

Computer Simulation of Ligand Shells of Colloidal Cadmium Selenide Quantum Dots

A. V. Nevidimov and V. F. Razumov

*Institute of Problems of Chemical Physics, Russian Academy of Sciences,
pr. Akademika Semenova 1, Chernogolovka, Moscow oblast, 142432 Russia
e-mail: nevidimovsasha@yandex.ru*

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Abstract—The full-atomic molecular dynamics approach has been employed to study the structure and composition of ligand shells of colloidal cadmium selenide quantum dots produced by high-temperature colloidal synthesis in a trioctylphosphine–trioctylphosphine oxide mixture. The influence of solvents (chloroform and methanol) on the composition of the shells has been investigated. The number of ligand molecules optimal for complete covering the surface of a considered particle without its deformation has been found. The fraction of passivated surface ions has been calculated.

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1. INTRODUCTION

High-temperature colloidal synthesis is a method for the production of semiconductor nanoparticles (NPs) with narrow size distributions [1]. The reaction is carried out at a temperature of about 300°C in a special high-boiling solvent which is in a liquid state at this temperature. Molecules of such a solvent contain functional groups, which enable it to play the role of not only a solvent, but also a ligand capable of bonding to NP surface atoms. This bonding gives rise to the formation of a stable dense ligand shell around a particle, which prevents the NPs from coagulating and stabilizes their sizes. The structure of the ligand shells surrounding NPs is, to some extent, similar to that of shells that are formed by surfactant molecules in reverse micelles and hinder the coagulation of NPs synthesized in them [2]. After the synthesis is completed, a mixture is cooled to room temperature, at which the solvent passes to the solid state. For subsequent investigation or practical application of NPs at room temperature, they are transferred to another solvent, while the shell composed of initial ligand solvent molecules surrounding the NPs remains preserved with retention of the particles in a dispersed state and prevent them from coagulation for a long time.

Initially, the high-temperature synthesis was employed to produce NPs of cadmium chalcogenides (CdS, CdSe, and CdTe), with a mixture of trioctylphosphine (TOP) and trioctylphosphine oxide (TOPO) being used as a high-boiling solvent [1]. As a rule, thus-synthesized NPs are then dissolved in chloroform and the initial solvent (TOP/TOPO mixture) is washed-out by repeated reprecipitation of the quantum dots with methanol followed by washing with chloroform [3]. Nanoparticles transferred into chloroform

have stable sizes; however, their optical properties gradually deteriorate under the action of air [4]. The properties deteriorate most rapidly for CdTe NPs and somewhat slower for CdSe ones. CdS particles are most stable. The optical properties of the particles do not deteriorate in an inert dark medium. The properties of NPs deteriorate due to the interaction of cadmium cations and chalcogenide anions with atmospheric oxygen in accordance with the following scheme [5]:



At room temperature, the spectral luminescent properties of NPs dispersed in a TOP/TOPO mixture remain almost unchanged for very long time, while, in chloroform, the luminescence quantum yield rapidly decreases when no additional stabilization measures are undertaken [4]. The optical properties of NPs become more stable when a hexadecylamine–octadecylphosphonic acid mixture is used as an initial ligand solvent instead of TOP and TOPO [6].

Various functional optical nanomaterials are often developed based on colloidal quantum dots used in the form of nanoclusters composed of a large number of diverse NPs. Such nanoclusters possess a new set of properties and characteristics that are necessary to create a targeted nanostructured functional material [7–9]. In the nanoclusters, NPs may be rather densely packed, with the degree of packing being essentially dependent on NP size, number ratio between NPs of different types and sizes, and the structures and compositions of their ligand shells. Therefore, detailed studying the structure of ligand shells surrounding NPs is an important problem. Therewith, it is necessary to determine not only the quantitative ligand

composition, but also its dependence on the nature of different solvents.

