Theoretical analysis of structures and electronic spectra in molecular cadmium chalcogenide clusters

Nguyen, Kiet A.; Pachter, Ruth; Day, Paul N.; Su, Haibin

2015

Nguyen, K. A., Pachter, R., Day, P. N., & Su, H. (2015). Theoretical analysis of structures and electronic spectra in molecular cadmium chalcogenide clusters. *The Journal of Chemical Physics*, 142(23), 234305-.

<https://hdl.handle.net/10356/81096>

<https://doi.org/10.1063/1.4922320>

© 2015 American Institute of Physics. This paper was published in *Journal of Chemical Physics* and is made available as an electronic reprint (preprint) with permission of American Institute of Physics. The published version is available at: [<http://dx.doi.org/10.1063/1.4922320>]. One print or electronic copy may be made for personal use only. Systematic or multiple reproduction, distribution to multiple locations via electronic or other means, duplication of any material in this paper for a fee or for commercial purposes, or modification of the content of the paper is prohibited and is subject to penalties under law.

Downloaded on 26 Apr 2023 16:00:51 SGT

Theoretical analysis of structures and electronic spectra in molecular cadmium chalcogenide clusters

Kiet A. Nguyen, Ruth Pachter, Paul N. Day, and Haibin Su

Citation: *The Journal of Chemical Physics* **142**, 234305 (2015); doi: 10.1063/1.4922320

View online: <http://dx.doi.org/10.1063/1.4922320>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/142/23?ver=pdfcov>

Published by the [AIP Publishing](#)

Articles you may be interested in

Symmetry-adapted cluster and symmetry-adapted cluster-configuration interaction method in the polarizable continuum model: Theory of the solvent effect on the electronic excitation of molecules in solution

J. Chem. Phys. **133**, 024104 (2010); 10.1063/1.3456540

Molecular geometry and polarizability of small cadmium selenide clusters from all-electron ab initio and Density Functional Theory calculations

J. Chem. Phys. **124**, 071101 (2006); 10.1063/1.2173236

HF in clusters of molecular hydrogen. I. Size evolution of quantum solvation by parahydrogen molecules

J. Chem. Phys. **122**, 244306 (2005); 10.1063/1.1927528

Structural and electronic properties of CdS and CdSe clusters

J. Chem. Phys. **114**, 943 (2001); 10.1063/1.1329126

Structures and electronic phases of the bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) clusters and κ -(BEDT-TTF) salts: A theoretical study based on ab initio molecular orbital methods

J. Chem. Phys. **111**, 5986 (1999); 10.1063/1.479894

The logo for AIP APL Photonics. It features the letters 'AIP' in a large, white, sans-serif font, followed by a vertical yellow bar and the words 'APL Photonics' in a smaller, white, sans-serif font. The background is a red gradient with a bright yellow sunburst effect.

APL Photonics is pleased to announce
Benjamin Eggleton as its Editor-in-Chief

Theoretical analysis of structures and electronic spectra in molecular cadmium chalcogenide clusters

Kiet A. Nguyen,^{1,2,a)} Ruth Pachter,^{1,a)} Paul N. Day,^{1,3} and Haibin Su⁴

¹Air Force Research Laboratory, Wright-Patterson Air Force Base, Ohio 45433, USA

²UES, Inc., Dayton, Ohio 45432, USA

³General Dynamics Information Technology, Inc., Dayton, Ohio 45431, USA

⁴Nanyang Technological University, Singapore 639798, Singapore

(Received 2 April 2015; accepted 28 May 2015; published online 16 June 2015)

We present calculated structural and optical properties of molecular cadmium chalcogenide non-stoichiometric clusters with a size range of less than 1 nm to more than 2 nm with well-defined chemical compositions and structures in comparison to experimental characterization and previous theoretical work. A unified treatment of these clusters to obtain a fundamental understanding of the size, ligand, and solvation effects on their optical properties has not been heretofore presented. The clusters belong to three topological classes, specifically supertetrahedral (T_n), penta-supertetrahedral (P_n), and capped supertetrahedral (C_n), where n is the number of metal layers in each cluster. The tetrahedrally shaped T_n clusters examined in this work are $\text{Cd}(\text{ER})_4^{2-}$ (T1), $\text{Cd}_4(\text{ER})_{10}^{2-}$ (T2), and $\text{Cd}_{10}\text{E}'_4(\text{ER})_{16}^{4-}$ (T3), where R is an organic group, E and E' are chalcogen atoms (sulfur or selenium). The first member of the P_n series considered is $\text{M}_8\text{E}'(\text{ER})_{16}^{2-}$. For the C_n series, we consider the first three members, $\text{M}_{17}\text{E}'_4(\text{ER})_{28}^{2-}$, $\text{M}_{32}\text{E}'_{14}(\text{ER})_{36}\text{L}_4$, and $\text{M}_{54}\text{E}'_{32}(\text{ER})_{48}\text{L}_4^{4-}$ (L = neutral ligand). Mixed ligand clusters with capping ER groups replaced by halogen or neutral ligands were also considered. Ligands and solvent were found to have a large influence on the color and intensity of the electronic absorption spectra of small clusters. Their effects are generally reduced with increasing cluster sizes. Blueshifts were observed for the first electronic transition with reduced size for both cadmium sulfide and cadmium selenide series. Due to weakly absorbing and forbidden transitions underlying the one-photon spectra, more care is needed in interpreting the quantum confinement from the clusters' lowest-energy absorption bands. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4922320>]

I. INTRODUCTION

Chalcogenide clusters with well-defined size and structure serve as building blocks for new materials with size-dependent properties.^{1,2} Advances in synthetic methods have been very successful in producing a wide variety of nonstoichiometric molecular clusters with unique structures and sizes that overlap in size with ultrasmall stoichiometric quantum dots. The progress in the synthesis and characterization of II-VI molecular clusters containing over 100 metal-chalcogen sites^{3–5} with well-defined chemical compositions has led to a number of systematic studies aimed at understanding the role of size variance,^{6–8} solvent, and surface ligands in optical properties, including a number of theoretical studies.^{9–14} As pointed out in the review by Feng *et al.*,¹⁵ these clusters belong to three topological classes¹⁵ named supertetrahedral (T_n), penta-supertetrahedral (P_n), and capped supertetrahedral (C_n), where n is the number of metal layers in each cluster (Figure 1). T_n clusters are regular tetrahedrally shaped fragments of the cubic ZnS type lattice. The tetrahedral clusters examined in this work are $\text{M}(\text{ER})_4^{2-}$ (T1), $\text{M}_4(\text{ER})_6\text{L}_4^{2-}$ (T2), and $\text{M}_{10}\text{E}'_4(\text{ER})_{12}\text{L}_4$ (T3), where the metal ion M is cadmium, R is an organic group, and E and E' are chalcogen (sulfur or

selenium) atoms. L is a coordinating ligand such as a halogen atom, water, PR_3 , or an ER group. The small T2 and T3 clusters are made up of adamantane-like cages. For T3, the six inner M atoms (M^i) form an octahedron while the outer M atoms (M^o) constitute a tetrahedron. Each P_n is an assembly of four T_n clusters tetrahedrally distributed onto four faces of one T_n cluster with interconverted cationic and anionic sites. The first member of the P_n series is $\text{M}_8\text{E}'(\text{ER})_{12}\text{L}_4^{2-}$, which has been synthesized with various bridging and coordinating ligands: $\text{Cd}_8\text{E}'(\text{EPh})_{12}\text{L}_4^{2-}$ (E, E' = S, Se, Te, L = SPh, Ph = phenyl)¹⁶ and $\text{Cd}_8\text{Se}(\text{SePh})_{12}\text{Cl}_4^{2-}$.⁸ For the C_n series, the first three members are $\text{M}_{17}\text{E}'_4(\text{ER})_{24}\text{L}_4^{2-}$ (C1), $\text{M}_{32}\text{E}'_{14}(\text{ER})_{36}\text{L}_4$ (C2), and $\text{M}_{54}\text{E}'_{32}(\text{ER})_{48}\text{L}_4$ (C3). The core of these molecular clusters forms a tetrahedral bound M-E network consisting of primarily fused adamantane cages similar to the bulk structure. For the C1 class, neutral $[\text{Cd}_{17}\text{S}_4(\text{SCH}_2\text{CH}_2\text{OH})_{26}]$,¹⁷ cationic $[\text{Cd}_{17}\text{S}(\text{SEtOH})_{24}^{2+}]$ and $[\text{Cd}_{17}\text{Se}_4(\text{SePh})_{24}(\text{PPh}_2\text{Pr})_4^{2+}]$,^{18,6,8} and anionic $[\text{Cd}_{17}\text{E}'_4(\text{EPh})_{28}^{2-}]$; E = E' = S, Se; E = S, E' = Se¹⁹ cluster species have been prepared and characterized. Crystal structures and spectra of the larger C_n series have also been reported for $\text{Cd}_{32}\text{S}_{14}(\text{SPh})_{36}\text{DMF}_4$ (DMF = *N,N*-dimethylformamide),²⁰ $\text{Cd}_{32}\text{S}_{14}(\text{SCH}_2\text{CHOHCH}_3)_{36}(\text{H}_2\text{O})_4$,²¹ $\text{Cd}_{32}\text{Se}_{14}(\text{SePh})_{36}(\text{PPh})_4$,^{6,8,22} $\text{Cd}_{32}\text{S}_{14}(\text{SPh})_{40}^{4-}$, and $\text{Cd}_{54}\text{S}_{32}(\text{SPh})_{48}(\text{H}_2\text{O})_4^{4-}$.³ These clusters could be useful, for example, for two-photon absorption applications, as has been shown by Zhang *et al.*²³

