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Electronic excitations of cytosine in water: how to describe solvent effects?

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Benchmark studies provide fair comparisons of accuracy and computational cost of different methods; as such, they play a critical role in forming community knowledge base. However, to date, benchmarks for methods capable of describing photochemistry in condensed phase are scarce and incomplete.

We work on development of condensed-phase photochemistry database by (i) creating and documenting model systems covering wide range of photochemical phenomena in various environments and (ii) providing benchmarks on these systems with various solvation models such as quantum mechanics / molecular mechanics (QM/MM), QM with the effective fragment potential (EFP) embedding, and fragment molecular orbital (FMO) method.

The test set will include DNA nucleic bases such as molecule of cytosine in natural environment and in water solution. A preference will be given to systems with available experimental data such as absorption, emission and transient absorption spectra.

The following information is documented and stored for general use on external website (cophee.efpdb.org): (i) gas phase geometries; condensed phase snapshots from MD trajectory, (ii) gas phase excitation energies at different levels of theory, (iii) QM/MM, QM/EFP, FMO excitation energies for specific geometry snapshots, (iv) plots of excitation energy distributions (i.e., absorption spectra) at different levels of theory, (v) statistical analysis of various sets of data, including average solvatochromic shifts and widths of spectral lines, (vi) information on reference experimental data, (vii) detailed description of all computational protocols, and (viii) sample inputs for gas phase, QM/MM, QM/EFP and FMO calculations. *This work was supported by RSF (project № 14-43-00052-II).*

Predictive power of classical MD calculations for n-alkanes rheological properties

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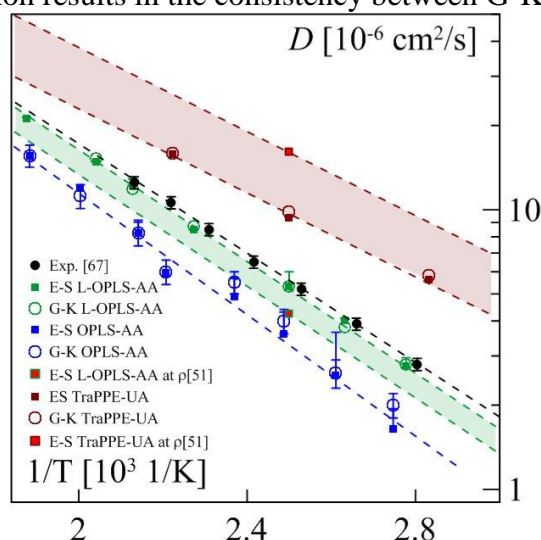
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Modern industry is strongly interested in research of liquid hydrocarbon properties since they are parts of lubricants, insulators and fuels. One of the main properties of such liquids are transport coefficients (diffusivity, viscosity and thermal conductivity).

Diffusion is one of the key subjects of molecular modeling and simulation studies. However, there is an unresolved lack of consistency between Einstein-Smoluchowski (E-S) and Green-Kubo (G-K) methods for diffusion coefficient calculations in systems of complex molecules. We analyze this problem for the case of liquid n-triacontane. The nonconventional long-time tails of the velocity autocorrelation function (VACF) are found for this system. Temperature dependence of the VACF tail decay exponent is defined. The proper inclusion of the long-time tails contributions to the diffusion coefficient calculation results in the consistency between G-K and E-S methods¹⁻³.



The comparison of the n-triacontane diffusivity D obtained by the E-S (the filled squares) and G-K (the open circles) methods at different T with the experimental data (the black circles).

Our calculations of the viscosity of liquid hydrocarbons have demonstrated the applicability of the Green-Kubo time-decomposition method⁴ in the case of single-component n-alkanes systems. The obtained values of the viscosity coefficients for the hydrocarbons under study coincide with the non-equilibrium method⁵ and the experimental data within 10%. The experimental dependence of viscosity on temperature is reproduced.

The work is supported by the grant No. 17-79-20391 of the Russian Science Foundation.

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Computational search for new superhard transition metal borides

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Superhard materials are used in many industrial applications. Nowadays it is a big challenge to search for new cheap and effective materials which can substitute traditional materials in many many of industrial applications. Traditionally material can be called as superhard if its Vickers hardness is higher than 40 GPa[1].

We predicted new transition metal borides based on W, Mo etc. using the evolutionary crystal structure prediction algorithm USEPX[2]. Some of the predicted phases are promising hard materials that are expected to be thermodynamically stable in a wide range of conditions. The composition-temperature phase diagram was calculated for W-B systems, where the new boron-rich compound WB₅ is found to have Vickers hardness of 45 GPa and at the same time it possesses high fracture toughness of ~4 MPa·m^{0.5}[3]. Newly predicted tungsten and molybdenum boride (WB₅ and MoB₅) are found to be thermodynamically stable in a wide range of temperatures at ambient pressure. Temperature dependences of the mechanical properties of WB₅ were studied using quasiharmonic and anharmonic approximations. Our results suggest that WB₅ and MoB₅ remains a high-performance material even at very high temperatures.

The work was supported by Russian Science Foundation (Grant No. 17-73-20038).

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The ultrahard fullerite model. Computational study

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Materials which are harder than diamond always attracts great attention from the scientific community. Thus, each experimental confirmation of the synthesis of new ultrahard materials initiates a new wave of investigations in this field. One of the successful attempts to synthesis of new material harder than diamond was made by Blank et al.[1][2], who synthesized a new amorphous materials based on fullerenes C₆₀ called as “tisnumit”. Later, similar materials based on polymerized fullerite with outstanding mechanical properties were synthesized.[3][4] However, the crystal structure and the origin of unique mechanical properties still unknown.

Here we considered the model of the nanocomposite consisted on the hard fullerite grain made of SH-phase, predicted by Prof. Chernozatonskii et al.[5], surrounded by the single crystal diamond matrix. SH-phase was chosen as a hard grain of the nanocomposite, because its atomic parameters and X-ray diffraction data agrees well with experimental data from [5].

In proposed model nanocomposites differs from each other by the size of fullerite grain and the thickness of diamond matrix. We studied in detail the atomic structure of proposed materials using the simulation of X-ray diffraction patterns, which nicely describe the experimental data. We also calculated the dependence of bulk modulus on the geometrical parameters showing that some nanocomposites approach the bulk modulus value of 1 TPa, caused by the compression of fullerite grain inside the diamond matrix.

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Теоретическое исследование двумерных структур на основе переходных металлов

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В настоящей работе методами DFT изучены соединения на основе переходных металлов, FeO [1] и CoC [2], расширяющие класс структур с несвойственной двумерным кристаллам орторомбической симметрией.

В первой части работы были исследованы атомная структура, а также электронные и магнитные свойства ультратонких пленок FeO. Продемонстрирован эффект расслоения таких пленок с последующим формированием отдельностоящих монослоев, обладающих двумерной орторомбической решеткой. Подробно изучена возможность стабилизации монослоя FeO в матрице графена, в частности, аналитически определены оптимальные формы границ раздела 2D-FeO/графен. Смоделированные ПЭМ-изображения 2D-FeO в поре графена (Рисунок 1а) демонстрируют хорошее согласие с экспериментом [3], что позволяет предположить о возможности экспериментального наблюдения структур на основе двумерного оксида железа.

Во второй части работы были изучены атомная структура (Рисунок 1b), а также электронные и механические свойства двумерного карбида кобальта, также обладающего орторомбической симметрией. Показана динамическая стабильность такого монослоя, описаны особенности формирования химических связей, а также получены оценки упругих констант, модуля Пуассона и коэффициентов жесткости.

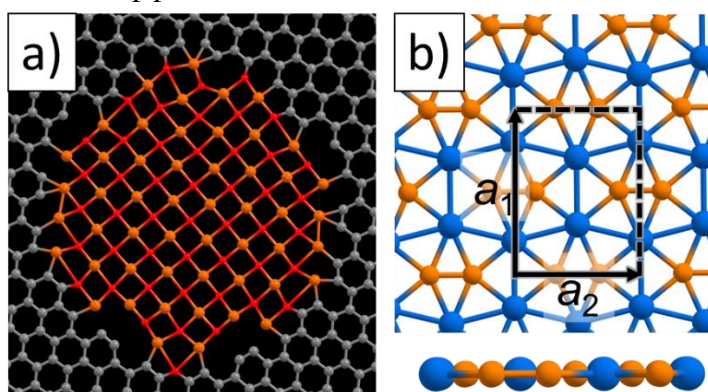


Рис. 1. Атомная структура а) монослоя оксида железа в поре графена и б) монослоя карбида кобальта.

Работа выполнена при поддержке гранта РФФ 17-72-20223.

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Fluctuation enhancement of ion diffusivity in liquids

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Dependence of ion diffusivity on the ion radius is calculated for different liquids via molecular dynamics. It is found that there are multiple ion sizes with enhanced diffusivity. This is caused by destabilization of the ion solvation shell and only happens at the ion radii that correspond to changes of the ion coordination number, which happen with an increase in the ion size. Solvation shell fluctuations are activated which leads to an additional ion motion with rearrangement of the shell. A model of the ion motion is made to describe this effect.

The ion motion can be separated into the motion together with solvation shell as a whole and the motion inside the solvation shell. The total diffusivity of the ion is a sum of two diffusivities associated with each of these motions. The motion of the entire solvation shell can be described using the Stokes-Einstein relation. It is independent on the ion size. The motion inside the solvation shell is associated with fluctuation of its structure. Such fluctuations can be described as fluctuations of ion coordination number. Thus, diffusivity enhancement can be found by the examination of ion coordination number. This allows to determine regions of high and low diffusivity value.

This model is universal and it predicts diffusivity enhancement. It is in a good agreement with the molecular dynamics simulation of ions diffusion in Lennard-Jones liquid and water.

Enhanced diffusivity is caused by fluctuations of liquid in the local vicinity of the diffusing particle. Thus, it can be calculated from the molecular dynamics only considering a rather small number of particles in the simulation box. The results of diffusivity calculation should be size corrected. It is known that diffusivity of liquid decreases with decrease of the number of particles in simulation. Additionally, the statistical error of calculated diffusivity decreases with the decrease of the number of particles. As a consequence, the smallest possible number of particles provides the best statistical accuracy.