The quantitative compositions of the shells surrounding CdSe NPs were studied as early as in the early experimental works [3, 10]. The authors of [3] used tributylphosphine (TBP) rather than TOP, assuming that the former will be completely replaced by TOPO in a shell. They established that the fraction of surface atoms coordinated with ligands was in a region of 0.3–0.6 depending on NP size. The cases, in which this fraction was higher than 0.5, were explained by the presence of residual amounts of TBP. In [10], NPs were studied directly in an initial TOP/TOPO mixture without washing it out. The authors considered particles 3.7 nm in diameter composed of nearly 1000 atoms. According to their estimates, about 300 atoms in these NPs belonged to the surface, while the shell contained 150–170 molecules of TOPO coordinated with Cd atoms. Therefore, they concluded that all Cd atoms on NP surface were coordinated with TOPO ligands.

The structure of a ligand shell surrounding a CdSe NP was also studied by computer simulation in [11–13]. The authors of these works investigated solvent-free CdSe NPs with different sizes coated with TOPO shells. TOPO molecules were rigidly bonded to Cd atoms, while its shortened analog, trimethylphosphine oxide, was used in [13]. Although TOPO was covalently bonded to Cd in [12], the authors prepared shell-coated NPs in a manner that enabled them to determine the fraction of surface Cd atoms bound with TOPO. This fraction varied from 1.0 for the smallest particles (0.7 nm in radius) to 0.7 for the largest particles (1.8 nm in radius).

Computer simulation of CdSe NPs (both with and without shells) has been the subject of some recent works [14, 15] and remains an urgent problem. For example, a shell composed of acetic acid molecules covalently bonded to Cd was studied in [14]. The authors of [15] studied structural transformations of ligand-shell-free CdSe NPs in vacuum.

In this work, the molecular dynamics (MD) method was used to study the composition and structure of TOP/TOPO mixed shells of CdSe NPs and shells composed of TOPO alone in solvents with different polarities (chloroform and methanol). Moreover, the case in which the solvent was absent was also considered. In contrast to previous studies [11–15], the molecules of ligands were not covalently bonded to NP atoms in this work, whereby allowing ligand molecules to be freely transferred into the solvent in the course of simulation. This approach was assumed to give the most detailed information on the qualitative and quantitative composition of a shell and to enable us to determine the effect of the solvent polarity on it and explain the aforementioned experimental data.

2. MOLECULAR MODELS AND SIMULATION DETAILS

Molecular-dynamics calculations were performed in terms of the freely distributed software package NAMD 2.10 [16] using the computational potential of the Lomonosov supercomputer at Moscow State University [17], Interdepartmental Supercomputer Center of the Russian Academy of Sciences [18], and Institute of Problems of Chemical Physics of the Russian Academy of Sciences [19]. Each problem was solved with the use of 8–32 ordinary and 0–8 graphics processors.

A cadmium selenide nanoparticle was formed by locating 499 Se and 499 Cd atoms in a random manner at the sites of a $10 \times 10 \times 10$ cubic lattice. The parameters of interatomic interactions (charges and Lennard-Jones potential) were taken from [20]. The starting distance between adjacent atoms was assumed to be 0.4 nm to provide free displacements of the atoms. The cell volume was kept constant. Temperature was initially slowly elevated from 0 to 2000 K, and the system was exposed at this temperature to ensure a more efficient intermixing of the atoms. Then, the system was slowly cooled to a final temperature of 298.15 K. The total time scale was 1000 ns. As a result, an almost ideal spherical CdSe NP was formed with a radius of about 1.85 nm, which corresponded to the bulk density of CdSe substance.

A shell containing equal numbers of TOP and TOPO molecules was formed around the CdSe NP thus prepared. The total number of ligand molecules was 60, 100, or 150. The shell was created with the use of the software described in our previous work devoted to the simulation of reverse micelles [21]. The software placed TOP and TOPO molecules by turns uniformly over a sphere with a preset radius (2.2 nm) without connection with specific surface Cd or Se atoms. This system was equilibrated for 100 ps.

At the next step, a medium was formed from molecules of a solvent (pure chloroform or pure methanol) around particles with different contents of ligands also using the software described in [21], but having replaced hexane molecules by chloroform or methanol molecules, which were located at distances corresponding to the densities. The thickness of a solvent layer was 4 nm, which was in consistent with about 7000 or 13000 molecules of chloroform or methanol, respectively.