^{a)}Authors to whom correspondence should be addressed. Electronic addresses: kiet.nguyen.2.ctr@us.af.mil and ruth.pachter@us.af.mil

FIG. 1. Structures of molecular chalcogenide clusters belonging to supertetrahedral (T_n), penta-supertetrahedral (P_n), and capped supertetrahedral (C_n) topologies: $M_4(ER)_6L_4^{2-}$ (T2), $M_8E'(ER)_{12}L_4^{2-}$ (P1), $M_{10}E'_4(ER)_{12}L_4^{2-}$ (T3), $M_{17}E'_4(ER)_{24}L_4^{2-}$ (C1), $M_{32}E'_{14}(ER)_{36}L_4$ (C2), and $M_{54}E'_{32}(ER)_{48}L_4$ (C3).

In this work, we present a systematic study of molecular cadmium sulfide and cadmium selenide clusters (shown in Figure 1) using electronic structure theory to predict their optical and photophysical properties and to obtain a fundamental understanding of the effects of size, structure, ligation, and solvation on the properties. Each cluster in Figure 1 was considered at least once in the literature, but a unified treatment of these families of molecular clusters ranging in size from less than 1 nm to more than 2 nm has not been heretofore presented. Size dependence of the excited state transitions in clusters has been previously examined using electronic structure theory using the singly excited configuration interaction (CIS) approximation and the CNDO/2²⁴ and CNDO/S^{9,10} semi-empirical Hamiltonians. Interestingly, the experimental and simulated spectra of $Cd_4(Sph)_{10}^{2-}$ and smaller clusters show a blueshift with increasing sizes, directly opposed to simple predictions based on quantum confinement.¹⁰ However, the lowest excitation energies computed using time-dependent density functional theory (TDDFT) and the tight-binding Hamiltonian for CdS clusters with hydride ligands were found to redshift with increasing particle size. In the work of del Puerto *et al.*,^{12,13} TDDFT and Green's function (GW-BSE) methods were applied to predict optical properties of hydride passivated neutral CdSe clusters [$Cd_4(SeH_2)_6$, $Cd_8H_4Se(SeH_2)_{16}$, $Cd_{10}H_4Se_4(SeH_2)_{12}$, $Cd_{17}H_4Se_4(SeH_2)_{24}$, and $Cd_{32}H_4Se_{14}(SeH_2)_{36}$] in the gas-phase. Similarly, structures and excitation energies of model compounds [$Cd_8Se(SeH)_{12}Cl_4^{2-}$, $Cd_{10}Se_4(SeH)_{12}(PH_3)_4$, $Cd_{17}Se_4(SeH)_{24}(PH_3)_4^{2+}$, and $Cd_{32}Se_{14}(SeH)_{36}(PH_3)_4$] of the larger CdSe clusters with hydride ligands have been reported using density functional theory (DFT) and TDDFT with the BP-86 functional.¹¹ The same functional was also used in a recent study of the $Cd_8Se(SePh)_{16}^{2-}$ and $Cd_{17}E'_4(EPh)_{28}^{2-}$ ($E = E' = S, Se$; $E = S, E' = Se$) clusters.¹⁹ However, due to the charge transfer (CT) nature in the excited states, the BP-86 predicted excitation energies for these molecular chalcogenide clusters were found to have very large errors (larger than 1 eV in some cases) in comparison with experiment. Since functionals based on the generalized gradient approximation are generally

found to significantly underestimate CT excitation energies, a benchmark study of hybrid and long-range corrected functionals was carried out for small bare and ligated stoichiometric $(ZnS)_n$ and $(CdSe)_n$ clusters using results from coupled cluster (CC) method with singles, doubles (CCSD), and noniterative triples (CCSD(T))²⁵ and the second order approximate CC (CC2)²⁶ methods. The PBE0 functional was found to provide a good description for both the ground and excited states for such small clusters.²⁷ Thus, the PBE0 hybrid functional is also used in this work to study structures and ground state spectra of the molecular CdSe and CdS clusters in order to shed light into the influence of size, topology, ligand, and solvent on spectral properties (see Table 1S in the supplementary material²⁸ for a summary of the clusters presently considered). The paper is organized as follows. Section II provides computational details. Section III presents results and discussion for ground state structures and spectra, starting with the cadmium sulfide clusters and then the cadmium selenide series. Finally, we summarize the findings and conclude the paper in Sec. IV.

II. COMPUTATIONAL METHODS

Kohn-Sham (KS)²⁹ DFT and TDDFT electronic structure calculations with the PBE0 functional were done using the Def2-TZVP basis set for small clusters [$Cd(Sph)_4^{2-}$, $Cd_4(Sph)_{10}^{2-}$, and $Cd_4(SePh)_6Cl_4^{2-}$]. For larger clusters, the Stuttgart/Dresden (SD) valence basis set and effective core potential were used for Cd, $(7s7p5d)/[5s5p2d]$,^{30,31} and Se, $(4s5p2d)/[2s2p2d]$,³² including two additional sets of d -functions for Se ($\zeta = 0.475\,412, 0.207\,776$)³³ atoms for better structures and energetics. Additional polarization functions for atoms with high coordination in the clusters were previously^{34,35} found important. Other atoms were treated with the 6-31G(d) basis set.^{36,37} For selected cases, calculations were carried out using the larger correlation consistent valence triple- ζ basis set. The $Cd(Sph)_4^{2-}$ cluster requires the larger Def2-TZVP³⁸ basis set for accurate excitation energies. However, the effects of basis sets were found to be

small for the larger $\text{Cd}_4(\text{SPh})_{10}^{2-}$ and $\text{Cd}_4(\text{SePh})_6\text{Cl}_4^{2-}$ clusters (see supplementary Table 2S).²⁸ The PBE0/SD-6-31G* results are discussed throughout, unless mentioned otherwise. To account for bulk solvent effects for the ligated clusters, TDDFT calculations were done using the nonequilibrium polarizable continuum model (PCM)^{39,40} with the united atom cavity using scaled (by a factor of 1.1) Universal Force Field atomic radii previously described.⁴¹

Starting points for geometry optimization are X-ray crystal structures that were determined by previous experimental work. For clusters with less than 54 Cd atoms, the low-energy structures were verified to be minima on the potential energy surface by harmonic frequency calculations using the Gaussian 09 program.⁴² TDDFT singlet excitation energies and oscillator strengths using the length representation were calculated using the Gaussian 09⁴² and GAMESS⁴³ programs.

