Molecular design of a sensor for small analyte molecules based on a dye adsorbed on silica nanoclusters and nanopores

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Quantum-chemical (QC)/molecular dynamics (MD) studies of the interaction of various compounds with fluorescent dyes adsorbed on amorphous silica surfaces are quite important in the design of optical chemical sensors based on adsorbed dyes. Such sensors were proposed for the determination of small molecules by changes in the optical signal (absorption or luminescence spectrum) of a receptor centre (adsorbed dye) upon its interaction with various analytes [1]. QC and MD calculations for such systems can provide an atomic-scale insight into the structure and properties of the receptor centre. The computational results can be used to predict structures; adsorption energies; and changes in the positions, intensities, and widths of spectral bands of a receptor centre interacting with analyte molecules. We considered a set of both polar and non-polar compounds comprising acetone, ammonia, methanol, ethanol, water, benzene, naphthalene, toluene, and dinitrotoluene. These molecules can form complexes with corresponding sensing components of the sensitive layer (receptor centre). The resulting changes in the absorption or fluorescence spectra provide an output signal of the sensor, so that even rather low concentrations of analytes can be detected [2].

As the indicator dye in this study we used 9-(diphenylamino)acridine (DPAA) adsorbed on a silica substrate, for which we chose different cluster [3] and nanopore models with a diameter from one to several nanometres. Silica clusters were built by MD simulations [4]. To do this, an amorphous SiO2 structure was obtained by simulated annealing of the alpha quartz crystal structure, after which cluster and porous SiO2 structures were cut off from the obtained amorphous structuers. We optimised the structures of DPAA/silica/analyte complexes and estimated the interaction energies between the adsorbed dye and analyte molecules and between the dye and the silica surface using a QC DFT-D approach with the PBE0+D functional, including explicit corrections for vdW forces. One of the optimized structures consisting of DPAA, $Si_{10}O_{11}(OH)_{18}$ (Si10) and ethanol is shown in Figure 1.

To determine the effect of silica gel porous surface irregularities on the receptor centre properties, we built model nanopores of different radii. The adsorption of the dye was simulated using genetic algorithms [5]. Next, after cutting off a structure suitable for QC calculations, dye adsorption energies were calculated. The interaction energy of the dye in pores of the lowest investigated diameter reach a maximum value (40–42 kcal/mol, D ~ 1 nm) and decreases with increasing pore size. For pores with a diameter greater than 3 nm, the interaction energies do not differ from similar results for cluster models (25–30 kcal/mol). The construction process is illustrated in Figure 2.

The electronic absorption and fluerescencse spectra of molecular complexes were determined by the vertical electron transition energies at the equilibrium geometries of complexes in the ground and excited electronic states. We calculated the positions of the 1st absorption and fluorescence bands in the systems DPAA/silica/analytes and the system without analytes by TDDFT method (PBE0/6-31G**(cc-pVTZ)) [6] and evaluated the displacements of spectra, whose values determine the efficiency of the detecting device. The calculated band shifts are shown in Figure 3.

Another important characteristic of the optical response of a chemical sensor is the shape and the width of the corresponding electronic band. The spectra of adsorbed substances exhibit no rotational structure; therefore, taking into account the vibrational structure should be sufficient in our case.

One of the most convenient first-principles approaches to calculating the band shapes in the electronic spectra of complex molecular systems is based on the classical Pekar model [7]. In this model, each electronic transition is broadened into a structureless band of an approximately Gaussian shape due to linear vibronic coupling. In practice, only a single-point evaluation of the excited state gradient is required in this approach. The following data are required from the ground state calculations: equilibrium geometry, nuclear Hessian, harmonic frequencies, and normal modes. These data are calculated by QC methods, such as DFT, DFT-D and TDDFT. The results of calculations of the bands are in good agreement with the experimental data for DPAA in solutions, which leads to the conclusion that the developed approach can be used for the estimation of the shapes of spectral bands in the absorption spectra of organic dyes adsorbed on silica particles and their complexes with analytes. This offers new possibilities for the design of optical chemical sensors on the basis of such systems. The proposed procedure can be used for the preliminary screening of materials (dye + substrate) as receptor centers for optical chemical sensors. It is shown that the DPAA/silica receptor centre can be used to detect compounds in a gas phase by changes in fluorescence and absorption spectra.

