

Structure, Stability and Vibrational Properties of CdSe Wurtzite Molecules and Nanocrystals: A DFT Study

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Structure, Stability and Vibrational Properties of CdSe Wurtzite Molecules and Nanocrystals: A DFT Study

Abstract

Bare and hydrogen passivated CdSe wurtzite molecules and nanostructures are investigated. The investigation is performed using wurtzoid structures that represent the wurtzite structure at the molecular and nanoscale region. The results show that the energy gap of bare and hydrogen passivated CdSe molecules is higher than and converges to the experimental bulk energy gap. Vibrational analysis of wurtzoid molecules shows that the experimental longitudinal optical mode is in between bare and hydrogen passivated CdSe molecules and very near to bare molecules. The stability of wurtzoid molecules against transition to CdSe diamondoids and cuboids that represent the molecular scale of diamond and rock-salt structures respectively is investigated. The results show that CdSe wurtzoids are the most stable followed by cuboids and diamondoids respectively according to their calculated Gibbs free energy. This order is different than the bulk order of wurtzite, zincblende, and rock-salt respectively. The stability of wurtzoids is attributed to their compact and symmetrical surface structure. The analysis also shows that dangling bonds on bare wurtzoids are responsible for the differences between bare and passivated molecules including lower energy gap, higher vibrational force constants, and lower vibrational reduced masses.

Keywords

CdSe, Density Functional Theory, nanocrystals

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1. Introduction

Cadmium selenide is an important II-VI semiconductor, especially at the nanoscale region. The importance of the nanoscale region is due to the value of bulk CdSe energy gap at the range 1.74–1.83 eV [1,2] in comparison with the visible spectrum at the range 1.65–3.26 eV [3]. As the size of the particles reaches the nanoscale region, the energy gap becomes larger. The increase in the energy gap changes the color of these particles. Since CdSe bulk energy gap is near the lower end of the visible spectrum (red), the color of nanoparticles changes from black red to blue as particle size decreases [4]. Because of the value of the energy gap, the applications of CdSe nanoparticles span wide optical phenomena such as mid-infrared laser applications [5], and solar cells [6].

At the molecular and nanoscale region surface and quantum effects are more dominant than in bulk. To show these effects, models for bulk solids are made by introducing small molecules that can represent the bulk by periodical repetition of these molecules. Examples of these molecules are wurtzoids and diamondoids that can represent the wurtzite and diamond structure in their properties when enlarged enough [7–12]. In the same way, rock-salt cuboids shapes can be seen to grow from nanoscale to mm size crystals [13]. The motivation and aim of this work are to compare the stability of these various molecules (wurtzoids, diamondoids, and cuboids) at the nanoscale.

2. Models and simulation details

Recently, a model for the wurtzite structure is made so that it resembles this structure with a bundle of capped (3,0) nanotubes [7,8]. This resemblance is used successfully to simulate physical properties of wurtzite materials in addition to their use as gas sensors [9,10]. The new molecules are called wurtzoids. These wurtzoids are similar to diamondoids that resemble diamond and zincblende structures at the molecular and nanoscale region [11,12]. Both of the two structures (diamondoids and wurtzoids) share the same property of having four bonds for each atom in the bulk system except surface atoms. All the atoms at the surface have one dangling bond in the wurtzoid bare molecules while the surface of bare diamondoids has one or two dangling bonds. The wurtzoids are said to be in the boat conformation while diamondoids are in the chair

conformation [14]. The effect of such surfaces will be discussed later in the results and discussion section. Bare molecules can exist in a vacuum or inert surroundings.

