Alexander Bagaturyants, Michael Alfimov TNT2011

Atomistic Multiscale Simulation of Nanostructured Materials for Photonic Applications

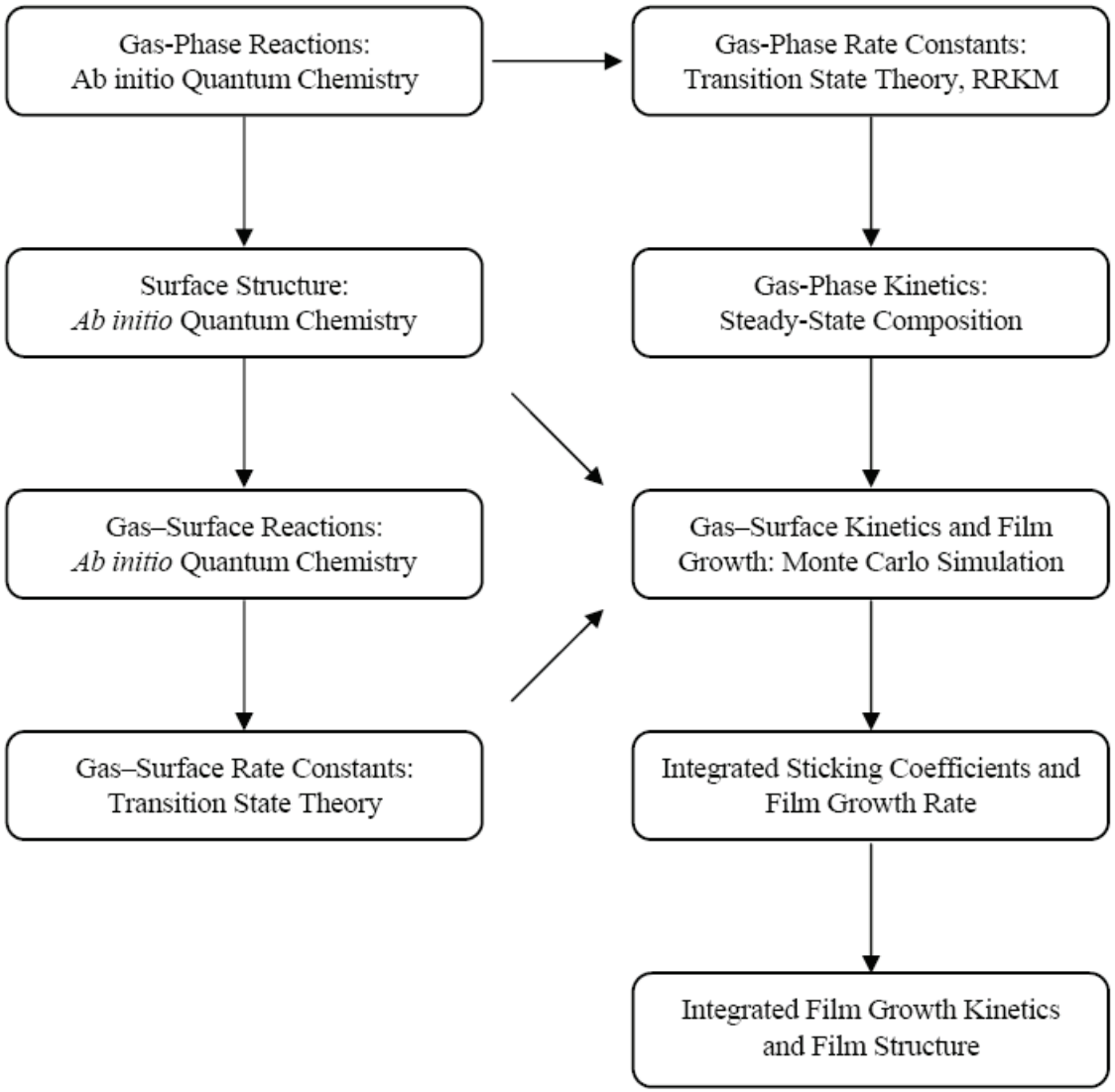
Paul Gauguin. Where Do we come from? Who are we? Where are we going?

Where Do we come from? Who are we? Where are we going?

Paradigm Change: From understanding the nature of chemical bond to predicting the molecular structure and properties and to predicting the structure and properties of materials

- The formation of materials (deposition and growth of thin films and nanoparticles)
- The structure and properties of materials
- The structure of a hierarchically designed material exhibits several levels of organization: atomic-molecular (1–2 nm), supramolecular (2–10 nm), nanosized (10–100 nm), and microscopic (100–1000 and more nm).
  1. Methods: quantum chemistry for molecular structure and properties and for gas-phase and surface reactions;
  2. Methods: molecular dynamics for microstructure and fast growth processes
  3. Methods: Kinetic Monte Carlo for rare events (chemical reactions)
  4. Methods: band structure (plane-wave) slab calculations for surfaces and interfaces

Where Do we come from? Multiscale simulation of semiconductor film deposition and growth



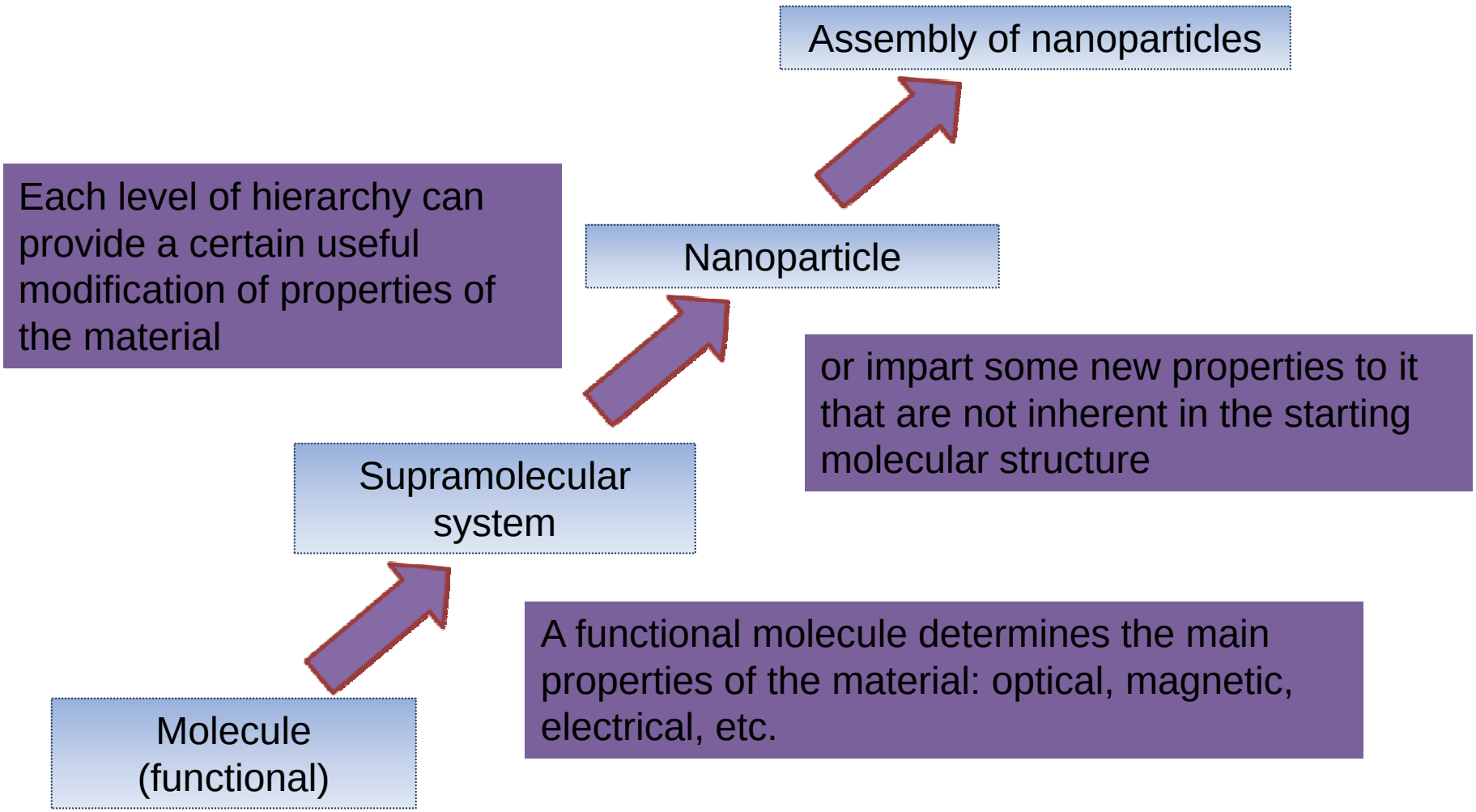
A.A. Knizhnik, A.A. Bagaturyants, I.V. Belov, B.V. Potapkin, A.A. Korkin, Comput. Mater. Sci., 2002, vol. 24, no. 1-2, pp. 128-132.

A.A. Bagatur'yants, A.A. Korkin, K.P. Novoselov, L.L. Savchenko, S.Ya. Umanskii, in Computational Materials Science, IOS Press, Amsterdam, Eds: C.R.A. Catlow and E. Kotomin, 2003, pp. 388-418.

