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HOLE BURNING, SINGLE MOLECULE,
AND RELATED SPECTROSCOPIES:
SCIENCE AND APPLICATIONS

BOOK OF ABSTRACTS

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HBSM-2018 continues the series of symposiums started in 1987 and hosted in USSR, USA, Switzerland, Japan, France, Taiwan, France, Australia, Germany, Estonia. HBSM has been exceptionally successful in bringing together participants from the leading research teams around the world to discuss the latest developments in the fundamental science and the applications of site-selective and single-molecule spectroscopies and numerous related topics (condensed matter physics and physical chemistry, nanoscopy, quantum dots, rare-earth ions, nanodiamonds, biophysics, medical nanodiagnostics, quantum technologies, photovoltaics, on-chip technologies).

HBSM-2018 was organized by the Moscow State Pedagogical University and the Institute for Spectroscopy of the Russian Academy of Sciences and managed by the Interinstitutional scientific team working in laser selective spectroscopy and nanoscopy of single molecules, condensed matter and nanostructures (www.single-molecule.ru).

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INTRODUCTION

Foreword

XIII International Conference on Hole Burning, Single Molecule, and Related Spectroscopies: Science and Applications (HBSM-2018) is organized by the Institute for Spectroscopy of the Russian Academy of Sciences (Troitsk, Moscow) with the Moscow State Pedagogical University. The conference will be held in the heart of Russia in one of the oldest Russian cities called Suzdal. It is known as one of the best places that illustratively and vividly tells about the centuries of eventful and dramatic history of this land and its people.

Laser selective spectroscopy has a particular significance and value for the Russian scientific community. The emergence of quasi-linear spectra of complex organic compounds in specially selected solvents at low cryogenic temperatures known as “Shpol’skii matrices” was first observed in 1952 by Prof. Eduard Shpol’skii’s group from the Department of Theoretical Physics of the Moscow State Pedagogical Institute. In 1972, a former student of Prof. Shpol’skii, Prof. Roman Personov, and his colleagues at the Institute for Spectroscopy of the USSR Academy of Sciences demonstrated successful site-selective laser excitation of narrow luminescence spectra in organic molecules. Two years later, in 1974, Personov’s group with their colleagues from the Institute of Physics in Tartu, Estonia (USSR) conducted the fundamental experiments on the persistent spectral hole burning. That work had formed the basis of laser site-selective spectroscopy of molecules which has now evolved in single-molecule spectroscopy.

HBSM was known under a few different names. It started in 1987 in Tallin, Estonia (USSR) as “All-Union Symposium on Modern Methods of Laser Spectroscopy of Molecules in Low-Temperature Media”. The second meeting took place in Monterey (California, USA, 1991) as “Persistent Spectral Hole Burning: Science and Applications” while the third became “Spectral Hole Burning and Luminescence Line Narrowing: Science and Applications” and moved to Ascona (Switzerland, 1992). Later it was organized as “International conferences on Hole-Burning and Related Spectroscopies (HBRS): Science and Applications” in Tokyo (Japan, 1994), Brainerd (Minnesota, USA, 1996) and Hourtin (France, 1999). In 2001, the conference finally found its current name “Hole Burning, Single Molecule, and Related Spectroscopies (HBSM): Science and Applications”. It paved its path through Taipei (Taiwan, 2001), Bozeman (Montana, USA, 2003), Aussois (France, 2006), Palm Cove (Australia, 2009), Tübingen (Germany, 2012) and Tartu (Estonia, 2015). This conference series has been exceptionally successful in bringing together participants from the leading research teams around the world to discuss the latest development in the fundamental science and the applications of site-selective and single-molecule spectroscopy and related topics.

We look forward to meeting you in Suzdal and Moscow!

Head of the HBSM-2018 Organizing Committee Prof. Dr. Andrei Naumov, Sci. secretary Dr. Kamil Karimullin.
The Shpol’skii – Rebane – Personov Prize for outstanding scientific achievements in the area of site-selective spectroscopy

The International Advisory and Program Committee (IAPC) of the International Conference on Hole Burning and Single Molecule Spectroscopy (HBSM) has established a special Prize and a medal named after Prof. Eduard Shpol’skii, Prof. Karl Rebane, and Prof. Roman Personov that will be awarded for outstanding scientific achievements in the area of site-selective spectroscopy.

The Prize bears the names of three outstanding scientists – the founders of the scientific direction of selective spectroscopy of complex organic molecules.

Prof. Eduard Shpol’skii and his colleagues from MPSU in 1952 discovered the effect of quasilinear spectra of organic chromophore molecules in the substances later named “Shpol’skii matrices” at cryogenic temperatures, which opened the way for the fine-structure spectral analysis of a huge number of complex organic compounds. The term “Shpol’skii effect” has now become a commonly used term in scientific communities around the world.

Prof. Karl Rebane, who headed the Institute of Physics of the Academy of Sciences of the Estonian SSR, and his colleagues made a great contribution to understanding the appearance the zero phonon spectral lines of single impurity molecules. He developed the theoretical foundations of optical spectroscopy of impurity centers, which subsequently led to the discovery of the narrow stable hole burning simultaneously in the Institute of Physics in Tartu and the Institute for Spectroscopy of the USSR Academy of Sciences in 1974. K.K. Rebane predicted and then discovered hot luminescence in crystals.

Prof. Roman Personov and his colleagues at the Institute for Spectroscopy of the USSR Academy of Sciences in 1972 were among the first to conduct unique experiments on laser narrowing of fluorescence lines in impurity organic compounds. Many authors both in Russia and worldwide call the effect of laser excitation of the fine-structure luminescence spectra the Personov effect.

The discoveries of these three scientists stimulated numerous studies in the area of site-selective spectroscopy all over the world, culminating in the detection of spectra of single molecules, which later played a decisive role in the emergence of a new interdisciplinary direction of ultra-high spatial resolution optical spectroscopy, now known as nanoscopy. Numerous investigations in this field have been the basis and the reasons for organizing the HBSM conference series.
**Statue of the SRP-Prize**

1. The International Advisory and Program Committee (IAPC) of the International Conference on Hole Burning and Single Molecule Spectroscopy (HBSM) following the suggestion from Moscow State Pedagogical University (MSPU, Russia), Institute of Physics of the University of Tartu (IP Tartu, Estonia), and Institute for Spectroscopy of the Russian Academy of Sciences (ISAN, Russia) have established a Prize to be awarded in the future HBSM meetings in the memory of Professor Eduard Shpol’skii, Professor Karl Rebane and Professor Roman Personov (Shpol’skii–Rebane–Personov Prize).

2. These three scientists are recognized to give the key contributions to the field of the site-selective spectroscopy and help its development to the modern state of the art:
   – Prof. E.V. Shpol’skii with his colleagues from MSPU in 1952 discovered the effect of quasi-linear spectra of organic chromophore molecules in specific hosts (named later “Shpol’skii matrices”) at cryogenic temperatures. This discovery paved the way to the fine-structure spectral analysis of complex organic condensed matter.
   – Prof. K.K. Rebane, heading IP Tartu, with his colleagues made strong contributions to understanding the phenomenon of zero-phonon lines by developing in 1960s the theoretical background for impurity centers spectroscopy. It was followed by co-discovery in IP Tartu of persistent spectral hole burning simultaneously with ISAN in 1974.
   – Prof. R.I. Personov with his colleagues from ISAN in 1972 performed the pioneer experiments of laser fluorescence line-narrowing in dye-doped organic solids, and in 1974 co-discovered (with the researchers from IP Tartu) the effect of persistent spectral hole burning.

   These discoveries stimulated research activities world-wide and made site-selective spectroscopy of complex organic solids an important area. It culminated in the detection of spectra of single molecules and now, in general, it has become one of the key components in development of modern nanooptics. Numerous investigations in this field have been the basis and the reasons for organizing the HBSM conference series.

   For these reasons, the IAPC HBSM felt it is appropriate to establish a prize in the honor which would recognize outstanding contributions made by researchers in the field of Site-Selective Spectroscopy of Complex Condensed Matter.

3. Eligible nominees are researchers in the active phase of their scientific work, who have performed outstanding investigations in the field of site-selective spectroscopy of complex condensed matter, including such topics as: Photoinduced phenomena in solids, Single nanosystems and nanooptics, Functionalized nanomaterials, Quantum technologies. The Prize winner should be a leader of scientific school in corresponding field, advising Ms.S. and Ph.D. students. The results obtained by nominee should be world-wide recognized, published in hi-ranking journals and presented in prestigious conferences (incl. HBSM) advertising the HBSM community and results obtained therein.
4. Nominations should consist of a letter of citation, a copy of the nominee's curriculum vitae (by form presented in the Application below) and at least one letter of endorsement by people acquainted with the nominee's contributions. Self-nomination is possible with endorsement letter only.

5. The Prize includes the monetary part of 1,500 Euro, plaque and diploma citing the contributions for which the winner is being recognized.

6. The Financial support for SRP-Prize will be fulfilled in equal parts by MSPU, IP Tartu, and ISAN. In future some additional support may be applied by special decision of IAPC HBSM or other sponsors.

7. SRP-Prize Jury consists of members of IAPC HBSM, and includes the representatives form MSPU (Shpol’skii Chair of theoretical physics), IP Tartu (Laboratory of laser spectroscopy), ISAN (Laboratory of electronic spectra of molecules), and headed by the Head of Local Organizing Committee of the forthcoming HBSM conference. The total number of Jury members should be not less than 5. The votes of Prize committee members should be submitted confidentially to the Jury Head, who is to announce the final result.

8. The winner of SRP-Prize will be obliged to present the honor lecture at the coming HBSM conference where the awarding ceremony is scheduled.

The 1\textsuperscript{st} winner of the Shpol’skii–Rebane–Personov Prize – Prof. Fedor Jelezko

Shpol’skii–Rebane–Personov Prize is awarded for the first time during HBSM-2018 to Professor Fedor Jelezko (Ulm University, Germany) for his pioneering experiments on quantum optics with single molecules, on NV color centers in diamonds and their applications for magnetometry and quantum information.

Prof. Dr. Fedor Jelezko
Born in 1971 in Minsk, Belarus
Feb 2011 – to date: Full Professor and Director of the Institute for Quantum Optics and, Department of Physics, Ulm University, Ulm, Germany.
Mar 2007 – Jan 2011: Lecturer, Senior lecturer (tenured): Physics Department, University of Stuttgart
Oct 1999 – Mar 2007: Research Assistant, Physical Institute, University of Stuttgart

Made full use of zero-phonon line of organic molecules and of color centers to test quantum optical concepts such as light shift, Rabi resonances, etc. and to develop new applications such as sensitive magnetometry.

In pioneering work over the last decade, Fedor Jelezko has made ground-breaking contributions that have established atomic scale lattice defects, so called colour centers, in diamond as a technology that can harness quantum coherence and entanglement even under ambient conditions. Furthermore, Fedor Jelezko has developed applications in such devices that are ranging from quantum information processing to the realization of new quantum sensing and imaging technologies and he has demonstrated their in-principle feasibility in experiments.

Main related papers


Photon echoes and coherent magneto-optical phenomena in semiconductors

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Abstract. Coherent optical phenomena such as photon echoes are well established for investigation of energy structure and coherent evolution of exciton complexes in semiconductors. We concentrate on photon echoes from charged exciton complexes in n-type direct band semiconductor structures subject to transverse magnetic field (Voigt geometry). A stimulated step-like Raman process induced by a sequence of two laser pulses creates a coherent superposition of the ground state doublet (Raman coherence) which can be retrieved only optically because of selective excitation of the same subensemble with a third pulse. This approach can be used for remarkably high resolution spectroscopy of the ground state levels. Moreover the decay of Raman coherence in an electron spin ensemble measured by photon echoes provides unique access to the local spin relaxation processes of resident electrons.

Ultrafast coherent optical spectroscopy provides essential information on dynamical properties of charge and spin states in condensed matter [1]. Optical techniques such as ultrafast pump probe and transient four-wave mixing (FWM) in combination with magnetic field and polarization sensitive excitation and detection represent a powerful set of methods. Particular interest is attracted by systems with more than two states interacting with light. The most representative examples are V- (Λ-) type energy level orders where the single ground (excited) state is optically coupled to an excited (ground) state doublet. These level schemes make it possible to observe several fascinating phenomena such as quantum beats, coherent population trapping and electromagnetically induced transparency (EIT) which may be used for applications in quantum information technology. The main feature of a Λ-scheme is a possible long coherence time of the ground states. In semiconductors, the Λ-scheme can be obtained for optical excitation of localized resident carriers, e.g., electrons in the conduction band or holes in the valence band, using their spin degree of freedom. In the case of resident electrons, localized charged exciton (trion X−) and the donor-bound exciton (D\textsuperscript{0}X) are possible optically excited states. Optical manipulation of the resident carrier spin states and their coherent dynamics after excitation with short picosecond laser pulses has been studied in different semiconductor systems [2]. However, the majority of the FWM and photon echo studies in semiconductors did not use so far the spin degree of freedom in the ground state.

Here, we present an overview of photon echo spectroscopy in transverse magnetic field which allows us to address selectively the spin degrees of freedom and to investigate coherent

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evolution of ensemble of conduction band electrons. In particular, the step-like stimulated Raman process following after the excitation of the system by the two optical pulses allows the coherent transfer of the optical excitation into the spin ensemble of the resident electrons and observation of the magnetic field induced long-lived photon echoes [3,4]. The main effects are demonstrated for a model system – CdTe/(Cd,Mg)Te quantum wells, where inhomogeneous broadening of the optical transitions is small and it is possible to excite selectively the various exciton complexes with the different degree of localization. Recently we have also observed magnetic field induced photon echo signals for D\textsubscript{0}X complexes in the hexagonal epitaxial ZnO layers, where the similar energy level scheme and selection rules for the optical transitions are realized if the optical excitation is performed along the c-axis of the crystal [5].

We demonstrate that the amplitude of long-lived echo oscillates at the frequency of Larmor precession frequency which corresponds to the Zeeman splitting of a resident electron spin levels in transverse magnetic field. Thus our approach can be used as tool for remarkably high resolution spectroscopy of the ground state levels: We are able to resolve splittings between the spin levels with sub-µeV precision and to distinguish between different types of electrons in the ensemble, namely electrons either bound to donors or localized on QW potential fluctuations [6].

Next, our results demonstrate that the decay of Raman coherence in an electron spin ensemble measured by photon echoes provides access to the local relaxation processes, such as hopping of carriers between localization sites or spin interactions between electrons within the ensemble (e.g., spin flip-flops). This is because every individual electron in the ground state contributes to the coherent optical response only if it is addressed by all three optical pulses sequentially. Moreover, in photon-echo experiments, because of dephasing of optically excited states between the first and second optical pulses, no macroscopic spin polarization is created in the ground state after the stimulated Raman process.

References


Longitudinal current in single-atom interacting with laser field

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Abstract. We present the results of calculations of high-harmonic spectra at different mutual orientations of laser field and atomic angular momentum. The presented results show that the atomic current induced by the external laser field can include the longitudinal component orthogonal to the polarization vector of an incident field. Moreover, it provides an insight into the physics of processes which cause the polarization of generated harmonics. In addition, it hints at the way for the polarization control over high at harmonics.
Imaging and force transduction in correlative scanning force and confocal fluorescence microscopy

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Abstract. Correlative scanning force and confocal fluorescence microscopy has been used to study individual molecules, nanoparticles and nanoparticle oligomers. By applying a compressive force via the AFM cantilever, spectral blue and red shifts in the range of several meV/GPa have been observed for single dye molecules and semiconductor quantum dots. Moreover, individual Au nanoparticle dimers linked by a chlorophyll binding protein have been imaged in both modes and plasmonic fluorescence enhancement of the chlorophyll emission of up to a factor of 15 has been found.

Correlative microscopies are gaining increasing attention, since they allow for correlating structure or morphology of individual nano-sized objects from a potentially heterogeneous population with their electronic or photo-physical properties. An early example have been measurements of the emission spectra and polarization of single semiconductor nanocrystal quantum dots as well as their crystallographic structure by a combination of confocal fluorescence microscopy and transmission electron microscopy. [1] Recently, relying on the same approach it has been shown that the fraction of “on”-times of single CdSe/CdS nanocrystals decreased when stacking faults were present.[2] Besides transmission electron microscopy, single molecule spectroscopy has also been combined with scanning electron microscopy or scanning probe techniques. [3]

We have used confocal fluorescence and scanning force (AFM) microscopy of single molecules and nanoparticles for two purposes: i) To correlate structural information with photo-physical properties, and ii) To apply compressive stress and track the effects of the impact on the electronic states by fluorescence spectroscopy.

In a first set of experiments we applied compressive forces via the AFM cantilever to single terylenediimide molecules decorated with large side-groups and deposited on a mica surface. Reversible blue and red-shifts as well as irreversible shifts were observed and attributed to different conformations of the terylene core induced by the compressive force. [4] Similar experiments were conducted with CdSe/CdS/ZnS nanocrystals and again blue and red shifts were registered under the directional force. [5] These experiments clearly have shown that a given particle either shifts to the red or blue under pressure (see Fig.1), resolving a controversial issue remaining from bulk studies of semiconductor quantum dots in diamond anvil cells. The direction of the spectral shifts largely depends on the crystallographic axis of the quantum dot onto which the non-hydrostatic pressure is applied. However, the orientation of the approximately spherical core-shell particles typically is not known. This obstacle can be mediated by the use of nanocrystal platelets which can be deposited in a well-defined way and therefore expose a known crystallographic face.

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Fig. 1. Scheme how to apply force to a single nanoparticle with the tip of an AFM-cantilever. For the case shown the emission spectrum of a single CdSe/CdS/ZnS-nanocrystal was shifted to the blue with increasing force. After force was released, the spectrum shifted back to its original position.

Correlative atomic force and confocal microscopy has also been employed to study the properties of Au nanoparticle oligomers, linked by the water-soluble chlorophyll binding protein (WSCP). For individual dimers - as identified by AFM - fluorescence enhancements of up to a factor of 15 with a clear dependence on the excitation polarization were observed and attributed to mainly plasmonic enhancement of the Chl excitation rate. Promising features of this protein-directed assembly of a plasmonic nanoantenna are the simple transfer of the construct into different environments and the structure-driven positioning of the pigments in the plasmonic hotspot.

References

Coherent spin dynamics of erbium doped crystals at sub-Kelvin temperatures

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Abstract. We investigate electron spin coherence properties of erbium (Er³⁺) ions in YSO and YLF crystals with a view to their potential application in optical and microwave quantum memories. We perform optical coherent spectroscopy at sub-Kelvin temperatures by using two and three-pulse echo experiments. By cooling our samples below conventional temperature 1.5 Kelvin, we show that the deep freezing of erbium doped crystals results in 5 to 100-fold increase of optical phase memory time depending on the crystal type, doping concentration and orientation.

Rare-earth (RE) doped solids represent today one of the widely exploited materials for the modern laser and telecommunication industry. Yet, recently, they have raised a strong interest in the field of quantum information storage, signal processing and communication. The RE ions possessing a half-integer spin are also known as Kramers ions. The exclusive feature of some Kramers ions, such as Nd³⁺, Yb³⁺, and Er³⁺, is the presence of optical transitions within the standard telecommunication bands, which is very attractive for quantum repeater applications. There, RE-doped crystals can be used as quantum memory elements for a long-lived storage of entangled photons.

One of the main challenge associated with using crystals doped with Kramers ions in memory applications is their quite strong unquenched electronic magnetic moment, which in the case of Er³⁺ reaches nearly 8μB. At weak magnetic fields and conventional temperatures of T>1.5K, large electronic spins mediate a rapid spin–lattice relaxation process which limits the spin coherence time. Another contribution to the decoherence is caused by magnetic dipolar interactions with another electronic spins. Therefore, in order to attain long coherence time, high magnetic field up to 7T and low temperatures of 1.5K are used to polarize an electronic spin bath. By following this prescription the longest optical coherence time of 4.4 ms among solid-state systems has been demonstrated for 0.001% Er³⁺:Y₂SiO₄ (Er:YSO). Also, in the very recent experiments Rančić et al. demonstrated optically addressable nuclear spin states of ¹⁶⁷Er:YSO with coherence time of 1.3 s [1].

Contrary to that, we propose to follow another strategy. The detrimental role of spin–lattice and spin–spin relaxation processes on quantum coherence can be reduced by deep freezing of RE-doped crystals down to ultra-low temperatures, i.e. at T<<1K, and at much weaker fields of 10-100 mT. We will report on investigation of spin decoherence properties of erbium doped YSO and YLF crystals at such extreme conditions [2]. The measurements are performed by using continuous and pulsed optical vector network analysis setup [3]. In

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addition, I will briefly report on confocal microscopy of a single SiV-center in diamond and implementation of all-optical control of its spin states at ultra-low temperatures [4].

References

Comparison of different schemes for temperature read-out from luminescence

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Abstract. This contribution presents the comparison of luminescence spectroscopic schemes for the read-out of temperature. Schemes are classified to as time-integrated and time-resolved ones depending on the temporal nature of the luminescence measurements. The former includes methods based on reading temperatures from the intensity of emission, the ratio of emission intensities, the changes of excitation and emission band positions and bandwidths with temperature, and luminescence anisotropy (polarization). The later includes methods based on measurements of emission decay-times and rise-times. The contribution also presents a comparative analysis of the advantages/disadvantages between of time-integrated and time-resolved temperature read-outs.

1 Introduction

Temperature sensors comprise a market of USD 5.13 billion (in 2016) and are used across a broad spectrum of human activities, such as in medicine, home appliances, meteorology, agriculture, industry, and military [1]. Scientific and technological developments and awareness of environmental and health problems generate a continual need for the development of novel temperature measurement methods. Even more importantly, new temperature measurement concepts and temperature probes are required for applications in emerging environments, the most important of which being nanotechnology, biotechnology, and integrated optics. A significant growth in demand is expected in the near future for contactless temperature sensors, which are not only easy to use, but are less complex and more accurate than contact temperature sensors. For example, there is an immediate need for noncontact thermometry for moving objects or objects which are sensitive to contact, difficult to access, or in hazardous locations [2].

Thermometry based on changes in the optical properties of materials is considered a promising route to meet these needs. The largest attention among emerging optical methods is in the luminescence thermometry because of the ease of detection of luminescence signal in comparison to other methods, relatively fast response, and a good spatial resolution. Luminescence thermometry can be utilized with probes prepared from wide variety materials of which lanthanide and transition metal ion activated phosphors [3], semiconductor quantum dots, organic dyes, and metal-organic complexes are the most exploited ones [1]. Also, different temperature dependent features of luminescence can be exploited for the determination of temperature. Herein, the comparison of schemes for the temperature read-outs from luminescence is given.

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2 Temperature read-outs

Luminescence thermometry methods can be classified as time-integrated (steady-state) or time-resolved with respect to the temporal character of the observation of luminescence. Time-integrated methods are executed with an illumination that has constant intensity over the time period of detection of luminescence and signal integration. These methods are founded on the changes in temperature caused by excitation and emission band energies and bandwidths, emission intensities, ratios of intensities of different emission bands (spectral shape), and polarization/anisotropy. The lifetime of the material’s excited state provides information about the material’s temperature and can be evaluated from the decay of emission originating from a particular excited state. The initial rise of emission after excitation is also a temperature sensitive feature of luminescence [4]. Comparison of different temperature read-outs from luminescence is given in Table 1. Regarding the complexity and the cost of equipment, time-integrated measurements are favorable to time-resolved ones since they are simpler and cheaper. However, time-resolved measurements are self-referencing, are not compromised by inhomogeneity of the probe, and by using delayed the problem of strong background luminescence can be eliminated.

Table 1. Comparison of different temperature read-outs from luminescence

<table>
<thead>
<tr>
<th>Read-out</th>
<th>Temporal character</th>
<th>Self referencing</th>
<th>Sensitivity to disturbance</th>
<th>Processing time</th>
<th>Precision</th>
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</thead>
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<tr>
<td>emission intensity</td>
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<tr>
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</tr>
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</table>

References

Optical resonances of Si-nanoparticles for dielectric photonics

Andrey Evelyukhin

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Abstract. Strong resonant light scattering by individual Si nanoparticles is theoretically discussed and experimentally demonstrated. It is shown that the pronounced resonances associated with the excitation of magnetic and electric multipole modes in the nanoparticles. For fabrication of Si nanoparticles the laser printing technologies have been used. The scattering properties were studied by single particle spectroscopy. It is shown that it is possible to design silicon nanoparticles for which the electric and magnetic multipole resonances are overlapped at a given spectral range providing special directional scattering.

Recently it has been demonstrated that spherical Si nanoparticles can strongly scatter optical waves. It was established that the resonances of 200-300 nm Si nanoparticles in the visible spectral range are associated with the excitation of magnetic and electric dipole moments of these nanoparticles [1-3]. In this work we discuss the origin of the magnetic dipole (multipole) resonance in dielectric nanoparticles using the quasi-static electromagnetic approach and Mie theory [4].

Fig. 1. (Left) SEM image of spherical Si nanoparticle on a glass substrate fabricated by the laser printing technology. (Right) Scattering spectrum of the nanoparticle. Two peaks correspond to electric dipole (ED) and magnetic dipole (MD) resonant scattering.

Then theoretical and experimental results concerning the resonant optical properties of Si nanoparticles are presented. For example, figure 1 demonstrates SEM image of a spherical Si nanoparticle and its corresponding scattering spectrum recorded by a fibre-coupled spectrometer. The scattering spectrum clearly demonstrates two resonances around 520 nm and 630 nm, respectively. Theoretical analysis [1,2] of the experimental spectrum shows that resonant peaks correspond to excitation of electric and magnetic dipole modes of the nanoparticle.

A new theoretical approach [3,5,6] allowing multipole analysis of light scattering by arbitrary-shaped nanoparticles located in free space and on flat substrate surface is demonstrated as well. This approach is applied to investigations of light and surface plasmon polaritons (SPPs) scattering by Si nanoparticles and Si nanoparticle structures [7,8]. It is shown...
and discussed how the particle magnetic multipoles can affect spatial distribution of the scattered light and SPP (Fig. 2).

Applications of Si nanoparticles for realization of nanoantennas and metamaterials are suggested and discussed.

**Fig. 2.** Simulated intensity distributions in systems with Si nanoparticle structures. (Left) Scattering of a light beam by 2D Si nanoparticle structure in free space. (Right) Scattering of a SPP beam by a circle Si nanoparticle structure placed on a silver substrate. Positions of the nanoparticle structure are shown by white dashed-dot and dashed lines. Frequencies of the light and SPP correspond to the magnetic dipole resonances of Si nanoparticles.

**References**

Correlation between the maximum wavelength and the line width in the emission of a single semiconductor colloidal quantum dot at different temperatures

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The very first measurements [1] of the spectrally resolved photoluminescence of single colloidal semiconductor quantum dots CdSe (QDs) revealed the phenomenon of very slow spectral diffusion (SD) with a characteristic time scale in order of hundred seconds. Usual explanation of this phenomenon [2-5] is based on the quantum-confined Stark effect by the movement of charge carriers around individual QDs. Gomez et al. [4] found correlation between linewidth and peak position of the single QD spectrum at room temperature.

A unique spectroscopic experiment on single QD under slow heating and cooling was carried out by our group. Fluorescence images and spectra of single quantum dots were measured via home-build fluorescence microscope equipped by prism spectrometer. Two optical schemes: wide-field and scanning confocal schemes were combined in one microscope in order to simplify procedure of single quantum dots preliminary searching (by fluorescence image processing and antibunching determination) and sequential measuring of fluorescence spectra of the selected QD.

Quantum dots (CdSe/ZnS, Sigma Aldrich with Fluorescence peak at 620 nm) were dispersed in toluene solution of polyisobutylene in low concentration and then spincoated onto a cover glass. Thicknesses of polymer films with single quantum dots were varied in the range of several tens of nanometers. Sample temperature was controlled by LakeShore temperature controller and regulated by Peltier element attached to the sample. In our experiments temperature was varied in the range from 306 K C up to 353 K. Tunable dye laser (Coherent CR599) was used to excite quantum dots at the wavelength of 580 nm near the quantum dot absorption band edge. Excitation laser intensity (~ 100 W/cm² in a focused spot) was attenuated by neutral spectral density filters (Standa) and controlled by Newport Power meter. Set of interference filters (Semrock and Thorlabs) separated fluorescence signal from scattered laser radiation. Two highly sensitive cooled EMCCD cameras were utilized to capture single quantum dot images (Andor Luca) and spectra (Andor Ixon Ultra). Hanbury Brown and Twiss scheme with broadband 50% splitter (Thorlabs) and two identical SPAD detectors (EG&G SPCM-200PQ, time resolution 1 ns, dead time 200 ns, QE ~ 50 %) were used to measure autocorrelation function for QD fluorescence intensity. Sample space position was controlled by piezo-driven stage (NanoScanTechnology), which allows us to move the selected QD to the laser spot position with high (nanometer) precision.
Fig. 1. The dependence of the linewidth on the peak wavelength. The points correspond to the experimentally obtained values at room temperature. The solid line indicates the theoretical dependence obtained in the proposed model based on the fluctuations of the electron-phonon interaction.

Fluorescence spectra sequences for single quantum dots were measured with exposure time 200 ms and spectral resolution $\sim 0.7$ nm, which was enough to rich good signal to noise ratio. A systematic displacement of the emission line caused by temperature changing was observed as well as spectral diffusion at each given temperature.

The experiments show a correlation between the position of the maximum and width of the QD emission spectrum (see Fig. 1). In order to explain experimental results we propose a new model of the QD spectral diffusion and temperature dependent shift. In the model both the peak position and the linewidth are determined by the electron-phonon interaction value. Slow variations of this value in time lead to correlated fluctuations of the wavelength and linewidth at given temperature. The increase in temperature changes the average value of the electron-phonon interaction, which leads to a systematic shift in position of the peak. As seen on Fig. 1 the theoretical dependences of the line width on the peak position at different temperatures very well describes the experimental data.

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References

Long lived optical and spin coherences in rare earth doped nanomaterials

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Abstract. Nanoscale systems that coherently couple to light and possess spins offer key capabilities for quantum technologies. However, an outstanding challenge is to preserve properties, and especially optical and spin coherence lifetimes, at the nanoscale. We investigate rare earth doped nanoparticles and show that narrow optical and nuclear spin linewidths can be obtained in these materials. These results open the way to new quantum light-atom-spin interfaces for optical quantum technologies.

Nanoscale systems offer new functionalities in quantum technologies, like single qubit control and detection, or extremely localized sensing [1,2]. The ability to couple qubits with light is an attractive feature for these systems for interfacing with photonic qubits, creating light matter entanglement or fast processing of quantum information. In this work, we will review recent results obtained in rare earth doped nanoscale materials, with a focus on the optical and nuclear spin properties of Eu$^{3+}$ doped Y$_2$O$_3$ nanoparticles that we recently reported [3-5].

The 0.5% Eu$^{3+}$:Y$_2$O$_3$ particles were prepared using homogeneous precipitation followed by high temperature annealing. Their average diameter was 400 nm, with crystalline domains of 130 nm. The particles were placed between two glass plates in a helium bath cryostat and measurements performed in transmission (Fig. 1). A 2-pulse photon echo sequence was used to determine the homogeneous linewidth of the $^5$D$_0$-$^7$F$_0$ transition at 580.88 nm (vacuum). Although the light was strongly scattered by the powders, we could use heterodyne detection, which increased a lot signal to noise ratio.

We studied homogeneous linewidth dependence on temperature, applied magnetic field, and measurement time scale, and determined the dominant broadening interactions for various temperature ranges. These results provide strong evidence that for 400 nm diameter nanoparticles the minimum linewidth achieved (45 kHz at 1.3 K) is not fundamentally limited by phonon processes [4] (Fig.1).

Experiments on nuclear spin coherence were also performed on the $^{151}$Eu isotope (I = 5/2), which has a natural abundance of about 50%. The ground state $\pm1/2$-$\pm3/2$ hyperfine transition at 29.33 MHz was probed using an all-optical scheme. Two-color laser pulses resonant with the optical $^5$D$_0$-$^7$F$_0$ transition and detuned from each other by the hyperfine transition frequency were used to excite and rephase spin coherences. Spin echoes were detected using Raman heterodyne scattering.
We measured spin coherence lifetime ($T_2$) of 1.3 ms at 5 K [5]. To our knowledge, this is the longest $T_2$ for an optically addressable spin in a nanoparticle. Moreover, this is only one order of magnitude shorter than what was observed on transparent ceramics and high quality bulk single crystals [6]. The additional dephasing is attributed to magnetic perturbations, that are likely to be trace impurities or defects carrying electron spins. Using an all-optical dynamical decoupling sequence, $T_2$ were extended up to 8 ms, limited by a large spread in Rabi frequency due to the strong light scattering in the powder and the random orientation of the particles.

Rare-earth doped nanoparticles are thus the only nano-material in which optically controlled spins with millisecond coherence lifetimes, as well as optical linewidths have been reported. These results open the way to providing quantum light-atom-spin interfaces with long storage time within hybrid architectures. For example, these particles could be placed in optical micro-cavities [7] to enhance light-matter interactions and single ion readout efficiency, with applications to quantum processors and memories.

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**References**

Quantum photonic integrated circuits with waveguide integrated superconducting nanowire single-photon detectors

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Abstract. We show the design, a history of development as well as the most successful and promising approaches for QPICs realization based on hybrid nanophotonic-superconducting devices, where one of the key elements of such a circuit is a waveguide integrated superconducting single-photon detector (WSSPD). The potential of integration with fluorescent molecules is discussed also.

Currently, many physical systems for the realization of qubits including superconducting circuits, trapped ions and atoms, quantum dots, color centers in a solid and photons are intensely studied. Here we focus only on the last item in the list - photons. Because photons interact only weakly with an optically transparent medium but not with each other, have several degrees of freedom for encoding of quantum information and provide fast propagation speed, they are an attractive choice for creating quantum networks. However, while individual photons can be manipulated conveniently, the creation of two- and three- deterministic qubit gates requires strong nonlinear interaction between photons. In this case, the advantages of the photons are compensated for by their shortcomings, which for a long time limited the use of photons as qubits. Fortunately, Knill, Laflamme and Milburn (KLM) proposed the concept of linear optical quantum computing (LOQC), allowing to create non-deterministic gates using photons, linear optical elements and single photon detectors. While the implementation of the KLM-protocol is possible in free space, the need for a large number of optical components and their precise configuration requires a more complex solutions. Due to a number of advantages, such as scalability, small footprint, inherent stability, no need for optical alignment as well as low power consumption and CMOS-compatibility, quantum photonic integrated circuits (QPICs) can successfully overcome these challenges.

Popular material platforms for the realization of QPICs include silicon, gallium arsenide, and diamond. Each platform has its own advantages and disadvantages and is currently in different stages of development [1]. Nevertheless, all of the platforms rely on combining single photon sources, linear optical elements and single-photon detectors on chip.

Recently, a fully integrated circuit including a single photon source (carbon nanotube), detectors (superconducting nanowire single-photon detectors) and silicon-nitride waveguides has already been implemented on a single chip [2]. Despite the demonstration of the working concept, the purity of the emulsion of electroluminescent photons is not yet sufficient for large scale processing and new single-photon sources are constantly being investigated.
Fluorescent molecules are one of the promising single-photon sources. Recently the emission of single photons from Dibenzoterrylene (DBT) molecules into Si3N4 ridge waveguide at room temperature was demonstrated. DBT was placed on a Si3N4 waveguide to couple emitted single photons through the evanescent waveguide mode into the guided mode. The advantages of this approach include a small footprint, simple fabrication methods and scalability towards arrays of integrated single photon sources for QPICs. However, unlike the on-chip integrated electroluminescent nanotube [3], a more complex photonic circuit is required. The next step in the integration of a single-photon emitted molecule and QPIC including effective pump rejection (CDC) and superconducting nanowire single-photon detectors (WSSPDs) is proposed in Fig. 1b. As an efficient on-chip filter a contra-directional coupler (CDC) can be used. After optical pumping of a single molecule, the residual pump is rejected to the neighboring waveguide and routes to the optical absorber. Emitted photons are directed to WSSPD, reproducing the Hanbury Brown-Twiss scheme. By measuring the on-chip second order correlation function, one can detect non-classical light for QPICs, as well as to study the molecules itself.

Going beyond such proof-of-principle concepts, the realization of large scale QPICs is expected to have profound impact on science and technology, material engineering, as well as quantum information processing including quantum computing, simulation and metrology.


References

Impact of single point mutations on the excitonic structure and dynamics in Fenna–Matthews–Olson complex

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Abstract. Hole burning (HB) spectroscopy and modeling studies reveal significant changes in the excitonic structure and dynamics in several mutants of the Fenna–Matthews–Olson (FMO) trimer from the green sulfur bacterium Chlorobaculum tepidum. In particular, the excited state decay times of the high energy excitons levels are significantly modified when mutation occurs near bacteriochlorophyll (BChl) 1 (with valine replaced by asparagine; V152N mutant) or BChl 6 (where tryptophan 184 near BChl #6 is replaced with phenylalanine; W184F mutant). Longer (averaged) excited-state decay (T₁) times of highest energy excitons in V152N and W184F mutants suggest that site energies of BChls 1 and 6, believed to play an important role in receiving excitation from the baseplate BChls, likely play a critical role to ensure the femtosecond (fs) energy relaxation observed in wild-type FMO complexes. HB spectroscopy reveals preferentially slower T₁ times (about one picosecond on average) since fs excited-state decay times prohibit HB process due to extremely low HB quantum yield and decreased peak absorption cross-section. Mutation induced heterogeneity, the composition of exciton states, and average, frequency dependent, excited-state decay times are discussed.

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Diamond based quantum technologies

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Abstract. Diamond is not only the king gemstone, but also a promising material in quantum technologies. Optically active impurities (colour centers) in diamond show unique coherence properties under ambient conditions. Their quantum state can be readout and manipulated using a combination of single molecule spectroscopy and magnetic resonance techniques. In this talk it will be shown how engineered spins in diamond can be used for creation of non-classical (entangled) quantum states. I will also demonstrate the potential of atomic magnetometers based on single color centers for nanoscale sensing and imaging. New photoelectric detection technique allowing efficient readout of single color centers will be discussed.