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Excited State Dynamics of Photoexcited Charge Carriers in Halide Perovskites: Time-Domain Ab Initio Studies

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Photo-induced processes play key roles in photovoltaic and photo-catalytic applications of halide perovskites. They require understanding of the material's dynamical response to the photo-excitation on atomic and nanometer scales. Our non-adiabatic molecular dynamics techniques,¹ implemented within time-dependent density functional theory,²⁻⁴ allow us to model such non-equilibrium response in the time domain and at the atomistic level. The talk will focus on photo-initiated energy and charge transfer, relaxation and recombination in hybrid organic-inorganic perovskites. Considering realistic aspects of perovskite structure,⁵ we demonstrate that strong interaction at the perovskite/TiO₂ interface facilitates ultrafast charge separation,⁶ how dopants can be used to both decrease and increase charge recombination,⁷⁻⁹ that grain boundaries constitute a major reason for charge losses,⁹ that moderate humidity increases charge lifetime, while high humidity accelerates losses,¹⁰ that hole trapping by iodine interstitial, surprisingly, extends carrier lifetime,¹¹ that collective nature of dipole motions inhibits nonradiative relaxation,¹² that organic cation orientation has a strong effect on inorganic ion diffusion and current-voltage hysteresis,¹³ that surface passivation with Lewis base molecules decelerates nonradiative charge recombination by an order of magnitude,¹⁴ and that the experimentally observed dual (hot/cold) fluorescence originates from two types of perovskites substructures.¹⁵ Our simulations provide a unifying description of quantum dynamics on the nanoscale, characterize the rates and branching ratios of competing processes, resolve debated issues, and generate theoretical guidelines for development of novel systems for solar energy utilization.

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***Ab initio* simulation of formation of the conducting solid hydrogen at high pressures**

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The assumption of the existence of metallic hydrogen was advanced by Wigner and Huntington in 1935[1]. An estimate of the metallization pressure at zero temperature at 25 GPa was obtained. The topic was continued by many theoreticians who increased the required pressure. V.L. Ginzburg included this problem in the list of especially important and interesting physics problems. Developed and experimental research. However, it was only in 2017 that a sharp increase in the reflection coefficient of hydrogen was observed at a pressure of 495 GPa and a temperature of 5.5 K, which was interpreted as the transition of solid hydrogen to the conducting phase[2]. The report reviews theoretical and experimental works, as well as proposals on practical applications of metallic hydrogen. The emphasis is on the latest theoretical and experimental research and the original results of the authors of the report.

The dependences of the pressure, electrical conductivity, and profiles of hydrogen proton-proton pair correlation function (PCF) on the density at temperatures of 50 and 100 K are calculated within the framework of the density functional theory. The range of densities $\rho = 1.14 - 2.0 \text{ g/cm}^3$ is considered, the calculated pressure range is $P = 300 - 1200 \text{ GPa}$, which corresponds to the solid phase of hydrogen. The calculations are carried out using the VASP package. A pseudopotential approach is used to describe internal electron shells (core electrons) the nonlocal potential of the projected augmented waves (PAW) is applied. For the valence electrons, the Kohn-Sham set of equations with the PAW potential is solved.

In order to describe the exchange-correlation interaction, the generalized gradient approximation with parametrization in the form of the PBE functional is used. The monoclinic lattice of the C2/c space group, with 24 particles in the unit cell, is used as the initial configuration, since this structure is the most stable in the pressure region above 260 GPa, which corresponds to solid hydrogen phase III at the temperatures under consideration.

A structural transition is observed at a pressure of 607 GPa, characterized by a considerable jump in electrical conductivity and a sharp decrease in the number of H₂ molecules. The first peak of the PCF arises at 0.92 Å, which corresponds to the interatomic distance in the H₃⁺ ion. The value of the distance corresponding to the first maximum of the PCF remains the same in the pressure range $P = 607-630 \text{ GPa}$. Thus, the nature of the transition combines ionization with structural changes. With the further compression, the first maximum of the PCF corresponds to the average distance between the particles at a given density, which indicates the complete dissociation of hydrogen ions.

Strong ionization during the phase transition in dense solid hydrogen / deuterium brings this transition closer to the prediction of the Norman-Starostin plasma phase transition.

The work is supported by the grant 18-19-00734 of the Russian Science Foundation.

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² Dias R.P., Silvera I. F. *Science* 2017, **355** 715.

Novel push-pull quinoxalinone-based chromophores with high sensitivity of emission and absorption to small structural modifications

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Push-pull type organic molecules attract considerable attention in a number of important applications in non-linear optical (NLO) materials, organic light-emitting devices, sensory and photovoltaic applications. The molecules demonstrate perfect sensitivity of their optical absorption/emission properties to the external stimuli or structural modifications. The latter may dramatically influence photophysical properties of the molecules allowing the rational design of the systems with desirable properties.

In the current study the photophysical properties of a series of novel push-pull quinoxalinone-based chromophores (Figure 1), strongly absorbing and emitting light in the broad range of visible spectrum, were comprehensively studied both experimentally and quantum chemically.

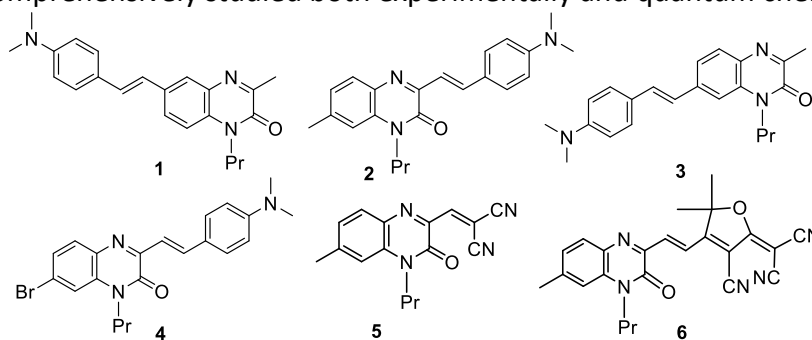


Figure 1. Chemical structures of the considered systems.

The drastic influence of the electron-donor dimethylaminostyryl group (DMAS) position in the quinoxalinone core on the absorption and emission intensities and on solvatochromic behavior of the considered isomers has been established. No dependence of the photophysical properties of the chromophores on the conformation of DMAS group is found. Quantum chemical computations provided reliable theoretical description of observed spectral features, in particular, related to the important Stokes shift. The local or intramolecular charge-transfer (ICT) character of the main electronic transitions has been quantitatively assessed on the basis of natural transition orbitals analysis and the novel topological descriptors of the electronic density rearrangement. It is shown that the ICT effects are not the main factors of drastic differences in the emission efficiency of the structurally very similar push-pull chromophores.

The reported study was funded by RFBR according to the research project № 18-33-00128 mol_a

Modeling of carrier transport in thin layers of two-phase organic materials by the Monte Carlo method

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The study of non-stationary transport of charge carriers in very thin layers (less than 100 nm) of organic materials is important, both for a fundamental point of view, because it allows to investigate the features of the energy distribution of hopping centres and the morphology of thin layers, and for applications, since layers with such thickness are used in light-emitting diodes, field-effect transistors, photovoltaic cells and other basic elements of organic electronics^{1,2}. In particular two-phase structures of materials are of interest to researchers, since such materials are promising in increasing the energy efficiency of organic photovoltaics³. In addition, at the moment there is extensive knowledge of how the molecular weight of the polymer, the solvents used and the processing methods control the morphology of the material.

In this work, the drift mobility in ultrathin organic layers was studied by the Monte Carlo method in the framework of the Gaussian Disorder Model of transport and Miller-Abrahams model of the hopping rates, in structures with different morphologies. The results of all models are compared. In the case of a two-phase structure, there is a considerable change in the mobility dependence on the thickness of the layer when the size of the crystallites (individual regions of high orderliness in the polymer material) varies at small thicknesses and when their part in the material varies at large thicknesses. The reason for the obtained dependencies is analysed.

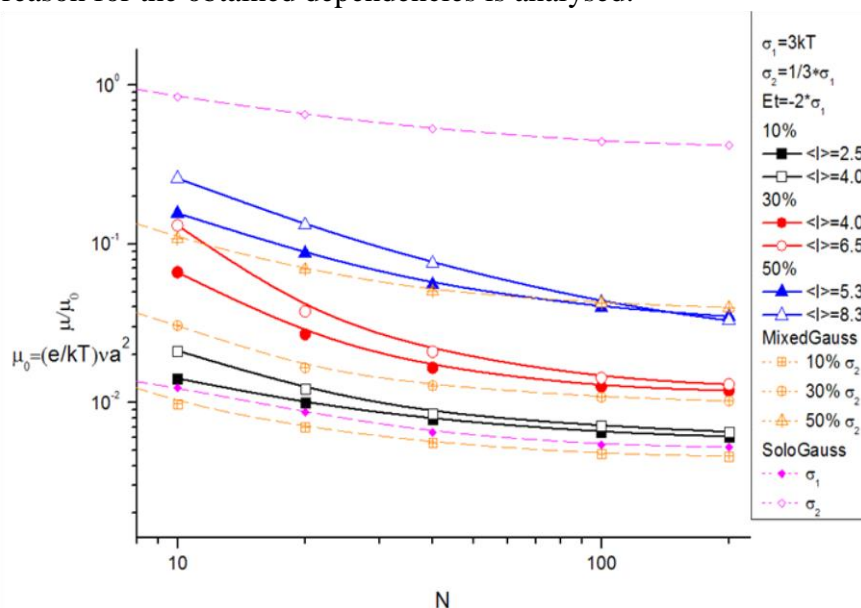


Fig. 1. Comparison of drift mobility dependencies on thickness in models with different morphology.

This work was supported by Volkswagen Foundation (Germany), the project "Understanding the dependence of charge transport on morphology in organic semiconductor films".

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Моделирование процесса взаимодействия дипептида с фрагментом ионной мицеллы

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В настоящей работе изучен процесс взаимодействия α -Ala- α -Ala с фрагментом ионной мицеллы додецилсульфата натрия, моделируемой димером SDS. Дипептид рассмотрен в цвиттер-ионной форме, наиболее устойчивой в водных растворах.

Квантово-химическое моделирование исследуемых объектов выполнено методом DFT/B97D/6-311++G(2d,2p). Для учета сольватационных эффектов использована модель предельной поляризации Томаси – РСМ. Для подтверждения того, что оптимизированные комплексы являются минимумами на поверхности потенциальной энергии, был проведен анализ нормальных колебаний; мнимых частот не обнаружено.

На основании выполненных расчетов получены супрамолекулярные структуры двух типов, отличающихся расположением α -аланил- α -аланина. В ковровой модели (рис. 1а), дипептид существует в двойном электрическом слое мицеллы, при этом образуется межмолекулярная водородная связь типа N-H...O ($r=1.744$ Å), а ион Na⁺ оказывается тетраденратно координированным относительно атомов кислорода. В случае, когда α -Ala- α -Ala находится в так называемой «поре» мицеллярного агрегата (рис. 1б), между молекулами возникает не менее прочная, чем в первом случае, Н-связь с $r=1.741$ Å. Отметим, что энергии образования комплексов оказались близки 46.8 и 44.7 ккал/моль, соответственно. Таким образом, можно утверждать, что обе модели имеют вероятность к реализации.