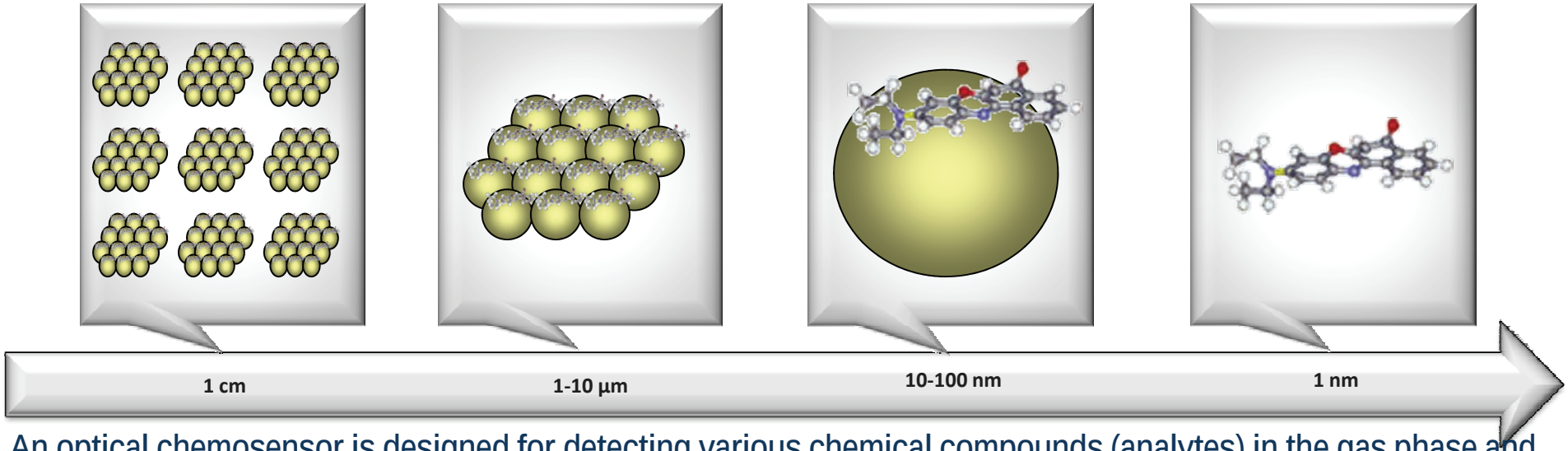
A.A. Bagatur'yants, A.Kh. Minushev, K.P. Novoselov, A.A. Safonov, S.Ya. Umanskii, A.S. Vladimirov, A. Korkin, in Springer Series in Materials Science, Vol. 72, Dabrowski, J. and Weber, E.R. (Eds.), Springer Verlag, 2004, pp. 295-356.

A.A. Bagatur'yants, M.A. Deminskii, A.A. Knizhnik, B.V. Potapkin, S.Ya. Umanskii, in Thin Films and Nanostructures: Physico–Chemical Phenomena in Thin Films and at Solid Surfaces, L. I. Trakhtenberg, S. H. Lin, O. J. Ilegbusi, eds., Elsevier (2007) 468–522.

Who are we? Hierarchically designed nanostructured materials



Who are we? Material for optical chemical sensing as an example of hierarchically designed nanostructured material



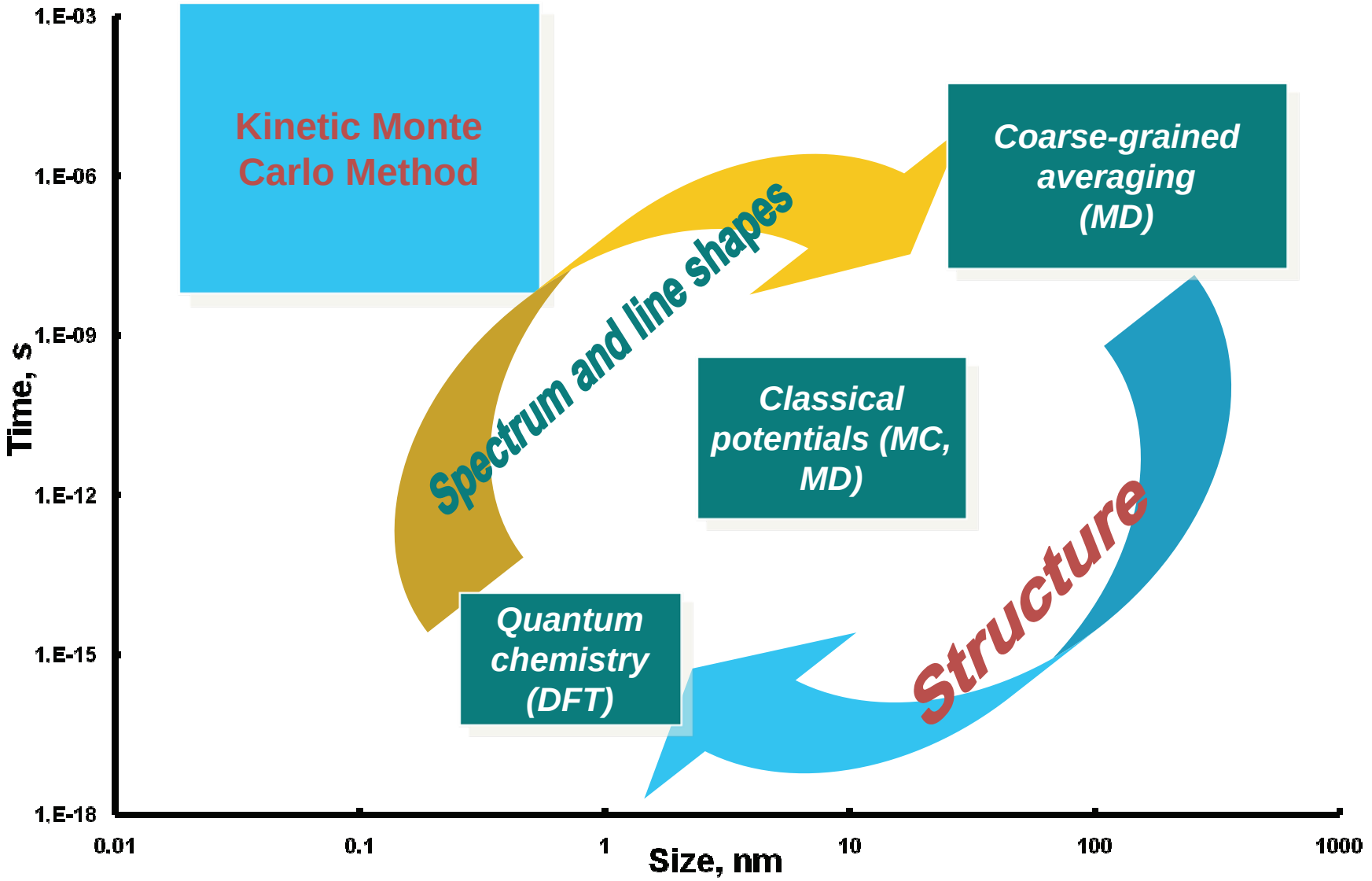
An optical chemosensor is designed for detecting various chemical compounds (analytes) in the gas phase and represents a hierarchically organized array of sensing elements constructed from various sensor materials.

An organic “indicator molecule” (IM) is in the basis of the construction of a sensing material and is responsible for the generation of an optical signal on its interaction with an analyte.

IM along with its local environment forms a “receptor center” (RC). The local environment can be selected so that the signal can be enhanced and its selectivity can be improved.

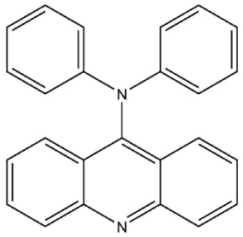
RC are arranged on the surface or in the particle bulk (nanoparticles) and the nanoparticles themselves are assembled in an organized structure (which may, for example, exhibit properties of a photonic crystal.

Who are we?: Multiscale approach in atomistic simulation of hierarchically designed nanostructured material

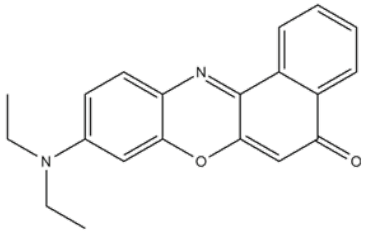


Who are we? Models and methods

Dye as a functional molecule, silica (SiO2) and polystyrene (PS) as substrates:



9-(Diphenylamino)acridine = DPAA

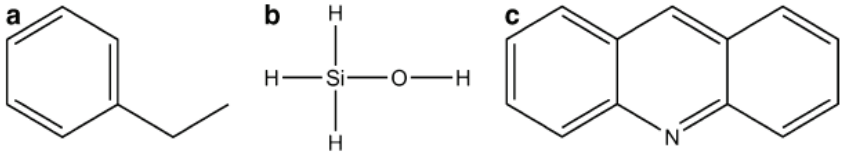


Nile Red = NR

Two systems were considered: DPAA/SiO2 and NR/PS

1. The structure of the substrates was amorphized by classical molecular dynamics (MD) simulations. Silica was heated to 6000 K for 7 ps, and then the temperature was consecutively decreased to 4000, 2000, 1000, and 300 K at simulation times of 7, 7, 17, and 17 ps, respectively. PS was heated to 500 K, thermalized for a few nanoseconds and then cooled to 298 K. Empirical potentials by Feuston and Garofalini were used for modeling amorphous silica, while the OPLS-aa force field was used for polystyrene.
2. Quantum-mechanical cluster was cut off from the simulated amorphous structure, and dangling bonds were saturated with H atoms.
3. QM calculations were performed mostly using DFT-D approximation for the ground states and TDDFT for the excited states. Various exchange-correlation potentials (PBE, PBE0, B3LYP, etc.) and various basis sets of double-zeta and triple-zeta quality supplemented with polarization functions were used in the QM calculations.
4. Band shapes were calculated using the Pekar approximation (S.I. Pekar, 1953)

Who are we? Calculations of molecular interactions between analyte molecules and simple substrate models by a DFT-D method



Ethylbenzene (a) and silanol (b) served as models of polystyrene and silica substrates.
Acridine (c) served as a model of an acridine dye

Formaldehyde, acetaldehyde, ammonia, methylamine, methanol, ethanol, acetone, benzene, acetonitrile, ethyl acetate, chloroform, and tetrahydrofuran were considered as gas-phase analytes.

