

LETTERS

Size and Electric Dipole (Hyper)polarizability in Small Cadmium Sulfide Clusters: An ab Initio Study on (CdS)_n, n = 1, 2, and 4

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We report conventional ab initio and B3LYP/DFT calculations for the static electric (hyper)polarizability of small CdS clusters. Our results indicate a strong reduction of the (per atom) mean dipole polarizability with size, supporting the recent LDA findings by Troparevsky and Chelicowsky [*J. Chem. Phys.* **2001**, *114*, 943]. The same trend is observed for the second dipole hyperpolarizability. The computational complexity of the determination of the electric properties varies considerably with cluster size. B3LYP and conventional ab initio values are not in good agreement for the monomer but the gap is drastically reduced for the dimer and the tetramer.

The electric properties of cadmium sulfide clusters are currently of interest due to the dramatic increase of work on semiconductor particles and their potential applications in materials science.¹ As applications vary from electronic/optical properties^{2,3} to solar cell technology⁴ and DNA analysis,⁵ nanomaterials-oriented synthetic work on CdS clusters is actively pursued by many research groups.^{6–8} The emergence of nonlinear susceptibility measurements on CdS clusters,⁹ nanoparticles,^{10–12} and thin films of CdS nanocrystals¹³ is worth noticing. Little theoretical work has been published on (CdS)_n. The electric (hyper)polarizability of the monomer was studied by Raptis et al.¹⁴ The structure of (CdS)_n was investigated by Joswig et al.¹⁵ We are aware of only one study on the polarizability of cadmium sulfide clusters, a pseudopotential approach based on the local density approximation (LDA).¹⁶ Troparevsky and Chelicowsky¹⁶ showed that the mean dipole polarizability per atom of (CdS)_n decreases rapidly with cluster size, approaching the bulk limit of $23.7 e^2 a_0^2 E_h^{-1}$ from the

tetramer onward. The aim of this paper is to present conventional ab initio and density functional theory (DFT) results for the static dipole (hyper)polarizability of (CdS)_n, n = 1, 2, and 4. We have designed a basis of Gaussian-type functions (GTF) especially for this kind of molecular system. We expect to obtain clear indications for the performance and relative merit of these two important classes of theoretical methods in CdS cluster calculations. A most important part of our investigation is to offer a first aperçu on the nonlinear polarizability of small CdS clusters and to compare the observed trends to those available for the linear polarizability. Overall, given the scarcity of ab initio work on (CdS)_n, we expect the present gleanings of computational experience to be of use to future endeavors by other researchers.

A detailed presentation of the theoretical methods used in this paper may be found in standard references.^{17–21} Thus, along with the self-consistent field (SCF) we rely on Møller–Plesset perturbation theory (MP) and coupled-cluster (CC) techniques. The MP based methods are MP2, SDQ-MP4, and MP4, second, partial, and complete fourth-order, respectively. The highest order methods are CCSD (single and double CC) and its

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TABLE 1: Electric Properties^a of CdS^{b,c}