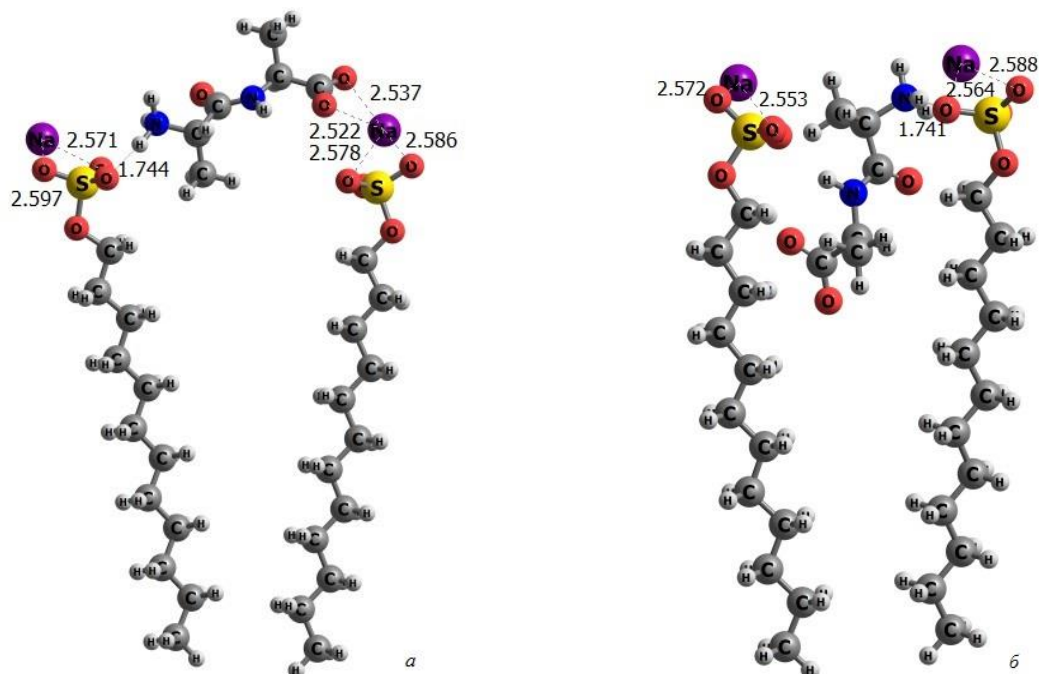


Рис. 1. Оптимизированные структуры комплексов SDS... α -Ala- α -Ala: ковровая модель (а) и модель «поры» (б).

Работа выполнена при финансовой поддержке гранта РФФИ № 18-03-01032-а

An analytic description of transient current in disordered organics for a broad range of temperature and electric field by the joint application of transport level and effective temperature concepts

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Disordered organic semiconductors are the subject of intensive investigations due to growing applications in electronics. Charge carrier transport, being characterized by mobility in general, is one of the basic processes, determining parameters of electronic devices. The combination of steady-state and time resolved measurements, like the well-known time-of-flight (TOF) technique[1], seems to be the most reliable way to obtain the information about the mobility and other parameters of disordered materials. The Monte-Carlo (MC) modelling of charge transport is a very pertinent, but the time-consuming, although model-dependent, tool for the theoretical modelling of charge transport in disordered organics. Hence, an alternative approach, i.e. the analytic modeling of charge transport using simple heuristic models, like the transport energy[2] and effective temperature[3], employing MA or Marcus models, is promising. The first concept allows describing the hopping transport by the relatively simple formalism of the multiple-trapping model in the low-field limit, while the second provides a simple way to describe both the field and temperature dependence of mobility. Both these analytic tools used typically for the analysis of the mobility in quasi-equilibrium transport mode. The description of non-equilibrium transport[4], including dispersive mode, still considered as questionable, although qualitative description of TOF transient current has been shown.

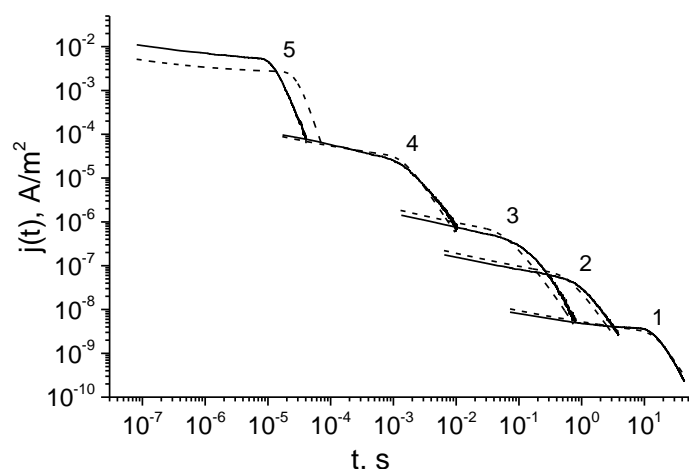


Fig. 1. Comparison between the results of MC (solid lines) and analytic modeling (dash lines) for temperature 250 K and different fields: 1 - 10^6 , 2 - 10^7 , 3 - 3.6×10^7 , 4 - 10^8 , 5 - 2×10^8 V/m.

In this work we perform calculations of transient current in time-of-flight conditions, using both the concepts, transport energy and effective temperature, simultaneously. Our calculations provide good enough fitting for the results of MC modelling (see fig. 1), approving this approach.

This work was supported by the "Improving of the competitiveness" program of the National Research Nuclear University MEPhI (Moscow Engineering Physics Institute).

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Noncovalent interactions in the design of nonlinear-optical polymer materials

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Organic nonlinear-optical (NLO) materials engage much attention due to their attractive potential in photonic devices. Molecular sources of the NLO activity are organic chromophores incorporated into polymer material, which should have noncentrosymmetric structure to exhibit quadratic nonlinearity. This is achieved by chromophores orientation in the electric field applied to the polymer heated up to the glass transition temperature. The long-term stability of the chromophores orientation can be provided by using polymer matrices with high glass transition temperatures, or by means of polymers chains cross-linking. Noncovalent interactions between chromophores and polymer matrix as well as between chromophores inter se can serve alternative way of fixing the orientation order. Here different types of the chromophore aggregates, π - π stacks (so-called H-aggregates), and head-to-tail clusters (J-aggregates) of azochromophores are investigated quantum-chemically.

Recently, in the course of atomistic modeling of epoxy-based oligomers with multichromophore dendritic fragments, H-aggregates of co-directed chromophores were revealed. Stacked azochromophores were studied in the framework of the DFT-based approach. It was shown that the formation of stacks results in moderate increase of NLO characteristics, the effect depending on the relative shift of the chromophores. According to the QTAIM analysis, the binding between chromophores occurs due to the noncovalent van der Waals interactions.

Supramolecular organization of the azochromophores DO3 in composite materials with PMMA-based or epoxy-based polymer matrix was studied. H-bonding between chromophores and polymer matrix in composite PMMA-based material and between chromophores in solution is studied both theoretically and experimentally.

Quantum chemical modeling in combination with vibrational and electronic absorption spectroscopy has shown that the neat DO3 contains both antistacked forms and hydrogen bonded associates of the "head-to-tail" type. In PMMA/DO3 films with low concentration of the chromophores, DO3 is mainly H-bonded to PMMA matrix, while in the composites with high concentration of DO3 molecules, the latter form hydrogen bonds both with PMMA and with each other. Infrared, Raman, and UV-vis spectroscopic markers of isolated DO3 molecules and various modes of their supramolecular associations are revealed.

The addition of DO3 to the host matrix of chromophore functionalized epoxy amine oligomer, CFAO, enhances the NLO coefficient compared to that for CFAO by ca. 40%. Molecular modeling in an amorphous cell has shown the presence of hydrogen bonding and π - π interactions between the chromophores-guests and polymer matrix. The energy of H-bonds is of the order of 3 kcal/mol, what is rather small, but the number of such bonds is large, and we hope they could contribute to the conservation of the chromophores relaxation order.

All calculations were performed with Materials Science Suite.¹

This work was supported by Program of Presidium of RAS № 32.

¹ Schrödinger Release 2018-1: Materials Science Suite, Schrödinger, LLC, New York, NY, 2018.

Spin-dependent electronic structure and transport in deformed platinum nanotubes

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The spin- and deformation-dependent electron structures of the single-walled chiral and achiral Pt nanotubes are investigated using a relativistic linear augmented cylindrical wave method.

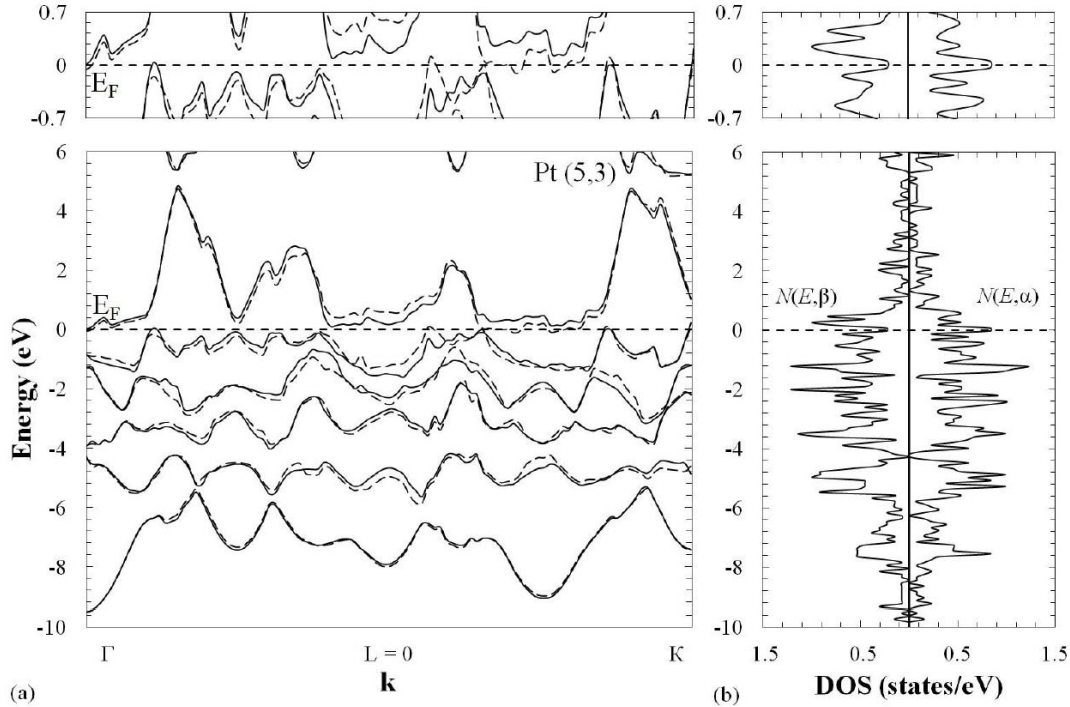


Fig. 1. Electron structure of the (5,3) Pt nanotube. The dashed and solid lines correspond to the spin α and β . The dispersion curves and DOS in the Fermi energy region are presented in enlarged energy.

