constant values.

Frequencies of v(P=N) vibrations of phosphineimines are not characteristic and revealed in two bands of absorption v_s and v_{as} . High frequency peak $v_{as}(P=N-Y)$ is usually used for correlation with P=N bond characteristics.

	$v_{as}(P=N)$ cm ⁻¹	$\begin{array}{c} r(P=N) \\ A^0 \end{array}$	$\frac{k_{P=N}}{10^6 \text{cm}^{-2}}$
$(Me_2N)_3P=O$	-	1.65	6.16
$(Me_2N)_3P=NH$	1110	1.55	10.4
$Me_3P=NH$	1170	-	10.7
$Ph_3P=NH$	1200	1.55	11.5
$(Me_3Si_2)NP=NSiMe_3$	1232	-	12.0

The problem of applying scaling multipliers in quantum chemical calculations with the objective of obtaining actual force field for predicting spectra of new molecules is discussed.

Estimation of the H_2O_2 molecule moment of momentum in gas and condensed state

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Molecular chirality is one of nature asymmetry phenomenon that is characterized by the existence of pairs of molecules that have a different configuration - namely being mirror reflections of each other. Chirality affects chemical and physical properties of a molecule. Although energetically chiral configurations are equivalent, only one of them dominate in the animate nature. Therefore, a close examination of the molecular chirality as well as methods of its control constitutes a matter of practical and theoretic interest. H_2O_2 molecule of C_2 symmetry that is being examined in this paper belong to the class of substances that are characterized by chirality.

Authors expressed a supposition that a simultaneous excitation of several vibrations of H_2O_2 molecule may cause a appearance of a vibration moment of momentum different from zero.

In order to check this hypothesis, a number of preliminary calculations were carried out for the "right" and "left" configurations of the H_2O_2 molecule in gas and condensed state.

A reverse spectral problem was solved by means of using H_2O_2 molecule normal vibrations in both gas and condensed state, as well as normal vibrations of its isotope modification in appropriate states [1]. The problem was solved without preliminary assumptions about the nature of the force field [2]. Normal vibrations forms of the molecule were built.

Obtained results have confirmed the existence of the vibration moment of momentum that appears when two vibrations of H_2O_2 molecule with close frequencies ($\nu_1 = 3607 cm^{-1}$, ($\nu_2 = 3608 cm^{-1}$) are excited simultaneously. A certain difference in the vibrations of the chiral molecule configurations was found while the orientation and the value of moment of momentum were found to be equal.

Authors express an idea that taking into account the interaction between the vibration and rotation motion of the molecule in further calculations will allow to find the configuration of the eclectro-magnetic field able to influence the racemic mixture.

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Quantum-chemical investigations of an electronic and geometrical structure of squaraine dyes

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Influence of the polar solvent on behavior of the excited polar molecule of a solute is not restricted to stabilization of its fluorescent condition with stationary values the dipole because of reorientation enclosing dipoles of the solvent. The electronic and geometrical structure of donor-acceptor molecular systems can be subject to change as a result of interaction with polar molecules of the solvent.

Hamiltonian of the system which are powering up a solute and the solvent: $H = H_0 + H' H_0$ - the Hamiltonian of a solute in absence of the solvent, H' -features interaction between a solute and the solvent.

By consideration inside and intermolecular systems with transposition of a charge the wave function can be presented by the wave function: $\Psi = C_1 \Psi(A - D +) + C_2 \Psi(A * D) + C_3 \Psi(AD)$. Where the first member features a configuration with transposition of a charge, the second - corresponds locally to the excited configuration, and the last member - to the basic state. The contribution of a profile $\Psi(A - D +)$ in an excited state is more, than basically. It is even more augmented at interaction of a solute with polar molecules of the solvent. For consideration of the given problem it is necessary to calculate energy for each case, using wave function Ψ and having selected Hamiltonian H' in submission of a sample piece of a dielectric continuum: $H' = -\mu F$, where μ - an operator of the dipole, F - Onzagers reactionary field.

Within the framework of introduced sample energy, geometrical and electronic structures of squaraine dyes in polar solvents are determined. The obtained results come allow explaining mechanisms of processes of a quenching of a bloom and intermolecular interactions.

Interpretation of acoustical spectra of chain-molecule liquids (rotational isomeric approach)

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A multilevel model based on rotational isomeric approach was proposed for interpretation of acoustical spectra of chain-molecule liquids. The model was checked for liquid n-alkanes from n-pentane to n-nonane. It describes noncollective rotational isomeric transitions, in other words, transitions that take place around the only one C-C bond at the moment. It was considered that the same energy was necessary to rotate around the bond no matter where such bond was located - in the center or at the sides of the molecule. Thus one could divide all the possible conformers into n-3+1 (the number of C-C bonds around which rotations were possible plus plain trans-form) groups with the same energy. The energy differences and the energy barriers were considered independent of the number of the level. Two cases were examined. In the first case the state of the link was independent of the sates of its neighbor links, in other words, so called "pentane effect" that implied the certain conformations were banned was not taken into account. In the second case "pentane effect" was taken into account. The frequency dependence of sound absorption coefficient was determined in the frame of non-equilibrium thermodynamics. It was shown that the spectrum of sound absorption in the first case was characterized by one relaxation time. Taking "pentane effect" into account makes the spectra more complicated - additional relaxation times arise.

0.2 H-Bond

An effect of dissolved gas content and the type of gas on the strucrure of water as studied by Raman spectroscopy

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Using the Raman spectroscopy we have studied the spectral patterns of water with different content of dissolved gas and the type of gas within the 64000 cm^{-1} and the 3350 cm^{-1} spectral ranges. It occurred that the low-frequency spectrum of water is drastically changed at removing dissolved gas. After a complete outgassing of several water samples we dissolved helium, argon and perfluoropropilene in these samples (note that the latest gas cannot at all be dissolved in water as shown in literature). We obtained that after this procedure the low-frequency spectra became different for each specific dissolved gas. We also studied the spectra in the chosen ranges at removing each gas. It occurred that there exists strong dependence of the low-frequency spectra on the specific gas content. It also occurred that at lowering the content of dissolved argon and helium the optical breakdown (induced by a YAG:Nd³⁺ laser pulses) vanishes while the breakdown behavior is indifferent as related to perfluoropropilene content. The results can be qualitatively interpreted in the framework of supposition that the dissolved gas can exist in liquid in the form of equilibrium stable nanobubbles.

Molecular mobility and the H-bonds lifetime as the reflection of peculiarities of the liquid water structure on the Raman spectral Data

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The structure of hydrogen-bonded compounds is closely related to these molecular mobility and molecular dynamics. One of the principal questions related to liquid water state is the question of mobility of water molecules forming the spatial hydrogen bonds network.

Raman spectral data by the temperature and concentration influence on the O-H(O-D) stretching water bond was received.

Our conclusions are the next. Liquid water forms a continuons network of hydrogen bonds containing various cells corresponding to four conformations of a fully hydrogen-bonded five-molecule structural unit with the different orientations of the central water molecule [1, 2].

The share of each "conformer" as defects of the spatial H-bonds network depends on the temperature and on the nature of the solute. These factors influence on the molecular mobility mechanism of water molecules in the spatial H-bonds network. The dynamics of this process takes place in the picosecond time interval. The lifetime of different H-bonds was determined.

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Investigation of Peculiarities of Structure and Phase Transitions in Hydrogen-bonded Crystals by NQR and Vibrational Spectroscopy Methods

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The investigated in this work hydrogen-bonded iodate crystals $(AIO_3 \text{ and} \text{ some mixed crystals obtained on their base, where } A = H^+, K^+, NH_4^+)$ are very convenient for study of the symmetry hydrogen bonds problem. The main peculiarity of this crystals consist in possibility to pick out the rigid covalent-bonded iodate groups IO_3 , the oxygen atoms of which can form the hydrogen bonds of different energy. These facts are well known from numerous experimental data obtained by structure and vibrational spectroscopy studies. However to investigate the behavior of hydrogen bonds in these crystals at phase transition and under different outside effects (for instance, temperature and pressure) are difficult problems, it requires the complicated neutronographic investigations. The Raman and Infrared absorption spectra obtained in the wide temperature ranges give, as a rule, integrated information about the changes of structure and energy of hydrogen bonds in the critical temperature range.

Using the unique possibilities and simplicity of the NQR method as structure probe we try to solve this problem starting from the analysis of the temperature and pressure dependencies of the NQR spectra parameters. First of all, the calculations of electronic structure of different iodate groups $(H_x IO_3, where$ x = 0 and 1) with different by MO LCAO method were made. This allows to obtain parameters of the ${}^{127}I$ NQR spectra: quadrupole coupling constant $e^2 Qq_{zz}$ and asymmetry parameter η including different states of hydrogen atoms which can form relative strong covalent O - H part or weak $O^{\cdots}H$ bond of hydrogen bond $O - H^{\cdots}O$. Then the obtained theoretical data were compared with experimental results. The analysis of the hydrogen bond structure for different crystals in the wide temperature range was made. The type of the phase transitions and changes of hydrogen bonds structure near the phase transition points was determined. The analysis of the pressure dependencies of the NQR spectra parameters lead to detection of the symmetrization effect of "so called" interionic hydrogen bonds under hydrostatic pressure. It was shown, that this effect has a general character and is valid for both symmetric hydrogen bonds with disordered proton and asymmetric bonds. The main sense of the symmetrization effect consists in some moving of proton to geometrical center of the hydrogen bonds $O^{\cdots}H^{\cdots}O$ or $O-H^{\cdots}O$ when hydrostatic pressure increase. In a pure appearance the symmetrization effect developers for $\alpha - HIO_3$ crystal for which the decreasing of asymmetry parameter on resonance nuclear ^{127}I with increasing hydrostatic pressure was observed.

Technique and accuracy of definition of parameters of low-frequency Raman spectra of weak water solutions.

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Importance of studying low-frequency (LF) of spectra (0-350 cm⁻¹ - a Rayleigh wing) weak water solutions consists they change at entering impurity [1, 2, 3]. Therefore spectra can be applied to diagnostics of water and weak solutions. Thus arises questions of interpretation of spectra and accuracy determination of spectra parameters.

Now for the description of the mechanicm of occurrence of these spectra there are three basic approaches. Historically the first is relaxation mechanicm [4]. It is used three parameters. Another mechanicm developed at the end of 20 centuries, fractal, is connected with difficult topology of intermolecular connections (see, for example, [5]).

Approximately at the same time enough wide circulation the mechanicm in which more high-frequency part of a spectrum (20-300 cm⁻¹)) is connected with intermolecular translation movements, and low-frequency (has received 0- 50 cm^{-1}) - with chaotic slow strong damped movements of molecules of a rotary kind [6]. Unlike first two mechanicms last well approximates a spectrum down to 300 - 320 cm⁻¹. (In [7] the similar approach with a slightly other ideology is considered.)

In considered area connection of dynamic susceptibility $\chi''(\nu)$ and Raman intensity $I(\nu)$ is given by connection

$$\chi''(\nu) = (\nu - \nu_i)^{-4} [n(\nu) + 1]^{-1} \cdot I(\nu)$$

where $n(\nu) = [\exp(hc\nu/kT) - 1]^{-1}$ - Bose-Einstein factor, (ν_i - frequency of exciting laser radiation in cm⁻¹, T - temperature.

For weak water solutions in spectral dependence of a susceptibility there are two precisely expressed wide humps with feature on LF a slope of LF of a hump. A high-frequency hump explain movements of two molecules of the water connected by hydrogen connection along connection, low-frequency - the movement of molecules bending this connection. These humps are well enough described Lorenzian (see, for example, [6]). For satisfactory approximation it is necessary to add a pedestal which intensity for many substances investigated by us is described to proportional frequency by dependence, that we connect with a luminescence. For practical the relaxation part managed to be described quite well dependence $\chi''(\nu) = I_r \nu/(1 + (2\nu/\delta\nu_r)^2)$. Approximating function has 9 fitting parameters: $I_r, \delta\nu_r, I_l, \nu_l, \delta\nu_l, I_h, \nu_h, \delta\nu_h, I_lm$, where I_{α} - intensity

of a corresponding member (I_{lm} - factor of proportionality of a luminescent pedestal), ν_{α} - frequency of a Lorenzian maximum, $\delta\nu_{\alpha}$ - its width on half of height. Approximation was means of the program realizing Marquard algorithm

Definition of accuracy was spent on a set of spectra of the water sealed-in in an ampoule intended for injections. All spectra were normalized on value of intensity valent full symmetrical vibration of water ($\nu = 3400 \text{ cm}^{-1}$), which was accepted equal 10000. Accuracy of measurement of the majority of parameters has made 1 - 4%, , and, basically, has coincided with a confidential interval which was given with the program. Thus accuracy of definition of parameter I_{lm} has made 10%. Exception has made position of a maximum of low-frequency Lorenzian which accuracy was made with 0,15%, and was much less than a confidential interval.

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Experimental Study of Continuous Background in Raman Spectra of Water

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Raman spectra of water preliminarily attributed as structured after its contact with fumed silica (Aerosil A300 with a specific surface area approximately $300 \text{ m}^2/\text{g}$) in water filter supplied by "Clorovinil", Kalush, Ukraine.

We observed significant (up to few times) increasing of continuous background in Raman spectra of distilled water passed through such filter as compared with continuous background in spectra initial distilled water.

Special study of spurious contribution of residual scattered light in triple grating monochromator "Coderg" T-800 shown that the said background is not artefact and really exist even in double distilled water.

We found that this background drastically changes during few days. The probable reason may be change of concentration of solute gases, i.e. air in water.

Rapid increasing of continuous background in Raman spectra of water after its passing filter with developed surface occurs due to washing-out of gases absorbed at this surface.
Theoretical study of proton transfer in diflavonol derivatives

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Diflavonols are the compounds, which can be used as models for investigation of the intramolecular proton transfer in the excited state (ESIPT). Diflavonol mole-cules contain two ortho-hydroxycarbonyl fragments, where hydroxyl and carbonyl groups are connected by hydrogen bonds. The transfer of hydroxyl proton onto car-bonyl group occurs in the excited state.

Recently diflavonol (3,7-dihydroxy-2,8-diphenyl-4H,6H-pyrano-[3,2-g]-chromene-4,6-dione) and its 4',4"-bis(dimethylamino) derivative have been studied [1].

The transfer of the first proton in diffavonol molecule have been found to pre-vent ESIPT from the second hydroxyl group.

Quantum chemical analysis of the molecular structure, spectral properties and possibility of mono / double ESIPT processes are in a good agreement with experimental data. In presented work we have used quantum chemical analysis (AM1/CI) of spec-tral characteristic and proton transfer peculiarities in diflavonol molecules of another symmetry. The possibility of double proton transfer and factors influencing on this process (solvent properties, electrondonating substituents) have been considered.

 A.D. Roshal, V.I. Moroz, V.G. Pivovarenko, A. Wroblewska, and J. Blazejowski. J. Org. Chem. 68 (2003), P.5860-5869.

Periodic DFT dynamic simulations of $H_2O_n: H - CHA, n=1,2,3.$

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Structure, proton dynamics and vibrational spectra of the hydrated zeolite (HSSZ-13, periodical boundary conditions, stoichiometry $AlHSi_{11}O_{24}$ per unit cell) were studied by density functional theory using BLYP and PBE. The 1:1 complex exists as a neutral complex corresponding to the global minimum. This structure enables one to explain, in harmonic approximation, all experimental frequencies with the only exception of the C zeolite band (ca. $2900cm^{-1}$). Possible other local-minimum structures (the ion-pair species) are not accessible at the room temperature. The potential energy surface of the 2:1 complex is broad and shallow. It accommodates different neutral and ion- pair structures. The ion-pair species can be treated as the $H_3O^+(H_2O)$ clusters. According to BLYP, the ion-pair structures are less stable than the neutral species, however, corresponding minima are accessible at temperature of IR experiments (T > T)300 K). The neutral species have no vibrations with the frequencies in the 1800- $3200 cm^{-1}$ region. Each ion-pair structure has only one vibration, that locates in the considered region. PBE, in comparison with BLYP, overestimates the strength of the H-bond between the first water molecule and the acidic proton. As a result, the ion-pair species of the 2:1 complex are more stable the neutral species in the PBE approximation. The first stable protonated cluster in the 3:1 complex is $H_3O^+(H_2O)_2$, because the bridging proton locates near the first water molecule and only several proton jumps to the second water molecule can be observed on the MD trajectory.

Clusterization processes in dilute water-alcohol solutions

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The results of our investigation of clusterization processes in water-alcohol solutions are presented. Especial attention is paid to water-glycerol solution. From the structural and thermodynamic reasons is concluded that the structural subunit in dilute water-glycerol solution - an elementary cluster - is formed by two glycerol molecules and 10-12 water molecules. Elementary clusters in solution can be considered as the subsystem of admixture particles.

The equation of state for clusterized solution is constructed. It is taken into account that different pseudoparticles interact by means of 1) Van der Waals forces and 2) ones caused by fluctuation-multipole mechanism. The position of the pseudospinodal in water–glycerol solutions is determined. The increase of the concentration fluctuations at approaching the pseudo–spinodal is described within the Landau–Ginsburg formalism. The behavior of integral intensity of molecular light scattering is studied in details.

It is shown that the numerical values of the coefficients of the Landau-Ginsburg Hamiltonian, calculated in the framework of cluster representations are close to those determined from experimental data. This fact and also the computer modeling of cluster and the successful description of the crystallization in water-glycerol solution are weighty arguments in favor of micro-inhomogeneous structure of water-alcohol solutions.

Structure and stability of protonated complexes $(DMF)_2H^+(H_2O)_2$

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The properties of solutions of acids are determined mainly by the presence in the latter of protons, which appear on dissociation of the acid. In solution the protons form stable solvates. The simplest stable proton solvates actually participate in the majority of the processes occurring in solutions of acids. The fact that they play a primary role in homogeneous acid catalysis should be specially mentioned. In the chemical reactions of organic and inorganic compounds, stable proton solvates act as reactants and ionising agents, forming various intermediate complexes. Thus they participate in the equilibrium and nonequilibrium stages of the acid-catalytic process.

The aim of this work was to study the conditions of formation and the structure of stable proton solvates present in acid solutions in N,N-dimethylformamide and in trinary liquid system acid-H₂O-DMF. The data necessary for this purpose were obtained by quantum-chemical calculations at B3LYP/6-31++G(d,p) level for the positively charged complex $(DMF)_2H^+(H_2O)_2$. Eight stable conformers of the complex were revealed having cyclic, chain or branched structure. The enthalpy of their formation varied from 104 to 85 kcal/mol. The length of the hydrogen bridge involving excess proton is in the range of 2.40-2.67 A. The results of present calculation were compared with the data on proton disolvate $(DMF)_2H^+$ and $(DMF)_mH^+(H_2O)_n$ (m = 0-1, n = 0-3) complexes obtained in our previous study.

Analysis of tendencies of $(DMF)_m H^+(H_2O)_n$ complex formation, the peculiarities of the structure, and relative stability of various topology conformers allows one to draw the following conclusions. The experimental fact that the formation of proton disolvates with strong symmetric hydrogen bond in acid solutions of DMF is impossible is conditioned by the proton-anion interaction (not full dissociation of acid molecules). The modelling of the structural fragments of trinary system acid-H₂O-DMF shows that $H_5O_2^+$ ion cant form in this system because the proton affinity of DMF molecule far exceeds (by 34 kcal/mol) the proton affinity of water molecule. The most stable proton solvate in trinary solutions with equal mole concentrations of DMF and H₂O is apparently H_3O^+ ion. The formation of structural fragment with quasi-symmetric hydrogen bond $((CH_3)_2NCH)O...H^+...O(H_2)(H_2O)_n$ is likely if the content of DMF in solution is relatively low. The obtained data on the structure and properties of stable positively charged complexes composed of DMF and water molecules enabled us to reveal some characteristic features of the intermolecular interactions.

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Hydrogen bonds of 2-aminothiazoles in intermolecular complexes (1:1 and 1:2 composition) with proton acceptors in solutions.

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IR spectra of the free molecules of 2-aminothiazole and 2-aminoben-zothiazole and their H-bonded complexes of 1:1 composition with acetonitrile, dioxane, tetrahydrofourane, dimethylformamide, dimethylsulfoxide and hexamethyl-phosphoramide in CCl_4 were studied in the region of the stretching and deformational vibrations of the amino group. The complexes of 1:2 composition were studied in undiluted aprotic solvents.

The absorption bands spectral characteristics of monomers and complexes were determined: $M^{(0)}$ - zero spectral moment (integrated band intensity B), $M^{(1)}$ - first spectral moment (band's centre of gravity) and effective half width $(\Delta \nu_{1/2})_{eff}$ which is related to the second central moment $M^{(2)}$ $(\Delta \nu_{1/2})_{eff} = 2(M^{(2)})^{1/2}$.

The temperature influence on the absorption band spectral characteristics of the amino group stretching vibrations for monomers and 1:1 complexes were studied in the interval 283-323 K. It was shown, that within the range mentioned above, spectral characteristics have practically linear dependence on temperature. Parameters of the linear regression equation Y=aT+b (Y=B, $M^{(1)}$, $2(M^{(2)})^{1/2}$) were determined. It was stated, that the temperature sensitivity $a=\partial Y/\partial T$ of spectral characteristics for 1:1 complexes of 2-aminothiazoles with proton acceptors is approximately by a degree higher than for monomers.

The monomer-complex equilibrium constants K(T) (1:1) were calculated and the thermodynamical characteristics - ΔH and ΔS were determined on the Vant-Hoff equation basis.

For free (R-NH₂, R-NHD, R-ND₂) and H-bonded (1:1 and 1:2, with various proton acceptors) molecules of 2-aminothiazoles the vibrational and electrooptic problems were solved in the approximation of the six-coordinate valence force field model. The valence angles γ (HNH), force constants K(NH), electrooptic parameters $\partial \mu / \partial q$ (derivative of the dipole moment by the length of the same NH-bond) and $\partial \mu / \partial q'$ (derivative of the dipole moment by the length of the neighboring NH-bond) were determined. The correlations were stated between spectral, geometrical, force and electrooptic parameters of free and H-bonded molecules.

The comparative analysis was performed on the influence of the pyridine, pyrimidine and thiazole cycles in $R-NH_2$ molecules on the amino group parameters of free molecules and on the thermodynamical characteristics of 1:1 complexes of aminothiazoles with proton acceptors.

In the approximation of DFT-B3LYP/6-31G** and ab initio MP2/6-31G** the calculation of the on-atoms charge distribution (according to Mulliken), geometrical and force characteristics and dipole moments μ_0 of 2-aminothiazoles was performed.

Conformity between the quantum mechanical calculations, valence force field calculations and the experimental results were found to be satisfactory.

Determination of composition of stable heterocomplexes forming in binary liquid system

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Vibrational spectroscopy is one of the main methods of studying systems with hydrogen bonds. The determination of the molecular and ion-molecular complex composition and structure is indissolubly linked to the analysis and interpretation of their IR spectra. In the present work the original method is suggested and tested to find the stoichiometric ratio in stable H-bonded heterocomplexes, which may form in a binary liquid system. The method addresses the analysis of the concentration trend in the systems IR absorption spectra. Normalizing of the optical density at frequencies of heterocomplex absorption to the total number of moles of solution components in the measuring cell volume (N) is the essence of the method. In that case according to the law of mass action investigated optical density will reach its peak if the molar ratio of solution components equals the stoichiometric ratio of molecules in heteroassociate. The suggested method has been applied to determine the composition of stable complexes forming in three binary liquid systems: HF–N,N-dimethylformamide, HF-acetone, and HF-acetonitrile. The stoichiometric ratio HF : Solv. in these systems was found to be 4: 1, 6: 1, and 4-5: 1, respectively.

These results were compared with the data on composition of complexes under investigation deduced from the concentration dependence of HF-Solv. solution density. The method, which is recently formulated and grounded in order to treat the density data, is similar to the suggested spectral method. It corresponds to the law of mass action and stems from the following fact. If the measured solution density differs from the calculated for a mixture of the same components using the additivity scheme (such condition is realized in studied systems, as well as in other binary mixtures with strong intermolecular interaction) the maximum of the concentration dependence of the excess density normalized to N will occur when the molar ratio of solution components and the stoichiometric ratio in heterocomplex are equal. The use of this method made it possible to conclude that upon solution of HF in DMF or in acetonitrile the 4 : 1 complexes are formed whilst in acetone the complexes 7 : 1 are formed. The reasonably good agreement of the results deduced from two different experimental methods testifies that the suggested method to determine the composition of stable heterocomplexes forming in binary liquid system is correct.

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Conformational dynamics and polymorphizm of fatty acids

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It is known that in long-chain aliphatic crystals in the temperature range below the melting point the molecules can perform the orientation disorder motions of the different kinds. It is clear that any distortions in periodic location of the atoms in the plane perpendicular to the long axis of the molecules must result in some peculiarities in the intermolecular interactions. In particular, one could expect changes in resonance dynamic intermolecular interaction (Davydov splitting of vibrational excitons) in orientationally disordered phase. In the present paper we report on temperature dependent FTIR spectra studies of the value of Davydov splitting for CH₂ rocking vibrations of pure crystalline normal chain carboxylic acids $CH_3(CH)_{n-2}COOH$ with odd (n=15,17,19) and even (n=10,14,16,22) number n of carbon atoms in the temperature region from 100 K to the crystal melting temperature. The analysis of given temperature dependencies has allowed to discover the following regularities. For all acids in the region of low temperatures the Davydov splitting value practically does not depend on temperature. When temperature is increasing for acids with odd number and even number n=22 of carbon atoms it takes place the slow decreasing of splitting value with consequent sharp decreasing of this one to zero in the nearest region of crystal melting point. For acids with odd number of carbon atoms n=10,14,16 the splitting value decreases to zero without sharp changes. A statistic and dynamic model is proposed which provides adequate description of the observed effect. In the framework of this model, two different mechanisms are responsible for the temperature changes of the splitting value of vibrational modes. In addition to thermal expansion of crystals under heating, the damping of vibrational excitons on orientational defects of different nature takes place. Genesis of such defects is connected with excitation of conformational, librational and rotational degrees of freedom of H-bonded molecular dimers at the different temperatures. Theoretical analysis of the effect of resonance dynamical intermolecular interaction on the spectra of intramolecular vibrations of the crystals was performed in terms of stochastic equations with account for mentioned mechanisms. The explicit expression for theoretical dependence of Davydov splitting value on temperature was obtained. Computer simulation of such dependence was performed for crystalline normal chain carboxylic acids. Good agreement between the experimental and computer simulation results was obtained.

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Anharmonic effects in quantum-chemical calculations of 3,5- dimethylpyrazole and diphenylformamidine H-bonded complexes

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Quantum-chemical calculations of H-bonded complexes formed by 3.5- dimethylpyrazole (DMP) and diphenylformamidine (DPFA) as proton acceptors and carboxylic acids and hydrogen halides as proton donors were carried out by the DFT method at the $B3LYP/6-31G^{**}$ level with the use of Gaussian 2003 program. Earlier we calculated the equilibrium geometry and vibrational frequencies in the harmonic approximation for monomers, dimers, trimers and H-bonded complexes of DMP and DPFA with carboxylic acids. As a rule, the theoretical harmonic frequencies differ significantly from the experimental data. To minimize this error, we attempted calculations of frequencies and intensities with the anharmonic effects taken into account. Three approaches were used in the calculations. (1) To calculate the ν NH mode of DMP (DPFA) free molecule, we replaced the molecule by a hypothetical diatomic molecule consisting of the H atom of H-bond and the remaining atoms. The 1D anharmonic vibrational equation was solved numerically using an ab initio potential computed at a large number of uniformly spaced points. (2) The second approach was a version of variational multidimensional anharmonic calculations of vibrational electrooptical parameters in space of normal coordinates [1]. In this case, the Hamiltonian matrix was evaluated by Gauss - Hermite quadratures. The use of a basis set of ten harmonic oscillator eigenfunctions ensured convergence of wave function expansion. (3) We also performed anharmonic calculations using the option provided by the GAUSSIAN 2003 package. The first method can yield the frequencies in good agreement with experimental findings for very characteristic modes. For example, the ν NH stretch frequency obtained by different methods for isolated DMP was as follows: $3676 \ cm^{-1}$ (harmonic approximation), 3522 cm^{-1} (1), 3532 cm^{-1} (2), 3496 cm^{-1} (3); the experimental gas phase value is 3520 cm^{-1} . For the DMP-acetic acid cyclic complex, the ν NH...O stretch values are 3414 cm^{-1} (harmonic), 3244 cm^{-1} (2), 3200 cm^{-1} (3), the experimental value in solution is $3320 \ cm^{-1}$. For the OH...N stretching mode, using approach (2) yields the best result. For DPFA-acid complexes, the NH stretch frequency of the NH...O H-bond was found to be 3263 cm^{-1} (harmonic) and 3258 cm^{-1} (2); the experimental frequency is 3200 cm^{-1} . The calculated ν OH frequency of the OH...N H-bond in a cyclic complex equals to $2731 \ cm^{-1}$ (harmonic) and 2229 cm^{-1} (2). The results obtained show that the second approach is more preferable for calculating the high-frequency XH stretch in systems where the corresponding normal mode is less characteristic and involves motions of many atoms. Approach (3) seems also promising for calculating the frequencies of DMP monomer and DMP - acetic acid complex. Simulation of experimental spectra with the help of vibrational transition frequencies allows us to describe about 20 characteristic and noncharacteristic vibrational bands of DMP-acid complexes unstudied earlier.

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Spectroscopic studies and quantum chemical harmonic calculations of H-bonded complexes of N-containing molecules

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The results of experimental studies by IR, ¹H and ¹⁵N NMR spectra and of quantum chemical calculations of vibrational frequencies and structure of Hbonded complexes formed by strong nitrogen-containing bases (B) 3,5-dimethylpyrazole (DMP) and diphenylformamidine (DPFA) with carboxylic acids are presented. The monomers and trimers of DMP and monomers and dimers of DPFA were found in solutions in CCl_4 and CH_2Cl_2 under the variation of Ncontaining base concentration. IR spectra of systems B - RCOOH in CH₂Cl₂ solution show that the complexes with weak acids have the cyclic molecular structure, and the interaction with strong acids results in formation of cyclic H-bonded ionic pairs with proton transfer to the N atom. The frequency shift of ν_{as} COO of RCOOH under the transition from weak to strong acid (from molecular to ionic structure of complex) for complexes formed by pyrazole and amidine are discussed. The analysis of spectra with excess concentrations of strong acid enables to identify the bands of complexes of 1:1 and 1:2 compositions; the last structure contains the homoconjugated anion with the strong H-bond C-O-H ... O-C. The analysis of spectra of B - HHal systems supported the formation of ionic-pair complexes B⁺ ... Hal⁻. Low-temperature NMR spectra of DMP-CCl₃COOH system in freon solution support the formation of 1:1 and 2:1 (under excess of pyrazole) ionic-pair complexes. The complexes 2:1 contains homoconjugated cation with the N-H ... N hydrogen bridge. The cooperative effect of H-bonds in cyclic structure for this system was studied additionally by use of NMR spectra of partly deuterated samples, and it was concluded that two O⁻ ... ⁺HN H-bonds are anti-cooperative.

Quantum chemical calculations were carried out using with DFT–(B3LYP) method with different basis sets by GAUSSIAN-98 program and gave the structure and harmonic frequencies of complexes, which show good agreement with the experimental data. The results obtained support that pyrazole and amidine form the cyclic molecular complexes with two H-bonds with weak acids; no proton transfer takes place in these complexes in solvent. The proton transfer and formation of the ionic structures have been found for the complexes with stronger proton donors (dichloro-, trichloro- and trifluoroacetic acids). Inclusion of polarized environment effect (in the framework of Onsager or Tomasi models) changes the relative depth of potential minima in favor of the ionic form.

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Analysis of Infrared Spectrum of 2-(2'-hydroxyphenyl)benzoxazole by DFT Calculations

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A molecule of 2-(2'-hydroxyphenyl)benzoxazole (HBO) has an OH...N intramolecular hydrogen bond and exhibits excited state proton transfer [1]. Vibrational spectrum of HBO was analyzed by semi-empirical calculations, however, the wavenumbers were significantly overestimated and different scaling factors were required for different regions of the spectrum [2]. Density functional theory (DFT) was successfully applied to calculations of vibrations of various organic molecules including H-bonded systems [3].

We performed DFT calculations for an isolated HBO molecule to analyze an IR spectrum of solid state HBO. The IR spectrum was measured in the region of intramolecular vibrations (400-4000 cm^{-1}) in KBr pellets at room temperature. DFT geometry optimization was done with B3LYP functional and 6-311++G(d,p) basis set. Optimized ground state geometry of the isolated HBO molecule is planar even when no symmetry constraints are used for the optimization. The calculations of vibrations were performed for C_s symmetry of the molecule. Computed frequency values were scaled by constant factor 0.98 in the whole range. The intensity and scaled wavenumbers are in good agreement with experimental values. Deviations from the experimental wavenumbers do not exceed 10 cm^{-1} except the band at 710 cm^{-1} . In this case the difference is 20 cm^{-1} and observed frequency is lower than calculated one. This band is assigned to the three out-of-plane fundamental modes involving the hydrogen bond where significant anharmonicity is expected. In-plane O-H stretching vibration demonstrates the wide band at 3300 cm^{-1} . Such a wide band is specific for H-bonded system and implies interaction with other modes [4].

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The influence of the methoxy- and nitro- substituents in pyrimidine ring on the amino group spectral, geometrical, dynamical, electrooptic and energetical characteristics of free and H-bonded (1:1 and 1:2) with various proton acceptors molecules of 2-aminopyrimidine.

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Different forms of amino- and imino- pyrimidines are a part of the various drugs: antibiotics, vasodilators, coronary (heart) deficiency correcting medications and metabolic stimulators.

The amino and imino groups participating in the hydrogen bond play very impotant role in the interaction mechanism between medical products and living organism. Therefore, the investigation of the substituents influence in the pyrimidine ring on proton donation ability of the substituted aminopyrimidines seems to be very actual.

The aim of the present work is the investigation of the methoxy and nitro substituents on the amino group spectral, geometrical, dynamical and electrooptic characteristics of 2-amino-4,6-dimethoxy- and 2-amino-5-nitropyrimidines.

Acetonitrile, tetrahydrofourane, dimethylformamide, dimethylsulfoxide and hexamethyl-phosphoramide were used as proton acceptors. Their proton- accepting properties vary in a wide range.

The absorption spectra of the amino group stretching and deformation vibrations of free molecules and H-bonded 1:1 complexes were studied in CCl₄, 1:2 complexes - in undiluted aprotic solvents.

The absorption band spectral characteristics of the amino group stretching vibrations of free and bonded molecules were determined: $M^{(0)}$ - zero spectral moment (integrated band intensity), $M^{(1)}$ - first spectral moment (band's centre of gravity) and $M^{(2)}$ - second central moment which is related to the effective halfwidth: $(\Delta \nu_{1/2})_{eff} = 2(M^{(2)})^{1/2}$.

It was shown, that within the range 288-330K, the absorption band parameters of the amino group stretching vibrations of free molecules and 1:1 complexes have virtually linear temperature dependency.

The linear regression parameters Y = aT + b ($Y = M^{(0)}, M^{(1)}, 2(M^{(2)})^{1/2}$) were determined. It was stated, that the thermal sensitivity of the spectral characteristics ($a=\partial Y/\partial T$ parameter) for H-bonded complexes (1:1) is several times greater than for free molecules in CCl₄.

For free and H-bonded molecules of the substituted 2-aminopyrimidines the vibrational and electrooptic problems were solved in the R-NH₂ framework of the valence force field model.

Valence angles γ (HNH), force constants K(NH), electrooptic parameters $(\partial \mu / \partial q)$ (derivative of the dipole moment by the length of the same NH-bond) and $(\partial \mu / \partial q)$ (derivative of the dipole moment by the length of the neighboring NH-bond) were determined.

The comparative analysis was performed on the influence of the methoxy and nitro substitution in anilines, aminopyridines and aminopyrimidines on the amino group spectral, geometrical, dynamical and electrooptic characteristics.

It was stated, that the methoxy and nitro substituents in the pyrimidine cycle have little influence on the position of the absorption bands in spectra, but their influence on the band intensity is significant.

The linear correlations were established between the amino group spectral, geometrical, dynamical and electrooptic parameters of free and H-bonded (1:1) with proton acceptors molecules of 2-aminopyrimidines. These correlations will allow to find important molecular characteristics on the basis of the spectral measures.

The thermal dependency of the monomer-complex equilibrium constant (1:1) was studied and the thermodynamical characteristics $(-\Delta H_1, \Delta S_1)$ of 1:1 complexes were determined. The enthalpy $-\Delta H_2$ of 1:2 complexes was determined on the basis of the Johancen empirical correlation in assumption that the coefficient α in equation $\Delta H = \alpha \Delta B^{1/2}$ does not depend on complex's composition.

The thermodynamical characteristics of complexes have a weak dependency on the individual properties of the substituents.

It was shown, that the H-bond strength in 1:1 complexes is greater than in 1:2 complexes. This is also confirmed by the independent force constants K(NH) calculations for complexes with different composition.

The quantum mechanical calculations of the amino group parameters for free and H-bonded (with proton acceptors) molecules were performed in the DFT-B3LYP/6-31G^{**} approximation.

It was shown, that the charge transfer through the hydrogen bridge from the acceptor molecule to proton donor molecule is observed in H-bonded complexes.

IR spectra of binary liquid systems HF - aprotic solvent at molar ratios ranging up to 9 : 1

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Fluorination is an important process of preparative and industrial chemistry. Therefore, the physicochemical and spectral properties of hydrogen fluoride solutions in inorganic and organic solvents are of great interest. In the present work a systematic study of IR spectra of HF solutions in aprotic solvents were carried out for the first time. The binary liquid systems HF-Solv. (Solv. = N,N-dimethylformamide, acetone and acetonitrile) at molar ratios ranging up to 6: 1-9: 1 was chosen as the subjects of inquiry. Because of high corrosiveness of hydrogen fluoride, the measurements of vibrational spectra were taken using a CaF₂ cell in the frequency range 4000 - 1000 cm⁻¹. Along with the spectral study the density of HF solution in acetonitrile was measured for the first time over the entire concentration range. The largest density value was observed at molar ratio of about 18 : 1.

The spectra of two systems under investigation (HF-DMF and HF-acetone) exhibit absorption bands at 3500, 2600, 1800 cm^{-1} , and continuous absorption (CA) in the frequency range from 3500 to 1300 cm⁻¹. At molar ratios 1 : 12 - 3 : 1 the intensities of these bands and CA increase in proportion to the concentration of HF in solution. The difference between the experimental density of HF solution in acetonitrile and the calculated additive sum of the densities of the solution components behaves similarly. At higher percentage of HF all obtained concentration dependencies become nonlinear. The comparison of these results with analogous data for systems HF - CH₃OH and HF - nC₃H₇OH shows that they are very similar. At the same time the spectra of HF solutions in acetonitrile has several distinctive properties. The most essential of them are the absence of absorption band 1800 cm^{-1} and the appearance of new bands at 3320 cm^{-1} (at molar ratios 1 : 12 - 2 : 1), 3700, 1700, 1600, 1245, 1200, 1150 cm⁻¹ (at molar ratios 1: 1 - 7: 1), 1745, and 1765 cm⁻¹ (at molar ratios exceeding 4 : 1). It is also worth noting that the characteristic absorption bands 2600, 3500 cm^{-1} , and CA appear in the spectra of HF-acetonitrile only at high molar ratios.

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Electrooptical parameters of hydrogen bridges in molecular complexes B...HF (B = DMF, H₂O, AND HF)

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By means of quantum-chemical calculations performed by the density functional method (B3LYP, basis 6-31++Gdp) with the use of GAUSSIAN-94 program the structures and the charges on the atoms in the molecular complexes DMF...HF, H₂O...HF, and (HF)₂ were calculated. By varying the lengths of the hydrogen bonds and the adjacent covalent bonds the finite differences of the dipole moments of the bonds in the hydrogen bridge were found and their derivatives with respect to coordinates of the lengths of the bonds HF and F(O)...H were estimated. The obtained results allow us to reveal a number of common regularities.