III. RESULTS AND DISCUSSION

A. Structures

The average computed and X-ray crystal structure bond distances and angles for the CdS and CdSe molecular clusters (Figure 1) are listed in Table I for comparison. The $\text{Cd}(\text{SPh})_4^{2-}$ structure was found to possess S_4 symmetry with Cd-S bond distances of 2.586 Å and S-Cd-S angles of 116.8°. In comparison with the average bond distance and angles from the crystal structure of $\text{Cd}(\text{SPh})_4^{2-}$ with two Ph_4P^+ counter ions which was found to distort to C_1 symmetry,⁴⁴ the average computed Cd-S distances are 0.05 Å longer while the S-Cd-S angles are 6.7° larger. For $(\text{Et}_4\text{N}^+)_2\text{Cd}_4(\text{SPh})_{10}^{2-}$, the X-ray crystal structure contains an adamantane-like complex with the Cd_4S_6 cage distorted from T symmetry of adamantane.⁴⁵ The mean of the Cd-S_i (2.467 Å) bond lengths is 0.09 Å smaller than that of Cd-S_o (2.56 Å) bonds. These values are about the same as the corresponding distances in $\text{Cd}_4(\text{SPh})_{10}^{2-}$ with two *trans*-4-(4-dimethylanilino)styryl)-*N*-methyl-pyridinium ions.²³ The phenyl ligands are pyramidal at the bridging positions, adopting either axial (a) or equatorial (e) orientations in the four fused six-member rings of the adamantane-like cage.⁴⁶ Four structures (Figure 1S in the supplementary material²⁸) identified by the orientations of three phenyl ligands in the fused-six-member rings were found to be within 1 kcal/mol of one another for $\text{Cd}_4(\text{SPh})_{10}^{2-}$ without counter ions (see supplementary Table 3S²⁸). The mean computed Cd-S distances for the lowest energy structure are 0.03-0.04 Å longer than those of experiments. Similarly, the large number of isomers for the T3 cluster of $\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}^{4-}$ stems from the stereochemistry of the phenyl group at each of the 12 bridging thiolates. Experimentally, the capping phenyls in $\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}^{4-}$ (supplementary Figure 1S²⁸) were found to distort the T_d core ($\text{Cd}_{10}\text{S}_4\text{S}_{16}$) to S_4 symmetry.⁴⁶ One of the three nearly isoenergetic S_4 isomers (supplementary Table 4S²⁸) was observed in the crystal structure.⁴⁶ The average computed Cd-S distances for the low-energy isomers are in a range 0.03-0.04 Å longer than the corresponding values in the X-ray structure with $\text{N}(\text{CH}_3)_4^+$ counter ions.⁴⁶ The C1 structure of $\text{Cd}_{17}\text{S}_4(\text{SPh})_{17}^{2-}$ with $\text{N}(\text{CH}_3)_4^+$ counter ions was found to possess D_2 symmetry with a central Cd^c atom

TABLE I. Calculated^a and experimental^b average bond distances (in angstrom) and angles (in degree).

	Expt.	PBE0
$\text{Cd}(\text{SPh})_4^{2-}$		
Cd-S	2.535	2.586
S-Cd-S	110.1	116.8
$\text{Cd}_4(\text{SPh})_{10}^{2-}$		
Cd-S ⁱ	2.460	2.505
Cd-S ^o	2.554	2.591
S ⁱ -Cd-S ⁱ	112.2	112.4
$\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}^{4-}$		
Cd ⁱ -S ⁱ	2.484	2.512
Cd ⁱ -S ^o	2.608	2.608
Cd ^o -S ^o	2.565	2.580
Cd ^o -S ⁱ	2.473	2.544
MAE		0.029
Cd ⁱ -S ⁱ -S ^o	112	111.4
$\text{Cd}_{17}\text{S}_4(\text{SPh})_{17}^{2-}$		
Cd ^c -S ^c	2.508	2.533
Cd ⁱ -S ^c	2.529	2.562
Cd ^c -S ^o	2.542	2.579
Cd ⁱ -S ^o	2.524	2.545
Cd ^o -S ^o	2.569	2.606
Cd ^o -S ⁱ	2.464	2.481
MAE		0.028
S ⁱ -Cd ⁱ -S ^o	111.4	112.5
$\text{Cd}_4\text{Cl}_4(\text{SePh})_6^{2-}$		
Cd-Cl	2.459	2.492
Cd-Se	2.647	2.688
C-Se	1.934	1.934
MAE		0.025
Cl-Cd-Se	108.8	108.0
$\text{Cd}_8\text{SeCl}_4(\text{SePh})_{12}^{2-}$		
Cd ⁱ -Se ⁱ	2.614	2.652
Cd ⁱ -Se ^o	2.640	2.675
Cd ^o -Se ^o	2.668	2.675
Cl-Cd ⁱ	2.442	2.446
Se ⁱ -C	1.946	1.932
MAE		0.020
Cl-Cd ⁱ -Se ^o	108.4	109.5
$\text{Cd}_8\text{Se}(\text{SePh})_{16}^{2-}$		
Cd ⁱ -Se ⁱ	2.604	2.639
Cd ⁱ -Se ^o	2.628	2.676
Cd ^o -Se ^o	2.687	2.734
Cd ^o -Se ⁱ	2.572	2.605
Se ⁱ -C	1.886	1.925
MAE		0.040
Se ⁱ -Cd ⁱ -Se ^o	111.3	112.1
$\text{Cd}_{10}\text{Se}_4(\text{SePh})_{12}(\text{PPr}_3)_4$		
Cd ⁱ -Se ^o	2.672	2.707
Cd ^o -Se ^o	2.634	2.665
Cd ⁱ -P	2.607	2.643
Se ^o -C	1.921	1.917
MAE		0.026
P-Cd-Se ^o	107.4	106.2
$\text{Cd}_{17}\text{Se}_4(\text{SePh})_{24}^{2+}$		
Cd ^c -Se ^c	2.625	2.660
Cd ⁱ -Se ^c	2.654	2.701

TABLE I. (Continued.)

	Expt.	PBE0
Cd ^I -Se ^o	2.644	2.680
Cd ^I -Se ^o	2.648	2.669
Cd ^I -S ^I	2.564	2.623
Se ^o -C	1.929	1.934
MAE		0.034
S ^I -Cd ^I -S ^o	104.1	103.2
Cd ₁₇ Se ₄ (SePh) ₂₈ ²⁻		
Cd ^c -Se ^c	2.624	2.651
Cd ^I -Se ^c	2.653	2.690
Cd ^I -Se ^o	2.649	2.679
Cd ^I -Se ^o	2.646	2.673
Cd ^I -S ^I	2.684	2.730
Se ^o -C	2.578	2.609
MAE		0.033
S ^I -Cd ^I -S ^o	109.5	109.2

^aUsing the Def2-TZVP basis set for Cd(SPh)₄²⁻ and Cd₄(SPh)₁₀²⁻, and the SD-6-31G* basis for others. Average SD-6-31G* bond distances and angles for Cd₄(SPh)₁₀²⁻: 2.499 (Cd-S^I), 2.597 (Cd-S^I), 112.7 (S^I-Cd-S^I). The computed Cd₄SeCl₄(SPh)₆²⁻(NPr₄⁺)₂ structure has a MAE of 0.02 Å and the following average bond distances: 2.481 (Cd-Cl), 2.686 (Cd-Se), and 1.934 (C-Se).

^bExperimental X-ray structures with counter ions: [P(Ph)₄]₂Cd(SPh)₄²⁻,⁴⁴ (Et₄N⁺)₂Cd₄(SPh)₁₀²⁻ with two *trans*-4-(4-dimethylanilino)styryl-*N*-methylpyridinium ions has the following average bond distances: 2.460 (Cd^I-S^I), 2.554 (Cd^I-S^o),²³ Cd₁₀S₄(SPh)₁₆⁴⁻ with Me₄N⁺ counter ions,⁴⁶ Cd₁₇S₄(SPh)₂₈²⁻ with Li⁺ ion complex of 1,2-dimethoxyethane ([Li(dme)₃]₂),¹⁹ [N(CH₃)₄]₂Cd₁₇S₄(SPh)₁₇²⁻ has the following average bond distances: 2.497 (Cd^c-S^c), 2.53 (Cd^I-S^c), 2.52 (Cd^I-S^o), 2.52 (Cd^I-S^o), 2.556 (Cd^I-S^o), 2.482 (Cd^I-S^I).⁴⁷ Cd₄SeCl₄(SPh)₆²⁻(NPr₄⁺)₂,⁸ Cd₈Se(SPh)₁₆²⁻-Cd₁₇Se₄(SePh)₂₄²⁺.⁸

connected to four S^c atoms (Figure 1).⁴⁷ Each S^c atom is connected to three tetra-coordinated Cd^I atoms forming a cuboctahedron. For Cd₁₇S₄(SPh)₁₇²⁻ without counter ions, bond distances of the computed PBE0 *D*₂ structure are on an average 0.03 Å longer than the experimental structures with N(CH₃)₄⁺⁴⁷ and dimethoxyethane (Li(dme)₃)¹⁹ counter ions.

