Spectral signatures of semiconductor clusters: (CdSe)₁₆ isomers

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Abstract

The sensitivity of several experimentally accessible properties to the geometrical structure of the semiconductor (CdSe)₁₆ cluster is explored by density functional theory. Our test set consists of eleven (CdSe)₁₆ isomers belonging to various topological groups. For all isomers, the UV-visible and IR spectra have been simulated and vertical and adiabatic ionization energies, adiabatic electron affinities, polarizabilities and hyperpolarizabilities have been computed. The hyperpolarizability is found to be the most sensitive property to the isomer geometrical structure followed by optical and IR spectra. This work leads to the conclusion that reliable identification of an isomer requires a combination of experimental methods.

Keywords: semiconductor Qdots, CdSe clusters, optical spectra, polarizability, ionization energy, electron affinity.

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1. Introduction

CdSe quantum dots (QD) have extensively been studied over the last 20 years in the size range of 1-100 nm. The interest in these II-IV type semiconductor QD's is due to their promising applications in such areas as medical imaging [1,2], opto-electronic design [3], bioactive fluorescent probes [4], and solar cells [5 ,6]. The preferred lattice of bulk CdSe has the wurtzite type and correspondingly core geometrical structures of CdSe QDs [7] often have the wurtzite type as well; however, QDs with zinc-blende cores have also been actively studied [8]. CdSe clusters with small diameters, which are precursors for CdSe QDs, are less studied and no experimental structures for these clusters are generally available.

Experimentally, magic-sized clusters of $(\text{CdSe})_n$ produced by laser ablation appear at $n = 33$ and 34 and are stable in solution both with and without ligation [9]. A joint experimental and computational study was performed for $(\text{CdSe})_n^+$ cations ($n = 1 - 16$) and the corresponding neutral parents have also been computed [10]. It was found that computed atomization energies of the cations correlate with their stability determined from experiment. Neutral $(\text{CdSe})_n$ clusters with $n \leq 16$ have been characterized using density functional theory (DFT) [11]. In both studies, the $(\text{CdSe})_n$ clusters with $n \leq 5$ have been found to possess ring geometrical structures whereas the energetically preferred geometrical structures in the range of $n = 6 - 16$ are three dimensional spheroids. On the basis of DFT calculations, neutral $(\text{CdSe})_n$ clusters have been predicted to possess core-shell structures for $n = 13, 29 - 35$ [12] and $n = 36$ [13].

Theoretical absorption spectra of small $(\text{CdSe})_n$ clusters have first been obtained [14 , 15] using time-dependent density functional theory (TDDFT) for $n = 1 - 8$. In a subsequent work, absorption spectra of $(\text{CdSe})_n$ clusters have experimentally been measured in the range of $n = 2 - 16$ and compared to the results of accompanying calculations [16]. A basin-hopping global method has been applied for the search of magic-sized $(\text{CdSe})_n$ clusters in the range of $n = 1 - 37$ [17] and absorption spectra have been simulated using their TDDFT results for the

selected states with energetically preferred geometries. Light absorption by CdSe nanoclusters with sizes up to 1.5 nm has been studied using DFT and the results of computations have been compared to experiment [18].

Electric polarizability has been computed for small $(\text{CdSe})_n$ clusters ($n = 1 - 4$) [19, 20] and the polarizability anisotropy has been shown to be consistently overestimated when using hybrid Hartree-Fock-DFT functionals. Static and dynamic polarizabilities have also been calculated [21] for $(\text{CdSe})_n$ clusters in the range of $n = 1 - 16$. It has been found that both the polarizability and its anisotropy vary substantially with the cluster size. Frequency-dependent hyperpolarizability tensors have also been calculated [22] for small $(\text{CdSe})_n$ clusters in the range of $n = 1 - 4$.