basis set	method ^d	μ	α_{zz}	α_{xx}	$\bar{\alpha}$	$\Delta\alpha$	β_{zzz}	β_{zzx}	$\bar{\beta}$	γ_{zzzz}	γ_{xxxx}	γ_{xxzz}	$\bar{\gamma}$
[7s6p4d/5s4p2d]	SCF	-3.3754	124.87	65.91	85.56	58.95	1986.4	836.1	2195.1	49.7	49.1	66.0	88.9
	MP2	-3.0582	99.89	69.86	79.87	30.02	-939.5	365.2	-125.5	-3.6	39.8	29.5	44.1
	SDQ-MP4	-2.8486	116.24	72.41	87.02	43.83	-143.3	702.4	756.9	-50.5	37.7	62.7	60.2
	MP4	-2.7963	107.91	72.55	84.34	35.36	-476.1	531.0	351.6	41.7	44.0	59.5	79.5
	CCSD	-2.8218	122.99	75.13	91.08	47.86	394.2	1102.4	1559.5	-45.2	6.4	117.6	88.5
	CCSD(T)	-2.7362	120.36	77.59	91.85	42.77	406.2	1290.9	1792.9	21.0	-12.7	164.9	129.3
	ECC ^e	0.6392	-4.50	11.68	6.29	-16.18	-1580.1	454.8	-402.3	-28.7	-61.8	98.9	40.4
[7s6p5d1f/5s4p3d1f]	SCF	-3.3420	124.05	65.69	85.14	58.36	1977.2	798.7	2144.8	50.6	52.7	63.2	88.8
	MP2	-2.9646	99.73	70.53	80.26	29.20	-877.6	375.4	-76.1	-3.4	46.4	30.2	48.2
	SDQ-MP4	-2.7784	114.53	72.63	86.59	41.90	-117.1	695.0	763.8	-35.9	43.6	62.7	66.2
	MP4	-2.7142	106.38	73.16	84.23	33.22	-495.4	519.0	325.6	44.8	50.5	57.6	81.9
	CCSD	-2.7568	121.59	74.90	90.47	46.68	473.7	1056.5	1552.0	-32.3	16.2	111.0	90.9
	CCSD(T)	-2.6616	119.39	77.50	91.46	41.89	477.1	1228.2	1760.1	25.6	-0.3	153.7	127.9
	ECC	0.6803	-4.67	11.81	6.32	-16.48	-1500.1	429.5	-384.6	-25.0	-53.1	90.4	39.0
[7s6p4d/5s4p2d]	B3LYP	-2.6111	103.87	61.98	75.94	41.89	453.8	374.0	721.0	41.5	39.7	44.5	65.1
[7s6p5d1f/5s4p3d1f]	B3LYP	-2.5543	103.14	61.77	75.56	41.36	495.6	347.9	714.8	38.9	45.6	41.3	65.2
[7s6p5d2f/5s4p4d2f]	B3LYP	-2.5548	103.35	61.69	75.58	41.66	471.2	353.4	706.9	49.1	49.5	44.4	71.7
[7s6p5d3f/5s4p4d3f]	B3LYP	-2.5384	103.34	61.81	75.65	41.52	458.1	349.3	694.0	48.2	50.7	44.1	71.7

^a Definitions: $\bar{\alpha} = (\alpha_{zz} + 2\alpha_{xx})/3$, $\Delta\alpha = \alpha_{zz} - \alpha_{xx}$, $\bar{\beta} = (3/5)(\beta_{zzz} + 2\beta_{zzx})$ and $\bar{\gamma} = (3\gamma_{zzzz} + 8\gamma_{xxxx} + 12\gamma_{xxzz})/15$. ^b The molecule on the z axis, with the center of mass at the origin and S on the positive part of the axis. ^c All values in atomic units. The second hyperpolarizability values are given as $10^{-3} \gamma_{\alpha\beta\gamma\delta}/e^4 a_0^4 E_h^{-3}$. ^d The 23 innermost MO were kept frozen in the post-Hartree-Fock calculations. ^e Defined as ECC = CCSD(T) - SCF.

extension CCSD(T), which is an estimate of connected triple excitations via a perturbational treatment. Last, we include B3LYP, a widely used DFT approach. The finite-field method used to obtain the electric properties has been exposed in sufficient detail elsewhere.^{22,23} We follow Buckingham's conventions in our electric property definitions and independent tensor component specification.²⁴

The basis sets used in the calculations were built upon a relatively small-sized but sufficiently flexible substrate, the split-valence 3-21G basis (as implemented in the GAUSSIAN 98 set of programs²⁵). The construction of the four basis sets used in this work follows a well-tested computational philosophy.²² Their composition is succinctly presented as (GTF exponents in a_0^{-2} in parentheses):

$$\begin{aligned}
 \text{SV0} &\equiv [7s6p4d/5s4p2d] \text{ for CdS, from 3-21G} \equiv \\
 &\quad [6s5p3d/4s3p]^{25} \\
 &\quad + \text{Cd: sp}(0.012761) + d(0.0374) \\
 &\quad + \text{S: sp}(0.0442605) + d(0.2420, 0.0544) \\
 \text{SV1} &\equiv [7s6p4d1f/5s4p3d1f], \text{ from SV0} \\
 &\quad + \text{Cd: d}(0.1255) + f(0.0374) \\
 &\quad + \text{S: d}(0.1147) + f(0.0544) \\
 \text{SV2} &\equiv [7s6p5d2f/5s4p4d2f], \text{ from SV1} \\
 &\quad + \text{Cd: d}(0.0111) + f(0.0111) \\
 &\quad + \text{S: d}(0.0258) + f(0.0258) \\
 \text{SV3} &\equiv [7s6p5d3f/5s4p4d3f], \text{ from SV2} \\
 &\quad + \text{Cd: f}(0.1255) \\
 &\quad + \text{S: f}(0.2420)
 \end{aligned}$$