Thus, nine systems with different numbers of TOP/TOPO ligand molecules were studied in chloroform, methanol, and without a solvent, as well as a system containing 150 TOPO molecules in chloroform. The starting characteristics of all systems are presented in the table.

For solvent-containing systems, periodic boundary conditions and isobaric-isothermal *NPT* ensemble were used. A pressure of 1 atm was maintained with the use of the Berendsen barostat. Spherical boundary

Characteristics of simulated systems. Starting (index 1) and final (index 2) numbers of TOP and TOPO molecules

| System number | N_{TOP1} | N_{TOPO1} | Solvent | N_{TOP2} | N_{TOPO2} |
|---------------|-------------------|--------------------|------------|-------------------|--------------------|
| C1 | 30 | 30 | — | 30 | 30 |
| C2 | 30 | 30 | Chloroform | 24 | 30 |
| C3 | 30 | 30 | Methanol | 16 | 30 |
| C4 | 50 | 50 | — | 49 | 50 |
| C5 | 50 | 50 | Chloroform | 42 | 50 |
| C6 | 50 | 50 | Methanol | 31 | 50 |
| C7 | 75 | 75 | — | 37 | 68 |
| C8 | 75 | 75 | Chloroform | 38 | 63 |
| C9 | 75 | 75 | Methanol | 34 | 69 |
| C10 | — | 150 | Chloroform | — | 126 |

conditions were imposed on solvent-free systems, with the sphere radius being essentially larger than the size of a simulated object. The temperature was in all cases maintained by the velocity reassigning procedure. For rapidly decreasing Lennard-Jones interactions, a cut-off radius equal to 1.3 nm was applied. The classical motion equations were integrated using the velocity Verlet algorithm with a time step of 1 fs. The constructed systems were initially equilibrated for 100 ps; then, the calculation was performed for 10–15 ns.

Cd^{2+} and Se^{2-} ions were described in terms of the model [20], in which the absolute values of their charges were 1.18. The absolute values of the charges for O and P atoms in TOP and TOPO molecules were also equal to 1.18. This charge of P in TOPO was slightly higher than the value of +1.13 obtained in work [22], where the structure of trimethylphosphine near a CdSe NP was optimized in terms of the density functional theory or the value of +1.031 that was used in the MD simulation of phosphine oxide containing phenyl substituents [23]. Oxygen charge had substantially higher absolute values than those reported in the same works (−0.81 and −0.803, respectively). The higher negative charge of O atoms may result in stronger bonding of TOPO molecules with NP surface. The charge of phosphorus atoms in TOP was also markedly higher than the value of +0.75 used in the MD calculations of a trimethylphosphine molecule [24]. This may also lead to a stronger interaction of a TOP molecule with a CdSe surface. The selection of charges for phosphorus and oxygen is complicated by the absence of works in which TOP and TOPO ligands would not be bonded to NP surface, with the particle itself being remained nonrigid. The charges of carbon and hydrogen atoms were selected based on the CHARMM27 force field. Therewith, the positive charge of phosphorus in TOP molecules was compensated by additional negative charges of near-phosphorus carbon atoms. The models for chloroform and methanol molecules were taken from [25, 26].

3. RESULTS AND DISCUSSION

3.1. Formation of CdSe NPs from Separate Ions

Based on the density and molecular mass of cadmium selenide, a spherical particle of it composed of 499 molecules has a radius of 1.867 nm. In our simulation, the radius of a particle obtained by the self-assembly of individual cadmium and selenium ions was nearly equal to this value. Each Se atom was surrounded with four Cd atoms, while each Cd atom was in the environment of four Se atoms. Given this, the particle structure was not ideally ordered; it contained both surface and interparticle defects (Fig. 1). Of the 998 atoms composing the particle, 198 selenium and