As the number of atoms in a cluster increases, the number of possible geometrical structures grows rapidly. States with different geometrical structures generally possess different total energies, and the main problem is to find a geometrical structure which corresponds to the state with the lowest total energy. Under normal experimental conditions, the ground state has to be the most populated and will be responsible for the main features in spectra measured for a given cluster. Excited states of a cluster can be close in total energy to the ground state, and the presence of isomers in experimental samples greatly depends on a sample preparation [9, 23]. Since both the size and the shape of a cluster may seriously influence experimental spectra, the identification of species used in experiment is highly desirable.

The aim of this paper is to explore the dependence of different properties of a semiconductor cluster, which can be measured experimentally, on its geometrical structure. As test clusters we chose eleven isomers of the $(\text{CdSe})_{16}$ cluster belonging to different topological groups. For each isomer, we simulated absorption and IR spectra and computed its ionization energies and electron affinities along with polarizabilities and hyperpolarizabilities. All of these cluster signatures can be measured experimentally and this work could help in choosing the most sensitive method for identification of isomers of semiconductor nanoparticles.

2. Computational details

Our calculations were performed using density functional theory within the generalized gradient approximation (DFT-GGA) as realized in the Gaussian 09 suite [24]. As in our previous work [25,26], we chose the Becke-Perdew-Wang (BPW91) [27, 28] exchange-correlation functional. The small 18-electron effective core potentials (ECP) [29] and the cc-pVDZ-pp basis sets were used for Cd (*4s4p3d1f*) [30] and Se (*5s4p3d*) [31].

In order to test reliability of the chosen BPW91/cc-pVDZ-pp approach, we performed optimizations [13] of the ground singlet state of a CdSe dimer using the coupled-cluster method with singles and doubles and non-iterative inclusion of triples [CCSD(T)] [32] and a larger cc-pVTZ-pp basis sets. The equilibrium bond distance r_e and harmonic vibrational frequency ω_e obtained at the BPW91/cc-pVDZ-pp level of theory are 2.368 Å and 261.0 cm⁻¹, respectively. These values are in close agreement with the values obtained at the CCSD(T)/cc-pVTZ-pp level of theory: 2.361 Å and 260.6 cm⁻¹, respectively.

The convergence threshold for total energy was set to 10⁻⁸ eV and the force threshold was set to 10⁻³ eV/Å. Each geometric optimization was followed by harmonic frequency computations in order to confirm the stationary character of the state obtained. If an optimization arrived at a transition state, optimizations following the imaginary frequency modes were performed until all imaginary frequencies were eliminated. In order to estimate ionization energies and adiabatic electron affinities, the geometries of the isomer cation and anion states have also been optimized.

3. Results and discussion

We first select geometrical structures of (CdSe)₁₆ belonging to different topological groups and optimize singlet states with the chosen geometries. All possible geometrical structures can be divided into two classes: fullerenes and non-fullerenes. Unlike carbon fullerenes which are composed of hexagons and 12 pentagons, binary (AB)_n fullerenes are composed of hexagons and rhombi when each atom is bound to three atoms of the opposite type.

According to the Euler theorem, such fullerenes contain exactly 6 rhombi and $(n - 4)$ hexagons, except for $n = 5$, where no fullerene structure exists. With these optimized geometrical structures, we simulate absorption spectra using transition energies and oscillation strengths obtained from our TDDFT computations followed by simulations of IR spectra using the vibrational energies and corresponding IR intensities obtained from our harmonic vibrational frequency calculations. Next, we compute and discuss polarizabilities and hyperpolarizabilities of the isomers. The dependence of ionization energies and electron affinities on the isomer geometry is discussed in the last section.

3.1. Geometrical structures

For generating geometrical structures we used the literature data on geometrical structures of $(\text{BN})_{16}$ [33, 34], $(\text{GaAs})_{16}$ [35], $(\text{CdSe})_{16}$ [16-18], and $(\text{CdTe})_{16}$ [36]. It was found in previous studies that the states of semiconductor $(AB)_n$ clusters with Cd_nSe_n fullerene-type geometrical structures typically possessed the lowest total energies for $n < 29$ whereas the states with core-shell geometrical structures became energetically more favorable for larger n . An exception presents the $(\text{CdSe})_{13}$ cluster with a single Se atom as a core. As for the $(\text{CdSe})_{16}$ cluster, different geometrical structures have been found for its ground state in the previous studies.