5D and 7F GTF were used in the calculations. The following molecular geometries were used in this work. For CdS the bond length is 2.311 Å, taken from the work of Raptis et al.¹⁴ For the dimer, we performed a MP2(Full)/3-21G*(6D) calculation which yielded a Cd-S bond length of 2.521961 Å and a S-Cd-S angle of 109.8243°. For the tetramer (T_d) we used a B3LYP/3-21G*(6D) calculation which predicts a structure with

Cd-Cd distance of 3.207119 Å and S-S distance of 4.096006 Å (see footnote b, Table 3). With the exception of geometry data, atomic units are used throughout this paper.²⁶ To simplify the notation, all properties are reported as pure numbers, i.e., $\mu/e a_0$, $\alpha_{\alpha\beta}/e^2 a_0^2 E_h^{-1}$, $\beta_{\alpha\beta\gamma}/e^3 a_0^3 E_h^{-2}$, and $10^{-3} \gamma_{\alpha\beta\gamma\delta}/e^4 a_0^4 E_h^{-3}$. All calculations were performed with GAUSSIAN 98.²⁵

Our SV1 basis set yields for the monomer the following SCF values: $\mu = -3.33420$, $\bar{\alpha} = 65.69$, $\Delta\alpha = 58.36$, $\bar{\beta} = 2144.8$, and $\bar{\gamma} = 88.8$. Electron correlation reduces the dipole moment but has a non uniform effect on the components of $\alpha_{\alpha\beta}$. The same trend is obvious with the components of both hyperpolarizabilities $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$. Consequently, despite the very large electron correlation correction (ECC, defined as ECC = CCSD(T) - SCF) calculated for the Cartesian components, the overall effect on the mean values (and $\Delta\alpha$) is relatively smaller. The CCSD(T)/SV1 values are $\mu = -2.6616$, $\bar{\alpha} = 91.46$, $\Delta\alpha = 41.89$, $\bar{\beta} = 1760.1$, and $\bar{\gamma} = 127.9$. The results obtained with the smaller basis set SV0, reveal more or less a similar picture. Overall, the conventional ab initio methods are far from displaying a converging behavior for the hyperpolarizability of CdS. In comparison, the B3LYP method gives a reasonable value for the dipole moment but underestimates systematically the dipole polarizability components. The same is true for the components of both polarizabilities. It can be stated that the B3LYP values are relatively stable for all basis sets SV0 \rightarrow SV3. The B3LYP method is not in good agreement with the CCSD(T) results, but given the poor convergence of ab initio methods, one can hardly conclude with a too severe judgment on its performance.

It is interesting to notice that the overall picture is greatly improved for the dimer (CdS)₂. For this system electron correlation has a uniform effect on all tensor components. All methods are in good agreement. Our CCSD(T) values for the mean and anisotropy of the dipole polarizability are $\bar{\alpha} = 128.68$, $\Delta\alpha = 50.40$, 17.0, and 23.4% above the respective SCF values. The magnitude of the ECC for the components of $\gamma_{\alpha\beta\gamma\delta}$ increases as $\gamma_{zzzz} < \gamma_{yyyy} < \gamma_{xxxx}$. The SCF/SV0 and CCSD(T)/SV0 values for the mean $\bar{\gamma}$ are 70.7 and 100.5. The ECC corresponds to a strong increase of 42.1% of the SCF value. We have obtained MP2 values with the larger SV1 basis set. The results are very close to the analogous SV0. The B3LYP method performs much better in the case of the dimer.