The molecular CdS clusters discussed above are isostructural with the CdSe counterparts. Thus, the chlorinated Cd₄Cl₄(SePh)₆²⁻ also adopts an adamantane-like cage with low-lying isomers arising from the orientations of the three phenyl ligands in each of the four fused-six-member rings. Compared with the crystal structure,⁸ the average PBE0 bond distance for the lowest-energy isomer is 0.03 Å longer. Using the Cd₄SeCl₄(SPh)₆²⁻(NPr₄⁺)₂ crystal structure⁸ with counter ions as a starting point, the PBE0 optimized structure slightly (0.02 Å) reduces the mean absolute error (MAE). This is consistent with X-ray data for the Cd₈SeCl₄(SePh)₁₂²⁻ crystal structures with different counter ions displaying similar bond distances.⁴⁸ The larger CdSe P1, T3, and C1 analogs were found to retain the symmetries found in the CdS clusters. Tetrahedral (*T*) symmetry was predicted for the tetra-chlorinated P1 Cd₈SeCl₄(SePh)₁₂²⁻, neutral T3 Cd₁₀Se₄(SePh)₁₂(PPr₃)₄, and C1 Cd₁₇Se₄(SePh)₂₄²⁺ clusters. Overall, the MAE for the computed bond distances for CdSe clusters is about the same (0.03 Å longer) as the corresponding CdS values. Previous PBE structures for model CdSe clusters with hydrogen atoms (instead of phenyls) were reported to have bond distances of 0.06 Å longer in comparison to X-ray data.¹¹

B. Electronic spectra

1. CdS clusters

Computed and experimental spectral maxima and extinction coefficients for CdS and CdSe clusters are given in Table II. The computed excitation energies, oscillator strengths (*f*), and character of transitions for *f* > 0.1 are tabulated in Tables 3S-10S (see the supplementary material).²⁸ We begin with the smallest T2 adamantane-like cluster followed by the T3, P1, and larger clusters (Figure 1). The T3 cluster is composed of only adamantane-like cages with fused six-membered rings. Since the ER ligand is pyramidal at each E position, there are two possible orientations at each of the ER group, leading to a number of conformational isomers.⁴⁶ Thus, Boltzmann averaging of excited state properties was done for clusters with low-energy isomers. The computed excited state maxima are given in Table II and Figures 2 and 3 along with the experimental values for comparison. The influence of counter ions on the computed (supplementary Table 8S²⁸) and experimental electronic spectra was found to be quite small.⁴⁸ Thus, they are not included in computed spectra. For Cd₄(SPh)₁₀²⁻, isomerization can occur through the axial-equatorial inversion of the phenyl groups at the bridging chalcogen atoms.⁴⁹ The variation in the ground state energies is small (0.3-0.5 kcal/mol in the gas-phase and 0.6-3.2 kcal/mol in solvent, see supplementary Table 3S²⁸). The Boltzmann averaged value for the first allowed one-photon absorption (OPA) maximum in CH₃CN is 4.60 eV, which is in good agreement with the experimental value of 4.51 eV (Table II).⁵⁰ The larger Def2-TZVP basis set improves the maximum extinction coefficient (9.35 × 10⁴ M⁻¹ cm⁻¹) but does not significantly change the OPA maximum (4.55 eV). Weakly absorbing first excited state energies of about 4.0 eV (4.2 eV in CH₃CN) were predicted for different T2 isomers (supplementary Figure 1S and Table 3S²⁸). Thus, the first band is largely derived from the more intense transitions at higher energy. The first four transitions arise from excitations from the highest occupied molecular orbital (HOMO) and lower-energy MOs to the lowest unoccupied molecular orbital (LUMO), which has contributions from the 5*s* orbitals of the metal atoms and the π orbitals from the SPh ligands that are significantly reduced in contribution for the larger clusters (Figure 4). The four highest occupied MOs have contributions mainly from the π orbitals involving the terminal SPh groups, while bridging SPh ligands have major contributions in the lower-energy occupied MOs. Moving to the larger Cd₈S(SPh)₁₆²⁻ cluster, the first excited state is predicted to be slightly redshifted and more intense (gas-phase: 3.9 eV, *f* = 0.1). In CH₃CN solvent, the first three virtually degenerate (¹B₂, ¹B₃, and ¹B₁) transitions are predicted to underlie the strong lowest-energy band at about 4.3 eV (total *f* = 0.75). No experimental absorption data exist for Cd₈S(SPh)₁₆²⁻, although the cluster has been synthesized along with other M₈E'(EPh)₁₆²⁻ (M = Zn and Cd; E, E' = S, Se, Te) clusters.¹⁶ For Cd₁₀S₄(SPh)₁₆²⁻, the three different crystal structures determined⁵¹ for the cluster were found to be within 0.5 kcal/mol in energy in the gas-phase. However, larger deviations in energy were obtained in CH₃CN (see supplementary Table 4S²⁸). The first excited state in CH₃CN is predicted to occur at about 4.1 eV (Figure 2). This

TABLE II. Summary of computed^a and experimental absorption bands^b (in eV) and extinction coefficients (in parentheses, in M⁻¹ cm⁻¹) in the gas-phase and solvents.^c

Cluster	Computed	Expt.
CdS		
Cd(SPh) ₄ ²⁻	4.55 (9.35 × 10 ⁴) ^(a)	4.40 (2.03 × 10 ⁴) ^{(a),50}
Cd ₄ (SPh) ₁₀ ²⁻	4.60 (4.96 × 10 ⁴) ^(a)	4.51 (1.16 × 10 ⁵) ^{(a),50}
Cd ₈ S(SPh) ₁₆ ²⁻	4.38 (9.59 × 10 ⁴) ^(a)	
Cd ₈ S(SCH ₂ CH ₂ OH) ₁₆ ²⁻	4.75 (7.59 × 10 ⁴) ^(d)	4.77 ^{(d),18}
Cd ₁₀ S ₄ (SPh) ₁₂	4.34 (7.84 × 10 ⁴) ^(c)	>4.13 ^{(c),52}
Cd ₁₀ S ₄ (SCH ₂ CH ₂ OH) ₁₂	4.75 (4.45 × 10 ⁴) ^(d)	4.86 ^{(d),18}
Cd ₁₀ S ₄ (SPh) ₁₆ ⁴⁻	4.45 (1.42 × 10 ⁵) ^(a)	4.25 (1.38 × 10 ⁵) ^{sh,(a),5,50}
Cd ₁₀ S ₄ (SPh) ₁₆ ⁴⁻		4.1 ^(c) (or mineral oil) ^{5,52}
Cd ₁₀ S ₄ (SCH ₂ CH ₂ OH) ₁₆ ⁴⁺	4.77 (5.46 × 10 ⁴) ^(d)	4.88 (6.87 × 10 ⁴) ^{(d),54} 4.90 (6.63 × 10 ⁴) ^{(d),18}
Cd ₁₇ S ₄ (SCH ₂ CH ₂ OH) ₂₄ ²⁺	4.25 (5.50 × 10 ⁴) ^(d)	4.28 (3.89 × 10 ⁴) ^{(d),18}
Cd ₁₇ S ₄ (SCH ₂ CH ₂ OH) ₂₆	4.27 (7.84 × 10 ⁴) ^(d)	4.3 (8.4 × 10 ⁴) ^{(b),(c),(d),17}
Cd ₁₇ S ₄ (SPh) ₂₆ (H ₂ NCSNH ₂) ₂	4.35 (1.20 × 10 ⁵) ^(b)	4.26 ^{(b),3}
Cd ₁₇ S ₄ (SPh) ₂₈ ²⁻	4.0 (5.0 × 10 ⁴) ^(a)	4.2 (1.0 × 10 ⁶) ^{sh,(a),19}
Cd ₃₂ S ₄ (SCH ₂ CHOHCH ₃) ₃₆ (H ₂ O) ₄	3.87 (8.94 × 10 ⁴) ^(b)	4.81 ^{(b),21}
Cd ₃₂ S ₁₄ (SPh) ₄₀ ⁴⁻	3.92 (1.30 × 10 ⁵) ^(b)	3.79 ^{(b),3}
Cd ₅₄ S ₃₂ (SPh) ₄₈ (H ₂ O) ₄ ⁴⁻	3.58 (1.27 × 10 ⁵) ^(b)	3.51 ^{(b),3}
Mean absolute error	0.11	1.2 × 10 ³
CdSe		
Cd ₄ (SePh) ₆ Cl ₄ ²⁻	4.34 (1.01 × 10 ⁵)	4.2 ^{(f),7}
Cd ₈ Se(SePh) ₁₆ ²⁻	4.00 (1.33 × 10 ⁵)	3.86 ^{(f),19}
Cd ₈ Se(SePh) ₁₆ ²⁻	4.05 (1.06 × 10 ⁵) ^(a)	4.1 (1.0 × 10 ⁶) ^{sh,(a),19}
Cd ₈ Se(SePh) ₁₂ Cl ₄ ²⁻	4.02 (1.1 × 10 ⁵)	4.08 ^{(f),7,48}
Cd ₁₀ Se ₄ (SePh) ₁₂	4.03 (8.23 × 10 ⁴)	>4.5 ^{(f),55}
Cd ₁₀ Se ₄ (SePh) ₁₂ (PnPr ₃) ₄	4.13 (1.26 × 10 ⁵)	3.88 (5.7 × 10 ⁵) ^{(f),7} 3.92, 4.17 ^{(f),53}
Cd ₁₇ Se ₄ (SePh) ₂₄ (PPh ₂ Pr) ₄ ²⁺	3.67 (7.08 × 10 ⁴)	3.42 ^{(f),7}
Cd ₁₇ Se ₄ (SePh) ₂₈ ²⁻	3.54 (4.55 × 10 ⁴)	3.64 ^{(a),19} 3.57 ^{(f),53}
Cd ₃₂ Se ₁₄ (SePh) ₃₆ (PPh) ₄	3.38 (1.04 × 10 ⁵)	3.32 ^{(f),7}
Cd ₃₂ Se ₁₄ (SePh) ₃₆ (OC ₄ H ₈) ₄		3.24 ^{(f),53}
Cd ₅₄ Se ₃₂ (SPh) ₄₈ (H ₂ O) ₄ ⁴⁻	3.05 (1.05 × 10 ⁵)	
	3.19 (2.46 × 10 ⁵) ^(b)	3.18 ^{(b),3}
Mean absolute error	0.11	