Fig. 1 shows the building block of bare surface CdSe wurtzite structure that is called wurtzoid (Cd_7Se_7). Elongating this wurtzoid in its main axes (c axis in the wurtzite structure) will produce wurtzoid2c as in Fig. 2. Adding three parallel wurtzoids to form a bundle of wurtzoids will produce CdSe triwurtzoid as in Fig. 3. Quantum confinement effects as the size of these molecules change will be investigated [15]. Passivating the surface of these wurtzoids completely by hydrogen will make these wurtzoids inert and increase their band gap as we shall see later. Fig. 4 shows the CdSe triwurtzoid after passivating with H atoms (hereafter hydrogen passivation is abbreviated HP). Surface passivation is not necessarily performed by using hydrogen atoms. Passivation can be made using oxygen, chlorine or even other semiconductors such as CdS. The effect and stability of passivating atoms will be discussed in the later sections. Vibrational properties of the molecules mentioned above are calculated and corrected using 0.966 scale factors [16] that depend on DFT method and basis sets. All calculations are performed using the Gaussian 09 software [17]. B3LYP/6-31G**/3-21G method and basis sets are used. The B3LYP method and basis set had proved

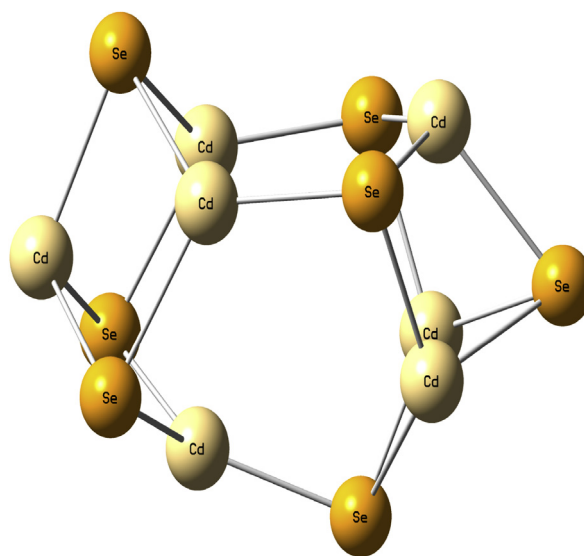


Fig. 1. Bare CdSe wurtzoid molecule after geometrical optimization.

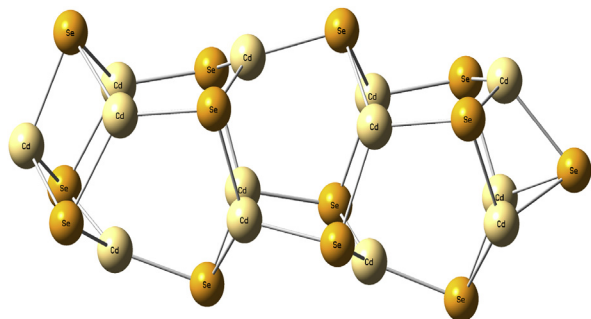


Fig. 2. Bare CdSe wurtzoid2c molecule after geometrical optimization.

convenient for use in previous wurtzoid calculations [8–10]. Heavy elements such as Cd atoms in the present compound cannot be performed using the same basis (6-31G**) used for lighter elements (Se, H) and resorting to simpler basis states such as the 3-21G basis for Cd atoms resolved the problem.

3. Results and discussion

Fig. 5 shows the variation of the energy gap (highest occupied molecular orbital to lowest unoccupied molecular orbital (HOMO-LUMO)) of bare and hydrogen

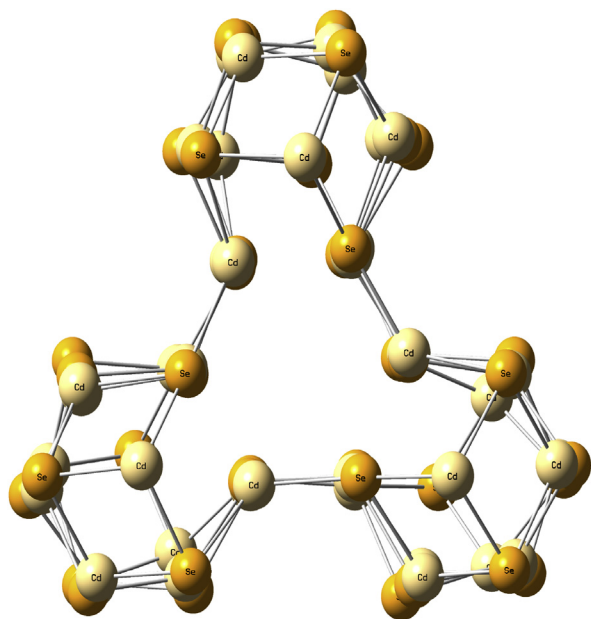


Fig. 3. Bare CdSe triwurtzoid after geometrical optimization.