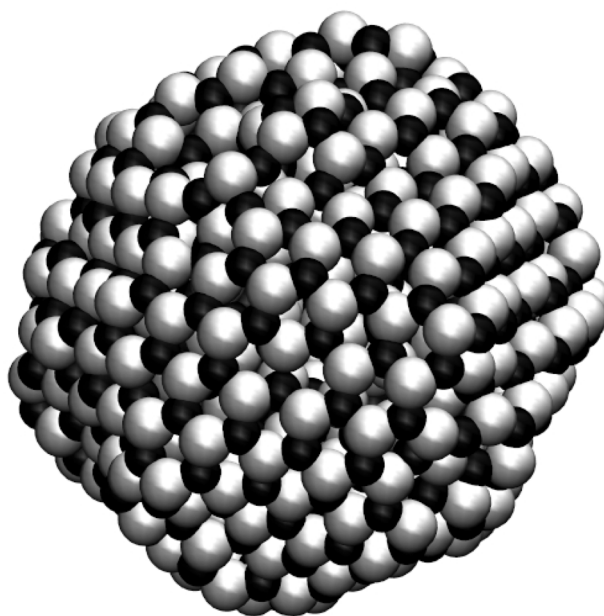


Fig. 1. Structure of CdSe NP obtained by self-assembly of ions after 1000-ns simulation. Black and white symbols refer to cadmium and selenium, respectively.

198 cadmium atoms were located on its surface. This result substantially differs from the theoretical estimate of ≈ 300 surface atoms obtained in [10] for CdSe NPs with the same size and content of atoms.

Let us estimate the number of atoms that must be located on the surface of a CdSe particle 1.867 nm in radius containing 998 atoms. Assuming that Cd and Se atoms form a smooth surface monolayer, its thickness must be equal to 0.185 nm, i.e., the average diameter of one atom calculated from the average atomic volume. The volume of a spherical layer with this thickness amounts to 27% of the total sphere volume. Hence, under the above assumption, nearly 30% of atoms must be located on the surface, as was reported in [10]. However, the surface atoms do not form a smooth monolayer; they are somewhat shifted relative to adjacent ones. As a result, the thickness of the surface layer is nearly 1.5 times larger, and its volume fraction is about 39%. This is in good agreement with the number of surface atoms counted manually. Furthermore, the number of 396 was used when calculating the fraction of surface atoms bonded to ligands.

3.2. Selection of the Number of Ligand Molecules

The surface area of a formed CdSe NP is approximately 44 nm². According to the quantum-chemical calculation of the structure of a trimethylphosphine molecule bonded to a CdSe particle [22], the wide part of a ligand molecule is located at a distance of 0.4 nm (the sum of the Cd–O interatomic distance and the O–P bond length) from a solid CdSe particle surface. Taking into account the thermal motion, this distance may be assumed to be 0.5 nm. Thus, the surface area of the sphere on which the branched moieties of TOP and TOPO molecules are located is nearly 70 nm². The number of ligand molecules could be calculated from the surface area occupied by one molecule; however, this value is unknown. It may be assumed that TOP and TOPO molecules must occupy the surface area equal to that per one molecule of a surfactant Aerosol OT on the surface of a reverse micelle, i.e., about 0.75 nm² [21]. Of course, this estimate is not quite correct, because AOT and TOP molecules have different structures: AOT has two branched hydrocarbon tails and a large polar head group, while TOP and TOPO molecules contain three linear hydrocarbon chains and a small polar moiety; however, the average areas may be approximately equal. Thus, about 94 ligand molecules may be optimally located around a CdSe particle, e.g., 47 TOP and 47 TOPO molecules.

Three different numbers of ligand molecules were selected in this work. The first one was (100) approximately corresponded to the optimal amount. The second one was equal to 60. Ligands taken in these amounts could be freely located on the NP surface without displacing each other from it. In this way, the strengths of TOP and TOPO bonding could be estimated in the absence of their competition. The third

number of ligand molecules was equal to 150. This is a fortiori excessive number that causes competition between the molecules for the place on the surface and the formation of a dense “coat” from them.

3.3. Ligand Molecules on a Free Surface

At the beginning of simulation in C1–C3 systems, 30 TOP and 30 TOPO molecules were uniformly distributed over CdSe NP surface. The C1 system contained no solvent around the particle, while the C2 and C3 systems contained chloroform and methanol, respectively.