^aComputed values for Cd₁₇S₄(SPh)₂₆(H₂NCSNH₂)₂ are obtained using a model cluster with hydride ligands Cd₁₇S₄(SH)₂₆(H₂NCSNH₂)₂. Computed values for Cd₁₇Se₄(SePh)₂₄(PPh₂Pr)₄²⁺ were obtained with Cd₁₇Se₄(SePh)₂₄(PCH₃)₄²⁺, Cd₃₂ × 10¹⁴(ER)₄₀⁴⁻, Cd₃₂ × 10¹⁴(ER)₃₆(PR)₃₆, and Cd₅₄ × 10³²(ER)₄₈ clusters (E = S, Se) are computed with hydride ligands (R = H). Computed spectra were obtained using Gaussian line shape with the following FWHM: CdS: 0.5 eV for Cd(SPh)₄²⁻, Cd₈S(SCH₂CH₂OH)₁₆²⁻, Cd₁₀S₄(SCH₂CH₂OH)₁₂, Cd₁₀S₄(SCH₂CH₂OH)₁₆⁴⁺, and Cd₁₇S₄(SCH₂CH₂OH)₂₄²⁺; 0.4 eV for other clusters. CdSe: 0.4 eV for Cd₈Se(SePh)₁₆²⁻ and Cd₁₇Se₄(SePh)₂₈²⁻; 0.2 eV other clusters.

^bShoulder bands are indicated by “sh.”

^cSolvent: CH₃CN (a), DMF (b), pyridine (c), water (d), DMSO (e), and Nujol (f).

is much higher than the recently reported¹⁹ value of 2.45 eV for the lowest excited state obtained with the conductor-like screening model (COSMO) and the BP-86 functional, which is known to underestimate CT transitions. The first strong transitions in CH₃CN involving a number of states were found to occur at about 4.3–4.4 eV, followed by strong and higher energy transitions starting at about 4.5 eV. This is consistent with the experimental spectrum with a shoulder at 4.25 eV.^{5,50} Removing four thiophenolate groups from Cd₁₀S₄(SPh)₁₆²⁻ leads to a stable neutral Cd₁₀S₄(SPh)₁₂ intermediate with the predicted first strong transitions of about 4 eV in the gas-phase, which are more intense and blueshifted to about 4.1–3.4 eV in pyridine solution. The TDDFT results are consistent with the experimental assignment for the first absorption band of Cd₁₀S₄(SPh)₁₂, which is to be below 300 nm (4.13 eV) in pyridine solution; absorption bands at lower energies were attributed to aggregation⁵² and the presence⁵ of larger clusters.

The structures of CdS and CdSe *C_n* series are isostructural. They are found to be tetrahedral with phosphine ligands at the apex positions but only possess *D*₂ symmetry for L = SeR and SR. However, the absorption spectrum for the first *C_n* initially reported was a neutral Cd₁₇S₄(SEtOH)₂₆ (EtOH = hydroxyethyl) cluster with two instead of four capping ligands.¹⁷ Thus, the structure of the C1 with hydroxyethylthiolate ligands is reduced to *C*₂ symmetry. The predicted spectrum for Cd₁₇S₄(SEtOH)₂₆ in water reveals two nearly degenerate strong (total *f* = 0.6) transitions at 4.2 eV and four nearby transitions at 4.3 eV with the combined oscillator strength of ~0.4. The weakly absorbing first excited state of Cd₁₇S₄(SEtOH)₂₆ is predicted to slightly redshift (to about 4.0 eV) from these intense transitions. The TDDFT computed maximum (4.27 eV and 78 000 M⁻¹ cm⁻¹) is in good agreement with the observed first intense spectral band at 4.28 eV in aqueous solution.¹⁷ Nearly the same intensity

FIG. 2. Computed (blue) and experimental (red) excitation energies of the lowest and/or intense levels for different CdS cluster sizes (n = number of Cd atoms) with phenolate (square) and hydride (diamond) ligands in the gas-phase (open), DMF (filled), CH_3CN (half-filled), and Nujol (dot).

FIG. 3. Computed (top) and experimental (bottom) absorption spectra in CH_3CN for CdS clusters with phenolate (SPh) ligands: $\text{Cd}(\text{SPh})_4^{2-}$ (black), $\text{Cd}_4(\text{SPh})_{10}^{2-}$ (red), $\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}^{4-}$ (blue), and $\text{Cd}_{17}\text{S}_4(\text{SPh})_{28}^{2-}$ (green). The computed spectra were obtained using Gaussian line shape with FWHM of 0.5 eV for $\text{Cd}(\text{SPh})_4^{2-}$ and 0.4 eV for other clusters.

FIG. 4. Lowest (L) virtual, highest (H), and lower-occupied orbitals with symmetry labels at cutoff value of 0.015 a.u. for CdS clusters. Orbital energies (in eV) are in parentheses. Only one of four nearly degenerate occupied HOMOs comprising linear combinations of π -orbitals of the S atoms and phenyl groups at the apex positions is shown for $\text{Cd}_8\text{S}(\text{SPh})_{16}^{2-}$, $\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}^{4-}$, and $\text{Cd}_{17}\text{S}_4(\text{SPh})_{28}^{2-}$ clusters.

(84 000 $\text{M}^{-1} \text{cm}^{-1}$) and position of the spectral maxima in *N,N*-dimethylformamide (DMF) and in dimethyl sulfoxide (DMSO) were also reported.¹⁷ Experiment and theory concur on this observation. The first absorption maximum of the related $\text{C1 Cd}_{17}\text{S}_4(\text{SPh})_{26}(\text{H}_2\text{NCSNH}_2)_2$ was observed at about the same energy in DMF.³ Absorption spectra in the gas-phase or in non-polar solvents were not reported. The computed gas-phase value of 2.7 eV for the $\text{Cd}_{17}\text{S}_4(\text{SEtOH})_{26}$ cluster is obtained for the first excited state, a redshift of about 1.3 eV from the corresponding value in aqueous solution. All transitions in the gas-phase up to 4 eV are predicted to be very weak in intensity. Thus, solvents have a strong influence on the spectral color and intensity.