Electron and nuclear spin resonance is a spectroscopic technique that provides very detailed information on almost every possible substance but also as very insensitive. This may be contrasted to the excellent sensitivity of optical single molecule spectroscopy which is able to demonstrate the detection of single molecules in condensed matter. A recent development is a combination of these techniques making it possible to detect magnetic resonance transitions of single quantum systems. While first experiments were done with aromatic molecules at low temperatures, recently single spin magnetic resonance techniques were also applied to the study of defect centers in diamond allowing coherent single spin control and readout under ambient conditions. This new approach opened a number of interesting applications, such as quantum information processing and communication, secure quantum communication and sensing with nanometer resolution.

A particularly interesting application of diamond based quantum sensing is the detection of nuclear magnetic resonance on nanometer scales, including the detection of individual nuclear spins or small ensembles of external nuclear spins. Single nitrogen vacancy (NV) color centers in diamond currently have sufficient sensitivity for detecting single external nuclear spins and resolve their position within a few angstroms. The ability to bring the sensor close to biomolecules by implantation of single NV centers and attachment of proteins to the surface of diamond enabled the first proof of principle demonstration of proteins labeled by paramagnetic markers and label-free detection of the signal from a single protein. Single-molecule nuclear magnetic resonance (NMR) experiments open the way towards unraveling dynamics and structure of single biomolecules. However, for that purpose, NV magnetometers must reach spectral resolutions comparable to that of conventional solution state NMR. New techniques were proposed for this purpose and realized recently including technique that employs quantum entanglement. The ability to sense nuclear spins by NV centers also enables the transfer of polarization from optically polarized spins of NV centers to external nuclear spins. Such diamond based techniques for dynamic nuclear spin polarization are very promising for the enhancement of sensitivity of conventional MRI imaging.

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Most of mentioned above results obtained so far with diamond centers are based on optical
detection of single NV color centers. Recently it was shown that photoelectrical detection of
NV centers base on spin selective photoionization can provide robust and efficient access to
spin state of individual color centers
Light controls light: single molecules as optical switches

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Abstract. In recent years much attention has been given to design multistate molecular components with functionalities that cover the range from simple switches to logic gates [1-3]. In this regard photochromic molecules, i.e., molecules that can be interconverted between two bistable forms by light, have played an important role. Promising candidates that fulfill obvious demands such as high photochemical/photophysical stability and high fatigue resistance are compounds of the family of diarylethenes [2,3]. However, a serious drawback of this class of molecules is a low fluorescence quantum yield. Therefore we adapted the strategy developed by Irie and coworkers [2,3], to chemically synthesize complex tailor-made triads consisting of a photochromic dithienylcyclopentene (DCP) unit covalently linked to two perylene bisimide (PBI) molecules that are known as strong fluorophores, see fig.1 inset top left. This facilitates the combination of high fatigue resistance and high fluorescence quantum yield. Illumination with light in the UV spectral region induces a ring-closure reaction of the DCP and leads to a state with suppressed fluorescence from the PBIs, whereas light in the VIS spectral region yields a ring opening reaction of the DCP and restores the fluorescence from the PBI units. This allowed us to verify functionalities like optical gating and amplifying, yet where the electrons have been replaced by photons as signal carriers [4-6], see fig.1.

Fig.1. Relative change of the fluorescence of the photochromic triads as a function of the intensity of the UV/VIS conversion beams. The flow of (many) fluorescence photons from the PBI units can be controlled by (few) UV and VIS photons that induce the photocyclization/photocycloreversion reactions of the photochromic DCP unit, respectively.

Switching of photochromic molecules at the single molecule level has been demonstrated

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before [7], yet in those experiments no distinction was made between deliberate switching and unavoidable blinking of single molecules. The switching process is manifested as a finite delay between the onset of the fluorescence and the onset of the VIS laser. For a sequence of 8800 switching events the distribution of delay times can be reasonably well approximated as an exponential decay, in agreement with the expectation for a switching process that obeys Poissonian statistics [8]. From a statistical analysis, that takes results from reference experiments performed on the same triad without switching into account, we determined the positive predictive value $p(S|+)$ for deliberate light-induced switching. In words: The conditional probability that the triad indeed has switched given that we observed a finite delay for the onset of the fluorescence. For 15 triads studied the average of this probability amounts to $0.8 \pm 0.1$. In the best cases it reached about $96\%$, insufficient for optical memories with single triads, yet exceptionally good for super-resolution microscopy.

References

Single nanostructure extinction spectroscopy

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Abstract. In this talk I describe recent work we have conducted on the extinction spectroscopy of individual nanostructures. The first part describes how we have measured and assigned the size-dependent excited state transitions of individual, quantum confined CdSe nanowires. I then describe work to measure the dimensionality-dependent evolution of CdSe as it transitions from a nanowire to a quantum dot. This has entailed measuring the extinction spectrum of individual CdSe nanorods. The second part of the talk describes work we have done on single layer graphene oxide (GO). GO is an inherently disordered material with oxygen containing functional groups decorating its basal plane. Light-induced reduction removes these groups. Unfortunately, the photoreduction mechanism of GO is not well understood. In what follows, I therefore describe how we have rationalized this photoreduction through the photolysis of GO’s oxygen containing functional groups. Fluorescence intermittency arises naturally as a consequence of this process. The end of my talk focuses on recent work we have done to develop super-resolution single nanostructure infrared absorption measurements as a technique for probing semiconductors such as GO.

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One might regard the emission and absorption of light by a single atom in free space as one of the most fundamental processes in quantum optics, which has not yet been fully explored on the experimental side:

1. A single atom should be able to act as an efficient 100% reflector for narrow band coherent light provided the light power is not too high.
2. A single atom should be able to efficiently shift the phase of a narrow band coherent light by up to 180° if the light power is not too high. (First results, see [1].)
3. A single photon should be able to deterministically excite a single atom.

We are developing and testing a set-up for the demonstration of this reversal of spontaneous emission by placing a single atom at the focus of a deep parabolic mirror. Using an ionized atom one can hold it in place by electrodes, a variation of the Paul trap for ions. It is expected that such a 100% excitation by a single atom require sending in the time-reversed version of the photon, which would be emitted by the same atom if it were to decay. Regarding the spatial structure, a parabolic mirror generates the required ingoing spherical wave fronts. Concerning the temporal shape, the single photon wave packet should have an exponentially rising leading edge as opposed to the exponentially falling trailing edge of the wave packet created in a spontaneous emission process [2].

References

1/2 Fabry Pérot micro-resonators in single molecule spectroscopy

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Abstract. Embedded in a tuneable 1/2-FabryPérot micro-resonator the radiative relaxation of a dye molecule or quantum dot can reproducibly be modified allowing to determine their quantum yield, control Förster energy-transfer or localize them with nanometer precision.

1 Introduction

Small optical micro-resonators are structures that confine light to volumes with dimensions on the order of a wavelength and hence have become increasingly important for controlling and studying light-matter interaction in integrated optics [1]. The spontaneous emission rate of an atom or molecule depends on both the transition dipole moment (TDM) between the electronically excited state and the electronic ground state as well as on the density of optical modes of the electromagnetic field in the surrounding medium. In an optical subwavelength micro-resonator with piezo-controlled mirror separation the density of optical modes can be varied with respect to the free space in a controlled manner, and hence, also the radiative coupling of the dipole transition of the emitter to the optical field can be tuned.

2 Results

We demonstrate controlled modification of the vibronic relaxation dynamics of a single fluorescent molecule fixed in a solid host matrix by varying the distance between the cavity mirrors. While it is well known from quantum electrodynamics nowadays that the spontaneous emission is not an intrinsic property of an atom but can be modified by tailoring the electromagnetic environment, the situation for a molecule or quantum dot embedded in a solid host is more complex since the radiation rate and relaxation pathways depend on the balance between the radiative (the far-field) and non-radiative (the near-field) relaxation dynamics, the latter being sensitively dependent on the interaction with the local chemical environment. Hence, by controlling the electromagnetic environment of a single molecule or quantum dot, we can select the vibronic transition where fluorescence will mostly occur [2] and we can tune its radiative transition and determine its fluorescence quantum yield [3] as shown in Fig.1.

Using a tuneable optical micro-resonator with subwavelength spacing, we demonstrate controlled modulation of the radiative transition rate of a single molecule, which is measured by monitoring its fluorescence lifetime [4]. By comparing the experimental data with a theoretical model, we extract both the pure radiative transition rate as well as the quantum yields of individual molecules. We observe a broad scattering of quantum yield values from molecule to molecule, which reflects the strong variation of the local interaction of the observed molecules with their host environment. Finally, we will also discuss the possibility of controlling Förster resonance energy transfer in a tuneable micro-resonator [5, 6, 7] and

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nanometer precise localization [8].

![Diagram](image)

**Fig. 1.** Adopted from ref. [5] (1) Chemical structure of a typical dye molecule. (2) Jablonski-like diagram with an electronic ground state $X_0$ and excited state $X_1$. After pulsed excitation (violet arrow) into the excited vibronic level $X_1'$ the system relaxes to the purely electronic level $X_1$. The electronic relaxation occurs either non-radiatively or radiatively into possible vibronic levels of the electronic ground state. Each fluorescent transition can be described by a spectrally broadened Gaussian band due to thermal energy level fluctuations and phonon interactions with the environment. (3a–3c) Tuning the micro-resonator with the on-axis spectral emission to the emission wavelength of a specific vibronic transition enhances resonant and suppresses off-resonant radiative transitions.

**References**


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The Story of Single Molecules, from Hole-Burning and Early FM Spectroscopy in Solids, to Super-Resolution Nanoscopy in Cells and Beyond

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Abstract. In the late 1970s and 1980s, many researchers around the world were exploring a novel optical storage concept, frequency domain optical storage, which was based on spectral hole-burning in the zero-phonon lines of impurities in solids at low temperatures. In 1989, experiments aimed at establishing the ultimate limits this optical storage idea led to the first optical detection and spectroscopy of a single molecule in the condensed phase using laser FM spectroscopy. At the unexplored ultimate limit of individual molecules, many surprises occurred where single molecules showed both spontaneous changes (blinking due to spectral diffusion) and light-driven control of emission, properties that were subsequently also observed in 1997 at room temperature with single green fluorescent protein variants. In 2006, PALM and related approaches showed that Abbe’s optical diffraction limit of ~200 nm can be circumvented to achieve super-resolution fluorescence microscopy, or nanoscopy, with relatively nonperturbative visible light. Essential to this advance is the combination of single-molecule fluorescence imaging with active control of the emitting concentration and sequential localization of single fluorophores decorating a structure. Super-resolution microscopy has opened up a new frontier in which biological structures and behavior can be observed in live cells with resolutions down to 20-40 nm and below. Examples range from protein superstructures in bacteria to bands in axons to details of the shapes of amyloid fibrils and much more. Current methods development research addresses ways to extract more information from each single molecule such as 3D position and orientation, and to assure not only precision, but also accuracy. Still, it is worth noting that in spite of all the interest in super-resolution microscopy of extended structures, even in the “conventional” single-molecule tracking regime where the motions of individual biomolecules are recorded in solution or in materials, much can be learned about nanoscale processes when ensemble averaging is removed.
Looking back on 28 Years of Cryogenic Single-Molecule Experiments

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Abstract. Starting with the first single-molecule fluorescence experiments in 1990, the field of cryogenic single-molecule spectroscopy exploits the narrow zero-phonon lines of single molecules, usually in molecular crystals and glasses. Occasionally, similar experiments can also be done at room temperature, as illustrated by the case of the NV\(^-\) center in diamond. In this review contribution, I shall illustrate the variety and scope of the experiments performed in the past 28 years, highlighting some important points and outlooks.

1 Spectroscopy and magnetic resonance

From the first high-resolution optical experiments on single molecules [1], it was clear that this fine spectroscopy enables accurate mapping of molecular electronic and vibronic states through excitation spectra and molecular vibrations from fluorescence spectra. Blinking single-molecule fluorescence yields information about triplet population and depopulation rates, and optically detected magnetic resonance provides the positions of the triplet sublevels split by magnetic spin–spin and spin–orbit interactions [2]. Later work identified hyperfine interactions and achieved magnetic resonance experiments of single nuclear spins through ENDOR [3].

Fig. 1. Example of a single-molecule fluorescence excitation spectrum showing the lifetime-limited lines of single pentacene molecules in a p-terphenyl crystal at 1.8 K (from Ref. 1).

2 Quantum optics

The narrow zero-phonon lines are often lifetime-limited, which opens unique opportunities for quantum optics. Antibunching in the emission of single molecules was demonstrated early on at low temperature [4]. Single-photon emission at low temperature [5] provides indistinguishable photons, that have been used in Sandoghdar’s group for pioneering quantum optics experiments in solid-state phases for the first time, before the experiments with self-assembled quantum dots. Today, single molecules at low temperature are still attractive contenders for single-photon sources delivering indistinguishable photons.
3 External field effects and local probing

Being ultra-narrow oscillators, single molecules are very sensitive probes for all kinds of perturbations, by pressure or mechanical strain, electric fields, magnetic fields. This sensitivity can be exploited to detect small changes in the surroundings of the molecules, for example from acoustic or mechanical deformation [6] or from charge carriers diffusing or trapped in the matrix.

4 Spectral diffusion

The time-dependent dynamics of single-molecule lines has clarified the concepts of spectral diffusion in molecular solids, glasses and polymers at low temperature, by displaying individual two-level systems, and quasi-local vibration modes [7]. Many other causes of spectral diffusion have been identified or proposed in more specific systems, such as phenyl ring flips in p-terphenyl crystals, or rotational-translational coupling in methylated matrixes.

In conclusion, the knowledge and experience accumulated in the previous two decades have made single organic molecules uniquely attractive quantum emitters. Along with self-assemble quantum dots and color centers in diamond, these fascinating systems are excellent candidates for a broad variety of nanophysics experiments, including optomechanics, localized probing, or as the cores of devices for the storage and treatment of quantum information.

References

Investigation of evaporation of sessile droplets using luminescent nano-probes and other applications of NV centers in diamond

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Abstract. The paper describes application of diamond nano crystals to research on dynamic processes in small (less than 1 mm across) evaporating droplets deposited on a solid substrate. Such droplets are used as a model system for testing proposed bio applications of nitrogen-vacancy centers in diamond. We demonstrate that a high spatial resolution of our methods reveals unexpected features of the evaporation and fluid mechanics in such droplets.

Research on nitrogen-vacancy centers in diamond (NV-centers) has gained its momentum about 30 years ago and since then the field has developed in several directions. One direction of research mainly exploits very stable luminescence of these centers, which may escape photo bleaching for weeks. If such centers are embedded in very small (tens of nanometers or less) crystals, these crystals can be used as luminescent labels in bio imaging applications (such as tracking and targeted visualization) where they compete with conventionally used organic dyes and quantum dots. However the necessity to use nano-crystals has a number of undesired consequences [1] of practical significance.

In this report we also demonstrate applications of nano-diamonds for investigation of mechanical dynamics in small evaporating droplets deposited on a solid surface. This system (where physics is not yet completely described with quantitative models) is interesting by itself but also provides a simple playground for developing and testing concepts employed in corresponding intracellular applications.

A very popular physical model for the evaporating droplet has been suggested 20 years ago in a seminal paper [2] and it predicts that the velocity of the fluid in the evaporating droplet deposited on a solid substrate increases towards the rim. This velocity is proportional to $x^{-\lambda}$, where $x$ is the distance to the rim, the value of $\lambda = (\pi-2\theta)/(2\pi-2\theta)$ and $\theta$ is the contact angle between the droplet and the substrate.

The experimental results obtained by tracing a 35-nm diamond with about 80-nm accuracy are shown in Fig. 1. Contrary to the theoretical predictions, the data do not show acceleration towards the rim and careful analysis of diffusion points to a decrease of velocity of liquid within less than 2-μm distance from the rim.

A very interesting prospect for NV centers is their sensitivity to various external parameters such as magnetic and electrical field and temperature [3]. Magnetic field sensors based on NV-centers exploit a not zero spin of the electronic ground state of these defects in diamond lattice and the dependence of the luminescence intensity on the spin state (the value if its projection on the center axis). Temperature measurements can either use the sensitivity of the ODMR frequency to the crystal temperature (the resonance shifts with a gradient of 75 kHz/K) or the thermal sensitivity of the zero-phonon line (ZPL) in the luminescence spectra (ZPL of NV-centers is clearly visible even at room temperature).

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Fig. 1. The $x$-position vs. time for a nano-diamond when it approaches the rim of a droplet. The initial position on the $x$-axis and the time are set to zero at the start of tracing. The position of the rim corresponds to the displacement $x \approx 21 \mu m$. For $\approx 2$ s the diamond drifts towards the rim with a constant velocity of about $11.4 \mu m/s$ and then its movement is described near the rim as constrained diffusion in a steady liquid flow. The inset shows the droplet and the direction of the $x$-axis.

Temperature measurements inside biological cells have raised recently a hot debate among physicist, biophysicists and biologists. The discussion is focused on the temperature rise in single cells under physiological conditions. Simple physical arguments suggest that a cell generate very small temperature gradients (even on a 100-nm scale the estimated temperature difference is less than 1 mK). But some experimental results show a local temperature rise on the order of 1 K. The contradiction has been even named as “The $10^5$ gap” paradox [4]. Most of the measurements in this area are done using thermo sensitive dyes and their reliability is questioned. The solution of this contradiction requires new methods for sensitive and ultra local temperature measurements. Because most of the reported measurements of temperature in evaporating droplets also lack reliability, we investigate evaporative cooling in droplets using NV-centers as thermometers. Such a model system is a reasonable proxy to the complex intracellular measurements.

References

Multiphoton spectroscopy: An optical window into molecular electrostatics

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Abstract. Quantitative knowledge about static molecular electric dipole moments is essential for understanding of intramolecular charge transfer as well as nanometer-scale static electric interactions. However, measuring or determining the molecular electrostatic properties with sufficient accuracy remains a challenging task. In our experiments, we measure the femtosecond two-photon absorption spectra- and cross sections of a range of organic- and organometallic chromophores in solution and use these data to determine the electric dipole moment change in corresponding lowest-energy dipole-allowed transition. Good correspondence of our experimental dipole moments with the quantum-chemical calculations as well as reports by other groups using conventional dipole moment measurement methods suggests that quantitative multiphoton spectroscopy may offer all-optical alternative to the traditional techniques such as Stark effect and electrochromism.

Two-photon absorption (2PA), first proposed by Maria Goeppert-Mayer [1], consists in an instantaneous 3rd-order nonlinear-optical process, where two simultaneously incident photons induce a transition from molecule’s ground state to an excited electronic state. Under ambient illumination conditions, the probability of 2-photon transitions as well as higher-order multiphoton absorption (MPA), remains notoriously low. However, recent proliferation of high peak intensity, wavelength-tuneable femtosecond lasers, make 2PA and MPA conveniently accessible in many laboratories, rendering these effect particularly useful for microscopy and biological imaging. Furthermore, recent progress towards higher accuracy and reliability of nonlinear spectroscopic measurements [2], have transformed 2PA into a precision quantitative method, with increasing range of applications.

Two-photon spectroscopy is able to take advantage of the empirical fact that if, in a dipolar chromophore, the lowest-energy 1-photon electronic transition is dipole-allowed, then the 1PA and 2PA spectral profiles of to the same purely electronic transitions, have coinciding shapes, and that the corresponding 2PA cross section is proportional to the square of the permanent electric dipole moment change in that transition [3]. This approach was recently used to evaluate static dipole moments of some dipolar dyes in solution and also estimate the strength of local dielectric reaction field [4]. On the other hand, if a molecular system maintains inversion symmetry, then according to Laporte spectroscopic selection rule, all permanent electric dipole moments vanish, and the 2PA transitions between opposite parity states are forbidden. However, under certain conditions, e.g. if the molecule undergoes steric distortions or is placed within a complex nano-environment, then actual ground state symmetries may be lowered. In this case, experimental comparison between 1-photon and 2-photon absorption spectra may also yields useful insights regarding spontaneously induced permanent electric dipole moment change [5].

We describe our recent experiments, where we apply 2-photon excitation with a wavelength-tuneable femtosecond laser to measure the 2PA spectra with high accuracy in a

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broad range of wavelengths of a variety of molecular systems, including organometallic charge transfer complexes [6-8], fluorescent proteins [9], as well as DNA nucleotides [10]. In particular, ferrocene complexes show in their UV-vis absorption spectra prominent features associated with metal-to-ligand charge transfer (MLCT) transitions, where a notable fraction of the electron density shifts from the Fe atom(s) in the ground electronic state towards the organic group(s) in an excited state. We used our novel 2PA spectroscopy approach to quantify the corresponding large change of the molecular permanent electric dipole moment, both in non-centrosymmetric as well as nominally symmetric ferrocene oligomer structures, whereas in the latter case spontaneous symmetry breaking was attributed to ground state steric distortions [7]. Most recently, we used accurate measurement of the 2PA spectrum of ruthenium(II) tris-complexes of 2,2’-bipyridine and 1,10-phenanthroline ligands to determine the molecular electric dipole change in the corresponding MLCT transitions [8]. Where applicable, our experiments show good correspondence with reports by other groups using conventional dipole moment measurement methods such as Stark effect and electrochromism. We will also compare our experimental findings with quantum-chemical theoretical calculations and discuss how to optimize the calculated 2PA spectra and dipole moment values by choosing appropriate methods [11]. In summary, our results indicate that our 2-photon absorption based approach may be a viable alternative to more traditional methods of determining the electric dipole change based, while offering higher versatility associated with all-optical access.

References
Organic Molecules Coming of Age in Quantum Optics

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Abstract. The interaction of light and matter at the nanometer scale lies at the heart of quantum optics because it concerns elementary processes such as absorption or emission of a photon by an atom. Over the past decade, we have shown that direct coupling of a photon to a single two-level atom should be possible via tight focusing. However, because transitions in quantum emitters are typically not closed, laboratory demonstrations of this idea fall short of the theoretical prediction. In this presentation I shall report on recent achievements, where the branching ratio of a single organic molecule is improved by a substantial Purcell effect when coupled to a microcavity. Furthermore, we will discuss coherent linear and nonlinear experiments on molecules coupled to subwavelength waveguides on a chip. Together with their ability to generate narrowband stream of single photons, these developments make organic molecules viable candidates for integration in chip-based quantum optical circuits.
Non-radiative processes in metal halide perovskite semiconductors probed by photoluminescence microscopy

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Abstract. Organo metal halide perovskites are solution processed semiconductors that recently attracted a great attention. They possess a rather “soft” and (photo) chemically active solid structure allowing for ion migration and other mass diffusion processes. This is a likely reason why non-radiative recombination centres in these materials are activated and de-activated on relatively slow time-scales. This dynamics reveals as photoluminescence (PL) fluctuations (blinking) of individual microcrystals and local areas of films and allows for application of a broad range of single molecule spectroscopy methods including optical super-resolution. Studying PL blinking resolves properties of individual non-radiative centres and helps to unravel their chemical nature.

Non-radiative charge recombination in semiconductors sets a fundamental limitation to the efficiencies of light emitting devices and solar cells. Recently re-discovered organo-metal-halide perovskites (OMHP) have become the most popular and, in a way, mysterious optical semiconductors showing a great potential for industrial applications. It was quickly realized that spectroscopy methods able to monitor the fate of photogenerated charge carriers locally with high spatial resolution are of a high demand. [1] The resolution in space is needed because these solution-processed semiconductors possess highly inhomogeneous properties in terms of polycrystallinity, defect state distributions, formation of intermediates and degradation. Photoluminescence (PL) micro-spectroscopy is one of such methods. OMHPs possess phenomena of photo-brightening, defect curing, ion migration, and other light-induced photochemical processes which can be nicely monitored by PL micro-spectroscopy. [1] In several publications we have successfully used ideas coming from single molecule spectroscopy to study perovskite films and individual nano- and micro-crystals. [2–4] OMHP materials are highly dynamic in terms of local chemical structure leading to easily observable temporal fluctuations of PL yield of localized regions of perovskite films [5] or individual crystals. [2–4] PL flickering or blinking is the direct indication of switching processes in efficient non-radiative recombination centres.

Non-radiative recombination in semiconductors is a difficult process to comprehend in detail. [6] [7] It occurs due to the presence of intra-band defect states (traps) or complex non-radiative centres. The concentration of these quenchers and the charge trapping cross sections per one quencher are usually not known. Luckily OMHPs possess properties that allowed us to see and count each individual non-radiative channel in a small particle. These properties are crystal structure dynamics and mass (ion) diffusion, leading to transformation of the material

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at slow time scale of milliseconds, seconds and beyond. It turned out that these dynamics lead to activation/deactivation of individual non-radiative channels observed experimentally as PL blinking. The efficiency of just one channel can be very large, allowing for on/off switching of the PL of 500 nm sized MAPbI$_3$ crystals and substantial fluctuations of the PL of 10 micrometer long MAPbI$_3$ rods with a volume of about 1 $\mu$m$^3$. [2,4] It was suggested that such an efficient quencher (a super-trap or a “killing” centre) can be a donor-acceptor complex. [2] Monitoring of PL fluctuations allows us to obtain information about charge carrier and exciton diffusion, trapping and trap concentrations. Moreover, the switching allows for application of optical super resolution spectroscopy to localize trapping and emitting sites in space with nanometer accuracy.[2,8]

Single molecule fluorescence and its blinking gave birth to super-resolution optical microscopy (Nobel Prize 2014 in chemistry). Similarly, fluctuating activity of individual quenchers in OMHPs allowed us to get a mechanistic view beyond ensemble averaging on the non-radiative recombination in these semiconductors. We were able to resolve the temperature-dependent action of each defect state individually by observing 50 nm sized MAPbI$_3$ crystals and studying the increase of their PL intensity upon cooling from 300 K to 77 K. We suggest that the temperature activation of PL quenching is related to the potential barriers present in charge carrier diffusion and in charge trapping process. Contrary to some literature [9] we propose that the apparent activation energy of the PL intensity is not directly related to the exciton binding energy. Individual crystals showed highly diverse temperature dependencies of PL, which in many cases could not be approximated by the Arrhenius equation. Further studies are on the way towards Monte-Carlo simulations of the PL blinking dynamics and estimation of activation energies of the non-radiative centre formation and passivation and correlating these energies with the activation barriers of mass diffusion processes in perovskites including ion migration.

References

Photophysics and electroluminescence of single nanocrystals of halide perovskites and related nanomaterials

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Abstract. We report simultaneous photoluminescence and electroluminescence single-particle study of nanocrystals of inorganic halide perovskite CsPbBr₃, as well as of ternary I-III-IV semiconductor quantum dots.

Due to their exceptional excitonic properties such as strong absorption and efficient narrow-band emission, lead halide perovskite nanocrystals (NCs) have been recently rediscovered as possible alternatives to semiconductor quantum dots for electroluminescence (EL) devices and other light-emitting and sensing applications, and research into their basic photophysical properties is attracting increasing attention. While dispersions of NCs generally show high photoluminescence (PL) quantum yields, the efficiencies of electrically driven luminescence devices are considerably lower. We have shown previously that simultaneous characterization of PL and EL on single-molecule level can bring valuable insight into these emission processes in conjugated polymers [1] and small molecules [2]. Especially, the differences in luminescence blinking and spectral dynamics between the two processes can provide information on the different dynamics of the excited states and their relaxations. Here, we report a simultaneous study of EL and PL of inorganic halide perovskite nanocrystals with the aim to uncover the origin and ways of suppression of blinking in both EL and PL to maximize the emission quantum yield, as well as to study the origin of spectral diffusion and spectral shifts, in relationship with structural/compositional stability.

We use nanocrystals of CsPbBr₃ prepared by methods reported in literature. In solution, the NCs show efficient and narrow emission in the green part of the spectrum. We first examine the influence of a surrounding matrix on their spectral properties and blinking behavior by dispersing the NCs in an inert matrix of PMMA and in a conductive matrix of PVK/PBD, both on the level of single NCs and aggregates (arrays) of tens of NCs. The differences in the blinking characteristics appear as different parameters of truncated power law distributions of the on-times, both for bright and dim (grey) states. These findings are further corroborated by an effect of externally applied electric field on the blinking dynamics and PL spectra. The applied field enhances the blinking in both matrices, and causes a linear Stark shift, the extent and direction of which differs from particle to particle. Based on the above characterization, we next fabricate a single-particle organic light-emitting device (OLED) by dispersing the NCs at very low concentrations in PVK/PBD matrix as an emitting layer in an ITO/PEDOT:PSS/PVK/PBD/TPBi/LiF/Al device and study the device by PL and EL single-particle spectroscopy. As shown in an example in the Figure 1, the same NC can exhibit dramatically different brightness and blinking behavior upon the different modes of excitations. Such differences in PL and EL characteristics can be attributed partly to influence of charge injection and trapping in the device, but intrinsic properties of the NC arrays also play a role in the observed phenomena.

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Fig. 1. Electroluminescence (a) and photoluminescence (b) microscopic images of CsPbBr$_3$ nanocrystals in an ITO/PEDOT:PSS/PVK/PBD/TPBi/LiF/Al device. (c) Spectral time traces measured from one bright spot in the images upon excitation by light, electric field and combined show different blinking and lineshape dynamics.

Apart from the work on perovskite nanocrystals, we report on recent progress in single-particle photophysical characterization of ternary I-III-IV semiconductor nanocrystals which have been explored as a non-toxic alternative to II-VI semiconductor quantum dots. For NCs of (AgIn)$_x$Zn$_{2(1-x)}$S$_2$ we explore the origin of defect emission, multiple emitting sites and suppression of blinking [3], and report the emergence of narrow band-edge PL in core/shell structures.

References

Optical Properties of a Novel Metamaterial made of Carbon Intercalated with Au/Ag Nanoparticles

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Abstract. We study experimentally the optical properties of a novel self-assembled carbon-metal hybrid metamaterial. It is comprised of a crystalline carbon matrix intercalated with bi-metal nanoparticles. For the experimental analysis, we use a microscopic Müller matrix approach. The material shows an extraordinarily high linear birefringence as a direct consequence of its substructure. This unique metamaterial can find applications in optoelectronics and nanoplasmonics, extending the corresponding toolbox.

1 Introduction

Carbon-based materials are known for the extraordinary optical and electrical properties [1]. By combining carbon with metal nanostructures, the range of applications can be even extended [2]. Recently, a novel carbon material intercalated with bi-metal nanoparticles was reported [3]. A laser-induced growth process was used to fabricate this special type of self-assembled hybrid metamaterial in a bottom up approach. In the following, we refer to the resulting structures as flakes. These flakes exhibit a crystalline carbon lattice, with gold-silver nanoparticles (diameter: 3nm) embedded in it. Based on this unique composition, the novel flakes are expected to have applications in high speed opto-electronics, integrated polarization manipulation and beam shaping. Therefore, we performed a detailed investigation of individual flakes to reveal their optical properties.

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2 Experimental analysis of carbon flakes

Due to the small lateral dimensions of the flakes (on the order of several microns), standard optical measurement techniques could not be used. For our study we thus utilize a custom-built setup (similar to [4]) and perform the aforementioned detailed polarization analysis on the individual carbon flakes. A light beam was tightly focused using a microscopic objective with numerical aperture of $NA = 0.9$, which reduces the beam diameter in the focus to a size comparable to the wavelength. The flake was then scanned through the focal spot, and at each position the forward transmitted light is collected by an oil-immersion microscope objective of NA 1.3. A full polarization analysis of the transmitted light was performed. This was done by preparing different input polarization states with Stokes parameter $\hat{s}$ and measuring the output parameter $\hat{t}$ after transmission through the flake. The Stokes analysis was done using two liquid crystals variable retarders [5]. By selecting the right combination of voltages applied to the retarder cells, all six polarization states necessary for a full Müller matrix analysis were generated. The experimentally measured Müller matrices of the flake recorded for different wavelengths (400 nm to 700 nm) can be used to retrieve the optical properties such as attenuation, birefringence and diattenuation [5]. Our results indicate a linear increase in attenuation $A$ towards smaller wavelengths, while diattenuation stays negligibly small across the investigated spectral range. Most importantly, the investigated structure shows a strong optical birefringence $\Delta n$ on the order of 0.1. The finite-difference time-domain (FDTD) method has been exploited to simulate alloy nanoparticles intercalated with sheets of a graphene-like material. Simulations confirm the plasmonic nature of the peak observed in the measured absorptance. The simulated birefringence is demonstrated by using the local-field theory for noncubic lattices. Our experimental findings are in good agreement with the theoretical modeling results.

3 Conclusion and outlook

We performed a detailed polarization analysis of novel carbon flakes using a microscopic Müller matrix measurement technique. The experimental results show a very high optical birefringence in the visible spectral range. Hence, the carbon flakes hold great potential as all-integrated optical components in on-chip light manipulation and shaping. Furthermore, interesting nonlinear properties are expected as well due to the hybrid structure.

References

3. A. Manshina and et. al, "Novel 2D carbon allotrope intercalated with Au-Ag nanoclusters. From laser design to functionality," in Advance Photonics 2017
Photoluminescence intermittency (blinking) beyond nano-confinement: the Curious case of hybrid perovskite microcrystals

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Fluorescence blinking or temporally random, discrete photoluminescence (PL) intermittency between two or more intensity levels has been long recognized to be characteristic of single quantum nano-emitters such as organic molecules, conjugated polymers and dimensionally-confined (typically in 3D) semiconductor nanocrystals. However, PL intermittency is seldom reported beyond ~100 nm dimensions not only because spatiotemporally uncorrelated emission intensity fluctuations average out over the ensemble, but also due to nominal contributions of surface-states in radiative-recombination processes compared to that of the bulk material. There are a few scattered examples where multi-level fluorescence intermittency is exhibited by single spatially extended (~µm) yet nano-confined (in 1 or 2 D) objects, however, such blinking dynamics is almost overwhelmingly spatially heterogeneous, i.e., spatiotemporally uncorrelated.¹⁻³

We have investigated the spatio-temporal variation of PL spectra and emission dynamics of various organo-metal (hybrid) halide perovskite microcrystals (MCs), some of which have been shown to exhibit heterogeneous PL blinking within local nanodomains under ambient conditions.⁴ In this presentation, we will demonstrate the occurrence of a highly unusual phenomenon, where entire individual methylammonium lead bromide (CH₃NH₃PbBr₃) MCs, bulk polycrystalline materials (volume ~0.1-3 µm³) with no dimensional confinement, undergo discrete, prominent intensity fluctuations between multiple levels (blinking or flickering).⁵ Moreover, such abrupt PL blinking is spatially-synchronous (i.e., temporally correlated) across each single MC, which is most intriguing because this implies extremely long-range communication (> micrometers!) amongst majority of photogenerated carriers at distal locations in each crystal. Such remarkable long-range correlation in intra-crystal blinking is attributed to extensive delocalization of carrier wavefunctions, and is intricately related to high carrier diffusion propensities reported for hybrid halide perovskites. We provide a phenomenological model which invokes the formation and removal of a few metastable non-radiative traps which act as PL quenchers, the details of which will be discussed. While further investigations are essential to indentify the nature of the transient quenchers as well as to understand the role of organic cations in concerted blinking of hybrid halide perovskites, these experimental results will hopefully stimulate theoreticians to ponder upon and elucidate alternate possible mechanism(s).

References


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Breakup of adiabatic alignment of two coupled molecules within a long-pulse optical field

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Abstract. The necessary and sufficient conditions for quantum adiabatic theorem and approximation are actively investigated in current quantum state engineering and quantum computation. Molecular alignment within a pulsed far-off-resonant optical field could provide a platform for these researches. We have investigated quantum adiabaticity of alignment of molecules coupled by laser-induced dipole-dipole interaction (LIDD), and found that when LIDD presents, the $e^{-1}$ width of the Gaussian pulse much longer than the rotation period is not sufficient for adiabatic alignment, due to time-varying degree of degeneracy of instantaneous eigenstates and LIDD-induced internal resonance. This internal resonance leads to excitation of molecules to rotation states with odd angular momentum quantum numbers which is forbidden in conventional single molecular alignment experiments, such that a stationary field-free alignment (FFA) can be generated, in contrast with the fast time-varying FFA by a short optical pulse.
Fluorescence nanoscopy of single quantum dot pairs

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Semiconductor colloidal nanocrystals (quantum dots, QD) are artificial luminophores with size-dependent spectral properties. Quantum dots are promising objects for laser gain media, single photon sources, single fluorescent labels and for development of effective light emitting diodes, solar cells, QD-lasers, etc.

QDs have been investigated since early 1980-s. At single particle level the research activities have been going since the pioneer work in 1996 [1]. Many intriguing effects have been discovered for single QDs. They include stochastical switching between emitting and dark states (fluorescence blinking or intermittency) and spectral diffusion (see review [2] and references therein). The nature of blinking is still the matter of discussion [3].

Localization accuracy for single emitters (coordinates determination accuracy) can be as small as several Angstroms and is usually limited by a single emitter photo-stability, its quantum yield and small dynamical range of highly sensitive 2-dimensional detectors (EMCCD). Implementation of fluorescence localization nanoscopy for single QDs and small QD clusters create a range of opportunities for investigation of underlying processes, which determine fluorescence and spectral properties of such artificial “atoms” and “molecules”. In this sense reconstruction of emitters’ spatial coordinates with the nanometer accuracy in such a cluster is an essential step in this type of experimental studies.

In the present work we consider the case when the cluster is represented by two closely-spaced QDs (inside a diffraction limited volume). The task was numerically simulated for QDs separated by a distance in the range from 20 nm to 120 nm for different types of blinking dynamics, which are well known from experiments. The technique based on statistical studies of sub-diffraction coordinate distributions [4] was proposed and the errors of the processing algorithm were estimated. The developed method allows us to recover distances between single emitters in pairs in real experiment with CdSe/ZnS colloidal QDs embedded inside a thin polymer film. Fig. 1 (inset) shows an example of a super-resolution image of a single QD pair, i.e. the spatial distribution of the recovered coordinate’s density, obtained in a series of laboratory experiments in a short period of time (during which the experimental conditions and spatial coordinates of QD in a pair remained constant). The distance between QDs was estimated using the distribution of the recovered coordinates along the line connecting quantum dot super-resolution image centres.
Fig. 1 Super-resolution image of single CdSe/ZnS quantum dot pair in a thin polymeric film. Distribution of the recovered coordinate along the line through quantum dot super-resolution image centers.