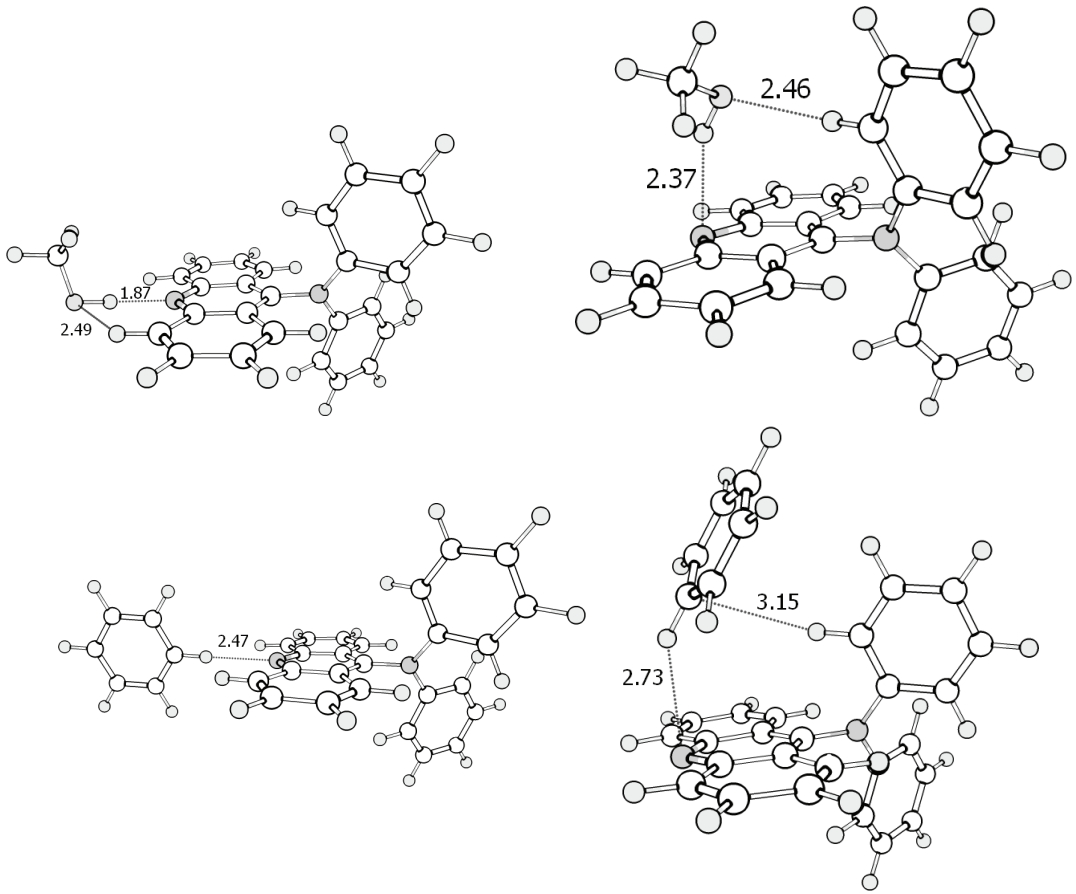
The calculated interaction energies indicate that the dyes of the acridine series adsorbed on a polystyrene or silica substrate are not promising indicator molecules for acetone and acetonitrile.

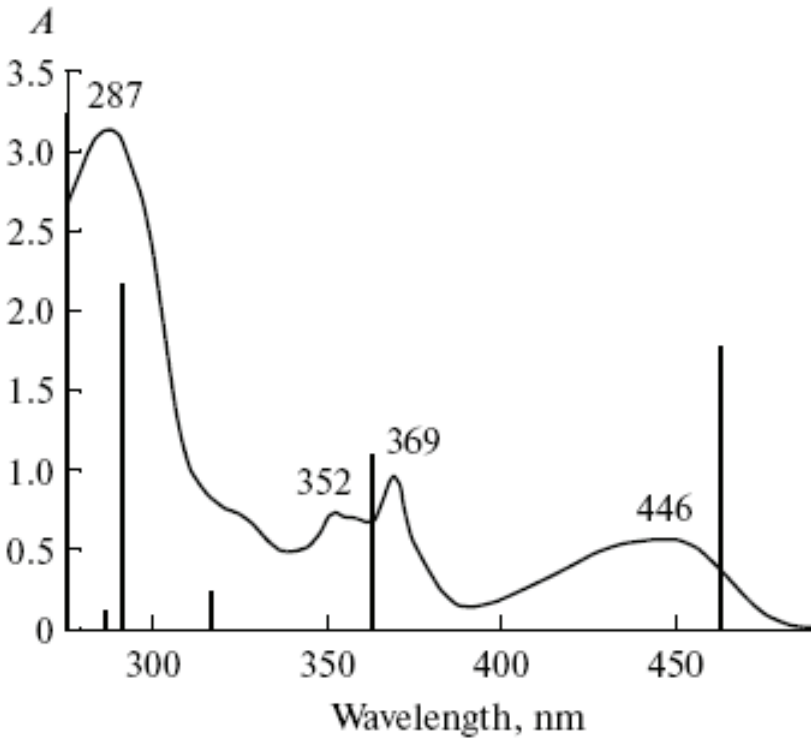
For all other analyte molecules, polystyrene can be considered a suitable substrate for an acridine dye indicator.

Finally, silica might be considered a suitable substrate for the detection of methanol, ethanol, benzene, ethyl acetate, and chloroform using an acridine dye as a molecular sensor.

A.A. Safonov, E.A. Rykova, A.A. Bagaturyants, V.A. Sazhnikov, M.V. Alfimov, Atomistic simulations of materials for optical chemical sensors: DFT-D calculations of molecular interactions between gas-phase analyte molecules and simple substrate models, J. Mol. Mod., (2011) 17:1855–1862.

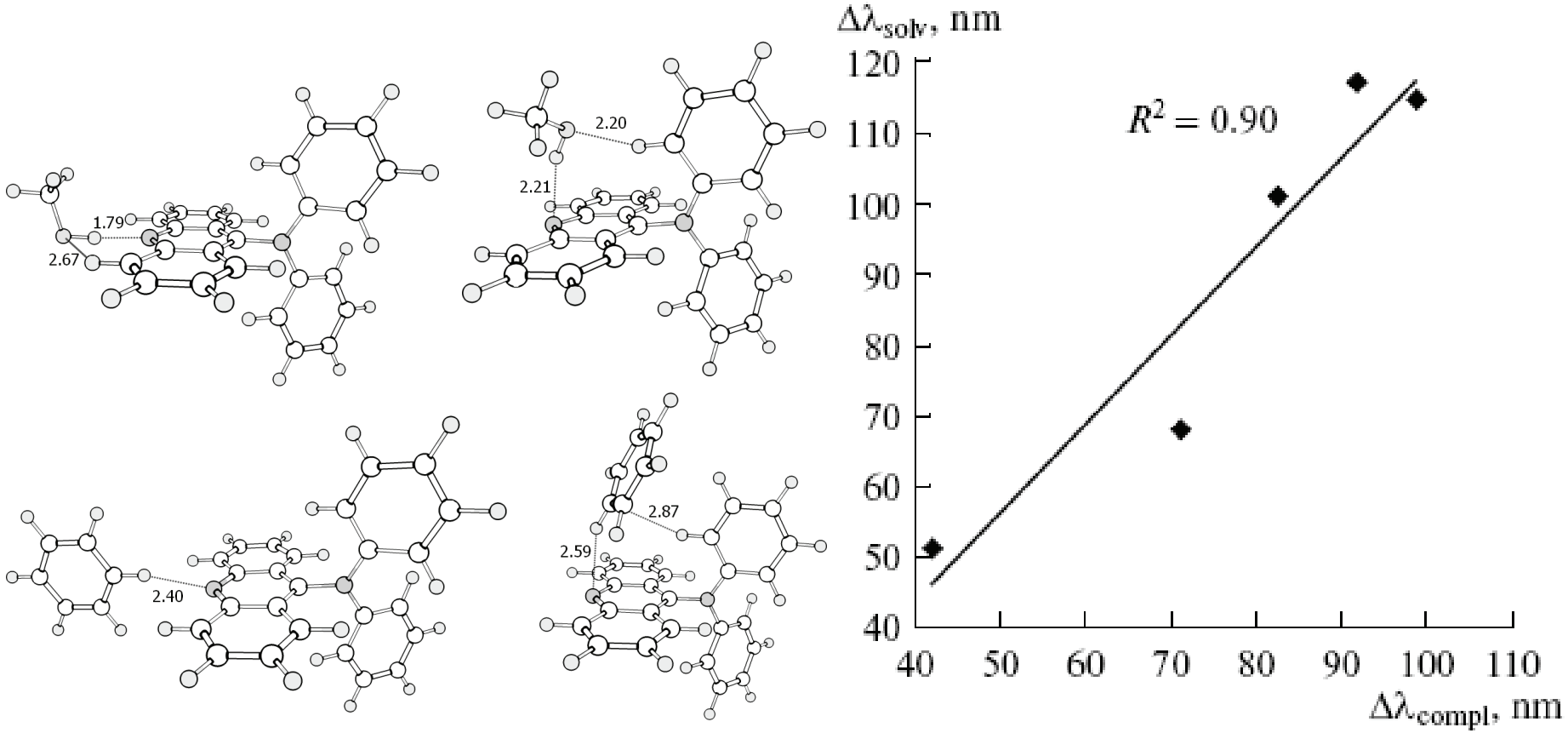
Who are we? Calculations of molecular interactions between analyte molecules and an indicator molecule: Two types of diphenylaminoacridine (DPAA) complexes