For the C_n anions series, the first band at 4.2 eV in CH_3CN for the $\text{Cd}_{17}\text{S}_4(\text{SPh})_{28}^{2-}$ cluster¹⁹ was derived from a Gaussian fit to its lowest-energy absorption shoulder. Upon going to the larger clusters, the first band progressively redshifts to 3.79 eV and 3.51 eV (in DMF) for $\text{Cd}_{32}\text{S}_{14}(\text{SPh})_{40}^{4-}$ and $\text{Cd}_{54}\text{S}_{32}(\text{SPh})_{48}(\text{H}_2\text{O})_4^{4-}$, respectively.³ For $\text{Cd}_{17}\text{S}_4(\text{SPh})_{28}^{2-}$, the computed first four nearly degenerate and weak transitions are not expected to be observed, lying at about 3.9 eV in CH_3CN solvent (3.3 eV in the gas-phase). The corresponding first excited state of 2.05 eV obtained with BP-86/COSMO is much lower.¹⁹ A large number of excited states of the C1 cluster are predicted to contribute to the first experimentally observed band, which appears as a broad shoulder due to band overlapping.¹⁹ A first band was found to occur at about the

same energy region (~ 4.0 eV) using Gaussian line shapes with FWHM of 0.40 eV with 20 computed excited states. These transitions mainly originate from excitations from the occupied MOs involving π orbitals of the outer and apex S atoms to the LUMO, which has 5s orbitals of the inner tetra-coordinated Cd atoms (Figure 4). Thus, substitutions of the phenyl ligands with methyl groups and hydrides have weak effects on the position of the first strongly allowed transition of the $\text{Cd}_{17}\text{S}_4(\text{SPh})_{28}^{2-}$ cluster. Due to the low intensities of the transitions associated with the phenyl groups, the methyl and hydride substitutions induce spectral blueshifts of 0.05 eV and 0.13 eV, respectively, for the first maximum of the $\text{Cd}_{17}\text{S}_4(\text{SPh})_{28}^{2-}$ cluster in CH_3CN (see supplementary Figure 2S for oscillator-strengths-weighted-sum of orbitals involved).²⁸ The larger $\text{M}_{32}\text{S}_{14}(\text{SR})_{40}^{4-}$ and $\text{M}_{54}\text{S}_{32}(\text{SR})_{48}$ clusters are, therefore, examined with hydride ligands ($\text{R} = \text{H}$). The first bands of the C2 and C3 clusters in DMF are predicted to be strong in intensity, located at around 3.8 eV and 3.5 eV, respectively. Taking into account the small ligand shifts, the computed maxima are in good agreement with observed maxima (3.79 eV for C2 and 3.51 eV for C3) in the same solvent. The computed C3 maximum is obtained with a cluster with four coordinating water molecules. However, the variance of coordinating ligands is found to induce very small spectral shifts in the low-energy region of the spectrum. Overall, the predicted TDDFT excitation energies have a MAE of 0.11 eV for the CdS clusters considered. The predicted absorption

FIG. 5. Computed (blue) and experimental (red) excitation energies of the lowest and/or intense levels for different CdSe cluster sizes (n = number of Cd atoms) with phenolate (square) and hydride (diamond) ligands in the gas-phase (open), DMF (filled), CH₃CN (half-filled), and Nujol (dot). Experimental values for Cd₈Se(SePh)₁₂Cl₄²⁻ and Cd₁₇Se₄(SePh)₂₄(PPr₃)₄²⁺ were estimated from a [Cd₁₇Se₄(SePh)₂₄(PPr₃)₂²⁺-Cd₈Se(SePh)₁₂Cl₄²⁻] complex.

intensities are largely consistent with experiment with the MAE error for the extinction coefficients of 1200 M⁻¹ cm⁻¹.

2. CdSe clusters

Experimental investigations were carried out to study structures and optical properties of a series of CdSe cluster molecules from the smallest T2 (0.7 nm) to the C2 (2 nm) families, consisting of 4-32 metallic sites.⁶⁻⁸ The spectra maxima obtained in the chemically inert Nujol oil for these cadmium selenide clusters are expected to have weak electrostatic interactions that will not induce significant spectral shifts, making them amenable to comparison with computed gas-phase values (Table II, and Figures 5 and 6). A spectral maximum of 4.2 eV was reported for the Cd₄(SePh)₆Cl₄²⁻ cluster.^{7,8} The maxima for larger clusters were shifted to 4.08 eV, 3.88 eV, 3.42 eV, and 3.32 eV for the Cd₈Se(SePh)₁₂Cl₄²⁻, Cd₁₀Se₄(SePh)₁₂(PET₃)₄, Cd₁₇Se₄(SePh)₂₄(PPr₃)₄²⁺, and Cd₃₂Se₁₄(SePh)₃₆(PPh₃)₄ clusters, respectively.^{7,8} For the P1 Cd₈Se(SePh)₁₂Cl₄²⁻ cluster with different counter ions, the absorption spectra were found to be virtually identical, suggesting that electronic transitions within the spectral region are of the anion cluster.⁴⁸ Slight redshifts were reported for the first absorption band in the same solvent for the P1 cluster with SePh ligands [~4.8 eV for Cd₈Se(SePh)₁₆²⁻]¹⁹ and the neutral C2 cluster with different terminal ligands [3.24 eV for Cd₃₂Se₁₄(SePh)₃₆(C₄H₈O)₄].⁵³ The spectral maxima of the P1 and C1 clusters were estimated from the Cd₁₇Se₄(SePh)₂₄(PPr₃)₄²⁺-Cd₈Se(SePh)₁₂Cl₄²⁻ complex by assigning the higher energy peak to the smaller P1 cluster and the low energy peak to the larger C1 cluster.^{7,8} For the C1 anion, the absorption spectrum of Cd₁₇Se₄(SePh)₂₈²⁻ taken in a mull with Nujol showed with a weakly resolved lowest energy maximum around 3.54 eV (347 nm), a blueshift of 0.12 eV from the C1 cation.^{19,53} However, spectral redshifts for the first transitions are generally observed upon going from cations to the corresponding anions. The experimental spectrum for the larger C3 cluster was obtained in DMF

solvent, showing the first absorption band of 3.2 eV for the Cd₅₄Se₃₂(SPh)₄₈(H₂O)₄⁴⁻ cluster.³

The first excited states for the T2 structure of Cd₄(SePh)₆Cl₄²⁻ (4.0 eV) and the C1 structures of Cd₁₇Se₄(SePh)₂₈²⁻ (2.9 eV) and Cd₁₇Se₄(SePh)₂₄(PCH₃)₄²⁺ (3.4 eV) are predicted to be very weak, unlikely observed in the OPA spectra (see supplementary Tables 8S and 10S²⁸). In contrast, the first transitions of the P1 and T3 clusters, at 4.0 eV for Cd₈Se(SePh)₁₂Cl₄²⁻ and 4.1 eV for Cd₁₀Se₄(SePh)₁₂(PPr₃)₄, respectively, are found to be strong in intensity (supplementary Tables 9S and 10S²⁸). These predicted values are in good agreement with the lowest-energy observed maxima (4.1 eV^{7,8} and 3.9 eV^{7,8,53}) in Nujol. Interestingly, substituting the four terminal chlorine of Cd₈Se(SePh)₁₂Cl₄²⁻ with phenyl groups significantly (0.39 eV) redshifts the first excited state (to 3.63 eV). The first strong band of Cd₈Se(SePh)₁₆²⁻ is predicted to occur at about 4.0 eV, in good agreement with the observed shoulder of ~3.9 eV in Nujol and ~4.1 eV in CH₃CN.¹⁹ The corresponding BP-86/COSMO value of 2.45 eV is much lower.¹⁹ Similarly, the previously¹¹ predicted weak and low energy transitions using the BP-86 functional for the model P1 and T3 clusters [3.3 eV and $f = 0.06$ for Cd₈Se(SeH)₁₂Cl₄²⁻, 3.0 eV and $f = 0.05$ for Cd₁₀Se₄(SeH)₁₂(PH₃)₄] are also at variance with our computed values and experiment.^{7,8,53} Using the same functional, the first excited state was predicted to be stronger in intensity slightly redshifted (2.93 eV and $f = 0.17$) upon going to the C1 cation Cd₁₇Se₄(SeH)₂₄(PH₃)₄²⁺ cluster.¹¹ A much more intense (total $f = 1.10$) and higher transition energy (3.91 eV) is obtained with the PBE0 functional for the same cluster. The transition energy for this band is predicted to be less intense (total $f = 0.79$) and shifted to the red for the methylselenate (3.73 eV) and the phenylselenate (3.67 eV) C1 clusters, a blueshift of 0.25 eV for the Cd₁₇Se₄(SePh)₂₄(PCH₃)₄²⁺ cluster in comparison to the first transition observed for the Cd₁₇Se₄(SePh)₂₄(PPr₃)₄²⁺-Cd₈Se(SePh)₁₂Cl₄²⁻ complex.^{7,8} From the KS orbital picture (Figure 7), the first transitions arise from the HOMO-LUMO