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References

Upconversion nanoparticles: on the way from diagnostics to theranostics

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Abstract We report surface modification approaches of luminescent upconversion nanoparticles (UCNPs) structured as inorganic hosts NaYF4 codoped with Yb3+ and Er3+ or Tm3+. These approaches enabled the facile, lossless preparation of hybrid polymer-encapsulated UCNPs suitable for bioassays. These probes inherited UCNP properties, such as excellent photoluminescence under excitation with NIR light from the biotissue “transparency window”, as well as they were dispersible in aqueous media and physiological buffers, exhibiting chemical stability. The feasibility of the hybrid UCNPs was demonstrated for in vitro bioassay and in vivo optical whole animal imaging using a home-built epi-luminescence imaging system.

Introduction

Lanthanide-doped upconversion nanoparticles (UCNPs) represents a flexible platform, where various surface moieties can be attached to, enabling targeting, bioimaging and therapy in a broad physiological context. UCNPs are characterized by sharp emission, high conversion efficiency, long lifetimes, low cytotoxicity, negligible photobleaching, and high spatial-temporal resolution during bioimaging. The efficient conversion of near-infrared (NIR) excitation at the wavelength of 980 nm into the shorter-wavelength IR, visible and UV spectral range emission (known as “upconversion”) represents its most acclaimed property. Under the NIR excitation of UCNPs the excitation of tissue autofluorescence is almost negligible. Additionally, the excitation light penetration in biological tissue is greater in comparison with visible light, up to one centimeter. Generally, the UCNPs are based on efficient host matrix NaYF4, which produce anti-Stokes luminescence, co-doped with lanthanide ions: Yb3+ as a sensitizer, and Er3+ or Tm3+ as activator.

Results and Discussion

Typically, UCNPs are synthesized in organic solvents, resulting in UCNPs stabilized with hydrophobic oleate ligands. This fact limits their biological applications. Therefore, surface modification of UCNPs is a crucial step in an effort to create the water-dispersible and biocompatible UCNP probes.

Modification method using amphiphilic polymer poly(maleic anhydride-alt-1-octadecene) have been developed, which made it possible to create target-based UCNP hybrid
nanocomplexes for \textit{in vitro} labeling the HER2 / neu cancer-specific marker (Fig. 1, way 1)\cite{1}. We exploited the original design of UCNP nanocomplexes, where a "corona" was obtained from chemically bound PEG molecules, in order to increase the circulation time in the blood system \textit{in vivo} and deliver UCNPs to the tumor (Fig. 1, way 2)\cite{2}. UCNP encapsulation into polyacrolein particles in the course of radical heterophase polymerization was the basis for production the reagents capable to study the particle biodistribution by organs at intravenous injection (Fig. 1, way 3)\cite{3}. Unique optical properties of UCNPs enabled formation of hybrid nanocomplexes with riboflavin (Rf) responsible for generating active oxygen forms under the NIR-radiation through the realization of FRET effect. Hybrid nanocomplexes were successfully applied for photodynamic therapy and showed tumor regression in mice, following the Rf-UCNPs peritumoural injection and near-infrared light photodynamic treatment of the lesions (Fig. 1, way 4)\cite{4}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{Fig. 1. Approaches of UCNP surface modification for various bioapplications.}
\end{figure}

This work was supported by Russian Foundation for Basic Research [RFBR research project №17-03-01033, RFBR research project № 17-00-00122 (K) (17-00-00118)]

\section*{References}
2. A.N. Generalova, V.V. Rocheva, A.V. Nechaev, et al., RSC Advances, 6, 30089 (2016)
Local and macroscopic characterization with single molecules and single quantum emitters

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Abstract. We introduce an experimental approach for mapping effective local values of dielectric characteristics of solid films and the analysis of the related local-field effects. The characterisation technique is based on the imaging and spectroscopy of single chromophore molecules at cryogenic temperatures. The progress in the theory of fluorescence enhancement due to the local field effects is reported.

We report the progress in development of the experimental approach for mapping effective values of local dielectric characteristics of frozen solid films and the analysis of the effects either enhanced or suppressed by the local fields. This probing technique is based on imaging and spectroscopy of single chromophore molecules at cryogenic temperatures. Since the fluorescence lifetime of a single dye molecule imbedded in a transparent matrix depends on the properties of the encapsulating medium at different spatial scales it has long been a challenge to detect inhomogeneities in the host material by simply measuring the lifetime of individual molecules distributed over the sample. The factors that change the excitation lifetime in the matrix are known to be related to existence of the local density of the photon states and the local response of the medium to incident light. Both factors may be attributed to local effective values of the dielectric function describing the continuous surroundings of each chromophore light emitter. Thus, measuring the radiative lifetime distribution may help revealing the distribution of effective susceptibilities or refractive indices as well as the pattern of the local fields. In our experiment the spatial mapping of the local values is accomplished by localizing the corresponding chromophores with nanometer accuracy. We demonstrate this approach for a polycrystalline film doped with terylene molecules. We also report a significant progress in the theory of light emission enhancement due to the local field effects. This work was partially supported by the Russian Foundation for Basic Research (RFBR № 17-02-00652).

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Ion implanted defects in diamond: optical spectroscopy of the Xe center

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Abstract. A review of the photoluminescence spectroscopic studies of diamond crystals implanted with Xe⁺ ions will be given. We will focus on the optical center yield of the formation and the mechanisms for zero phonon line shape and thermal broadening in the broad temperature range 1.8 – 300 K.

The current attention to the optical and the spin properties of impurity centers in diamond is stimulated by recent progress in the understanding and the applications of the nitrogen-vacancy (NV) center [1]. Diamond possesses unique material properties, e.g. extreme hardness, high thermal conductivity, a wide band-gap, high Debye temperature, biocompatibility, and photo-stability of the defect centers. Due to these reasons, diamond is considered as a potentially useful material for advanced photonics applications such as single photon emitters and light emitting diodes, bio-imaging and magneto-sensing, quantum optics, communications and computing. Optical centers in diamond can be formed during diamond growth or by ion implantation followed by thermal annealing. The latter method gives one control over the accuracy of the spatial distribution of the implanted ions, as well as the number of vacancies near the implanted ion, which are capable of facilitating the formation of an optical center. Due to a variety of implanted ions and corresponding optical centers, the search for centers having suitable properties, supplementary to NV centers, is in progress. The XeV center is of particular interest as it is one of a few centers (Si, Ni, Cr) in diamond having sharp zero phonon emission lines (ZPL) in the infrared spectral region, both in photo- and electroluminescence.

The conventional ion implantation technique allows one to introduce into diamond different optical centers having emission lines in a broad spectral range, including the near-infrared region. Focused ion implantation and electron beam lithography enables nanoscale patterning of diamond, and may be used to fabricate single optical center structures. A serious problem related to ion implantation is the low conversion efficiency of implanted ions into optical centers (yield of the formation) at desirable ion implantation energy, e.g., for NV centers the yield is typically about 2% for the 10 kV energy of N⁺ implantation [2]. This parameter is critical for the fabrication of quantum devices, especially those using single ion implantation technique. It is difficult to estimate the conversion efficiency value theoretically due to complex physical and chemical processes in solids during ion implantation and thermal annealing. Experimental determination of the yield of desirable defects can be performed by the direct counting of single emitting centers from known numbers of implanted single ions in an ion array [3]. We developed a different approach based on collecting the optical signal from ensembles of centers and establishing the statistics of the emitting centers [4]. The former method requires a sophisticated single ion implantation setup. The latter method is simpler experimentally and more universal, but one has to establish the relationship between the statistics of emitting centers and the statistics of the collected luminescence signal. It was found

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that the observed yield of formation of XeV center (Xe$^+$ 180 keV implantation, dose $10^{10}$ ion/cm$^2$) in our single CVD samples is about 28%.

At low temperatures the photoluminescence spectra of the XeV center feature a single narrow ZPL at 811.7 nm and a weak phonon sideband (the Debye-Waller factor is more than 0.9). We will focus on the mechanisms of ZPL shape and thermal broadening in the broad temperature range 1.8 – 300 K. The width of the ZPL at $T < 20$ K and low implantation doses could be less than 0.2 cm$^{-1}$ - similar to lines of rare earth ions in good crystals. The lineshape investigation indicates inhomogeneous broadening with the non-gaussian line shape due to a 2D distribution of the implanted Xe$^+$ ions [5]. At higher temperatures the interactions with phonons becomes essential: the ZPL becomes broader and its shape develops an unusual significant asymmetry. We attempt to describe the thermal changes, not just in the linewidth but also in the much more sensitive spectral shape of the ZPL, in terms of vibronic couplings without free parameters. The following topics will be discussed: low and high temperature luminescence spectra, manifestation of pseudolocal vibrational modes in the low-frequency Stokes and anti-Stokes phonon sidebands, mechanisms of optical dephasing and the lineshape due to quadratic vibronic coupling, fitting of the ZPL shape and width for the temperature range 30 - 200 K in the model of quadratic interaction with pseudolocal modes [6], fitting of the ZPL width for the temperature range 200 - 300 K taking into account Orbach processes in the exited electronic state.

References

Entangled plasmon generation in nonlinear spaser systems

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Abstract. The work is focused on the investigation of features of quantum dynamics for localized plasmons in spaser systems consisting of metal nanoparticles (NP) and semiconductor quantum dots (QDs). The non-classical plasmon states generation in a three-particle spaser system with nonlinear plasmon-exciton interaction is predicted.

In this paper we propose a model of three nanoobjects (NP-QD-NP) coupled by nonlinear dipole-dipole interactions in the presence of an external magnetic field. The nonlinear regime of this ensemble corresponds to the two-quantum processes of the QD biexciton decay in the case $|\delta| > \Omega_{1,2}, |\Delta|$, where $\delta = \omega - \omega_{p}$ and $\Delta = \omega - \omega_{p}$ is the spasing frequency, and $\Omega_{1,2}$ are the Rabi frequencies of dipole-dipole interactions between the QD and NPs. As a result of this nonlinear process, one can expect the appearance of strongly correlated plasmon pairs. In the technical framework, the presented spaser systems can be used to generate nonclassical states of the electromagnetic field at the nanoscale. Such systems can be integrated in the individual plasmonic waveguides [1] and plasmonic circuits for quantum information processing [2]. Nonlinear regimes of interaction between NP and QD can be realized, firstly, in the presence of a two-photon pump in the system and secondly, under the condition that the coupling energy between two electron-hole pairs is of the same order of magnitude as the internal coupling energy of a single pair. The energy of biexciton state $XX$ differs from the double energy of the exciton $X$ by the biexciton binding energy $\Delta_{bb}$ (see Fig. 1).

The Hamiltonian of exciton-plasmon interaction has the following form [3]:

$$H = \hbar \omega_{\mu} \hat{c}_{\mu}^{\dagger} \hat{c}_{\mu} + \hbar \omega_{\nu} \hat{c}_{\nu}^{\dagger} \hat{c}_{\nu} + \hbar \omega_{XX} D / 2 + \hbar \mathcal{O}(2) \left( \hat{c}_{X}^{\dagger} \hat{c}_{X}^{\dagger} \hat{S} + \hat{c}_{X}^{\dagger} \hat{c}_{X}^{\dagger} \hat{S} \right),$$

(1)

where the last term in the brackets comprises the annihilation operator $\hat{S}$ of the biexciton $XX$ state and the creation operators $\hat{c}_{X}^{\dagger}$ and $\hat{c}_{X}^{\dagger}$ of a pair of plasmons, whose energies differ slightly for the different intermediate levels $X_{+}$ ($X_{-}$) with frequencies $\omega_{X_{+}}$ ($\omega_{X_{-}}$). The
parameter $\Omega^{(2)} = \Omega_1 \Omega_2 / |2| \delta |$ is the effective two-quantum Rabi frequency, $D$ is the population imbalance. Parameters $\delta = \sigma - \omega_x$ and $\delta^{(2)} = 2\sigma - \omega_x$ are the effective detunings, where $\omega_{xx} = \omega_x + \omega_x - \Delta_{2b}$ is the biexciton frequency. The Rabi frequency of interaction between the QD and NP is $\Omega_1 = \Omega_2 = \mu_{QD} / \sqrt{\omega \alpha_{NP} / \left(4\pi \hbar \epsilon_0\right)}$, where $\alpha_{NP}$ is the NP radius, $\omega_p$ is the plasmon resonance frequency of NPs, $\mu_{QD}$ is the dipole moment. In this work we analyse the dynamics of the parameter

$$G_{12}^{(2)} (t, \tau) = \frac{\langle \hat{c}_1^+ (t) \hat{c}_1^+ (t) \hat{c}_2^+ (t + \tau) \hat{c}_2^+ (t + \tau) \rangle}{\langle \hat{c}_1^+ (t) \hat{c}_1^+ (t) \rangle \langle \hat{c}_2^+ (t + \tau) \hat{c}_2^+ (t + \tau) \rangle},$$

which corresponds to the cross-correlation function and is a criterion for establishing correlations between plasmonic modes $\hat{c}_1$ and $\hat{c}_2$. In particular, the condition $G_{12}^{(2)} (t, 0) > 1$ is associated with the intermode plasmon bunching. Moreover, the violation of the Cauchy-Schwarz inequality $C \equiv \frac{G_{12}^{(2)} (t, 0)^2}{g_1^{(2)} (t, 0) g_2^{(2)} (t, 0)} \leq 1$ indicates the nonclassical character of the correlations, where $g_{12}^{(2)} = G_{12}^{(2)} (t, 0) + 1$. The maximum value of $C$ parameter is $C_{\text{max}} = 15.15$ and the stationary regime value is $C_s = 1.2$, which demonstrates the nonclassical character of correlations between plasmon modes in spaser system. Thus, the main result of our simulation is a demonstration of the development of quantum correlations between two localized plasmonic modes and the possibility for formation of an entangled state of plasmons. Further development of this work may be aimed on a complex simulation of nonlinear collective processes [4] with non-classical states of surface plasmon-polaritons (SPP) [5] and SPP waves structures [6].

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References

Auger recombination observed in ensemble of CdSe nanocrystals

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**Abstract.** The temperature dependence of photoluminescence intensity of 5 nm colloidal CdSe nanocrystals passivated with oleic acid was studied. It was demonstrated that the photoluminescence intensity exhibits a hysteresis at temperatures below 220 K. This effect was explained by a model taking into account formation of an additional nonradiative relaxation channel associated with Auger recombination promoted by hole trapping on the surface of the nanocrystal.

Semiconductor nanocrystals are advanced materials exhibiting unique optical properties. They can be employed in light sources, biological markers, lasers and other photonic devices. The developed surface of the nanocrystals gives rise to additional luminescence bands and long-lived states. The aim of this work is to detect and characterize the trap states in 5 nm colloidal CdSe nanocrystals passivated with oleic acid using thermally stimulated luminescence techniques [1,2].

It is possible to detect the traps even in the presence of nonradiative relaxation using a modified technique of thermally stimulated luminescence. In the proposed approach cooling and heating of the sample is accompanied by its continuous optical excitation with simultaneous registration of the photoluminescence spectra. In this case the properties of the traps are determined from their indirect influence on the temperature dependence of the photoluminescence intensity.

The dependence of the luminescence intensity of the nanocrystals on the temperature within 90-300 K range is shown in Fig. 1. At temperatures below 220 K hysteresis is observed. Moreover, with heating the photoluminescence intensity is lower that with cooling. At the same time, the intensity of the laser radiation transmitted through the sample is almost constant during the experiment. After switching the optical excitation off the luminescence signal of the nanocrystals vanishes.

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Fig. 1. Photoluminescence intensity of CdSe nanocrystals (1) and intensity of transmitted laser radiation (2) upon cooling and heating.

The origin of the hysteresis in the temperature dependence of the photoluminescence intensity of the nanocrystals was explained on the basis of the analysis of the obtained data. When a photon is absorbed an electron-hole pair is generated. On one hand, both radiative and nonradiative recombination mechanisms are possible. On the other hand, one of the charge carriers can be trapped on the surface of the nanocrystal. Then the electron remaining in the bulk of nanocrystal gives rise to a new nonradiative recombination channel associated with Auger recombination of newly generated electron-hole pairs. The same mechanism observed in the experiments on blinking fluorescence of single nanocrystals [3-5] was shown to be responsible for the transition of the nanocrystals to the «dark» state.

In accordance with this reasoning, a model for excitation relaxation in nanocrystals was developed. The trap emission rate and activation energy were obtained.

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References

1. A.V. Katsaba, V.V. Fedyanin, S.A. Ambrozevich et al. Semicond. 47, 1328 (2013)
2. A.V. Katsaba, V.V. Fedyanin, S.A. Ambrozevich et al. Semicond. 49, 1323 (2015)
Time Resolved Femtosecond Spectroscopy of Nanocomposites

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Abstract. Characterization methods of nanocomposites consisted of semiconductor metal-oxide quantum dots (QD) incorporated into a dielectric matrix have been elaborated on the base of time resolved four-wave mixing and photon echo. Large permanent dipole moment, inherent to QDs under study, local field effect, the QD spatial dispersion and distribution function of the transition dipole moments in QDs are taken into account. New responses at multiple frequencies in directions differed from spatial synchronism conditions of well-known signals have been predicted.

As it is well known, nanocomposites attract attention of scientists due to their unique properties. So, nanocrystals TiO\textsubscript{2} incorporated into potassium dihydrogen phosphate (KDP) crystals provide enhancement of the second harmonic generation efficiency at higher than 60\% in comparison with pure KH\textsubscript{2}PO\textsubscript{4}. Macroscopic and microscopic features of such nanocomposite is actively discussed but the origin of observed effect is still under question. Bearing in mind high potential for frequency up- and down-conversion of nanocomposites composed of semiconductor metal-oxide quantum dots (QD) incorporated into a dielectric matrix we study exciton states in these materials and elaborate characterization methods accounting for large permanent dipole moment (PDM) of quantum dots (QD).

We dwell on the nanocomposite consisted of semiconductor spherical QD with the permittivity $\varepsilon_2$ surrounding insulating matrix with the permittivity $\varepsilon_1$, and suppose, that $\varepsilon_2 \gg \varepsilon_1$. In such a system QD-matrix interface forms a potential barrier to electrons not allowing them to penetrate into the QD. The Coulomb interaction of the electron with the QD-matrix interface leads to localization of the electron in the potential well near the QD surface. With increasing QD radius $a$, so that $a \gg a_B$, where $a_B$ is the exciton Bohr radius, the spherical QD-matrix interface transforms into a planar interface between the semiconductor and the matrix. The exciton formed from the spatially separated electron and hole becomes two-dimensional (2D) with maximal binding energy. Another dielectric enhancement effect is originated from the field produced by the nanoparticles in matrix, when $\varepsilon_2 \gg \varepsilon_1$. Under these conditions, rich structure of exciton levels is formed with a multitude of possible transitions. It should be noted that in such a nanosystem the PDM and transition dipole moment can exceed the same parameters for volume samples by two orders of magnitude. As a sequence, methods of time resolved laser spectroscopy should be modified accounting PDM impact. Thus, our task reduces to the elaboration of characterization technique of noncentrosymmetric multilevel system by femtosecond pulses. Below we more specifically consider features of time resolved

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four wave mixing (TRFWM) and photon echo (PE) methods for nanoparticles embedded in noncentrosymmetric matrices with quadratic nonlinearity.

For simplicity, we consider three-level system, which is in resonance with pump pulses at the lowest transition between exciton states. Due to the PDM interaction with the light pulses the Hamiltonian of the light-matter interaction contains fast oscillating diagonal elements that makes impossible traditional theoretical technique application to calculate responses of medium on pulse excitation. After unitary transformation

\[
\hat{L} = \begin{pmatrix}
\exp(i\lambda) & 0 & 0 \\
0 & \exp(-i\lambda) & 0 \\
0 & 0 & 1
\end{pmatrix}
\]

where \( \lambda = \frac{P_{11}}{\hbar} \int E_i dt = \sum_{m=1}^{\infty} \frac{P_{1i}}{\hbar\omega} E_i \sin \varphi(z,t), \varphi(z,t) = (\omega t - \vec{k}_i \vec{r}) \), we arrive at Hamiltonian describing QD interaction with a number of fields at multiple frequencies. Here \( P_{11} \) is the PDM, \( E_i \), \( \omega \) and \( \vec{k}_i \) are the envelope, carrier frequency and wave vector of \( i \)-th pulse, correspondingly. Applying successively a number of unitary transformations, we obtain Hamiltonian for generalized two-level system in rotating reference framework. This Hamiltonian does not contain fast oscillating terms and describes one- and two-quantum transitions. While one-quantum transitions occur in the field of excitation pulse \( E_i \) two-quantum transitions are induced by its components \( E_i J_s(a) \) and \( E_i J_{s-1}(a) \) at multiple frequencies \( s\omega \) and \( s\omega \) due to the PDM contribution. Elaborated approach allows us to deduce the Bloch equations for the QD with PDM in slowly varying envelope approximation and to solve them by means of well-known computational procedures. Besides resonant component macroscopic photoinduced polarization contains multiple harmonics, which can be sources of responses at corresponding frequencies in the nanocomposite. We have calculated TRFWM and PE signals under noncollinear excitation taking into account excitation induced shift of absorption frequency, the QD spatial dispersion and distribution function of the transition dipole moments in QDs. In addition to signals at resonant frequency under well-known spatial synchronism conditions, we predict observation of responses on two-pulse excitation of nanocomposite at multiple frequencies. The observation time and spatial synchronism conditions of new responses will differ from signal in \( 2\vec{k}_s - \vec{k}_i \) direction. The signals at multiple frequencies and terahertz responses are originated from the PDM interaction with excitation pulses. The most intensive signals among all responses will be at double and terahertz frequencies. Signals related to local field effect are discussed. It should be noted that for short time delay between pulses the nonresonant nonlinear matrix will contribute to the TRFWM signals mainly to resonant, second and terahertz harmonics.
Emerging upconversion nanoparticles for industry and biomedical application

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Abstract. In recent years, the overwhelming majority of the upconversion nanoparticles (UCNPs) prominent applications have originated from their unique luminescent properties. Due to original properties of inorganic UCNPs they attract the interest in numerous fields. We discussed a number of UCNP assisted techniques, such as biomedical imaging, therapy agents, anti-counterfeit labels and 3D printing, showing highly versatile and translatable UCNP photoluminescent nanotechnology for the applications in industry and biomedicine.

The main engineering advantage of UCNP platform, unlike conventional luminescent labels, is based on the nature of the anti-Stokes luminescence. UCNPs consist of an inorganic host matrix (usually NaYF4, YF3, LiYF4) co-doped with lanthanide ions act as the sensitizer (e.g., Yb3+ or Nd3+) and as the activator (e.g., Er3+/ Tm3+ or Ho3+). The network of closely spaced sensitizer-ions resonantly absorbs NIR radiation and non-radiatively couples excitation energy to neighboring activator -ions. Activators provide the multiple photon absorption due to their ladder-like arranged levels and emit upconverted photons [1].

1 Near-infrared polymerization and security printing

We demonstrated the effective and straightforward strategy for the NIR-activated polymerization of photocurable compositions containing UV-emitting upconversion nanomaterials. For this aim, the rationally-designed core/shell upconversion nanoparticles NaYF4:Yb3+,Tm3+/NaYF4, with the distinct ultraviolet-emitting lines have been used. Their ability to activate commercially available photoinitiators in the process of radical polymerization of light-sensitive resins at moderate NIR light intensities and irradiation doses opens unique possibilities for the implementation of novel NIR triggered photopolymerization technique. This technique allows fabrication of 3D polymeric structures inside the volume of photocurable compositions.

We developed invisible biocompatible inks visualized under infrared irradiation for security printing applications. To produce stable water inks the surface of UCNPs was modified by amphiphilic polymer. Undetectable under daylight security printing was performed by ink-jet printing on paper. Upconversion of the printed patterns under near infrared laser irradiation was observed and imaged. Higher levels of security were achieved

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based on optical multiplexing capable combinations of Ln3+ in nanoparticles. The developed technology is promising for fast, easy and low cost inkjet printing for anti-counterfeit and security applications.

Fig. 1. Image of 3D polymer microstructure obtained by NIR-light-activated photopolymerization (left). The graphic image printed with upconversion inks (middle). UCNP biovisualization - the tumor exhibited high luminescent contrast (red color) demonstrating superiority of the UCNP-assisted imaging (right).

2 Bioimaging and Photodynamic therapy

Photodynamic therapy (PDT) is a clinical tumor treatment that utilizes cytotoxic reactive oxygen species (ROS), generated by photosensitizer, which is excited by external light source. However, conventional PDT is limited by the penetration depth of light required for photosensitizer activation. We demonstrate a solution to this problem by the rational photoluminescent nanotechnology design. Specifically, upconversion nanoparticles (UCNPs) offer a lucrative possibility to kindle UV or visible light at the sub-centimetre depth in tissue, owing to their property to convert infrared radiation at the wavelength in the biological tissue transparency window 975 nm. We designed upconversion nanoparticles (UCNP) of the composition NaYF4:Yb3+:Tm3+ that yielded UV/blue emission bands critical for the photosensitising of vitamin B2. We achieved a high Förster resonance energy transfer (FRET) efficiency from UCNPs to vitamin B2, which facilitates a large production of cytotoxic singlet oxygen and thus an enhanced PDT efficacy. Design UCNPs was used as PL probes for tumor labelling. The comparison of the image acquisition in the Stokes and anti-Stokes channels shows much greater contrast in the anti-Stokes channel. This clearly demonstrates the advantage of UCNP-assisted imaging.

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References

New schemes of compact modal LC modulators for control of light spatial structure

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Abstract. The results of numerical simulation of new schemes of compact modal LC spatial modulators are presented. Special configurations of contact electrodes and predetermined values of applied voltages provide the jump in the profile of phase delay of light passing through the modulator or reflecting from it. This leads to the appearance of a vortex field. Ring-shaped light fields and light fields with intensity distribution in the form of two maxima, which rotate in the transverse plane during propagation were obtained. These devices may be valuable for use in the spectroscopy of single molecules.

Structured light has a huge number of applications, including microscopy and spectroscopy [1]. Formation of light fields with various (arbitrary) intensity distributions and dynamic control of their parameters is possible using multi-pixel LC SLM. For practical applications the reducing cost of modulators as well as the simplification and reducing the sizes of the optical schemes on their base are of interest. In this paper we present new schemes of compact modal LC light modulators which can form certain types of vortex light fields.

The modal principle of control has been proposed in studies [2, 3]. The important feature of those modulators is the presence of additional homogeneous transparent high-resistance layer. This layer covers the low-resistance coating with the hole and performs the function of a control electrode. Tunable spherical and cylindrical lenses were designed in this way. Next, we developed LC focusator (or 4-channel LC modulator) [4, 5]. By using LC focusator as an optical transparent it is possible to focus light into a point spot or a line segment and to form transverse distributions of intensity. Shaped beams can be of various forms, with sizes, position and orientation controlled by means of applied voltages [6 - 8]. Since only a few control electrodes and low control voltages are used in modal LC devices they are easy to control, have relatively low cost and are easy to manufacture.

To obtain light fields with angular momentum, it is necessary to provide a jump in the phase profile of the light passing through the device. This can be done with the special geometry of electrodes. It is found that axially symmetric light intensity distributions can be obtained for two electrode configurations. In the first case, the contact electrode on one of substrates is divided in half, and in the second one, two narrow stripe electrodes are applied on one of the substrates. Thus, a spiral focusator and spiral phase plate can be realized. Selecting the amplitudes of the potentials in such a way that the magnitude of the jump in the phase profile varies by a factor of 2π, it is possible to control the diameter of the ring (Fig. 1). It is also possible to move the light ring in the observation plane. This case may be of interest for example for STED-nanolithography.

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If the conductive coating and contact strip electrodes on one of the substrates are divided in the middle by a narrow nonconducting transparent strip, then on this substrate four contact electrodes are formed. With the help of such a device, one can obtain an intensity distribution with two maxima that rotate during propagation. Incident light of different curvatures will produce maxima at different positions in the observation plane. (Fig. 2). This configuration of the modulator can be used in fluorescent nanoscopy [9].

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References
Anomalous doping of a molecular crystal monitored at the single-molecule level

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Abstract. Terrylene molecules in a $p$-terphenyl crystal usually occupy substitution sites where one guest molecule replaces one host molecule. But in highly terrylene doped crystals we were able to observe also molecules anomalously embedded between two layers of the host crystal. Such an orientation of terrylene in respect to laser excitation beam results in much more efficient absorption and collection of fluorescence photons than in the case of previously investigated molecules embedded in the substitution sites.

Fluorescence images of a highly terrylene (Tr) doped $p$-terphenyl ($p$-T) crystals resembled the images observed for lightly Tr doped crystals, with bright spots deposited on a darker background [1]. The background in this case has however contribution from Tr molecules embedded in the substitution sites $X_1$-$X_4$ [2], as clearly seen in the excitation spectrum recorded from any point between the bright spots – see spectrum (a) in Fig. 1, Right.

![Fluorescence image and excitation spectrum](image)

**Fig. 1.** Left: Confocal ($30\times30$ $\mu$m$^2$, 100×100 points, 5 ms at each point) fluorescence image for a highly Tr doped $p$-T crystal. Right: Fluorescence excitation spectrum collected at 5 K from the area between bright spots (a) and from one of the bright spots (b).

The fluorescence excitation spectrum recorded from each of the bright spots composed of the $X_1$-$X_4$ lines and one or several new narrow lines indicating that Tr molecules occupied also new sites. In Fig. 1 Right (b) the lines corresponding to new sites were numbered by letters from A to E.

One step blinking and bleaching (time gate 0.6 s) of the lines suggested that new sites were occupied by single molecules. Polarization of the fluorescence excitation spectra and saturation behaviour led us to the conclusion that the planes of Tr molecules in the new sites

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were oriented perpendicularly with respect to the excitation beam. Such an anomalous embedding of Tr molecule between the layers of $p$-T crystal is shown in Fig. 2.

![Diagram of Tr molecule and crystal structure](image)

**Fig. 2.** Structure of an anomalous Tr trap. Laser excitation beams was applied along the axis c.

Estimated concentration of Tr molecules in anomalous traps was about 3 orders of magnitude lower than for trapping in the substitution sites X$_1$-X$_4$. We postulate that anomalous doping, considered and observed for the first time in the present work, should be typical in molecular crystals with the herringbone structure.

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**References**

Experimental realization of revival of silenced echo memory protocol in optical cavity

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\textbf{Abstract.} We demonstrated a photon echo quantum memory for weak input optical pulses on the ROSE protocol in a Tm\textsuperscript{3+}:Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} crystal placed in impedance-matched optical cavity. The quantum efficiency of 21\% for a storage of time of 36\,\mu s was achieved for single light pulses.

Active development of optical quantum technologies including optical quantum computing and long range quantum communications stimulates the creation of quantum memory (QM). The creation of highly-efficient QM will not only significantly expand the capabilities of these technologies, but also leads to fundamental impact on the creation of new directions in their development \cite{1}. In last decade, there was proposed and experimentally realized a number of protocols of QM \cite{2}. The schemes based on photon echo in solid state systems \cite{3} demonstrated very promising results for achieving high quantum efficiencies and information capacity. Herein, the \textit{revival of silenced echo} (ROSE) memory protocol seems especially attractive due to the possible use of natural inhomogeneously broadened line \cite{4-6} that could significantly simplify practical implementation of QM. It was also recognized that the photon echo approach in free space schemes needs for a large optical density and requires backward spatial geometry for efficient quantum retrieval. However, these limitations can be eliminated by placing a QM cell in an optimal optical cavity \cite{7,8}. Crystals doped by rare-earth ions are very attractive for this scheme due to its parameters of homogeneous and inhomogeneous broadening of the optical transitions \cite{9}. By placing this crystal into impedance matched optical cavity we can increase the light-matter interaction up to complete absorption of input optical signals which leads to higher efficiencies \cite{7,8}. In recent years there were several experimental demonstrations of photon echo QM in optical cavities \cite{10,11,12}.

In this work for the first time we experimentally realized ROSE protocol in a Tm\textsuperscript{3+}:Y\textsubscript{3}Al\textsubscript{5}O\textsubscript{12} crystal placed in a concentric optical cavity. As in previous work \cite{6} we used \textsuperscript{3}H\textsubscript{6}-\textsuperscript{3}H\textsubscript{4} optical transition ($\lambda = 793$\,nm) of thulium ions with concentration of 0.1\% and orthogonal geometry for propagation of signal and control fields in the cavity. The concentric optical cavity was constructed from two spherical dielectric mirrors with reflection coefficients of $R_1=70\%$ for the front (coupling) mirror and $R_2\approx100\%$ for back mirror. The overall cavity length was ~90\,mm which corresponded to 1.65 GHz free-spectral range. The impedance-matching condition for the ideal cavity with coupling mirror reflection $R_1$ and without any losses inside is achieved when weak total absorption $\alpha$ of the crystal with length $L$ satisfies $2\alpha L = -\ln(R_1)$. In our case this condition is satisfied for $\alpha L \approx 0.15$. So the experiment was performed on absorption line wing because $\alpha L$ is close to 1.4 at the line center. The crystal was placed in Montana Instr. closed-cycled cryostation and cooled down to the temperature $T=4$\,K. Typical behavior of the input light pulse and detected revived silenced echo is depicted in Fig.\,1.

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input pulse was reflected. This could be caused by misalignment of the cavity. For no cavity case, the unabsorbed (reflected) signal could be 85% in this scheme. So the impedance-matched cavity provides 10-fold enhancement of the signal absorption. Using this property, we obtained retrieval efficiency of 21% of input signal pulse for a storage time of 36 µs which is the best result for ROSE experiments and third in implementation of QM in optical cavity.

![Echo signal Efficiency - 21%](image)

**Fig 1.** The signal of the revived silenced echo obtained by using Tm³⁺:Y₃Al₅O₁₂ crystal in impedance matched optical cavity. The signals from scattered π-pulses (red curve) can be seen between the input pulse and echo signal. The echo signal efficiency was 21% with storage time 36 µs.

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**References**

3. W. Tittel, et.al., Las. Photon. Rev. 4, 244 (2009)
Live-cell nanoscopy enabled with transient labeling and the control of fluorophore blinking

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Abstract. Live-cell super-resolution of proteins labeled with genetically encoded fluorescent tags is a challenging task because of the imperfect labeling and the inevitable deterioration of the signal in the course of the experiment. Incomplete maturation of the covalently attached fluorescent tags, inefficient photoconversion, and photobleaching further complicate prolonged live-cell nanoscopy. We have implemented two strategies for lowering the photodamage: ensuring the dynamic replacement of damaged molecules and establishing conditions for the robust intrinsic blinking of the tags at lower illumination powers.

Typical super-resolution localization microscopy setup requires illumination powers at the levels harmful to living cells [1]. These harsh conditions are necessary for both squeezing out the maximum possible number of photons from the fluorophore and for the robust blinking of the dye. Alternative means of achieving blinking established for fixed samples, such as the use of strong reductants, are also inadequate for live-cell experiments. Therefore, the photoactivatable and photoswitchable fluorescent proteins (such as Dendra2, mEos3.2, Dronpa, PA-GFP) currently occupy the niche of fluorescent tags for live-cell super-resolution. For that type of probes, the precise control of the number of fluorophores in the light-emitting state is achievable via the additional light source, typically in the near-UV range. We have recently shown that the intrinsic blinking of some genetically encoded proteins can be robust enough even at low-light setup to allow nanoscopy applications [2]. Still, the labeling quality inevitably deteriorates in the course of the experiment due to the depletion of the pool of the available fluorophores. Unfinished maturation of the covalently attached fluorescent marker, incomplete photoconversion, and photobleaching hinder prolonged live-cell nanoscopy and reduce effective labeling density (Fig. 1A).

The general principles of PAINT (Point Accumulation for Imaging in Nanoscale Topography) resolve many challenges in super-resolution microscopy by replenishing the photobleached or defunct dye from the pool of undamaged molecules [3]. We have recently shown the protein-PAINT with a specific transient binding of cell-permeable fluorogenic dyes to genetically encoded protein tags, engineered from bacterial lipocalins [4]. In protein-PAINT, the concentration of externally added chemical dye controls the number of blinking events (Fig. 1B).

While the photon budget of these dyes does not exceed one of the fluorescent proteins, an almost infinite supply of undamaged dyes allows for nanoscopy even at the low-light regime.

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**Fig. 1.** Challenges of live-cell super-resolution with genetically encoded tags. (A) scheme depicts an enlarged region of the cytoskeleton, the problems in labeling are stated; (B) scheme depicts an enlarged region of a cellular structure, labeled with (left-to-right) a fluorescent protein, the protein-PAINT two-component system with a pool of renewable fluorophores, or with entirely genetically encoded protein-PAINT implementation based on transient protein-protein interactions.

Here we further extend the range of compatible fluorogenic dyes and test other applications of the labeling system, including FRET. We then show the Protein-PAINT implementation based on fluorescent protein and the transient heterodimerization of artificial peptides. Similarly to the protein-PAINT with synthetic dyes, we confirm the improvement in the signal photostability and the labeling density in confocal and super-resolution regimes. Also, we provide the data on the effect of the amino acid residues near the chromophore on blinking of photoactivatable green fluorescent proteins. In conclusion, we show how all the techniques mentioned above could be combined to allow prolonged low-light nanoscopy in living cells with minimal photodamage.

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**References**

Site-selective spectroscopy of nanoconfined dye molecules in liquid and at room temperature

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Abstract. There is ongoing debate about whether or not nanoconfined water freezes at room temperature. Optical persistent hole-burning spectroscopy has been conducted for nanometer-sized reverse micelles within which a dye molecule-containing water droplet resides. We definitely demonstrate that the water surrounding the dye molecule is in a glassy state for the reverse micelle with an aqueous cavity radius of ~1 nm. Moreover, we show dependence of the glassy behaviour of the water on the size of the reverse micelle.

