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Zinc Selenide Nanoclusters: Static Dipole Polarizability and Electronic Properties

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ABSTRACT: The structural stability and electronic properties of stoichiometric zinc selenide (ZnSe) nanoclusters up to 20 atoms have been systematically investigated in the framework of density functional theory. The similarity function has been used to investigate the extent that the clusters are similar to the pure ZnSe or to each other. Energetically, the relative stability of ZnSe clusters at different sizes is studied by calculating the second-order difference in total energy. The size evolution of several reactivity descriptors such as static dipole polarizability and chemical hardness has been determined for ZnSe clusters. In addition, the minimum polarizability principle and principle of maximum hardness are used to characterize the magic clusters. Moreover, it is shown that the differential mean polarizability can be also a useful quantity to characterize the stability of the studied clusters. It is found that there is a strong inverse correlation between the static dipole polarizability and the ionization potential of the ZnSe clusters. Similarly, the softness has also been shown to mostly correlate with the static dipole polarizability of these clusters. This work thus will have some important implications for the calculation of polarizability of ZnSe clusters in terms of the corresponding ionization potentials and softness. For each property, a comparison between studied clusters here and the zinc sulfide clusters from our recent article is presented. © 2010 Wiley Periodicals, Inc. Int J Quantum Chem 111: 3888–3896, 2011

Key words: zinc selenide nanoclusters; static dipole polarizability; similarity function; reactivity descriptors

1. Introduction

During the last two decades, the perusal of the chemical and physical properties of II–VI semiconductor materials has been carried out by both theoreticians and experimentalists. These materials are currently under intense investigation in various fields of science and have generated great importance in the development of technology. Applications of these species in diverse fields such as photocatalysts [1, 2], optical sensitizers [3], solar cells [4–9], emissive flat screens and ultraviolet

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light-emitting diodes [10, 11], quantum devices [12], and so on have led to extensive studies in this context. Theoretically, the electronic structure of these semiconductors has been investigated in previous studies [13–17]. To comprehend the applications of these compounds, it is necessary to study their structures and electronic properties. Moreover, there are some properties related to these compounds that have been seen to be local phenomena, that is, they happen in a certain well-defined domain of the surface. Clusters by their nature represent the link between an ensemble of separate atoms or molecules and a bulk of these materials. So, it is important to study small clusters of these materials, whose electronic and structural properties could give an insight into understanding the bulk properties. In fact, to understand the features of experimentally observed properties, theoretical studies would be valuable. In this respect, II–VI clusters are especially interesting and represent a remarkable focus of studies. In recent years, different clusters of group II–VI materials were investigated in the literature [18–31]. Nonetheless, studies that involve structures and properties of stoichiometric zinc selenide (ZnSe) clusters are scares and only few reports are available for theoretical works on these clusters. Matxain et al. [32] made one of the first structural studies for ZnSe clusters and obtained the most stable structures of small $(ZnSe)_n$ clusters with $n = 1$–9. They found ring-like structures as global minima for clusters as large as $n = 5$ and three-dimensional spheroid structures for larger ones $n = 6$–9. Also, they have reported some properties such as natural orbital charges and cohesive energies for these clusters. A potential energy surface study for small ZnSe clusters up to heptamer was carried out by Deglmann et al. [33]. Another theoretical work on the structures and some of the properties such as incremental atomization and first excitation energies for $(ZnSe)_n$ clusters up to $n = 16$ has been done by Burnin et al. [34]. More recently, Nanavati et al. [35] studied the structures and properties such as binding energy, highest occupied molecular orbital-lowest unoccupied molecular orbital energy gap, and optical absorption of bare and passivated small ZnSe clusters. However, no systematic density functional theory (DFT) investigation on the correlations of the stability, the static dipole polarizability, and the electronic properties of ZnSe clusters has been conducted thus far. So, in the present article, we extend our previous work on the optical, electronic, and structural properties of the zinc sulfide (ZnS) nanoclusters to get further insight into various properties of ZnSe clusters too [36]. In fact, we focus on the static dipole polarizability, similarity function, second-order difference in total energy, and chemical hardness and softness that so far have not been studied in the literature for ZnSe clusters. The size dependence of these descriptors has been investigated in this work. Moreover, as ZnSe clusters have similar structure to what we previously found for the ZnS clusters [36], we performed a comparative analysis for various properties of these two types of II–VI clusters.