FIG. 6. Computed (top) and experimental (in Nujol, bottom) absorption spectra for CdSe clusters. Top: $Cd_4(SePh)_6Cl_4^{2-}$ (black), $Cd_{10}Se_4(SPh)_{12}Cl_4^{4-}$ (red), $Cd_8Se(SePh)_6Cl_4^{2-}$ (blue), and $Cd_{17}Se_4(SPh)_{24}(PCH_3)_4^{2+}$ (green). Bottom: $Cd_4(SePh)_6Cl_4^{2-}$ (black), $Cd_{10}Se_4(SPh)_{12}Cl_4^{4-}$ (red), $Cd_8Se(SePh)_6Cl_4^{2-}$ - $Cd_{17}Se_4(SPh)_{24}(PPh_2Pr)_4^{2+}$ (blue). The computed spectra were obtained using Gaussian line shape with FWHM of 0.2 eV for all clusters.

excitations. For $Cd_4(SePh)_6Cl_4^{2-}$, the HOMO has the main contributions from the π orbitals involving the SePh ligands while the LUMO from the $5s$ orbitals of the Cd atoms and the π orbitals from the ligands (SePh, Cl), which are significantly reduced for the larger clusters. The triply degenerate HOMOs of $Cd_{17}Se_4(SePh)_{28}^{2-}$ are linear combinations of π -orbitals of the Se atoms and phenyl groups at the apex positions while orbitals from SePh ligands located at different regions are involved in the HOMOs of the other clusters. The oscillator-strength-weighted-sum of orbitals involved in the band of $Cd_4(SePh)_6Cl_4^{2-}$ and $Cd_{17}Se_4(SePh)_{28}^{2-}$ clusters is given in supplementary Figure 2S.²⁸

For the C1 anion clusters, the first four nearly degenerate transitions are predicted to occur at about 3.0-3.1 eV for $Cd_{17}Se_4(Seh)_{28}^{2-}$ and about 2.9 eV $Cd_{17}Se_4(SePh)_{28}^{2-}$ (supplementary Table 11S²⁸). The latter value is about 0.8 eV higher than the corresponding reported value using the BP-86 functional.¹⁹ Note that the shifts induced by the phenyl groups for the first four transitions are small. Similar to the CdS analog, these transitions involve excitations from HOMO and lower-energy MOs to the LUMO. Note that the HOMO orbital energies remain about the same from $Cd_8Se(SePh)_{12}Cl_4^{2-}$ to

$Cd_{17}Se_4(SePh)_{28}^{2-}$, while the orbital energy of the LUMO decreases as the molecular size increases (Figure 7). The first four highest occupied MOs are linear combinations of nonbonding π orbitals involving the four Se atoms and minor contributions from the phenyl groups located at the apex positions while the LUMO has dominant contributions from $5s$ orbitals of the inner Cd atoms. These transitions include the forbidden (1A) and three weakly allowed (1B_1 , 1B_2 , and 1B_3) states that are unlikely observed with linear absorption spectroscopy. Stronger transitions for the C1 clusters are obtained from excitations from the lower energy occupied MOs with π orbitals of the outer and terminal Se atoms to the LUMO. Going to the larger C2 cluster, the first excited states obtained for $Cd_{32}Se_{14}(SeH)_{36} \cdot 4PH_3$ with TDDFT in the gas-phase are triply degenerate with T symmetry at about 3.4 (total $f = 0.81$) and are in good agreement with the experimental maximum of 3.3 eV taken in Nujol. The three excited states of $Cd_{54}Se_{32}(SH)_{48} \cdot 4H_2O$ are accidentally degenerate and are redshifted to 3.05 eV (total $f = 0.78$) in the gas-phase. This is slightly lower than the lowest energy experimental maximum of 3.2 eV taken in DMF, which is predicted to occur at 3.18 eV. The overall errors of the predicted TDDFT excitation energies

FIG. 7. Lowest (L) virtual, highest (H), and lower-occupied orbitals with symmetry labels at cutoff value of 0.015 a.u. for CdSe clusters. Orbital energies (in eV) are in parentheses. Only one of four nearly degenerate occupied HOMOs comprising linear combinations of π -orbitals of the S atoms and phenyl groups at the apex positions is shown for $\text{Cd}_{17}\text{Se}_4(\text{SePh})_{28}^{2-}$ cluster. For the $\text{Cd}_{17}\text{Se}_4(\text{SePh})_{24}(\text{PCH}_3)_4^{2+}$ cluster, H-3 instead of H-2 is shown.

for the CdSe clusters are similar to the corresponding CdS clusters. The same MAE error of 0.11 eV was obtained in comparing the predicted and available experimental energies for CdSe clusters.

3. Size-dependent properties

The effects of quantum confinement are often examined by inspecting the experimental OPA spectral shifts of the first absorption bands. However, they are not necessarily the first transitions since weakly absorbing and forbidden (two-photon) states are unlikely to be observed in the OPA spectra. Electronic charge of the clusters may also induce natural variations in the spectral shifts as the first transitions of cations and anions are generally shifted to the blue and red, respectively, from the corresponding neutral species. Thus, effects of quantum confinement might be better studied using computed first excited transitions (Figures 2 and 4) from a reliable level of theory, as established in the discussion in Secs. III B 1 and III B 2. The effects of ligands and solvent must be taken into account, as their induced shifts can be large. Thus, a systematic spectral blueshift with reduced cluster size does not always indicate the effects of size dependence, unless the variables discussed above have been considered. For the cadmium clusters with thiophenolate/selenophenolate ligands, a spectral shift of 1.0 eV for the first absorption band was obtained by theory and experiment upon going from $\text{Cd}_4(\text{SPh})_{10}^{2-}/\text{Cd}_4(\text{SePh})_{10}^{2-}$ to

$\text{Cd}_{54}\text{S}_{32}(\text{SPh})_{48}(\text{H}_2\text{O})_4^{4-}/\text{Cd}_{54}\text{Se}_{32}(\text{SPh})_{48}(\text{H}_2\text{O})_4^{4-}$. About the same redshift of the first excited state is predicted upon going from $\text{Cd}_4(\text{SH})_{10}^{2-}$ to $\text{Cd}_{54}\text{S}_{32}(\text{SH})_{48}(\text{H}_2\text{O})_4^{4-}$ in the gas-phase and in DMF. However, much larger shifts were obtained for CdSe clusters with hydride ligands in the gas-phase (1.9 eV) and in DMF (1.6 eV) (see Figure 5).

IV. SUMMARY AND CONCLUSIONS

A systematic study for the ground and excited states' properties of CdS and CdSe cluster molecules with different sizes and ligands was carried out in the gas-phase and in solvent using electronic structure theory. The results provide an understanding on the influence of ligands, solvents, and cluster size on optical properties of the nanoclusters. Ligand and solvent were found to induce a large shift in the color and intensity of the electronic absorption spectra of small clusters while the effects are reduced with increasing cluster size. Blueshifts were obtained for the first transition with reduced size for both cadmium sulfide and cadmium selenide series. Consistent with our previous work, DFT and TDDFT with the PBE0 functional provided effective tools at relatively low computational cost for predicting ground state structures and spectra, respectively. Comparing the calculated results with experimental data confirms that the PBE0 functional does provide a good description for both the ground and excited states of CdS and CdSe cluster molecules. Preliminary calculations suggest that the same methodology is applicable

to linear and non-linear spectral predictions/assignments for larger CdS and CdSe clusters and for other chalcogenide clusters.

ACKNOWLEDGMENTS

We gratefully acknowledge support from the Air Force Office of Scientific Research and the Air Force Research Laboratory DoD Supercomputing Resource Center.