1). The dipole moments of the hydrogen- and HF- bonds are directed in the same direction.

2). The derivatives of these dipole moments with respect to the HF-bond length are positive in all cases. The derivatives of the hydrogen bond and HFbond dipole moments with respect to the H-bond length are negative.

3). It is appropriate to calculate the intensities of the hydrogen bridge B...HF stretching and translational bands using the total dipole moment of this bridge instead of the dipole moments of its constituent bonds.

4). The absolute values of the derivatives of the hydrogen bridge dipole moment with respect to the covalent and hydrogen bond lengths (these derivatives are opposite in sign) increase linearly as the H-bond strength rises.

The listed data make the solution of the inverse electrooptical spectral problem unique. Thereby they open up an opportunity of using the data of numerous experimental measurements of the stretching vibration band intensity of HF bond in various complexes for studying of their electrooptical properties. The obtained results also can be used in solving the direct spectral problems for the wide range of H-bonded systems involving the molecules of hydrogen fluoride.

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The Effect of Temperature and Pressure on Hydrogen Bonding in Liquid and Supercritical Fluids

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Raman spectra of 1-butanol have been obtained along the isobar of 500 bar up to 375C and along the isotherms of 250, 300, and 350C in the pressure range from 25 to 600 bar. The data are compared to the IR absorption spectra obtained earlier for ethanol, iso-propanol, and 1-butanol at pressures up to 1000 bar in the temperature range from 20 to 450?C. A large body of new interesting results has been obtained but here we concentrate only on the effect of temperature and pressure on hydrogen bonding, in particular, on the intensity of scattering and absorption for bonded and non-bonded species. As was found, the intensity of Raman scattering depends on the strength of hydrogen bonds to a much lesser degree than the intensity of IR absorption. However, just this circumstance helps to reveal that non-bonded OH groups exist even at low temperatures and high pressures. Another important fact gathered from the experiment is that the energy distribution of bonded molecules is certainly discrete. At least two distinguishable species may be recognized in the contours of stretching bands of H-bonded 1-butanol and iso-propanol at low temperatures. Both the Raman and IR spectra confirm the existence of cooperativity effect of hydrogen bonding. The effect means that each additional molecule added to a chain of bonded molecules enhances the average energy of bonding. Fast strengthening of hydrogen bonding begins as the mole fraction of bonded OH groups exceeds 0.6?0.7. At a larger mole fraction an avalanche-like process of forming long chains or large rings takes place. Such a phenomenon resembles very much the surmounting of percolation threshold.

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0.3 Inorganic crystals

Exciton-phonon interaction in CdS_xSe_{1-x} nano- and bulk crystals

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The structural and electronic properties of semiconductor nanocrystals are becoming an expanding field of interest in physics of semiconductors. Excitonphonon interaction is a very important factor in determining the physical properties of bulk and nanocrystals. The size-dependence of the coupling between electronic and vibrational excitations is a long lasting issue of the physics of nanostructures. There are several mutually contradictory publications on this problem. The studies of phonon modes in these materials allow one to understand optical properties of semiconductor quantum dots, including excitonphonon coupling.

In this work, the electron-phonon interaction in $\operatorname{CdS}_x\operatorname{Se}_{1-x}$ nanocrystals have been investigated and compared with those in bulk crystals of the same composition x. For this goal we fitted our experimental Raman spectra by using the theoretical expression taking into account the strong interaction of the exciton with the lattice vibrations. We describe the whole spectrum, the structure of which depends on the ratio of (X/w), where X is the exciton-phonon coupling constant w is the phonon frequency.

The lattice frequencies w_1 , w_2 we can obtain from the experiment, the ration of the intensities of two first phonon replica were fitted by variation of X_1 , X_2 constants. All spectra can be fitted by varying these two constants. The result of fitting have shown that coupling constant for bulk is by a factor of 1.2 larger than that for nanostructures (at close compositions), which is in agreement with other theoretical works.

Optical spectra of RB_6 and RB_{12}

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The RB_6 hexaborides and RB_{12} dodecaborides (R is rare-earth, alkaline-earth, or early transition metal) have been widely studied due to their peculiar physical properties, such as superconductivity (YB₆, ZrB₁₂), Kondo and valence fluctuation effects (CeB₆, SmB₆, YbB₁₂), anomalous magnetism (EuB₆), and narrow gap semiconductor properties (YbB₆, YbB₁₂). Also, LaB₆ is known as a very good emitter of electrons, and ferromagnetism was recently reported at unexpectedly high temperatures in La doped alkaline-earth hexaborides. Therefore, these borides are of great scientific and technological interest due to their extraordinary properties, especially in the field of spin electronics.

The aim of this contribution is to perform *ab initio* calculations of electronic energy structures and optical spectra of representative series of rare-earth hexaborides and dodecaborides, and to shed more light on the origin of intriguing properties of these borides. The RB_6 structure can be described in terms of a simple CsCl lattice, where R atoms occupy Cs sites, while B_6 octahedra are in Cl sites. The basic structural elements of the cubic dodecaborides are stable cubooctahedral boron clusters B_{12} . The RB_{12} structure is described in terms of simple rock-salt lattice, where R occupies Na sites and B_{12} cubooctahedrons are located in Cl sites. The electronic structure calculations have been carried out for corresponding paramagnetic, ferromagnetic and antiferromagnetic phases by using the full-potential linear muffin-tin orbital method (FP-LMTO) within the density functional theory. The densities of electronic states (DOS) and the balanced crystal orbital overlap populations (BCOOP) were calculated for the RB_x systems. The calculations have revealed a small overlap between the conduction and valence bands in the majority of RB_6 and RB_{12} compounds. The features of a band overlap (or the presence of a small band gap) have important implications for models proposed to explain the properties of RB_x .

The spectral quantities were evaluated by using the calculated real and imaginary parts of the dielectric tensor. The optical dielectric tensor was calculated in the momentum representation, which requires matrix elements of the momentum, \mathbf{p} , between occupied and unoccupied eigenstates. The imaginary part of the dielectric function, $\epsilon_2(\omega) \equiv \operatorname{Im}\epsilon(\mathbf{q} = 0, \omega)$, was calculated by:

$$\epsilon_{2}^{ij}(\omega) \simeq \omega^{-2} \sum_{\mathbf{k}nn'\sigma} \frac{\langle \mathbf{k}n\sigma \big| p_{i} \big| \mathbf{k}n'\sigma \rangle \langle \mathbf{k}n'\sigma \big| p_{j} \big| \mathbf{k}n\sigma \rangle \times}{f_{\mathbf{k}n} \left(1 - f_{\mathbf{k}n'}\right) \delta \left(e_{\mathbf{k}n'} - e_{\mathbf{k}n} - \hbar\omega\right)}$$

Here $f_{\mathbf{k}n}$ is the Fermi distribution, and $|\mathbf{k}n\sigma\rangle$ is the crystal wave function corresponding to the nth eigenvalue with crystal momentum \mathbf{k} and spin σ . Fi-

nally, the real part of the dielectric function, $\epsilon_1(\omega)$, as well as other optical spectral functions, can be obtained from $\epsilon_2(\omega)$ by using the Kramers-Kronig transformation. In order to reproduce experimental conditions, related to the finite lifetime of the excited states and the instrumental smearing, the calculated spectra have to be broadened.

Optical properties of RB_x in the VUV energy range have been investigated experimentally by Kimura et al. In their studies, the reflectivity measurements for RB_6 and RB_{12} single crystals were done in the energy range 0.001—40 eV. Also this group studied the total electron yield spectra around the boron 1s absorption edge in YB₆, YB₁₂, and LuB₁₂. In order to shed light on these experimental data in connection with the band structures of RB_x , the reflectivity spectra, optical conductivity, as well as boron 1s absorption spectra, were calculated for corresponding rare-earth borides RB_6 and RB_{12} .

The optical conductivity spectra of LaB₆ and YB₆ above 15 eV appeared to be different from each other due to differences of corresponding 5p-5d and 4p-4d transitions at La and Y, whereas below 15 eV these spectra are rather similar. Also, one should take into account that LaB₆ contains the unoccupied 4f band, which is hybridised with the conduction p-d band. The calculations indicate that the optical conductivity spectra originate mostly from the intramolecule absorption of B₆ clusters. Thus, the transitions to the unoccupied 4fstates are almost forbidden in LaB₆, and the 4f states do not contribute directly to the optical conductivity spectra.

The B 1s XAS absorption reflects the partial density of states of the unoccupied *p*-states of boron. The 1s XAS spectrum of LuB₁₂ appeared to be different from those of YB₁₂ and YB₆, and this is related to differences in electronic structures of these compounds. Since the 4*f* level of LuB₁₂ is occupied, the valence band of LuB₁₂ appeared to be close to that of YB₁₂, though there is some difference between Lu 5*d* and Y 4*d* states. For these compounds the calculated *p* partial DOS of boron above the Fermi level appeared to be consistent with the B 1s absorption spectra. The reason for the experimentally observed core exciton absorption in YB₆ is presumably the strong covalency bonding in the B₆ cluster. The possibility and appearance of the core-hole effects in these XAS spectra are also studied in the present calculations.

The optical conductivity spectra of RB_{12} do not depend substantially on rare-earth atom, except for the high peak above 20 eV. It is expected, that the main contribution to these spectra is due to the electronic structure of the B_{12} cluster. The higher peak in the RB_{12} spectra is probably originates from the 5p-5d transitions at R site, whereas the main part of the optical conductivity spectra presumably comes from the bonding s - p states of B_6 and B_{12} clusters in RB_6 and RB_{12} , respectively.

The experimental optical spectra of YbB_{12} can be represented as a superposition of the calculated spectra with di- and trivalent ions of Yb. This clearly demonstrates the intermediate valence nature of ytterbium in YbB₁₂. On the other hand, the origin of the assumed Kondo insulator state in YbB₁₂ and the reported tiny energy gap is still controversial both experimentally and theoretically.

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Reflectance spectra of bare and impregnated synthetic opal photonic crystals

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Interest in optical phenomena in photonic crystals is caused by presence of gaps in their photonic band structure. The most interesting phenomenon is complete photonic band gap which is a range of wavelengths in which light cannot propagate through photonic crystal in any direction [1, 2, 3]. Photonic band gap emerges from scattering of light on a three dimensional lattice which is formed by modulation of dielectric constant with the period close to the wavelength of light. Advance in fabrication of synthetic opal photonic crystals and wide range of possible modifications of their optical properties by impregnating them with various substances stimulates experimental study of these materials [4].

The purpose of the present research was to study reflectance spectra of synthetic opal photonic crystals. Samples of synthetic opal made of $a-SiO_2$ spherical particles have been studied. The samples were kindly provided by S.M. Samoilovich. Dimensions of the samples are approximately 1.0x0.5x0.5 cm. Reflectance spectra for reflection from the plane of growth (111) for both a bare opal sample and the sample with interstitials filled with $Ba(NO_3)_2$ have been measured.

The samples were illuminated with an incandescent lamp and LEDs. Light from the source was collimated with a collimator of goniometer GS-5 and an iris diaphragm. Reflected light, which included diffuse component, was collected with a lens positioned on two focal distances from the sample and a fiber-optical cord with cross section diameter 3.5 mm positioned on two focal distances from the lens. The other end of the fiber-optical cord was placed in the plane of the entrance split of a double grating monochromator of spectrometer DFS-12. Reflectance spectra were measured in geometry of specular reflection for angles of incidence of 20° , 30° and 45° .

The obtained spectra contained an asymmetrical peak with parameters dependent on the angle of incidence. For sample 1 (bare synthetic opal) maximum reflectance for the angles of incidence of 20° , 30° and 45° was detected at the wavelengths of 506 nm, 482 nm and 445 nm correspondingly. For sample 2 (synthetic opal with interstitials filled with Ba(NO₃)₂) maximum reflectance for the abovementioned angles of incidence was detected on the wavelengths of 590 nm, 564 nm and 510 nm correspondingly. Magnitude of reflectance in the point of maximum for the angle of incidence of 20° reached 25% for both samples. With increase of the angle, reflectance decreases: for 30° it was 24% for both samples; for 45° it was 18% for sample 1 and 20% for sample 2.

Analysis of obtained spectra was made using a well known expression for Bragg diffraction of light in opals $\lambda(\theta) = 2d \left[\sqrt{\langle n \rangle^2 - \sin^2 \theta} \right]$ where *d* is the distance between (111) planes of opal: $d = (2/3)^{1/2}a$, *a* is diameter of silica spheres; θ - angle of incidence; $\langle n \rangle = xn_{sph} + (1-x)n_{int}$ - effective refractive index of opal (*x* is packing fraction of the spheres, n_{sph} and n_{int} are refraction indices of materials of spheres and interstitials).

Theoretical relation between the wavelength of diffracted light and angle of incidence have been calculated.

The following values were used for sample 1: $n_{sph} = 1.47$; $n_{int} = 1$; x = 0.74; a = 237 nm (a was calculated from data for normal reflection). The wavelengths of 505 nm, 484 nm and 444 nm were obtained for the angles of incidence of 20°, 30° and 45°. For sample 2, the following values were used: $n_{sph} = 1.47$; $n_{int} = 1.57$; x = 0.74; a = 248 nm. The obtained wavelengths for the abovementioned angles of incidence were 590 nm, 571 nm and 534 nm correspondingly. Thus, for sample 1, the experiment and calculations give similar results while those for sample 2 differ considerably. It seems to be due to features of filling of interstitials with a substance.

The halfwidth of the peak in reflectance spectra is generally defined by the width of the stopgap. For sample 1 the halfwidth of the peak for the angles of incidence 20° , 30° and 45° is 30 nm, 30 nm and 36 nm; for sample 2 the halfwidth of the peak for these angles is 47 nm, 47 nm and 50 nm correspondingly. Broadening of the peak is due to scattering of light on defects of opal structure among which these are misalignment of densely packed growth planes (111) in domains from which bulk opal consists [5], interfaces of the domains and defects in the domains like stacking faults and point defects. With increase of the angle of incidence intensity of scattering increases which results in additional spectral broadening for big angles. Additional spectral broadening of the peak in reflectance spectra for impregnated opal possibly is due to defects in filling of interstitials.

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Molecular Spectroscopy of Subthreshold Inelastic Radiation-Induced Processes in Rare-Gas Crystals

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The fundamental excitation of non-metallic solids by photons and beams of particles with kinetic energy below the threshold of knock-on of atoms from lattice sites — subthreshold excitation — is a powerful tool for materials modification [1]. The scission of the bonds, stabilizing the ground-state configuration, by transfer of electronic excitation energy to the lattice requires the trapping of the electronic excitations. However the range of materials, which exhibit inelastic processes induced by electronic excitation, is limited to specific classes of materials, such as alkali halides, alkali earth fluorides and fused quartz [1].

Recently the rare-gas crystals (RGC) — solid Xe, Kr, Ar and Ne — manifest themselves as a new class of insulators, which demonstrates pronounced inelastic processes induced by electronic excitations [2]. As a consequence of the closed electronic shells, RGS are the simplest solids known to us with smallest binding energy between atoms in the lattice. On the other hand, solid Ar and Ne have band-gap energies exceeding that of LiF and may be cited as widest band-gap insulators. Therefore, RGC — well-known model systems in condensed matter physics — are very promising for investigation the mechanisms of subthreshold inelastic electronically induced processes. Because of strong interaction with phonons the excitons and holes are self-trapped in RGC. Local elastic and inelastic lattice deformation around trapped electronic excitations, population of the antibonding electronic states during relaxation of the molecular-like centers, and excitation of the Rydberg states of guest species are the moving force of point defect formation in the bulk and desorption from the surface of RGC.

RGC-samples exist only at cryogenic temperatures and most of the optical spectroscopy of electronic processes must be done in the vacuum ultraviolet. It requires from experiment the indispensable combination of liquid-helium equipment with window-less VUV-spectroscopy devices and synchrotron radiation as a photon source. To investigate the electronic excitation energy pathways and variety of subthreshold inelastic radiation induced processes in RGS we used the complementary advantages of cathodoluminescence (possibility to vary the excitation depth beneath the sample surface) and photoluminescence (selective excitation of luminescence by synchrotron radiation at high-flux SUPERLUMIstation at HASYLAB, DESY, Hamburg) [3]. The paper reports the recent spectroscopic studies of mechanisms of desorption and defect formation processes induced by exciton self-trapping in RGS.

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Spectroscopy of electron traps in solid Ne

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Solid inert gases are convenient model systems for investigation of electronically-induced processes in insulating materials in particular defect creation. These substances give a possibility to understand such processes at the atomic level due to their specific properties: comparatively simple electronic and crystal structure, small binding energy of atoms and strong electron-phonon interaction. Electron traps play an important role in various stages of energy relaxation processes in irradiated solids. In the case of solid Ne such structural defects as pores or vacancies are effective traps for electrons because of the negative electron affinity of solid Ne [1]. Excitation of the electronic subsystem of the crystal (by means of irradiation) results in formation of ionized species in the lattice: self-trapped holes, guest ions and electrons trapped by electron scavenger or at defect sites. Relaxation processes in cryogenic matrices, are of considerable interest both from the point of view of fundamental condensed-matter physics, and in a number of important applications especially in solid-state photochemistry. Energy stored by the species formed during irradiation of the sample can be released by heating or by photons. It induces a complex series of reactions followed by energy conversion and transfer processes. We have studied electronic and atomic relaxation processes on the model system - solid Ne doped with N. This system is attractive for elucidating the role of radiative transitions in relaxation cascades because of the intense afterglow, which is caused by the formation of N atoms in metastable states after irradiation. We prepared samples of Ne cryocrystals from the gas phase by condensation on a cooled substrate. Then they were exposed to a beam of electrons. After the irradiation we detected a long afterglow from the samples maintained at the constant low temperature. The total yield of afterglow decay can be described by the exponential function with the characteristic decay time $\tau = 195$ sec. The sources of this emission are dopant atoms and molecules. Note that before irradiation of the sample the impurities (for example N and O) are present in a molecular state. The irradiation results in dissociation of molecules into atoms. The long afterglow is caused by radiative decay of metastable states. We also registered a similar behavior of the excelectron emission yield from the sample after irradiation - "afteremission". It occurs simultaneously with the afterglow. We measured exoelectron emission using a movable electrode under small positive potential. One can suppose that the afterglow in the visible range of spectrum is responsible for the "afteremission". Visible photons of afterglow can release electrons from the traps. In rare gas solids free electrons are highly mobile. Due to negative electron affinity of solid Ne there is no barrier for electron to escape the surface. Because the conduction band in solid Ne is wide the electrons can be released by visible light both from deep and shallow traps.

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Molecular aspect in investigation of the electronic structure of tungstate crystals

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Dielectric oxide crystals AWO_4 (A = Zn, Cd, Pb) are used as scintillation materials in different applications of science and technology ranging from high-energy physics to medicine. Their optical and scintillation properties are investigated intensively during the last decade. Successful understanding of mechanisms and of the origin of the luminescence processes in these crystals cannot be achieved without the detailed study of their electronic structure. In our works on this problem, we developed a complex approach in theoretical calculations of the electronic structure of AWO_4 crystals, which combines two different methods of the calculations. The choice of these methods was determined by the objectives of the investigations.

In our aproach, the electronic properties of a whole crystal are studied via calculations carried out in band formalism by a full potential Linear Augmented Plane Wave (LAPW) method implemented in WIEN2k program code [1]. However, it is commonly recognized that a spatially separated objects, i. e. lattice defects, impurities, crystal surfaces forming the shapes of macro-defects in the crystal, etc, in general determine the luminescence properties of AWO_4 crystals. On the other hand, it is well known that the spectroscopic properties of perfect AWO_4 crystals are in great measure determined by tungstate groups WO_4^{2-} , complex molecular anions with mostly covalent character of inter-atomic bonds, which are situated in anionic sites of the crystal lattice. The localized electronic states of such objects can be successfully considered, if the calculations of the electronic structure are carried out in molecular cluster approach. For this purpose, we use the Restricted Hartree-Fock (RHF) method developed in GAMESS program package [2].

The aim of this work is to reveal advantages and drawbacks of the molecular cluster RHF method when it is applied to dielectric oxide crystals AWO_4 . The sets of clusters of different sizes (from 12 to 100-110 atoms) of AWO_4 (A = Pb, Cd, Zn) crystals are considered for these purpose. Several types of defects like the oxygen vacancies, the impurities of Mo and Pr are modeled in clusters. The densities of electronic states (DOS), spatial distributions of electronic charges, and the joint DOS are calculated. The results obtained for different clusters are compared with experimental data on luminescence, excitation and absorption of corresponding AWO_4 crystals and with analogous results obtained in band calculations carried out by means of WIEN2k code. Similar features in the results of the two methods are emphasized, and possible explanations of discrepancies found in the results are presented. Some general remarks concerning the principal applicability of a cluster method to the study of the electronic structure of the luminescence centres in dielectric crystals are done.

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Resonant Raman scattering, ab initio calculation and band-gap states in $g - GeS_2$

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Raman spectra of $g - GeS_2(T_i, V_i)$ [samples were synthesized by melt quenching from different temperatures ranging from 1173 K (T_1) to 1473 K (T_4) and cooling rate variations from 100 K/s (V_1) to 150 K/s (V_2)] were measured firstly using a photon energy of 2.41 eV (514.5 nm), less than the Tauc optical gap (E_0) of GeS_2 glasses ($E_0 \sim 3.2 \text{ eV}$). As these spectra are similar to those measured with longer wavelengths: 632.8 and 785 nm, corresponding to 1.96 and 1.58 eV respectively, we assign these to be non-resonant Raman spectra. A pronounced differences between the spectra is that both the (T_1, V_1) and the (T_3, V_2) samples shows similar small increases in the 370 and 433 cm^{-1} vibrational modes in comparison with (T_2, V_2) condition, and for the (T_4, V_2) sample these peaks broaden and merge with the main peak at 342 cm^{-1} . Altogether the non-resonant Raman results combined with the ab initio calculations support the idea about co-existence of single GeS_4 tetrahedra, corner-shared and edge-sharing GeS_4 tetrahedra. A very weak mode at $200 \ cm^{-1}$ is observed for all samples while a weak Raman mode at 490 cm^{-1} is detected only for (T_2, V_2) . Among ab initio computed Raman spectra for the $Ge_n S_m$ clusters only $SGe_3 - S_{6/3}$ contributes to first weak mode.

The most pronounced differences, however, occur at the low frequency side of the main peak: new peaks arise at 256 and 237 cm^{-1} , especially strong for (T_4, V_2) condition. The experimental peaks at 256 cm^{-1} correlates with the calculated Ge-Ge stretching mode in the ethane-like $Ge_2S_{6/2}$ cluster (250 cm^{-1}) or the mode calculated at 246 cm^{-1} obtained for $SGe_3 - S_{6/3}$. However, the shoulder at 237 cm^{-1} can only be related to the formation of new structural units all having tri-coordinated S or Ge ($SGe_{3/3}$, $SGe_3 - S_{6/3}$) as no other clusters have any peaks below 250 cm^{-1} . The band near 237 cm^{-1} is a breathinglike A_g mode in the polarized spectra of c-GeS.

Intensity increases for the two Raman modes at 370 and 433 cm^{-1} are observed for both (T_1,V_1) and (T_2,V_2) samples with increasing of exciting photon energy. The intensity ratios of the 370 and 433 cm^{-1} modes was compared with the intensity of the main mode at 342 cm^{-1} , (I_{370}/I_{342}) and (I_{433}/I_{342}) , respectively, as functions of excitation photon energy, that shows clearly the mainly common nature of these peaks.

The calculated band gaps of Ge_nS_m were estimated by the differences of the HOMO and LUMO energies (BLYP) and by the differences of energies of ground first excites states (TD BLYP). The band gap states of $g - GeS_2$ we proposed

to consider as superposition of electronic states of Ge_nS_m clusters with weight coefficients [1].

 R. Holomb, P. Johansson, V. Mitsa and I. Rosola // Phil. Mag., 2005, in press.

Peculiarities of spectroscopy of 2H-PbI₂ layered crystals with high concentration of Mn impurity

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Semiconductors with iron-group transition ions are of high interest because they can reveal spin effects and thus are promising materials for application in spintronics. However, contrary to the case of diluted magnetic semiconductors on the basis of traditional II-VI and III-V compounds, much less attention has been paid to highly anisotropic layered crystals.

Present report deals with spectroscopic investigation of 2H-PbI_2 layered crystals with high concentration of Mn impurities. To obtain information on the peculiarities of phonon and exciton states and paramagnetic centres in these crystals, we applied the Raman, exciton and EPR spectroscopies. It is shown that Mn-doped crystals belong to 2H-polytype. The resonance increase of some Raman lines attributed to a new type of the Fermi resonance (local impurity vibration + two phonon lines) is registered. Exciton and EPR spectra indicate on the formation of $Pb_{1-x}\text{Mn}_x\text{I}_2$ solid solutions with x = 0.1.

Birefrigence of the inorganic crystals

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Interferometric method has been used in order to determine the birefringence of some uniax and biax inorganic crystals.

Additionally a spectral method for the birefringence determination in the visible range is appliedd. The channeled spectra were recorded for thin layers of some uniax inorganic crystals placed between two crossed polarizers and having their main axes at 45 degrees relative to the transmission directions of the polarizers. The wavenumbers of the channels were used for the birefringence dispersion estimation.

Experimental results refer to some inorganic crystals originary in the Carpathians Mountains. Good agreements between the data interferometrically obtained and those from the channeled spectra.

Excitons and structure phase transition in $Cs_3Bi_2I_9$ layered ferroelastic crystals

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Cs₃Bi₂I₉ crystals belong to an extensive family of poorly studied threecomponent A₃B₂X₉ layered substances and are actual object of investigations from both scientific and practical point of view. Interest in Cs₃Bi₂I₉ crystals is due to the manifestation of the ferroelastic second-order phase transition at the temperature $T_c = 220$ K (accompanied by a reversible change of crystal symmetry from hexagonal 6/mmm into centrosymmetrical monoclinic 2/m), to the prediction of incommensurate phase at T < 220 K and to the possibilities of usage in recorder systems, pressure and γ -emission sensors, acousto- and optoelectronics.

This review report deals with the experimental studies of the effect of temperature variation on the exciton and Raman spectra of $Cs_3Bi_2I_9$ crystals. The results of the investigations are discussed on the basis of exciton-phonon interaction and phase transitions.

We have found that $Cs_3Bi_2I_9$ crystals are not typical layered ones. They are layered semiconductors in the hexagonal phase and behave like conventional semiconductors in the monoclinic phase. The registered transition region in the temperature broadening of the half-width of the exciton band in the temperature interval 150–220 K and a surge at T = 220 K are caused by the formation of the heterophase structure region (where ferroelastic and paraelastic phases coexist) and ferroelastic phase transitions, respectively.

We have simulated the optical functions of the system of two non-interacting classical oscillators using traditional extrapolation by Philipp-Taft and Yahoda methods. It is shown that the calculated functions are in good agreement with model functions only in the second case. We have proposed the self-consistent method for dividing of dispersion dependence of complicated optical functions into individual compounds and determined the parameters of critical points of Cs₃Bi₂I₉ reflection spectra. The analyses of Argand's diagram gives us possibility to suppose that the shape of the absorption bands 2.583, 2.956 and 3.075 eV (T = 4.2 K) may be Lorenzian. The energy gap $E_g = 2.857$ eV (T = 4.2 K) and the exciton binding energy Ry = 279 meV, oscillator force $f = 5 \cdot 10^{-1}$ and radiative time $\tau_R = 1.2 \cdot 10^{-8}$ sec.

We have studied the $Cs_3Bi_2I_9$ Raman spectra in conditions of increasing of temperature from 5 to 300 K in unpolarized light and did not observe any soft modes or softening of modes. The effect of equality of the intensities of lines 114.8 and 125.3 cm⁻¹ at the point of the phase transition is observed without any peculiarities in the behaviour of their frequencies. The doublets in the lines 37.0, 45.0, 61.4, 68.3 and 97.4 cm⁻¹ (T = 4.2 K) are registered too. The reason of its manifestation may be nonequivalent position of $[Bi_2I_9]^{-3}$ ions in monoclinic lattice or take off the degeneration and splitting of degenerated states of *E*-symmetry. One should note that Cs₃Bi₂I₉ Raman spectra in light polarization z(y,y)z and z(y,x)z at T = 100 K are similar to those in unpolarized light.

The obtained and known data have testified that the studied ferroelastic phase transition is of the first-order close to the second-order.

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Alteration in glasses As-S during micro-Raman spectra at different energies of excitation

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In this report we present the analysis of the energy dependent transformations of micro-Raman scattering spectra of As-S glasses. Micro-Raman spectra of glassy materials were measured at room temperature using Raman spectrometer equipped with microscope. The laser sources used for Raman scattering excitation were follows: (i) a diode laser (785 nm, $E_1=1.58$ eV), (ii) a He-Ne laser (632.8 nm, $E_2=1.96$ eV), and (iii) an Ar-ion laser (514.5 nm, $E_3=2.41$ eV and 488 nm, $E_4=2.54$ eV). Optical filters, limiting the output power near 80 μ W and lower, were used in order to avoid visible photo-structural changes of the materials. The vibration frequencies of realgar and pararealgar As_4S_4 molecules were calculated [1] using ab initio method.

Firstly we note that exciting line with energy E_1 is located on the low-energy part of weak absorption ($\alpha < 1 \ cm^{-1}$) of As-S glasses edge absorption spectra, where $\alpha \sim \exp(h\nu/E_{\omega})$ ($E_{\omega} \sim 200\text{-}300 \text{ meV}$) is adjacent to the Urbach edge. The photon energy of E_2 exciting line is correspond to the Urbach edge, $\alpha > 10 \ cm^{-1}$. The light with the photon energy of E_3 is closed to the Tauc band-gap (E_0), $\alpha > 5 * 10^3 \ cm^{-1}$. Finally, at the photon energy $E_4 > E_0$, $\alpha > 10^4 \ cm^{-1}$ the absorption of As-S glasses is maximal. So different exciting energies $E_1 - E_4$ are correspond to the different levels of edge absorption.

The most visible changes occur during measuring arsenic-reach $As_{45}S_{55}$ composition but similar tendency has been observed for stoichiometric composition of As-S glasses. In comparison with $As_{45}S_{55}$ a micro-Raman spectrum of $As_{40}S_{60}$ sample has no such significant influence of excitation energy on the intensities of several bands. It is known that arsenic-reach glasses are phase separated and consists of β -As₄S₄ micro-crystals embedded in glassy matrix. Using the E_1 exciting line the sharp features in the micro-Raman spectrum of g- $As_{45}S_{55}$ are correspond to the β - As_4S_4 modes. In measured spectrum using E_2 exciting line a drastic changes in comparison with spectrum registered at E_1 exciting line observed - the intensities of realgar-like peaks at 358, 220, 187 cm^{-1} are decreases but pararealgar-like peaks at 346, 334, 231 cm^{-1} are increase in intensity. Further increases in exciting photon energy (E_3) the gradual spectral changes of Raman bands are appearing. The half-width of complex band centered at 346 cm^{-1} is notedly increased. Instead the peak at 358 cm^{-1} in micro-Raman spectra excited with low photon energies (E_1, E_2) in corresponded spectrum exciting with E_3 line only shoulder is presented. The broadening of complex band at 346 cm^{-1} may be connected not only with pararealgar bands at 334, 346 cm^{-1} but furthermore also with broken weak As-As bonds in realgarlike As_4S_4 molecules due to the laser illumination and formation of extra As-S stretching modes typical for As-rich $As - (S - As)_3$ and $As - (S - S)_3$ clusters [1]. Existence of weak band at 490 cm⁻¹ in micro-Raman spectra measured using the E_3 , E_4 lines are supported this conclusion. Furthermore, the peaks typical for pararealgar (P), $\beta - As_4S_4$ phases and amorphous (a) matrices based on $AsS_{3/2}$ s. u. are observed in spectrum measured using the E_1 , E_2 , E_3 exciting lines. We suggest possible coexisting of these phases (P, β , a) with different proportion in the illuminated sample using different photon energies.

The As-As band intensity of pararealgar As_4S_4 molecule at 230 cm^{-1} is increasing at E_3 exciting photon energy and this is one of the maximal among intensities of four $E_1 - E_4$ exciting lines. It means that at $E_3=2.41$ eV, P~1000 W/cm² per 60 sec. of laser irradiation of $As_{45}S_{55}$ sample during spectrum recording the rate of alteration of β - As_4S_4 in pararealgar is more fast. In case of E_4 exciting energy the penetration depth is ~ 1 nm and during exposure time a laser beam has modified only surface of the sample. In this case the intensity of 230 cm^{-1} band is decreased in comparison with As-S band at 346 cm^{-1} .

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Raman spectra of Hafnia based ceramics

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Hafnia- (HfO₂) based ceramics are some of the most interesting high-temperature materials used in current technologies, having applications similar to ZrO_2 . HfO₂ materials can be used in solid electrolytes for fuel cells, oxygengas sensors, refractories, coating for oxidation resistance, and control rods for a water-cooled reactor. The significant attention to these materials is caused by their unique combination of properties such as high strength and fracture toughness, resistance to effect of aggressive chemical conditions, low thermal conductivity, etc.

The crystal structure of HfO_2 has monoclinic *m* symmetry under ambient conditions and exhibits a structural phase transition to tetragonal *t* forms at ~1720-2270 K. The application of Raman spectroscopy considerably expands the possibilities of study of the material structure, the phase transformation peculiarities, the quantum size effect, compositional effects, the material evolution with sintering and treatment.

In present work we have investigated materials on the basis of hafnia with monoclinic m and tetragonal t type of structure in order to study the manifestation of the peculiarities of each phase in Raman spectra. Spectra were excited by emission of argon ion laser with 514.5 nm and 488.0 nm wavelengths and recorded with DFS-24 double grating spectrometer. The nanocrystalline powders and policrystalline materials have been investigated.

We have carried out the group theoretical analysis of phonon states both tetragonal and monoclinic phases. The symmetries and forms of the normal vibrations for these structures also have been obtained for correct correspondence of spectral lines. Changes in the frequencies of the Raman modes with the phase content of materials have been carefully detected.

Observed Raman spectra contain all fundamental optical modes as predicted by the group theoretical analysis both for powders and policrystalline pressed pellets of the same composition. The band intensity relationship depends on the type of sample. The band widths and positions change as function of the dopant content and its quality

The vibrational spectra of $Li_2B_4O_7$ crystals doped with potassium and silver ions

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The effect of point defects of varying physical nature on the optical vibrational spectra of crystals is discussed in many papers which represent preferably theoretical model calculations. However, experimental works devoted to this question are considerably smaller in number, especially, for such dielectric crystals with a complex structure as lithium tetraborate $Li_2B_4O_7$ (LB4). This work was aimed at the experimental study of vibrational spectra of LB4 crystals doped with potassium and silver ions by using Raman and Infra-Red (IR) spectroscopy methods.

LB4 crystals were grown by the Czochralski method. The impurity concentration in a charge was 0.1-0.2%. Raman spectra of pure and doped LB4 crystals were excited by the second harmonic of the Nd³⁺:YAG laser radiation at 532 nm. Spectra in the X(ZZ)Y, X(YY)Z, Z(YZ)X, X(ZX)Y and X(YX)Z geometries were measured in a region of wavenumber 0-1000 cm⁻¹ at room temperature. IR reflection spectra were obtained in a region of 100-400 cm⁻¹ for an incident angle at 6⁰ by using Fourier spectrometer LAFS-1000 and in a region of wavenumber 200-2000 cm⁻¹ for an incident angle at 20⁰ by using IR spectrometer SPECORD M80. Reflection spectra were measured in $E\perp z$ geometry. The fitting of all spectra has been performed in order to determinate the oscillator parameters. Raman spectra were fitted within the framework of the model of weakly interacting oscillators. For IR reflection spectra the four parametric dispersion (Kurosawa) relation was used.

It has been found that the influence of impurity ions was in changing of integral intensity and halfwidth of the majority of polar A_1 and E modes in Raman spectra. As for IR reflection spectra, the changes of the oscillator strength were most noticeable for the low (100-250 cm⁻¹) and high (650-1200 cm⁻¹) wavenumber regions. Dielectric ϵ_0 and ϵ_{∞} parameters were also changed significantly in doped crystals. Oscillator parameters obtained from Raman and IR reflection spectra of LB4 crystals doped with silver ions are quite different from those for pure and potassium-doped crystals. The effect of potassium ions on the vibrational spectrum has been found to be much smaller. In all spectra there were not any manifestations of local or resonant vibrations caused by impurity existence. Thus, obtained results give evidence of the fact of impurity ions influence on the vibrational spectrum of LB4 crystal. This influence is different because of the difference in ionic radii. It has been also found that impurity ions in both doped crystals are positioned in interstices.

Lattice Dynamic Properties of ReO₃

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The Infrared and Raman spectra have been applied to calculate the parameters of lattice dynamics for ReO_3 crystals. In the framework of a rigid-ion model, lattice dynamics for the cubic phase involves only five parameters. These parameters characterize the interaction constants parallel and perpendicular to Re-O and O-O bonds and the electric charge of the oxygen ion. The phonon-dispersion curves and the phonon density of states are calculated. The phonon spectra have two characteristic regions.

The calculated phonon spectra are used to determine the mean square displacement of rhenium and oxygen ions. The mean square displacement of an oxygen ion show the well-pronounced anisotropy. The mean square relative displacement are calculated for ion pairs Re-O and Re-Re. The obtained results are compared with the experimental data of X-Ray diffraction and EXAFS.

Application of method of projective representations to analysing of Raman circular dichroism in tetragonal girotropic objects

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Raman circular dichroism (RCD) is manifestated as dependence of Raman cross-section on sign (handedness) of circularly polarized incident laser light. It was observed for components of some low-frequency E-modes in first-order Raman spectra of gyrotropic tetragonal crystals ZnP_2 , CdP_2 and TeO_2 (central positiom of these doublets are 99 cm⁻¹ for ZnP_2 , 93 cm⁻¹ for CdP_2 , and 122 cm⁻¹ for TeO_2). Each of the said crystals exists in right of left enantiomorphous modifications, characterised by space groups P4₁2₁2 and P4₃2₁2, respectively. Above mentioned E-mode splitting is proportional to value of component of phonon wave vector which parallel to Γ - Z direction.

Therefore point Λ of Brillouin zone was examined in longwave approximation. By use of projective operator it was shown that in this point two circularly polarized TO phonon states exist. Right polarized phonon in group P4₁2₁2 corresponds to representation Λ_3 and left polarized phonoin corresponds to representation Λ_4 of the same group. In group P4₃2₁2 picture is opposite. All these features were observed experimentally.

The high-temperature Raman spectra anomalies in isotopic substituted $Li_2B_4O_7$ crystals

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Lithium tetraborate crystals $Li_2B_4O_7$ (LB4) attract a considerable attention owing to possibilities of their wide practical applications in acoustoelectronic devices, ultraviolet solid state lasers and solid state sources of electrical power.

The study of these materials within a wide temperature region allowed finding out a number of anomalies of physical properties in 214-238 K, 370-520 K and 700-900 K which were connected with structural changes in lithium sublattice. However, detail investigations of Raman spectra in the high-temperature region have not been performed by now.

This work is devoted to the study of LB4 Raman spectra in the range of frequencies of vibrations with lithium ions participation in the high-temperature region in order to clarify the nature of vibrational spectrum of LB4 crystals and to expose structural changes in lithium sublattice.

Raman spectra for LB4 single crystals with various content of lithium isotopes LB4-7-10 (Li⁷-96%; B¹⁰-97,3%) and LB4-6-10 (Li⁶-95%; B¹⁰-97,3%) have been measured within a wide temperature region of 300-1000 K in the X(ZZ)Y, X(YY)Z, X(ZX)Y geometries, corresponding to A₁(TO), A₁(IO)+B₂ and E(TO + LO) modes, respectively. The intervals of 60-350 cm⁻¹ and 420-550 cm⁻¹ have been studied. The samples have been excited by the second harmonic of the Nd³⁺:YAG laser radiation at 532 nm. Analysis of scattered light has been performed by using the double monochromator of DFS-12 spectrometer. The sample heating has been performed in a resistance furnace in air.