In the C1 system, none of the ligand molecules escaped from the NP surface during the entire time scale (15 ns) of the molecular dynamics (Fig. 2a). Therewith, the particle surface was not covered completely and contained large free areas, with one of them being clearly seen in the figure. In the C2 and C3 systems, some ligand molecules were gradually transferred into the solvents for a few nanoseconds at the beginning of the calculation (Figs. 2b, 2c). Only TOP molecules were transferred, while TOPO molecules remained on the surface. In the cases of chloroform and methanol, 6 and 14 TOP molecules escaped from the surface, respectively (see table). It should be noted that different numbers of molecules are transferred into the solvents in these systems; therefore, this transfer cannot be attributed to an improper starting arrangement of molecules. The transfer of TOP molecules into chloroform may be explained by the solubility of nonpolar molecules in the nonpolar solvent. Even an overestimated energy of TOP interaction with the surface does not hinder this transfer. Methanol is much more polar than chloroform is; therefore, it would be more reasonable to expect a smaller number or the absence of TOP molecules in it. The larger number of TOP molecules in methanol may be explained by the fact that this polar liquid more intensely interacts with Cd²⁺ and Se²⁻ ions and displaces TOP from the CdSe surface. If we used a lower bonding energy between TOP and the surface, the number of escaping molecules could increase. However, we are, at this stage, interested in the very fact of this transfer from the free surface in the presence of a solvent.

3.4. Ligand Molecules on a Densely Packed Surface

In the C4–C6 systems, 50 TOP and 50 TOPO molecules were located on the surface at the initial moment. The C4 system contained no solvent, while the C5 and C6 systems contained chloroform and methanol, respectively.

In the C4 system, only one ligand (TOP) molecule escaped from the nanoparticle surface. At the same time, actually no open regions were present on the surface. Particle deformation similar to that occurring for, e.g., a reverse micelle core in the presence of

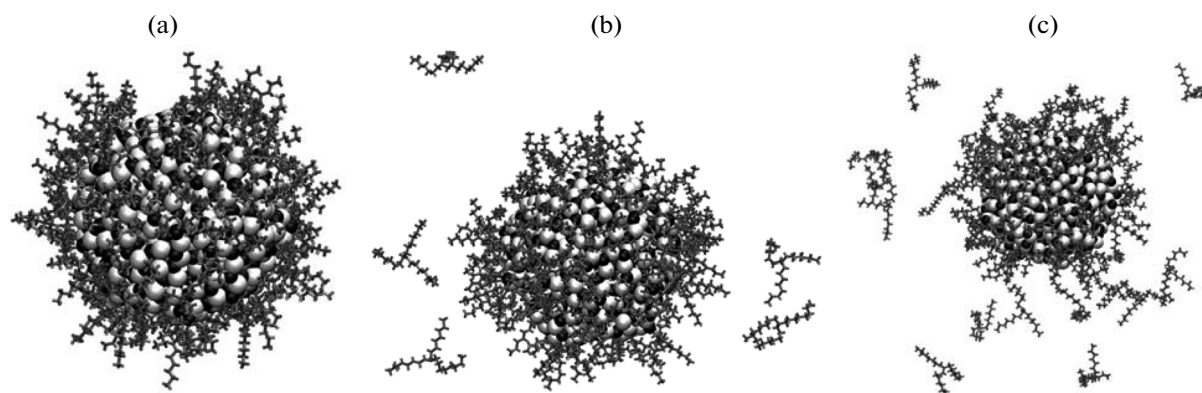


Fig. 2. (a) C1, (b) C2, and (c) C3 systems after 15-ns simulation. Black, white, and gray symbols refer to cadmium, selenium, and TOP–TOPO mixed ligand, respectively. The solvent is not shown.