passivated CdSe wurtzoids. The variation shows that

both bare and HP CdSe wurtzoids tend to converge to the bulk experimental gap. However, there are differences in the way that bare and HP wurtzoids converge to bulk experimental gap. Both of the bare and HP wurtzoids obey quantum confinement rule of approaching bulk energy gap with increasing size [15]. However, due to a large number of dangling bonds in both CdSe and Cd₃Se₃ molecules (first two bare molecules in Fig. 5) with respect to the actual number of bonds of the two molecules, the energy gap is lowered since the dangling bonds create energy levels inside the original energy gap that decrease its value. As the molecules increase in size, the number of dangling bonds decreases with respect to the total number of bonds that prevents gap reduction and renders quantum confinement rule of approaching bulk energy gap as the size of nanocrystals increases.

Fig. 6 shows the variation of CdSe molecules vibrational reduced mass as a function of the frequency of both bare and HP wurtzoids. The longitudinal optical mode (LO) can be deduced from this figure [9]. The LO mode is the last vibrational mode in the bare case. In the same way, the LO mode is the last vibrational mode in the HP case before hydrogen vibrations begin. Hydrogen vibrations are characterized by a reduced mass that is nearly equal to 1. LO modes of both bare and HP wurtzoids are shown in Fig. 6 in comparison with experimental LO value at 207 cm⁻¹ [18]. As we can see from Fig. 6, the experimental LO mode is situated between bare and HP LO modes and very near to the bare case. This phenomenon can be correlated with Fig. 4 that shows the weak bonding between surface hydrogenated atoms and the rest of the molecule. Surface hydrogen atoms are easily removed so that these molecules are partially hydrogenated in real experiments.

Fig. 7 shows the variation of CdSe vibrational force constant as a function of frequency for both bare and HP CdSe wurtzoid2c. As we can see from Fig. 7 that vibrational force constant of the bare case is several times stronger than that of HP case. Surface dangling bonds are the cause of this large increase. The electronic charge of dangling bonds strengthens other real bonds so that nearly double bonds are created in other bonds. Various hydrogen vibrations can be seen in the HP case in addition to the Cd–Se vibrations discussed previously in Fig. 6. Cd–H and Se–H bending vibrations can be seen in the range 252–505 cm⁻¹ in Fig. 7. These bending vibrations are followed by an island of Cd–H stretches at the range 1537–1564 cm⁻¹. Finally, an island of Se–H

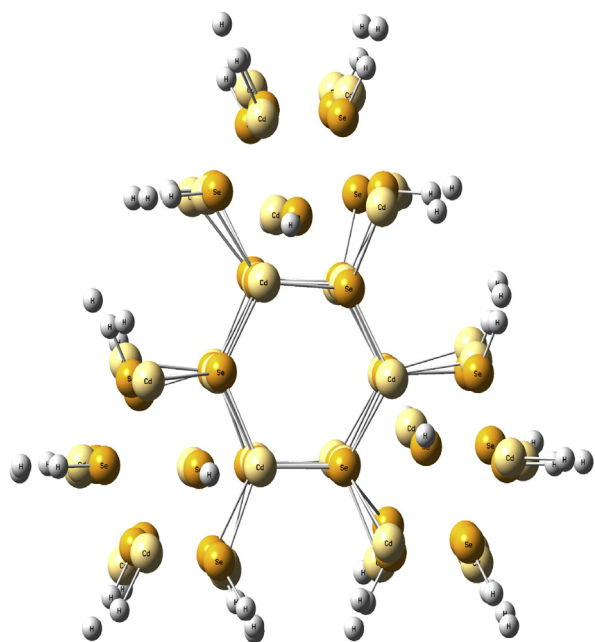


Fig. 4. Hydrogen passivated CdSe triwurtzoid after geometrical optimization.

stretching can be seen at the range $2287\text{--}2308\text{ cm}^{-1}$ of Fig. 7.