Figure 1 shows the results of calculations of the band structure and DOS of tubule (5,3). This is the chiral system without rotational symmetry having 98 atoms per translational unit cell. However, due to account of screw symmetry, the cell is reduced to one atom and the results are presented in a very simple form with only ten spin-dependant energy bands in the valence band and two low-energy curves in the conduction band. The Fermi level clearly separates the valence and conduction band curves. There is no crossing of the occupied and vacant dispersion curves, but only slight overlap of a top of valence and of a bottom of conduction states typical for semimetallic systems. In the band structure, the spin-orbit coupling appears as the large splitting of nonrelativistic dispersion curves equal up to 0.5 eV for the bands in Fermi energy region. The spin-polarization of eigenstates relative to the nanotube axis is almost perfect. The spin-orbit interaction is also manifested in the DOS. Particularly, the electron DOS on the Fermi level for the spin up $N(E_F, \alpha)$ and spin down $N(E_F, \beta)$ states differs about three times resulting in a possibility of spin-dependent ballistic transport in this system. The total DOS $N(E_F) = N(E_F, \alpha) + N(E_F, \beta)$, the spin-dependent components, and, therefore, spin transport can be controlled by mechanical deformation of the tubes. The torsional, uniaxial, and uniform strain results in the drastic change of the total and spins densities of state and spin pairing. The spin-dependent transport can be controlled by mechanical deformation of the tubes and used in spintronic devices.

Characterization of the ground and excited states properties in the series of selected diazines

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Diazines possessing highly π -deficient character effectively act as the electron-withdrawing part in π -conjugated push-pull structures. Intramolecular charge transfer (ICT) in the molecular scaffold can induce tunable photophysical properties. A wide library of fluorescent diazine derivatives has been described (see for example[1][2][3]). Moreover in very recent reports it was shown that the quinoxalinones/quinoxalines used as π -bridging fragments represent a valuable addition to the pool of NLO systems.[4][5] At the same time the various possible structural modifications could considerably and unexpectedly affect the photophysical properties of the systems making predictions and interpretations of the latter to be the challenging task. In order to reliably rationalize and establish the “structure-properties” relationships available modern quantum chemistry tools are very helpful. In particular, time-dependent density functional theory (TDDFT) provides cost-effective and accurate approach allowing to shed light on the spectral properties of the chromophores for both ground and excited states. In this work we present the use of TDDFT for predicting the electronic transitions energies in the series of recently synthesized quinoxaline/quinoxalinone derivatives with push-pull architecture and demonstrating a number of outstanding properties important for material applications. Their thermal- and photo-stability, electrochemical reversibility and high molar absorptivity in the visible spectral region¹⁻² opens perspectives for use the compounds under study for design of functional materials. Furthermore obtained theoretical results are in the good agreement with experimental characteristics pointing to the reliability of the chosen approach for a treatment of their photophysical properties and for a rational design of the push-pull chromophores.

The work was supported by Young Researchers Grant of Tatarstan Academy of Sciences (research project № 04-136-у-Г 2018)

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⁵ A.A. Kalinin, S.M. Sharipova, T.I. Burganov, A.I. Levitskaya, Yu.B. Dudkina, A.R. Khamatgalimov, S.A. Katsyuba, Yu.H. Budnikova, M.Yu. Balakina, *Dyes and Pigments*, 2018, **156**, 175-184

A fresh look on the nature of dual-emission of the octahedral Cu₄I₄ clusters

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Copper(I) complexes have attracted considerable interest because of their rich structural and photophysical properties and potential applications as inexpensive, abundant materials in optoelectronics, catalysis, and biological systems. The most common motif for Cu₄I₄ clusters reported in the literature is a cubane-like structure consisting of a copper tetrahedron with iodides capping the four faces (Figure 1a).

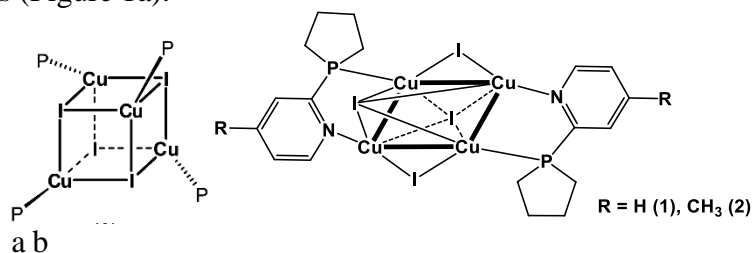


Fig. 1. Structures of a) cubane Cu₄I₄ cluster, b) studied complexes with octahedral Cu₄I₄ core

Generally, the cubane clusters exhibit two distinct emission bands, one at high energy (ca. 450 nm) and the other at low energy (ca. 600 nm), arising from metal-halide-to-ligand charge-transfer (³(M+X)LCT) excited states and triplet cluster-centered (³CC), respectively. The former band is quite prominent at low temperature (LT), the latter band dominates at room temperature (RT).

Recently, the dual-emissive tetranuclear copper (I) complexes with Cu₄I₄ core of rather rare octahedral type (Figure 1b) have been synthesized[1]. Emission of complexes of this type reported in a few existing studies demonstrates temperature dependence similar to cubanes case. For the complexes under study the observed tendency is opposite: the LE band strongly dominates at low temperature whereas at RT the HE/LE ratio intensity increases. To understand the origin of the above non-typical thermal sensitivity of two emission bands, the quantum chemical computations have been undertaken.

Two lowest triplet excited states, T₁ and T₂, have been found. The symmetrical computed geometries of Cu₄I₄ core in T₂ state are characterized by almost equal Cu-Cu distances. In T₁ state all four Cu-Cu distances are essentially different. According to computations the highest occupied molecular orbitals (HOMO) for both T₁ and T₂ states are located at metal-halide core and the lowest unoccupied molecular orbitals (LUMO) are contributed by pyridyl moieties. Thus, one can conclude that both bands are of ³(X+M)LCT character unlike to previous interpretations of dual emission origins of cubane-like and octahedral complexes.

Obtained in this work results demonstrate the alternative interpretation of LE band for octahedral Cu₄I₄ complexes, which should be taken into account.

The emission spectra were registered on the equipment of the Center for Optical and Laser Materials Research of St. Petersburg State University

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[3+2] Cycloaddition of the nitrilimines and thiosulfines as effective atom-economic way for C-C, C-O and C-S bonds formation

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Five-membered heterocyclic compounds are the base for huge amount of the bioactive substances. In particular, derivatives of the diazoles obtain the antiseptic, analgesic, anticancer and psychotropic activities. Some oxadiazoles contained two nitrogen atoms and oxygen atom in five-membered cycle are perspective hypnotic drugs. Derivatives of the 1,2-dithioles, for example Oltipraz, are characterized by high anticancer activity.

Effective atom-economic way for synthesis of the five-membered 1,2-diazoles and 1,2-dithioles is [3+2] cycloaddition (1,3-dipolar cycloaddition) (Fig. 1).[1]

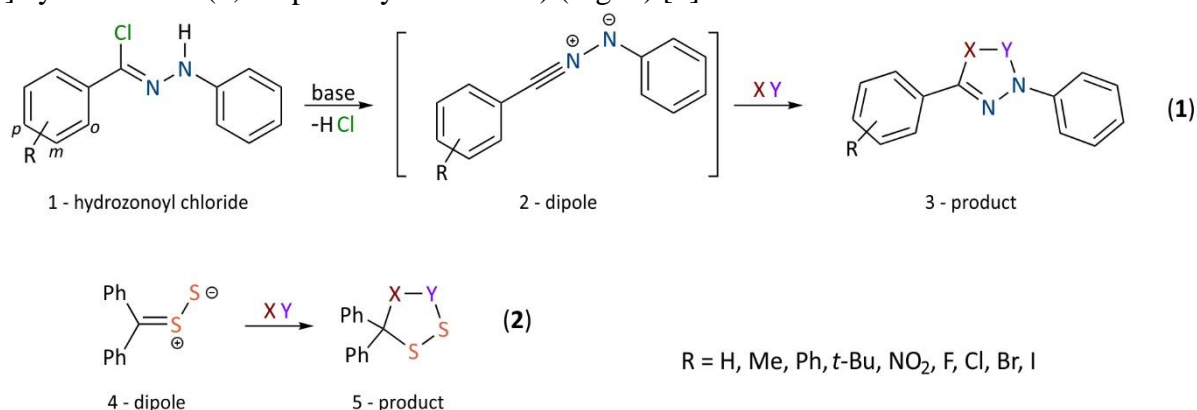


Fig. 1. Schemes of the [3+2] cycloaddition reactions for nitrilimines with various substituents (1) and thiosulfines (2); XY is an alkyne, alkene, ketone or thioketone molecule.

The mechanism of the reactions (1) and (2) was investigated by wB97X-D/6-311G(d,p) method (SMD model for chloroform media). It was shown that activation energy of the acetylene addition to 2-dipole (reaction 1) systematically higher for dipoles with *ortho*-position of the substituent R, and exergonic effect of the [3+2] addition stage for *ortho*-substituted dipoles is smallest. However, the activation energies for the *ortho*-, *meta*-, and *para*-positions of the substituent R differ insignificantly.

The mechanism of the reactions (1) and (2) was studied for various XY substrates: acetylene, ethylene, 2-methylpropene, acetone, thioacetone, thiobenzophenone. It was established that addition of these XY substrates may occur in mild conditions and characterized by high exergonic effect.

Based on analysis of the electron localization function (ELF) and bond orders in the transition states of the [3+2] cycloaddition stage it was shown that addition of acetylene and ethylene molecules to the 2-dipole (reaction 1) is characterized by asynchronous bonds formation, whereas addition of the acetone and thioacetone is synchronous process, i.e. C-O (C-S) and C-C bonds of the five-membered cycle in 3-product are formed simultaneously.

For reaction (2) acetylene and ethylene addition is synchronous reaction, but addition of thiobenzophenone is very asynchronous due to steric effects from two Ph-groups.

This work was supported by RFBR (project № 17-03-01148).