excess surfactant molecules [21, 27] was not observed. The interaction between Cd^{2+} and Se^{2-} ions is realized only via the Coulomb and van der Waals forces; therefore, the core can be easily transformed when needed. Since this does not take place, the considered number of ligand molecules (nearly 100) can be accommodated on the NP surface. Although the molecules are rather densely packed, we cannot state that a larger number of molecules cannot be accommodated on the surface. In the C5 and C6 systems, 8 and 19 TOP molecules, respectively, were gradually transferred, whereas all TOPO molecules remained on the surface. As a result, small ligand-free regions were observed on the particle surface. Hence, the observed transfer of TOP molecules is due to the presence of a solvent in a system rather than their excessive number or disadvantageous starting arrangement. In order to determine the maximum number of ligand molecules that can be located on the surface of a CdSe particle in question, systems with a fortiori excessive numbers of them were considered.

3.5. Ligand Molecules on an Excessively Packed Surface

In the C7–C9 systems, 75 TOP and 75 TOPO molecules were placed onto the surface at the initial moment of simulation. The C7 system contained no solvent, while the C8 and C9 systems took the forms of particles in the environments of chloroform and methanol, respectively.

An abundant escape of ligand molecules was observed already at the very beginning of simulation for the systems of this series. In all cases, slightly more than 100 ligand molecules remained on the surface (see table), i.e., nearly the same amount as was in the C4 system. TOP molecules amounted to 80–90% of the escaping ones. Therewith, the particle itself underwent no deformation (Fig. 3a), thus indicating that the surface of the considered particle can accommodate at least 105 ligand molecules.

Thus, 105 molecules remaining in the solvent-free system give us grounds to suppose that this number of ligand molecules is optimum for a dense packing formation around a CdSe NP with a radius of 1.86 nm. This number agrees with the data of [3], according to which the ratio between P and Cd atoms for CdSe NPs 1.8 nm in radius is 0.21. In our case, it is $105/499 = 0.21$. Since, of the 998 atoms of this particle, about 396 atoms belong to the surface and each atom coordinates no more than one ligand molecule, the fraction of passivated surface atoms is 27%. This value also agrees with the data according to which this fraction for particles of a larger radius is 30% [3]. At the same time, the value of this fraction substantially differs from the result obtained in [10] for particles of the same size. In [10], this fraction was as large as almost 55%. It was obtained in [10] by dividing 160 (the number of ligand molecules) by 300 (the number of surface atoms). In our work, we dealt with a particle for which the number of surface atoms could be counted manually. As for the number of 160, which was also obtained in [10] by comparing experimental data with a mathematical model, the following can be noted. When simulating the C7–C9 systems, we initially covered the NP surface with 150 ligand molecules; however, slightly more than 100 molecules subsequently remained on the surface, although overestimated energies were used for the interaction of ligand molecules with NP atoms. Since, in the presence of a solvent, TOP molecules are prone to escaping from the surface even when the surface is not completely covered, we prepared the C10 system, in which 150 TOPO molecules were placed onto a CdSe particle in the presence of chloroform. In this system, 126 TOPO molecules remained on the surface, while others were transferred into chloroform. Therewith, the particle was strongly deformed (Fig. 3b), thereby indicating an excessive number of ligand molecules. Due to the very strong bonding to the surface, these excessive TOPO molecules do not escape from it. If we used an oxygen atom charge with a lower absolute value, the bonding