Water is nanoconfined in various situations, such as hydration water surrounding proteins, water in channel proteins, water layer on hydrophilic and hydrophobic surfaces, and clay swelling. Hence, nanoconfined water is an important state of water in science and technology, and so its properties have been extensively studied. There is ongoing debate about whether or not nanoconfined water freezes at room temperature [1-4]; here, we note that the diffusional relaxation process of bulk water has a time scale of a picosecond. Studies using atomic force microscopy (AFM) have demonstrated that water confined between AFM tip and a substrate exhibits very slow relaxation processes of ~ms at room temperature, and the glassy behaviour was discussed, where the water has a few molecular layers [1-4]. However, the water does not freeze from their measurement.

Recently, we have shown from the optical absorption spectroscopy of a dye molecule in reverse micelles that the water surrounding the dye molecule exhibits no diffusional relaxation within minutes at room temperature, and hence it was regarded to be in a glassy state; here, surprisingly, the outside of the reverse micelle, that is, the nonpolar solvent is in the liquid state [5]. A reverse micelle serves as a model of cells. It is formed by self-assembly of surfactant molecules in a nonpolar solvent, and becomes a microscopic spherical cage filled with water, as schematically displayed in Fig.1 [6]. Excellent properties of reverse micelles are that their size (nm–sub-μm) can be controlled experimentally, and that water-soluble molecules, such as proteins and DNA, can be dissolved within them. These properties allow us to study the confinement effect on the properties of water and molecules dissolved. In the present study, in order to definitely confirm the glassy state of the confined water in reverse micelles without any spectral analysis, persistent hole-burning (PHB) spectroscopy has been performed for a dye molecule encapsulated in reverse micelles by use of an experimental system whose signal/noise ratio was improved compared with that in the previous studies [7], and the site-selective effects were examined.

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A dye-containing reverse micellar solution was prepared using the injection method [6]. Rhodamine 6G, AOT [=bis (2-ethylhexyl) sulfosuccinate], isoctane, and sterile Millipore-filtered water were used as a dye, surfactant, oil, and water, respectively.

An optical parametric oscillator pumped with the third harmonic pulse of a nanosecond Q-switched Nd:YAG laser was used as a wavelength-variable excitation source for PHB spectroscopy. PHB spectra were obtained by the difference between absorption spectra before and after the laser irradiation, where the absorption spectra were measured with an experimental system constructed by a combination of white light from a Xenon lamp and spectrometer. The measurement time of PHB spectroscopy was at least of the order of minutes; this time was determined by a sum of laser-irradiation time and acquisition time of the PHB spectrum. The sample was optically excited on the long-wavelength side of the absorption spectrum.

The PHB spectra of the reverse micellar solution with an aqueous cavity radius of ~0.8 nm and ~80 water molecules were shifted to longer wavelengths from the absorption one depending on the excitation wavelength, and the spectral width of the former is narrower than that of the latter. This demonstrates that the surroundings of the dye molecule are in a glassy state because the site-selective effect is observed in the PHB spectrum. On the other hand, it was found for the reverse micelle of ~5 nm and ~2×10^4 water molecules that the PHB spectra agree with the absorption spectrum. The large reverse micelle is filled mostly with bulk-like waters, and so its inside is liquid-like at room temperature. As a result, the site-selective effect is not observed for the large reverse micelle in the PHB spectrum owing to the diffusional relaxation. In the small reverse micelle, the water molecules are confined between the surfactant and dye molecules and will have the hydrophilic interaction between them, where the water will be one or two molecular layers. This confinement effect is thought to lead to a glassy behaviour of water even at room temperature. We are going to also present the dependence of the PHB spectra on the size of the reverse micelle to clarify the size at which the liquid-glass transition takes place.

References

Synthesis and PL properties of quantum-dot chains: gel electrophoresis and hybridization of DNA-functionalized quantum-dots

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Abstract. We report our recent study on the synthesis and PL properties of quantum-dot (QD) linear chains linked by double-stranded DNA. In order to fabricate the linear chains of closely-spaced QDs, the QDs are first functionalized with thiolated short single-stranded DNA, and then are separated using agarose gel electrophoresis according to the number of attached DNA molecules, and finally selected QDs are hybridized with similarly selected QDs functionalized with the complementary DNA.

1 Introduction

Closely-spaced Quantum-dot (QD) oligomers, e.g., dimer, trimer and tetramer, have been attracted attention for the last two decades because of the interest in the optical properties due to energy transfer and/or electronic coupling among constituent QDs [1-3]. The optical properties, however, are still not yet thoroughly understood. One of the reasons is the difficulty to fabricate the oligomers with controlled structure, especially in the case of linear chains composed of three or more QDs. We have recently been investigating the synthesis and photoluminescence (PL) properties of closely-spaced QD chains linked by short double-stranded (ds) DNA in order to understand and control their optical properties. Here, we present the results of the studies.

2 Experimentalas

The QD chains are fabricated in the following way. First, CdSe/ZnS core-shell QDs capped with trioctylphosphineoxide are synthesized by a pyrolytic decomposition method of organometallic compounds [4]. Then, the QDs are rendered water-soluble by ligand exchange with mercaptopropionic acid [5]. Next, the QDs are functionalized with thiolated short single-stranded (ss) DNA (15-mer) in a borate buffer solution (pH=8.3), and after that the DNA-functionalized QDs are separated using agarose gel electrophoresis according to the number of attached DNA molecules (Fig.1(a)). Finally, the selected QDs (B (or A) shown in Fig. 1 (a)) are hybridized with the similarly prepared QDs that are functionalized with the complementary DNA (B’ (or A’) as shown in Fig.1(b)). The structure of the QD chains were characterized by

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TEM, and spectral and time-resolved photoluminescence studies were employed to investigate their optical properties.

3 Results and Discussions

Figure 1(c) shows a PL image of the agarose gel after electrophoresis. It is turned out that the DNA-functionalized QDs can be separated discretely into several bands in spite of the shortness of the ssDNA. And it can be considered that the PL bands correspond to the DNA-functionalized QDs illustrated in Fig. 1(a) (the correspondence can be understood from the results for the samples having different mixing molar-ratio between the QD and the DNA). Figures 1(d) show TEM images of the typical QD oligomers obtained after hybridization. Even though precise control of the shape and particle-number is not yet achieved, linear chains of closely-spaced QDs can be fabricated by using the method. In the presentation, we will describe the synthesis and the detailed results of the TEM and PL measurements of the QD oligomers.

Fig. 1. Schematic diagram of (a) the agarose gel electrophoresis of the DNA-functionalized QDs (b) QD chains linked by double-stranded DNA. (c) the PL image of the agarose gel (4% NuSieve GTG agarose; Lonza) under 365-nm light irradiation. Mixing molar-ratio of the QD and the DNA was 1:8. (d) TEM images of the typical QD oligomers.

References

FRET in single donor-acceptor pair attached to a biomolecule as a nano-ruler

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Förster Resonance Energy Transfer (FRET) in single donor-acceptor pairs differs considerably for FRET in bimolecular ensembles because formula $E(R) = \left[ 1 + \left( \frac{R}{R_F} \right)^6 \right]^{-1}$ for FRET efficiency includes distance R between molecules of the pair. Here $R_F$ is a Förster radius. Hence the change in R can be detected by measuring the change in FRET efficiency. Therefore FRET efficiency can serve as a nano-ruler. For instance, fluorescence of single D-A pair attached to a protein molecule can be used as a nano-ruler for the measurement of folding/unfolding in the protein molecule. In principle, the changes in R we can detect by measuring change in FRET efficiency.

Folding/unfolding processes will create fluctuation of FRET efficiency. By now these processes are studied with the help of the distribution function P(E) for FRET efficiency. Gopich and Szabo [1] presented function $P(E)$ for protein as sum of three Gaussians. Comparing the theoretical expression with distribution $P(E)$ measured in an experiment they can find two efficiencies $E_{1,2}$ and rate of folding/unfolding. However, the Gopich-Szabo theory: 1) didn’t enable one to find distance R from measured $P(E)$, 2) didn’t take into account existence of triplet states in D-A pair. Influence of both factors will be considered in this talk.

We consider single D-A pair attached to a protein molecule in which the donor molecule has two singlet and one triplet states. Fig. 1 describes such system.

Eight rate equations can be written for this scheme. Applying Monte Carlo method to these equations we can find random time instances for emission of D- and A-photon. These fluctuating intensities $I_{D,A}(t)$ enable one to find FRET efficiency trajectory, $E(t) = \frac{I_A(t)}{I_A(t) + I_D(t)}$. This trajectory enables us to find distances $R_1$ and $R_2$ in two conformations of the protein molecule allowing for triplet state in the donor molecule. If the donor molecule reaches triplet state D-fluorescence stops. However, A-fluorescence stops as well because there is no excitation of A-molecule if D-molecule occupies triplet state. Therefore, off-intervals of both fluorences coincide with each other. Fluorescence of D-A pair with triplet state has two sources of fluctuations: 1) interconformational transitions in biomolecule, 2) singlet-triplet transitions in the donor molecule. Therefore, we have two types of on-intervals with average durations:

$$
\tau_{on}^{(1)} = \left[ \frac{kG}{\Gamma_D + G + F_1} + B \right]^{-1} \quad \tau_{on}^{(2)} = \left[ \frac{kG}{\Gamma_D + G + F_2} + b \right]^{-1}
$$

Let us consider a case when interconformational transitions are faster than singlet-triplet transitions. Then trajectory for FRET efficiency looks as follows (see Fig. 2 on the left).
After statistical treating of this trajectory we find: \( E_1=0.33, \ E_2=0.83, \ \tau_{on}^{(1)} = 5\text{ms}, \ \tau_{on}^{(2)} = 10\text{ms}. \) Since bin time is shorter as compared with times of interconformational and singlet-triplet transitions equation for FRET efficiency is simplified and takes the following form: \( E_{i,2} = E_{i,2} \left( \frac{1}{(F_{i,2} + \Gamma_o)} = 1 + (R_{i,2} / R_{i}) \right)^{-1}. \) It enables us to find changes in \( R. \) Distributions of two types of on-intervals found from trajectory in Fig.2 have the following average rates: \( \tau_{on}^{(1)} = 1/203\text{ms} \approx 1/B, \ \tau_{on}^{(2)} = 1/100,83\text{ms} \approx 1/b. \) We see that if singlet-triplet transitions are slower than interconformational transitions we can find from statistical analysis of FRET trajectory both ratio \( R_1/R_2 \) and rate of folding/unfolding.

Let us consider now a case when singlet triplet transitions are faster than interconformational transitions. Then trajectory of FRET efficiency looks as right side of the Fig. 2 shows.

After statistical treating of this trajectory we find the following values: \( E_1=0.3, \ E_2=0.8, \ \tau_{on}^{(1)} = 23\text{ms}, \ \tau_{on}^{(2)} = 75\text{ms}. \) Theoretical eq.(1) give \( \tau_{on}^{(1)} = 23\text{ms}, \ \tau_{on}^{(2)} = 75\text{ms}. \) Theoretical and experimental results are close with each other. Distributions of two types of on-intervals found from trajectory in Fig.3 have the following rates: \( \tau_{on}^{(1)} = 23\text{ms} \neq 1/B = 100\text{ms} \)
\( \tau_{on}^{(2)} = 77\text{ms} \neq 1/b = 200\text{ms} \).

We can formulate the following conclusions: 1) Maxima \( E_1 \) and \( E_2 \) of the distribution functions \( P(E) \) do not depend on rate of singlet-triplet transitions. Therefore, ratio \( E_1/E_2 \) can be found with the help of D-A pair in presence of triplet state in the donor. 2) However, rate of singlet-triplet transitions influence considerably on the distribution functions for on-intervals and their average rates \( \tau_{on}^{(1)} \) and \( \tau_{on}^{(2)} \) measured in trajectories. Instead of values \( 1/B = 100\text{ms} \) and \( 1/b = 200\text{ms} \), which determine times of interconformational transitions, we shall measure in experiment more fast average times \( \tau_{on}^{(1)} = 23\text{ms}, \ \tau_{on}^{(2)} = 77\text{ms}. \)

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References

Integration of the atomic force microscopy and laser spectroscopy

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Abstract. We demonstrate application of integration Raman microscopy and atomic force microscopy for investigation of materials. This integration is made by using innovative optical and micromechanical components. Optical measuring head with cantilever holder was designed for both Raman microscopy and atomic force microscopy modes.

Integration of atomic force microscopy and laser spectroscopy traditionally makes it possible to obtain more information about the object under investigation: whether it is a living cell, a polymer composite, or nanotubes. In the report are given an examples of combined AFM and Raman microscope NTGERA Spectra II (NT-MDT Spectrum Instruments) application to study both physical properties of the surface (topography, surface potential, magnetic or piezoelectric properties, conductivity, local stiffness) and structural properties measured by Raman spectroscopy. Usually Si cantilevers of top-visual shape are used for optical access to the tip from above by high-res objective (100x, 0.7 NA). It is also possible to use metal needles in the tunneling current microscopy or tuning fork based feed-back. It is possible to carry out combined measurements in a controlled gas or liquid environment, which may be important to maintain the properties of the sample or to eliminate the background low-wavenumbers Raman peaks from the N2 and O2 molecules present in the air. The design of the spectrometer makes it possible to use either edge filters or notch filters to suppress laser radiation and provide both Stokes and anti-Stokes scattering, including the THz range down to 10 cm−1 from Rayleigh scattering.

The most intriguing possibility that appears when integrating atomic force microscopy and Raman spectroscopy is to overcome the diffraction limit due to local amplification of the field near the tip apex [1]. To achieve strong enhancement of the Raman scattering in the Tip Enhanced Raman Scattering (TERS), it is necessary to keep the tip at the surface of the sample as closely as possible. The mode of nonresonant intermittent-contact microscopy, also known as Hybrid mode [2] allows the probe to be held in contact with the surface up to 70% of the time, while eliminating lateral forces during scanning and minimizing the pressing force. In addition, this method is also applicable to keep feedback in the liquid and when the sample is heated, when an significant drift of the cantilever tilt is observed.

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Fig. 1. The presented results using the example of graphene oxide flakes, show that HybriD mode allows one to effectively enhance the Raman scattering and, at the same time, significantly reduces the mechanical effect on the sample and on the probe during scanning.

References

Thin layer fluorescence microscopy based on one-dimensional photonic crystal

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Abstract. A new method of specimen illumination for wide-field fluorescence microscopy has been presented. This method allows to excite the fluorescence in a thin near-surface layer of the studied object. As a result, the captured images have greater contrast and signal-to-background ratio in comparison with the epifluorescence ones. The long-range surface waves in one-dimensional photonic crystal have been used to localize the electromagnetic field exciting the fluorescence. An experimental setup has been created to excite the surface waves and obtain images of the objects from the near-surface layer. For an illustration of the possibilities of our method, we conducted several experiments with specimens that are typical for fluorescence microscopy, such as bacteria and eukaryotic cells.

1 Introduction

One-dimensional photonic crystal (1D PC) is a multilayer meta-structure with periodically changing refractive indices of the layers. As shown by V. Konopsky et al. [1], it is possible to create the special conditions for existence of one or several modes of long-range surface optical range electromagnetic waves on the surface of 1D PC. The main idea of our work [2] is to use a small penetration depth of the long-range surface waves to improve the contrast and signal-to-background ratio of the images that could be captured with the help of a wide-field fluorescence microscope. One of the most frequently used methods of such kind image improvement is the so-called Total Internal Reflection Fluorescence Microscope (TIRFM). However usually, this approach requires permanent fine-tuning of optical setup and works only with high numeric aperture lenses. It will be shown that our method does not have such limitations.

2 Materials and Methods

The 1D PC structure was calculated using the method of complex impedance [3]. The dispersion characteristic of the calculated structure corresponded to the excitation spectra of green fluorescent protein (GFP). This structure provides an opportunity to initiate long-range surface waves with 473 nm wavelength on the 1D PC surface. The PC was fabricated using the magnetron sputtering and consisted of 3 layers of SiO₂ and Ta₂O₅ (134.4 nm and 78.4 nm thickness respectively) and a final layer of SiO₂ 300 nm thick. In order to excite the long-range surface waves, an experimental setup based on the Kretschmann configuration with a cylindrical lens was created (see Fig. 1). This configuration does not require permanent fine-tuning of the laser illumination angle.

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Laboratory mutant strain of GFP labeled *E. coli* and a mutant line of GFP labeled HeLa cells were used as the representative specimens for fluorescent microscopy. Cells were fixed on the PC surface. The images of the PC surface were captured with the help of a wide-field fluorescence microscope.

### 3 Results and Conclusion

The experiments showed that fluorescence is excited only inside a thin near-surface layer (~150 nm) of a specimen. Moreover, in the obtained images the signal-to-background ratio is on the average 7 times greater than the value of this parameter in the epifluorescent images of the same specimens. Thus, the localization of the initiating radiation reduces a background signal from the specimen bulk. As a result, it became possible to study a more detailed structure of a specimen. This new method of specimen illumination can be used as a cheap and simple alternative to the TIRFM method. Also, it potentially can be combined with a surface waves biosensor [4].

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### References

Large linear Stark effect on single molecules of dibenzoterrylene in crystals of substituted naphthalenes

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Abstract. Zero-phonon line energies of fluorescent molecules can be tuned in external electric fields—a phenomenon commonly referred to as the Stark effect. In appropriate crystalline environments, dibenzoterrylene (DBT) molecules show narrow optical resonances but the response of individual molecules to an external electric field is not uniform and is often weak in magnitude. Here, we introduce a novel single-molecule host-guest system based on DBT in 2,3-dibromonaphthalene (DBN). The probe shows large linear electric Stark effect in the order of 1.5 GHz/(kV/cm), corresponding to an electric dipole moment change of 2 D. Remarkably, nearly all DBT molecules show similar values of Stark coefficients and excellent spectral stability, indicating well-defined embedding of DBT guest molecules into the crystalline lattice of the host. The results suggest four symmetry-equivalent insertion sites that induce permanent electric dipoles on DBT.

The advancements of quantum technologies and devices depend in part on the integration between quantum optics and nano-electronics. Organic fluorescent molecules can provide an excellent platform for this integration as well-defined, reproducible, and highly responsive quantum systems. When performed at cryogenic temperatures, single-molecule fluorescence experiments can provide narrow zero-phonon lines (ZPLs). These resonances—typically limited by the fluorescence lifetimes of the excited states—can be used as highly sensitive probes of nearest molecular environments or external electric fields.[1] The latter could expand the scope of quantum applications to integrated electronic devices based on single organic molecules. To reach this goal, single-molecule emitters should provide i) high degree of uniformity among individual emitters, ii) high photostability with minimized spectral diffusion, and preferably iii) large linear Stark response. Here, we show that the crystal growth of a host-guest combination with such properties is possible and we provide experimental evidence for the large linear Stark shift in ZPLs of DBT.

Recent results have shown that molecular crystals based on disubstituted naphthalenes can be suitable hosts for fluorescent polycyclic aromatic hydrocarbons, such as terrylene.[2] Furthermore, fluorescent molecules of dibenzoterrylene (DBT) are considered as bright and photostable single-photon emitters which have recently received increasing attention of researchers. Motivated by these developments, we have grown crystals of 2,3-dibromonaphthalene DBN doped with DBT by a co-sublimation method. The crystals were further mounted on an electric chip specially designed for Stark effect experiments, providing typical electric fields in the order of 1-10 kV/cm between the electrodes. Finally, single molecule fluorescence experiments were performed at 1.2 K by using a confocal fluorescence microscopy setup.

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The DBT/DBN crystals showed relatively high concentration of single molecules, with a large number or resonances available around the absorption maximum (Figure 1a). This enabled quick selection of individual ZPLs, with molecules centred in the middle of the electrodes (typical distance of 10 µm). We find linear Stark response with typical Stark coefficients in the order of ±1.5 GHz/kVcm⁻¹ (Figure 1b). Most remarkably, all individual emitters show Stark shifts with similar strengths, a lifetime-limited linewidth (40 MHz), and no visible signs of spectral diffusion.

![Figure 1a](image1.png) ![Figure 1b](image2.png)

**Fig. 1.** a) Stark effect for a large number of single DBT molecules within a single-point scan. b) Histogram of the Stark shifts (absolute values) for more than 130 measured molecules.

We find two values of the Stark shift (with equal magnitude but opposite slopes) for the crystals perfectly aligned with the vector component of the electric field (see Figure 1a). The observed Stark shift corresponds to the electric dipole moment change of 2 D for nearly all studied molecules. In other (non-aligned) orientations of the crystals we find four values of the Stark coefficients. This observation indicates four symmetry-equivalent insertion sites with the electric dipole moment change vector (Δµ) slightly inclined in respect to the vector of the electric field. The maximum recorded Stark shift was found to be close to the mean value for the measured ensembles of molecules, stressing again the highly uniform response of individual molecules in the electric field.

**References**

Plasmonic magneto-optical nested 2D nanostructures: tailoring responses through effective refractive index

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Abstract. Spectra of a nested square two-dimensional lattice of metal nanospheres encased in a magneto-optical host were studied. We show that the magneto-optical response of the nanostructures considerably increases due to the plasmon resonances. Moreover, the optical and magneto-optical responses can be strongly altered with a negligible change in structural parameters.

Nanophotonics encompasses studies on artificial nanostructures that support various optical resonances [1]: surface propagating plasmon resonance (SPR) and localized surface plasmon resonances (LSPR). These plasmonic resonances in various magneto-optical (MO) plasmonic systems are useful for the control of light intensity or polarization. The enhancement of polarization rotation is observed in the polarization rotation spectra of plasmonic MO nanostructures and should be understood as a reciprocal phenomenon [2], however, can be useful for a tunable waveplate [3].

To demonstrate a new view on plasmonic MO nanostructures, we introduce a nested square two-dimensional (2D) lattice of gold (Au) nanospheres encased in a magnetic host (a layer bismuth-substituted yttrium iron garnet, Bi:YIG). We analyze spectra of 2D Au-Bi:YIG nanostructures with square lattices having different periods and discuss LSPRs on single nanospheres and their ensemble. Then, we select a 2D lattice and insert additional nanospheres with radius \( R \), composing another square lattice, into it, thus forming a nested 2D lattice. We will show that the number and spectral positions of the LSPR bands in spectra of the nested Au-Bi:YIG nanostructure are governed by the radius of nanospheres, the MO response can be enhanced at frequencies of LSPRs and it becomes extremely sensitive to the radius of the nanospheres. Two main features are in spectra of such structures: LSPR (\( D_1 \)) band is defined by the lattice period \( D \) and has a large spectral shift as \( D \) changes and LSPR on single spherical nanoparticle in the short-wavelength (SW) band at approximately 600 nm (see Fig. 1(a)).

We compare MO responses of the Au–Bi:YIG nanostructures with square and nested lattices and find interesting features. Unexpectedly, the sign of the angle of polarization rotation \( \theta(\lambda) \) oscillates in the vicinity of LSPR (\( D_1 \)) and is same as that of Bi:YIG at LSPR (\( D_2 \)) band. Moreover, for the SW range, a negligible change in \( R \) results in the drastic flip-over of the MO response at \( \lambda = 630 \) nm [see the left graph in Fig. 1(b), (c)]. Another interesting feature in the spectra is that the presence of the additional scatterers having the coordinates of \((iD_3x, jD_3y)\) strongly influences the spectral position of LSPR (\( D_1 \)). A small change in \( R \) results in the following spectral shifts: \( \Delta \lambda(\text{LSPR}(D_1)) \approx 5 \) nm and \( \Delta \lambda(\text{LSPR}(D_2)) \approx 1 \) nm at \( \Delta R = 1 \) nm. The observed peculiarities, result from the out-of-phase field oscillation on the neighbor nanoparticles in the case of LSPR (\( D_1 \)). In contrast, there is an in-phase dipole-to-dipole interaction of the neighbor nanoparticles in the case of LSPR (\( D_2 \))—the likely reason why the MO response does not change sign. It is worth noting that in the vicinity of strong polarization rotation at 635 nm the light emerging from the Au–BiYIG layer is elliptically polarized, see
Fig. 1 (b) and (c). As for polarization states of the waves at LSPR (D₂) and LSPR (D₁), they are linear (λ = 733 nm) and elliptical (λ ≈ 925 nm) polarizations correspondingly, see Fig. 1 (c).

Fig. 1. a) Calculated transmittance (b) polarization rotation spectra and (b) phase shift between the \( E_x \) and \( E_y \) components for a nested 2D structure with \( D_1 = 350 \) nm. The pairs of spectra demonstrate their dependence on a negligible change of \( R \). Spectra of the square 2D structure with \( D_1 = 350 \) nm is shown for comparison.

References
Abstract. We demonstrate the routing of exciton emission in an external transverse magnetic field in hybrid magneto-plasmonic semiconductor nanostructures. In order to realize magnetic control over the direction of emission and its strength we exploit spin-momentum locking by combining a magnetic material as a source of polarized photon emission with metallic gratings, which support surface plasmon polaritons at the metal-semiconductor interface. Here, we distinguish between the far field effects with a strength of ~1% and the nearly one order of magnitude stronger near field effects.

Plasmonic structures provide a pathway for control of light at the nanoscale. Here, we demonstrate that the use of hybrid magnetic semiconductor nanostructures as a source of exciton emission allows one to acquire magnetic field control over the direction of surface plasmon polariton (SPP) propagation, which are launched via exciton recombination. Moreover, we show that far field effects due to superposition of diffracted electromagnetic waves also contribute to the directionality of the emission.

**Fig. 1.** Scheme of routing exciton emission from the magnetic QW via surface plasmon polaritons. In Figure 1 we illustrate SPPs propagating along the y axis, perpendicular to the direction of magnetic field $B \parallel x$. As shown in the left panel (a), for zero magnetic field ($B = 0$), the QW emission is determined by the heavy hole excitons with angular momentum projections $\pm 1$ along z-axis, which correspond to circularly polarized dipoles rotating in opposite directions.
in the QW plane (x, y). Both dipoles excite left- and right-propagating SPPs with equal intensity. The right panel (b) shows, that the application of a magnetic field along the x-axis modifies the selection rules for optical transitions. The polarization of excitons turns to the (y, z)-plane due to the mixing with light hole states, which results in the excitation of a SPP wave propagating to the right/left depending on the direction of magnetic field. In this way, the magnetic field controls the emission direction. We quantify the strength of this effect by the quantity

$$\rho(\theta) = \frac{(I+(\theta) - I-(\theta))}{(I+(\theta) + I-(\theta))}. \quad (1)$$

Here, \(\theta\) is the emission angle and \(I_+ / I_-\) are the detected intensities at this angle for magnetic fields in positive or negative x-direction respectively. We use a CdMnTe / CdMgTe quantum well structure with large Zeeman splitting and thus strong polarization as source of light. On top of this structure rectangular gold gratings with 250 nm grating period are applied for supporting SPPs. The emitted light is detected in a Fourier imaging setup with the sample being placed inside a liquid helium flow cryostat at \(B = 520\) mT, \(T = 10\) K. Figure 2 shows an exemplary measurement of directional emission. Left and right colored panels correspond to measured and calculated \(\rho(h \omega, \theta)\)-patterns, respectively. Side plots at the calculated pattern shows cross-sections along fixed photon energy \(h \omega = 1.656\) meV as indicated by the dotted line (upper plot) or fixed angle \(\theta = 10^\circ\) as indicated by the dash-dotted line (right plot). Blue and red curves in these plots correspond to cross-sections of experimental data and calculation results, respectively. Yellow curves in the side plots show PL signal measured in s-polarization.

Fig. 2. Angle- and spectrally-resolved directionality measurement of the near field effect.

In conclusion, we observe directional magnetic field controllable emission with a strength of round about 5% in the near field. As shown in [1] the effect decreases with increasing spacer thickness down to about 1% in the far field.

References

Quantitative description of MLCT transitions in ruthenium polypyridyl complexes probed by two-photon absorption spectroscopy

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Abstract. Quantitative two-photon absorption (2PA) cross section and 2PA spectrum measurements were used to determine the molecular electric dipole change in the metal-to-ligand charge-transfer transition of ruthenium(II) tris-complexes of 2,2'-bipyridine ([Ru(bpy)₃]²⁺) and 1,10-phenanthroline ([Ru(phen)₃]²⁺) in several solvents.

1. Introduction
Ruthenium(II) polypyridyl complexes are well studied systems with the ability to form metal-to-ligand charge-transfer (MLCT) excited states with visible light absorption. This charge-transfer makes these complexes useful for numerous applications, but also makes them sensitive to local electric fields due to the formation of a dipole moment, Δμ. Quantitative two-photon absorption (2PA) spectroscopy is a versatile technique that can measure changes of permanent electric dipole moment.[1,2] We investigated the 2PA spectra of [Ru(bpy)₃]²⁺ and [Ru(phen)₃]²⁺ dissolved in water (H₂O), dimethylsulfoxide (DMSO), acetonitrile (ACN), and dichloromethane (DCM), and use a two-level model of 2PA applied to the lowest-energy transitions to estimate the value of Δμ in different solvents.

2. Results and Discussion
The 2PA cross-sections over the wavelength range of 680 – 1020 nm for [Ru(bpy)₃]²⁺ and [Ru(phen)₃]²⁺ are shown as solid lines in Figure 3. Applying the two-state model of 2PA[1] to the lowest-energy transitions, we can evaluate the difference in the ground- and excited state dipole moments according to the equation:

\[ |Δμ| = \frac{13650}{n^2 + 2} \sqrt{\frac{n \sigma_{2PA}(2λ)}{λ \varepsilon_{1PA}(λ)}}, \]

where \( n \) is the index of refraction, \( ε_{1PA} \) is the molar absorption coefficient at wavelength \( λ \), and \( σ_{2PA} \) is the 2PA cross section at twice that wavelength. The calculated Δμ values (Table 1) are in the range 5 – 8 D and show a decrease with decreasing solvent polarity. Our all-optical measurements agree with previous electroabsorption measurements,[3,4] but are the first to show the dipole moment solvent dependence for both complexes, which is important in their function as a charge-transfer photosensitizers.

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Fig 1. Absorption spectra collected for [Ru(phen)$_3$]$^{2+}$ (A) and [Ru(bpy)$_3$]$^{2+}$ (B) in H$_2$O (Black), DMSO (Dark-Gray), ACN (Mid-Gray), and DCM (Light-Gray). 2PA (solid lines) are in units of Goeppert-Mayer (GM), and 1PA molar absorption coefficients (M$^{-1}$cm$^{-1}$, dashed lines) are scaled for comparison. The calculated dipole moment ($\Delta \mu$) is displayed with units on the right-hand axis.

Table 1. Comparison of the 1PA molar absorption coefficient ($\varepsilon$) and 2PA cross section ($\sigma$) at $\lambda_{max}$ for both complexes in the four solvents studied, as well as the relative permittivity ($\varepsilon_r$) for each solvent.

| Solvent | $\varepsilon$ (M$^{-1}$ cm$^{-1}$) | $\sigma$ (GM) | $|\Delta \mu|$ (D) | $\varepsilon$ (M$^{-1}$ cm$^{-1}$) | $\sigma$ (GM) | $|\Delta \mu|$ (D) |
|---------|----------------------------------|---------------|-------------------|----------------------------------|---------------|-------------------|
| H$_2$O  | 78                               | 14450$^a$     | 56                | 19000$^a$                        | 83            | 7.4               |
| DMSO    | 47                               | 11100$^b$     | 32                | 19900$^e$                        | 93            | 7.4               |
| CAN     | 36                               | 14600$^c$     | 27                | 19900$^d$                        | 73            | 6.6               |
| DCM     | 9                                | 14400$^e$     | 26                | 16600$^e$                        | 54            | 6.0               |

$^a$ref [5], $^b$ref [6], $^c$ref [7], $^d$ref [8], $^e$ref [9].

References

Influence of solid matrices on spectral features of metalloporphyrins

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Abstract. A way of simultaneously forming in the ground electronic state a planar, as well as two distorted forms was established for a set of metalloporphyrins in solid matrices at cryogenic temperatures. Experimental data together with results of theoretical DFT calculations are combined for analysis and assignment of possible types of distorted porphyrin macrocycles conformations.

Metallocomplexes of porphyrins are biologically relevant compounds known for many years. On other side metalloporphyrins are suitable compounds for single molecule spectroscopy as molecules with wide variable different spectral features at cryogenics temperatures. However, despite intensive studies by many groups, their spectral features and photophysical properties are still the subject of long debates and new experiments. The spectroscopic studies at low temperatures belong to effective and proven methods of investigation of fine details such as a vibrational structure of molecules in both the ground and excited states. One of the most spectacular methods for recording fine-line luminescence spectra is the fluorescence line narrowing (FLN) \cite{1}.

In this report, we discuss the results, obtained for set of the simplest metalloporphyrins in different solid solutions, crystals and rare gas matrices at liquid helium temperature. The interest in such type of study was motivated by a unique possibility to obtain the spectra of the different spectral conformation of metalloporphyrins.

For example, fluorescence spectra of three different spectral forms Zn-porphine (ZnP), embedded in solid argon matrix are presented on Fig. 1. Fluorescence excitation spectra were recorded upon detection of fluorescence bands for corresponding spectral conformation also. These spectral features are caused by realization the structures with position of Zn- atom «in plane» (Form F\textsubscript{0} - Fig1a) and two types «out of plane» of porphyrin macrocycles in matrices (Form F\textsubscript{I} - Fig1b and F\textsubscript{II}- Fig1c) \cite{2}. Above mentioned forms of ZnP in argon matrix have the different positions of the 0-0 transitions of the first electronic states at 552.3, 562.4 and 566.45 nm. The energy gap between positions of the 0-0 transitions more than 300 cm\textsuperscript{-1} of Form F\textsubscript{0}, for Form F\textsubscript{I}. Spectral gap between Form F\textsubscript{0} and Form F\textsubscript{II} have the value about 450 cm\textsuperscript{-1}. In a Soret band range the position of long-wave transitions for three forms are manifested at 385, 388 and 404 nm, correspondingly.

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Fig. 1. Fluorescence spectra of ZnP (1) in solid argon matrix onto a sapphire substrate under nonselective excitation: $\lambda_{\text{exc.}} = 385$ (a), 388 (b), 404 nm (c) at $T = 5$ K and FLN spectra (2) of ZnP in $n$-octane, $\lambda_{\text{exc.}} = 556.8$ nm (a) and ZnP in $n$-octane with pyridine $\lambda_{\text{exc.}} = 573.1$ nm (b) at 4.2 K.

Relative intensities of the 0-0 and vibronic transitions are very different for these forms (Fig. 1). Upon the fluorescence line narrowing conditions there are essential difference in intensities of vibronic transitions. It is connected with different character of vibronic borrowing intensities for vibrational transition upon formation of vibrational structure of fluorescence spectra for above-mentioned forms. FLN spectra of Form F0 (realized for ZnP in $n$-octane) and Form FII (ZnP in $n$-octane with pyridine) were recorded upon laser selective excitation. The modes with frequencies 1578 and 1622 cm$^{-1}$ (Form F0) decrease to 1566 and 1606 cm$^{-1}$ in spectrum of Form FII, correspondingly. An empirical interpretation of this effect can lead to wrong conclusions Density Functional Theory (DFT) and time dependent DFT methods were used for optimization of the ground and excited states together with calculation intensities and frequencies of normal modes of metallocomplexes. Based on performed calculations, an assignment of experimentally observed forms was proposed. The FI form was attributed to a complex of metalloporphyrin with one extra ligand placed above its plane. The FII form corresponds to a structure with two additional ligands located at opposite sides of the porphyrin macrocycle. Complexes of metalloporphyrins with rare gas may be realized as Van der Waals complexes between metalloporphyrin and rare gas. Upon condensation of the molecules into rare gas matrix, the distance between the matrix and the chromophore is less than one nanometer, which can lead to a significant increase of the probability of Van der Waals complexes formation [3].

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References
Spectroscopy of rare-earth ion-doped crystals for optical quantum memory applications

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Abstract. Rare-earth ion doped crystals (REICs) are of particular interest in domains of quantum information processing and quantum communication. Thanks to their long optical and spin coherence times at low temperatures and wide optical inhomogeneous linewidths (in the GHz range) they have been actively studied to realize optical quantum memories and quantum processors. In this context the precise spectroscopic information is of particular importance in order to realize quantum light-matter interface. In this work we present an extensive spectroscopic study of various REICs for optical quantum memory applications, including \textsuperscript{151}Eu\textsuperscript{3+}:Y\textsubscript{2}SiO\textsubscript{5}, \textsuperscript{145}Nd\textsuperscript{3+}:Y\textsubscript{2}SiO\textsubscript{5} and \textsuperscript{171}Yb\textsuperscript{3+}:Y\textsubscript{2}SiO\textsubscript{5} crystals.

1.1 \textsuperscript{151}Eu\textsuperscript{3+}:Y\textsubscript{2}SiO\textsubscript{5}

Europium-doped yttrium orthosilicate Eu\textsuperscript{3+}:Y\textsubscript{2}SiO\textsubscript{5} is one of the most attractive solid-state systems to realize optical quantum memory for quantum repeater application. This is due to the long optical coherence times of a few milliseconds, which together with excellent spin coherence properties of tens of milliseconds lifetime offer the possibility to realize spin-wave storage of photonic states. Recently, the extension of the spin coherence lifetime in Eu\textsuperscript{3+}:Y\textsubscript{2}SiO\textsubscript{5} up to one minute has been demonstrated using the zero-first-order Zeeman shift (ZEOFOZ) condition at high magnetic [1]. Further use of the ZEOFOZ transition for storing optical excitations requires knowledge of optical properties for this material under an applied magnetic field. The excited state spin Hamiltonians have been previously characterized for other non-Kramers crystals.