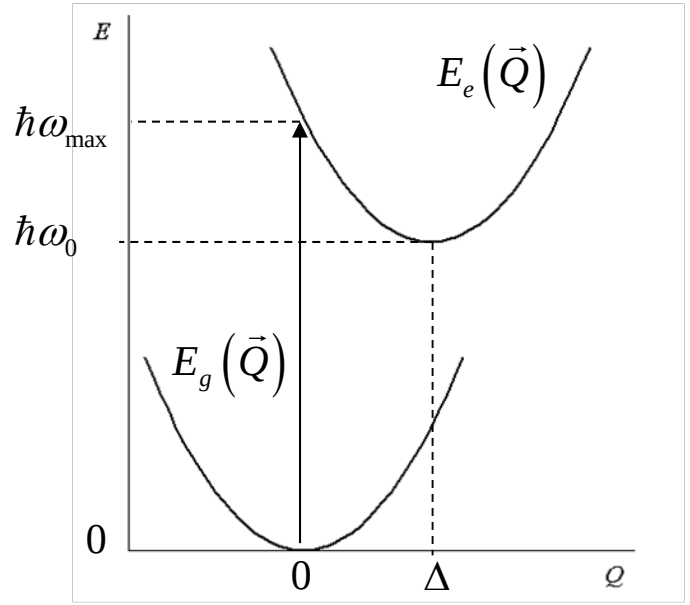
A. A. Safonov, A. A. Bagaturyants, V. A. Sazhnikov, and M. V. Alfimov, “Density Functional Calculations of 9-Diphenylaminoacridine Fluorescent Indicator and Its Interactions with Analyte Molecules: I. Structures of Complexes in the Ground Electronic States and Absorption Spectra,” High Energy Chemistry, 2011, Vol. 45, No. 3, pp. 229–236

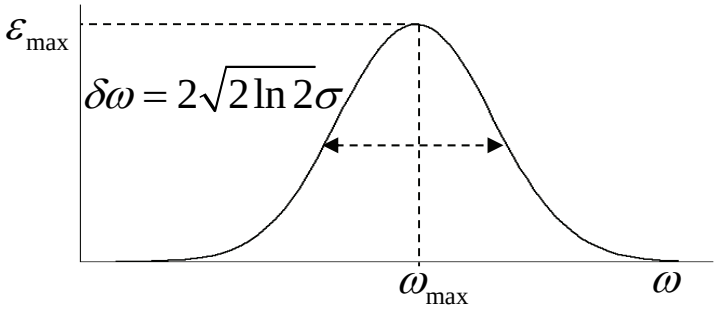
Who are we? Molecular interactions between analyte molecules and a DPAA indicator molecule: Structure of complexes in the excited state and emission spectra



Correlation between calculated band shifts for stacking complexes and experimental shifts of DTAA fluorescence bands in corresponding solutions. A. A. Safonov, A. A. Bagaturyants, V. A. Sazhnikov, and M. V. Alfimov, “Density Functional Calculations of 9-Diphenylaminoacridine Fluorescent Indicator and Its Interactions with Analyte Molecules: II. Structures of Complexes in the Excited Electronic States and Emission Spectra” High Energy Chemistry, 2011, Vol. 45, No. 4, pp. 265–272

Who are we? Modeling of vibronic bands





Simple harmonic model of two potential surfaces

$$E_e(\vec{Q}) = \hbar\omega_0 + \frac{1}{2}\sum_x \hbar\omega_x (Q_x - \Delta_x)^2$$

$$E_g(\vec{Q}) = \frac{1}{2}\sum_x \hbar\omega_x Q_x^2$$

Gaussian shape of an electronic transition band (S.I. Pekar, 1953):

$$\alpha(\omega) \propto |\mathbf{M}|^2 \omega \exp\left\{-\frac{(\omega-\omega_{max})^2}{2\sigma^2}\right\}$$

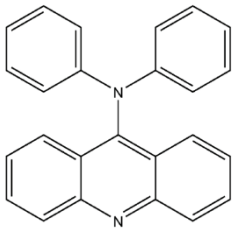
$$\sigma^2 = \sum_x \Delta_x^2 \omega_x^2 \left(\overline{n_x} + 1/2\right)$$

$$\overline{n_x} = \left[\exp\left(\hbar\omega_x / kT\right) - 1\right]^{-1}$$

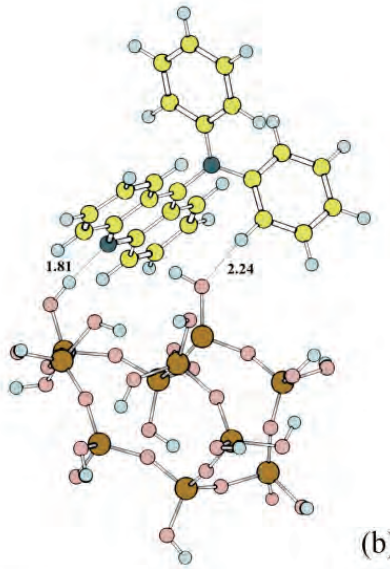
Parameters ω_{max}, Δ_x, ω_x, and $|\mathbf{M}|$ can be estimated by quantum-chemical methods

V. Chashchikhin, E. Rykova, A. Scherbinin, A. Bagaturyants, M. Alfimov, to be published

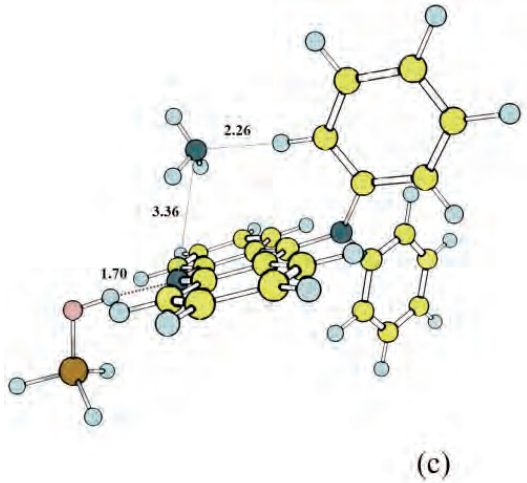
Who are we? Modeling of a 9-DPAA/silica gel receptor center



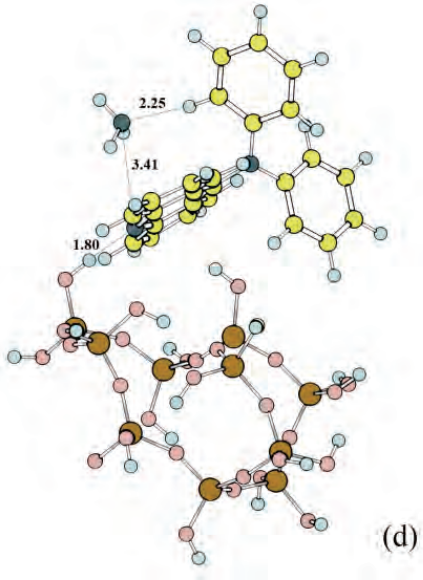
(a)



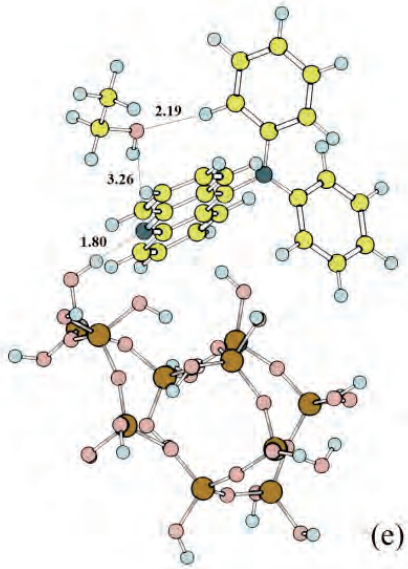
(b)



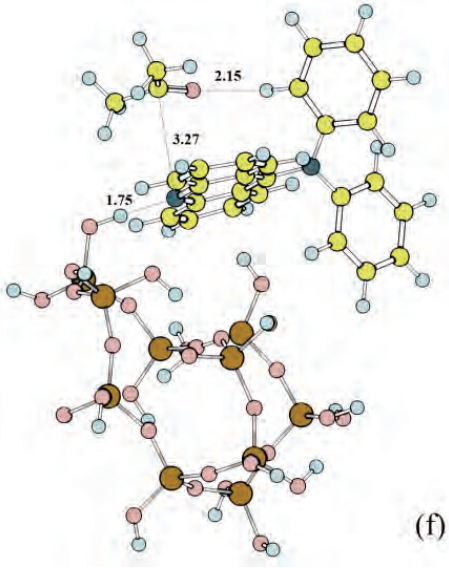
(c)



