

Structure and Optical Properties of Tetrahedral CdSe Clusters with Carboxylate and Amine Ligands

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RPA calculation of $\text{Cd}_{35}\text{Se}_{20}\text{X}_{30}\text{L}_{30}$

The imaginary part of the dielectric function ($\varepsilon = \varepsilon^{(1)} + i\varepsilon^{(2)}$) is given by the Cartesian tensor

$$\varepsilon_{\alpha\beta}^{(2)}(\omega) = \frac{4\pi^2 e^2}{\Omega} \lim_{q \rightarrow 0} \frac{1}{q^2} \sum_{c,v,\vec{k}} 2\omega_{\vec{k}} \delta(\varepsilon_{c\vec{k}} - \varepsilon_{v\vec{k}} - \omega) \times \langle u_{c\vec{k}+\vec{e}_\alpha q} | u_{v\vec{k}} \rangle \langle u_{c\vec{k}+\vec{e}_\beta q} | u_{v\vec{k}} \rangle^*,$$

where ω is in units of energy; Ω is the volume of the cell; $\vec{e}$ are unit vectors for the three Cartesian directions; c and v are conduction and valence states, respectively; $u_{c\vec{k}}$ are the cell-periodic orbitals at $\vec{k}$.³ In the calculation of $\varepsilon_{\alpha\beta}^{(2)}(\omega)$, $\vec{k}$ is restricted to the irreducible wedge of the first Brillouin zone. The real part of the dielectric tensor is obtained from Kramers-

$$\varepsilon_{\alpha\beta}^{(1)}(\omega) = 1 + \frac{2}{\pi} P \int_0^\infty \frac{\varepsilon_{\alpha\beta}^{(2)}(\omega') \omega'}{\omega'^2 - \omega^2 + i\eta} d\omega',$$

where P denotes the principal value of the integral. Spectra were calculated using $\alpha_{ij}(\omega) = \frac{\sqrt{2}}{ch} E \sqrt{\sqrt{\varepsilon_{ij}^{(1)}(\omega)^2 + \varepsilon_{ij}^{(2)}(\omega)^2} - \varepsilon_{ij}^{(1)}(\omega)}$, where $i, j = x, y, z$. Here we

used the average absorption coefficient, defined by $\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$, and the calculations were carried out at

the RPA (random phase approximation) level of theory.

Calculations were performed with the Vienna ab initio simulation package VASP 5.4,^{1,2} based on the structure optimized with the DFT/PBE0 functional (see main text), including and excluding spin-orbit coupling (SOC). A plane wave basis set with an energy cutoff of 500 eV was used. The k -sampling is Γ point sampling. A 15 Å vacuum is added in the x, y , and z directions.

The RPA optical absorption spectra for CdSe quantum dots are shown in the Figure below for clusters that are passivated by pseudohydrogens (a), formate-ammonia ligand pairs (b), and formate-methylamine ligand pairs (c,d). In the case of pseudohydrogen passivation, In the case of H passivation, the first peak is not split without SOC and is at 2.69 eV, while when SOC is included, the peak is split into two peaks, located at 2.61 and 2.81 eV, with an intensity ratio of 2.3. For formate-ammonia (b), formate-methylamine clusters (c, d), the absorption spectra are quite similar with and without SOC. With SOC, the first peak is split into two peaks, at 2.28 and 2.41 eV with an intensity ratio of 0.95 for (b), and 2.24 and 2.38 eV with a ratio of 1.45 for (c). With SOC, the first peak is not split for (d). The peak is at 2.12 eV.