Figures 1 and 2 present six fullerene and five non-fullerene isomers of $(\text{CdSe})_{16}$, respectively. As can be seen in Figure 1, the states of isomers with fullerene geometrical structures are lower in total energy than the states of isomers with non-fullerene geometries except for the state of an isomer with geometrical structure **IV** obtained from optimizations of a state whose initial geometrical structure consisted of a CdSe dimer inserted in the center of a $(\text{CdSe})_{15}$ fullerene. The state of an isomer with a fullerene geometry of T_d symmetry is found to possess the lowest energy in agreement with one of the previous studies [17]. The states of isomers with fullerene geometries of C_{3v} and C_s symmetries are higher by 0.11 eV in total

energy. The state of an isomer with non-fullerene structure **IV** is higher in total energy by only 0.02 eV than the previous two states, followed by three states of isomers with fullerene-type geometries of C_1 , C_{2h} , and S_4 symmetry.

Non-fullerene geometrical structures presented in Figure 2 possess different topologies; namely, structure **IV** contains a Se atom inside the cage (this atom is bound to a single Cd atom only and cannot be considered as a core); structure **VIII** contains an eight-member ring $(CdSe)_4$ and the state of an isomer with this geometry is nearly degenerate in total energy with the states of isomers whose geometrical structures **VI** and **VII** are fullerenes; structure **IX** is amorphous; structure **X** contains single Cd – Cd and Se – Se bonds; structure **XI** contains three Cd and three Se atoms doubly bonded to the rest of atoms which are triply bonded. The states of isomers with geometrical structures **X** and **XI** are considerably higher in total energy than the states of other isomers considered. It is worth noting that the formation of Cd – Cd bonds has to be highly unfavorable since the free-standing Cd_2 dimer is a Van der Waals dimer with a Cd – Cd binding energy [37] of only $\sim 200\text{ cm}^{-1}$.

3.2. Optical Spectra

In order to simulate absorption spectra of the states with geometrical configurations presented in Figures 1 and 2, we performed TDDFT computations for the first 200 singlet-singlet transitions. Note that singlet-triplet transitions are forbidden in the first order. The energy of the first optical transition is found to be considerably larger than the CdSe bulk band gap of 1.73 eV [38]. For the ground state (**I** in Figure 1), the energy of the first singlet-singlet transition is 2.21 eV whereas the HOMO-LUMO gap (HLG) is 2.19 eV. It was shown in our previous work [39], that the HLG value obtained using the BPW91 approach produces a good approximation for the first singlet-triplet transition energy. The latter energy can be computed directly as the difference in total energies between the lowest singlet and triplet states or using the TDDFT results for the singlet state.

According to the effective mass approximation model [40],[41] quantum confinement effects are expected to dominate when QDs have a radius smaller than the Bohr exciton radius which represents an average electron-hole distance in the Wannier-Mott exciton theory. According to this model, the band gap increases (blue-shifted) as the size of nanoclusters decreases. However, experimentally measured values for small QDs begin to seriously diverge from the theoretical estimates obtained using the effective mass approximation model [42, 43] as the QD size decreases. The experimentally measured Bohr exciton radius for CdSe is 5.6 nm [44], whereas the radii of our (CdSe)₁₆ isomers are around 1 nm. The largest internuclear distance in the prolate isomer **VII** is 1.46 nm. Therefore, one should expect the isomers to show strong quantum confinement effects.