(d)



(e)

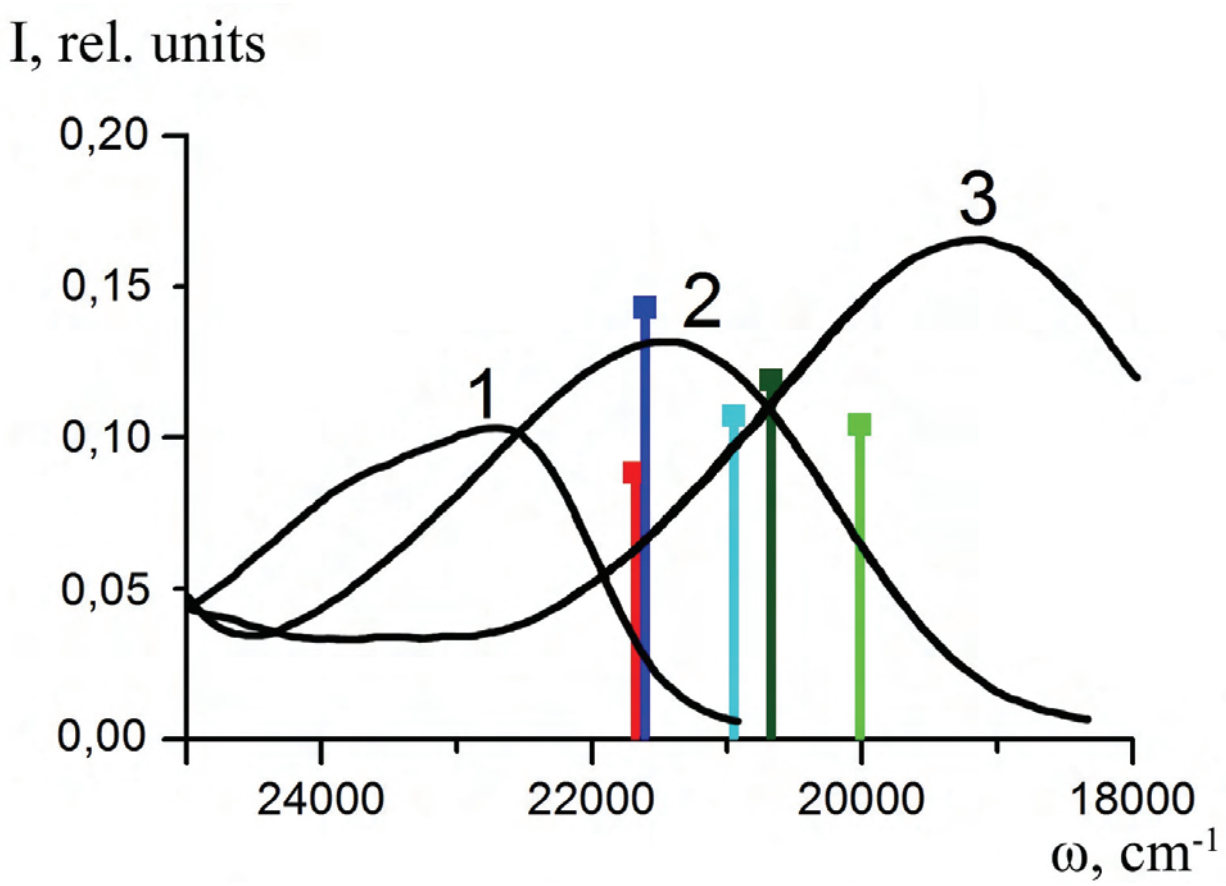


(f)

(a) 9-DPAA and optimised structures of complexes
(b) DPAA–Si10,
(c) NH3–DPAA–Si1,
(d) NH3–DPAA–Si10,
(e) C2H5OH–DPAA–Si10,
(f) (CH3)2CO–DPAA–Si10.

Silicon atoms are given by brown circles; oxygen, by pink; hydrogen, by blue; carbon, by yellow; and nitrogen, by sea-green circles.

Who are we? Modeling of a 9-DPAA/silica gel receptor center

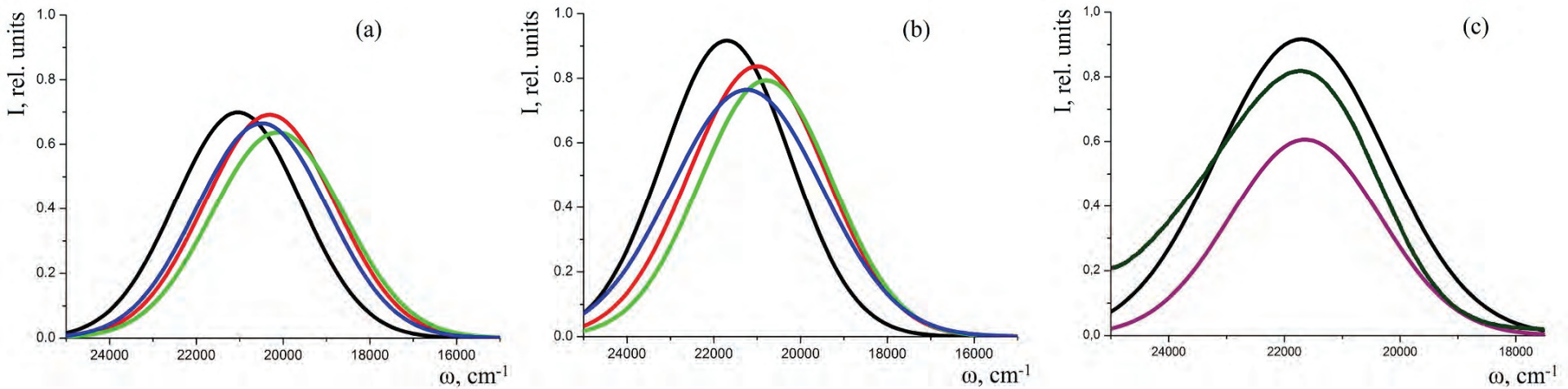


Calculated (TDDFT, PBE0/6-31G(d,p)) vertical electronic absorption spectrum of isolated DPAA molecule (red line), DPAA–Si1 complex (green line), and DPAA–Si10 complex (blue line).

Experimental absorption spectra of DPAA in (1) pentane, (2) methanol, and (3) protonated DPAA in methanol.

The experimental spectra are scaled in proportion to the oscillator strengths of the first absorption band

Who are we? Complexes of 9-DPAA/silica gel receptor center with analytes



Band shapes calculated using the Pekar model for complexes

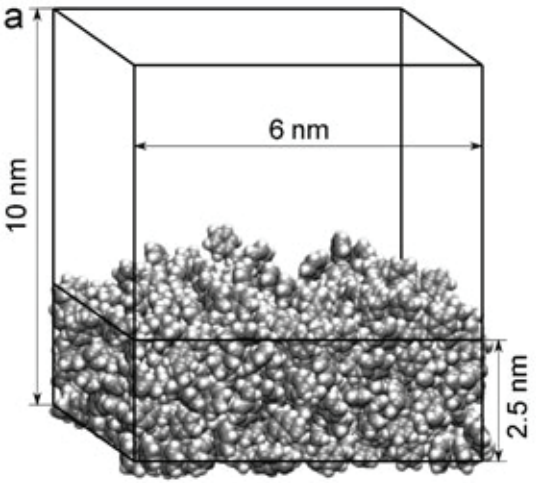
(a) analyte–DPAA–Si1

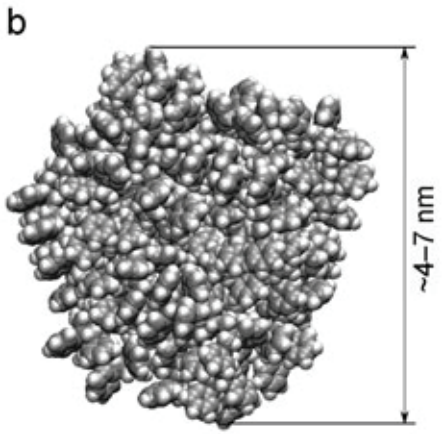
(b) analyte–DPAA–Si10 (black line, adsorbed dye; red line, complex with ammonia; green line, complex with ethanol; blue line, complex with acetone)

(c) experimental spectrum of DPAA solution in methanol (dark green line) and calculated spectra of isolated DPAA (violet line) and DPAA–Si10 complex (black line).

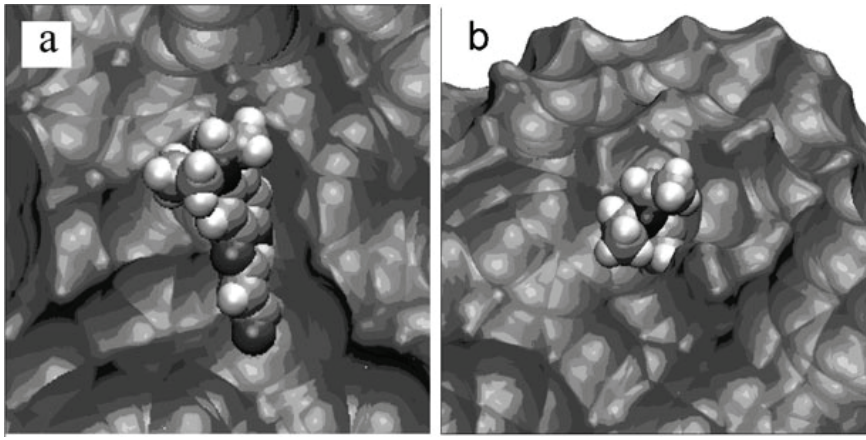
V. Chashchikhin, E. Rykova, and A. Bagaturyants, "Density functional theory modeling of the adsorption of small analyte and indicator dye 9-(diphenylamino)acridine molecules on the surface of amorphous silica nanoparticles" Phys. Chem. Chem. Phys., 2011, 13, 1440–1447.