2. Theoretical Framework

The static dipole polarizability is one of the most important quantities in chemistry and physics. The study of linear optical properties of semiconductor clusters such as polarizability has become a considerable area of theoretical and experimental predictions in recent years [37–45]. The interplay between theory and experiment is a powerful tool that serves to identify which cluster is observed in the experiments through the comparison of the calculated polarizabilities with the experimental ones. Therefore, the thorough understanding of the polarizabilities from theoretical calculations is important in cluster science. Moreover, polarizability is sensitive to the structural geometry and delocalization of valence electrons of clusters, and it can provide information on the electronic properties and geometrical features of the clusters.

The measured data in experiments are usually the mean static dipole polarizability, which can be obtained by the trace of the polarizability tensor to be as follows [46]

$$\langle \alpha \rangle = \frac{1}{3} \left(\alpha_{xx} + \alpha_{yy} + \alpha_{zz} \right) \qquad (1)$$

In this work, we focus on the static dipole polarizability per ZnSe unit, which is calculated as $\langle \alpha(ZnSe)_n \rangle / n$. In addition, a more sensitive quantity of interest is the differential mean dipole polarizability per ZnSe unit,

$$\langle \alpha \rangle_{\text{diff}} / n = \frac{\langle \alpha(ZnSe)_n \rangle}{n} - \langle \alpha(ZnSe) \rangle \qquad (2)$$

This quantity is also instrumental in characterizing the electronic density of the clusters and in

analyzing binding effects. This property has been previously used to analyze the dipole polarizability of small silicon and gallium arsenide clusters [47, 48].

The other interesting motif is the similarity function that has been introduced by Grigoryan and Springborg [49]. This function is used to quantify structural differences and similarities in a set of clusters [50–52]. Using ZnSe bond distances in various clusters, the quantity q is defined as

$$q = \left[\frac{1}{N} \sum_{i=1}^{N} (r_i - r_o)^2 \right]^{1/2} \quad (3)$$

where r_is and r_o are the ZnSe bond lengths in $(ZnSe)_n$ clusters and pure ZnSe unit, respectively. N is the total number of Zn—Se bonds in $(ZnSe)_n$ clusters under consideration. Subsequently, the similarity function, SF, can be introduced as

$$SF = \frac{1}{1 + q/r'} \quad (4)$$

in which $r' = 1$ Å to have appropriate dimensionality. In this work, this function is used to compare the similarity between clusters with different sizes.

To analyze the stability and the size-dependent physical properties of $(ZnSe)_n$ clusters, we compute the second-order difference in total energy of clusters, $\Delta_2 E(n)$, as follows:

$$\Delta_2 E(n) = E(ZnSe)_{n+1} + E(ZnSe)_{n-1} - 2E(ZnSe)_n \quad (5)$$

The chemical hardness is another property, that is, an indicator for overall stability of the system. In DFT, the chemical hardness of a species is defined to be second derivative of the ground state energy E with respect to the number of electrons N at constant external potential $v(r)$ [53],

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{v(r)} \quad (6)$$

Using the finite difference approximation, the chemical hardness is computed as [53–55]

$$\eta \approx \frac{1}{2} (IP - EA) \quad (7)$$

in which IP and EA are the vertical ionization potential and electron affinity of the cluster under study, respectively. Moreover, the global softness

is defined as the inverse of chemical hardness ($S = 1/2\eta$).