Two bulk phases of CdSe are known to exist in standard conditions, i.e., wurtzite and zincblende phases [19]. The third bulk phase namely rock-salt phase exists only at high pressures [20]. The three

phases differ in their bulk energy gap and vibrational frequencies. At the molecular-nanoscale limit, these phases are represented by wurtzoids, diamondoids, and cuboids for wurtzite, zincblende, and rock-salt phases respectively. To compare the three phases at the molecular-nanoscale range we choose CdSe wurtzoid (Fig. 1), diamondane (Fig. 8) and dicuboid (Fig. 9) in both bare and HP surfaces since they have a close number of Cd and Se atoms. Table 1 show some of these differences.

Gibbs free energy of atomization ($\Delta_a G$) in Table 1 is calculated by subtracting the theoretical Gibbs free energy of the molecule from that of constituting atoms. Table 1 reveals several interesting things about CdSe three phases of wurtzite, zincblende, and rock-salt at the molecular-nanoscale level:

- 1 The difference in energy gap between the two phases $E_g(\text{wurtzite}) - E_g(\text{zincblende})$ is in the order of 0.1 eV at the bulk limit [19]. However, at the extreme molecular limit, this difference is larger and is somewhere between 0.869 and 2.652 eV depending on surface passivation. The reason for this difference is quantum confinement effects and the excess surface dangling bonds of the two phases that introduces energy levels inside the gap.
- 2 The Gibbs free energy of atomization ($\Delta_a G$) reveals that the wurtzite phase is more stable than the zincblende phase of CdSe at the molecular limit. This is also the case at the bulk limit [21].

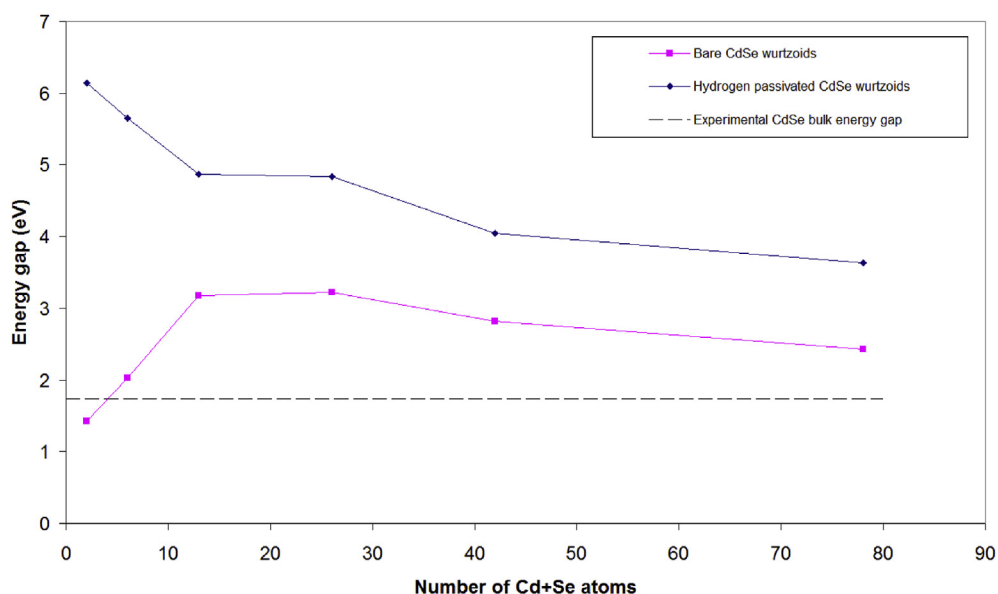


Fig. 5. The variation of the energy gap of bare and HP CdSe wurtzoids. The experimental bulk energy gap is shown [1].

