XIX International School-Seminar

"Spectroscopy of molecules and crystals"

devoted to the

175th Anniversary of Kyiv Taras Shevchenko University

ABSTRACTS

XIX ISSSMC is organized by
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Ministry of Ukraine on Education and Science
National Academy of Sciences of Ukraine
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Professor **Galyna Oleksandrivna Puchkovska**

On 22nd of June, 2009, Galyna Oleksandrivna Puchkovska, one of the outstanding Ukrainian woman scientists working in the field of solid state physics, molecular physics and vibrational spectroscopy, an associate member of the European Academy of Sciences, Arts and Humanities, Doctor of Science in Physics and Mathematics, Professor, Honored Worker of Science and Technology of Ukraine, Head of the Photoactivity Department of the Institute of Physics NAS of Ukraine, celebrated her 75th birthday.

She was born on June 22, 1934, in Kyiv, in a medical family. Her father, Oleksandr Mytrofanovych Puchkovskii, a well-known Ukrainian scientist in the field of otolaryngology, a founder of the Otolaryngology Chair in Kyiv Medical Institute, was tragically lost in 1937. Since her three-year-old, she was brought up with her mother, Vira Gavrylivna Boiko, otolaryngologist, who during the years of the Great Patriotic War was working as a medical officer in the evacuation hospital. After the war, she worked as a senior research associate in the Institute for Hygiene and Industrial Disease in Kyiv. High standards of hard-working and devotion to science were also set to Galyna by her older sister, Nadiya Oleksandrivna, the outstanding ophthalmologist, Member of the National Academy of Sciences of Ukraine and Member of the Medical Academy of Ukraine, who for many years headed the V.P. Filatov Institute of Eye Disease and Tissue Therapy in Odessa.

After having graduated from 13th Young Ladies School in Kyiv in 1951 with silver medal, Galyna Puchkovska attended the Physics Department of Taras Shevchenko Kyiv National University where she obtained her MSc degree in molecular physics in 1956. Since 1956, she works at the Institute of Physics of the National Academy of Sciences of Ukraine. Just after graduating from the university, she was first appointed at the Institute of Physics of the National Academy of Sciences of Ukraine as an engineer and then as junior Research Associate in the Department of Infrared Detectors headed by Anton Fedorovych Malnev. During 1960-1963 she studied as a postgraduate student at the Institute of Physics of the National Academy of Sciences of Ukraine, and in 1966 she obtained her Ph. D. degree. Her Ph. D. thesis was focused on studies of the IR spectroscopic behavior of n-paraffins in different phase states. Since 1966, she was appointed as Senior Researcher (1966-1990), Chief Researcher in Photoactivity Department (1990 -1993), and Head of Photoactivity Department (1993 onwards). In 1972 she and her team joined the Photoactivity department headed by Marat Terentijovych Shpak.

In 1988 she received her D. Sci. (habilitation) degree at Taras Shevchenko Kyiv National University for applications of vibrational spectra to elucidation of structure, molecular dynamics and polymorphism in molecular crystals. In 1993 she received her professorship, and in 2000 she was awarded with Soros Professorship Grant.

During 1964-1974 years she also participated in the development of the first domestic instrument for measurements of spectral parameters of IR detectors in 0.4-300 micrometers spectral range built on the basis of an absolutely pyroelectric detector. For this research she was honored by the State Prize of Ukraine in 1984. For her outstanding scientific achievements, G.O. Puchkovska was honored with four state medals.

For many years of scientific activities of Galyna Puchkovska, her creative forces were related to different aspects of solid state physics, molecular physics, as well as vibrational spectroscopy of disordered systems.

Since 1960, the main scientific interest of G.O. Puchkovska was focused on systematic studies of molecular dynamics in condensed states, which allowed to discover and study in detail the phenomenon of conformational polymorphism in long-chain aliphatic compounds (mono- and dicarboxylic acids, cholesterol esters, etc.), and to understand a variety of properties and structures of molecular systems appearing in different phases using optical vibrational spectra.

At the beginning of 80th years of XX century, one of the important problems in solid state physics was experimental verifications of an exciton theory developed by O.S. Davydov and its application to vibrational excited states of molecular crystals. For the first time, Prof. Galyna Puchkovska found that interactions of alkyl chains in a condensed phase may be estimated using the spectral value of dynamic resonance (Davydov) splitting of IR absorption bands related to rocking vibrations of alkyl chains.

Among her most outstanding scientific achievements are studies of temperature dependence of Davydov splitting in the IR spectra of n-paraffins and their binary mixtures, carboxylic acids, which allow to determine the temperatures of phase transitions in these systems and to discover solid rotator phases where orientational motions of molecules are activated.

An important field of Prof. G.O. Puchkovska's activities is IR and Raman spectroscopic studies of the structure and lattice dynamics of hydrogen-bonded crystals. For a family of alkali iodates and their acid salts, homologous series of n-alkane cholesterols, n-alkylbensoate cholesterols and their fluorinated derivatives, she has elucidated the effect of different kinds of hydrogen bonds (formed in a condensed state between molecules, molecules and complex molecular ions, or between ions) on the structure of the hydrogen-bonded systems and found a correlation between a spectral behavior and structural properties of these systems. The results of these studies were summarized in a monograph "IR Spectra of H-bonded Crystals" (with co authorship of L. Babkov, S. Makarenko, and T. Gavrilko) published by "Naukova Dumka"publishing house, Kyiv, in 1989.

Among the most significant achievements of Galyna Puchkovska is also her contribution to the studies of surface phenomena in anisotropic crystals of alkali iodates, ZnO and BeO. For the first time, surface polariton dispersion curves were studied for massive crystals, thin films and ceramics allowing to obtain important parameters of these materials. These results were additionally confirmed by Raman scattering and ellipsometry measurements. Prof. Galyna Puchkovska is the author or co-author of well over 250 original research papers published in most respected scientific journals.

Her aspiration to all the new always serves as a creative incentive for her scientific activity, and her exceptional intuition and ability to find prospective trends in the scientific research distinguish her among others. In recent years, she fruitfully works in the field of nanophysics and coordinates the complex investigations of the physical phenomena, relating to the self-organization processes and organic molecule interactions in the nanosized heterogeneous structures of the organic-inorganic type, the photochemical and luminescent properties of nanostructures, photophysical processes in the nanosized semiconductors, and nanostructure based systems for the information optical recording. These studies are being run in the department headed by her.

Ukrainian scientific school in the field of vibrational spectroscopy of nonmetallic and liquid crystals, disordered and nanostructure heterosystems has been actually created under the direction of Prof. G.O. Puchkovska. Galyna Puchkovska has trained 19 young Candidates of Physico-Mathematical sciences, also stimulated the three thesises for Doctor Degree, by O.I. Barabash, L.M. Babkov and V.I. Melnyk. Her grateful pupils work successfully in the educational and scientific research establishments in Ukraine (Lutsk, Sumy, Zaporizhya, Kyiv), Russia, USA, and never forget the years spent together with Galyna Oleksandrivna, the warm environment she creates, her continual care and help. The papers, written by G.O. Puchkovska and representatives of her school, are commonly recognized in the scientific society and have a reasonable authority in Ukraine, as well as abroad.

G. O. Puchkovska takes an active part in the international scientific collaboration, and during almost 20 years she keeps in close scientific touch with the scientists from different countries, in particular, from Germany, Romania, Poland. Many years she also fruitfully cooperates with the researchers from Russia (Moscow, Saint-Petersburg, Saratov Universities, the Institute of General Physics RAS), Uzbekistan (Samarkand University), and the ones from Tartu, Riga, Vilnius, Erevan etc. G.O. Puchkovska is an indefatigable participant of the scientific-social activities, with endless energy and enthusiasm. She is a member of Scientific Council on solid-state physics NAS of Ukraine, Scientific Council of the Institute of Physics NAS of Ukraine, Specialized Scientific Councils of the

Institute of Physics and F.D. Ovcharenko Institute of Biomolecular and Colloidal Chemistry NAS of Ukraine. For many years, she executes the duties of members for national and foreign scientific publishing editorial boards and organizing committees of different international scientific forums. In 2001, she was elected to the members of European Academy for Sciences, Arts and Humanities (Paris, France).

Starting from 1973, G.O. Puchkovska is a permanent chief of National (from 1989 - International) School-Seminar "Spectroscopy of Molecules and Crystals", which is held systematically during above 35 years, due to her persistence and organizing abilities. Till present time, 18 such School-Seminars have been held together with the scientists from national educational establishments, universities and institutes in different cities of Ukraine (Uzhgorod, Lutsk, Lviv, Chernivtsi, Mukacheve, Cherkasy, Poltava, Ternopil, Kharkiv, Nizhin, Sumy, Odessa, Chernihiv, Sevastopol, Beregove). A wide involvement of outstanding national and foreign scientists and scientific youth to this scientific meeting encourages the propagation of the advanced scientific approaches and spectroscopic methods, the establishment of international scientific relations and the growth in authority of Ukrainian science around the world.

The year of her jubilee, Galyna Oleksandrivna meets in creative research, as always, full of new scientific ideas and goals, projects and plans, sincerely shared with her pupils and colleagues, drawing them in intense scientific activities. We wish our dear and respected Galyna Oleksandrivna good health, creative inspiration, new touches with beautiful and always new world; and also, to remain fond of science, art, history and culture, to save a sincere and rich soul, not indifferent to people for many-many years.

We love You!

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The 19th International School-Seminar "Spectroscopy of Molecules and Crystals", RSC of Kyiv National Taras Shevchenko University, Crimea, Beregove, September 20 - 27, 2009

Abstracts

Preface

The Book contains abstracts of papers presented to 19 International School-Seminar ”Spectroscopy of Molecules and Crystals” (19ISSSMC). The School was founded by Professor Galyna Puchkovska and is held bi-annually 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.

Contents

1 THEORY

O-1 ⇓

The Investigation of Excitons at Boze-condensation State Applying Anti-stocks Comporent of Hyperraman Scattering

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The intensive electromagnetic radiation allows to obtain the high densinties $10^{17} \div 10^{18} sm^{-3}$ of excitons. Such densinties make the collective properties of the mentioned quariparticles more significant, namely Boze condensation. The authors of the given article have no information about any experimental data related to the observation of the mentioned states. The "needle-shaped" peak in the luminescence spectrum does not prove the presence of Boze-condensation states. The authors of the given article intend to consider the possibility to study the mentioned states within the limits of the polariton model which shows the propagation of electromagnetic waves in crystal. The excitons condensation is expected to appear at the minimum of the polariton spectrum upper branch (the point, where the wave vector $k \approx 0$). It is impossible to achieve the transition from the state $k = 0$ into the electromagnetic radiation outside the crystal, as the law of wave vector preservation does not take place at such transition. Hiper-Raman scattering allows to study the states which can not be studied by means of luminescence. The theory of scattering is presented in monograph [1]. Four quasiparticles participate here. The primary state is represented with three polaritons. One of them is located at the point $k = 0$, two other are located at the area of transparence. The polariton is at the transparence area in its final state. Applying the methods presented in [1], we have obtained the formula for spectrum density of the secondary radiation in the form:

$$I(\omega) = D\alpha(\omega_1\omega_2\omega_3)\delta(\omega_1 + \omega_2 - \omega + \frac{E}{hbar})_{01}(\omega_1)I_{02}(\omega_2)f(E)$$

where $I_{01}(\omega_1)$, $I_{02}(\omega_2)$ - are the spectrum densities of two primary streams, $f(E)$ - is the spectrum of quasiparticles, which are considered to be in the state of Boze-condensation, α - is the tensor of Hyper-Raman scattering,

δ - is delta - function, D - is the constant, depending on crystal sizes, refraction index and some other characteristics of an object. Formula (1) allows to find the function of quasipaticles of distribution around the point $k = 0$ and to conclude if the mentioned quasiparticles are in the state of Boze-condensation or not.

[1]. Zavorotnev Y.D., Ovander L.N. Non-linear optical effect in molecular crystals. Nord Press Donetsk 2005.(in Russian).

O-2 ⇓

To What Extent are Thermodynamic Properties of Water Argon-Like?

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Surprising properties of water in its liquids states are well known. Among them, the special attention is usually paid to the non-monotonous temperature dependence of density, the large values of dielectric permittivity and the local structure, close to that in hexagonal ice. All these as well as other surprising properties are connected with the existence of H-bonds in water.

However, the role of H-bonds should noticeably change with temperature. Let τ_H be the average lifetime for typical local configurations of H-bonds. In the wide temperature interval, from the melting point T_m to the critical one T_c , τ_H has the same order of magnitude as the soft collision time.

This conclusion about the temperature dependence of τ_H is practically self-evident if we take into account the behavior of the kinematic shear viscosity of water. For temperatures $T < T_m$, the latter has the same order of magnitude as for argon.

Our analysis shows that in the wide temperature interval the main thermodynamic properties of water are argon-like. In particular, for the fraction volume and the evaporation heat per molecule such a similarity takes place practically in the whole temperature interval 315 K < T < 550 K for liquid states. At T < 315 K , i.e. in the supercooled and normal states joined to the melting point, the properties of water are determined by clusters, the lifetime τ_c of which is essentially greater than the characteristic time τ_H . At temperatures, closed to the critical point (550 K < T < 648 K), the properties of water are determined by both the fluctuation effects and the dimerization ones. In this region, the lifetime τ_d of dimers is also essentially greater than τ_H.

The similarity of the thermodynamic properties of water and argon in the wide interval 315 K < T < 550 K is naturally explained by the effective intermolecular potential between water molecules, which is obtained from the strongly anisotropic microscopic potential owing to the averaging on the rotation degrees of freedom.

In this report we consider 1) the structure of the averaged intermolecular potential for water, 2) the closeness in the thermodynamic behavior of normal and heavy water and argon on their coexistence curves and 3) the cause of strong difference in the positions of the melting points for water and its nearest homologue H_2S .

Thermalization in Heavy-Ion Collisions

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The model of isotropization and thermalization in the system formed after collision of two N-particle systems (two nuclei) is proposed. Two-particle collisions are taken into account. The model is based on two ingredients: three collisions of every particle results in the full randomization of the particle momentum and the single-particle momentum transfer space is restricted from above. We show that these features lead to a smearing of the nucleon momenta around initial values and as a consequence this results in a partial isotropization in momentum space. In the frame of proposed [1] Maximal Isotropization Model (MIM) we derive a “double” single-particle distribution function which reflects that every of two nuclei possesses its own initial condition.

$$D_M(\boldsymbol{p}) = \left(\frac{1}{2N}\frac{d^3N}{d^3p}\right)_M = \frac{1}{2}e^{-\beta\omega(\boldsymbol{p})}\left[\frac{I_M(\boldsymbol{p}-\boldsymbol{k}_0)}{z_a(\beta)} + \frac{I_M(\boldsymbol{p}+\boldsymbol{k}_0)}{z_b(\beta)}\right].$$

The distribution function carries the memory about initial state of each nucleus. These memory effects are washed out with increase of the number of effective collisions, or the memory effects disappear with time and the nonequilibrium distribution function becomes a regular equilibrium Boltzmann distribution in the momentum space.

The partition function of nonequilibrium distribution which was obtained in MIM is exploited to extract physical information from experimental data on the proton rapidity and transverse mass distributions. We propose to separate all amount of nucleons into ensembles in accordance with a number of collisions.

$$\frac{dN}{d^3p} = \sum_{M=1}^{M_{\rm max}} C(M)D_M(\boldsymbol{p}) + C_{\rm therm}D_{\rm therm}(\boldsymbol{p})\,.$$

On the base of our model we analyze rapidity distribution and get a number of particles in every collision ensemble [2]. We argue that even a large number of effective nucleon collisions cannot describe the central rapidity region and the thermal source appears as a result of thermalization of the collective (parton) degrees of freedom. The obtained number of nucleons which corresponds to the thermal contribution is treated as a nucleon power of the created quark-gluon plasma.

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P- 1 ⇓

External noise effects on relaxation process in resonant tunneling structures

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In recent years, the investigation of nonlinear systems far from equilibrium under the influence of stochastic forces (or noises) has received great attention. Of particular interest and importance are noise-driven phenomena that occur near instability points of the deterministic (noise-free) system. In the present work, we studied noise effects on the process of tunneling of electrons through a double-barrier resonant tunneling structures. Understanding of transport properties in such structures is very important in the sight of solid-state electronics. The process of tunneling in the resonant case is characterized by the existence of a negative differential conductivity and a hysteresis cycle in a current-voltage characteristic. We studied effects of intensity fluctuations of an incident electron flow which were described by a Gaussian white noise of a zero mean. We considered a case when the system was originally in a state of low transmission determined by a small value of the incident intensity. If this parameter was changed to a value close to the end point of the lower branch of the hysteresis cycle, the system eventually relaxed to a state of high transmission in the upper branch. A simplified Langevin equation was used to describe the system near the critical point. By numerical simulation of this equation, dependencies of a mean first passage time (MFPT) to reach the upper state on the noise intensity and the deviation of the incident electron flow intensity from the critical point have been obtained. Numerical results satisfactory agree with analytical results obtained with the use of the method of Ref. [1]. The change of the behavior from the case when the average value of the incident intensity is less or bigger than the critical one indicates the change from relaxation via activation by fluctuations to relaxation via deterministic dynamics. It was shown that in the region below the critical point MFPT increases with decreasing of the incident intensity. At fixed distances MFPT decreases with increasing of noise intensity. For those values of incident intensity for which the transition in deterministic limit was impossible, adding of noise makes it possible.

[1]. P. Colet et al. Phys. Rev. A. 39, 149 (1989)

P- 2 ⇓

General Dynamic Properties of Quasi-Particles Under an External Field

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The features of dynamic properties of free quasiparticles as represented by Frenkel excitons were analyzed in paper [1]. The Frenkel excitons are electrically neutral. Therefore a field of elastic stresses which are caused by crystal deformation or by lattice defects can serve as an example of external field for them. In case of electron injected into a semiconductor, which is considered in this work, the influence of external electric field is analyzed.

The analysis of dynamic properties of quasiparticles under an external electric field of general spatial configuration was done. To separate a contribution of an external field to dynamics of the quasiparticle from other physical influences, the most simplified model of the crystal was used: nearest neighbor approximation, the cubic crystal lattice approximation and continuous approximation of the second order. Also, this analysis was performed under approximation of homogeneous external field and generalized approximation of amplitude-modulated plane wave. The generality of approximation manifests itself in the fact that the wave vector and energy phase component of wave function depend on time. As in the case of absence of an external field [1] (uniform dynamics), in the case of non-uniformity it is also possible to provide different descriptions of quasiparticle dynamics (the quantum-mechanical (base) description and the description of classical type) that are in mutual agreement. The relations obtained allow us to define basic dynamic characteristics of quasiparticle identically to the case of no external field (in particular, speed vector and the dynamical mass tensor are kept identical).

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P- 3 ⇓

Structure of Fluids in Pores of Various Shape

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It is known that in pores external field can cause significant rearrangement of density (particles) in the system. Namely, for pores of small size filled with fluids (i.e. finite-size liquid systems) wall potential as well as gravitational field affects essentially distribution of fluid. Such non-uniform distribution can be measured by experiments on neutron refraction. Peculiarities of density fluctuations correlation at critical state are studied by light scattering as usual. Those experiments give interesting information about critical state of the system at critical region.

In our work we consider problem of fluid distribution in pores of different shape from theoretical point of view. We find profiles of density distribution in systems of several geometries and analyze results for some special cases (i.e. for particular types of wall potential and for the case of gravitational field). Here we use methods that were developed previously for simple one-component systems and several particular types of wall potential and multi-component systems under influence of external field of general type. We complete our theoretical results with numerical calculations and compare results with experimental data and other results are exist.

P- 4 ⇓

On Nature of Broadband Background in Spectra of Raman Scattering of Light

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In spectra of spontaneous Raman scattering of light (RS) of liquids and polycrystalline objects side by side with narrow lines of intramolecular vibrations a broadband background is observed. The broadband background is stretched up to 5000 cm^{-1} in the Stokes region and sharply decreased in anti-Stokes one. Experimental dependencies of formation of this background were studied in many works, however, the nature of appearance this background is still uncertain.

In the present work we propose a mechanism of formation of the broadband background in spectra of Raman scattering. As a result of self-organization and self-compression in atomic-molecular systems there is a process of formation of collectivized electrons or electronic subsystem. Formation of collectivized electrons should not be considered as a process of formation of quasi-free or Brownian electrons. As a result of oscillating influence of the physical vacuum and surrounding particles there occurs an additional volume polarization of valency electrons or induction of beats of frequency of vibrations (spins). This process leads to formation of oscillating WFR of electrons, and the phase correlation between WFR of electrons leads to formation of self-coordinated field of electrons [2]. We present a broadband background in Raman spectrum of D tirozyne at =300 at different power of exciting radiation. One can see that the rise of power of exciting radiation is accompanied by rise of intensity in the maximum of the scattering spectrum. Such dependence can be explained by self-organizing influence of the exciting radiation on the energy structure of the self-coordinated field of substances electrons. There is the additional polarization of electrons, and this process leads to rise of intensity of the broadband background.

The broadband background in spectra of Raman scattering should be considered to be a manifestation of the self-coordinated field of electrons on main electronic energy level. Energy transition to excited electronic level with absorption of excitation energy leads to formation of electronic absorption spectrum, and the energy transition to the main electronic energy level leads, in the process of formation of electronic liquid, to luminescence phenomena.

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2 MOLECULES

O- 1 ⇓

Intermolecular Hydrogen Bond in Solutions of Quinoline. Spectroscopic Studies

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The half-width of bands 1414 cm^{-1} and 1033 cm^{-1} of Raman scattering spectrum of quinoline at the dilution of it in neutral solvents (benzene, CCl_4) markedly narrowed (in 1,3-1,5 times) at high dilution. The effect is associated with increased time of vibrational relaxation.

In solutions with isopropyl alcohol band 1033.8 becomes of doublet character, with a reduction of quinoline in a mixture of high-frequency component increases in intensity and in these concentrations the doublet character of the band is clearly detected. Resolution of bands becomes better in the dilution of the binary solution of quinoline-alcohol in a large number of neutral solvent (benzene). Wave number of bands in the triple mixture of 1033 cm^{-1} and 1039 cm^{-1}. Doublet nature of the band in the binary and triple mixtures is associated with the presence in a liquid mixture of monomer molecules and aggregates of quinoline-isopropyl alcohol (high-frequency line). Quantum-chemical calculations showed that between molecules of quinoline and alcohol molecules can form hydrogen bonds. For example, between the hydrogen atom of OH group of ethanol and the nitrogen atom of quinoline molecules is formed H-bond with length 1,938 and the energy profit 23.1 kJ/mol. Apparently, intermolecular hydrogen bond to form between the molecules of isopropyl alcohol and quinoline. Formation of aggregates is seen in the band 820 cm^{-1} isopropyl alcohol in a solution with quinoline - band width with decreasing content of alcohol goes through a maximum, which accounts for 0.1 m.f. of alcohol content. A similar picture is for the band 667 cm^{-1} of chloroform in a mixture with quinoline. In both cases, the observed picture is associated with the complexity of the bands of alcohol 820 cm^{-1} or chloroform 667 cm^{-1}. The above method of the triple mixture allowed to improve the resolution of the complexity of the band 667 cm^{-1} of chloroform.

O- 2 ⇓

Spectroscopic Studies of Formation of Intermolecular Hydrogen Bonding in Alcohol Solutions of Pyridine

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Quantum-chemical calculations and experimental data on Raman spectra show that the possible aggregation of dimer molecules of pyridine in pure liquids, at this the molecules form two hydrogen bonds with each other. The bonds are formed between two molecules with participation of neighboring nitrogen and hydrogen atoms of one molecule with similar atoms of other molecule. The length of hydrogen bond is 2,570 . Note that the distance between the nitrogen atom and the nearest hydrogen atoms in the monomer molecule is 25% less than the length of intermolecular hydrogen bond. Intermolecular H-bond is weak and it corresponds, according to calculations, the energy of 7.37 kJ/mol. In the Raman spectra 992 cm^{-1} band of pyridine, with a strong dilution in heptane is narrowed in about two times, partly due to, in our opinion, the destruction of dimers of pyridine. Narrowing of the 992 cm^{-1} band may also be associated with increased time of vibrational relaxation, which usually occurs in the dilution of a substance in a solvent of low density. The difference in frequencies of monomers and dimers of pyridine, according to calculations, is small - 0.6 cm^{-1}.

In pyridine solution with isopropyl alcohol in the Raman spectra along with a band of monomers pyridine 992 cm^{-1} we observed in the high-frequency part two other bands with the wave number of 998 cm^{-1} and 1001 cm^{-1}, which are associated with the presence in a mixture of pyridine aggregates of various types.

Calculations showed that in mixtures of pyridine with methyl alcohol it is possible through hydrogen bonding formation of dimers - pyridine, methyl alcohol and trimer pyridine with two molecules of alcohol with the energy profit, respectively, 23.1 kJ/mol and 59.78 kJ/mol. In the trimer aggregate is involved in hydrogen bonding a hydrogen atom nearest to the nitrogen atom of pyridine molecule. Formation of these aggregates is possible also in pyridine - isopropyl alcohol solutions. With the use of the triple mixture - dilution of the binary mixture of pyridine-isopropyl alcohol a large amount of heptane - we were able to improve the resolution of the bands 992 cm^{-1}, 998.5 cm^{-1} and 1001 cm^{-1} (respectively, monomers, simple and complex aggregates) and to determine from anisotropic components of the bands the relaxation times of the orientation of aggregate formations, which were equal to 4.1, 11.0 and 21.0 ps.

O- 3 ⇓

2D NMR and DFT Study of Proton Transfer and H-bond in Ionic Liquids and Super-Polar Media

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The picolinic acid N-oxide (PANO) can be attributed to the series of systems with strong intramolecular H-bonds. However, it can be suspected that in super-polar media (e.g. formamide, $\epsilon = 109.6!$) the intramolecular H-bond system may convert into intermolecular neutral H-bond complex of PANO with formamide molecule.

NMR experiments were carried out on a BRUKER AVANCE^{II}/400 NMR spectrometer (details are given in [1]). ^{1}H and ^{13}C chemical shifts of PANO were confirmed by the analysis of 2D homo- and hetero-nuclear NMR experiments (^{1}H^{1}H COSY, ^{1}H^{13}C HSQC and ^{1}H^{13}C HMBC).

Our computations of H-bonded structures of PANO and PANO/formanide were based on density functional theory (DFT). Molecular geometries in vacuo and solutions were derived from the PBE1PBE geometry optimization in combination with the 6-311++G** basis set. The same level of theory was also utilized to calculate magnetic shielding tensors within gauge-including atomic orbital approach. We have used the polarizable continuum model (PCM) to account for solvent effects. Because formamide is not a built-in solvent within PCM in the Gaussian 03 program, we have provided the value of dielectric constant of formamide at room temperature in the liquid-phase calculation explicitly.

The obtained NMR and DFT data indicate that formamide being extremely polar solvent (maybe the most polar found among liquids) indeed can act on certain H-bond systems as their destroyer. It can even affect the systems with such a strong H-bond, as PANO molecule. The bridge proton can be removed from its primary motion path and placed to a newly appeared one due to the short-range order structures build with one or several solvent molecules.

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Influence of Fluorescent Probe Hydrophobicity on Cell-Probe Binding in Cell Tracing Applications

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Fluorescent cyanine dyes are widely used as markers and sensors in biological systems. They can be introduced in bio-systems either by covalent-labeling or by adsorption. Due to the different strength of electrostatic, hydrophobic and van der Waals forces between the dye and the target, the adsorption interaction can be very specific. According to their adsorption state, the fluorescence and absorption behavior of the dye molecules can change remarkably upon adsorption.

In the present study we try to found out the role of such a parameter as dye hydrophobicity on the efficiency of it binding with cell membranes. For this purpose, a series of cationic dialkyloxacarbocyanine perchlorate (DiOC_n) dyes has been used. As a model system of cell membrane we use micelles of anionic sodium dodecylsulpate (SDS) surfactant. Based on the study of changes in DiOC_n dyes absorption depending on the surfactant SDS concentration, the efficiency of the dye surfactant micelle interaction has been analyzed. The increase of the SDS concentration leads to the increase in the absorption of all dyes and shift of the absorption maxima toward long wavelengths that is evidence of the dyes incorporation into SDS micelles. Using Benesi-Hildebrand equation, the binding constants (K_b) of the dyes to the surfactant micelles, the fraction of the dyes bound to the micelles (f_{mic}) and the standard free energy change (ΔG^0) of the dye transfer from water phase to micellar phase have been calculated. It has been shown that the interaction of oppositely charged dyes and surfactant micelles is controlled by both electrostatic and hydrophobic interactions. The increase of the dye hydrophobicity by lengthening alkyl chains increases the tendency to associate, the K_b, f_{mic} and ΔG^0 values increase with increasing dye alkyl chain length. For DiOC_2 dye with the shortest alkyl chains the electrostatic attraction between the dye and a micelle is found to be not enough for effective binding. In this case only 50% of the dye molecules are incorporated into SDS micelles. However, a small increase in the dye alkyl chain length causes an abrupt nonlinear increase of the f_{mic} value that points to the fact that the hydrophobic interactions plays a major role in the dye to micelle incorporation.

O- 5 ⇓

Fermi Resonance of New Type

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The lecture is devoted to manifestation and study experimentally and theoretically of Fermi resonance of new type: the resonance between a local vibration and the two-phonon spectrum in layered crystals (H-PbI2) with transition metals. The plan lecture is the following:

INTRODUCTION. Fermi resonance and particular interest to investigation of layered crystals with ferro-group transition ions.

Exciton reflection spectra.

Influence of temperature on energy position and half-width of exciton absorption band (n=1).

Electron magnetic resonance studies.

Manifestation of Fermi resonance of new type by Raman spectroscopy method.

Theory and simulation.

Fermi resonance between impurity and two-phonon states.

CONCLUSIONS.

O- 6 ⇓

Spectroscopic and Thermodynamic Parameters of Liquid n-alcohols

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Primary monohydric alcohols are the polar solvents associated by H-bond. They have naturally changing physical and chemical properties. These properties affect their spectroscopic and thermodynamic parameters. In the present work these characteristics of liquid n-alcohols from methanol up to octanol at 5 - 55^0 (over 10 ^{0}) are analyzed.

Far IR-spectra maxima (ν_{max}) (accordingly to [1]) using structure-related parameters (compressibility, density) are calculated. Shift viscosity and ν_{max} experimental data, relaxation times of transmitting oscillatory conditions (τ_E) and a structural relaxation (τ_D), self-diffusion factors (D) this n-alcohols according to works [2-5] are calculated and analyzed using the values we define. Calculated at 5 55 ^{0} values of ν_{max}, τ_E, τ_D and D is in accordance with available experimental data.

Association constants and part of monomers in structure of n-alcohols are estimated over the same temperature range on the basis of model proposed in [6]. H-bond, dispersive, dipole and inductive contributions in total energy of intermolecular interactions (IIA) have been determined for the alcohols mentioned above. Change of a part of each contribution with temperature growth and hydrocarbon radical rise has been shown quantitatively, also as their influence on structure of liquid n-alkanols.

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O- 7 ⇓

Analysis of Solvent Effects on Parameters Of IR-Spectrums of Organic Molecules and its Complexes in Single and Binary Solvents. Role of Cooperativity

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Properties of organic molecules significantly changes during transition of them from gas phase to solution. Intermolecular interactions between solute and solvent are the reason of these changes. They influence on conformation equilibrium, on organic reactivity and others properties. IR-stectra parameters are especially sensitive to manifestation of intermolecular interactions. This gives opportunity to use IR-spectroscopy as the basic method for studying them. Nowadays different approaches are used for estimation of solvent effects influence on IR-spectrums. They can be divided on methods based on physical models and methods using empirical scales of solvents.

In present work we have studied influence of media on IR-spectrums of different molecules and its complexes in single and binary solvents. The most widely spread models of solvent effects assessment on IR-stectra (gutman scale (an), hildebrand scale of density of cohesion energies, allerhand-schleyer scale (g) and multi-parameter equation of kamlet-abboud-taft) were used. It was shown that they are not universal. Some of them have good capacity of quantitative description of observed solvent effect on frequencies; others possess opportunity adequately to mIRror the mechanism of solvent involvement in studied process. In general all studied models cant account contribution of cooperative hydrogen bonding in solute-solvent interaction. Cooperativity is the important property of all types of intermolecular interactions in condensed media.

New model for analysis of solvent effects on IR-spectrums was applied. This model is based on thermodynamics of solvation of alkanes in organic non-electrolytes. According to this model experimentally measured stretching vibration frequency shifts (relative to a gas phase) of molecule x-h in solution is presented as the sum of contribution of van der waals interactions, hydrogen bonds formation and cooperative effects. Assessment of van der waals interactions values is carried out using the new solvent parameter S_{VW}, proposed in our work.

Solvent effects on stretching vibration bands of C=O, S=O AND P=O groups of free molecules in aprotic solvents were studied. Applicability of different models to describe frequency shifts was analyzed. It was shown that sensitivity to media of studied objects depends on structure of molecules and polarizability of characteristic group. Frequency shifts due to van der waals interactions in some cases were more than 30 cm^{-1}.

Stretching vibration frequencies of h-bonded complexes in different aprotic and proton donor solvents were measured. Analysis of value and mechanism of solvent influence were carried out. The methods of an assessment of cooperative influence of proton donor and proton acceptor solvents on strength of hydrogen bonds in complexes of alcohols, polyhydroxyphenols, amides with different molecules was proposed based on IR-spectroscopic data solvent effects on stretching vibration frequencies of different molecules acetone, butanone, octanone-2, dimethylsulphoxide and ethanol in binary mixture acetonitrile-tetrachloromethane were studied. It was shown that there is no linear correlation between frequency shifts of studied groups at different composition of components and solvent parameters due to preferential solvation. Consequently, the solvation shell around the standard solutes which were used for determination of solvent scales is changed than we dissolve other molecules. Deviation from additivity is increased with increasing of molecules polarity. The same situation was observed for solutions of one solute in different binary solvents. Some regularity between compositions of mixtures and value of solvent effects were determined.

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The Kinetics of Cluster Formation During the Phase Transition Gas-Liquid in Alcohols

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The processes of the molecular cluster formation of monohydric alcohols (from methanol to hexanol) were investigated by FTIR using the matrix isolation technique in Ar matrices. The transformation of FTIR bands of free hydroxyl groups (3600–3800 cm^{-1}) into diffuse bands (3000–3600 cm^{-1}), which were assigned to the stretching vibrations of the H-bonded O–H groups in various clusters, was monitored in its initial stage softening the matrices by heating from 20 K to 50 K. The band shape analysis was carried out for all investigated systems. The FTIR bands of alcohol molecules trapped and solidified in the matrices without annealing were found very close to be Gaussian-shaped. The magnitude of inhomogeneous broadening due to the matrix effect was evaluated. The values of hydrogen bond dissociation time of alcohols trapped in matrices were evaluated from the bandwidths of dimers, trimers and higher aggregates after broadening factor was taken into account. These data correlate with those directly measured in ultra fast infrared experiments of alcohols in solutions.

O- 9 ⇓

Luminescence Properties of Dyes in a Strongly Scattering Medium

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Being inherent in dyes the significant overlapping of luminescence and absorption spectra causes reabsorption of luminescence radiation. It results in significant dependence (long-wave shift and spectrum contour change) of luminescence spectra (LS) on the parameters influencing the absorption efficiency: the sample thickness and the dye concentration. In the strongly scattering medium these parameters are supplemented with scattering efficiency. The efficiency increases luminescence path length in the sample influencing in such a way the reabsorption. Multiple scattering also influences the excitation redistribution in a sample. Thus one can expect the significant dependence of the LS and excitation spectra (ES) on the scattering centers concentration and the center refractive index.

The mentioned influences can be substantially described theoretically by successive considering of reabsorption and reluminescence in each sample point. But this method of the problem solution is laborious that results in formulas complicity and being difficult for analyses. On the general conclusion basis we obtained the simple expressions determining luminescence radiation dependence on excitation and luminescence wavelength, scattering and absorption coefficients, sample thickness. The main feature of the expressions is obvious including of all main actual mechanisms that allow us to analyze their influences: the influence of absorption and multiple scattering on the excitation redistribution in the sample, and absorption, multiple scattering and reabsorption influence on the LS. The multiple scattering influence was introduced via photon path length dependence on the scattering centers concentration been calculated by Monte-Carlo method.

It were experimentally investigated the dependences of LS and ES of rhodamine 6G in solid polymer suspension of scattering particles (silica, BN) on the particles concentration and the sample thickness. The LS and ES concentration-dependencies were shown to be observed under essentially different particle concentration and sample optical thickness (D¡¡1 and D¿1 correspondingly). The obtained experimental and calculated results are in good agreement.

As the LS determine the gain contour of a dye, the similar spectral dependences have to be observed for random lasing as well. It agrees with experimental results too. Thus the obtained results can be useful for random lasing spectra calculation and for strongly scattering medium (as abrasive tools) diagnosing.

O- 10 ⇓

Anharmonism Effect on Chemical Bond Deviation of the Deformed Methane Molecule

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The force matrix for free methane molecule has been computed without using tentative assumptions about force field pattern. The calculations have been carried out by the relatively new method of $3N$-matrices [1] using experimental frequencies of normal vibrations of CH_4, CD_4 and CT_4 molecules.

The deviation scope of valence-force field from real molecule force field has been ascertained the "addition" of central force field amount near 11%. The effect of anharmonicity has been taken into account using two stages: calculating zero frequencies of normal vibrations using four independent parameters of anharmonism for each vibration and constructing model potentials for all eigenmodes according to their forms.

The deviation of chemical bond C-H (the term "deviation" was proposed in [2] for chemical bond "bending" effect) for deformed molecule has been calculated using both harmonic and anharmonic approximations. The chemical C-H bound deviation by certain preliminary molecule deformation is the one of the manifestations of central-force field "addition" to the valence-force field. The C-H bond deviation can be explained by changing the equilibrium position of hydrogen atom.

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Coefficient of density and temperature broadening of ν_1 band of Raman spectra of methane and its gaseous mixtures with argon and krypton

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Problems of intermolecular interaction and manifestation of this interaction in the spectra of molecules is not only scientific but also practical significance. Of particular interest are studies of molecular spectra of hydrocarbons, particularly methane. Problems of the spectroscopic determination of methane in the atmosphere (damp) or in the atmosphere of other planets is still important. Spectroscopic methods are expected to play an important role.

In this report we present the results of the study of spectra of ν_1 band of isotropic Raman scattering (IRS) of methane and in mixtures with Ar and Kr in the gas phase in the temperature range 140 ÷ 380 K and densities up to 380 Amagat. In all cases ν_1 band of CH_4 in the gas phase at densities up to 10 Amagat not alter its half-width, and then with the increase in density increases almost linearly with the density of the gas. According to the linear dependence of the half-band of ν_1 band on density we determined the factors of the density broadening K.

For the studied systems running the following ratio.

$$K(CH_4 + CH_4 \approx K(CH_4 Kr) > K(CH_4 + Ar) > K(CH_4 + He)$$

The change in temperature leads to a qualitatively similar change in the coefficient of broadening for all the studied systems: the increase in temperature from 140 K the broadening coefficient initially decreases, reaching a minimum in some temperature T_{min}, depending on the buffer gas, and then begins to rise. Nonmonotonic dependence of the coefficient of broadening on the temperature was predicted in the model ML Strekalova and AI Burstein [1], which showed that the cause of this behavior can be influenced in the collisional processes of attraction, the relative role of which is dependent on temperature. Calculated by the model ML Strekalova and AI Burshtein correlation of the broadening coefficient of ν_1 band of gaseous pure methane on the density and temperature were compared with the experiment. The shape of both curves are similar, but the calculation predicts a weaker dependence than is observed in the experiment. Model ML Strekalova and AI Burshtein only qualitatively explains the shape of curves, there is no quantitative agreement.

.. mechanism of intermolecular interactions in molecular spectrometry is still largely open.

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O- 12 $\Downarrow$

Dimensional Effect in IR Absorption Spectra of Benzene

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We studied the shape of IR absorption band (ν_{max} = 673 cm^{-1}) of gaseous and liquid benzene in dependence on thickness of absorbing layer. The band of IR absorption ν_{max} = 673 cm^{-1} is related to non-plane vibration of the benzene ring. In gaseous state the contour of IR absorption band of benzene represents lateral P and R branches and the central Q branch. Distance between maximums of intensity of P- and R-branch is $\Delta\nu_{PR} \approx 26cm^{-1}$ in the process of transition to liquid state there is a significant deformation of the bands contour. Normal spectrum of IR absorption in liquid benzene can be obtained when the thickness of benzene layer is 3-4 μ m the bands contour consists of intensive central dispersion contour and lateral high-frequency contour.

We studied the dependence between the absorption bands contour and the thickness of benzene layer. With rising thickness we observe, firstly, a deformation of the contour in its maximum, and when the thickness is higher than 15-20 μ m we observed a disappearance of the central dispersion part. The band's contour of liquid benzene becomes similar to that in the gaseous state without the central Q branch. Distance between the maximums of P and R branches is about $\Delta\nu_{PR} \approx 24cm^{-1}$, i.e. like if it would be in gaseous state.

The obtained results can be explained in terms of field-substance interaction [1]. As a result of oscillating influence of molecules on each other and the physical vacuum, an oscillating wave-function of response (WFR) is induced on each molecule. As a result of phase correlation between WFR of molecules a self-coordinating field of molecules is formed. Energy structure of WFR of molecules is identical to the energy structure of the self-coordinated field of matter. That is why the WFR of molecules is an order parameter for molecular systems. Observable P and R branches in the gaseous state should be referred to manifestation of oscillating WFR of molecules. Due to difference in spatial dimension and frequency of oscillations we observed the difference between the frequencies and intensities of lateral P and R branches. As a result of break of phase correlation in the self-coordinated field of molecules the Brownian particles are formed.

Dynamics of mass-center and orientation of the particles are of chaotic character. The Brownian molecules lead to formation of the central Q branch in vibrational spectra. In the process of transition from gaseous state to liquid one there occurs a mutual compensation of dipole moments of WFR of molecules, as a result of which there occurs a significant decrease in intensity of lateral P and R branches. The Brownian molecules, as in case of gaseous state, form the central Q branch.

With rising thickness of layer there occurs a process of restoration of the phase correlation of WFR of molecules in the self-coordinated field of liquid. As a final result, realization of total phase correlation between WFR of molecules leads to disappearance of the central Q branch. Approximate coincidence of PR in gaseous and liquid states testifies on insignificant change of the frequency of FWR of molecules in the process of transition of matter from one aggregate state to other.

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O- 13 ⇓

Stimulated Raman Scattering in Strongly Scattering Active Medium

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Nowadays considerable attention has been focused on the investigation of stimulated emission in random strongly scattering medium (RSSM) resulting in random lasing (RL). But the other possible stimulated process - stimulated Raman scattering (SRS) - has not been investigated in RSSM so far. Due to multiple light scattering the both emission processes are developed along broken trajectories and reveal itself as undirected emission. But the corresponding emission spectra are quite different. RL spectrum is usually continuous under diffusive conditions of light propagation $L \sim l$ (L - characteristic medium size; l - light wavelength and photon mean free path) because the scattered wave interference is destroyed in this case. Linear view of the RL spectrum is possible only under a unique condition of the weak photon localization ($l \sim \lambda$) being usually difficult to achieve. But SRS is characterized with linear spectrum.

We showed experimentally that SRS can be obtained when it accompanied with stimulated emission in RSSM. This effect for dye molecules was obtained in two type of RSSM: concentrated suspensions of silica in polyvinylacetate and vesicular polymeric films. Pumping was performed by the second harmonic of either YAG Nd^{3+} or wavelength tuneable phosphate glass Nd^{3+} laser. SRS and stimulated emission jointly form in RSSM united non-linear process. In this case the quasilinear spectrum of RL under diffusive regime of light propagation in dyed RSSM was experimentally revealed. Initially the observed emission spectrum was continuous. Under pump intensity increasing it narrows down rapidly to saturation value ~3-8 nm (depending on the dye and spectral region) corresponding to the RL rise. Further pump increasing caused reformation of narrow lasing spectrum into quasi-line spectrum with not-equidistant lines. The lines spectral position in observed quasi-line spectra is strongly reproducible and depends on excitation wavelength. For rhodamine 6g dyed RSSM the line frequency shifts relatively to the pump frequency as well as the lines intensity are in good agreement with corresponding parameters of the inverted Raman scattering [1] and SERRS (surface-enhanced resonant Raman scattering) [2] lines for this dye. On this basis we can assert that the lines in RL spectrum arise from Raman scattering on dye molecules.

The lines formation in the RL spectra is quasi-threshold process and it adheres to certain rules. The lines arise within RL spectral region only [3]; their intensities (against the smooth background) are linearly dependent on emission intensity of RL at the same wavelength and pump intensity. It testifies the lines formation is conditioned by both these processes. The quasi-threshold behavior of line formation testifies about stimulated mechanism of dye Raman scattering in RSSM. Unlike the "classic" SRS observed for one or several high-Q Raman lines only the RL spectra reveal almost all active Raman lines. It testifies about specific conditions realized in RSSM which impede transition from enhanced Raman to "classic" SRS and thereby destroyed competition between different Raman lines.

Having the interrelated intensities the Raman scattering together with RL form a united non-linear process in the RSSM and influence each other. These processes can be described by means of system of the equations in Stokes and simulated emission intensities at Raman frequencies and molecules state population as well.

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O- 14 ⇓

Abnormal Shifts in Raman Spectra of Deuterated 6-azacytidine and Cytidine: Possible Role of H-bonds

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Anomalous nucleoside 6-azacytidine (6-azaC) is known as an antimetabolite with wide spectrum of therapeutic activities. Raman study of 6-azaC dissolved both in H_2O and D_2O revealed that some Raman peaks of 6-azaC dissolved in D_2O have manifested abnormal high frequency shifts with respect to their position in water solution while the other have been shifted normally to low frequencies. Similar results were obtained for canonical nucleoside cytidine and its related nucleobase cytosine [1,2]. Recently there was reported so called blue shift in Raman spectra of methanol in water solutions due to improper hydrogen bonding involving the methyl group of methanol with solvent [3]. To discriminate effect of deuterated solvent and deuteration effect of the nucleoside molecule itself we have made recrystallization of 6-azaC and cytidine from their H_2O and D_2O solutions. Raman spectra of 6-azaC microcrystals recrystallized from H_2O solution proved to be the same as spectra of the initial 6-azaC microcrystalline sample. But in spectra of 6-azaC microcrystals recrystallized from D_2O solution in addition to the initial peak at 760 cm^{-1} appeared new peak at 750 cm^{-1} and in addition to the initial peak at 1290 cm^{-1} appeared new peak at 1301 cm^{-1}. It confirms noticeable deuteration effect of the nucleoside molecules itself in D_2O solution and existence of abnormal Raman isotopic shift in 6-azaC crystal too. Similar results were obtained for recrystallized cytidine. To the best of our knowledge this is the first observation of abnormal Raman frequency shifts of intramolecular modes under deuteration unlike to reported in [3]. To elucidate principal possibility of such abnormal shifts Raman spectra of the above three compounds and their water solutions were calculated using PCM model, Gaussian 03 package, B3LYP hybrid density functional in 6-31+G (d,p) basis set. For 6-azacytidine and cytidine were obtained both normal and abnormal frequency shifts close to the experimentally observed (except abnormal shift in spectrum of cytosine. We assume that abnormal shift occurs due to deuteration of intramolecular H-bonds. To test such possibility we calculated Raman spectra of benzophenone and fully deuterated benzophenone that has no H-bonds and of 2,2?-dihydroxybenzophenone that contains two adjacent OH groups. No abnormal shift occurs for benzophenone in view of excellent agreement of calculated and experimentally measured Raman spectra. On the contrary after replacement of OH with OD in the 2,2?-dihydroxybenzo phenone molecule calculations predict abnormal shift of initial 1060-cm^{-1} peak for 5.4 cm^{-1} to higher frequencies. .

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P- 1 ⇓

Comparision of Spectral Shifts of Benzene, Naphthalene, Phenanthtrene and Fullerene-60 in Oxygen Containing and N-Alkane Solvents

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Solvent-induced shifts of bands in $S1 < S0$ and high-energy transitions of benzene, naphthalene, phenanthrene and fullerene-60 in oxygen containing (heavy water, light water and the first alcohols) and n-alkane solvents are compared. It was shown that ratios of shifts of bands belonging to high-energy transition to corresponding shifts at $S1 < S0$ transitions in in oxygen containing solvents noticeably exceeded the similar ratios in n-alkane solvents. Probable nature of such effects and peculiarities of fullerene-60 spectral shifts are discussed. It was speculated that excess values of spectral shifts can be provoked by electronically excited state of molecules in form of charge-transfer complexes (exciplexes).

Probable mechanisms of such effect and peculiarities of spectral shifts are discussed. An assumption is expressed that excess values of spectral shifts provoked by oxygen atoms in solvent molecules are connected with short-time imbedding oxygen electrons into high-energy states of solutes (exciplexes in high-excited solute states)[1].

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P- 2 ⇓

The Pecularities of NMR Spectra of Cobalt Semiquinolates Transformed by Hyperfine Coupling

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The valence tautomerism of Co semiquinolate complex ($Co(SQ)_3$) has been studied in wide temperature range 183 383 (toluene D_8) and 293 423 (DMSO D_6) using ^{1} NMR technique.

The ^{1} NMR spectrum of $Co(SQ)_3$ recorded at 293 K just after the dissolution in DMSO D_6 is drastically broaden and shows signals of aromatic protons (6-8 ppm) and tret-butyl moieties (0-4 ppm.). The increase in temperature leads to the significant narrowing the signals in the spectrum which is accompanied by slight changes of their chemical shifts. The reverse change in the sample temperature is attended with separation of resonance signals at 343 . Such transformation of the spectrum can indicate to the fact that the complex exists in solution as two tautomers [1] where noticeable delocalization of unpaired electron spin density on protons of the ligand molecule does not occur. Therefore, the values of chemical shifts of signals of aromatic proton and signals tret-butyl moieties differ insignificantly from diamagnetic analogs.

Analysis of the chemical shifts alteration points to the presence of intramolecular exchange process which is not associated with valence tautomerism.

The transformation of the ^{1} NMR spectrum of $Co(SQ)_3$ in DMSO D_6 unexpectedly results in the appearance of two broaden signals of low intensity with chemical shifts at 12.2 and 16.3 ppm. The location and width of the signals change in the course of the temperature varying according to Curie law [2]. Analysis of the spectral data reveals the linear dependence of chemical shifts on temperature.

Similar signals are observed in the ^{1} NMR spectra of $Co(SQ)_3$ recorded in toluene D_8 at various temperatures. The signals appear at 313 and become strongly broaden at 233 . however, like in the case with DMSO, the change in chemical shifts depends linearly on temperature and is obeyed to Curie law. The data obtained can be explained by NMR theory applied for paramagnetic systems.

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P- 3 ⇓

^{1}H, ^{13}C NMR and DFT study of intermolecular interactions in ionic liquids

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Ionic liquids (hereinafter - ILs) are materials consisting exclusively of anions and cations, which melting temperatures are lower than +100 C. The discovery of ILs is one of the most recent and most successful breakthroughs creating the multifunctional materials. ILs demonstrated their unique characteristics in various high technology areas, from which particular mention: enzyme catalysis, protein synthesis, membrane techno-logy, fuel cells, dye-sensitized solar cell (DSSC), gas sensors, and others. Dielectric studies show that the ILs are not super-polar systems. It is thought that the most of exclusive properties of ILs are due to mezoscopic effects - in particular with a heterogeneous formation of nanostructures and the dynamic process between them [1]. Intermolecular interactions between the anions and cationic in IL should be one of the most important factors determining formation of such structures.