TABLE 2: Electric Properties^a of (CdS)₂^{b,c}

basis set	method ^d	α_{xx}	α_{yy}	α_{zz}	$\bar{\alpha}$	$\Delta\alpha$	γ_{xxxx}	γ_{yyyy}	γ_{zzzz}	γ_{xxyy}	γ_{yyzz}	γ_{zzxx}	$\bar{\gamma}$
[7s6p4d/5s4p2d]	SCF	120.85	82.87	126.18	109.97	40.90	69.9	47.7	83.5	20.4	22.6	33.3	70.7
	MP2	140.17	94.49	145.67	126.78	48.67	108.1	75.0	97.0	31.3	32.8	42.6	98.7
	SDQ-MP4	138.27	92.98	145.51	125.59	49.32	105.3	71.5	92.2	30.6	30.8	45.3	96.5
	MP4	144.18	96.78	152.03	131.00	51.77	122.0	85.4	102.3	35.3	36.4	49.8	110.6
	CCSD	136.66	92.23	143.67	124.19	48.31	97.6	66.0	84.6	29.6	28.4	43.0	90.1
	CCSD(T)	141.24	95.36	149.43	128.68	50.48	109.2	76.2	89.4	33.9	32.6	47.4	100.5
[7s6p5d1/5s4p3d1f]	ECC	20.40	12.49	23.25	18.71	9.58	39.3	28.5	5.9	13.6	10.0	14.1	29.8
	SCF	122.73	83.55	126.68	110.98	41.29	74.0	53.7	83.6	21.4	22.7	34.9	73.9
[7s6p4d/5s4p2d]	MP2	142.76	95.33	147.48	128.52	49.96	114.7	83.0	95.5	32.6	31.8	44.0	102.0
	B3LYP	144.36	88.12	139.05	123.81	53.74	97.5	59.7	71.4	27.2	26.7	27.6	78.3
[7s6p5d1/5s4p3d1f]	B3LYP	145.36	88.47	139.33	124.39	54.13	99.2	66.3	69.1	27.6	25.0	27.5	79.0

^a Definitions: $\bar{\alpha} = (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})/3$ and $\Delta\alpha = (1/2)^{1/2}[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2]^{1/2}$ for the dipole and $\bar{\gamma} = (\gamma_{xxxx} + \gamma_{yyyy} + \gamma_{zzzz} + 2\gamma_{xxyy} + 2\gamma_{yyzz} + 2\gamma_{zzxx})/5$ for the hyperpolarizability. ^b The molecule is on the xz plane, with z as the reference Cd–Cd axis. ^c The second hyperpolarizability values are given as $10^{-3} \gamma_{\alpha\beta\gamma\delta}/e^4 a_0^4 E_h^{-3}$. ^d The 46 innermost MO were kept frozen in the post-Hartree–Fock calculations.

TABLE 3: Electric Properties^a of (CdS)₄^{b,c}

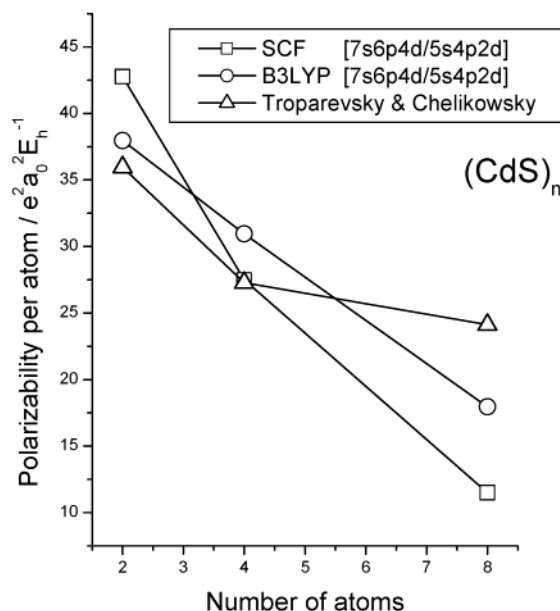
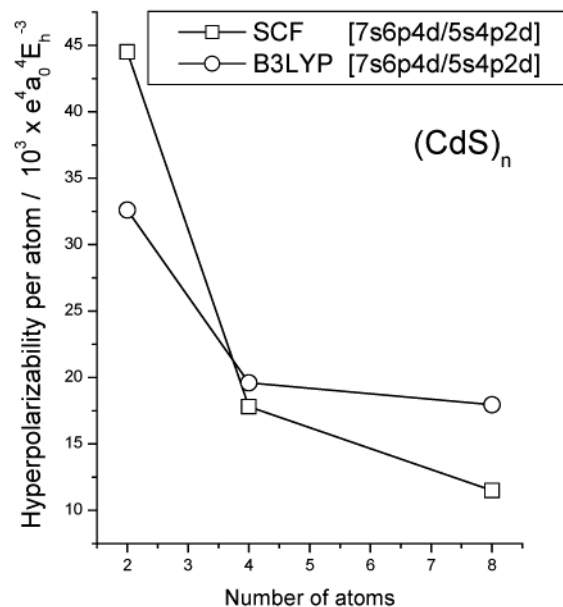
basis set	method ^d	α	β	γ_{zzzz}	γ_{xxxx}	$\bar{\gamma}$
[7s6p4d/5s4p2d]	SCF	182.91	−77	86.9	33.2	92.0
	MP2	209.25	−113	140.0	54.7	150.0
[7s6p4d/5s4p2d]	B3LYP	212.50	−107	130.4	54.5	143.6