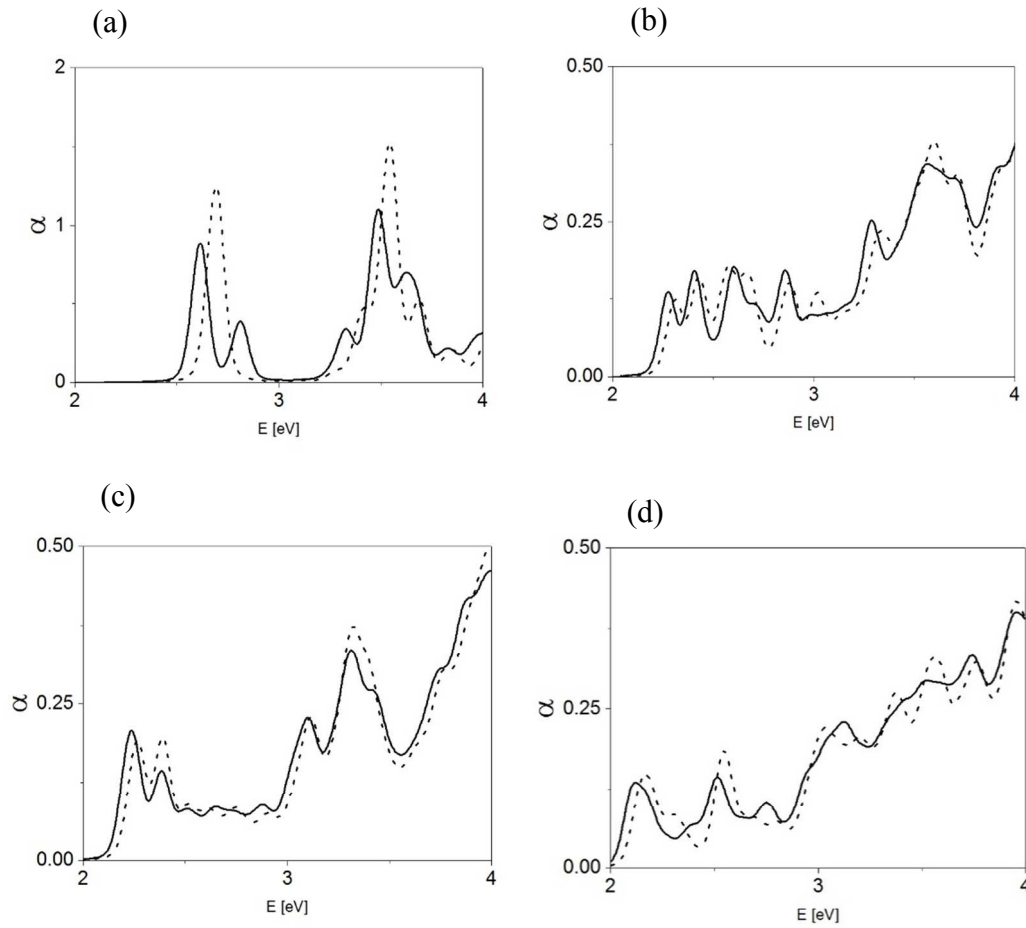


Figure: RPA optical absorption for CdSe quantum dots passivated by (a) pseudohydrogen atoms, (b) ammonia, (c) L, and (d) M ligands, with (solid) and without (dash) SOC.

- (1) Kresse, G.; Furthmüller, J. Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set. *Computational Materials Science* **1996**, *6*, 15-50.
- (2) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Physical Review B* **1999**, *59*, 1758-1775.
- (3) Gajdoš, M.; Hummer, K.; Kresse, G.; Furthmüller, J.; Bechstedt, F. Linear optical properties in the projector-augmented wave methodology. *Physical Review B* **2006**, *73*, 045112.

Table 1S. Summary of computed relative energies (in kcal/mol) in the gas-phase and diethyl ether for $\text{Cd}_4\text{SeX}_6\text{L}_6$ ($\text{X} = \text{O}_2\text{C}-\text{C}_6\text{H}_5$, $\text{L} = \text{H}_2\text{N}-\text{CH}_3$). Values in parentheses are obtained with the Def2-TZVP basis set.

Method/Isomer	Gas-phase	Diethyl ether
a	0.0	0.0
b		
PBE0	6.5	5.3
PBE0-D3//PBE0	8.6	7.5
MP2//PBE0	8.3	7.3
PBE0-D3	4.1	4.6
MP2//PBE0-D3	2.3	3.3
MP2	2.4	2.1
c		
PBE0	7.3	7.7
PBE0-D3//PBE0	3.3	3.7
MP2//PBE0	-2.6	-1.8
PBE0-D3	2.0 (1.6)	3.7 (3.0)
MP2//PBE0-D3	-3.4	-1.4
MP2	-3.3	-2.3
d		
PBE0	9.0	9.8
PBE0-D3//PBE0	4.5	5.4
MP2//PBE0	-1.0	0.2
PBE0-D3	10.6	10.5
MP2//PBE0-D3	4.6	4.7
MP2	5.4	4.5
e		
PBE0	17.7	14.0
PBE0-D3//PBE0	15.5	11.8
MP2//PBE0	11.0	7.3
PBE0-D3	21.6	18.5
MP2//PBE0-D3	14.1	11.1

Mean unsigned errors compared to MP2 in the gas-phase: 0.3 (MP2//PBE0-D3), 4.1 (PBE0-D3), 4.3 (MP2//PBE0) 6.1 (PBE0). Mean unsigned errors compared to PCM-MP2//PBE0-D3 in diethyl ether: 0.8 (MP2//PBE0-D3), 4.8 (PBE0-D3), 3.3 (MP2//PBE0) 6.2 (PBE0)

Table 2S. Summary of computed relative energies (in kcal/mol) in the gas-phase and diethyl ether for $\text{Cd}_{10}\text{Se}_4\text{X}_{12}\text{L}_{12}$ ($\text{X} = \text{O}_2\text{C}-\text{C}_6\text{H}_5$, $\text{L} = \text{H}_2\text{N}-\text{CH}_3$). Values in parentheses are for $\text{X} = \text{O}_2\text{CH}$, $\text{L} = \text{H}_2\text{N}-\text{CH}_3$.