In this research of ionic liquid 1-decyl-3-methyl-imidazolium bromide [C_{10}mim][Br], the neat material, and also dissolved (0.01 mol. concentration of solution) in various dielectric permeability media (chloroform, acetonitrile, ethanol, 2-butanol, H_2O, etc.) research using ^{1}H and ^{13}C NMR method was carried out. The most important interaction in this compound is considered to be the hydrogen bond, which forms between the anions and cationic $BrHN^+$.

Experimental studies were performed with AVANCE^{II}/400 NMR Bruker spectrometer using a 5 mm BBO probe. 297 K temperature in the probe was maintained with accuracy of 0.5 K. Chemical shifts were measured respect the TSPSA standard [2] in D_2O solution in capillary. The same D_2O capillary was used for lock.

In order to obtain supplementary insights into the experimental observations the ^{1}H and ^{13}C chemical shifts of [C_{10}mim][Br] were calculated using density functional theory (DFT). Calculations were performed using modified hybrid Perdew, Burke and Ernzerhof functional (PBE1PBE/6-31++G**) and the GIAO atomic orbital approximation. For compounds geometry optimization were used B3LYP functional and 6-311++G(2d, 2p) base function set.

The ^{1}H chemical shifts of various groups of [C_{10}mim][Br] dependences on the dielectric constant are measured. It is worth to note that the most considerable variation of the chemical shifts is observed in small dielectric permittivity range (10 - 20), in particular at the transition from the neat IL to solutions.

The obtained results show that signals of terminal methyl groups retain the most stable shape of the spectrum. Dielectric medium mostly influence the behavior of the $BrHN^+$ proton, which is characteristic of H-bonds. Also noteworthy 'central' [C_{10}mim][Br] parts groups of NMR signal shifts. This may be due to the relatively 'long' decyl- hydrocarbon chain conformational transformation during the transition from the neat material to the solution.

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2D Raman Correlation Spectroscopy Study of Ionic Liquids Conformation

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Ionic liquids (ILs) are one of the most successful breakthroughs of the last years creating novel multifunctional materials those posses many appealing features [1]. It makes these systems very attractive as for high technologies as well as for research. By their dielectric properties IL systems are not super-polar [2]. Their extraordinary action in certain molecular processes is mainly due to the supra-molecular structuring and other short-range (in nano-scale) order effects [3]. The vibrational spectro-scopy (FTIR, Raman) can be particularly powerful method studying these effects. Perhaps the most informative are the low frequency modes that are coupled with phonons, Hbonding, skeletal vibrations, etc. Unfortunately their spectral contours often are very broad and not resolved in the conventional 1D spectra. The two-dimensional (2D) correlation analysis, developed by Noda [4], can be effective tool solving this problem. This has been already demonstrated on the FTIR spectra of IL systems [5, 6]. In the present work 2D correlation technique was applied on the Raman spectra. One of imidazolium-based room temperature ionic liquids, namely - 1-decyl-3-methyl-imidazolium bromide (short name: [C_{10}mim][Br]) was chosen for the study.

This substance has a rather low melting point ($T_m = 289$ K) and is totally miscible with water and other solvents of technological importance. Just above its melting point [C_{10}mim][Br] is extremely viscous (7892.9 mm^2/s at 293 K, data from Merck KGaA). The low frequency Raman bands (50 - 200 cm^{-1}) are indeed overlapped under a broad envelope contour in the 1D spectrum. These modes are resolved in the 2D asynchronous spectrum obtained using the thermal perturbation of the sample in the range of $296 < T < 433$ K stepping by 20 K.

The vibrational modes of different conformers of [C_{10}mim][Br] were identified and fairly good agreement between experimental and calculated (DFT B3LYP/6-31++G**) frequencies was achieved.

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P- 5 ⇓

H-bond Clustering of Methanol in Ar Matrix: 2D FTIR Correlation Spectroscopy

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The clustering phenomena and structural peculiarities of partially ordered liquids are of great interest in the context of recent trends and developments in studies on modern multifunctional materials, heterogeneous systems and nanotechnologies. Monohydric alcohols, that usually build broad variety of H-bond aggregates, are quite simple and convenient models to investigate the properties of molecular systems sized over the mezoscopic scale (1 - 100 nm). The purpose of present studies was to register the dynamical FTIR spectra of the simplest alcohol, i.e. methanol trapped in Ar matrices using temperature perturbation and to analyze the changes in spectra applying 2D correlation analysis [1].

Dynamic FTIR spectra $I_{dj}(\omega) = I_d(\omega, T_j), j = 1, .., m$ have been measured by heating of the sample from T = 13 K to 42 K stepping by 1 K.

The synchronous 2D correlation spectrum was obtained by the inner product of two spectrum vectors

$$\Phi(\omega_1, \omega_2) = \frac{1}{m-1} \sum_{j=1}^{m} I_{dj}(\omega_1) \cdot I_{dj}(\omega_2),$$

while the asynchronous correlation spectrum was calculated by a cross product of the spectrum vector and its Hilbert transformation H_{dj} [1]:

$$\Psi(\omega_1, \omega_2) = \frac{1}{m-1} \sum_{j=1}^{m} I_{dj}(\omega_1) \cdot H_{dj}(\omega_2).$$

The obtained results provide qualitatively new information concerning methanol clustering kinetics and the role of water impurities on the clusters structure.

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P- 6 ⇓

Raman Scattering and Boson Peaks in a Glass-Forming Liquid: phenyl-2-hydroxybenzoate

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Low-frequency Raman scattering as a function of temperature was carried out on molecular compound phenyl-2-hydroxybenzoate ($(HO)C_6H_4CO_2C_6H_5)$) from far below to above the glass transition at 223 K. Glassy phase shows a broad feature in the frequency range from 14.5 to 17.2 cm^{-1}; the 'Boson peak', which is associated with the inhomogeneous glass nanostructure [1, 2].

We have found that Boson peak could be interpreted in terms of its relationship to the formation of structural clusters, i.e. generation of crystal nuclei, through fluctuation of liquid structure below 258 K. Moreover, it was shown that the crystalline structures of the nuclei formed in supercooled liquid state differ from the initial state structure of crystalline phenyl-2-hydroxybenzoate. During subsequent cooling the nuclei become an important element of the glass structure, and thereby are considered as a measure of the intermediate range order in this glass. Complementary differential scanning calorimetry measurements of phenyl-2-hydroxybenzoate were done in the temperature range from 104 to 360 K to confirm the results of the Raman study.

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P- 7 ⇓

Molecular and Crystal Structure and Spectral Properties of New Squarylium Dyes

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Squarylium dyes have high selectivity and intensity of absorption and high photostability, therefore they find an application for different areas: information recording and saving, analytical determination of cations for a number of different metals, etc. Recently some squarylium dyes have been used as luminescent mark on the biopolymers. Squarylium dyes derivatives of pyrilium which include heteroatom connected with the four-spatial ring, absorb in near IR region, so powerful and portable semi-conducted lasers could be used for their photoexcitation.

Spectral-luminiscent properties of new squarylium dyes (4E)-2-[(2,6-ditert-butyl-4H-pyran-4-ylidene)methyl]-4-[(2,6-ditert-butylpyrylium-4-yl) methylene]-3-thioxocyclobut-1-en-1-olate 1, (4Z)-2-[(2,6-ditert-butyl-4H - pyran-4-ylidene)methyl]-4-[(2,6-ditert-butylpyrylium-4-yl)methylene]-3 -(dicyanomethylene)cyclobut-1-en-1-olate 2 and (4Z)-2-[(2,6-ditert-butyl-4H-pyran-4-ylidene)methyl]-4-[(2,6-ditert-butylpyrylium-4-yl)methylene]-3-(dicyanomethylene)cyclobut-1-ene-1-thiolate 3 in solution were studied under by UV spectroscopy.

As a result of single-crystal X-ray diffraction method it was found that in contrast to all previously known squarylium dyes these compounds have not the trans-trans, but cis-trans configuration. Investigation of crystal packing has showed that in 3 there is a stacking molecular organization, whereas in 1 and 2 the parallel molecules are connected in pairs that are oriented in the herring-bone type.

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Characterization of Organic Semiconductors by Spectroscopic Techniques

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Organic electronics is the field where organic chemistry, material science and engineering and technology interrelate [1]. The modern organic synthetic methods allow chemists to develop the organic semiconducting materials with the optimal set of properties. In order to obtain materials with the required properties the sets of similar derivatives, e.g. varying the heterocyclic system or junction position, should be synthesized and characterized. The synthetic strategy for 2- and 3-substituted functionalized carbazole stilbenes was developed. The reaction of 2-(3-)bromo-9H-carbazole with various vinylic compounds under Heck conditions and alkylation of stilbene derivatives with epichlorohydrin gave monomers containing benzyl, pentafluorophenyl, carbazolyl and triphenylamino chromophores. Polyethers were obtained by cationic polymerization initiating with BF3OEt2.

Various spectroscopic techniques were used for the studies of synthesized materials. For example ionization potential (Ip) or HOMO energy was measured by the electron photoemission in air method (photoelectron spectroscopy). It was showed that changing chromophores in the molecules the Ip could vary from 5.3 eV to 5.9 eV. The investigation of optical and photophysical properties by UV-VIS and fluorescence spectroscopies enable to characterize the materials as emissive materials for organic light emitting diodes. It was showed that fluorescence maxima of diluted solutions in THF could vary from 380 nm to 450 nm. Such differences could be explained by the different conjugation length in the molecules.

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New Heterocyclic 3-hydroxychromone Derivatives as Highly Effective Ratiometric Fluorescent Probes

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The derivatives of 3-hydroxychromone is a numerous group of natural and synthetic compounds, characterized by high biological activity and possessing powerful antioxidant and anti-inflammatory properties [1]. In the last decades, they became a subject of extensive interest of researchers all over the world due to their unique spectral and fluorescent characteristics. At the electronic excitation of these molecules, the process of the excited state intramolecular proton transfer (ESIPT) occurs, determining the existence of dual-band fluorescence spectra [2]. This feature gave birth to the new approach of the luminescent analysis application - ratiometric detection. In this method, the normal-to-phototautomer bands emission intensity ratio plays the role of the analytical signal independent of the dye concentration. This advantage makes ratiometric fluorescent compounds very useful as probes for investigating physico-chemical characteristics of natural objects and even living organisms [3].

The new derivatives of 3-hydroxychromone with highly effective fluorophore moieties in position 2 - 2,5-diphenyloxazole [4] and 1,3,5-triphenyl-2-pyrazoline [5] - were synthesized. High fluorescence quantum yields are typical to both these groups of compounds (up to 50-70%), which places them among the most effective fluorescent dyes of the 3-hydroxychromone family. At the same time they exhibit high sensitivity to different parameters of their microenvironment. Thus, remarkable positive solvatofluorochromism was observed for the title compounds (bathochromic shift of the normal form emission maximum reached 4500 cm^{-1} in case of the 1,3,5-triphenyl-2-pyrazoline derivative, passing from hexane to ethanol). The intramolecular proton transfer reaction is very sensitive to the polarity itself, demonstrating the increase of the normal-to-phototautomer bands emission intensity ratio in polar surrounding. This effect allows using the title compounds in different applied investigations, for example, for water admixtures analysis in organic solvents. This was particularly exemplified by fluorimetric titration of 1,3,5-triphenyl-2-pyrazoline-substituted

3-hydroychromone acetone and dioxane solutions by water.

Temperature also influences the spectral and fluorescent properties of the compounds under study. The effective temperature quenching and fluorescence termochronism was observed in our experiments. The ratiometric temperature effects determined by the simultaneous action of the acceleration of proton phototransfer reaction and non-radiative processes, which entail the asynchronous changes of the two bands intensities in their fluorescence spectra were outlined. This performs significant prospects for practical application of these dyes as ratiometric temperature probes.

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P- 10 ⇓

Estimation of Solvent Effects On N-H And C=O Frequencies of Amides and Amines, of its H-Bond Complexes and Self-Associative Species by IR-Spectroscopy Method

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Intermolecular interactions significantly influence on properties of many supramolecular and biological systems. Especially they are important in conformational stability of proteins and nucleic acids. Model objects such as amides and amines usually are used for investigation and analysis of such systems. Intermolecular interactions influence on the characteristics of absorption spectrums. Today large quantity of models for analysis and estimation of influence of intermolecular interactions on IR frequencies are known.

In present study solvent effects on N-H and C=O stretching vibration frequencies of pyrrol, N-methylformamide (NMF), N-methylacetamide (NMA) and C=O stretching vibration frequency of N,N-dimethylformamide (DMFA) and its complexes with proton acceptors and proton donors were investigated. For analysis of solvent effects model (Solomonov B.N., Varfolomeev M.A., Novikov V.B., Klimovitskii A.E. (2006) // Spectrochimica Acta A. V64, P.404.) was applied. It is based on solvent parameter s_{vw}.

On the first stage absorbance of free molecules of pyrrol, nma, nmf and dmfa were analyzed. It was shown that obtained C=O frequencies of these substances in proton acceptor and inert solvents linearly depend on solvent parameter s_{vw}, responsible for van der waals interactions. Sensitivity to solvent is changed by next way NMF>NMA>DMFA. Deviations of frequencies from obtained linear dependencies were induced by hydrogen bond formation and proton transfer. The absorbance of N-H groups was analyzed in the same way. The frequency shifts induced by different types of interactions were calculated. In work frequencies of H-bonded N-H groups of pyrrol, nmf and nma in complexes with proton acceptors (N-H…b) in different solvents were obtained. In aprotic solvents frequency shifts were induced only by occurrence of van der waals interactions. In proton donor environment ternary or more complicated complexes are formed. The strength of hydrogen bonds N-H…b in these complexes is changed due to cooperative effect. The obtained cooperativity factors were analyzed from view of molecules structure.

Influence of solvent effects on self-association of pyrrol, nmf and nma in different solvents was studied. Formation of associative species induces occurrence of new N-H and C=O stretching vibration bands shifted to low frequencies. It was shown that increasing of polarity, proton acceptor and donor abilities of solvents decreases degree of association. Obtained IR-spectra give opportunity to make consequences about the predominant structure of self-associative species of pyrrol, nmf and nma. Comparison of solvent effects contribution on frequencies of H-bonded O-H, N-H and C=O groups was carried out. The work was supported by grants MK-1462.2008.3, BRHE NO Y5-C-07-12 and RFBR NO 09-03-00751-A.

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Spectroscopic Studies of Dye-Surfactant Interactions in Aqueous Solutions in Pre- and Postmicellar Regions

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Dye-surfactant interaction is a subject of numerous studies. Surfactant micelles, which have polar and hydrophobic regions and form in solutions at the concentration of a surfactant above the critical micelle concentration (CMC), are considered to be simple model systems of biological membranes, because cell membranes consist of surface active components (lipid bilayers). The study of interactions between organic molecules and surfactant micelles can help to understand complex processes of substance delivery and transport taking place in a variety of biological processes. Optical analysis based on fluorescence labeling has been extensively used to study these processes and organic fluorophores are used most often for these purposes. Therefore, studying the interaction between dyes and surfactant micelles is also important from this standpoint.

In the present work, the interaction between cationic diethyloxacarbocyanine perchlorate dye ($DiOC_2$) and anionic surfactant sodiumdodecylsulfate (SDS) has been studied spectrophotometrically in aqueous solutions in surfactant pre- and postmicellar concentrations. In aqueous solutions of $DiOC_2$ with SDS at SDS concentrations far before the CMC, the formation of ion-pair complexes of 1:1 composition between the dye cation and surfactant anion has been revealed and studied by the method of continuous variations. In the higher premicellar region of SDS concentrations, the formation of dye-rich induced micelles has been revealed. Further increase of the SDS concentration (above the CMC) causes the dye solubilization by SDS micelles. Using absorption spectra of the dye in solutions at SDS concentration above the CMC, binding constant (K_b) of the dye to the surfactant micelles and a fraction of the dye bound to the micelles (f_{mic}) have been calculated by means of the Benesi-Hildebrand equation. It has been shown that binding of oppositely charged dye and surfactant micelles is controlled by both electrostatic and hydrophobic forces and the latter play a key role, because just 50% of the $DiOC_2$ dye molecules are incorporated into SDS micelles. It means that for the dye with a short alkyl chains the electrostatic attraction between the dye and a micelle is not enough for an effective binding. Thus the hydrophobic interactions play a major role in the dye to micelle incorporation.

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Non-Uniform Broadening of The Low-Frequency Raman Bands and the Parameters of Intermolecular Vibrations in the Weak Water Solutions of Hydrogen Peroxide

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In our articles [1-2] the experimental data on parameters dependence study of low-frequency Raman spectra in the weak solution of hydrogen peroxide (concentration of peroxide less than 3 on the concentration have been published. Within the limits of widely accepted oscillatory model the vibration component of spectrum of water dynamic susceptibility is well described [3] by two lorentians with average frequency of high-frequency (HF) peak on measurements in our conditions of 170 cm^{-1} with a dispersion of 1.5 cm^{-1} and LF: 45.5 cm^{-1} with a dispersion of 1.5 cm^{-1} . These values are considerably less than water infra-red absorption frequencies (183.4 cm^{-1} and 50 cm^{-1} [4]). Thus the frequency and peaks width dependence on concentration of peroxide is very noisy. But the dependence of frequency on width is much less noised, that testifies to their correlated change owing to some other factor influence. The dependence is linear with negative coefficient of absolute size much less than 1 : -0.19 for HF [2] and -0.14 for LF. Such behavior is similar to that of the c lassical oscillator, which has frequency and width of spectrum of free oscillations (without influence of other forces except the friction force), is described by the expression $\nu_0^2 = \nu^2 + \delta^2$, where ν_0 is the resonant (eigen) oscillator frequency . If the eigen frequency is constant and the width changes in small limits, from the relation : $-(\delta/\nu) * (\Delta\delta/\Delta\nu) = 1$ is obtained, where $(\Delta\delta/\Delta\nu)$ is the inverse value of the declination in dependence of frequency on width. For this relation to be done it is necessary to assume, that the width of the line of oscillations in a spectrum is nonuniform, i.e. there is the oscillators $^{-1}$-1 (with a dispersion of 1.3 cm^{-1}), the eigen frequency - 183.6 cm^{-1} (1.0 cm^{-1}), that of the LF line is 25.9 cm^{-1} (0.7 cm^{-1}) and 51.5 cm^{-1} (1.6 cm^{-1}) accordingly, that quite well coincides with data on IR absorption of water [4].

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P- 13 ⇓

The IR and Raman Spectra of 2-biphenylmethanol and Anharmonic Structural-Dynamical Molecule Model

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Using B3LYP/6-31G (d) method the energy minimization, structure optimization, dipole moment and polarizabilities calculations for the 2-biphenilmethanol (2BPM) molecule were performed. The force field was built and the frequencies of the normal modes with their overtones and combinational frequencies were calculated using anharmonic approximation. With the anharmonicity taken into account the agreement between the calculated and measured frequencies was considerably better than in the case of using harmonic approximation. This approach allows avoiding the scaling procedure for the calculated force constants and vibrational frequencies. On the basis of the modeling results obtained by authors in their previous experimental and theoretical investigations of the 2 BPM crystalline sample structure in stable triclinic modification and its vibrational spectra, a full interpretation of the measured IR and Raman spectra was given.

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Low Temperature Time-Resolved Fluorescence of Merocyanines and Nature of Their Electron Transitions

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The merocyanines as donor-acceptor conjugated compounds with the high polarizable collective system of ?-electrons are excellently important for numerous applications because of their specific electronic, linear and non-linear optical properties; also, they are favorite model molecules to verify the new theoretical approach and to study of the dependence of the electron structure in the ground and excited states as well as the nature of the electron transition on an extension of the conjugated chain, symmetry, total charge, topology of terminal groups, etc. [1]. Upon excitation, merocyanine molecules show considerable intramolecular charge transfer, especially in the polar solvents. Such mobility of the charge wave could be detected by the time-resolved low temperature investigations (4.2 K). This paper presents the results of the combine quantum-chemical and experimental investigation of dependence of the fluorescence spectra of merocyanines derivatives of malodinytriles on changes of the chemical constitution. It was found the existence of two components in the fluorescence spectra at low temperature detecting as two spectral peaks. The intensities of each spectral bands depends strongly on the polarity of the solvent. Basing on the spectral and quantum-chemical investigation, we have concluded that the observed spectral effects at 4.2 K point on the appearance of the solitonic charge waves in the excited state and their mobility upon relaxation.

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Use of Spectral Methods for the Characterization and Studies of Carbazolyl-Containing Semiconductors

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Film-forming charge transporting organic materials are known for various applications such as organic light-emitting diodes used in displays and for lightning [1,2], photovoltaic cells [3], photorefractive materials [4], organic thin film transistors [5] and electrophotographic photoreceptors [6]. Organic semiconductors containing electronically isolated carbazolyl groups how rather poor hole drift mobilities and relatively high ionization potentials [7]. Recently we have synthesized several families of glass-forming compounds with larger conjugated electron systems. They exhibit lower ionization potentials and enhanced hole transporting properties [8,9].

In this presentation we report on the synthesis and spectral characteristics of 3(6)-substituted derivatives of 9-alkylcarbazole, i.e., 9-ethyl-3-(carbazol-9-yl)carbazole, 9-(2-ethylhexyl)-3,6-bis-(carbazol-9-yl)carbazole, 9-(2-ethylhexyl)-3-[(carbazol-9-yl)iminomethyl]carbazole, 9-(2-ethylhexyl)-3,6-bis-[(carbazol-9-yl) iminomethyl]carbazole. All the reported compounds were identified by ^{1}H NMR, ^{13}C NMR, FTIR and mass spectroscopy. The data found were to be in good agreement with the proposed structures. The signals in the ^{1}H NMR spectra of the compounds containing iminomethyl groups can be exactly assigned to the characteristic hydrogen atoms of these compounds. The well-distinguished signals of methine protons are at 9.2 ppm in the spectra. The typical proton signals of carbazole rings are at 7.3-9.0 ppm. The analysis of IR spectra of the synthesized compounds has shown, that the spectra have characteristic absorption signals of aromatic groups at 3045-3055 cm^{-1}(CH stretch), at 1584-1593 cm^{-1}, 1490-1460 cm^{-1} (C=C stretches) and characteristic absorption signals of aliphatic groups at 2970-2930 cm^{-1} and 2871-2855 cm^{-1} due to CH stretches of alkyl chains.

The certain information concerning applicability of organic semiconductors in optoelectronic devices can be obtained by UV spectrometry. An important role in the charge transport of carbazolyl-containing materials is assigned for ? electrons. The comparison of UV spectra of organic semiconductors often enable to estimate indirectly the extent of conjugation of ? electrons. Condensed carbazole derivatives reported in this presentation absorb in the range of 220-420 nm. All the reported compounds exhibit strong bands attributed to p-p* transitions. The absoption maxima of investigated C-N bond conjunct compounds are at the similar wavelengths. The absoption maxima of iminomethyl group having compounds are shifted bathochromically with respect to the absorption maxima of C-N bond conjunct compounds.

Ionization potentials (I_p) of the condensed carbazole derivatives established from the electron emission spectra range from 5.32 eV to 5.80 eV. From the point of view of I_p values the reported compounds are applicable as hole transport materials in electrophotographic photoreceptors [10-13]. Time of flight measurements were used to characterize the magnitudes of the hole drift mobility of the compounds reported. Hole drift mobilities of carbazole derivatives molecularly dispersed in bisphenol Z polycarbonate reach 10^{-5} cm^2/Vs at high electric fields.

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Excited State Symmetry Breaking in Anionic Polymethine Dyes Detected by Low-Temperature Time-Resolved Fluorescence

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According to the current views [1], the charge (electron or hole) injected to the highly-polarized collective system of -electrons is not delocalized uniformly over the whole -system, but is self-localized in the form of a charge wave, i.e. as a kink or soliton. The quantum-chemical calculations have shown that the charge wave is of a finite length, approximately, 15-17 carbon atoms. Simultaneously with a charge wave, there is a generation of a solitonic-like wave of the alternated bond lengths, so called, geometrical or topological soliton. The shapes and the locations of the charge and bond length waves are mutually connected. When the length of the conjugated chain exceeds the dimension of the solitonic wave, the soliton becomes mobile. It was previously shown that the movement of the solitonic waves in the cyanine dyes with the terminal groups could lead to a symmetry breaking in the electron density distribution and equilibrium molecular geometry. Symmetry breaking results in the considerable broadening of the absorption bands for near IR dyes, which can be explained by the co-existence in the ground state of two molecular forms with the symmetrical and asymmetrical charge distributions [2]. In the excited state the dimension of the solitonic wave becomes smaller, and therefore, the symmetry breaking effect can occur at the shorter polymethine chain. We performed a detailed quantum-chemical analysis and time-resolved spectroscopic investigation of a series of the anionic polymethine dyes.

Time-resolved low temperature investigations (77 K) have shown a transformation of the fluorescence spectra in both series of the dyes and an appearance of the additional bands in the long wavelength region. The intensity of these additional bands increases with time (up to 10 ns), while the intensity of the main bands decreases. Room temperature spectra in the time scale 500 ps - 10 ns remain unchanged indicating that the emission originates mainly from the symmetrical molecular geometry. We conclude that a restriction of possible conformational processes at 77 K results in the registration of the fluorescence from the asymmetrical form generated by the mobile excited-state geometrical soliton.

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P- 17 ⇓

Use of Spectral Methods for Monitoring of the Synthesis and Investigation of the Properties of New Derivatives of Triphenylamine and Carbazole

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Organic charge-transporting materials are currently widely used in optoelectronic devices such as electrophotographic photoreceptors, organic light emitting diodes, solar cells and electronic devices, such as organic thin film transistors. In most of the organic optoelectronic devices hole-transporting materials prevail. They are used both in bulk heterojuction solar cells and in dyes sinsitized solar cells. For the later devices glass-forming low-molar-mass materials with high chrge carrier mobilities and low ionization potentials are required.

Four new 1,1-bis(4-aminophenyl)cyclohexane based triarylamines including those with mehoxy-substituted triphenylamino groups and those with 9-butylcarbazole-3-yl moeties were synthesized by improved Ullman condensation. 9-(4-methoxyphenyl)carbazole-3,6-diyl containing triarylamine was synthesized usind the same method. 1,1-bis(4-aminophenyl)cyclohexane based enamine was prepared by the condensation reaction of the mentioned primary amine and diphenylacetaldehyde.

The reactions were monitored by 1HNMR, FT-IR and mass spectroscopy techniques. These techniques were also used for characterization of the chemical structure of the compounds obtained. The dissappearance of the signals of amino protons at 3.55 ppm in CDCl3 and at 3.40 ppm in DMSO-d6 was observed in 1HNMR spectra of the target compounds as compared with the spectra of the starting amines. The dissappearance of the absorption bands of primary or secondary amino groups in 3500-3300 cm-1 region was observed in FT-IR spectra of target compounds as compored with those of the starting amines. The appearance of the additional signals of aromatic fragments in 6.60-8.00 ppm region of 1HNMR spectra of the target compounds was also observed . Optical and photophysical properties of the diluted solutions of the compounds synthesized were investigated by UV-VIS and fluorescence spectroscopy methods. The absorbtion in the region of 200-420 nm was observed and the flourescence peaks in the range from 356 to 449 nm were established.

The synthesized compunds were studied by the method of electron photoemission spectroscopy and the values of ionisation potentials ranging from 4.97 to 5.55 eV were established. The charge transport properties of the new derivatives and of their molecular dispersions in bisphenol-Z polycarbonate were estimated by time-of-flight technique. Hole drift mobilities up to $3.210^{-4} cm^2 V^{-1} s^{-1}$ were observed.

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On Structure of Water'S Raman Spectra and its Dependence on Temperature

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Raman spectra of water in temperature range 20-3 ^{o}C and pressure up to 70 atm was investigated. Spectra were excited by laser irradiation with wavelength 532 nm. Raman signal was collected at an angle of 90^{o} to exciting laser beam and was detected by PMT which works in "photon counting" mode. For complex Raman spectra approximation a few Gaussian-shaped peaks were employed, and the best result was obtained with five ones. Positions of maximums of these five constituents were 3070, 3230, 3440, 3600 and 3650 cm^{-1}. The most intensive constituents are 3230 and 3440 cm^{-1} lines which contribute more than 90% to Raman spectrum of water. The most sensitive to temperature changing the 3230 cm^{-1} line was unveiled. So, under decreasing of temperature from 20 ^{o}C to 3 ^{o}C: i) position of its maximum moves from 3232 cm^{-1} to 3224 cm^{-1}; ii) and its magnitude increased on 14%. Authors could not detect any changings in constituents positions and its magnitude under pressure increasing up to 70 atm.

Methods Of Enhancement Of The Luminescence Efficiency Of Europium And Terbium Aromatic Carboxylates

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Europium and terbium aromatic carboxylates with the high luminescence quantum yield can be used in devices of molecular electronics and photonics, applied as light transforming materials, sensors, etc [1, 2]. In this paper, some paths of enhancement of the Ln^{3+} luminescence efficiency will be discussed. The efficiency of the excitation energy transfer from ligands to Ln^{3+} ions and the luminescence quantum yield depend on the structure of compound. That can be adjusted by the change of the architecture of carboxylate anion and other ligands [3, 4].

Luminescence, phosphorescence and luminescence excitation spectra of europium, gadolinium and terbium benzoates, salicylates, phenylcarboxylates, naphthylcarboxylates and corresponding complexes with 1,10-phenanthroline derivatives were examined. Lifetimes of metastable $^5D_4$ (Tb^{3+}) and $^5D_0$ (Eu^{3+}) states were measured. To correlate paths of the excitation energy transfer with the ligand architecture, known X-ray data on crystal structures were analyzed. The influence of introduction of donor and acceptor radicals in the aromatic ligand on the ln^{3+} excitation efficiency (manifestation of a push-pull effect) was studied. The effect of the methylene bridges breaking the $\pi-\pi-$conjugation in the ligand on the structure of coordination centre and on the excitation energy transfer to Ln^{3+} ions was analyzed.

The influence of relative positions of the lowest triplet state of the complex referred to one of the ligands and $^5D_4$ (Tb^{3+}) or $^5D_0$ (Eu^{3+}) electronic states on the energy transfer was investigated. The lifetime of $^5d_4$ state and the Tb^{3+} luminescence efficiency decrease noticeably in some investigated compounds at increasing the temperature owing to the energy back transfer. Correlation between the lowest triplet state energy of terbium compounds and $^5D_4$ (Tb^{3+}) state lifetime at 300 K was demonstrated.

It was shown, that the high luminance of europium salicylates can be reached by introduction of two electron-withdrawing nitrogroups in the ligand. This effect was connected with noticeable lowering the energy of the anion lowest triplet state and with increase of the energy of the ligand metal ion charge transfer states (LM CTS). In contrast to that, the decoupling of ligand π-electronic system in europium carboxylates leads to lowering the LM CTS energy. Therefore, the probability of participation of the LM CTS in the degradation of excitation energy increases resulting in the low luminance of europium compounds.

The studies presented can facilitate a selection and application of coordination lanthanide compounds as effective luminophors. The work was supported by the russian foundation for basic research (grant no. 08-02-00424-a).

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P- 20 ⇓

Features of Absorption, Fluorescence and Fluorescence Excitation Spectra of Styryls and Methoxystyryls

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Unsymmetrical cyanine dyes, including styryls and their methoxyanalogues, continue to be used widely, in parallel with symmetrical dyes, in numerous applications connected with the light conversion. Going from symmetrical dyes to unsymmetrical ones causes significant changes in distribution of the total positive charge in the polymethine chromophore, molecular geometry and, hence, in spectral properties.

This work presents the results of the spectral and quantum-chemical studies of the dyes type $R_1 - (CH)_m - R_2$ as unsymmetrical cyanines with an extremely high degree of asymmetry. They are styryls and metoxystyryls that differ by R_2 group which contains $\mathrm{N(CH_3)_2}$ or OCH_3 groups, correspondingly. Here R_1 is the terminal group: indolenine, benzthiazole, benzoxazole, pirydine and quinoline.

The most intense and distinct spectral band observed in the absorption and fluorescence excitation spectra is connected with the first electronic transition $S_0 \rightarrow S_1$. The second transition $S_0 \rightarrow S_2$ is detected by the fluorescence excitation anisotropy spectra.

The study has shown that the two lowest electron transitions in the styryls containing both nitrogenic terminal groups are coupled transitions (*i. e.*, they have the same polarization), similarly to the symmetrical cyanine dyes. Whereas in the oxystyryls, the nature of the second transition differs from that of the first transition.

Experimental results have shown that substitution of styryl by metoxystyryl causes a blue shift of the peak of the intense absorption band by nearly 100 nm. An energy level diagram that accounts for the abovementioned shift is proposed.

The Modeling and Interpretation of the 4-butil-4-cyanobiphenyl IR Spectra

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The IR spectra of the 4-butil-4-cyanobiphenyl in the liquid and solid crystal states in the region 400-400 cm-1 were measured at the 2870? temperature interval. The transformations of the spectra at the temperature changes are conditioned by the conformational mobility of molecules. This conclusion follows from analysis of results of IR spectra calculations of the 4-butil-4-cyanobiphenyl possible conformers. The calculations are realized by method of fragment by using LEV-100 program complex. A supposition about the conformational changes in the molecule made. The bands sensitive to the changes in its conformational structure of molecule were found. The interpretation of the IR spectra was given. The conclusions about conformational composition of specimen in solid crystal and liquid phases were made.

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Conformational Mobility Investigation in Behenic Acid Molecule Using IR Spectroscopy and Quantum Mechanical Method

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In wide temperature interval (11-330) IR absorption spectra of the carbonic acid C3(2)20COOH (behenic aid, kC22) were measured. The changes revealed in the spectra at the temperature increasing can be explained by the assumption about the conformational mobility of the molecules in the sample. The modeling of the structure and vibrational spectra of conformers of C3(2)20COOH molecule have been carried out to confirm this assumption. These conformers were differed by the orientation of carboxylic group and by the orientation of fragment including carboxylic group and the closest CH2 group relatively to the remaining part of the plane carbonic frame of alkyl radical (AR). Also the modeling of the C3(2)20COOH molecules H-bond dimer, in which the AR carbonic frames and dimer ring are lying in the same plane, was performed. Using density functional method (B3LYP/6-31G) the energies, structures, dipole moments and polarizabilities of conformers of the C3(2)20COOH molecule with different orientation angles and of the H-bond dimer were calculated. The force fields were built and the frequencies of normal vibrations with intensities in IR spectra were calculated for all mentioned above quantum molecular systems. On the basis of the analysis of the calculated and measured IR spectra the authors made a conclusion about the conformational mobility of the molecules in C3(2)20COOH carbonic acid sample.

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Investigation of the 2-, 4-bromobenzophenones Structures and Their Vibrational Spectra Using Anharmonic Approximation

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Using density functional method (B3LYP/6-31G) the energies, structures, dipole moments and polarizabilities of the 2-, 4-bromo- (2BrBP, 4BrBP) molecules were calculated. In harmonic and anharmonic approximation the force fields of the mentioned above molecules were built and the frequencies of the fundamental normal modes, their forms and intensities in the vibrational spectra together with overtones and combinational frequencies were computed. The comparison of the calculated and measured frequencies pointed to the significant improvement of the modeling results at the transition from harmonic approximation to the anharmonic one. It has been found that it is possible to avoid the scaling procedure for the calculated force fields and vibrational frequencies. On the basis of the modeling results a full interpretation of the measured spectra of the crystalline samples of investigated compounds was given.

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IR sPectrum of the methyl-?-D-glucopyranoside and its Interpretation on the Basis of StructuralDynamic Model Construction Using Density Functional Method

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Structuraldynamic models of the methyl-?-D-glucopyranoside molecule are constructed by density functional method in bases 6-31 G(d), 631+G (d, p). Energies, structures, dipole moments, polarizabilities, frequencies of normal modes in harmonic approximation and IR intensities have been calculated. Interpretation of IR absorption spectrum is presented in range 400 - 3700 cm^{-1}. Advantages of model, which was constructed, compared with model, which bases on using valence-force field method and valenceoptical theory, are discussed.

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Structure and Infrared Spectra of Small Biomolecules Trapped in Low Temperature Inert Gas Matrixes

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Matrix-isolation IR spectroscopy and *ab initio* calculations performed at the DFT, MP2, MP4 and CCSD(T) levels of theory were employed to establish the structure of small biomolecules and their intermolecular complexes isolated in solid inert gases. The conformational behaviour of the aminoacids and their derivatives were investigated with accounting for influence of the matrix environment on structure and vibrational spectra of the molecules studied. This approach includes the molecular dynamics (MD) simulation of the rare gas crystals with isolated molecule. The MD simulation was performed with the set of the force field parameters which was constructed based on the precise *ab initio* calculations of the interaction energies between inert gas atoms and guest molecules performed at the CCSD(T) level of theory. It allowed us to determine the trapping site distribution and the structure of the microenvironment around the guest molecules. These data were used in subsequent calculations of the structure and vibrational spectra performed at the DFT level of theory for the systems which were consisted of a guest molecule and up to 100 neighbor matrix atoms. In these calculations we used the new generation density functional M05 modified by us for best performance in simultaneous prediction of the vibrational spectra and intermolecular interaction energies. We demonstrated that the matrix environment influence both the structure and vibrational frequencies of the trapped molecules. The competition between hydrogen bonding and stacking interactions of the dimers of nucleic acid bases and their derivatives was also studied using the same approach.

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Unsymmetrical 7,8-dihydrobenzo[c,d]furo[2,3-f]indole Dyes: Interrelationships Between Structural, Electronic and Spectral Features

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Based on the 7,8-dihydrobenzo[c,d]furo[2,3-f]indole nucleus [1], a number of unsymmetrical carbocyanines as well as styryl dyes have been synthesized and their absorption spectra have been measured. Combined spectro-scopic and quantum chemical study of the novel near-infrared absorbing dyes has been performed to elucidate the relationships between the positions of their long-wavelength maxima, on the one hand, and end-group basicities, bond-length alternations, and frontier level energies, on the other hand. Starting from the deviations of dye long-wavelength maxima [2], the value of electron-donor ability D [3] has been estimated for the 7,8-dihydrobenzo[c,d]furo[2,3-f]indol-4-yl residue; as shown, it is significantly increased as compared to the initial 2-benz[c,d]indolyl nucleus due to dihydrofuran annelation. It has been found that the hemicyanine obtained from the new heterocyclic nucleus and the dyes containing, as the second end group, the residues of indolenine, benzothiazole, and thiopyran exhibit negative deviations in spite of regular C-C bond alternation in the polymethine chromophore. This phenomenon suggests that the mentioned dyes are characterized by the predomination of the topological part of the deviation over the contribution from alternating bonds. Importantly, negative deviations which are often regarded as an obscuring factor in studying dye end-group basicities are invoked here, as well as positive deviations, to assess the electron-donor properties of various residues. On this basis, the deviation-based basicity series has been constructed which agrees fairly well both with the previously known empirical scale [3] and with the computational data on bond alternation and energy level positions in the dyes concerned.

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P- 27 ⇓

Spectroscopic Investigations of Luminescent Centers in Solutions with Ag^+ Impurity

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In this report the investigations of optical properties of oxygen-containing salts and acids activated with Ag^+ ions were carried out in the temperature range 4.2 – 290K.

The absorption spectra of concentrated aqueous solutions $HClO_4$, H_2SO_4, Na_2SO_4, Na_2SO_3 with silver impurity (10^{-5} – 10^{-3} mol/l) are similar to those of solutions of phosphorus-containing and haloid salts and acids with Ag^+ impurity. In general case, they consist always of short-wave band and a group of low-intensity long-wave bands. The emission spectra are also complex, depending substantially on the wavelength of the exciting light.

A detailed study of the excitation spectra on different regions of emission bands was carried out. It was found that silver oxygen-containing solutions are characterized by three types of structured bands of absorption (excitation) and emission.

The observed bands may be associated with the certain transitions in the free Ag^+ ion, the energy levels of which are deformed due to interaction with the external environment.

The obtained experimental results enable to cognize fundamentally the mechanism and nature of absorption and emission of light by solutions and crystal phosphors containing an impurity of the same heavy-element ions.

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Exiton Migration and Relaxation in PPI and PAMAM Dendrimers

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Due to unique branched structure dendrimers represent large opportunities for fabrication of new functional materials for organic electronics. Dendritic materials are promising for application in organic light emitting devices and Solar cells. Pheripheral end groups constitute a large molecular structure, which may serve as a light harvesting system for Solar energy collection. Since light absorption and emission in organic materials involve excitonic states, operation of organic photoelectrical devices to a high extent depends on the exciton properties. In this work we present femtosecond time resolved transient absorption spectroscopy study of PPI and PAMAM dendrimers functionalized with azobenzene (CAzPA) terminal groups. Dendrimers in solvents and in thin films were investigated. Ultrafast excited state relaxation takes place in both dendrimers with time constant of about $\tau =$3ps in solvents and several times longer of about $\tau \approx$ 25ps in solid films.The relaxation dynamics is very similar to that observed in solutions of azobenzene molecules. Therefore we conclude that the excited state properties of the dendrimers are determined by the azobenzene functional groups, which only weakly interact with the dendrimer core.

P- 29 ⇓

Features of Structure and Optical Properties of ZnO Films

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Nowadays ZnO generates great interest due to specific optical and electronic properties. It is widely used in transparent electric contacts and gas sensors, as well as in piezoelectric transistors, luminescent devices and UV lasers. Al doped zinc oxide is used in sun batteries.

It is necessary to determine the influence of deposition technique on physical properties in order to obtain the films with proper operational characteristics. In this work, the properties of the films produced at various substrate temperatures and various pressures of residual gases were determined.

The samples were produced by reactive magnetron sputtering at SiO_2 substrates. The O_2 and Ar partial pressures were $1.7\dot{1}0^{-3}$ mbar and $7.4\dot{1}0^{-3}$ mbar, respectively. The samples 1-4 were deposited at room temperature of the substrates whereas the substrate for sample 5 had the temperature of 550 . The pressures of residual gases were $2.7\dot{1}0^{-5}$ mbar (sample 1), $3.4\dot{1}0^{-6}$ mbar (sample 2), $2.2\dot{1}0^{-7}$ mbar (sample 3), $9.7\dot{1}0^{-6}$ mbar (sample 4) and $2.5\dot{1}0^{-7}$ mbar (sample 5). The thickness of the substrate was about 210 nm.

The measurements were done by Beatties method within the spectral range 1-4.3 eV at room temperature. The ellipsometric parameters Δ and Ψ were obtained. The Atomic-Force Microscopy and Scanning Elecronic Microscopy gave information about morphology structure of the surfaces.

The dispersion curves in 3.4-4.3 eV area show the decrease of refractive indices when reducing the pressure of residual gases. It might be due to more disordered structure of the films deposited at lower pressures. Meanwhile, AFM doesnt show essential difference of the structure of the samples 1-4 and SEM shows nanostructures in the samples 2-4. Thus, no clear conclusion could be made yet. On the other hand, both AFM and SEM show clear crystallites on the surface of sample 5. But, the refractive indices of the samples 3 and 5 are similar and the presicion doesnt enable us to determine the true behaviour of the refractive index when elevating the temperature up to 550 .

P- 30 ⇓

On the Possibility pf Observing Coherent States in Fluids of Depolarized Component of Molecular Scattering of Light

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Coherent properties of matter are manifested in such phenomena as superconductivity, super fluidity, Josephson Effect (interference currents). The phenomenon of super radiance properties associated with coherent collective state of matter "of two" molecules. There coherent properties of layered systems is coherent dissociation, ionization coherent. Summarizing the above said, it is possible to approve that the coherent (or cooperative), the phenomenon is global in nature and are observed for all the states of matter-crystals, liquids, gas, plasma.

Our work is related to the study form the band depolarized components of the molecular scattering of light (DCMRS) a number of organic liquids, consisting of asymmetric polarizability of molecules (benzene and its derivatives). In such fluids DCMRS the band took a broad spectral region 200-250 cm^{-1}. And if the central part (area 0-50 cm^{-1}) is a superposition of two dispersion contours and is due to rotational and vibrational steppes of freedom [1], the long sections DCMRS (60-200 cm^{-1}) does not describe the dispersion dependence and, in general, this area is little studied. Even the experimental data in the form of distant wings are contradictory.

Our data on the form of distant wings show that the damping wings are damped by Gaussian.

To explain such forms of distant wings, we used the idea proposed by Fischer [2], which suggested that the long wings as part of the spectrum DCMRS carrier for information about the initial temporal evolution of a collision less scattering system. Scattering is related fluctuations. Fluctuations are an ensemble of particles, including some 10^6 molecules. This ensemble of molecules is in the potential field created by the environment. The lifetime of such an ensemble is $\approx 10^{-12}$ (relaxation time of anisotropy). After this time moving from one potential well to another, from one configuration space to another. Therefore, we can suggest that fluctuations in the transition from one state to another occurs in the coherent (phased-array condition), but more must be even distribution of the phases of individual molecules, which are achieved through a process of diffusion.

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P- 31 ⇓

Kubelka-MunkS Theory Applicability to the Random Active Media

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Modeling and theoretical treatment of the lasing in random active media is very difficult problem. Therefore the development of the comprehensive model and theory is the task of the future. But one should attempt to deliver different approach to this problem solving. We try out to extend the Kubelka-Munk's theory over the random active media and to study the applicability this theory to the light propagation and lasing in a random active media.

Within the framework of the two-flux Kubelka-Munk theory (the radiation passing through an inhomogenouos material is represented as two opposite fluxes, exchanging by the energy because of multiple scattering) we considered passing of the incident radiation through the random active medium with the negative absorption coefficient K. Solution of the proper equations shows that the change of the absorption coefficient sign from positive to negative results in substitution of the direct flux intensity I decrease vs depth x by the increasing one. The rate of this increasing enhances considerably under K and scattering coefficient S increasing. The intensity of the opposite flux J rises towards medium surface of the light incidence regardless of the K sign but the amount of this increasing dependence strongly on K and S. Maximal intensity I and J (at the end and input of medium respectively) became equal and functions I(x) and J(x) dependence weakly on boundary conditions under high value of this parameters ($K \sim 200cm^{-1}$ and $S \sim 100cm^{-1}$). This condition corresponds to regenerative amplification in conventional lasers.

In a random laser the lasing develops along random broken trajectories where scattered light moves. Thus as a rough approximation one can present a random laser as a set of scattered centers chains dipped into an active medium. Distance between scattering centers and the chain length are distributed according to random law (for example according to Gauss law). While propagating along the chain the light is amplified and scattered. Thus its propagation can be described by Kubelka-Munk's theory. But in contrast to previous case the light originates from spontaneous emission within the chain itself, and the luminescence appeared at both chain edges equiprobably. The situation is described by four-flux Kubelka-Munk's theory that can be reduced to two-flux model with equal boundary condition on the entrance and exit surfaces of the pattern. The equation shows the origination of two opposite equivalent fluxes which intensity grows under gain and scattering coefficients increasing. As random lasing consists of a number of the chains the lasing intensity depends on K and S in similar way. It agrees completely with main features of random laser.

Thus the results testifies that extended Kubelka-Munk's theory appropriately describe main features of lasing in random laser and can be a base for appropriate theory developing.

3 CRYSTALS

O- 1 ⇓

Low-Energy Excitation Spectrum of the Crystal $KTm(MoO_4)_2$.

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The $KTm(MoO_4)_2$ crystal belongs to the series of the isostructural compounds in which the low-temperature phase transitions caused by the cooperative Jahn-Teller effect (CJTE) are observed. The characteristic feature of these materials is their layered crystal structure [1] which yields in the acoustic and optic-acoustic vibration branches with low limit frequencies in the vibration spectrum. In the $KTm(MoO_4)_2$ crystal the low local symmetry of the Tm^{3+} ions (C_2) results in complete splitting of the ground multiplet $^3H_6$ of Tm^{3+} ion by crystal field with forming of the quasi doublet with the gap $\Delta E = 2.3$ cm^{-1} [2]. The long-wave infrared transmission spectra previously studied allowed us to determine the structure of the $KTm(MoO_4)_2$ low-frequency vibration spectrum in Brillouin zone. The problem to concern with this work was to investigate the interaction of the first excited Stark level of Tm^{3+} ion with the acoustic vibration branches depending on its position in the energy spectrum of the crystal.

For this purpose the measurements of dependences of transmission of $KTm(MoO_4)_2$ crystal on external magnetic filed at different microwave pumping frequencies (85 – 333 GHz) were carried on at low temperatures ($T = 2K$). The experiments allowed us to make the following conclusions:

- the dynamic bond of electron excitation of Tm^{3+} ion with crystal lattice vibrations gives rise to the features shaped as side bands of the ground transition in the microwave radiation absorption.
- the dynamic interaction of the electron excitation of the Tm^{3+} ions with crystal lattice vibrations is enhanced when electron level crosses the acoustic branch in the frequency range with the wave vector corresponding to crystal lattice vibrations with the wavelength equal to the integer number of periods.

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O- 2 ⇓

Electronic Spectra and Magnetic Properties of Layered FeAs Systems

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The discovery of superconductivity (SC) with $T_c \sim 26$ K $\div$ 56 K in the rare earth oxypnictides RFeAsO$_{1-x}$F$_x$ (R=La, Nd, Sm, Pr), and in the ternary oxygen-free arsenides AFe$_2$As$_2$, where A are alkaline earth metals Ca, Sr or Ba, has triggered an enormous amount of research activities. These materials exhibit a crystal structure with layers of Fe–As separated by spacer layers, where the dopants are introduced by replacing some of the oxygen in RFeAsO with fluorine. The reported high T_c SC has raised a number of questions about the nature of SC state and the pairing mechanism, and encouraged the studies of high T_c SC outside of the cuprate family. The parent compounds of these pnictides are poor metals with a spin density wave (SDW) ground state, and SC emerges as soon as the orthorhombic distortion and the SDW magnetism are suppressed.

The performed here DFT electronic spectra calculations show that the energy bands at the Fermi level E_F in RFeAsO$_{1-x}$F$_x$ and AFe$_2$As$_2$ are formed by the hybridization of d-(Fe) and p-(As) states, while the R-O bands are far from E_F. It is found, that the Fermi surface of iron pnictides consists of slightly warped tubular sections running along the c direction. These bands in most cases can be considered as two effective 2D bands. The density of electronic states at E_F comes essentially from the d electrons of Fe, and the partial contributions of other states are substantially smaller. Therefore, SC is presumably located in the Fe–As layers, and the R–O layers provide the charge reservoir. Also, the LaFeAsO compound is found to be close to magnetic instability.

We also present a systematic experimental study of magnetic properties of the polycrystalline LaFeAsO$_{0.9}$F$_{0.1}$ in the fields up to 5 T and at temperatures of 4.2 K – 300 K. Comparing experimental data to DFT calculations suggests that the electron correlations are less important in the pnictides and a competition is anticipated between the spin ordering and SC. Also, the susceptibility calculated in external magnetic field appears to be close to the experimental value at the theoretical lattice parameter. Our DFT calculations for LaFeAsO indicate, that the doping and pressure shift the system away from magnetic instability, which is expected to be unfavourable for SC. It should be noted that in the undoped LaFeAsO the calculated susceptibility is larger, and the experimental one is smaller, than in the doped systems. This suggests that there are also other important spin excitations in RFeAsO, which suppress SDW state.

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O- 3 ⇓

Investigation of Raman Mode Relaxation in Molecular Ionic Crystals

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Raman modes in molecular ionic crystals can be divided into two main groups: high frequency vibrations that are originated inside molecular ion, so called internal modes and lattice phonons, external vibrations. Internal modes are well isolated from lattice phonons, that's why the number of their possible relaxation channels is limited and they can be easily interpreted in terms of multiphonon decay mechanisms.