It has been found that $A_1(TO)$ modes at 152 and 491 cm⁻¹, and B_2 mode at 207 cm⁻¹ in LB4-7-10 crystal were most sensitive to isotopic substitution. Temperature dependences of frequency and halfwidth of modes at 491 cm⁻¹ in LB4-7-10 and 497 cm⁻¹ in LB4-6-10 have anomalies in the region of 750-810 K which indicate structural changes in lithium sublattice.

Besides, the $A_1(TO)$ mode at 152 cm⁻¹ has been found to be caused by contribution of two vibrations. The resonance interaction between these vibrations is accompanied with intensity redistribution from the high-frequency oscillator to the low-frequency one. Similar behavior has been also observed for the E(TO+LO) modes at 135 and 159 cm⁻¹.

Thus, temperature anomalies observed in Raman spectra testify the existence of phase transition that is due to structural changes in lithium sublattice in the temperature region of 750-810 K.

Laser induced quenching of luminescence of lead centers in borate glass

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As is well known, lead ions in glass matrixes form luminescence centers which emit blue luminescence under UV excitation. This luminescence is usually attributed to ${}^{3}P \leftrightarrow {}^{1}S_{0}$ transitions in Pb^{2+} ions. In borate glasses doped with Pb^{2+} ions, three types of luminescence centers (0-, I-, and II-centers) are revealed. Investigations of spectral properties of lead-doped borate glasses provide useful information on the symmetry and structure of these centers. Under powerful pulsed laser excitation, Pb-centers of type I and II demonstrate excited state absorption and nonlinear luminescence, similar to other mercury-like ions in glasses.

Previous investigations of glasses doped with mercury-like ions show that irradiation by powerful UV laser radiation produces new types of luminescence centers in the glass. Similar effects are observed in glasses irradiated with γ -rays. For example, in glasses doped with indium, irradiation-induced transformations of spectral characteristics can be explained with the following mechanism $\text{In}^+ \leftrightarrow \text{In}^{2+} \leftrightarrow \text{In}^{3+}$.

In the present work we investigate laser-induced quenching of luminescence in borate glasses with the composition of K₂O-mB₂O₃ - 0.1wt.%PbO (m=2, 3, 4). Such glasses initially contain 0-centers with Pb²⁺ ions. In the experiments, a Q-switched YAG-Nd³⁺ laser (1064, 532, 266 nm, 15 ns) was employed. γ irradiation was performed with a Co⁶⁰ source.

The experiments show significant laser-induced quenching of Pb^{2+} luminescence. Depending on the laser wavelength, the mechanism of quenching includes excited state absorption and stimulated emission in Pb^{2+} centers. A model is proposed for interpretation of the experimental data obtained. Besides, we investigated the laser-induced luminescence of γ -irradiated lead-doped glasses. The experiments show intense infrared luminescence of γ -produced lead centers. This infrared luminescence is effectively quenched by laser radiation due to stimulated emission.

Dependence of kinetic phosphorescence of ceramics ZnS - Cu on a doze of a proton irradiation

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Was studied kinetic of the light sum accumulation at an isothermal mode after an irradiation by protons of ceramics ZnS - Cu by dozes 10^{14} , 10^{15} p/cm² with energy 50 Mev. The excitation luminescence and the light sum accumulation were carried out by integrated study x-ray tube (Mo, 35 kV, 10 mA) at temperature 85 K. In work the method accumulation of the light sum is used at increase of time of excitation. The method allows qualitatively estimating changes in system of local levels of samples. The researches stationary luminescence have shown, that at an irradiation of initial samples the doze 10^{14}p/cm^2 observes increase of intensity roentgen luminescence (RL) and the size reserved the light sum under a curve phosphorescence (Ph) grows. The fall of intensity RL and strong reduction reserved the light sum under a curve Ph is characteristic for samples irradiated by a doze 10^{15} p/cm². For all three sets of samples experimental dependences of recession of intensity Ph after the first minute of attenuation is satisfactory approximation by hyperbolic dependence. After an irradiation of ceramics by protons has changed kinetic radiation relaxation Ph. The increase of a parameter of a degree hyperbola $\alpha = Ln(J)/Ln(t)$ is established, for the irradiated samples, where J - intensity Ph, t - the time of registration Ph, from time of excitation, in an initial sample α decreases with increase of a degree of excitation. The received dependences of rate of accumulation the light sum (t)during an interval of registration Ph testify to participation in attenuation of two grades of traps differing on the mechanism radiation of transitions. And, the presence of radiating defects differently changes processes of the light sum accumulation on these grades of traps. For initial sites Ph τ depends on time of achievement of saturation Ph and size of intensity RL, it is supposed that this grade of a trap is a part of a uniform complex responsible for green a luminescence in ZnS - Cu. The character of change τ for the second grade of traps explains by increase of channel recombination after a proton irradiation. The reduction increase of values τ for samples irradiated by a doze 10^{14} p/cm² contacts to increase of concentration interstitial of zinc (Zn_i) responsible for long low-temperature Ph. For samples irradiated by a doze 10^{15}p/cm^2 the received values t are explained by possible displacement Zn_i in regular places, that is reduction of concentration Zn_i and vacancies S. The easing radiation of ability of samples irradiated by a doze 10^{15} p/cm² is explained by occurrence of the centers nonradiative recombination generated by a proton irradiation.

Optimisation of luminescence efficiency of europium and terbium compounds for OLEDs by modification of aromatic ligands

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This work is a continuation of investigations of processes of excitation of europium and terbium compounds depending on the details of the structure [1, 2]. Its goal is a search of lanthanide compounds with high luminescence efficiency that could be used in organic light emitting diodes (OLEDs) [3].

The opportunity of optimisation of luminance of the lanthanide compounds by modification of ligands is discussed. The effects of changing of the excitation and luminescence efficiencies at introduction of the nitro- (NO_2) , sulfo- (SO_3-) , hydroxy- (OH), amino- (NH_2) , and phenylamino- (NHC_6H_5) groups in the aromatic ligands were studied. Investigations of luminescence and luminescence excitation spectra of europium and terbium compounds with 10 derivatives of benzoic acid, 2-furancarboxylic acid and corresponding adducts with 1,10-phenanthroline and 2,2-bipyridine as well as of 8-hydroxyquinolinates were undertaken. Luminescence efficiency was measured at 77 and 300 K. Paths of the energy transfer from the ligands to Ln³⁺ ion were examined. Influences of radicals on the energies of the ligand triplet state and on the ligand-metal charge transfer states (LM CTS) in europium compounds were analysed. Influence of relative positions of the lowest triplet levels of two non-equivalent ligands of compound on the energy transfer to Eu^{3+} and Tb^{3+} ions was considered.

It was found, that the luminescence efficiencies of europium and terbium benzoates and furancarboxylates are high, in contrast to very low efficiencies of europium and terbium nitrobenzoates. In the nitrobenzoates channel of dissipation of the excitation energy through the NO₂-group π^* -n transition was found.

The luminescence efficiencies of majority of europium anthranylates and salicylates are low, on the contrary to terbium anthranylates and salicylates having high luminance. The weak luminance of europium anthranylates and salicylates is caused by energy dissipation through the low-energy LM CTS. Effect of increasing of the luminescence efficiency of europium compounds due to introduction of the electron-withdrawing nitro- and sulfo-groups in the aromatic ligands was revealed. An increase of luminescence efficiency by a factor of 10^2 was obtained for europium 5-sulfo-8-hydroxyquinolinate, and by a factor of 10^3 for europium 3,5-dinitrosalicylate.

The influences of radicals on quantum yield of luminescence should be taken into consideration at engineering of red and green luminophores.

P-10

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Influence of LO-phonon dispersion on exciton energy loss in molecular crystals

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The influence of longitudinal optical phonons dispersion on the process of excitons scattering in molecular crystal was investigated theoretically. For the first time, the modified Davydov's function of Frenkel exciton coupling with optical lattice vibrations was used for the calculations. A special attention was paid to the study of frequency and temperature dependence of scattering intensity. We have revealed the relation between the dispersion and the width of energy interval of phonon absorption and/or emission. It was found that depending on frequency, the LO-phonon dispersion can lead to increasing as well as to decreasing of the magnitude of exciton damping. In addition, absorption peaks, associated with the energies of a phonon creation or annihilation, behave in an opposite way with respect to the phonon dispersion growth: the first one increases and the second falls. Temperature peculiarities of exciton relaxation in molecular crystals have been investigated with different values of LO-phonon dispersion.

Electronic structure and the luminescence centres of zinc and cadmiumtungstate crystals

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The zinc $ZnWO_4$ and cadmium $CdWO_4$ tungstate crystals are perspective scintillation materials, which are used in different technical applications. Significant numbers of works dedicated to investigation of the luminescence and scintillation properties of these crystals were published in recent years. However, the composition and structure of the luminescence centers in zinc and cadmium tungstate crystals are still the subjects of discussion. In order to clarify the origin of luminescence in $ZnWO_4$ and $CdWO_4$ we carried out theoretical calculations of their electronic structure.

Electronic structures of perfect and defective $ZnWO_4$ and $CdWO_4$ are calculated in molecular cluster approach. Two types of defects are considered: the oxygen vacancy and the molybdenum impurity. The molecular clusters of the crystals were constructed of about 100 atoms. The electronic structures (the energies of molecular orbitals, densities of electronic states, inter-band densities of states) of the clusters are ab-initio calculated by the Restricted Hartree-Fock (RHF) method using GAMESS quantum chemistry package [1]. The electronic states of the Cd^{2+} and Zn^{2+} cations and the WO_4^{2-} tungstate groups are evaluated. The influence of defects on these states is studied. Results of the calculations are analyzed together with experimental results on luminescence and absorption spectra of zinc and cadmium tungstate crystals.

The origin of several bands in absorption and reflection spectra of the crystals is discussed on the base of the obtained results of calculation and existing experimental data. Possible schemes of luminescence processes in perfect and defective $ZnWO_4$ and $CdWO_4$ crystals are drawn.

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Acoustic emission and electroluminescence GaAsP diodes at threshold direct current density

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Additional internal mechanical and termomechanical tensions usually provoke in epitaxial diodes of origin of spontaneous chaotic radiation of acoustic waves - acoustic emission (AE) [1]. Appearance of AE means that in local regions to the crystal the irreversible changes took place is appearance of new defect or change of metastable state of existing. At intensive enough the AE such local changes engulf considerable part of volume of crystal, irreversible changing his properties - there is degradation of electro-physical parameters. However much the display of AE allows to regulate a size and speed of change of the external influencing (direct current of transition) for warning of premature destruction to the diode. On the dynamics of AE correlation influences between high-energy discrete AE, which is conditioned usually by the change of the state ("by the wearing-out") of the 3-d defects or dislocation complexes, and low-power continuous AE, which is conditioned usually by synchronous motion (by tearing-fixing off on a stop) of dislocation segments (on evaluation information [1] for forming of one impulse of AE needs to $10^3 - 10^4$ dislocation segments). It follows to notice that AE, at the change of the state only points defects in general is not registered [1]-[4], through too small energy separately emitted impulse. As composition and state of points defects which can change in the process of reorganization of local structure (origin of AE), and the direct current of transition is one of basic factors, which determine a spectrum and integral intensity of electroluminescent (EL), speed and size of degradation of basic parameters of light-emitting diodes, cause interest comparative researches of spectrum evolution EL of epitaxial light-diodes $n^+ - n - p$ -structures GaAs_{0,15}P_{0,85}:N/GaP but GaP:N/GaP, that was accompanied by the radiation of AE, in step-up process of direct current of heterotransition. In [2, 3] it was show that subject to the condition certain in epitaxial LED $n^+ - n - p$ -structuresGaAs_{0.15}P_{0.85}:N/GaP the origin of AE is accompanied by the change of bands ELL. These changes for in relation to small currents had circulating character [3]. For large currents, after forming of infra-red (I) band, this smooth change was closed on different - with renewal of initial positions of red (R) and green (G) bands [3] at the decline of density of current of J_i , or change of G-band (565...580 nm) to 720 nm and disappearance of R- band [4] even for small J_i Evolution of spectrums ELL in liquid nitrogen (77 K) and at a temperature 300 K differs substantially. At 300 K and small J_i change of maximums of R- and G- bands ELL from primitive positions (710 and 580 nm) insignificant (to 10 nm) and is described within

the framework of the known models (in particular - overheat of active region) of based on the use of correlation of Warshny. Intensity in an I- band grows droningly, but a change is not observed. In liquid nitrogen at those J_i change of R- and G- bands ELL considerable - to 20 nm for a G-bar and to 30 nm for a R-bar in which ELL carries threshold character. At small J_i ELL in a R-band is practically absent, at $J_i = J_{rel} = 20...30 \text{ A/sm}^2$ a maximum is formed 680 nm, $\sim 100 \text{ A/sm}^2$ this maximum is displaced to 710 nm. In an I- band at and at J_i J_{rel} intensity ELL grows a jump from a sound-level in 10 times, and with growth of J_i there is expansion of I- band in a long-wave region. In a G- band intensity of ultralinear grows up to J_{rel} , and farther is the maximum of band (585 nm) is displaced in a short-wave region to 565 nm. It should be noted that evolution of G-band for structures GaAs_{0,15} P_{0,85} : N/GaP at low (77 K) temperatures does not answer evolution of G-band in GaP : N/GaP (120 K). The change of maximum at them takes place in a long-wave region, and I-band ELL is not formed. In structures $GaAs_{0,15} P_{0,85}$: N/GaP radiative recombination in a red band concernes by the complexes of Zn-O, that insignificant GaP : N/GaP. It confirms expressed in [3] supposition, that growth ELL in an I-band can be related to disintegration of complexes of Zn-O at high J_i , that is accompanied discrete AE.

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An XPS examination of intercalation of alkaline atoms in the host framework of phosphate tungsten bronzes

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New cathode materials for secondary power cells were recently synthesised and tested in model electrochemical cells L/Na(+) PP-membrane ClO4 in EC-1,2-DMC monophosphate tungsten bronzes. The monophosphate tungsten bronzes (MPTB) are promising cathode materials with specific capacity values in the range 150-350 (mAg)/h. These parameters satisfy the materials requirements and can put forward elaboration of the modern cathode materials. Structurally, the MPTB framework forms by perovskyte-like layers of WO_6 octahedra, interconnected by PO_4 tetrahedra and respective host-framework cavities can be filled by cations. However, it is necessary to perform the modelling of intercalation-deintercalation for optimization of work of the electrochemical cell and to gain the optimal parameters of the cathode material and to optimize exchange processes in the electrochemical cell. The chemical process during the electrochemical cell working was mimicked using the chemical intercalation of small exchanging cations in the MPTB cavities via organometallics reductant. Red-ox processes during the chemical intercalation and spectral characteristics of the intercalated materials were tested in complex by XPS, FTIR, Raman and EDX/WDS spectroscopy. The respective spectra modelling was performed using simple structural models in a cluster approach. The numerous unexplained phenomena which can not be assigned directly using the results of examination were observed. Consequently, SEM/HRTEM electron microscope equipped with a high-sensitive X-ray photoelectron and EDX/WDS microprobes was applied to monitored the light-elements content in the thin section or layers of MPTB in situ during a charge-discharge cycle. The complex of spectroscopic technique enables to found interdependences of voltage or specific capacity of cell as a function of the exchanging cations content and clarify some of the phenomena observed. It was determined, that the bend in these dependences corresponds to formation of fixed stoichiometry phases containing L/Na, which can be utilized for controlled preparation of the respective ionic conductors. Additionally structural and spectral studies of isolated intercalates were performed by XPS, neutron diffraction study, XAS and PXRD methods.

Oscillations of magnetic anisotropy in superlattices Co/Cu(111)

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Magnetic resonance in multilayer $[Co(8\text{\AA})/Cu(d_{Cu})(111)]_{20}$ in magnetic fields parallel or a perpendicular film plane on the frequencies f = 9,4 GHz has been investigated. Oscillations of magnetic anisotropy and resonance line width ΔH_{res} were found for thicknesses of copper layer $d_{Cu} = 7-19$ Å. Extremal values of and ΔH_{res} were observed at $d_{Cu} = nd_{(111)}$, where n - is integer or half-integer and $d_{(111)} = 2.087$ Å is the distance between Cu(111) planes. The intervals between neighboring maximums and minimums are $1d_{(111)}$, $1.5d_{(111)}$ and $2d_{(111)}$.

It is shown, that the absorption of a microwave capacity is caused by ferromagnetic resonance in the ordered planes of Co atoms. The frequencies of ferromagnetic resonance for directions of field $\theta_H = 0$ (the direction of magnetic field is perpendicular to film) and $\theta_H = \pi/2$ (the direction of magnetic field parallel to film) are described by expressions

$$\omega/\gamma = H_{\perp} + H_{eff}$$

when $\theta_H = 0$, and

$$(\omega/\gamma)^{2} = H_{||}(H_{||} - H_{eff})$$

when $\theta_H = \pi/2$.

 $H_{eff} = 2K_A/M - 4\pi M, \ H'_{eff} = 2K_1/M - 4\pi M, \ K_A = K_1 + K_2.$

Oscillations of K_A and ΔH_{res} at change of d_{Cu} are accompanied synchronous oscillations of specific resistance in external magnetic field equal to a field of saturation, and also magnetoresistance.

In thickness region $d_{Cu} = 8-11$ Å and $d_{Cu} \ge 18$ Å the manifestations of interlayer antiferromagnetic exchange interactions between Co layers were revealed.

Results of the presented researches magnetoresonance and magnetoresistance properties of system $[Co(8\text{\AA})/Cu(d_{Cu})(111)]_{20}$ demonstrate synchronous oscillations dependence on thickness of copper layers d_{Cu} with a characteristic step in 1-2 copper monolayers. Observed effects are connected with nonmonotonous varying of layers borders roughness when d_{Cu} grows, because interlayer diffusion in this system is minimal (physical properties of samples, including their resistance, are stability during several years).

EPR spectrum of powder sample $[Cu(HIm)_2CO_3]H_2O$

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The results of investigation of EPR spectrum of metal-organic complex $[Cu(HIm)_2CO_3]H_2O$ are reported. This compound was synthesized as powder. EPR spectrum of a powder sample is the superposition of spectra of small single crystal particles, which are randomly oriented relatively of applied field direction.

In the case the Lorentzian shape of resonance absorption line of individual crystals the form of paramagnetic resonance absorption band can be written as:

$$I(H) \sim \int_{H_{\perp}}^{H_{\parallel}} \frac{(1+H_{\parallel}^2 H^{'2}) dH^{'}}{[(H-H^{'})^2 + (\Delta H/2)^2] H^{'2} (H_{\perp}^2 - H^{'2})^{1/2}}$$

where extremal values of resonance field H_{\parallel} and H_{\perp} are determined by values of effective g-factor (g_{\parallel} and g_{\perp}).

According to this the absorption band have the specific form. As the intensity in every point will be determined by as a number of particles with given orientation as a transition probability for this orientation. As a result the resonance curve looks as a wide band. With next feature on the band end in region of H_{\perp} the narrow peak is formed whereas in region of H_{\parallel} the absorption intensity will be minimal and form the step with following small height shelf if ΔH is small. The form of absorption band was calculated by computer simulation with g_{\parallel} , g_{\perp} and ΔH (absorption line width of individual crystals of powder) as fitting parameters.

Electron paramagnetic resonance was measured in $\lambda \approx 3$ cm wavelength band (9.4 GHz) at room temperature. At this temperature g-factor components $g_{||} = 2.194$, $g_{\perp} = 2.056$ and $\Delta H = 48$ Oe were obtained. The orbital singlet $|x^2 - y^2\rangle$ is a ground state because for this Kramers doublet the unequality $g_{||} > g_{\perp}$ and ratio $(g_{||} - 2)/(g_{\perp} - 2) \approx 4$ are proper. This orbital state is formed by elongated octahedron of local surrounding of magnetic ion.

Charge accumulation layer on the GaN(0001) n-type surface with Cs and Ba overlayers

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We report on observation of new phenomena that arise under Cs and Ba adsorption on the n–GaN(0001) surface. First, photoemission by excitation of visible light in the transparency region of GaN has been found. Second, appearance of an oscillation structure in photoemission spectra has been revealed. Third, surface bands induced by Cs and Ba adsorption are found to emerge at submonolayer coverage around 0.5 ML.

III-nitride materials have attracted great interest due to both fundamental reasons and technological applications in light emitting devices and high power electronic. In this work, Cs/n-GaN(0001) and Ba/n-GaN(0001) interfaces are studied using a photoemission technique with the s- and p-polarized light excitation. Details are presented in [1]. Experiment was performed *in situ* in a vacuum of ~ 5 10¹¹ Torr. Employed samples were Si-doped GaN epilayers of $3 - 4\mu m$ thickness grown on a (0001) sapphire substrate by MOCVD. Cs and Ba flux was accurate calibrated to dosage using original technique [2].

It is found that Cs and Ba adsorption produces drastic change in both the photoemission properties and downward band bending of the n-GaN(0001) surface. Upon Cs and Ba adsorption, minimum value of the thresholds are obtained to equal to ~ 1.4 eV at Cs coverage of ~ 0.5 ML and to ~ 1.9 eV at Ba coverage of ~ 0.4 ML. It was shown that photocurrent from Cs/n–GaN system under light excitation exhibit an unexpectedly high intensity comparable with photocurrent from Cs/GaAs(100) system. Note that GaN is among wide-banggap semiconductors with a band–gap width of 3.4 eV. Therefore, photoemission under light excitation in the transparency region of GaN cannot be originated from the valence-band states. This is the principal distinction from the photo emission processes for all the known semiconductor photocathodes when the valence electronic states are excited. Thus, the data obtained evidence that the photoemission proceeds from a quasi-metallic bulk states in space-charge region of length L $\sim 20-30$ nm near the surface, that is, an electron accumulation layer AC induced by Cs adsorption in the close vicinity of the GaN surface is revealed.

We assume that the formation of the accumulation layer can be explained with a view of downward band-bending when the conduction band edge at the surface lies below the Fermi level [3]. In this case, photoemission is originated from the two-dimensional free-electron gas layer in the conduction band. Then, the photoemission threshold corresponds to the work function. Surface photoemission spectra for both the Cs/n–GaN and Ba/n–GaN interfaces have been studied at coverages up to 2 ML. Two surface bands induced by Cs adsorption are found in surface photoemission spectra. Energy positions of induced surface bands are obtained at 0.3 eV and at 0.5 eV below the Fermi level. It is found that Ba adsorption leads to formation of three surface bands. However, accumulation layer induced by Cs adsorption is more powerful than that by Ba adsorption.

A new phenomenon is revealed, namely, the appearance of oscillation structure in photoemission spectra. To explain origin of oscillation structure, a model taking into account both the electron accumulation layer and multi-beam interference in parallel-sided plate of GaN is suggested.

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Optical-absorption edge and birefrigence of $(Sn_xZn_{1-x})_2P_2S_6$ crystals under hydrostatic pressure

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Hexachalhypodiphosphate crystals of $A_2^{IV} B_2^V C_6^{VI}$ - group combine semiconductor and ferroelectric properties, possess high pyroelectric, piezoelectric and electrooptical characteristics what makes them promising for various applications. The interest to the studies of these crystals is also determined by the presence of Lifshitz points (LP) in (x,T) and (p,T) phase diagrams, separating phase transitions to commensurate and incommensurate phases. Here we report the studies of the effect of hydrostatic pressure on the absorption edge and birefringence near Lifshitz point of $(Sn_xZn_{1-x})_2P_2S_6$ crystals. In $(Sn_xZn_{1-x})_2P_2S_6$ crystals the exponential shape of the absorption edge is observed, its temperature behaviour being shown to be described by the Urbach rule. The Urbach law parameters and absorption edge energy position along the p, T-diagram at approaching to LP is investigated. The temperature dependences of the birefringence in $Sn_2P_2S_6$ crystals at different values of the hydrostatic pressure have been explored. The behaviour of the critical indexes of the β order parameter and α heat capacity along the p, T-diagram of $(Sn_xZn_{1-x})_2P_2S_6$ crystals has been determined. Based on the studies of pressure and temperature effects on the absorption edge and birefringence, a (p, T)-phase diagram is built.

Investigation of cadmium tellyride film by the ellypsometry and X-ray diffraction methods

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The property of the cadmium tellyride films on the single crystal silicon, distributing of thickness and index of refraction on the area of sample are determine by the methods of ellipsometry and X-ray diffraction. Research is realized on the CdTe thin films, got on the epitaxial vacuum setting by the method of "hot wall". By a x-ray diffraction method it is explored the film structure.

The structure of the CdTe thin films was analyzed by powder X-ray diffraction (XRP, Siemens D5000). XRD spectra were measured within diffraction angle 2? range of 5 to 105 with step size 0.02° and measuring time 1 s/step. Cu-Ka radiation from a Cu X-ray tube (30 mA, 40 kV) was used. Polycrystalline phases could be distinguished by comparison with powder diffraction files (PDF) from the JCPDS (Joint Committee on Powder Diffraction Standarts) database. All measured samples of CdTe thin films deposited on single crystalline Si(111) showed film structures with two crystallographic orientations: (111) and (511).

The ellipsometric measurments are executed on a wave-length 632.8 nm by means the compensator laser ellipsometer and on wave lengths of 579, 546, 435, 405 and 366 nm of the mercury lamp spectrum radiation by means nonstandard photometric ellipsometer, calibrated with the help of the single-crystal silicon plate. Ellipsometer is built on a non-compensator scheme analyzersample-polarizer. The ellipsometric parameters both measured at fixed angle of incidence 60, and in the wide region of angles of incidence. Measurements on different lengths of waves and on different angles of incidence allowed to define a thickness, the coating indexes of refraction and absorption. A sounding light beam fell on areas of the explored sample with a different interference colouring (to seven areas), located along the radius of spraying spot, that allowed to get distributing of thickness and optical constants on the area of sample. For determination of three unknown parameters of film the method of diagrams of the measured values is applied, when distributing of the experimental points got at the variable (unknown) values of the layer thickness, try to describe by the consistent set of parameters of the investigated system. It is obtained, that index of refraction of telluride cadmium films is considerably less from the index of refraction of single-crystal CdTe and depend on the film thickness, growing with its increase. In our opinion this circumstance is conditioned to those, that the explored film is not monocrystallic, and in actually is loose, has the changed structure which includes pores between the separate corns of basic material. The pores sprinkled in the volume of film, contain air and effective index of refraction of film is less than index of refraction of continuous material. Obviously, the degree of loosess diminishes with the increase of thickness of film, and the value of index of refraction grows.

The influence of lattices field on the radial wave functions of Tl^+ in alkaline-haloid crystals

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The radial wave functions of free ion for theoretical estimation of luminescent centres are often used. Such approach is justified in most cases because of little influence of ions environment on its electron shells. But sometimes this approach cannot be used and some luminescent and absorption bands cannot be associated with electronic transitions of free ion. Creation of simple and sufficiently exact model for taking into account of the crystal lattice field influence is necessary in this case. Offered model differs from earlier ones of taking exchange interaction of activator ions electrons with electrons of ions of the lattice into consideration.

Lets assume that identical cubic cells divide space of the lattice. The size of each cells edge is equal to the distance between the nearest ions of the lattice. Location of these cells is such that an ion of the lattice is located on center of each cell. The potential inside a cell consist of three parts (U_m, U_s, U_p) . The fist one corresponds the potential created by all ions of the lattice except for the nearest one. Calculations show that this potential is invariable with high fidelity within the bounds of suggested cell. This potential is equal to Moudelung potential. The second potential is the electrostatic potential created by the nearest ion. The electron density distribution of the suggested ion was taken into account to calculate this potential. The third one is the potential of repulsion stipulated by the overlapping the ion of activator electronic orbitals with orbitals of suggested ion. This potential was calculated with help of Slaters simple approximation. The potential of lattice can be obtained by the summing U_m, U_s and U_p potentials and posterior spherical averaging.

5f radial wave function of 5d96s25f exited state of Tl^+ ion doped into KCl lattice was calculated using offered model. Hartree-Fock-Slater method was used. Calculations have shown, that under influence of an environment the collapse of a radial wave function of a f-electron of ion Tl^+ is observed - the maximum of electronic density is displaced from 9 (a.u.) for the free ion up to 1.5 (a.u.) for the condensed state. The obtained result confirms the validity offered before interpretation of absorption spectrums and a luminescence.

Luminescent and vibration spectroscopy of zinc manganese (magnesium) diphosphates

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At present, chemistry of phosphates of individual divalent metals compounds is widely studied and possibilities of creation on their base materials those characterize with certain complex of physical, chemical and operational requirements are exhaust. On the contrary, optical and, in particularly, spectroscopic characteristics of diphosphates those simultaneously comprise cations of various divalent metals, f.g. zinc-magnesium (manganese) are investigated in limited frames. Such compounds are solid solutions those differ one other not only by compositions but by structures too. Directed management by composition has to allow obtaining of the diphosphates with adjusting contents of the cations and the same time with the set of multifunctional properties. In the work luminescence characteristics and the data of investigation of vibrations spectra in IR absorption and Raman scattering (RS) both of hydrated and dehydrated solid solutions of the $Zn_{2-x}Mg_xP_2O_7n_2$ (0? ? 0.61; n = 5, 1) and $Zn_{2-x}Mn_xP_2O_7n_2$ (0? ? 2,0; n = 5, 1) diphosphates are presented. The solid solutions of the hydrated diphosphates of certain compositions were obtained by combined precipitation of suitable cations by diphosphate -ion from water solutions of a mixture of their sulphates. Water solutions of the $M^{II}SO_4$? nH_2O ($M^{II} = Zn, Mg, Mn$) and $_4P_2O_7$ sulphates were used as initial reagents. Dehydratation was made by means of thermal treatment of the samples. Synthesized and treated diphosphates were identified by using diffraction X-ray phase analysis. IR and RS spectra were obtained at room temperature in the frequency regions 20 1500 and 200 $4000 \ cm^{-1}$ respectively. Luminescence properties were investigated in the spectral region 350 850 nm in temperature interval 4.2 300 K. As result the groups of lines were separated in vibration spectra of the $Zn_{2-x}Mg_xP_2O_7n_2$ and $Zn_{2-x}Mn_xP_2O_7n_2$ compounds and some of these lines were identified as caused by the intrinsic vibrations of the diphosphate anions and especially those ones caused by vibrations of the PO_3 groups and bridge P-O-P vibrations. As for luminescence, the set of bands in blue green and orange red region of visible light was found in luminescence spectra of studied materials. Spectra of excitation of luminescence in various emission bands were measured too. Dependences of luminescence and vibration characteristics on the composition, concentration of manganese ions and content of water were analyzed. Most part of emission band is explained as caused by radiation transitions in manganese ions two plus charged. Correlations between luminescent and vibration characteristics were observed and had been discussed.

hromium ions effect on the spectroscopic properties of the $MAlP_2O_7$ (M = Na, K, Rb, Cs) crystals

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The purpose of the work is to investigate spectroscopic properties of the $MAlP_2O_7$ (M = Na, K, Rb, Cs) double alkali metal and aluminum pyrophosphate crystals doped with chromium ions. Polycrystalline samples of the $MAlP_2O_7$ (M = Na, K, Rb, Cs) crystals were synthesized from a melt of the mixture of the $M_2 - Al_{23} - 25$ oxides those chemical qualifications were "Chemically pure". Impure chromium ions were incorporated into the sample composition by adding of the Cr_2O_3 oxide in the mentioned above mixture.

Photoluminescence spectra (PL), spectra of the luminescence excitation, reflection and vibronic (infrared and Raman) spectra were obtained for the $MAlP_2O_7$ crystals doped with the Cr ions. PL and excitation spectra of the luminescence were obtained in temperature range 4.2 300 K. Luminescence spectra of the investigated crystals reveal one wide structural band in 350 - 800 nm spectrum regions. It consists of two bands: short wave length band that lies in the 350 650 nm region and the "red" long wave length band extended in the 700 800 nm region. The short wave length band consists of several structural components. The maximum positions of the luminescence bands and their components depend on the impurity ions concentration, temperature of the samples, excitation light wave lengths and of the type of the alkaline metals. Made analysis has shown the short wave length luminescence band is a superposition of the proper matrix luminescence (short wave length components) and emission of the distorted CrO_4^{2-} molecular groups. The long wave length band can be caused both by the electron-vibronic transitions in the Cr^{3+} ions and in the complex centers formed on the base of r_4^{2-} molecular groups and defects of crystal lattice. Effect of the alkali cations on the reflectance, luminescence and vibronic characteristics of investigated compounds is analyzed.

Obtained experimental results were compared with the results of the abinitio calculations of the electronic structure of $MAlP_2O_7$ crystals carried out by full potential LAPW method implemented in WIEN2k program [1]. Comparison of experimental and calculated data allowed us to make the following conclusions concerning effect of the alkali cations and chromium doping on the electron structures of mentioned double pyrophosphates.

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Properties of own luminescence of orthophosphate and vanadate crystals

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Spectral-luminescent properties of double alkali metal titanium orthophosphate and calcium vanadate apatite crystals pure and doped with rare earth ions were investigated. Luminescence spectra of both types of investigated compounds contain broad nonstructural bands in wide spectral regions. Positions of maximums of the bands depend on temperature of the samples and type of cations. The bands are complex and characterized at least by three components.

Luminescence spectra of the $MTi_2(PO_4)_3$ crystals (where M is alkali metal) consist of two bands: the short-wave luminescence band in a range 460–700 nm with maximum position at about 545 nm and the long-wave luminescence band in a range 720–800 nm with maximum position at 765 nm. The first band has two shoulders of small intensity which are observed at 570–585 and 595–625 nm. The second band consists of wide unstructured component with /greekl?m = 765nmand two sharp peaks at /greekl?m = 740nm, and /greekl?m = 745nm, and a weak shoulder at /greekl?m = 750nm on its short wave length wing.

Luminescence spectra of the $Ca_{(5} - 2x)M_xLa_x(O_4)_3OH$ crystals (where M is alkali metal) consist of wide luminescence band in a range 460–700 nm that is characterized by three components with maximum positions in the 470 - 480, 520 - 550, and 570 - 590 nm spectral regions: the blue, green and yellow components.

Decreasing of samples temperature leads to increasing of intensity of the integral luminescence intensity. At the same time the intensity of some spectral component increases more strongly with temperature decreasing compared to intensity of the other spectral components. Thus, redistribution of intensities of the total spectra of the both types of crystals with temperature was observed. Obtained wide nonstructural emission bands for vanadate crystals are in a good agreement with the well known emission of vanadate luminophores, which luminescence is connected with radiation transitions in $VO_4^{\ell}3-$) anions. Taking into account a fact that bands are similar and they were observed by us for all investigated vanadate apatites, we assign these bands to the transitions in the emission centers formed on a basis of the $VO_4^{\ell}3-$) vanadate oxyanions.

The short-wave luminescence band of the $MTi_2(PO_4)_3$ crystals is characterised by the same properties and therefore we assign it to radiation transitions in the emission centers formed on a basis $PO_4^{(3-)}$ phosphate oxyanions.

At the same time we have obtained evidences of existence of more than one type of emission center in the investigated compounds. We assume that observed complex composition of the photoluminescence spectra is a result of existence in these crystals of several types of the emission centers like to "oxyanion group + neighbor defects". The made conclusion agrees with a data on investigation of the $Ca_5(O_4)_3$ calcium phosphate apatites (= OH, Cl, F) [1], [2].

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Role of group and multiple noncritical phase-matchings in laser physics, spectroscopy and processes of energy relaxation

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The concept of vectorial group and multiple noncritical in frequencies and phase-matching (PM) angles is evolved and that is of great importance in quantum electronics, in particular, at generation of sum- and difference frequencies. Broadband in frequencies and divergence (angles) of interacting waves PMs hold promise for creation of sources of tunable coherent radiation, and also visualization of the IR and UV "colour" images. In anisotropic crystalline media the vector group PM is realized when the projections of group velocities of signal and resulting radiations $V_{S,R}$ onto a direction of a signal wave V_S are equal. It can be scanned in frequencies at change of the geometry of interaction. When the group velocity vectors V_S and V_R are equal (the group centre (GC)), the large angular aperture is realized simultaneously with broadbandness of PM. It is established that the scanning of GC along the all transparent region of crystals, when tuning the laser pump in long-wavelength region, is possible in uniaxial crystals LiJO₃, AgGaS₂, HgGa₂S₄, CdSe etc., and also in biaxial ones KTP, RTA and LBO. The GC tuning is considered when passing from the XZto the YZ-plane in biaxial crystals. The comparison of crystals with weak (KTP, RTA) and stronger (LBO) anisotropy in the XY-plane is carried out. By using the considered crystals the GC can be realized in the region of 0,8-18 μ m. Noncritical PMs are very actual for frequency conversion of femtosecond pulses. For the majority of types of interaction the line of GC tuning ends with a critical point (CP), whereupon PM is not realized. The triple noncriticality of PM is achieved in CP. By the behavior of many characteristics, the vicinity of CP is similar to a critical point of a liquid-vapor transition.

For the first time it is shown experimentally, that vectorial noncritical PMs show itself in the overtones and combined tones spectroscopy. In particular, in Raman spectra of a dWO₄ crystal the occurrence of sharp (in intensity) peaks 1231 and 1521, 1537, 1552 cm⁻¹ is revealed in the region of a total tone of oscillatory modes 390 and 901.6 cm⁻¹, and also overtone 2x775 cm⁻¹ at tuning of the laser excitation wavelength $514.5 \rightarrow 496.5 \rightarrow 476.5$ nm. The peak 1231 cm⁻¹ arises at 496.5 nm, and peaks in the overtone region 1400-1600 cm⁻¹ – at 476.5 nm. Thus, the maxima in the second order spectra can be connected not only to areas of maxima of oscillatory state density. The greatest peaks in the second and higher order spectra arise under realization of conditions of multiple noncritical PMs at the coordinated change in dispersion of phonon branches in any given region of a Brillouin zone. The known singular points of a

phonon zone $\omega(k)$, in which $d\omega/dk = 0$, are a special case of PM, noncritical only in wave vectors of phonons. This case of noncritical PM is realized practically more often, than the peaks corresponding GC.

Noncritical PMs show itself completely at cascade nonlinear wave interactions in the processes of relaxation of the excited electronic and oscillatory states. Processes of relaxation in water are investigated in detail at excitation in the region up to 60 V. There are found numerous noncritical PMs, including CP. When not only group velocities, but also their derivatives in frequency are matched, the superbroadband conversion of radiation with spectral width $\sim 10^4$ cm⁻¹ is realized. Such situations are realized in some crystals and water media. The phenomenon of energy concentration is revealed, when at difference-frequency generation the intensive narrow-band radiation is generated when using broadband radiation. This phenomenon, apparently, play the important role in biophysics. The conception of noncritical PMs opens the new directions in spectroscopy of overtones and combined tones and allow to create the new types of frequency transformer.

0.4 Surface

Spectroscopy of surface plasmon polaritons in subwavelength structures

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In connection with development of nanoelectronics nowadays two different ways have been used for enhancement of light-matter interaction in solids: i) fabrication of co-called photonic crystals, in which the band gap for the propagation of light (analogous to the electronic band gap in single crystal semiconductors) is achieved by using some periodic nanostructures with different dielectric properties, and ii) utilizing of surfaces (localized) plasmon polaritons excitation on the flat metal-dielectric interface or in small metal particles. In the second branch of polaritonic optoelectronics (sometimes called plasmonics) recently have been fulfilled interesting experiments:

-on propagation of light through subwavelength holes in metal slabs, when the usual diffraction scale constraints are removed;

-on excitation and propagation of surface plasmon waves on the metallic tip of near-field microscope what leads to increasing of its resolving power;

-on strong interaction of light with one-, two-, and three- dimensional arrays of closely spaced interacting nanoparticles.

So, due to achievements of nanotechnology the investigation of the resonant excitation of surface plasmon waves (polaritons), propagation and damping of them in subwavelength structures became possible.

