# Computational Study of Magic-Size CdSe Clusters with Complementary Passivation by Carboxylic and Amine Ligands

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**S** *Supporting Information*

**ABSTRACT:** The electronic and optical properties of tetrahedral CdSe magic clusters (average diameter ~1.5 nm) protected by carboxyl and amine ligands, which correspond to previously reported experimental structures, are studied using density functional theory. We find extreme ligand packing densities, capping every single dangling bond of the inorganic core, strong dependence of the Z-type metal carboxylate binding on the amount of excess amine, and potential for improved photoluminescence upon replacing phenyl ligands with alkanes. The computed absorption spectra of the $Cd_{35}Se_{20}$ cluster agree well with experiments, resolving the 0.2 eV splitting of the first exciton peak due to spin−orbit coupling. We discuss the origin of the significant broadening of the optical spectra as due to phonons and structural variations in the ligand configurations and inorganic core apexes.
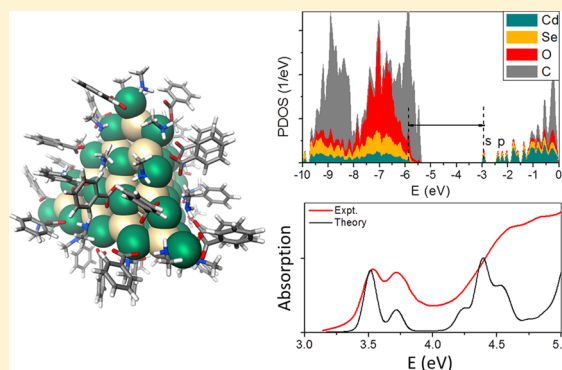
## I. INTRODUCTION

The properties of semiconductor quantum dots typically are very sensitive to the size and shape, as well as to surface passivation. They can be synthesized with high quality and have dimensions such that their optical gap can be tuned over the entire visible spectrum. Consequently, they find applications in light emitting devices,[1−3] solar cells,[4−7] and lasers.[8,9] The exact structure of the quantum dot surface remains often unknown despite being crucial for optoelectronic applications.[10] In this regard, ultrastable (so-called magic) clusters attract a lot of attention as promising candidates to shed light on the quantum dot surface chemistry, because their precise atomic structure can be resolved using X-ray diffraction techniques,[11−13] while their small size allows for comprehensive modeling using density functional theory.[14,15]

Tetrahderal CdSe clusters with thiolate ligands were reported more than two decades ago,[11,12] and mass-spectroscopy characterizations are available for CdSe clusters with ligands removed by laser ablation.[16,17] However, clusters with carboxylate ligands, more relevant for a typical synthesis of larger quantum dots,[18,19] have been isolated only recently.[13] Here we report the first comprehensive modeling of CdSe clusters including the full ligand shell. In particular, we verify the experimental predictions on the achievable ligand packing density. We explore the stability of the clusters and the variability of their geometry due to ligand rearrangements around the well-defined inorganic core. The role of the ligand

frontier orbitals in the photoluminescence properties of the clusters is studied and the absorption spectra are obtained within density functional theory, resolving a 0.2 eV splitting of the first absorption peak due to spin−orbit coupling. We also discuss the effect of thermal vibrations on the optical properties.

## II. COMPUTATIONAL ASPECTS

Structural optimizations with full ligand shell are performed using the Perdew−Burke−Ernzerhof (PBE) exchange-correlation functional and the CP2K software.[20] Full benzoic acid ligands and their shorter acetate analogues are explored. First, the ideal zincblende structure is frozen to allow for ligand relaxation, followed by unconstrained relaxation of the cluster as a whole. Further, the energy alignment of the ligand and inorganic core orbitals is verified with the B3LYP hybrid functional.[21,22]

We find that the PBE calculations do not capture the correct ligand and core energy alignment, resulting in ligand-localized trap-like states near the valence band even for acetate ligands, which is not the case in B3LYP calculations (see Figure S1 in the Supporting Information). To avoid this effect while maintaining a reasonable computational cost, optical properties