Previously there was a number of publications on the vibration relaxation of internal modes in some molecular ionic crystals, like $CaCO_3$, K_2SO_4, $NaNO_3$ et al. The obtained results for different molecular ionic crystals have shown that the temperature dependence of the line broadening provided the fundamental information on the dominant mechanism leading to vibrational relaxation. The developed theory [1] showed that the full bandwidth for an internal vibron in an ideal crystal equals to the sum of several contributions, each arising from a specific depopulation or dephasing mechanisms. The simplest depopulation process is a two-phonon splitting process, when high frequency vibration w_i is annihilated with emitting two lower energy phonons w_j and w_k, so that $w_i = w_j + w_k$. There can be two-phonon up-conversion process, which corresponds to the fusion of a w_i phonon with another one w_j with producing of a higher energy vibration w_k, so that $w_k = w_i + w_j$. There can be higher order relaxation processes with the interaction of three, four and more phonons. The probability of higher order relaxation process is strongly reduced with the number of involved phonons. There is a dephasing process which involves the interaction of excited vibron w_i with the thermally excited lower energy lattice phonons w_j andw_k. In this case these low frequency phonons scatter on high frequency vibration that can be presented as an immediate absorption and emission of phonons with the same energy but with different phases $w_i + w_j = w_i + w_k$. All the above processes has a certain contributions to the total relaxation probability.

In this report the dominant relaxation processes of Raman modes were obtained for a number of nitrate, tungstate, molybdate and vanadate molecular ionic crystals. It was found that the Raman mode linewidth depends on spontaneous Raman spectrum. The increase of energy gap between the investigated mode and the closest mode reduce the probability of the relaxation process that results in the increase of the mode lifetime and narrowing of its linewidth. The slope and curve of the temperature dependence of the linewidth was analyzed by the sum of variable relaxation mechanisms. It was found that with high accuracy in many molecular ionic crystal the relaxation of internal mode excitation can be described by the sum of two processes: the splitting and the dephasing processes. These results allowed to explain some favorable properties of barium nitrate and barium tungstate crystals as a perspective nonlinear materials for developing Raman converters.

The results on investigation of temperature dependencies of spectroscopic parameters of the most intensive Raman modes in molecular ionic crystals were applied for analysis of the stability of nonlinear parameters of the active and nonlinear crystals in Raman converters and lasers.

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O- 4 ⇓

Spectroscopy of New Compounds from the Family of Rare-Earth Orthoborates

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My lecture is devoted to the rare-earth (RE) borates $RM_3 (BO_3)_4$, M = Al, Fe, and Cr, that have non centrosymmetric trigonal structure of the natural mineral huntite. It gives a brief review of a spectroscopic research on $Yb_3 (BO_3)_4$ (YbAB) and a big group of magnetic iron borates. This work was carried out by my group in cooperation with the Kazan' State University (Russia) and the Laboratory of Condensed Matter Chemistry, ENSCP (Paris, France) The crystals of good optical quality have recently been grown in the L.V. Kirensky Institute of Physics (Krasnoyarsk, Russia).

Spectroscopic study of YbAB was stimulated by a recent report of the highest power ever achieved by self-frequency doubling (SFD) laser, using the YAB:Yb crystal. We have measured high-resolution temperature-dependent polarized absorption, luminescence, and Raman spectra of YbAB. Energies and symmetries of crystal-field (CF) levels were determined, vibronic structure analyzed, multiple additional Yb^{3+} centers were found and discussed.

Borates with magnetic M ions (like Fe and Cr) have interesting new properties and promising new application potential connected, in particular, with magnetoelectric interactions in them. We have performed a systematic study of polarized RE spectra in the $RFe_3 (BO_3)_4$ single crystals, with the aim (i) to find the energies, symmetries, and, finally, wave functions and magnetic g-factors of the CF levels and to obtain a set of the CF and exchange interaction parameters for the whole series of the RE iron borates; and (ii) to study different phase transitions and, possibly, magnetoelastic interactions. Main results of this study are reviewed. The most interesting spectral peculiarities are discussed. First results on the RE chromium orthoborates are also presented.

A part of the results has recently been published in Refs. [1-3]. This work was supported by the Russian Foundation for Basic Research (grant 07-02-01185), by the Russian Academy of Sciences under the Programs for Basic Research, and by the CNRS - RAS exchange program (project No 21241).

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O- 5 ⇓

Spectral Properties and Processes of Interaction of Er^{3+} in Disordered Laser Crystals Calcium Niobium Gallium Garnet Doped with Er^{3+}

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The development of Er-doped solid-state lasers for 3 μm sources is useful for medical and meteorological applications. The lamp-pumped YAG:Er 3 μm laser (transition $^4I_{11/2} \to ^4 I_{13/2}$ of Er^{3+}) was reported in [1]. Laser generation on 3 μm at electron-phonon branch of $^4I_{15/2} \to ^4 I_{13/2}$ transition excited by 1.34 μm laser was reported in [2].

The transition $^4I_{11/2} \to ^4 I_{13/2}$ of Er^{3+} ions in YAG:Er^{3+} is self-limited ($\tau(^4I_{11/2}) = 100\ \mu$s, $\tau(^4I_{13/2}) = 6.4$ ms). Processes of up-conversion lead to deactivation of lower laser level $^4I_{13/2}$ for high concentrations. Therefore effective laser generation on crystals of YAG:Er is possible only at high concentrations of activator ion ($C_{\mathrm{Er}} > 30$ at. %) [1].

Although crystals with regular structure such as YAG:Er are widely used for laser generation, disordered crystals are very interesting for laser physics as well. Disordered structure crystals doped with TR3+ ions are characterized by strongly inhomogeneously broadened absorption and luminescence spectra. This fact provides the best overlap with emission spectrum of pumping diode and gives possibility for creation of tunable laser operating with ultra shot pulses.

In order to evaluate the possibility of laser generation on transition $^4I_{11/2} \to {}^4I_{13/2}$ of Er^{3+} ion in disordered calcium-niobium-gallium garnet (CNGG) crystals doped with Er^{3+}, we have investigated the structural and spectroscopic properties of these crystals at different concentrations of Er^{3+} ions. We have also studied processes of Er^{3+} ion interaction.

The CNGG:Er crystals were grown by the Czochralski method from melt. We have found by structural studies (RSA investigation) that structu-ral perfection is impaired for CNGG:Er crystals with concentration higher 12 at.%. Therefore CNGG:Er crystals with concentration not higher than 12 at. % of Er^{3+} can be used in laser generation experiments.

We have obtained oscillator strength for the transitions from the $^4I_{15/2}$ level to the excited multiplets of Er^{3+} ion $^4F_{5/2}$, $^4F_{3/2}$, $^4F_{7/2}$, $^4H_{11/2}$,

$^4S_{3/2}$, $^4F_{9/2}$ $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$. With the help of the Judd-Ofelt method [3,4] we have calculated the intensity parameters Ω_t $(t = 2, 4, 6)$. Using this parameters we have estimated the probabilities $A_{JJ'}$ for some radiative transitions from the excited states of Er^{3+} ions in CNGG:Er crystals. Using the value of experimentally measured lifetime of $^4I_{11/2}$ level of Er^{3+} ion and value of probability of radiative transition from the level $^4I_{11/2}$ we have found that quantum yield of luminescence from the level $^4I_{11/2}$ level is equal 14%. This value is similar to analogous values for YGG:Er and GGG:Er crystals, but differs by an order of magnitude from YAG:Er crystals [1]. This fact is caused by decrease of probability of multiphonon intracenter transitions from the upper laser $^4I_{11/2}$ level of Er^{3+} in CNGG:Er. That is stipulated by larger mass of Ga^{3+} ions compared to mass of Al^{3+} ion.

To understand the formation of inverse population at laser levels $^4I_{11/2}$, $^4I_{13/2}$ in CNGG:Er crystals we have investigated processes of nonradiative energy transfer from levels $^4S_{3/2}$, $^4I_{11/2}$, $^4I_{13/2}$ of Er^{3+} ions.

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O- 6 ⇓

Interaction of Femtosecond Laser Pulses with Chalcogenide Glasses

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Outstanding non-linear optical properties of chalcogenide glasses make them promising materials for fast optoelectronics devices [1]. We performed a set of Z-scan and time-resolved pump-probe experiments investigating ultrafast nonlinear properties of as-prepared As2S3, As50S50, and As4Ge30S66 chalcogenide glasses. Femtosecond regenerative amplifier Legend F-1K-HE with 140 fs pulse duration was used as a pump source at 780 nm (intraband pumping) and frequency doubled 390 nm (interband pumping). Using Z-scan technique [2] we measured nonlinear refraction (NR) indices and Two-Photon Absorption (TPA) coefficients in the said media. Temporal behavior of NR and Transient Absorption (TA) has been studied in time-resolved pump-probe experiments. Excited by the same laser source white supercontinuum with controllable time delay in a 0 - 300 ps interval was used as a probe pulse. The pump pulses were focused in samples of chalcogenide glass 0.5 mm and 3 mm thick. White probe beam was directed to the center of the excited spot. After passing the sample, the probe beam was analyzed with spectrograph. Change of optical density induced in the test sample by the pump pulse at different delays was measured. Temporal resolution of the setup is 300 fs. At intraband pumping in all the studied glasses the TA dependence of the spectrally wide probe beam on the time delay shows two decay times. The fast component depends strongly on the mutual polarization of the pump and probe beams, increasing tree times in As2S3 at equal polarizations in comparison with crossed ones. The width of the TPA peak roughly equals to the temporal resolution of the setup. Polarization dependence of the fast part can be explained assuming that two components of TPA are involved. One component is formed by polarization dependent direct two-photon absorption involving one pump and one probe photon, and the second - by two-step absorption, the first step being two-photon generation of short-living free carriers by two pump photons, or/and one-photon excitation of the gap states, followed by the second step - probe absorption by free carriers, not depending on the probe polarization. Slowly decaying part of the induced absorption relaxes between two consequent laser pulses. As50S50 and As4Ge30S66 demonstrate similar behavior. At interband pumping the transmission dependence of the probe beam on the time delay shows only a single 11 ps exponential decay in As2S3, not depending on the probe polarization, in qualitative agreement with the results of [1] for As2Se3. Ultrafast optical Kerr effect was for the first time measured in bulk As50S50, As4Ge30S66 and in As2S3. The sample was placed between two crossed polarizers. Kerr birefringence induced by pump beam caused appearance of the elliptic component in the probe beam polarization, which passed second crossed polarizer. The probe beam, which survived crossed polarizers, was analyzed by spectrograph in the same way, as in previous experiments at different time delays. The temporal width of the measured Kerr signal equals to the temporal resolution of the setup. Cubic non-linear susceptibility responsible for Kerr signal generation was estimated for the said glasses. The authors acknowledge the support from Science and Technology Center in Ukraine (Project #3745).

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Features of Electroluminescence of Light-Emitting Gaasp/Gap Structures After Natural Ageing

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Significant for stable work without degradation of light-emitting diodes is prevention of occurrence and duplication of defects of different dimension in their active area and in the field of their ohmic contacts. One of powerful methods of research of the defective subsystem is the spectroscopy, in particular research of electroluminescence (el) spectra. Earlier has been established [1], that in light-emitting GaAsP/GaP structu-res due to process of natural ageing there is a reduction of defects number with small aact which accept active participation in defects-formation processes and micro-destructions that proceed in their active area and area of the contacts accompanied be acoustic emission (aa) and leading to degradation both el intensity [1] and other characteristics of light-emitting structures. Processes of ageing occur mainly due to linkage of dot defects and dislocations in clusters, i.e. Formations of new complexes of defects with greater aact that has led to increase of local strength of a crystal. Also in light-emitting diode structures at natural ageing there is an increase in adhesive durability of contacts to a structure surface. In work the electroluminescence of natural aged light-emitting structures based on the gap and gaasp (the maximal constant direct current - 10 mA) is investigated. The current raised step-by-step due to technique [1], which allowed simultaneously with record of el spectra to register aa. Irreversible and reversible degradation of GaAsP: N, Zn-O/GaP structures at currents up to 350 mA is found out. It is revealed, that a part natural aged structures at currents 500 mA (and more) and also at ambient temperature 500-600 N Degrade slowly and do not fail, unlike new, without ageing, structures of such type for which these currents are not achievable. Reversible degradation of the red band can be explained by thermal ionization on isoelectronic complex ZnGa$-OP$. At the raised temperatures (SINCE 300 N) disintegration of excitons on far donor-acceptors pairs (DAP) ZnGa$-OP$ starts to occur and accordingly radiating recombination between energy levels ZnGa$-OP$ - Zn (and EV) sharply decreases. This effect is not connected with el intensity reduction due to increase of phonon absorption at temperature increase. The exciton strip (1,78 aV) passes in a strip 1,4 aV, caused by donor OP. THus due to a significant warming up by passage current up to 450 mA (the overheat temperature of active area 600 N), and at external source (up to 500 N), occurs significant displacement of the green strip from 2,18 aV up to 2 aV due to band gap change which is caused recombination on the isoelectronic centers of nitrogen np. due to it color of light of the aged structures monotonously changes from green to red. Irreversible el degradation corresponds as defects-formation in the area of contacts that leads to reduction of injection coefficient, and also defects-formation in active area and accordingly to growth of non- radiative recombination. Simultaneous significant shift and disappearance (both reversible and irreversible) band 1,78 eV and formation of the strip 1,4 eV which it is accompanied by ae, explains domination of the channel of radiative recombination at the donor of oxygen [1] (reversible degradation) or diffusive disintegration of dap ZnGa$-OP$ (irreversible degradation).

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O- 8 ⇓

Elegant Example of Using the Perturbation Theory: Manifestations of Magnetic Ordering in The Optical Spectra of $PRFE_3(BO_3)_4$

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In this presentation, we report on several effects observed in the optical spectrum of Pr^{3+} in the magnetically ordered state of $PrFe_3(BO_3)_4$ and explained using the perturbation theory. The splittings and shifts of energy levels appear as the first and, respectively, the second order corrections of the perturbation theory. Besides, a new effect was observed, namely, the emergence of new spectral lines at the magnetic ordering temperature [1]. The transitions between singlet crystal-field sublevels of Pr^{3+} ion with the same transformational properties, strictly forbidden for the trigonal D_3 point symmetry of this ion in $PrFe_3(BO_3)_4$, appear below the Nel temperature and grow in intensity as a square of the order parameter. We show that the forbidden spectral lines appear not due to changes in the symmetry of the crystal lattice structure as the magnetic phase transition is crossed but due to mixing of wave functions of an optical center by the exchange interaction in the magnetically ordered state. The perturbation theory delivers corrections to unperturbed wave functions and, as a consequence, to the intensities of optical transitions. Using the perturbation theory and the results of crystal-field calculations, we were able to perform a quantitative estimate of the observed effects [1].

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O- 9 ⇓

Discrete States of OH-groups and Water in Volume and Near to the Surface of Solid Bodies

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Water impurity in solid bodies change their mechanical, optical, electrophysical and other characteristics that regularly was not studied.Especially important role plays water interaction with various silicate mediums which are very widespread in the nature (in lithosphere of the Earth 58% SiO_2) and are widely used in manufacture. By methods of IR spectroscopy with use of Fourier spectrometer Nicolet NEXUS-470 various states of OH-groups and molecular water in a number of monocrystals (NaCl, KBr, LiF, $LiNbO_3$, $LiJO_3$, $LiTaO_3$, $Ba_3NaNb_5O_{15}$ (a banana), $CdWO_4$, $Bi_{12}GeO_{20}$, Al_2O_3, $Y_3Al_5O_{12}$, Ge, SiO_2 (quartz, amethyst), $Al_2[SiO_4](F,OH)$ (a topaz)) were studied, various samples of fused quartz, disperse silica (silica gels, aerosils, porous glass). Samples $\alpha-$ and $\beta-$ phases $Ni(OH)_2$ in which except hydroxyl OH-groups contained molecules $_2$ in crystal kind ($3Ni(OH)_2$-2_2) or the adsorbed water, and also thin plates of muscovite $KAl_2[Si_3AlO_{10}](OH,F)_2$ and teflon were in addition studied. In disperse silicate mediums it was studied both the water adsorbed from air, and capillary water. The existence of six discrete states of internal OH groups and water molecules in volume of solid bodies in addition to superficial OH groups (3690-3749 cm^{-1}) for the first time is established. Various states of OH-groups and solid bodies were identified by discrete positions separate spectral components (3379, 3428-36, 3484, 3545, 3583-96, 3640-75 cm^{-1}), and also by change their intensities.

In monocrystal NaCl narrow peak of 3583 m^{-1} OH-groups has half-width $\delta\nu = 1,5cm^{-1}$, and for bonds about 3485 cm^{-1} in crystals $LiNbO_3$, $LiTaO_3$ and $Ba_3NaNb_5O_{15}$ $\delta\nu = 27 - 29cm^{-1}$. Strips of the condensed water in the field of 3430 cm^{-1} have considerably the big width. Resonant bond of a valency water mode ? and the second overtone $3\nu_3(SiO_4)$ a valency asymmetric mode of structural tetrahedrons is essential feature of crystals of quartz, a topaz and related it substances. For a band of an overtone $3\nu_3$ of quartz crystals four components connected with LO-TO splitting are observed, that allows to easily interpret them. In a spectrum sharper lines of internal OH-groups 3380, 3484 and 3595 cm^{-1} are observed. For fused quartz, absorption bands of OH-groups are wider and also displaced in high-frequency area (6675 cm^{-1}). The same position of bands is observed in muscovite, nickel hydroxyls, silica gels and porous glass. The isolated OH-groups on SiO2 and Ge surface have the greatest frequency of 3748-49 cm^{-1}. Except area of valency vibrations OH-bonds length -, overtones $2\nu_{OH}$ and compound tones with participation ν_{OH}, deformation, libration, and also screen water modes were in details studied. The maximum number of ν lines was observed by us in IR spectrum of $\mathrm{Bi_{12}GeO_{20}}$. And to narrow lines of $\mathrm{H_2O}$- molecules and OH-groups 3440, 3567,3625, 3683 and 3749 cm^{-1} in overtone areas corresponds approximately doubled frequencies of 6875, 7130, 7235, 7358 and 7458 cm^{-1} that specifies on very small anharmonicity of investigated vibrations. The same situation is observed for topaz, $\beta - Ni(OH)_2$ and other substances.

Presence of molecular water forms is proved by direct supervision of deformation mode $\nu_\delta = 1662cm^{-1}$ in $\mathrm{CdWO_4}$ and 1617 cm^{-1} in $\mathrm{Al_2O_3}$, 1637 cm^{-1} in $\beta - Ni(OH)_2$, and also supervision of compound tones $\mathrm{nu}_{OH} + \nu_\delta$ near 5200 cm^{-1} in fused quartz, $\mathrm{Ni(OH)_2}$ and disperse silica. Relationship of characteristic band of 4520 cm^{-1} intensity with the water maintenance in disperse silicate mediums is proved. Spectral changes at increase of quantity of the adsorbed both capillary water and strengthening of collective properties of their vibration modes are studied.

Research of Phase Composition and Structure of Systems is on Basis of TiO2.

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One of intensive methods of research of structure of crystals there is a x-raying. It is based on research of conformities to the law of dispersion of coherent x-ray photography waves the electrons of atoms of the condensed systems. We study phase composition and structure of the system by x-raying method from nanocrystals components on the basis of TiO2 and cobalt in an amount 10 and 20% mass in our work.

The structure and physical and chemical properties of the mixed nanocrystals materials of oxide depends on their composition and method of synthesis in majority. Oxides, based on a titania with the admixtures of transitional metals, are mixed, have high photocatalytic activity in the reactions of disintegration of organic compounds, and also examined as non-reactive materials for sun small holes in the devices of transformation of light. The mixed oxides were synthesized chemically, by introduction of cobalt on the surface of polydiscontinuous particles of TiO2 and next burning at temperatures 350, 600 and 900 C.

Information of x-raying analysis show that after here gigue at temperatures 350 and 600 C crystalline structure of example in tetragonal with the parameters of a=3,785 and c=9,514, that answers the grate of TiO2 is an anataze. Sciagraphy, being of cobalt in the free state can be related to disguise of lines of cobalt from considerable expansion of lines of anataze.

The analysis of size of blocks of coherent dispersion is resulted on expansion of x-ray photography lines of anataze shows that structure of standards after burning at the temperature of 350C shallow with the size of blocks of order of 80 - 90 nm. Burning at the temperature of 600C results in a jumboizing blocks to 120 nm. Standards, heated at the temperature of 9000s presented three phases (are an anataze (77-78%), tetragonal rutile of TiO2 (18-20%), (a=4,593, c=2,959) and connections of Sotio3 at initial maintenance of cobalt 20% is 6%. Burning at the temperature of 900C results also in a substantial jumboizing blocks of mosaic of anataze to d=300nm.

P- 2 ⇓

Low Frequency Vibrational Spectrum of Crystal KYb(MoO$_4$)$_2$

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Crystal KYb(MoO$_4$)$_2$ belongs to a family of double alkali – rare earth molybdates with the general formula KRe(MoO$_4$)$_2$, where Re is a rare-earth metal ion. These compounds have an orthorhombic crystallographic structure (D_{2h}^{14}, z = 4) [1]. Their common features are low temperature phase transitions induced by the cooperative Jahn-Teller effect (CJTE) [2,3]. The compounds have a layered crystalline structure formed by the weakly-bonded K^+ – layers and the Re(MoO$_4$)$_2$ – layer packets with stronger bond. It induces low-frequency vibrational modes in the excitation spectrum and a strong electron-phonon coupling between the electron excitations of the rare-earth ions and the lattice vibrations, provided that their energies coincide.

To identify the structure of the low-energy vibrational and electron excitation spectrum of KYb(MoO$_4$)$_2$ we measured the long-wavelength IR transmission. Two absorption bands with the energies 25.3 cm^{-1} in the polarization E||c and 16.8 cm^{-1} in the polarization E||a were detected. They are interpreted as interlayer vibrational modes. The acoustic and optico-acoustic vibrational branches of the crystal KYb(MoO$_4$)$_2$ in the Brillouin zone were calculated using a one-dimensional model [4].

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P- 3 ⇓

Kinetic Study of Frenkel Pairs Accumulation and Aggregation in Rare-Gas Solids by Analytical Luminescence Technique

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Materials modification by electronic excitation is an important prerequisite for many novel technological applications in material and surface engineering, photochemistry, micro- and nanoelectronics. At the same time the relevance of integration of techniques of materials modification by electronic excitations into the modern industry requires the development of remote nondestructive continuous analytical approaches to monitor the correspondent technological processes of material parameters changing [1], and the problem of analytical control of crystal composition and structure modification processes is one of the central problems in solid state radiation physics and chemistry [2].

The basis for the electronically induced lattice modification technologies is a localization of the excitation energy followed by the energy transfer to the material surroundings. A variety of inelastic processes induced by electronic excitations have been studied, but many details of the electronically induced modification of solids are still not understood in deep. Rare-gas solids are the model systems in chemistry and physics of solids, and a lot of information about dynamics of electronic excitations has been documented in several books and reviews (see e.g. Ref. [3] and references therein). It is generally recognized that creation of electronic excitations in rare-gas solids results in self-destruction of crystal lattice. Recently, harnessing the intrinsic luminescence of rare-gas solids, the kinetic model for description of radiation-induced subthreshold inelastic elementary processes in rare-gas solids has been proposed, which allows the real-time analytical monitoring of the crystal structure of the samples [4]. Exciton self-trapping induced defect accumulation progress curves – time dependence of intensity of characteristic "defect" luminescence subbands – show pronoun-ced linear growth at the beginning of irradiation, saturation at longer times, and, finally, fading behavior [5].

In the present study we apply our kinetic approach to such a progress curves and propose an explanation of the slow decay of the "defect" subband as a result of defect phase formation induced by Frenkel pairs creation during relaxation of self-trapped excitons. The experiments were carried out at the SUPERLUMI-station at HASYLAB, DESY, Hamburg. Initial increase of the intensity of the characteristic luminescence subband during irradiation reflects the accumulation of stable long-lived point defects (Frenkel pairs) in the lattice as a result of exciton creation and self-trapping in the consecutive process

$$E + T \rightleftharpoons MTE \rightarrow D,$$

where E is the mobile excitation (free exciton), which is trapped at trapping center T (lattice imperfection) and forms an excited metastable trapped center MTE [4]. Radiation decay of short-live MTE-center either returns the lattice into the initial state, or creates the stable defect D (Frenkel pair). The kinetics of growth of characteristic luminescence intensity under steady-state conditions of irradiation may be expressed as

$$I(t) = I_0 + \frac{K \cdot t}{L + t},$$

where $I_0 = I(0)$ is the initial intensity of characteristic luminescence of the sample; K is the saturation value of $(I(t) - I_0)$ at $t \rightarrow \infty$; $L \sim n_E n_T (n_{MTE})^{-1}$ is a specific constant of a sample; n – concentration [4]. Numerical fitting of experimental dose curves for the samples of solid xenon and neon allows to obtain the values of these constants $K_{\mathrm{Xe}} = 1.6 \cdot 10^3$ cps, $K_{\mathrm{Ne}} = 6 \cdot 10^2$ cps, $L_{\mathrm{Xe}} = 2.4 \cdot 10^3$ s, $L_{\mathrm{Ne}} = 1.4 \cdot 10^4$ s. After long exposure, when the point defect concentration in the sample, n_D, will exceed the critical value, the exciton self-trapping near existent defects will not stimulate the creation of the new defect, but will induce the aggregation of the existent defects in the process

$$MTE + D \rightarrow DD.$$

In this case the fading kinetics of the characteristic luminescence may be expressed as

$$I(t) = \frac{K \cdot L'}{L' + t},$$

where $L' \sim n_{MTE} n_D (n_{DD})^{-1}$. Numerical fitting of the dose curves allows to determine the value of this constant $L' = 4.8 \cdot 10^3$ s for the particular case of xenon cryocrystal.

Proposed analytical luminescence method provides a way of qualitative and quantitative analysis and certification of rare-gas cryocrystals, which is indispensable at any attempt of comparison of data from experiments with different samples [6]. Analytical applications of this method enable an estimation of the "defectiveness" of the sample and maximum radiation dose, above which the growth of the defect phase occurs in the sample.

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P- 4 ⇓

Crystal Engineering and Luminescent Properties of New 4,4?-Bipyridines and Related Compounds

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4,4?-bipyridine derivatives are widely used in the practice as the electrochromic materials, electron transfer mediators, biosensors, matrices of molecular electronic devices, etc. The viologens, 4,4?-bipyridine tertiary salts, are the most useful of them.

We have recently synthesized new substituted viologens contained various functional groups (amide, amino, urea, carboxylic, etc), conjugation-extended viologen analogues bearing stilbene motif as a spacer between the pyridine moieties and some other principally new 4,4?-bipyridine derivatives. Single-crystal X-ray diffraction was used for the determination of the molecular and crystal structure peculiarities of these compounds. It was found that in the most cases the dipyridine core of viologens and their analogues is planar. But there are also some exceptions that demonstrate twisted bipyridine structures. It was found by X-ray diffraction that the viologens bearing hydrogen-contained functional groups depending on the type of H-bonding could be organized in the solid state not only in the intermolecular chains, but also in the helices or nets. Spectral-luminescent properties of the all new compounds in microcrystalline state were studied under excitation with UV laser diode operated at 405 nm. It was found that the extended viologen-analogues demonstrate strong intensity of luminescence in contrast to the corresponding original viologens. Structure-luminescence dependence has been studied.

Domain Walls in Ferroelectrics as Nano-Dimensional Crystalline Objects

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180°-domain walls (DW) which are ones of kinds of borders between the neighbor domains, are a typical example one-dimensional nanostructures (the characteristic sizes 7-12 $\AA$ for ferroelectrics $BaTiO_3$ and $Pb_5Ge_3O_{11}$ with phase transitions of type of "displacement" and nearby 100$\AA$ for ferroelectric triglycine sulfate (TGS) with phase transition of type "order-disorder"). These one-dimensional nanostructures are the plane defects of crystal lattice. These defects create the additional branches of acoustic and optical vibrations in the vibration spectrum of a ferroelectric and ones are localized near to DW. The temperature dependence of parameters of these local vibrations strongly influences the nature of nanodimensional objects.

Within the limits of this research a behavior of dependences of characteristic size d of these one-dimensional nanostructures from microscopic parameters of ferroelectrics with phase transitions of both kinds have been theoretically studied.

On the basis of microscopic model for ferroelectrics with phase transitions of type of "displacement" it has been established, that for motionless domain walls there is critically possible minimal size d_{min} of this nanoobject

$$d_{min} = \sqrt{8S_{S0}/\Omega_{S0}},$$

where S_{S0} is the parameter which characterizes a dispersion of soft mode, O_{S0} is the value of soft mode in the centre of the Brillouin zone.

Within the limits of model which was used for consideration by methods of the Lagranges formalism moving with a speed V domain borders, it is established, that width d of such moving nanoobject is defined in the form of

$$d = C\sqrt{2\alpha(1 - V^2/C^2)/a},$$

where C is the velocity of a sound in the crystal, a and α are the parameters of the ferroelectric model with the double-minimum anharmonic potential.

By research of spectra of pseudo-spin excitations for ferroelectrics with phase transitions of type "order-disorder" it has been established, that for moving domain walls the width d is defined in a similar way, but with parameters of this model.

The temperature dependences of parameters of these models specify that characteristic size d the mentioned nanostructures in the ferroelectric phase has a following appearance

$$d \sim (T_C - T)^{-1/2}.$$

In this case the nanostructure object at approach of the temperature ? to the point of phase transition T_C is delocalized, increasing the characteristic size.

The experimental researches of temperature dependences components of dielectric permittivity along a polar axis for monodomain ε_m and polydomain ε_p crystals TGS have been spent. These researches have qualitatively confirmed results of theoretical calculations which have defined decrease of the contribution from movement domain walls in this parameter at temperatures approach to T_C:

$$\varepsilon_p - \varepsilon_m \sim (T_C - T)^{3/2}.$$

P- 6 ⇓

Crystal Structure of Merocyanine Dye Based on the 2-acetyldimedone Boric Chelate

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In the view of the possibility of practical application of the merocyanine dyes and their analogues unrelenting interest in them develops. These dyes serve as NLO-materials and could be used in OLED displays production. For investigation the correlation of structure and spectral-fluorescent properties of merocyanine dyes, 2,2-difluoro-1,3,2(2H)-dioxaborine dye was synthesized. The goal of the present work was the determination of the bonds lengths distribution in these compounds by single-crystal X-ray diffraction method. It was found, that these dyes depending on conditions could be crystallized in two forms: classic single crystals and crystals with through canals inside. In the most cases these canals reiterate the outward form of crystals and their size varies depending on the solvent, which compound was crystallized from. It is worth to note that the indexing of X-ray reflections for the both types of crystals (with canals and single crystals of classic form) give the same cell parameters. It means that structure of crystals with canals isn't generated in the way of growing of different facets together. It is possible that crystals' growing was caused by the specific influence of proton-donor solvents which able to block separate parts of molecules of dye in such a way that crystals growth on the free of salvation areas of compound occurs.

Influence of a Proton Irradiation on Rate Recombination of Interaction in Ceramics ZnS-Cu

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The influence of defects of structure on rate recombination is defined by their concentration, factors of capture electron, hole and power level of traps. With other things being equal this influence the is less, than more finely power level of a trap concerning one of zones. Physically it designates that the majority of carriers of a charge seized from the nearest zone, at once are thrown out in a zone. Such of defects of structure are the good suppliers equilibrium electron or hole and strongly change electrical conduction's. On the contrary, the impurity with deep levels of energy low-grade influence on equilibrium electrical conduction's, but can strongly change times of life (recombination's defects of structure).

The change of rate recombination was studied at isothermal and not isothermal modes after an irradiation by protons of ceramics ZnS-Cu. The excitation luminescence and the light sum a accumulation were carried out by integrated study x-ray tube (Mo, 35V, 10 mA) at temperature 85 and 295 .

During experiment samples (initial and irradiated by protons by dozes 10^{13}, 10^{14},10^{15} /cm^2 with energy 50 Mev) were raised during different intervals of time, from 2 sec till 3 hours. The change of rate recombination and was analyzed on linear sites of curve accumulation the light sum on all area of afterglow. The analysis τreceived on the formula for located electron at short-term excitation used time from 2-3 sec up to 60 sec testifies to dependence of this parameter on a level impurity doping process by protons.

The received dependence of rate of accumulation up the light sum $\tau()$ of an initial sample in an interval 100 up to 440 testifies to presence of several grades of traps participating in accumulation up the light sum. After an irradiation of ceramics has changed kinetics of accumulation up the light sum during an interval of registration thermostimulated luminescence (TSL). And, the presence of radiating defects differently changes processes of accumulation up the light sum on different grades of traps. The increase of values τ for samples irradiated with a doze 10^{13}, $10^{14}/cm^2$ (area of registration 100-250) contacts to increase of concentration interstitial of zinc (Zn$_i$) crucial for low- temperature peaks TSL. The peaks 110 and 125 are caused by sulphide of zinc, the peak TSL at 160 communicates - with V_s (vacancy of sulfur).

For deeper traps the value τ has changed concerning the appropriate values of an initial sample a little. The changes τ in these sets of samples can be connected with increase of concentration of the canters participating in recombination processes, i.e. increase of channels recombination of carriers in a material.

The increase of value τ on the average in 2-3 times (temperature area 250-450) is characteristic for samples irradiated by a doze $10^{15}/cm^2$. In this temperature area the selective change τ, showing about occurrence after an irradiation of new local levels selectively influencing of accumulation up the light sum by the certain groups of traps is observed. The relation reserved up the light sum under curves TSL enables to assume occurrence of the canters of suppression in the irradiated samples by depth 0,5 eV, and the concentration them is comparable to concentration before the available canters of capture. For finer traps, the linear growth of value ? with increase of temperature is observed. The received values τ in low- temperature an interval TSL can be connected by probable displacement Zn$_i$ in regular places that is reduction of concentration Zn$_i$ and V$_s$ for low- temperature peaks TSL. The radiating defects, generated by a proton irradiation, result in change kinetics of luminescent processes and change of a spectrum of local statuses in a researched material. The selective change of speed of accumulation up the light sum after a proton irradiation testifies to presence in sulphide of zinc tunnel recombination of processes.

The Influence of Temperature on Raman Modes in Lead Nitrate Crystal

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The temperature broadening and shift of phonon lines is a manifestation of the phonon-phonon and phonon-lattice interaction. The investigation of Raman mode temperature dependencies allows to study the anharmonicity of lattice and molecular ionic vibrations.

The spontaneous Raman spectrum of $Pb(NO_3)_2$ crystal was investigated in [1]. The internal vibronic modes of $(NO_3)^-$ molecular ionic group in lead tungstate are well isolated from lattice vibrations with energy gap about 500 cm^{-1}. This simplifies the analysis of phonon-phonon and phonon-lattice coupling. In this report the results on temperature dependencies of Raman mode parameters in the range 15300K are presented. The frequency shift and line broadening were measured for F_g (96 cm^{-1}), E_g (730 cm^{-1}), F_g (733 cm^{-1}), F_g (736 cm^{-1}), F_g (1047 cm^{-1}) and A_g (1049 cm^{-1}) Raman modes. The temperature shift of Raman mode frequencies exhibit similar behavior. The mode energies are reduced with heating due to lattice expansion and lowering of the crystal field influence on $(NO_3)^-$ molecular ion. The Gruneisen parameter that characterize the mode coupling with crystal field were estimated for these Raman modes.

The increase of temperature results in Raman mode broadening. The value of the linewidth at 0^oK and the slope and curve of temperature dependence are determined by the coupling processes. The analysis of temperature broadening allows to predict the dominant relaxation mechanisms. High frequency Raman vibrations in molecular ionic crystals are originated inside molecular ion and are well isolated from lattice phonons. That's why the number of their possible relaxation channels is limited and they can be interpreted in terms of multiphonon decay mechanisms. Our analysis showed that with high accuracy the relaxation of high frequency $A_g(n_1)$ vibronic mode can be described by a combination of two processes. At low temperature the dominant relaxation process is a two-phonon splitting with the excitation of a lower energy internal vibron and a lattice phonon. At higher temperature the dominant is a dephasing process due to the interaction of the $A_g(n_1)$ internal vibron with highly populated low energy lattice phonons. The dominant relaxation mechanisms are proposed for all investigated Raman modes in lead nitrate crystal.

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Crystal and Molecular Structure of New N-trifluoromethylsulfonyl-N-(4-fluorophenyl)carboximidoyl Chloride Derivatives

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Fluorine substituents have become a widespread and important drug component, their introduction facilitate the development of protecting and selective fluorinating agents. Organofluorine substituents affect nearly all physical and biological properties of the initial compound: absorption, distribution, metabolism, excretion, etc. Their inductive effects are relatively well understood (for example, they enhance bioactivity by reducing the basicity of neighboring amines). In contrast, exploration of the specific influence of carbon-fluorine single bonds on docking interactions, whether through direct contact with the protein or through stereoelectronic effects on molecular conformation of the drug, has only recently begun [1]. We have recently synthesized and investigated a number of new heterocyclic compounds containing trifluoromethanesulfonylimino-, methylsulfonylimino groups and some N-trifluoromethylsulfonyl-N-(4-fluorophenyl)carboximidoyl chloride derivatives. As a result of single-crystal X-ray diffraction it was found that in the most cases the molecules are characterized by the very strong intramolecular hydrogen bonds which significantly influence on their spatial structure. The peculiarities of intramolecular hydrogen bonds in solid state and solutions were investigated by IR-spectroscopy. X-ray diffraction has also shown that in crystals the hydrogen-contained functional groups usually form intermolecular chains or nets by different types of hydrogen bonds which often include solvent or water molecules.

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Phonon and Magnon Raman Scattering in $Ni_5(TeO_3)_4Cl_2$ Single Crystal

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The new transition-metal tellurium oxycloride has clearly a pronounced layered structure. Each layer is made of groups of five distorted nickel-octahedra into a "claw unit" with some unusually short nickel-nickel distances [1]. The magnetic properties should therefore be dictated by strong magnetic interaction within each "claw unit". The powder sample undergoes a transition in antiferromagnetic ordering state at temperature 23 K [1].

In high-field electron-spin resonance investigations of $Ni_5(TeO_3)_4Cl_2$ single crystal, ten spin-resonance modes with characteristic magnetic-field dependencies were discovered [2]. The two-dimensional model discussed by Mihaly et al. [2] reproduces only a part of the observed excitations and further investigations including neutron and Raman scattering are necessary for a complete exploration of the magnetic structure in this compound.

The transition metal tellurium oxychloride, $Ni_5(TeO_3)_4Cl_2$, has been investigated by Raman scattering method at temperatures 2 - 300 K. Sixty two phonon modes (of the total 69 Raman-active phonon modes allowed for the monoclinic structure) were identified in the spectra and their behavior was analyzed. The temperature behavior of the phonon modes testifies the absence of a structural phase transition in the temperature range 2 - 300 K.

At low temperature range 2 K, a number of additional weak peaks at 13.1, 16.8, 24.4, 29.2, 31.9, 46.2, 48.2, 56.3, 69.4, 69.9 cm^{-1} appear in the low-energy Raman spectra. The energy of additional peaks is consistent with results of spin-resonance investigations [2]. Additional peaks (except peak at 56.3 cm^{-1}) vanish at around T_N with temperature rising. This is a typical behavior for the one-magnon scattering. Moreover, wide band at 50 cm^{-1} perhaps two-magnon scattering in origin was observed.

The behavior of additional peaks have investigated in magnetic field 0 - 25 kOe in different geometries. It was discovered that line at 56.3 cm^{-1} did not respond on magnetic field. Moreover, this line displays a strong interaction with the phonon mode at 55.1 cm^{-1} and exhibits the anomalous temperature dependence. Line observes at temperature well above T_{N}. The interesting features of behavior this line is discussed.

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Investigation of Low-Energy Electronic Excitations of Terbium Ion in $KTb(WO_4)_2$ Single Crystal by Raman Scattering

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Resonance studies show that in $KTb(WO_4)_2$ the non-Kramers terbium ion possesses in the bottom part of the electronic spectrum a quasidoublet of states separated by an energy gap ~ 1 K [1]. The experimental results obtained for the static magnetic properties of $KTb(WO_4)_2$ show this compound to be an Ising antiferromagnet with critical temperature $T_N \approx 0.7$ K [2]. Phase transition induced by external magnetic field has been observed [1]. The experimental dependence of the susceptibility [2] has been described in assuming a model included three excited electronic quasidoublets. A correctness of the two-level model may be verified by new experimental information about the arrangement of the energy levels of the terbium ion.

Spectrum of the Raman light scattering is investigated in $KTb(WO_4)_2$ single crystal in the frequency range 3-950 cm^{-1} in the temperature range 5-300 K. All 36 vibrational modes predicted by group theory analysis were detected and their symmetries were determined. The temperature behavior of the phonon spectra testifies the absence of a structural phase transition in the investigated temperature range. To extract electronic spectrum contribution the isomorphic compounds of yttrium and dysprosium were investigated.

In $KTb(WO_4)_2$ ten of the 11 predicted Raman-active low-energy electronic transitions were found between the levels of the ground state multiplet of terbium ion split by the crystal field with the symmetry C_2. It is determined that the first excited electronic quasidoublet consists of two singlet levels with different symmetry, and it is separated from the main quasidoublet by enough big energy (~ 75 cm^{-1}). The behavior of all experimentally observed levels in external magnetic fields is investigated. Study of electron transition from first thermal populated level in external magnetic field gives opportunity to evaluate an energy spliting of quasidoublet ground state in zero field (~ 0.7 cm^{-1}). Spectroscopic g-factor of quasidoublet ground state and excited electronic states evaluated from

electronic Raman lines field dependence.
The results of investigations confirm that at low temperatures a case of the pure Ising anisotropy is realized, and that the considered magnet may be regarded as a system of two-level magnetic ions.

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Modelling of space ionizing fields action on the optical properties of diode pumped solid state laser elements

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A detailed analysis of investigation state-of-art on the ionizing radiation influences on laser systems has been conducted. The research has concentrated on estimation of predictable level of space radiation and other radiation field environments influences on optical materials, laser elements and solid state lasers.

The diode pumped laser output functional dependence of the main parameters of pumping and characteristics of basic laser elements is well known for the basic modes of generation [1]. Features of major types of lasers, such, for example, as Nd:YAG lasers, full enough taken into account in a number of works. In this connection, for a development of model, allowing to estimate influence of ionizing radiation on a laser, the experimental information is needed about influence of radiation on absorption and scattering of light in optical elements, change of reflectivity of multi-layered dielectric mirrors, change of transmission and absorption of laser crystal on a wavelengths of pumping and lasing. The following models have been analyzed [2]: (a) solar flare influences on laser systems; (b) forecasting of ionizing radiation influences; and (c) risk assessment in laser safety analysis. The possibility of using statistical probability risk assessment and nonlinear forecasting models of laser dynamics under ionizing radiation influences has been analyzed. This is a so-called black box or input-output model, which seeks only to reproduce the behaviour of the systems output in response to changes in its setpoint or inputs. The model inputs are radiation influences on lasers and output parameters are indexes (integral characteristics) of laser elements.

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Crystal Structure and Photoluminescence Properties of Complex Lanthanide Oxides from Molten Phosphate–Molybdate (Tungstate) Media

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Lanthanide (Ln) doped phosphates, vanadates, molybdates and tungstates have been the subject of recent investigations as potential materials for luminescent applications. M^I_2O–P_2O_5–$M^{VI}O_3$–Ln_2O_3 (LnF_3) ($M^I = Na$ or K; $M^{VI} = Mo$ or W) melted systems were investigated as following binary sections: M^IPO_3–$M^I_2M^{VI}_2O_7$, $0.5(M^I_4P_2O_7 \times M^IPO_3)$–$M^I_2M^{VI}_2O_7$ and $M^I_4P_2O_7$–$M^I_2MoO_4$ containing 5 % mol. $M^{III}_2O_3$ ($M^{III} = La$, Nd–Gd, $Dy - Lu$) or 7 % mol. $M^{III}F_3$ ($M^{III} = La - Lu$). Two main methods were used: FTIR-spectroscopy and single crystal XRD. Three types of compounds were revealed. One of them, namely $K_2Ln(PO_4)(M^{VI}O_4)$ has attracted our attention to study luminescence properties.

Isostructural analogue $K_2Bi(PO_4)(MoO_4)$ doped with Eu^{3+} has been chosen to investigate the concentration series up to $K_2Eu(PO_4)(MoO_4)$. Luminescence spectra measured under 4.2 and 300 K have been discussed taking into account structural data.

Luminescent properties of the concentration series of mentioned above undoped and doped with Eu^{3+} ions compounds were investigated and discussed.

Luminescence of the RE^{3+} ions doped compounds is a superposition of own matrix luminescence and luminescence of RE^{3+} ions caused by intrinsic $f - f$ radiation transitions. Besides, manifestation of interaction between matrix and impurity ions was found. Correlation between number of various Eu^{3+}-luminescence centers and local structures of mentioned typed of compounds was established.

Thus, the results obtained show a perspective of mentoined compounds doped with Eu^{3+} to be used as effective white and color light-emitting photoluminophores.

Photoluminescence of Titanium Perovskite-Like Compounds Doped with EU^{3+} Ions

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Oxid compounds with rare earth (RE) ions are attractive materials for multicolor luminofors which can be used in plasma and catodoluminescent displays and detectors of ionizing radiation as well. There were undertaken some effort to design new phosphors on the base of doped with praseodymium ions $Ca/Ba/SrTiO_3$ perovskites. Such type phosphors could be used in combined LEDs. PL intensity of these phosphors is very low and researchers aimed to enhance it have to introduce some additional impurities, Al or Ga ions, e.g., into mentioned matrix.

$BaLa_2Ti_3O_{10}$ belongs to Dion-Jacobson family of layered perovskite-like titanates of common formulae $Ba[Ln_{n-1}Ti_nO_{3n+1}]$ where Ln is RE element from La to Sm. The some part of the La atoms in $BaLa_2Ti_3O_{10}$ can be easily replaced by another RE atoms. Surely, active in visible photoluminescence RE ions can be among them. We synthesized and investigated here the structure and PL properties of the $BaLa_{2-x}Eu_xTi_3O_{10}$ compounds, where x=0–2.

Synthesis $BaLa_{2-x}Eu_xTi_3O_{10}$ microcrystalline powders were made using termotreatment (T = 1520 K, t = 2 hours) of simultaneously precipitated barium, titanium, and rare earth hydroxycarbonates.

Luminescence spectra were investigated using synchrotron radiation from the region 50-330 nm. Experiments with synchrotron radiation were carried on at SUPERLUMI station at HASYLAB (Hamburg, FRG). In some cases luminescence was excited by radiation from the N_2 (λ_{ex} = 337.1 nm) lasers or powerful xenon lamp DKsL-1000 and MDR-2 or DFS-12 diffraction spectrometers which cover wide spectral region from 225 to

1200 nm were used.

The $BaLa_2Ti_3O_{10}$ compounds doped with europium manifest red "by eye" PL typical for emission of Eu^{3+} ions. The PL spectra of the samples consist of three well-distinct groups of lines. One group lies in 670–750 nm region and others lie in 550–725 nm region. The intensity of lines of the first group is rather low in comparison with the one of the lines in 550–725 nm region. The shape of the spectra does not depend considerably on excitation wave length either it lies in the region of absorption of lattice or it corresponds to inner transitions of Eu^{3+} ions. The diffusion of spectrum components shows that arising of content of Eu^{3+} ions (x=0.5–2.0) follow with accumulation of Eu^{3+} ions, in positions which differ from La ions positions in $BaLa_2Ti_3O_{10}$ compound that leads to destroying its layered crystal lattice and different crystal phases can be formed as result. It is possible also that crystal structure of high concentrated $BaLa_{2-x}Eu_xTi_3O_{10}$ samples is closer to the structures of crystalline solid solutions.

For the first time, the main luminescent characteristics of compounds $BaLa_{2-x}Eu_xTi_3O_{10}$ (x varies from 0 to 2) were investigated. It was found that the luminescence of mentioned materials is caused by radiation transitions in luminescence centers formed by Eu^{3+} ions. The sets of lines observed in the regions 578–582, 580–604, 604–640, 640–675 and 675–725 were related with $^5D_0 \rightarrow {}^7F_J$ ($J = 0, 1, 2, 3$ and 4) manifold transitions respectively. Two types of luminescence centers which differ by symmetry of neighborhood of Eu^{3+} ions are found in luminescent emission. Concentration quenching depending on Eu^{3+} ions content takes place and luminescence intensity is the most at x=0.5. Luminescent characteristics of Eu^{3+} ions are in close relation with composition of $BaLa_{2-x}Eu_xTi_3O_{10}$ compounds that can be caused by both changing their crystal structure and phase composition as well.

Experimental investigation of lattice dynamics and anharmonicity of SRS Raman modes in $BaWO_4$ crystal

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Spontaneous Raman spectra for Raman-active modes in the $BaWO_4$ were measured in the temperature range 15÷295K for a body-centered tetragonal phase [1]. The temperature dependencies of linewidth of four Raman modes ($333 cm^{-1}$, $345 cm^{-1}$, $833 cm^{-1}$ and $926\ cm^{-1}$) were analyzed numerically using TDOS due to cubic term according to the lattice dynamical calculations approach described in Ref. [2]. The calculated results well describe the experimental ones in this temperature range. Also, the variation of linewidth of lower-frequency modes ($333 cm^{-1}$ and $345\ cm^{-1}$ peaks) is about 2.0 times greater than that for higher-frequency modes ($833 cm^{-1}$ and $926 cm^{-1}$ peaks). We concluded that the TDOS for the lower-frequency modes is dominated by the decay and the scattering processes, while phonon-phonon interactions on the higher modes are dominated by the decay of the observed phonons into two phonons having lower energies. We found that this originates in a clearly large phonon band gap [3] in the phonon density of states that produces a difference in anharmonic effects on each peak's channels. This result is similar to that in the high-temperature phase in the case of $LaGaO_3$ [4].

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Self-Association of Quinacrine on Polyphosphate Matrix

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Likely a key agent in evolution from prebiotic time, polyphosphate (Poly P) is found as a chain of tens to hundreds of phosphate residues linked by highenergy,phosphoanhydride bonds as in ATP. Poly P has been conserved in every cell in nature: bacterial, fungal, plant and anymal. Polyanion Poly P interacts with cationic compounds. The reaction, in which high-molecular-weight Poly P cause a shift in the absorption maximum of cationic dyes, is well known. This reaction essentially involves polymerization of the dye on the macromolecular anion. The conformational analysis of the Poly P chain shows that it can shape helix in which P atoms are draqwn up into two diametrically oppositely situated linear rows with the step of 0.36 nm, as well as PO^{2-} groups. Upon construction of this geometry the P-O bond distance of 0.156 nm was taken from X-ray diffraction data and valence angle between P-O bonds of 109.5 was used. The obtained step of negative Poly P groups corresponds with an interplanar separation of π-systems of two parallel neighboring chromophore (0.34-0.36 nm). That promotes formation by quinacrine of stacking associates on polyanionic matrix of Poly P due to attractive interaction between positive charged groups of the quinacrine and negative charged oxigen atoms of Poly P. Since the quinacrine molecule has mutually spaced two positive charges that set conditions for forming of several steric type associates. We studied the interaction of quinacrine to Poly P in water solutions under small molar polymer-to-dye ratio (P/D) corresponding to the saturation of the binding. Methods of absorption and polarized fluorescent spectroscopy were used. The change in absorbance and fluorescence spectra evidences rearrangement of the complex structure depending on P/D value. Models of the complex formation is suggested.

4 LIQUID CRYSTALS

O- 1 ⇓

Dispersions Of Carbon Nanotubes In Liquid Crystals: State-Of-Art, New Results, Further Prospects

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Dispersions of carbon nanotubes (CNT) in liquid crystals (LC) are examples of liquid crystalline colloids or, in other terms, anisotropic nanostructured systems. Growing interest to these objects is based both on their promising applications as advanced materials for electrooptical LC devices and on their properties as model objects for fundamental studies in molecular physics of anisotropic media. The integration of nanometer-long LC molecules and micrometer-long CNTs may result in a unique self-organization of a composite governed by the highly anisotropic excluded-volume interactions. It has been shown that the orientational order of LC can be transmitted to carbon NTs, which results in a high level of nematic order in organisation of NTs [1-2].