In the present work, the influence of the periodic or non-periodic (rough) interfaces in the thin dissipative films on transmittance through these films into substrate have been considered theoretically in the case of small deviation from flat surface in comparison to wavelength (nanoscale reliefs). Our theoretical description is based on the using of Maxwells vector equations with homogeneous permittivity in each media consisting of the structure. The surface deviation is considered as perturbation for the flat interface problem. In the nanoscale reliefs case we search analytical solution in first order of perturbation theory with using of the Greens tensor for Maxwell equations (the poles of this Greens tensor correspond to surfaces and waveguide modes).

The non-periodic (rough) interfaces have been assumed to be statistically isotropic and homogeneous and described by Gauss correlation function. The correlation between different surface modes is appeared in the system with closely spaced interfaces. This surface modes coupling give possibility to the investigation of the contacting media by the spectral and angle dependencies of the transmittance (reflectance). Also, the passing of electromagnetic energy through layered structures may be possible due to the conversion of the bulk waves to surface ones at one interface and the re-conversion of surface to bulk waves at another interface by the surface modes coupling.

The transmittance correction due to nanorelief interfaces have been calculated numerical for metallic films (Au, Ag, Al) with various thicknesses (10-50 nm) on GaAs substrate. The obtained spectral, angle and azimuthal dependencies are non-monotonic and demonstrate that the transmittance rising in the comparison to the flat interfaces is about 10.

Photoluminescence of polysilane nanocomposite confined into mesoporous silica

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Nanosized semiconducting polymers in confined area are widely used in various technological applications such as light emitting devices, transport layers for holes or sensors. We have successfully prepared such materials by introducing a semiconducting polymer poly(di-n-hexilsilane)-PDHS into two different mesoporous silica: MCM-41 and SBA-15. This allowed us to investigate the optical properties of polymers for controlled enlargement of pore diameter within 2.8 and 10 nm. Particular, the dependence of low-temperature photoluminescence and absorption spectra of PDHS/mesoporous silica composites as well as FTIR spectra was studied. Spectra obtained were compared with those of bulk films and polymer solutions. The location of the polymer inside the pore was systematically controlled due to the structure of silica framework monitoring by X-ray diffraction method.

For these composites an essential influence of space confinement on observed spectra was found. The shifts of absorption and luminescence bands, the arising of new visible luminescence band and the display of forbidden electronic transition proved to be critically dependent on the size of pores and on the area where polymer inside a pore interacts with the pore walls.

In case of composite PDHS/MCM-41, only one polymer chain can be embedded into the pore. Here the narrow band, which related to the $\sigma^* - \sigma$ transition, shifts to the blue side from its position in the film, a new broad band arises in visible region of photoluminescence and the higher excitation state is manifested in the one-photon absorption spectrum. Simultaneously, CH₃ and CH₂ vibrations in various regions of FTIR spectra shift essentially. It was shown that observed peculiarities of optical spectra are connected with the conformation change of polymer chain, embedded into the mesoporous silica MCM-41, due to the interaction of this chain with pore surface.

In case of composite PDHS/SBA-15, the quantity of polymer chains embedded into separate pore increases with the enhancing of pore size, the interaction between the polymer chains becomes dominative, above-mentioned peculiarities of optical spectra inherent in composite PDHS/ MCM-41 disappear. The luminescence spectrum becomes structural, where the amount and intensity of arising new bands depend on the pore size. It was shown that new bands correspond to the transitions from spatial-independent states between which the energy migration is absent. The nature of the observed structure in photoluminescence spectra is discussed. The fabrication of such functional composites with welldefined mesoporosity opens a route to controlled change of optical properties of nanosized polymer in course of the passing from the isolated polymer chain to the polymer film.

Interaction of adsorbed molecule vibrations with a surface: repulsion of energy levels and swap of spectral lines intensities

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A study on the IR-spectra of polyatomic adsorbed molecules revealed a manifestation of the effect known in quantum mechanics as a repulsion of closely positioned levels. It is an accepted fact that a dipole placed near a surface generates polarization charges which may be considered in terms of image dipoles. Treating each vibrational mode of the adsorbed molecule as a point dipole, one can obtain a frequency shift and a change in the integral intensity, both depending on the molecular orientation with respect to the surface normal and induced by the original-image interaction. The corresponding formulas for the squared frequencies λ_l and the integral intensities γ_l take the form:

$$\lambda_l = (1 - \chi_{vl} W_{ll}) \omega_l^2, \quad \gamma_l = \chi_{vl} \omega_l^2,$$

where χ_{vl} is the vibrational polarizibility of the *l*-th mode, ω_l is its frequency for a substrate-free state of the molecule. The parameter W_{ll} describes the interaction of the *l*-th mode with its own image dipole and depends on the molecular orientation with respect to the surface.

Taking into account indirect interactions of different modes via the substrate $(W_{ll'}, l \neq l')$ leads to the mixing of individual modes. For the case of two mutually perpendicularly polarized vibrational modes, the formulas for squared frequencies and integral intensities look as follows:

$$\nu_q = \frac{1}{2} [\lambda_1 + \lambda_2 + (-1)^q \sqrt{(\lambda_1 - \lambda_2)^2 + 4\gamma_1 \gamma_2 W_{12}^2}],$$

$$A_q \propto \frac{1}{2} (\gamma_1 + \gamma_2) + \frac{(-1)^q}{2} (\gamma_1 - \gamma_2) \frac{\lambda_1 - \lambda_2}{\sqrt{(\lambda_1 - \lambda_2)^2 + 4\gamma_1 \gamma_2 W_{12}^2}}, \quad q = 1, 2$$

Judging from the orientational dependences of the above values, it is clear that the image forces cause the repulsion thus preventing intersection of the levels obtained without regard for the substrate-mediated interaction between different modes. This effect is accompanied by a swap of integral intensities (a change in their ratio) for the relevant spectral lines which may occur if the orientation of the adsorbed molecule changes.

With electronic polarizabilities included, the relations presented become more complicated and describe the additional spectral line shifts and the corresponding integral intensity enhancements.
Synenergetics of friction and boundary lubrication

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The melting of ultrathin lubricant film by friction between atomically flat surfaces is represented as a result of action of spontaneously appearing shear stress that is caused by the external supercritical heating. The kinetics of this solidlike-liquidlike transition is described by Maxwell-type and Kelvin-Voigt equations for viscoelastic matter as well as by relaxation equation for temperature. It is shown that these equations coincide formally with the synergetic Lorenz system, where the stress acts as the order parameter, the conjugate field is reduced to the shear strain, and the temperature is the control parameter. Taking into account the deformational defect of the shear modulus I show that lubricant melting is realized according to mechanism of the first-order transition. The critical temperature of friction surfaces increases with growth of the characteristic value of shear viscosity and decreases with growth of the shear modulus value linearly. The Ginzburg-Landau scheme is constructed describing the spatial distributions of the shear stress and stain, and the temperature in the lubricant film. The additive noises of these quantities are introduced for building the phase diagrams, where fluctuations intensities and frictional surfaces temperature define the domains of sliding, stick-slip, and dry friction. It is shown that increase of the strain noise intensity causes the lubricant film melting even at low temperatures of the friction surfaces.

The melting of lubricant film is studied taking into account the correlated fluctuations of its temperature defined by Ornstein-Uhlenbeck process. The behaviour of the most probable shear stress, appearing in the lubricant, is studied and phase diagrams are calculated for the case of second-order transition — the melting of amorphous lubricant and for the first-order transition — the melting of crystalline lubricant. It is shown that for the first case the fluctuations of lubricant temperature result in appearance of stick-slip friction domain, dividing the regions of dry and sliding friction, inherent in the first-order transition. In the second case the three stick-slip friction domains arise characterized by transitions between dry, metastable, and stable sliding friction. The increase of correlation time of lubricant temperature fluctuations leads to increasing of frictional surfaces temperature needed for realization of sliding friction.

Interrelations of the vibration and electronic states of water and quartz

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The interaction between liquids and solid state surface plays an important role in nature and technical processes. The problems of the surface physics and chemistry can be conveniently studied by example of the water-quartz interaction. The Raman and IR absorption spectra methods have been used for studying of these processes on the level of the atoms and molecules interaction forces. The interrelations between vibration and electronic states of water and quartz were observed. It is the fundamental result, which exhibits in strong changes of not only water vibration bands but also amorphous quartz, and appearing new electronic bands at the interaction of water with developed surfaces of the silica gel, microporous glass or the sand. It should be noted the great decreasing of the valence band ν_{OH} intensity in Raman and IR spectra, the changes increase with the medium dispersion increasing. For example, at the silica gel dimensions ~ 0.2 mm the capillary water (CW) band intensity decreases in more than 8 times comparatively with the bulk water. In IR absorption the intensity of this band decreases in more than two orders. It shows a considerable decreasing of the electronic polarisability and dipole moments at the OH-bond vibrations what can be explained by the weakening of the water collective features. In the ν_{OH} band can be outlined the bands of the strongly and weakly bound water. At the same time the overtone bands $3\nu_{OH}$ and the complicated tone with the deformation mode $3\nu_{OH} + \nu_{\delta}$ intensity increases in more than two orders, what is caused by the strong anharmonicity increasing.

Unexpected were the changes in vibration bands of the quartz at its interaction with CW water: some fundamental quartz modes, overtones and compound tones can as increase in ~ 2 times so decrease, depending on the water quantity. At increasing these bands shift to the high frequency region and vice versa. The changes in vibration spectra caused by changes in the water and quartz electronic states. We first observed the appearing of the new electronic bands in IR absorption spectra in the region of compound tones $3\nu_{OH} + \nu_{\delta} + \nu_{HB}$ and the more high frequency region 500-1000 cm⁻¹. So, the electronic bands are induced by vibration modes. In Raman spectra induced electronic states exhibit as a wide range background with maxima in the range of 2000-2500 cm⁻¹. At interaction with water it decreases in ~ 3 times, what points out on the electronic subsystem ordering. At decreasing of the water quantity the background increases again. For α -quartz the background decreases in ~ 20 times and shifts in the ~ 500 cm⁻¹ region. Both in Raman and IR spectra the narrow electronic bands are observed which connected both with the mode 464 cm^{-1} disordering and the water librations modes.

Performed study opens up the new field in surface phenomena spectroscopy.

Abnormal variation of absorption band intensity of the capillary and adsorbed water in porous silicates behavior

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The abnormal behaviour of the adsorbed water (AW) on a quartz surface is well known. But the water states on a solid surface were not adequately investigated with vibration spectroscopy methods and observable phenomena were not clearly physical understood. We have found out an abnormal increase of the absorption band intensity of the high vibration modes $3\nu_{OH}$, $3\nu_{OH}+\nu_{\delta}$ and $2\nu_{OH} + \nu_{\delta}$ for the capillary and adsorbed water in porous silicates (silicagel, sand, aerosil). Here $3\nu_{OH}$ and $3\nu_{OH} + \nu_{\delta}$ are frequencies of valence and deformation water modes. Intensity of weak bands $3\nu_{OH}$, $3\nu_{OH} + \nu_{\delta}$ of capillary water (KW) increases more than on two times comparatively to an equivalent thickness of the volumetric water layer. But at that time decreases the intensity of absorption bands ν_{OH} and $\nu_{OH} + \nu_{\delta}$. Thus the strongest band ν_{OH} for KW in silicagel with the grain size 0.16-0.2 mm decreases in $10^2 - 10^3$ times and a band of combination tone $\nu_{OH} + \nu_{\delta}$ - more than in 10 times. It is essential, that absorbance for an overtone $2\nu_{OH}$ at 1.45 mk does not change. It allows to quantitative define the water content in porous medium used spectral methods by the comparison with spectral data for a volumetric water. The abnormal intensity increasing of the high vibration modes is caused by weakening of hydrogen bonds (HB) and gigantic anharmonicity of the connected water. The intensity variation of vibration bands for AW was smaller, but the increasing absorption for the high vibration modes indicates the weakening of HB. The variation of absorption bands was less at the full water filling of pores in disperse silicate medium.

Opposite changes of high-frequency and low-frequency absorption bands by a content growth of AW were clearly demonstrated by bands of positive and negative polarity in difference spectra. Intensity of bands of the high vibration modes increases with growth of water content, meanwhile were the bands of positive polarity in the difference spectra observed. However the ν band was in the fine-porous glass weakened and in a difference spectrum the strong band of negative polarity was observed. A form of vibration bands of AW and KW changes also essentially. The bands were expanded and displaced, have the complex form, which is especially shown for AW. By comparison of normalized band forms of the capillary, adsorbed and distilled were allocated the absorption bands for the strongly and poorly connected water. Analyse of vibration band series allowed to calculate the anharmonicity of vibration modes and to define the bonding energies for all water states. The nonmonotonic changes of a background broadband is characteristic for AW and KW spectra. This is caused by an influence of a multiple light scattering and also by the change of electronic states. The strong intensity changes of water absorption bands are caused by its interaction with SiO_2 surface. As a result of it essentially change the electronic states which define potential energy for vibration modes. Studying of water interaction with porous silicates has independent scientific and practical value, and also allows to studying the water nature.

Two-layers thin film metal sensors on the basis of the measured ellipsometric parameters for small molecular contaminations

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Optical sensors of small molecular contaminations, which work on the principle of excitation of surface polaritons by Kretchman's method, are constructed on the basis of thin films of gold. The last related to a small oxidizing ability of gold. But gold is at first precious metal and secondly, gold films have a weak adhesion to the dielectric substrate, which they are sprayed on. With the purpose of reduction of prices of sensors and increasing of adhesion we calculated two-layers sensors on the basis of thin metal films, where the film of ordinary metal was the first layer, and on top of it for prevention of oxidization of the first film gold film was pasted. Sensors works on the basis of measuring of ellipsometric parameters, namely shift of phases between p- and s-component of the reflected lights Δ and azimuth of the restored linear polarization Ψ . For sensor on the basis of a pure film of gold the deepest polariton minimum on the curve of the dependence of azimuth of the restored linear polarization Ψ from the angle of incidence φ is observed on the thickness of gold film equal 56 nm for length of light wave 620 nm. For calculated by us two-layers sensor Al-Au the deepest minimum is observed on this curve at the same angle of incidence $\sim 44^{0} - 45^{0}$ and at length of light wave 620 nm at the thickness of films φ equal 6 nm for Al and 25 nm for Au. The last let to economize the precious u. The second calculated sensor was two-layer sensor on the basis of the thin tapes of r and Au. It is known that transitional metals, to which Cr belongs too are characterized by high adhesion. The carried out calculations shown, that deep polariton minimum on a curve $\Psi(\varphi)$, which belongs to the pure film r, is remained after the pasting the thin protective film of Au. This minimum is in the range of the angle of incidence $58-60^{\circ}$ depending on the thickness of the film of gold. So for the thickness of the film of r 10 nm and the film of gold 10 nm this minimum corresponds to the angle of incidence 58° . Except for a polariton minimum a high sensitivity to the ellipsometry parameters at adsorption of thin molecular film on sensor for both sensors has also the polariton maximum on a curve $\Psi(\varphi)$ at the angle of incidence φ $\sim 42^{\circ}$.

Ellipsometric investigation of the polished layer on the surface of optical glass

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Knowledge of properties of damaged layer which arises by abrasive treatment is the actual task of the fields of knowledges, that are engaged in development of devices, in particular optical. At the same time, existent information on the given question is am-biquous. So, thickness of the polished layer (a few ten nm) on optical glasses are in-comparably less, then the size $(1 \ \mu m)$ of the polishing abrasive corns. The index of refraction of layer is got both greater, and less than index of refraction of the undam-aged material. A question about applicability of the homogeneous layer model to the polished layers remains opened. In this work ellipsometric investigation of the surface layer properties, which arises up at long time mechanical polishing of optical glass type K8 by the diamond abrasives, were realized. It is determined, that the model of homogeneous dielectric layer can be applied to the polished layer, his parameters are definite. The ellipsometric measurements were executed on the wave-length 632.8 nm by means the compensate laser ellipsometer and on a few lengths of waves of the mer-cury lamp radiation spectrum by means photometric ellipsometer. Ellipsometric angles were measured in the wide region of angles of incidence on both sides about the Brew-ster angle of given material. Determination of the refraction index and thickness of layer is executed in the model of the one-layer homogeneous system, which includes the substrate (glass) with the known index of refraction. For the calculations of pa-rameters of layer the Newton iterating method was applied. In this method two un-known parameters of layer calculated by two values of ellipsometric parameters, which measured on each angle of incidence. If the calculated values of parameters on all angles of incidence remain the same within the definite statistical dispersion, the model, which we chose for calculations, coincides with the real model of the damage region. At the fixed values of optical constants of medium, which forms the reflection system, the measured ellipsometric angles are the periodic functions of the layer thickness, and period depend on the refraction index, angle of incidence and length of light wave. In the previous publications the authors always determined the least possible value of thickness and did not paid attention to possibility of existence of other. Our multiangular measurments on a few lengths of waves allowed to determine more prob-able value of polished layer thickness. The applied iterating procedure gave the index of refraction and the least thickness. The other possible thicknesses we calculated by the known formula for period on all lengths of waves and on all angles of incidence. The true value of thickness is that value, what same (within the definite statistical dis-persion) for all angles of incidence and all lengths of waves. It was determined, that the refraction index of the polished layer always less than the substrate refraction index (1.51) on 0.02 0.04 and his value changes approximately on 0,02 with the in-crease of angle of incidence from 54 to 60°. It was determined by the model calculations, that observed angular dependencies of index of refraction it is possible to ex-plain by the instrumental error of setting of angle of incidence within the limits of 5 angular minutes. By introduction of the angle amendment angular dependence of index of refraction reach the value $1,500\pm0,001$, and the layer thickness is evened 212 ± 1 nm.

Optical properties of Fe-based amorphous alloys

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All the alloys of $Fe_{80}M_5B_15$ analyzed are doped with 5% additional transition metal: Ti(4s²), V(4s²), Cr (4s¹), Mn(4s²), Co(4s²) or Ni(4s²). In periodic table all of the elements are close to basic metal Fe (4s²). According to reflectance spectrum, the specimens are separated in two groups due to doped element, namely Cr, Ti, V and Mn, Co, Ni. Such division appears due to impurity band appearance and therefore an additional pseudo-gap emerges. This effect considerably affects the optical conductivity in the IR and therefore the reflectivity of such alloys.

A methodique of pre-calculating reflectance spectrum is proposed. In case there is no interaction and specimen is homogenious, the reflectance is defined as:

 $R_0 = s_1 R_1 + s_2 R_2 + s_3 R_3 + \dots$

where si is atomic concentration of element in a compound and Ri is it's reflectance. The real value of reflectance will be different due to interaction, therefore real value of $R = R_0 \delta$. The value δ contains information about interaction between elements and may be effectively analyzed. Obviously, the elements used in combination may be complex alloys, increasing accuracy and opening new possibilities for analyses. Such modelling allows obtaining very precise extrapolations to use in Kramers-Kronig transform and even predicting electronic parameters of a given amorphous alloy in a wide spectral region.

Ellipsometrical properties of thin metal films with different conductivity at surface polariton excitation by Kretchmans method

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Ellipsometric parameters (shift of phases Δ and azimuth of the restored linear polarization Ψ) under surface polaritons excitation by Kretchman's method for a number of thin films with high and low conductivity were theoretically calculated. Calculations were carried out by Airy's formulas. The length of light wave was 620 nm. Thickness of films varied from 0.2 nm to several tens nm. For every material a maximal thickness was a value, when ellipsometric parameters become similar to the massive specimens. In a role of high-conducting metals were l, Au, Ag, Cu. In a role of metals with less conductivity were got out Cr, Ti, Ni. The researches demonstrated, that angular dependences of ellipsometric parameters of all without the exception films of both groups of metals at small thickness about 0,2 nm were identical and practically coincided with angular dependences of ellipsometric parameters at the total internal reflection. But at larger thickness of films angular dependences of ellipsometric parameters for both groups of metals differ cardinally. Although for the metals of one group they are alike. So for the group of metals with high conductivity under increasing of the film's thickness a narrow polariton minimum at the curve of the dependence $tg\Psi$ from the angle of incidence φ appears on the angle of incidence $\varphi \sim 44-45^{\circ}$. The depth of the minimum depends on the thickness of the film, and it's location does not practically change with the variation of the thickness of the film. At the subsequent increasing of the thickness of the film this minimum disappears gradually, and another one minimum appears. The last one corresponds to the minimum at the main angle of incidence of the massive metal. It remains at large thickness of films, which correspond to a massive metal. Absolutely different situation is observed for films of transitional metals. At the increasing of the thickness of the film from 0.2 nm a wide polariton minimum on the curve of dependence of $tg\Psi(\varphi)$ appears by degrees. But when the thickness of the film is increasing this minimum is shifting towards greater angles of incidence, approaching to the main angle. Otherwise it gradually runs into the minimum at the main angle.

These disagreements in angular dependences of $tg\Psi$ for both groups of metals are explained on the basis of electromagnetic theory of light, namely by a different contribution to formation of this minimum of jumps of phases on both boundaries of the film and differences of phases due to passing by the light of the film for metals of a different conductivity.

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New types surface polaritons in diphosphides single crystals

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Present research paper deals with research of new type surface polaritons (SP) in diphosphides ZnSiP₂, ZnP₂ and CdP₂ single crystals which are characterized by anisotropy of phonon subsystem.

Surface polariton represents an electromagnetic wave which propagate along the surface of the crystal and has maximum of amplitude of it's electric field on the surface of the crystal. Electric field of the surface polariton damps by exponential law while moving away from the surface of crystal. Surface polaritons (SP) in ZnSiP₂ have not been researched yet. In ZnP₂, CdP₂ SP were investigated in [1], but these authors used data [2] to model dielectric permittivity of ZnP₂, CdP₂ single crystals and they did not take in account high-frequency dielectric constant and damping coefficients of oscillators. The main goal of this research is investigating SP of new types in the diphosphides using data about their phonon and plasmon subsystems, obtained from our experimental IR reflection data.

In present study we have obtained spectral ranges of existence of the SP of the first and second type in the phosphides. Spectral ranges of existence of the singular SP in ZnSiP₂ were obtained as well. We have calculated SP (of of the first and second type) dispersion curves in the ZnSiP₂, ZnP₂ and CdP₂ single crystals for these orientations of the system: $C \parallel x \ (K \perp c, xy \parallel C), C \parallel y \ (K \parallel C, xy \parallel C)$ and $C \parallel z \ (K \perp C, xy \perp C)$. Where z axis is perpendicular to the surface of the crystal (plane xy), C - optical axis of the crystal and K - wave vector of the SP. Anisotropy of the properties of phosphides crystals shows itself in the different quantity of the dispersion curves of the SP for each orientation. We have study an influence of concentration of free charge carriers dispersion curves of the singular SP in ZnSiP₂.

Surface polaritons in diphosphides were investigated by ATR method. ATR spectra have been obtained for such system: ATR element (KRS-5, n = 2, 37) - air gap ($d = 15 \ mkm$) - single crystal. Dispersion curves of the SP corresponds to the minima of the ATR spectra. We obtained three-dimensional theoretical ATR image - dependence of reflection of above-mentioned system on frequency and angle of incidence.

Thus, in present research paper the results of investigation of the SP of new types in ZnSiP₂, ZnP₂, CdP₂ single were presented. Spectral range of existence, dispersion curves of the SP, ATR spectra and surfaces were obtained in the phosphides using such method.

0.4 SURFACE

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Gold surface influence on vibration modes of glycine in zwitterionic and monoionic forms and guanine

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It is known that molecules adsorbed on island metal film or colloidal metal particles show 10-1000 times more intensive IR absorption than those without metals [1]-[4]. This effect was named SEIRA - surface enhanced infrared absorption [2].

However, along with undoubted SEIRA advantages (high sensitivity of the method, detection of monolayer film or less, and up to 10 pg [3], a possibility for determination of orientation of the molecular groups, enhancement of intensity of some bands to $10 \cdot 10^3$ times, etc.) the method has some disadvantages. One of them is metal surface influence on the SEIRA spectra in comparison with conventional FTIR spectra. Indeed, high enhancement is achieved in the case when the absorbed molecules tightly come to the metal surface [2]. As usually, these distances are about tens of angstroms or less. Naturally, the question arises, how gold influences the structure of molecules, what type of interaction exists between adsorbed molecules and gold. Here we study a gold surface influence upon vibration modes of glycine (Gly) in zwitterionic and monoionic form deposited on rough gold surfaces.

We studied SEIRA spectra of Gly on gold substrate at pH within range of 2-11 in comparison with those on CaF_2 substrate. It is well known that in aqueous solution at pH about 5-6 and in solid-state Gly shows zwitterionic form. The experiment showed drastic SEIRA spectra dependence on pH at gold substrate in comparison with CaF₂ substrate. At pH close to 2 the enhancement of COOH stretching vibration at 1745 cm⁻¹ on gold to 10 times, weakening of H-bonded both stretching NH^{3+} at 3167 cm⁻¹ and deformation NH^{3+} at 1604 cm⁻¹ and their narrowing have been observed. In this case a clear enhancement of the second tone modes (more than 10) in the 3300-1900 $\rm cm^{-1}$ were registered. We suppose that gold shows proton acceptor properties at low pH, influencing the reorganization of H-bonded groups. In the case of high pH close to 10-11 a low-frequency shift of H-bonded stretching NH_2 from 3392 to 3385 cm⁻¹ and high-frequency shift of NH_2 deformation vibration from 1619 to 1594 cm⁻¹ on gold as well as their widening have been observed. No enhancement of COOmolety has been observed. In this case a supposition about proton donor gold properties is arised. We supposed an orientation of Gly so manner that NH₂ is located close to gold surface at high pH and COOH is close to gold surface at low pH. The shift of different vibrations on gold are equaled to $8-25 \text{ cm}^{-1}$, so the interaction between molecular groups and gold is weak that is why it is very difficult for registration the gold effect. As usually, the intermolecular interactions are more than gold influence.

In the case of zwitterionic form of Gly on gold pH 6, the shift of vibrations is less than in monoionic forms. So, in this case the gold influence is essentially less. If it is so, the Gly molecule should be turned to the gold by both moieties. We practically do not observed an enhancement in the spectra of zwitterionic form of Gly deposited from the solution on the gold. In the case of vacuum deposition we can induce the certain orientation of Gly molecule at gold surface and reach of the enhancement (more then 10) of vibrations in SEIRA experiment.

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Investigation of the interphase epoxy composites

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The composite interphase can significantly affect the mechanical and thermal properties of the composite.

Fourier transform infrared spectroscopy has been used to investigate the interfacial chemical bonding at the interfaces of the coupling agent and epoxy matrix in glass fiber-reinforced composites.

As objects researched the glass fiber mark VMS-6, coupling agent the processing aids N 80 on based γ -aminopropyl- triethoxysilane and epoxy matrix polyglycidyl esters of p-aminobenzoic acids (consisting 9 % NH groups) without/ with curing agent 4,4¹-diaminodiphenylsulfone (DDS) selected.

The results indicate that chemical bonds are formed in the interfacial region the matrix and components of the coupling agent. It is found that from hydrogen bonds between the functional groups of molecules this epoxy matrix and corresponding donor-acceptor groups of processing aids N 80 (coupling agent).

The effect of the presence of an interphase of the composites was determined by mechanical analysis.

The amount of the interfacial bonding depends on the composition (epoxy resin without or with curing agent DDS).

In addition experimental results also clearly show the dependence of the crosslinking process on the concentration of the coupling agent treated surface.

The Pecularities of Rhodamine 6G degradation in presence of nanosized anatase films under changes of their specific weight and porosity

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Porous nanocrystalline titania anatase films of high optical quality with various structure, morphology and specific surface area have been synthesized by a dip-coating process using sol-gel solutions. The effects of the addition of complexing molecules polymer polyethylene glycol (PEG) with molecular masses of 300, 600 and 1000, and viscous solvent alfa-terpineol on the physical properties (thickness, crystallite size, porosity) and kinetics of photocatalytic degradation of Rhodamine 6 G (R6G) have been evaluated.

2 films have been characterized by the ellipsometry, UV-VIS and XRD spectroscopy , TEM and SEM. XRD measurements revealed crystalline modification of anatase. Films are porous, transparent (almost 100% of transparency). The nanocrystalline particles demonstrate bimodal diameter distribution as 4-5 nm and 15-20 nm. Film thickness is between 150 and 280 nm, porosity from 15 to 40% and specific weights $1,8*10_{-5} - 3,9*10_{-5} \text{ g/cm}^2$.

Photocatalytic activity of the films relative to R6G degradation depends on the size of the crystallites and is higher in the case of small particles of titania film, which corresponding to the more developed specific surface area and porosity. When crystallite size increased, Ssp decreased in parallel with the decrease of photocatalytic activity.

The thickness of the film is an important point in the photodegradation kinetics also and depends on the viscosity of the initial precursor solution. This dependence is complex, and the increase of the viscosity in time resulted in the crystalline growth, and as a result, small decrease of the photocatalytic activity, and kinetic of R6G photodegradation.

It is shown that the optical characteristics and photoactivity of the titania films critically depend on the synthesis conditions. The structure processes in the initial solution using for the precursor preparation define the photoactivity of the titania films.

Influence of solid subtrate on properties of liquid solutions in thin interlayers

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Joint action of asymptric surface field of lyophilic solid substrate and dispersion intermolecular forces on the organic liquids, which consists of anisometric molecules, leads to liquid crystalline orientational arragement and dimerization effect of ultrathin wall-adjacent layers [1, 2]

It seems to be interesting to estimate the relative contribution of these factors into observed effects. Logically we may assume that increasing of the solution consentration causes the enlargement of intermolecular interaction relative contribution and diminution of the effect of subtrate influence.

In order to test this hypothesis we carried out the spectral measurements of absorption spectra of ultrathin interlayers of nitrobenzene and anisole solutions in n-heptane and ethanol and studied the dependence of the band shape on the solution concentration.

It was found a brightly expressed manifestation of isobestic points in series of electronic spectra (normalized by the area) of the nitrobenzene main absorption band measured for various concentrations of nitrobenzene solution in ethanol. Two isobestic points ($\nu^1 = 37700 \text{ cm}^{-1}$ and $\nu^2 = 44300 \text{ cm}^{-1}$) define the existence of two-component structure of the studied object. According to [2, 3] we associate one of those components with monomers and another one with dimers. Further each of the normalized spectra was decomposed into two subspectra and we suppose tha the spectrum of the solution with the lowest concentration corresponds to the monomer spectrum and with the highest concentration (within ultrathin interlayer) to the dimer spectrum.

The procedure of spectral decomposition allowed us to estimate the concentrational dependence of relative dimer part. Analysis of experimental results in the framework of the theory of two-component orientationally ordered system allowed us to establish that main factor of associate formation process is the action of the solid substrate surface field.

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Photoluminescence spectra of porous silicon treated by nucleic acid solutions

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The behavior of porous silicon (PS) luminescent characteristics after application of water solutions of nucleic acids, such as thymus deoxyribonucleic acid (DNA), polyadenylic acid, polyuridine acid, adenosine monophosphate (AMP) and adenosine triphosphate (ATP), to the sample surface is studied. The measurements are carried out after drying the applied drop.

The main luminescence band at 1.7 eV is observed in photoluminescence (PL) spectra of PS samples obtained by electrochemical etching. At low temperatures (80 K), an infrared (IR) band with a peak near 1.4 eV manifests itself in some samples.

The PL intensity of PS samples increases after application of polynucleotide solutions. The PL rise is observed when storing the samples for 10 days and thereafter the PL is stabilized. The most efficient luminescence is found for the DNA coated sample. A small shift of the main PL band peak to short waves is observed in some cases. Application of the ATP and AMP solutions does not affect PL efficiency of the PS samples.

The variations of low-temperature PL spectrum after polynucleotide application consist in a rise of the visible band intensity with simultaneous degradation of the IR one.

It is concluded that the effect of nucleic acid solutions on the PS luminescent properties is not limited by the passivation of silicon structure. Formation of the additional recombination centers contributing to the PS main luminescence band takes place. The hydrate envelope of nucleic acids is suggested to play the main role in modification of the PS surface.

The theature of the photoluminescence of the annealing porous silicon carbide with titanium atoms introduced

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Here we consider the effect of rapid thermal annealing (RTA) on the properties of layers of por-SiC with titanium in its pores. Diffusion of titanium atoms into silicon carbide pores was performed in the course of RTA in the argon atmosphere. The starting material was 6H-polytype of silicon carbide (6H-SiC).

The PL spectra were measured in the $1.8 \div 3.2$ eV range. Radiation from a nitrogen laser with wavelength of 337 nm (photon energy of 3.67 eV) was used for PL excitation.

It was shown that the surface play as assentiat role in the forming of PL spectra. So, the PL spectra of the initial sample and that with unopened pores are practically the same. This is in agreement with absence of pores at the sample surfaces. These PL spectra involve two broad bands (with peaks at 2.4 and 2.75 eV) that are due to the impurity-defect centers and donor-acceptor pairs, respectively.

Appearance of pores on the sample surface is lead to appearance of a weak band (with a peak at 2.15 eV) in the PL spectrum, to increase of intensity of the PL band with a peak at 2.75 eV, and to disappearance of the band with a peak at 2.4 eV. The above changes in the PL spectrum may be related to the appearance of fine-disperse cubic phase of silicon carbide.

After titanium introduction in the por-SiC pores, the PL band with a peak at 2.15 eV disappears. The only broad band (with a peak at 2.8 eV) is observed in the PL spectrum. This band is characteristic of por-SiC obtained with anodization of 6H-SiC. Disappearance of the band with a peak at 2.15 eV correlates with disappearance of pores at the por-SiC+Ti structure surface.

Thermal annealing in the vacuum of the sample of por-SiC with introduced titanium results in narrowing of the PL band with a peak at 2.8 eV. This may serve as indication at decrease of surface defect concentration due to interaction between the titanium atoms and the intrinsic defects of silicon carbide in the course of thermal treatment.

RTA at temperatures of 700 and 900 in the dry oxygen flow does not affect considerably both the form and position of the PL band peak at 2.8 eV. When RTA temperature is increased up to 1000 C, the PL band becomes broader. This seems to be related to formation of structure defects at such temperature. It was shown that RTA leads to modification of the por-SiC structure with titanium atoms introduced into the pores. Thus one can modify purposely the properties of por-SiC + Ti structure by varying the RTA mode.

Optical properties and photocatalytic activity of mesoporous TiO_2 , TiO_2/Al_2O_3 and TiO_2/ZrO_2 films

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Strongly reductive/oxidative effect of titanium dioxide is based on the electron/hole pair formed upon photoexcitation and cause TiO_2 catalytic activity. A great deal of research has been conducted recently to optimise the performance of the TiO_2 photocatalysts, especially mesoporous films, with high surface area and enhanced optical properties.

Mixed oxide composite materials can often be more efficient photocatalysts than pure substances. This phenomenon arises through the generation of new active sites due to interactions between titania and dopant oxides, through improved mechanical strength and thermal stability and surface area of doped titania.

Optically transparent, crack-free mesoporous titania and zirconia or aluminadoped titania thin film photocatalysts were fabricated by sol-gel technique, using nonionic amphiphilic block copolimer Pluronic P123 as template. The structure and optical properties of these films were characterized using SEM, low-angle XRD and UV/Vis spectroscopy, hexane adsorption investigation. Band gap energy and the position of flatband potentials were estimated by photoelectrochemical measurements.

The Brunauer-Emmett-Teller (BET) surface area measurements show that samples with low dopant content (5-10uniform structure with rough surface, as was shown by AFM, adsorption-desorption investigation and SEM measurements.

Surface acidity of prepared films has been estimated from measurement of dimethylaminoasobenzole (DMAAB) adsorption from the gas phase onto unsupported powders prepared from the precursors. The assignment of the DMAAB absorption bands has been done by the analogy to the spectra for this substance in neutral and acidic solutions. Catalytic activity of mesoporous TiO_2 , TiO_2/Al_2O_3 (5-10(5-30 organic intermediates to inorganic. Enhancing of photocatalytic activity of doped films relatively to pure TiO_2 originates from an anodic shift of the valence band edge potential, correlates with crystalline size, and growth with increasing of surface acidity and specific surface area of the samples.

Phase diagram of generalized Ashkin-Teller model on the Bethe lattice

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A statistical model with the generalized Ashkin-Teller Hamiltonian,

$$H = \begin{pmatrix} \Sigma - J_1(\sigma_{mn}\sigma_{m+1,n} + s_{mn}s_{m+1,n} + \sigma_{mn}\sigma_{m,n+1} + s_{mn}s_{m,n+1}) - \\ J_2(\sigma_{mn}s_{m+1,n} + s_{mn}\sigma_{m+1,n} - \sigma_{mn}s_{m,n+1} - s_{mn}\sigma_{m,n+1}) - \\ J_4(\sigma_{mn}s_{m,n}\sigma_{m+1,n}s_{m+1,n} + \sigma_{mn}s_{m,n}\sigma_{m,n+1}s_{m,n+1}) \end{pmatrix}$$

is considered on the Bethe lattice with the coordination number 4. Alternatingsign bilinear interactions, so-called fluctuation interactions, are included in (1), in contrast to the normal Ashkin-Teller model. Interactions of this kind are typical of adsorbate lattice systems characterized by dipole-like intermolecular forces and a strong azimuthal angular dependence of the C4-symmetrical adsorption potential [1]. They can result in a new type of orientational ordering, viz., a preferential direction of long molecular axes in the absence of spontaneous polarization [2].

Here we report an analytical solution of the problem which is an exact one for the Bethe lattice with the coordination number 4 and also gives a qualitatively correct description of phase transitions on a square lattice. The exact solutions found in the framework of this model (i) determine the second-order phase transitions between paraphase I with $\langle \sigma \rangle = \langle s \rangle = \langle \sigma s \rangle = 0$ and two ordered phases, phase II with $\langle \sigma \rangle = \langle s \rangle \neq 0$, $\langle \sigma s \rangle \neq 0$ and phase III with $\langle \sigma s \rangle \neq 0$ at $\langle \sigma \rangle = \langle s \rangle = 0$; (ii) specify the conditions for the conversion of second-order to first-order transitions. With regard to these solutions, the phase diagrams are constructed for K1, K2, K4, where Ki = J_i/k_BT , J_1 is the interaction constant between $\sigma - \sigma$ and s-s spin subsystems, J_2 is the constant of bilinear fluctuation $\sigma - s$ interactions, J_4 is the constant of biquadratic $\sigma - s$ interactions, k_B is the Boltzmann constant, and T is the absolute temperature. First-order transitions are detected numerically by comparing the free energies of the phases concerned. It is shown that phase II is gradually replaced by phases I and III with rising J_2 and vanishes at all if $J_2 = J_1$.

For the 2x1 monolayer of CO molecules adsorbed on the NaCl(100) surface, it is found that $J_2 = 0.6J_1$, $J4 = 0.2J_1$, and $J_1 = 0.8 \ meV$ [1, 2]. Monte Carlo simulation with these parameters provides the phase transition temperature within the experimentally observed temperature range 17.5 - 21.5K [3]. Though phase III is not characteristic of the CO/NaCl system, it can be detected for nonpolar adsorbates provided their dispersion interactions are strong in comparison with quadrupole-quadrupole interactions [1].

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Asymmetric potentials of hindered rotation due to image forces: application to Brownian motors

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Nonequilibrium fluctuations leading to the unidirectional motion of Brownian particles in asymmetric media even in the absence of an external field are of methodological and applied interest in connection with the study and design of so-called Brownian motors. These include "nanomotors" converting various types of energy into mechanical energy, systems segregating nanoparticles, molecular pumps driven by the energy of adenosine triphosphate splitting, etc [1, 2]. A necessary condition for generation of the unidirectional motion is the presence of a periodic and asymmetric potential.