The lower total energy clusters generally possess larger HLG values and the maxima in their simulated absorption spectra are close to 400 nm as can be seen in Figure 3. For example, the ground state (**I**) has a single maxima at 414 nm (3.00 eV) and its HLG is 2.19 eV whereas the states with C_{3v} and C_s fullerene geometries [**II**] and [**III**], respectively] have maxima at 415 nm and 401 nm and an HLG of 2.12 eV and 2.22 eV, respectively. The absorption spectrum (**III**) has a noticeably broader peak with a shoulder in the long wavelength region. The next state in total energy possesses a non-fullerene geometrical structure (**IV**) and its absorption spectrum has two peaks, the taller one at 382 nm and the shorter one at 500 nm.

The absorption spectra of the remaining fullerene isomers (**V**) and (**IV**) are quite broad and possess a single strong peak with shoulders. The corresponding states possess somewhat smaller HLG's: 1.90 eV and 2.03 eV for C_{2h} and S_4 isomers, respectively. The absorption spectra of non-fullerene isomers presented in Figure 4 are quite different and the HLG of the corresponding states decreases as isomer total energy increases (see Table 1). The general feature of all spectra is the presence of a peak at ~400 nm. In general, the HLG decreases as the isomer total energy decreases.

3.3 IR spectra

The IR spectra simulated with a full width at half maximum of 3 cm^{-1} are presented in Figures 5 and 6. As can be seen, the peaks of the IR bands with the highest intensity are located above 200 cm^{-1} in most cases. In particular, the IR spectrum of the ground state (**I**) has three strongly IR active modes at 208 cm^{-1} . The spectrum (**II**) of the isomer next in total energy (the C_{3v} isomer) has two IR active modes belonging to the E irreducible representation at 209 cm^{-1} and the mode belonging to the A_1 representation at 211 cm^{-1} . The closeness of these values causes the major feature of the spectrum to be similar to that of spectrum (**I**).

Other isomers possess more complex spectra. For example, the spectrum belonging to isomer (**III**) possesses three major peaks at 214 cm^{-1} , 207 cm^{-1} , and 202 cm^{-1} . The spectrum (**IV**) belonging to an isomer **IV** (see Figure 1) with the lowest total energy among all other non-fullerene isomers has a noticeably distinct shape with a quite strong feature at 271 cm^{-1} . The spectrum (**V**) belonging to the fullerene isomer of symmetry C_1 has the major feature at 208 cm^{-1} , followed by a closely-spaced peak at 215 cm^{-1} and a broad feature around 184 cm^{-1} . The spectrum (**VI**) of the C_{2h} fullerene isomer has also a peak at 208 cm^{-1} as well as a few smaller peaks surrounding it. The IR spectrum of the last fullerene of S_4 symmetry is the most unique among the spectra of isomers with fullerene-type geometrical structures. The spectrum possesses the major peak at 184 cm^{-1} with a relatively small feature at 208 cm^{-1} which is likely because of the isomer tube-like structure.

The spectra of isomers with non-fullerene structures presented in Figure 6 are much more diverse in their shapes and had less in common with one another. The spectra of isomers with spheroid-like structures like the spectra of isomers with fullerene-type structures possess the major features at 208 cm^{-1} . These non-fullerene isomers include structures **VIII** of C_{2v} symmetry and **X** which is lacking symmetry. The spectra belonging to the isomers with other shapes, such as the bulk-like isomer (**XI**) or the C_1 (**IX**) cluster are unique.

3.4. Polarizability and Hyperpolarizability

Static dipole electric polarizabilities correspond to coefficients in the Taylor expansions of total energy perturbed in the presence of a weak uniform external static electric field [45, 46]:

$$E^p = E^0 - \sum_{\alpha} \mu_{\alpha} F_{\alpha} - \frac{1}{2} \sum_{\alpha, \beta} \alpha_{\alpha\beta} F_{\alpha} F_{\beta} - \frac{1}{6} \sum_{\alpha, \beta, \gamma} \beta_{\alpha\beta\gamma} F_{\alpha} F_{\beta} F_{\gamma} - \frac{1}{24} \sum_{\alpha, \beta, \gamma, \delta} \gamma_{\alpha\beta\gamma\delta} F_{\alpha} F_{\beta} F_{\gamma} F_{\delta} + \dots \quad (1)$$