In this report, the properties of NT+LC composites are briefly reviewed. Recent results on optical, electrophysical, thermodynamical and structural studies of CNT dispersions in LC matrices of different chemical nature (cyanobiphenyls, azomethines, etc.) and in different LC states (nematics, smectics, cholesterics) are discussed [3]. Similarities and differences are noted for LC dispersions of CNT and other types of particles, e.g., platelets of organomodifed montmorillonites. Implications of the results obtained for applications (e.g., LC memory cells [4]) and fundamental questions related to anisotropic condensed matter are discussed.

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O- 2 ⇓

Specific Features of Luminescence Spectra in Liquid Crystalline and Isotropic Solvents

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Luminescence spectra of several substances of different molecular structure were studied in liquid crystalline (LC) and standard organic solvents. The LC solvents used (nematic alkylcyclohexanecarboxylic acids and their mixtures with cholesterol alkanoates) showed practically no luminescence under excitation at wavelengths above 280 nm; even at 260 nm, their luminescence could be considered as negligibly small as compared with such commonly used nematics as alkylcyanobiphenyls. Several behavior types of luminescence spectra could be noted as for shifts of the luminescence maximum in LC with respect to the isotropic solvents. Thus, luminescence peaks for stilbene and o-POPOP were shifted to longer wavelengths, reflecting effects of incorporation of these molecules into the orientationally ordered LC structure. With pyrene, no shift was observed, and the excimer fluorescence at higher wavelength grew in intensity with concentration. In other cases (e.g., chromenoacridines), the shifts were towards shorter wavelengths, presumably due to molecular aggregation. Possible mechanisms and implications of such behavior are discussed.

Optical Transmittance and Electric Conductivity in Nematic Dispersions Containing Carbon Nanotubes and Organomodified Montmorillonite

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Optical transmission and electric conductivity were measured for dispersions of multiwalled carbon nanotubes (MWCNT), organomodified montmorillonite (MMT) and for hybrid dispersions of MWCNT+MMT in 5CB nematic liquid crystal (LC). The optical transmittance jump at the nematic-isotropic transition was observed in MMT+LC (0.1% wt of MMT). This behaviour was qualitatively similar to that of reported earlier for MWCNT+LC (0.1% wt of MWCNT) nanocomposites, suggesting exfoliation of the organoclay plate-like particles and their incorporation into the orientationally ordered nematic structure. In hybrid dispersions the effect of MWCNT and MMT on optical transmission was additive. Noticeable differences in the electric conductivity behaviour for composites filled with MWCNTs and organomodified MMT were observed. It was shown that MWCNTs facilitated and MMT hindered the electric field-induced transition from planar to homeotropic state in the LC cell.

Laser with Distributed Feedback Based on Doped Nematic Liquid Crystal

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Lasers with the distributed feedback (DFB) on the basis of natural periodic structures of cholesteric liquid crystals (CLC) are known for a long time [1], however interest to similar systems is maintained [2]. Practical value of such lasers is restricted due to lack of operative methods of lasing frequency tuning. Temperature change of frequency due to change of a helix pitch is inertial also demands the thermostability. Imposition of an electric field along an helix axis destroys the macroscopical structure of a mesomorphous body though such expedient of tuning can be used for waveguide lasers with imposition of a field perpendicularly of helix axes.

The electric field can be used also for frequency tuning of lasing in dye doped nematic liquid crystal (NLC) if to build up in an arbitrary periodic structure and to change by the field the orientation of NLC-director and accordingly an average refractive index [3].

In the report results of studying of lasing in dye doped NLC are presented at making the dynamic distributed feedback in two ways of excitation: at an interference of colliding beams pumping and at an interference of passing beam pumping. The pumping contribution in amplitude and phase parts was estimated and quantity of modulation of a complex refractive index was evaluated. Numerical estimates for typical NLC with the positive anisotropy have shown an opportunity of tuning within the limits of an dye amplification band $n \approx 50nm$ for both schemes of excitation. Spectroscopic performances (absorption, fluorescence, quantum yield, photostability) dyes of different classes in NLC are studied.

On a pyrrometane dye solution No metricconverterProductID567 in567 in NLC-654 with a quantum yield 98 n % laser oscillation is gained in the scheme of dynamic DFB with colliding beams pumping. Tuning of a oscillation spectrum from an angle of an interference of pumping beams and presence of spectral narrowing (with the advent of a spectrum of a amplified fluorescence emission at the particular angles), testifies to excitation of typical oscillation in requirements dynamic DFB on NLC. With the purpose of optimization of laser performances their threshold, spectral and spatial dependences from the spatial grating period (an angle of an interference) and an optical density of a dye solution in NLC are studied. Lasing in the scheme of excitation dynamic DFB with an interference of passing pumping beam it was used pirrometane dye No metricconverter ProductID597 in597 in NLC 5. In this case also results on frequency the oscillations corresponding theoretical estimates are gained also. Are analysed and tested some ways of optimization of basic lasing characteristics with frequency tuning for both pumping schemes.

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Hysteresis of Freedericksz Transition in Bounded Light Beams

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Influence of form and boundedness of lateral dimension of incident light beam on hysteresis of light induced Freedericksz transition in nematic liquid crystal cell is considered. Threshold values of director orientational nonstability at increasing and decreasing of light beam intensity are calculated in dependence on the beam lateral dimension and form. It is shown that the width of hysteresis loop changes nonmonotonically with increasing of the light beam lateral dimension. In contrast to the case of homogeneous light beam the domain of hysteresis existence is determined not only by values of parameter $(K_3 - K_1)/K_3$ but parameter K_2/K_3 as well. In this case the critical values of parameter $(K_3 - K_1)/K_3$ increase and of parameter K_2/K_3 decrease with decreasing of beam lateral dimension.

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Influence of Director Anchoring Energy on Freedericksz Transition Hysteresis

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Influence of finite director anchoring energy with surface of homeotropic nematic cell on Freedericksz transition hysteresis in field of homogeneous light beam is considered. Values of director reorientation thresholds at increasing and decreasing of incident light intensity are calculated. Analytical expressions for thresholds and hysteresis loop are derived in the limiting cases of strong and weak director anchoring. Analytical criteria of existence of optical Freedericksz transition hysteresis is obtained in dependence on the cell parameters. It is shown that influence of finite anchoring energy is most significant at the weak director anchoring.

O- 8 ⇓

Nonlinear Optical Properties Of Ionic Mesomorphic Glasses Of The Homological Series Co(II) Alkanoates

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Ionic liquid crystals (ILC) of metal alkanoates form non-traditional class of liquid crystals. Most uni- and divalent metal alkanoates form ionic liquid crystals (smectic A) by heating, which is easy subcooling with creating mesomorphic glasses [1-2]. Such glasses are characterized by ordering and good optical quality. We investigate the mesomorphic glasses (MG) of the homological series CoC_{n+1}, where n=7,9,11, and the common structural formula is $\mathrm{Co}^{2+}(\mathrm{C}_n\mathrm{H}_{2n}\mathrm{COO})_2^-$. The particular feature of MG is their layered structure, which consists of cation-anion electrostatic layers and hydrophobic alkanoate chains between them.

We provide complex study of structural, spectral and nonlinear optical properties of homologous series of cobalt (II) alcanoates, namely octanoate, decanoate and laurate.These ILC and their glasses are coloured due to presence of cobalt ions. The absorption spectra of (II) in alkanoate systems are characterized by two absorption bands with the maximums at 512 nm and at 570 nm, which indicate the existence of two coordination states of cobalt ions: the octahedral and the dodecahedral ones. The nonlinear optical properties are investigated by the impulse holographic method. Dynamic holographic gratings are recorded with nanosecond times both for recording and for relaxation. The coefficient of the nonlinear refraction is calculated from the experimental data. We found that the value of nonlinear refraction coefficient is decreased linearly with increasing the length of the alkanoate chain. A mechanism of optical nonlinearity is considered. This property makes it possible to use ILC of metal alkanoates as new holographic recording materials for applications in fast information processing.

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P- 1 ⇓

Optical Vortices Generated in a Laser Beam Propagating Through Nematic Liquid Crystal Doped with Carbon Nanotubes

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An optical vortex core is zero-intensity point/line in 2D/3D what is actual for high resolution imaging. The wave front with singularities possesses quantified parameters and quit new topology against an usual smooth wave front [1]. Therefore, it's most suitable for investigation of liquid crystals (LCs) doped by carbon nanotubes (CNTs). LCs doped by CNTs displayed many unique properties and have attracted attention due to possible applications in material science, photonics and electronics [2]. Recently, the interesting electro-memory and percolation effects were demonstrated for CNT-LC composites [3,4].

We have observed firstly to our knowledge optical vortices generated in a laser beam propagating through LC cells with CNTs dispersed in a nematic LC 5CB (4-pentyl-40-cyanobiphenyl). The multiwalled carbon nanotubes with high aspect ratio $L/d \approx 300 - 1000$ were used. The composites were prepared by introduction of NTs (0.005-1%) into LC solvent with subsequent 20-30 min sonication. The LC/CNT composites were placed in a thin electrooptical cell with thickness of 100 μm. The optical singularizes were absent in the neat LC media, however, they appeared in the samples at some threshold concentration of NTs ($\approx$ 0.01%). It indicates that optical singularities are generated by presence of NTs. It can be speculated that optical singularities arise as a results of interaction of an incident laser beam with LC shells covering the NTs. The electrical conductivity of LC/CNT composites demonstrated the similar percolation-like threshold behavior. The properties of optical singularities were studied at different NT concentrations corresponding to the tunneling, percolation-like and multiple-connected mechanisms of electrical conductivity.

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Optical Films Based on Plasma Beam Aligned Layers of Reactive Mesogens

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Plasma beam alignment technique earlier developed for alignment of conventional nematic [1] and ferroelectric smectic [2] liquid crystals (LCs) is successfully applied for alignment of so-named reactive LCs widely used in technology of anisotropic optical films. Along with mesogenic core, RM molecules contain one or several polymerizable groups [3]. Due to this structure, RM film can be aligned in a conventional way by the aligning substrate(s) and then solidified via illumination or other action causing polymerization.

In our studies RM films are excellently aligned with the plasma beam alignment technique. As aligning substrates for RM films bare and polyimide coated glass slides and plastic films are used. As RM materials we utilized several mixtures from Merck designed for planar (RMM256C, RMM141) and homeotropic (RMS04-007) alignment. The phase retardation of RM films was characterized by using null ellipsometry [4].

The following types RM films are realized.

(1) Single films with planar and homeotropic alignment having properties of positive A (+A) and positive C (+C) optical retardation films, respectively.

(2) Single films with patterned alignment optically acting as +A/+A, +A/+C, +A/I and +C/I patterned retarders.

(3) Single films of dyed RM with uniform and patterned alignment acting as dichroic polarizers.

(4) Multiple films of neat and dyed RM layers acting as complex retarders (e.g. achromatic retarders) or stacks of retarders and polarizers.

The mentioned films were characterized by high uniformity and good reproducibility.

The obtained results open excellent perspectives for plasma alignment technique as a constituent part of the technology of optical films based on RMs.

These studies were carried out within the projects VC30/04-13 and VC140 of NASU.

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Orientation Effects of Nematic Liquid Crystal on Photosensitive Surface of Chalcogenide Glassy

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Photoinduced phenomena in chalcogenide glasses are of the large interest due to strong and diverse effects produced by light. Irradiation of chalcogenide glasses by polarized light results in different anisotropic and gyrotropic effects. Formation and next orientation of photoinduced defects, orientation of main covalent bonds of the glass and enhancement of the fluidity of the glass under a light polarization are just one of the numbers of mechanisms resulting in light-induced anisotropy and gyrotropy. Photoinduced anisotropy makes chalcogenide glasses attractive materials for application as active and passive photoaligning layers.

We report on the first observation of reversible light-induced changes of the pretilt angle of a nematic liquid crystal (NLC) on As_2S_3 and $As_{50}Se_{50}$ chalcogenide glassy. Irradiation of a LC cell containing an chalcogenide films covered glass substrate with a Gaussian beam of a low power cw-laser (wavelength,$\lambda = 0.47, I < 90W/cm^2$, $\lambda = 0.53, I = 100W/cm^2$) leads to a spatially modulated pretilt angle and the corresponding modulation of the phase retardation of the pump and test light beams. The spatial inhomogeneity of LC anchoring results in the formation of a strong nonlinear Gaussian lens in the LC bulk and the appearance of aberration rings in the far field zone. The characteristic rising and relaxation times of the lens formation and decay are of several minutes. To model theoretically the characteristics of the observed lenses we first minimized the total free energy functional subject to the time dependent anchoring. Having found the director spatial profile we studied the light beam propagation through the cell with a spatially modulated pretilt angle and anchoring energy. We determined the focal length and the number of aberration rings depending on the properties of the LC cells. We believe that the observed effect is promising and can be used in recording of dynamic holograms, light-controlled electro-optical devices and lasing.

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P- 4 ⇓

Aggregation and Phase Transitions in Nematic Liquid Crystal EBBA Doped with Carbon Nanotubes

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Electrical conductivity, optical transmittance and microstructure of multiwalled carbon nanotubes (MWCNTs) dispersed in nematic liquid crystal 4-ethoxy - benzylidene-4'-n-butylaniline (EBBA) were studied in the temperature range between 287 and 363 K. The concentration C of MWCNTs was varied within 0.01-1%. The percolation threshold with noticeable increase of electrical conductivity (by many orders of magnitude) was observed in the vicinity of $C \approx 0.1\%$. The heating - cooling hysteretic behaviour of electrical conductivity and optical transmittance thermal prehistory effects were studied. These effects reflected strong agglomeration and rearrangement of nanotubes during the thermal incubation. The estimates show that transient behaviour during the thermal incubation can be caused by Brownian motion of MWCNTs. The solidification of MWCNT + EBBA composite in the nematic range extended by conditions of supercooling was also studied as a function of temperature using electrical conductivity measurements. The solidification lag-time dependence on supercooling temperature followed the classical heterogeneous nucleation law, with MWCNTs serving as centres of EBBA solidification.

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Selective Reflection Features of Luminescent Substances in Cholesteric Solvents

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Selective reflection in cholesteric solvents was studied for a set of luminescent substances of different chemical structure. Unusually high solubility in cholesteric matrices with selective reflection peaks clearly recorded up to 10% concentration was noted for pyrene and o-POPOP. With pyrene, unusually large shift of the selective reflection band to longer wavelengths was noted, while introduction of o-POPOP, on the contrary, led to shorter helical pitch values, i.e., additional helical twisting. This behavior is interpreted in terms of molecular geometry factors and corresponding short-range interaction features between the dopant molecule and steroid ring of cholesterol esters. Other substances studied (stilbene, p-terphenyl) had much lower solubility, with concentration dependences of the selective reflection maximums close to theoretically expected. These results, together with luminescence data obtained in parallel, can indicate the ways of search for new efficient functional materials combining useful properties of luminescence and liquid crystalline phase state.

P- 6 ⇓

Theoretical Modelling of Tunable-Focus Liquid Crystal Lenses with Non-Plane Electrodes

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We study a tunable-focus lens with convex and flat tip electrodes in homogeneous liquid crystal (LC) cell. When a voltage is applied to the electrodes, a centro-symmetric gradient refractive index is generated within the LC layer, which causes the focusing behavior for the extraordinary wave. There has been the experimental studies of the systems with spherical and parabolic shape of the top electrodes [1,2] and there is a need in the theoretical modeling.

We present a theoretical model of the lens operation and analyze its properties. We solve the Maxwell equations that are coupled to the Euler Lagrange equations from the variational principle applied to the total free energy minimization. LC director spatial profile is found subject to the applied voltage. After that the phase retardation profile of the test light beam is calculated and thus a focal length dependence on the applied field. The model is in the good agreement with the experimental data. This LC lens has advantages of relatively large focal length range, low control voltage and good mechanical stability.

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Lateral and Longitudinal Aberration Modeling of Liquid Crystal Lens

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A gradient polymer stabilized liquid crystal (G-PSLC) structure has been proposed for a tunable-focus lens application [1]. The mixture of homogeneous planar oriented nematic liquid crystal (NLC) and few percent of photopolymerizable monomer are illuminated by a laser beam with Gaussian spatial intensity distribution. This exposition induces a spatially inhomogeneous polymer network in the cell. As a result, the electro-optical response of this system to a uniform electric field reveals an inhomogeneous, centrally symmetric character. Freedericksz transition threshold appears to be maximal in the centre of the illuminated spot and minimal in the nonilluminated regions. Thus it is possible to obtain a corresponding distribution of the NLC director in the cell and form a circularly symmetric distribution of the refractive index, with a maximum in the cell centre. Such cell represents a lens for the extraordinary polarized light. By applying the voltage one can vary the profile of the refractive index and so, the focal length of the lens.

In this presentation we further develop theoretical model [2] that describes the dependence of the G-PSLC lens focal length on applied voltage and present a theoretical study of lens aberrations. Using geometric optics [3] we find the optical path of a ray inside the nematic layer in the cell. According to Fermat's principle we minimize the optical path of a ray functional and calculate the ray angles output from the cell. Using these results lateral and longitudinal aberrations are estimated. Obtained results can be applied to develop G-PSLC lenses that have no moving parts and allow the electro-optical zooming.

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Deep Integration of Liquid Crystal Molecules and Carbon Nanotubes: Effect of Electro-Optic Memory

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Deep integration of liquid crystal (LC) molecules and micrometer-long carbon nanotubes (CNTs) may result in many unique properties. LC is an excellent host for CNTs and orientational order of LC can be transmitted to carbon CNTs. From the other side, the LC is strongly anchored to the CNT surface, so that aligned ensemble of CNT may induce alignment of LC. CNT dopant essentially changes performance of LC layers allowing to improve operational parameters of LC devices. The LC-CNT composites demonstrate improved electro-optic response with reduced driving voltage and switching time, suppressed parasitic effects like image sticking and back flow. These features make LC-CNT suspensions rather attractive for electro-optic LC applications.

A present work discusses electro-optic effects of liquid crystals with negative dielectric anisotropy doped with multiwalled CNTs (0.01-0.5 wt.%). EBBA (Reakhim, Russia), MLC6608 and MLC6609 (Merck) were used as LCs. The layers of LC-CNT suspensions were homeotropically aligned in a sandwich type LC cells. Observation of these samples between crossed polarizers revealed that in the field on state they switch to the random planar alignment, which remains after the field is off. The obtained memory state was stable in the temperature range of mesophase. However, it was possible to erase it thermally (by bringing sample to the crystalline or isotropic state and its subsequent return to mesophase), or mechanically (deformation of LC cells).

The mechanism of electro-optic memory is discussed. Electric field application caused homeotropic-to-planar reorientation of LC and resulted in development of electro-hydrodynamic flows (EHDF) in the LC phase. A breakdown of large initial CNT aggregates was facilitated by EHDF. This effect suggests unique method for in-situ dispergation of CNT in a LC medium. This dispergation results in a deep integration of CNTs in a LC host and formation of strong CNT network in the vicinity of the percolation threshold. The network formed may stabilize the planar state of LC which resist to homeotropic alignment force of the boundary layers.

The efficiency of electro-optic memory may further be increased by doping LC with a chiral dopant. A small amount of chiral dopant (0.1-0.2 wt.%) does not disturb homeotropic state of LC suspensions, but weakens homeotropic anchoring caused by the boundary layers of the cell. Thus, jointly with CNT network, a chiral dopant stabilizes the planar LC alignment, thus causing the memory effect. The observed effect allows us to suggest a new principle of information storage in LC media.

These studies were carried out within the frame of 10-07-H Project of NASU and "Dnipro" program of French-Ukrainian scientific collaboration.

P- 9 $\Downarrow$

Dielectric Spectra and Percolation Behavior of Liquid Crystal-Carbon Nanotubes Dispersions

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The dielectric spectra $\varepsilon''(f)$ and $\varepsilon'(f)$ of planarly aligned layers of nematic liquid crystal 5CB doped with multiwalled carbon nanotubes (CNT) are investigated in a wide range of frequencies ($f = 10^{-2} - 10^{6}$ Hz) and CNT concentrations (c=0-0.25 wt.%). It is shown that studied frequency range can be divided in three parts according to behavior of $\varepsilon'(f)$ and $\varepsilon''(f)$ curves. The low-frequency range ($10^{-2} < f < 10^{1}$ Hz) reflects the near-electrode processes in the cell. The ratio $\varepsilon''(f)/\varepsilon'(f)$ used to characterize these processes sharply grows if concentration of CNT exceeds 0.05 wt. %. The moderate frequency range ($10^{1} < f < 10^{5}$ Hz) corresponds to alternating current conductivity, σ_{AC}. At the nanotubes concentration less than 0.025 wt.%, σ_{AC} does not depend on the frequency that implies its ionic origin. In turn, at the $c \geq 0.025$ wt. %, σ_{AC} is a power function of the frequency that is typical for electronic hopping mechanism. The transition from the ionic to electronic conductivity can be explained by percolation theory with a critical concentration of nanotubes 0.03 wt.% and percolation parameter 2.5. The high-frequency range ($10^{5} < f < 10^{6}$) is mainly attributed to dipole volume polarization. For $c < 0.05$ wt.% such polarization is well described by Debye equation. The time of dielectric relaxation in this frequency range increases with nanotubes content. This is explained by effective interaction of nanotubes with LC molecules.

These studies were carried out within the frame of 10-07-H Project of NASU and "Dnipro" program of French-Ukrainian scientific collaboration.

5 NANOBJECTS

O- 1 ⇓

Features of Energy Transport in Luminescent Molecular Nanoclusters (J-aggregates)

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A rapid development of nanotechnologies observed today requires novel delivery systems which provide energy transport to the nanoscale reaction centers. Nature demonstrates us a prominent example of such delivery systems light harvesting complexes (LHC), which provide extremely fast and efficient energy transport of the absorbed light to the photochemical reaction center of plants and photosynthetic bacteria. Recently J-aggregates of amphiphilic cyanine dyes have been shown to be the most promising artificial system to mimic LHC. J-aggregates are luminescent well-ordered nanoensembles of non-covalently coupled luminophores. Due to high order degree of molecular packing in J-aggregates and strong dipoledipole interaction between molecules forming the J-aggregate, an electronic excitation is delocalized within a molecular chain, as in case of LHC, forming Frenkel excitons. That explains unique optical properties of J-aggregates: extremely narrow (for organic molecules) spectral width of the absorption band, resonant luminescent, giant oscillator strength, giant optical nonlinearities etc.

To study the mechanism of the exciton transport in amphi-PIC J-aggregates, special energy traps (organic dye molecules) were embedded into the J-aggregate chain. As an exciton trap, amphiphilic cyanine dye dioctadecyltetramethylindodicarbocyanine perchlorate (DiD) was used. To estimate the efficiency of the exciton migration to the trap, J-aggregate luminescence quenching by the trap was analyzed using the well-known modified SternVolmer equation. It has been shown that 50accessible for quenching is quenched at the ratio 1 trap molecule per 120 amphi-PIC monomer ones. It is large enough value for such type of nanoobjects. However, we can increase the efficiency of exciton migration in amphi-PIC J-aggregates by improving their structure via a formation of a surfactant shell around the aggregates. In such case 50at the ratio 1 trap molecule per 160 amphi-PIC monomer ones.

O- 2 ⇓

Multiply Resonances in Raman Spectra of C60 Fullerite, Davydov Splitting and Polymerization Mechanisms

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Molecular crystals and polymerized forms of C_{60} fullerites are subject of great interest due to their prominent properties that can be used in technological and scientific applications.Big size of $_{60}$ molecules and a number of normal vibrations lead to appearance of new regularities that are absent in the simple molecules and crystals. We have studied Raman scattering (r^{+} laser, 514,5 and 488 nm), infrared absorption and diffuse reflection forboth pure films of 60 (thickness 600, 1200 and 2000 nm, Si(100) substrate) and doped with Cu, In, Bi films of $_{60}$, and $_{60}$ films irradiated with electrons (doses D=1-25 MGy, Ee=1,8MeV). Crystal structure was studied by means of X-rays diffraction ($?_{Co}$ =1,7902 A). High excited states were controlled by photoluminescence (PHL) within spectral region of 1-2,2 eV. Analysys of resonance Raman scattering in the C_{60} fullerite was performed with taking into account of the stimulated resonance processes.

We report about existence of number of Fermi-Davydov resonances in which all observed and nonactive modes are involved. It is well-known that IR spectrum of C_{60} fullerite consists from 4 vibrations F_u(i) (i=1-4), Raman spectrum - from 10 vibrations (A_g(1,2) H_g(j), j=1-8). Lowering of the symmetry due to natural contain of isotopes ^{13}, molecular interaction, influence of crystal field leads to appearance of new vibrations, for example F_u(1,2), G_g(1) in Raman spectrums and $_g$(2) in IR spectrums. Vibration resonances $H_g(1)+H_g(2)=H_g(3)$; $H_g(1)+_g(1)=H_g(4)$; $2H_g(1)=F_u(1)$; $F_u(1)+F_u(2)=H_g(5)$; $H_g(3)+F_u(1)=H_g(6)$; $2H_g(3)=H_g(7),F_u(4)$; $2H_g(4)=H_g(8)$; $H_g(3)+H_g(4)=_g(2)$ are observed in whole region of low-frequent and high-frequent excitations. Respective nonlinear interactions $H_g(2)+H_g(4)=_g(1)+H_g(3)$; $H_g(1)+H_g(6)= H_g(2)+H_g(2)$ and other cause the energy redistribution between different states. Strengthening of low-frequent lattice vibrations ?lat=60-180 $^{-1}$ at doping of the C_{60} fullerite with Cu (2%) and shifting of bands to the high frequencies during increasing of the irradiation dose for case of the electron irradiation have allowed to determine resonance of the first overtone with low-frequency mode $H_g(1)$. Resonances with participation of ?lat appear in the region of high-frequency bands $H_g(5\text{-}8)$ and $_g(2)$. Therefore resonances of normal vibrations of C_{60} molecules are supplemented with many resonance interactions of the lattice and intramolecular vibration modes. This can be confirmed by nonmonotonic changes of majority of frequencies of C60 vibrations and intensities of maximums of peaks on XRD diffraction pattern at increase of irradiation dose.

We have studied fine structure of vibration bands that is associated with overlapping components of Davydov and isotopic splitting. It is shown that IR bands $F_u(1\text{-}4)$ and low-frequent bands $H_g(1)$, $_g(1)$ in Raman spectrum Davydov splitting at room temperature is more intensive than in the low temperature phase of the C_{60} fullerite. That points on amplification of intermolecular interaction due to appearance of nonequilibrium vibration excitation. We have determined correlation of intensity of Davydov splitting in molecular crystal $_{60}$ with splitting of vibration bands at polymerization of the fullerites. It is shown that shifting of C_{60} vibration frequencies at polymerization agree with vibration resonances.

All the observed regularities can be connected with nonlinear resonance interaction of thermally excited vibration modes and cascade excitation of higher vibration states. The latter are located near exciton and electron states that leads to amplification of vibration-electron interaction and change of the electron states. Delocalization of vibration modes in the crystals leads to spatial amplification of nonlinear interaction processes. The proposed nonlinear conception can be confirmed by the observed components of resonance differential frequencies, eg.,$H_g(1)=H_g(3)\text{-}H_g(2)$; $H_g(4)\text{-}_g(1)$. The idea of amplification of molecular interaction in strongly excited state of the substance can be confirmed by use of high-energy electron irradiation.

Transformation of electron states due to nonequilibrium vibration excitation of fullerite reveals in appearance of background in vibration spectrums and shoulder of excitant line in Raman spectrums and small-angle scattering on the XRD pattern. The intensive shoulder of excitant line in Raman spectrums has complicate structure and contains few exponential regions that characterizes the electron structure collectivization. Change of electron states reveals also in considerable change of the intensities of vibration bands and splitting of peaks of XRD pattern. Interaction of vibrationally excited molecules $_{60}$ and change of the electron states is accompanied by appearance of spatial heterogeneity of the fullerite that has regions with weak and tightly bonded molecules. Very important is correspondence of atomic-vibration and electron subsystems, thanksgiving to that a number of vibration resonances are observed and new types of chemical interactions are revealed due to vibration motion. New electron states can be also conditioned by absorbed water that has the most high-frequent vibrations.

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Frequency Tunable Sources of Light on the Base of Photonic Crystals

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Photonic crystals are new type of physical objects, revealing a number of unique physical properties. In this work the results of theoretical and experimental investigations of different types of three dimensional photonic crystals are presented.

Description of photonic crystals growth technology has been discussed. Such technology is based on artificial opal obtaining as a result of nanoglobule of amorphous quartz packing into face centered cubic lattice. The next step was thermal annealing of the samples at 500-600 C for ordering of the crystalline structure. Then different substances have been embedded into the artificial opal pores for modifying of the physical properties of photonic crystals. Artificial opal pores were filled by some liquids, aromatic substances, ferroelectrics, ferromagnetics, noble metals, and carbon structures. As a result we have obtained new hybrid materials as: dielectric-ferroelectric, dielectric-ferromagnetic and dielectric-metal. In the case of opal pores filling by high fusing temperature substances (ZrO_2 , carbon and metals as Au, Pt, Pd) additional annealing was made at high temperature (1200 C). The samples, annealed at high temperature became homogenous and transparent for visible radiation. Its structure was periodically placed quantum dots of high fusing temperature substance inside homogeneous quartz matrices and corresponds to new type of photonic crystal: so called quantite.

We have established that obtained photonic crystals may emit quasi-monochromatic radiation in different spectral regions in dependency with photonic band gap position. Such emission has revealed due to photonic crystal excitation by continuous source of visible light, ultraviolet emission or high frequency electromagnetic field excitation. The conditions of frequency tunable laser generation taking place from three dimensional photonic crystals have been analyzed.

Photonic Crystals in Nature and Science

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At the beginning of XXI century the attention of numerous physicists was attracted to new physical objects so called photonic crystals. The properties of electromagnetic waves and also visible light in photonic crystals seemed to be very different from the known properties of usual optical media. It was established that group wave velocity of electromagnetic emission at some frequency in photonic crystals may become very small; the refraction index may be negative and accordingly the refraction law is changed; photons, moving inside photonic crystal, become massive qausi-particles and its mass may be positive or negative and so on. Experiments and theory have shown, that in photonic crystals so called photonic band gap should exist. Inside photonic band gap the propagation of electromagnetic emission is forbidden. Accordingly in reflectance spectrum of photonic crystal is the region of strong light reflection, spectral position of which depends on the photonic crystal structure. Recently three dimensional photonic crystals have been obtained. One of the examples of three dimensional photonic crystals is artificial opal, known before in nature as precious stone. Important property of artificial opal is the presence inside of its structure free pores, size of which is several tens nanometers. Such pores may be filled by different substances quantum dots: liquids, organic and inorganic substances, biologic molecules, ferroelectrics, magnetic, metals and also superconductors. Now for us new opportunities have appeared for modifying of substance physical properties with the help of hybrid materials construction: dielectric-ferroelectric, dielectric - magnetic, dielectric-metal, dielectric- superconductor and others. Photonic crystals are also realized in living nature and in cosmos; such crystals are used in technique as new type mirrors and may be effective media for laser generation; new opportunities have appeared for quantum computers creation and for numerous other applications.

O- 5 ⇓

Magic Clusters of CdSe and ZnO: Synthesis, Structure, Spectroscopy

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Stable clusters sized between molecules and solid state attract much attention now from both fundamental science, as specific objects of unique structure and unusual properties, and from applied science, as perfect probes and promising building blocks for assembling of nanostructures. Among the variety of materials, clusters of semiconductors are of particular interest due to their size-dependent optical properties and implied novel applications in solar energy conversion, optoelectronics, photochemistry and photobiology.

CdSe and ZnO both are well known and deeply studied semiconductors. However, stable small clusters of these materials have been synthesized with atomic precision just recently [1, 2], and now they are a subject of extensive investigations. Namely, essentially different features on their time-of-flight mass spectra, obtained by pulsed laser ablation, stimulated us to perform computer simulations of their structure by quantum chemistry calculation methods. As a model, several cage-like structures have been considered, as well as fragments of the bulk wurtzite structure. Semiempirical (AM1, PM3), as well as first-principles (B3LYP functional for DFT on 6-31G and 3-21G basis sets) calculations confirm the enhanced stability of the clusters of suggested structures over the bulk fragments.

An investigation on the ways for CdSe magic clusters synthesis resulted in two wet chemistry methods of their production in mass quantities [1, 3]. Synthesized colloidal solutions of the clusters have been studied by spectroscopic (absorption, photoluminescence, Raman) and other (XRD, electron microscopy) methods. The results confirm predicted by calculations caged structure of the clusters. The achieved photoluminescence quantum yield (about 30% of Rhodamine 560) is high enough to inspire work on applications of the magic clusters.

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O- 6 ⇓

Ways of Formation and Spatial Stabilization of Ag Clusters and Nanostructures in Mesoporous Titania Thin Film

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It is believed that an ordered, continuous network of porous titania would improve the efficiency for many useful application e.g. as the semiconductor component of the Gratzel photovoltaic cell. A standard application of TiO2 has been as a photocatalyst for decomposition of organic molecules. Immobilization of titania on a rigid support as a thin film can avoid many drawback for photoreactor. Variety of attempts has been made to introduce various metal species into the TiO2 matrix in an effort to enhance the photocatalytic activity and/or broaden the absorption of the solar spectrum by the doped TiO2. Methods that have been used include ion exchange, impregnation and co-precipitation have used for preparing doped TiO2.The ideal morphology of titania would 1) maximize the internal surface area, (titania accepts electrons), and 2) have surfaces spaced every 20 nm or less (pore diameter), such that excitons may diffuse to a surface before recombining. A method for creating such morphology has been developed using block-copolymers as a structure directing agent in a sol-gel spin-coating process. The purpose of this investigation was to determine the best condition for formation titania coating with incorporating silver for inhibition the recombination carriers and improving of photocatalytical efficiency. Different ways for Ag nanoparticles stabilization was examined. Composite titania mesoporous films with spatially determined and stabilized Ag nanostructures were prepared. Green synthesis approaches for preparation of silver nanoparticle and nanostructures organization were realized by assembled in the mesoporous TiO2 network films. Analyses of these systems were based on XRD, AFM, FTIR, and elipsometry porosimetry data. The confinement effect of mesoporous TiO2 network of hexagonal pore configuration towards Ag nanostructures was demonstrated by the enhanced thermostability and photoactivity. The method of stabilization of the nanostructures in matrixes accompanied shifted and broadened of the plasmon absorption peak due to interaction with host matrixes proposed. Received composites have favorable electronic and photocatalytical properties.

O- 7 ⇓

Exciton Dephasing in Single-Walled Carbon Nanotubes

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Results obtained by means of three-pulse-photon echo obtained on semiconducting single-walled carbon nanotubes embedded in polymer matrix at room temperature will be presented and discussed. The results demonstrate a striking dependence of the peak shift on the excitation intensity. The theoretical model based on a interacting boson model and subsequent numerical simulations demonstrate that the intensity dependence originates from a highly nonlinear optical response initiated by exciton-exciton annihilation.

Synthesis, Structure and Optical Properties of Nanoomposite *CdMnS* nanoparticles / polyvinyl alcohol

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Polymer-nanoparticle composites have been increasingly studied because of their enhanced optical and electronic properties. Composites containing semiconductor nanocrystals are promising for applications in optoelectronics as the materials for light-emitting devices. Also, this research is motivated by fundamental interest in nanoparticles interactions with different matrixes.

We studied the nanoparticles that were prepared by chemical routes. The colloidal access to nanoparticles is achieved by carrying out a precipitation reaction in a homogenous solution in the presence of stabilizers, whose role is to prevent agglomeration and further growth. Colloidal methods have not yet excelled at preparing doped nanocrystals, but recent advances portend an exciting future for this area.

CdMnS nanoparticles were synthesized in aqueous solution using cadmium chloride ($CdCl_2$), sodium sulfide (Na_2S) and manganese chloride ($MnCl_2$) as starting materials. Polyvinyl alcohol was used as a capping reagent. All steps of the synthesis were performed at room temperature under ambient conditions. In order to keep the system in the focusing regime (the formation of nearly monodisperse nanocrystals) for a long time, it is possible to perform additional slow injections of precursors during the growth, effectively keeping the concentration of free species in a solution above a critical threshold. Thus obtained nanocomposites - semiconductor nanoparticles/polymer matrix - were characterized by , SEM and optical methods.

The EM studies of the material synthesized demonstrated the presence of nanoparticles with the average size less than 10 nm. The SEM studies of the material synthesized demonstrated the structure of the matrix that influences the embedded particles.

Optical spectra revealed band gap change due to quantum size effect and composite. Photoluminescence studies showed that the nanocrystals embedded in polyvinyl alcohol give bright emission in the visible range. Three photoluminescence bands were attributed to the residual photoluminescence of the polyvinyl alcohol matrix, the near band edge luminescence of CdS and the emission corresponding to the surface traps in CdS. Doping with manganese contributed to the emission in the spectral range of surface traps. It is also shown that the polymer matrix participates in the excitation of nanocrystals.

O- 9 ⇓

Spontaneous Parametric Light Scattering in Spatially-Nonuniform Materials Based on Globular Photonic Crystals

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A great interest in studying globular photonic crystals based on synthetic opals is caused by presence of forbidden gaps in their photonic band structure [1-3]. Optical properties of these materials may be easily modified by infiltrating them with different substances. An origin of secondary emission of such synthetic opals is now discussed being explained in terms of parametric scattering [4] or impurity luminescence [5]. The aim of present work is to clear up the origin of emission of synthetic opals infiltrated with nonlinear optical materials. Measurements were performed on samples of synthetic opals grown by us. The photonic stop-band position was determined from Bragg reflection and transmission spectra. An infiltration with $Ba(N0_3)_2$ and $LiIO_3$ was made by soaking samples into a water solution of subsances with a following high-temperature annealing at temperatures lower than melting ones (595^oC and 120^oC respectively). Secondary emission of samples was excited by LED Edixeon EDST-3LAx at 400 nm. The exciting radiation frequency was in the range of upper photonic dispersive branch at significant distance from the band edge. Spectra were measured in the forward scattering geometry. In all spectra a wide structured continuum in the range of 425 nm - 640 nm was observed as before annealing as after one. According to [5], the main criterion of its origin is the spectral position and intensity after annealing. In case of impurity luminescence due to the structural OH group defects this continuum is disappeared as water is evaporated. In our case it is shifted to blue side becoming more than 20 times intensive. Thus, the origin of this band may be explained by spontaneous parametric scattering (SPS) in spatially-nonuniform samples with regular structure. Observed SPS spectral distribution is due to the overlapping of bands shifted relative to that in uniform medium in correspondence with the quasi-synchronism condition with regard for the reciprocal lattice vector and an interference of bands [6]. SPS is most probably observed in the range of the maximums of photon density of states which correspond to the stop-band edges in photonic crystals. A change of SPS spectral position and intensity after annealing is due to the shift of a stop-band position and the disappearance of the OH group luminescence.

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Surface Enhanced Raman Scattering in Synthetic Opals Infiltrated with Salts of Metals

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Optical phenomena in structures with space modulation of dielectric constant with period close to the wavelength of light are of a great interest now because of the presence of forbidden gaps in their photonic band structure (photonic crystals) [1-3]. Synthetic opals constrained from silica globules serve as a good prototypes for 3D photonic crystals. By infiltrating them with dielectrics the study of surface enhanced Raman scattering phenomena becomes quite urgent [4].

The aim of present work is to clear up the nature of emission of bare opals and opals infiltrated with salts of metals in the vicinity of the exciting line within a Raman scattering spectral region.

Measurements were performed on samples of synthetic opals grown by us. The photonic stop-band position was determined from transmission spectra. An infiltration with salts of metals ($CuCl_2$, $Ba(N0_3)_2$, $CdSO_4$ and LiOH) was made by soaking samples into a water solution of corresponding substances with a following high-temperature annealing at temperatures lower than melting ones. Secondary emission of samples was excited by LED Edixeon EDST-3LAx at 400 nm. The exciting radiation was in the range of upper photonic dispersive branch at significant distance from the band edge. Spectra were measured in the forward and back scattering geometries with the use of modernized spectrometer DFS-12. They were detected within an aperture of ¡0.17π sr in the ¡111¿ direction. Registration of a useful signal was carried out in a regime of the photon counting with accumulation.

For all emission spectra of bare opals there was an intensive band whose spectral position was independent of the stop-band position and previous technology conditions. It is situated in the vicinity of the excitation line and corresponds to the vibrational spectrum range. The spectral intensity distribution in infiltrated opals was quite dependent from kind of substance. This intensive band is most probably due to the surface enhanced

Raman scattering in amorphous substances which compose samples under study. It results in appearance of scattered radiation whose spectrum is determined by the density of phonon states of corresponding substances. Such process becomes possible to be detected owing to the essential increase of the radiation field caused by the slow diffuse motion of incident photons into sample volume and as a result of surface enhanced conditions inside of opal pores.

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Experimental Determination of Local Field Enhancement Factor at the Surface of Metal Nanoparticles

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New method of experimental determination of local field enhancement at metal nanoparticles is suggested [1]. It uses surface plasmon as a probe. In the present report we investigate spectral characteristics of surface plasmon resonance, namely, its position, intensity, and halfwidth. We report observation of alternating-sign shift of surface plasmon resonance frequency under laser irradiation. It is a manifestation of two phenomena with different influence on surface plasmon and with different kinetics. The faster one observed during the action of pump pulse can be attributed to laser-induced changes in dielectric constant of studied composite medium. In previous studies performed at lower pump intensities the influence of dielectric matrix was a priori considered negligible. Simple estimates show that even at the higher intensities of the order of 10^{11} W/cm^2 used in the present paper changes of optical constants of silica and consequent their influence on characteristics of surface plasmon have to be almost undetectable. However, these phenomena became so prominent due to surface enhancement of local electric field well-known from surface enhanced Raman scattering (SERS) and surface enhanced infrared absorption (SEIRA). Comparison of the expected and observed changes of the frequency of surface plasmon allowed us to suggest an alternative method of experimental determination of field enhancement factor at the surface of metal nanoparticles, which is important for better understanding of enhancement mechanisms in SERS and SEIRA.

The samples containing spherical copper nanoparticles with $d = 35 - 60$ nm and narrow size distribution in pure silica matrix have been prepared by modified sol-gel method [2]. High optical quality of the samples and high stability of silica allowed us to conduct measurements at higher intensities of pump beam compared to other studies [3]. Pump-probe measurements have been performed with a Coherent femtosecond laser system consisting of a Mira-900F oscillator and a Legend HE amplifier. Output pulse energy was 2.5 mJ at 1 kHz repetition rate, pulse duration estimated from autocorrelation function was approximately 130 fs. Probe "white light" was generated in a sapphire plate. We used part of the amplifier output at 780-800 nm or its second harmonic (390-400 nm) generated in BBO crystal as a pump beam. Measurements were performed at room temperature.

Characteristic feature of absorption spectrum of copper nanoparticles is a peak of surface plasmon at 2.175 eV (for $d = 47\ nm$ particles). Under the intense pump it decreases in amplitude and broadens. More details can be obtained from analysis of the shape of plasmon peak and its evolution during and after the pump pulse. In the case of copper, the spectral position of surface plasmon is close to an onset of band-to-band transitions. Absorption background caused by band-to-band transitions changes its shape under intense pump. To separate plasmon peak from the background we have performed multi-peak analysis. At first, the red shift of plasmon is observed in almost any case of first or second harmonic excitation. It is observed for very short time approximately equal to the pump pulse duration. After the end of the pump pulse the plasmon peak shifts to the blue side and then gradually relaxes to its original position with a time constant of 0.5 ps. We can explain the plasmon red shift observed during the pump pulse by decrease of resonance frequency of surface plasmon $\Omega_{SP} = \frac{\omega_p}{\sqrt{\epsilon_1(\Omega_{SP})+2\epsilon_m}}$, where ω_p is plasma frequency of bulk copper, $\epsilon_1(\Omega_{SP})$ is a contribution of bound electrons to dielectric constant of copper. Plasmon frequency decreases as a result of optical Kerr effect, which causes increase of dielectric constant of silica matrix surrounding nanoparticle $\epsilon_m = n_m^2 = (n_0 + n_2 I_1)^2$, where $I_1 = \frac{cE_1^2}{8\pi}$ is intensity of the pump beam, n_0 is refraction index of silica for low-intensity light. Validity of presented above supposition about the origin of the plasmon red shift is supported by its instantaneous character. Obviously, after the end of pump pulse when the influence of the optical Kerr effect disappears, the dielectric constant relaxes to its original value, that causes back shift of plasmon resonance frequency at 0.25 ps. In this case, from the value of the red shift of plasmon band we can calculate a necessary value of electric field, which causes the shift. Comparing it with the electric field of the femtosecond pump pulse we can determine the enhancement factor G, because due to small value of Kerr constant quantitative agreement cannot be obtained without taking into account field enhancement effect. In the vicinity of nanoparticle electric field of incident light is enhanced with factor $G = \frac{E_1}{E_0}$, where E_0 and E_1 is the electric field of incident electro-magnetic wave in silica far from nanoparticles and electric field in the vicinity of copper nanoparticle, respectively. Estimates performed with $\hbar\Delta\Omega_{SP} = 0.019\ eV$ observed in our experiments at $I_0 = 4.46 \times 10^{11} W/cm^2$, $n_0 = 1.45$, and $n_2 = 2.48 \times 10^{-16}\ cm^2/W$ [4] give $G \approx 20$ for copper nanoparticles with average size $d = 47\ nm$.

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O- 12 ⇓

Influence of Structure Transformation on Optical and Electronic Properties of Cobalt

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For the purpose of studying of influence of immediate environment on electronic properties optical properties of cobalt in different structural conditions : crystal massive, crystal film, amorphous and liquid have been studied. Besides spectra interband conductivity $\tilde{\sigma}\,(h\nu)$ of cobalt in the specified structural conditions on the basis of theoretical data about density of electronic state been calculated. Optical properties of cobalt are investigated at a room temperature on the massive and film samples by thickness 40 μm received by a method magnetron sputtering on cooled liquid helium leucosapphire's substrate. Owing to the big speed of cooling (˜10^5 /) was persistent amorphous structure of films, in due course they were transfered to a crystal condition. Cobalt mirror surface in a spectral interval 0,25-17,0 μm (0,07-4,96 eV) by methods of spectral ellipsometry were investigated, using Beatty's method. On experiment near the main angle of sight was measured ellipsometric parametres D and y and on their basis optical constants n and c, permittivity $\varepsilon^2 = n^2 - \chi^2$, optical conductivity $\sigma = 4\varepsilon_0 \pi \nu n \kappa.$, ($v$ - frequency of light) and reflexion factor paid off atnormalangleofsightonsample$R = \frac{((n-1)^2+\chi^2)}{((n+1)^2+\chi^2)}$. The analysis of dependences of optical characteristic from of energy of photons h in an interval h = 0,07-4,96 eV has allowed to receive the information on electronic structure of investigated systems. On a curve $\sigma\,(h\nu)$ amorphous Co it is revealed three prominent features: a wide maximum at 0,77 eV and less intensive two narrow maxima at 0,38 and 0,16 eV while for crystal Co in this area of a spectrum it is observed only two maxima: the basic - at 0,88 eV and additional - at 0,18 eV. Besides, at transition to a crystal condition the peak of the basic band is displaced on 0,11 eV almost coincides with a maximum Co in a liquid condition. However at energy h $\langle$*0,6 eV* absorption starts to increase in a liquid condition monotonously. Let's specify, that the most intensive band of absorption which responsible interbands to transitions, practically does not change the position on a energy scale in crystal samples: massive and film Co. It testifies to a dominating role of a near environment on formation of power conditions which are responsible for interbands absorption. Having compared curves for cobalt films in a crystal condition with results for the massive sample, it has been established, that in massive Co the double structure of the basic strip of absorption which is located in a vicinity 1 eV is shown, and the long-wave maximum disappears at 0,18 eV. Instead of it in massive Co the excess of curve $\sigma\,(h\nu)$ which, in our opinion, is caused by imposing of a long-wave band of absorption with the basic which intensity the higher is observed. Besides, in this area of a spectrum insidebands transitions become more intensive, than interbands. Caused by exchange interaction of splitting of the basic band of absorption of massive cobalt in the field of 1 eV in film systems it is not shown. Displacement of the basic maxima for a crystal condition concerning amorphous (approximately on 0,11 eV) in high - energetic area of a spectrum and increase in semiwidth of the basic maxima on curves *s (hn)* is connected with zones broadening as a result of structural transformations. It is shown, in an electronic spectrum Co the new energetic zone which is located on 0,38 eV more low Fermi level E_F which is connected with defects of structure is formed. It is established, that at structural transformations from amorphous in crystal conditions, character immediate environment essentially does not change, though occurrence of a structural order leads to broadening energetic bands of metal and their displacement in area high energy photons. Structural transformations lead to reorganisation electronic to a cobalt spectrum, and, occurrence of an additional band of absorption in a long-wave site of a spectrum specifies that essential changes in an electronic spectrum occur near Fermi's level.

Spectroscopic Investigations of Nanohydroxyapatite Powders

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In the biological system, apatites are of great interest as an integral constituents of vertebrate hard tissues like bone, teeth. In the form of carbonated hydroxyapatite they provide stability and hardness to these skeletal tissues. All normal hard tissues of humans are apatitic. Furthermore, hard tissues that form in pathological calcification are also apatitic. The biogenic minerals in these hard tissues are formed through a process called biomineralization and these minerals are usually termed as biominerals.

Relevant aspects of the functional behaviour of the calcium phosphate particles in their working medium (ion exchange with the body fluids, dissolution/re-precipitation during the remodeling/readsorption in the host tissue) depend significantly on their structural (bulk) order but whether there is an effect of the surface order at atomic level on the chemical properties of the calcium phosphates and their interaction properties with water is unknown.

In this respect, we compared two nano-hydroxyapatites (HA) with very similar surface area, bulk carbonate content, constituted of particles about 10x30x60 nm^3 in size, crystalline in their bulk, but exhibiting, as shown by high resolution transmission electron microscopy (HR-TEM) analysis, different surface structures. In the first material, HA-x, the bulk order extends up to the surface of the materials, that, although stepped and irregular, are actually resulting from the interruption of a HA crystal. Conversely, the second material considered, HA-a, exhibits a surface amorphous layer about 1-2 nm thick, so that the only difference between the two materials is actually in their surface structure. By using IR spectroscopy of adsorbed H_2O, D_2O, CO and CO_2, used as probe molecules, we described the nature and the properties of surface species. H_2O/D_2O isotopic exchange indicated that both materials exhibit a low amount (⟨10% of surface sites) of surface hydroxyls, slightly more abundant in the case of HA-a, as expected for a non stoichiometric surface. Both the surface Lewis acidity, monitored by CO adsorption on Ca^{2+} sites, and surface basicity, monitored by the formation of surface carbonates as a result of the interaction with CO_2, resulted more marked for HA-x. These differences, likely arising also by a different arrangement of the reciprocal positions of surface sites, has a significant effect on the structure of the surface water ad-layers: while, in the case of HA-x, from the third layer of H_2O adsorbed on the surface, the structure of water is comparable with the one of bulk liquid water, for HA-a a H-bond network significantly stronger than in liquid water is observed up to the fourth water layer. Finally, the crystalline surfaces showed a less pronounced modification of the interaction properties with water as a consequence of thermal treatments.

Europium Oxide Nanoparticles as Fluorescent Probes for DNA

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The integration of nanotechnology with biology and medicine is expected to produce major advances in molecular diagnostics, molecular biology and bioengineering.

In this work, we describe an original chemical approach for the quantitative synthesis of colloidal solutions of europium oxide nanoparticles. The study of the structure and optical properties of these materials is not only of fundamental interest, but also of technological importance for the development of advanced phosphors for different applications, for example, fluorescent probes for cell biology.