For surface atomic groups with a rotational (or hindered rotational) degrees of freedom [3, 4], such a potential can arise from the inclination of the rotational axes relative to the surface plane. This may occur, for instance, on irregular (amorphous) substrates. An inclined rotating dipole interacts via image forces with a surface, which creates asymmetry of the initial symmetric potential of hindered rotation. The types of the arising asymmetry are analyzed. For a twowell potential (such potentials can be realized by OH groups on Al₂O₃), dipoledipole terms of the image forces lead only to a shift and an amplitude change, but do not give rise to asymmetry. Only when dipole-quadrupole components diminishing with group-surface distance as r^{-4} are taken into consideration, the asymmetry appears. For a three-well potential (OH groups on the SiO₂ surface), dipole-dipole interactions generate asymmetric potentials. In this case the asymmetric contribution to the potential depends on group-surface distance as r^{-3} .

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Destruction of a surface of solid substance under action of laser radiation

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Theoretical interpretation of destructive effect of a powerful pulse of radiation on a substance surface is offered in research. A purpose of this work is the theoretical study of features in formation of conditions of a dynamics of surface destruction of a material and peculiarity of space-temporal dynamics of a gas phase. This phase arises due to local phase transitions at a quick heating of the substance surface by a laser pulse and it reduces to formation (to burnup) of a corrosion crater.

The system of the differential equations which describes dynamics of development of a corrosion crater on a substance surface and burning of a plasma plume is formulated. The general solution for dynamics of a plasma-gaseous phase is obtained and its behavior is analyzed for different levels of interaction of radiation with gas. Influence of frequency on such interaction was taken into account. It was shown that an increase of region of gas- radiation interaction has a great influence on dynamics of a gas phase. It happens due to the enlargement of length of a plasma plume. Space-temporal dynamics of crater formation on an irradiated surface is analyzed

Temperature dynamics of a material surface with the arbitrary nonlinearity of radiation absorption

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The problem of action of a powerful pulse of radiation on a surface of a material is examined. It is essential that a stream of energy in a pulse is below its threshold value for destruction of a material surface. As a result of solution of the problem where the inhomogeneity is given implicitly by the Lambert equation the strict analytical generalized solution as a spatio-temporal behavior of temperature was obtained.

On the basis of this solution it is possible to analyze dynamics of temperature of a surface for any concrete nonlinear dependence of an absorption constant on value of a radiation flow. This enables us to analyze the influence of nonlinearity of absorption of any kind on value of a destruction threshold of a material. In particular, it is shown that account of a nonlinearity of a volume absorption based on the two-level model of absorption of radiation by a solid always gives increase in a threshold of a material destruction.

Efficiencies of Brownian motors

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Great recent interest in the mechanisms of high-efficiency energy conversion in living objects has given rise to a diversity of models, the favorite being the flashing potential model of a Brownian motor [1, 2]. This approach implies that a Brownian particle moves unidirectionally in an asymmetric periodic potential which is assumed to fluctuate by means of random (or regular) shifts by half a period L with the frequency γ [3, 4]. Fluctuations of this kind can be caused by an external cyclic process generating the potential profile, such as an external signal or a far-from-equilibrium chemical reaction resulting in a conformational change of the particle or of the track [5]. It is just the fluctuations that are responsible for a high efficiency of the motor, provided certain additional conditions are imposed on the potential shape. These are, first, the presence of a barrier V blocking the backward motion of a Brownian particle on each period of the potential profile [3, 4] and, second, the same potential shape, with a certain energy shift, on both half-periods (this is a prerequisite for minimized energy losses arising from the potential fluctuations) [4]. This mechanism of high efficiency is realized in the near-equilibrium region. Another mechanism acting far from equilibrium is typical of strongly asymmetric potentials which are shaped identically on both half-periods with a large energetic shift W [6]. The two mechanisms exhibit radically different limiting behavior of the maximum possible efficiency: $1 - \exp(-V/2kT)$ for the former and $1 - kT \ln(2W/kT)/W$ for the latter. The flux and the efficiency for a Brownian motor with a piecewiselinear potential are calculated using the transfer matrix method [6]; an exact analytical solution can thus be obtained for an extremely asymmetric sawtooth potential, the simplest example of the second high-efficiency mechanism. As demonstrated, the mechanisms considered are also characteristic of a two-well periodic potential treated in terms of the kinetic approach.

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Directional Transport of Brownian Particles in Asymmetric Sawtooth Potentials

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In recent years the problem of unidirectional motion of Brownian particles caused by induced non-equilibrium fluctuations in asymmetric media has attracted considerable interest due to multiple biophysical applications. By now a number of models have been proposed for describing the ordered motion of particles in asymmetric potentials fluctuating due to external factors [1, 2].

A simple switching between two states in which a potential is present (the "on" state) or absent (the "off" state) is implemented when a Brownian particle changes its charge as a result of repeated chemical reactions [1]. An asymmetric stationary potential can be induced by a chain of dipoles with collinear dipole moment orientations along the chain axis. The electric potential of this chain at a certain distance from its axis can be approximated with a high accuracy by a sawtooth potential [3]. Switching on and switching off such a potential with certain frequency gives rise to unidirectional motion of Brownian particles. Using the adiabatic approximation of this model, we have simulated, in explicit analytical form, a flow defining an average velocity of unidirectional motion and efficiency depending on model parameters. Models of this kind referred to as on-off flashing ratchets are characterized by a low efficiency owing to a purely diffusional stage of motion in the "off" state. Molecular motors of an alternative model, so called rocking ratchets, in which the unidirectional motion of Brownian particles is caused by an external fluctuating force applied in the field of stationary asymmetric sawtooth potential are also characterized by a low efficiency, though higher than that of on-off flashing ratchets.

We have proposed a much more efficient flashing ratchet model in which an asymmetric sawtooth potential fluctuates between two identical states spatially separated by half a period [4]. The efficiency of this model tends to unity provided that an extremely asymmetric high-amplitude potential is involved [4, 5].

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Stochastic theory of transitions between the modes of ultrathin lubricant film melting

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Using the Lorenz model the melting of ultrathin lubricant film by friction between atomically flat surfaces is studied. The additive noises of the elastic shear stress and strain, and the temperature in the film are introduced for building the phase diagram where the noise intensity of this temperature and temperature of friction surfaces define the domains of sliding, dry, and stickslip friction. The conditions are found at which the last regime corresponds to the intermittency mode inherent in self-organized criticality phenomenon. The self-similar distribution of the stress is represented allowing for their nonlinear relaxation and fractional feedbacks in the Lorenz system and it is provided with temperature fluctuations. Such fractional scheme is used for building the phase diagram determining various modes of friction. The study of corresponding fractional Fokker–Planck equation shows that stick-slip friction corresponds to the subdiffusion process.

The self-similar behaviour of lubricant film is studied taking into account correlation fluctuations of its temperature defined by Ornstein-Uhlenbeck process. The behaviour of the most probable shear stress, appearing in the lubricant, is considered and phase diagrams are calculated for the case of second-order transition - the melting of amorphous lubricant and for the first-order transition the melting of crystalline lubricant. It is shown that the fluctuations of lubricant temperature result in disappearance of sliding friction region at presence of dry and stick-slip friction domains in both above cases. In the second case the stick-slip motion arises characterized by three stationary values of shear stresses at which dry, metastable, and stable sliding friction are realized. The increase of correlation time of lubricant temperature fluctuations leads to increasing of frictional surfaces temperature needed for realization of stick-slip friction.

0.5 Liquid crystals

Optical properties of viologens introduced into ionic liquid crystal and polymeric matrixes

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With fast development of optical information technologies, it is important to search new functional materials, which could be used in different optical devices. In our work we present the results of investigation of new type of liquid crystals, namely lyotropic ionic metal-alkanoate LCs, and polymer material, namely polyvinyl spirit. We introduce into these matrixes electrochromic admixtures viologens with the aim to colour them. It is known, that in water solutions viologens form strongly coloured cation-radicals under applying of the electric field or under ultra-violet irradiation. After the introduction of viologens into different matrixes their property of colouring remains the same. Moreover, the lifetime of cation-radicals in LC and polymer is much more longer.

We study electron absorption spectra of obtained LC and polymeric materials depending on the viologen type and on the voltage applied. Also we have provided the analysis of the optical density value on the concentration of the admixture.

We investigate the structure of liquid crystal materials using the method of small-angle X-ray scattering. Taking into account these data we have evaluated some main values characterizing liquid crystal ordering. Weve discovered that low concentrations of viologen admixture do not influence LC structure and organically built into it.

We have obtained the recording of the holographic grating for samples of lyotropic liquid crystals doped by viologens. We measured the diffraction efficiency of the first diffracted order depending on the grating period and on the energy and proposed the possible mechanism responsible for holographic recording.

Liquid Crystal Interaction with Hydrated Pore Surface of MCM 41 Molecular Sieves: FTIR and DSC Studies

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The beaviour of liquid crystals in porous matrices is of great interest in current research of novel nanostructured materials. Mesoscopically structured porous molecular sieves MCM-41 have a highly uniform geometry, very large inner surface and small pore diameter of about 4 nm, and are often used as an ideal host for different organic species. The properties of these materials depend on the chemistry of the surface active sites being largely determined by the structure of hydrate and hydroxyl coverage of the pore surface. In this work we report on the results of temperature variable FTIR and calorimetric DSC studies (in the temperature range from -10 to 250°C) of adsorption of 4-n-pentyl-4'-cyanobiphenyl (5CB) liquid crystal on MCM-41 molecular sieves. MCM-41 molecular sieves treated with transition metal cations were used. FTIR spectroscopy results demonstrate that implantation of bivalent metal cations (Me^{2+} , Me = Cu, Co, Fe, Ni, Mn) onto the surface of MCM-41 affects the nature of adsoprtion sites on the pore surface changing the relative proportion of Lewis and Bronsted active centers. The DSC studies demonstrated that LC in such narrow pores do not exhibit any phase transitions, and only one broad peak originating from thermal desorption of physisorbed water is observed. Incorporation of metal cations onto the pore surface changes the shape and position of the observed specific heat peak depending on the Me2+ cation. After filling of MCM-41 with 5CB, the specific heat curves exhibit different behavior depending on the type of metal cation. In the case of CuMCM-41, the dehydration process clearly demonstrates step-wise behavior which is likely related to the existence of different surface active sites. Correlatation between DSC results and temperature variation of the intensity of OH stretching bands of physisorbed water in FTIR spectra is explained by interplay between the molecular interactions in the near surface layers in the studied systems.

Spectral studies of the nematic liquid crystal layers in external electric fields

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The channeled spectra of some nematic liquid crystals at room temperature were recorded in external electrostatic as well as alternate electric fields with different intensities and frequencies.

The birefringence dispersion in the visible range has been estimated from the channelled spectra. The influence of the field intensity and of the frequency in the case of alternate electric fields has been revealed by these studies.

An increase of the degree of order with the electrostatic field intensity followed by a saturation plateau in the case of MBBA and its mixtures has been revealed.

The increase of frequency of the external alternate electric field decreases the order degree of PPAMAECOBA in TCM lyotropic liquid crystal, showing that the dipolar collective interactions of the side chains of polymer are responsible for the liquid crystal characteristic of this mixture.

Optical properties of ionic thermotropic liquid crystal glasses

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With fast development of optical information technologies, contemporary investigations are aimed at searching of new low-cost functional materials possessing the properties of holographic recording. One of such materials are ionic liquid crystals (ILC). It is new insufficiently explored group of liquid crystals, which have number of advantages in contrast to molecular liquid crystals. Most uni-and divalent metal alkanoates form ionic liquid crystals (smectic A) under their melting [1]. These compounds are perspective in the developing systems of information recording and the laser techniques due to own ionic conductivity, high solvent capability, good thermal stability and inclination to vitrification [2].

In this work electronic absorption spectra of Co^{2+} in the isotropic melt, ionic smectic mesophase and crystal phase of the systems based on cobalt decanoate were studied as a function of temperature. From absorption spectra of Co^{2+} in decanoate matrix obtained data about region of wavelength and intensity of absorption depending on temperature and molecules ordering. On the base of small angle X-ray scattering was determined structure of cobalt decanoate mesophase. Presence of absorption on the wavelength of laser beaming and exceptional stability of smectic glasses of these systems force us to check the possibility of holographic recording for such samples. We obtain dynamic hologram recording in samples of ionic smectic glasses of cobalt decanoate. The diffraction efficiency of the first diffracted order reaches up to 6 % at room temperature.

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Threshold periodic structure of director in flexoelectric nematic cell

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The influence of finite planar director anchoring with the substrates of planeparallel flexoelectric nematic cell on the threshold and the spatial period of the director structure, which arises at the director reorientation in the external electric field, is theoretically investigated. Before this problem was considered in the case of homeotropic director anchoring [1]. The arising of periodic director structure in planar flexoelectric nematic cell at the threshold director reorientation was only studied in the case of infinitely rigid director anchoring [2].

The analytical expressions for director reorientation threshold and spatial period of director structure are obtained in the case of strong (but finite) planar director anchoring. In other cases the numerical calculations were fulfilled. The most important qualitative results are as follows, i) finiteness of director anchoring energy changes not only the values of director instability threshold and director structure period but the character of their dependence on the flexoelectric parameters as well; ii) in the case of finite azimuth director anchoring the director spatial period non-monotonously depends on the director anchoring value; iii) the region of existence of periodic director structure, which is determined by the flexoelectric parameters values, now essentially depends on the director anchoring value, at that it increases with decreasing of azimuth director anchoring and decreases with decreasing of polar director anchoring.

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Influence of flexoelectricity on correlations of thermal director fluctuations in filled liquid crystals

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Spatial correlation function of thermal director fluctuations in flexoelectric nematic liquid crystals filled with small macroscopic particles is calculated in long field approximation. We show that static flexoelectric polarization, which can arise in some liquid crystals due to the director field static deformations around the particles, gives the significant contribution into the screening of spatial correlation of the thermal director fluctuations. The value of contribution is compared with that caused by the director interaction with the particles surface [1] and significantly exceeds the contribution from the thermal flexoelectric polarization [2]. It means that decreasing of Rayleigh light scattering on the thermal director fluctuations observed in experiments in filled liquid crystals has to be stronger in the flexoelectric ones.

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Interface interactions in liquid crystal organoclay nanocomposites

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Combined systems, consisting of nematic liquid crystal (NLC) and nanostructured inorganic substance, are widely used in the modern technologies, such as the development of scattering displays, windows with controlled transparency, devices of information recording and storage etc. Due to the interactions between organic and inorganic components, these systems can possess some unusual for their individual components properties (for instance, memory effect, high stability with time, the absence of flocculation during the isotropic liquid-NLC transition etc.). The absence of understanding of interface interactions mechanisms and methods of their efficient regulation is a main problem in the field of organic - inorganic nanocomposites.

The present work is devoted to the investigations of structure and phase transitions of composites, based on 4-pentyl-4-cyanobiphenyl NLC and organophilic montmorillonites (MMT), which are mainly managed by intermolecular interactions on interfaces of these layered materials. In order to make particles of initial Na-MMT organophilic, dioctadecyldimethylammonium and alkylbenzyldimethylammonium chlorides were used as modifiers. The experimental methods, used in this work, are FTIR-spectroscopy, X-ray diffraction and differential scaninnig calorimetry (DSC). The composites were obtained by accurate mixing of components with the subsequent ultrasound treatment at the presence of small amount of acetone. The mass fraction of the solid compound in the composite has been varied in the range of 2 - 8 %.

Investigations of changes in spectral parameters of absorption bands, corresponding to vibrations of LC molecule bonds (C–C at $\nu = 1606 \ cm^{-1}$, and C≡N at $\nu = 2226 \ cm^{-1}$), Si-O-Si bonds vibrations of the clay mineral (at $\nu = 465 \ cm^{-1}$) etc. allowed to analyze the peculiarities of interface interactions in mentioned systems. It should be notes, that the majority of the interactions are of Van-der-Vaals type. By DSC method is shown the decrease of the temperature point of NLCisotropic liquid phase transition at increase MMT concentration, compared with that one for the pure LC, is observed to have a non-linear behaviour, which is due to their different structure formations. By means of X-ray diffraction experiments it is demonstrated the presence of two reflexes corresponding to $d_{001}\approx 2$ and $\approx 4~nm.$ All experimental results are discussion.

The effects of chemical nature of the modifier on the structure and properties of composites is shown. It has been established, that the maximum structuring is observed in these composites at the concentrations of 46% and accompanied with the strong increase of viscosity and extreme dependencies of phase transition temperatures. The model for the description of the structure alignment in the studied composites has been proposed.

About Implementation of the Electrically Tunable Distributed Feedback Laser on Dyed Nematic Liquid Crystal

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The distributed feedback(DFB) lasers on the basis of natural periodical structures of cholesteric liquid crystals (CLC) are known comparatively for a long time [1]. The urgency of their research is recently conditioned by application prospects of such lasers in information displays, as screens of heightened brightness. But problem of operating and controlled frequency tuning in such laser has not solved yet because a such inertial method as temperature change of a CLC pitch is not favorable [1]. It is known also that imposing of electrical field along of CLC axis of spiral destroys its macroscopic texture so a such frequency tuning is applicable only for a field oriented perpendicularly to CLC axes of a spiral, i.e. for waveguide lasers.

We consider and study an electrical frequency tuning a bulk DFB laser with dynamic phase-amplitude grating recorded in the dyed nematic liquid crystal (NLC) simultaneously with 2 pumping beams. The calculated and set angle of get-together of pumping beams and its wavelength determine the spatial frequency of the grating and middle laser oscillation frequency at a given bulk index refraction of NLC. Under imposing of an electrical field there is a turn of NLC molecules in initial planar texture and change of middle refractive index in NLC and variation of laser grating period.

The experimental laser cell is made, which one allows to realize considered idea for the single-beam interference scheme at pumping and to provide a unidirectional output of laser radiation of such DFB laser. The numerical calculations demonstrates a wavelength tuning capability approximately on 50 nm within the limits of a amplification band of the laser dye at given angle of pumping/interference. Are studied the spectral characteristics (absorption, a fluorescence and its polarization, quantum yield) of some dyes in NLC and tested for lasing by second harmonic Nd-YAG laser.

The made experiments showed the expected results.

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Features of previtamin D cis-trans isomerization in the nematic LC matrices

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Photomodulation of orientations of liquid crystals (LCs) induced by photochemical reactions of doped photochromic molecules is of great current interest. It has been found that photochemical phase transitions depend significantly on the molecular shape of each isomer of photochromic molecules. Here we discuss the opposite case the effect of LC microenvironment on the photoisomerization of 7-dehydrocholesterol (provitamin D3) that underlies the complex network of vitamin D synthesis.

UV irradiation of provitamin D within its absorption band (240-315 nm) yields previtamin D by hexadiene ring-opening and further it undergoes a number of side photoconversions among which cis-trans isomerization into tachysterol is the most efficient one ($\varphi_{cis-trans} = 0.48$). Studies of provitamin D photoisomerization in heterogeneous media established pronounced effect of microenvironment on the previtamin D cis-trans isomerization [1] that is coordinated with the principle of ground state conformation control and reflect the reaction medium effect on the conformational equilibrium of previtamin D molecule. However, recently a new reaction mechanism (so-called "Hula-Twist") has been postulated which becomes dominant under conformational mobility constraints [2], and the first experimental evidence of the Hula-Twist of previtamin D cis-trans isomerization was found in a rigid glass at low temperature.

For the first time we studied provitamin D3 photoisomerization in nematic LC matrices (ZLI-1695, ZhK-805) by UV absorption spectroscopy. Dissolution of chiral 7-DHC molecules in the nematic LCs induces cholesteric phase, and dramatic effect of the cholesteric pitch value on the spectral kinetics has been revealed. Significant increase in trans-isomer accumulation was observed as the cholesteric pitch was reduced from 2200 to 25 μ m. Noticeable effects of the LC viscosity and orientation were observed as well.

As is known, under irradiation at 254nm in ethanol the trans-isomer is accumulated in high concentration (up to 70%) that is accompanied by the absorbance increase. For the LC matrix dramatic increase in the absorbance has been revealed that testified significant growth of the cis-trans isomerization efficiency.

Similar behavior of spectral kinetic was observed in the LC cells of different thickness, different LC orientation and dopant concentration. It appeared that in all cases the more is previtamin D molecule constrained the higher is its cis-trans isomerization efficiency. This effect is hardly understandable within the limits of classical mechanism of cis-trans isomerization which is highly sensitive to a medium viscosity. We believe the result obtained support a "Hula-Twist" mechanism in the nematic LCs where torsional relaxation is prohibited and the layer LC structure is more favorable for sliding motion of the two halves of the molecule between the layers.

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Luminescence and IR spectral peculiarities of 5CB liquid crystal – benzophenone molecular complexes

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Nowadays much attention of scientists are concentrated on the composite materials, based on the liquid crystals and some organic impurities, for instance, organic dyes. The main idea of such investigations is to find an optimal combination of components for further practical use of these complex systems in the fields of information display and processing technologies. There are many works, dealing with the study of both orienting action of a liquid crystal on the doping organic molecules and induced anisotropy. Nevertheless, only few of them concern possible mechanisms of intermolecular interactions between components in mentioned composites. In organic solvents various processes of intermolecular interactions may occur, such as solvation, aggregation of impurity molecules, formation of donor –acceptor and/or charge – transfer (exciplex) complexes by impurity and solvent molecules.

Biphenyl derivatives are interesting compounds from both theoretical and practical points of view. Some biphenyl compounds, in particular, 4–pentyl – 4'– cyanobiphenyl (5CB) display properties that are characteristics of liquid crystals and therefore, are important for technical applications in electro-optical devices. Recently, they also found application for surface studies in porous materials and molecular sieves.

In this work we investigated photoluminescence spectra of benzophenone (BP) in the liquid- and solid-crystalline 5CB matrices in a wide temperature range (from 4.2 K to the room one). These molecules do not form strong bonds between each other, therefore, no new chemical substances appear in such solutions. This fact has been also proved by means of IR-spectroscopy method.

Fluorescence spectroscopy is a powerful tool for investigating microscopic environments, because of the rich information content of this method. Our experimental data showed significant changes in the photoluminescence spectra of 5CB liquid crystal – BP system and the appearance of new spectral bands, in the comparison with spectral features of both neat components, which are well known from our previous studies and literature sources.

5CB molecule contains a cyanic group, which is a strong acceptor of electrons. This fact enables one to assume that even in the ground state 5CB and BP molecules form $D^{d+} - A^{d-}$ complexes. BP molecules serve as electron donors, while cyanic groups are electron acceptors. Spectral parameters and temperature behaviour of photoluminescence spectra of 5CB liquid crystal – BP molecular complexes have been carefully analyzed and discussed.

The modelling of 4-n-alkyl-4-cyanobiphenils,structure and phase transitions

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The peculiarities of the structure and of the intermolecular interaction in homological series of 4-n-alkyl-4-cyanobiphenils (nCB) have been investigated by IR spectroscopy methods. IR absorption spectra of nCB samples (n=2, 4, 5, 8, 9) were measured in 400-4000 cm⁻¹ frequency range, in 26100 temperature interval for solid crystal (SC), liquid crystal (LC) and isotropic liquid (IL) states. Theoretical modelling of IR spectra of the molecules with taking into consideration of the conformational mobility using LEV-100 program package was performed. On the basis of modelling results the analysis of measured spectra with consideration of the intermolecular interaction was carried out. The interpretation of them is given. A distinguish in spectra transformations is determined between of lowest and highest homologues at the change of temperature. The separation of homologues into lowest and highest according with spectral criterion correlate with ability to possess with anisotropic melt. In IL state the samples are represent a mixture of conformers. In nematic LC and IL the identical associates are dominate.

Breaking of associates is not exerting to the melting and blooming temperatures. Odd-even alteration of melting and blooming temperatures is not associating with the change of type of intermolecular interaction (IMI) with participation of cyano group. With increasing of n a new strips and its components appeared including strips, which are belong to different conformers. These conformers are differently packed in cells of SC and in layers of LC because of difference in IMI between lowest and highest homologues. At the temperature change and phase transitions the conformation of molecule is changing and owing to this the spectrum of compound is changing too. Spectrum changes are lag from phase transition and appear when the temperature exceeds of 2-7 degrees the critical one. This fact is in agreement with experimental data obtained by positron annihilation spectroscopy method for the phase transformations of nCB homologues.

Conformational Transformations of 4-cyano-4'-n-alkyloxybiphenyls as Liquid Crystals

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IR spectral data were received on some 4-cyano-4'-n-alkyloxy biphenyls (nalkyloxy groups = $C_3H_7O_7$, $C_4H_9O_7$, $C_5H_11O_7$, $C_7H_15O_7$, $C_8H_17O_7$) as liquid crystals. Conformational transformations play the principal role on the transition from isotropic liquid to mesophase.

In course of study one can see the correlation on changing of vibrational bands as alkyloxy- so and biphenyl- and also $C \equiv N$ groups.

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Dependence of diffraction efficiency of H-PDLC film on shape of liquid crystal droplets

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In many applications however it is desirable to have a post-exposure control over the diffraction efficiency to obtain, for example, electro-optically adjustable holographic multiplexers, data storage units and dynamically variable focal length lenses. In this connection there has recently been growing interest devoted to holographic polymer dispersed liquid crystal (H-PDLC) materials, a dispersion of liquid crystal (LC) submicrometer sized droplets in a polymer. The refractive index modulation as well as the diffraction efficiency of such H-PDLC materials strongly depends on LC director orientation within droplet. Early we reported on studying of diffraction properties of such films composed of spherical droplets [1]

In the present paper we constructed model of HPDLC cell for studying the dielectric properties of HPDLC containing bipolar liquid crystal droplets. Shape of droplets can vary from sphere to ellipsoid. The LC director profile in each of the LC droplet is controlled by the balance of elastic energy associated with director inhomogeneity within droplet, anchoring energy at the droplet surface, droplet size and shape, and magnitude of the externally applied electric field.

To find director profile within single LC droplet upon applied voltage we used Monte Carlo simulations, Lebwohl-Lasher (LL) lattice model and strong tangential anchoring conditions (bipolar droplets). We simulated system of $3 \cdot 10^5$ nematic spins starting from a random initial configuration. The standard Metropolis scheme was then employed to update nematic spins orientations, maintaining a rejection ratio close to 0.5. The final result appeared not depending on the choice of the starting configuration. To describe the diffraction properties of anisotropic holographic gratings under the action of externally applied voltage we used coupled-wave theory [2].

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0.6 Nanoobjects

Single J-aggregate spectroscopy

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Molecular aggregation into well-defined supramolecular structures, like Jaggregates, plays a significant role in cell biology and in molecular electronics, and thus has attracted a great deal of attention in both fundamental and applied research. Since aggregate supramolecular structure strongly impacts its spectroscopic properties such as the spectral line shape and peak energy, interest in direct observation or visualization of J-aggregates has greatly increased.

Confocal luminescence microscopy has been used to excite and collect luminescence from single amphi-PIC J-aggregate. Two types of J-aggregates have been revealed in the luminescence image: bead-like J-aggregates, which diameter is less than 1 mkm and rod-like ones, which length is about 3 mkm and diameter is less than 1 m. It has been found that single rod-like and bead-like J-aggregates exhibit different luminescence bands with different decay parameters. At the off-resonance blue tail excitation, J-aggregate exciton luminescence disappeared within a certain time period and a new band appeared, which can not be attributed to the monomer emission. The luminescence image shows that the J-aggregate is not destroyed. However J-aggregate storage in darkness does not recover its exciton luminescence.

Ultrafast exciton-exciton annihilation in semiconducting single-walled carbon nanotubes

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Semiconducting single-walled carbon nanotubes (SWNT) represent a novel class, one-dimensional nano-scale materials with diameter-tunable electronic transition energies coupled with their quantized electronic structures. Currently, there are greatly increasing interests in understanding the optical spectra, ultrafast dynamics and related physical mechanisms due to their fundamental importance and direct relevance to many of the potential applications.

In this presentation, we will report detailed femtosecond fluorescence upconversion and spectrally resolved transient absorption measurements designed to probe the dynamics of several specific nanotube types throughout the range of their optical response. Our measurements are carried out on a SWNT preparation consisting of individual nanotubes isolated in sodium dodecyl sulfate micelles. The clearly resolved spectroscopic transitions associated with specific semiconducting nanotube structures allow us to independently access specific nanotube types. The time-resolved fluorescence measurements were performed by exciting the second electronic transitions (E2) of selected tube structures (8,3), (6,5), (7,5), (7,6) and (9,5) with 30 fs pulses at appropriate wavelengths and detecting the fluorescence emission at the corresponding first electronic transitions (E1). We find that the relaxation from the state associated with E2 to the state of E1 occurs within 100 fs, and the subsequent fluorescence decays are strongly dependent on the initial excitation density, namely an increase of excitation intensity induces a faster decay. The excitation-intensity-dependent fluorescence decays can be satisfactorily described by a simple model involving ultrafast exciton-exciton annihilation with time-independent annihilation rate.

In the frequency-resolved transient absorption experiments, selective tube types, (6,5), (8,3) and (11,0), are excited by tuning pump pulses to be resonant with the corresponding E1 and E2 transitions and the photo-induced absorption changes in the visible and near-infrared spectral regions are probed. Analyses of the data collected for a selected nanotube type, the (8,3) tube, further enabled us to reveal the spectroscopic and dynamic signatures of the exciton-exciton annihilation as summarized below. (1) The electronically resonant excitation of the E1 state of the (8,3) tube at 953 nm induces an instantaneous spectral

response at 660, the corresponding E2 transition. (2) The dependence of the amplitude of transient absorption signal on the intensity of pump pulses at 953 nm differs for the kinetics probed at 660 and 953 nm. The former exhibits a linear dependence, whereas a saturating behavior is seen for the signal amplitude obtained at 953 nm. (3) The kinetics probed at 660 and 953 nm upon resonant excitation of the E1 transition are strongly correlated with each other. This correlation is manifested by the excellent match between the squared profile of the kinetics recorded at 953 nm and the kinetics measured at 660 nm. Our observations provide experimental evidence for the excitation in individual semiconducting nanotubes.

Temperature dependent excitaton relaxation in nanotubular $TPPS_4$ J-aggregates in water solution and in polymeric matrix

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J-aggregates are nice example of the self assembled structures, where self assembly crucially changes their spectral and other functional properties. Effective manifestation of the exciton coherence makes them ideal model systems for investigation of the excitonic properties of molecular materials. High and fast optical nonlinearities suggest a wide perspective for the J-aggregate application in various nonlinear opto-electronic devices. Because of similarity to porphyrin-based biological molecules J-aggregates of porphyrin derivatives are of particular interest for biological and medical applications. Recent investigations of the meso-Tetra(4-sulphonatophenyl) porphine $(TPPS_4)$ J-aggregate geometry by AFM and X-ray methods and theoretical modeling have shown that they form tube-like structures. Such nanotubes are of particular interest in molecular nanotechnology. However, these aggregates are not typical J-aggregates, since clear J-aggregate type spectrum forms only from the higher energy, Soret band, whereas J-aggregate features of the lowest Q absorption band are not so clearly expressed. Therefore, excitonic theory developed for "classical" Jaggregates cannot be straightforwardly applied to explain fluorescence, exciton diffusion and relaxation peculiarities in TPPS₄ aggregates.

In this investigation we compare exciton properties in $TPPS_4$ aggregates in aqueous solution and in polymeric PVA matrix. We use ultrafast absorption pump-probe spectroscopy to reveal exciton relaxation dynamics. In order to get deeper insight into the exciton relaxation mechanism we investigated temperature dependence of this process and its dynamics in photoannealed samples.

Our experimental data reveal that the nonradiative exciton relaxation in $TPPS_4$ aggregates in water solution and PVA matrix is determined by the exciton quenching by the quenching centers, which are formed by defects, impurities or aggregate chain ends. Due to different quenching center distribution exciton life-times in various aggregate species are different, what causes nonexponentiality of the exciton density relaxation. Excitons created in more perfect aggregate species with more red-shifted absorption bands have longer life-times. Both, exciton-exciton annihilation and linear relaxation are controlled by the exciton diffusion rate, which determines time interval needed for exciton to "meet" another exciton or relaxation center and annihilate or decay nonradiatively. Due to weak excitonic interaction in the lowest excited state, the excitons are rapidly localized and propagate in noncoherent way. The exciton diffusion rate is determined by the energetical disorder, therefore at low temperature the excitons are rapidly trapped before meeting another exciton or relaxation center. An-

nealing of the PVA film doped with TPPS_4 aggregates by high intensity laser pulses destroys part of the TPPS_4 molecules and creates additional relaxation centers, which significantly reduce the exciton life time, particularly at room temperature, when the exciton diffusion range is not reduced by trapping.

About size dependence of electron Auger scattering and its manifestation in luminescent properties of nano-Si

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Electronic Auger process involving three charge carriers is a basic channel of non-radiative losses in semiconductors. Its efficiency W depends on distance between interacting particles as r^{-6} . In nanoscale range of objects sizes R dependence W=f(R) is expected caused by the influence of R to r. Results of experimental studies of nonlinearities of photoluminescent properties of various structural forms of nano-Si, for the first time confirming such size dependence in dynamic electronic processes are given. Spectral and temperature dependences of 'radiation fatigue' effect having the same as the hole-burning in spectral contour of inhomogeneously broadened radiation bands, are analyzed. Arguments are given which show that inhomogeneous broadening of main radiation band is genetically associated with dispersion of function of size distribution f(R) in nanoSi.

'Charge pump' effect is proposed, whose driving force is an electronic Auger process taking place in conditions of spatial confinement on charge transport. Peculiarities of photo-, thermo and tunnel luminescence of nano-Si are explained from the position of this effect.

New trends in nanoplasmonics

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I present the review article in which new trends in nano-optics and nanoplasmonics are discussed. The explosive growth of nanoscience and nanotechnology during a few last years led to great interest and improved understanding of nanoscale optical fields and to the development of tools for studying and exploiting them. Such fields are excited at metallic nanoparticles where they are greatly enhanced due to high quality-factors surface plasmon (SP) resonances. These local fields are singular, exhibiting large spatial fluctuations and energy concentration in nanosize volumes. In vicinity of these "hot spots" optical responses are gigantically enhanced and can to allow, in particular, observation of Raman scattering from single molecule. Among the most remarkable effects associated with such giant fields are near-field fluorescence microscopy based on two-photon excitation, nano-manipulation of the particles by enhanced optical fields at a metal tip (optical nano-tweezers), linear- and nonlinear optical probing and nano-modification and many others. New ideas about quantum generation of coherent surface plasmons in nanosystems, efficient nanolens as self-similar linear chain of several metallic nanoparticles with progressively decreasing sizes end separations, nano-focusing of optical energy in tapered plasmonic waveguides, radiative decay engineering of quantum systems in the nano-proximity of nano-bodies are analyzed..

Ultimate sensitivity of optical microsensors feasible to monitor dielectric nanobodies

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Recently, spherical micrometer-sized optical cavities are proposed to be applied as sensors of nanometer-sized dielectric bodies (such as DNA molecules) [1]. This report reviews the principles of operation of such sensors.

The evidences of the presence of a dielectric body near or inside of an optical cavity are analyzed. We consider (i)a change in the frequencies of the morphology dependent resonances in spectra of the cavity emission, (ii)a change of the amplitudes of individual MDRs, and (iii)relative changes of the MDR amplitudes correspondent to the resonant modes of different orders. The ultimate sensitivity of sensors using these principles is estimated. The ways of improvement of the sensitivity by use of active optical cavities are discussed.

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Molecular spectra of fullerene silica photo active nanocomposites

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Fullerenes and their derivatives show unique physical and chemical properties which allow using them in biological systems as medical preparations or for target delivery of biologically active compounds and a medicine in a cell. In addition of being nontoxic, they are also capable to contact biological molecules showing influence on biological processes at rather low (even physiological) concentration. Fullerenes are effective antioxidants, but on the other hand Fullerenes under photo excitation can assist a formation of singlet oxygen and other radical forms of oxygen (RFO), which are the endogenous factors of damage to biological molecules especially nucleic acids. This fact testifies to a perspective of using fullerene based materials. For example it can be a photodynamic therapy. To make fullerene active in biological solutions they were hydrophilized by covalent bonding to the nanosilica surface. It is shown, that composites where fullerene is chemically bonded to the surface, can generate RFO and destruct DNA under irradiation. To strengthen the property to generate active forms of oxygen and to destruct transformed cells, nanocomposites were modified by photosensitive organic molecules. The properties of such compounds strongly depend on their structure. That is why the main part of our work was devoted to investigation of obtained composites. By the means of IR spectroscopy we can show the formation of azomethine group 1630 cm^{-1} on the surface which is the proof of covalent bounding of organic molecules to the surface. The presence of bounded fullerene was investigated by UV-VIS diffuse reflectance spectroscopy. It can be identified by displacement of the absorption peaks maximum at region from 18000 to 22000 cm^{-1} . To investigate the influence of organic antenna on the properties of the fullerene we have study fluorescence spectra. We have obtained interesting results which testifies an interaction between fullerene and organic molecule even without direct contact. The nanocomposites is investigated by TEM. The molecular spectroscopy results agrees with TEM images.

Optical study of self-assembled GeSi nanoislands

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Semiconductor structures several nanometers in size typically exhibit quantum confinement effects. By varying the geometrical dimensions and configuration of such objects, one can control the properties of the nanostructure, primarily the energy spectra of carriers and phonons. Nanostructures can be formed in different ways, for example, through self-assembly of growing nanoislands via the Stranski–Krastanow mechanism. In order to develop perfect devices, one needs information on the optical and electronic properties of QDs, which depend on various factors, such as QD size, shape, stresses, composition, as well as the spatial ordering and areal density of QDs.

The structures under study were grown, using molecular-beam epitaxy (MBE), on a Si(001) substrate covered with a preliminarily grown Si or SiGe buffer layers. MBE was performed at substrate temperatures varied in the range 400-750 C from sample to sample. The structures were studied by Raman spectroscopy and atomic force microscopy.

It is known that deposition of Ge layer with nominal thickness of 4-11 monolayers on Si substrate leads to the formation of coherent pyramidal and/or domelike nanoislands. Thanks to the larger height-to-lateral dimension ratio of domes, they are more relaxed as compared to pyramids. This fact, in turn, effects the composition of the islands. However, Raman spectrum from such a two-modal ensemble does not allow one to determine the parameters of the islands of a particular shape, due to the superposition of the contributions from both subensembles. By tuning the substrate temperature and nominal thickness of the deposited Ge, we have obtained the monomodal ensembles of the islands of a particular shape. That allowed us to study the structures with nanoislands of only certain shape.

It is found from the Raman spectra on nanostructures that among uncapped islands the most strained are pyramidal and the most relaxed are dome-shaped islands. For the islands of the same shape, the strain relaxation due to the islands three-dimensionality is larger for smaller islands. The composition of the islands grown at Tg \geq 500C, as follows from the three-band structure of corresponding Raman spectra, is mixed SiGe due to the significant interdiffusion with Si substrate. The intermixing is highly enhanced with increasing Tg. An overgrowth of the islands with Si even at low temperatures results in increasing of both Si content and strain in them.

The morphology of the self-induced nanoislands formed on $Si_{0.9}Ge_{0.1}$ differs from those grown on Si by larger surface density and size of the islands. The differences observed are found to be due to the larger critical volume of the pyramid-to-dome transition in the case of the $Si_{0.9}Ge_{0.1}$ buffer. The latter fact is explained by a larger Si content in the islands on $Si_{0.9}Ge_{0.1}$ at the very early stage of growth.

Study of carbon nanotubes interactions and interfaces with DNA and proteins

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Recent years have exited a significant interest to biological application of carbon nanotubes. The unique electrical and mechanical properties of singlewall carbon nanotubes (SWNT) and multi-wall carbon nanotubes (CNT) in combination with biomolecules could lead to creation of novel miniature electronic and optical devices, sensors, etc. The mechanism of these effects is still not clear both for simple molecules (water, monomers) and complex molecules such as DNA and proteins.

The presented data include a study of conformational states of DNA and proteins adsorbed on single-wall carbon nanotubes. FTIR and Raman spectroscopy, electron and atomic force microscopy were used for characterization of SWNT and CNT [1]. SEIRA (surface enhanced infrared absorption) spectroscopy method that allows to get an enhancement in IR absorption spectra of molecules on rough metal surface up to 10 times [2, 3] was used for registration of conformational structure of biomolecules and their complexes with SWNT and CNT.