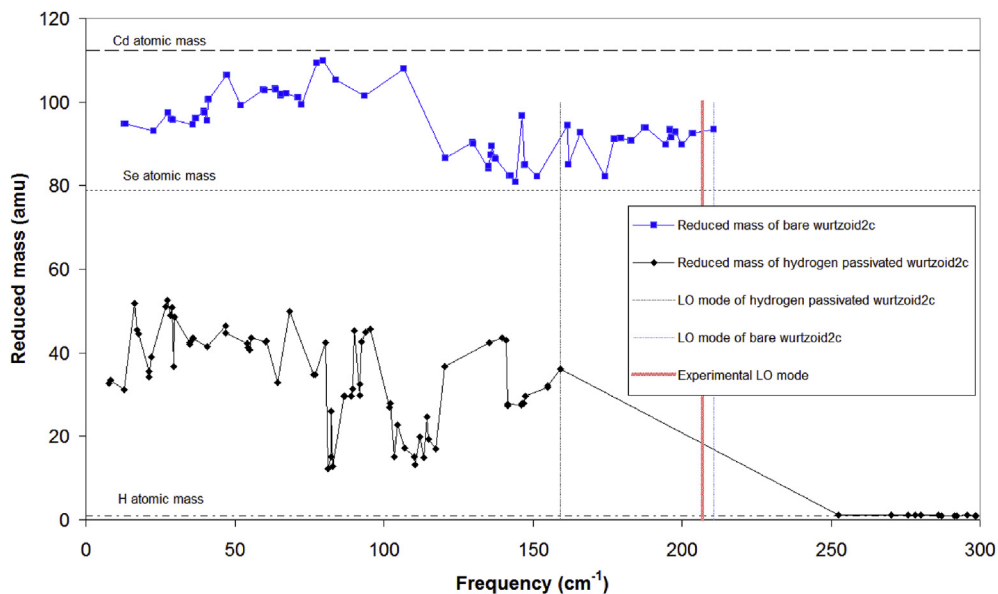


Fig. 6. The variation of CdSe vibrational reduced mass as a function of the frequency of both bare and HP wurtzoid2c. The experimental nanocrystals LO vibrational mode is shown [18]. The atomic masses of Cd, Se, and H are also shown. Only part of HP reduced masses is shown since the remaining reduced masses are all near the value (1) which is equal to H atomic mass number.

3 The present theory shows that the LO vibrational mode should be higher for the zincblende phase than the wurtzite phase because of a higher number of surface dangling bonds at the extreme molecular limit. However, no experimental frequency number is given in the literature for the zincblende phase. Most literature assigns the

same LO mode frequency for the two phases [22].

The bare and HP CdSe dicuboid molecules have a different number of Cd and Se atoms than their comparable wurtzoid and diamantane. To compare these molecules, one has to consider the averaging of the