3. Computational Details

One of the major issues arising in molecular property calculations is the performance of proper quantum chemical method. It is well known that the electronic exchange and correlation effects play a primary role in determining molecular polarizabilities [56]. DFT methods, which attempt to include both exchange and correlation effects, have been widely used to be a practical and effective computational tool especially for metallic clusters and polarizability calculations. However, it is not easy to propose sufficiently quantitative arguments on the performance of DFT methods in comparison to conventional ab initio ones. In this respect, quantitative analysis of the performance of large sample of DFT approaches on the polarizability calculations have been reported by Maroulis et al. [57–60]. In this work, we used the Becke's three-parameter hybrid functional incorporating the Lee–Yang–Parr correlation functional known as B3LYP [61, 62], which has been proven to be reliable for the geometric, stabilities, and electronic properties of clusters [32, 63, 64].

On the other hand, the selection of suitable basis set is another task, which should be carried out with care to advance safely to the prediction of reliable properties. However, experimenting and testing several classes of basis sets are needed to make a judicious choice. Recently, more efforts have been devoted to analyze and construct the proper basis sets for prediction of dipole polarizability [65–67]. Here, we rely on 6-31+G(d) basis set for both zinc and selenium atoms, which has been previously shown that is sufficiently accurate to explore the molecular polarizability [68]. Each stationary point was then characterized at the same level of theory by computing the vibrational frequencies within the harmonic approximation to make sure that the resulting structures were the minima. All the geometry optimizations and frequency calculations were carried out with the GAUSSIAN 03 suite of programs [69]. Then, single-point calculations at the same level of theory were performed on positively and negatively charged clusters having the optimized geometries of the corresponding neutral clusters to calculate the vertical ionization potentials and electron affinities.

4. Results and Discussion

Previous investigations have shown that the potential energy surfaces of heteroatomic clusters are rich of stable local minima very close in energy. In such kind of potential energy surfaces, the determination of the ground state is not an easy task. Although the scope of this article is not the structural analysis of ZnSe clusters, the identification of correct ground state is important because there is strong dependence between various properties and cluster shape. Therefore, to avoid trapping in the local minima of the potential energy surface, we optimized the geometries of clusters up to $n = 10$ that have been established in the literature. However, before discussing our results for various properties of ZnSe clusters, we are going to compare our calculated energy minima of these clusters with the previous theoretical results that have been reported for ZnSe clusters. In Figure 1, we illustrate the structure of the ground states of $(ZnSe)_n$ clusters with $2 \leq n \leq 10$ optimized at the B3LYP/6-31+G(d) level. The obtained structures and geometrical parameters agree with those reported in previous works [32–34]. Almost all of the neutral clusters take on structures predicted by Euler's theorem, which provides the relationship among the number of faces, vertices, and edges, in any simple, closed polyhedron. This theorem predicts that the number of four-membered rings, N_4, is equal to 6 and the number of six-membered rings, N_6, is given by $N_6 = n - 4$ in which n is the total number of monomer units. We found the ring-like structures with planar or near-planar geometries to be the global minima for clusters as large as $n = 5$, and three-dimensional spheroid structures for larger ones, $n = 6$–10, which have the geometry predicted by Euler's theorem for closed-cage polyhedra with all atoms in a three coordinated state. In the next sections, we deal with various properties of the lowest energy structures of ZnSe clusters and follow-up the comparison between these properties with those obtained for ZnS clusters [36].

4.1. SIMILARITY FUNCTION

The comparison and classification of cluster structures are prior step to infer the principles that relate structure and function. Accordingly, in this work, the evolution of the structure with respect to the size of cluster has been studied based on the similarity function. The similarity function is calculated through Eq. (4) and is depicted in Figure 2 as a function of cluster size. Similarity function shows to what extent the clusters are similar to the pure ZnSe. In addition, similarity function can be used to compare structural similarities between clusters with different sizes. From Figure 2, it can be seen that similarity is useful quantity to delineate the structural likeness in clusters with different sizes. It is obvious that ring-like structures with $n \leq 5$ exhibit similar behavior. A sudden decrease in this quantity appears in $n = 6$, which is accompanied to its three-dimensional structure and elongation of ZnSe bond length. Clusters with the size of $n = 7$–10 which are all containing four- and six-membered rings show more similarity in their structures. To compare the structural similarities between ZnS and ZnSe clusters, the calculated similarity function for ZnS clusters [36] has been also shown in Figure 2. It is observed that both clusters exhibit a similar structural behavior for all sizes.