The single-wall carbon nanotubes were synthesized by arc discharge between two graphite electrodes in He atmosphere in the Natural Science Centre of General Physics Institute (RAS, Moscow). The length of SWCNT was 1-2 μ m and diameter was 1.3-1.5 nm. The CNT were synthesized in Institute of Surface Chemistry (NASU, Kyiv).

Interaction of SWNT with ?-helix protein (bovine serum albumin) and ?sheet protein (ribonuclease) was registered. Under interaction with SWNT the increase of random coil and turns as well as the changes in orientation of protein molecule were registered though the initial conformation prevalence preserved for both proteins. We did not observe such changes in protein structure after interaction with soot.

Study of the interaction of SWNT with DNA showed formation of a stable DNA-carbon nanotube complex [3]. The wrapping of DNA molecules around carbon nanotubes probably occurs under this interaction, however, non-wrapping process appears in some cases. Van-der-Waals bonding and ?-stacking take part in the interaction for both proteins and DNA with carbon nanotubes. Study of SWNT and DNA interaction could be used not only for development of new devices but for characterization and identification of nanotubes. Study of SWNT and CNT interaction with proteins could be used in different sensor applications.

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UV spectra of photopolymerized fullerene films

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We present results of the combined UV-spectroscopic and theoretical study of the polymerized C_{60} films. UV spectra of photopolymerized fullerene film obtained by simultaneous deposition and UV-irradiation were observed in the range of 200-800 nm. The degree of the polymerization of the C_{60} films was estimated as about 95%. To assist the assignment of the experimental UV spectra of the polymerized C_{60} films we performed quantum chemical calculations of electronic transitions of C₆₀ monomer, dimer, trimers, and tetramers using semiempirical ZINDO as well as ab-initio CIS/6-31G* and TD DFT(B3LYP)/6-31G* methods. Geometries of the monomer, dimer, five trimers and two tetramers were fully optimized at the DFT(B3LYP)/3-21G level of theory. The calculations showed that the lowest-energy trimers are: Trimer A (with the angle between the monomer centers equal to 90°) and Trimer B (with the angle between the monomer centers equal to 120°). The UV spectra of the polymerized fullerene film were compared with the calculated energies of electron transitions. Based on this comparison and on the analysis of the IR spectra obtained earlier, we concluded that the main components of the films are the C_{60} dimer and the orthorhombic (O) polymer phase.

Struktural properties of short-period C/SiC superlattices

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Extensive studies of carbon nanostructured materials (CNM) properties and production techniques have got high progress last decades. As known, structural modification of many substances depends on external properties, such as pressure, temperature, symmetry of magnetic, electric and stress fields include gravity. In case of crystalline modifications and nanostructures a great importance has a potential energy distribution for atoms and electrons and its symmetry. For example, nanocrystals have usually increased crystalline period and crystal subsurface layers undergo the reconstruction depends on surface orientation and adsorption conditions It was shown earlier [1], that strong short periodic potential superimposed by wide gap dielectric on thin semiconductor layers in SL can act on their crystallization similar Kronig-Penny potential in case of bulk crystals. So by the control of nanoscale potential distribution and its symmetry one can expect to manage carbon crystallization process and even to get unknown yet carbon crystalline modification. A very short period C/SiC superlattices (SL) were prepared and avalanche annealed. Raman structural investigation indicated that the structure of annealed SL reveals strong dependence of thickness of SiC barriers and C wells. Clear confirmation of graphite and diamond features were obtained for structures prepared with carbon thickness correlated with size of interplane crystalline lattice distances of graphite and diamond. It was observed that the ordering effect took place only in case of thin enough barriers of SL. It was shown early that by choosing of anodization conditions one can promote of decreasing of number of defects and impurities of initial crystal [2]. The anodization has shown to improve crystalline perfection of layers and increase their photoluminescence. The role of one-dimensional superimposed periodic potential on crystallization processes and the features of electrochemical etching of non-equilibrium system are discussed.

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Spectroscopy and Nonlinear Optical Response of Fe/TiO2 Nanocomposite Films

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Among different semiconductors used in photocatalysis, titanium dioxide turned out to be the most suitable for photocatalytic environment cleaning as it is non-toxic, relatively cheap, and it demonstrates high photoactivity and inertness (optical stability). TiO_2 is a wide-gap semiconductor and it absorbs only 5% in UV spectral range of the ordinary sunlight that essentially limits its applications. Much effort is applied to extend the range of photosensitivity of TiO_2 from UV into visible range of spectrum. This can be achieved by addition of organic (dye molecules) or non-organic (3-d-metals, Fe^{3+} in particular) sensitizers.

Transparent, nanostuctural high quality Fe/Ti films were prepared (synthesized) from titanium tetra-iso-propoxide and iron chloride by sol-gel method with Fe:Ti ratio of 1:1 [1]. Films where characterized by ellipsometry, UV-Vis spectroscopy, FTIR, XRD, and electron microscopy (TEM).

According to electron microscopy measurements, Fe-containing TiO_2 films with Fe:Ti ratio of 1:1 consist of nanostructural matrix that contain 15-20% of cubic crystals 150 nm in diameter [1]. The ratio Fe//=1/1/3,5 was determined using energy-dispersive X-ray analysis (EDX).

Optical transmission spectra of Fe/Ti film demonstrate considerable absorption edge shifting into visible range (500 nm) in comparison with 380 nm for TiO_2 . It allowed using these films as photocatalyst to decompose dichloracetic acid while illuminated by visible light [1].

We have studied the laser beam selfaction phenomena in Fe/TiO_2 films with spatial profile analysis technique. The photoinduced absorption and nonlinear optical (NLO) refractive index variation have been observed in transparency range and at the absorption edge region with fundamental (1064 nm) and second harmonic (532 nm, 30 ps FWHM) radiation of pulsed Nd:YAG laser.

The estimated two-photon absorption coefficient ($\beta \sim 103 \ cm/MW$) and real parts of the effective cubic susceptibility ($\chi^{(3)} \sim 10^4 \ esu$) at 1064 nm give possibility to say about extremely efficient NLO response of the film in the transparency range. The phenomenon is similar to the effect of the giant NLO response of TiO_2 nanoparticle porous films [2] with ($\chi^{(3)} \sim 10^{-5} \ esu$). For both materials the efficiency of the response is caused by resonant excitation of carriers due to the existence of the states in the gap of titanium dioxide.

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Nonradiative recombination centers in SiO_x composite films

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During last years the silicon-based materials with visible photoluminescence are of increasing research interest due to the possibilities to create optoelectronic devices using traditional silicon technology. One of them is SiO_x which contains nanosize clusters of silicon. This composite material is characterized by more intensive and high-frequency photoluminescence in comparison with radiation of bulk silicon. There are two types of models that attribute visible photoluminescence to silicon nanocrystallites or/and different surface complexes. Nonradiative processes in this material are still under the debate. The present study deals with the investigation of paramagnetic defects in the composite SiO_x films and their influence on the photoluminescence of the materials.

The SiO_x films under investigation were fabricated by thermal evaporation of SiO in vacuum. To create silicon nanoclusters the thermal annealing was applied. Depending on the annealing temperature we obtained two modifications of SiO_x material. Both types were analyzed using the following techniques: Raman scattering, photoluminescence, electron paramagnetic resonance and optically detected magnetic resonance. Raman scattering studies demonstrated the presence of amorphous silicon clusters in SiO_x matrix in the material formed by 750 C annealing while silicon nanocrystallites embedded in SiO₂ were observed in the material annealed at 1000 C. Both types of SiO_x composites revealed the photoluminescence in red and near infrared range with the maxima at $\sim 1.64 \text{ eV}$ and ~ 1.46 eV, respectively. Electron paramagnetic resonance investigations evidenced the presence of the silicon dangling bonds in different surroundings in both types of the samples. In the samples with silicon nanocrystallites these defects were characterized by g-value of 2.0055 while in the samples with amorphous silicon clusters the g-value equals to 2.0045. All types of paramagnetic defects were also found in the spectra of optically detected magnetic resonance. The sign of the optically detected magnetic resonance signal evidenced that these defects are the centers of nonradiative recombination in both types of samples.

Nonlinear properties of *PbS* nanoparticles in polymer

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This work is devoted to the creating and investigating properties of a new optical nonlinear material based upon poly(vinyl alcohol)-PVA containing nanoparticles of PbS. PbS concentration in polymer composite is about 4vol%.

Using X-ray diffraction peaks widening we have determined that the mean size of a PbS particle is 5nm. According to the hyperbolic zone model [1] the band gap E_g of PbS semiconductor particles in our polymer composite is 1.05eV.

Refraction index dispersion $n(\lambda)$ in our polymer composite has been studied by direct method of Jamin interferometer crossed with spectrograph. Our experimental data are based on direct measurements of phase change of the light wave passed through the sample. We have obtained a value of $n(\lambda = 0.532 \mu m) = 1.87$. The measured values of $n(\lambda)$ and $k(\lambda)$ were used for calculation of the real and imaginary parts of dielectric constant of PbS in PVA.

Nonlinear refraction of our samples with the thickness of $1\mu m$ has been studied in the scheme of the degenerate four wave mixing.

A frequency doubled YAG: Nd^{+3} laser ($\tau_p = 10ns, \lambda = 0.532\mu m$) was used as a source of radiation. Reading out of the dynamic holographic gratings recorded in the material was carried out by means of CW He-Ne laser. Our materials was shown to exhibit third-order nonlinear response characterized by the optical nonlinear susceptibility $\chi^{(3)}(\omega; \omega, -\omega, \omega)$. The value of the susceptibility was calculated using diffraction efficiency of the recording gratings. We have obtained a value of $\chi^{(3)} = (4.2 \pm 2.1) \times 10^{-16} m^2/V^2$ which is higher than that of both known non-organic optical nonlinear materials and other composites containing nano-particles of other origin. Nonlinear refraction time response of our composite was measured to be not longer then 10 ns.

The experimental technique used in our studies made it possible to register optical nonlinear response caused by fast electronic mechanisms. Since the PbS nanocrystal size (5nm) is a factor four less then the exciton diameter in bulk PbS (21.4 nm) so the electronic mechanism of nonlinear refraction in our material could be connected with the strong spatial limitation of the charge carriers. This factor may be a reason for the observed large third order optical nonlinear susceptibility χ^3 [2].

The material under study is perspective for optical data processing.

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Chemical synthesis and photocatalytic properties of nitrogen-doped $Zn_xTi_vO_z$ nanostructures

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For successful broad scale application of nanosized TiO_2 and ZnO photocatalysts is the need to shift their optical absorption spectra from the UV to the visible spectral range. One of the recently developed promising approuches includes the incorporation of nonmetal ions (e.g. N, S, C, F) into TiO_2 [1, 2]. Of particular interest to us is extending the absorptivity of TiO_2 and ZnO into the visible by nitrogen doping. However the possibility that N-dopped TiO₂ would catalyse the photooxidation of organic compounds remaines conjectural [3].

The new wet chemical route to colored $\operatorname{Zn}_x \operatorname{Ti}_y \operatorname{O}_{w-z} \operatorname{N}_z$ powders and nanocrystalline layers was developed recently [4]. In presented work the rout of sol preparation was modified and used for $\operatorname{Zn}_x \operatorname{Ti}_y \operatorname{O}_w$ layers deposition on the glass. The anniling of these films under ammonia gas at temperatures between 550°C and 800°C shifts the optical absorption edge into the visible. The nitrogen incorporation and oxonitrides formation was confirmed by XPS analysis.

The photoactivities of the films were examined in Methylene Blue degradation under UV-Vis and Visible irradiation. Under MB infiltration study we observed the high adsorption capacity of $\text{ZnTiO}_x N_y$ layers produced by replacing oxygen by nitrogen. In MB infiltrated films we revealed the unexpected blue shift of the optical absorbance spectra. This metachromatic effect in MB infiltrated films evidences about high hydrophilicity of the film.

Nitridated and nonnitridated films were active in MB photodecomposition under irradiation with UV-Vis light. The highe activity of nitridated film under UV-Vis light can be explaned as well its wider light absorption region as higher MB adsorption capability. We observed the MB degradation during the exposure of MB-infiltrated nitridated film to the visible part of a Xenon lamp. Interestingly the photodegradation is additionally accompanied by blue shift of MB spectra. Thus, $Zn_x Ti_y O_{w-z} N_z$ film shows the hydrophilic conversion property when irradiating with light. At the same conditions we didn't observe MB degradation with nonnitridated films. This excludes the posibility of MB sensibilisation of $Zn_x Ti_y O_{w-z} N_z$ films.

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Quantum-dimension effects in optical properties of nano-structures

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On the base of ideas on properties of nano-structures [1] a mechanism of quantum-dimension effects in optical properties of nano-materials is proposed.

On of the first discovered unique properties of nano-particles was change of the melting temperature of metals with respect to size of the particles. For example, for aurum the melting temperature decreases on 1000 K when the size of particles becomes 2 nm (for compact aurum it is 1340 K) [2]. Some nanocrystalline substance are the materials, in which one metal is implanted into other one. In such cases the melting point may vary to increase or decrease with respect to compact materials when the size of particles changes.

Quantum-dimension effects in optical properties of nano-materials are observed when the radius of the nano-particle $R\sim10$ nm [3]. A shift of the absorption band towards the region of smaller wavelengths was observed when the size of nano-particles decreased [4].

The mechanism of quantum-dimension effects in properties of nano-particles was discussed by many authors [5, 6]. We assume that the mechanism of formation of the properties of nano-particles, including the quantum-dimension effects in properties of nano-particles, should be discussed in terms of fieldsubstance interaction [1]. According to experimental data, the energy density of cosmic vacuum exceeds significantly the energy density of atomic nucleus [7]. All structural-dynamic processes in substances take place in high-frequency field of the physical vacuum, and they cannot be discussed without taking into account the field substance (F-S) interaction.

In a set of particles as a result of influence of the physical vacuum and surrounding particles an oscillating wave function of response (WFR) of particles is formed [8]. The phase correlation among WFRs of particles leads to formation of a self-coordinated field of the substance. Energy structure of WFR of particles is identical to the energy structure of the self-coordinated field of the substance. That is why the WFR of particles is an internal parameter, which plays the principal role in formation of macroscopic and mesoscopic properties of substances. Mutual repulsion of WFRs of particles leads to formation of a coherent cover of particles. Realization of the phase coherency among harmonics of WFRs of particles leads to formation of the surface energy or coherent cover of the substance. Formation of the surface energy or the coherent cover in a set of particles leads to formation of the condensed state of matter. Properties of the coherent cover of the material as a whole are different from those of WFR of a single particle. For example, it was discovered that the density of particles changes by several order of magnitude in a thin boundary layer, which thickness is several nanometers [9].

In atomic-molecular systems as a result of self-organization and self-compression the collectivized electrons are formed. Oscillating influence of the physical vacuum and surrounding particles leads to formation of WFR of the collectivized electrons. As a result of the phase correlation among WFRs of electrons formation of the self-coordinated field of electrons occurs. Energy structure of the absorption and luminescence spectra allows one to obtain information on the oscillation frequency and energy distribution in WFR of electrons.

When the volume of substance becomes lesser than the spatial dimension of WFR of particles there occurs a disturbance of integrity properties of the material. The disturbance leads to mesoscopic behavior of the properties of substances, i.e. dependence of material properties on its quantity. In small volume of substances the role of the physical vacuum in formation of materials properties becomes significant.

In nano-scale volumes while decreasing the size, as a result of influence of the physical vacuum, the process of self-compression and increase of coherent properties of nano-structures cover continues. The coherent cover of nano-structures limits the spatial dimension of WFRs of atoms and molecules. They appear to be locked inside the nanostructure (in a sense of interaction with environment). That is why the properties of nano-structures can be compared with those of nuclei. It is known that in nuclei the nucleon interaction forces are not spread outside the nucleus.

When nano-liquids and nano-materials are formed from nano-structures the high-frequency self-coordinated field and coherent cover of nano-structures provides unique properties for those materials.

At super-low amount of the substance, as a result of self-organizing influence of the coherent cover, there occurs significant increase of the frequency of selfcoordinated field and density of the substance in nano-scale dimension. Change of the energy structure of the self-coordinated field of nano-structures depending on size leads to the dimension effect of physical-chemical and, particularly, optical properties of nano-materials. Increase of the frequency of self-coordinated field of electrons with decreasing the size of nano-particles leads to a shift of the maximum of absorption and luminescence bands towards higher frequencies [4].

As a result of self-compression of nano-structures there occurs a change of the lattice period and inter-particle distances [9]. This process leads to increase of decrease of the coherent properties of covers of nano-structures, and influences on the melting temperature of nano-particles. In case of decrease of the covers coherent properties there occurs a disturbance of the self-coordinated field and formation of Brownian particles, and the melting temperature of nano-particles decreases. Obviously, in case of gold there occurs the decrease of the covers coherent properties with decreasing the size of nano-particles that leads to sig-
nificant decrease of the melting temperature. In cases when other metals are implanted into structures the coherent covers of nano-particles may increase that will lead to increase of the melting temperature [2].

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Substrate effect and interparticles interaction in optical properties of isolated metal nanoparticles and their array

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Formation of small metal particles on surfaces of various materials and selfassembling of them into desired surface arrays has been the subject of many studies during last years. Especially interesting are one-, two, and three-dimensional arrays of closely spaced nanoparticles in which short- and long-range interactions between plasmons may lead to new optical properties, such as light induced coherent interaction between metal nanoparticles arranged in two-dimentional arrays [1]. This phenomenon results in the formation of a plasmon mode with an extremely sharp and strong resonance representing the cooperative interaction of several particles with light.

In this work photostimulated chemical (electroless) deposition of Au from aqueous solution of AuCl₃ salt for gold nanoparticles fabrication on different semiconductor surfaces and vacuum sputtering of Au on semiconductor and glass surfaces was used. As for the benefits of the chemical deposition method, self-organized formation of uniform surface structures of metal nanoparticles opens an elegant and efficient route towards fabrication of large-scale arrays of uniform metal-semiconductor nanostructures. Besides Au films were subjected to vacuum annealing at temperature from 100° to 300° C. AFM and SEM measurements were used to characterize shape and size of nanopaticles and statistical parameters of their arrays.

Optical properties of nanosystems were investigated by multim angle of incidence and spectral ellipsometry, and the reflectance spectroscopy of polarized light at several angles of incidence. In spectral region 300-900 nm plasmon resonance in Au nanoparticles was observed. The plasmon minima location depends on the nanoparticles size and shape, the mean distance between nanoparticles, the total gold amount on surface, etc. To describe optical data different models of effective medium approximation and new approach [2] for polarizability of gold clusters on the surface were used. In particularly, this approach includes a generalization of the microscopic theory of the electrostatic response of a system of spheres on a substrate. The generalized theory allows to treat spatial systems of spherical particles of different sizes, made of different materials and located arbitrary near a boundary surface. For a system of two spheres above a substrate, an analytical expression for the spheres polarizability was used in the dipole approximation, and the substrate influence on the polarizability and the optical properties of nanodimensional sphere is analyzed.

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New fluorescence dynamics of single Y_2SiO_5 : Pr_3 +nanocrystal

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Confocal fluorescence microscopy has been used to study the fluorescence spectrum and decay of the Pr^{3+} ion doped into a Y_2SiO_5 nanocrystal freely attached at the glass-air interface. In spite of room temperature, surprisingly sharp spectral lines (less than 1 cm⁻¹) have been observed in the ${}^{1}D_{2}$ - ${}^{3}H_{4}$ fluorescence spectrum of the Pr^{3+} ion. The electronic relaxation within the ${}^{1}D_{2}$ manifold characterized by the average splitting value of about 200 cm⁻¹ has been strongly suppressed that has resulted in an intense fluorescence from the high ${}^{1}D_{2}$ crystal field components. The effects observed are very sensitive to cluster environment and clustersubstrate interaction. Obtained results open a new spectroscopic way, which allows us to explore directly the excited states of J-manifolds of RE ions, control the electronic relaxation rates and create a new type of quantum systems for surface monitoring.

Noble metal nanoparticles reductively grown in silicon nanoparticles suspension and in porous silica

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Metal (Ag, Au, Pt) nanoparticles of 2 - 10 nm were prepared in two different systems: in the solution of silicon nanoparticles obtained from porous silicon and in the nanopores of porous silica, usually called as porous glass (PG). They show similar reduction activities, probably due to high surface curvatures and dangling bonds of silicon.

In the first method, porous silicon was produced by a typical electrochemical etching of crystalline p-type Si in HF:H₂O₂-based etchant. AgNO₃, HAuCl₄ and HPtCl₆ were used as metal precursors. Metal nanoparticles were grown by sonicating the porous silicon in the aqueous solution of corresponding metal precursors, thus silicon nanoparticles were used as a reducing agent. Surfactant prevented metal nanoparticles from aggregation. Scanning electron microscopy (SEM) together with energy dispersive X-ray analysis (EDX) and tunneling electron microscopy (TEM) including selected area electron diffraction measurements (SAED) were utilized to study the prepared metal nanoparticles. It was found that the particles were well separated each other and had spherical shape, narrow size distribution and crystalline structure. Optical absorption data in the region of plasmon resonances confirmed elelectron microscopic observation. Gel electrophoresis separation technique was successfully utilized to check the particles size distribution.

The second method utilized porous glass as a reducing agent and matrix for metal nanoparticles growth. The metal precursors were spread inside the pores by soaking the PG in aqueous solution of the precursors followed by drying the PG in air or in vacuum. Reductive growth of metal clusters in the pores started during drying process and its rate was significantly accelerated upon heating of the PG. The size of the grown metal nanoparticles is natively limited by the size of the PG pores. Pore size distributions of the porous glasses, obtained by nitrogen adsorption isotherms measurements, were very narrow and centered at 2 nm, 4 nm and 10 nm for different sets of samples. The particles in the pores were surely separated each other and well fixed in the matrix. Obtained nanocomposite material (porous glass with metal nanoparticles inside) was studied mainly by optical absorption spectroscopy in the UV-vis region of metal plasmon resonance and in the NIR region of the absorption of hydroxyl groups, which cover the surface of pores in PG. The particle size and concentration calculated from the optical measurements agree with the pores size and specific pore volume obtained from the gas sorption measurements. The role of water in metal nanoparticles reduction has been discussed.

Energy migration in single J-aggregates of pseudoisocyanine

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Molecular aggregates, called J- or S- aggregates in honor of their discoverers Jelley and Scheibe, are clusters of noncovalently coupled organic dye molecules, which form linear or closed chains. They reveal a narrow and intense absorption band (J-band) bathochromic shifted relative to the monomer band. Due to excitonic nature of the J-band, J-aggregates exhibit coherent excitation phenomena, such as superradiance or coherent energy transfer, which can be used for the creation of artificial lightharvesting complexes. Despite more than sixty years of their research, a lot of questions, concerning optical properties of Jaggregates depending on their structure or preparation conditions, still remain, even for pseudoisocyanine (PIC, 1,1'-diethyl-2,2'-cyanine) J-aggregates, which are the most investigated ones.

Using fluorescent microscopy and microspectroscopy we have studied Jaggregates of PIC-iodide in an aqueous electrolyte solution. J-aggregate morphology transformation from stringlike structure to rod-like one during ageing has been revealed, similar to TC ones [1]. Contrary to TC, two new bands, redshifted relative to J-band, have been observed in the fluorescence spectrum of rodlike PIC J-aggregates. But the most interesting result is fluorescence of the ends of the rod, which can be observed at the distance up to 20 m away from the exciting spot. That is much longer than 50 nm distance of energy migration for PIC J-aggregates, which was reported in [2]. The best of our knowledge, it is the first direct observation of energy migration to a such large distance in J-aggregates.

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Features of exciton transport in J-aggregates of amphi-PIC

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Since their first discovery by Jelley and, independently, Scheibe in the mid thirties, molecular aggregates named J-aggregates or S-polymers in honor of their discoverers have been the subject of keen interests in both fundamental and applied aspects. J-aggregates are specific assembles of noncovalent coupled organic dye molecules organized in the form of linear or closed molecular chains, which in their turn form complex cylindrical patterns. These supramolecular assemblies are characterized by a narrow intense absorption band redshifted with respect to the relevant monomer band that reflects the exciton nature of electronic excitations in J-aggregates. Due to a chain arrangement, optical and luminescence properties of J-aggregates are well described within the 1D Frenkel exciton model. Recently, J-aggregates have attracted a great deal of attention as a new type of luminescent probes to control mitochondrial membrane potential in living cells and as an artificial analogue of light-harvesting (LH) complexes.

In this work, we present results concerning an efficiency of exciton migration under the exciton selective excitation within the absorption band (J-band) of amphi-PIC at different temperatures. To detect exciton migration, the luminescence of exciton traps, which are molecules capable of energy capturing at the exciton approach, has been used. It has been found out that the absorption spectrum of amphi-PIC J-aggregates and the excitation spectrum of trap luminescence differ in their longwavelength edges. That is associated with the fact that on the longwavelength edge of the J-band of amphi-PIC J-aggregates exiton states remain localized and the energy transfer to traps is impeded essentially. In presented work the temperature dependence of exiton motion has been studied and the influence of static disorder in amphi-PIC J-aggregate structure on exiton motion has been revealed.

0.7 Biomolecules and polymers

The pecularities of the DNA and some model compounds luminescence

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The deoxyribonucleic acid (DNA) is the very important biopolymer macromolecule that plays the main role in the transfer and realization of genetic information in every living organism. But until now the nature of the electronic processes in the DNA was not described completely. The aim of the present work is the investigation of the luminescence and electronic excitation transfer in the DNA.

The spectral peculiarities of the DNA, d(CCCGGGTTTAAA), poly-(dAdT)₂ and the low molecular model compounds of them (dGMP, dAMP, dCMP and dTMP) were examined. The system of energy sites and electronic processes in the DNA and d(CCCGGGTTTAAA) (specially designed and synthesized) were analyzed. It was shown the absorbing centers in the DNA macromolecules and d(CCCGGGTTTAAA) are the basic groups. To the other hand, phosphorescence of the DNA and d(CCCGGG-TTTAAA) (due to migration of the electronic excitations) is close to emission of other type centers. The nature of these centers was found by comparing of the DNA, d(CCCGGGTTTAAA) and poly(dAdT)₂ phosphorescence spectra.

New Trends in the Development of Photopolymers for Holography: Polymer / Nanoparticles Composites

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Photopolymer systems possess many advantages as attractive recording materials for 3D holography. Polymers, like other organic materials, have more flexible chemical structures and can be modified more readily than inorganic media thus providing control over their physical and holographic properties. In addition self-developing photopolymers can provide formation and fixing of holograms directly during recording. Polymeric recording materials for 3D holography have been a subject of intensive investigation since the late 1960's. The fabrication of convenient low-cost photopolymer holographic materials has led to the creation of various holographic devices. In the same time development of the nanotechnologies over the last decade opened up a new application of photopolymers. The photopolymerization in the interference field, which is the typical method for holographic recording in photopolymers, is also used for the spatial ordering of organic and inorganic impurities (G) distributed in polymeric matrix. The interest to these structures is caused by the following reasons. Different substances - liquid crystals or nano- and micro-particles of various types having specific physical properties can serve as Gs. The combination of their intrinsic physical-chemical properties with the diffraction properties of the periodic structures is promising to design new functional optical and electro-optical components and devices for data storage, communication networks (switches, add-and-drop systems, and beam deflectors), and also for liquid crystal displays and photonic bandgap structures for wave-guiding. Furthermore the embedding of inorganic impurities improves polymer holographic materials, namely increases the amplitude of refractive index modulation and its temporal stability.

The photo-reactive syrup being used for holographic creation of well-ordered structures contains a mixture of monomers, photoinitiator of polymerization and G. The spatial ordering of G is obtained due to: (i) the local polymerization and phase separation of the mixture on polymer-rich and G-rich phases and (ii) the photo-induced counter-diffusion of the components, providing a periodic distribution of the mentioned phase during the exposure to the interference pattern. The resulting structure consists of the alternating polymer-rich and G-rich regions having different refractive indices and represents the phase volume Bragg grating. The variation of the refractive index of G under the influence of high-power laser beam can cause a nonlinear diffraction in the periodic structure. Such gratings can be used for the fabrication of modern electro-optical components, for example, for all-optical switching devices. The elimination of polymer

matrix allows obtaining 1D bandgap structures.

In this report we present a holographic technique to produce volume gratings, based on photopolymerizable composites containing different nanoparticles. We compare various methods of introduction of nanoparticles into monomer syrup; discuss the mechanism of their ordering that are important for further improvement of the holographic technique. We also report the holographic and optical properties of polymer/nanoparticles gratings.

Prototropic tautomerism of nucleotide bases in model protein-nucleic acid contacts. Spectroscopic and theoretical results

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The problem of nucleotide bases tautomerism arose in the course of experimental investigations of elementary processes of protein-nucleic acid recognition via carboxylic group of amino acids. To interpret UV, IR and NMR spectroscopic data, in some cases tautomeric transformations of a nucleotide bases were suggested in their complexes in DMSO with deprotonated carboxylic group modelled by sodium acetate $(CH_3COO^-Na^+)$.

Quantum mechanical ab initio calculations of energies of the Ade, isoGua and Xan tautomer complexes with CH_3COO^- gave evidence of transitions from ground-state tautomers to high-energy ones: $AdeN9H \rightarrow AdeN7H$, $isoGuaN9H \rightarrow isoGuaN7H$ and $XanN7H \rightarrow XanN9H$, which agrees with experimental data.

In the case of Ura the MP2/6-31G(d,p)//HF/6-31G(d,p) calculations of its tautomer complexes of the CH_3COO^- :Ura type failed to explain vanishing of both imino proton signals in ¹H NMR spectrum. Only taking into account an impact of Na^+ in the triple complexes of the CH_3COO^- :Ura: Na^+ type, it was shown that both enolic tautomers of the base proved to form much more stable complexes (with slight energy gap between them) than the ground-state diketo one. Coexistence of two enolic tautomers explains experimental results.

The B3LYP/6 - 311 + +G(d, p) calculations of similar triple complexes of Ade tautomers showed that, except the groundstate complex of high-energy AdeN7H tautomer, two more high-energy tautomers (imino-AdeN3H,N9H and AdeN1H) form complexes more stable than the ground-state one AdeN9H. According to calculations of the same level of theory, in the ground-state triple complex m^9 Gua exists as the ground-state tautomer m^9 GuaN1H, but energy of high-energy tautomer m^9 GuaN3H in triple complex is 8 time reduced (as compared to isolated state).

Every triple complex of all the base tautomers studied is stabilized by two H-bonds with CH_3COO^- and the most favourite coordination with Na^+ . In all the cases theoretical data completely agree with conclusions extracted from spectroscopic study.

Thus, tautomeric transformations of nucleic acid bases were first detected in model systems of protein-nucleic acid recognition and role of Na^+ in this process was elucidated. Biological role of high-energy tautomers of nucleotide bases is discussed.

Internal dynamic investigation of modified steroid hormone analogues by NMR spectroscopy in liquid

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Modified analogues of steroid hormones are widely used to treat a number of serious diseases. The therapeutic properties of the applied preparations are largely determined by the steroid conformation in solution and intramolecular dynamic in liquid. Among the methods that help us to determinate the existence of conformational exchange in molecules and to define its kinetic and thermodynamic parameters NMR spectroscopy occupies an important place. This application is based on well-known dependencies of spectral and relaxation parameters on temperature [1].

This report is devoted to the analysis of the problems related to the use of NMR methods in one and two dimensions for the investigation of internal mobility in some analogues of steroid hormones [2]. Among them are: a) - analysis of the variable-temperature 1H spectra at slow exchange condition which are substantially hampered due to the overlapping of multiplet signals of ~20 aliphatic protons for each conformer, b) - determination of populations PA and PB at fast exchange condition (A – B) on base values of averaged chemical shifts, scalar coupling constants and nuclear Overhauser effects and c) discovering of fast exchange between two or more conformers on base measurement of cross-relaxation rates between scalar coupled protons.

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Random Lasers on Vesicular Polymer Films

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Random lasers are new class of coherent light sources where random nonresonant positive feedback is formed due to multiple light scattering in the active medium[1]-[3]. Lasing threshold decreases with growth of the multiple scattering efficiency. There are several different types of random laser: dyed liquid suspensions of scattering particles, dyed polymer with embedded scattering particles and simple powder of semiconductor particles.

The scattering efficiency in the suspension depends on relative refractive index $n_{rel} = n_{part}/n_{polym}$ of the particles, and their concentration. But as the refractive index of polymeric matrix is high the relative refractive index of the highly refractive materials (rutile, diamond) is less than $n_{rel} = 1.6$. Moreover the homogeneity of particle distribution in the medium is difficult to be achieved that influences the random laser parameters.

The close value of the relative refractive index $(n_{rel} = 1.5)$ can be obtained using vesicular materials as a matrix. Among the various methods of vesicle realization it is perspective to produce nitrogen bubbles by UV irradiation of the many component polymers containing azines. Variation of the intensity and duration of UV irradiation can vary those centers concentration. Their size depends on hitting time of the films. The samples are prepared as films up to 30mkm films. While the bubbles are used it negotiates the problem of homogeneity of the redistribution of the scattering centers. Furthermore, the bubbles use obviates the necessity of the particles purification from the absorbing impurities decreasing energy yield.

In the work we investigated the lasing threshold and the lasing spectra parameters of the random laser based on films of solid polymeric dye (R6G, concentration $10^{-3}M$) solution with N_2 vesicles as scattering centers. The laser was pumped by the second harmonic of Q-switched YAG: Nd^{3+} source. The investigation were carried out depending on the bubbles concentration (time of UV exposition), films thickness (15-30mkm) and polymer composition.

The distinguish features of the investigated films are essentially lower lasing threshold (more than an order) in comparison with the other random lasers and small spectrum width ($\sim 2nm$).

The lasing spectrum 20% widening was founded under pump four and more times increasing over the lasing threshold. The widening contains reversible and irreversible which relative contributions depend on polymer composition. It conditioned by two mechanisms: the gain band widening under increasing of the inversion between dye molecules electronic laser layers, and polymer decomposition under thermal influence of pump radiation.

The obtained results allow asserting that vesicular polymer films can be perspective to produce compact random and photonic laser in the nearest future.

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Manifestation of intramolecular H-bonds of 1',2'-deoxyribose conformers in IR-spectra. Non-empirical quantum chemical investigation

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Elucidation of structural and dynamic properties of 1',2'-deoxyribose conformers, e.g. from the point of H-bonds presence, is important for base-modifies 2'-deoxyribonucleosides structure clarification.

In this context the intermolecular OH...O H-bonds were firstly found by DFT method at the B3LYP/6-31C(d,p) level of theory. It was shown that 16 conformers from the full 1',2' deoxyribose conformational family containing 64 conformers have H-bonds of the type O5'H...O4', as well as 2 conformers of the type O5'H...O3' and 2 conformers of the type O3'H...O5'. These H-bonds have been identified applying geometric, electronic and spectral criteria. The last one is especially emphasized.

It is established that all H-bonds are characterized by O...O distance which does not exceed 3 Å and has a range of values from 2.724 Å to 2.991 Å; in these cases OH...O average angle for O5'H...O4' type H-bonds is 110.371° and 136.42° for O5'H...O3' of O3'H...O5' type H-bonds.

We observed the hydroxyl OH bond elongation in the range of values 0.003-0.005 Å. The hydroxyl groups involvement to the H-bond exerts influence on their characteristic vibrational values: torsion vibration frequencies $N_{I_{OH}}$ increase by ~ 170 cm⁻¹ and stretching vibration frequencies N_{OH} decrease by ~ 50 cm⁻¹, which is accompanied by growth in their intensities.

The biophysical importance of the obtained results is discussed.

Sensitized intrinsic phosphorescence from a poly(phenylene-vinylene) conjugated polymers

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Intrinsic phosphorescence in a phenyl-substituted poly(phenylene-vinylene) (PhPPV) film sensitized by a phosphorescent dye dopant has been directly observed for the first time for PPV class conjugated polymers. This study enables direct spectroscopic measurements of the S0 T1 gap in PPV polymers. To overcome the problem of very low population of triplet levels in a PPV via intersystem crossing after optical excitation of the polymer, we have doped polymer films with the red emissive phosphorescent platinum porphyrin dye (PtOEP). It has been chosen due to the following reasons; (i) PtOEP can efficiently capture singlet excitations of the PhPPV host since its LUMO energy is below of that of PhPPV as determined by cyclovoltammetry, (ii) the efficiency of ISC is almost 100%, and (iii) the lowest triplet state (T1) of PtOEP is above than the T1 state of the host polymer so that efficient triplet energy transfer can be expected. Therefore, after excitation of PhPPV almost all singlet excitations are captured by the dye molecules and, in its turn, subsequent quenching of PtOEP triplets by the host polymer enhances the population of T1 states of PhPPV. Since the T1 state is then populated orders of magnitude more efficient than by intersystem crossing in undoped polymer matrices triplet emissions are available to direct spectroscopy. Efficient triplet energy transfer from the platinum porphyrin dye molecules to the PhPPV polymer was found to occur as the triplet level of the dopant (1.91 eV) is above the triplet level of PhPPV, which was determined to be at 1.63 eV. Intrinsic phosphorescence emission has been observed at room temperature as well. A significant decrease in emission intensity of phosphorescence has been found, if the sample was measured in air indicating quenching of triplets by oxygen.

The spectral manifestation of some fluorescent probes photoxicity

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One of the DNA and other biological objects detection methods is the use of fluorescent probes. For such type detection the dyes (quantum yield of which greatly increases under interaction of the dyes with another biological object) are used. Recently the papers that show the phototoxicity of some of these dyes (for example, TO-TO) have appeared.

In this paper the spectral method of fluorescent probes phototoxicity phenomenon investigation was proposed. As it is well known one of the phototoxicity manifestation is the damage of a biological object under excitation of the fluorescent probe which contact with this object. The absorbtion spectra typical peculiarity of many of the dyes using as the probes is the existence of "relative transparency window" in the spectral region between the first and the second electronic transitions. The DNA and RNA absorbtion bands that are connected with the first electronic transitions in them "hit" in this region ($\sim 260 \div 300$ nm). In our experiments optical density D(t) in mentioned above region of the DNA+dye solutions increased under irradiation in the first absorbtion band of the dye that was evidence of the DNA basic groups photochemical modification. The dynamics of D(t) was not monotonous. In the paper the results of the investigations carried out on a number of dyes were analyzed and discussed. The versions of possible phototoxicity mechanisms are proposed.

On-line monitoring of immobilization of small organic molecules in polyoxymethylene films by means of low temperature mass spectroscopy

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A problem of immobilization of biological molecules in polymeric films with preservation of their activity is essential for design of bionanodevices, in particular biosensors. Application of both high and low temperature technologies in polymerization can be equally damaging for biomolecules. However, a peculiar polymerization process can be found, which requires moderately low temperatures, namely, oligomerization of formaldehyde, which proceeds actively at temperatures lower than $+10^{\circ}$ C; freeze-drying of thus formed polyoxymethylene (POM) films under vacuum can be conducted at about -50° C.

In the present communication a method of on line monitoring of phase transformations in the frozen samples of solutions of small organic molecules (nitrogen bases and organic dyes) in formalin by means of low temperature secondary emission mass spectrometry is described. The mass spectra of frozen formaldehyde solutions contained sets of peaks corresponding to POM oligomers incorporating up to 11 monomers and their hydrates. On thawing of the frozen samples the decrease of viscosity, melting, dehydration and subsequent solidification of the sample layer were reflected in the characteristic changes of the spectral pattern, that is the peaks distribution and their relative abundance. The incorporation of the intact organic molecules within the polymeric structure was evidenced by the corresponding peaks of their molecular ions. This result confirms, that phase separation does not take place on cooling and freezing of formalin and the dissolved small organic molecules are trapped between the growing POM oligomers. Thus, the desirable effect of immobilization of small biomolecules and dyes in POM films is achieved. No noticeable chemical modification of small molecules under study by formaldehyde was observed under the conditions applied, although possible toxic effects of formaldehyde are to accounted in further work with biological objects.