In our work [2], we investigate the hyperfine properties of the excited state \textsuperscript{5}D\textsubscript{0} of \textsuperscript{151}Eu\textsuperscript{3+}:Y\textsubscript{2}SiO\textsubscript{5} by fully reconstructing its effective spin Hamiltonian. To this end we use an optical free induction decay method on the optical transition, which allows us to measure all hyperfine splittings under weak external magnetic fields applied in various directions. With this approach, all hyperfine splittings can be measured for both the ground and excited states at the same time, which is an efficient method to precisely characterize the relative orientation of the two spin Hamiltonians. This is crucial in order to predict optical branching ratios for various optical pumping tasks, like quantum memory applications.

1.2 \textsuperscript{145}Nd\textsuperscript{3+}:Y\textsubscript{2}SiO\textsubscript{5}

In Kramers ions such as erbium, neodymium or ytterbium, the ground state is an electronic Zeeman doublet \textit{S}=$1/2$ in low-symmetry doping sites. In terms of applications, Kramers ions are interesting as the large Zeeman and hyperfine splittings allow large bandwidth quantum
memories and could be interfaced with superconducting qubits working in the 1-10 GHz regime. 

In our study [3] we explore spectral hole lifetimes in moderate magnetic fields and a temperature of about 3K in an isotopically $^{145}$Nd$^{3+}$:Y$_2$SiO$_5$ crystal, where $^{145}$Nd also has a nuclear spin I=7/2. We demonstrate that the spectral hole lifetime depends strongly on the duration of the hole burning pulse. By burning for durations of around one second, the spectral hole is dominated by a slow decay process with a lifetime that can reach 4 seconds. As a result the optical pumping is enhanced by the longer hole lifetimes, with an absorption background of 1-2% of the peak absorption. By applying these results to an optical storage experiment based on an atomic frequency comb memory, we reach storage efficiencies of up to 33%, which is mainly limited by the peak absorption rather than the residual background absorption.

1.3 $^{171}$Yb$^{3+}$:Y$_2$SiO$_5$

Ytterbium has a number of advantages comparing with other rare-earths. The favorable optical branching ratio connecting lowest crystal field levels, in comparison to other REIC system, gives additional advantages for the single ion detection using optical cavity enhancement. Another advantage comes from the specific isotope $^{171}$Yb, which has the lowest non-zero nuclear spin I=1/2. This fact greatly simplifies the energy level structure facilitating the spectral tailoring and the spectroscopic study using standard methods.

In our latest work [4] we determine the hyperfine tensors for the ground and excited states on the optical transition by combining spectral holeburning and optically detected magnetic resonance techniques. The resulting spin Hamiltonians correctly predict the magnetic-field dependence of all observed optical-hyperfine transitions, from zero applied field to the high-field regime. These results pave the way for realizing solid-state optical and microwave quantum memories based on a $^{171}$Yb$^{3+}$:Y$_2$SiO$_5$ crystal [5].

References

Optical detection of single transparent nanoparticles

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Abstract. We will present the novel experimental far-field optical microscopy technique for detection of single nanoparticles, which weakly absorb a visible light and are characterized by refractive index close to its value in nearby environment (including particles of organic and biological origin: polymer nanoparticles, micro- and extracellular vesicles, liposomes, viruses etc).

Visualization of small nanoparticles is one of the basic challenges of the modern optical microscopy. Extremely low level of light signals makes this task very difficult. It is especially difficult to detect the so-called “invisible” nanoparticles, which weakly absorb a light of a visible band and are characterized by the index of refraction close to its value in nearby environment. Such objects are typical in biology media and are often used in modern technologies (for example, solution of polymer nanoparticles in water).

Despite the evident success of the fluorescence microscopy in high sensitive nanoparticle detection it has a set of fundamental shortcomings. First, a necessity of sample labelling that might alter properties of particles, and secondly, an undesirable photobleaching of fluorescence emitters and a fluorescence saturation, that limited the number of emitted photons.

We present the novel optical technique for high sensitive image of nearly invisible nanoparticles based an elastic scattering detection. Our approach uses the modified suffer plasmon assisted microscopy and waveguide technique that allows to increase significantly the efficiency of sample illumination. The original scheme of optical signal detection, sensitive to distortion of scattered light, allows to increase noticeably signal to noise ratio. The important advantage of our microscope is the possibility to detect the same particles simultaneously by two different methods. It can be realized by collecting light signals from two different sides of the sample. This way allows to raise the reliability of nanoparticle detection with the assumption that the origin of the experimental errors in two methods is different.

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Fig. 1. Fragment of the detected image of polysterene nanospheres of 80 nm diameter

Fig. 2. Fragment of the detected image of liposomes of ~100 nm diameter
Multifocus self-focusing of a femtosecond optical vortex

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Abstract. We analyze formation of multifocus structure during the propagation of optical vortex with topological charge \( m = 1 \) in fused silica at wavelength 1800 nm, which corresponds to region of anomalous group velocity dispersion. Propagation of pulse is accompanied by sequence of nonlinear focuses, where each focus is a high intensive ring.

Self-action of femtosecond pulses may tend to formation of spatially long structures with high intensity – filaments [1]. Propagation of laser pulses in the regime of anomalous group velocity dispersion (GVD) may be accompanied by formation of localized in space and time high intensive structures – “light bullets” [2, 3]. Filamentation in beams with smooth phase has been widely studied for Gaussian beams, Airy and Bessel beams [4]. Annular beams with spiral phase dislocation have zero field on optical axis and are often called optical vortices. Self-focusing of optical vortex in a medium with normal GVD was studied in [5, 6]. Filamentation of vortices often tends to breaking up into several hot points due to modulational instability [7], but the distance of nonlinear focus can be less than the distance of modulational hot points formation. Thus, nonlinear focus preserves annular symmetry.

The formation of tubular filament with peak intensity \( 5 \times 10^{13} \) W/cm² and plasma electrons concentration \( 10^{-3}N_0 \) of neutrals, was demonstrated in [9] for femtosecond optical vortex in fused silica with normal GVD at central wavelength 800 nm. This work is devoted to numerical simulations of optical vortex filamentation in the presence of anomalous GVD. We analyze dynamics of light bullets and evolution of fluence distribution of the pulse.

Numerical simulation of the optical vortex self-action is based on the system of equations for slowly varying complex amplitude of laser field \( A_V(r, \varphi, t, z) = A(r, t, z)\text{e}^{im\varphi} \) and free electron concentration \( N_e(r, t) \):

\[
\begin{aligned}
2ik_0 \frac{\partial A}{\partial z} &= \hat{T}^{-1} \left( \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} - \frac{m^2}{r^2} \right) A + \hat{T}^{-1} \hat{D} A + \frac{2k_0^2}{n_0} \hat{T} \Delta n_k A + \frac{2k_0^2}{n_0} \hat{T}^{-1} \Delta n_{pl} A + i\hat{T}^{-2} \sigma A - i k_0 (\alpha + \delta) A, \\
\frac{\partial N_e}{\partial t} &= W(N_0 - N_e) + N_e (\nu_i - \beta).
\end{aligned}
\]

Operator of the wave nonstationarity \( \hat{T} \) [9] is used to describe such effects as femtosecond pulse wavefront self-steepening.

Initial shape of optical vortex was considered as annular vortex beam with Gaussian envelope:

\[
A_V(r, \varphi, t, z = 0) = A_0 \left( \frac{r}{r_0} \right)^m e^{-r^2/2r_0^2} e^{-t^2/2t_0^2} e^{im\varphi},
\]

where \( m = 1 \) is topological charge, \( \varphi = \arctan x/y \). Spatial parameter \( r_0 = 100 \, \mu m \), pulse duration \( t_0 = 36 \, fs \), central wavelength \( \lambda_0 = 1800 \, nm \). Peak power of initial beam was \( P_0 = 5P_V \), where \( P_V \) is the critical power of self-focusing for optical vortex [5, 6] with topological charge \( m = 1 \).

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In the initial stage of vortex beam propagation the self-action yields narrowing ring in the beam cross-section, its radius being practically the same $r_0 = 100 \, \mu m$ at $z = 0.9 \, cm$ (Fig. 1). Peak intensity rises up to $1.5 \times 10^{13} \, W/cm^2$, ring width decreases in $\sim 10$ times, peak fluence is $0.07 \, J/cm^2$. This wave packet corresponds to the first nonlinear focus and can be considered as vortex bullet. Kerr’s self-focusing is then stopped by linear diffraction, which is accompanied by flowing pulse energy towards the optical axis. Phase singularity prevents the appearance of the light field in the beam center and interference rings are formed at $z \sim 1.2 - 2.5 \, cm$ around the optical axis with fluence up to $0.04 \, J/cm^2$. The next nonlinear focus takes place at distance $z = 4.1 \, cm$. The light bullet corresponding to the second focus has approximately the same peak intensity as in the first focus, ring radius being about $50 \, \mu m$. Energy flowing towards beam axis remains up to the distance of $z \sim 4.3 \, cm$, where the last focus is situated. Peak intensity reaches the global maximum, which is about $5 \times 10^{13} \, W/cm^2$, fluence is $0.24 \, J/cm^2$, the ring radius decreases up to $10 \, \mu m$. Plasma electrons concentration is reached for the first time noticeable value $0.5 \times 10^{-3} N_0$, where $N_0$ is neutrals concentration.

Fig. 1. Fluence evolution of optical vortex in fused silica at wavelength 1800 nm

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References
Temperature related shift in the hyperfine structure of NV center ground state

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Abstract. In an ensemble of NV centers temperature related shift of hyperfine structure of the ground state was measured at room temperature using NV associated thermometer and NV related NMR techniques. We show a good correlation with a theoretical estimation and make an estimate on spin density distribution inside NV center nearby the N atom.

Over the past decade various color centers in diamond attracted a lot of interest of researchers and among them well-known NV center[1]. Thanks to room temperature operation [2], ability to optically polarize and detect electron spin state, long coherence time in a solid state it become promising platform for many quantum applications and fundamental tests of quantum physics [3]–[6]. Nuclear spin and hyperfine interaction plays important role, giving a possibility to control nearby nuclear spins and use them as a sensory or memory resource[7]. It was shown that temperature variations lead to significant drift of electron quadrupole term in the Hamiltonian, and it was shown that temperature drifts during the Ramsey sequence microwave pulses after switching off the laser source could limit the performance of a possible electronic spin sensor [8].

In this work we show for the first time, that apart from electron spin fine structure, nuclear spin associated hyperfine structure also have a temperature related shift, which is of importance for ultraprecise diamond-based quantum sensors. The drift is attributed to the expansion of the diamond crystal lattice. Comparison of the experimental results with the exact theoretical estimation give an insight into the structure of spin density around nuclear spin, which was discussed previously in several works.

References


Multi-photon luminescence of single gold nanoparticles: Exploring the dynamics of plasmons and electron hole pairs

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Abstract: We investigate the dynamics of the multi-photon excitation of single, isolated gold nanoparticles and show that the one/two/three emission can be actively switched by changing the excitation pulse duration.

Luminescence of bulk gold has first been reported in the pioneering experiments of Mooradian in 1969 [1] and was attributed to the radiative recombination of electron hole pairs. In the recent years it was pointed out that their optical properties, like elastic scattering [2] or one photon luminescence [3], are dictated by the particle plasmon.

Here we utilize multi-photon excitation to investigate the optical properties of single gold nanoparticles and report on efficient two and three photon luminescence emission based on the excitation of electron hole pairs. Furthermore, we show that the emission of the same gold nanoparticle strongly depends on the excitation conditions and can be actively switched by changing the excitation pulse duration from 500 fs (Fig.1(a)) to 100 fs (Fig.1(b)).

Fig. 1 (a) shows the emission spectrum of a single gold nanosphere exited with one (black line) and two (red line) photons exhibiting a single emission band at 550nm. This emission follows closely the plasmonic properties of the gold nanosphere. In Fig. 1(b) the gold nanosphere is excited with one (black line) and two (red line) photons and the green line displays a corresponding simulation. In this case a shorter excitation pulse duration was used, which drastically changes the emission properties. This emission can be described by the radiative recombination of electron hole pairs. Additionally, we are using single gold nanorods with different aspect ratios to investigate the interplay between the particle plasmon and electron hole pairs, which enables us to develop a quantitative model to fully describe the two and three photon luminescence emission of single gold nanoparticles.

These findings greatly increase the understanding of the physical processes underlying the luminescence of gold and hence help to increase the usefulness of gold nanoparticles in various application fields, e.g. in material science, bio imaging, microscopy and spectroscopy.
Fig. 1. (a) shows the typical plasmonic emission spectrum of a single gold nanosphere exited with one (black line) and two (red line) photons exhibiting a single emission band at 550nm. (b) displays the emission excited with one (black line) and two (red line) photons. In this case the pulse duration was reduced from 500 to 100fs causing a drastic change in the emission behaviour. The green line shows a corresponding simulated spectrum.

References


Exciton fine-structure splittings in single perovskite nanocrystals

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Abstract. Semiconductor perovskite nanocrystals (NCs) have just emerged as a novel type of fluorescent nanostructure capable of emitting single photons with superior optical properties. Here we show that bright-exciton fine-structure splittings as large as several hundreds of μeV are observed in single perovskite CsPbI\textsubscript{3} nanocrystals due to the enhanced electron-hole exchange interaction. The above finding implies that the fundamental studies and practical applications of semiconductor colloidal NCs have now stepped into the quantum information processing regime.

The electron-hole exchange interaction is greatly enhanced in quantum-confined semiconductor nanostructures, leading to the energy-level splitting between bright- and dark-exciton states. In semiconductor epitaxial quantum dots (QDs), the dark excitons are generally nonemissive without applying a magnetic field and the bright-exciton state is further divided into two orthogonally- and linearly-polarized ones. A complete elimination of this bright-exciton fine-structure splitting (FSS) has been actively pursued to realize a polarization-entangled photon-pair source for fundamental tests in quantum mechanics and optics, as well as for practical applications in quantum communication. Interestingly, the dark excitons in colloidal semiconductor nanocrystals (NCs) are normally emissive, while the bright-exciton FSS was rarely observed. Overall, the random orientation of the crystallographic axis of the traditional colloidal NCs, together with the photoluminescence (PL) blinking and spectral diffusion effects, posed severe obstacles to investigating the polarized bright-exciton FSS so that its very existence is still questionable.

Semiconductor colloidal perovskite NCs have just emerged as a novel type of semiconductor nanostructure capable of emitting single photons without the influence of dark-exciton emission [1]. Moreover, the suppressions of both the PL blinking and spectral diffusion effects were successfully demonstrated in single perovskite CsPbI\textsubscript{3} NCs [2]. Here we show that the bright-exciton FSS can be easily observed in single CsPbI\textsubscript{3} NCs at the cryogenic temperature of 4 K (Fig. 1), with an energy separation as large as hundreds of μeV between the two orthogonally- and linearly-polarized states [3]. With the laser excitation at an intermediate power, this PL doublet of neutral single exciton would switch to a single peak of singly-charged single exciton. When the laser power is further increased, PL doublets from neutral biexciton, charged biexciton and doubly-charged single exciton could be additionally observed. Based on the FSS values obtained from various exciton species, the isotropic and anisotropic e-h EI energies can be roughly estimated, which have provided valuable information on the fundamental electronic processes in these novel perovskite NCs.
Fig. 1. (left) PL spectrum measured at 4 K for a single CsPbI\textsubscript{3} NC with the FSS of two orthogonally- and linearly-polarized peaks. (right) Time-dependent PL spectral image of a single CsPbI\textsubscript{3} NC showing the long-time stability of the FSS.

References


Simultaneous coherence enhancement of optical and microwave transitions in $^{171}$Yb:Y$_2$SiO$_5$

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Abstract. Rare-earth ions doped crystals are promising systems for quantum information processing. In particular, paramagnetic rare-earth centres can be used to realize quantum coherent interfaces simultaneously for optical and microwave photons. $^{171}$Yb$^{3+}$ is an interesting candidate for those kinds of applications, since it is the only paramagnetic rare-earth with a one-half nuclear spin ($I=1/2$), which makes its hyperfine structure the simplest possible. In this paper, we show the promising properties of an isotopically enriched $^{171}$Yb:Y$_2$SiO$_5$ single crystal such as narrow inhomogeneous linewidths, strong oscillator strength and long coherence times for both optical and spin transitions.

Crystals doped with paramagnetic rare earth (RE) ions are promising materials for quantum information processing because they can be coupled to microwave photons [1] or provide large bandwidth memories [2]. Furthermore, we recently demonstrated that coherence transfer with high fidelity was possible between electron and nuclear spins in these materials, opening the way to long storage time capability [3].

Yb$^{3+}$ presents in Y$_2$SiO$_5$ high oscillator strengths associated with narrow inhomogeneous linewidths at low concentrations [4]. Here we report on the hyperfine structure of $^{171}$Yb$^{3+}$, which is the only paramagnetic rare earth ion with a nuclear spin $I=1/2$, leading to a simple energy level structure. Thanks to the narrow optical inhomogeneous linewidths ($<1$ GHz), the nuclear spin transitions can be selectively addressed with a laser, which is convenient for an efficient optical pumping into the spin levels and can facilitate a state preparation for quantum processing applications.

In order to know precisely the spin energy structure for an arbitrary magnetic field, we determined the strongly anisotropic hyperfine tensors for the ground and excited states on the optical $^2F_{7/2}(0) \leftrightarrow ^2F_{5/2}(0)$ transition by combining spectral holeburning (see fig. 1 A), optically detected magnetic resonance and electronic paramagnetic resonance techniques [5]. This knowledge allowed us to find particular magnetic field positions for which the energy states are insensitive to small magnetic field perturbations. Those points, which are called ZEFOZ or “clock transitions”, show an exceptional coherence time enhancement [6, 7]. For the first time, we demonstrate a simultaneous enhancement for both microwave and optical domains, reaching coherence times of above 100 µs and 1 ms in the optical and microwave domain, respectively. Our results show the great potential of $^{171}$Yb$^{3+}$:Y$_2$SiO$_5$ for quantum processing applications relying on both optical and spin manipulation, such as optical quantum memories [2, 7], microwave-to-optical quantum transducers [1, 9], and single spin detection [10].
Fig 1. A) Recorded optical spectral holeburning (SHB) spectra of site I of $^{171}$Yb$^{3+}$:Y$_2$SiO$_5$ crystal measured for different magnetic field amplitudes applied in the direction close to D$_1$-axis. Zero frequency detuning corresponds to the central frequency at which spectral holeburning is performed. Black regions correspond to lower absorption (holes), while white lines correspond to lower transmission (antiholes) regions. White and black dashed lines indicate the energy level splittings of ground and excited states calculated with the determined spin Hamiltonian. B) and C) Optical and electron spin coherence lifetimes measurements as a function of the external magnetic field.

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Study of the dynamics of the nuclear spin bath in europium-doped yttrium orthosilicate

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There is growing interest to use nuclear spin states of rare earth ions doped crystals to store and manipulate quantum information due to the potential of optically manipulating the spin states [1, 2]. Eu³⁺:Y₂SiO₅ is a good candidate for such quantum-memory applications due to its good coherence properties for both hyperfine and optical transitions of the Eu³⁺ ions [3, 4].

In previous work, when we demonstrated a hyperfine coherence time of six hours in this system, we also determined that the interactions between the Eu³⁺ and the host Y³⁺ spin bath are still the dominant decoherence source [4].

Further extension of the coherence time is beneficial for quantum memory applications. Here we present techniques to study the detailed dynamic interactions between the Eu³⁺ ions and the spin bath, with the aim of further extending the hyperfine coherence times of the Eu³⁺ ions through higher precision control over these interactions. These techniques will be applicable to a wide range of spin systems.

Fig. 1. The measured spin-transition spectrum of Y³⁺ spins near the Eu³⁺ ion in a strong magnetic field. The detuning of the Y³⁺ spin frequencies is produced by the induced magnetic moment on the Eu³⁺ by the magnetic field. Here p₁ - p₅ represent different Y³⁺ sites given by the separation from the Eu³⁺ ion.

References

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Vibrationally-selective, infrared absorption microscopy and spectroscopy of individual single layer graphene oxide sheets

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Abstract. Infrared photothermal heterodyne imaging (IR-PHI) is a recently developed, super-resolution mid-infrared imaging technique that circumvents the infrared diffraction limit. It enables spatial resolution on the order of 300 nm and overcomes one of the primary limitations of infrared absorption microscopy. Here we apply IR-PHI to directly investigate in-plane chemical heterogeneity in single layer graphene oxide (GO) grown atop holey Si₃N₄. Despite a decade of research on GO, ambiguity still exists regarding its chemical structure. This limited understanding stems from the fact that techniques employed to characterize it have largely been ensemble-based. IR-PHI measurements reveal spatial heterogeneity in intrasheet non-carboxylic acid carbonyl C=O and cyclic ether C-O distributions. GO chemical compositions near holey Si₃N₄ regions additionally exhibit large C=O to C-O ratios. Correlated photoluminescence measurements indicate that these C=O rich regions exhibit sizable spectral shifts relative to the rest of the sheet. In tandem, these measurements reveal links between GO’s chemical functionalities and its local optical properties during photolysis. These studies open the door to better understanding the chemical structure of single-layer GO as well as establishing detailed mechanistic insight into its photolytic chemistries.
Spectroscopic investigation of Eu$^{3+}$ complexes with different fluorination degree of ligands

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Abstract. We present a spectroscopic study of four Eu$^{3+}$ complexes with 1,3-diketonate ligand environment having different fluorination degrees of the carbon chain. Based on our results, we conclude that the “antenna” effect occurs in the studied compounds. The efficiency of the energy transfer from the ligands to the ion was shown to be increased with the growth of the fluorination degree. For highly fluorinated complexes saturation of the transfer efficiency was observed. The obtained results are associated with suppression of the CH oscillations responsible for nonradiative relaxation.

Rare-earth coordination compounds are promising materials for fluorescence microscopy, biological and medical applications as well for fabrication of active layers in organic light-emitting diodes and other photonic devices. In the present paper we provide the results of the spectroscopic study of four complexes involving Eu$^{3+}$ ion and the ligand environment composed of Bphen and 1,3-diketonate ligands with different fluorination degrees. Increasing the fluorination degree in the 1,3-diketonate ligands provides a means to reduce luminescence quenching via CH oscillations [1 varaksina].

Bonding BPhen and one of the 1,3-diketonate ligands to Eu$^{3+}$ results in ion-centered luminescence of the complexes with complete suppression of the ligand emission providing the evidence for the “antenna” effect. The observed narrow emission bands with the maxima at 583 nm, 588 nm, 615 nm, 655 nm and 680 nm are assigned to $^5D_0\rightarrow^7F_0$, $^5D_0\rightarrow^7F_1$, $^5D_0\rightarrow^7F_2$, $^3D_0\rightarrow^7F_3$, $^3D_0\rightarrow^7F_4$ transitions in Eu$^{3+}$.

The rate of $^5D_0\rightarrow^7F_1$ magnetic dipole transition in Eu$^{3+}$ corresponding to a wavelength of 590 nm does not depend on the electric field induced by the ligand environment. Therefore, it is possible to evaluate the internal quantum yield from the normalized emission spectra with the intensities of the respective spectral bands divided by the intensity of the magnetic transition [1, 2, 3]. Increasing the fluorination degree in the investigated complexes leads to a successive increase in the internal quantum yield from 27% to 56%. Saturation of the internal quantum yield is demonstrated for highly fluorinated complexes. It indicates that further increase in the fluorination degree is unlikely to improve the quantum efficiency.

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Fig. 1. Photoluminescence spectra for solid-state samples of neat BPhen (1), one of 1,3-diketonate ligands (2) and complex (3) of Eu$^{3+}$ ion; samples were excited by 365 nm CW radiation; inset: fine structure of $^5D_0 \rightarrow ^7F_2$ transition band in Eu$^{3+}$.

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References


3. I. V. Taidakov, B. E. Zaitsev, A. N. Lobanov, A. G. Vitukhnovskii, N. P. Datskevich, A. S. Selyukov, Synthesis and luminescent properties of neutral eu(III) and gd(III) complexes with 1-(1,5-dimethyl-1h-pyrazol-4-yl)-4,4,4-triuoro-1,3-butanedione and 4,4,5,5,6,6,6-heptauro-1-(1-methyl-1h-pyrazol-4-yl)-1,3-hexanedione, Russian Journal of Inorganic Chemistry 58 (4) (2013) 411{415. doi:10.1134/s0036023613040190. URL https://doi.org/10.1134/s0036023613040190
Spin colour centres in SiC as a material platform for sensing and information processing at ambient conditions

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Abstract. Atomic-scale colour centres in bulk and nanocrystalline SiC are promising systems for quantum photonics compatible with fiber optics, quantum information processing and sensing at ambient conditions. Colour centres which acts as stable single photon sources in SiC can be key elements for quantum photonics and communications. It has been shown that there are at least two families of colour centres in SiC with $S = 1$ and $S = 3/2$, which have the property of optical alignment of the spin levels even at room temperature and above. The spin state can be initialized, manipulated and readout by means of optically detected magnetic resonance (ODMR), level anticrossing and cross-relaxation. Recently, we observed the effects of “hole burning” in the ODMR spectra, which made it possible to narrow the ODMR line by approximately an order of magnitude, which substantially increases the possibilities of technological applications of spin centres.

The unique quantum properties of the NV centre in diamond [1, 2] have motivated efforts to find defects with similar properties in silicon carbide (SiC), which can extend the functionality of such systems. Atomic-scale colour centres in bulk and nanocrystalline SiC are promising for quantum information processing, photonics compatible with fiber optics and sensing at ambient conditions. Their spin state can be initialized, manipulated and readout by means of optically detected magnetic resonance (ODMR), level anticrossing (LAC), cross-relaxation (CR) and hole-burning radio-frequency spectrum analysis. It has been shown that there are at least two families of colour centres in SiC with $S = 1$ and $S = 3/2$, which have the property of optical alignment of the spin levels and allow a spin manipulation. For the $S = 3/2$ family, the ground state and the excited state were demonstrated to have spin $S = 3/2$ and a population inversion in the ground state can be generated using optical pumping, leading to stimulated microwave emission even at room temperature and above. By controlling the neutron irradiation fluence, the colour centres concentration can be varied over several orders of magnitude down to a single defect level. Furthermore, these atomic-scale spin colour centres can be also attractive for local or environment sensing. Several, separately addressable spin-3/2 centres (spin qudits) have been identified in the same crystal for each polytype (4H-, 6H- and 15R-SiC) which can be used either for magnetic field or temperature sensing. Some of these spin colour centres are characterized by nearly temperature independent zero-field splitting, making these centres very attractive for vector magnetometry. Contrarily, the zero-field splitting of the centres in the excited state exhibits a giant thermal shift, which can be used for thermometry applications. Finally coherent manipulation of spin states has been performed at room temperature and even at temperatures higher than room temperature by hundreds of

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degrees. SiC is taking on a new role as a flexible and practical platform for harnessing the new quantum technologies, it is a technologically friendly material, used in various devices (LED, MOSFETS, MEMS). Fabricating various types of microstructures and nanostructures in SiC, including SiC grating structures with colour centres, has increasingly attracted owing to their potential applications in electronic and photonic devices.

Here, we apply a two-frequency to excite and image multiple qudit modes in a SiC spin ensemble under ambient conditions. Strikingly, their spectral width is about one order of magnitude narrower than the inhomogeneous broadening of the corresponding spin resonance.

Figure 1 (a) show familie of spin colour centres in 4H-SiC, 6H-SiC and 15R-SiC with unique mechanism of an optical alignment of the spin sublevels. Each spin colour centres of the is divided into several possible configurations, as there are different lattice positions in the crystal. Family of the centres, labeled as a V1, V2, V3 and V4 is a negatively charged silicon vacancy VSi− in the paramagnetic state that is noncovalently bonded to the neutral carbon vacancy VC0 in the nonparamagnetic state, located on the adjacent site along the SiC symmetry c axis having quadruplet ground and excited states (S=3/2). We apply a two-frequency to excite and image multiple qudit modes in a SiC spin ensemble under ambient conditions. Strikingly, their spectral width is about one order of magnitude narrower than the inhomogeneous broadening of the corresponding spin resonance.

We have presented a review of optical and spin properties of colour centres in different polytypes of SiC, which were studied two-radiofrequency hole-burning spectrum analysis. This study will allow SiC is taking on a new role as a flexible and practical platform for harnessing the new quantum technologies.

References

Low-temperature ultrafast optical dephasing in the ensemble of semiconductor quantum dots

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Abstract. We obtained ultrafast (with characteristic times about picoseconds) optical dephasing in an ensemble of double-coated colloidal quantum dots at cryogenic temperatures. The possible mechanisms which may lead to such a dephasing are discussed.

Recently semiconductor nanocrystals or quantum dots (QDs) have become widely used in various scientific and technological applications. Due to their unique photo-physical properties, namely, a narrow symmetric fluorescence spectrum, depending on the size of the QD, a wide absorption band, high photostability, and a high quantum yield. The coating of QD’s improves quantum yield by passivation of nonradiative recombination sites, and also makes them more resistant to oxidation [1]. Quantum dots are especially important for optical applications due to their bright, clear colors, as well as their ability to radiate a rainbow of colors in combination with their high efficiency, longer lifetime and a high extinction coefficient. Examples include LEDs and solid-state lighting, displays and photovoltaic cells [2].

We studied double-coated colloidal CdSe/CdS/ZnS (QD-Light, Russia) QDs. Samples with a thin film prepared from QDs solution should have a high optical density and a sufficient concentration for detection of photon echo signals. To obtain a high optical density, we have developed a method for preparing thin films from colloidal solution of QDs in toluene [3].

Photon echo (PE) is widely used to study ultrafast dynamics in different media, including solid-state structures, liquids and gases. A large number of works devoted to the using of photon echo technique to study disordered structures: polymers, glasses and molecular crystals (see, e.g. [4] and references therein). In recent years, there is a considerable interest to study semiconductor quantum dots and their ensembles [5] by means of PE. The PE-measurements were performed using the home-build incoherent photon echo spectrometer based on a resonator-less super-luminescence dye-source (see, e.g. [4] for detailed description).

PE decay curves (dependence of PE signal intensity on the delay time $\tau$ between 1st and 2nd pulses) were measured by controlled moving of reflecting prism along mechanical delay line. The typical 2-pulse PE (2PE) decay curve consists of sharp intensive peak in the region of zero delays and tail. In order to find the optical dephasing time $T_2$ we fit this tail with the standard expression: $I_{2PE} = I_0 + C \exp(-4\tau / T_2)$, where $I_0$, $C$ and $T_2$ are fitting parameters. By changing the temperature in range from 50K to 4.5K with accuracy of 0.1K, different PE decay curves were obtained (Fig 1.).

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Fig. 1. PE decay curves measured in ensemble of 3-7 nm CdSe/CdS/ZnS at cryogenic temperatures (4.5 – 10K).

The ultrafast times of optical dephasing can be explained by the following models: blinking [6] – phase loss due to fast relaxation of the electron-hole pair into a long-lived trap state (defects at the boundary of two interfaces), which leads to lifetime broadening [7]; the interaction of electron-hole pairs with low-frequency acoustic phonons; dispersion by the size of quantum dots in a sample.

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References

1. A.M. Smith, S. Nie, Nature Biotechnology 27, 8 (2009)
2. A.D. Yoffe, Advances in Physics 50, 1 (2001)
Slow drift compensation in long-term measurements in fluorescence nanoscopy with blinking colloidal semiconductor quantum dots

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Abstract. In this work we present an approach for image processing accuracy increasing in fluorescence nanoscopy of single colloidal quantum dots with blinking fluorescent behavior. The approach is based on the estimation of parameters, describing the slow collective drift, according to the information about a long series of frames with fluorescent images of single blinking quantum dots. The results of collective drift compensation for single colloidal quantum dots CdSe / ZnS super-resolution image are demonstrated.

The presence of a slow drift - spatial image shift in time - is one of the serious problems of various microscopic techniques: probe microscopy, luminescent nanoscopy, etc. The characteristic values of the shifts can vary from tens to several hundred or more nanometers per hour. The potential reasons are instabilities in the sample positioning system, slow changes in the spatial position of the optical elements in the recording system associated with mechanical and temperature instabilities. As a result, the super-resolution images of particles are "blurred", which leads to a decrease in the accuracy of the estimation of their parameters. In this paper, we propose an approach that reduces the effects of slow drift in long-term measurements in experiments on luminescent nanoscale with single flickering quantum dots. The approach is based on estimating the parameters of a function describing the collective drift and sub-pixel shift compensating in each CCD-camera frame in image post-processing.

In present time there exist a few approaches to compensate nanodrifts: by measuring the interframe shift based on calculating the cross-correlation function between frames [1], by using the special embedded markers [2], etc. In this paper, we propose an approach based on the use of information on the subdi-fractional coordinates of flickering quantum dots recorded in a sufficiently long series of frames (from several hundred to several thousand frames) that does not require special markers. This approach makes it possible to obtain drift-corrected superresolution images of single quantum dots without additional markers. To do this, information about the coordinates of all the QDs found in the series of frames under study is grouped into a common data array by subtracting the mathematical expectation of the coordinates of the QDs within the track from the coordinates of each QD. The set of points thus obtained is approximated by a polynomial of a given degree. The obtained functional dependence will characterize the law of global drift of all marks.

To show the possibilities of suggested approach we use the experimental data on fluorescence images of single colloidal QDs CdSe/ZnS (with diameter of emitting core ~4 nm) kindly provided by the Single-molecule research team from the Institute for Spectroscopy of the Russian Academy of Sciences [3-5]. The fluorescence of single QD were excited by CW laser (Coherent Verdi V6) on the wavelength 532 nm with excitation intensity ~100 W/cm². The fluorescence images were detected by emCCD camera (Luca Andor) with exposure time 100 ms per frame.

Figure 1 demonstrates the dependence of the change in the subdiffractional coordinate Y for several single QDs and corresponding functions which describe observed global drifts for the coordinates X (red line) and Y (green line).
Fig. 1. Dependence of the change in the subdi-coordinate Y for several quantum dots (a). The result of calculating the global drift for the coordinates X (red graph) and Y (blue graph) (b). The abscissa is the frame number.

The Figure 2 (a) shows an example of the “superresolution” image of single QD subjected to the slow drift. This superresolution image is constructed from restored (from each CCD-frame) QD coordinates as 2D-histogram of coordinates distribution. The significant drift along the Y coordinate is clearly observed. The “superresolution” image is elongated along the drift direction.

Fig. 2. Fragment of the histogram of the distribution of the single colloidal CdSe/ZnS QD coordinates, as restored from 5000 CCD-frames without (a) and with (b) compensation of the global drift.

Figure 2b shows the image obtained for the same series of frames, after compensation for global drift. The density of the restored coordinates is a symmetrical figure, i.e., a circle of the radius equal to the accuracy of coordinates determination in a single measurement. Thus in this paper we show that slow drifts can be compensated by extended measurements and correct polynomial analysis.

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References

Light shift of the Ramsey resonance of coherent population trapping in optically dense medium

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Abstract. In this work we calculate the Ramsey resonances of coherent population trapping effect in cold atomic ensembles. The main goal is to investigate the light shift of the resonance on the different parameters in optically dense medium, because such medium can to distort and absorb the interrogating laser pulses.

Coherent population trapping (CPT) effect [1,2] allows us to detect the microwave transitions in atomic ensembles only by radiation of optical range. The two-frequency laser radiation interacts in simply case with the three-level $\Lambda$-system and induces the microwave atomic coherence. Atoms cease to scatter the light and the transparency window appears. Due to the fact that the microwave atomic coherence is long lived, the width of the transparency window is small compared with natural line width. It makes it possible to use this effect in wide range of practical applications such as quantum frequency standards [3], magnetometers [4], recording and processing of quantum information [5].

One of the ways to improve the accuracy of the metrological devices is to reduce the width of the reference resonance. Detection of the CPT resonance by the Ramsey method [6] allows us to further narrow the resonance line. The idea of this method consists of interrogation the atoms by the radiation not continuously, but in discrete periods. It can be done both by spatial separation of the interaction regions [7,8] and by using pulsed radiation [9-12]. The Ramsey method using pulsed radiation has been actively researched in the last years. One of the main problems affecting the accuracy of the atomic clock is the light shift of the reference resonance. At present, a new direction of research is the search for ways to suppress the light shifts of CPT-resonance when using the Ramsey method by varying of the shapes of the pulses, their phases and amplitudes – the so-called generalized auto-balanced Ramsey spectroscopy [13]. The work [14] uses a two-stage pulse shape to simultaneously suppress light shifts and improve the signal-to-noise ratio. In [15] the density matrix formalism is constructed for atoms in an arbitrary periodic field.

Despite the large number of modern works on the investigation of Ramsey detection method, there remain some open questions related to the influence of an optical density [16] of the medium at the Ramsey signal. The optically dense medium is the atomic medium where the mean free path of the quasiresonant photon is much smaller than the size of the medium. In such medium the laser radiation can be absorbed significantly, the form of the interrogation laser pulses can be distorted and different modes are absorbed in different ways. This can drastically affect the total light shift of the CPT resonance, which is not taken into account in modern theoretical works in this direction. Moreover, the effects of dense medium can suggest new ways of suppressing the light shift of the Ramsey signal. The radiation modes can be equalized in intensity due to a different absorption coefficient, which will result in an auto-balancing effect. Such effect has already been observed by us in the excitation of the CPT resonance by continuous radiation [17].

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In this work we investigate the influence of the optically dense medium on the light shift of the Ramsey resonance of coherent population trapping in cold atomic ensembles. The dependencies of the light shift on the intensity of radiation, durations of the laser pulses and dark pause, dipole moments of the atomic transitions, length of the medium and atomic concentration have been found.

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References

8. I. M. Sokolov, Quantum Electronics, 45, 947 (2015)
Au/Ag-containing DNA-based nanowires

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Abstract. Direct conductivity measurements of thin uniform gold-coated DNA nanowires conductivity are presented. Gold-coated DNA conductive wires deposited on a mica surface are visualized by SEM and conductivity of the wires are measured using nanomanipulators built inside the microscope. The measurements show that the conductivity is limited by defects, and the thicker the coating the higher the conductivity of the wires. These gold-coated DNA nanowires are promising candidates for molecular electronics. DNA-base nanomaterial to be used in new to explore DNA-based molecular electronics.