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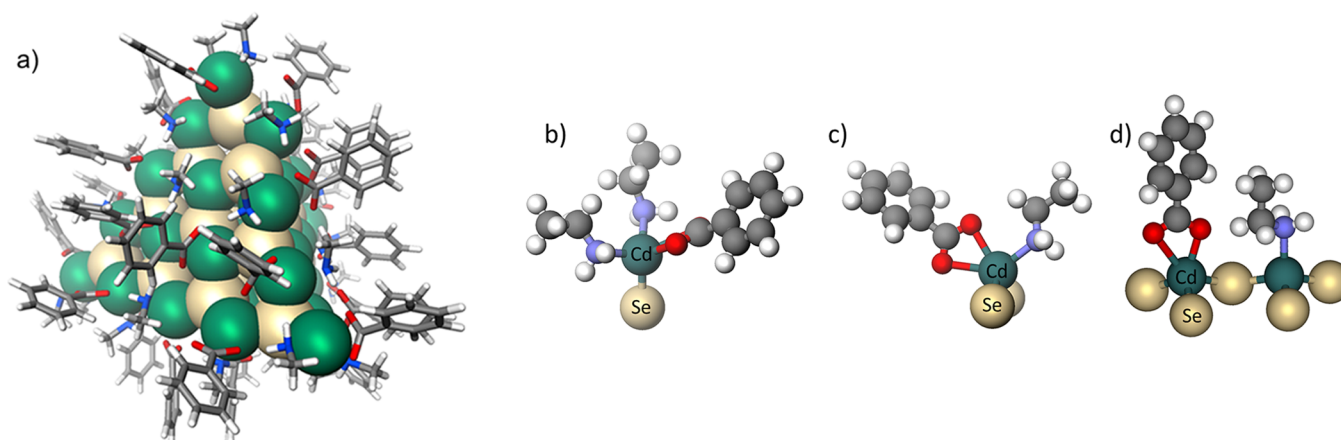**Figure 1.** (a) Relaxed structure of the $Cd_{35}Se_{20}$ cluster with all dangling bonds fully saturated by carboxylates and amines. Binding motifs of ligands on (b) apex Cd, (c) ridge Cd, and (d) Cd on (111) facet.

are calculated by the Vienna Ab-initio Simulation Package[23] within the frequency dependent dielectric matrix methodology,[24] using the PBE functional and passivating every dangling bond with pseudohydrogen with noninteger ionic charge.[25] The role of pseudohydrogen is to saturate each dangling bond to exactly two electrons. Thus, pseudohydrogen with charge 1.5 is used to saturate surface Cd atoms. This is a reasonable approximation at least for the first few absorption peaks, since the cluster frontier orbitals are not affected by the ligands and are localized on the inorganic core. The structure is fully relaxed but remains very close to the ideal zincblende structure. Effects of the spin−orbit coupling on the optical properties are also explored.

Molecular dynamics simulations are performed in CP2K for a cluster with ammonium and acetate ligands at 300 K, using a 1 fs time step for a total time of 6 ps. The first 1 ps of equilibration time is discarded. The bandgap variation due to thermal vibrations over the remaining 5 ps is fitted with a Gaussian. Since density functional theory underestimates the bandgap, we shift the conduction band states in all presented figures for direct comparison with experimental spectra.