The synthesis method is based on a direct rare-earth oxide precipitation in high boiling alcohol (diethylene glycol). The nanoparticles synthesized by this method are homogeneously dispersed and distributed within a very narrow range of sub-20nm sizes. The synthesize nanoparticles of europium oxide were tested with biological objects: bovine serum albumin, dextrane, polyvinyl alcohol (such plasma substitute), DNA and RNA.The materials obtained have been characterized by high-resolution TEM and luminescence microscopy.

P- 3 ⇓

Analysis of Interaction Colloid Nanocrystalls $GdVO_4$:Eu^{3+} with Cellular Components and Isolated Cells

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The nanoprobes are widely used in the biomedical investigation in order to solve a great variety of problems from the surface and intracellular proteins labeling up to a genetic analysis and observation of cellular processes dynamics. The main requirements imposed upon them are their biocompatitibility, ability to be dissolved in water and low toxicity.

In the present study, the $GdVO_4$:Eu^{3+} - based aqueous colloidal solute nanoparticles having a negative surface charge and average diameter of 3. 20 and 120 nm have been used as the nanoprobes. Their interactions with bimolecules as well as the peculiarities of their accumulation by cells and isolated cellular organelles have been estimated. For this purpose the aqueous 0.1dextran 70000, bovine serum albumin were used. The concentration of the nanoparticles in the incubation solution was about 0.4 mg ml-1. Isolated rat hepatocytes nuclei and cells (5x105 cell/ml in dimension) together with the nanoparticles were incubated in the 5in nuclei and cells was observed by a microscope Olympus IX71 (X 100 objectives) on excitation by a xenon lamp of 75 W over range 460-490 nm with an emission wavelength of 500 and more. The character of nanoparticles - biomolecules interaction was found to depend on the peculiarities of molecular structure and surface properties of the nanoparticles. In the absence of Mg^{2+} ions the aggregation of the particles in the solution of biomolecules studied was expressed weakly. However, addition of Mg^{2+} ions resulted in both adhesion nanoparticles to nucleic acid and appearance amorphous areas clusters and threats in the visible range. This fact is a indicative of the aggregation of nanoparticles on the nucleic acids which are in the state close to a native form. In the isolated hepatocytes nuclei, the accumulation of nanoprobes accompanied by increased red luminescence was observed that correspond to EU emission line. Thus, the magnesium DNA and RNA complexes have been predominantly painted by the nanoparticles as well as the nucleic acidrich nuclei in the native form. The particle size had a significant effect on their accumulation by the cells. The particles of 120 nm in diameter clustered along the cell periphery whereas on application of the particles of fewer diameters (20 nm and less) the intracellular accumulation most likely by endocytosis mechanism, has been noted, followed by their accumulation in nuclei. The results obtained demonstrated opportunities for an application of the nanoparticles as luminescent nanoprobes in biomolecules and cells as a whole in the biomedical investigations.

Size Dependent Surface Plasmon Enhanced Photoluminescence From Silver Nanoparticles

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We report the strong photoluminescence from the spherical silver nanoparticles with sizes of 8 - 30 nm incorporated in silica matrix. Two bands were observed in PL spectra of Ag nanoparticles. The high energy band was observed only in the samples with smallest 8 and 11 nm Ag nanoparticles. It was attributed to the radiative recombination of the electrons in sp conduction band of silver with holes in d valence band. The low energy band was observed in all the samples with the nanoparticles of sizes of 8 30 nm. The intensity of PL spectrum was found to increase with decrease of nanoparticle size. The quantum yield of the photoluminescence was measured. It was found to be maximum in smallest 8 nm Ag nanoparticles, namely about 10^{-2} that is in 10^{8} times higher than in bulk silver. We performed the calculation of the theoretical photoluminescence spectra of Ag nanoparticles with various sizes working in the frame of the model1 of the local field enhancement by surface plasmons in Ag nanoparticles. The calculations is in good agreement with the experimental results that proves that the strong size dependent enhancement of the luminescence from Ag nanoparticles is the results of the enhancement of the electric fields of exciting and outgoing photons due to coupling of photons to surface plasmon resonance in Ag nanoparticle.

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Influence of Interparticle Interaction on Melting of Gold Nanoparticles in Au/PtFe Nanocomposites

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We studied the temperature behaviour of the absorption spectra of Au/PTFE nanocomposites with various filling factors at 77-936 K. The obtained temperature dependences of surface plasmon energy and bandwidth in gold nanoparticles with size of 5 nm proves the aggregation of nanoparticles due to thermal softening of polymer matrix and consequent melting of nanoparticles with formation of isolated large (about 25 nm) nanoparticles. The melting of gold nanoparticles occurs at temperatures considerably lower than the melting point of bulk gold. The interaction between the gold nanoparticles significantly affects the melting of the nanoparticles. When the filling factor increases the melting point of gold nanoparticles decreases and the spectral signature of their melting become stronger.

P- 6 ⇓

Spectroscopic Characterization of II-VI Semiconductor Nanocrystals in a Glass Matrix

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Diffusion-limited growth is a well-known technique to produce ternary II-VI semiconductor nanocrystals in a glass matrix. Their electronic spectrum, determining the optical properties, can be effectively varied by the nanoparticle size and chemical composition. Spectroscopic techniques, used to determine the main parameters of the nanocrystals, can be complementary and often competitive to transmission electron microscopy and X-ray diffraction-based techniques.

Here we report on obtaining and spectroscopic characterization of ternary ($CdS_{1-x}Se_x$ and $CdSe_{1-x}Te_x$) and quaternary ($CdS_{1-x-y}Se_xTe_y$) nanocrystals grown in a borosilicate glass using heat treatments at 600 to 700° C. Optical absorption spectra of the obtained samples, measured with a LOMO MDR-23 monochromator at room temperature, enabled the average nanocrystal size to be derived from the spectral position of the confinement-related exciton absorption peaks. Resonant Raman spectra measured at room temperature using a Dilor XY 800 monochromator as well as Ar^+ and Kr^+ lasers were used for the determination of the nanocrystal composition.

For two-mode $CdS_{1-x}Se_x$ and $CdSe_{1-x}Te_x$ ternary systems the nanocrystal composition was determined from the corresponding LO phonon frequency difference, taking into account the effects of the glass matrix pressure, confinement-related relaxation of the selection rules as well as surface phonon scattering. The composition of the obtained $CdS_{1-x}Se_x$ nanocrystals is shown to depend on the heat treatment parameters: the content of the predominant chalcogen (S or Se) increases with the heat treatment duration and temperature.

The measured Raman spectra clearly confirm the formation of quaternary $CdS_{1-x-y}Se_xTe_y$ nanocrystals in a glass matrix which are characterized by a three-mode behaviour of the phonon spectrum. The frequencies and intensities of the CdS-like, CdSe-like, and CdTe-like LO phonon bands in the spectra correspond to the related component content.

P- 7 ⇓

Conformational Transitions iIn Nucleic Acids Located on Carbon Nanotubes

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Functionalization of single-walled carbon nanotubes (SWNTs) by biopolymers opens ways for designing nanodevices in which the unique physical properties of nanotubes combine perfectly with recognizing abilities of biological molecules. To solve successfully fundamental and practical tasks connected with the formation of the nucleic acid (NA)-carbon nanotube complex, it is important to be informed in the structure of NA being the main functional element of the complex.

In this study SWNT functionalization was performed by single- and double-stranded deoxy- and ribonucleic acids in aqueous salt buffer solutions. Heating-induced transitions from the ordered helix to the disordered coil as well as converse processes - hybridization of single-stranded complementary nucleic acids with formation of double-stranded structures were studied by UV-spectroscopy methods and computer simulation. The results obtained are compared with data for free solution polymers.

It is shown that, upon adsorption of single-stranded molecules on SWNT, intensities of main transitions in bases are re-distributed due to π-stacking interactions with carbon hexagonal cells of nanotubes. As well, it was revealed that the helical structure of the polymer and interplane interactions of its heterocyclic bases disrupt significantly during adhesion on the SWNT surface.

At adsorption of double-stranded DNA and RNA on the nanotube, thermostabilization of the polymer structure was observed, resulted from the decrease of the effective density of charges of the sugar-phosphate backbone. As well, losses in entropy because of limitation of freedom degrees of the polymer backbone at adsorption on SWNTs contributed to the stabilization.

The process of the double helix formation (hybridization) on the nanotube when one of the polymers is bound with the nanotube surface and the complementary polymer is in solution was studied. It is shown that, in comparison with quick hybridization kinetics of free poly(rA)-poly(rU) (the double helix is created for tens of minutes), the process of the double-stranded molecule formation on SWNT lasts tens of hours at 20°C. Double-stranded poly(rA)-poly(rU) formed on the nanotube by hybridization are of lower thermal stability than that for molecules without nanotubes. Computer simulation revealed that destabilization may result from the imperfection in the structure formed as the significant part of bases is unable to form regular Watson-Crick pairs because of interactions with the carbon surface.

P- 8 ⇓

Interface Interactions in Benzophenone Doped by Multiwalled Carbon Nanotubes

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The interface interactions were studied by methods of conductometry, low-temperature phosphorescence and differential scanning calorimetry (DSC) in multi-walled carbon nanotubes (MWCNT) and benzophenone (BP) composite. The concentration of MWCNTs was varied within 0-1% wt. A percolative threshold was found at MWCNT concentrations exceeding 0.1 % wt. The integration of MWCNTs caused melting temperature increase (3K for 1% wt of MWCNTs). The effect of positive thermal resistively coefficient, as well as substantial hysteretic behaviour of electrical conductivity in a heating-cooling cycle, was observed near the melting point of BP (T_m= 321.5 K). The activation-type temperature behaviour of electrical conductivity was observed in the temperature range of supercooled BP. The activation energy was decreasing with increase of MWCNT concentration. The observed nonlinear dependencies of electrical conductivity versus applied voltage U reflect the transport mechanism of the charge carriers through amorphous interface films formed near the surface of the MWCNTs. The thermal shifts of phosphorescence spectra measured within the temperature range of 5-200 K evidence existence of such interface films of amorphous BP with width of the order of 0.1 μ m.

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Optical Studies of A_2B_6 Semiconductor Nanowires

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In this paper we studied the spectra of resonance Raman scattering at room temperature in the structures with nanowire ZnSe; ZnTe; ZnMTe; ZnSe / CdSe (each wire is an alternating segments ZnSe and CdSe); in film ZnSe; in crystal ZnTe. Samples ZnSe; ZnTe; ZnMTe represent a quantum filament with a diameter of 10 - 30 nm, grown by molecular beam epitaxy at substrate GaAs, catalyst - Au. Spectra of ZnSe were measured in samples with varying thickness of the film Au (2, 10 and 100 A, film thickness determines the diameter of Au nanowire). ZnMnTe spectra were measured for different concentrations of Mn. Raman spectra were recorded on a u-1000 spectrometer in backscattering geometry. The source of laser radiation used He-Cd, ar and Ar-Kr laser. In the spectra of structures with nanowire ZnSe (film thickness of au 2 and 10A) and ZnTe, observed boundary of luminescence peak shift towards higher energy. We assume that this shift is due to increase in the effective width of the band gap, due to effects of size quantization. We estimated nanowire radius based on the magnitude of this shift. It is concurring in order of magnitude with the data of electron microscopy. Spectra of samples with thickness of Au, equal to 100A, are identical to the spectra of the ZnSe film. This is probably due to the fact that nanowire in this sample is covered by ZnSe film. This fact is confirmed by measuring the infrared reflection coefficient. One can see visible peaks corresponding to lo and to phonons GaAs, lo phonons ZnSe, and mode at a frequency of 248 cm^{-1} on the spectrum of resonance Raman scattering in nanowire ZnSe / CdSe. Perhaps this is vibration mode in the ZnCdSe alloy, which demonstrates the mutual diffusion of components. Spectra of ZnMnTe alloy nanowire is characterized by double mode behavior. The L_o-phonon repetition can also be observed. By comparing the spectra for ZnSe nanowire and films, one can see change in the intensity of L_o phonon-repetition (maximum intensity in the film are $4L_o$, while in the one-dimensional sample - at 1 and $2L_o$).

Presumably, these differences are related features of hot luminescence in quantum-dimensional structures.

P- 10 ⇓

The pH effect on spectral characteristics of single-walled carbon nanotubes in aqueous solutions

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Single-walled carbon nanotubes (SWNTs) are new type molecular nanowires. They have got unique physical and chemical properties and wide prospect of using in nanotechnology. SWNTs can be used as the basis new bio/chemical sensors thanks to their chemical inactivity. Depending on their diameter and chirality, SWNT possess metal or semiconductor properties. Peaks of the electronic density of states van Hove singularities, between which transitions occur when a photon is absorbed or emitted, are present in the valence and conduction bands of semiconductor nanotubes. Luminescence of semiconductor nanotubes is observed in the near-IR range of the spectrum.

The bulk synthesis processes yield SWNTs in the bundled form with large intertube van der Waals attraction. Under ordinary conditions, nanotubes form bundles because of the strong van der Waals interaction between individual nanotubes. In bundles, nanotubes with metallic conductivity quench luminescence of semiconductor SWNT. The bundles can be separated in a water medium by means of ultrasonic dispersion in the presence of a surfactant or watersoluble polymers. This molecules absorbs onto the SWNT prevents the nanotubes from re-aggregating into plaits after the ultrasonic treatment has been completed. Luminescence of nanotubes in a water suspension is very strongly influenced by the external environment, variations of the surfactant or polymer type as well as properties of the solution itself (pH, ionic strength, and so on).

Herein, we report our work on studying the pH effect on spectral characteristics of SWNT in aqueous solutions with surfactants (sodium dodecyl sulphate and sodium dodecylbenzenesulfonate) or polymer (DNA) in 0.85-1.45 eV range of the spectrum. pH has varied in 3-11 range. The luminescence spectrum of SWNT consists of a series of peaks due to the emission from nanotubes of different chirality and diameters. The intensity of spectral bands rises as pH of SWNT solution with surfactant or polymer increase. Therefore, it can be stipulated by (1) decreasing interaction of adsorbates with the nanotube surface because of their deprotonation and hydrophily increase and/or (2) structural changes of absorbates [1]. The intensity of the spectral bands lowers as pH of SWNT solution with a surfactant or polymer decreases. It can be stipulate by the increase of protonation of carbon nanotube and adsorbates [2]. We have discussed various models pH effect on complexes of nanotubes with polymers and surfactants.

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The Mechanism of Magnetic Anisotropy Temperature Dependence Formation in Co/Cu (111) Superlattices

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The temperature dependence of ferromagnetic resonance (FMR) spectra of superlattices Co/Cu was studied for establishing of forming of magnetic anisotropy mechanism. We have investigated the series of samples $[\mathrm{Co/Cu(111)}]_{20}$ with fixed thickness of ferromagnetic cobalt layers $\mathrm{d}_{Co} =$ 8 Å , while the thickness of nonmagnetic copper interlayers valid from 7 to 22 Å with step 1-2 Å . The samples were obtained on mica by magnetron sputtering. The measurements of FMR spectra were performed with a JEOL-XK spectrometer in 3-cm wavelength range in temperature interval from 230 to 350 K. From the values of resonance field quantitative determinations of effective anisotropy constant K_{eff} have been made. The temperature dependence of effective anisotropy constant K_{eff} is close to linear behavior for all samples of series ($\Delta K_{eff} \approx 25\%$).

For same multilayer magnetic films the magnetic anisotropy consists of four main contributions:

$$K_{eff} = K_{MC} + K_{ME} + 2K_S/d_{Co} - 2\pi M^2$$

where K_{MC} - magnetocrystalline contribution, K_{ME} - magnetoelastic contribution, connected with the pseudomorphyc state of Co and Cu layers, K_S - surface anisotropy constant, $-2\pi M^2$ - magnetodipole contribution, determined by the value of saturation magnetization. Magnetoelastic and magnetodipole contributions are dependent on temperature.

In this work the actual parameters of the lattice were calculated in consideration of a pseudomorphic interface [1]. In view of the actual lattice parameters and the values of the coefficients of linear expansion for cobalt and copper ($a_{Co} = 17.9 \cdot 10^{-6}$ deg^{-1}, $a_{Cu} = 15.2 \cdot 10^{-6}$ deg^{-1} [2]) the magnetoelastic contribution for given temperature interval was calculated ($\Delta K_{ME} = 0.1\%$). The changes of magnetodipole contribution were evaluated and makes from 10% [3] to 50% [4].

So, the main contribution to the temperature dependence of effective magnetic anisotropy is given by the magnetodipole contribution, determined by temperature dependence of saturation magnetization.

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Optical Spectroscopy of Polysilane/SiO_2-Film Nanocomposites

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The investigation of optical properties of the photoconducting polymers confined in the nanosize volume is stimulated by the expansion of the application area of these materials to the optoelectronic devices. Recently the possibility to manipulate properties of conjugated polysilanes by incorporating them in nanoporous silica matrices has been demonstrated [1-3]. It was shown that proper manipulation of the polymer chain conformation and interchain interaction allows for the development of highly efficient polymer-based devices. However the use of the silica in a powder form was a significant limitation to their investigation and application.

In this work the novel hybrid composites were fabricated on the basis of poly (di-n-hexylsilane)-PDHS incorporated into porous SiO_2 films with different pore diameters. For this purpose, at first the composite fabrication procedures were developed in order to find optimal conditions for the polymer incorporation (concentration, temperature, the film surface cleaning).

The fluorescence and excitation spectra of these nanocomposites have been studied in the temperature range from 5 to 240 K and the absorption spectra from 293 to 353 K. The spectra were measured versus the PDHS concentration, the type of the porous film and the pore diameter. It was shown that optical spectra of the PDHS confined in the nanoporous SiO_2 films depend on the pore diameter and differ from those of the bulk film, polymer solution, as well as from those of PDHS/silica nanocomposites. This difference is due to a decrease of both the intermolecular and the exciton-photon interactions in the composites. It was proved that polymer chains located in the pore volume of SiO_2 have both separate and aggregate forms. Temperature dependence of the fluorescence and absorption bands intensities enabled us to explain optical properties of their conformational structure and to obtain information about the thermochromic transition of the confined PDHS and the excitation energy transfer pathways.

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Photoluminescence of CdSe Nanoparticles on Porous SiO$_x$ Layers

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Nanostructured materials which are formed by introduction of nanoparticles in a porous matrix of other material have been extensively studied. In the present work the photoluminescence (PL) spectra of the structure obtained by introduction of CdSe nanocrystals in porous SiO$_x$ layers have been investigated. Porous SiO$_x$ layers were produced by thermal evaporation of silicon monoxide in vacuum and oblique deposition onto polished Si substrates. During deposition, the substrates were oriented at the angle 75 between the normal to the substrate surface and the direction to the evaporator. Obtained SiO$_x$ layers have column-like structure and porosity of these samples (volume share of pores) was equal to 53-57 %.

Precipitation of CdSe nanocrystals onto Si-SiO$_x$ substrates was carried out by two ways. In the first case the CdSe nanoparticles were deposited onto porous SiO$_x$ layer as colloidal solution, with the subsequent evaporation of the hydrocarbon solvent. After evaporation of hydrocarbon samples were exposed to additional processing in hydrocarbon. The second way of nanoparticles precipitation is the direct formation of CdSe nanoparticles on the porousSiO$_x$ layers.

It is shown, that after precipitation of CdSe nanoparticles from colloidal solution in PL spectrum of obtained sample two broad PL bands are observed. One, more intensive with maximum at ˜ 550 nm and second, less intensive, maximum at ˜ 420 nm. Additional processing of samples by hydrocarbon results in redistribution of PL bands intensity.

At precipitation of nanoparticles from colloidal solution on porous surface influence of this substrate results in disturbance of equilibrium conditions at which the size of particles in the solution is stable, that results in rearrangement of part of the nanoparticles in fraction with the new sizes. Occurrence of fractions with the new sizes is shown in PL spectra as broadening of the basic band with $_{max}$˜550 nm and occurrence of additional PL band with$_{max}$˜ 420 nm. As follows from experimental data, additional processing by hydrocarbon results in change of the both PL bands half-width. Probably, it is caused by exchange processes between particles and CdSe clusters, adsorbed on surface of porous sample, and formation of fractions of the nanoparticles with the new optimal sizes for the given conditions of precipitation. Growth of intensity of the shortwavelength PL band confirms the formation of particles with smaller sizes.

At chemical precipitation of the CdSe on Si-SiO$_x$ substrate, it is observed shift of PL maximum in the short-wave side in comparison with position of PL maximum for colloidal solution of CdSe nanoparticles ($_{max}$˜548 nm). This shift can be caused by decreasing of the nanoparticle size as results of their formation in restricted volume of pores between SiO$_x$ nanocolumns.

Thus, using of porous SiO$_x$ layers as a substrate for precipitation of CdSe nanoparticles allows to realize process of nanoparticles synthesis in the limited volume. It enables to control process of synthesis and to obtain nanoparticles of the different sizes.

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Effect of Carbon Nanotubes on Molecular Dynamics and Phase Transitions of Benzophenone: FTIR Spectroscopy and Thermodynamic Studies

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Molecular dynamics and phase transition temperatures in multi-wall carbon nanotube (MWCNT)/benzophenone (C13H10O, BP) nanostructured binary systems were investigated by means of FTIR absorption spectroscopy and differential scanning calorimetry. The MWNTs were prepared from ethylene using the chemical vapor deposition (CVD) method, and typically have the outer diameter de about 10 20 nm, and length about 5 10 m. The MWNTs BP composites were obtained by adding the appropriate weights of NTs (0 1%) to the organic matrix in the isotropic liquid state with their subsequent 20 30 min sonication using a UZDN 2T ultrasonic disperser. The differential scanning calorimetry (DSC) data (transition temperatures and enthalpies) were measured by Perkin-Elmer DSC7 instrument in the heating and cooling modes in the range of 278-330 K, at the rate of 8 K/min. FTIR adsorption spectra were measured with Bruker IFS-88 FTIR spectrometer in 380-4000 cm-1 spectral range with 1 cm-1 resolution in parallel experiments for the nanocomposites and the undoped organic matrix.

It was found that the phase transition temperatures of the BP component increased by up to 3 K with incorporation of small amount of MWCNT. However, BP crystallization was not observed in our DSC measurements suggesting that MWCNTs promote BP supercooling in the MWNTs BP composites. The noticeable increase of the BP melting temperature could reflect the presence of strong interface interactions between MWCNT and BP. Our FTIR spectroscopic data confirmed strong binding interactions between MWNTs and benzophenone in the studied binary systems, which mainly involve terminal C=O groups.

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Brownian Motors: Transition Processes in Dichotomic Fluctuations of a Potential Energy

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Using a high-temperature Brownian motor with unidirectional motion provided by symmetric deterministic dichotomic fluctuations of a potential energy as an example [1], it is shown that taking into account the transition duration between the dichotomic-process states has essential influence on the average velocity of the motion, when this duration becomes greater than the characteristic diffusion time of the particle on the period of potential energy. Analytical dependences of the average velocity on time parameters of the system have been obtained [2]. Their comparison with harmonic time dependence of potential energy has been undertaken.

In the theory of Brownian motors, nonsymmetrical dichotomic process with different state lifetimes allows to govern the direction of motion at definite conditions by varying of the lifetimes. The competition of the lifetimes difference with the transition duration between the dichotomic-process states leads to interesting phenomena discussed in this presentation.

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Adsorption of Organic Molecules on Au Nanoparticle Surface as Studied By SEIRA And UV-VIS Absorbance Spectroscopy

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Self-assembly of organic compounds on metal surfaces has attracted much attention due to its importance both from the view of scientific perspective and for potential applications in molecular electronics, non-linear optics and nanoscale electroluminescent (EL) devices. Recently we demonstrated a new type of planar nano-scale EL device built from an island metal and organic compound film [1]. It was shown that the electroluminescence from such planar devices to a large extend depends on molecular organization at the interface between the metal and organic components. For better understanding of the EL mechanisms, is it necessary to study the influence of the processes of the film growth and self-assembly in metal-adsorbate systems on their structure and optical properties.

Here we report on the studies of SEIRA (Surface Enhanced IR Absorption) and UV-Vis absorption spectra of several organic compounds (light-emitting complexes terbium(III) tris(2,2,6,6-tetramethyl-3,5-heptanedionate), Tb(thd)3, and europium (dibenzoyl-methanato)3(bathophenanthroline), Eu(DBM)3bath, as well as polymers polynaphthalimide-methacrylate, and polymethylmetacrylate) layers deposited on Au nanoparticle surface. Au nanoparticles of controllable size (80 100 nm) were obtained according to the procedure described in [2]. Thickness of the organic layers was controlled by digital quartz balance monitor, and varied from 35 to 120 nm. Room-temperature SEIRA spectra of the composites were measured using IFS-66 Bruker FTIR spectrometer with 2 cm 1 resolution. UV Vis absorption spectra were measured in the range 400 800 nm with a LOMO MDR-23 monochromator equipped with photodetectors.

The changes observed in the SEIRA spectra of the studied molecules are explained in terms of different molecular orientation with respect to the nanoparticle surface. In addition, it was shown that the surface plasmon peak in UV-Vis absorption spectra of all studied metal-adsorbate systems is shifted compared with its position in the spectra of the island metal substrate, the shift value being dependent on the type of organic compound. Correlation between the plasmon peak shift and SEIRA enhancement factor for different compounds is discussed.

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Nonlinear Optical Properties of Porous Nanostructured Oxyhydroxide of Aluminum

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The ultraporous nanostructured oxyhydroxide of aluminium (NOA) is a medium with high specific surface, so it is suitable for molecular adsorption and nanoparticles deposition. For applied reasons it is interesting to study optical and nonlinear optical (NLO) properties of such a medium, considering it as a suitable way for designing novel guest-host functional materials. Incorporation of various guest systems into the NOA matrix allows to investigate its interaction with adsorbates, also it may even enhance NLO response of the guest subsystems by the local field of the matrix.

Synthesis of the NOA is based on selective aluminium oxidation upon exposure to humide atmosphere through a mercury film [1]. The monoliths grown posess extra high porosity and specific surface of the order of $\sim$ 300 m^2/g. The NAO structure consists of amorphous nanofibrils of $\sim$ 100 nm length and 5 nm in diameter, forming nanopores with an average size of 10 nm.

The described technique allows to obtain monoliths of sufficient size for optical and nonlinear optical diagnostics. However, due to the ultralight structure of the monoliths, they are very brittle. So the samples for the characterization were prepared via compression into pellets 0.25-0.4 mm thick and 13 mm in diameter, the fibrous nanostructure remaining undamaged.

NLO transmittance of NOA samples annealed at different temperatures was studied using continuous laser excitation at 532 and 633 nm. The behavior of NLO responses of different samples are compared and discussed.

Nonlinear interaction of non-annealed sample with picosecond-range laser pulses (1064 and 532 nm) was under investigation. The scale of the effect observed reminds of the giant NLO response of the porous layers of

TiO_2 nanocrystals [2]. In the intensity range less than 10 MW/cm^2 the cubic NLO susceptibility $\mathrm{Im}(\chi^{(3)}) \sim 10^{-8}$ esu was measured at 1064 nm.

The NOA samples under study are very high-dispersive. The homogenius scattering type observed proves that the process of compression does not affect the fibrous nanostructure of the samples.

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Laser-Induced Incandescence of Carbon Microparticles in Polymeric Matrixes

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For the last two decades, the interaction of carbon microparticles with high-power pulsed laser radiation has attracted much interest. The majority of the publications is devoted to research of carbon suspensions (primarily aqueous) and of soot microparticles in air, which are formed as a result of combustion of organic fuel. The laser-induced behaviour of light-absorbing microparticles in solid and high-viscosity matrixes is investigated insufficiently.

The main physical effect of the laser radiation on light-absorbing microparticles in air and in condensed matrixes is their warming up to temperatures of approximately 4000 K. Thermal radiation of laser-heated microparticles is easily observed and is referred to as LII (laser-induced incandescence). The optical signal of LII allows estimating the amount of soot in the exhaust or in the combustion chamber, which gives the valuable information for the operative control over the engine.

In the present work, LII of carbon microparticles in condensed matter with high viscosity, such as synthetic resins (epoxy resin); solutions of polymers (polystyrene) and water-soluble gels (gelatine gel), is investigated under powerful laser irradiation (Q-switched YAG:Nd^{3+} laser). High viscosity of the matrix essentially reduces the influence of convective streams on the investigated phenomena and allows studying the properties of suspensions depending on the dose of the laser irradiation. Besides, for laser irradiation of non-stirred matrixes, the stable local changes of optical properties are expected. At last, the investigation of laser-induced effects in carbon-doped high-viscosity matrixes can create a bridge for gradual transition from liquids to solids activated by light-absorbing microparticles, which are poorly investigated.

The experiments reveal essential differences in behaviour of water suspensions and suspensions in polymers. In the polymeric non-aqueous matrixes, under irradiation by a sequence of powerful nanosecond laser pulses, the phenomenon of LII building-up is observed. The increase of LII intensity with the irradiation dose is accompanied by the increase of LII pulse duration. A model is proposed for interpretation of the observed phenomena. The model includes the laser heating of carbon microparticles to temperatures of about several thousands of kelvins with the pyrolysis (thermal decomposition) of oligomers around the overheated carbon particle. The products of pyrolysis – gases and nonvolatile carbonized products – form gas bubbles and carbonized shells around the particles. As a result, the increase of size of light-absorbing center causes the observed increase of LII intensity with the irradiation dose.

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Absorption of Ultrashort Double Laser Pulses by Aspherical Metallic Nanoparticles

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The theory is developed [1] which allow the energy absorbed by nonspherical particles of small sizes from laser-induced irradiation of double pulse of given duration to calculate in the region of surface plasmons excitation (Mie-resonances). For particles of oblate or prolate spheroidal shape [2] the dependences of this energy on degree of deviation from spherical form, pulse duration, particle volume and on the polarization of laser beam electric field with respect to spheroid axis of revolution are obtained. It is shown, that depending on the time delay between two pulses the energy absorbed by a nanoparticle can be higher or less than the total absorbed energy of two no correlated pulses.

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Condition of Equilibrium of Inhomogeneous Nano-Fluctuation System Under the Earth Gravity Near the Critical Point

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On the basis of the contemporary fluctuation theory of phase transitions (FTPT) [1] a substance near the critical point (CP) is a gas of the clusters of fluctuations. The compressibility of the system goes to infinity near the CP. Due to this fact the characteristics of the substance (correlation length R_c, a mass of the cluster of the fluctuation $m_f = \frac{4}{3}\pi R_c^3 \rho_f$) change along the height of the system in the external field $h = \rho_c g \Delta z P_c^{-1}$ [2]. The condition of equilibrium [3]

$$|\Delta\mu = \frac{\mu - \mu_c}{\mu_c}| = |h = \rho_c g \Delta z P_c^{-1}| \qquad (1)$$

cannot be considered as correct one for such inhomogeneous systems under gravity near the CP. Here ρ_c , P_c , μ_c are the critical density, pressure, chemical potential; g is the gravitational acceleration; Δz is a level in the sample cell, measured from the level with the critical density of substance.

Some new peculiar properties of such inhomogeneous systems near the critical point have been obtained experimentally for the first time [4-6] by using the molecular light scattering and refractometry methods.

1) The action of the gravity field of the Earth causes the appearance of the internal nonuniform field $U(h)$ in the inhomogeneous liquid at the critical state. It changes in the range of magnitudes $\Delta U(h) = \mu(h) = (10 \div 10^2) \cdot h >> h$ for different substances.

2) The value of this internal field $|\Delta\mu(h)| >> |h|$ depends on the critical temperature of substance ($\Delta U(T_c) = \Delta\mu(T_c) \sim T_c^3$), i.e. on the forces of intermolecular interaction.

3) ΔU depends on the linear size of the system ($\Delta U(L) = \Delta\mu \sim f(L) \sim L^{-x}$);

4) ΔU depends on the average density $\overline{\rho}$ of the system filling with the substance $\Delta U(\overline{\rho}) = \Delta\mu(\overline{\rho}) = f(\overline{\rho})$.

Hence it follows that the condition of the equilibrium of an inhomogeneous substance under the gravity field of the Earth is different from (1), namely

$$|\Delta\mu = \frac{\mu - \mu_c}{\mu_c}| = |\Delta U(T_c, L, \overline{\rho})| >> |h| \quad (2)$$

It means that the condition of equilibrium in the inhomogeneous substance depends on the system vicinity to the critical state.

The inhomogeneous field $U(h)$ is not external, but internal critical field, induced by the field of Earth gravity.

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Diffusion in The Nano-Fluctuation System Isobutyric Acid-Heavy Water Under the Critical State

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The temperature dependence of the half-width of the central Rayleigh line in the scattered light spectrum of the solution isobutyric acid - heavy water near the consolute critical temperature has been study in the work by using the method of spectroscopy of optical mixing [1]. On the basis of these measurements the temperature dependences of the diffusion coefficient, $D(t) = D_0 t^{\nu}$, and the correlation length, $R_c(t) = r_0 t^{-\nu}$, of this solution have been obtained along the thermodynamic directions: critical isochore-isoconcentrate ($t = (T - T_c)/T_c > 0$) and the liquid-liquid phase interphase ($t = (T - T_c)/T_c < 0$). The values of critical indices, ν , the amplitude of correlation length, r_0, and the diffusion coefficient, D_0, of isobutyric acid-heavy water solution along these critical directions were calculated.

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Spectroscopy of Sol-Gel Films on Germanium Oxide with Gold Nanoparticles

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This paper reports about investigation of the series consists of samples with undoped germanium oxide films, films doped only with gold, films doped only with europium, and films co-doped with gold and europium. Concentrations of activators were 3% and 10% for the gold and europium dopants, respectively. Spectra of the undoped films ($100GeO_2$) contain wide very weak bands in the region 400 800 nm. Spectra of the $97GeO_2 - 3Au$ films at low temperature consist of two wide bands with maximums near 500 and 600 nm as well as the most intensive narrow complex band with maximum at 685 nm and additional spectral features at its long wave length side. Only this band forms spectra at room temperature. Spectra of the $87GeO_2 - 10Eu_2O_3 - 3Au$ films consist of the intensive narrow band emission in the spectral region from 550 to 750 nm. Intensity of this emission increases by 4 times with rising of temperature from 10 K to RT. Spectra of the $90GeO_2 - 10Eu_2O_3$ films contain wide very weak band with maximum at 611 nm intensity of which at room temperatures by about 50 times lower than intensity of the similar band for the $87GeO_2 - 10Eu_2O_3 - 3Au$ films.

The weak wide bands in the region 400 800 nm in the spectra of the $100GeO_2$ films could be attributed to the emission of quartz substrate. The broad emission bands with maximums 500 and 600 nm in the spectra of the $97GeO_2 - 3Au$ films are similar neither to the luminescence spectra of oxygen deficiency centers (-Ge-O-)2Ge:, nor to the substrate emission. The first band may be assigned to the $d^9s- > d^{10}$ luminescence transitions of the Au+ ions arising as a result of Au^0 ionization or to the recombination luminescence in the GeO_2 matrix. The latter one has to be assigned to luminescence of gold nanoparticles. Maximums of the main narrow bands in the spectra of the samples with $87GeO_2 - 10Eu_2O_3 - 3Au$ films are at 591, 611, 652 and 702 nm that allow us to attribute all of them to intrinsic f?f emission transitions in the Eu^{3+} ions. The weak luminescence band observed in the spectra of the samples with $90GeO_2 - 10Eu_2O_3$ films is also corresponded to the similar radiation transitions in the Eu^{3+} ions.

Therefore, it has been established that multiple increase of the Eu3+ luminescence intensity takes place for the $87GeO_2 - 10Eu_2O_3 - 3Au$ sol-gel films compared to the $90GeO_2 - 10Eu_2O_3$ films annealed at Tann = 800 C. In our opinion, this effect is caused by photo-ionization of Au atoms on the surface of (Au0)n nanoparticles and follow transfer of excitations from formed Au^+ ions to Eu^{3+} ions.

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Optical and Photoelectric Properties of Different Chemically Cross-Linked Fullerene Thin Films

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Special structural and chemical properties of C_{60} molecules can be successfully employed as building blocks of nanostructured hybrid materials (especially in form of thin films) based on functional fullerenes and metals. Thus, fullerene films provide bonding sites which could be exploited as molecular templates. Different organic cross-linkers discovered to be very attractive to assemble nanoparticles in the formation of covalently linked superstructures. The cross-linking molecules with spacers of various lengths allow, to some extent, to control over interparticle spacing, and in its turn, the interparticle spacing influences the lattice properties such as conductivity.

The method of direct solvent-free functionalization of C_{60} films with aliphatic bifunctional amines and thiols, aminopirene, pyrenemethylamine, diaminenaphtalene, porphyrin was applied to prepare covalently functionalized, cross-linked C_{60} films. The pristine and cross-linked with octane-1,8-diamine and octane-1,8-dithiol fullerene films were decorated with silver and gold nanoparticles. To characterize photoelectric properties photodiodes were fabricated by evaporation of a semitransparent gold electrode layer through an opaque mask onto pristine and functionalized C_{60} films, and by making an ohmic contact to the rear side of Si substrate. Optical and photoelectric properties of nanostructured hybrid films in comparison with the undecorated ones were studied.

Photoluminescence (PL) spectra of the functionalized fullerene films have been measured in wide temperature range (from room temperature to 2 K). The low temperature PL spectra demonstrate significant changes of the band intensity and appearance of fine structure for bands connected with radiative transitions of self-trapped and localized excitons, and their phonon replicas. The changes of recombination properties of fullerene films in consequence of the process of chemical functionalization and decoration with nanoparticles determine the observed changes of PL intensity.

Photoelectric properties of $Au/C_{60}/n-Si$ surface-barrier structures considerably depend on chemical agents employed in the process of chemical modification of fullerene films. Thus, the gas-phase reaction of films with diamine-octane results in the decrease of photocurrent value by an order of magnitude, unlike the reaction with dithiol-octane. The deposition of Au nanoparticles onto the surface of the dithiol-octane modified films causes the increase of photocurrent value in the range of local plasmons excitation in such kind of nanoparticles. It should be also noted, that the modification of fullerene films with molecules of porphyrin leads to the increase of photocurrent value by a factor of 1.5-2.

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Peculiarities of the Raman Spectra of Polyurethane/arbon Nanotube Composite

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Carbon nanotubes are among the promising constituents of carbon nanonscale composites because of their unique properties, such as a one-dimensional structure (small diameter of 1 nm and long length of many microns), high thermal and chemical stability, very good heat conduction, and high mechanical strength (elastic modulus comparable to that of a diamond). Currently, a large number of materials allow the implementation of SWNTs for the improvement of their properties or the acquisition of new qualities. Crucial for a successful design of nanocomposites is the knowledge of interactions between SWNTs and the matrix (polymers, epoxy resins, inorganic material) in the structural material.

The morphology, orientation and dispersion of carbon nanotubes in polymer matrix were studied by AFM, using an Autoprobe CP (ThermoMicroscopes Inc.) machine in different modes. The Raman spectra were detected by an automated double spectrometer DFS-24 (LOMO, Russia), equipped with a cooled photo multiplier and registration system working in a photon counting mode. The light source used was a linearly polarized, cylindrical focused 514.5 and 488 nm A+-laser.

In present work we have studied the Raman spectra of pristine Carbon SWNT and composite SWNT/Polyurethane in terms to investigate the interaction with SWNT and PU.. These spectra demonstrate, that the SWNTs retain their pristine properties and display the characteristic features of semiconducting SWNT. The spectra demonstrate significant influence of the polymeric matrix on the carbon nanotube bundles. The nanocomposite Raman bands become broader and are shifted to high-frequency area of the spectrum in comparison to the corresponding bands of the SWNT material. Redistribution of the intensity in a vicinity of a G-band and increase of splitting of the radial breathing mode are also observed for the nanocomposite Raman spectrum. We suggest that these

Raman shifts have been resulted by intrusion the polymer into nanotube bundles. The polymer exerts a pressure on the individual tubes, thereby increasing the breathing mode frequencies. On the other hand, as a result o this intrusion some bundles can be combined with the lesser number of nanotubes, until to presence of single tubes.

6 SURFACE

O- 1 ⇓

Electro and Photo Physical Properties of the Ordered Dyed SiO2 Films on the Gold Surface Manufactured by Sol-Gel

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Quasi ordering of silicate glass pores with application of Zola-gel technology is reached owing to spatial self-organizing micelles taking place at the second critical concentration forming micelle mphiphilic molecules. According to the morphology of the starting molecule (like hyper-branched precursors) or the nature of some bonds (hydrophobic Si-CH_3 or Si-H groups), it is possible to build up a network with controlled pore size and Interpore space. It is possible to select starting molecules to tailor physical and chemical properties of xerogel. As walls of such xerogel serves arising during chemical reaction silicon dioxide. In the current literature there is a set of data on preparation porous and mezoporous materials on this technology for the first time offered in 1999 by authors [1]. Similar materials are important both for basic research of complex wafers and for their potential applications in modern optics and electronics [2].

Tasks of the given work concern both subjects and are based on ability ordered structured SiO_2 to include in a film body organic dyes in concentration 1mol/l compared with pore concentration. Spectral appearance of this feature has been described in ours work[3]. It was expected, that at equality of concentration of R6G cations and pores formed by Pluronix-123 (a three block-copolymer, peo20ppo70peo20 (peo-(polyethylene oxide, pop-polypropylene oxide, Aldrich (m.w.5800) not ionic, 100 % active, non-toxic al SAS), are possible field interactions and the ordered orientation of molecules what to be shown in the reinforced migration of vibronic excitations and dichroic absorption. Thus it is important to determine the places of dye molecule localization in the structure, possibly dependent from an ion charge. Indeed absorption and luminescence spectra of ionic dyes at so high concentration have found out significant changes concerning their known spectra for the case of independent molecules.

In connection with expected photosensitivity of dye doped SiO_2-films measurements of a photo current had been carried out. It has appeared that photocurrent was very insignificant for voltage up to 12 v For understanding of the similar response conductivity of undoped SiO_2 200nm films deposited on a gold surface has been measured. In measurements 4-point scheme eliminating of contact resistance influence was used. Longitudinal specific conductivity structured and nonstructural SiO_2- films appeared high as for insulator and equal 510-4(.)-1,, but it explained low photosensitivity of the dye doped material. Lateral macro conductivity such a film remained very low (less 1mS). The preliminary analysis of results on conductivity with use data of work [4] allows to consider as responsible for the high conductivity a nonstechiometry of SiO_2 at a lot of Si share through the measured index refraction 1,47 is typical for the glass.

The phenomenon of amplification of light scattering (SERS) by a surface of precious metals [5] arising at simultaneous excitation of the surface plasmonic polaritones is known . In work [6] it was possible to experience even laser emission in visual spectra on surface plasmon polaritones (SPP), compensating losses in metal by light amplification in dye solution. SPPs are confined to the proximity of metal-dielectric interface and decay exponentially to both media.

When SPP is excited an evanescent wave arises near to a surface corresponding metal (up to 4-5nm). Molecules that are in the field of localization evanescent waves respond to a greater signal of a scattering light or a luminescence emission. We have observed the similar effect of amplification for a part of a fluorescence spectrum on the dye doped SiO_2-films deposited on a gold substrate at excitation by the linearly- polarized p-wave at comparison with results for the same samples on a usual glass substrate.

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O- 2 ⇓

Influence of the Substrate Nature On The Orientational Ordering In Thin Wall-Adjacent Liquid Layers

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It is known, that the solid substrate may induce orientational ordering state in the wall-adjacent layers of some organic liquids.

This special epitropic liquid-crystal (ELC) state stretches up to the 100 molecular distance lengths into the liquid.

Taking into account facts, mentioned above, it is possible to describe the current system by methods, which was developed earlier for classical LC. First of all these methods consider the effects of dipole-dipole interaction and anisotropy of intermolecular dispersion interaction, connected with the anisometry of the molecules shape.

In this work we analyzed the influence of the substrate treatment and its nature on the formation and peculiarities of ELC phase and on the appearance of molecular associates. The dichroism of electronic-vibrational absorption spectra of thin liquid interlayers and wetting films of nitrobenzene was studied. It allowed us to ensure the diversity of symmetrical and unsymmetrical boundary conditions for studied systems: "quartz-quartz", "metal-metal", "quartz-metal" and "quartz-air".

In last case the wetting film was formed in porous cell with simultaneous measurement of its thickness. It was found that the homeotropic type of molecular texture in ELC layers was formed in all of above mentioned situations.

Quantative characteristics (order parameter, equilibrium layer thickness) of ELC layer depend essentially on the type of boundary conditions. The largest effect of ordering degree was observed in case of conductive bounding substrates. Note, that in all of studied situations the orientationally ordered phase was separated by relatively sharp boundary from the bulk liquid and that in ELC phase dimers prevail, as compare with the bulk liquid where monomers prevail usually.

These peculiarities of ELC structure are explained in the framework of theoretical model which takes into account the effects of dipole-dipole interaction between pairs monomer-monomer, dimer-dimer, anisotropy of intermolecular disperse interaction, caused by anisometry of molecular shape and orientational interaction of liquid particles with solid substrate.

O- 3 ⇓

Transmission Spectroscopy for Nanostructured Conductive Films on Semiconductor Surface

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Transmission enhancement through a front conductive layer into semiconductor substrate is very important for many photonic or optoelectronic devices (photodetectors, sensors, solar cells etc.). Recently, it was predicted the application of surface plasmon polaritons (SPP) excited in thin metal film for this aim. Besides, the excitation of surface (localized) plasmons (SP) in ledges of micro(nano)relief of a thin conductive texturized film or on the array of metal nanoparticles on the semiconductor surface also changes the scattering/absorption of light into below laying semiconductor substrate. This increases the light intensity in substrate too.

Therefore in this report the light transmission through: i) conductive (metal) thin films with stochastically texturized interfaces; ii) thin metal films with mutual correlation of both periodically texturized film interfaces; iii) 1D periodic metal nanowires ensembles on the semiconductor substrate and iv) arrays of metal nanoparticles on the substrate has been considered theoretically.

The influence of nano-scale roughness on the transmittance of three-media structures with a homogeneous permittivity value in each layer has been analyzed using the Greens functions formalism. The spectral dependencies of the light transmission through a thin metal (Au, Ag, Al) continuous film deposited onto GaAs substrate were calculated for the cases of roughness inherent to "airmetal", "metalsemiconductor" or both surfaces. The increase of the transmittance caused by the nano-roughness reaches about 10% compared to that in the case of flat surface [1].

The interaction between 1D periodic reliefs of a thin absorptive film in the framework of differential formalism has bee considered. The anticorrelated films have demonstrated an essential increase of transmittance through the absorptive film in some spectral and angular vicinities of SPP excitation [2]. For typical plasmon-carrying media as noble metals (Ag, Au and Cu) has been predicted anomalous enhancement of transmittance through thin film with anticorrelated reliefs of its opposite sides. Besides the usual resonant excitation of SPPs (Fano modes), almost nonresonant excitation of strongly dissipative damped Zenneck-Sommerfeld modes takes place in the strong absorption region of plasmon-carrying medium [3].

The transformation of SP into SPP at an increasing metal filling factor while changing the width of rectangular nanowires was predicted theoretically. The theoretical calculations are based on differential formalism using curvilinear coordinate transformation and Fourier modal methods, and its comparison in the case of nanowires with rectangular cross section was performed. The essential enhancement of SP oscillator strength at transformation to surface plasmon polariton was obtained too [4].

The photocurrent of Schottky diodes (Au/GaAs) with different type of interface has been studied. Significant contribution of SPP and SP modes has been shown in all cases by analysis of experimental spectral dependencies of photocurrent and theoretical calculations of light transmittance into semiconductor. The structure with diffraction grating shows narrow and intensive peak of photocurrent while it is broader and less intensive for structure with low ordering (quasigrating, nanoparticles).

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O- 4 ⇓

Manifestations of Orientational Effects in IR-spectra of Adsorbates

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As a result of the adsorption on substrates with regular structure monolayers of orientationally ordered adsorbates are formed. The facts proving the orientational ordering of the adsorbate are furnished by numerous experiments [1]. Rather large number of experiments deal with CO/NaCl(100) and $CO_2/NaCl(100)$. The IR-spectra of these systems reveal Davydov splitting, related to presence of more than one non-equivalent molecule per unit cell of quasi-2D lattice of adsorbed monolayer. The Davydov splitting observed, proves the orientational structure of the adlayer is ordered and the value of the splitting helps in estimation of the structure parameters as well as of their changes.

The general theory of calculating vibrational spectra is being developed by the author with electronic component of molecular polarizability regarded [2]. Such regard allows to diminish the discrepancy in the value of Davydov splitting till less than 5% for CO/NaCl(100) and CO_2/NaCl(100) systems. While prior calculation for CO/NaCl(100) without molecular polariziblity regarded showed discrepancy of 25%. Besides the Davydov splitting integral intensities of spectral lines were calculated. Though the coincidence is worse in this case still qualitatively the correlation is evident. E.g., the obtained analytic formulas give the null value of the integral intensity of s-polarized symmetric collective vibration band, while in p-polarization this band is very intensive.

The variety of orientational structures furnished by monolayers adsorbed on substrates with regular structure is the result of competition of two types of interactions: lateral interactions between the molecules of adlayer and interactions with the substrate. The former reveal themselves in monolayers with regular structure, while the latter reveal themselves in orientational effects even for single adsorbed molecules (or for highly diluted adlayers). Such effects result in changes of IR-spectra (indirect interaction of vibrational modes via the substrate, swap of integral intensities of near bands, their converging) compared with gas-phase spectra of the same molecules. Besides this, scanning radiation during spectroscopic measurements reflects from the substrate giving rise to additional orientational dependencies in IR-spectra affected both by orientational parameters of the adsorbate and by incidence angle.

Some adsorbed systems possess hindered rotation of the adsorbed molecules when temperature increases, that is the jump-like reorientations between several equivalent orientations. This effect results in temperature dependence of IR-spectra for such systems. E.g., the system CO/NaCl(100) possesses temperature phase transition between the ordered phase with (2x1)-structure and the disordered phase. As a result of growing dispersion in the orientations of long axes of the molecules, the band corresponding to antisymmetric collective mode vanishes in the phase transition point. The other result is the decreasing of the Davydov splitting, still, unlike in bulk molecular crystals, this value remains non-zero up to the phase transition point. This unusual behaviour is due to the substrate. The value of Davydov splitting of the layer is determined by the value of average dipole moment of the layer. In adsorbed layer molecular orientations are constrained by the substrate and the resulting dipole moment is non-zero, while in bulk samples molecules have no constraints in orientations and when thermodynamic fluctuations grow the resulting dipole moment turns zero. Still zero value of Davydov splitting in phase transition point is also intrinsic for planar orientational structures of adsorbed monolayers.

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Optical Properties and Thickness of a Transitive Surface Layer on a Newly Polished Ni and Fe Mirrors

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Newly polished mirrors of metals and metal alloys are usually used for determination of their optical constants by ellipsometric methods. Thus in most cases the transitive surface layer formed in the course of polishing is set aside. Such layer consists of the adsorbed molecules and chemical compounds (as a rule, oxides of corresponding metals). Therefore we have conducted research of optical properties and a thickness of a transitive surface layer on newly polished Ni and Fe mirrors. Optical constants of newly polished mirrors were defined by ellipsometric Beatty's method. After that mirrors were annealed in high vacuum (10^{-6} mm hg) for two hours. As it has been shown by Roberts in [1], annealing of the oxidised copper mirror in vacuum $2 \cdot 10^{-5}$ mm hg restored optical constants of the sample made in vacuum and which constants were also measured in vacuum. Further it is known that annealing restores crystal structure of a surface. Therefore after annealing the optical constants of samples Ni and Fe were measured by ellipsometric Beatty's method. Using known formulas of Drude for a transitive surface layer on a metal surface, we have defined a thickness and an index of refraction of a transitive surface layer of Ni and Fe for different lengths of waves of visible spectrum. Angle of incidence of light on the sample was 75°. Optical constants of annealed samples in formulas of Drude were accepted as optical constants of pure Ni and Fe surfaces, and optical constants of newly polished samples as the oxidised surfaces. As a result, dependences of index of refraction of a transitive surface layer for Ni and Fe from length of a wave λ in visible spectrum, and also from thickness of surface layers have been received. For Ni the thickness has appeared equal 3 nm, and for Fe 3,9 nm. For Ni spectral dependence of an index of refraction has an abnormal course, and for Fe normal. It is known [2] that for pure Ni in the ultra-violet spectrum there is an intense fundamental absorption band, which begins at 3 V (λ $400nm$). Thus, if transitive surface layer on the Ni surface consisted from Ni dependence of an index of refraction would be normal, as is observed in work [2]. On the other hand, absolute values of the index of refraction received by us for Ni surface layer coincide with the data of work [2] and change from 2 to 2,8 as a length of a light wave increases. The explanation of abnormal dependence can be as follows: in a transitive surface layer of oxide on Ni there is a surplus of atoms of pure Ni that displaces the absorption band towards the bigger length of waves, i.e. a visible spectral range. The normal dispersion of an index of refraction for a surface layer on Fe shows that in a visible spectrum for it there is no strong absorption, as in case with Ni. Values of an index of refraction for a surface layer on Fe are from 3,66 to 3,9 as length of a wave λ reduces.