1 Introduction

DNA is considered to be one of the the most promising candidates for future molecular electronics. Several types of DNA-based metalized nanowires have been recently reported. Among them are: new metalized form of DNA, E-DNA \cite{1} and thin gold nanoparticles-coated DNA wires \cite{2}. In this work we present direct conductivity measurements of such gold-coated DNA wires.

2 Materials and Methods

The suspension of gold seeds (diameter of about 1.5 nm) was poured on a mica substrate with deposited DNA and left on the surface for 4 h. The surface was then washed with ultrapure distilled water and dried by a nitrogen flow. The mica surface was subsequently flowed with a freshly premixed enhancement solutions of ascorbic acid. The ascorbic acid and the gold solutions were inserted into a mixing chamber by two peristaltic pumps, such that the mixture flushed the surface \(\approx\)1 s after the mixing. Treatment of the surface with the mixture was conducted for 10 s. The surface was then rinsed with water and dried with nitrogen gas \cite{2}.

This samples were visualized by Zeiss Merlin with GEMINI II Electron Optics SEM. The measurements of gold-coated DNA wires conductivity were performed with Kleindiek nanotechnik MM3A-EM micromanipulators mounted on an SEM adaptor plate inside the SEM vacuum camera and Keithley 2636A System SourceMeter (see Fig. 1).
Fig. 1. Measurements of VAC of gold-coated DNA wires inside the Zeiss Merlin SEM.

3 Results and Conclusion

The thin gold-coated DNA wires display long-range conductivity. Our measurements show that the conductivity is limited by defects. Moreover, the thicker the gold coating the less the number of defects and the longer the conduction distance of the wire. The preparation method enables the formation of molecular wires with dimensions and uniformity that are suitable for molecular electronics.

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References

Investigation of optical properties in ultrasmall nanodiamonds carrying SiV centers

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Abstract. Here, we experimentally investigate optical properties of SiV centers in artificial ultrasmall nanodiamonds with sizes lower than 10 nm.

Single photon sources are of great interest for various application in quantum information, in particular quantum cryptography. Also, color centers in diamond attract a lot of attention due to possibility to generate single photons at room temperature, low spread in spectral characteristics and access to electron spin[1]. Besides single photon applications ultra-small nanodiamonds, containing color centers are of great interest for bioimaging[2] and biosensing[3].

Recently, SiV centers were suggested as an alternative to NV centers due to their strong zero-phonon line (ZPL), containing about 70% of emission and narrow, with width of 5 nm at room temperature[4]. Another advantage of SiV centers is their emission at 738 nm in a spectral region where the background fluorescence of the surrounding material is weak.

In this work, we report on high pressure high temperature (HPHT) synthesis of nanodiamonds with sizes lower than 10 nm (see Fig. 1(a)) containing optically active single SiV color centers (see Fig. 1(b)). The HPHT synthesis was realized in metal-free grown system based on mixtures of hydrocarbon and silicon-organic compounds. The high quality nanodiamonds display intense narrowband (4.6 nm, see Fig. 1(c)) emission of SiV defects centered at 738 nm with spread about 1 nm. This ultra-small low-strain artificially produced diamonds have substantial potential for quantum information processing and biomedical applications.

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References

Upconversion nanoparticles with anti-Stokes luminescence as bioimaging agents

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Abstract. Lanthanide-based upconversion nanoparticles attract great attention in theranostics due to their unique physicochemical and optical properties. It is innovative platform possessing peculiar properties for luminescent imaging, temperature mapping, sensing, and therapy. In present work we demonstrate advantages of new luminescent agents based on upconversion nanoparticles and hydrophylic biocompatible polymer.

1 Introduction

Theranostics is a new interdisciplinary research area, which is an integration of therapy and diagnostics [1]. Upconversion nanoparticles (UCNPs) are promising nanoplatform for theranostics.[2] Lanthanide-based UCNPs are composed of inorganic crystalline ceramic host matrix, co-doped with pairs of different trivalent lanthanide ions (Ln3+), usually the Yb3+, Er3+ or Tm3+. Its distinctive feature is the ability to convert near-infrared (NIR) light into higher energy visible or ultraviolet (UV) light [3]. UCNPs have been successfully used for in vivo bioimaging due to the low biotissue autofluorescence. The most common mechanism for passive nanoparticle delivery into solid tumors is the enhanced permeability and retention effect (EPR) allowing UCNPs to preferentially diffuse and accumulate in tumor tissues [4]. The efficiency of the EPR-effect in UCNP delivery into the tumor is associated with the circulation half-lifetime in blood.

In present work we developed nanocomplexes with prolonged circulation time in the blood at intravenous injection by UCNP surface modification with colominic acid (CA). CA is endogenous non-immunogenic, biodegradable, non-toxic compound with low serum protein adsorption [5]. These properties determine the prospects of using for solid tumour visualization in vivo. We studied chemical and photophysical properties of CA-modified UCNP agents and demonstrated its effective accumulation in tumour due to prolonged blood circulation time for 3 hours in comparison with UCNPs-polyethylene glycol complexes.

2 Results

Nanoparticles are synthesized in organic solvent that determines their hydrophobic surface properties. The development of hydrophilization methods for obtaining hydrophilic UCNP probes, which can be homogeneously dispersed in an aqueous medium, biocompatible and colloidal stable in a biological environment is crucial. Firstly, we hydrophilized UCNPs through coating nanoparticles with polyethyleneimine (PEI) having NH2 groups, without

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removing the oleic acid from the UCNP surface. Then, we modified the surface in two different ways: 1) by forming a covalent bond between the PEI and the CA using the carbodiimide activation method (CA-CDI); 2) by adsorption of the CA on the UCNP surface due to electrostatic interactions (CA(+/-)). The obtained samples are hydrophilic retaining their colloidal stability in PBS, pH=7.2 for 1 month. IR spectroscopy successfully confirmed the modification.

The minimal adsorption of blood proteins on the particles provided the prolonged particle circulation time in blood and effective accumulation in the tumor. Our study showed that after incubation CA-modified UCNPs with mouse serum at T=37°C for 1 hour the probes practically did not adsorb the serum proteins as compared to UCNPs/PEI. These data were obtained by detection the protein concentration in the supernatants using the Bradford method. Thus, CA-modified UCNPs have potential to prolonged circulation in the body.

The UCNP accumulation in cells was studied by flow cytometry on the cell lines of murine macrophages RAW 264.7 and human monocytes THP-1. The cell suspension (106 cells per ml) was incubated with 0.1 mg/ml modified UCNPs for 30 min in a CO2 incubator (37 C, 5% CO2). UCNPs covered with CA-CDI showed a higher level of accumulation in the cells than CA(+/-). It is worth noting that the level of CA(+/-)-UCNP accumulation was comparable to the accumulation of PEG-modified UCNPs.

We studied in vivo circulation time in blood after intravenously injection in mice Balb/c and collected blood samples from the tail vein at several time intervals. The samples were analyzed using home built anti-Stokes fluorescent microscope [6]. Images from four random areas were taken and calculation of UCNP number in all areas was made.

CA coating of UCNPs made it possible to reduce the UCNP interaction with serum proteins, leading to longer circulation in the bloodstream of small animals (up to 3 hours) as compared to UCNPs, modified with PEG, which are in the bloodstream no longer than 1 hour.

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References

Two decades have passed since the first observation of long-term fluorescence intensity fluctuations (blinking) of single colloidal CdSe quantum dots (QDs) with a ZnS shell [1]. In further experimental studies it was found (see [2-4]) that these fluctuations have a wide spectrum of characteristic timescales, from hundreds of microseconds to hours.

Another interesting phenomenon manifested in the emission of single quantum dots is spectral diffusion showing the characteristic time scales in order of hundreds of seconds [5-6]. It is not surprising that there are a number of models connecting the fluctuations of the emission intensity with the slow motion of the exciton energy. The first model of that kind suggested by Shimizu et al. [7] is based on the Efros/Rosen charging mechanism [8]. More advanced version of this idea was suggested by Tang and Marcus [9-10] as the diffusion-controlled electron transfer model (DCET). In 2014 Zhu and Marcus [11] presented an extension of the DCET model by introduction of an additional biexciton charging channel. Simultaneously with the Tang and Marcus, the model based on the alternative fluctuating rate mechanism of blinking was suggested by Frantsuzov and Marcus [12]. The mechanism assumes that the variations of the non-radiative exciton recombination rate $k_n$ generate fluctuations of the emission intensity on a long time scale. The Frantsuzov and Marcus model connects the recombination rate with the fluctuating energy difference between 1S and 1P states.

The predictions of the DCET model [9-10], the Expend DCET model [11], and the Frantsuzov and Marcus model [12] were compared by the analytical analysis and numerical simulations. It was found that the DCET model [9-10] predicts the appearance of extremely long ON and OFF time periods in a single QD emission trace. As seen on Fig. 1 such a period could last years, which is much longer than the duration of a typical experiment. Thus the QD can become permanently bright or permanently dark after about a hundred blinking cycles with a high probability. The presence of a second ionization channel in the Extended DCET [11] model resolves the problem with very long ON times, but not with the very long OFF times. As a result, the most of the QD has to become permanently dark in this model as confirmed by numerical simulations. These predictions significantly differ from the experimentally observed behaviour of single quantum dots. On the contrary, the predictions of the model of Frantsuzov and Marcus [12] correspond to the basic properties of the quantum dots blinking obtained in experiment, such as a nearly continuous set of emission intensities, the power-law form of the ON-time and OFF-time distributions obtained by the threshold procedure, and a change in behaviour the of the emission intensity power spectral density on millisecond time scales.
Fig. 1. The ON time distribution function within the DCET model (thick black line), the first interval power law (blue dashed line), the second interval power law (blue dashed-dotted line), the Tang-Marcus approximation (thin black line) and the long-time exponential asymptotic (red line).

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References

The study of a new family of phase masks for three-dimensional fluorescence nanoscopy

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Abstract. The question of the axial coordinate determination accuracy is quite sophisticated in far field 3D fluorescence nanoscopy. The accuracy of a point emitter axial coordinate reconstruction depends among other things on the conversion efficiency of the phase mask and the microscope objective instrumental function. It was found that the instrumental functions of different microscope objectives differ significantly from each other, most have a strongly non-uniform spatial distribution of the radiation intensity in a parallel beam created by an objective focused on a point emitter. It was shown that taking into account the actual microscope objective instrumental function when calculating the phase masks allows to increase significantly the axial coordinate reconstruction accuracy.

Fluorescence microscopy with ultra-high spatial resolution (far field fluorescence nanoscopy, FFN) is currently one of the most effective and in-demand tools for research in the fields of biological and medical physics, biology, and chemical physics. It is also of interest for applications in solid state physics. Many of these far field fluorescence nanoscopy techniques (STORM, PALM, etc.) are based on the possibility of fluorescence imaging of single point-like emitting labels with nanoscale reconstruction of their lateral spatial coordinates, and subsequent computer rendering of object nanostructure by mapping plenty single labels positions (see [1,2] and references therein). Application of the technique based on the theory of spiral beam optics allows to reconstruct all three spatial coordinates of a single point emitter with nanometer accuracy. In this technique the spatial phase modulation of the light beam is used for the transformation of the single emitter point spread function into double helix point spread function [3].

The accuracy of a point emitter axial coordinate reconstruction depends on a variety of experiment parameters: the number of recorded photons, the conversion efficiency of a phase mask, the microscope objective instrumental function, and the characteristics of the optical scheme used in the registration channel.

FFN methods can be especially informative if fluorescent single molecules (SM) of organic dyes are used as emitting point light sources at cryogenic temperatures, when zero-phonon lines (ZPL) which correspond to purely electronic transitions in SMs are reachable for the observation. First, the analysis of ZPL of single molecules makes it possible to study the dynamic processes in impurity solid media, since the ZPL parameters are sensitive to the SM local environment characteristics. Second, the very large ratio of inhomogeneous absorption bandwidth to the very narrow ZPL homogeneous spectral width gives the opportunity to measure the fluorescence excitation spectra and coordinates for a huge number (up to all)
efficiently fluorescing SMs in doped bulk solid samples - crystals, glasses, polymers (see [1,2] and references therein).

To perform measurements at cryogenic temperatures, it is necessary to use special micro-objectives designed for the operation at liquid-helium temperature, including in superfluid helium. In the case of an ideal microscope objective the propagation of light from a single point emitter located in a focal plane will be described after the objective by a plane wave with a Gaussian spatial intensity profile. However, in reality there are a variety of aberrations that degrade the picture. Manufacturers of the microscope objectives try to compensate for certain aberrations, depending on the tasks for which an objective is calculated. As a result, in most cases the spatial distribution of the radiation intensity in a parallel beam created by an objective focused on a point emitter, - the microscope objective instrumental function, - is significantly different from the ideal one. In particular, it is peculiar to micro-objectives designed to operate at cryogenic temperatures.

In the case of such micro-objectives the use of phase masks calculated for the spatial distribution of the radiation intensity with a flat (or Gaussian) profile gives a low efficiency of conversion of the microscope objective instrumental function to the two-lobe function. In this connection the actual task is the calculation of new effective phase masks taking into account the shape of the microscope objective instrumental function.

In the present work with the use of single-crystal semiconductor colloidal quantum dots (QDs) as point emitters of radiation the instrumental functions of a number of micro-objectives were measured and analysed. It was found that the instrumental functions of different micro-objectives differ significantly from each other, most have a strongly non-uniform spatial distribution of the radiation intensity in a parallel beam. With the use of an objective with the radiation intensity spatial distribution profile closest to a flat one, for a number of original calculated phase masks [4] the efficiency of the microscope objective instrumental function to the two-lobe function conversion was estimated. It was found that taking into account the actual microscope objective instrumental function when calculating the phase masks allows to increase significantly the conversion efficiency.

It was also shown that during the calculation of the optimal phase mask, it is necessary to take into account the actual diameter of the light beam and the pixel size of the phase modulator. Calibration curves – the correspondence between the two-lobe function rotation angle and the position of the radiating QD along the optical axis (axial coordinate) - were measured for a number of phase masks using specially developed technique. In addition, the question of the accuracy of the QD axial coordinate reconstruction was experimentally investigated.

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References

Fluorescence lifetime imaging microscopy in the frequency domain (FD-FLIM): Study of self-assembled nano-fibers

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Abstract. A custom-built fluorescence lifetime imaging microscope operating in the frequency domain (FD-FLIM) was used for mapping the fluorescence lifetimes of different samples containing self-assembled nanofibers. Two materials were investigated, the conjugated polymer poly-(3-hexylthiophene) (P3HT) and a carbonyl-bridged triarylamine derivative. Excitation was performed with a diode laser (λ = 488 nm) amplitude-modulated at frequencies between 104 and 160 MHz. The measured lifetimes in the P3HT samples are distinctly below 100 ps with the longest values found in the vicinity of needle-shaped crystals which were added as a nucleating agent. This result is ascribed to higher order of the H-aggregated P3HT nanofibers close to the crystals.

1 Materials

Poly-(3-hexylthiophene) (P3HT) is a polymer with a conjugated π electron system along its backbone. It has semiconducting properties and is a benchmark system for applications in organic photovoltaics. Its electronic properties depend strongly on the microscopic order of the polymer chains [1]. The formation of highly ordered nano-fibers of P3HT can be induced by addition of a small amount of needle-shaped crystals with lengths of a few hundred micrometers, which act as nucleation sources. P3HT has an absorption band in the blue-green part of the spectrum and emits red-shifted photoluminescence.

A second material which was investigated is a carbonyl-bridged triarylamine derivative (S-CBT) with a flat molecular core [2]. The disk-like S-CBT molecules self-assemble into long nano-fibers driven by van-der-Waals interactions between the π electron systems and by intermolecular hydrogen bonds [2, 3]. By self-assembly, these nano-fibers can form bundles of varying diameter which also emit phosphorescence.

2 Experimental method and data analysis

Spatial mapping of fluorescence lifetimes was performed with a custom-built fluorescence lifetime imaging microscope operating in the frequency domain (FD-FLIM). The excitation source was a diode laser at 488 nm wavelength which was amplitude-modulated at frequencies between 104 and 160 MHz. The rf signal was provided by a computer-controlled precision direct digital synthesizer (DDS). Signal processing and demodulation was performed with standard rf electronics. Excited-state lifetimes were calculated from the modulation amplitude

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of the fluorescence and its phase shift with respect to the excitation light [4]. All experiments were conducted at room temperature.

For data evaluation and visualization, the polar-plot (also Cole-Cole plot or phasor) representation was used. It consists in plotting the quadrature-phase versus the in-phase component of the modulated fluorescence signal for each spatial data point. In case of single-exponential decay, the data points lie on a characteristic semi-circle with radius 0.5 around the position (0.5, 0); for more complicated relaxation behavior, the data points are located inside this semi-circle [5].

3 Results

Figure 1 shows the fluorescence intensity (left) and the modulation (middle) and phase lifetimes (right) in a sample of P3HT with several needle-shaped nucleating agents present. The lifetimes are distinctly longer in the vicinity of the needles, which is ascribed to higher order of the H-aggregated P3HT nano-fibers forming around the needles. The lifetimes calculated from the modulation amplitude and phase shift are different, which indicates that the excited state does not decay single-exponentially. This is corroborated by the polar-plot analysis. The data show that spatial variations of fluorescence lifetimes can be mapped even for lifetimes well below 1 ns. The absolute values of the lifetimes have large error margins, however; an accurate measurement would require higher modulation frequencies.

**Fig. 1.** Fluorescence intensity (left) and fluorescence lifetimes as calculated from the modulation amplitude (middle) and phase shift (right) in a sample of P3HT nano-fibers.

References

Low-Temperature Dynamics in a Dye-Doped Polymer: Correspondence between the Data Obtained by Photon Echo and Single Molecule Spectroscopy

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Abstract. The tunneling and vibrational relaxation processes in doped polyisobutylene film has been reinvestigated using incoherent photon echo (IPE) and compared with single-molecule spectroscopy (SMS) data. It has been shown that at T = 4.5 – 20 K the IPE gives optical dephasing times which correspond to the narrowest electronic spectra of single dye molecules. From this analysis we can conclude that the former contradiction between IPE and SMS data has been resolved.

Combined photon echo (PE) and single-molecule spectroscopy (SMS) technique is a very powerful tool for detailed study of low-temperature dynamics in dye-doped disordered polymers and glasses. However this type of studies reveal discrepancies when comparing dephasing time T\(_2\) and single-molecule (SM) zero-phonon spectral lines (ZPL) width obtained from PE and SMS, correspondingly. For tetra-tert-butylterrylene (TBT) PE-experiments obtained T\(_2\)-times much shorter than it is sufficient to cause the corresponding ZPL broadening in the temperature range of a few – dozen of Kelvins \([1, 2]\). We experimentally solve this problem and show that at T = 4.5 – 20 K the incoherent PE (IPE) technique gives T\(_2\)-times which correspond the narrowest SM ZPL \([3]\).

The PE-measurements were performed using the home-build IPE spectrometer that was constructed originally in the mid of 1990ies \([1, 4]\), and recently reconstructed to achieve modern experimental possibilities \([3, 5]\). We used a thin (0.5 mm) film of PIB with TBT molecules. PIB (M\(_w\) = 4.2 \times 10^6 g mol\(^{-1}\), Sigma Aldrich) was dissolved in spectrally pure toluene (Sigma Aldrich) together with TBT. The sample was prepared by disposing of the solution between two glass slides and further pumping for toluene removal.

We measured 2-pulse IPE (2IPE) decay curves at different cryogenic temperature, and obtained the temperature dependence of the inverse optical dephasing time 1/\(\pi T_2\). This dependence is shown in Figure 1 (large solid circles) together with previous 2IPE-data as measured originally in \([6]\) (solid squares); T-dependences of ZPL for several single TBT molecules in PIB (small colour dots), as measured in \([7]\); and T-dependence of average spectral ZPL widths for a number of TBT SM in PIB (black stars) as measured in \([8]\).

In both experiments \([7, 8]\) the fluorescence excitation spectra of single TBT molecules in thin (0.5 – 1 µm) PIB film were measured by tuning of frequency of narrowband (1 – 2 MHz) dye CW-laser and detection of Stokes-shifted luminescence. In Ref. \([7]\) the confocal scheme together with avalanche photodiode (time of measurement for one spectrum was \(t_m\approx250\) s), whereas in Ref. \([8]\) the wide-field luminescence microscope was used with detection by EM CCD camera (\(t_m\approx10\) s).

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While the effective $t_m$ for 2IPE ($\sim 10$ ns) is much less than the effective $t_m$ in SMS-measurements ($\sim 250$ s), the average value of $1/\pi T_2$ should be in the region of narrowest SM ZPL widths. It is exactly what was observed in the comparative SMS/PE-studies at $T=2$ K [7]. At higher temperatures (4–20 K) the ZPL broadening (as well as optical dephasing) is mainly caused by electron-phonon coupling, although the spectral diffusion processes are also intensified with $T$. Again, the value of $1/\pi T_2$ should be in the region of the narrowest ZPL widths. However, this was not observed in previous studies [1, 6, 7] for a broad range of temperatures. If we compare previous PE data with SM and average SM ZPL widths, we see that $1/\pi T_2$ comparable or even larger than average SM ZPL widths, that has not reasonable explanation.

In the present work we have carefully re-measured dephasing times for TBT in PIB at $T=4.5–15$ K. The high sensitivity of the updated IPE-setup allows careful measurement of power dependences, thus any saturation and light induced effects were eliminated. As one can see from the Figure the new 2IPE data are in reasonable agreement with theoretical considerations. The $1/\pi T_2$ values correspond to the narrow ZPLs.

As possible explanations for the question why the previous PE-data did not agree with SMS, we can suggest the following two: (1) The additional contributions into the effective dephasing processes were observed to be due to high laser excitation power. Now the modern detectors, adjustment optical scheme gives opportunity to diminish the laser pulse energy enough to obtain unsaturated values of $1/\pi T_2$. (2) Second possible reason is difference of molecular weight of PIB used in PE- and SMS-data. As it is known now [9] when diminish the $M_w$, additional spectral diffusion processes are strongly activated. As in-information about molecular weight of PIB is absent in first original PE researches, one can assume, that it was PIB with lower $M_w$ in comparison with SMS-experiments, that leads to larger values of $1/\pi T_2$ measured by IPE. In this case the main role plays the spectral diffusion processes in nanosecond time scale.

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References
Superconducting Single-Photon Detector for Integrated Waveguide Spectrometer

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Abstract. We present our recent achievements in the development of an on-chip spectrometer consisting of arrayed waveguide grating made of Si\textsubscript{3}N\textsubscript{4} waveguides and NbN superconducting single-photon detector.

Superconducting single-photon detectors (SSPD) \cite{1} became recently a device of choice in many applications ranging from quantum dots characterization to quantum cryptography \cite{2} and long distance space communication \cite{3}. The key factor of their success is superior performance: above 90\% detection efficiency \cite{4}, very low dark count rate \cite{5}, picosecond timing jitter \cite{6} and high photon count rate. The superb performance makes SSPD especially attractive for advanced applications in quantum optics.

At the same time, there is a long-term trend in practical quantum optics to switch to optical integrated circuits on a single chip in which the light is delivered from the source to the detector by the dielectric waveguides. The waveguide were realized by means of several materials platforms, such as silicon on insulator (SOI) \cite{7,8}, gallium arsenide (GaAs) \cite{9,10}, silicon nitride (Si\textsubscript{3}N\textsubscript{4}) \cite{11-14} and polycrystalline diamond \cite{15-17}.

In \cite{7} integration of SSPD with dielectric optical waveguides was demonstrated featuring near unity absorption for the wave travelling in the waveguide. At the same time, due to shorter nanostrip length compared to the traditional meander-shaped SSPD it features also shorter dead time and thus is capable of higher photon counting rates. Advanced photon detection capabilities offered by SSPD make such integrated circuits feasible for applications in optical signal processing, optical sensing and linear optical quantum computing.

In this paper, we present an approach to the realization of an on-chip spectrometer based arrayed waveguide grating (AWG) multiplexer integrated with SSPD as shown in Fig 1(a). The AWG is patterned from silicon nitride Si\textsubscript{3}N\textsubscript{4} on silicon substrate by e-beam lithography. The input light is split by the AWG in several output channels, each with its own wavelength. The transmission spectrum of the AWG is shown in Fig. 1(b). Each output waveguide is integrated with the SSPD which is a 100-nm-wide U- or W-shaped strip made of superconducting NbN film. The whole device is operated at 1.7 K temperature providing best performance of the SSPD. Fig. 1(c) shows detection efficiency of the SSPD as a function of its bias current normalized to the critical current at which superconducting state is destroyed.

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Fig. 1. (a) Schematics of AWG spectrometer integrated with SSPD; (b) spectral transmission of the AWG in different channels, (c) on-chip detection efficiency and dark counts rate of SSPD as functions of SSPD bias current $I_b$ normalized to its critical current $I_c$.

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References


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Single photon detection in micron scale NbN and α-MoSi superconducting strips

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Abstract. We experimentally demonstrate the single photon detection in straight micrometer-wide NbN and α-MoSi bridges. Width of the bridges is 2 µm, while the wavelength of the photon changes from 408 to 1550 nm and critical current exceeds 50% of the depairing current. Obtained results offer the alternative route for design of detectors without resonator and meander structure and indirectly confirm vortex assisted mechanism of single photon detection.

Until recently the operation of superconducting single photon detectors SSPD [1] was described by the "geometric hot spot model" first presented in Ref. [2] and improved further in subsequent works (a good review is given in Ref. [3]). In the framework of this model it is assumed that the single photon detection occurs only in a superconducting strip with a width comparable to the size of the hot spot, being in the range of 50 to 150 nm. It has led to devices consisting of fairly narrow and very long strips arranged in such a way that they fill a much larger area for good optical coupling. Recently, a more thorough theoretical approach [4] was applied to the problem of photon-detection in a superconductor. It is based on the standard theory of non-equilibrium superconductivity capable of treating processes depending on space and time. It predicts that in samples with a supercurrent up to about 0.7 to 0.8 of the depairing current, and uniform over the cross-section of the strip, the detection efficiency is not dependent on the width of the strip. We have experimentally demonstrated single-photon detection in 5-micron-wide constriction-type bridges made of polycrystalline NbN, using radiation of wavelength ranging from 408 nm to 1550 nm [5].

In this work we obtain the similar results for straight 2-µm-wide and 10-µm-long NbN strips. We measure close to unity internal detection efficiency (Fig. 1) at wavelengths 408 nm and 637 nm in agreement with the theoretical expectations [4]. As an additional check on the generality of this finding we also made wide strips of the amorphous silicide α-MoSi. Unlike polycrystalline films, this amorphous material can be brought more easily in the required regime of a uniform superconducting gap and supercurrent. Additionally, amorphous α-MoSi is claimed to be attractive due to its lower critical temperature T_c compared to NbN which allows to obtain larger hot spot (for the same photon energy and film thickness). Experimentally α-MoSi wide bridge demonstrates IDE close to unity at wavelength up to 1 µm.

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(Fig.1 b). We will present the results of the single-photon detection with the emphasis on the straight strips and compare them with the theoretical predictions.

Fig. 1. Internal detection efficiency (detection efficiency normalized to absorption) and dark counts rate of NbN (a) and MoSi (b) samples.

Table 1. Parameters of the studied samples at the temperature $T = 1.7$K. The thickness of the film $d$ was determined from time of deposition and deposition rate, $w$, width of the bridge, $T_c$ is the critical temperature determined from the midpoint of the resistive transition, $\rho(20K)$ is resistivity at $T=20$ K, $j_c$ is critical current density, $j_{dep}$ is the calculated depairing current density at $T=1.7$ K, using $j_{dep}(0)$ the calculated critical depairing current at $T = 0$ following from Eq.1 and Eq 2 from Ref.[5]

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d$ (nm)</th>
<th>$w$ (µm)</th>
<th>$T_c$ (K)</th>
<th>$\rho(20K)$ (µΩ cm)</th>
<th>$j_c$ (A/cm²)</th>
<th>$j_{dep}$ (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NbN</td>
<td>5.8</td>
<td>2</td>
<td>8.35</td>
<td>396</td>
<td>$5.3*10^6$</td>
<td>$7.8*10^6$</td>
</tr>
<tr>
<td>MoSi</td>
<td>2.8</td>
<td>1</td>
<td>3.1</td>
<td>203</td>
<td>$0.79*10^6$</td>
<td>$1.7*10^6$</td>
</tr>
</tbody>
</table>

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References

Raman spectroscopy of methylammonium lead iodide (MAPI) perovskite

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Abstract. In recent years, there has been an impressive fast technological progress in the development of highly efficient lead halide perovskite solar cells. However, the stability of perovskite films are respective solar cells is still an open point of concern and calls for advanced characterization methods. In this work, we identify appropriate measurements conditions for a meaningful analysis of spin-coated absorber – grade perovskite thin films based on methylammonium (MA) lead iodide (MAPI) by Raman spectroscopy.

As emerging photovoltaic materials, organic–inorganic lead halide perovskites (e.g., CH$_3$NH$_3$PbI$_3$) have attracted much attention since their initial application in dye sensitized solar cells in 2009. The unique merits, including the excellent optical absorption, the long-balanced carrier diffusion length and the low-cost processing methods, have allowed them to be extremely promising for the next-generation photovoltaics. In this work, we identify appropriate measurements conditions for a meaningful analysis of spin-coated absorber – grade perovskite thin films based on methylammonium (MA) lead iodide (MAPI) by Raman spectroscopy. MAPI films were formed on glass substrate through the simple “one-step” deposition process based on the stoichiometric mixture of Pb(Ac)$_2$ and MAI in DMF (sample 1) and from the anhydrous N,N-Dimethylformamide (DMF) (Aldrich) solution containing equimolar mixture of CH$_3$NH$_3$I and PbI$_2$ (sample 2).

The Raman spectra of the CH$_3$NH$_3$PbI$_3$ samples were obtained with LabRAM HR Evolution (Horiba, France). The He-Ne laser (excitation wavelength 633 nm) was used as a source of excitation radiation. The diffraction grating 600 lines/mm provided the 1.5 cm$^{-1}$ spectral resolution. The CCD camera was cooled at 200 K for detecting Stokes-side Raman scattering at a wide spectral range. The precision motorized stage and on-board Olympus BX41 microscope were used for the laser beam focusing on the investigated area. The calibration of the LabRAM HR spectrometer was verified before and after each investigated sample by acquiring Raman spectra of a standard silicon wafer.

The normalized experimental Raman spectra of investigated samples are shown in Fig. 1. The maximum at near 100 cm$^{-1}$ was chosen for normalization, since its peak was found in almost every investigation. The intensity and shape of the Raman spectra for both samples are close.

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Fig. 1. Raman spectra of CH$_3$NH$_3$PbI$_3$ thin films: a – laser power was 0.01 mW, accumulation time was 10 s; b – laser power was 0.5 mW, accumulation time was 0.1 s.

However, the increase of the laser power from 0.01 mW (Fig. 1,a) to 0.5 mW (Fig. 1,b) leads to a changes of Raman spectra. It should be noted, that after excitation of 0.5 mW, significant changes in the surface morphologies of the thin films were observed. In accordance with [1], important markers of the inorganic component have been found at 60 and at 94 cm$^{-1}$, which are mainly associated to the I–Pb–I bending and Pb–I stretching. The region between 100 and 200 cm$^{-1}$ is instead associated to librational motions of the MA cations.

The study was supported by the Russian Science Foundation (project 18-13-00409).

References

Cryogenic and large-base Fabry-Perot cavities for ultra-stable laser systems

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Nowadays most of high-precision spectroscopy experiments are based on lasers with spectral linewidth less than 1 Hz. Best systems now provide fractional frequency instability 4×10⁻¹⁷ on 1-100 seconds averaging time [1]. Such systems are a “hart” of most accurate frequency standards: their frequency is locked to ultra-narrow clock transitions in atomic and ionic ensembles. Stability of optical clock on short averaging times (less than ensemble preparation time) is completely defined by clock laser. On longer times Dick effect, that is determined by level of laser noise, limits stability as well.

Basic technique to obtain ultra-low fractional instability is locking laser frequency to the mode of a passive monolith ultra-stable high-finesse Fabry-Perot cavity. It has to be vibro-isolated and thermostabilized, is usually kept in ultra-high vacuum. Under those conditions fractional instability is fundamentally limited by thermal noise of cavity’s mirrors (i.e. instability of length).

Allan variance of thermal noise—σ_y—can be used to predict best achievable fractional instability of cavity’s eigenmode. In dependency on major parameters it is given as:

σ_y ∝ \sqrt{T × \phi_{coat}}

Here, T—temperature, \phi_{coat}—loss angle of mirror coating, L—cavity length, \lambda—laser wavelength, E—Young’s modulus of mirror’s substrate.

Our main goal is to improve efficiency of ultra-stable laser systems, and, as a result, to provide laser systems with fractional frequency instability about 10⁻¹⁶ on 1 second averaging time. According to equation for σ_y, main ideas to diminish thermal noise influence are: using high-Q materials, low temperatures and enlarging base of reference cavity. In present work we consider four ultra-stable systems.

The idea of lowering temperature with stabilization at the point of zero extension is presented by two cryogenic single-crystal silicon cavities - one with dielectric SiO₂/Ta₂O₅ mirrors (1) and one with crystalline GaAs/AlGaAs mirrors (2). Silicon is a very promising material for upcoming ultra-stable cavities because it has a temperature of zero extension at 124K and has a very low mechanical loss angle. It is also transparent for 1.5 µm wavelength, which is covered by convenient erbium fiber lasers. Accurate calculations, proceeded for silica systems, resulted in following fundamental fractional instability limits: 3×10⁻¹⁶ and 6×10⁻¹⁷ for cavities with dielectric (1) and crystalline mirrors (2) respectively [2]. We have systems (1,2) assembled at this moment. (1) has finesse about 580'000, measured by ring-down method; (3)—about 250'000. Both silica cavities are mounted in UHV cryogenic chambers and stabilized at 124K with precision better than 3 mK. Fractional instability characterization via frequency correlation for two silica cavities will be performed in future.

The idea of enlarging cavity’s base is presented by two large vertical and horizontal (3,4) cavities made of Ultra-low Expansion glass, operating on 698 nm wavelength. These systems are being assembled at this moment. Fundamental frequency instability limit calculations resulted in 7×10⁻¹⁷ for both large systems [2]. Also, vertical and horizontal cavities were

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numerically analyzed with finite element method to find out proper shape and optimal vibration-immune suspension configuration. Was found out that biconical is the best shape for (3): it affords least vibration susceptibility. For system (4) vibration-immune suspension system was developed, where bearings are located at the Airy points. Deformations under the action of horizontal and vertical accelerations were simulated for (3,4) as well.

Presented systems (3,4) will be used as clock lasers in Sr optical lattice clock in VNIIFTRI [3], systems (1,2)— as optical frequency synthesizer stabilizers and for stabilizing long fiber-optic communication lines.

References

Thermally activated luminescence blinking in methylammonium lead iodide nanocrystals

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Abstract. Organo-metal halide perovskites have attracted considerable attention during the last years because of their promising performance as light harvesting materials. However, non-radiative recombination still limits the efficiency of the resulting devices. By investigating the Photoluminescence (PL) flickering or blinking in small perovskite crystallites we resolved the contribution of individual quenchers to the overall non-radiative processes. We also found that the blinking process is thermally activated, which is consistent with ion migration as suggested by previous works. Our findings add to the understanding of blinking behavior and non-radiative processes in MAPbI₃.

Organo-metal halide perovskites have attracted considerable attention during the last years as a promising material for photovoltaic and opto-electronic devices. Remarkably, the efficiency of the perovskite-solar cell climbed from a few percent to 22 % in a few year only. To reach the higher efficiencies, there is a need to better understand the non-radiative processes occurring in the material as they are among the limiting factors to the device efficiencies. These non-radiative processes are due to defects in the material, but the nature of these defects is still poorly understood. If such defects are efficient luminescence quenchers and if they are activated and deactivated on a timescale of milliseconds to seconds, it can result in an easily observable effect: Photoluminescence (PL) flickering or blinking. When the quencher is active, the PL intensity of the crystal will go down while it will return to its initial value if the quencher is inactive. Consequently, one can study the contribution of individual quenchers by studying PL flickering. In practice, it is, of course, far more complicated as it is difficult to control the amount of defects as well as their nature. Fortunately, Perovskites are dynamic materials meaning that the lattice is less rigid than e.g. in III-V semiconductors and different species (e.g.) ions can migrate in the material.[1,2,3] We speculate that ion migration causes activation/deactivation of quenchers on an observable timescale. To avoid having contributions from too many quenchers, one can control the size of the object that is studied. Thus, by studying small crystals (~50nm) of perovskite, we can ensure that only a few (~5) quenchers are present in one entity. In the presented work, we resolved the contribution of individual quenchers to the overall non-radiative processes. Additionally, we investigated the temperature dependence of the activity of the quenchers between 77 and 295 K by studying PL blinking using fluorescence microscopy.

Our results (see Fig.1) show that blinking is temperature activated. Indeed, the relative blinking amplitudes decrease substantially upon cooling. Additionally, the number of blinking

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events also decreases. Remarkably, the behavior is highly reproducible when cooling and heating subsequently the same region of the sample.

Our study provides a link between the microscopic properties of individual quenchers and the PL quantum yield, which is a common observable in many studies. We find that the slope of the temperature dependent PL quantum yield is very sensitive to the diverse properties of individual PL quenchers, which is important to consider when this material is characterized via luminescence studies.

Figure 1: Temperature dependence study of PL flickering. a) Blinking traces of one of the studied crystal at various temperature upon cooling and heating. b) Average PL intensity for all crystal for cooling and heating c) Cumulative distribution function of relative blinking amplitude. d) Number of switches per crystals.

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References

Spontaneous transitions to enhanced fluorescence for GeV centers in a single microcrystalline diamond

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Abstract. We propose a theoretical explanation of spontaneous transitions between dim and bright fluorescence intensity states observed experimentally in a nanocrystal of diamond doped with germanium driven by a continuous wave laser. We use a generalized system of optical Maxwell-Bloch equations derived for an emitter in an ensemble of motionless similar particles embedded in a dielectric medium, which is transparent for the incident light. A numerical analysis of transient regimes and several models of slow damping of the bright luminescence mode are reported.