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FRET study of M13 major coat protein: simulation-based fitting approach

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The geometry determination of membrane proteins is still at the frontier of the structural biology. The complexity and delicacy of membrane-protein systems substantially impede the application of standard methods of protein study, such as X-ray crystallography and NMR [1]. As a successful alternative to named techniques, the Forster resonance energy transfer (FRET) spectroscopy was proposed [1, 2]. However, the complexity of protein-lipid systems hampers and limits the analytical interpretation of FRET data. On the other hand, the simulation modeling of photophysical processes in the experimental system during a fluorescence measurement was proved to be a powerful alternative to analytical modeling, not restricted to special conditions [3].

The goal of the current work is developing and testing the methodology for fluorescent data analysis and simultaneous determination of membrane protein geometry and protein-protein aggregation by the means of steady-state FRET experiments. To perform this goal the model of the energy transfer in a protein lipid system was built. It includes the simplified structural model of a proteinlipid system and steady-state FRET simulation. The developed model is applied to experimental data analysis via the simulation-based fitting approach, which intend approximation of the experimental FRET data by their simulated analogues.

The developed methodology was tested on a well-known bacteriophage M13 major coat protein [4]. Different Cys mutants of this protein were produced and specifically labeled with AEDANS. By observing the energy transfer from natural Trp26 to AEDANS and application the simulation-based fitting approach the structural parameters of the protein were determined and the protein-protein aggregation characterized. The found values of structural parameters are in a good accordance with previously reported ones, obtained from ESR experiments and fluorescence polarity probing [4]. The main advantage of the proposed technique is a simultaneous determination of parameters describing protein state in a bilayer by only one series of experiment.

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Combining the thermally stimulated luminescence and the thermally stimulated current studies in conjugated polymers

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Thermally stimulated current (TSC) controlled by thermal release of excess charge carriers (holes) from intrinsic traps in a conjugated polymer poly(9,9bis(2-ethylhexyl) fluorene-2,7-diyl) (PF2/6) has been studied at different readout voltage applied during the heating run. We found that TSC peak measured at low applied electric field is located at somewhat higher temperature than the thermally simulated luminescence (TSL) detected in this material; however the TSC peak shifts towards lower temperature with increasing read-out voltage and at high electric fields approaches the temperature spectra of TSL. The present work is aimed to get deeper insight into a possible origin of discrepancy between TSL and TSC temperature spectra in the studied PF2/6 conjugated polymer which is chosen in the present work as a model system where the TSC definitely is not affected by charge pair dissociation. The low temperature TSC peak in PF2/6, being measured after photoexcitation at sufficiently large positive load voltage, depends on read out voltage was found. The shift of TSC peak is not accompanying with substantial increase of TSC intensity usually observed in TSC of organic solids, which implies absence of recombination of liberated charge carriers, whereas such behaviour of TSC peak is most probably a manifestation of thermally stimulated dispersive transport of holes in the polymer. We formulated the model of dispersive TSC, which consider the partial filling of deep traps. Results of calculations agree well qualitatively with the experiment. Possible implication of dispersive character of TSC for evaluation of the energetic distribution and spatial concentration of traps from TSC data is analyzed.

FTIR spectroscopic and STM studies of novel polymer thin films: poly(naphtalimidphenylacrylate) deposited on gold surface

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Since organic electronic materials are now widely used in many nano-structured electronic devices, the properties of organic thin films and interfaces attract much interest. The characteristics of devices using thin organic films depend strongly on the molecular structure and orientation of the films. In the present work, we investigated for the first time the molecular structure and orientation of pendant groups at the surface of poly (naphtalimidphenylacrylate) (PNIPhA) thin films using FTIR adsorption and reflection spectroscopy as well as STM. The compound PNIPhA, synthesized in this work, belongs to the class of donor-acceptor polymers having a good electron and hole transport ability. Polymers of this class have also potential use for light-emitting device (LED) applications, since they enhance LED emission as well as provide for color tuning. LED technology employing polymer thin films makes possible the electronic interactions between the neighboring chains in the film and the creation of new excited states. Hence, the interfacial properties of the individual layers in the devices, as well as polymer-metal interface interactions, should be studied. In this communication we focuse on FTIR spectroscopic and STM studies of the structure of PNIPhA thin films deposited by thermal evaporation in vacuum on gold substrates. The thickness of the vacuum deposited (VD) films varied from 35 to 120 nm. The FTIR transmission and reflection-absorption spectra of the initial compound and of VD thin films were measured with Bruker IFS-88 FTIR spectrometer in the 380-4000 cm-1 spectral range. Spectroscopic characterization of the VD PNIPhA films showed no evidence for impurities or degradation of the initial compound during its thermal evaporation in vacuum. The differences in the peak intensities of particular bands observed between the transmission and RA spectra of the VD films on gold may suggest either that the pendant groups of the polymer are oriented at a particular angle to the substrate or that the interchain interaction in the films plays a significant role. STM study showed that the VD thin PNIPhA films consisted of rather large clusters 100

nm in size. The chains of smaller clusters of about 10 nm in diameter were also clearly seen on the large grains. Local current-voltage characteristics measured for nano-sized areas within individual organic grains have a shape symmetrical relative to the polarity of applied voltage. At voltages above 0,5 V, the characteristic becomes superlinear, which is typical of the most organic films. This work was supported in part by Ministry of Education and Science of Ukraine (Project No M/230-2004).

Spatial structure and energy transfer in synthetic nucleic macromolecules

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Correlation of transfer effectiveness with temperature was observed during investigation of direct excitation transfer in π -electron containing molecular systems. There were some situations when it disappeared. We think it happens when molecules spatial structure changes in such way that the energy transfer is impossible.

For estimation of energy transfer effectiveness we use classical Forster-Dexter theory of sensitized luminescence. There are 3 the most effective additive energy transfer ways: dipole-dipole, dipole-quadrupole interactions and additional exchange effects, which represent electrostatic interaction between the two charge clouds of donor and acceptor. We analyze them separately in order to investigate what way is most relative to spatial structure. We dont take into account through-bond interaction because the distance between π -electron systems of donor and acceptor is less than nanometer.

The primary task was to understand the spatial structure of investigated molecules. We use molecular mechanics and semi-empirical methods for this task. We model molecules spatial structures in vacuum and in water surroundings in order to understand wagging of solvent on delocalization of molecular orbitals and consequently on interaction mechanisms. It was calculated overlap weighting factors for π - π electrons in order to normalize UV spectra, connecting to experimental data.

Investigated synthetic macromolecules were synthesized from nucleo-tides. So, these investigations are simplified. They may be used for explanation interaction ways between DNA or RNA and drugs molecules. These investigations are applicable for practical use, because there is need to know the majority way of interaction.

Conformation transitions in polyA·polyU complexes with Cd²⁺ ions, studied by UV-VIS spectroscopy

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In spite of the strong evidence for the carcinogenic activity of cadmium, the underlying molecular mechanisms that lead to malignant transformation in cells exposed to cadmium remain unknown. Because its DNA-damaging potential is rather weak (A.Hartwig et al. Environ Health Perspect (2002)), it is interesting to study a cadmium interaction with nucleic acid noncanonical structures being of biological significance. The double (polyA·polyU) and triple (polyA·2polyU(A2U)) helices are used as a model structures.

Due to great complexity of heating- and Cd²⁺-induced conformational transitions in polynucleotides of different levels of structural organization, efforts to modify the method of differential UV(DUV)-spectroscopy were made. To identify possible conformational transitions with unclear disproportionality characteristics, thermally induced DUV spectra of polyA·polyU (AU) and A2U were measured in the interval (20-92)°C. These spectra permit to observe behaviour of polymer extinction upon conformational transformations in some characteristic points simultaneously. Destruction of the ordered helical structure (hyperchromic effect) was traditionally registered at the spectral absorption maximum of the polymer ($\nu \sim 38500 \text{ cm}^{-1}$). Formation of triple and double helices were recorded at $\nu \sim 35700 \text{cm}^{-1}$ and 35273 cm^{-1} , respectively. Aggregation and condensation processes in polynucleotides were observed in the visible region of the absorption spectra.

UMP absorption spectra do not change up to $3 \cdot 10^{-2} \text{ Cd}^{2+}$ that evidences the ion interaction only with the nucleotide phosphate group. N7 and N1 are atoms coordinating Cd²⁺ in AMP and polyA. In the range $2 \cdot 10^{-4} \leq [\text{Cd}^{2+}] < 10^{-3}$ this interaction type results in disordering of polyA helical parts. At $[\text{Cd}^{2+}] \geq 10^{-3} \text{ M}$ intramolecular condensation of polyA and polyU into a highly-ordered structure is observed that follows from strong hypochromicity of absorption spectra at $\nu \sim 40000 \text{ cm}$ -1. These particles are of high thermal stability and destruct at temperatures $\sim 80^{\circ}\text{C}$, forming light-scattering intermolecular aggregates. The chelate complex N7-Cd²⁺-O(P) is the main type of interaction in A·U double helix. Cd²⁺ binding to A·2U phosphates leads to restoration of the helical structure of disordered triplex parts. The character of the heating-induced conformational transition in A·2U changes with the $[\text{Cd}^{2+}]$ content: two subsequent transitions A·2U \rightarrow A·U+U \rightarrow A+U+U take place in the region 10^{-6} - $4 \cdot 10^{-4}$; at $[\text{Cd}^{2+}] > 4 \cdot 10^{-4}$ single-stage unwinding of the triplex into single strands A·2U \rightarrow A+U+U is observed.

Detection of Mg²⁺-induced highly-cooperative conformational transition in poly I poly C

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Interest in metal complexes of polynucleotides of different structures and contents is conditioned with a problem of environmental contamination with metal salts. This problem is especially urgent in Ukraine economics of which is significantly based on ferrous and nonferrous metallurgy.

Materials: Potassium salt of double-stranded poly I·poly C (IC), MgCl₂ ·6H₂O, cacodylate buffer (pH7, 0.001M Na⁺), NaCl (0.099M).

Method: Differential UV spectroscopy.

Results: The increase of the IC thermal stability is observed in the range of small magnesium contents but when the Mg²⁺ ion concentration reaches its critical value ($[Mg^{2+}]_{cr} \sim 10^{-4}M$), the IC melting temperature decreases about unevenly.

As a result, two melting temperatures differing by ~8°C correspond to the same value of the magnesium concentration. It is supposed that, as in the case of AU, at this concentration the transition $2(IC) \rightarrow C2I+C$ (the 2 \rightarrow 3 transition) takes place. Upon the further increase of the magnesium content, the thermal stability of the polynucleotide rises again. This change in T_m corresponds to the C2I \rightarrow I+I+C transition (the 3 \rightarrow 1 transition). Correlation is observed between changes in the melting temperature and in the value of hmax (h_{max} is the hyperchromic coefficient of IC absorption at ν =40300 cm⁻¹, induced with heating of its solution from 20 to 92°C). So, the value of hmax decreases but at [Mg²⁺]~[Mg²⁺]_{cr} rises again reaching a magnitude close to the value of h_{max} at [Mg²⁺]=0 ((h_{max})₀ = 0.82÷0.03).

As the value of h_{max} is proportional to the initial degree of the polynucleotide helicity, the data obtained permit to conclude that Mg²⁺ ions induce its lowering at [Mg²⁺] < [Mg²⁺]_{cr}. This result agrees with the data of [1], according to which, hydrated Mg²⁺ ions interact not only with phosphates but also with π -electrons of rings of polynucleotides nitrogen bases (the cation- π interaction). The last leads to disordering in stacking of bases [1].

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Comparative analysis of Ni²⁺ ion effect on conformational equilibrium of three-stranded helices A2U and A2I

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Interest in three-stranded polynucleotides has been generated with a possibility of their application in treatment of viral, inherited and oncological diseases.

The aim of the work: To get information on effects of temperature and the concentration of ions of carcinogenic and mutagenic nickel on conformations of three-stranded poly U·poly A·poly U (A2U) and poly I·poly A·poly I (A2I).

Materials: A2I, A2U and their components poly A, poly U, poly I, AMP, UMP and IMP. Aqueous solution of acetate and cacodylate buffers (pH $6\div7$, $0.03\div0.1M$ Na⁺).

Methods: Differential UV- spectroscopy and thermal denaturation.

Results: In polynucleotides and single-stranded structures N7 of pyrines are atoms coordinating Ni²⁺ ions. But in A2U, N7A is included into the system of hydrogen bonds that makes it inaccessible to bind to Ni^{2+} . Therefore, Ni^{2+} effect on the A2U conformation is similar to Mg^{2+} influence: only binding to phosphates of A2U takes place, not changing its structure. Upon heating, two stages of A2U disruption are passed through: A2U \rightarrow AU+U (the $3\rightarrow$ 2 transition) \rightarrow A+U+U (the 2 \rightarrow 1 transition). Ni²⁺ ions increase the thermal stability of A2U and AU in the whole range of ion concentrations. In this case the interval of the $3\rightarrow 2$ transition is 3 times larger than that of the $2\rightarrow 1$ one . It is caused by the fact that enthalpy of the $3\rightarrow 2$ transition is significantly lower than for the $2\rightarrow 1$ transition. The increase of the A2U and AU thermal stability observed in the ion presence is mainly conditioned with a difference in the nickel binding to multi-stranded helices and poly U. Accessibility of N7 of hypoxanthine (H) in A2I polyinosinic chains leads to the formation of macro- $(N7H-Ni^{2+}-PO_{4}^{-})$ and inner $(N7H-Ni^{2+}-O6H)$ chelates. The last chelate induces a partial destruction of A2I triplexes even at room temperature and to a decrease of the polynucleotide thermal stability observed at [Ni²⁺]>0.0002M. In this case cooperativity of heating-induced melting of A2I decreases continuously. These effects are conditioned with a preferential nickel binding to single-stranded poly I (in comparison with an interaction with A2I) and with an entropy rise due to the increased number of binding sites upon the destruction of the triple helix. A2I melting, unlike that of A2U, is a single-stage process: $A2I \rightarrow A+I+I$ (the $3 \rightarrow 1$ transition).

Spectroscopic study of poly(rA) and poly(dA) complexes with $(dT)_{14}$ modified by imidazophenazine dye

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Fluorescent nucleoside analogues incorporated into antisense oligonucleotides instead of the natural nucleosides are used as effective fluorescent probes in the study of structure and dynamics of nucleic acids due to definite fluorophore location [1]. In the frame of this conception we studied the imidazo(4,5-d)phenazine N1- β -D ribofuranoside (Pzn) which can be built into oligonucleotide chain like a usual nucleoside. Besides, the intercalative capability of the dye chromophore [2] can be realized in stabilization of antisense oligonucleotide hybridization. These properties of the Pzn we have investigated on model systems of oligothymidylate interacting with poly(rA) and poly(dA).

The imidazo(4,5-d) phenazine N1- β -D ribofuranoside was covalently attached to 3'- end of (dT)₁₄ via a ribose residue of dye ((dT)₁₄Pzn). The investigations were carried out using buffered solutions, pH 6.9, containing 0.1 M sodium ions.

It was shown earlier by the titration method [2], that upon the interaction of Pzn with poly(rA) its fluorescence was quenched. Now we have investigated the temperature dependence of Pzn - poly(rA) as well as Pzn - poly(dA) complexes stabilities and have found thermodynamic parameters of binding. The formation of duplex complex of $(dT)_{14}$ Pzn with both poly(rA) and poly(dA) was followed by thermal denaturation method with registration by UV-absorption and fluorescence. It was shown that the attached Pzn substantially enhanced the thermal stability of duplex complexes formed by poly(rA) and poly(dA) with $(dT)_{14}$ increasing the temperature of transition midpoint by 6-7 °C. Thermodynamic parameters of the modified and unmodified complexes were obtained using simple two-state model. Values of transition enthalpies and entropies were evaluated from the concentration dependence of the melting temperature and analysis of the shape of absorption melting curves. Molecular modeling method was used to construct geometries of free and covalently attached Pzn incorporation into both poly(rA) and poly(dA) strands. They turned out to be in conformity with the quenching of the Pzn fluorescence.

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Reactions in dense nonstationary microsystems

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We investigate particle reactions in dense microsystem where particle motion can be expressed in terms of space-time localized quantum states.

Such a short lived system is created in relativistic heavy nuclei collisions.

Due to the dense hadron environment, the pions and quarks produced during a collision emerge as localized quantum states which finite lifetime is scaled as the lifetime of the system.

The medium-induced modifications of the pion-pion and quark-quark annihilation reactions which result in lepton pair production are analyzed.

Spectral properties of some biological tissues

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A difference between fluorescence spectra of sound and affected tissues of internals of mammals opens up possibilities for luminescent diagnostics of tumour diseases. The advantages of that kind of diagnostics consist in its being non-invasive, proximate and timely, which allows one to reveal a disease at an early stage of its development.

In this work we studied the fluorescence spectra of the rat stomach and liver tissues as well as the human stomach tissues *in vitro*. The aim was to elucidate the nature of intrinsic fluorescence centers in the tissues in order to examine the possibility of realization of a technique for fluorescent diagnostics of human internal diseases.

The fluorescence was excited by radiation of a pulsed UV-laser with a wavelength of 337 nm at room temperature. Two bands with peaks at 390 and 480 nm are distinguished in the sound rat tissue spectra while only one band at 420 nm is revealed in the human tissue spectra.

Also studied is the dependence of fluorescence spectra on the time that passed after the tissue preparation. It is found that the band intensities decrease with time, which indicates a decay of corresponding molecular centers.

It is proposed that the 480 nm band may be attributed to the presence of NADH molecules in the cells of tissues under study, the content of the former in the tissue decreasing as its vital functions terminate. The two other bands at 390 and 420 nm may be due to pyridoxine and elastin molecules, respectively. It is supposed that decrease in the fluorescence band intensities with time that passed after tissue preparation is caused by irreversible oxidation of the respective molecules, while for the NADH molecule by its transition to the NAD+ form which does not exhibit any noticeable fluorescence.

0.7 BIOMOLECULES AND POLYMERS

Investigation of interaction actinocin derivatives with DNA by the methods of spectrophotometry and Raman spectroscopy.

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The binding ways of drugs to DNA and polynucleotides are various for different ligands. The types of DNA-ligand complexes are strongly influenced by the spatial pattern of drugs. In present study complexation of new actinocin derivatives with DNA were investigated by the methods of spectrophotometry titration and Raman spectroscopy. The side chains of examined ligands are different.

No differences in ultraviolet and visible absorption spectra of examied ligands were observed. However, the comparison of concentration dependences at the same wavelengths showned, that 1200 formed more number of aggregates than 11299. Binding parameters (the binding constants and values of the site sizes) were obtained from the Scatchard isoterms. The similarities and differences of Raman spectra of free and bounded to DNA ligands were analysed. The atom groups of actinocin derivatives participating in complexation have been determined by the analysis of Raman spectra. Possible models of ligand binding with DNA matrix are discussed.

Complexation of daunomycin with the self-complementary deoxyhexanucleotide, d(GCTAGC), in aqueous solution: 1D- and 2D-NMR analysis

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500 MHz 1D- and 2D-1H NMR spectroscopy have been used to determine the structural and thermodynamical parameters of self-association of the deoxyhexanucleotide, d(GCTAGC) and its complexation with the anthracycline antibiotic daunomycin (DAU).

Thermodynamical parameters (enthalpies H, entropies S) of the self-association of the hexamer have been determined from the concentration and temperature dependences of the proton chemical shifts of the hexamer. It is worth noting that extrapolation of the concentration dependences to zero concentration results in substantially lower values of the proton chemical shifts with respect to their values measured at high temperatures, when it may be assumed that the hexamer exists practically in the single-stranded state. This conclusion is not consistent with the normal monomer-duplex two state model. It may be assumed that the observed differences of the concentration and temperature curves are due to formation of a compact structure (similar to a hairpin) in the single-stranded deoxyhexanucleotide d(GCTAGC), with the magnetic shielding of the protons close to that in the hexamer duplex.

Molecular mechanics calculations using X-PLOR, NAMD software and Charmm 27 force field confirm that the single-stranded hexamer d(GCTAGC) can adopt a rather compact conformation, the value of the energy minimum for the folded structure of this hexamer is lower than that for the isomer sequence, d(GCATGC), studied earlier [1]

A quantitative determination of the complexation parameters of DAU with the oligonucleotide was based on analysis of the chemical shift dependences of the ligand non-exchangeable protons on concentration at different temperatures and on temperature. The experimental results were analysed in terms of the equilibrium reaction constants, limiting proton chemical shifts and thermodynamical parameters of different drug-DNA complexes.

The most favourable structure of the DAU-hexamer intercalated complex has been determined taking into consideration both intra- and intermolecular NOE contacts in the complex. The calculations show that the DAU chromophore is oriented nearly perpendicular to the base pair axis of the double helix of the hexamer duplexes, which is similar to that found for other intercalated complexes of DAU with hexamers [2]. The sequence-specificity and thermodynamics of intercalative binding of DAU with other self-complementary oligonucleotides, including tetramer and hexamer duplexes studied under the same experimental conditions, is discussed.

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NMR and molecular mechanics investigation of sequence-specifity of daunomycin binding with deoxyhexanucleotides

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Daunomycin (DAU) is a prominent member of the anthracycline antibiotics, a class of compounds that possesses anti-cancer activity. The chemo-therapeutic efficacy of DAU has been attributed to its intercalative binding with DNA, resulting in inhibition of DNA replication and RNA transcription. In contrast to other DNA intercalating drugs, it was suggested previously that DAU does not show pronounced sequence specificity, though more recent work based on theoretical calculations and solution studies show contradictory results [1, 2].

In this work 500 MHz NMR spectroscopy has been used to investigate the complexation of DAU in aqueous solution with self-complementary deoxyhexanucleotides of different base sequence; viz. d(CGCGCG), d(TAC-GTA), d(GCATGC) and d(CGTACG). 2D homonuclear 1H NMR (TOC-SY and NOE-SY/ROESY) and 1H-31P NMR spectroscopy (HMBC) have been used for complete assignments of non-exchangeable proton and phosphorus signals, respectively, and for a qualitative determination of the preferred binding sites of the drug. A quantitative determination of the complexation of DAU with the hexanucleotides has been made using experimental concentration and temperature dependences of the drug proton chemical shifts; which have been analyzed in terms of equilibrium reaction constants, limiting proton chemical shifts and thermodynamical parameters (enthalpies Δ H, entropies Δ S).

A comparison of the complexation parameters of DAU with the deoxyhexanucleotides shows preferential binding of DAU with the 5'-d(GCA) triplet compared with other sequences; analysis also shows that there is some sequence specificity for intercalation at d(GC) compared to d(CG) sequences in the terminal sites of the hexamers.

The energy parameters of different interactions of DAU with the hexamer duplexes were studied by molecular mechanics calculations using X-PLOR software and the Charm22 force field. The most favorable structures of the DAU-hexamer intercalated complexes have been calculated by taking into consideration the induced limiting proton chemical shifts of the drug in the intercalated complex as well as both the intra- and intermolecular NOE contacts.
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1H NMR study of the hetero-association of caffeine with anthracycline antibiotics

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It has been shown previously that a typical methylxanthine, Caffeine (CAF), is a mediator of biological activity of a number of aromatic mutagenic dyes and anticancer antibiotics [1]. The action of CAF has been explained both by its hetero-association with aromatic drugs and competitive binding of CAF and Drug with a DNA molecule in the cell [2]. It follows that investigations of hetero-association are necessary to elucidate the molecular basis of the action of aromatic compounds, as mediators of the pharmacological activity of drugs and as protectors of DNA from binding with mutagenic aromatic molecules.

In the present work the hetero-association of Caffeine with the anthracycline antibiotics, Doxorubicin (DOX) and Nogalamycin (NOG), in aqueous solution has been investigated analysing the concentration and temperature dependences of 1H NMR chemical shifts of the interacting molecules using a statisticalthermodynamical model of molecular hetero-association [2]. The model provides the magnitudes of equilibrium hetero-association constants, the enthalpy and entropy of the association reactions and the induced proton chemical shifts in the 1:1 hetero-complexes of CAF with DOX or NOG.

Analysis shows that the parameters of complexation of CAF-Antibiotic fall between the corresponding quantities for self-association of CAF/ DOX/ NOG. The same conclusion has been reported previously for complexation of CAF with other aromatic drug molecules (including the Doxorubicin analogue, Daunomycin) [2], indicating stabilization of the hetero-complexes by stacking interactions of CAF with DOX/ NOG. However, both the CAF-NOG and CAF-DOX interactions are characterized by an elevated value of the hetero-association constant, as well as lower absolute value of entropy with respect to CAF-Daunomycin hetero-association [2], which is consistent with more significant contribution of hydrophobic interactions in the CAF-NOG/ DOX complexation compared with the CAF-Daunomycin system.

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Non-covalent interactions of flavine-mononucleotide with aromatic drug molecules studied by NMR

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² Department of Physics, Sevastopol National Technical University, Ukraine Dedicated to the memory of Prof. Alexei Veselkov, friend and collaborator in research for many years

Riboflavine (RBF) is a Vitamin that is widely used to treat various human diseases and reduce some undesirable consequences of chemotherapy. Several studies are available in literature reporting a change of biological activity of certain aromatic drugs being given simultaneously with Riboflavine or its analogues. For example, the toxicity of some anticancer antibiotics and aromatic mutagens changes significantly in the presence of RBF, which has been explained by formation of complexes between them in vivo [1]. It follows that the heteroassociation between aromatic Vitamins and aromatic drugs (Antibiotics and Mutagens) can play a crucial role in regulation of the medico-biological activity of aromatic drug molecules in vivo.

In the present work, the hetero-association of a Riboflavine analogue, Flavinemononucleotide (FMN), with different aromatic anticancer antibiotics, Daunomycin (DAU), Nogalamycin (NOG), Novatrone (NOV), Actinomycin D (AMD), and aromatic mutagens, Ethidium Bromide (EB) and Proflavine (PF), has been studied by means of 500 MHz 1H NMR spectroscopy and molecular mechanics calculations. The concentration and temperature dependences of proton chemical shifts of the interacting molecules and two-dimensional through-space correlation spectroscopy (NOESY/ROESY) were used to determine the structural and thermodynamical properties of the Vitamin-Drug complexation in aqueous solution. Induced chemical shifts, equilibrium constants and enthalpy/entropy of the hetero-association reactions have been obtained using the BASE model approach [2].

Analysis of the structural and thermodynamical parameters of Vitamin-Drug hetero-association is consistent with a sandwich-type aggregation of aromatic molecules in solution, characterized by parallel alignment of the chromophores of the molecules in the complexes. The hetero-complexes are mainly stabilized by stacking interactions involving dispersive van der Waals and hydrophobic interactions of aromatic chromophores. The presence of an intermolecular H-bond in the hetero-complexes is consistent with additional stabilization of the complexes of FMN with EB/ PF/ NOV/ AMD observed by the elevated magnitudes of the thermodynamical parameters, and with intermolecular NOE contacts observed in 2D spectra. In general an effective intermolecular association between FMN and the Mutagens or Antibiotics supports the idea that the toxicity of aromatic drug molecules may be altered in vivo in the presence of the Vitamin.

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The Manifestation in Raman Spectra of the Influence of Berberin on the DNA Molecules

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The problem of elucidating of the mechanisms of interaction between the DNA molecules and other macromolecules, in particular, of the antitumour agents, is the very actual now. Here we report about the manifestation in Raman spectra of the influence of berberin on DNA molecules (DNA of erythrocytes of kitchen). Berberin and its preparations now have aroused particular interest because of its wide range of antitumour activity. We have obtained Raman spectra of the DNA water solution (40-50 mg/ml) in the region of $500 - 1800 \ cm^{-1}$ firstly at excitation of the $\lambda = 5145$ Å line of the Ar-laser. Since the intensity of scattering was very weak, we had to work in mode of time accumulation (10-12 passes). Besides, the obtained spectra must be treated specially by some computing programs. After that treating the spectra were identified reliably. So Raman spectra of DNA of kitchen erythrocytes were obtained for the first time. Raman spectrum of the berberin powder was obtained at 6328 Å excitation of the He-Ne-laser (berberin is yellow) in the area of its vibration modes $(1000 - 1700 \ cm^{-1})$, but the spectrum of the saturated water solution of the berberin we could not obtain and identify trustworthy. Reliable Raman spectra of DNA solutions at 6328 Å excitation were not obtained too because of the small power of the He-Ne laser. But a very interesting result was gained for the mixture solution of the DNA and berberin at 6328 Å excitation. The intensity of the DNA and berberin lines increased greatly over the whole area of overlapping of regions of the DNA and berberin vibration modes $(1000 - 1700 \ cm^{-1})$, the spectra are identified reliably. Out of the range of berberin vibrations the DNA Raman lines were kept weak and could not be identified. Now we can not explain such resonance interaction between the DNA molecules and berberin, but the problem is under further study. From the preliminary calculations performed by the mathematics modelling methods follows that berberin molecules build in the major groove of the DNA molecule.

Binding of antibacterial antibiotic norfloxacin with DNA oligomer in presence of caffeine studied by NMR

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It is known that the efficacy of drugs can be changed if they are used in combination with other biologically-active molecules. For some aromatic drugs the major molecular mechanisms of this phenomenon are assumed to be heteroassociation of aromatic molecules and their competitive binding to receptors such as DNA [1].

Aromatic antibiotic Norfloxacin (NOR) is a synthetic antibacterial drug showing broad spectrum of antibacterial activity which has found a wide application in clinical practice. Biological activity of NOR is often related to its ability to bind with DNA [2] as well as to form complexes with xanthines such as Caffeine (CAF) [3]. In the present work we studied the interactions of NOR with CAF and with a model DNA oligomer 5-d(TpGpCpA) in aqueous solution (0.1M Na-phosphate buffer, T=298K, pD 7.1) by means of 1H NMR spectroscopy (500 MHz). Equilibrium constants, enthalpies and entropies of complex formation were obtained which enabled the binding of NOR with the oligomer in the presence of CAF to be quantitatively evaluated.

The results on antibiotic-caffeine interactions evidence a formation of p-p type NOR-CAF complexes in solution stabilized by planar stacking interactions of aromatic chromophores in the hetero-complexes. Based on NMR data an intercalation-like interaction of NOR with the oligomer duplex was proposed.

By using the calculated values of equilibrium complexation constants a relative contribution of the hetero-association of NOR-CAF and complexation of CAF-d(TGCA)2 to the decrease of NOR binding with the oligomer was estimated. It was found that under physiological interrelation between the NOR (mM) and CAF (mM) concentrations both processes contribute to the modification of the NOR-DNA interaction depending much on the concentration of CAF and DNA in solution.

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The Luminescent Manifestation of the DNA – Amitozine's Alcaloid Interaction

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The complete understanding of the therapy mechanism action of drugs is impossible without studies of the interaction of these compounds with biological objects on the molecular level. In our work some results of the investigations the DNA – amitozine (plant origin - *Chelidonium majus L.* - drug with anticancer and immune modulation properties) are presented.

The absorbtion, fluorescence and phosphorescence of amitozine were studied in water solution without and in presence of the DNA. The fluorescence maximum amitozine without DNA depends on excitation wavelength but fluorescence maximum amitozine in presence DNA doesn't depend. Simultaneously the fluorescence intensities increase approximately 10 times. This phenomenon is connected, to our opinion with the adsorption one of the one amitozine's alcaloid on the DNA macromolecules (amitozine molecule consists from several alkaloids).

According to our investigations the triplet excitations in DNA are localized mainly on amitozine's alkaloid - berberine (the phosphorescence spectra DNA+berberin are very close to berberine water solution spectra). It was obtained from studies of the phosphorescence dependence of DNA+berberine solution on berberine concentration, that average value of the triplet excitation displacement at least reaches the 20 base sequence length (7 nm).

The data obtained open the way to establish the molecular mechanism of the amitozine therapeutic action.

About the possibility of application of microwave reflection in medicine diagnostics

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One of the main parameter for an electromagnetic emission interaction with different objects is a reflectivity coefficient at the boundary between air and a body influenced by the radiation. It is of a great practical interest to use the microwave reflectivity coefficient from biologically active points on a skin, sensitive to pathological changes in organs and tissues, as a diagnostic parameter.

In this report, methods and results of measurements of the reflectivity power coefficient $|\Gamma|^2$ in the range of 54 ÷ 78 GHz for some parts of a human body are given. Optimally consistent waveguide systems in direct contact with the body were used for microwave reflectivity coefficient measurements from the human body in an open space.

The measurements show that the values of $|\Gamma|^2$ for the most parts of a body do not exceed 0.1. Respectively, an absorption capability A of a human body in a millimetre diapason approaches to 1, so more than 90% of the emission power are absorbed.

The research results give an evidence of an individual character of a person respond to the external microwave emission and that is a reason for optimistic forecasts for applications of microwave reflection in medical diagnostics. In particular, the values of $|\Gamma|^2$ from different parts of one person body and from relative parts of bodies of different persons definitely differ from each other, change in time and depend on a skin state.

Small values of the reflectivity coefficient from a human body, observed in the experiments, are due to the fact that skin layers having the lack of water near the surface play the role of an "antireflection" wideband transformator of wave impedances that facilitates the penetration of the microwave emission in a human body without large reflection.

Application of ATR-IR spectroscopy to nucleic acid films

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To our knowledge, in literature there is no example of ATR-IR spectroscopy application to nucleic acids, despite variety of molecular and supramolecular objects were investigated by this method. In our efforts to use ATR-IR spectroscopy for dry DNA and RNA films we became certain that main obstacle to application it to investigation of these patterns is connected with difficulties in removing films from the working surface of germanium prism (internal reflection element) without damage. Special buffer (our finding), being somewhat heated, permitted us to cope with this problem. ATR-IR spectroscopy, combined with molecular biological methods, was used to prove that RNA, unlike DNA, binds to aurintricarboxylic acid via valence bond under procedure of their isolation from biological materials. Attempts to solve this problem by traditional IR spectroscopy has turned out a failure. Our result allow to study ATR-IR spectra of nucleic acids, their constituents and complexes with their natural and unnatural ligands. ATR-IR spectroscopy seems to be perspective in molecular biology and biophysics of nucleic acids, as well as in pharmaceutics and medicine.

Molecular Structure of Beta-D-Glucosylated Thymine

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The molecular structure and relative stability of conformers of hyper-modified nucleoside Beta-D-Glucosylated Thymine [1] and corresponding nucleotide (Beta-D-Glucosylated Thymine-5-monophospahte) have been obtained and analyzed at the DFT/B3LYP level using the 6-31++G(d, p) basis set. Baders Atoms in Molecules (AIM) theory [2] have been applied for analysis of intramolecular hydrogen bonds.

In the nucleoside and the nucleotide the formation of multiple additional intramolecular hydrogen bonds in comparison with canonical nucleoside has been observed. The formation of intramolecular hydrogen bonds between modified nucleotide and neighboring bases is possible. Additional intramolecular hydrogen bonds could stabilize B-conformation of DNA containing this hypermodified nucleotide.

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Spectral investigation of the slow-electrons inelastic interaction with nucleic acid bases

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The study of low energy electrons interaction with biomolecules is of particular interest not only for physics, but also in biomedical and ecological applications. Such investigations allows one to obtain the information unreachable by using other methods. In the present work we report on the results of spectral and mass-spectrometric studies of slow electrons collisions with nucleic acid bases molecules.

Investigation were carried out using crossed electron and molecular beam method. The experimental setup consists of such principal components as: molecular and electron beam sources, collision chamber, vacuum system, photon and ion detection systems. The molecular beam was obtained using special microchannel source, the electron beam – by means of five-electrode electron gun. The energy of the monoenergetic electron beam was varied in the 0,3-300 eV range. The molecules concentration was determined directly in experiment and was equal to $8 \cdot 10^{10}$ cm⁻³. The electron beam current was about $2 \cdot 10^{-6}$ A with an energy spread of $\Delta E_{1/2} \sim 0.3$ eV (FWHM). The electron gun was located in lengthwise magnetic field with induction $1,2 \cdot 10^{-2}$ Tl. The energy scale was calibrated using SF₆⁻ anions recorded in the same experimental conditions. The peculiarity of this experimental setup is the possibility of analysis not only radiation but also the positive and negative ions.

The emission spectra of the nucleic acid bases molecules excited by electron impact were obtained within the 200-600 nm range. This spectra have the compound structure, noticeably to differ from the photoexcitation ones. The excitation functions (the energy dependences of the excitation cross section) of biomolecules were measured in the electron energy range from the threshold up to 300 eV. Compound spectra are the results of various physical processes that take place simultaneously at the electron interaction with biomolecules. First of all, there are the direct excitation of singlet and triplet molecular levels and dissociative excitation too. The ionization function (for positive and negative ions) and threshold features are investigated. The absolute value of the cross sections positive and negative ions formation of the nucleic acid bases molecules was found in the direct experiment for the first time using our original technique. For example, the energy dependence of the effective cross sections for cytosine negative ions formation has the distinct resonance at 1.5 eV electron energy. Maximal ionization cross section is $4.2 \cdot 10^{-18}$ cm² and include the cross sections of the negative ion formation both for the whole molecule and its fragments. It is important, that probable damage of the nucleic acid molecules at low electron energy would have a place in consequence of the resonant, practically nonthreshold mechanism of the negative ions formation. The absolute value of the cross sections for positive cytosine ions is $7.8 \cdot 10^{-16}$ cm².

Thus, the physical processes (excitation, ionization, dissociative excitation and dissociative ionization) induced by low-energy (0,3-300 eV) electrons were investigated in the nucleic acid base molecules. Biophysical and radiological consequences of the inelastic processes caused by electron impact in biomolecules were analyzed.

Local parametrizaiotn in modified Karlpus equation for steroid molecules

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Most important application of NMR spectroscopy in conformational analysis of molecules in liquid is found on well-known dependence of vicinal coupling constants ${}^{3}J_{ij}$ on dihedral angles θ_{ij} [1]. Correct determination of θ_{ij} values on base experimental coupling constant data ${}^{3}J \stackrel{exp}{ij}$ is substantially hampered because in general the magnitude of scalar coupling constant ${}^{3}J_{H-H}$ in ethane fragment $R^1 R^2 H_i C_i ? C_j H_j R^3 R^4$ besides θ_{H-H} depends also on electronegativity of α - and β -substituents, valence angles H-C-C, bond length C-C and throughspace interaction between the closest non-bonded groups [2]. During last years some some modified Karplus equations on base Mullay's group electronegativity approach [3] and different additive calculation schemes were applied and widely discussed to improve the accuracy of calculated vicinal spin-coupling constant calccalc ${}^{3}J H - H$ and dihedral angle values $\theta H - H$. As a rule the knowledge of some empirical parameter values is needed for successful application of these calculations.

In this report the differences between experimental and calculated vicinal coupling constant $\{{}^{3}J^{exp} - {}^{3}J^{calc}\}_{ij}$ and dihedral angle $\{\theta^{exp} - \theta^{calc}\}_{ij}$ data for modified steroid estrogens obtained from NMR [4], X-ray and molecular mechanic calculations were used to determine the optimal sets of local empirical substituent constants ΔS_{1-4} and parameters A, B and C in Colucci's relationship [5]:

$${}^{3}J_{H-H} = \frac{A + B\cos(\theta) + C\cos(2\theta + \cos(\theta[(\Delta S_{1} + \Delta S_{4})\cos(\theta - 120^{0}) + (\Delta S_{2} + \Delta S_{3})\cos(\theta + 120^{0})]}{(\Delta S_{1} + \Delta S_{2})\cos(\theta + 120^{0})]}$$

for different ethane fragments in rings "B", "C" and "D" of these steroid molecules.

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Infrared study of cholseteryl n-alcanoates

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Thermo-physical and X-ray structural investigations have shown that physical properties of cholesteryl n-alkanoates do not exhibit such features characteristic to most of homologic series as even-odd alternation, but they do exhibit different types of solid and liquid crystal structure and of polymorphism that are however similar within few consequent groups of cholesteryl n-alkoates homologous.

Investigation of cholesteryl n-alkanoates infrared absorption spectra, which carry information on structure (conformations) and intermolecular interactions are of great interest. However, the indications of conformational mobility of cholesteryl n-alkanoates molecules have not been investigated to a sufficient extent. Structural and spectral data have not been sompared. There is no information on cholesteryl n-alkanoates spectral studies at low temperatures.