Method/Isomer	Gas-phase	Diethyl ether
a	0.0	0.0
b		
PBE0	4.5	4.5
PBE0-D3//PBE0	1.6	1.6
PBE0-D3	0.2	0.4
c		
PBE0	5.8	4.3
PBE0-D3//PBE0	1.8	0.3
PBE0-D3	-5.8	-6.4
d		
PBE0	3.0	2.7
PBE0-D3//PBE0	-3.5	-3.5
PBE0-D3	-7.4	-6.6
e		
PBE0	4.4	2.7
PBE0-D3//PBE0	-0.3	-1.9
PBE0-D3	-5.9	-6.4
f		
PBE0	5.5	4.4
PBE0-D3//PBE0	2.5	1.4
PBE0-D3	-9.3	-6.9
MP2//PBE0-D3	-7.5	-4.9
g		
PBE0	6.9	9.6
PBE0-D3//PBE0	-1.0	1.6
PBE0-D3	-13.3 (-14.5)	-9.6 (-8.8)
MP2//PBE0-D3	-9.9	-5.3

Mean unsigned errors compared to MP2//PBE0-D3 in the gas-phase: 2.6 (PBE0-D3), 9.5 (PBE0-D3//PBE0), 14.5 (PBE0). Mean unsigned errors compared to PCM-MP2//PBE0-D3 in diethyl ether: 3.2 (PCM-PBE0-D3//PBE0-D3), 6.6 (PCM-PBE0-D3//PBE0), 12.1 (PCM-PBE0//PBE0).

Table 3S. Summary of computed relative energies (in kcal/mol) in the gas-phase and diethyl ether for $\text{Cd}_{20}\text{Se}_{10}\text{X}_{20}\text{L}_{20}$, $\text{X} = \text{O}_2\text{C}-\text{C}_6\text{H}_5$ and $\text{L} = \text{H}_2\text{N}-\text{CH}_3$. Values in parentheses are for $\text{X} = \text{O}_2\text{C}-\text{CH}_3$ and $\text{L} = \text{H}_2\text{N}-\text{CH}_3$. Values in brackets are for $\text{X} = \text{O}_2\text{C}-\text{H}$ and $\text{L} = \text{H}_2\text{N}-\text{CH}_3$.

Method/Isomer	Gas-phase	Diethyl ether
a	0.0	0.0
b		
PBE0	2.2 [1.1]	-0.9 [-1.1]
PBE0-D3//PBE0	15.4 [7.2]	12.4 [5.0]
PBE0-D3	1.1 [5.8]	-0.3 [3.0]
c		
PBE0	7.3 [2.4]	3.7 [0.6]
PBE0-D3//PBE0	18.1 [12.0]	14.5 [10.2]
PBE0-D3	14.3 [14.8]	13.0 [11.1]
d		
PBE0	6.5 [7.9]	0.0 [1.5]
PBE0-D3//PBE0	13.8 [9.8]	7.3 [3.4]
PBE0-D3	14.3 [9.7]	8.9 [1.3]
e		
PBE0	0.3 [0.2]	0.8 [0.0]
PBE0-D3//PBE0	0.1 [0.8]	3.2 [0.6]
PBE0-D3	1.5 [-0.2]	-0.1 [-0.3]
f		
PBE0	2.6 [0.1]	0.4 [0.3]
PBE0-D3//PBE0	9.6 [4.2]	7.5 [4.4]
PBE0-D3	6.5 [7.3]	2.3 [3.8]
g		
PBE0	14.0 [6.3]	12.0 [6.8]
PBE0-D3//PBE0	17.1 [5.7]	15.1 [6.2]
PBE0-D3	[7.9]	[4.8]
h		
PBE0	26.4 [29.7]	19.6 [23.0]
PBE0-D3//PBE0	36.3 [31.0]	29.6 [24.3]
i		
PBE0	38.6 [36.9]	29.3 [26.6]
PBE0-D3//PBE0	55.4 [39.3]	46.1 [27.1]

Table 4Sa. Summary of computed relative energies (in kcal/mol) in the gas-phase and diethyl ether for $\text{Cd}_{35}\text{Se}_{20}\text{X}_{30}\text{L}_{30}$ (X = O_2CH , L = NH_3).