^a Definition: $\bar{\gamma} = (3/5)(\gamma_{zzzz} + 2\gamma_{xxxx})$. ^b T_d symmetry, center at the origin (0,0,0), the four Cd atoms on the directions defined by the origin and the points (1,1,1), (1,−1,−1), (−1,1,−1), (−1,−1,1) and the four S atoms on the directions defined by the origin and the points (−1,−1,−1), (−1,1,1), (1,−1,1), (1,1,−1). ^c The second hyperpolarizability values are given as $10^{-3} \gamma_{\alpha\beta\gamma\delta}/e^4 a_0^4 E_h^{-3}$. ^d The 92 innermost MO were kept frozen in the post-Hartree–Fock calculations.

Only the SV0 basis set was used in calculation on the tetramer. The MP2 results give a strong indication of the size of electron correlation effects. The MP2/SV0 for the mean values are (SCF results in parentheses): $\alpha = 209.5$ (182.91), $\beta = -112.6$ (−77.2), and $\bar{\gamma} = 150.0$ (92.0). The increase in size of these values is 14.4, 45.9, and 63.0%, respectively. It is rather encouraging that the B3LYP results are in reasonable agreement with the above values. Overall, one observes that although the computational difficulties increase considerably with cluster size, DFT methods might be used with some success at a much lower cost.

Consider now the comparison of our results to the findings of Raptis et al.¹⁵ and Troparevsky and Chelikowsky.¹⁶ The former authors have reported a model study of ZnS, CdS, and HgS. Their SCF values for the monomer are $\mu = -3.42020$, $\bar{\alpha} = 81.369$, $\beta = 2370.8$, and $\bar{\gamma} = 101.7$, in good agreement with ours. We refer to their work for additional information on the monomer, as their efforts extend to the study of vibrational and relativistic effects. Our values for CdS are in essential agreement with theirs. In Figures 1 and 2 we present our SCF and B3LYP data for the evolution of the mean (per atom) (hyper)polarizability of the studied systems. In Figure 1 we have also included the values reported by Troparevsky and Chelikowsky.¹⁶ For the polarizability our SCF/SV0 and B3LYP/SV0 data show an almost linear evolution with cluster size. Our values for the tetramer are systematically lower than theirs. In Figure 2, we show that the mean (per atom) hyperpolarizability follows the same trend as the polarizability.

In conclusion, we have brought forth the formidable difficulty of the extension of ab initio studies of (hyper)polarizability effects to cadmium sulfide clusters. There is evidence that DFT methods might predict reliable (hyper)polarizability values for large clusters. Our small SV0 basis set provides a reliable theoretical description of the studied molecules and could be used for electric polarizability calculations on clusters as large as (CdS)₁₅. It is worth emphasizing that considerable computational work has to be done to elucidate fundamental aspects

**Figure 1.** Mean dipole polarizability in small (CdS)_n clusters.**Figure 2.** Mean second dipole hyperpolarizability in small (CdS)_n clusters.

of the evolution of (hyper)polarizability with cluster size. This can be attributed to drastic changes in bonding patterns as cluster size increases. Such effects have been reported in the case of

the polarizability of silicon clusters.^{27,28} Also, in the case of the tetramer Si₄ the mean hyperpolarizability per atom is significantly lower than that of Si.²⁹ This is similar to the conclusions of the present investigation.

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