In this work the molecular conformation of cholesteryl n-alkanoates CH_3 $(CH_2)_{n-2}$ COOC₂₇H₄₅ (n = 1-18) is investigated by infrared spectroscopy in different phases.

It is shown that cholesteryl n-alkanoates may be divided into three groups with similar conformation and packing of alkyl chains in solid state and mesomophism types within each of them.

Molecular dynamics simulation of single-stranded polyribocytidylic acid

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The molecular dynamics simulation of single-stranded polyribocytidylic acid with explicit water and K+ as counterions in AMBER8 was carried out. The conformation of poly(rC) obtained after 2.1 ns production run differed significantly from its initial helical conformation though stacking between subsequent bases in poly(rC) still was observed. The RMSD of poly(rC) backbone with respect to the initial conformation fluctuated around 3 ? in the course of simulation run. Single-stranded poly(rC) was found to be a very flexible structure with bases flipping out and in during the simulation.

The molecular dynamics trajectory of poly(rC) was analyzed using essential dynamics method in order to separate functionally important large-scale correlated motions from local harmonic fluctuations. The conformations of poly(rC) obtained after essential dynamics analysis were used as targets for flexible docking with actinocin derivative (actIII). Actinocin derivatives are known to cause cytotoxic activity due to their binding to nucleic acids. Therefore the study of their complexes with polynucleotides is important for the determination of molecular mechanisms of interaction of actinocin derivatives and nucleic acids. Among the docked actIII-poly(rC) complexes the most probable ones were selected according to the known IR- and Raman spectroscopy data.

The Shift of the Melting Temperature of DNA-Ligand Complexes Compared with Melting Temperature of Pure DNA.

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It is known that the melting curves of DNA-ligand complexes might shifting to the high or low temperature area as compared with the melting curve of "pure" DNA. So some types of ligands are stabilizer or distabilizer of the native DNA. The shift of the melting temperature of DNA-ligand complexes (Tm) compared with melting temperature of "pure" DNA (To) may be estimated by different methods.

The complexes of actinocin derivative (ActII) with some types of poly-nucleic matrixes: DNA from Micrococcus lysodeikticus (\sim 72% GC), Clostridium perfringers (\sim 28% GC), DNA from calf thymus (\sim 48% GC), poly (rC) were investigated. The complexes of 6-azacytidine (6-AZC) with calf thymus DNA and DNA samples extracted from epididymis of the Wistar male rats exposed to chronic radiation were investigated also.

The analysis of Tm for all DNA-ligand mixtures was carried out by some different ways. The shift of the melting temperature of complexes was estimated using experimental melting curves of DNA-ligand complexes and of "pure" DNA. The melting temperatures (Tm and To) were obtained as half of helix-coil transition temperature. The temperature dependence of absorption spectra of DNAligands mixtures were used to determine the thermodynamic parameters of the binding. These temperature dependencies of binding constant have been used to obtain H, S, G values by vant Hoff equation and Marky's approach. Different approaches for determination of Tm (the methods of Frank-Kamenetskii and McGhee) values in considered DNA-ligand systems have discussed.

The using of approaches from simple equations of chemical equilibria for estimation of Tm have discussed also.

The ultrasound fragmentation of DNA: spectroscopy and electrophoresis study

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The development of fast and sensitive biosensors for use in monitoring of environment is of great interest now. DNA-sensors can ideally offer rapid and reversible detection of different bacteria, viruses and others. To do this requires that target DNA is available in single-stranded (ss) form to provide hybridization of nucleic acids and sufficiently short to decrease the detection time. The ultrasound can be select as rapid and simple methods to convert genomic DNA into (ss) form of short sequence length. In this report the influence of genomic DNA time sonication on IR spectra (in range 800-1700 cm⁻¹) of the polymer in D_2O solution has been studied. The DNA sonication leads to the some bands shift and intensity redistribution. The length of fragmented DNA was controlled by dielectric electrophoresis. The estimation of DNA fragmentation after 15 minutes sonication (44 kHz, 20 Wt) showed that the mean length of a fragment was about 200-300 base pairs. To study variations in the DNA structure the thermal denaturation method was applied in which the dependences of the DNA solution optical density at 38500 cm^{-1} on the temperature was measured. DNA aqueous solution was also sonicated with single-walled carbon nanotubes to prepare a steady suspension of this nanomaterial. Comparison analyses of obtained solutions was performed. Possible model of genosensor based on carbon nanotubes is discussed.

Artificial neural network as s tool for preliminary analysis of time resolved fluorescence data

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The time resolved fluorescence spectroscopy is a very important experimental tool for study the complex biomolecular objects and systems, including lipids, membranes, proteins, DNA, etc. These methods provide detailed information about structure and dynamic of these systems [1]. The analysis of spectroscopic data may be complex because of several reasons: there could be a number of unknown parameters in an experimental system; almost all dependencies between them and the processes taking place are non-linear; and experimental data are distorted by noises and inaccuracies of a registration system. These facts impel to analyze experimental data via the multi-parametric optimization approach (fitting). General scheme of the proposed method is the following: the model that describes studied processes is selected from all possible models, initial estimations for the model parameters are made, and the optimization algorithm is starting to modify these parameters trying to achieve a coincidence between experimental and calculated data [2]. For the successful application of the fitting procedure, the selected model must be an adequate and the initial estimation for its parameters should be sufficiently good. Consequently, the tasks of model recognition and initial estimations arise. The first task can be accomplished using a priori knowledge about the system. Unfortunately, it is not always possible, because this information may be the object of the research itself. To perform the second task, specific algorithms of data analysis can be implemented. However, these algorithms are strictly specialized, and cannot be applied in the general case. For example, the Laplace transform allows analyzing multi-exponential fluorescence decay model but it cannot be used for stretched exponential model.

Therefore, in this paper we propose to use artificial neural networks [3] to solve the tasks of model selection and initial parameter estimation. Neural networks are widely used in a variety of disciplines, including the application of such techniques to the data acquisition and triggering of high energy physics detectors. Their robustness provides successful data analysis in the presence of statistical fluctuations and noise.

The proposed approach was tested on the simulated fluorescence decays and ESR spectra. It showed rather good results in prediction of the model for fluorescence data. For the case of multi-exponential fluorescence decay analysis, the mean probability to obtain the correct lifetime values within the error range of 10% was approximately 80%. It should be noted that the method is applicable in the case of non-exponential decays. The method works with convoluted data. The absence of the deconvolution procedure gives a significant increase to the noise stability of the method.

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Two-photon excited fluorescence of styrilbased dyes at DNA presence

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Styryl dyes are widely used in different biological techniques, particularly in two-photon fluorescence imaging.

A series of novel styryl dyes was synthesized, spectral-luminescence properties of obtained templates in free state and in NA complexes were studied. All dye-DNA complexes from current series were studied for their capacity to emit upon two-photon excitation by 20 ns pulsed YAG: Nd^{3+} laser with wavelength 1064 nm. The intensities of two-photon excited fluorescence spectra of dyes-DNA complexes from series are close to the same of Rodamine 6G (the solution in EtOH of the same concentration). The calculation of two-photon absorption cross-sections of dyes is on hold.

It could be concluded that designing of styryls based on benzothiazolium template seems to be perspective way for the elaboration and synthesis of efficient DNA-sensitive two-photon excitable molecular probes.

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Spectrophotometric investigation of competitive binding of actinocine derivative ActII and 6-Azacytidine to DNA

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Spectrophotometry is one of the most convenient methods to investigate interaction of biologically active small molecules and drugs to nucleic acids. Competitive binding can be used to analyse a complexation in any three component systems ligand1 DNA ligand2 to obtain binding parameters of ligands to polynucleotides in solution. Interaction of 6-azacytidine (6-AZC) and actinocine derivative ActII, analogue of actinomycin D with calf thymus DNA have been investigated.

A novel method of investigation of competitive binding in triple systems ligand1 DNA ligand2 have been proposed. We used DALSMOD optimization programs to calculate binding parameters of ligands to polynucleotides in such systems. Using spectrophotometric data obtained in VIS and UV regions complexation in systems ActII DNA 6-AZC have been studied. Our calculations shown that when both competitors are present in solution they interact with nucleic acid simultaneously. 6-AZC forms one type of complex on DNA with binding constant K=1000.

This method can be used also to investigate a complexation in any three component systems even in the case when one of the competitors has a weak affinity to DNA or does not absorb neither in VIS, nor in UV region.

Spectroscopic characterization of the inclusion complexes of electron donor substituted bis-pyrasolopyridine with cyclodextrins on the titania-silica surfaces

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Large π -electron donor-acceptor compounds like electron-donor substituted bis- pyrasolopyridine (in particular DEA-DMPP) have been recently the subjects of intensive investigation [1]. DEA-DMPP are highly emissive in non-polar solvents; they show charge separation in polar solvents and dual fluorescence in polar protic solvents due to solvent-solute interactions and the existence of twisted or conformational relaxed TICT states. In the heterogeneous media of titania-silica colloids the formation of the ICT state of DEA-DMPP inhibited probably because of H-bonding between of amino group of DEA-DMPP and OHgroup localized on the colloid surface [2]. In this work we apply the luminescence spectroscopy technique to follow changes in the electronic properties of adsorbed DEA-DMPP molecule in presence of β - and γ -cyclodextrin (CD) on porous silica and titania-silica dependent on the polarity of the added intra-porous solvent. The variations of the fluorescence emission and excitation following the addition of ?- and ?-cyclodextrin in ethanol/water solution of DEADMPP were attributed to the formation of inclusion complexes.

The measurements of the fluorescence spectra and kinetic decay of fluorescence were performed in vacuum cells and in presence of acetonitrile or water vapors added to the sample as well. The fluorescence spectrum of DEA-DMPP adsorbed on the silica surface under vacuum is complex. Both the short-wave and long-wave emissions are present. Dual fluorescence might mainly be affected by the different position of adsorbed molecule on the polar silica surface. Short wavelength, primary emission is caused from the molecules adsorbed on low-acid OH group via strong electron donor amino group. Long-wave emission might be cause due to adsorption of bulk electron-acceptor part of DEA-DMPP on the silica surface. In presence of high polar acetonitrile vapors on silica, longwavelength fluorescence grows. This should indicate that the character of the emitting state changes from low polar to highly dipolar.

DEA-DMPP inclusion into voluminous γ CD cavity possessed the possibility for the ICT state formation; inclusion complex remains stable on the silica surface and showed sensitivity to intra-polar solvent changing. Lack of CT band in the spectra of DEA-DMPP inclusion complex with β CD adsorbed on

acetonitrile vapor addition were attributed

the vacuum ed silica and it grows after acetonitrile vapor addition were attributed to guest to host orientation with the diethyl-amino-group pointing out of the larger ring of β CD cavity and strong interact with surface OH groups.

On the TiO_2/SiO_2 surface the long wavelength ICT emission is totally quenched as well for DEA-DMPP molecules as for DEA-DMPP/CD inclusion complexes. After addition of acetonitrile to DEA-DMPP on the Ti/Si surface fluorescence spectra DEA-DMPP only short-wave emission has been observed.

The competition between the interaction of DEA-DMPP with cyclodextrins, surface active centers and with the solvent molecules defines the fluorescence behavior and ICT processes in adsorbed DEA-DMPP molecule.

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Fluorescent probes as the tools for study of the radiation-induced structural disorders of the enterocyte plasma membrane

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The functional specialization of the small intestine - one of the most radiosensitive organ, is determined to a great extent by the highly specialized structure of the epithelial cells - enterocytes. Plasma membrane of enterocyte contains diverse transport enzyme systems that regulates transmembrane and transcellular transfer of the ions and nutrients. The cell membranes are one of the crucial targets of the ionizing irradiation effect on organism.

Fluorescent probes (ANS and pyren) were used for the monitoring of the membrane structure. The spectral characteristics of the ANS bound to plasma membrane (fluorescence intensity, probe binding parameters) indicate the existence of the complex processes (probe micro-environment changes, surface charge increase, structural rearrangement of the membrane components, etc.), occurring in the membrane after X-ray irradiation of the rats in dose range from 0,5 to 3,0 Gy.

More detailed information on the surface accessibility of the tryptophane residues and intramembrane mobility of the protein molecules in plasma membrane was obtained in studies of intrinsic trytophane fluorescence quenching by external quenchers with different properties. The method of inductive-resonance transfer of energy between the pair of fluorophores tryptophane-pyrene was applied. The transition of the protein mass center in the direction from the lipid/water border into lipid phase of plasma membrane was calculated. At the same time the reduction of the protein component participating in energy transfer and decrease of the effectiveness of the energy transfer due to the increase of the distance between donor and acceptor are observed in plasma membrane.

Thus, there are the following changes of the membrane physical properties after irradiation: the decrease of the thickness of the hydrophobic region of the lipid bilayer and surface accessibility of the tryptophanyls; protein mass transition into lipid bilayer; the decrease of the effectiveness in the energy transfer in tryptophane-pyrene as the result of the donor-acceptor distance increase. The aggregation of the protein molecules due to disorders in the protein-lipid interactions and appearance of the non-specific protein-protein interactions (as the result of the SH-groups oxidation and/or conformational changes in proteins and lipids) are supposed.

The membrane structural reorganization, accompanied by disorganization of

the native protein-lipid interactions may be the reason of the revealed enhancement of the plasma membrane permeability for ions and metabolites.

It is concluded that destructive changes of the enterocyte plasma membrane induced by X-ray irradiation include the changes of the dynamic properties of the membrane components, their topology and modification of the protein-lipid interactions.

Fluorescence resonance energy transfer between two dyes in a surfactant micelle

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Development of new multi-functional luminescent probes on the base of nanoclusters ("cage") containing several dyes for high-selective interaction with biological objects is a very actual task. Such probes are very promising for cell tracing applications. The case when between dyes incorporated in such a "cage" fluorescent resonance energy transfer (FRET) takes place is of special interest.

We present result on FRET between two amphiphilic dialkylcarbocyanine dyes 1,1'-dioctadecyl - 3,3,3',3' - tetramethylindocarbocyanine perchlorate (DiI) 1,1'-dioctadecyl - 3,3,3',3' - tetramethylindodicarbocyanine perchlorate (DiD) which were incorporated into surfactant micelles. Using forced concentration of the dyes in sodium dodecylsulphate micelles, FRET has been observed at a low concentration of dyes in a solution. Luminescence decay and luminescence anisotropy decay experiments have shown that dyes are incorporated into micelles in such way that charged fluorophore localizes the dye at the micelle's surface and lipophilic aliphatic "tails" inserts into the micelle and thus anchor the dye to the micelle. Luminescence anisotropy decay analysis has revealed that rotation diffusion of DiD acceptor molecules in micelles is less restricted due to its structural feature.

0.8 Applications, methods, equipment

Fiber Optic Lasers and Amplifiers in Terabit Rate Telecommunication Systems

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Spectroscopic features of the modern lasers and optical amplifiers realization in the optical fibers based on the fused silica are considered. The spectroscopic data analysis shows, that optical fibers as the active media for lasers and optical amplifiers, can possess the spectral width of the amplification band exceeding 10 THz that has allowed to create a number of practical devices with terabit rates for data transfer and the information processing. The analysis of spectroscopic features of the laser and optical amplifier designs in the fibers with the core activated by rare-earth ions is submitted. The comparative analysis of the lasers and optical amplifiers parameters in the rare-earth doped fibers with fiber lasers and optical amplifiers based on the stimulated Raman scattering (SRS) is carried out.

Already at the first applications of the fiber Raman amplifiers (FRA) with several pump sources on different wavelengths it has been demonstrated the high-quality amplification of optical signals with bandwidth close to limiting for silica fibers, up to 13 THz. These results have made FRA the first nonlinear optics device which has received already wide practical application in long-distance fiber optical communication. Simultaneously it was found some problems, connected with FRAs, two of which, in our opinion, have fundamental character. At first, the signal quality after FRA appears above maximum permissible and it is in the contradiction with modern theoretical representations about the optical amplifiers noise. This problem still waits for the decision, and the experimental aspect of this decision, from our point of view, lays in additional researches on spontaneous and stimulated Raman scattering in the optical fibers. At second, extreme simplicity of the FRA design is accompanied by the physical processes complexity of the nonlinear energy exchange along the optical fiber between several pump sources and hundreds the information channels are divided on wavelengths of the optical beam carrier. Our spectroscopic approach to analysis of the multiwave pumping FRA allows to simplify essentially the simulation and design optimization at the practical realization of such amplifiers in comparison with usual methods of direct numerical modelling. Research results on new optical fibers with the help spontaneous Raman scattering, traditionally used for search of new materials, in particular for the SRS lasers creation are given.

The practical schemes of the fiber optical devices based on the photonics and the nonlinear optics elements, which are realized the monolithic full fiber integration of the traditional optical devices functions, are considered at demonstration of the terabit rate opportunities of the information processing. Such devices possess the bandwidths and they bit rate is exceeded the limiting opportunities of modern electronics on several orders.

Numerical modeling of optical transmission through subwavelength hole arrays

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We present numerical modeling of the fine structure of optical field by diffraction on subwavelength hole arrays. Different configurations of geometrical parameters was analyzed and correlative field distributions are obtained. Qualitative coincidence with experimental data is demonstrated.

Spectroscopic techniques for making temperature measurements in air plasma

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Generation and investigation of the non-equilibrium atmospheric pressure plasma are topical questions in present plasmachemistry. Special emphasis must be attended to development methods of determining the character of population distributions in non-equilibrium plasma flow. Features of the diagnostic techniques based on optical emission spectroscopy for making temperature measurements were considered in this paper. To solve low-resolution problem during interpretation and processing of plasma emission spectra the computer simulation, with taking into accounts apparatus function parameters of real spectrometers, was proposed. Developed techniques were used for investigating parameters of the plasma generated by electric arc in a transverse blowing airflow, the experimental scheme of which previously described in [1].

The method of determining parameters of the excited level populations from multiplets with low resolved structure was designed. Oxygen multiplet lines (777 nm, 844 nm, 926 nm) observed in emission spectrum of the investigated plasma were simulated with taking into accounts the apparatus function of spectral device. It was shown that developed technique could be applied for computation in cases, when half-width of apparatus function is order to spectral distance between multiplet components.

The character of electronic, vibration and rotation population distributions of oxygen and copper atoms and nitrogen molecule was investigated. The temperatures T_e^* , which characterise the excited electronic level populations, of Cu and O atoms were determined from Boltzmann plot. Obtained T_e^* values of oxygen are slightly smaller than corresponding values of copper atom. Its temperature distributions in the investigated plasma down to the blowing airflow z were studied. The T_e^* of copper is shown to decrease slightly near the electrode (small z) and to be almost permanent value for oxygen atom. It was supposed that the difference between T_e^* values of Cu and O atoms and its distributions indicate that gas heating occurs due to the convective heat exchange between its particles and the current channel.

The character of the excited vibration populations was evaluated from the relative intensity of (0,0), (2,4), (1,3), (0,2) and (1,4) bands of the 2nd positive system $N_2(C^3\Pi_u^+ - B^3\Pi_g^+)$ and its Boltzmann distribution was shown. The vibration temperature T_v^* profile down to the airflow was measured and its distribution was studied. It was shown that temperature T_v^* slightly increases down to the airflow and approaches to the T_e^* value at the periphery.

The method of determining the rotation temperature T_r^* , which characterises rotational population distribution, based on comparison computer simulated molecular (1,4) band of the 2nd positive system N₂(C³\Pi_u^+-B³\Pi_g^+) with experimental ones was used. This procedure allows the use of spectra with low resolution for the estimation of plasma parameters. The (1,4) band of the 2nd positive system N₂(C³\Pi_u^+-B³\Pi_g^+) was simulated since it is free from overlapping with other lines. The rotational temperature evaluated from N₂(1,4) band shape is much smaller than T_e^* value determined for Cu and O atoms. The T_r^* distribution down to the airflow z was analysed for different discharge currents. The temperature is shown to increase by moving away from electrodes because of blowing gas penetration inside the current channel and its heating.

It was shown that the T_r^* value is much smaller than T_e^* and T_v^* . Such temperature discrepancy and its different distributions down to the airflow indicate that plasma generated by the electric arc discharge in transverse airflow is highly non-isothermal.

 V.Ya. Chernyak, V.V. Naumov, V.V. Yukhymenko, I.L. Babich, V.A. Zrazhevskyy, Yu.V. Woewoda, T.V. Pashko Problems of Atomic Science and Technology. Series: Plasma Physics, 2, p.164 (2005)

What are the research activities in the Molecular Spectroscopy Labs of the Al.I.Cuza University from Romania?

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In Faculty of Physics of Al.I.Cuza University from Iasi, Romania, there are special sections for masterands and doctorands in which lectures in Spectroscopy are organized for two years.

Some chapters of Molecular Spectroscopy (electron spectroscopy, IR, NMR) are used for molecular recognition. The students can identify substances analyzing their spectra and can attribute the spectral lines and bands on the bases of molecular symmetry studied at Physics of Atoms and Molecules.

The solvent influence on the electronic emission and absorption spectra is an intensively studied problem initiated by Prof.dr.doc. Constantin Mihul and continued by the group of prof. Valer Pop. Many PhD theses had subjects bounded to this problem. In spite of the insufficient modern equipment, good results were obtained and published in international devoted journals.

Some spectral measurements of the diluted solutions of the spectrally active molecules are used in order to estimate some molecular parameters (dipole moments, polarizabilities or ionization potentials) or the contribution of the different types of intermolecular interactions to the total spectral shift.

Specific interactions of the type donor-acceptor are studied especially by means of IR and NMR spectroscopy. The supplementary shifts, measured in the active from the point of view of specific interactions solvent, permit to evaluate the strength of the quasichemical interactions.

In the Plasma Labs students are able to estimate the discharge temperature from the emission spectra of the gases contained in the discharge vessels. The spectral intensities are very sensitive parameters both at temperature and concentration of the spectrally active species. Doppler bandwidths are also used in plasma temperature determination.

Studies regarding the spectral characterization of the kinetics of some chemical reactions, such as dimerization reaction of the cycloimmonium ylids or protonation reactions are also made in the Department of Spectroscopy.

Some from the above mentioned activities and the obtained results will be detailed in this communication.

At the finish of their two master years, the students must prepare an original paper publishable in the ISI Journals. In this way, the School of Spectroscopy has good traditional results and the graduated are easily accepted to work as doctorands or post doc. persons in the modern labs of Europe and USA. Now, about 40 percents from our graduated persons work in the modern labs of the world.

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0.8 APPLICATIONS, METHODS, EQUIPMENT

Stimulated Raman adiabatic passage in the fields with stochastic amplitude

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Stimulated Raman adiabatic passage is a well-known technique to selectively populate states of atoms and molecules [1]. In the most elementary applications of this technique a three-state atom (initial, excited and target states) is exposed to two sequential partially-overlapping laser pulses with carrying frequencies resonant to transition frequencies. The Stokes pulse coupling the target and excited states precedes the pump pulse coupling the initial and target states. As a result the population transfer from initial to target state is close to 100%. In the report we theoretically investigate STIRAP in three-level atom in the fields with stochastic amplitude not studied before.

Two models of stochastic field are discussed. In the Gaussian amplitude model the electric field exhibits Gaussian fluctuations about zero. In the chaotic field model the real and imagine parts of the complex electric field fluctuate independently. We show that amplitude fluctuations do not prevent effective population transfer if the amplitudes of Stokes and pump fields fluctuate synchronically (amplitude ratio of the fields does not fluctuate). A possible experimental scheme with synchronous fluctuations of the fields is discussed.

In the case of Gaussian amplitude model, rapid synchronous fluctuations and short pulses (correlation time G^{-1} of fluctuations and spontaneous emission time are much shorter than time duration of pulses) the expression for the population of the target state reads

$$\eta = \exp\left[-2\int_{-\infty}^{\infty} \dot{\theta}(t')^2 \int_{-\infty}^{t'} \exp\left(-\frac{1}{4G^2} \langle \Omega_p(t')^2 + \Omega_S(t')^2 \rangle \times \left(-1 + G(t' - t'') - e^{-G(t' - t'')}\right)\right) dt'' dt'\right]$$

where $\langle \rangle$ denotes ensemble averaging, $\Omega_p(t)$ and $\Omega_S(t)$ are fluctuating Rabi frequencies of pump and Stokes pulses, $\theta(t) = \arctan(\Omega_p(t)/\Omega_S(t))$. For specific pulses shape this expression is much simplified. Monte-Carlo simulations are in good agreement with derived analytical expressions.

The results of Monte-Carlo simulations for chaotic field model resemble the results for Gaussian amplitude model.

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The relation between metamerism phenomenon and parameters of the uniform color space

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Is it possible to build uniform color space? The question, to this day, still remains undetermined. Firstly, the space must be three-dimensional space with Euclidean metric and secondly, a distance between any two points in the space must be proportional to the number of color limens. In the general case, a linear element expression corresponds to Riemann metric and ability of transition to Euclidean metric remains unproved. But, taking into account practical needs of colorimetry, different approximate expressions were proposed in the past decades. The best were recommended to use by CIE.

Better known, that different spectral energy distributions correspond to the same color stimulus. This phenomenon was named metamerism and color stimuli metameric. Metamerism depends on illumination and viewing conditions. For example, two paper sheets that seem identical at the day light illumination may differ from each other when the light source is incandescent lamp.

The goal of research was eduction affinity between color stimuli characteristics and color limens values. Greatest and least energy values of metameric stimuli were chosen as parameters that describe color stimulus. To find these values the certain functional was tested for maxima and minima. Calculated results were extreme values of metamer energy and spectral energy distribution for these values. Successive approximation method was used for the calculation.

Preliminary results demonstrate the correlation between values of color limens and metamerism parameters. The further moves would allow to build uniform color space using metameric color stimuli characteristics.

Simulation of light propagation in the strongly scattering medium under amplification and absorption conditions

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Strong scattering essentially changes the process of light propagation in the medium and can lead to the effects of lasing or additional absorption if the medium is amplifying or absorbing. Up to now the effects were investigated only experimentally that is inadequate to understand the mechanisms of their behaviour. Thus the simulation of light propagation in the strongly scattering medium under the amplification and absorption conditions is a pressing problem.

To solve the problem we created an original program simulating by Monte-Carlo method the photon propagation through the absorbing (gaining) medium with evenly distributed scattering particles. The program allows computation of the photons trajectories and can make a statistical analysis of the photons according to the determined criteria: a number of the photons scattered certain times, or a number of photons coming certain pass through the medium, or a number of photons reaching the detector, or those ones which trajectories are within the determined volume.

It was shown the portion of photon exposed by scattering of certain multiplicity significantly depends on the scattering particle concentration n_{part} . Under the n_{part} increasing the portion of multiply scattered photons grows both within the scattering medium and in the beam reaching the detector. Just this portion is the most sensitive parameter to the absorption and amplification in the medium. The portion of multiply scattered photons is sharply decreases under absorption and grows under amplification. These phenomena appear as additional absorption and lasing.

The additional absorption and lasing appear under the multiple scattering regime only originating under the particle concentration to be over the certain value $(n_{part} \ge 2 * 10^8 \div 6 * 10^8 cm^{-3}$ for the particles of 5mkm in diameter). The value of the additional absorption depends on absorption coefficient (amplification) of the medium α . It increases under the k decreasing. It resulted from the fact the less α the higher scattering multiplying is needed for the additional absorption appearing.

In the absorption medium the further 1.5-2 times increasing of the n_{part} leads to the sharp increasing of the extinction coefficient K up to complete disappearing of the transmitted beam. In the amplifying medium the n_{part} . increasing leads to the transmission T sharp increasing and proceeding to lasing (T > 1). At the higher absorption (amplification) coefficient value the n_{part} range of K (or T) increasing extends to lower concentration region. Under the α increasing the range of sharp K (T) increasing become narrower and the rate $d\alpha/dn$ increases. This is resulted from higher multiplicity of the photon scattering within the region of high n.

Obtained results make the interpretation of the experimental results on strongly scattering media properties to be more reliable and can be useful for the random laser development.

Detection of extra-small amount of substances by SEIRA spectroscopy

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It is known that molecules adsorbed on island metal film or colloidal particles show 10-103 times more IR absorption than those without metals. Registration and study of extra-small amount of substances up to 10 pg or concentration of about 10 nM is a subject of interest in biological, electrochemical, surface, sensor etc. applications [1]. During the last decade the effect of enhancement of optical signal from molecules near metal surface (namely, Raman scattering SERS, infrared absorption, luminescence) is effectively used for detection of small amount of substances, monolayer films or less, as well as separate macromolecules [1]-[3]. In the beginning of 90s the effect of enhanced infrared signal was named SEIRA (surface enhanced infrared absorption) by Osawa and Ikeda [1] analogously to SERS and the scientists came back to it due to very low limit (up to 10 pg) of the molecules that could be detected by SEIRA.

However, essential enhancement (about 500 times) in SEIRA spectra could be achieved in the following case:

i) thin film of the adsorbed molecules at metal surface;

ii) molecules should be attached to the metal surface or colloidal particles by covalent bonding;

iii) specific geometry of the metal surface, namely peak island film or steplike surface;

iv) usage of ATR attachment with ATR crystal covered with metal of 20-70 A thickness;

v) usage of MCT detector;

vi) special method of molecule deposition on metal surface. In some cases, e.g. glycine, quinone, etc., thermal vacuum deposition gives bigger enhancement factor than deposition from solution.

Calculated factors of enhancement ?(?) were determined as coefficient that is proportional to ?'/?". Being based on the experimental data for our gold film and Bruggeman model and we calculated coefficients proportional to enhancement factor and compare them with experimental data for monomers of biological molecules.

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Self-phase modulation of laser pulse on the border of Kerr liquid

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Experimental results are given to prove existence of the transition effect, which generates new spectral components on a physical boundary of environment under self-phase modulation of nanosecond laser radiation pulses in consequence of queasy-stationary self-focusing in Kerr-liquids. New spectral components generated as result of the transition effect have shift up to 100 inverse centimeters and predominantly in Stokes side relatively to the frequency of stimulating radiation.

Computations are carried out for additional phase lag, instantaneous frequency and spectrum of pulse. The results of computation and obtained experimental data have satisfactory agreement.

Plasma temperature determination by spectroscopic measurements

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Oxygen plasma have a wide range of applications (surface treatment, polymer etching, etc) and the investigation of an oxygen glow discharge led to a better understanding of the medium and of the processes involved in these applications. In particular, plasma temperature plays an important role in all these applications. Optical emission spectroscopy and Langmuir probe measurements were performed in a capacitively coupled 13, 56 MHz argon rf discharge. Those diagnostics are important for characterizing plasma temperature relevant to etching applications. At low pressures, an increase in plasma potential values induces an increase in O^+ ion temperature. At high pressures and high rf powers, an increase in the number of ion/ neutral collisions causes Doppler broadening of the emission from O atoms.

An exponential dependence of spectral lines intensities with pressure has been founded. A simple theoretical model has been verified to calculate atom temperatures and a very good concordance with Doppler measurements was relieved.

Determination of Lens Transmittance Using Matrix Method in Z-Scan Technique

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Matrix technique in optics approach has been suggested for the determination of the lens transmittance using Z-scan technique. It has been shown that the lens transmittance can be determined within the geometrical optics approximation, provided that effect of the finite radius of the focused gauss beam is taken into account. An expression for the lens transmittance in terms of parameters of the Z-scan input gauss beam has been obtained.

Optical golograph interference of fluids at millimetre irradiation

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At this report, investigations of refractive indices variations based on the method of holograph interference at the wavelength $\lambda = 632.8$ nm in a number of fuilds (organic liquids, waterm cell cultivations in nutritious medium) under their irradiation by an electromagnetic emissikn in a frequency range of $37.5 \div 78$ GHz are presented. Fluid temperature was controlled during the process of measurement with an accuracy not less than 0.1 K by a copper-constantan thermo-couple having sensitivity of $\sim 40 \ \mu W/K$. The magnitude and dynamics of a refractivity index variation under the irradiation in the frequency range of 37.5÷78 GHz depend on the irradiation power and physical parameters of objects (molecule dipole moment, viscosity, heat capacity, and heat conductivity of fuilds, and their thermal refractivity index) and do not depend on the mutual orientations of polarization vectors of millimetre and optical fields in limits of experimental errors. The investigations have shown that mm-radiation with power up to 10 mW produces thermal variations in optical refractivity index in fluids of the order of 10^3 . The variations of refractivity index in various fluids are different in magnitude but have the same sign refraction index decreases under the irradiation. At large values of an absorption coefficient α_{mm} of mmemission (for instance, in water, where $\alpha_{mm} \approx 22 \text{ cm}^{-1}$), the optical refractivity index variations exponentially depend on the depth of penetration and that is an essential feature of the process of heat transfer (mm-emission is absorbed by a thin layer of material just under a wave-guide, where the heating of a fluid may reach $5\div7$ K). In liquids with symmetric molecules having no constant dipole moments (such as CCl₄ and benzene), mm-emission is absorbde weakly $(\alpha_{mm} < 0.003 \ cm^{-1})$, ortho-zilol $(\alpha_{mm} \approx 0.4 \ cm^{-1})$, ethanol, butanol, and aceton, complicated interference fields were observed caused by a bulk absorption of mm-emission penetrating in medium on the depth of $\sim \alpha_{mm}^{-1}$.

Comparative study of optical limiting caused by nonlinear absorption and scattering

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Optical limiting is a phenomenon of self-induced attenuation of powerful laser radiation in nonlinear media. In a simple instance, it manifests itself as a decrease of optical transmittance at high levels of incident laser intensity. There are several physical mechanisms responsible for optical limiting in various media, for example, excited state absorption in molecules (impurity centers), absorption in photo-ionized centers, absorption in photo-chemical products, etc.

In turbid media containing absorptive particles, propagation of powerful laser radiation demonstrates effective optical limiting in a wide spectral range. The mechanism of optical limiting in absorbing suspensions is a nonlinear light scattering caused by laser-induced evaporation and plasma formation in the neighborhood of suspended micro-particles.

Optical limiting can be treated as a process determined by odd-order nonlinear susceptibilities, $\chi^{(2n-1)}$. In a great number of instances, a non-zero imaginary part of third-order susceptibility, $\chi^{(3)}$, is enough for describing the observed limiting properties.

In the present work we report on a comparative analysis of optical limiting in the media with different mechanisms of optical nonlinearity. The experiments were performed with nanosecond laser pulses on crystals, glasses, and aqueous suspensions. We observed that experimental curves of nonlinear transmission differ significantly in media with excited state absorption and nonlinear scattering mechanisms. In case of excited state absorption, nonlinear transmission curves are well fitted with a $\chi^{(3)}$ -model, whereas suspensions demonstrate nonlinearity of higher order. Here we propose a simple method for distinguishing $\chi^{(3)}$ and $\chi^{(5)}$ nonlinearities with the use of nonlinear transmission curves.

Ultrafast static stokes meter

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Measurement the Stokes parameters of the light beam bring more information about investigated object then measurement only the light intensity. But the traditional methods determination the Stokes parameters demand precision measurements intensity by using several photodetectors simultaneously or the high stable power source of light. Trand to apply very short light pulses to study fast phenomena in photochemical and biological processes. Unfortunately stability pulse light sources and operating speed of the photodetectors are low. Thus development of principle new method measurement the Stokes parameters of the light is topical. We present method measurement the Stokes parameters based on analysis distribution intensity from digital images. Computer simulation and first successful experiments was made. Our method has certificate of authorship.

The extension of possibilities of physical researches with using of an automatic regulating system of temperature

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It is often important to maintain the precise temperature of a sample in a range of cryogenic temperatures at research of properties of substances by spectral methods. Low temperature experiment allows to minimize influence of thermal movement of molecules on quantum effects that is especially important at studying radiating and optic absorbing ability of material. For setting and long maintaining of low temperature at the required level optical cryostats are used.

The so-called three regime "PID" regulators are applied widely enough in the industry and the general principles of their creation are well covered in the corresponding literature. The given type of regulators is most the common one of the regulators used in control systems applied when it is required to improve the kind of transient process and accuracy in the established mode at the same time.

However development and creation of temperature controllers for a range of cryogenic temperatures have some specific features. Among the range of difficulties in creation of the managing device for broad-band cryostat the following basic problems can be allocated.

1. In a diapason of cryogenic temperatures the characteristics of existing temperature sensors, including temperature sensitivity, undergo significant changes. It makes the sensor choice and also development of the measuring secondary equipment for work with it more complicated;

2. As the result of significant changes of a thermal capacity and heat conductivity of a material of cryostat walls, the temperature regulator should provide a program choice of parameters of automatic control due to temperature range required.

To solve the above mentioned problems the Universal Cryogenic Thermoregulation systems UTREKS have been developed by the Institute of Physics Science Academy of Ukraine. They are widely used both in Ukraine and abroad.

For the last system upgrading the managing program allowing setting of the temperature in a diapason from 4,2 to 373 K with step-type ability 0,02 K and stability of maintenance of the set temperature not worse then 0,01 K. As the basic standard of temperature sensor the broad-band silicon diode temperature sensor is used.

The cryogenic system UTREKS managing program provides an automatic choice of regulation modes depending on the current temperature and makes the scanning process with various speed of temperature changing at the required range.

The cryogenic system developed has allowed to accomplish the experiment on an establishment of temperature dynamic dependence of intensity of luminescence and optic absorption.

Heterodyne spectrometer on the base of femtosecond laser

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The investigation and development of high-stability lasers are carried out in the Institute of Physics more than 30 years. During this time a diversity of iodine and methane stabilized gas lasers having record performance was built up. The absorption iodine cells created in the Institute have let to get the frequency instability of the lasers of $10^{-11} - 10^{-12}$ and keep their performance more than 5 years. This allow to use the lasers as secondary length standard and also for metrological measurements and high resolution spectroscopy.

The $HeNe/^{127}I_2$ lasers pumped by transverse rf-discharge, which have high metrological parameters, were developed in the Institute during the last years. The parameters correspond to the criteria of Recommendation 1 (CI-1997) of the *Bureau International des Poids et Mesures* (International Bureau of Weights and Measures, or BIPM) [1]. Due to the low level of amplitude fluctuations in transverse rf-discharge, the frequency instability of such lasers reaches $5 \cdot 10^{-13}$ for the integration time 100 s, and it is about six times as small as the stability of the lasers pumped by dc-discharge [2].

We propose here the spectrometer based on the femtosecond laser and stabilized gas or semiconductor lasers. The spectrum of the femtosecond laser is a comb of equidistant modes what can be used as a frequency scale in the optical region [3]. The He-Ne laser stabilized by the components of the hyperfine structure of iodine will serve as the frequency reference for precise measurement of the femtosecond laser mode frequency. The semiconductor laser will form the frequency marks, which corresponds to the center of the investigated spectral line, for example the hyperfine structure component of heteroisotope iodine molecule.

Thus, the proposed design of heterodyne spectrometer combines the high accuracy of the heterodyne technique of frequency measurements and wide working frequency region, defined by the width of the femtosecond laser spectrum. The working region can be essentially increased by generation of optical harmonics in the nonlinear optical fiber. The spectrometer can be used as a powerful tool for high precision spectroscopy of molecular gases in visible and near IR regions.

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PerkinElmer instruments for the molecular spectroscopy

Larissa Pelieva

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PerkinElmer instruments established in 1937 is one of the biggest analytical equipment producer in the world for today. Its instruments are successfully used in the various branches including molecular spectroscopy research. PerkinElmer manufactures various instruments for this purpose such as: polarimeters (series 341/343); UV/VIS spectrometers (Lambda 25/35/45, 650/850/950); IR-spectrometers (Spectrum RXI Spectrum BX II, Spectrum One, Spectrum GX); luminescence spectrometers (LS-30).

There are a lot of applications of these instruments:

- Polarimeters (series 341/343) are an important technique for the investigation and analysis of optically active substances. The proven optical null principle, with automatic rotation of the analyzer, is the basis of PerkinElmers reputation for excellence in polarimetry. This principle, combined with stateof-the-art microprocessor electronics, results in an instrument which combines the highest possible accuracy and precision with simple operation;

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