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Born-Oppenheimer molecular dynamics reveals the origin of calixarene selectivity to cesium cations

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Solvent extraction and separation techniques are widely used to decrease the amount of the radioactive wastes, especially radioactive cesium isotopes presented in the liquid phases. Calixarenes are known to be good candidates for the selective extraction of the heavy alkali metal cations with the selectivity coefficient of around 1000 to Cs^+ . The molecular mechanism of selectivity remains unknown. We performed Born-Oppenheimer molecular dynamic (MD) simulations of the complexes of calixarene with the alkali cations (Li^+ , Na^+ , K^+ , Rb^+ and Cs^+) in water solution. The model system comprised 291 water molecules, calixarene with one deprotonated OH group and metal cation, all together 929 atoms. This system was treated at the DFT/PBE-D3/DZVP-MOLOPT-GTH level of theory in the CP2K program package. We performed sets of MD simulations with the biasing harmonic potentials centered at different values of the reaction coordinate. The latter was chosen as the distance between the metal cation and oxygen atom of the phenolate group of calixarene. Weighted histogram analysis method as well as umbrella integration approach were applied to reconstruct free energy profiles and calculate corresponding dissociation constants for all complexes. We got the values of around 10^{-2} M for Li^+ , Na^+ and K^+ whereas the dissociation constants for Rb^+ and Cs^+ were 10^{-5} M and $6 \cdot 10^{-6}$ M, respectively. These computational results explain the experimental observations and reveal the molecular mechanism of complex formation.

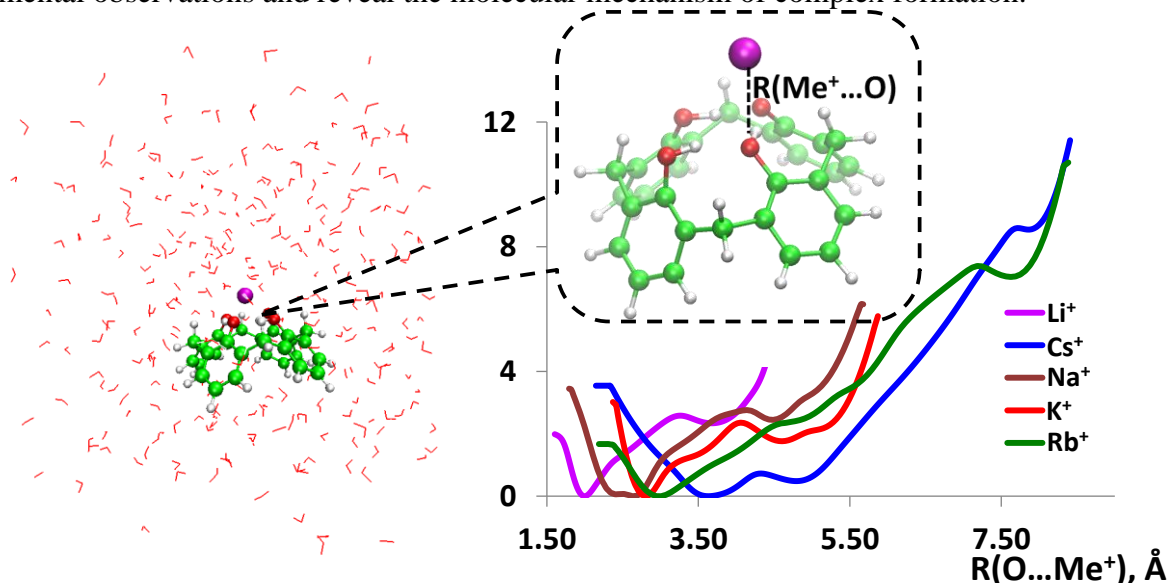


Fig. 1. Free energy profiles of calixarene – alkali metal complex formation

This work was supported by Russian Foundation for Basic Research (project № 18-03-00605).

Вязкость расплава кобальта: теория, моделирование и эксперимент

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Представлены результаты теоретического и численного исследования вязкости расплава кобальта в температурном диапазоне $T=[1400; 2000]$ К. Получены теоретические выражения для спектральной плотности временной корреляционной функции тензора напряжений и сдвиговой вязкости, определяемые через частотные релаксационные параметры. Установлено хорошее согласие результатов теоретических расчетов для температурной зависимости вязкости расплава кобальта с экспериментальными данными и результатами моделирования атомарной динамики.

Введение. Транспортные процессы играют важную роль во многих природных и технических процессах. Так, например, коэффициенты самодиффузии и вязкости являются ключевыми величинами при исследовании фазовых переходов, в частности, процессов стеклообразования и кристаллизации. По сравнению с коэффициентом самодиффузии, который достаточно трудно экспериментально измерить точно, коэффициент сдвиговой вязкости может быть непосредственно определен в экспериментах по вискозиметрии. С другой стороны, вязкость может быть рассчитана с помощью моделирования равновесной и неравновесной молекулярной динамики. Вязкость является одной из простейших транспортных характеристик, которая с одной стороны, связана с микроскопической коллективной динамикой частиц в системе через временную корреляционную функцию поперечного потока, а с другой стороны, связана со временем структурной релаксации системы через известное соотношение Максвелла.

Детали моделирования. Моделирование динамики атомов расплава кобальта было выполнено в изотермически-изобарическом (NpT) – ансамбле в температурном диапазоне $T=[1400; 2000]$ К при давлении $p=1.5$ бар. Система состояла из $N=4000$ атомов, находящихся в кубической ячейке с периодическими граничными условиями. Взаимодействие между атомами учитывалось через EAM-потенциал [1]. Переохлажденный расплав кобальта (при $T < T_m$, где $T_m=1768$ К) был получен быстрым охлаждением равновесного расплава (при температуре $T=2000$ К) со скоростью охлаждения $\gamma = 10^{12}$ К/сек [2]. Интегрирование уравнений движений было выполнено по схеме Верле в скоростной форме с временным шагом $\tau = 10^{-15}$ с [3]. Для приведения системы в состояние термодинамического равновесия и расчета спектральных характеристик при каждой температуре $T=[1400 \div 2000]$ К было выполнено 100000 и 5000000 временных шагов соответственно.

Результаты и выводы. Для проверки корректности потенциала межчастичного взаимодействия [1] в воспроизведении структурных и динамических свойств расплава кобальта были рассчитаны радиальная функция распределения атомов $g(r)$ и статический структурный фактор $S(k)$. На рис. 1 представлены рассчитанные с помощью атомарной/молекулярной динамики функции $g(r)$ и $S(k)$ в сравнении с экспериментальными данными по дифракции рентгеновских лучей [4]. Из рисунка видно, что результаты моделирования находятся в хорошем согласии с экспериментальными данными: верно воспроизводят как интенсивности, так и положения пиков в функции радиального распределения и статическом структурном факторе.

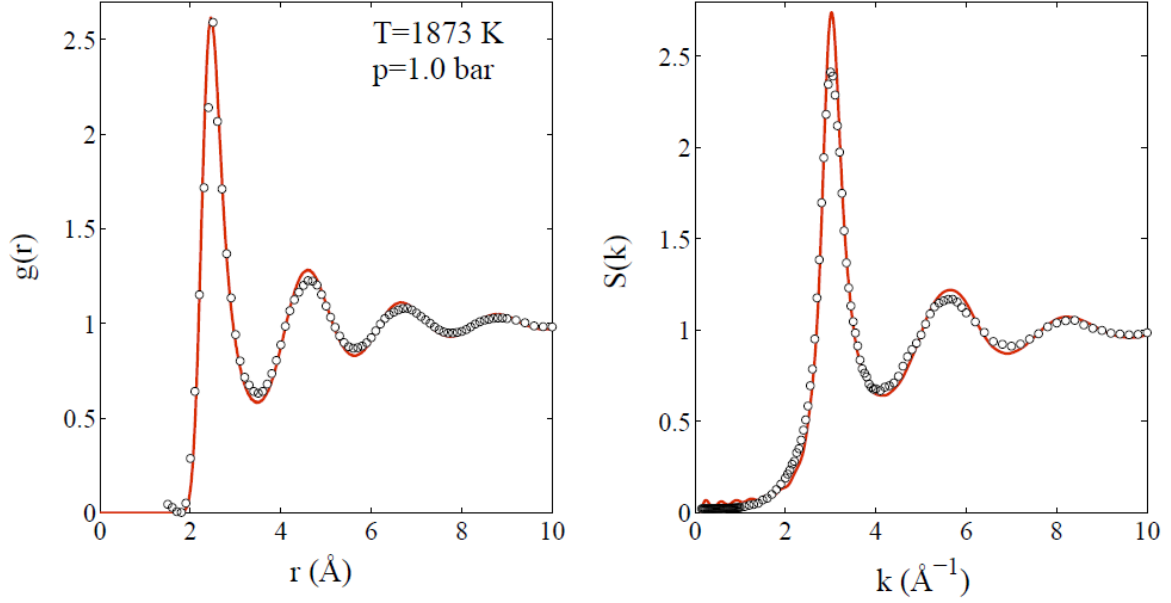


Рис. 1. (Левая колонка): Радиальная функция распределения атомов кобальта при температуре $T=1873$ К. (Правая колонка): Статический структурный фактор. Сплошная линия представляет результаты моделирования атомарной/молекулярной динамики; (o o o) - экспериментальные данные по дифракции рентгеновских лучей [4].

Сдвиговая вязкость расплава кобальта рассчитывалась с помощью соотношения Кубо-Грина [5]

$$\eta = \frac{V}{k_B T} \int_0^{\infty} S(t) dt. \quad (1)$$

Здесь $S(t) = \langle \sigma_{\alpha\beta}(0), \sigma_{\alpha\beta}(t) \rangle$ есть временная корреляционная функция (ВКФ) тензора напряжений, V и T - соответственно объем и температура системы, k_B - постоянная Больцмана. Коротковременное разложение $S(t)$ может быть представлено в виде

$$S(t) = 1 - S^{(2)} \frac{t^2}{2!} + S^{(4)} \frac{t^4}{4!} - S^{(6)} \frac{t^6}{6!} + \dots \quad (2)$$

Здесь $S^{(2m)}$ – четные частотные моменты

$$S^{(2m)} = \frac{\int \omega^{2m} \tilde{S}(\omega) d\omega}{\int \tilde{S}(\omega) d\omega}, \quad m = 1, 2, \dots \quad (3)$$

спектральной плотности ВКФ тензора напряжений

$$\tilde{S}(\omega) = \frac{1}{2\pi} \operatorname{Re} \int_{-\infty}^{\infty} \exp(i\omega t) S(t) dt. \quad (4)$$

С другой стороны, спектральная плотность ВКФ тензора напряжений $\tilde{S}(\omega)$ может быть представлена в виде

$$\tilde{S}(\omega) = \frac{S(t=0)}{\pi} \operatorname{Re} \left\{ \frac{1}{-i\omega + \Delta_1 \tilde{M}_1(\omega)} \right\}, \quad (5)$$