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Surface Excitations of Spheroid

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According to tradition, the MDS spectrum for spatially confined systems is calculated in the presence of external electromagnetic field. For spatially confined systems their polarizability and SEM frequencies are calculated in appearance of anomalous growth of their polarizability. In other words, a heterogenous system of differential equations is solved for corresponding system though the spectrum itself of surface MDS can be found from the homogeneous system of Maxwell equations for the specific problem as the condition of existence of nontrivial solutions [1, 2]. It is this method was used in the given work for calculation of surface plasmones spectrum in spherical metallic particle. The frequencies of surface modes $\omega_{lm}(\xi)$ are calculated. Dependences of these frequencies is calculated numerically from ellipsoids' oblongness $\xi = 1/e$ (e is an ellipse eccentricity) for different values l and m.

In any spatially confined media, fluctuations electromagnetic field always take place [3]. The spectrum of possible excitations in the media is formed by Maxwell equation and boundary conditions corresponding to given problem. For electrostatic approximation for the case of spheroid these equations and boundary conditions look like [4]

$$\Delta V = 0, (\vec{E} = -grad\ V), \tag{3}$$

$$E_t^{(in)} = E_t^{(out)}; \varepsilon_{in} E_n^{in} = \varepsilon_{out} E_n^{out}, \tag{4}$$

where $V(x, y, z)$ is an electric field potential in an arbitrary point of space (x, y, z) , E_t^{in} and E_n^{in} – tangential and normal components to the surface arranging electrical field $\vec{E}$ inside spheroid, E_t^{out} and E_n^{out} – the same components $\vec{E}$ outside of the spheroid. Taking symmetry of the problem into consideration, the solving of the problem can be exposed in a spherical coordinates' system (ξ, η, φ) [5, 6].

Taking into consideration a physical idea about limited nature of the potential V and its first derivatives' in any space points, solution of equation (3) for internal (in) and external (out) space regions relatively to the ellipsoid surface can be exposed:

$$V_{in} = P_l^m\left(\xi\right) P_l^m\left(\eta\right)\left[A\ \cos m\varphi + B\ \sin m\varphi\right], \tag{5}$$

$$V_{out} = Q_l^m\left(\xi\right) P_l^m\left(\eta\right)\left[C\ \cos m\varphi + D\ \sin m\varphi\right], \tag{6}$$

where $P_l^m(\xi)$, $Q_l^m(\xi)$ are Legendre polynomials of the first and the second kind.

Taking into consideration boundary conditions (4) and formulae (5), (6), it can be found

$$\varepsilon_{in}\frac{P_l^{\prime m}\ (\xi_o)}{P_l^m\ (\xi_o)} = \varepsilon_{out}\frac{Q_l^{\prime m}\left(\xi_o\right)}{Q_l^m\left(\xi_o\right)}, \tag{7}$$

where the stroke at Legendre polynomials means differentiation by ξ for specific spheroid. Eq. (7) is the basic one for determining surface modes' frequencies of an arbitrary spheroid.

Let us analyze a metallic spheroid disposed into a dielectric space with permittivity $\varepsilon_{out} = \varepsilon_a$ independent of frequency ω. Dielectric function for spheroid is taken in Droude form [7] $\varepsilon_{in} = \varepsilon_\infty - \Omega_p^2/[\omega(\omega + i\nu)]$. Finally, we obtain an equation for calculating spectrum of surface plasmons (SP) in metallic spheroid for the general case:

$$(1 - \frac{\omega_p^2}{\omega_{em}^2})\frac{P_l^{\prime m}\ (\xi_o)}{P_l^m\ (\xi_o)} = x\frac{Q_l^{\prime m}\left(\xi_o\right)}{Q_l^m\left(\xi_o\right)}, \tag{8}$$

where $\omega_p^2 = \Omega_p^2/\varepsilon_\infty$, $x = \varepsilon_a/\varepsilon_\infty$, and ω_{em} are the frequencies of the surface modes for the metallic spheroid.

Using recurrent dependencies for Legaundre polynomials $P_l^m(\xi)$ $Q_l^m(\xi)$ [6], numerical procedure was realized of calculating dependencies SP of the spheroid $\omega_{lm}(\xi)$ from $\xi = 1/e$ for different l and m values.

The formulae obtained for calculating frequencies ω_{lm} of elongated ξ can be easily generalized in case of flattened ellipsoid using a simple change of ξ_0 to $i(\xi_0^2 - 1)^{1/2}$ $(i = \sqrt{-1})$. It comes from Legaundre polynomials abilities [6].

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P- 3 $\Downarrow$

Rotational Motion of Surface Molecular Rotors

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Molecular rotors created artificially on surfaces provoke a great interest at the last time. Molecular rotors allow to study physical principles of generation of guided mechanical motion and friction on the molecular level. Also it allows the accidental thermal motion effects which distinguish nanomachines from the widely used macromachines.

Molecular rotary motion on solid surfaces reveals itself in various experiments. Vibrational spectroscopy fixes specific lines of absorption in angular (deformational) vibration frequency range as well as in frequencies of stretching vibration range where the supplementary spectral lines arise. Moreover, such motion leads to characteristic spectrum-line broadening. Thermal dependence of this broadening is determined by the re-orientation frequencies. Rotational motion of hydroxyl groups on oxide surfaces is caused by the low value of the re-orientation barrier ($\Delta U_\varphi \approx 55\,\mathrm{meV}$) with respect to typical thermal energy ($k_B T \approx 26\,\mathrm{meV}$; $= 300$). It reveals in the appearing of the IR absorption spectral lines in frequency range of 100–200 cm-1 and of characteristic temperature dependence of the line width of OH-valence vibrations (Arrhenius type dependence) [1] . Another way to determine such rotations is dielectric measurements.

The temperature dependence of dielectric loss tangent fixes stochastic resonance [2] which arises when the frequency of applied electrical field is comparable with the thermal re-orientation frequency of molecules between equilibrium angular positions. These measurements are sensitive to the structure of the local surrounding of the surface centre and give the important information about it. Therefore it is actual the development of the models allowing to obtain the frequency dependence of the polarizabilities for the rotating polar surface centers.

We have calculated the polarizability of the flat dipole rotator with hindered rotation potential $U_n(\varphi, t) = U_n(\varphi) - \mu(\varphi) \cdot E(t)$[3]. Here the angular part of potential energy of polar molecule $U(\varphi) = (1/2)\Delta U_\varphi(1 - \cos n\varphi)$is n-well hindered rotation potential, and temporal part arises from the interaction of the dipole moment $\mu(\varphi)$ of the molecule with external alternating field $E(t)$. Implicit analytic expressions have been obtained for the temporal dependence of the average dipole moment, the frequency dependence of polarizability, and dielectric loss tangent ($\tan(\delta) = Im\varepsilon(\omega)/Re\varepsilon(\omega)$, where$\varepsilon(\omega) = 1 + 4\pi C_V\chi(\omega)$, C_V is the bulk concentration of hydroxyl groups) . These dependencies are characterized by evident stochastic resonance. The influence of the asymmetry of two-well potential on dielectric losses spectra and other characteristics of Brownian motion has been studied. When local average fields are sources of the asymmetry emerging due to orientation phase transition in the system of dipole rotators, the regarded characteristics have peculiarities permitting to record phase transition and its parameters.

At $n = 2$, the system has a selected direction along two wells of the hindered rotation potential. If the field is oriented at the angles $\varphi_E \neq 0,\ \pm\pi/2,\ \pi$ to this selected axis, the alternating field modulates both minima and maxima of potential relief [4].

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Temperature Dependence of a Brownian Motor with Spatial-Temporal Asymmetry

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Nonequilibrium fluctuations of potential energy is one of operating mechanisms in Brownian motors [1]. Typical example of a such fluctuation can be catalytical chemical reaction which occurs in Brownian particle, resulting in changes of its electrical charge $q(t)$ that varies between two values q_+ and q_-. Assuming persistence of periodical potential $\varphi(x)$, leads to temporal dependence of particles potential energy $U(x,t) = q(t)\varphi(x)$ [2]. In this case potential energy $U(x,t)$ fluctuates between two potential profiles $U_+(x)$ and $U_-(x)$ which have same shape with different scaling for energy in + and - states. Special interest is attended to sign fluctuations of potential energy that described by $f(t) = f\sigma(t)$, where f is charge or dipole moment, and $\sigma(t) = \pm 1$. In this case assuming high temperature value [4] was shown, that the directed motion arise only at the expense of difference in life time for τ_+ and τ_- states.

In order to calculate explicitly particle velocity in wide temperature specter, low frequency assuming were used $\tau_\pm \gg \tau_D$, where typical diffusion time $\tau_D = L^2/D$ for distances order of potential period L, and D is the diffusion coefficient. It turns out that the dynamic effect considered above does not depend on used assumption. Temperature dependence of velocity is monotonic. Dependence of velocity from parameters (temperature, time and spatial asymmetry) were obtained by computer simulations for potential profile in the form sum of two harmonics and stopping points were found.

Before we offered conception of photomotors [4], special category of brownian motors, in which the dipole moments of particle are in the field of spatially-periodic asymmetric potential.Within the framework of this conception the numeral simulation of the directed stream arising for brownian particles for a sowtooth potential consisting of two linear areas of variable spatial asymmetry was conducted, the system similarly possessed spatial asymmetry. As a result characteristic dependences of average velocity of the directed motion from a temperature, asymmetries of the system and relation of dipole moments of particles were obtained. It appeared that combination of spatial and temporal asymmetry allows to change direction of motion, in other words at fixed other parameters average speed of photomotor depending on a temperature can change a sign. We in detail explored this question, the phase diagrams of stop points of photomotor for different parameters of the system are plotted.

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P- 5 ⇓

Continuous Approximation of Calculation of Dipole Sums for Low-Dimensional Objects

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To describe observed vibrational spectra of adsorbed monolayer calculation of components of the tensor of dipole-dipole interaction of the monolayer is needed. Such calculation implies awareness of the exact geometry of the monolayer. In some cases the calculation of geometrical parameters of arbitrary layer is hindered. However, if the parameters of the lattice of the adsorbent are known, the calculation can be executed in continuous approximation with error within 10% [1]. Such precision is enough for estimation. The idea of the continuous approximation is to substitute chain structures of dipole moments by a system of opposite-charged parallel threads.

To calculate the components of the tensor of dipole-dipole interaction, fields generated by two parallel threads are found, as well as the fields of periodic structures formed by such pairs of threads. Besides this the internal interactions between the dipoles of the regarded chain should be taken into consideration. These interactions are calculated exactly with no approximation involved. For the [2x1] structure on the square lattice with two non-equivalent molecules in the unit cell the following formulae for the components of the tensor of dipole-dipole interaction are obtained:

$$\begin{aligned} a^3\hat{D}_{11} &= \begin{pmatrix} -4\zeta(3) & 0 & 0 \\ 0 & 2\zeta(3)-\zeta(2) & 0 \\ 0 & 0 & 2\zeta(3)+\zeta(3) \end{pmatrix}, \\ a^3\hat{D}_{12} &= \begin{pmatrix} 0 & 0 & 0 \\ 0 & -3\zeta(2) & 0 \\ 0 & 0 & 3\zeta(2) \end{pmatrix}; \quad \zeta(k)=\textstyle\sum_{n=1}^{\infty} n^{-k}, \end{aligned} \tag{9}$$

where $\zeta(k)$ – Riemann zeta function, a lattice constant, $\hat{D}_{11}$ $\hat{D}_{12}$ - dipole tensors of the monolayer, describing interactions with equivalent and non-equivalent molecules of the layer respectively.

The eigenvalues of the tensor of dipole interaction for CO/NaCl (100) calculated by the formulae (1) show less than 10% discrepancy with the result of exact calculation carried out by the authors earlier [2]. It indicates that the continuous approximation in use is correct.

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P- 6 ⇓

Modeling of lIght Scattering of Scatter Pattern Samples Based on Mie Theory

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For effective use of modern devices, including optical, they occasionally need to be calibrated. To do that patterns are often used. Cause their main characteristics were measured with definite accuracy. In colorimetry such system of standards is used. But its use is limited by 4 standardized schemes of scattering measurements, which cant give full information about general scattering properties of pattern samples. For enhancement of their use it is desired to describe theoretically their scattering indecatrix by equation with small parameters quantity. To analyze possibility of Mi theory usage for scattering parameters description we used atomic force microscope to study structure of two working surfaces, polished and rough, of sample made of glass MS-20. According to obtained data we calculated correlation radius of both surfaces. With the help of program designed in NASA (method described in book which can be found by address http://www.giss.nasa.gov/ crmim/books.html), which basing on Mi theory and transport theory can calculate scattering indecatrix by known particle size distribution of scattering surface, we obtained scattering indecatrix for certain illumination angles. Calculated data was compare with experimental data gained earlier with goniophotometr.

Structure Properties, Phonon Raman Spectra and Optical Properties of Nanocrystalline Mixed Oxides TiO_2/MnO

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The composition of binary oxides promotes new physical and chemical properties depend on the synthesis procedure. The couple TiO_2/MnO seems to present interesting optical, catalytic and ptotocatalytic properties, as well as it may be perspective material for solar energy conversion. The mixed oxides TiO_2/MnO with different Mn content (235 at.%) have been prepared by chemical precipitation of manganese hydroxide on polycrystalline TiO_2 particles (rutile, anatase) with thermal processing at different temperatures 300, 850 900 and 1000C. The characterization of the structure and surface properties of the samples was performed by FT-IR and FT-Raman spectroscopy using ISF-88 FT-IR spectrometer (Bruker), X-ray and X-ray-fluorescent analysis. UV-VIS absorption spectra of mixed TiO_2/MnOsamples were measured in the range of wavelengths 250-700 nm. Spectra were measured using the standard deuterium lamps and portable PC-operated CCD-based multichannel optical spectra analyzer SL40 (grating 600 l/mm, blaze 350 nm, 3648-pixel TCD1304AP linear sensor, spectral resolution 0.3 nm).

According to X-ray data, synthesized mixed oxides are polydisperse compounds of different composition. It was shown that the samples calcined at 300 and 850 contain TiO_2 and Mn_2O_3oxides, while the high-temperature samples (heated up to 900 and 1000) contain also $MnTiO_3$in their structure. The mean size of $Mn_2O_3$and $MnTiO_3$ crystallites was determined and was shown to be 2560 and 30-70nm, correspondingly.

From the UV-VIS absorption spectra of mixed TiO_2/MnOsamples, it was found that the absorption edge shifts significantly to longer wavelength comparing with pure TiO_2, which is due to decrease the optical band gap E_g. The derived E_g of the samples with Mn content of 15at.% is 2.4 eV which is in good agreement with [1]. The red shift of E_g can be interpreted as mainly due to the *sp-d* exchange interaction between the conduction band electrons and the localized *d*-electrons of the Mn ions substituting Ti ions [2].

In FT-IR absorption spectra of TiO_2/MnOsamples, some broadening and shift of main absorption bands related to TiO_2 are observed. In addition, several new bands are registered centered at 200, 319, 342, 527, 659, 682, as well as 1078, and 1140cm^1 characteristic of new structure phases and several types of surface defects, e.g. terminal Ti=O, TiO or Mn=O bonds. A broad absorption band ranging from 4000 to1000cm^{-1} is also observed, which may result from free charge carriers (electrons and holes) generated due to IR light absorption by shallow traps in the conduction band caused by polyphase structure of the oxide samples. From the width of Raman lines centered at 145cm^1 (anatase) and 446cm^1 (rutile), a stoichiometric Ti/O ratio is evaluated. It is shown that the number of oxygen vacancies in TiO_2/MnO binary oxides increases comparing with initial TiO_2, moreover, the manganese ions hinder anatase-to-rutile phase transition.

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Optical Constants Spectra of CdTe Films

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Thin CdTe films, deposited on the monocrystalline Si and Cd_xTe(x=0,2) substrates were studied.

Cadmium telluride films were obtained by the hot wall epitaxy. Before loading into the setting substrates were chemically polished in HF acid for oxide and contaminations removing. Formation of CdTe films was conducted in a high vacuum $\approx 10^{-7}$Torr. For achieving conditions of film growth, that would be maximally approximated to the balanced conditions, evaporation is conducted in the quasiclosed area formed by the source, wall and substrate, that are keep up at different temperature. Values of the parameters, that defined growth conditions of thin CdTe films are the next: $T_{source} = 380°C$, $T_{wall} = 400°C$, $T_{substrate} = 50 \div 80°C$. Time of evaporation were varied for obtaining films with different thickness. Nominal thicknesses of CdTe epitaxial films were obtained by continuous growth of thin layer during the evaporation time, that was 6, 8, 10 and 14 minutes.

The ellipsometric investigations were conducted wave length of visible area of spectra at the nonstandard photometric ellipsometer at the fixed angle of incident $\varphi = 65°$. Sounding light ray fell on the areas of investigated film with different interference coloring (up to 7 areas), that is with different film thickness in the area of sounding.

Optical constants, reflective index n_2 and index of absorption κ_2, and film thickness d_2 were calculated from the results of ellipsometric measurements using the package of ellipsometric programs Ellipsometric calculator.

The most impress fact is fundamental change of optical spectra that appears with the increasing of deposition time. This effect is observed on the films deposited both on the Si and CdHgTe substrates. It was detected, that maximum, which appears on the spectral curve in the studied spectrum area, moves to the long wave area of the spectrum with the film thickness increasing. According to this refractive index increase at all wave length, where measurements were conducted. Features of optical constants spectra moves to the long wave area of the spectrum with the increasing of deposition time and with film thickness increasing correspondingly. In particular, refractive index maximum, that is observed at 400nm for monocrystalline CdTe, moves approximately to the 550 nm in the case of film thickness of 130 nm. According to this absorption is increasing at the whole studied area of the spectrum.

Change of the energy band structure could be the reason of the studied optical parameters changes. In the area of presented investigation optical spectra are stipulated by the electron transition from the valence band, that is splited by the spin-orbit interaction, into the lower conduction band. These transitions are achieving at different points and directions of Brillouin zone, and formate the crystal fundamental absorption zone. The energy band structure reconstructs with the increasing of deposition time and with corresponded film thickness increasing, that is concerned with the possible changes of film structure.

7 BIOMOLECULES AND POLYMERS

O- 1 ⇓

Peculiarity of Free Poly(rU) Hybridization with Poly(rA) Adsorbed to the Carbon Nanotube Surface

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Hybridization between two complementary single-stranded DNA is a main recognition process on which a genosensor is based. The development of sensitive and cheap DNA sensors with miniaturized analytical systems is one of the main problems in biosensoring which can be solved using carbon nanotubes. The first step in this direction is to ascertain a possibility of DNA hybridization on the nanotube surface.

In this work we report results of investigation on adsorption of synthetic polyribonucleotides (poly(rA)) on the single-walled carbon nanotube surface in aqueous suspension and its hybridization with a free complementary strand of poly(rU), employing NIR luminescence, UV absorption spectroscopy, atom force microscopy (AFM) and computer modeling. After mixing of these two components, the double-stranded polymer is formed the appearance of which is confirmed with the characteristic S-like form of its melting curve (the dependences of UV light absorption of polymers on the temperature in the range 20-900 °C). However, the melting temperature of this polymer is decreased in comparison with that of the free poly(rA)·poly(rU). This result indicates that poly(rU) hybridization with poly(rA) adsorbed to the SWNT surface occurs with defects along the whole polymers length because of the essential π-π stacking interaction between nitrogen bases and the nanotube surface, which hinders the usual hybridization process. Computer modeling demonstrates different possible structures of hybridized polymers on the nanotube surface and confirms the defect hybridization on the nanotube surface. Hybridization of polynucleotides induces aggregation of nanotubes. At hybridizing free poly(rU) with two complementary poly(rA) adsorbed to different individual tubes local cross-linking can occur between them. Nanotubes aggregation is accompanied with light scattering and can be observed by AFM. The size of the assembly increases with time, and then this process results in nanotubes precipitation. This work was partially supported by Grant 4918 of the Science and Technology Center in Ukraine.

O- 2 ⇓

The Effect of Noble Metal Atoms on The Spectral Properties of the Polynucleotides

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It is known the incorporation of the heavy atom into the pi-electron containing molecular systems leads to the changes in photochemical and photophysical properties of pi-electron containing polymer macromolecules. The same processes take place in the vitally important biopolymer macromolecules - the nucleic acids RNA and DNA that play the main role in the transfer, storage and realization of the genetic information. In the present work the investigation results of the dynamics of electronic excitations, the nature of the emitting centers and the effect of noble metals atoms (Pt) incorporation in the nucleic acids macromolecules are presented. The optical absorption, fluorescence and phosphorescence of the DNA and the nucleic-acid-platinum complexes (DNA-Pt) that are used for anticancer chemitherapy were examined. It is shown the phosphorescence of the DNA is connected with AT-sequences are the traps for migrating triplet excitations in the DNA. The effect of Pt centers on the spectral properties and electronic processes in the DNA was studied. Also the optical absorption of the samples of the DNA and DNA-Pt complexes under irradiation by UV-light were studied. The conclusions concerning the influence of Pt-atoms on the DNA photostability were made.

O- 3 ⇓

Hydration of Oxyethylated Derivatives of Glycerol

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Nowadays, oxyethylated derivatives of glycerol are considered as promising cryoprotectants for low-temperature preservation of biological objects. There is a strong correlation between cryoprotecting ability and hydration ability of a compound since formation of hydrogen bonds near a cryoprotectant considerably decreases mobility of water molecules and therefore prevents formation of ice crystals causing damage and death of biological cells. In the present work, hydration of oxyethylated glycerol (OEG) of polymerization degree n = 5, 25 and 30 was studied by IR-spectroscopy. IR-spectra of OEG solutions of different concentrations were recorded using spectrophotometer UR-20 (GDR, Carl Zeiss). Formation of hydrogen bonds between ether groups of OEG and water was observed in the form of low-frequency shift of the absorption band of asymmetric stretching vibrations of the ether groups (1100 cm1) when water content in the samples increased. The maximal shift of the wavenumber indicated completion of hydration of the ether groups. We showed that the other type of polar groups of an OEG molecule hydroxyl groups is hydrated earlier than the ether groups. Therefore completion of hydration of the ether groups of an OEG molecule corresponds to completion of hydration of the whole OEG molecule. According to the experimental results, about 20 water molecules bind to an OEGn=5 molecule, about 75 water molecules bind to an OEGn=25 molecule and about 90 water molecules bind to an OEGn=30 molecule. Each element of the polymeric chain can bind to about 3 water molecules. Thus OEG molecules have sufficiently high hydration ability that explains the mechanism of OEG cryoprotective activity.

Excited State Relaxation in Polyspirobifluorene-co-Benzothiadiazole Films

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Investigations of photoinduced processes in polymers helped to develop a picture of electronic processes in these materials. However, over the past decade studies on photophysics of polymers have mainly focused on *homo*-polymers such as poly(phenylene-vinylene)s or polyfluorene. Current state-of-the-art materials, however, are often *co*-polymers with four or more chemically different subunits. Each of the units carries one or more functionalities ranging from enhancing the solubility, the suppression of aggregation, to charge transport, recombination and light emission. It turned out that *co*-polymers based on fluorene are suitable as emitters to cover the entire visible spectrum in OLED or lasing applications. Mixtures (blends) of electron and hole transporting fluorene *co*-polymers are efficient as charge generation and transport layers in bulk heterojunction photovoltaic devices. To increase the thermal and electrical stability of polyfluorenes the introduction of a spiro linked fluorene has proven to be successful.

Here we present investigations of the excited state dynamics in poly(spirobifluorene-*co*-benzathiadiazol) (PSF-BT) thins films.
The fluorescence in PSF-BT is characterized by an unusual long lifetime with non-trivial decay characteristics. We investigate the temperature dependence of the fluorescence decay and transient absorption kinetics to delineate a picture of the excited state kinetics. To shine light on the influence of the conjugated spiro-fluorene we compare our data to the data for well-known poly(fluorene-*co*-benzathiadiazol. The experimental results and their comparison with the similar data obtained for poly(fluorene-*co*-benzathiadiazol) show that the long-lived excited state with reduced transition to the ground state dipole moment is formed on a subpicosecond time scale due to the exciton localization on a polymer backbone and spirobifuorene side group. Excited state stabilization reduces the transition dipole moment still further causing fluorescence relaxation on

a nanosecond time scale faster than the excited state relaxation. We conclude that the excited state properties are heavily dependent on the nature of the substituents. This is partly due to a higher internal charge transfer character of the excited state compared with a *homo*-polymer or *co*-polymer without conjugated side-groups.

O- 5 ⇓

Triplet Excitation Dynamics in Triplet-Emitter Containing Semiconducting Conjugated Polymers

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Organic light-emitting diodes (OLEDs) have been extensively investigated for full-color plat-panel display applications and illumination light sources because of their merits of high luminance, low drive voltage, and variety of emission colors. Internal quantum efficiency of electro-fluorescence OLEDs is limited to be around 25% according to simple spin statistics. In order to overcome this efficiency limit of fluorescent OLEDs, phosphorescent (triplet) emitters doped into host material have been used. Triplet emitters are low-molecular weight phosphorescent dye molecules incorporating a heavy metal atom with strong spinorbit cou-pling that mixed singlet and triplet states. The radiative decay of triplet states becomes al-lowed and the efficiency of intersystem crossing is also enhanced. As result, the lowest triplet state is efficiently populated and produces light emission with large quantum yield. Triplet emitters in both small organic molecule hosts and polymer hosts allow for harvesting singlet and triplet excitons and, therefore, internal quantum efficiency of the OLED devices can be greatly enhanced approaching 100%.

In the present work [1] the phosphorescent materials consisting of the red triplet-emitting iridium complex Btp2Ir(acac) doped into poly(2-(6-cyano-6-methyl)-heptyloxy-1,4-phenylene) (CNPPP) and polystyrene (PS) host matrices, as well as frozen diluted solution of Btp2Ir(acac) were characterized by time-resolved photoluminescence techniques. The excitation intensity dependence of the phosphorescence (Ph) emission and the Ph decay kinetics measurements in Btp2Ir(acac) (1wt.%) doped CNPPP films reveled that the triplet-triplet an-nihilation inevitably occurs even at a moderate (about 50 $/cm^2$ x pulse) excitation intensi-ties due to the annihilation with movable host triplets. It was also found that oxygen has a profound effect on the apparent lifetime of Btp2Ir(acac) in the doped polymer films at rela-tively large Btp2Ir(acac) concentration (ca. 10 wt%) even in inert PS host. The latter evi-dences on triplet energy migration occurring through the triplet-emitter manifold, that was further supported by the observation of the spectral diffusion effect at such doping level. Elimination of the oxygen by the film encapsulation does prevent the Btp2Ir(acac) triplet quenching.

Further, phosphorescence and delayed fluorescence of polyfluorene polymer films doped with cyclooctatetraene (COT) and anthracene were investigated by time-resolved photolumi-nescence measurements. Occurrence of an anomalous nonvertical triplet energy transfer in solid conjugated polymer films is demonstrated for the first time [2] employing the nonverti-cal COT triplet acceptor, which appears to behave not much different from conventional vertical triplet acceptors like anthracene. Both dopant molecules are found to quench effi-ciently host phosphorescence without affecting the host fluorescence of the polymer owing to the large singlet-triplet (S1-T1) splitting of these molecules. This S1-T1 splitting is exception-ally large in COT due to its low-lying relaxed triplet state capable of accepting host triplet excitations. In contrast to anthracene, the triplet lifetime of COT molecules is reasonably short, making a fast deactivation of triplet excitations possible. This suggests that nonvertical triplet scavengers might be promising candidates for quenching of host triplet excitations in future electrically-pumped fluorescence organic lasers, which suffer from excessive triplet state losses.

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FTIR Spectrometry on γ-irradiated Polytetrafluoroethylene

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Radiation-chemical modification of polymers is widely used for the manufacture of advanced materials with improved properties or unique combinations of characteristics. It was revealed that γ-irradiation at room temperature induces the polymer degradation process leading to a rapid fall in the molecular mass. It was also found that irradiation of the polymer in the molten state at 360380C results in its depolymerization. Chemical transformations and alteration of properties induced by ionizing radiation in PTFE above its melting point were investigated by IR, ESR, NMR, TGA, and DSC and X-ray diffraction techniques.

The quantum-chemical investigation of tentative products of radiation-chemical transformations in PTFE under the action of radiation at a temperature higher than the melting point of the crystalline phase was carried out earlier publication [1]. The excited electronic states of fluorinated alkylpolyenes of F_3C-$(CF{=}CF)_n$-CF_3 *(n=*1-7), the same compounds with CFO terminal groups, and the dimers of monomer fragments containing two and more conjugated double bonds have been calculated.

In the present work partial degradation of samples of polytetrafluoroethylene which has absorption and luminescence in the visible region of spectra caused by γ-irradiation were investigated by using attenuated total reflection (ATR) and transmission IR. The quantum-chemical calculations of modeling fragments chains of fluorocarbon molecules were performed and were used to interpretate the experimental data about molecular structure.

We studied the influence of the γ-radiation dose and atmospheric conditions on the structure γ-irradiation produces COF groups with a band at 1885 cm^{-1} in the transmission spectra. The presence of terminal $CF{=}CF_2$ and COF groups in chain is characterized by the presence of bands at 1785 and 1885 cm^{-1}, respectively, in the IR spectrum of PTFE. The IR spectra of PTFE are sensitive to the formation of defects related to emerging of branching CF_3 groups in side chains of the PTFE structure. The presence of branching -CF_3 groups in a chain is characterized by the band at 986 cm^{-1} in the PTFE IR spectra. In case of branches formation in chains, the sensitivities of vibrations C=C and C=O in olefin and carbonyl groups depend on the place of branching, and the frequency of $CF=CF_2$ vibrations can change at their close location.

The quantum-chemical calculation of possible centers of absorption and luminescence spectra is done, taking into account the reactions of radicals formation in the process of irradiation. Cyclic connections containing three attended double by connections take in the visible region of spectra and can determine colouring of the radiation-exposed polymer. Bands of absorption in IR regions at 982-986 cm^{-1} were delivered due to vibrations of cycle is perfluorocyclobutyl and perfluorocyclopentyl. Intensive bands in the spectra at 900-990 cm-1 of perfluorocyclic structure located at 985, 990, 965 and 980 cm^{-1} for perfluorocyclohexane, perfluorocyclopentane, perfluorocyclobutane, and perfluorocyclobutene accordingly. These bands behave to vibrations of ring in cyclic molecules.

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Transmittance of Powerful Laser Pulses in Polymers Doped with Carbon Microparticles

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The interaction of high-intensity laser radiation with light-absorbing microparticles (carbon) is well investigated in gases, as well as in aqueous suspensions.

The basic physical effect at the laser irradiation of light-absorbing microparticles both in gases and in condensed matter is their heating up to high temperatures of approximately 4000 K. Thermal radiation of such microparticles (laser-induced incandescence, LII) is clearly visible. In aqueous carbon black suspensions (CBS) LII is accompanied by the phenomenon of optical limiting (OL), which includes the significant decrease of optical transmittance with the increase of laser power. The main application of optical limiting effect in CBS is the protection of optical devices (for example, photodetectors) against accidental overshoot by pulsed laser radiation.

In this work, we investigate optical limiting of carbon suspensions in high-viscosity matrixes: synthetic resin (epoxy resin) and water-soluble gel (gelatin gel). The experiments were performed with the dependence of optical transmittance on the laser irradiation dose. A Q-switched YAG:Nd^{3+} laser (wavelength 1.064 μm, pulse width 25 ns, power density 100 MW/cm^2) was used. Besides, a pump-probe technique with a c.w. He-Ne laser beam was also used for the investigation of optical transmittance kinetics.

The experiments reveal significant differences in the processes and consequences of interaction of laser radiation with carbon in aqueous and non-aqueous matrixes. A model is proposed which explains the interaction of the investigated suspensions with powerful pulsed laser radiation. While in aqueous suspensions the high local temperatures in the vicinity of microparticles cause the evaporation of water, in the synthetic resins the main mechanism is the pyrolysis (thermal decomposition) of oligomers around the overheated carbon particle. The gaseous products of pyrolysis form gas bubbles and the condensed products of pyrolysis form carbonized shells around the particles.

Spectral Properties of Furosemide

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Furosemide (chemical formula $C_{12}H_{11}ClN_2O_5\mathrm{S}$) is 5-aminosulfonyl-4-chloro-2-furanylmethyl acid and is used widely as an effective diuretic in the treatment of edematous states caused by cardiac and renal failure, hypertension, congestive heart failure and cirrhosis of liver.

The work presents a study of spectral properties of furosemide solutions (dissolved in distilled water, etanol, solvents with different pH indices) in order to elucidate the mechanism of light absorption and emission as well as the electron energy structure of furosemide molecule. Investigated were the spectra of absorption, fluorescence, fluorescence excitation of furosemide dissolved in the abovementioned solvents in different concetrations. The spectra were found to be dependent on the pH index of solvent. The solutions were also checked for optical activity.

The electron energy spectrum was calculated with the help of the LCAO method using the HyperChem computer propram. A satisfactory agreement was obtained between the experimentally determined position of electron energy levels and the results of calculations.

P- 4 ⇓

Determining Thermodynamic Parameters Mg^{2+}, Ni^{2+} AND Cd^{2+} Ion Binding With Single-, Double- and Three-Stranded Polynucleotides Containing Adenine and Uracil

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Interest in studies on the dependence of polynucleotide conformational states on metal (Mt) ion concentrations and temperature is generated with ecological problems and with a possibility of polynucleotide metal complexes use in therapy (as therapeutic agents). Binding constants (K) and stoichiometry (n) of the complexes are main thermodynamic parameters conditioning the concentration range of stabilities of Mt ion-nucleic acids complexes.

By phase diagrams of polyU·polyA·polyU (A2U) complexes with Mg^{2+} [1], Ni^{2+} [2] and Cd^{2+} [3] ions and by the clip theory [1], K and n values were calculated for three-, double- and single-stranded polynucleotides consisting of adenine and uracile, with these ions. The data obtained permitted to ascertain the physical nature of different effects of the above ions on temperature of 2(polyA·polyU) (AU)→A2U+polyA transition (2→3 transition) $(Tm)_{23}$, observed in phase diagrams of these ion complexes with AU. It is shown that widening of the AU existence region in the presence of large Ni^{2+} concentrations is caused with the fact that the difference between association constants of these ions with AU and polyA is larger than that one between association constants of these ions with A2U and AU. As a result, opposite relations of differences in binding constants of Mg^{2+} ions and these polynucleotides lead to $(Tm)_{23}$ lowering. As Mg^{2+} ions, Cd^{2+} lower $(Tm)_{23}$. But, unlike the case with magnesium, such a decrease is conditioned with the strong interaction of Cd^{2+} ions with single-stranded polyA bases.

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P- 5 ⇓

Fulerene Containing Three-Particle Nanosystems for Medicine Applications

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The nanosystems containing SiO_2 nanoparticles with covalent bounded fullerene molecules attached by gold nanoparticles have been designed and synthesized.

The aim of such nanodevices is to penetrate to cancer cell (due to SiO_2 nanoparticles) to generate excited states of the molecular oxygen that have to destroy the cell (due to fullerene groups). The gold nanoparticles attached to SiO_2 nanoparticle have to increase oscillated force of fullerene species. The functionality of such systems and their characterization can be realized by spectroscopic methods.

Another three-particle nanosystem consists of SiO_2 nanoparticle, fullerene and fluorescein species. The role of fluorescein - to mark with he help of intensive green fluorescence the penetration of mentioned above system into the cell.

The absorption, fluorescence and Raman scattering have been applied to study the structure and functionality of these nanocomplexes.

The phototoxic effect of these nanosystems on oncotransformed T-lymphocytes (jurkat cell line), but not on normal T-lymphocytes (isolated from Wistar rat thymus) have been demonstrated.

P- 6 ⇓

The Peculiarities of the DNA and RNA Luminescence

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The brief review of the DNA and RNA optical properties studies together with recent results on this topic of the authors team are presented.

The results on optical absorption, fluorescence, phosphorescence of the pure and doped by number of dyes DNA and RNA were examined. The obtained results allowed us to evaluate the positions of DNA and RNA electronic energy levels, to suggest the nature of the electronic excitations traps. The errors in the determination of the positions of the polynucleotides electronic triplet levels were analyzed. It was shown that namely the position of the lowest triplet levels for DNA and RNA (belong to theadenosine base) determines the phenomena of the self-protection of these vitally important biologic macromolecules.

The results of the investigation of the singlet and triplet excitation energy transfer in DNA macromolecules were analyzed. The data obtained proved that mobile singlet excitations (S-exciton) spread on the short distances that corresponds several base pairs; the triplet excitons spreading way correspond to 18-20 base pair length along the DNA. Due to triplet excitons intra-DNA migration and their annihilation the delayed fluorescence is observed similar to manifestation of these processes in synthetic macromolecules.

Some applied problems connected with polynucleotide detection and imaging, the spectral manifestation of the DNA and RNA interactions with other biological molecules were examined and discussed.

P- 7 ⇓

Spectroscopic Study of Pheophorbide-*a* Methyl Ether Binding to Synthetic Polynucleotides and DNA

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Binding of the pheophorbide-*a* methyl ether (Mepheo-*a*) to the synthetic double-stranded poly(A)·poly(U), the poly(G)·poly(C) polynucleotides, four-stranded poly(G), and native DNA was studied by methods of absorption and polarized fluorescent spectroscopy. Measurements were carried out in aqueous buffered solutions pH6.9 of low ionic strength (2 mM Na^+) in a wide range of phosphate-to-dye molar ratios (P/D). Absorption and fluorescent characteristics of complexes formed by the dye with the biopolymers were determined. It is established that binding of neutral Mepheo-*a* to four-stranded poly(G) is accompanied by significant spectral transformations, namely, by dye absorption hypochromism, bathochromic shift of Soret absorption band (~26 nm), bathochromic shift of fluorescence band maximum (~9 nm) and 50-fold increase of dye fluorescence intensity. Unlike that, Mepheo-*a* binding to double-stranded poly(A)·poly(U), poly(G)·poly(C) polynucleotides and to calf thymus DNA is accompanied by insignificant spectral shifts of absorption and fluorescence bands, as well as by no more than 4-fold rise of fluorescence intensity. Observed substantial spectral changes and the high value of fluorescence polarization degree (0.26) evidence the intercalation of dye chromophore to four-stranded polynucleotide structure. Insignificant increase of the dye fluorescence polarization degree (0.12) and weaker spectral transformations point to another binding mode, namely, the incorporation of MePheo-*a* to a groove of the double helix, presumably, in the dimeric form. Since binding of MePheo-*a* to four-stranded poly(G) polynucleotide induces substantial changes in fluorescent characteristics of the dye, this derivative is promising as a fluorescent probe for monitoring the G-quadruplex structure.

Spectroscopic Features of Interaction of Azanucleoside with Water and Organic Solvents

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We have compared raman spectra of anomalous nucleoside 6-azacytidine (6-azac), cytidine and cytosine in different solutions in order to get spectroscopic features of their interaction with solvents. The close similarity of raman spectra of 6-azac in crystalline form and dissolved in different solvents in the region from 500 to 1800 cm-1 allows us to assume that parameters of intramolecular modes in crystal and in solutions are approximately the same but depend on solvent. After dissolving of 6-azac in h2o all raman peaks in above region experience low frequency shift with respect to their position in crystalline state while after dissolving in d2o some peaks manifest high frequency shifts with respect to their position in water solution. Similar behavior of raman spectra of canonical nucleoside cytidine and its related nucleobase cytosine was observed [1]. These shifts apparently are caused by interaction between nucleoside and solvent due to h-bonds particularly so called improper hydrogen bonding as was recently reported for raman spectra of methanol in water solutions [2] but in high frequency shifts in d2o solutions also contribute dueterated intramolecular h-bonds of nucleosides themselves. After dissolving of cytidine in dmso we observed both shifts of raman peaks of cytidine as well as dmso itself that may be regarded as spectroscopic features of their interaction. We suppose that analogous shifts of solvent peaks in water solutions are not observable through their large width as compared with dmso. Raman spectra of 6-azac after adding it to dna water solutions showed definite shifts of some 6-azac peaks as compared with 6-azac water solutions that could indicate on interaction between nucleoside and dna. Absorption spectra of 6-azac in dna water solution proved such assumption. Authors thank prof. V.yashchuk from physics department of taras shevchenko national university of kyiv for useful discussion. This work was supported by the fundamental researches state fund of the ministry of education and science of ukraine (grant #F25/137).

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P- 9 ⇓

Abnormal Decrease in Thermal Stability of Double-Stranded polyI·polyC and Native DNA in Presence of Mg^{2+} Ions

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The tasks on ascertaining molecular mechanisms of the metal ion biological action, related to ecological problems and, recently, to applications of oligo- and polynucleotide metal complexes upon creating nanoelectronic schemes [1,2], require studies on dependences of conformational states of polynucleotides of different contents on Mt^{2+} ion concentrations and temperature.

Mg^{2+} ion effects on thermal stabilities of double-stranded polyI·polyC (IC) (0.1 M Na^{+}, pH7) and salmon sperm DNA (0.015 M Na^{+}, pH8.5) were studied with thermal denaturation and UV-spectroscopy methods. The initial rise of the magnesium ion concentration ($[Mg^{2+}]$) induce the increase of their melting temperatures (T_m), resulted from ion-induced neutralization of the charge on oxygen atoms of phosphate groups. On reaching the critical $[Mg^{2+}]$ value (10^{-4} M and $2{\cdot}10^{-4}$ M for IC and DNA, respectively), T_m lowers sharply up by 8°C (for IC) and 26°C (for DNA). In both the cases the value of derivative $|\gamma| = |\frac{dT_m}{d[Mg^{2+}]}|$ is about $2{\cdot}10^5$ degree/mole that is by 2 orders larger than the $|\gamma|$ value in the region of the ion binding to polynucleotide phosphates. Such a high cooperativity of T_m decrease can be an evidence of Mg^{2+}-ion induced conformational rearrangement of polynucleotides, being realized as the phase transition. It is supposed that the transition is a result of cation-π-interactions of Mg^{2+} ions with nitrogen bases. The principle possibility of realization of the above interactions was shown for complexes of hydrated Mg^{2+} ions with duplexes of Dickerson decamers and dodecamers [3].

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Mass-Spectrometric Studies of Glycine Molecule Fragmentation

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A mass-spectrometric apparatus based on the magnetic mass-analyzer has been applied to study the single and dissociative ionization of the glycine molecule by electron impact. A primary emphasis was given to the production of ionic fragments. Such data are of specific interest in view of tracing the possible effects occurring in the live tissue under the influence of ionizing radiation accompanied by the production of slow secondary electrons, which, in turn, cause a series of structural transformations in the cells resulted in degradation of constituent elements of human body [1]. Amino acids, which glycine belongs to, are one of the basic building blocks of the live body. Moreover, recent investigations have shown that amino acids are present in various space objects (say, meteorites and/or comets), proving, thus, the idea of life ”import” to the Earth [2]. Of special interest is the fact that such molecules take an active part in constructing live cells and repairing damaged tissues, in particular, in forming antibodies, which fight against the viruses and bacteria that destroy the immune system of living organism. Experiment was carried out using a crossed-beam technique combined with mass separation of electron-molecule interaction products. The measuring procedure was fully automated using the PC control. Besides measuring the mass-spectra of the initial molecule, we have determined the energy dependences of the ionized fragment yield with the 0.3 eV energy step and the $0.2 - 0.5$ eV (FWHM) energy resolution from the threshold up to 150 eV using a specially-designed electron gun instead of the conventional one used in the original version of mass-spectrometer ion source. It has been found that the main ionic fragments of the initial $C_2H_5NO_2$ molecule are CH_4N^+, CH_3N^+ and CH_2N^+, which can be produced in various isomer states. Since the initial molecule may undergo strong fragmentation due to the thermal processes, special studies of possible temperature-induced fragmentation of the glycine molecule were carried out allowing one to choose the regime of molecular beam generation, minimizing, thus, the influence of thermal effects. Application of special least-square fitting procedure [3] enabled the absolute values of the appearance potentials for the above fragments to be found. Out data demonstrate fairly good agreement with the results of recent photoioniozation studies [4]. More detailed analysis of experimental data and possible mechanisms of electron-impact glycine molecule fragmentation will be presented at the conference.

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Structural Organization of Polyethers Oligomers Complexes with Inorganic and Organic Cations

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Synthetic polymers based on organic polyethers are widely used in pharmacology, cryoprotection, green chemistry and design of bionanodevices. Knowledge on parameters of interactions of polyethers with biomolecules is necessary for elaboration of advanced materials and technological procedures.

In the present work structural features of supramolecular complexes formed by oligomers of polyethylene glycol PEG-400 and oxyethylated glycerol derivatives OEG-5 (synthesized in the Institute for Problems of Cryobiology and Cryomedicine of NAS of Ukraine, Kharkov) with ions of alkali metals and organic cations of amino acids (proline, histidine, ornitine, valine) are studied by mass spectrometry with fast atom bombardment (FAB) and electrospray ionization (ESI) and theoretical simulation by molecular dynamics. A peculiarity of synthetic polymers is that they have no a single molecular mass (M) but are characterized by a definite molecular mass distribution (M_n). Parameters of low mass oligomers interactions with any other compound are dependent on the oligomers length (number of monomers, n).

FAB and ESI mass spectra of PEG-400 and OEG-5 contain sets of protonated M_nH^+ and cationized M_nNa^+, M_nK^+ oligomers [1]. In some earlier works [2, 3] it was shown that stabilization of the complexes of PEGs with alkali metal ions in the gas phase is achieved due to wrapping of the polymer chain around the monoatomic cation. The polymer chain accepts semi-circle configuration similar to that of crown ethers with the ether oxygens are turned to the cation. Our molecular dynamics simulation have confirmed wrapping of OEG-5 oligomers (with n¿4) around Na$^+$ and K$^+$ cations.

In the ESI mass spectra of systems containing OEG-5 and the above amino acids protonated associates of the amino acids and OEG-5 oligomers were recorded [4]. Increase of efficiency of binding of amino acids by oligomers with n¿7 was observed. We have suggested a possibility of wrapping of the OEG-5 oligomers around charged moieties of amino acids. Molecular dynamic modeling allowed us to follow a spontaneous bending of the extended oligomer chain around the charged imino group of proline amino acid being either in neutral zwitterionic or charged protonated form. The supramolecular complexes of oligomers with n=9-10 with zwitterionic proline are stabilized by four-point contacts: two bonds between hydrogens of NH_2^+ group with the ether oxygens and two bonds of COO^- group with terminal OH groups of the oligomer. Thus, stabilization of the oligomer-amino acid complexes due to wrapping of the polyether chain around an organic cation (positively charged group) is demonstrated for the first time. Modeling of OEG-5 oligomers (n = 2-12) with amino acids in various charge states is in progress.

A competition for binding of inorganic and organic cations with oligomers is observed, since there are no triple complexes of oligomers with alkali metal ions and amino acids. Obviously, addition of the third component to a compact positively charged binary complex is unfavorable. At the same time binding of COO- group of zwitterionic amino acid to the cationic alkali metal-oligomer cluster is possible; the resulting comlpex, however, is neutral and thus invisible in the mass spectra.

The results obtained can be applied to explanation of molecular mechanisms of cryoprotective function of OEG-5 oligomers which are connected with stabilization of the solvation shell of separate amino acids present in biological fluids as well as of the positively charged sites of proteins.

Experimental details: FAB mass spectra were obtained on MI-1201E magnetic sector mass spectrometer (SELMI, Sumy, Ukraine); ESI mass spectra were obtained at the Chemical Research Center of the Hungarian Academy of Sciences (Budapest) on API 2000 Triple Quadrupole MS (Applied Biosystems, Canada); molecular dynamic simulation was performed using CHARMM force field on grid-platform computer cluster of the ILTPE NAS of Ukraine.

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1H NMR Study of the Hetero-Association of Anti-Cancer Antibiotic Topotecan with Aromatic Drug Molecules

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Antitumor antibiotic Topotecan (TPT) is a camptothecin derivative and has long been known as Topoisomerase I - targeting drug exerting clinically important anticancer activity in certain types of cancer. It has also been shown that the integral biological effect of TPT can be altered by addition of another aromatic drug, such as Caffeine or Vitamin B2, which provides a way to directed regulation of biological response. The principal mechanism for such regulation suggested in recent years was solely based on the hetero-association between TPT and other aromatic drugs present in solution along with TPT. With an aim to estimate the strength of hetero-association involving TPT and its influence on binding to bioreceptor, in the present work we have studied by 1H NMR spectroscopy the hetero-association of TPT with various aromatic biologically active drugs: antibiotic Daunomycin, Proflavine and Ethidium Bromide mutagens, Caffeine, Flavine-mononucleotide (analogue of Vitamin B2) and Nicotinamide. We used concentration and temperature dependences of proton chemical shifts in order to obtain the magnitudes of equilibrium constants, thermodynamic parameters and magnetic shielding. The results of numerical analysis have enabled to build the most probable structures of 1:1 hetero-complexes, make conclusions on the contribution of principal physical factors into stabilization of the hetero-complexes. It was shown that the binding of TPT to Daunomycin and Proflavine occur with the highest affinity whereas its binding to CAF and NMD is characterized by the lowest hetero-association constant. Some consequences of this knowledge on the interceptor mechanism influencing the TPT biological effect in the presence of aromatic drugs are discussed.

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The Spectral Response of the RNA-Proteine Interaction

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The electronic (spectral) properties of the biopolymers (the DNA, RNA, oligonucleotides) in the optical range are connected with the presence of the pi-electronic groups in the nucleotide cells in their macromolecules. The biopolymers belong to the type of polymers in which the pi-electron systems are localized in separate groups and, as the result, their energy structure determined mainly by individual properties of such groups. Taking this into account the optical absorption and luminescent spectra of the biopolymers give the possibility: to evaluate the positions of the singlet and triplet energy levels of the biopolymers and to determine the centers of the electronic excitations localization in these macromolecules. To the other hand the fluorescence and phosphorescence of the biopolymers are very sensitive to interaction with other molecules, f.e. proteins. The optical absorption, fluorescence and phosphorescence spectra of the different RNA, ribonucleotides and some complex proteins were investigated. Positions of the first excited singlet and triplet electronic energy levels of the RNA bases were evaluated. Comparing the phosphorescence spectra of the RNA macromolecules and rAMP it was found: the main triplet excitations traps in the RNA are adenosine groups. The phosphorescence spectra of the RNA-, DNA- and oligonucleotide-complex-proteins show the facts of the binding of these biopolymers with complex proteins.