Who are we? Modeling of Nile Red dye adsorption on an amorphous polystyrene surface





The structures of polystyrene used as substrate for the adsorption of the dye:
(a) film, the integration cell is shown;
(b) ball, the integration cell in this case has no boundaries.

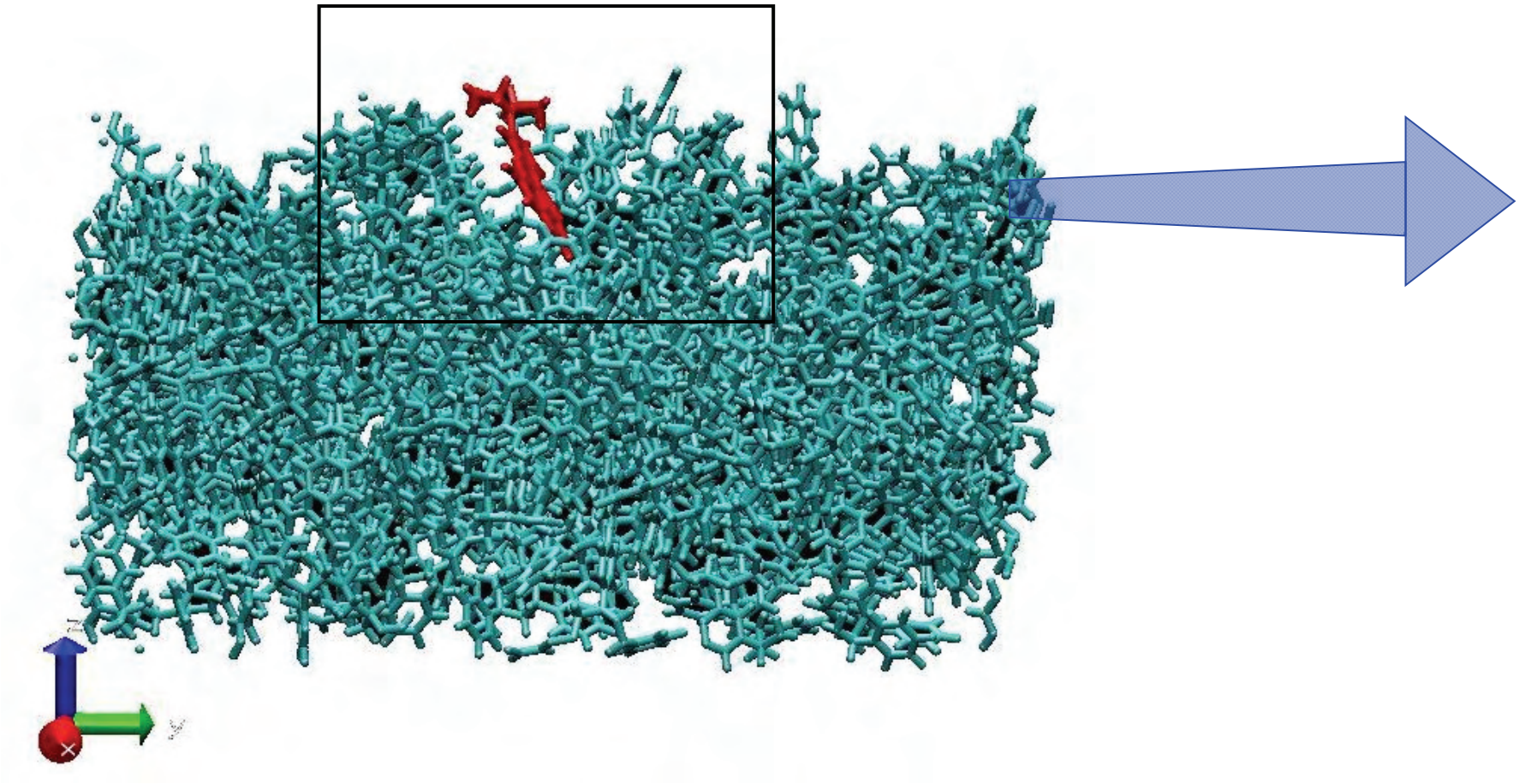


A section of the solvent-accessible surface (SAS) of polystyrene with the adsorbed dye.
Acetone was a test particle, R = 0.35 nm:
(a) film;
(b) ball, a chain of 200 monomers.

V. A. Tikhomirov, A. V. Odinokov, A. A. Bagatur'yants, M.V. Alfimov, "Modeling the Surface of Polystyrene and the Adsorption of Dye Molecules on this Surface," Theor. Experim. Chemistry, v. 46 (6), 342-349, 2011.

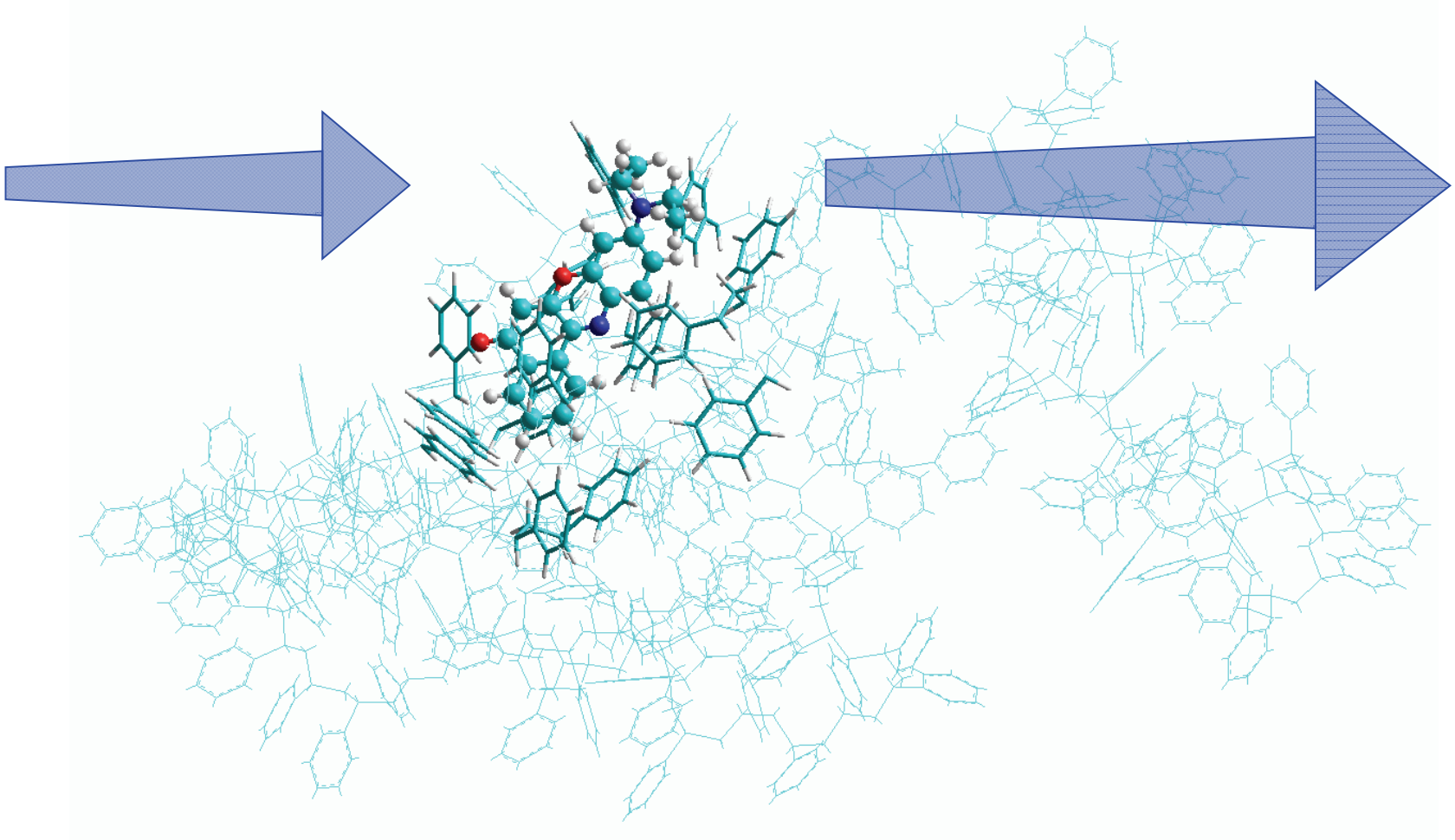
Who are we? Multiscale simulation of sensing material properties. Molecular dynamics

Adsorption of the Nile Red dye on polystyrene: MD trajectories at room temperature. The dye molecule is placed in a cavity on the polystyrene surface.