где $\tilde{M}_1(\omega)$ – есть спектральная плотность так называемой функции памяти первого порядка, которая связана с функциями памяти старших порядков $\tilde{M}_n(\omega)$ при $n > 1$ рекуррентным соотношением

$$\tilde{M}_n(\omega) = \frac{1}{-i\omega + \Delta_{n+1} \tilde{M}_{n+1}(\omega)}, \quad (6)$$

Δ_n – есть частотные параметры, которые выражаются через спектральные моменты $S^{(2m)}$, $n, m=1, 2, \dots$:

$$\Delta_1 = S^{(2)}, \quad \Delta_2 = \frac{S^{(4)}}{S^{(2)}} - S^{(2)}, \quad \Delta_3 = \frac{S^{(6)}S^{(2)} - S^{(4)^2}}{S^{(4)}S^{(2)} - S^{(2)^3}}, \dots \quad (7)$$

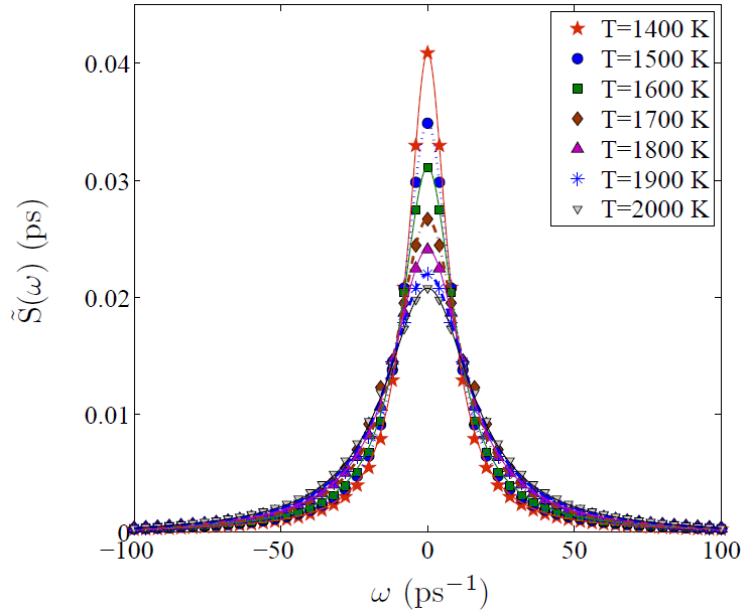


Рис. 2. Спектральная плотность ВКФ тензора напряжений расплава кобальта при различных температурах: маркеры представляют результаты моделирования; линии - результаты теоретических расчетов.

В соответствии с формулой Кубо-Грина для сдвиговой вязкости η имеем

$$\eta = \frac{V}{k_B T} \int_0^\infty S(t) dt = \frac{V}{k_B T} \tilde{S}(\omega=0). \quad (8)$$

Как было показано в работе [6], для транспортных процессов в однокомпонентных жидкостях реализуется условие вида $\tilde{M}_2(\omega) = \tilde{M}_1(\omega)$, что позволяет найти выражение для спектральной плотности $\tilde{S}(\omega)$:

$$\tilde{S}(\omega) = \frac{1}{\pi} \frac{2\Delta_1\Delta_2\sqrt{4\Delta_2 - \omega^2}}{\Delta_1^2(4\Delta_2 - \omega^2) + \omega^2(2\Delta_2 - \Delta_1)^2}. \quad (9)$$

Отсюда, получаем простое выражение для сдвиговой вязкости

$$\eta = \frac{VS_0}{\pi k_B T} \frac{\sqrt{\Delta_2}}{\Delta_1}, \quad (10)$$

которое содержит частотные параметры Δ_1 и Δ_2 , определяемые через функции распределения частиц и потенциал межчастичного взаимодействия.

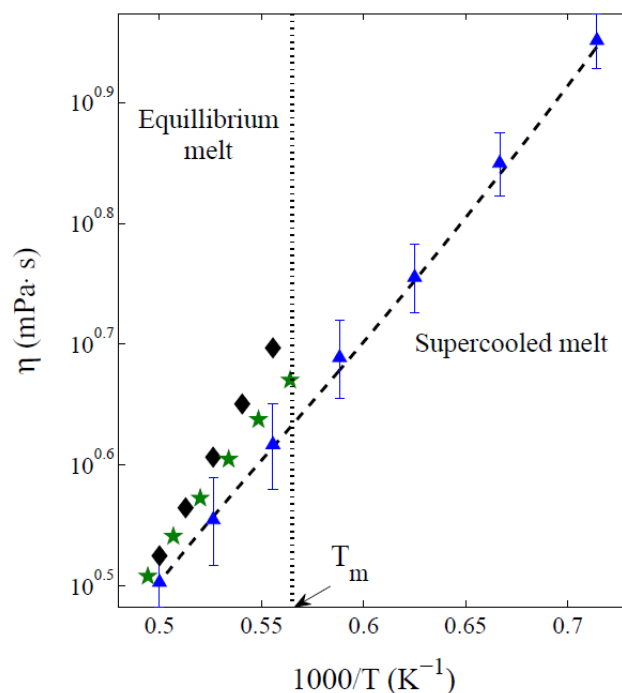


Рис. 3. Температурная зависимость сдвиговой вязкости расплава кобальта: маркеры (▲▲▲) - представляют результаты моделирования атомарной/молекулярной динамики; (◇◇◇) и (звездочки) - экспериментальные данные, взятые соответственно из [7] и [8]; штриховая линия - результаты теоретических расчетов [выражение (10)].

На рис. 3 представлены результаты моделирования и теоретических расчетов для температурной зависимости сдвиговой вязкости расплава кобальта в сравнении с экспериментальными данными [7,8]. Из рисунка видно, что результаты моделирования и теории адекватно описываются термоактивационным законом Аррениуса. Также, установлено хорошее согласие результатов теоретических расчетов для вязкости расплава кобальта с экспериментальными данными [7,8] и результатами моделирования атомарной/молекулярной динамики.

Крупномасштабные молекулярно-динамические расчеты были выполнены на вычислительном кластере Казанского федерального университета и суперкомпьютере Межведомственного Суперкомпьютерного Центра Российской Академии Наук. Работа выполнена при финансовой поддержке гранта РФФИ (№ 18-02-00407_a).

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Modeling of the structure of lead-containing ferroelectrics-relaxors at low temperatures

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The ferroelectric relaxors, whose properties were discovered more than fifty years ago, are now actively used for the needs of electronics. A wide range of physical properties makes the problem of correlating the structural features of these compounds with the observed and predicted functional properties relevant. Ferroelectric relaxors with a diffuse phase transition have a large temperature interval in which a phase transition occurs, in the consideration of which two cases are distinguished:

- the case when the anharmonicity is small and the potential $V(r)$ has one minimum;
- the case when the strongly anharmonic potential $V(r)$ is multiminimum, determines transitions of the order-disorder type with dynamic or static disordering of ions. It was established earlier that both cases of phase transitions can exist near the Curie point [1, 2].

In this paper we present data on the modeling of the structural features of the classical model object of this class of compounds-lead magnesium niobate (PMN) at temperatures of 203 K, 183 K, and 103 K.

In the case of a relaxor ferroelectric phase transition in PMN, the long-range interaction in the electronic subsystem of the crystal (reduction in the correlation interaction radius) is attenuated in the vicinity of the phase transition. This obviously can lead to a phase transition accompanied by coordinated rotations of the oxygen octahedra BO_6 ($B = Mg / Nb$). Chains ...B...O...B...O...B...O... become zigzagged. Based on the calculations of the thermal and positional parameters of the atoms of the given compound, a simulation of the behavior of sublattices of atoms of A-, B- type and oxygen in the perovskite structure at the indicated temperatures was carried out based on the experimental data of the X-ray diffraction study carried out at low temperatures.

An analysis of the results obtained by us suggests that with an approximation of the temperature values to the temperature T_m , ordering of the displacements of lead atoms in neighboring cells and associated antiparallel shifts of oxygen atoms can occur, which indicate possible rotation of oxygen octahedra. Such ordered displacements of atoms in PMN can be the reason for the appearance of superstructural reflexes, indicative of doubling the parameters of an elementary perovskite cell [3,4]. The possible mechanism of rotation of oxygen octahedra and associated displacements of lead atoms is simulated in this work. In favor of such a model, the temperature dependence of the peaks of super structure reflexes noted by many authors, whose nature is actively discussed, attests to the temperature dependence [3,4]. Various scenarios of the ordering process in the PMN are considered.

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Стабильные сайты связывания атомов в кристаллах инертного газа

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Вариативность стабильных конформаций ближайшего матричного окружения внедренного атома в матрицах инертных газов (RG) является установленным фактом многочисленных спектроскопических исследований[1]. Несмотря на то, что структура занимаемой вакансии редко может быть непосредственно установлена из эксперимента, простой эвристический подход, исходящий из сопоставления эффективных размеров полости и атома, позволяет предсказать возможные геометрии окружения примесного центра и оценить их относительную стабильность. Для ГЦК решетки кристаллических RG обычно рассматриваются 5 основных типов сайтов захвата, возникающих в результате: внедрения в тетраэдрические и октаэдрические пустоты, замещения одного атома RG, и встраивания в третра- и гексавакансию. Для атомов Yb и Mn такое интуитивное отнесение сайтов было подтверждено в рамках классической модели[2-3], которая включает в себя гибкую стратегию поиска структуры в поле кристаллической решетки и анализ термодинамической стабильности[4] методом “выпуклой оболочки”.

В данной работе похожая техника была применена к более общей проблеме, а именно к задаче отображения параметров, характеризующих взаимодействие атома и матрицы, на совокупность термодинамически стабильных сайтов захвата. При этом рассмотрение было ограничено матрицей ГЦК решетки аргона. Для описания взаимодействий как между атомами аргона, так и матрицы с внедренным атомом (в S состоянии) использовались парные межатомные потенциалы Леннарда-Джонса (LJ). При каждом значении пары параметров ϵ и σ потенциала взаимодействия производился обширный поиск глобального минимума, цель которого состояла в определении всех структур минимальной энергии для ряда систем с различными значениями числа удаленных атомов аргона $N = 0, 1, \dots$, замещаемых атомом внедрения. Концепция метода выпуклой оболочки для параметра “фазового состава” N затем использовалась при идентификации структур стабильных сайтов. Схожесть стабильных структур, найденных при различных значениях параметров, оценивалась методами иерархической кластеризации на основе геометрических и лексикографических метрик. В результате было обнаружено пять типов внедрения, которые практически полностью исчерпывают разнообразие возможных геометрий стабильных сайтов для малых и средних энергий связи с атомами матрицы, где выбранная модель потенциалов взаимодействия имеет смысл.