## III. RESULTS AND DISCUSSION

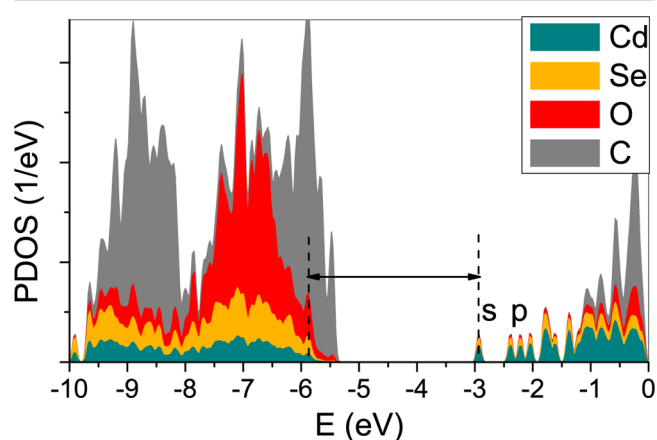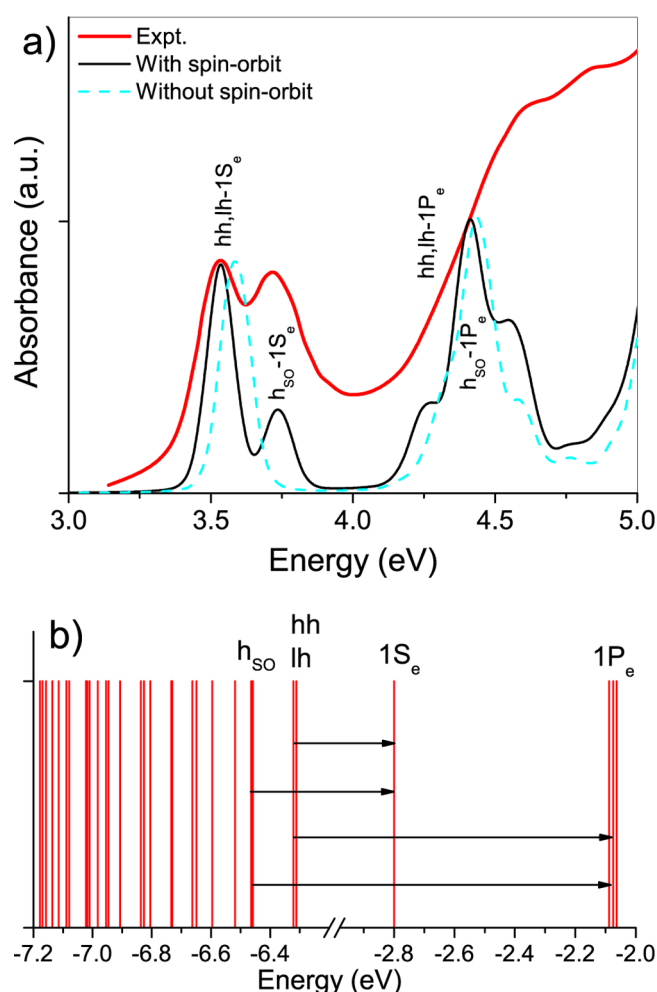**A. Structural and Electronic Properties.** Pristine CdSe quantum dots have many dangling bonds, since the surface Cd





**Figure 3.** (a) Absorption spectra and (b) interband transitions responsible for the absorption peaks of $Cd_{35}Se_{20}$ clusters passivated by pseudohydrogen.

and Se atoms are undercoordinated. Ligands typically saturate the unpaired electrons. On the basis of the measurements of the ligand concentration by nuclear magnetic resonance, it has been suggested that, at least in magic clusters, all dangling bonds are fully saturated with ligands.[13] However, it is not clear whether steric constraints would indeed allow for such a dense