where E^p is perturbed total energy, F is a static electric field, E^0 is total energy in the absence of the field, μ_{α} is the permanent dipole moment, $\alpha_{\alpha\beta}$ is the static dipole electric polarizability tensor (or linear polarizability), $\beta_{\alpha\beta\gamma}$ and $\gamma_{\alpha\beta\gamma\delta}$ are the first and second dipole electric hyperpolarizability (or the second and third order nonlinear polarizability) tensors, respectively. Greek subscripts denote indices running over x , y , and z . The mean static dipole electric polarizability ($\bar{\alpha}$)

$$\bar{\alpha} = \frac{1}{3} (\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

The $\bar{\alpha}$ components can be obtained as the second and first derivatives of the total energy and the dipole moment, respectively, with respect to the applied field, provided that the Hellman-Feynman[47] theorem is satisfied. The anisotropy of the polarizability tensor is

$$\Delta\alpha = \left(\frac{1}{2}\right)^{1/2} \left[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{xx} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{yy})^2 + 6(\alpha_{xy}^2 + \alpha_{xz}^2 + \alpha_{zy}^2) \right]^{1/2} \quad (3)$$

The first-order hyperpolarizability is defined as

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} \quad (4)$$

where

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$

$$\beta_y = \beta_{yxx} + \beta_{yyx} + \beta_{yzz}$$

$$\beta_z = \beta_{zxx} + \beta_{zyy} + \beta_{zzz}$$

One can also define the vector component of the first hyperpolarizability tensor in the direction of the ground-state dipole as

$$\beta_{||} = \frac{3}{5} * \frac{\beta_x \mu_x + \beta_y \mu_y + \beta_z \mu_z}{|\mu|} \quad (5)$$

It has been previously observed[48 - 50] that the polarizability of a species depends essentially on their geometrical structures and our results lend further support to this observation. As can be seen in Figure 1, geometrical structures **I** – **III** which correspond to the most energetically stable isomers of (CdSe)₁₆ are approximately spherical. The corresponding average polarizabilities $\bar{\alpha}$ are quite close to each other, but differ significantly from the $\bar{\alpha}$ values calculated for more prolate clusters of S_4 or C_{2h} symmetry (see Table 1).

On the contrary, the first hyperpolarizabilities of the first three most energetically stable isomers greatly differ from each other (see Table 2). Similarly, the components of the first hyperpolarizability tensor in the direction of the ground state dipole are also very different. The isomers with prolate geometrical structures; however, show a relatively small first hyperpolarizability. The isomers with inverse symmetry (T_d , C_{2h} , S_4) possess no dipole moment and the $\beta_{||}$ values are identically zero in these cases. Therefore, the combined information from polarizability and hyperpolarizability could be very useful in identifying the presence of various isomers in a sample.

3.5. Vertical detachment energies and electron affinities

The vertical ionization energy of a neutral isomer i is computed as

$$IE_{\text{vert}}(N_i, R_e^i) = E_{\text{tot}}^{\text{el}}(C_i, R_e^i) - E_{\text{tot}}^{\text{el}}(N_i, R_e^i) \quad (6)$$

where $E_{\text{tot}}^{\text{el}}(N_i, R_e^i)$ and $E_{\text{tot}}^{\text{el}}(C_i, R_e^i)$ are the total Born-Oppenheimer energies of the i -th neutral isomer and its cation, respectively, computed at the equilibrium geometry of the i -th neutral isomer. The energy of the adiabatic detachment of an electron is computed in a similar way

$$IE_{\text{ad}}(N_i, R_e^i) = E_{\text{tot}}^{\text{el}}(C_i, R_e^{+,i}) + E_0(C_i, R_e^{+,i}) - [E_{\text{tot}}^{\text{el}}(N_i, R_e^i) + E_0(N_i, R_e^i)] \quad (7)$$

where $R_e^{+,i}$ is the equilibrium geometry of the i -th isomer cation and E_0 is the zero-point vibrational energy computed in the harmonic approximation.