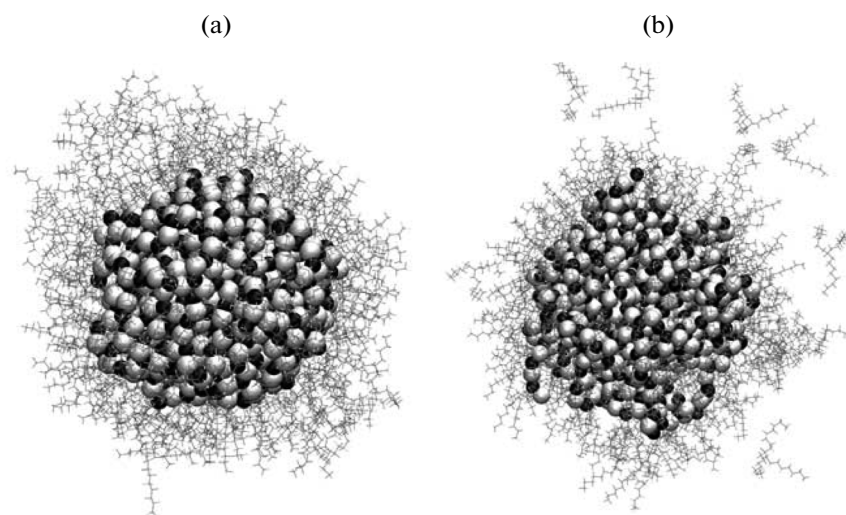


Fig. 3. Structure of CdSe NP in (a) C7 and (b) C10 systems after 10-ns simulation.

would be weaker, a larger number of molecules would escape from the surface, and the particle would not be deformed. Thus, the particle surface cannot accommodate 160 molecules; their number must be no larger than 126 even when TOPO strongly interacts with it.

The Cd^{2+} –O atoms of TOPO molecule pair correlation functions were plotted for NPs in all systems. Analysis of these functions has shown that oxygen atoms are located at a distance of about 0.19 nm from cadmium atoms (Fig. 4), which is somewhat smaller than the corresponding distance determined in [22].

In spite of the fact that we did not simulate a system in which TOP and TOPO molecules would play the roles of solvents, the following conclusions may be drawn. As a result of the synthesis, a CdSe nanoparticle is covered with a dense layer of TOP and TOPO molecules as ligands. Since a TOP molecule is bonded more weakly than a TOPO molecule is, it more readily escapes from the surface. While the particle occurs in an initial TOP/TOPO solvent, the place of a removed molecule is occupied by another one, thus leading the establishment of a TOP/TOPO equilibrium ratio

between ligand molecules and, above all, the dense ligand shell covering the particle remains preserved and prevents the particle from oxidation. After the initial solvent is replaced by another one (chloroform or methanol), ligand (TOP) molecules continue to gradually pass into the solvent, thereby giving rise to uncovered regions, which may undergo oxidation. This agrees with the results obtained in [4]. In order to increase the oxidation resistance of NPs, it is necessary to use a ligand more intensely interacting with the CdSe surface. In addition, the fraction of passivated atoms may be increased using ligands with unbranched nonpolar moieties. As follows from our data, the presence of even one oxygen atom in a ligand molecule substantially increases the ligand–particle bonding strength. Therefore, alkylphosphonic (with the general formula $\text{RPO}(\text{OH})_2$) or alkylcarboxylic (RCOOH) acids are preferable to be used instead of TOP and TOPO. Alkylamines (RNH_2) and alkylmercaptanes (RSH) are also known to be strongly bonded with the surface [6].

4. CONCLUSIONS

It has been shown that the fraction of surface atoms of a CdSe nanoparticle 1.85 nm in radius containing 499 CdSe molecules is about 40% of the total number of the atoms. The optimal number of molecules of TOP–TOPO mixed stabilizing ligands that can be accommodated on the surface of this NP to form coordination bonds with 27% of surface atoms is 105. When NPs are placed into chloroform or precipitated with methanol, some TOP molecules may pass into a solvent, while TOPO is not transferred into a solution because of its stronger bonding. The passage of TOP molecules into a solvent opens the surface and makes it oxidizable.

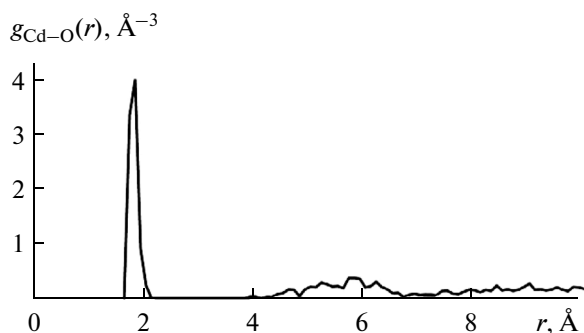


Fig. 4. Cd^{2+} –O (TOPO) pair correlation function for C4 system.

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