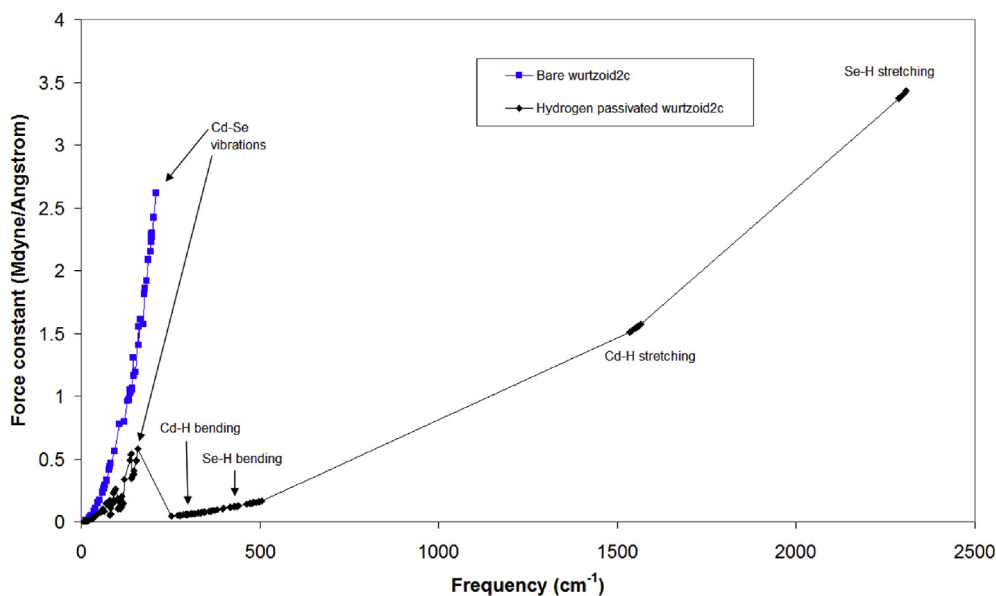


Fig. 7. The variation of CdSe vibrational force constant as a function of frequency for both bare and HP wurtzoid2c.

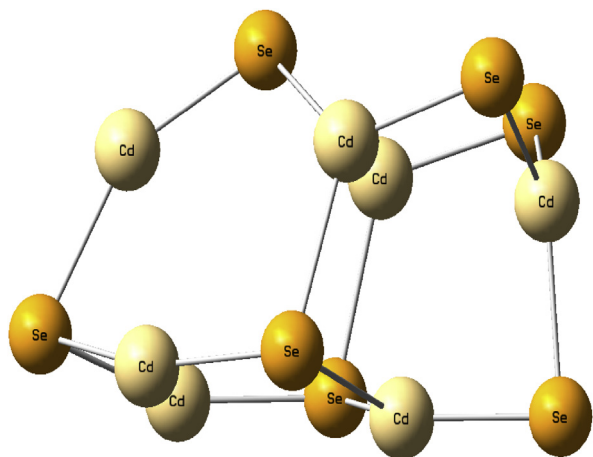
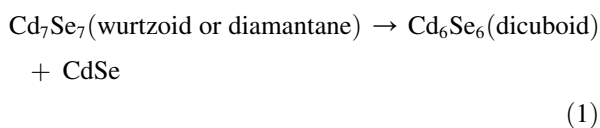


Fig. 8. CdSe bare diamantane (diamond cubic) optimized structure.

atomization energy of dicuboid and tricuboid (Cd_8Se_8). The value of the Gibbs free energy of atomization of CdSe bare tricuboid is 39.097 eV. The average of the two values is 33.963 eV. This value is higher than that of the diamantane and less than the wurtzoid. Another method is to consider the following dissociation reaction:



The Gibbs free energy of atomization of the products of Eq (1) is 31.144 eV. Comparing this value with those in Table 1 reveals that the CdSe bare wurtzoid will not dissociate to a dicuboid since its atomization

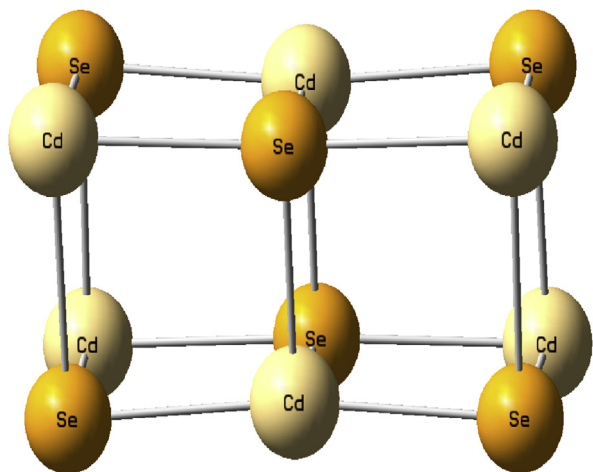
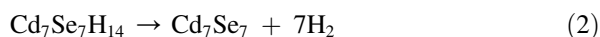


Fig. 9. CdSe bare dicuboid (rock-salt) optimized structure.

energy is 34.631 eV. On the other hand, bare CdSe diamantane will dissociate to a dicuboid since its atomization energy is 30.967 eV. This result makes the most stable bare structures in a descending order wurtzoid-cuboid-diamantane. This result is different than that in the bulk in which only wurtzite and zincblende are relatively stable under normal conditions. In Table 1 we also give the HP molecular species of the three phases. A similar result of that of bare molecules can be obtained for HP molecules. The most stable HP structures in descending order are also wurtzoid-cuboid-diamantane.