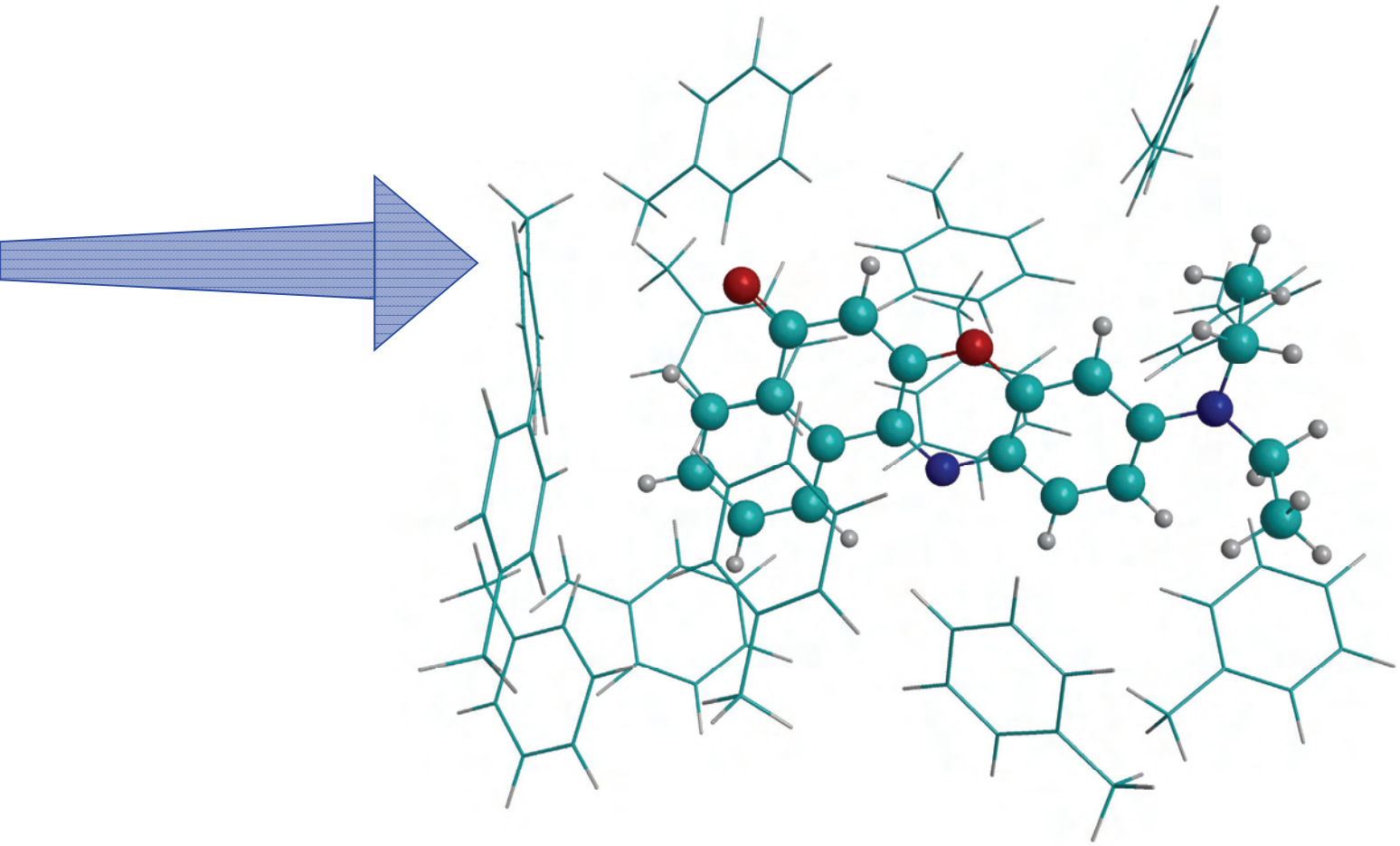


WHO ARE WE? MULTISCALE SIMULATION OF SENSING MATERIAL PROPERTIES: CONSTRUCTION OF A QUANTUM-MECHANICAL CLUSTER

A small fragment containing only nearest phenyl rings (shown in thick lines) was cut off from a large NR+PS cluster obtained by MD simulations.

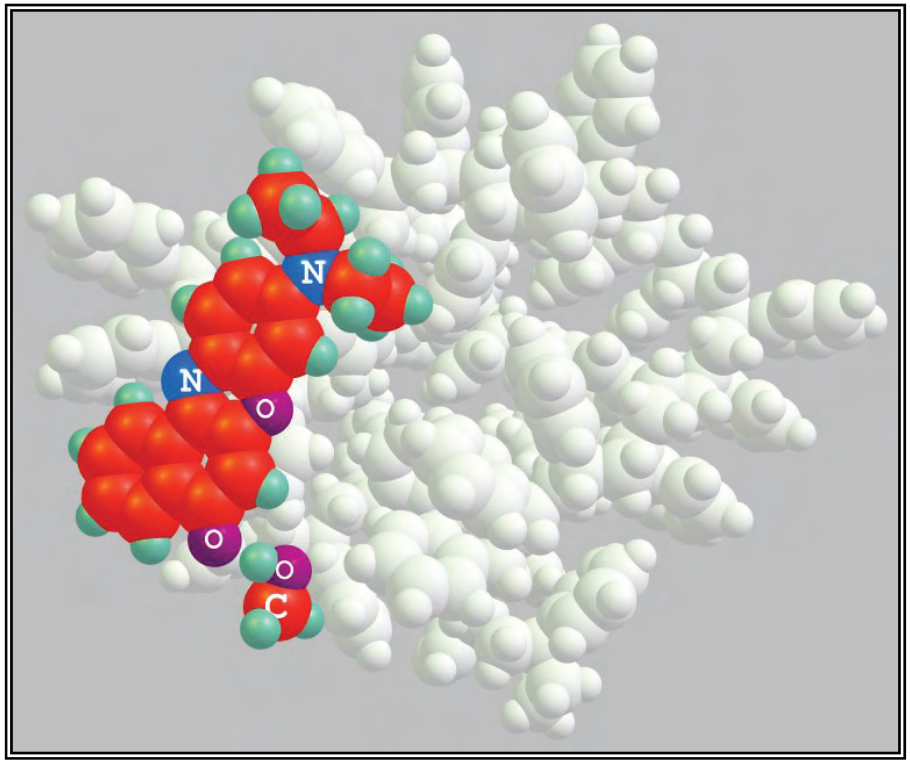


Who are we? Quantum-chemical modeling of dye properties with regard to environment (TDDFT)

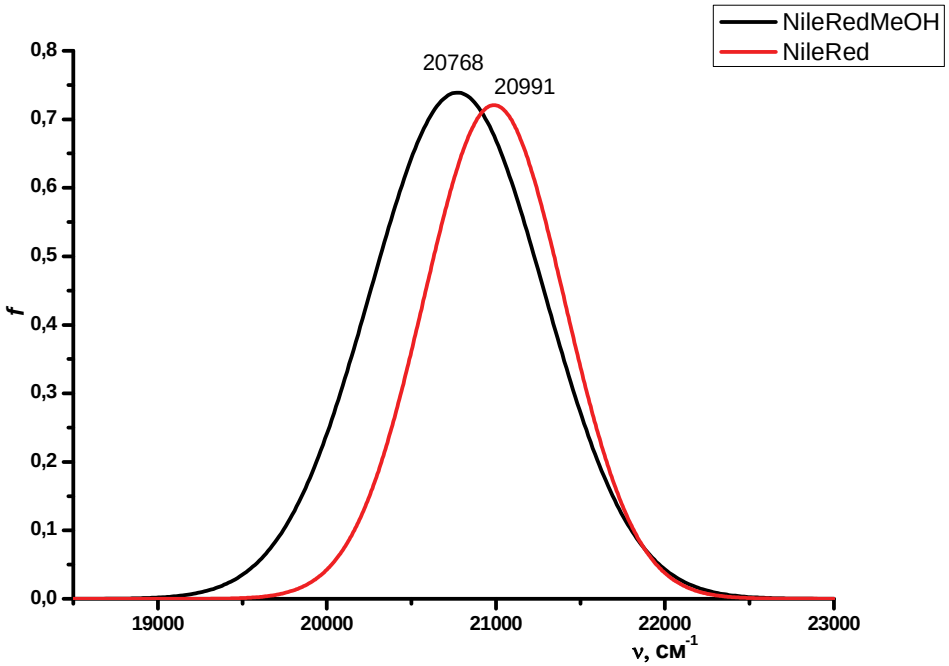


Who are we? Interaction of Nile Red dye on a polystyrene surface with small molecules

Search for the global minimum in the system using a genetic algorithm for the determination of the most stable configuration of a 1:1 complex between a small molecule and the Nile Red



Formation of a dye complex with methanol on a polystyrene surface, E_b = 9.7 kcal/mol



Luminescence band shift due to the formation of a dye complex with methanol D = 223 cm^{-1}

WHO ARE WE? CONCLUSION: A METHODOLOGY IS DEVELOPED FOR PREDICTIVE MODELING OF MATERIALS FOR OPTICAL CHEMICAL SENSORS

- **M.V. Alfimov, A.A. Bagatur'yants, A.A. Safonov, A.V. Scherbinin, K.G. Vladimirova, S.A. Belousov, M.V. Bogdanova, I.A. Valuev, A.V. Deinega, Yu.E. Lozovik, B.V. Potapkin**, Multiscale Computer Design of Photonic Crystal Based Materials for Optical Chemosensors, Nanotechnologies in Russia, 2010, Vol. 5, Nos. 3–4, pp. 250–258.