Spontaneous flickering of the fluorescence intensity was experimentally observed in a nanocrystal of diamond doped with germanium excited by a continuous wave laser light. The fluorescence intensity of the sample switched from bright to dim and vice versa. The effect took place on a time scale of the order of seconds and had a smooth transition dynamic. The phenomenon was strictly threshold in power. These characteristics are not similar to the effect of so-called “blinking” which has an abrupt behaviour. The blinking of a single object is a quantum effect due to the change of nonradiative decay rate which can lead to “switching off” the emitter. It can be assumed that the observed effect is most likely collective rather than individual and is associated with cooperative effects in the ensemble of emitters. It is known that the optical properties of dense atomic ensembles or complex materials can differ greatly from the optical properties exhibited by independent quantum emitters. In this report we propose a theoretical explanation based on the possibility for a cooperative ensemble of emitting centres to show intrinsic cooperative optical multistability. It is shown that the Maxwell-Bloch type equations describing such a system, even in the presence of large values of the phase relaxation rate, retain the possibility of having several stable steady state solutions that form a multistable optical response for certain combinations of the pump power and concentration of the emitters. A numerical analysis has shown that the transition time may exceed the lifetime by an order of magnitude. We report several models of slow damping of the bright fluorescence mode and discuss alternative reasons for such a behaviour.

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Spectral jumps of the single CdSe nanocrystal

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Abstract. CdSe nanocrystals synthesized in the liquid crystalline matrix were studied. The fluorescence trajectory of the single CdSe nanocrystal was obtained. Results show effect of jumps of the emission spectra.

The object under study is nanocomposite with CdSe nanocrystals (or quantum dots). Here we describe investigation of the thin film with CdSe nanocrystals with the size of 2.3 nm made from low-concentration toluene solution. Nanocrystals were grown in the ionic liquid crystalline matrix of cadmium alkanoate using template method of synthesis [1]. It’s quite a new method of synthesis to grow quantum dots inside liquid crystalline host medium. The resulting object combines peculiarities of semiconductor heterostructures and the liquid crystal anisotropic medium. In emission spectra of ensemble [2] samples under study show two separated bands in vicinity of exciton transition and wide band in the long wavelength region. Here we try to understand the nature of uncommon kind of spectra.

With the help of setup for a spatially resolved single molecule detection system based on the fluorescent microscope [3] with the prism spectrometer we managed to investigate emission peculiarities of the single particle.

Fig. 1. Different photoluminescence spectra of the single CdSe nanocrystal (a). Its luminescence trace (c) with the corresponding intensity histogram (b).

On the figure 1 (a) there are several examples of the recorded photoluminescence spectra of the same diffraction-limited area are shown. Effect is observed under continuous cw-laser excitation at room temperature. Observed random jumps in the emission wavelength called spectral diffusion lead to the broadening of the ensemble luminescence spectra of the nanocrystals. Luminescence from the quantum dots of different size going along with
phenomenon of spectral diffusion leads to massive inhomogeneous broadening of the spectra of the composite material [2].

On the figure 1 (c) fluorescence trace (track of the on- and off- fluctuations) of the single quantum dot is depicted. The duration of the on/off-intervals is random and characteristic of the single emitters. When several fluorescence tracks are summarized, the effect of fluorescence blinking is no longer observed. As shown first 1500 events fluctuations are complex with different amplitudes. If we propose that there are several emitting particles, then the probability of their simultaneous switch to the off-state (from 1500 to 2000) would be low. To support our assumption we need to mention, that investigated sample was prepared from solution with extremely low concentration of QD.

On the figure 1 (b) there is photocounts distribution function which is corresponded to the fluorescence track (figure 1 (c)). Such complicated fluorescence intermittency pattern cannot be explained in the context of the Efros-Rosen charge model [4]. In our case long on-intervals are absent and fluorescence fluctuates between multiple states with different intensity. The experimental results can be described in the general framework of the two models: 1st is multiple recombination center (MRC) model [5] and 2nd is combined model based on the modified charging model and the two-level system model [6].

References

Abstract. Photochromic molecules can be interconverted between two bistable conformations by light [1–3]. Irie and coworkers described a strategy to achieve superior fluorescence characteristics and outstanding switching characteristics of a photochromic unit by linking strong fluorophores covalently to photochromic building blocks [3,4]. Accordingly, we synthesised molecular triads that consist of two perylene bisimide (PBI) fluorophores covalently linked to a dithienylcyclopentene (DCP) photochromic switch, see fig 1. Such kinds of triads are promising candidates for super-resolution microscopy like RESOLFT and PALM [5,6], or can be used as optical transistors or memories [4,7].

Fig. 1. Top: closed (left) and open (right) state of the photoswitchable triad PBI-DCP-PBI, where the closed state is reached via illumination in the UV spectral range (325 nm) and the open state is reached via illumination in the visible range (488 nm). Bottom: Energy level scheme of the closed (left) and open (right) state of the triad. In the closed state, the excited state of the switch DCP lies below the excited state of the PBI, energy transfer is possible and the fluorescence of the PBI is reduced, whereas in the open state of the switch, energy transfer is not possible and the PBI shows fluorescence.

Regarding super-resolution microscopy and a demand for miniaturization for transistors and memories, single molecule applications are of great interest [8]. When studying the fluorescence of single photochromic triads under simultaneous illumination of visible and UV light, the on/off-durations of the telegraph-like fluorescence intensity vary as a function of the UV intensity [9]. The problem faced is that it is impossible to discriminate between off-states that are due to illumination with UV light and those that are due to spontaneous, yet unwanted and unavoidable blinking processes. However, a statistical analysis allows to determine the probability for transitions to the off state by deliberate switching of the triad. Such an analysis yields the positive predictive value \( p(S|+) \), that corresponds to the conditional probability that the triad indeed has been switched \( S \) given that a delay \( + \) between the onset of the excitation

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laser and the onset of the fluorescence has been observed. For the 15 triads we examined, this probability amounts on average to 0.8±0.1 with a maximum of approximately 0.96 [10], sufficiently large for application in super-resolution microscopy.

References

Exploiting of Stark effect in Tm: YAG crystal for addressable optical quantum memory

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Abstract. Rare-earth ions doped crystals are widely used in elements of quantum information processing. In this work, we demonstrated an optical quantum memory with the possibility of addressable recording and reading of the input weak light pulses in the Tm³⁺:Y₃Al₅O₁₂ crystal using revival of silenced echo (ROSE) memory scheme. The implementation of memory with addressing was possible due to the detected linear Stark effect in the Tm³⁺:Y₃Al₅O₁₂ crystal due to the presence of local crystal lattice distortions.

Crystals doped with rare-earth ions have attractive parameters of homogeneous and inhomogeneous broadening of the optical transitions [1]. In such crystals, it is also possible to realize a long lifetime of the electron-nuclear spin states [2]. These spectroscopic parameters enable the creation of a highly efficient solid-state quantum memory (QM), which is the main element of the quantum repeater. Along with the quantum efficiency, fidelity and storage time of QM, it is important to be able for addressable recording and reading of input pulses stored in QM. In this work we report on the implementation of addressable QM based on Tm³⁺:Y₃Al₅O₁₂ crystal by using revival of silenced echo (ROSE) memory scheme [3,4].

The $^3\text{H}_6$-$^3\text{H}_4$ optical transition of thulium ions in the Y₃Al₅O₁₂ crystal is interesting because its wavelength $\lambda = 793$ nm lies in the third window of optical fiber transparency. Moreover, it possesses quietly broadened inhomogeneous line ~20 GHz and long coherence times up to 75 μs in zero magnetic field. Tm ions in this material substitute Y ions in crystallographic sites with D₂ local symmetry. It is well known fact that linear Stark effect is absent in the crystals with central symmetries [5] such as D₂. Contrary earlier in this crystal we detected a quasilinear Stark effect [6].

Using the observed effect, we implemented writing and selective readout of the input light pulses stored in the QM cell by using control electric pulses (with duration of 5 μs and an electric field of 500 V / cm). Fig. 1 shows the effects of various electrical pulses on the readout of three input signal light pulses - a pair of the pulses and a separate third pulse in the revived of echo signal scheme. When recording the input pulses, an electrical pulse is also applied, due to which each excited thulium ion gets a certain phase shift different from the other ions. We observed, that for successful reading the input weak light fields, it is necessary to apply an electric pulse after the first or second $\pi$-pulse with the pulse area compensating the phase occurred when recording weak input light fields. It is worth noting that the addressing does not effect on quantum efficiency of the revived echo signals. So the efficiency of revival echo pulses remains the same with addressing Stark pulses (the highest curve in Fig.1) and if there is no external electric field (the lowest curve in Fig.1) that indicates to the new possibility of Tm³⁺:Y₃Al₅O₁₂ crystal in realization of optical QM.

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Fig 1. Addressable recording and readout of the weak input light pulses by using external electric field pulses in the ROSE scheme in Tm$^{3+}$:YAG crystal. The red solid lines show Stark pulses that suppress the echo and compensating pulses (after first $\pi$-pulse) that revive desired echo pulses. There are three incoming signal pulses – one pair and one single pulse. The highest (blue) and lowest (green) curves show the retrieval of all the input pulses with turned on Stark pulses for blue curve case and the original revived echo pulses in the absence of external electric field. Other curves show total suppression (black line), retrieving of only one pulse (purple line) and retrieving of only pair (blue line) of input pulses.

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References

A new approach for classification and evolution of statistics in blinking analysis of single emitter 
Quantum dots

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Abstract. Blinking in photo luminescence (from On- (higher) to Off- (lower) intensity state or vice versa) has rigorously been reported in single emitter semiconductor nano-materials. However, different blinking pattern of single emitters in same material system can be a signature for the co-existence of more than one electron-hole recombination mechanism at the same time. This work has focused on a particular thresholding method based on the intensity distribution of a blinking trace. Also we have put importance on the classification of blinking traces according to their %On-time and performed a thorough class-wise analysis of blinking properties which may be a more reliable way to present and comment on blinking mechanism for an ensemble of single emitters of same nano-crystal system.

Fluorescence or photo-luminescence (PL) intermittency, referred to as ‘blinking’ in semiconductor NCs has been explained through several theoretical models based on Auger ionization [1], influence of trap states [2] and structural diffusion [3] amongst others. However question remains whether a particular blinking mechanism is always operational throughout the NCs of a same system, like Mn doped ZnCdS QDs, located in different nano-environment which shows different blinking patterns as Figure 1(a). In general, blinking trajectory has been considered as a quasi-telegraphic signal between two states (On- or Off-) with respect to a single fixed threshold (FT) value. Further, the exponent m(On/Off) values of On-/Off-time distribution has often been used to propose theoretical models of blinking. Now, it is important to note here that the nature of On-/Off-time distribution and their exponent values can be affected by the chosen values of single FT, which has been reported earlier [4]. However, QDs frequently exhibit intermediate intensity states (say ‘grey’) between ‘On’ and ‘Off’ states for which often a continuous distribution of intensities over a range is observed rather than a clear bimodal intensity distribution. In this situation, FT in a blinking trace eludes the ‘grey’ states from blinking analysis. Here, we have developed intensity histogram dependent thresholding (IHDT) method for blinking analysis with particular single/multiple threshold(s) for each blinking trace, based on the intensity distribution pattern. IHDT easily detects and discards these ‘grey’ states between the multiple thresholds, where necessary, as shown in Figure 1(b).

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Further, the average exponent ($<m_{(on/off)}>$) value from a distribution considering many QDs has been reported, which is perhaps statistically more relevant because different individual NCs may undergo diverse blinking behavior [5]. In contrast, several experimental reports focus on a particular value of exponent ($m_{(on/off)}$), obtained from an individual emitter, which has been used to attribute a specific blinking mechanism for the ensemble of QD system [6]. Blinking behavior of the dopant emission from different Mn$^{+2}$ doped NC systems is reported either to be suppressed [6] or enhanced [7] or an intermediate type blinking [8]. It is therefore difficult to imagine why the exponent and other blinking parameters will have to be almost identical among different individual QDs of the same NC system. Therefore, we felt it is necessary to classify QDs which blink differently, using IHDT, into specific sub-ensembles with respect to their %On-time and performed a bottom up statistical analysis of blinking parameters to provide a more reliable scenario of diverse blinking process in a QD system.

References

Effects of photo induced changes in multilayer dielectric reflective coatings

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Abstract. The results of interaction of multilayer dielectric reflective coatings (Ta2O5/SiO2 and TiO5/SiO2 ) of laser mirrors with plasma of He-Ne discharge and discharge in oxygen are analyzed. There are formulated the requirements to the precise mirrors for laser gyro and gravitation interferometers measurements. The characteristics and the statistic parameters of the precise optical surfaces are discussed. The connection of the measured by the various metrological methods parameters with PSD function was theoretically described on the examples of experimental results received with help of AFM, WLI, ARS and TIS measurement methods. It is shown the correlation between of many layers coated mirrors surfaces profiles, scattering and their substrates by the comparison of PSD functions. The effects of the interaction of the generation radiation with the surface of the mirrors, manifested in the increase of the total losses in the resonator up to the threshold mode, the decrease of the generation threshold and the total losses on the mirrors after the start of generation, are also considered. The results of the inertial and hysteresis character, which are manifested in the reduction of the zone of synchronization of counter waves in ring lasers at a long stay near the zone and increase of the zone at a long stay in it, are discussed.

The quality of the modern high sensitive optical measuring devices, such as interferometers for seismic measurements and earthquakes predictions, opto-acoustical gravitational wave detectors [1,2], huge amount of laser devices and first of all ring lasers[3-6] mostly depends on the surfaces quality in the cavity both for mirror or prism cavity. Requirements to the optical surfaces parameters and laser mirrors characteristics are very high. Such, the irregularities of prism surfaces and mirror substrates in the range of spatial frequencies determined as “roughness” should be not more some angstroms, integral scattering coefficients should be not more some ppm. Ring laser mirrors have to satisfy in addition to the requirements of min back scattering into the mode of the ring laser cavity. The characteristics and the statistic parameters of the precise optical surfaces are discussed. It is shown that for characterizing of the surfaces shape, roughness and micro profile the function of the surface profile power spectral density (PSD) is the most informative, clear and convenient while the results of the surfaces analyzing by the different metrological methods are being compared.

Increase in total losses on mirrors under the influence of plasma radiation (operations: annealing in oxygen and operating time) under technological conditions. It was found that this effect is manifested as a result of insufficient focusing of the beam on the target or otherwise insufficiently pure sputtering material and the deposited oxide layer. The alleged cause was experimentally and statistically verified by target localization. The walls of the chamber on which the ion beam fell - Increase of total losses in the resonator in the pre-threshold mode - Reduction of the threshold and total losses after the start of generation - Decrease the capture area with a long stay near the measurement threshold zone - Increase the area after a long time in it.

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The connection of the measured by the various metrological methods parameters with PSD function was theoretically described. The values and shapes of the PSD-functions of the quartz substrates profiles were compared in its determination ranges of spatial frequencies with AFM, WLI, XRS and ARS methods. It is shown the good agreement of the measurements results, which permits to use those methods with the unified evaluation of the roughness with parameter $\sigma_{\text{eff}}$. It is discussed the experimental results of sitall, zerodur, CaF2, sapphire substrates PSD-functions.

Research work on the final treatment of the precise optical surfaces by the magneto-rheological suspension (MRS) has been made. It was demonstrated with the numerous experiments that in case of MRS final treatment the anisotropic surfaces are provided for any final level of roughness always. The direction of anisotropy coincides with the last treatment direction. Coated mirror surfaces repeat the anisotropic character of substrates texture. This result is interesting for application in the ring lasers. Multilayer interference coating of the laser mirrors to be coated at the such precise anisotropic surfaces have the min losses on scattering and min back scattering into the mode of the laser ring cavity, if the falling beam direction coincides with the mirror anisotropy direction. Analyzed the experimental results of sitall substrates finish polishing by gas cluster ion beams-method (GCIB) with help of PSD-functions measured by WLI and AFM.

It is researched the correlation between of many layers coated mirrors surfaces profiles and surfaces profiles of their substrates by the comparison of PSD functions. Results of the experimental measurements and the statistic analyses of the selected from production mirrors set demonstrated the connection between the substrates surface roughness and mirror scattering. Reflectivity of the mirrors has the direct connection with scattering being a part of mirror losses, which is seen from experimental data presented. Results of studying of the substrates roughness influence on the mirror scattering losses and analyzing of the substrates quality made by the different producers were followed by the work on the changing the technology of substrates surface treatment, that causes the mirrors parameters improvement and correspondingly the produced ring laser and interferometer accuracy increasing.

References
Eigen vibrational modes of phospholipid molecular layers in low-frequency Raman scattering

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Abstract. Molecular layers are unique objects, which are widely distributed in various areas of biology, medicine, and nanotechnology. It could be expected that molecular monolayers have peculiar vibrational dynamics in THz range. Here we studied THz dynamics of multilamellar phospholipid vesicles using low-frequency Raman spectroscopy. It was found that at temperatures below 273 K modes are observed at frequencies at 8-9 and 14-17 cm\textsuperscript{-1}. These modes are associated with eigen-vibrational modes of phospholipid layers in continuous approximation. Frequency of modes are defined by ratio between sound velocity and layer thickness. Thus, Raman spectroscopy allow us to follow the changes in sound velocity and layer thickness caused by temperatures, impurities and surrounding matrix.

1 Phospholipid molecular layers

Phospholipid molecules having hydrophilic polar head and two hydrocarbon hydrophobic tails are prone to organize a molecular layer, being in contact with a water surface. In most cases, they form multilayers of lipid bilayers separated by a nanometers water interlayers. Phospholipid layers are the subjects of many scientific researchers since they represent the cellular membranes, including plasma membranes, and are used for various biological and medical purpose, also as in sensor applications. Molecular layers of phospholipids are characterized by various structural and spectroscopic experimental techniques, among which Raman spectroscopy takes a particular place, since it is nondestructive, label-free technique with a high spatial resolution scattering. A progress in characterization of the conformational states of phospholipids tails by Raman spectroscopy was achieved recently \cite{1}.

The goal of the present work is to demonstrate that the THz dynamics, which is rich in the case of molecular layers, can be studied by low-frequency (4 - 100 cm\textsuperscript{-1}) Raman spectroscopy. This spectral range includes eigenmodes of phospholipid layers. This was firstly demonstrated in \cite{2} that below 273 K that the low-frequency Raman spectrum of multilamellar phospholipid vesicles at low temperatures contains two peaks near 8-9 cm\textsuperscript{-1} and 14-17 cm\textsuperscript{-1} attributed to the first eigenmode of phospholipids bilayer and monolayer.

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2 Low-temperature low-frequency Raman spectrum of phospholipid bilayers

In Fig. 1 a low-temperature ($T = 120$ K) Raman spectrum of a aqueous suspension of phospholipids 1,2-dihexadecanoyl-sn-glycero-3-phosphocholine (DPPC), prepared in spherical multilamellar vesicles with the lipid/water ratio about 1:0.3 w/w, is shown. Raman data are shown in the spectral density presentation. It is seen that minimization of bulk water presence allows us to reveal better the vibrational eigenmodes of lipid layers in comparison to a sample with the lipid/water ratio 1:1.5 w/w [2]. Fitting in Fig. 1 provides the frequencies of first eigenmodes of phospholipids bilayer and monolayer being 8.9 and 16.6, respectively. This values corresponds well to expected ones from

$$\nu_N = uN/(4cd)$$

where $d$ is molecular layer thickness $c$ is the light velocity, and $u$ is the acoustic velocity, $N = 1$ or 2 for bilayer and monolayer mode, respectively, is number of the normal mode. Taking known $2d \sim 5$ nm for gel phase of DPPC and estimating, $u$ as $\sim 2.4$ km/s (longitudinal sound velocity of dense polyethylene), one obtains $\nu_1 \sim 8$ cm$^{-1}$ and $\nu_2 \sim 16$ cm$^{-1}$.

Fig. 1. Raman spectra of DPPC suspension of the present work (circles) and from [2] (triangles). A five Lorentzian fit (thick line) is shown with its components. The dashed lines corresponds to the central peak, the thin solid lines to first three harmonics, the dotted lines reflect contribution from the rest of acoustic-like states.

References

Photobleaching of cytochrome Raman lines as the indicator of respiratory electron transport chain activity in cells during freezing

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Abstract. The intensity of resonance Raman lines of cytochrome haem depends on the cytochrome redox state. We applied this effect to characterize the activity of respiratory electron transport chain (ETC) in mouse early embryos and yeast cells during freezing. Green light radiation induces the formation of reactive oxygen species in biological cells resulting in oxidative stress and oxidation of cytochromes. Oxidation process leads to photobleaching of cytochrome Raman lines. We studied the temperature dependence of cytochrome photobleaching in the wide temperature range from frozen state at −120 °C to room temperature. In the case of cells freezing in glycerol aqueous solution, a sharp decrease in cytochrome photobleaching rate was found. Embryos freezing in propanediol aqueous solution demonstrate a gradual decrease in photobleaching rate with cooling. At temperatures below −50 °C, the effect of cytochromes photoreduction was found. It was shown that in photobleaching process are involved cytochromes of \textit{b} and \textit{c} types while in photoreduction effect only \textit{b} type cytochromes take part. The observed photoinduced transformations in cytochrome redox state indicate that at −50 °C changes in ETC occurs.

1 Introduction

Cytochromes are haemoproteins that participate in respiratory electron transport chain (ETC) – an essential process in cellular respiration. In the ETC cytochromes transfer electrons from one site of ETC to another. During electron transport, cytochromes change the redox state of the Fe-porphyrin complex called haem. Resonance Raman spectrum of cytochromes is known to depend on redox state of cytochromes (Fe\textsuperscript{2+}/Fe\textsuperscript{3+}) \cite{1}. For example, when excited by 532 nm radiation, Raman peak at 750 cm\textsuperscript{-1} (haem pyrrole rings breathing mode) for cytochrome in reduced redox state (Fe\textsuperscript{2+}) is by order of magnitude more intensive than for cytochrome in oxidized state (Fe\textsuperscript{3+}) \cite{2}. Under green light radiation, reactive oxygen species are formed in biological cells leading to oxidative stress and oxidation of cytochromes. This process can be visualized in a contactless label-free manner via photobleaching of cytochrome Raman lines \cite{3}. Thus, cytochrome photooxidation effect can be used to characterize the downregulation of cytochrome redox reactions in biological cells.

It is known that after cryopreservation, respiratory processes are suppressed in thawed cells \cite{4}. Therefore, we used cytochrome photobleaching effect to investigate the changes occurring in yeast cells and mouse early embryos during freezing.

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2 Results and Discussion

It was shown that in the case of yeast cells freezing in saline solution without cryoprotectant addition, temperature dependence of cytochrome photobleaching rate can be described by a combination of two thermal activation laws [5]. The first one corresponds to photoinduced reactions, depending on irradiation power, and native redox reactions [3,5]. This result indicates that downregulation of cytochrome redox activity occurs gradually during freezing.

When cells were freezing in presence of cryoprotectant (glycerol, propanediol) temperature dependences of cytochrome photobleaching rate was found to be different. In aqueous glycerol solution, both yeast cells and early embryos demonstrate gradual slowing of photobleaching rate with temperature decrease and an abrupt slowdown below −50 ºC [2]. In the case of mouse embryos, the replacement of glycerol by propanediol leads to a more gradual decrease in cytochrome photobleaching rate.

Analysis of difference spectra between Raman spectra measured at the beginning and the end of laser irradiation indicate that different types of cytochromes can undergo different photoinduced reactions. At temperatures above −50 ºC all types of cytochromes (b and c) demonstrate photoinduced oxidation. Below this temperature, c type cytochromes undergo oxidation, while b type cytochromes demonstrate photoreduction.

The observation of photoinduced transformations of cytochrome redox state inside freezing cells reveals peculiarity in downregulation of cytochrome redox reactions and the ETC activity. This peculiarity might be attributed to the protein dynamic transition related to the suppression of backbone peptide motion below a specific temperature.

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References

2. K.A. Okotrub, N.V. Surovtsev, Eur Biophys J (to be published)
Control of the direction of energy transfer in associates of colloidal quantum dots $\text{Ag}_2\text{S}/\text{TGA}$ and dye molecules

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Abstract. The possibilities for changing the direction of energy transfer in hybrid associates of colloidal $\text{Ag}_2\text{S}$ quantum dots (QDs) and thionine molecules are analyzed. The studies were performed by transmission electron microscopy, absorption and luminescence spectroscopy, PL decay study (time correlated single photon counting). An increasing of the average QDs size from 1.8 nm to 5.5 nm, and also a shift of the luminescence band from 630 nm to 950 nm, were found at using of TGA molecules and sodium sulfide as a sulfur precursor. Hybrid association of QDs (1.8 nm) with \textsuperscript{TH+} molecules leads to quenching of QDs luminescence with a simultaneous reduction of the luminescence lifetime from 13.7 to 6.5 ns. An association of QDs with a luminescence band maximum of 950 nm with \textsuperscript{TH+} molecules leads to quenching of \textsuperscript{TH+} luminescence and a reduction in its lifetime of luminescence from 0.43 to 0.3 ns. It was concluded that the reduction of lifetime of luminescence caused by the resonant nonradiative energy transfer between the components of the associates. An increasing in the average size of QDs leads to a change in the direction of energy transfer between the components of the associates.

In recent years, organo-inorganic associates of colloidal semiconductor quantum dots (QDs) and dye molecules (Dye) have been actively studied. They are used as luminescent sensors, photosensitizers of singlet oxygen, disinfecting systems. This is due to the appearance of new properties for associates that are not characteristic of individual components. The main role in the formation of new properties is played by the processes of exchange of electronic excitations.

Currently, the most detailed cases are considered when energy donors are QDs. Dye molecules are acceptors. The main energy transmission channels are: nonradiative Forster resonance energy transfer (FRET), transport of charge carriers. Herewith it has been showed the principal possibility of nonradiative energy transfer from QDs excitons to the dye and from the center of recombination luminescence to the dye. The situation when dyes are donors of an energy, and QDs are acceptors, is practically not considered.

The results of the study of nonradiative energy transfer in hybrid associates of colloidal $\text{Ag}_2\text{S}$ quantum dots, passivated with thioglycolic acid ($\text{Ag}_2\text{S}/\text{TGA}$) and thionine molecules ($\text{TH}^+$) are presented below.

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Figure 1 shows the absorption and luminescence spectra of the components of hybrid associates. Samples of QDs of I and II type have luminescence bands with maxima located in the region of 630 nm and 950 nm, respectively. For type I QDs, the luminescence band overlaps with the absorption band of thionine. For type II QDs, the luminescence band is located on the long-wave side of the absorption and luminescence bands of thionine.

At assembling of hybrid associates noticeable changes occurred in the absorption and luminescence properties of the components. The absorption spectra of thionine molecules increases in full width at half maximum toward shorter wavelengths to a few nanometers. For associates of type I QDs, thionine molecules were assembled into H aggregates. Also, the intensity and lifetime of the QDs luminescence decreased and simultaneously the luminescence of thionine increased. For associates of type II QDs, luminescence of thionine was quenched and luminescence of QDs increased. In addition, the lifetime of the luminescence of thionine molecules was reduced.

Thus, the quenching of luminescence and the shortening of its lifetime for one component and the increasing of luminescence of another component unambiguously indicate a nonradiative transfer of energy. In this case, the direction of the transfer is different for associates from the I and II type QDs.

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Nonlinear optical absorption of non-spherical silver nanoparticles and organic dyes mixtures

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Abstract. We study the features of the nonlinear optical response of silver nanoparticles (Ag NPs) of spherical and triangular shapes synthesized using a citrate-borohydride approach and their mixtures with methylene blue (MB⁺). The Z-scans at the wavelengths of 532 nm using 10 ns pulses were used to analyze the nonlinear optical absorption of MB⁺ solutions, Ag NPs of different morphology, particularly, the concurrence of saturable and reverse saturable absorption in the solution of triangular Ag NP and MB⁺. We show the significant contribution to the increasing in the normalized transmittance accomplished by photochemical degradation of the non-spherical Ag NPs (extinction maximum of 600 nm) and transformation into the spherical ones (extinction maximum of 400 nm). The nonlinear light scattering is analyzed as well, which showed the contribution to the variation of the sample transmission when it approaches the focal plane. It is shown that the nonlinear optical response is not additive in the mixture of Ag NPs and MB⁺. The increasing of the nonlinear absorption is probably due to both a change in the population of the triplet states of the dye and the efficiency of photochemical degradation of NPs in the presence of MB⁺.

At present, research in the field devoted to the development of control techniques for nonlinear optical properties of organo-inorganic nanostructures is relevant. The occurrence of interaction manifestations in other properties, in particular nonlinear optical, is of undoubted interest, including a practical one. For mixtures of plasmon nanoparticles (NPs) and dyes, studies of this kind are virtually unknown in the literature. In particular, the presence of plasmon NPs near MB⁺ can affect the probabilities of optical transitions and the mechanisms of photophysical processes in the molecule. However, the effect of plasmonic NPs on the two-photon absorption (TPA), the saturable absorption (SA), and the reverse saturable absorption (RSA) of MB⁺ has not been performed yet. In this paper, we report the studies of the nonlinear absorptive characteristics of mixtures of Ag NPs and MB⁺ in colloidal solutions using 10 ns pulses at the wavelength of 532 nm.

The measurements of the nonlinear optical properties of our samples were carried out by the standard Z-scan technique. The Nd:YAG laser generated single pulses (\(\lambda = 1064\) nm, \(\tau = 10\) ns) at 1 Hz repetition rate. The probe second harmonic (\(\lambda = 532\) nm) of this radiation generated in KDP crystal was focused by a 300-mm focal length spherical lens. The laser pulse energy was measured by a first calibrated photodiode and then registered by a digital voltmeter. The 5-mm-thick glass cells containing studied samples were moved along the z-axis through the focal plane of probe pulse using a translating stage. The open-aperture Z-scan scheme, i.e. the one without aperture in front of second photodiode allowed measuring all transmitted radiation to determine the dependence of the normalized transmittance on the position of sample on the z-axis. To observe the contribution to the Z-scan from nonlinear dynamic scattering, a scheme was also used in which a second diode was installed at an angle of 4.5º with regard to the

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optical axis.

We used Ag NPs obtained during the synthesis process, in which the reducing agents were trisodium citrate and sodium borohydride. According to poly-n-vinyl pyrrolidone and sodium citrate act as stabilizers preventing agglomeration of NPs during synthesis. The use of several stabilizers promotes the growth of non-spherical Ag NPs due to their ability to limit the growth of certain crystallographic planes of Ag NPs. Hydrogen peroxide, in turn, provided the necessary assistance to induce further oxidation of small particles to form NPs of different sizes and shapes.

The size and geometry of the synthesized ensembles of colloidal Ag NPs were determined using a transmission electron microscope (Libra 120, CarlZeiss). Size distribution for the ensemble of Ag NPs was obtained by digital analysis of TEM images. The extinction spectra of Ag NPs of different morphology were studied using the spectrophotometer USB2000+ with a source of radiation USB-DT (Ocean Optics).

It is shown that it is possible to obtain ensembles of spherical Ag NPs with average dimensions of 9±4 nm, whose extinction maximum was located near 420 nm. The NPs concentration in the solution was $4 \times 10^{14}$ cm$^{-3}$. Further holding of the colloidal solution for 30 minutes led to a change in the form of distribution of NPs and the appearance of two maxima on the histogram at 7 and 17 nm. The extinction maximum for such particles was located near 520 nm. The geometry of the NPs became non-spherical, resembling elongated droplets. The NPs do not have time to become triangular. Further holding of the colloidal solution for 60 minutes led to a change in size to 15±10 nm and a predominantly triangular geometry. The extinction maximum of these NPs was located near 600 nm.

We have demonstrated the dynamics of the nonlinear optical response of Ag NPs of spherical, mixed and triangular forms. It is shown that the reduction of the normalized transmittance in the focal plane of Z-scan can be induced, alongside the RSA, by photochemical degradation of the non-spherical NPs characterized by the plasmon resonance near 600 nm. Their transformation into spherical NPs characterized by the plasmon resonance near 420 nm can lead to a decrease in the optical density at a wavelength of 532 nm. We also analyzed the dynamic scattering of laser radiation, which may contribute to the formation of a symmetric dip in the Z-scan when samples with NPs approach the focal plane. In mixtures of Ag NPs and MB$^+$ in colloidal solutions using 10 ns pulses at the wavelength of 532 nm the enhancement of nonlinear response was observed. It was manifested in the enhancement of symmetric dip in the Z-scan which observed when sample approaches the focal plane. In this case, the intrinsic nonlinear response from the analogous volume of the dye without NPs was practically absent. The observed feature can be explained by a number of processes. On the one hand, near Ag NPs the changing in the probabilities of optical transitions of methylene blue molecules is probably. In this case, such an action is probably not only for singlet transitions, but also for triplet transitions. The change in the population of the triplet states can affect the enhancement of the RSA in MB$^+$. On the other hand, the optical absorption spectra indicate a substantial rearrangement of the mixtures. Probably photochemical transformation occurs both the dye and NPs, especially since for NPs in the absence of MB$^+$, the transformation of their geometry is observed.

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Spectral properties of hybrid associates of colloidal quantum dots Zn$_{0.5}$Cd$_{0.5}$S, europium tenoyltrifluoroacetonate and methylene blue

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**Abstract.** Hybrid associates formed from colloidal Zn$_{0.5}$Cd$_{0.5}$S quantum dots, passivated with thioglycolic acid, tenoyltritioacetate europium and methylene blue molecules, absorption, luminescence, IR and time-resolved spectroscopy technique are studied. The shift of the IR absorption bands of COO$^-$ and C=O groups of thioglycolic acid and europium thenoyltrifluoroacetonate has been detected. An increase in the efficiency of excitation of europium luminescence and a simultaneous increase lifetime of its luminescence upon adsorption on Zn$_{0.5}$Cd$_{0.5}$S quantum dots were found. Addition of methylene blue (thionine) molecules leads to quenching of the trap state luminescence of Zn$_{0.5}$Cd$_{0.5}$S and intracentric luminescence of Eu$^{3+}$. A conclusion about the adsorption of Eu$^{3+}$ on the surface of Zn$_{0.5}$Cd$_{0.5}$S quantum dots and the nonradiative energy transfer to methylene blue molecules was made.

Semiconductor crystals and dielectrics, doped with rare earth element (RRE), find extensive applications as materials for solid-state lasers, fiber amplifiers, biolables, solar cells, etc. Quantum dots (QDs) doped with RRE, whose own optical and electronic properties have a size dependence, have considerable interest. Among them are QDs doped with europium ions. An additional modification of the optical properties can be achieved by conjugating doped quantum dots with molecules of organic dyes.

The fig. 1 shows the luminescence spectra of QDs of Zn$_{0.5}$Cd$_{0.5}$S/ TGA in ethanol solution, and also their mixtures with europium tetrafluoroacetonate (Eu$^{3+}$: TTA), introduced at the stage of QDs crystallization. The luminescence in band with a maximum at 520 nm is occurred with participation of traps. In the luminescence spectrum of Eu$^{3+}$: TTA the peaks are present: at 592 nm, 615 nm, 653 nm and 702 nm - transitions between terms $^5$D$_0$$ightarrow$$^7$F$_1$, $^5$D$_0$$ightarrow$$^7$F$_2$, $^5$D$_0$$ightarrow$$^7$F$_3$ и $^5$D$_0$$ightarrow$$^7$F$_4$, respectively.

At introducing of Eu$^{3+}$:TTA into a colloidal solution with emerging QDs, the changes in luminescence properties were observed: - with increasing of QDs concentration, the luminescence intensity of Eu$^{3+}$ in all bands initially increases by 5 times, and then decreases; - with increasing of concentration of Eu$^{3+}$:TTA, the intensity of trap state luminescence decreases strongly, and the luminescence lifetime decreases; - at increasing of QDs concentration to 20%, luminescence decay in the Eu$^3+$ band slows down; - the intensity of the emission Eu$^{3+}$ grows at the initial point of decay of its luminescence, i.e. the effectiveness of its excitation is growing.

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Fig. 1. Spectra of luminescence of Zn$_{0.5}$Cd$_{0.5}$S/TGA+Eu$^{3+}$:TTA. In the insert is decay of luminescence of Zn$_{0.5}$Cd$_{0.5}$S/TGA and Eu$^{3+}$:TTA.

It can be concluded that there is an association of QDs and Eu$^{3+}$:TTA. Two types of similar associates are possible: i - some TTA molecules are replaced by TGA molecules and a carboxylate complex is formed. The structure of such a complex can be represented in the form Zn$_{0.5}$Cd$_{0.5}$S/TGA/Eu$^{3+}$. ii - Eu$^{3+}$ is adsorbed to QDs and integrated into the near-surface layer of QDs. The structure of Zn$_{0.5}$Cd$_{0.5}$S/Zn$_{0.5}$Cd$_{0.5}$S:Eu$^{3+}$:TTA (TGA), passivated by TGA and TTA molecules, is formed.

According to the IR absorption spectra, it was established on the basis of insignificant shifts in the absorption bands of the carboxyl group of TGA and the carbonyl group of TTA that the formation of Zn$_{0.5}$Cd$_{0.5}$S/Zn$_{0.5}$Cd$_{0.5}$S: Eu$^{3+}$:TTA (TGA), i.e. doping of QDs with Eu$^{3+}$ ions.

Fig. 2. FTIR spectra and structures of the investigated samples.

The conjugation of QDs of Zn$_{0.5}$Cd$_{0.5}$S/Zn$_{0.5}$Cd$_{0.5}$S:Eu$^{3+}$:TTA (TGA), with molecules of methylene blue (thionine) leads to quenching of trap state luminescence and intracentric luminescence and riseup of luminescence of the dye. At the same time, the luminescence lifetime in the bands of trap state luminescence and intracentric luminescence is reduced. A conclusion about the transfer of energy from the center of recombination luminescence and from the intracentral luminescence of Eu$^{3+}$ is drawn.