The adiabatic electron affinity of a neutral isomer is defined by the expression

$$EA_{\text{ad}}(N_i, R_e^i) = E_{\text{tot}}^{\text{el}}(N_i, R_e^i) + E_0(N_i, R_e^i) - [E_{\text{tot}}^{\text{el}}(A_i, R_e^{-,i}) + E_0(A_i, R_e^{-,i})] \quad (8)$$

where R_e^i and $R_e^{-,i}$ are the equilibrium geometries of the i -th neutral and anion isomer.

The vertical electron detachment energies of the i -th isomer anion are computed at the geometry $R_e^{-,i}$ of this isomer anion according to the expression

$$VDE_i(A_i, R_e^{-,i}) = E_{\text{tot}}^{\text{el}}(N_i, R_e^{-,i}) - E_{\text{tot}}^{\text{el}}(A_i, R_e^{-,i}) \quad (9)$$

The values computed according to Eqs (6)-(9) for all isomers are shown in Figures 1 and 2 are collected in Table 1. As can be seen, all four of these observables show a behavior quite similar to that of the HLG values. The IE_{vert} values decrease when moving along both fullerene and non-fullerene series in the ascending energy order, except for isomer **VIII** in the non-fullerene series. The anion of isomer **IV** with non-fullerene geometrical structure possesses the largest IE_{vert} value among all isomers. The adiabatic ionization energy follows nearly the same pattern except for the IE_{ad} value of isomer **IV** which is smaller than the IE_{ad} values of all isomers with fullerene-type geometries but isomer **VI**.

The adiabatic electron affinity do not show a regular behavior when moving along the isomer series in the ascending energy order with the minimal value of 2.52 eV belonging to isomer **VI** and the maximal value of 2.80 eV belonging to isomer **X**. All isomers from **I** to **IX** except for isomer **VI** possess the EA_{ad} values of 2.65 ± 0.05 eV and thus the EA_{ad} is a poor signature of these isomers when concerning their identification.

1 The vertical electron detachment energies of the isomer anions with non-fullerene
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3 geometries are all larger than those of the isomer anions with fullerene-type geometries, except
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5 for isomer **VII** which possess the largest total energy in the fullerene isomer series. Therefore,
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7 laser photodetachment can help in the identification of isomers which possess non-fullerene
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9 geometries.
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11 **4. Summary**

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13 Using density functional theory with generalized gradient approximation we computed a
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15 number of properties of (CdSe)₁₆ isomers whose geometrical structure belong to different
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17 topological groups. These properties can be experimentally measured and used for isomer
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19 identification. We found that the property which is most useful for distinguishing between the
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21 most energetically favorable isomers is hyperpolarizability because it is highly sensitive to even
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23 small changes in the geometry. The UV and IR methods are capable of distinguishing between
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25 clusters which spheroid and non-spheroid geometrical structures as well as between energetically
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27 similar clusters with fullerene and non-fullerene geometries. Ionization energies and adiabatic
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29 electron affinities of the neutral isomers can be useful for identifying those isomers which
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31 appreciably deviate from the general correlation between observable values and the total energy
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33 of isomer states. Especially it is true for the vertical electron detachment energies of the isomer
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35 anions where the values could vary in a large range. Overall, it seems that no one method is
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37 capable of reliably identifying an isomer because of the significant overlap of the different
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39 properties of the isomers. However, when one considers data obtained from different
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41 experimental measurements then an analysis of combinations of experimental data can help to
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43 reliably identify most of isomers.
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8 **Figure captions**
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10 **Figure 1.** The states and geometrical configurations of fullerene isomers. All energies are
11 relative to the total energy of the state with structure **I**.
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15 **Figure 2.** The geometrical configurations of non-fullerene isomers. All energies are relative to
16 the total energy of the state with structure **I** in Figure 1.
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20 **Figure 3.** Simulated optical spectra for the states with geometrical structures **I-VI**.
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22 **Figure 4.** Simulated optical spectra for the states with geometrical structures **VII-XI**.
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25 **Figure 5.** Simulated IR spectra for the states with geometrical structures **I-VI**. The full width at
26 half maximum is set to 3 cm^{-1} .
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30 **Figure 6.** Simulated IR spectra for the states with geometrical structures **VII-XI**. The full width
31 at half maximum is set to 3 cm^{-1} .
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Table 1