В конечном итоге, области стабильности каждого типа связывания были представлены на двумерной карте LJ параметров (ϵ , σ). Полученная карта позволяет качественно предсказывать геометрии стабильных сайтов захвата любого атома в S состоянии, для которого известен потенциал взаимодействия с атомами матрицы. Достоверность таких предсказаний была проверена сравнением с результатами для атомов H, Na, Mn, Ba, Eu и Yb, полученными на основе более сложных и затратных моделей или косвенно из экспериментальных данных.

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Correlations of Particle Motion in Supercooled Liquids

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This work considers the changes of transport coefficients, structure and correlations in particle motion in the metallic melts during the cooling from above the melting temperature to metastable state. The dynamics of the changes in correlation properties got extra attention. In particular, we studied the autocorrelation functions (ACFs) of shear stresses in a thin film, that define the shear viscosity of a liquid, and the correlations between the displacements of particles in the melt. The study is conducted for aluminum and copper melts using molecular dynamics method with many-body embedded atom method potentials.

At cooling of the thin film of aluminum melt below 600 K, the following changes are observed: (a) The growth of the dispersion of ACFs, which hints at the growing degree of inequilibrium; (b) oscillations in the shear stress ACFs in the planes normal to the film plane, which is an evidence of the transversal sound; (c) slowing down of the shear stress relaxation which is an evidence of the viscosity increase. All those changes happen in the same narrow temperature range.

Thus, we have obtained a direct evidence that the melt goes from quasi-equilibrium (metastable) to non-equilibrium state at high-speed cooling. We associate this transition with the glass transition. The transition temperature (i.e. the midpoint of the transition interval) increases with the increasing cooling rate which is also characteristic to the glass transition and not to the phase transitions.

The study of the correlations between displacements of atoms shows peculiar behavior of the $CC(t)$ function, which is the cosine between displacements of neighboring particles in the time t . At the temperatures above the equilibrium melting temperatures, the correlation function remains at virtually the same value, while it starts to grow when the melt transitions into the metastable region. That means that the motions of the neighboring particles are more correlated in the supercooled liquids than they are in the stable liquids. Thus, while the thermodynamic properties change smoothly at the transition to the metastable state, the kinetic properties, and correlation function in particular, may exhibit observable qualitative changes.

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Environment Effects on the Optical Properties of a Rhodamine Heterodimer-DNA Supramolecular Complex: A computational and Experimental Study

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Weakly bound homo- and heterodimers of organic chromophores serve as building blocks for electron/energy transfer in biological structures, amorphous organic semiconductor films and solar cells. In these multi-chromophoric systems optical properties are governed by the distance and relative orientation of the photoactive units. The inherent rigidity of the environment confines the system conformational space and consequently controls their vibronic profiles. Using molecular dynamics sampling we computationally investigate the effect of a restricted conformational space on the absorption lineshape of a weakly bound rhodamine heterodimer tethered on a DNA scaffold. The absorption profiles are compared with experimental spectra and with the spectra computed for π -stacking conformations of the bare dimers in solution. A substantial increase in the intensity of the initially low-intense S_0 - S_1 transition of the bare dimers is explained by the local character of the excitation in the conformationally restricted supramolecular hetero dimer-DNA complexes. Explicit sampling of the relative orientations of monomers provides an absorption lineshape which is in good agreement with the experimental spectrum.

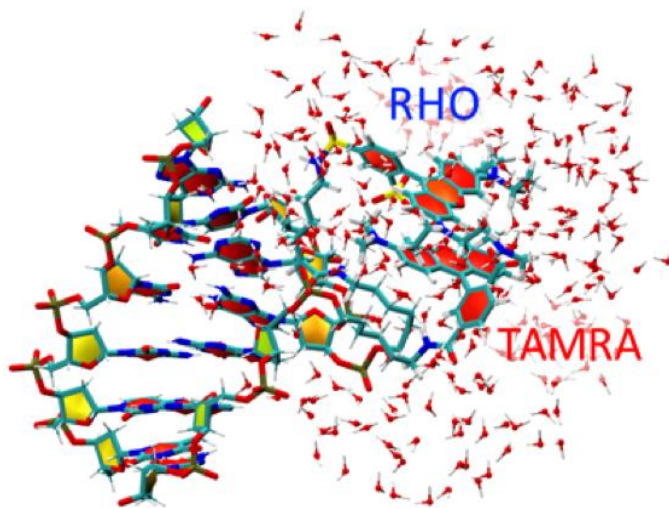


Fig 1. Rhodamine heterodimer tethered on a DNA scaffold

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“Side” conformers of some adamantane derivatives: DFT and Multi-reference insights

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The compounds from the diamondoids family (including adamantane as a simple diamondoid) and their derivatives have long been known as the best candidates for drug design, drug delivery, drug targeting etc.[1]. The incorporation of an adamantyl moiety into organic compounds changes their biological activities due to increase of the lipophilicity, which is promoting transport through biological membranes. Recently[2] we have shown that for *N'*-(adamantan-2-ylidene)benzohydrazide besides two “regular” *trans*- and *cis*-conformers (for C=O and N–H bonds) in solutions can exist two “side” *trans*-conformers, which correspond to left and right positions of the adamantyl moiety relatively molecular “frame” (i.e. rotation around N–N bond).

In this study, the structures of four adamantane derivatives, namely *N'*-(adamantan-2-ylidene)-R-hydrazides, where R = thiophene-2-carbo-, benzo-, adamantane-carbo-, and isonicotino-, have been obtained at DFT level of theory (B3LYP/cc-pVTZ) calculations. All of them demonstrate existence of four stable conformers (one *cis*- and three *trans*-). It is worth mentioning that “side” conformers are typical only for adamantane-containing compounds, because calculations of the model structures without adamantyl group did not confirm the stability of the “side” conformers.

Then *ab initio* multi-reference SA-CASSCF/XMCQDPT2[3] calculations for all conformers of all compounds were performed. The “side” conformers exhibit the more long-wave $S_1 \leftarrow S_0$ transitions than “central” ones. The differences in the values of the excitation energy for the “side” and “central” conformers may be caused by different positions of the adamantyl moiety relative to the molecular “frame”, leading to the differences in the values of the transition moments and their orientations relative to the molecular coordinate axes. Such regularities find confirmation in the UV/Vis spectra of the solutions of compounds under consideration in ethanol.

In continuation to our interest in the pharmacological and structural properties of the adamantane derivatives, the coexistence of all conformers should be taken into consideration when studying the pharmaceutical properties of such compounds and it may be useful in medicinal chemistry and for a drugs design.

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Nonlinear optical properties of mixed oxides crystals CsNbMoO₆ and CsTaMoO₆

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Materials with non-linear optical (NLO) properties underlie today many modern technologies, including those for creating tunable lasers, optoelectronic devices and information transmission and storage systems. Inorganic NLO crystals are especially promising for such a purpose because of their resistance to high-energy radiation beams. Among such crystals, the defective pyrochlores based on mixed oxides of MoO₃, Ta₂O₅, Cs₂O, Nb₂O₅ seems to be auspicious and were synthesized recently¹. However, the difficulty in studying of NLO properties for many inorganic compounds is the possibility of variation in the chemical composition and appearance of disordered configurations of the atomic structure, leading to a large number of crystalline modifications for the same stoichiometry. In this case, the important problem is a rapid theoretical screening of the properties of possible crystal structures. It can be solved by quantum-chemical calculations within the framework of various approximations. One of such approximations is the periodic coupled-perturbed Hartree-Fock (Kohn-Sham within DFT formalism) method CPHF/KS which was recently implemented in CRYSTAL program². In the present study, we assess the NLO properties of defective pyrochlore crystals CsNbMoO₆ CsTaMoO₆ by CPHF/KS method using HF and DFT/PBE0 formalism within two basis sets. Additionally, the crystals of KH₂PO₄ (KDP), LiNbO₃, (NH₂)₂CO (urea), and α -SiO₂ were evaluated as a benchmark compounds with reliable experimental data. The aim of the study is the evaluation of the ability of theoretical methods for calculating SHG activity by comparing the calculated and experimental NLO properties of test compounds and, on this basis, characterizing nonlinear optical properties of the crystals of defective pyrochlores, the experimental determination of which is difficult. Additionally, we studied the influence of the statistical disorder arising due to the different occupations of d-metal sublattice positions by atoms Mo or Nb(Ta) on the NLO properties. We calculated the linear optical properties (refractive indices and linear polarizabilities) and nonlinear ones (first hyperpolarizabilities and nonlinear optical tensors) for different isomers CsNbMoO₆ and CsTaMoO₆ on different levels of theory and compared them with the calculated and experimental data of benchmark compounds. We found that the best agreement of the calculated nonlinear optical parameters with experiment is achieved at the DFT/PBE0 level in the POB-TZVP basis. Significant improvement in the agreement between the calculated quantities and the experimental data takes place when the dimensionless relative NLO activity $\rho = \eta_i / \eta_X$ is used (here, η_i is the calculated ratio of powers of the single and double frequency rays for the unknown compound, η_X is the same ratio for the reference compound). The calculated NLO characteristics of the crystals CsNbMoO₆ and CsTaMoO₆ $\rho_{\text{CsNbMoO}_6/\text{LiNbO}_3} = 0.0161$ and $\rho_{\text{CsTaMoO}_6/\text{LiNbO}_3} = 0.0219$, $\rho_{\text{CsNbMoO}_6/\text{KDP}} = 0.3869$ and $\rho_{\text{CsTaMoO}_6/\text{KDP}} = 0.5249$. The symmetry of the sublattices of disordered atoms significantly affects the SHG parameters of the crystal and the values of the calculated parameters for sublattices of different symmetry can differ by an order of magnitude.

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Conditions for exciting soliton-type waves in A_3B stoichiometry crystals

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In work by method of molecular dynamics process of excitement of soliton-type waves and her distribution on a crystal of stoichiometric structure of A_3B is studied. Solitons are capable to move on crystals to considerable distances without change of a form and speed of the movement. This fact stimulates interest in such objects from a position of search of mechanisms of their excitement and studying of their properties.

Modeling is carried out with use of a package of molecular dynamics of LAMMPS[1]. As the potential of interatomic interaction the potential received by method of the embedded atom offered Zhou[2] was used.

Modeling of excitement of solitonic waves is closely connected with a concept of the nonlinear supratransmission[3] caused by external influence at frequencies outside of a phonon range of a crystal. The defining factor in excitement of such objects is the possibility of existence of discrete breather in the considered crystals. Discrete breather accumulate energy near area of influence and at achievement of some value of amplitude let out soliton-type wave. In fig. 1 the example of distribution of waves for two crystals of structure of A_3B is given: Pt_3Al and Ni_3Al . The crystal of Ni_3Al does not support existence of discrete breather unlike Pt_3Al .