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Quantum coherent modulating enhanced single molecule imaging microscopy

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Abstract. In the fluorescence imaging and detection, undesired fluorescence interference (such as auto-fluorescence), that cannot be suppressed by increasing integration time in traditional imaging microscopy, often hamper contrast and may even prevent the identification of structures of interest. Here, we develop a quantum coherent modulating method based on phase control of femtosecond pulses, which will effectively modulate the excited-state population probability of single molecule and thus its fluorescence intensity. Fluorescence imaging of the discrete Fourier transform (FFT) magnitude at modulation frequency dramatically improve signal decimation from strong interference, where the signal-to-interference (S/I) was enhanced by more than two orders of magnitude. This method with six orders of magnitude dynamic range for modulation frequency have been confirmed to be universal to organic dyes and that linked with biomacromolecules.
Near-infrared photopolymerization assisted by upconversion nanophosphors for biomedical applications

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Abstract. We present the concept and the experimental demonstration of near-infrared photopolymerization assisted by specially designed upconversion nanophosphors. The principle of this technique is based on conversion of 980 nm laser irradiation to ultraviolet photons subsequently absorbed by photoinitiator. The nonlinearity of upconversion allows for activation of the process locally in the laser beam waist. This approach enables precise fabrication of 3D constructs directly in the volume of photocurable composition. Furthermore, the presented technique is suitable for polymerization of a wide range of photocurable resins as well as gelation of hydrogels for biomedical applications.

A broad range of techniques based on photo-induced polymerization have been developed. The overwhelming majority of those employs the single-photon absorption. In this case, the polymerization of the exposed photocurable compositions (PCCs) is a linear process getting launched in every point within the irradiation penetration depth and depending only on exposure dose. This approach is widely used in laser stereolithography [1] and direct light processing [2] when the photocurable resin is patterned and recoated layer by layer. However, this technique is not always suitable for in situ formation of structures. In this case the two-photon photopolymerization can be implemented. The method is based on two-photon absorption of light by photoinitiator [3]. The nonlinearity of absorption process allows activation of polymerization locally in the laser beam waist. Furthermore, implementation of near-infrared light instead of UV exposure makes possible to increase the irradiation penetration depth. Two-photon polymerization represents a high resolution method for drawing structures directly in the volume of PCC. Nevertheless, the need to use complicated femtosecond laser systems in order to achieve the required high intensity in the beam waist limits the wide implementation of this technique.

In this paper, we report on formation of structures in the volume of PCC using near-infrared photopolymerization. We propose to impregnate the photosensitive resin with upconversion core/shell NaYF4:Yb3+,Tm3+/NaYF4 nanophosphors capable to absorb light at 980 nm and effectively convert it to ultraviolet lines (Fig 1 (left)) within the absorption band of photoinitiator launching the polymerization. The conversion coefficient was measured as $\eta_{\text{UC}}(\text{UV})=2\%$. In comparison to two-photon polymerization the excitation action is performed via real energy states. Therefore, formation of 3D structures in the depth of PCC volume can be carried out at moderate intensities using simple semiconductor lasers instead of expensive femtosecond systems.

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Figure 1(right) illustrates the scaffolds produced by near-infrared photopolymerization in the depth of PCC on the base of oligocarbonate methacrylate (OCM-2) containing 1 % of TPO photoinitiator and upconversion nanoparticles. The standard Irgacure or chlorine P6 can be also used as photoinitiators.

![Image of luminescence spectrum and scaffolds](image)

**Fig. 1.** Luminescence spectrum of core/shell NaYF$_4$:Yb$^{3+}$,Tm$^{3+}$/NaYF$_4$ nanophosphors under excitation at 980 nm (left). Scaffolds on the base of oligocarbonate methacrylate produced by near-infrared photopolymerization (right).

Implementation of near-infrared photopolymerization assisted with upconversion nanophosphors has a great potential for gelation of biocompatible hydrogels, e.g. on the base of polyethylene glycol diacrylate. For this aim NaYF$_4$:Yb$^{3+}$,Tm$^{3+}$/NaYF$_4$ nanophosphors can be modified with amphiphilic polymer in order to provide the hydrophilic properties. In this case the photoinitiator also should be water soluble. Therefore, the endogenous flavin mononucleotide [4] or chlorine P6 conjugated with polyethylene glycol can be the grate candidates. The ability to form the structures in the depth of biocompatible water-based PCCs makes the near-infrared photopolymerization assisted with upconversion nanophosphors extremely interesting for biomedical applications, when the polymerization process can be performed **in situ**.

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**References**

Structural peculiarities of the fluorescence excitation spectra and spectral diffusion of single Mg-tetraazaporphyrins in a polymer matrix at low temperatures

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The results of low-temperature measurements of spectral trails (temporal evolutions of individual fluorescence excitation spectra) of single Mg-tetraazaporphyrin molecules embedded in polyisobutylene are presented. Spectral trails were recorded in a broad spectral range (up to 4000 GHz) at a temperature 6K. Spectral diffusion in an anomalously wide spectral range up to 950 GHz has been found. Individual spectra of single molecules with a broad peak shifted with respect to zero-phonon line at ~14 – 15 cm⁻¹ were recorded. These broad peaks can be interpreted as the phonon sidebands.

Single molecule spectromicroscopy is a quite novel but well-established experimental technique. The method is especially powerful at cryogenic temperatures when bright and narrow zero-phonon lines (ZPL) are reachable for the observation in the single molecules (SM) spectra [1,2]. Ultra-high sensitivity of the ZPLs characteristics to the SM local (nanometer-scale) environment reveals the possibility to probe solid-state media at the microscopic level [2,3]. It is well known that stochastic spectral jumps of ZPL position in spectra corresponds mainly to the coupling of impurity chromophores with tunnelling two-level systems (TLS), in turn, the electron-phonon interaction leads to the appearance of homogeneous broadening and shifts of ZPLs and gives rise to the phonon sidebands (PSB).

In case of the electron-phonon coupling a very intriguing question is how impurity molecules interact with so-called quasilocalized low-frequency vibrational modes (LFM). One of the most actual issues in this area is related to the possibility of the PSB detection in the excitation spectrum of SM. The PSB contains the information about LFM energy spectra and in some cases theoretically can disclose even the individual parameters of LFM.

Mg-tetraazaporphyrin (Mg-TAP) molecules play an important role in the photosynthesis processes and consequently are of particular interest for studying the processes of energy storage and conversion in biological objects. Moreover, from the hole-burning experiments Mg-TAP molecules are known to be photochemically stable luminophores with narrow ZPL.

In present research at cryogenic temperatures (6K) individual spectra of single Mg-TAP molecules embedded in polyisobutylene were detected. The measurements of spectral trails in a broad spectral range up to 4000 GHz (~130 cm⁻¹) were also performed. SM fluorescence was excited by a Coherent CR-599 tunable dye laser (Rhodamine 6G) with an effective linewidth of 10 GHz (~0.33 cm⁻¹), the scan step was 5 GHz (~0.16 cm⁻¹). The spectra were recorded in a spectral range (570 – 595 nm) corresponding to the Q-band absorption maximum of Mg-TAP molecules. The Stokes component of single-molecule luminescence was recorded in the

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wavelength range from 612 to 644 nm using high-sensitive EM-CCD camera (Andor iXON Ultra).

The measured zero-phonon luminescence manifests different temporal dynamic and exhibits wide distribution of the values of spectral shifts in a broad range from 10 to 950 GHz (~0.33 – 31 cm\(^{-1}\)) that considerably exceeds the characteristic values observed earlier [4]. In the dipole-dipole approximation of the interaction between SM and TLS [5], the value of 950 GHz corresponds to the distance in the order of 1 nm between them. Another possible explanation of such anomalous behavior is switching between conformational substates in Mg-TAP molecules.

One of the recorded spectral trails consists not only from ZPL but also from the broad peak shifted with respect to ZPL by ~15 cm\(^{-1}\) and performing synchronous spectral jumps with ZPL. This corresponds to the peak in LFM\(^{a}\)s energy spectra – «bozon peak» that had been measured earlier in different independent experiments (see [6] and ref. there). This peak can be interpreted as PSB. In another individual spectrum a quite broad peak (~4.1 cm\(^{-1}\)) shifted with respect to ZPL at 13.9 cm\(^{-1}\) was observed. This peak possibly corresponds to the interaction of a SM with a single LFM.

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References

On-chip quantum optics in 1D: single molecules coupled to a ring resonator

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Abstract. We report on a device in which single molecules at low temperatures are evanescently coupled to on-chip dielectric structures. When coupled to a straight dielectric waveguide, single molecules demonstrate extinction of propagating light by up to 14\%. Furthermore, by using on-chip electrodes we achieve tuning of molecular resonances, which allows us to match frequencies of two molecules. When the waveguide is replaced by a ring resonator, the average coupling strength is increased, and we observe distinct Fano-shape molecule resonances.

One-dimensional subwavelength waveguides (nanoguides) promise efficient light-matter interactions between photons in the waveguide mode and individual emitters separated on length scales much longer than their transition wavelength [1,2]. We report on the coupling of organic dye molecules at low temperatures to the confined mode of a TiO\textsubscript{2} waveguide via the evanescent field.

We observe up to 14\% extinction of a propagating light in the nanoguide by a single molecule. In addition, we demonstrate external control on the resonance frequencies of the molecules via the DC Stark effect. This allows us to match the resonance frequencies of two emitters, thus enabling their coupling via the nanoguide.

To further boost our emitter-nanoguide coupling, we employ on-chip resonators [3]. We demonstrate molecules coupling to a resonator both by the characteristic Fano shape of their spectral response, and by direct imaging of molecules on the chip and matching their position with the ring structure. Furthermore, we observe an increase of the coupling efficiency, in accordance with theoretical expectations.

The two experiments above demonstrate flexibility and versatility the on-chip platform. In the future, this approach should enable us to build up a network of strongly coupled quantum emitters and study collective effects such as the emergence of polaritonic states [4].

References


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Deep tumor imaging by upconversion nanoparticles

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Abstract. In this work are shown the prospects of using upconversion nanoparticles (UCNPs) as markers for contrast optical imaging of a tumor. For using nanoparticles for biomedical purposes is implemented a technique for coating nanoparticles with polymers, such as PEG and PSA. This approach provides low non-specific adsorption, which prolongs the circulation of UCNPs in mouse bearing Lewis Lung Cancer (LLC) up to 10 hours. These properties allow nanoparticles to quickly accumulate in the tumor. Effective delivery of particles with different polymer coatings in the tumor is demonstrated with the help of an epiluminescent imaging system.

Today one of the topical directions in modern medical diagnostics is the creation of nanoprobes aimed at pathological targets based on photoluminescent nanoparticles possessing high photo- and chemical stability and their application in real time. Such nanoparticles are able to specifically label tumor tissues and ensure their visualization in real time [1].

Upconversion nanoparticles (UCNPs) are a special class of luminescent nanoparticles with a specific property - the ability to conversion low-energy photons into photons of higher energy. UCNPs are inorganic nanocrystals (NaYF4) doped with lanthanide ions. Their photophysical properties provide a bright and long-term visualization of the structures marked by them in the depth of biological tissues. UCNPs are characterized by photostability, low toxicity, and their surface, allows the creation of conjugates with targeting modules. The wavelength of excitation and photoluminescence UCNPs falls into the so-called "window of biotissue transparency", which allows them to be visualized in biological tissues from a depth of several centimetre [2]. They have chemically active functional groups on the surface, which is important for obtaining targeted drugs, and their optimal size determines the predominant accumulation of nanoparticles in the tumor tissue due to the morphological features of its vascular system due to the EPR-effect. It is important to note that one of the main difficulties in the targeted delivery of nanoparticles is their insufficient circulation time in the blood and significant absorption by macrophages, which reduces their accumulation in the tumor. To improve the targeted delivery and reduce non-specific absorption by macrophages, we modified their surface with hydrophilic biocompatible coatings based on polyethylene glycol (PEG) and polysialic acid (PSA), which increased the circulation time in the bloodstream from several minutes to 10 hours (in the case with PSA) (Fig.1A).

In order to visualize the tumor with the UCNPs with coatings, we performed a study on C57Bl/6 mice bearing Lewis lung cancer. To visualize the fluorescent signal, an imager of small animals DVS-02 (Institute of Photon Technologies of the RAS (Troitsk, Moscow)) was
used. UCNPs at a concentration of 800 μg/ml in physiological saline was administered intravenously to the animals in a volume of 0.15 ml. After the administration of UCNPs, a series of epiluminescent images and spectral characteristics of the tumor were obtained to study the accumulation of nanoparticles in the tumor.

According to the obtained data, an increase in the photoluminescent signal from the tumor begins after 1 minute, with an increase in contrast as compared to the surrounding tissues. In the range of 2-5 minutes, there is a slight decrease in the signal from the tumor, which is supposed to be due to the redistribution of nanoparticles with circulating blood. Five minutes after the administration of UCNPs, the signal grows in the tumor (due to the accumulation and retention of circulating UCNPs), reaching a maximum after 60 min after administration (Fig.1B).

![Graph](image1.png)

**Fig.1 (A)** Normalized dependence of the UCNPs without biocompatible coating, and UCNPs surface modified with PEG and PSA vs. blood circulation time. (B) Epiluminescent images of C57Bl/6 mice bearing Lewis lung cancer obtained after 60 min UCNP-PSA injection (left) and a general view (right)

The recorded photoluminescence signal was maintained for 24 hours after administration of UCNPs. The strongest photoluminescent signal was recorded from UCNPs coated with PSA, which is associated with a more significant accumulation of particles in the tumor. The smallest signal was recorded from hydrophilic UCNPs without a biocompatible coating. The conducted studies show the prospects of using nanoparticles of modified PSA for marking and intravital imaging of tumors. This technology can be in demand for intraoperative assessment of the boundaries of surgical intervention.

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**References**


Absorption and emission properties of QD-like particles

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Abstract. In this work we present the theoretical analysis of the absorption spectra of the probe field and the resonance fluorescence (hereinafter referred to as RF) spectra of two-level quantum system with properties of semiconductor nanocrystals. Semiclassical approach based on the method of a weak field was used to calculate the spectral dependences. Electron-phonon interaction, relaxation processes (including collective) are considered in phenomenological way.

Resonance fluorescence is the phenomenon of light emission by quantum systems in an external field. Specific spectrum known as Mollow triplet of was firstly observed from Na gas [1] and later from organic molecules [2]. Today quantum dots are being studied as objects that demonstrate resonance fluorescence. In the latest experiments the resonance fluorescence including asymmetric Mollow triplets were observed [3]-[4].

In this study we calculated the spectra of the collective ensemble of two-level emitters. It was considered that in a dense homogeneous ensemble in a laser light each atom is driven by an effective field. The work [5] was taken into account to consider the collective relaxation rate. A characteristic feature of the fluorescence spectrum of this system is that the side peaks in the Mollow triplet are spectrally moved from the center.

To simulate a resonance fluorescence spectrum of a single QD the model of quantum emitter was considered with the mechanisms of quantum transitions between its states and processes of cross-relaxation of coherences due to the electron-phonon interaction. The possibility of asymmetric Mollow triplet was demonstrated. The assumptions about the model of quantum dot were taken from work [6].

We carried out simulations of resonance fluorescence spectra and the probe signal absorption spectra of an ensemble of QD-like particles and demonstrated the possibility of the appearance of an asymmetric Mollow triplet with positions of the side peaks strongly dependent on laser detuning from the frequency of the transition in the emitter. This result qualitatively corresponds to the spectral dependences recorded in experiments with single quantum dots. Fig. 1 shows four typical spectral patterns for the models described.
**Fig. 1.** Spectrum of RF. Black line – two-level radiator. Red line – ensemble of two-level radiators. Green line – QD. Purple line – ensemble of QD.

**References**


Nanohybrid scaffolds with luminescent remote control

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Abstract. We report on hybrid nanocomposite scaffolds on the base of cross-linked hyaluronic acid derivative with embedded upconversion nanoparticles (UCNPs). The unique photoluminescence properties of specially designed hydrophilic UCNPs enable visualization of hydrogel using NIR irradiation. Formation of scaffold structure can be produced by means of 3D printing or direct laser writing. For the first time, we present visualization of nanohybrid scaffolds in live small animal aiming to demonstrate new possibilities of their luminescent remote control for tissue engineering.

1 Introduction

Hyaluronic acid (HA) appears to be one of the most suitable materials for tissue engineering and regenerative medicine. This naturally occurring polysaccharide is a priori biocompatible and biodegradable, still it lacks enough mechanical strength for constructing scaffolds. One of the methods to reinforce this polymer is photocrosslinking of HA derivatives containing double bonds. Addition of photoinitiator into hyaluronic acid glycidyl methacrylate (HAGM) water solution and irradiation it with UV/blue light makes possible crosslinking of composition resulting in solid insoluble hydrogel formation. Incorporation of UCNPs composed of NaYF4 crystals codoped with Yb3+ and Er3+ enables visualization of produced hydrogels under NIR light excitation as these UCNPs exhibit anti-Stokes luminescence under excitation at 980 nm. Since NIR light falls in so called “transparency window” for biological tissues, it can penetrate tissue and organs up to centimetres unlike visible light.

2 Results and discussion

In this work double bond moieties were introduced into HA by conjugation of the polysaccharide with glycidyl methacrylate (GMA) producing derivative capable of crosslinking (HAGM). Conjugation of GMA can be carried out via reaction mechanisms of reversible transesterification or irreversible epoxy ring opening with carboxyl or hydroxyl moieties of HA [1]. In order to make core/shell NaYF4:Yb3+/Er3+ UCNPs soluble in water their surface was first covered with amphiphilic SPAN-60 (sorbitan monostearate), then with polyethyleneimine for biocompatibility. HAGM (20 wt.%) was further dissolved in water solution containing UCNPs with following addition of polyethylene glycol diacrylate

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(PEGDA), Mn=575 (5 wt.%), and flavin mononucleotide (0.0004 wt.%) as an endogenous photoinitiator [2].

The produced photocurable composition (PCC) was subjected to exposure at 365 nm wavelength to gelate 150 µm thin hydrogel films 6 mm in diameter. The acquired scaffolds were implanted subcutaneously on dorsal side of mice with scaffolds without UCNPs as control. Animals were monitored with bioimaging system every day (Fig. 1, left). Intravital luminescent signal under NIR light irradiation was recorded up to 7th day after, then strong signal was recorded post mortem from extracted scaffold. Histological analysis displayed weak inflammation reaction and slight degradation. As an example of structured scaffold we produced the structure using PEGDA-based PCC by means of direct laser writing (Fig 1, right).

![Image](image.png)

Fig. 1. Left: Bright-field photo of mouse with implanted nanohybrid scaffold on day 1. The inset shows epiluminiscent signal from scaffold under irradiation at 980 nm wavelength. Right: Scaffold structure produced by direct laser writing.

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References

Spectral features of conjugated bichromophores: porphyrins with curcumin

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Abstract. Conjugated bichromophores of porphyrins with natural compound curcumin were synthesized and studied by methods of spectroscopy. The fluorescence spectra of bichromophore consist of four bands covered almost a whole visible spectrum from 450 to 700 nm. A relatively weak interaction between curcumin and metalloporphyrin allows to combine both effects: high generation efficiency of singlet oxygen by metalloporphyrin and an anticancer treatment of curcumin.

Design and characterization of novel types of polyheterocyclic compounds have a huge impact on development of methods for the selective transportation of photosensitizers to tumour cells, a crucial point of photodynamic therapy. Well known, that porphyrins are widely used as effective photosensitizers of singlet oxygen generation in photodynamic processes [1,2]. The idea to design a conjugated bichromophore based on porphyrin macrocycle with a natural compound - curcumin, isolated from the Curcuma longa plant, seems very promising. Nowadays curcumin isomers and derivatives attract a lot of attention of specialists in the field of medicine and biochemistry, primarily as a effective antitumor drugs [3]. Number of publications devoted to the study of the optical and photophysical properties of curcumin [4], as well as its structure modifications have been appeared recently.

In this report we presented of the first results of the synthesis of a structure based on metallocomplexes derivatives of tetraphenylporphyrin linked to curcumin molecule and studying of optical parameters newly-synthesized compounds at ambient and liquid nitrogen temperatures. The structures of Zn-5-(4-aminophenyl) 10,15,20-(triphenyl) porphinato (ZnATPP) and Zn-5-(4-aminophenyl)-1-(4-N-curcumin) 10,15,20-(triphenyl) porphinato (ZnATPP-CURC) are presented on Fig.1 (a, b).

Fluorescence excitation, fluorescence and phosphorescence spectra of ZnATPP and ZnATPP-CURC have been recorded at ambient and liquid nitrogen temperatures. Fluorescence excitation and fluorescence are presented on Fig.2 (a, b).

As evidently from absorption and fluorescence excitation spectra (Fig.2 a) absorption bands of curcumin and ZnAPTPP are practically coincided in the spectral range of 400-500 nm.

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\[ \text{\begin{align*}
\text{a} & \quad \text{b}
\end{align*}} \]
Fig. 1. Chemical structures of ZnATPP (a) and ZnATPP-CURC (b) compounds.

Fig. 2. Fluorescence excitation (a) and fluorescence (b) spectra of ZnATPP (1) and ZnATPP-CURC (2) in toluene at 77K.

The absorption bands of ZnATPP-CURC bichromophore exhibits a minor difference compare to ZnATPP in the range of 420 nm. While, the fluorescence spectrum of ZnAPTPP consists from two bands similar to well-known ZnTPP. In contrast, four bands in the spectral range from 450 to 700 nm (Fig. 2b.2) have been observed in the fluorescence spectrum of ZnAPTPP-CURC. Two “blue” bands in the spectrum (at 465 and 497 nm) refer to the curcumin emission, and two “red” bands at 608 and 659 nm correspond to the luminescence of ZnAPTPP. Upon formation of bichromophore with curcumin, the bands in the fluorescence spectrum of ZnAPTPP are shifted by more than 2 nm to the range of short wavelengths. A relatively weak phosphorescence of ZnAPTPP and ZnAPTPP-CURC were detected with a maximum at about 790 nm.

The complex of ZnAPTPP-CURC combines a high efficiency of singlet oxygen generation by one part of the complex (ZnAPTPP) with an anticancer effect of curcumin, that can provide to high efficiency of these species as therapeutic agents in the treatment of oncological diseases.

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References
Exciton spin precession detected by reflectance spectroscopy

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Abstract. Optically active excitons possess spin \( J = 1 \) and can precess in the external magnetic field. Usually, carrier spin precession in the external magnetic field is studied by the modulation or four-wave mixing spectroscopies. The high quality of the MBE-grown heterostructure and narrow spectral line of excitons allows us to experimentally study the exciton spin precession by conventional reflectance spectroscopy methods. Detailed analysis of reflectance spectra gives much more quantitative information about the studied physical phenomena.

A number of physical phenomena is observed in external and effective internal magnetic fields in semiconductor heterostructures. Effects of the electron, hole, exciton, and exciton complex spin precession are attractive for practical applications as a base for the memory elements in perspective quantum and classical computers.

The spin precession effects are usually studied by the modulation pump-probe Kerr/Faraday-rotation spectroscopy. It is considered in such experiments that the oriented magnetic moment of the spin system plays a role of an effective magnetic field, which rotates the polarisation plane of reflected or transmitted probe light. Only information about the angle of the polarization plane rotation is available in such experiments. A careful theoretical analysis is required to obtain valuable information about the energy levels shifts and the variation of oscillator strengths. The four-wave mixing experiments allows one to obtain information about the optical dephasing rates also.

In this paper, the results of experimental study of exciton spin precession in heterostructures with a quantum well (QW) in an external magnetic field are reported. The key feature of our report is a nonstandard experimental technique based on the non-modulated reflectance spectroscopy. The sample under study is a 14-nm AlGaAs/GaAs/AlGaAs QW grown by MBE technique. The main feature of the sample is a record quality, which is confirmed by the absence of nonhomogeneous broadening and of any shifts between the exciton lines in reflectance and PL spectra. The highest quality of the sample is also con-firmed by a small width of exciton resonances in reflectance spectra (HWHM = 76 μeV).

The sample is mounted in a helium cryostat and cooled down to 6 K. An electromagnet is used as a source of external magnetic field up to 0.8 T in the Voigt geometry. The radiation of a femtosecond pulsed Ti:S laser (100 fs, 80 MHz) is used for recording the reflectance spectra. The linearly polarized laser (probe) beam falls onto the sample at small angle incidence. The reflected light is split into two orthogonal circular components by a quarter-wave plate and a Wollaston prism. Each component is detected by an imaging spectrometer equipped a CCD. The pump beam is obtained from the same laser by spectral filtering. The circularly polarized spectrally narrow (1.8-ps) pump beam is tuned to the exciton resonance in the QW. In the experimental protocol, both the circularly polarized reflectance spectra are recorded at the each time delay between the pump and probe pulses.
Typical reflectance spectrum is shown in Fig. 1(a). All experimental spectra are fitted by a model described in Ref. [1]. An example of the fit curve is shown in Fig 1(a). There are four fitting parameters: radiative broadening $\Gamma_0$, nonradiative broadening $\Gamma$, exciton energy $\omega_0$, optical phase $\varphi$. All the parameters have a clear physical meaning and could be obtained from the fitting procedure with a high accuracy for the high-quality sample [2].

![Fig. 1. (a) Reflectance spectrum of the sample under study (blue curve) and the fit by model [1] (red curve). The heavy- and light-hole exciton transitions are marked as HH and LH. (b) The heavy-hole exciton energy dependence on the time delay between the pump and probe pulses for co- (red) and cross- (blue) circular polarizations at zero magnetic field (dashed lines) and at the field of 0.5 T (solid lines). The shift between the curves for different polarizations is introduced for a visibility.](image)

The experimental protocol and the fitting of each measured spectrum by the described procedure allow us to obtain information about all the parameters of exciton transitions. An example of the delay dependencies of exciton energies for co- and cross-polarizations is shown in Fig. 1(b) for magnetic fields 0 T and 0.5 T. We should note that, in traditional modulation pump-probe spectroscopy, only the data proportional to the energy splitting between the co- and cross-polarized exciton transitions can be measured. In our method, the absolute values of exciton energies are detected as well as the absolute values of other exciton parameters (radiative and nonraditive broadenings are not shown here). The quantitative data allows us to develop a quantitative model of exciton-exciton and exciton-carrier interactions.

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References

Room temperature optical thermometry based on the luminescence of the SiV defects in diamond

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Abstract. SiV-containing microcrystals of diamond are synthesised by using high-pressure high-temperature treatment of a mixture of pertinent organic-inorganic precursors. Photoluminescence of SiV defects were investigated with the aim to use the microcrystals for optical temperature sensing in near infrared at room temperature based on temperature-dependent shift of the 740 nm zero-phonon line of SiV photoemission.

1 Introduction

Biomedical applications require nontoxic photoresistant optical markers absorbing and emitting in the NIR biological window of biotissues. Several impurities in diamond, such as SiV and NE8 defect centres with spectrally narrow zero-phonon lines (even at room temperature), satisfy these demands [1,2].

2 Experimental

Diamond microcrystals (typical size ~1 µm) containing SiV defects were synthesized from a mixture of adamantane (C₁₀H₁₆) and tetraphenylsilane (C₂₄H₂₀Si) in a ratio of Si/C 0.28%. An apparatus of uniaxial compression and the high-pressure chamber of “Toroid-15” type were used for the synthesis [3]. The diamond sample was synthesized in titanium capsule at a pressure of about 9 GPa and a temperature of 1600 °C, the exposure time at the synthesis temperature was 10 seconds.

Under 488 nm laser excitation the SiV defects possessed an intense emission spectrum with a quite sharp zero-phonon line (ZPL) at 740 nm over a wide temperature range (Fig. 1). The spectral position of the ZPL shows a strong red-shift by increase of temperature (Fig. 2). Acceptable fitting could not be achieved by the conventional $T^4$ dependence but required additional $T^2$ term to take into account softening of bonds in the excited electronic state in accordance of a modified model of the ZPL of impurity centers in solids [4].

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Fig. 1. Temperature dependence of SiV emission in a diamond microcrystal. Excitation with 488 nm Ar⁺ laser line

Fig. 2. Thermally induced shift of the 740 nm ZPL in the emission spectrum of SiV defects in diamond micro-crystals.

3 Concluding remarks

A narrow 740 nm ZPL and its strong position dependence on temperature are promising for a sensitive (~1 K) optical thermometry around RT. Preparation of SiV-containing nano-diamonds by using the above described HPHT technique is in progress. We further intend to test the thermo-sensing capabilities of the nanoparticles in aqueous media and implement imaging and thermometry with different cell cultures.

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References

Spatially Asymmetric Transients of Propagating Modes in a CdZnTe/CdMgTe Guiding Structure

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Abstract. We report on ultrafast time-resolved pump-probe measurements in a CdZnTe/CdMgTe planar guiding structure covered with metallic gratings. In order to demonstrate propagation effects we scan the position of the pump focusing spot on the sample surface with a spatial resolution of 10 μm. We observe asymmetries depending on the direction of the relative displacement between the pump and probe beams. This is attributed to exciton-polaritons in the guiding layer propagating in opposite directions at different photon energies according to the guiding modes dispersion.

1 Introduction

Our subject is a CdZnTe/CdMgTe planar guiding structure covered with a metallic grating which is chosen to investigate propagation of modes in the guiding layer. We show that the time-resolved reflectivity signals in different excitation geometries which have a spatial shift between excitation (pump) and probe spot reveal asymmetries that we attribute to the propagation of the guiding modes.

2 Experimental Setup and Sample Structure

2.1 Femtosecond Pump-Probe

We measure the time-resolved differential reflectivity in a pump-probe setup. Starting from a Ti:Sa laser at 810 nm central wavelength and 50 nm (FWHM) wide spectrum, pulses of about 30 fs duration are split into pump and probe beams, whose relative delay time is varied. Both beams have incidence angles of 17 degrees but in planes perpendicular to each other and are focused to spot sizes of about 10 μm. The differential reflectivity of the probe beam gives an insight about the pump induced changes and dynamics of exciton-polaritons in the studied sample. To increase sensitivity the reflected probe beam passes a 760 nm bandpass filter (tuned near the exciton resonance). Additionally, we move the incidence spot of the pump on the sample surface, which allows us to measure a spatially resolved data set about the propagation of exciton-polaritons inside the sample.

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2.2 CdZnTe Waveguiding Sample

The sample studied in this work contains a 170 nm thick CdZnTe guiding layer bounded by 100 nm thick CdMgTe layers. On top, a 50 nm gold grating is applied. The steady-state dispersion relation shows a distinct exciton resonance at 755 nm, as well as a guiding mode, whose resonance wavelength strongly depends on the light incidence angle. It has two branches of opposite slope signs which both can be excited by the broad pulse of our laser system. The gold grating enhances the coupling of incident light to the guiding mode where p-polarized incident light results in a TM-polarized guiding mode. All measurements are taken at low temperatures of 10 K.

3 Experimental results

Fig. 1. (a) Scheme of propagation inside waveguiding layer. (b) Transient amplitudes evaluated at different delay times t: The instantaneous signal at temporal overlap (t=0 fs) and the longer-lived part at t>500 fs.

Pump-probe transients represent two distinct features: at the temporal overlap of pump and probe pulses (t=0 fs) we observe a sharp peak which is followed by a step-like signal of much longer lifetime. When moving the pump spot along the x-axis which means perpendicular to the grating slabs (see Fig. 1(a)), we detect an asymmetric behaviour of the amplitudes (and signs) of both of these features as shown in Fig. 1(b). The step-like component is present mainly at negative distances (x<0) and changes sign at positive x distances. Also, the instantaneous component at t=0 fs is much more pronounced in the positive x direction but disappears in the negative x direction. We interpret these observations as excitation of the two different polariton branches of the guiding modes travelling in opposite directions and corresponding different excitation mechanisms: The peak at temporal overlap is an indication of the optical AC Stark effect excited by the lower energy part of the guiding mode, whereas the higher energy part causes exciton bleaching and results in the step-like signal.
Investigation of NV centres in aggregates of detonation nanodiamonds

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Abstract. Here, we experimentally investigate optical and spin properties of NV centers in aggregates of detonation nanodiamonds. It was found out that despite the small size of nanodiamonds forming the aggregate, the NV centers in these aggregates have spin properties comparable to similar size nanodiamonds but with brightness enhanced by a factor of 2.

Currently, the color centers in the diamond have a huge community attention. So, NV (Nitrogen-Vacancy) color centers are actively being studied as a principal element of quantum information processing [1], and also have some applications as sensors for magnetic and electric fields, temperature [2,3]. Nowadays one direction of research is the searching optically active color centers and the study of their optical properties in nanodiamonds [4]. Interest in nanodiamonds is determined mostly by sensory applications, in which nanodiamond can play the role of a sensitive element of the detector. In addition, nanodiamonds can serve as natural single-photon sources, the radiation of which can be collected and intensified [5].

Fig. 1. a) TEM image of DND aggregation; b) g2 autocorrelation function.

In this research, we experimentally investigate optical and spin properties of NV centers in aggregates of detonation nanodiamonds (DND). Aggregate of DND is compound of diamond nanoparticles with size of 2-5 nm (see Fig. 1a), which forming an aggregate with size up to 100 nm. Because of a small probability of forming NV centers in DND (lower 1 % [6]) aggregate of DND often contains single NV center (see Fig. 1b). This fact allows us effectively investigate optical and spin properties of single spin in such an aggregate.

Optical properties of NV centers in DND are interesting. These are very bright centers, the number of emitted photons is 2.2 times greater with respect to 50 nm nanodiamonds using our confocal setup. Sensory applications, however, like applications for processing quantum information, are also extremely sensitive to the spin properties of NV centers. Therefore, we made a detailed study of the spin properties of the electronic system of NV centers in DND. In

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the presence of external magnetic field (see Fig. 2a) we performed a coherent manipulation of
the electron spin by a microwave field (see Fig. 2b), the damping of Rabi oscillations allowed
us to estimate the coherence time $T_2^*$ for the electron spin. Applying of Hahn echo sequence
allow us to measure the coherence time $T_2^*=3-5$ μs for the electron spin, which similar to
nanodimonds with bigger size [7].

![Fig. 2](image)

**Fig. 2.** a) Electron spin resonance of NV center obtained in continuous wave laser regime; b) Rabi
oscillations of electron spin of NV center.

Thus, bright and easily obtained aggregates may become successful replacement of bigger
nanodiamonds for sensing applications kite magnetometry and thermometry, in particular in
biology, due to its nontoxicity of diamond. In addition, reasonable results of the spin properties
of aggregates of DND indicate potentially good spin properties in the detonation nanodiamonds
themselves, which opens the possibility of using DND in nanophotonic applications.

**References**

   (2011)
   (2008)
Preparation of single-photon wave packets of infrared range wavelength with orbital angular momentum using phase "vortex" plates

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Abstract. We consider the peculiarities of formation and registration of axially symmetric vortex fields in the context of applying diffractive optical elements such as vortex lenses and vortex axicons for the generation of single-photon states with a nonzero orbital angular momentum in the process of spontaneous parametric down-conversion.

For the realization of free-space quantum communication channels, light beams with an orbital angular momentum (OAM) are of greatest interest \cite{1, 2}. Experimental and theoretical studies show that such beams are more stable when propagating in a turbulent medium compared to ordinary Gaussian beams \cite{3, 4}, and exhibit self-healing ability \cite{5, 6}.

Single-photon states at a wavelength around 800 nm corresponding to one of the atmospheric transparency windows can be effectively obtained in the process of spontaneous parametric down-conversion (SPDC) of light in a nonlinear medium \cite{7}. In this paper, we present the results of preliminary studies devoted to generation of single-photon states with a nonzero OAM in the process of SPDC with the use of diffractive optical elements.

To create optical vortices we used diffractive optical elements (DOE) in the form of a vortex lens and a vortex axicon \cite{8, 9}, which is one of the most flexible and energetically effective methods. We studied theoretically and experimentally the evolution of the generated fields during their propagation near the focusing region for a vortex lens and a vortex axicon. Fig. 1 shows the diameter of the beam ring as a function of the distance along the propagation axis. It can be seen that for the axicon the distance along the propagation axis, over which the intensity distribution remains practically constant, is about 2 times larger than that for the vortex lens. For the mask parameters used in the experiment, it is about 4 cm and 2 cm, respectively. On the other hand, the vortex lens provides a greater contrast of intensity distribution in the focal plane, which can be important when detecting the output signal. Therefore, when creating an experimental setup, the problem of choosing between vortex lenses and vortex axicons should be solved taking into account the geometry of the pump field and the geometry of the registration scheme.

One of the most effective methods for generating single photons is the process of SPDC, during which a photon from a strong pump field propagating in a non-centrosymmetric medium is annihilated with creating two photons, called idler and signal. This process satisfies the energy and phase matching conditions: \( \omega_p = \omega_i + \omega_s \) and \( \vec{k}_p = \vec{k}_i + \vec{k}_s \), respectively, where \( \omega \) and \( \vec{k} \) are the frequency and wave vector, respectively, of the signal (i), idler (s) and pump
In addition, for the collinear SPDC the following condition is valid for OAM: \( \ell_p = \ell_s + \ell_i \). We numerically simulated the collinear SPDC process for \( \ell_p = -1, 0, +1, +2 \), and calculated coincidences between the signal and idler photons for 49 possible combinations of orthogonal states. As should be expected, the coincidences observed in all cases when the sum of OAM of the generated photons is equal to that of the pump beam.

![Graph](image)

**Fig. 1.** The width of the beam ring as a function of the distance in the focus region for the axicon (circles) and for the vortex lens (squares).

The paper presents the results of experimental studies devoted to the generation of single photons with a non-zero OAM via SPDC. We consider the peculiarities of formation and registration of axially symmetric vortex fields with the use of diffractive optical elements: vortex lenses and vortex axioms. It was found that the position of the detection plane in the case of vortex lenses is more critical than in the case of vortex axioms. Compensatory method of measuring the topological charge allows one to achieve at least a tenfold increase in the signal compared to the method without compensation.

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**References**

8. E. Abramochkin et al., Optics Comm, **102**, 336 (1993)
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