References

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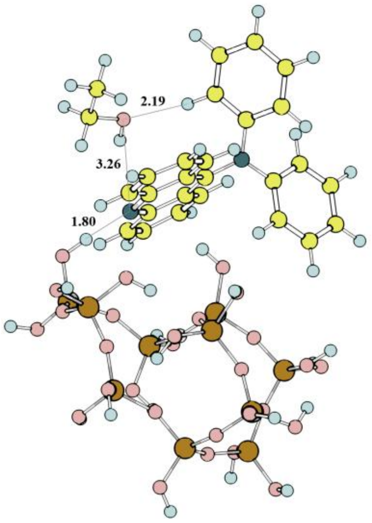

Figure 1. Structure of complexes C_2H_5OH–DPAA–Si10. Silicon atoms are given by brown circles; oxygen, by pink; hydrogen, by blue; carbon, by yellow; and nitrogen, by sea-green circles

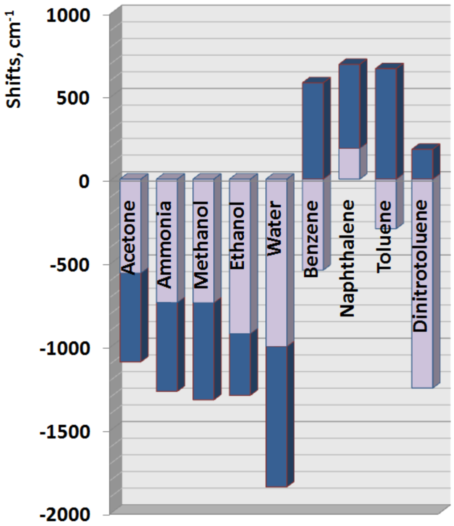

Figure 3. Band shift of fluorescence (dark blue) and absorption (light purple) spectra of complex DPAA/silica/anaytes corresponded to DPPA/silica system

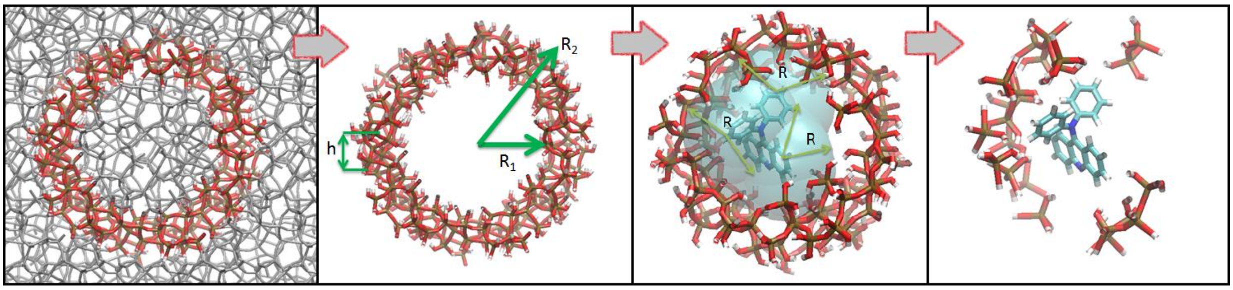

Figure 2. Stages of modeling complex dye in the pores of the amorphous silica gel: 1) Annealing of alpha quartz, 2) Cutting cylindrical pores (h = 2 nm, R_1 = 0.7 .. 1.5 nm, R_2 = 1 .. 1.8 nm); 3) adsorption of the dye, calculations with using a genetic algorithm and the MD methods; 4) Finding the structure comprising all atoms at a distance from the dye no more than 0.3 nm and subsequent geometry optimization by QC method

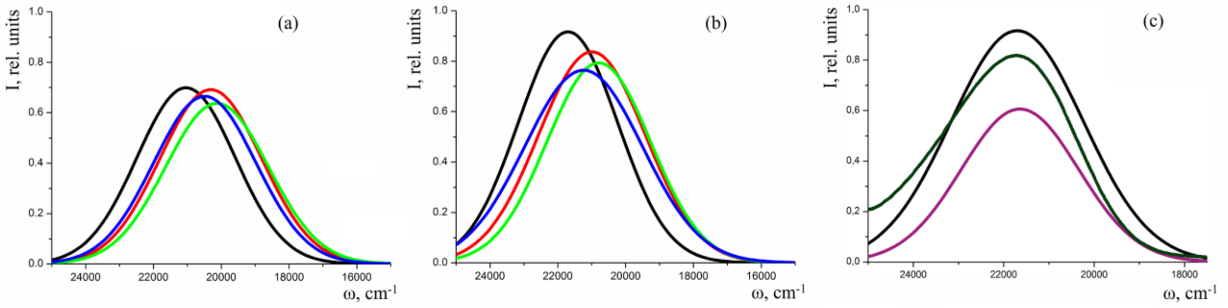

Figure 4. Band shapes for complexes (a) analyte–DPAA–SiH_3OH, (b) analyte–DPAA–Si10 (black line, DPAA–Si1(10); red line, complex with ammonia; green line, complex with ethanol; blue line, complex with acetone) and (c) experimental spectrum of DPAA solution in methanol (dark green line) and calculated spectra of isolated DPAA (violet line) and DPAA–Si10 complex (black line).