- ¹J. F. Corrigan, O. Fuhr, and D. Fenske, *Adv. Mater.* **21**, 1867 (2009).
- ²M. A. Malik, M. Afzaal, and P. O'Brien, *Chem. Rev.* **110**, 4417 (2010).
- ³N. Zheng, X. Bu, H. Lu, Q. Zhang, and P. Feng, *J. Am. Chem. Soc.* **127**, 11963 (2005).
- ⁴M. Bendova, M. Puchberger, S. Pabisch, H. Peterlik, and U. Schubert, *Eur. J. Inorg. Chem.* **2010**, 2266.
- ⁵M. Bendova, M. Puchberger, and U. Schubert, *Eur. J. Inorg. Chem.* **2010**, 3299.
- ⁶V. N. Soloviev, A. Eichhöfer, D. Fenske, and U. Banin, *J. Am. Chem. Soc.* **122**, 2673 (2000).
- ⁷V. N. Soloviev, A. Eichhöfer, D. Fenske, and U. Banin, *Phys. Status Solidi B* **224**, 285 (2001).
- ⁸V. N. Soloviev, A. Eichhöfer, D. Fenske, and U. Banin, *J. Am. Chem. Soc.* **123**, 2354 (2001).
- ⁹M. V. A. Kuz'mitskii, V. I. Gael', and I. V. Filatov, *J. Appl. Spectrosc.* **63**, 594 (1996).
- ¹⁰H.-J. Liu, J. T. Hupp, and M. A. Ratner, *J. Phys. Chem.* **100**, 12204 (1996).
- ¹¹K. Eichkorn and R. Ahlrichs, *Chem. Phys. Lett.* **288**, 235 (1998).
- ¹²M. L. del Puerto, M. L. Tiago, and J. R. Chelikowsky, *Phys. Rev. Lett.* **97**, 096401 (2006).
- ¹³M. Lopez del Puerto, M. L. Tiago, and J. R. Chelikowsky, *Phys. Rev. B* **77**, 045404 (2008).
- ¹⁴J. Frenzel, J.-O. Joswig, and G. Seifert, *J. Phys. Chem. C* **111**, 10761 (2007).
- ¹⁵P. Feng, X. Bu, and N. Zheng, *Acc. Chem. Res.* **38**, 293 (2005).
- ¹⁶G. S. H. Lee, K. J. Fischer, D. C. Craig, M. L. Scudder, and I. G. Dance, *J. Am. Chem. Soc.* **112**, 6435 (1990).
- ¹⁷T. Vossmeier, G. Reck, L. Katsikas, E. T. K. Haupt, B. Schulz, and H. Weller, *Science* **267**, 1476 (1995).
- ¹⁸Y. Nosaka, H. Shigeno, and T. Ikeuchi, *J. Phys. Chem.* **99**, 8317 (1995).
- ¹⁹K. Matheis, A. Eichhöfer, F. Weigend, O. T. Ehrler, O. Hampe, and M. M. Kappes, *J. Phys. Chem. C* **116**, 13800 (2012).
- ²⁰N. Herron, J. C. Calabrese, W. E. Farneth, and Y. Wang, *Science* **259**, 1426 (1993).
- ²¹T. Vossmeier, G. Reck, B. Schulz, L. Katsikas, and H. Weller, *J. Am. Chem. Soc.* **117**, 12881 (1995).
- ²²S. Behrens, M. Bettenhausen, A. C. Deveson, A. Eichhöfer, D. Fenske, A. Lohde, and U. Woggon, *Angew. Chem., Int. Ed.* **35**, 2215 (1996).
- ²³X. Zhang, Y. Tian, F. Jin, J. Wu, Y. Xie, X. Tao, and M. Jiang, *Cryst. Growth Des.* **5**, 565 (2005).
- ²⁴O. Kiyohisa, H. Toyoharu, and M. Akira, *Jpn. J. Appl. Phys., Part 1* **38**, 6107 (1999).
- ²⁵S. Hirata, P.-D. Fan, A. Auer, M. Noijien, and P. Piecuch, *J. Chem. Phys.* **121**, 12197 (2004).
- ²⁶O. Christiansen, H. Koch, and P. Jorgensen, *Chem. Phys. Lett.* **243**, 409 (1995).
- ²⁷K. A. Nguyen, R. Pachter, and P. N. Day, *J. Chem. Theory Comput.* **9**, 3581–3596 (2013).
- ²⁸See supplementary material at <http://dx.doi.org/10.1063/1.4922320> for excitation energies, oscillator strengths, and transition character.
- ²⁹W. Kohn and L. J. Sham, *Phys. Rev.* **140**, A1133 (1965).
- ³⁰M. Dolg, U. Wedig, H. Stoll, and H. Preuss, *J. Chem. Phys.* **86**, 866 (1987).
- ³¹D. Andrae, U. Haeussermann, M. Dolg, H. Stoll, and H. Preuss, *Theor. Chem. Acc.* **77**, 123 (1990).
- ³²A. Bergner, M. Dolg, W. Kuechle, H. Stoll, and H. Preuss, *Mol. Phys.* **80**, 1431 (1993).
- ³³J. M. L. Martin and A. Sundermann, *J. Chem. Phys.* **114**, 3408 (2001).
- ³⁴K. A. Nguyen, P. N. Day, and P. Pachter, *J. Phys. Chem. C* **114**, 16197 (2010).
- ³⁵J. M. Matxain, J. Mercero, J. E. Fowler, and J. M. Ugalde, *J. Phys. Chem. A* **108**, 10502 (2004).
- ³⁶W. J. Hehre, R. Ditchfield, and J. A. Pople, *J. Chem. Phys.* **56**, 2257 (1972).
- ³⁷M. M. Francl, W. J. Pietro, W. J. Hehre, J. S. Binkley, D. J. DeFrees, J. A. Pople, and M. S. Gordon, *J. Chem. Phys.* **77**, 3654 (1982).
- ³⁸F. Weigend and R. Ahlrichs, *Phys. Chem. Chem. Phys.* **7**, 3297 (2005).
- ³⁹M. Cossi, G. Scalmani, N. Rega, and V. Barone, *J. Chem. Phys.* **117**, 43 (2002).
- ⁴⁰M. Cossi and V. Barone, *J. Chem. Phys.* **115**, 4708 (2001).
- ⁴¹K. A. Nguyen, P. N. Day, and R. Pachter, *J. Phys. Chem. A* **113**, 13943 (2009).
- ⁴²M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.
- ⁴³M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. Su, T. L. Windus, M. Dupuis, and J. A. Montgomery, *J. Comput. Chem.* **14**, 1347 (1993).
- ⁴⁴D. Swenson, N. C. Baenziger, and D. Coucouvanis, *J. Am. Chem. Soc.* **100**, 1932 (1978).
- ⁴⁵K. S. Hagen and R. H. Holm, *J. Am. Chem. Soc.* **22**, 3171 (1983).
- ⁴⁶I. G. Dance, A. Choy, and M. L. Scudder, *J. Am. Chem. Soc.* **106**, 6285 (1984).
- ⁴⁷G. S. H. Lee, D. C. Craig, I. Ma, M. L. Scudder, T. D. Bailey, and I. G. Dance, *J. Am. Chem. Soc.* **110**, 4863 (1988).
- ⁴⁸A. Eichhöfer, O. Hampe, and M. Blom, *Eur. J. Inorg. Chem.* **2003**, 1307.
- ⁴⁹P. A. W. Dean, J. J. Vittal, and N. C. Payne, *Inorg. Chem.* **26**, 1683 (1987).
- ⁵⁰T. Turk, U. Resch, M. A. Fox, and A. Vogler, *J. Phys. Chem.* **96**, 3818 (1992).
- ⁵¹G. S. H. Lee, K. J. Fisher, A. M. Vassallo, J. V. Hanna, and I. G. Dance, *Inorg. Chem.* **32**, 66 (1993).
- ⁵²W. E. Farneth, N. Herron, and Y. Wang, *Chem. Mater.* **4**, 916 (1992).
- ⁵³A. Eichhöfer and O. Hampe, *J. Cluster Sci.* **18**, 494 (2007).
- ⁵⁴R. A. Haberkorn, L. Que, Jr., W. Gillum, R. H. Holm, C. S. Liu, and R. C. Lordic, *Inorg. Chem.* **115**, 2408 (1976).
- ⁵⁵A. Eichhöfer, *Eur. J. Inorg. Chem.* **2005**, 1245.