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The Spectral Properties of the pi-electron-containing Proteins

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Proteins are the vitally important biologic macromolecules for any living creature. The proteins are the main "constructional material" for any biological cell, defend them against bacteria and viruses, regulate the majority of chemical reactions and take part in the forming of the sequence of a gene, which is encoded in the genetic code etc. There are 3 pi-electron-containing classical proteins amino acids that take part in the photophysical processes in the proteins: tryptophan, tyrosine and phenylalanine. These compounds can be detected using optical spectroscopy methods. The optical absorption, fluorescence and phosphorescence spectra of the albumine and interpheron proteins as well as their pi-electron-containing components - amino acids (tryptophan, tyrosine and phenylalanine) were investigated. The spectral measurements were carried out at the temperatures of 4.2K and 77K. The positions of the first excited singlet and triplet electronic energy levels of the amino acids were evaluated. The centers of the electronic excitations localization in albumine and interpheron as well as singlet and triplet electronic excitation energy exchange between amino acids and oligonucleotides bind to proteins were examined.

The Spectral Properties of Carbazolecontaining Materials for Power Saving Light Sources

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The significant part of produced electrical energy is utilized in lighting. That is why the problem of design high efficient materials for effective energy saving source of light is very important.

In this paper some results of studies of the luminescence properties of carbazolecontaining compound (specially designed for electroluminescent devices production) are presented. The effect of various technology film deposition on their spectra and intensities of luminescence were discussed.

The compounds investigated are mainly chemical dimers, trimers of carbazole; two of them include five-six carbazole groups. The optical absorption, fluorescence and phosphorescence of these compounds in solutions, powders and films (obtained by two technologies of deposition) were studied at 293K and 77K.

The data obtained prove that the spectral properties of above mentioned compound in solutions are determined mainly by π-electron systems of carbazole groups and weak interaction between them. The films contrary to their (carbazole nature) absorbtion manifest the main impurity contribution in their fluorescence and phosphorescence spectra. In number of cases the influence π-electron groups each other leads to domination the phosphorescence in luminescence spectra. The effects of difference in deposition technology on spectral properties of investigated compounds as well as their applications in sensor systems and OLEDs are discussed.

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The Diffractive Elements on Basis of Self-Developing Polymeric Compositions for the Laser Spectroscopy Objectives

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Experimental methods of laser spectroscopy usually demand the probe beams with certain energy distribution by their cross-sections to be formed. Ideally this must be done independently of radiation wavelength, output energy, the time behavior of laser. This stipulates that appropriate diffractional laser radiation converters are designed. This task could be fulfilled by adapting existing methods of diffraction optics to specific conditions of laser experiment. Thus, material properties and production technology become crucial and provide for high diffractive efficiency, beam durability of an optical element, and possibility to operatively produce new elements with modified forming characteristics as well.

Based on these demands, research works to produce test series of diffractive elements were carried out. These elements provide for forming of so-called spiral laser beams with different kinds cross-sectional symmetry in them. Technology of production of such elements makes it possible to form laser beams in the range of wavelength 0.41.1 m. They keep well their forming characteristics up to energies 200300 MWt/cm^2.

The elements were produced on basis of self-developing polymeric compositions elaborated in Institute of Physics of National Academy of Science of Ukraine. The possibility of spatial phase modulation of both surface and volume of diffractional element along with keeping good quality of a specimen are the key advantages of such compositions. Thus diffractive efficiency of elements can be enhanced. It is important that the phase relief can be formed straight at the moment of specimen irradiation without additional processing. Comparatively fast production of specimens with new forming characteristics should also be noted.

Specimens were produced so that properly zoomed out amplitude transparency was projected, and exposed regions subsequently polymerized. The transparency represented a computed hologram of a beam, looking as interference bands with necessary distribution of amplitude. This pattern provided necessary distribution of energy on specimen, and thus, the required phase relief of the band. By changing degrees of blackening and exposition time, it was possible to adjust the depth and the form of phase relief in diffractional converter. The effective aperture of specimens designed to be installed in laser resonator was 35 mm. For an externally installed specimen, in a previously widened beam, the effective aperture was 510 mm. By means of interferometry in such specimens the profile of phase relief was measured in dependency of exposition, polymerization degree and other technological parameters.

Analysis of Conformational Transitions in Polynucleotide Complexes with Metal Ions, Using Equilibrium Binding Model

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Interest in studying metal complexes of nucleic acids forming both duplex and triplex structures is generated with their biological role and possibilities of application in biotechnological processes [1]. To describe in detail transitions in these complexes, more sophisticated theoretical approaches must be applied.

By the theory based on the equilibrium binding model, phase diagrams have been calculated for polynucleotide structures formed with single-stranded poly(rA) (A) and poly(rU) (U) (poly(rA)·poly(rU) (AU) and poly(rA)·2poly(rU) (A2U)) in solution with Mg^{2+}, Ni^{2+}, Cd^{2+} at 0.1M Na^{+}. Binding constants (K_A, K_U, K_{AU}, K_{A2U}) have been determined, the agreement with the early experimental results being observed. Calculations of diagrams with Mg^{2+} are shown to permit obtaining satisfactory results if steady mean constants of ion binding to polynucleotides of all the mentioned structures are used. But in the cases with Ni^{2+} and Cd^{2+}, constants dependences on ion concentrations must be taken into account, especially with high ion contents in the presence of which compaction of molecules of single-stranded poly(rA) emerges. It has been revealed that the main factor being responsible for differences in diagrams for Ni^{2+} and Cd^{2+} is a significant variation of their constants of binding to poly(rA). Temperature dependences of conformational transitions obtained by UV spectroscopy for low polymer concentrations are compared with those obtained by IR and VCD spectroscopy at high contents of these molecules and, accordingly, metal ions in solution. Differences and peculiarities conditioning irreversibility of the earlier observed disproportional AU to A2U transition are clarified.

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Interpretation of Vibrational Spectra of Polysilanes and Polygermanes

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Symmetry analysis and numerical calculations were done for polydihexylgermane and polydihexylsilane macromolecules which are characterized by zigzag structure of Ge- or Si-backbone, correspondingly. The results of analysis and calculations were used for interpretation of observed vibrational spectra.

Normal modes were constructed for model of endless zigzag chain of the same type atoms using method of symmetrical translations. Such system is described by two optical modes: longitudinal B_{2g} and transverse A_g which are allowed in Raman scattering.

Quantum-chemical calculations were done by means of Hartree-Fock method for basis 3-21G using Gaussian software for shot chains (from 2 to 15 atoms in backbone). Hexane radicals were not considered and dangling bonds were saturated by hydrogen atoms. It was found that dependence of frequency of vibrations on chain length n comes to saturation for n around 10 for most of modes. It proves that the frequencies of vibrations for endless chains have to be close to calculated ones.

Only modes A_g (460 cm^{-1} for Si-chain and 288 cm^{-1} for Ge-chain) and B_{2g} (416 cm^{-1} and 250 cm^{-1} for Si- and Ge-chain, respectively) having maximal intensity even for shot chains and obtained by symmetry analysis have to be observable for the endless chains. The rest of calculated vibrations with another symmetry type are the result of the finite chain length. Such additional oscillations are localized on the ends of a chain or they resemble the standing wave. Low frequency oscillations (54 cm^{-1}

for Si-chain and 34 cm^{-1} for Ge-chain) corresponding to constriction and stretching of chain are the acoustic longitudinal oscillations. Such kind of oscillations is observed only for shot chains as a result of the quantum size effect on phonons. Frequency of such oscillation decreases to zero with increasing of chain length because of approach to the center of Brillouin zone. The intensity of some oscillations doesnt increase monotonically with chain length. This fact is a result of the splitting of modes with similar displacement of atoms. This assertion is supported by monotonic dependence of total intensity. Such splitting takes place when the number of atoms in chain equals 8. When the chain consists of 11 atoms the non-monotony of the intensity of mode 416 cm^{-1} indicates the presence of the next detachment.

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Optical and Mass-Spectrometric Study of the Slow Electrons Interaction With Nucleic Acid Components

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Interest in experimental studies of the processes in the molecules of biological relevance by electron-impact is related, first of all, to the significance of the problem of intracellular irradiation of biological structures by secondary electrons produced in the substance in quite considerable amounts under the influence of different-type radiation. It has been shown in our preliminary experiments carried out with the heterocyclic components of the above molecules [1–3] that under electron impact different physical processes occur: i.e. molecules excitation, ionization, dissociative excitation and dissociative ionization. Physical modeling of these processes and estimation of their radiobiological consequences require knowledge of their basic characteristics – absolute ionization and excitation cross sections. Reliable data on the cross sections could be obtained only in the precise experiment, in which the role of environment is minimized. Such approach was applied in this work.

Production of positive and negative ions of nucleic acid base molecules has been studied using a crossed electron and molecular beam technique. The method developed by the authors enabled the molecular beam intensity to be measured and the electron dependences and the absolute values of the total cross sections of production of both positive and negative ions to be determined. A five-electrode electron gun with a tungsten cathode was used as an electron beam source. Measurements were carried out at the 10-7–10-metricconverterProductID6 A6 A electron beam current and the ΔE1/2˜0.3 eV (FWHM) energy spread. An electron energy scale was calibrated with respect to the resonance peak of the SF6– ion production, the position of which determined the zero point of the energy scale.

The emission (luminescence) spectra of nucleic acid bases were obtained in the wavelength range 200-600 nm, as well as the electron energy dependences of the effective excitation cross sections (excitation functions) of the molecular bands at their peaks.

Using the technique developed by the authors, the absolute cross sections of the positive and negative uracil ions formation have been determined within the 0–200 eV (positive ions) and 0.4–5.0 eV (negative ions) incident electron energy ranges. It has been found that the maximal positive ion production cross section is observed at 78 eV and reaches 7.8.10-16 cm2. Value of the ionization cross section obtained by us has a sense of the total cross section, i.e. it includes ion production cross sections for both initial molecules and its fragments. Formation of the primary molecular positive ion dominates. It has been found that the maximal negative-ion formation cross section is observed at 1.5 eV and is 4.2.10-18 cm2. Main contribution to the cross section was shown to result from the dissociative ionization cross section. It has been noted that due to the resonance mechanism of the negative uracil ions formation just at low incident electron energies considerable disorders in the nucleic acid macromolecules are probable.

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P- 20 ⇓

The Simple Physical Explanation How the Proteins of Replicative Complex Prohibit the Synthesis of DNA Base Pairs at Participation of Mutational Tautomers

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The *in vivo* replication processes of DNA have extremely high precision - on an average 10^{-9} mistakes per one nucleotide [1]. However, elementary physical mechanisms of these processes remain vague without regard to the important biological role of these processes in functioning of the cell. For the first time [2] we suggest and prove the simple physical model of Watson-Crick base pairs recognition and inhibition the biosynthesis of mispairs formed by bases in basic tautomeric form by the proteins of replicative complex from the side of major groove of DNA using modern non-empirical quantum-mechanical methods.

It is proved that only four aminoacids from 20 possible - asparaginic, glutaminic, asparagin and glutamine - can realize this function for each of four Watson-Crick pairs by the lateral radicals with the help of H-bonds. Actually such model eliminates the mistakes of biosynthesis of DN concerned with the formation of mispairs AC/CA and GT/TG by the bases in the canonic (basic) form.

In such a way emerge a natural question - as far as this approach is universal and whether it allows to inhibit the synthesis of DNA base mispairs at the participation of the mutagenic tautomers. The known approaches in particular the Poltev-Bruskov model [3] which is based on the ideology of the invariant atomic groups don't satisfy this question in this sense, as base pairs formed by the mutagenic tautomers are quasiisomorphic Watson-Crick base pairs that is to say have roughly the same spatial location of invariant atomic groups and so can't be blocked for their further biochemical insertion in the structure of DNA that is synthesized.

Various pairs of nucleotide bases formed by the rare tautomers which are quasiisomorphic Watson-Crick pairs and their complexes with the simplest models of the aminoacid residuals that belong to the proteins of the replicative complex were the studied objects.

We came to the conclusion using non-empirical quantum-mechanical calculations that suggested by us approach is universal and we proved that it can sufficiently block also the synthesis of mispars bases of DNA formed by the mutagenic tautomers of DNA.

We can confirm on the basis of our findings the assumption that complexes explored by us are not quasiisomorphic. Moreover it isn't possible to make them come back to an aforementioned state in the reasonable interval of energy. It certifies uniquely that they are incompetent from the point of view of the biochemical act of incorporation of presented pairs into the structure of the double helix of DNA.

It is done a conclusion that suggested by us physical mechanism that explain the high fidelity of the biosynthesis of DNA at elementary physical level is universall. It allows to recognize Watson-Crick nucleotide base pairs eliminating from the process of biosynthesis purine-pyrimidine mispairs as at participation bases in canonic tautomeric form so in rare filling with concrete physical sense the so-called "rule of compulsion".

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The DNA-sanguinarine Binding in an Aqueous Solution

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Sanguinarine is a benzophenanthridin biologically active alkaloid with antimicrobial, antiinflammatory, antioxidant and potentially antitumoral activities [1]. These medicinal activities are presumed owing to the sanguinarine-DNA interaction. In this report we present some spectroscopic aspects of sanguinarine binding with the Calf thymus DNA.

Absorption spectra of a sanguinarine solution consist of some complex bands in visible and UV region. If DNA is added, the intensity of absorption grows, the band maxima shift to the long-wave region up to 10 nm. The hypochromic and batochromic effects reveal in spectra and indicate the DNA-sanguinarine complex formation.

In the fluorescence spectra of sanguinarine two bands manifest themselves at 420 and 587 nm. The excitation spectra of those bands are different, which testifies to different origins of fluorescence centers. The 587-nm band is associated with the first electron level. From the analysis of obtained spectra we may assert that in our experiments both imine and alkanolamine forms of sanguinarine are present, and its characteristic peaks are at 587 and 420-nm, correspondingly. Besides, from our experiments it follows that both forms of sanguinarine interact with DNA, contrary to data [2].

The concentration dependencies of the sanguinarine-DNA absorption and fluorescence spectra were studied. The shifts of the maxima position and the intensity changes depending on P/D (the DNA base pairs/drug ratio) are measured. The shift of the fluorescence maxima increased with P/D and flattened out at P/D=8. The fluorescence intensity and the optical density have a minima at P/D~1-2. These and some other facts of the spectral behavior are indicative of certain optimal binding conditions. Analysis of these conditions was given too. According to the McGhee and Von Hippel's equation the binding parameters were calculated.

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P- 22 ⇓

A New Red Molecular Emitters for Energy Saving Light Sources

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Since the discovery of luminescence from an organic material organic compounds become attract attention as the promising material for LED. Moreover organic Pi-electron containing materials can be used in a wide spectrum of applications such as medicine, opto- and nanoelecronics, etc. One of the promising potential applications of such compounds is the creation of energy-saving luminescent light sources with emission spectrum similar to the visible range of sun emission spectrum. These light sources could be real alternative to the existing conventional illumination lamps. In our work a new luminescent dyes which emits light in red-orange region of the visible light spectrum were investigated. The absorption and luminescence spectra of these compounds solutions at ambient temperature were measured. Our measurements show a high luminescence quantum yield of the dyes that make them a promising compounds for luminescent LEDs and allows us to use it as red-orange molecular emitters for creation of white OLED.

P- 23 ⇓

Luminescence Diagnostics of Photosynthetic Processes in Algae

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The aim of the experiments was to study the behavior of the photoluminescence (PL) spectra of the green algae *Chlamydomonas actinochloris* Deason et Bold and *Chlorella vulgaris Bejer.* under microwave irradiation.

The magnetron with 2450 MHz frequency (wavelength is about 12 cm) was used as a source of radiation. Irradiation doses were 40, 85 and 140 J/g; control samples were not irradiated. The current functional state of the samples was controlled by the chlorophyll PL efficiency (two bands peaked at 685 and from 710 to 720 nm). Luminescence was excited by 488 nm argon laser with 19 mW power. The obtained PL spectra were normalized to the same number of cells to remove the effect of the influence of biomass growth on the emission efficiency.

It has been supposed that the peak within 685 to 692 nm corresponds to the chlorophyll a of photosystem II, while the band peaked form 714 to 726 nm belongs to photosystem I. Shifting the PL spectrum peaks to long waves is caused by microelements' deficiency in plants. The estimation of laser-induced PL intensities in plants at the wavelengths λII and λI, and their ratio $f = I(\lambda\mathrm{II})/I(\lambda\mathrm{I})$ allows to detect anthropogenic effects on the living organisms.

The analysis of data on the seventh day after irradiation shows that exposure of algae in a dose of 85 J/g significantly stimulates the luminescent processes compared with control, while 140 J/g, in contrast, almost completely reduces them. The intensity ratio of peaks at 685 and 720 nm in the old and young cultures of *Ch. actinochloris* changed on the 7th day after exposure. After irradiation of the old cultures at highest dose, the 685 nm peak in the PL spectrum of *Ch. actinochloris* disappeared completely, and the band at 720 nm of *Ch. vulgaris* shifted to short waves.

Significant reduction of the f ratio at high exposure levels is caused, in our opinion, disruption of the normal migration of energy in electron-transport chain of photosynthesis. Concerning the λI shift to short waves, one can say the following. It is known that the chlorophyll in the PSI reaction center can be in a state of a monomer, dimer or trimer. The last one is characterized by the most long-waved band of radiation and the highest f. Therefore, the decay of trimers or dimers under the influence of microwave radiation is accompanied by a λI shift and decrease of f, which has been observed.

P- 24 ⇓

Nonlinear Optical Properties of Nanosized Polymer Films Doped with Merocyanine Dyes

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Merocyanine dyes are one of the most promising molecules for development of composite materials with specified structure and nonlinear optical (NLO) properties [1]. They possess high polarizable π-electron systems that explains high interest in these materials for nonlinear optics.

In this work some NLO properties of polymethyl methacrylate (PMMA) films doped with merocyanine dyes with concentrations 0.1 %, 1 %, 10 % and 50 % as well as pure PMMA film are discussed. The results are compared with those for solid merocyanine film condensed on a glass substrate. The dependencies of the films NLO properties versus dye concentration gives the possibility to conclude about aggregation effects in the samples [2].

The samples of PMMA doped with merocyanine dyes were prepared using spin-coating technique. The solid organic film was prepared via method of condensing of organic compounds in vacuum. The thicknesses of the samples vary from 16 nm for 50 % to 92 nm for 0.1 % merocyanine concentration.

In this work optical and NLO properties of the samples were studied in a way of the excitation with second harmonic of Nd:YAG picosecond laser pulses (532 nm, 30 ps) and continuous wave (CW) radiation at 532 and 633 nm.

The total NLO transmittance and on-axis transmittance dependencies were measured as functions of laser intensity in both cases of pulse and continuous excitation of the samples. For all the samples both real and imaginary parts of the cubic NLO susceptibility were calculated at different excitation levels.

The main result of the investigation is that the total NLO response of PMMA doped with merocyanine dyes increases with the growth of the dye concentration in both cases for pulsed and continuous laser excitation, but at the same time the specific NLO response for the merocyanine dye decreases. We suggest that this is due to the dye molecules aggregation effect.

Also the scattering losses for all the samples were measured using CW laser radiation at 532 nm. They were found out to be 3 % for 1 % merocyanine concentration, 5.5 % for 50 % concentration, and 13 % for the condensed organic film. This indicates that the scattering losses also increase with the growth of the dye concentration in the samples.

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P- 25 ⇓

Modulation of indolo[3,2-b] Carbazole-Based Polymer Fluorescence by Applied Voltage

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Electric field induced photoluminescence quenching is a well known phenomenon widely used for the investigation of the charge carrier generation in organic materials. There are several processes, which may cause fluorescence intensity variations under applied electric field. These processes may influence operation of optoelectronic devices, organic light emitting diodes, solar cells and polymer lasers. Main functions of organic semiconductors are related to their ability to transport and interconvert electrical and light energy.

Here we report our optical and electrical studies of a new class of semiconductors. For our investigation we select a new indolo[3,2-*b*]carbazole-based polymer. The indolo[3,2-*b*]carbazole-based derivatives show good hole-transport properties and are environmentally stable. We investigated voltage induced fluorescence changes of the polymer material sandwiched between ITO and aluminium electrodes. Both fluorescence quenching and enhancement has been observed depending on the voltage direction and excitation intensity. Fluorescence decay kinetics showed that the fluorescence variation was caused by the changes of its life time.

Several mechanisms of the fluorescence quenching may take place in polymeric materials. They may be separated into three main groups: a) fluorescence quenching by the filed stimulated exciton splitting into charge pairs and b) fluorescence quenching by injected or generated charge carriers and c) the fluorescence intensity variation due to the Stokes shift of the material absorption band causing variation of the sample absorbance at the excitation wavelength.

Our experiment results show that the main effect causing the fluorescence variations is the fluorescence quenching by the mobile and trapped charge carriers. Numerical modelling of the experimental results show that the electric current caused by the carrier injection and photogeneration cause occupation of carrier trap states, while electric field also causes release of carriers from traps. Common action of both effects causes complex fluorescence dependence on applied voltage.

P- 26 ⇓

UV and X-Ray Irradiation Influence on the Fibrillar Biopolymer Luminescence

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UV and X-Ray irradiation influence on the fibrillar biopolymer (human hair) was investigated by the means of the photo - and X-ray luminescence. It was found that the long term exposure to the UV radiation effectively affect on fibrillar biopolymers regardless of the melanin content. Photoluminescence intensity monotonous decrease (of about 50 percent) for the 5 Hours exposure to radiation with the further on restoration of the intencity after the 16 hours period without the radiation was observed for the fibrillar biopolymers with now melanin (grey hair). As for the melanin saturated fibrillar biopolymers (dark blond hair) the stable glow was observed for the 5 hours exposure to radiation with the further on increase (for 25 per cent) after the 16 hours period without the radiation. The long term UV-irradiation haven't influenced the form of the photo luminescence spectra that is represented by a number of glow lines. The X-ray luminescence spectra were registered for the fibrillar biopolymers under the X-ray irradiation but there were no change in the intensity and form of the X-ray luminescence spectra of fibrillar biopolymers (regardless of the melanin content) even for the doses highly exceeding the allowed for the human body. The form and intensity of the photo luminescence spectra registered before and after the X-ray irradiation haven't changed either. The melanin presence in the fibrillar biopolymers doesn't' influence the intensity either photo or X-ray luminescence. The luminiscence intencity analysis has been made for the different samles.

Fullerene-containing Tree-particle Systems for Medical Application

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The nanosystems containing SiO_2 nanoparticles with covalent bounded fullerene molecules attached by gold nanoparticles have been designed and synthesized.

The aim of such nanodevices is to penetrate to cancer cell (due to SiO_2 nanoparticles) to generate excited states of the molecular oxygen that have to destroy the cell (due to fullerene groups). The gold nanoparticles attached to SiO_2 nanoparticle have to increase oscillated force of fullerene species. The functionality of such systems and their characterization can be realized by spectroscopic methods.

Another tree-particle nanosystem consists of SiO_2 nanoparticle, fullerene and fluorescein species. The role of fluorescein to mark with he help of intensive green fluorescence the penetration of mentioned above system into the cell.

The absorption, fluorescence and Raman scattering have been applied to study the structure and functionality of these nanocomplexes.

The phototoxic effect of these nanosystems on oncotransform T-lymphocytes (Jurkat cells, but not of normal thymocytes) have been demonstrated.

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IR Studies of Photochemical Processes in BIS-methacrylic Polymers

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Recently we disclosed excellent liquid crystal (LC) photoaligning efficiency of bis-methacrylic polymers [1]. They provide LC alignment characterized by high thermal and photo-stability, strong anchoring and controllable pretilt angle.

In the present study we are focused on photochemical transformations of bis-methacrylic polymers, which determine orientational ordering and LC alignment on the films of these compounds.

As representative of bis-methacrylic photoaligning polymers we choose poly(p-methacryloylaminophenyl methacrylate). Theoretically, three photochemical transformations in this polymer are possible: two Fries rearrangements and photocrosslinking/photopolymerization of side methacrylic groups. These reactions were studied by IR spectroscopy capable to monitor separately reactions in NH-C=O (amide group), O-C=O (ester group) and $C(CH_3)=CH_2$ (methylene group) groups during irradiation. To find positions of these groups, modeled compounds were synthesized in which one or more reactions mentioned above were excluded. The changes in FTIR spectra under ultraviolet illumination reveal an occurrence of both Fries rearrangements and a conversion of $C=CH_2$ methacrylic bonds in poly(p-methacryloylaminophenyl methacrylate).

The polarized absorption spectra measured in a UV/Vis range for all polymers suggest photoselection mechanism of photoorientational ordering [2]. Besides, all materials provide LC photoalignment. These facts allow us to conclude that all three photochemical reactions discussed contribute to LC photoalignment. However, as we checked, they differently influence photoalignment properties; while Fries rearrangement causes strong azimuthal anchoring, crosslinking reactions provide high alignment stability.

These studies were partially supported by 'Dnipro program' of French-Ukrainian scientific collaboration.

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8 METHODS AND APPLICATIONS

O- 1 ⇓

Saturated Absorption Resonances in Heteroisotope Molecular Iodine as References for Diode Laser Frequency Stabilization

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The iodine molecule is frequently used as a frequency reference for laser spectroscopic applications and laser frequency stabilization in a wide region of the optical spectrum from the green (500 nm) to the near infrared (900 nm). High frequency stability of He-Ne laser at 543 nm, 612 nm, 633 nm, 640 nm, Nd:YAG laser at 532 nm (second harmonic), Ar^+ laser at 514,5 nm is achieved by use of sub-Doppler techniques such as saturation spectroscopy for locking to an iodine molecular transitions.

The precise frequency locking onto the iodine hyperfine transitions is used now for the determination of the nuclear electric quadrupole interaction and the nuclear spin-rotation interaction parameters of iodine molecules. The$^{129}I_2$and$^{127}I^{129}I$ molecules are the attracting objects for these investigations. The very promising set of iodine transitions for laser frequency stabilization includes the wavelengths 502 nm ($^{127}I_2$R(51) 68-0), 633 nm ($^{127}I_2$ R(33) 6-3), 793 nm ($^{127}I_2$ R(92) 0-15). The additional references could be created with transitions of $^{127}I^{129}I$ molecules.

The diode lasers with external cavity are widely used now as sources of standard wavelengths for metrology, spectroscopy and interferometry with frequencies locked onto the iodine hyperfine transitions [1]. We present here the construction of a modified external-cavity diode laser based on a transmission diffraction grating in the Littman-Metcalf configuration [2] and its application for laser frequency stabilization. The photopolymer holography grating is used in laser design. The advantages of transmission grating cavity is discussed.

The absorption lines of molecular iodine $^{127}I_2$ and $^{127}I^{129}I$ are used as quantum references in red spectral region. The comparison of nonlinear resonances of both of iodine molecules parameters is presented.

The femtosecond laser based heterodyne laser spectrometer for direct measurement of optical frequencies is described. The first experimental results of optical frequencies comparison with MHz-precision are presented.

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Determination of Isothermal Compressibility of Solvent from Changes in the Absorbance of a Dye Solution Under Pressure

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Compressibility of the liquid and isothermal coefficient β_T are fundamental characteristics reflecting the change in the energy balance of the intermolecular attraction and repulsion with the pressure increase$^{[1,2]}$. $\beta_T = -(\partial V/\partial P)_T/V$ (1) Data on a change in the liquid volume determined in temperature and pressure intervals make it possible to describe the ratio of the main thermodynamic parameters $(P - V - T)$. In the present work we propose two simple methods for indirect determination of the dependence of $\Delta V/V$on P by data on the absorption of a dye solution under pressure. For this purpose it is necessary that the increase in the absorbance with the pressure increase would be caused only by an increase in the number of solvent molecules per volume unit. It was found$^{[3]}$ that with the pressure increase to 100 mpa the absorption bands undergo a small (2-3 nm), usually bathochromic shift. For purposes of the present study we chose the dye *rhodamine 6g* with a smooth maximum of the absorption band in the visible spectral region. When the pressure increases, the absorbance can change due to a change in the volume and, hence, in the concentration, and due to a change in the molar absorption coefficient. It can be checked that the molar absorption coefficient remains constant with the pressure increase only by comparison of the plots of $\Delta V/ V$ *VS.* P obtained from the data on the absorption of the dye solution under pressure and by direct precision measurements. For these measurements the special variable volume quartz cell was designed which filled up with dye solution and placed in a high pressure optical bomb disposed in the cell compartment of the spectrophotometer. The experimental results are in a good agreement with literature data of precision measurements (±1%) of compressibility of toluene and carbon tetrachloride. This work was supported by the russian foundation for basic research (Project 08-03-00219).

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O- 3 ⇓

Optical Frequency Comb as Spectroscopic Tool

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Since 1999 one of the hot topics of physics research has been the study of an optical frequency comb which is an optical spectrum comprising a set of equidistant discrete frequency components. To generate a frequency comb, a mode-locked laser can serve very well: the optical spectrum of a periodic pulse train, as generated in a mode-locked laser, consists of discrete spectral lines with an exactly constant spacing equal to the pulse repetition frequency. Nowadays, frequency combs are widely used for metrology purposes, mainly for the measurement of absolute optical frequencies [2]. A frequency comb has potential use also as spectroscopic tool, especially as a source of equidistant optical frequency components in experiments dealing with the coherent interaction of light with matter.

The quantum interference between excitation pathways is one of fundamental effects appearing in such interaction. It can eliminate the absorption at the resonant frequency of an atomic or molecular transition in gas medium, through the preparation of "dark states" that are immune to excitation. Such phenomenon, the so-called coherent population trapping (CPT) [1], can be observed in a system in which the two hyperfine components of the $S_{1/2}$ ground state of an alkali atom are coupled to a common excited state by two laser fields. If the frequency difference of the laser fields is close to the atomic hyperfine splitting ω_{12} the quantum coherence between the two hyperfine components is created, which leads to enhanced transmission of the optical fields in a narrow resonance around the difference frequency of the two optical fields. CPT resonances have recently been used for the slowing of light, storage of quantum information, magnetometry and in metrology.

To provide two optical fields with a frequency difference equal to ω_{12} one must use modulation techniques involving microwave radiation. An effective modulation of laser radiation with a few GHz modulation frequency is still a challenging problem. Let us consider the laser frequency comb overlapping with the absorption line of a three-level system and the frequency separation Δ of the comb components is chosen in such a way that $N\Delta \simeq \omega_{12}$ and N is a large integer. One can expect that there will be CPT resonances if the frequency Δ is tuned to exact two-photon resonance $\Delta = \omega_{12}/N$ [3].

We present a theoretical analysis of the CPT resonances excited by frequency comb including modelling of the short laser pulses interaction with ^{87}Rb vapour. An experimental study of the magneto-optical CPT resonances in ^{87}Rb and ^{85}Rb fluorescence, excited by the femtosecond Ti:Sa-laser radiation resonant with D_2 line has been performed too. In the experiments, the CPT resonances were detected as narrow dispersion shape features in the output of the lock-in amplifier which detects the amplitude of the first harmonic in the fluorescence signal in the presence of axial magnetic field, modulated with small amplitude at low frequency as a function of this field dc component. The experimental results show that these resonances can be detected with high signal to noise ratio, and their characteristics are well described by the developed theoretical model.

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O- 4 ⇓

Physics of Light Forces and Laser Cooling for Beginners

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Goal of the talk: understand how to use light to manipulate material objects at the microscopic level.

Observation of Daytime Atmospheric Optical Emission at 1.27 mu

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We designed the high-sensitive IR spectrometer by which register luminescence of singlet oxygen in solutions. Also we detected the band of daytime atmospheric optical emission at 1270 nm. It is known that on Earth, as well as on Mars and on Venus, on a daily side occur a photolysis of ozone as a result of which oxygen appears in excited state (singlet oxygen), which gives strong emission on a wave-length 1270 nm. We assume that intensity of this emission maybe the measure of maintenance of ozone in an overhead atmosphere.

P- 2 ⇓

Kinematic Controllability of Dipole Photomotors

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To get an insight into the kinematics of Brownian motors [1], we have considered a previously suggested dipole photomotor [2]. It operates due to a change in the molecular dipole moment which occurs on resonant laser-induced excitation of a molecule in a periodic asymmetric potential. The expression for the average motor velocity v assumes the form [3]:

$$v = \frac{\pi}{4}\frac{D}{L}\beta^3 V_1^2 V_2 \left(1-\alpha\right)^2 \left[\left(1+\alpha\right)\Phi_1\left(\xi,\delta\right) + \left(1-\alpha\right)\Phi_2\left(\xi,\delta\right)\right], \tag{1}$$

where D is the diffusion coefficient, L is the spatial period of the potential, $\beta = \left(k_{\mathrm{B}}T\right)^{-1}$ is the inverse temperature (with k_{B} denoting the Boltzmann constant and T the absolute temperature), V_1 and V_2 are the first two coefficients in the Fourier transform of the x-coordinate dependent potential energy $V\left(x\right) = V_1 \sin(2\pi x/L) + V_2 \sin(4\pi x/L)$, $\alpha \equiv \mu_-/\mu_+$ (the "+" and "-" subscripts referring to the states with the laser switched on and off), $\mu_- = \mu_0$, $\mu_+ = \left(\mu_0+\mu_1\right)/2$ (with μ_0 and μ_1 denoting respective dipole moments in the ground and excited states), $\xi \equiv \gamma\left(L/2\pi\right)^2/D$, $\gamma \equiv \gamma_+\gamma_-/\left(\gamma_+ + \gamma_-\right)$, $\delta \equiv \gamma/\gamma_-$ (with γ_+ and γ_- denoting the inverse lifetimes of the corresponding states), and the functions $\Phi_{1,2}$ are defined as follows:

$$\Phi_1\left(\xi,\delta\right) = \frac{3\xi(1+2z)}{(1+4z)^2(1+z)},\ \Phi_2\left(\xi,\delta\right) = \left(1-2\delta\right)\frac{6\xi z}{(1+4z)^2(1+z)},\ z \equiv \frac{\xi}{4\delta(1-\delta)}$$

It follows from relation (1) that the velocity direction at $\alpha > 0$ is governed solely by the spatial asymmetry of the potential energy (the sign of the component V_2). At $\alpha < 0$, a novel effect arises: the motor has stopping points at certain δ where the velocity changes its sign. The case of most interest is $\alpha = -1$ (the dipole moment fluctuates by the sign reversal); as a result, temporal asymmetry (the different state lifetimes, $\delta \neq 0.5$) is the only driving force for the directed motion.

For some selected organic compounds, with their molecular dipole moments drastically changing on excitation, kinematically interesting α values have been found by the AM1 method. Substituting them into Eq.

(1) and using the biologically relevant values of substrate and environmental parameters, we have obtained the values of the maximum average velocity which appear to be comparable to or even far exceeding those for typical protein motors (100-1000 nm/s [1]). One of the molecules under study for which the dipole moment changes on excitation both in magnitude and in sign is characterized by the negative parameter α. Thus, the corresponding photomotor, if placed under the same conditions as the other molecules (with positive α) should move with a significant velocity in the opposite direction. The examples presented show promise as dipole photomotors and demonstrate the possibility of kinematic control through varying molecular structure and instrumental parameters.

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P- 3 ⇓

Research is Maintenance of Heavy Metals in Air by Method of Absorption Analysis

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Heavy metals are threatenings the health of man and that's why maintenance them in the air basic attention is spared to that end maintenance of heavy metals is probed in vegetable tests. In the countries of the European union the bryophytess of certain sort undertake as vegetable tests, because they possess ability in a most degree to absorb in itself heavy metals [1, 2]. But in sew on to the bar, especially in city boundaries, bryophytess grow up very rarely, therefore we as vegetable tests took the leaves of poplars which also are the good absorbents of city dust, in particular, heavy metals.

The purpose of this work is research maintenance of cadmium, lead, zinc, coppers along the basic roads of city on a different delete from a route: 50, 100, 150. There was five directions that's why there was five series. Sampling was carried out along the street.

Research results show that from all of the considered metals maintenance of zinc mostly in all of the examined standards. The most high maintenance is fixed in the standards of series 3, because it is related to the casting production. The nonhomogeneous distributing of this element has such reason on different deletes from a route. The least maintenance of zinc is fixed in the standards of series 4 and 5.

Predictably, maintenance of all of the examined elements is most in the standards of series 1 and 3, that allows to draw a conclusion that air along these routes is most muddy.

Enhanceable maintenance of copper and cadmium as compared to the standards of other series is contained in the standards of series 6 and insignificantly changes as far as a delete from roads. Appeared unexpected circumstance that maintenance of heavy metals in all of standards of the probed series (2, 3, 4, 5, 6) practically does not change as far as a delete from a route. Yet more surprising is that in the standards of series 1, maintenance all and singular, examined heavy elements increased with the increase of distance from a route. More credible than all it is related to the closeness of chemical production. Nevertheless, this fact requires the detailed and careful consideration.

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The Holographic Sensor Response Depending on the Hydrogel Composition

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The holographic gauge represents hydrogel matrix on the basis of polymer in which layer are distributed nanocrystals the silver, forming a monochrom- atic mirror. This mirror reflects only light of the same wavelenght corresp- onding to distance between silver layers as the hydrogel matrix has proper - ties to bulk up and be compressed it conducts behind itself and distance change between silver layers and consequently also to change of wavelength of reflected light. Thus property of polymer to swelling directly is connec- ted with the holographic response. By introduction in structure of polymer of various sensitive groups, it is possible to change properties of a sensor control.

The sensors were prepared mainly following the protocol described early [1-4] , but the net construction and its fixing onto the plate were different as well as the technique of obtaining silver halogen nanocrystals [5-6].

The matrix represents a three-dimensional polymeric network on a basis akrilamide - (AAm) and N, N '-methylene-bis-acrylamide (BIS) as the sewing agent, with addition of sensitive copolymers such as acrylic acid (AK), N- acryloyl-3aminophenylboronic acid (AMPh), N- ϵ-methacryloyl-lysyn (Lys), 1-Vinyl-imidazol (IMI) and others.

Various sensor controls on structure were tested at titration of solution HCl(0.01N) by solution NaOH (0.1N), at change ionic strength solution NaCl to 0.3M, at studying of the response to glucose. Studying of sensor controls on influence ionic strength, has shown that introduction in what structure of polymer or the charged groups essentially influences polymer swelling and so character of this process is shown. In the course of titration of sensor con- trols, it has been revealed that the response of sensor controls (λ_{max} refle- xions) on various pH essentially changes according to pK groups entered into structure of a polymeric matrix. That is connected about change of charging structure and according to property to swelling. And increase in concentration of the added groups conducts to response increase at character preservation. At research of sensor controls of glucose, influence of concentration of the sewing agent on size of the response of a sensor control is established, non- linear dependence on concentration BIS is shown.

Studying of properties of holographic sensor controls allows to use the taught data at creation of new sensor controls, for the task it of additional pro- perties, for strengthening of the response to a target component, for achiev- ement of selective sensitivity.

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Pyroelectric Detector of Laser Radiation on The Base of Polimeric Film PVDF

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The pyroelectric crystals and pyroelectric ceramic materials are well-known objects for operation as the sensitive elements of the detectors both coherent, and incoherent radiation. The polymer PVDF is the most known material among other pyroelectric polymers as the detector of incoherent radiation. The elementary cell of this polymer contains two monomer units F_2 CH_2 and belongs to the space group Cm2m. This material is cheap and its area of ferroelectric phase extends up to the temperature 80 °C (for example, well-known ferroelectric crystal TGS has narrower similar temperature area, as its the Curie temperature TC = 49°C). All it allows to estimate this polymer as possible perspective use as sensitive element of the detector of laser radiation.

The polymeric films PVDF of company Precision Acoustics LTD (PAL) (Great Britain) have been selected as experimental research objects. These films have been preliminary stretched along one of the axes allocated in a plane of a film. It has allowed to reach higher maintenance of the ferroelectric β-phase. The films, which were used in experiments, had following sizes: a thickness 58 microns, diameter 35 mm. The aluminium electrodes have been put on films by a method of vacuum evaporation. Then films have been poled by the applied electric field with the strength $= 10^5$V/sm at temperature =85°C and the subsequent cooling to room temperatures at this field.

Experimental researches were spent as follows: the detector of radiation on the basis of film PVDF took places in the temperature sample cell and was irradiated with the Ge-Ne laser of the -113-type (the radiation wavelength λ=1,15 microns; the power P=5 mW). The continuous laser radiation was modulated by the mechanical modulator on the frequency f = 20Hz. The orientation of a laser beam which was defined by the angle ϕ in relation to a normal of a plane of a film, varied from 0° to 60°. The temperature T of a surface of a film from outside irradiations was controlled by the radiometer Fluke 576 (the accuracy of temperature measurements for the range 20 100 ° was the value ΔT = 0,1 K).

Measurements of the pyroelectric response of the detector of radiation have been fulfilled in a mode of dynamic pyroelectric effect, when the value of pyro-EMF U was defined by dependence

$$U \sim \gamma / C_V \varepsilon,$$

where γ is the pyroelectric coefficient, ε is the component of dielectric permittivity of a film along polar axis, C_V is the specific heat for constant volume.

The temperature dependences of the value of pyroelectric response U (T) and angular dependences of temperature T(ϕ) of a film on orientation of a laser beam have been obtained in the experimental results.

On the basis of the analysis of experimental results it has been shown that the detector of radiation on the basis of the PVDF-film can be used as the detector of laser radiation.

P- 6 ⇓

Holographic Glucose Sensors.

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Holographic sensors based on the hydrogels containing affinity groups sensitive to certain components of gaseous and liquid mixtures are perspective class of sensors. These sensors have the following advantages: the simple qualitative visual way of the information readout, the use simplicity, the reversibility, the wide spectrum of application, and the low coast at manufacturing. In same cases, for the semi quantitative or quantitative readout a corresponding design and reading equipment are needed. Sensor represents a thick hologram prepared in hydrogel films containing silver halogen nanocrocrystals. The sensor reflects a light of the same wavelength which was used for a hologram preparation. After the contact with an analyte, the analyte sensitive matrix changes its configuration, and the distances between layers of silver in the hologram are changed. As a result, the wavelength of a reflected light also changes.

The photosensitized silver halogen nanocrystals were synthesized in the hydrogel matrix, the matrix was immersed in water or the acetic acid (1%) solution and irradiated by the red He-Ne laser (power - 15 mW). The sensors were prepared mainly following the protocol described early [1-4] , but the net construction and its fixing onto the plate were different as well as the technique of obtaining silver halogen nanocrocrystals [5-6]. The matrix consisted of three-dimensional polymer net (N,N'-methylene-bis-acrylamide as crosslinking agent) based on the copolymers of acrylamide (AAm), N-acryloyl-3-aminophenylboronic acid (AMPh) and acrylic acid, N-ϵ-methacryloyl-lysin, 2-(dimethylamino)ethyl-methacrylate, N-acryloyl-D -2-glucosamine (NAG) as additive.

Differences in the replay of these sensors have been tested in the titration of the solution HCl (0,01 N) by NaOH (0,1 N). The wavelength reflection (λ_{max}) of these sensors agree whith pK of components in polymeric matrices, when the charge appears (or disappers) and matrices swelling (deswelling) takes place. The replay of the sensor (AAm-AMPh-NAG) pointed to the fast expansion when the pH solution approaching to pK AMPh (8,8) and slowly contraction of the polymeric matrix and at pH more 9,2 - only the expansion. These proceses agree with bindig NAG with tetrahedrical B of AMPh that to carry into effect of additional crosslinking.

The ability of boronic acids to bind glucose has long been known and sensors with the AMPh were sensitive to glucose concentrations in the solution. The wavelength reflection (λ_{max}) and the shift was influenced on the additive to polymer net and the buffer solution. The shift of λ_{max} was changed from -40 to 200 nm when glucose concentration was increased (1-16 mM).

The importance of glycemic control for the prevention of diabetes complications is well established. Future work will involve monitoring glucose in physiological fluids to access the performance of ligands in complex biological media and their suitability for incorporation into a suitable sensor format for continuous glucose monitoring in humans.

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Colorimetric Method for Measuring Wavelength Distribution of Narrow-Band Light Radiation with Digital Camera

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When working with holographic sensors [1-3], there is a problem of measuring the homogeneity of response of sensor properties over its surface. For these measurements, at the present paper we developed and applied the colorimetric method with the help of common camera. [4]. Inhomogeneity can emerge due either to inhomogeneities of the object under consideration, or to those of the sensor properties. The sensor is a thick layer hologram with width of few tens of micrometers. Its reflection spectrum has the spectral width 5-20 nm. Because of it, one suffices to use response from two color channels. As the main working camera we used 5-megapixel camera Sony F717. We have not managed to find its spectral characteristics (as well as those of many other cameras), hence, we made our own studies. Because of the constructive defect of the camera (similarly to many others), the working range turns out to be restricted by the two regions: 570-605 nm and 450-535 nm. The spectral response of camera was studied and gauged with the incandescent lamp. We constructed the characteristic function that allows one via color value of the pixel to determine wavelength of the radiation acting at this pixel. The approach is tested for image of the incandescent lamp spectrum obtained in the spectrograph with diffraction grating, and for image of the holographic sensor at the stationary state and at the transition process of dehydration of the sensitive layer in the alcohol solution. For the part of the lamp spectrum in the yellow working range of the camera the approach gives practically linear dependence of the wavelength on the coordinate and correct restoring the wavelengths of the yellow mercury spectrum doublet presented at the image. The wavelength is stable in the perpendicular direction. The standard deviation (SD) from the average over the window within the narrow slit window with width of 2 pixels and height of 50 pixels is from 0.27 till 1.35 nm depending on the wavelength. Being averaged over the whole spectral region it gives around 0.5 nm. When averaging over the whole image of the spectrum SD for this window is 0.75 nm. Within image of the hologram surface with size 3 cm at the stationary state there are around 500000 image points. A considerable part of them lies within the interval of 2 nm. Their SD from the average over the scanning window averaged over a considerable part of image is up to 0.33 nm for the scanning window containing 400 pixels. For a smaller window the value decreases to 0.16 nm for 4 pixels. The dependence on the window area is basically logarithmic. In the transition process one can observe a structure with different scales, in particular, a large scale inhomogeneity with the wavelength dispersion of 18 nm. The dependence of SD is similar to that in the stationary case, but with larger values. The SD for the 400 pixel scanning window is 14.8 nm and decreases to 0.52 for the 4 pixel window. The ratio of SD for the transition process to SD for the stationary process varies from 3.1 (4 pixels) to 4.5 (100-120 pixels). This is due to the hologram structure in the non-stationary regime. Thus, the colorimetric method is suitable for controlling inhomogeneous processes and hologram quality. The work is partly supported by the grant within the RAS Presidium program of fundamental research "Fundamental Science for Medicine"in 2007-2009.

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Adaptive Q-switching Using Absorbing Media

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The adaptive Q-switching [1] is the stepwise change from Q-factor Q_{ur} of the usual resonator (UR) to Q-factor Q_{ap} of the adaptive resonator (AR) with an intraresonator phase conjugation (PC) [2]. It is extensively used for laser resonator phase distortions compensation and energy characteristics enhancement. PC mirrors based on various types of stimulated light scattering (SLS) usually used for making such modulators in an optical range [3]. Usually, for their implementation, an nonabsorbing, medium is chosen, because an absorption worsens energy and time generation characteristics. It is valid without that fact [4], that in the SLS-modulator the reflectance region moves to a cell face. But for transparent mediums it does not influence on a Q-switching depth, is not considered, and earlier was not researched. However, generation characteristics of absorbing mediums vary considerably.

Features of the adaptive Q-switching at intraresonator SLS in absorbing mediums are considered. For the first time it is shown, that such adaptive Q-switching results not only in compensation of phase distortions, but also in compensation of absorption due to the displacement of the reflectance region. As the initial Q-factor of the laser resonator with absorption is lower, and while generating is commensurable in comparison with a case of nonabsorbing medium, such displacement allows increasing a Q-switching depth, to refine laser generation parameters.

Studies which have confirmed increase of Q-switching depth due to absorption compensation in the SLS-modulator are carried out. Time dependence changes of generated pulses, in particular their duration, in comparison with a case of nonabsorbing medium are registered.

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Sequential Photo-Bio Degradation of MCPA in the Presence of Humic Acids

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Halogenated pesticides are widely used class of chemicals. These toxicants are find out in soil and natural water. Chloroaromatic compounds are stable for microbiological degradation, that is why searching of new possibility of these compoundss degradation is still important task. Humic acids (HAs) is major component of bulk of organic matter in environmental. This compound effective absorbs the UV-radiation and can play a significant role in processes of photochemical transformation of organic compounds. Also HAs can change the rate of microbiological degradation of toxicants.

In the present work the data about phototransformation and sequential photo-biotransformation of MCPA in presence of HAs were discussed. Two sources of UV-radiation were used.

Photolysis and microbiological degradation of MCPA leads to formation of 2-methyl-4-chlorophenol (MCP) as a main product and further transformation of MCP. Phototransformation of MCP was accompanied by formation of non-chlorinated compounds including quinones. Microbiological degradation of MCP in a difference of photolysis is accompanied the cleavage of aromatic ring. Phototransformation of MCPA in presence of HA did not lead to the increasing of quantity of quinones in comparison of photolysis of pure herbicide. Microbiological degradation of MCPA was slowly in a presence of HAs.

It was shown that respiration activity of microbocenosis of active sludge (AS) in 3-7 days of cultivation was higher in the case with pre-irradiated solution of MCPA. Studying of influence of HAs shown that in presence of this compound and non-irradiated MCPA respiration of AS was more weakly than in presence only MCPA. Influence of simultaneous HAs and pre-irradiation on respiration of AS depends on used spectrum of UV-light.

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P- 10 ⇓

Ice and Water Luminscence

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Having used the method of luminescent analysis spectra of emission of ice and water tests in various sources were studied: in the Black Sea (Odessa coast) I, the Danube River (the district of Izmail) II, the Dnieper River (the district of Kiev) III, and also aqueduct water in Kiev IV and Odessa V, and also thawed Antarctic ice and distilled water. The measurements have been carried out on a spectrofluorimeter MPF-4 (Hitachi). Also, we had been selected for research samples of the Antarctic ice on the western slope of the glacier occupying the basic part of island Galindez in area of Ukrainian Antarctic station Academic Vernadsky.

The observed fluorescence is due to the dissolved impurities in the water. Their nature and concentration have an influence on the positions and intensities of the corresponding emission bands.

It has been shown that the shapes and frequencies of the bands in the fluorescence spectra of the distilled water and water obtained from Antarctic ice are similar, while they substantially differ from that for the spectra of the samples 1-V.

For the first time the luminescence of Antarctic ice (A) and ice prepared from distilled water (D) has been measured at T=4,2 K. The spectra consist of two bands: fluorescence (with a short lifetime) and phosphorescence (with a long lifetime). The emission spectrum (A) is shifted to the long-wave side on 35 nm in comparison to the spectrum (D). The mechanisms which are responsible for this emission are discussed.

The influence of the rapid cooling (strengthening) after preheating of the ice on the fluorescence spectra of the natural and distilled water, as well as melted Antarctic ice has been detected. It has been found that only in the case of Antarctic water the new emission band appears in the fluorescence spectra, while in the spectra of the other samples this band is absent. The obtained results are discussed in the framework of the model of water polymorphism and water structuring. The Antarctic ice was investigated with the aim to determine the presence of man-caused organic compounds dissolved in water.

P- 11 ⇓

Nanomembraine Microcantilever as a Spectroscopic Instrument

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The paper reports on a novel micro-calorimetric spectroscopy technique based on a micro(nano)-electro-mechanical-systems (MEMS/NEMS). It can be used for chemical and biological detection applications. A bimorphal nanomembraine micro-cantilever is used as an extremely sensitive thermal detector. The sensitivity of such a sensitive element is estimated and its optimization is discussed.

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P- 12 ⇓

Raman and Polarimetry Study of Monosaccharides Mutarotation

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Nowadays, optikal active materials widely use in allfields of our life. Optical activity of materials is given by the asymmetry of their chemical structures and strongly dependent on the conformation equilibrium, therefore, polarymetry cangiven valuable information about the spatial arrangemet of moleules in solution. We investigated monosaccharides as model objects using polarimetry and raman spectroscopy. In raman spectrum we see redistribution of intensity with time establishment of thermodinamic balance. Polarimetry displaied dependence optical activity in time,(mutarotation).namely we investigated glucose and fructose in solution with $H_2 0$, physiological and D_2O. Time constant of mutarotation in physiological in three times less then in H_2O and in 6 time less then in D_2O.