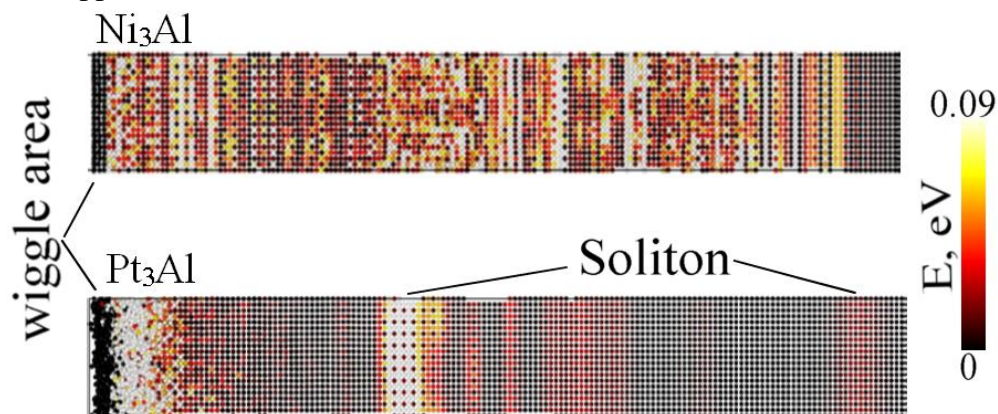


Fig. 1. Distribution of energy along model of crystals Ni_3Al and Pt_3Al

The received results demonstrate that formation of such waves is possible in crystals which are supported by slot-hole discrete breather, i.e. in this case in Pt_3Al . Waves are generated by discrete breather and extend from area of influence deep into of a crystal.

These solitary waves are capable to propagate to hundreds of nanometers without change of a form and speed. At the same time on each of atoms it can be concentrated the energy about 0.02 eV. The energy total volume transferred by a wave is defined by quantity of rows of the atoms involved in fluctuations and can be estimated at hundreds electron-volt.

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¹ LAMMPS Molecular Dynamics Simulator. URL: <http://lammps.sandia.gov/>

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Theoretical and experimental study of ground and excited state properties of the novel indolizine based chromophores

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Organic chromophores bearing donor-acceptor (D-A) topology attract considerable attention in the field of organic electronics acting as functional layers in dye-sensitized solar cells (DSCs), bulk heterojunction solar cells (BHJ), light-emitting diodes (OLED), non-linear optical materials (NLO) etc. To satisfy the general requirements for such materials the chromophores should possess a number of important characteristics: favorable electron energy levels arrangement, photo/thermal-stability, electro-chemical reversibility, broad and intensive absorption in the respective spectral region.

Frequently, strongly electron-deficient motifs result in too stabilized excited-state oxidation potentials preventing the successful electron injection and rendering these chromophores nonfunctional. Moreover, the search for stronger organic electron-donor materials matching well with the common electron acceptor motifs is ongoing. Commonly used arylamine or indoline donors are not the ideal systems since the electron donation strength is mitigated by many factors, one of those is nonoptimal nitrogen lone pair orbital alignment relative to π -conjugated system of chromophores due to sterical hindrances. At the same time indolizine shows an ideal planar nitrogen-substituent arrangement together with the opportunity of its nitrogen lone pairs to donate either into the 6- or 5-member ring and to productively deliver the donated electron. Limited reports including the red-NIR luminescent properties and DSCs characteristics of the indolizine-based systems have been described to date[1][2]. In the current work ground and excited state properties of the series of novel recently synthesized indolizine based derivatives[3] have been studied both experimentally and theoretically with the use of time-dependent density functional theory (TD-DFT). Namely, the electronic absorption/emission energies have been calculated for both the ground and excited states on relaxed geometries. Chosen computational approaches allow reliable interpretation and predictions of the important properties opening perspectives for the rational design of the novel systems toward the applications in organic electronics.

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Энергия образования Н-комплексов 4-фенилазофенола и 4-фенилазобензойной кислоты

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В современной химии наблюдается устойчивая тенденция перехода от традиционного молекулярного конструирования к супрамолекулярной химии как химии программируемых высокоселективных нековалентных взаимодействий, в которых особую роль играет водородная связь (ВС).

В данной работе исследовано строение молекулярных комплексов, связанных посредством водородной связи (Н-комплексов), между 4-фенилазофенолом (А) и 4-фенилазобензойной кислотой (В) методом DFT с функционалом B97D и базисным набором 6-311++G** (программа Gaussian09).

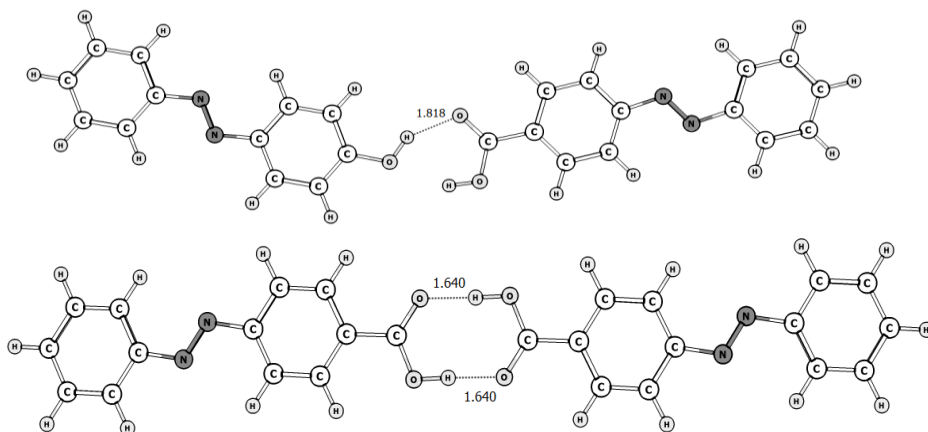


Рис.1. Геометрическое строение комплексов А••В и В••В

В обоих комплексах возникает по две межмолекулярные ВС, при чем в А атом кислорода является одновременно и донором и акцептором ВС.

Энергия комплексообразования определялась как разность полных электронных энергий участников процесса, соответствующих оптимизированным геометрическим параметрам молекул и составила для комплекса А••В – 10.0 ккал/моль, а для комплекса В••В – 17.1 ккал/моль. Также, оба комплекса имеют стержнеобразное строение и обладают наибольшей поляризуемостью ($\alpha_{xx} = 951.5$ и 891.3) в направлении директора x , а наименьшей ($\alpha_{zz} = 178.6$ и 173.3) в направлении перпендикулярном плоскости системы.

Рассмотренные структуры благодаря анизотропии электронных и геометрических параметров способны к проявлению жидкокристаллических свойств.

Работа выполнена при финансовой поддержке Министерства науки и образования РФ (4.7121.2017/8.9)

Молекулярная структура и ароматичность тиадiazол-аннелированного гетероазапорфириноида $C_{30}N_{15}H_{15}S_3$

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Изучены 17 возможных таутомеров тиадiazол-аннелированного гетероазапорфириноида $C_{30}N_{15}H_{15}S_3$ (рис. 1), отличающихся расположением трех протонов внутри координационной полости. Относительные энергии таутомеров вычислены в приближении B3LYP/pcseg-2. Минимуму энергии отвечает структура, в которой атомы Н принадлежат изоиндольному фрагменту (рис. 1). Остальные таутомеры имеют существенно (> 45 кДж/моль) большую энергию по сравнению с основным.

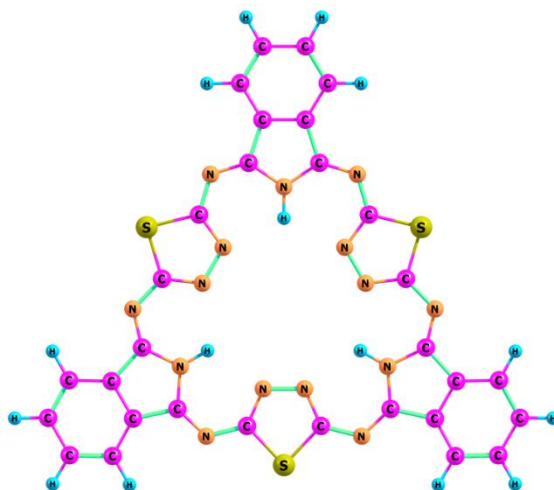


Рис. 1. Модель молекулы $C_{30}N_{15}H_{15}S_3$.

Ароматичность исследуемого макроцикла была оценена с помощью традиционных критериев NICS(1), HOMA, а также с использованием индекса FLU, рассчитанного в рамках формализма теории QTAIM[1]. Положительное значение NICS(1), рассчитанное в точке, находящейся на 1 Å выше центра макроцикла (+0.83 ppm) указывает на его неароматический характер. Напротив, величина критерия HOMA (0.864), рассчитанного для внутреннего контура макроцикла свидетельствует о его ароматических свойствах. Значение индекса FLU = 0.022 коррелирует с величиной HOMA и также подтверждает ароматичность макроциклической системы.

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Квантово–химическое моделирование покрывающих агентов квантовых точек селенида кадмия

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В настоящее время электронные и оптоэлектронные устройства на основе полупроводниковых квантовых точек привлекают широкий круг исследователей из самых разных областей науки. Особые физико-химические свойства квантовых точек обуславливают перспективность их дальнейшего изучения и применения в современной технике. Квантово-химическое моделирование свойств подобных объектов позволяет определить оптимальные условия их создания, объяснить экспериментальные данные и изучить преимущества и недостатки создаваемых на их основе материалов до проведения их синтеза. В настоящей работе была проведена разработка подходов к теоретическому моделированию физико-химических свойств квантовых точек селенида кадмия и некоторых широко используемых при синтезе квантовых точек покрывающих агентов (олеиновая кислота, триоктилфосфиноксид, гексадециламин, 1-октантиол и др.). С использованием метода теории функционала плотности проведено моделирование строения и физико-химических свойств квантовых точек селенида кадмия, строения и ИК-спектров покрывающих агентов. Произведен расчет энергии связи между покрывающими агентами и квантовыми точками, проведено моделирование диаграмм распределения электронной плотности и рассчитаны значения ширины запрещенной зоны. На основе данных квантово-химических расчетов установлено влияние природы покрывающих агентов на свойства квантовых точек, эффективность их излучения и перспективность использования в оптоэлектронике. Установлено, что заключение изученных квантовых точек CdSe в оболочку из гексадециламина позволит добиться хорошей стабилизации размера и свойств квантовых точек и высокого квантового выхода излучения. Полученные по результатам моделирования данные близки к экспериментальным.

Квантово-химические расчеты были проведены с использованием суперкомпьютеров МВС-10П и МВС-100К «Межведомственного суперкомпьютерного центра РАН» и вычислительных ресурсов системы «Ломоносов» суперкомпьютерного комплекса МГУ имени М.В. Ломоносова. Работа выполнена при финансовой поддержке Российского научного фонда, проект № 18-73-00100.