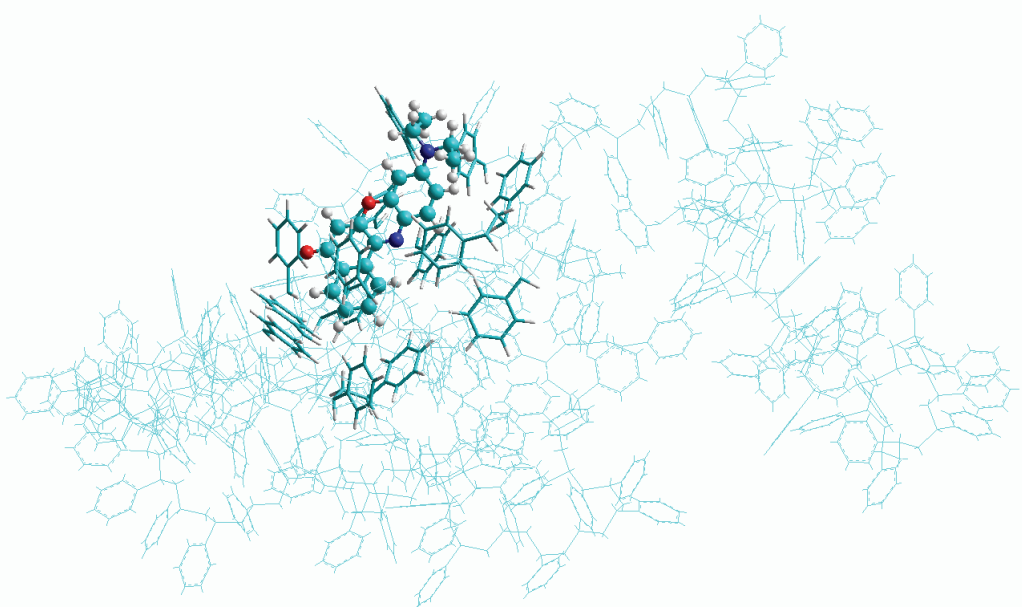
- **F.V. Grigor'ev, A.N. Romanov, D.N. Laikov, S.N. Zhabin, A.Yu. Golovacheva, I.V. Oferkin, A.V. Sulimov, M.V. Bazilevskii, A.A. Bagatur'yants, V.B. Sulimov, M.V. Alfimov**, Molecular Modeling Methods for Supramolecular Complexes: A Hierarchical Approach, Nanotechnologies in Russia, 2010, Vol. 5, Nos. 5–6, pp. 290–298..

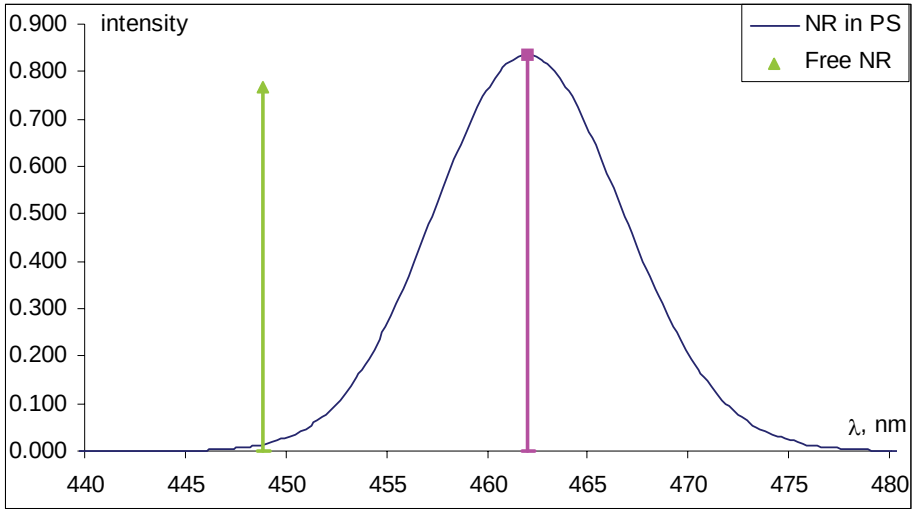
Where are we going? Quantum chemistry and atomistic simulation of materials for photonics applications (organic photovoltaic and light-emitting devices)

- Predictive simulation of the material microstructure using MD and MC methods
- Quantum-chemical calculation of electronic energy levels in a real material with regard to the calculated microstructure
- Quantum-chemical calculation of charge-transfer or excitation-transfer parameters (reorganization energy, hopping integrals, etc.)
- Combination of different approaches is necessary:

1. Molecular quantum chemistry
2. Solid-state quantum-mechanical methods
3. Methods based on the use of classical potentials (MD, MC, coarse-graining, etc.)
4. Methods of rare event simulation (kinetic Monte Carlo, accelerated MD, MD of rare events, …)

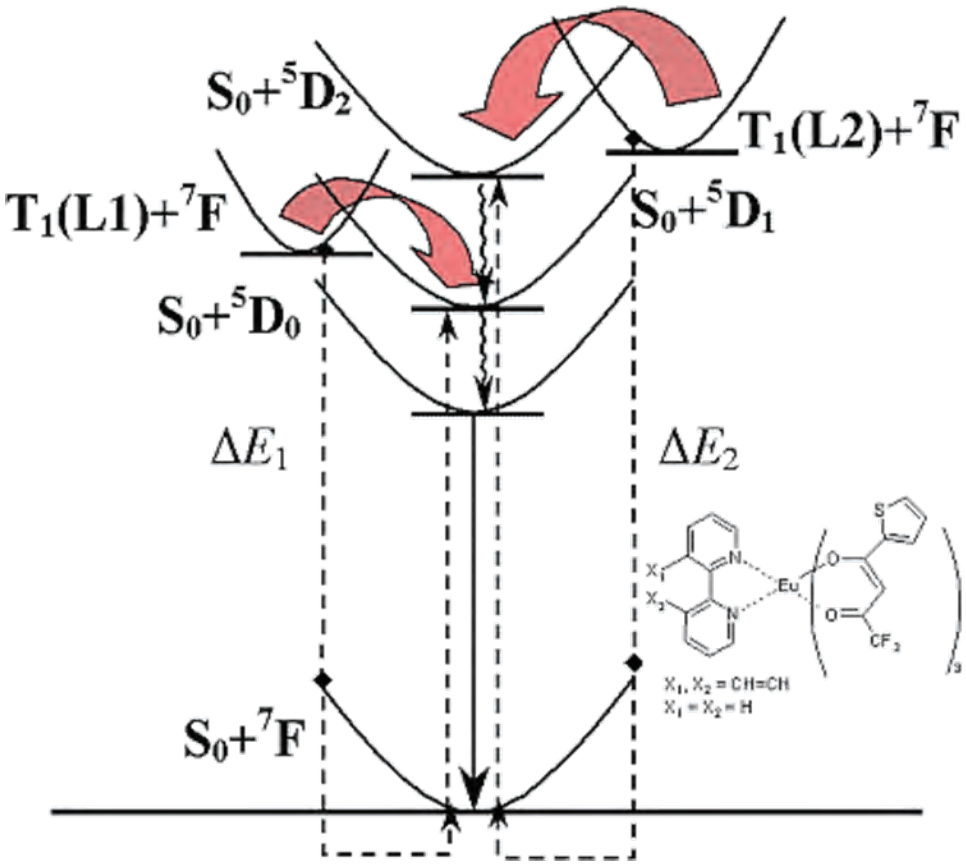
Where are we going? Quantum chemistry and atomistic simulation of materials for photonics applications: Simulation of dye spectra in a polymer matrix





An approach is being developed for modeling absorption and fluorescence spectra of dyes in a polymer matrix. The approach combines the use of molecular dynamics simulation for modeling the microstructure of the polymer matrix and the use of effective fragment potentials (QM/EFP) for quantum-chemical calculations of absorption and emission spectra of the dye adsorbed on the matrix surface.

Where are we going? Quantum chemistry and modeling phosphorescent europium complexes



An *ab initio* approach is being developed for the calculation of low-lying excited states of Ln^{3+} complexes with organic ligands. Using this approach the efficiency of antenna ligands used for phosphorescent emitters in organic light-emitting devices can be predicted and optimal antenna ligands can be selected in silico.

A.Ya. Freidzon, A.V. Scherbinin, A.A. Bagaturyants, M.V. Alfimov, “Ab Initio Study of Phosphorescent Emitters Based on Rare-Earth Complexes with Organic Ligands for Organic Electroluminescent Devices” J. Phys. Chem. A, 2011, 115, 4565–4573.

Final Conclusions

- **A methodology is developed for predictive atomistic multiscale simulations of the structure and functional properties of hierarchical organic and hybrid nanomaterials. The methodlogy is based on**

- Atomistic quantum-chemical modeling of the structure and functional properties of the material at a molecular level
- Atomistic quantum-chemical (quantum-mechanical) modeling of the structure and properties of the material at a supramolecular level using MD and/or MC (kMC) methods and classical potentials (with parameters fitted using results of quantum-chemical calculations)
- Quantum-chemical (quantum-mechanical) modeling of the absorption and emission spectra (or other required properties) for the system in a real environment (obtained from calculations at the supramolecular level) using DFT or even more accurate ab initio methods (CAS SCF, MCQDPT, etc.).
- This approach is suitable for predictive modeling of materials for optical chemical sensors, microchips, OLEDs, quantum dots, quantum wells, and for other photonic applications.

This work was made with the participation of

- My coworkers and coauthors from the laboratory of quantum chemistry and molecular simulation of the Photochemistry Center of Russian Academy of Sciences
- Our colleagues and coauthors from other institutions
- **Thank you very much for your attention!**

Thank You !!!