Some Problems of the Refractive Index Measurements of Thin Films Using Interference Methods

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In some papers [1, 2] the values of the refractive index (n) have been obtained using the Fabry-Perot interference method in thin crystal plates by simplified expression without a proper check of their applicability. As a result, the conditions of validity of this expression could be violated, and the dispersion curves n() would thus be uncorrected. Instead of the true curve n(), which characterizes the change in the phase velocity of light, one may obtain the dependence of the group velocity of a wave packet. The answer on the question, how to obtain the correct dispersion curves n(), stimulated the present study.

1. We have shown that the major requirement is that the existence of the wavelength range where variation ?n should not enlarge the interference order by more than unity; i.e., the assumption n = const should be valid.

2. We have proposed the method to extend the technique for measuring n( ) with the application of a Jamin interferometer combined with a spectrograph in the case when the zero-order fringe falls outside the field of the spectrograph.

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P- 14 ⇓

The Preparation Method of Detection Hexavalent Chromium at Gold Microensembling Electrodes in the Drinkable, Natural and Manufacturing Waters.

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The detection of hexavalent chromium is a challenging task because of the different possible oxidation states in which the element can occur. The two environmentally relevant valence states of chromium Cr(III) and Cr(VI) have a contrasting impact on environment and health. Trivalent chromium is relatively harmless plays an essential role in biological processes, whereas hexavalent chromium is about 100 1000 times more toxic. The maximum concentration limit of Cr (VI) is 0.05 mg L-1 (50 ppb).

Up to date methods for speciation and detection of chromium (VI) can be divided into indirect and direct approaches. Direct detection of chromium is spectrophotometric techniques and electrochemical methods.

The electrochemical detection of Cr (VI) has been reported at mercury electrodes, where it is claimed that hexavalent chromium is active over the entire pH range.

The purpose of our work is rejection of toxic mercure electrodes and a method preparation of detection Cr (VI) at the gold microensembling electrodes in the water.

The Cr (VI) detection was studied on analyzer TA - 4 (Tomanalit). Gold electrodserved as a working electrod and hloride silver elecyrodes are subsidiary electrodes. The gold drifted few time after electrod electrolisys (50, 100, 200 seconds).

The optimal conditions of voltammetric response of hexavalent chromium were found. Significant voltammetric responses towards the reduction of Cr (VI) were obtained only 0,03 M HNO3 by scaning rate 20 mV/s. Some artifact substances wereFe(III), Fe(II), HCl, NaCl, KCl, Cu(II), NO2-, Cr(III).

The method of detection Cr(VI) in water was suggested. We analysed some water samples (drinkable, natural and manufacturing). Method used was colorimetry with diphenylrdcarbazide to compare the results.

Advantages of the voltammetric method are high repeatability, apprehensibility, application minimal quantity of reagents and equipment.

P- 15 ⇓

Optical Tweezer with Tunable Spatial Profile of the Optical Trap

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The laser tweezers are the effective instruments in investigation of micron- and sub micron sized particles in physics, biology, materials science. The formation of three-dimensional structures in laser optical traps can be used in assembling of meta materials,self organization of nanoparticles etc. The basic principles of three-dimensional optical traps are presented , as well as the scheme of their implementation. The means of digital holography together with liquid-crystalline phase modulator of light are used for manipulation of spatial distribution of a light field in cross-section of a laser beam. This approach allows the flexibly transformation of the beam structure according to the solving tasks and gives the possibility of effectively using of the laser manipulator for capture, confinement, moving of small particles of the various natures, forming the three-dimensional structures of such particles in the created traps. Results of the device operation study are presented, the examples of particles capturing and three-dimensional structures formation are shown. The capability of the light field three-dimensional structure to keep up to 6 spherical glass particles 5 micrometer in diameter in water by He-Ne laser with moderate output power is experimentally shown.

The applications of laser tweezers with controllable trap configuration in laser spectroscopy of micro-and nano sized particles, atomic and molecular clusters and biological objects is discussed.

P- 16 ⇓

Magnetic Field Influence on the Polarization of The Radiation of the Quasi-Isotropic Gas Laser

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It is found by experiment that the quasi-isotropic resonator has a slight polarization anisotropy even the polarization elements arent brought in on purpose. In case of the helium-neon laser with the short resonator (0.2 0.3 m) it is shown by the generation of a red line 0,63 mkm: the laser generates two modes with the mutual orthogonal polarizations, and the position of the polarization squares about the resonator geometry is quite stable. This slight polarization can be connected with the multilayer cover of the mirrors or geometry of the activation of the active centers in the electric discharge.

It is found by experiment that the polarization of the emanation of such laser reacts on a slight longitudinal field in the area of the discharge.

To explain theoretically the influence of the magnetic field the classical dispersion theory and Lamb theory was used taking into account the Zeeman splitting of neon working layers. Also, the specific dispersion course for circular polarized waves in the bounds of Benet depressions and their shift due to the internal magnetic field are taken into consideration. The degree of activation of the active environment and the coefficients of the resonator losses are used as parameters. The theoretical dependence of the rotation of the polarization square of the laser emanation in the magnetic field for different frequencies in the bounds of the contour of the working transition is obtained. The calculations satisfactory correlate with the known experimental dependences.

9 COMPUTER SIMULATION

O- 1 ⇓

Correction of Intensity in Calculated Raman Spectra of Multi-Element Compounds

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One of the directions in the search of new materials for photonics and optoelectronics is incorporation of unusual atoms in organic molecules. Among many possibilities silicon and germanium are very promising since they are chemically similar to carbon and can readily substitute it but provide different energy levels for electrons and different physical properties of compounds. Important merit of silicon and germanium is that unlike many metals and halogens they pose no hazard to environment.

The Raman spectra of a series of phenyl-based organic compounds with silicon and germanium substituents have been studied in polycrystalline and powder samples. Comparison of Raman spectra of similar compounds with different substituents and side groups helps in assignment of vibrational modes. The experimental Raman spectra have been compared with the results of the first principles numerical calculations, performed with the 6-31G basis set of Gaussian 03 package. The geometry optimization was performed using the redundant internal coordinate procedure and the vibrational frequencies were calculated from the second derivative of the total energy with respect to atomic displacements about the equilibrium geometry.

Calculated frequencies are in good agreement with experimental ones while in intensities we found considerable discrepancies. The problem is already known but attracted much less attention than correction of frequencies. For vibrations of heavy elements (corresponding to low frequencies) calculated intensities are underestimated.

A simple empirical method is suggested for correction of calculated spectrum by increasing the intensities of the modes with vibration of C, Si, and Ge atoms with appropriate empirically found coefficients.

With suggested corrections calculated spectra are much closer to experimental ones. The only noticeable difference is strong low-frequency lines in the range $50 - 100$ cm^{-1} observed in all experimental spectra but absent in the results of calculations. Probably these lines belong to crystalline vibrations not considered in our calculations for isolated molecules.

Of course, suggested methods of correction are very crude since they are based on the displacement of atoms. Probably it would be better and more meaningful from the physical point of view to take into account deformation of different bonds C-H, C-C, C-Si, Ge-C and find the correction coefficient for each bond. Probably, it is possible but requires more complicated calculations.

Molecular Modelling as an Essential Tool of an Experimentalist

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When composing simple models of observed phenomenons, there is often need of an information not accessible from an experiment (or else hard-to-reach one). In such cases the molecular modelling might help. In the report, the author proposes his answers to the following questions:

- in which cases the use of quantum chemistry or molecular mechanics methods seems to be reasonable;
- what questions can be answered using molecular modelling;
- how to set the problem for molecular modelling;
- what are the computer programs accessible for molecular modelling;
- how to extract physically (chemically) significant information from the results of calculation.

Capabilities and defects of the most popular quantum chemistry methods are discussed very briefly.

Realization of the presented strategy is shown on the example of small molecules (O_2, CO, metal atoms) interaction with Pd nanoclusters, which have arisen when studying the mechanism of chemical modifier influence on the sensibility of atomic absorption analysis.

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Quantum Chemical Calculations of Conformations and Absorption Spectra of Alkylsubstituted Polysilanes in Solutions and Nanoporous Materials

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Condensed compounds in porous matrixes display a number of properties which are not observed at them in isolated state. Many works are devoted to studying of behavior of the polysilanes which form compositions of porous glasses and inorganic molecular sieves. Polysilanes are conjugated high polymers with a Si backbone and carbon-based side groups. Because of their remarkable optical properties having potential applications, a research of polysilanes and their derivatives has been the top agenda of many polymer chemists and physicists. Meanwhile, the poly(di-n-hexylsilane) which has two side chains of six methylene units each is probably the most well studied. It was shown that spectral properties of PDHS incorporated in nanoporous silica with different diameters of pores significantly differ from the spectra of the film and also depend from diameters of pores [1].

The photoluminescence spectra of PDHS incorporated in pores of 2.8 nm consist narrow band with a maximum at 350 nm and broad band in visible region at 450 nm. In the spectra of PDHS incorporated in matrix with pore of 6-10 nm the broad band in visible region is not observed [2]. In order to elucidate the nature of the observed spectral behaviors in solution and thereby to provide information about conformation of polymer incorporated into nanoporous silica, the quantum-chemical calculations were undertaken for PDHS. For calculations of the electronic spectra of the polymer compounds in the ground and excited state the PM3 methods were used (HyperChem).

Our calculations results shown that the appearance of the band at 420 nm in PDHS photoluminescence spectra can be explained by formation of complex between trailer atom Si of polymer and an oxygen ion of walls pores: -Si.-O-Al(Si). As follows from calculation results, the formation of such complex strongly decrease the energy of the lowest singlet level, ?=3957 cm^{-1}. The study involves the dependence of absolute energy of complex by changing the distances between trailer Si atom of polymer and an oxygen atom of nanoporous structure. The result of investigation shown that the minimum of absolute energy is obtained for point of 2.5 nm. It is well-known that formation of complex is resulted in appearance of long-wave band in fluorescence spectra that is observed experimentally in the work [2]. We are inclined to believe that formation of a broad band at 420 nm in spectrum of PDHS contained in the pores of 2,8 nm is due to formation of such complex.

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Analysis of Wave Function: to Translate the Information in Chemically Intelligible Language

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Many-electron wavefunction is defined in a many-dimensional phase space and is neither understandable directly nor easy to visualize. In order to extract chemically sensible information (such as atomic charges, bond orders and so on) from the wave function, many methods exist and are still under development.

In this survey report the most popular methods of ab initio wavefucntion analysis are discussed. In particular, Natural Bonding Orbitals method (NBO/NRT, [1]) and Atoms in Molecule method (AIM, [2]) are underlined. Also electron localization functions (ELF, [3]) and the excited state structural analysis [4] are briefly discussed.

The subject of the consideration includes the content of the methods of analysis, the resulting quantities, and their relation to the observed molecular properties. A frame of the questions, which can be reasonably answered using mentioned methods of wavefucntion analysis, is outlined.

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New Coupled Cluster Approach for Electron-Excited States. Test Calculations of Diatomic Molecules

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In the coupled cluster (CC) approach the wave function is represented by an exponentiated excitation operator acting on the Hartree-Fock wave function $|0\rangle$:

$$|\Psi_{CC}\rangle = exp(\hat{T})|0\rangle. \tag{10}$$

The excitation operator $\hat{T}$ in (10) includes operators representing different electron excitation levels:

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_M. \tag{11}$$

In the standard CC approach termed CCSD the operator $\hat{T}$ includes all single (S) and double (D) electron excitations from $|0\rangle$:

$$|\Psi_{CCSD}\rangle = exp(\hat{T}_1 + \hat{T}_2)|0\rangle = (1 + \hat{T}_1 + \hat{T}_2 + \hat{T}_1\hat{T}_2 + \frac{1}{2}\hat{T}_2^2 + \ldots)|0\rangle. \tag{12}$$

The most important excitations when quasidegenerate situation discussed are triple and quadruple ones. The CC methods that include these excitations are termed CCSDT (M=3) and CCSDTQ (M=4), respectively. When M is equal to the total number of electrons in the system the CC results are equivalent to the full configuration interaction (FCI) method. The exponential form of the CC wave function makes the CC approach size-extensive in describing the electron correlation effects. This is key feature contributing to the high effectiveness of the method in the calculations of atomic and molecular systems [1].

Standard expansion of the exponent in (12) produces superpositions of excitations of different orders from the reference $|0\rangle$. When more than one determinant provides a significant contribution to the wave function (as it happens in case of excited states calculations), the structure of the CC wave function *ansatz* has to be modified. To correctly describe the problem the CC $\hat{T}$ excitation operator has to generate excitations from all those important configurations. We propose the new state-specific multireference coupled cluster method for electronic excited states calculations (SSMRCC) [2]. Here, the configuration expansion of the CC wave function is generated from a single determinant $|0\rangle$ (called "formal reference") from the multiconfiguration reference space. All other reference determinants are generated as excitations from that formal reference. The reference space is defined by partitioning the all spin-orbitals into the inactive (core and virtual) and active (valence). And by including in the reference space only the determinants in which all core orbitals are doubly occupied by the core electrons and the active orbitals are occupied by the valence electrons. All possible distributions of the valence electron among the active orbitals are included into the reference space; this generates the complete active space of configurations. In our approach the reference function, which is the linear combination of the reference determinants, is generated from $|0\rangle$ by the CI-like operators $\hat{C}_1$, $\hat{C}_2$, etc.:

$$|CAS\rangle = (1 + \hat{C}_1 + \hat{C}_2 + ...)|0\rangle. \tag{13}$$

The "formal reference" can be selected as one of the determinants from the active space. In most cases it is chosen to be the determinant that provides the largest contribution to the wave function. We use the CASSCF method to obtaine orbitals and the reference function (13). From the CASSCF determinants the "formal reference" determinant is selected. We use the following form of the CASCC wave function in our approach:

$$|\Psi_{CASCC}\rangle = exp(\hat{T}^{(ext)})(1 + \hat{C}_1 + \hat{C}_2 + \ldots)|0\rangle, \tag{14}$$

where the operator $\hat{T}^{(ext)}$ generates excitations outside the CAS space. The CASCC wave function provides correct descriptions of any state of the system. Our calculations have demonstrated a very good ability of the CASCC method to describe potential energy surfaces (PES) of ground and excited states of molecular systems as compared with the FCI calculations and other *ab initio* approaches [2]. In this work we use (14) wave functions to calculate PES'es of BH and FH molecules in states with different spatial and spin symmetries ($^{1,3}\Sigma^{\pm}$, $^{1,3}\Pi$, $^{1,3}\Delta$). The calculated potential curves are fitted with generalized Morse (15) functions and used to solve the radial Schrodinger equation for the nuclear motion using a new variant of the Noumerov method [3].

$$U_{GM}(r) = \sum_m \alpha_m (1 - exp(-\beta_m (r - R_e)))^m, \tag{15}$$

where α_m and β_m are fitting parameters, R_e - the equilibrium internuclear distance. The calculated energies of the vibration states are compared with the (RKR) experimental data. The efficiency of different numerical methods for solving the nuclear-motion equation is investigated by calculating molecular constants (ω_e, $\omega_e x_e$, $\omega_e y_e$, α_e, $\hat{D}_e$).

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P- 1 ⇓

Cluster Structure of Monohydric Alcohols: Matrix Isolation and Quantum-Chemical Calculations

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The processes of the molecular cluster formation of monohydric alcohols were investigated by FTIR using the matrix isolation technique in Ar matrices. The transformation of FTIR bands of free hydroxyl groups (3600–3800 cm^{-1}) into diffuse bands (3000–3600 cm^{-1}), which were assigned to the stretching vibrations of the H-bonded O–H groups in various clusters, was monitored in its initial stage softening the matrices by heating from 20 K to 50 K.

The quantum-chemical calculations of different alcohol clusters were carried out with the program set Gaussian 03 (B3LY, 6-31G(d,p)). The comparison of the calculated vibrational spectra of the studied alcohols with the experimental IR spectra of alcohol clusters trapped in Ar matrices gives the possibility to determine the cluster structure of investigated alcohols.

Study of Luminescent Properties of 2-(2'-hydroxyphenyl)benzoxazole by DFT Calculations

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A molecule of 2-(2′-hydroxyphenyl)benzoxazole (HBO) possesses an intramolecular hydrogen bond and undergoes excited state proton transfer (ESIPT). Compounds that show ESIPT are considered to be useful for a variety of applications such as laser dyes, UV stabilizers, plastic scintillators, emitting layers for OLED and materials for non-linear optics.

Density functional theory (DFT) and time-dependent DFT calculations of geometry parameters and energies were performed for the ground and excited states of different tautomeric structures of HBO. The calculated values of energies of vertical transitions for the syn-enol (OH...N hydrogen bond), anti-enol (OH...O hydrogen bond) and planar keto (O...HN hydrogen bond) tautomers exceed the energies that corresponds to the bands in the absorption and fluorescence spectra measured in CCl_4 solution by about 0.16 eV . The most stable ground state structure of HBO is the syn-enol, whereas the anti-enol conformation is calculated to have the energy 6.5 kcal/mole above the syn-enol. This relation implies low concentration of the anti-enol rotamer and low intensity of the fluorescence band with normal Stokes shift. We did not locate any minimum that corresponds to the H-bonded keto species in the ground state. In the excited state rotation around the inter-ring bond between the benzoxazole and hydroxyphenyl moieties of the keto tautomer leads to significant decrease of the gap between the ground S_0 and excited S_1 states up to 0.25 eV that suggests existence of conical intersection of the S_0 and S_1 potential energy surfaces which causes non-radiative decay of the S_1 state decreasing quantum yield of the keto fluorescence of HBO.

Modeling of Interactions of Methylene Blue Dye With Nanotubes and Graphene

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Modeling of interactions of redox-active dyes with nano-forms of carbon is necessary in connection with design of nano-devices containing such constituents. In the present communication results of simulation of interactions of cation of methylene blue (MB) dye with fragments of carbon nanotube (CNT) and graphene sheet by means of ab initio DFT M05-2X method with 6-31++G(d, p) basis set and molecular dynamic simulation are presented. Preliminary calculations have shown that a fragment containing 56 carbon atoms is sufficient for adequate modeling of CNT interactions with relatively small ligands and optimization of geometry of the complex. For carbon bonds saturation hydrogen atoms were placed at the terminal carbons of the fragments both of the CNT and graphene. For frontier orbitals analysis a CNT segment of 160 carbon atoms was used.

In the optimized system MB-CNT the MB cation is located over the CNT surface at the distance of about 3-3.5 *Å* and the plane of its heterocycles is slightly distorted for better contact with the CNT surface. In the MB-graphene complex the plane structure of the MB cation remains intact; it is practically parallel to the graphene plane being at the distance of 3.4 *Å*. Relatively strong attraction between the π-system of carbon nanostructures and MB cation is observed. The energy of MB-CNT interaction was -159.0 kJ/mol and that of the MB-graphene was -176.0 kJ/mol. More high energy of interaction of MB with graphene (as completely unfolded tube) is due to better MB plane alignment and larger area of contact as compared to the MB-CNT complex.

Molecular orbitals analysis for MB-CNT system has shown that, as it was expected for such relatively small CNT fragment with terminal hydrogen atoms, frontier orbitals HOMO and LUMO are located at the hydrogens. More informative are orbitals HOMO-3 (-7.2 eV), HOMO-4 (-7.2 eV) located at CNT and LUMO+2 (-2.3 eV), LUMO+3 (-2.2 eV) located at MB. Localization of the orbitals on both the MB cation and CNT permits electron transfer in the system, which is essential for its functioning in nanodevices.

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Distribution Function of Swift Ions Energy Losses in Solid Targets

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Introduction. Equations for distribution functions of swift ions and their energy losses in a solid target have been derived about forty years ago [1, 2]. Last years authors [3, 4] proposed so called cumulants approach, and have created the corresponding numerical method. However this approach leads to an unexpected result for solution of the equations [2] for spatial distribution of energy losses of swift particles – ions and knocked atoms. So, equation for elastic energy losses of the particles has trivial solution $\nu(E) = 0$, and for the inelastic ones it is equal the ion energy E, in according to the energy conservation law.

Results. Research of the reasons for occurrence of the above results [5] has led authors to conclusion, that a not proved assumption was made in [2] about proportionality of energy losses inside of a small volume to its size δV. The similar assumption for number of implanted ions [1] certainly is valid, since the one ion can no more than once to stop inside δV. Hence the number of casual stops depends only on positioning of δV and stopping point. Since an ion borrows volume $\Delta V \approx 1/N_0$, where N_0 is atom concentration, after its stopping, then the probability of its stopping into a volume $\delta V \leq \Delta V$ is $\delta\mathcal{P} \approx \delta n \delta V/\Delta V \sim \delta V$. Hence the volumetric density distributions of implanted ions as a limit $\Pi\left(\vec{r}, E\right) = \lim\limits_{\delta V \to 0} \delta\mathcal{P}/\delta V$ can be introduced.

On the contrary to particle stopping, the losses of its energy occur in a set of collisions along their trajectory. They can happen many times into the same volume δV, if the particle free path length λ is enough small, or if its trajectory is curvilinear enough and it can fly many times through the volume δV. The lost energy is proportional to the collisions number δn if the particle comes into δV, or zero, otherwise. But $\delta n \approx \delta l/\lambda$, where $\delta l \sim (\delta V)^{1/3}$ is length of the particle path inside of δV, and number of casual collisions depends not only on positioning of δV and trajectories, but also on a measure of the δV. The area, where a swift particle transfers an energy $\langle T^\alpha \rangle$ to the target, is a cylinder with volume $\Delta V \approx \pi R^2 \lambda$, constant radiuse R, axis between two collisions of α type. Then the probable losses of energy inside $\delta V \leq \Delta V$ is $\delta\mathcal{P}^{\alpha} \approx \langle T^{\alpha}\rangle \delta n \delta V/\Delta V$. Hence we obtain $\delta\mathcal{P}^{\alpha} \sim (\delta V)^{4/3}$ and it is impossible to introduce the volumetric density distribution of energy losses of the fast particles. However it is possible to introduce the density of energy losses distribution of a fast particle along its path δl if probable loss of energy $\delta\mathcal{P}^{\alpha} \approx \langle T^{\alpha}\rangle \delta n \sim \delta l$ is considered.

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10 Minor Academy of Sciences

ГЛОРІЯ - ЗАГАДКОВЕ ОПТИЧНЕ ЯВИЩЕ

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У даній роботі подано дослідження і теоретичне обґрунтування глорії природного явища, яке автор вперше мала нагоду спостерігати, перебуваючи на високогір'ї українських Карпат. Явище, що нагадує колову веселку, в центрі якої завжди знаходиться спостерігач, є можливість побачити тільки за особливих умов, розгляд яких наведено у роботі.

За фізичні основи пояснення кілець глорії взято наведені в літературі розрахунки для клаплини води і зроблено узагальнення цієї теорії та поширення її на досліджувані явища. В роботі представлено світлини глорії, розглянуто умови її виникнення, утворення елементів штучної глорії, райдужних кілець.

Основною метою дослідження глорії, як оптичного явища є актуалізація даного питання з метою подальшого досконалого вивчення. Обмеженість умов спостереження звужує можливості щодо вивчення даного явища. В роботі запропоновано розрахунки залежності висоти спостереження від відстані до глорії. Останнім часом більшість пошуків спрямовано на ті об'єкти, які мають безпосереднє застосування на практиці. Людина має поринути в найпотаємніші куточки природи, щоб використовуючи її блага, залишити її в неспотвореному виді для наступних поколінь.

ДОСЛІДЖЕННЯ СИЛОВИХ ХАРАКТЕРИСТИК КОРОННОГО РОЗРЯДУ

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У цій роботі досліджено залежність сили, з якою діє «електричний вітер» на заряджений до високого потенціалу провідник із вістрям, від сили струму, що виникає під час цього розряду. Для реалізації цього дослідження було поставлено наступні завдання:

· розробити метод експериментального визначення значення цієї сили та виготовити відповідну експериментальну установку;

· здійснити фізичний експеримент та опрацювати його результати;

· теоретично пояснити результати експерименту та характер залежності досліджуваної сили від параметрів, що її спричиняють;

· сформулювати висновки та розглянути перспективні напрямки подальших досліджень;

У результаті було проведено фізичний експеримент, який дозволив зробити такі висновки:

· значення сили, яка діє на вістря, і сили розрядного струму у випадку негативної «корони» більші, ніж у випадку позитивної. Автори роботи схильні пов'язувати цей факт із більшою рухливістю негативних іонів, ніж позитивних;

· залежність F від I у межах здійсненого експерименту близька до лінійної;

· розміри самої «корони» становлять порядку 1 *см*, причому у випадку негативної корони вони дещо більші.

Подальші завдання вищевказаних досліджень автори роботи бачать у:

· розробці регульованого джерела високої напруги для дослідження коронного розряду за різних значень напруг;

· виготовленні більш чутливого динамометру і дослідженні характеру залежності F від I у випадку різних конфігурацій електрода та за його відсутності.

СПЕКТРАЛЬНЫЕ ИССЛЕДОВАНИЯ МОЛОДОЙ AE ЗВЕЗДЫ ХЕРБИГА HD179218

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Доклад посвящен анализу спектра высокого разрешения молодой звезды Хербига HD179218.

Приведены признаки молодости этой звезды, поставлена цель работы определить основные параметры фотосферы эффективную температуру и ускорение свободного падения. Найдено, что наилучшее совпадение рассчитанных синтетических спектров фотосферы с наблюдаемыми спектрами в области бальмеровских линий достигается при Teff = 11000K, и lg(g)=4.5, что соответствует спектральному классу звезды B9. Уточнено значение vsini и выявлено влияние околозвездной оболочки в наблюдаемые профили линий.

Обнаружен необычный для звезд данного типа эффект вуалирования в континууме и спектральных линиях на протяженном участке спектра.

Приведены косвенные доказательства существования второго компонента. К ним относятся эффект вуалирования в спектре молодой горячей звезды, не характерное для звезд данного типа значение lg(g). По интенсивности околозвездных линий сделано предположение о небольших размерах газового диска по сравнению с дисками у подобных звезд.

Результаты анализа показали необходимость учета влияния околозвездной оболочки на наблюдаемый спектр при проведении любых исследований молодых звезд, независимо от ориентации их диска.

КУМУЛЯТИВНІ ЕФЕКТИ В ГІДРОДИНАМІЦІ

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В даній роботі я досліджував явище утворення кумулятивного струменя в пробірці, кинутій на поверхню з деякої висоти. Мною була сформульована математична модель, що описує це явище. Основними положеннями її є:

- Розглядання наданої та витраченої енергії;
- Енергія надається за рахунок потенціальної енергії піднятої над водою пробірки та за рахунок енергії поверхневого шару рідини;
- Енергія іде на підняття струменя на деяку висоту та на подолання в'язкості.

При проведенні експерименту акценти ставились на:

- Вимірювання висоти підняття пробірки та висоти вильоту струменя з неї, що проводились візуально за допомогою лінійки, закріпленої на штативі.
- Вимірювання площі дотику дна пробірки з поверхнею, методом відбитків

Також було помічне часткове неспівпадання теорії з експериментом, що може бути обумовлене такими фактами:

- Вважання вилітаючого струменя конусом;

- Вважання потоку ламінарним, хоча при досягненні деяких швидкостей він стає турбулентним;

- Вважання переходу усієї потенціальної енергії воду у енергію струменя, хоча деяка її частина розсіюється.

ДОСЛІДЖЕННЯ ВЛАСТИВОСТЕЙ КОМПОЗИЦІЙНИХ БУДІВЕЛЬНИХ МАТЕРІАЛІВ

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В індивідуальному будівництві широко застосовуються будівельні матеріали на основі глини з додаванням цементу і ошурок із дерева. В роботі проведено дослідження важливих службових характеристик цих матеріалів теплопровідності і руйнівної напруги.

Досліджувалися властивості п'яти типів зразків, які готувалися на базовій суміші 3 об'ємні частини глини,1 частина цементу М400 і мали різний вміст ошурок із дерева від 0 до 33,3 об'ємних відсотків.

Введення ошурок покращує теплоізоляційні властивості композиційних матеріалів коефіцієнт теплопровідності зменшується від 0,71 до 0,51 Вт/мК.

Руйнівна напруга в межах вмісту ошурок до 25 об'ємних відсотків практично не змінюється і складає біля 1,6 МПа. Збільшення об'ємної частки ошурок вище 30% приводить до суттєвого пониження величини руйнівної напруги.

ЧОРНІ ДІРИ

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Робота виконувалася з метою розібратися у сучасній теорії чорних дір і «перекласти» на більш зрозумілу мову новітні теорії та представлення про походження й існування чорних дір. Ми не ставили за мету реферативний виклад цікавих досліджень і публікацій, хоча із захопленням прочитали багато з них.

В роботі нами оціночним методом розмірностей отримано важливі характеристики чорних дір: час їх життя, температуру Хокінга, швидкість зміни маси чорної діри.

Проаналізовано залежності між основними характеристиками чорних дір: залежності маси рівноважної чорної діри від температури; зв'язок між швидкістю зміни маси чорної діри з її масою m в певний момент та її «рівноважною» масою m_0 ; залежності часу зникнення чорної діри від її маси; залежності температури Хокінга від маси чорної діри.

Усі ці залежності, отримані елементарним способом збігаються з тими, які надаються у наукових публікаціях.

Практична значущість нашого дослідження полягає в тому, що нами показано, як за допомогою «шкільної» фізики та математики можна розібратися у складній і до кінця ще нерозробленій теорії чорних дір і пов'язаних з ними питаннях щодо структури і розвитку Всесвіту.

Вважаємо, що результати нашої роботи будуть цікавими учням і вчителям, які працюють за поглибленою програмою з фізики та математики.

РИБ'ЯЧЕ ОКО, ЛЕТЮЧИЙ ГОЛЛАНДЕЦЬ ТА ФАТА-МОРГАНА

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Робота присвячена вивченню умов виникнення міражів. За ***мету дослідження*** поставлено розробку методів отримання міражів у лабораторних умовах та їхнього пояснення за допомогою комп'ютерного моделювання.

У ході роботи виконано такі завдання:

1. Створено математичну модель для опису виникнення міражів різних видів, використовуючи існуючі в геометричній оптиці підходи.
2. Розроблено методику лабораторного експерименту для спостереження міражів та проведено відповідні досліди.
3. Створено комп'ютерну програму для моделювання виникнення міражів.

Об'єкт дослідження: проходження світла крізь оптично неоднорідні середовища.

Предмет дослідження: умови утворення міражів.

Наукова новизна та практична значущість дослідження

Науково-методична новизна роботи полягає в тому, що підготовлено комплекс доступних демонстрацій для наочного представлення викривлення світлових променів і утворення міражів у оптично неоднорідному середовищі.

Практичне значення полягає, по-перше, в узагальненні підходів математичного моделювання утворення міражів, і, по-друге, у розробці комп'ютерної програми для наочного представлення і доведення слушності математичної моделі утворення міражів.

ТЕРМОЕЛЕКТРИКА. ДОСЛІДЖЕННЯ ТЕРМОЕЛЕМЕНТІВ І ЇХ ЗАСТОСУВАННЯ

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Українські вчені і інженери нещодавно створили екологічний чистий пристрій, якій працює на газі і у будинку виконує зразу два важливих завдання: обігріває його і виробляє електрику. Кожна теплова батарея, що обігріває кімнату, дає ще 100-150 ватів електроенергії. При цьому економиться 40% газу, порівняно з звичайним центральними опаленням. В основі цього пристрою лежить термоелемент. Одна з провідних технологій майбутнього - отримання енергії з допомогою термоелектрики.

В своїй науковій роботі я розглянув питання природи термоелектрики в двох різних металах і напівпровідниках, розглянув прилад, в якому створюється електрична енергія за рахунок внутрішньої енергії іншого тіла термопапару. Аналізуючи фізичні і хімічні властивості металів я виготовив 9 термопар і виміряв їх терморушійну силу. В експериментальній частині своєї роботи я також дослідив залежність терморушійної сили термопари мідь-константин від різниці температур її спаїв, побудував графік цієї залежності, освітив питання використання термопар.

Я також звернувся до питання виникнення ТЕРС в напівпровідниках з різною природою провідності,розглянув питання дії термоелектричних холодильників, робота яких ґрунтується на ефекті Пельтьє, їх застосування і переваги над іншими типами холодильників. В заключній частині своєї роботи я розглянув питання використання термоелектрики і перспективи розвитку цього альтернативного джерела енергії.

ПОВЕДІНКА ГНУЧКИХ ПЛІВОК ПРИ ЗАГРУЗЦІ У ЦЕНТРІ

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Полімерні матеріали (біоматеріали) широко використовуються на сьогодні. Робота присвячена вивченню механічних властивостей полімерів, а саме залежності подовження плівки під навантаженням. Насправді, як це виявилось в ході досліджень, деформація полімерів не відбувається за законом Гука, який вивчається у шкільному курсі.

Запропонована в роботі модель наступна: поліетиленову плівку натягують на обруч та спостерігають, як поводять себе різні частини плівки (вимірюеться їх подовження в залежності від загрузки).

В процесі виконання роботи по вивченню механічних властивостей плівки були вирішені такі загальні питання:

· спостереження явища та причин, що його викликають,

· експериментальне дослідження,

· аналіз отриманих за планом експерименту значень,

· якісне пояснення спостерігаемих явищ.

В роботі запропонована проста модель, що дозволяє з прийнятною точністю, але простими засобами, дослідити явище та провести необхідні вимірювання. Результати роботи заслуговують довіри, що підтверджує успішність обраної моделі.

ЕКСПЕРИМЕНТАЛЬНЕ ВИЗНАЧЕННЯ ПОКАЗНИКА ЗАЛОМЛЕННЯ ПОВІТРЯ

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Метою роботи є експериментально довести, що показник заломлення повітря все-таки відрізняється від показника заломлення вакууму.

Задача визначити абсолютний показник заломлення повітря використовуючи призму з вакууму, на яку направлений вузький пучок світла.

Для детального пояснення багатьох цікавих явищ спостережуваних у природі, техніці, для визначення місцезнаходження астрономічних тіл, земних об'єктів використовується значення показника заломлення повітря рівне одиниці, хоча точне значення дорівнює 1,000292.

Якщо враховувати, що показник заломлення повітря дорівнює одиниці, то всі перераховані далі явища не спостерігалися б в природі: спостерігач бачить об'єкт не в тому напрямку , який відповідає дійсності: видима висота предметів над обрієм виявляється більше дійсності; виникнення міражів; дальності видимого обрію на 5 - 6%; збільшення довжини дня в середніх широтах на 8-13 хвилин, скорочення полярної ночі на 12 днів.

У науковій роботі запропоновано спосіб визначення абсолютного показника заломлення повітря, заснований на вимірюванні кута відхилення світлового пучка від первинного напряму при проходженні світла через вакуумну призму з великим заломлюючим кутом.

Проект має не тільки наукову, але і практичну цінність. Запропонований пристрій можна використовувати для визначення рівня забрудненості повітря, що сьогодні є дуже актуальним при низькому рівні екології. Наукова цінність полягає в тому, що запропонований експеримент можна використовувати при вивченні явищі рефракції світла, законів заломлення в середніх і вищих учбових закладах. Дана робота зацікавить учнів середніх та вищих учбових закладів, а також тих, хто цікавиться експериментальними дослідженнями.

$_2$:**PB**

СЦИНТИЛЯЦІЙНІ ВЛАСТИВОСТІ КРИСТАЛІВ CDI

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Вивчений вплив домішки свинцю на спектри оптичного поглинання, на фото-і рентгенолюмінесценцію, сцинтиляційні характеристики CdI$_2$ при кімнатній температурі. Для дослідження використовували кристали, вирощені методом Стокбаргера-Бріджмена. Активація CdI$_2$ з розплаву сполуками PdI$_2$ приводить до появи в спектрах поглинання в прикраєвій області активаторної смуги 395-405 нм, яка інтерпретується як А-смуга, генетично пов'язана з електронними переходами з $^1S_0$-стану на $^3P_1$-рівня у вільному іоні Pb^{2+}. При рентгенівському збудженні кристали CdI$_2$:Pb^{2+} з оптимальною концентрацією домішок характеризируются приблизно на порядок більшим світловиходом з максимумом в області 570-580 нм, аніж кристали CdI$_2$ в смузі 490-500 нм. При б-збудженні кінетика загасання люмінесценції неактивованого йодистого кадмію має дві компоненти: швидку ф$_1$ =3-4 нс і повільну - ф$_2$=10-70 нс. Загасання радіолюмінесценції CdI$_2$:Pb^{2+}описується в основному двома експонентами з параметрами ф$_1$?10 нс і ф$_2$=200-250 нс.

СПЕКТРОСКОПІЯ ОБ'ЄМНИХ КРИСТАЛІВ І НАНОЧАСТИНОК. ВИРОЩУВАННЯ КРИСТАЛІВ.

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Людину завжди цікавить все, що відбувається навколо неї, й вона сама. У неї виникає багато запитань про Природу, Всесвіт. Людина прагне дізнатись, що у світі найбільше, найдужче, найяскравіше, найменше, найміцніше...

Дослідження теоретичних знань з фізики немислиме без поєднання теорії із дослідами. Для того щоб дослідити будову об'ємних кристалів слід провести теоретичні дослідження дифракції у багатошарових системах та спектроскопію об'ємних кристалів і наночастинок. Для кращого розуміння будови кристалів доцільно провести експерименти із вирощування кристалів що і буде зроблено у даній роботі. В цій роботі проведено теоретичне дослідження багатохвильової дифракції у багатошарових системах, спектроскопію об'ємних кристалів і наночастинок. Показано як за допомогою спректрального аналізу досліджують будову Сонця, зір та газових хмар. В роботі проведені досліди із вирощування кристалів.

Багатохвильова дифракція є важливим методом високороздільного аналізу границі шар/підкладка. Інтерференція хвильових полів чутлива до зміни ширини перехідного шару порядку довжини хвилі і до порушення когерентності напівпровідникових структур. За її допомогою можна визначити ізоморфізм росту по відношенню до напрямку росту.

За допомогою багатохвильової дифракції можна визначити поля деформації (по зміні параметрів ґратки монокристалів), зумовлені наноструктурам
в підкладці ґратки навіть, якщо ці наноструктури приховані верхніми шарами. У випадку квантових точок, вирощених на ОаАз (001), гратка ОаАз тетрагонально спотворена і дещо викривлена поблизу поверхні підкладки.

ДОСЛІДЖЕННЯ СПЕКТРАЛЬНИХ ЗАЛЕЖНОСТЕЙ КВАНТОВОЇ ЕФЕКТИВНОСТІ ФОТОЕЛЕКТРИЧНИХ ПЕРЕТВОРЮВАЧІВ НА ОСНОВІ ТЕЛУРИДУ КАДМІЮ

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Практичний досвід Англії, Німеччини, США і Японії, переконливо показує, що, за умови державної фінансової підтримки, одній з складових вирішення енергоекологічних проблем людства є широкомасштабне використання сонячних елементів. У таких екологічно чистих відновлюваних джерелах енергії відбувається безпосереднє перетворення енергії сонячного випромінювання на електричну енергію. Економісти свідчать, що тільки плівкові сонячні елементи в майбутньому потенційно здатні конкурувати з традиційними джерелами енергії, оскільки собівартість вироблюваною ними електричній енергії може бути в чотири рази нижче, ніж в поширених зараз монокристалічних приладових структурах. Такий істотний економічний ефект зумовлений тим, що для ефективного фотоелектрично активного поглинання світла достатньо плівкового базового шару завтовшки всього декілька мікрометрів. Плівкові сонячні елементи з базовим шаром CdTe є одними з найбільш перспективних для наземного застосування, оскільки відповідно до ширини забороненої зони телуриду кадмію (Eg= 1,46 еВ) такі приладові структури мають максимальний серед один перехідних напівпровідникових фотоелектричних перетворювачів теоретичний коефіцієнт корисної дії (ККД) 29 %. Максимальний ККД кращих лабораторних зразків плівкових сонячних елементів на основі гетеро систем CdS/CdTe складає 16,5%. Таким чином необхідно продовжувати вивчення особливостей фотоелектричних процесів для визначення шляхів подальшого підвищення ефективності сонячних елементів. У представленій роботі вивчаються особливості фотоелектричних процесів в плівкових гетеро системах на основі CdS/CdTe/ITO. З цією метою проведені комплексні дослідження їх спектральних залежностей коефіцієнта квантової ефективності, які дозволяють аналізувати фізичні механізми формування фотоструму приладової структури поглинання фотонів з різною довжиною хвилі.

АНАЛІЗ ПОРФІРІНОВОГО ПІГМЕНТУ (ХЛОРОФІЛУ) ЗА ДОПОМОГОЮ МЕТОДУ МОЛЕКУЛЯРНОЇ АБСОРБЦІОННОЇ СПЕКТРОСКОПІЇ

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У медико-біологічних дослідженнях великий інтерес представляють комплекси перехідних металів. Дослідження комплексів перехідних металів доцільно проводити на основі визначення спектрів поглинання електромагнітного випромінювання молекулами речовини, що є завданням молекулярної спектроскопічної абсорбції.

У даній роботі описуються особливості будови комплексів перехідних металів на основі іона Co^{3+}. Показана залежність зміни забарвлення комплексів, створених на основі іона Co^{3+}, при зміні їх хімічного складу.

У роботі експериментально досліджен комплекс металу порфірінового пігменту хлорофілу. Вивчен спектр поглинання світла хлорофілом за допомогою дифракційного спектроскопа.

В результаті дослідів виявлено поглинання звичайним розчином хлорофілу червоного і синьо-фіолетового променів спектру, у разі концентрірованн розчину хлорофілу поглинання всіх променів спектру, окрім зелених.

Представлені результати колориметричного аналізу при дослідженні дії вихлопних газів на хвою сосни.

ОПТИЧНІ КВАНТОВІ ГЕНЕРАТОРИ СВІТЛА І МОЛЕКУЛЯРНИЙ СПЕКТРАЛЬНИЙ АНАЛІЗ

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Спектроскопія народилась на початку минулого століття, її методи і сьогодні залишаються одними із сучасних методів дослідження речовини. Як чисто емпірична наука за часів Фраунгофера і Кірхгофа, вона дала поштовх розвитку квантової механіки і, в свою чергу, активно використовувала отримані в ній результати.

Існує багато способів визначення складу речовини від таких природних і на перший погляд простих, як органолептичні, що використовують нюх і смак людини або тварини, до таких складних, як хроматографія або ультрамікрохімічний аналіз. Важливе місце серед них займають фізичні методи, і зокрема спектральний аналіз.

Напівпровідникові лазери з частотою, яка переналаштовується, дозволяють вивчати спектри в інфрачервоному діапазоні, де присутні спектральні лінії більшості молекул. На основі таких лазерів було створено ряд приладів, що відрізняються унікальною чуттєвістю і швидкодією, зокрема - трасові вимірювачі. Висока чуттєвість приладів забезпечує реєстрацію і точне вимірювання найменших концентрацій домішок на молекулярному рівні. Висока роздільна здатність і широкий діапазон перебудови частоти створюють умови для реєстрації практично будь-яких речовин в газовому середовищі. Спрямованість променя у просторі дозволяє проводити вимірювання у відкритій атмосфері або на відстані від досліджуваного об?єкта безконтактно. Завдяки застосуванню імпульсно-періодичної розгортки вдається записувати спектр речовини за рекордно малий строк і вивчати швидкодіючі процеси.

Перед лазерною молекулярною спектроскопією відкриваються широкі перспективи і в наукових дослідженнях, і в наукових розробках: контроль технології надчистих речовин, стану навколишнього середовища, чистоти повітря в цеху, геофізичні дослідження, дослідження в медицині і біології.

ВНУТРІШНЯ БУДОВА НАПІВПРОВІДНИКІВ

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Сьогодні, коли виробництво напівпровідників стало окремою галуззю промисловості і сьогодні, коли напівпровідники все в більшій мірі визначають рівень прогресу в таких галузях як радіоелектроніка, обчислювальна техніка, зв'язок, автоматизація виробництва, знання фізики напівпровідників стає потребою не тільки фахівців у даній галузі, але і більш широкого кола людей. Вимоги промисловості та техніки стимулюють у наш час розвиток науки і фізики напівпровідників зокрема. За п'ятдесят років свого розвитку фізика напівпровідників та промисловість із нею пов'язана, пройшла великий шлях, від перших діодів до мікросхем. У мікросхемі 1965 року випуску було 30 транзисторів, тоді як сьогодні чип Radeon HD 3870 містить 660 мільйонів транзисторів.

Для створення напівпровідникових виробів потрібно мати розвинуту промисловість, адже потрібно виготовляти чисті кристали кремнію та германію, вміст домішок у яких буде надзвичайно малим (до 10^{-10}). Довгий час це було неможливо. Потрібно вміти вводити в кристали кремнію точно дозовані кількості домішок, тощо. Але все це було б неможливим без знання внутрішньої будови напівпровідників. Фізика напівпровідників саме і вивчає будову напівпровідників, вона встановила певні загальні принципи їх функціонування, тощо.

Завданням даної роботи буде встановити внутрішню будову напівпровідників та пояснити на основі внутрішньої будови їх властивості.

1. У роботі було розглянуто поділ речовин на метали, діелектрики та напівпровідники, встановлено їх основні електрофізичні характеристики.

2. На основі рівняння Шредінгера встановлено зонний характер енергетичних спектрів електронів у кристалах напівпровідників. Розглянуто приблизні розв'язки рівняння Шредінгера для кристала напівпровідника.

3. Дане пояснення поняття зон Бріллюєна, та встановлена енергетична будова таких напівпровідникових матеріалів як германій та кремній.

4. На основі теорії будови напівпровідників показано введення поняття дірки, яка є певною мірою віртуальною частинкою, але введення такого поняття дозволяє складну задачу про рух величезного числа електронів валентної зони по вакантних рівнях замінити значно більш простою задачею про рух невеликого числа дірок, що розташовуються на цих рівнях.

5. У роботі розглянуто вплив домішок на структуру та електрофізичні властивості напівпровідників, утворення донорних та акцепторних рівнів, рівнів прилипання.

У СВІТІ КРИСТАЛІВ

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Наукова робота "У світі кристалів" висвітлює будову, властивості, практичне застосування кристалів.

У вступі представлено історію розвитку вчення про кристали від далекої давнини до сьогоднішніх днів. Адже ще в кам'яний вік людині були відомі кремінь, кварцит, нефрит. Камінь був головним знаряддям праці і надійною зброєю для захисту і нападу.

В першому розділі зроблено огляд літератури. Зокрема, в параграфі 1 висвітлюється загальна характеристика кристалічних тіл, їх форма, відмінності один від одного.

В параграфі "Будова кристалів" подана характеристика кристалічної структури тіл іонної, молекулярної, металевої. Наприклад, молекулярна кристалічна структура відрізняється просторовою решіткою, у вузлах якої нейтральні молекули речовини. Такі речовини легко руйнуються, на відміну від речовин з металевою кристалічної решіткою.

В третьому параграфі описано процеси росту кристалів. Реальні кристали не володіють правильною кристалічною решіткою, а містять цілий ряд порушень в розміщенні атомів, так звані дефекти.

Далі розкривається процес одержання монокристалів. В природі монокристали більшості речовин без тріщин, забруднень та інших дефектів зустрічаються рідко. Основні способи вирощування монокристалів це кристалізація із розплаву і кристалізація з розчину.

Завершує огляд літератури питання про застосування кристалічних тіл. Зараз існують цілі галузі промисловості, які працюють на штучних кристалах, повністю створених людиною. В першу чергу, це промисловість напівпровідникових кристалів, з яких роблять велику кількість різноманітних приладів. Коли люди навчилися вирощувати штучні рубіни, вони стали основним матеріалом для лазерів. Потужний промінь лазера досягає Місяця та інших планет, стежить за космічними кораблями і супутниками, допомагає бачити, як людина ходить по Місяцю.

В другому розділі описано процеси, які в лабораторії (в шкільних умовах) дають змогу виростити кристали.

Отже, кристали це не тільки символ неживої природи, але й основа життя на Землі.

НОВІ МЕТОДИ ТА МОЖЛИВОСТІ СУЧАСНОЇ ОПТИЧНОЇ СПЕКТРОСКОПІЇ МОЛЕКУЛ ТА КРИШТАЛІВ

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І. Предмет та завдання спектроскопії.

Предметом спектроскопії є вивчення спектрів атомних систем спектрів випромінювання, поглинання і розсіювання електромагнітних хвиль.

ІІ. Історичний огляд розвитку спектроскопії.

- розвиток спектроскопії розпочався з відкриття Ісааком Ньютоном білого світла в спектрі в 1666 році.

- відкриття і вивчення дискретних спектрів випромінювання і поглинання Фраунгофером в 1814 році.

- встановлення Кірхгофом в 1859 році співвідношення між випромінюванням та поглинальною здатностями тіл, що одержало назву закону Кірхгофа.

- встановлення закономірностей у розташуванні ліній в атомних спектрах у 1885 році Бальмером.

- теорія Бора (1913 рік) пояснила сутність закономірностей в атомних спектрах.

- відкриття в 1925 році спіну електрона Уленбеком і Гауцмітом.

- новий етап в розвитку спектроскопії пов'язаний зі створенням в 1924-1926 році квантової механіки.

- започаткування молекулярної спектроскопії з відкриттям в 1928 році Раманом, Мальдейштамом і Лансбергом явища комбінаційного розсіювання світла

ІІІ. Розділи спектроскопії.

- ядерна спектроскопія вивчає рівні енергій атомних ядер і переходи між ними.

- атомна спектроскопія вивчає електронні рівні енергій атомів і переходи між ними. Саме вона зіграла особливу роль у розвитку вчення про будову речовин.

- молекулярна спектроскопія вивчає електронні, коливальні й обертальні рівні молекул і переходи між ними.
- спектроскопія конденсованих систем кришталів, аморфних тіл і рідин, вивчає рівні енергій цих складних систем і переходи між ними.

IV. Реєстрація спектроскопії.

Оптичним приладом, призначеним для розкладу світла на спектральні складові й візуальне спостереження спектра є спектроскопія.

На сьогоднішній день спектральний розклад світла може здійснюватись трьома методами:

- дисперсією за рахунок заломлення в призмах;
- дифракцією на періодичних решітках
- з використанням явища інтерференції.

V. Застосування спектроскопії молекул та кришталів.

- в хімії та матеріалознавстві - для визначення елементного складу;
- в екології контроль за станом повітряного середовища;
- в астрономії - для вивчення інформації про будову та утворення зірок;
- вивчення структури біохімічних об'єктів, вивчення фотосинтезу й біохімії зору;
- вивчення можливостей використання лазерно-індукованої флуоресценції й комбінаційного розсіювання для діагностики раку, хвороб артерій і ряду інших захворювань.

ЛІОТРОПНІ РІДКІ КРИСТАЛИ ТА ПЕРСПЕКТИВИ ЇХ ВИКОРИСТАННЯ

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Рідкі кристали це речовини, що вдало сполучують у собі анізотропні властивості кристалів й текучість рідин. Існує багато речовин природного походження, які мають рідкокристалічні властивості. За способом утворення рідкі кристали поділяють на термотропні, ліотропні, фототропні. Усі ці види рідких кристалів широко використовуються в практиці. Ця обставина зумовлює необхідність дослідження властивостей рідких кристалів.

В теперішній час рідкі кристали широко використовуються. Нещодавно стало відомо, що важливі для життєдіяльності людського організму рідини це ліотропні рідкі кристали. Їх властивості повязані з станом людського організму. Ця обставина може бути викоритсана для діагностики різноманітних захворювань.

Мета роботи полягає в спробі визначення можливості використання особливих властивостей ліотропних рідких кристалів в біологічних об'єктах для дослідження станів цих об'єктів, зокрема, для діагностики захворювань людини.

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