4.2. SECOND-ORDER DIFFERENCE IN TOTAL ENERGY OF CLUSTERS

The structural, electronic, and optical properties of ZnSe clusters are summarized in Table I. To monitor relative stability of ZnSe clusters with increasing number of ZnSe units, we calculate the second-order difference in total energy via Eq. (5). Figure 3 plots the calculated $\Delta_2 E(n)$ for ZnSe clusters. As it is well known, $\Delta_2 E(n)$ is a measure of energy gain in formation of clusters of size n by cohesion of a unit to size $n - 1$ or due to fragmentation of size $n + 1$. Peaks in this quantity represent relatively more stable clusters. Inspection of Figure 3 reveals that the values of the magic numbers for local stability maxima are found to be 3 and 6 implying that these clusters are more stable than their neighboring sizes. This result has been confirmed by a time of flight mass spectrometry study of these clusters [34]. Also, clusters with $n = 8$ and 9 are found to be more stable than $n = 7$. For the sake of comparison, the calculated second-order difference in total energy of ZnS clusters [36] has been also shown in Figure 3. Although similar trend has been observed for both types of II–VI clusters, for $n = 4$, 6, and 7, ZnSe clusters being comparatively more stable than their ZnS analogous while for other sizes, ZnS clusters have greater stability. However, the differences are not very pronounced and the
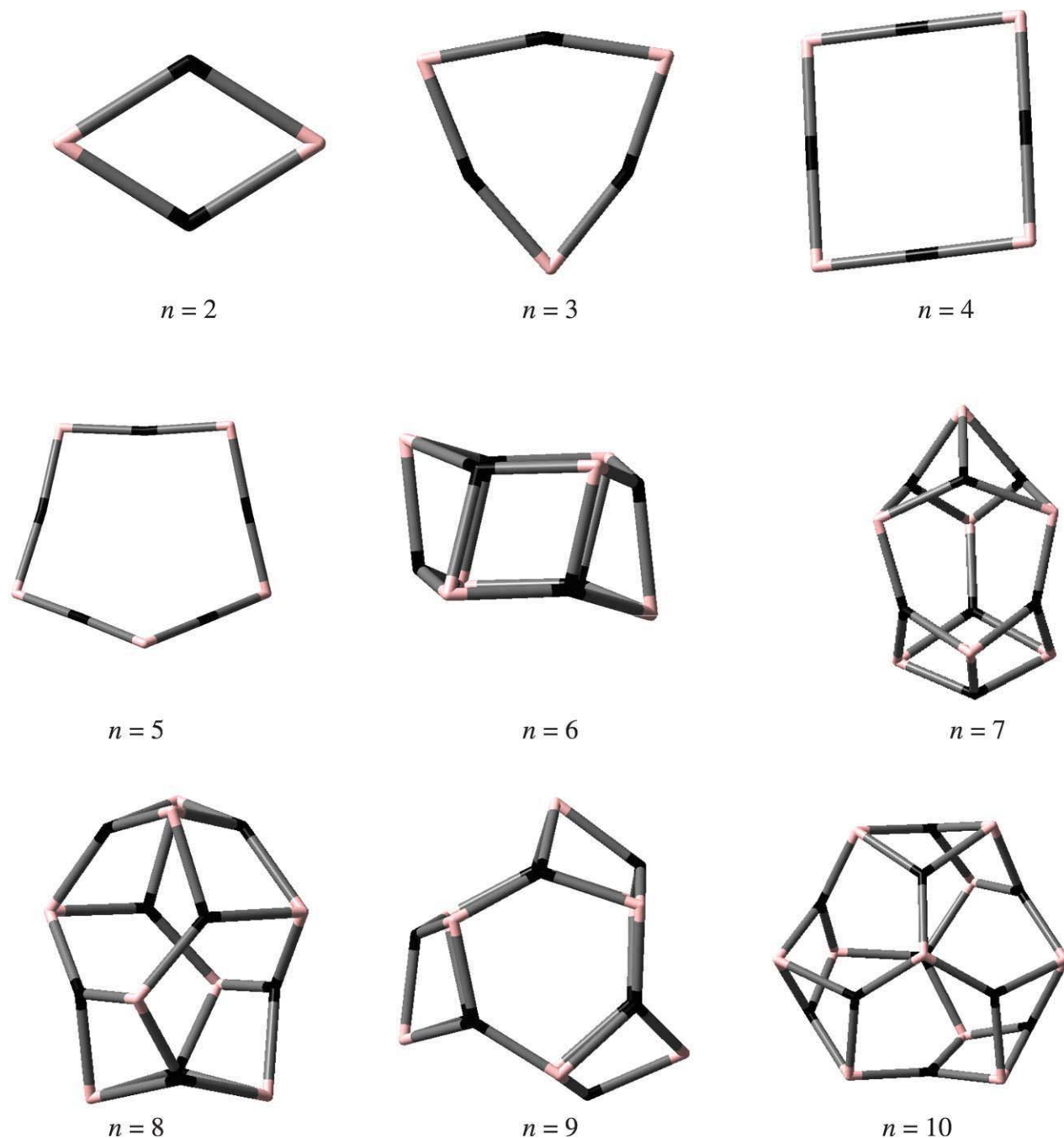
FIGURE 1. The lowest energy structures of (ZnSe)$_n$ clusters ($n = 2$–10). Black and pink vertices are zinc and selenium atoms, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