Comparison of the HLG, position of the main peak in absorption spectra, mean static electric polarizability per atom $\bar{\alpha}$, vertical and adiabatic ionization energies, and adiabatic electron affinity of the neutral (CdSe)₁₆ isomers along with the vertical electron detachment energies of the isomer anions.

Isomer	I	II	III	IV	V	VI	VII	VIII	IX	X	XI
Neutral											
ΔE_{tot} (eV)	0.0	0.11	0.11	0.12	0.65	0.89	0.90	0.90	0.93	1.76	2.05
HLG (eV)	2.19	2.12	2.22	2.05	2.00	1.90	2.03	1.99	1.55	1.42	1.51
Optical Max (nm)	414	415	401	382	387	396	510	397	517	402	396
$\bar{\alpha}$ ($\text{\AA}^3$)	4.73	4.75	4.67	4.62	4.83	4.87	5.16	4.83	4.70	4.93	5.14
IE_{vert} (eV)	7.08	7.07	7.04	7.13	6.98	6.90	6.95	6.99	6.68	6.44	6.51
IE_{ad} (eV)	6.99	6.97	6.97	6.83	6.88	6.82	6.78	6.91	6.49	6.03	6.47
EA_{ad} (eV)	2.60	2.62	2.52	2.65	2.66	2.71	2.61	2.69	2.69	2.80	2.72
Anion											
VDE (eV)	2.62	2.65	2.54	3.41	2.69	2.74	2.62	2.71	3.51	3.54	2.75

Table 2

Hyperpolarizabilities and dipole moments of the neutral (CdSe)₁₆ isomers.

	I	II	III	IV	V	VI	VII	VII	IX	X	XI
Neutral											
β_x	27.7	2.0	-73.7	-2083.2	83.2	10.2	16.0	7.8	-1651.0	-4898.9	-0.1
β_y	-3.2	-1.8	-633.7	31.4	-385.9	-8.9	-70.0	2.7	-305.1	796.7	-977.4
β_z	-19.5	198.5	39.5	15.5	555.6	-1.4	47.4	-672.5	131.9	1093.2	-11.5
$\langle\beta\rangle$	34.0	198.5	639.2	2083.5	681.6	13.6	86.1	672.6	1684.1	5082.3	977.5
$\beta_{ }$	0.0	119.1	339.3	1044.2	304.6	0.0	0.0	-403.5	742.0	-2077.8	-586.4
μ_x	0.0	0.0	0.4	-5.0	0.0	0.0	0.0	0.0	-4.0	1.5	0.0
μ_y	0.0	0.0	-1.0	2.4	0.1	0.0	0.0	0.0	1.4	-0.7	3.4
μ_z	0.0	0.1	0.0	2.4	0.9	0.0	0.0	0.0	3.2	1.0	0.0
$ \mu $	0.0	0.1	1.1	6.1	0.9	0.0	0.0	0.0	5.3	1.9	3.4

Figure

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Figure 1

Figure

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Figure 2

Optical spectra of $(\text{CdSe})_{16}$ fullerenes

Figure 3

Optical spectra of $(\text{CdSe})_{16}$ non-fullerenes

Figure 4

Figure

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Figure 5

IR spectra of $(\text{CdSe})_{16}$ non-fullerenes

Figure 6