**Figure 2.** Projected density of states calculated with the B3LYP functional, demonstrating ligand-localized in-gap states.
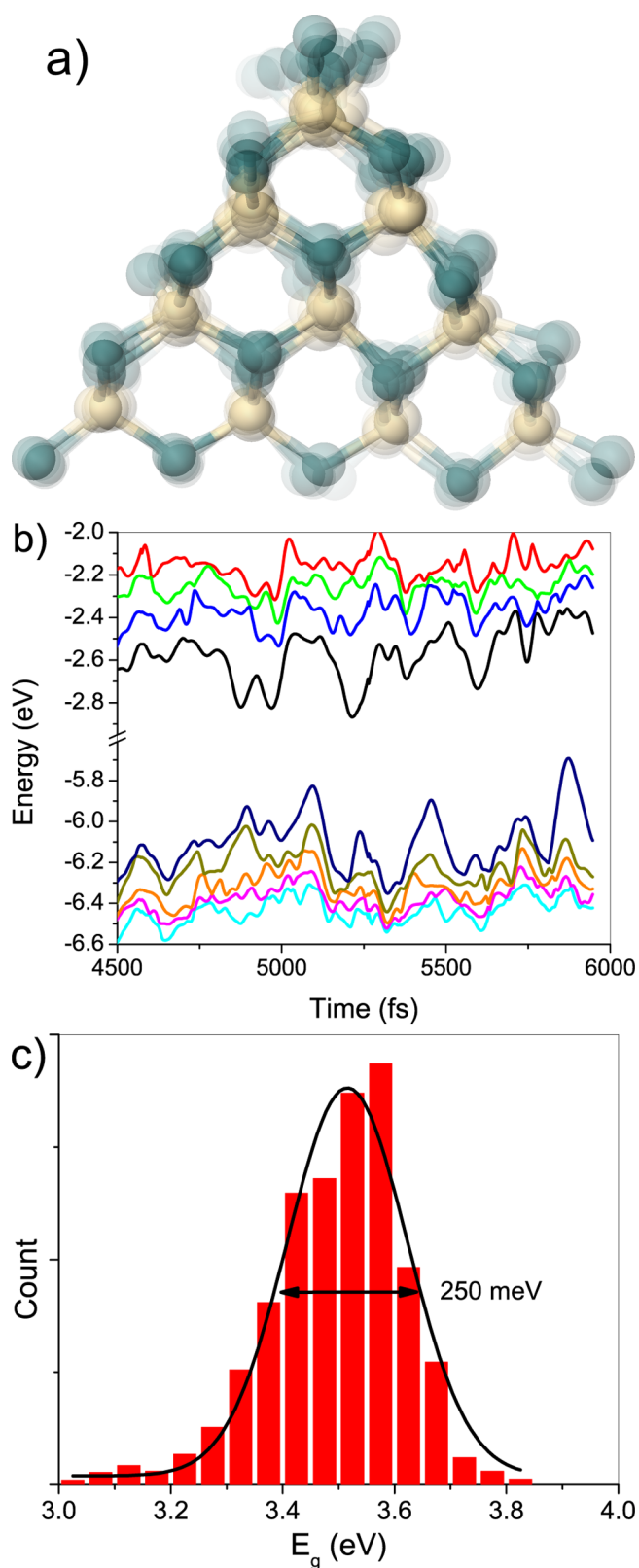
**Figure 4.** Molecular dynamics simulations showing the (a) atomic thermal deviations at 300 K, (b) resulting modifications of the electronic levels, and (c) bandgap distribution over a period of 5 ps.

ligands; see Figure 1a. The zincblende structure of the core is well retained, in agreement with experimental structures.[13] Without the ligands, the Cd atoms on (111) facets tend to planarize in a $sp^2$ configuration, whereas the presence of the ligands makes it possible to maintain a $sp^3$ configuration, as observed previously.[26,27] Extensive molecular dynamics simulations allow us to sample the most favorable ligand adsorption geometries; see Figure 1b−d. Corner Cd atoms have three dangling bonds, thus being saturated with three ligands, while the ridge Cd atoms fully utilize binding to two ligands, in contrast to previously published models with only one ligand.[27,28]

The projected density of states in Figure 2, calculated with the B3LYP functional, shows that the highest occupied molecular orbital of the cluster is located on the phenyl rings. This ligand-localization can explain the poor photoluminescence efficiency of the clusters and is consistent with prior experimental work on thiol-capped tetrahedral clusters.[29] We expect, however, that the clusters can become much brighter if alkane ligands are used instead.[11]

Saturation of all dangling bonds means that the edge Cd atoms have two ligands attached, and the apex Cd atoms have three ligands, as discussed above (Figure 1b). If two of them happen to be carboxylates, the apex species may be prone to desorption as a neutral $Cd(RCOO)_2$ molecule. Calculations confirm that such apex Z-type ligands have almost zero binding energy. However, the system stabilizes by 2.4 eV when one of the carboxylates from each apex is exchanged with an amine from the (111) facet of the cluster. Cd-carboxylate-amine complex desorption becomes favorable again upon solvation by an additional free amine molecule, suggesting that a loss of Cd apexes is possible when excess amines are available in the solution, consistent with experimental observations.[18,19] Closer inspection of the experimental pair distribution functions[13] indeed confirms that, at least for the smallest clusters, geometries lacking one or two apexes provide a better fit to the data. We thus consider all such configurations in the optical calculations described below.

**B. Absorption Spectra.** Absorption spectra are presented in Figure 3 together with the computed energy levels and transitions responsible for the optical peaks as well as the experimental spectrum.[13] Loss of Cd apexes exposes the Se dangling bonds. If left unpassivated, the highest occupied molecular orbital leaks into these dangling bonds, reducing the bandgap and forming sub-bandgap absorption peaks (Figure S2, Supporting Information). With all apexes intact, we find good agreement in terms of the overall shape of the spectrum, in particular the double peak structure at the absorption edge, with a 190 meV splitting. Calculations without inclusion of spin−orbit coupling result in a single peak, confirming that the doublet originates from a spin−orbit split hole state.