behavior of magic clusters is the same along both series.
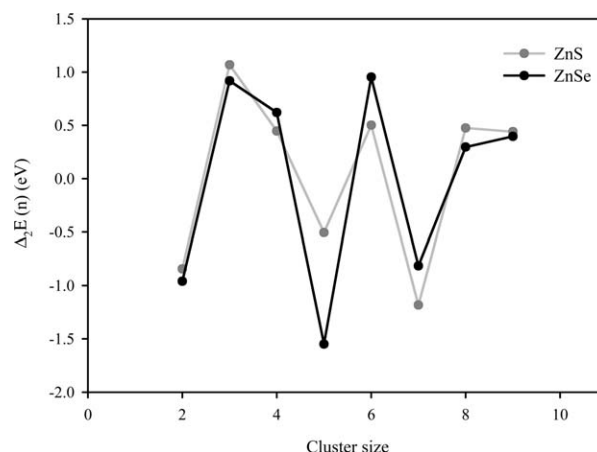
4.3. STATIC DIPOLE POLARIZABILITY

The static dipole polarizability is a quantity that is sensitive to the structural geometry and delocalization of valence electrons of clusters. To study the size and dimensionality effects, the evolution of the calculated mean polarizability per ZnSe unit has been shown in Figure 4 for ZnSe clusters. Also, in Figure 4, we compared these results with those obtained for ZnS clusters [36].
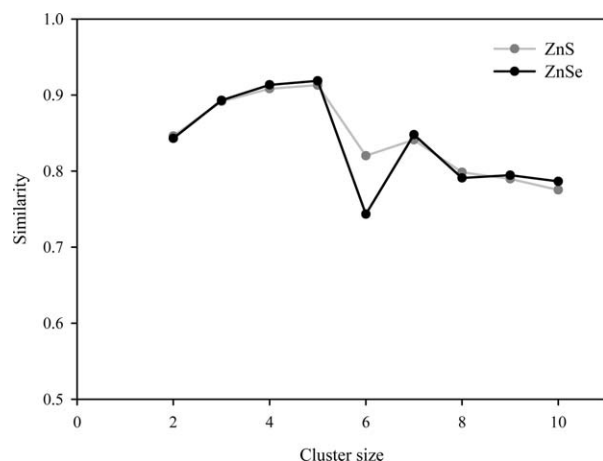
FIGURE 2. The similarity function versus the cluster size.

FIGURE 3. Second-order difference in total energy as a function of cluster size.