Finally, we can see from Figs. 4–7 that the hydrogen passivated CdSe structures are less stable, weaker and have an energy gap and vibrational frequencies that are relatively far from experimental values than in the case of bare molecules. This fact can be interpreted by the following reaction equation:



The Gibbs free energy of atomization of the products of Eq (2) is 64.227 eV. Comparing this value with that of the reactant from Table 1 (57.049 eV) reveals that the HP wurtzoid will eventually dissociate to hydrogen and bare CdSe wurtzoid. The HP wurtzoid is at a local potential minimum that prohibits fast dissociation. The dissociation time depends on the transition state between the reactant and the product. In fact, Se–H bond is strong enough to survive, which is also the case of Hydrogen selenide (H_2Se) molecule. However, Cd–H bond is less stable, and might decomposes at high temperatures as in the case of Cadmium hydride molecule (CdH_2) [23]. This explains why the experimental values are closer to the bare wurtzoids.

The Gibbs free energy of atomization is an efficient tool to check the relative stability of vacuum (bare) or gas surrounded materials (surface passivated) [24,25]. On the other hand, Gibbs free energy of formation can be used to check the quantum confinement effects on the formation energies of the nanostructured materials [26]. Gibbs free energy of formation should converge to the bulk experimental value of formation.

The bulk CdSe is known to have a red-black color which is what we expect from a material of 1.8 eV energy gap. As we reduce the size of CdSe nanocrystal to a quantum dot size, the color of these quantum dots changes to other colors such as blue-green color [27]. This change is expected from a material of 2.5 eV energy gap which is in excellent agreement with the results of Fig. 5 for the bare CdSe wurtzoids. This

Table 1

A comparison between bare and HP wurtzoid, diamantane and dicuboid CdSe molecules. The comparison includes energy gap (E_g), Gibbs free energy of atomization ($\Delta_a G$), longitudinal optical mode (LO), and the number of dangling bonds.

Molecule	Formula	E_g (eV)	$\Delta_a G$ (eV)	LO mode (cm^{-1})	Dangling bonds
Bare wurtzoid	Cd_7Se_7	3.182	34.631	210.704	14
Bare diamantane	Cd_7Se_7	0.530	30.967	251.206	20
Bare dicuboid	Cd_6Se_6	2.621	28.828	207.993	8
HP wurtzoid	$\text{Cd}_7\text{Se}_7\text{H}_{14}$	4.873	57.049	159.300	0
HP diamantane	$\text{Cd}_7\text{Se}_7\text{H}_{14}$	4.004	56.411	183.205	6
HP dicuboid	$\text{Cd}_6\text{Se}_6\text{H}_8$	3.946	42.177	181.276	0

result is also in agreement with our previous results that CdSe exist mainly in bare nanocrystals with minimum surface passivation. Additional useful information can be seen in Ref. [28].

4. Conclusions

Both bare and hydrogen surface passivated CdSe are discussed in the present work. These molecules show good convergence to bulk properties as their size increases. This includes the energy gap and vibrational properties in addition to the quantum confinement effects that reduce the value of the energy gap and increases longitudinal vibrational mode (LO) frequency. As the particles increases in size, the surface dangling bonds act in the reverse direction of decreasing the energy gap and increasing LO mode frequency. Gibbs free energy of atomization of wurtzoid, dicuboid and diamantane shows that the wurtzite phase is more stable in the molecular limit which is also the case at the bulk. Dicuboid is more stable than diamantane molecule which is the reverse situation in bulk case. Bare CdSe wurtzoid is more stable than hydrogen passivated CdSe wurtzoid which explains why the experimental energy gap and vibrational LO mode is nearer to bare CdSe wurtzoids results.

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