**C. Origin of the Spectral Broadening.** Since the first absorption peaks are dominated by only a handful of discrete transitions, we further seek to understand the origin of the significant broadening of the experimental spectra.[13] It is known that coupling to phonons can broaden the absorption and emission peaks and indeed significant narrowing is observed when cooling the nanocrystals down to low temperatures.[30,31] However, a typical broadening of ∼50 meV is observed for regular size nanocrystals, while it reaches 200 meV for the $Cd_{35}Se_{20}$ cluster explored here. We thus have performed molecular dynamics simulations; see Figure 4. We find that indeed, due to the small size of the cluster, thermal
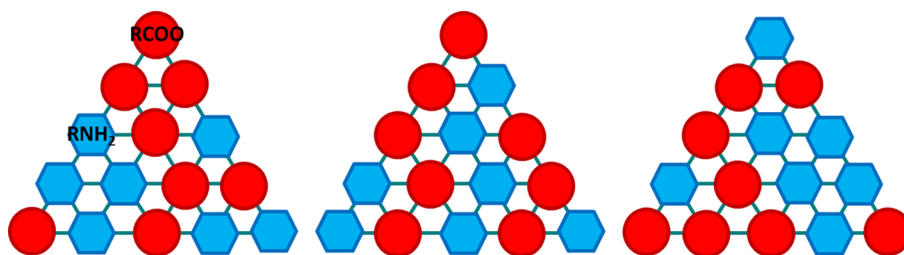
packing. We have created our models based on experimental suggestions, using short amines and benzoic acid as ligands, and indeed find that, due to the surface curvature, every dangling bond can be covered, despite the bulkiness of the phenyl

**Figure 5.** Schematic of different arrangements of carboxylates and amines on cluster (111) facets. Since each ligand can occupy any Cd site, swapping carboxylates and amines allows for multiple configurations, without affecting the surface passivation.

vibrations of the atoms constitute relatively large changes of the geometry, sufficient to broaden the bandgap by up to 250 meV.

In addition, experimental photoluminescence excitation spectra are shifted relative to the absorption,[13] suggesting the presence of not only homogeneous but also inhomogeneous ensemble broadening. We note that only 30 anionic benzoic acid ligands are required on a $Cd_{35}Se_{20}$ cluster to achieve electroneutrality. The rest of the surface sites are covered with amines, which saturate the Cd dangling bonds with dative bonds formed by the N lone pair. Since both types of ligands adsorb on Cd, a multitude of ligand arrangements is possible, with total energy variations below 0.2 eV; see Figure 5. Each such arrangement yields a slightly different surface relaxation and thus affects the band gap of the cluster, leading to an inhomogeneous broadening of the absorption spectrum of an ensemble with nominally identical cores.

## IV. CONCLUSION

We have presented a first-principles analysis of tetrahedrally shaped CdSe magic clusters with carboxyl and amine ligands, with and without structural imperfections at the apexes of the pyramid. We confirm a high ligand packing density (covering every dangling bond), as suggested by experiments, and a complementary role of carboxylates and amines, allowing to decouple the surface coverage from the charge neutrality. Calculated optical spectra show good agreement with experiment. In particular, the splitting of the first absorption peak is assigned to a spin−orbit split hole state. In addition to phonons leading to homogeneous line width broadening, a multitude of possible ligand configurations on the surface allows for a significant inhomogeneous broadening in an ensemble of nominally identical inorganic cores. We predict that the photoluminescence of magic clusters can be significantly improved if alkane ligands are used instead of phenyls. The ligand-capped clusters reported here can serve as prototypical models for further studies of the carrier relaxation dynamics, defects, phonon-assisted trap emission, and blinking of larger nanocrystals.

## ASSOCIATED CONTENT

**Ⓢ Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b10908.

> Figures showing calculated projected density of states and HOMO wavefunctions of the $Cd_{35}Se_{20}$ cluster with ammonium + acetate ligands and calculated absorption spectrum of a cluster with two apices removed (PDF)
> Input files and geometries (ZIP)

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**Notes**
The authors declare no competing financial interest.

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