Method/Isomer	Gas-phase	Diethyl ether
a	0.0	0.0
b		
PBE0	0.2	-2.6
PBE0-D3//PBE0	0.3	-2.5
PBE0-D3	8.2	1.9
c		
PBE0	4.8	-1.8
PBE0-D3//PBE0	5.7	-0.9
PBE0-D3	5.1	1.1
d		
PBE0	6.7	3.3
PBE0-D3//PBE0	10.1	6.7
e		
PBE0	7.0	2.0
PBE0-D3//PBE0	6.3	1.4
f		
PBE0	9.5	3.8
PBE0-D3//PBE0	13.3	7.4
g		
PBE0	11.2	15.2
PBE0-D3//PBE0	14.0	18.1
h		
PBE0	13.0	13.6
PBE0-D3//PBE0	15.7	16.3
PBE0-D3	14.5	17.0
i		
PBE0	14.4	18.8
PBE0-D3//PBE0	19.9	24.6
j		
PBE0	20.3	22.1
PBE0-D3//PBE0	22.6	24.4
k		
PBE0	21.6	14.3
PBE0-D3//PBE0	27.6	19.9
l		
PBE0	19.5	20.5
PBE0-D3//PBE0	23.2	24.2
PBE0-D3	16.7	20.4
m		
PBE0	26.1	29.9
PBE0-D3//PBE0	29.4	33.1
n		
PBE0	26.2	7.7
PBE0-D3//PBE0	29.4	10.7
o		
PBE0	40.6	38.4
PBE0-D3//PBE0	45.8	43.6
PBE0-D3	43.9	41.5

Table 4Sb. Summary of computed relative energies (in kcal/mol) in the gas-phase and diethyl ether for $\text{Cd}_{35}\text{Se}_{20}\text{X}_{30}\text{L}_{30}$ ($\text{X} = \text{O}_2\text{CH}$, $\text{L} = \text{H}_2\text{N-CH}_3$). Values in brackets are for $\text{X} = \text{O}_2\text{CC}_6\text{H}_5$, $\text{L} = \text{H}_2\text{N-CH}_3$.

Method/Isomer	Gas-phase	Diethyl ether
a	0.0	0.0
b		
PBE0	3.9	1.7
PBE0-D3//PBE0	11.5	2.0
c		
PBE0	2.9	3.0
PBE0-D3//PBE0	7.2	7.3
d		
PBE0	-9.9	-11.2
PBE0-D3//PBE0	15.7	5.6
e		
PBE0	0.5	-3.3
PBE0-D3//PBE0	11.1	7.3
f		
PBE0	-2.2	-2.2
PBE0-D3//PBE0	7.7	7.7
g		
PBE0	-22.8 [-23.5]	-13.9[-17.5]
PBE0-D3//PBE0	-9.6 [-21.1]	-0.7 [-28.4]
PBE0-D3	-11.3 [-29.2]	-1.5 [24.3]
h		
PBE0	-2.5	-0.9
PBE0-D3//PBE0	-0.3	1.3
i		
PBE0	-22.7	-13.8
PBE0-D3//PBE0	-12.0	-3.2
PBE0-D3	-20.2 [-34.2]	-12.4 [-28.0]
j		
PBE0	-16.1	-8.1
PBE0-D3//PBE0	0.8	8.8
k		
PBE0	2.4	-9.3
PBE0-D3//PBE0	2.8	6.6
l		
PBE0	-23.3	-14.5
PBE0-D3//PBE0	-17.1	-8.3
PBE0-D3	-18.6 [-32.5]	-11.5 [-23.4]
m		
PBE0	-18.4	4.9
PBE0-D3//PBE0	-4.4	8.1
n		
PBE0	-18.3	-10.0
PBE0-D3//PBE0	-4.3	4.0
o		
PBE0	-15.4	-7.6
PBE0-D3//PBE0	0.1	7.9

Table 5S. Computed lowest excitation energies (in eV) and oscillator strengths (in parentheses) in the gas-phase and diethyl ether.

Cluster	Gas-phase	Diethyl ether
T2 Cd₁₀Se₄X₁₂L₁₂		
X = O ₂ C-C ₆ H ₅	4.25 (0.12)	4.31 (0.18)
X = O ₂ C-C ₆ H ₅ , L = H ₂ N-CH ₃	4.06 (0.00)	4.06 (0.00)
T3 Cd₂₀Se₁₀X₂₀L₂₀		
X = O ₂ C-C ₆ H ₅	3.74 (0.13)	3.80 (0.20)
X = O ₂ C-C ₆ H ₅ , L = H ₂ N-CH ₃	3.68 (0.16)	3.78 (0.36)
T4 Cd₃₅Se₂₀X₃₀L₃₀		
X = O ₂ C-C ₆ H ₅	3.45 (0.12)	3.47 (0.17)
X = O ₂ C-C ₆ H ₅ , L = H ₂ N-CH ₃	3.47 (0.29)	3.54 (0.29)

^a Average core edge: 0.8 nm (T2), 1.2 nm (T3), 1.7 nm (T4).