According to the minimum polarizability principle (MPP), the natural direction of evolution of any system is toward a state of minimum polarizability [70]. As a natural extension of this aspect, those clusters with the local minimum polarizability are more stable than the neighboring clusters. The observation of minimum at $n = 3$ and $n = 6$ is consistent with our discussion on the stability by energetic analysis for ZnSe clusters. Moreover, the cluster size dependence of the differential polarizability exhibits similar trend to mean polarizability. This quantity reflects the delocalization of the electron density in the clusters with respect to an equivalent number of noninteracting units. From Table I, it is observed that the differential polarizabilities are negative for all clusters indicating strong binding effect. Thus, both the mean and differential polarizability are correlated

with stability of ZnSe clusters. These observations are similar to those obtained for ZnS clusters [36].

4.4. CHEMICAL HARDNESS

Using the computed vertical ionization potential and electron affinity values, the chemical hardness for each cluster is calculated through Eq. (7). In Figure 5, the plot of chemical hardness versus number of ZnSe unit is shown. Chemical hardness has been established as an electronic quantity which may be used to characterize the relative stability of molecules which is associated with the concept of principle of maximum hardness (PMH), which states "molecules arrange themselves so as to be as hard as possible" [71]. According to this principle, the larger chemical hardness indicates the more stable cluster. Assuming that the PMH holds in our investigated

TABLE I

Various properties of the lowest energy structure of (ZnSe)$_n$ clusters ($n \leq 10$) computed at the B3LYP/6-31+G(d) level of theory.

| Clusters	$\Delta_2 E(n)$ (eV)	$\langle\alpha\rangle/n$ (Å³)	$\langle\alpha\rangle_{\text{diff}}/n$ (Å³)	q (Å)	IP (eV)	EA (eV)
ZnSe	—	9.408	0.000	0.000	8.465	2.352
(ZnSe)$_2$	−0.960	8.186	−1.222	0.186	8.179	1.895
(ZnSe)$_3$	0.918	7.819	−1.588	0.120	8.504	1.303
(ZnSe)$_4$	0.621	7.975	−1.432	0.095	8.145	1.143
(ZnSe)$_5$	−1.550	8.194	−1.214	0.089	8.178	1.173
(ZnSe)$_6$	0.952	7.250	−2.157	0.345	7.996	1.814
(ZnSe)$_7$	−0.815	7.269	−2.138	0.179	8.086	1.938
(ZnSe)$_8$	0.296	7.226	−2.182	0.264	7.902	1.793
(ZnSe)$_9$	0.396	7.175	−2.233	0.259	7.948	1.803
(ZnSe)$_{10}$	—	7.221	−2.187	0.272	7.787	1.822
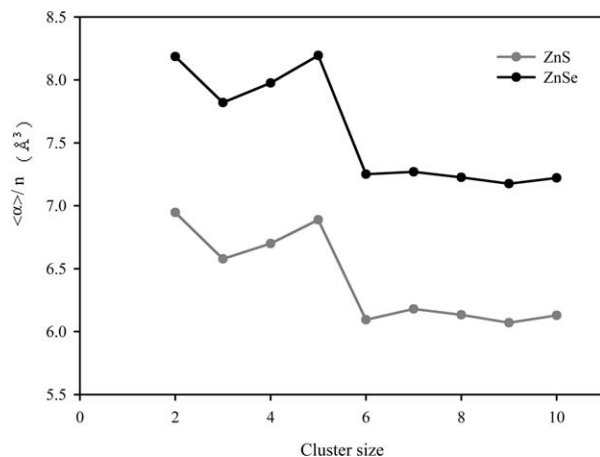
FIGURE 4. The mean static dipole polarizability as a function of cluster size.

systems, the hardness is expected to present a behavior with a local maximum at the magic clusters. Figure 5 clearly shows that the magic cluster $n = 3$ is harder than the neighboring clusters. In the case of $(ZnSe)_6$, despite this cluster is harder than $(ZnSe)_7$, its hardness is significantly less than $(ZnSe)_5$. This behavior can be attributed to the great structural difference between $(ZnSe)_6$ and $(ZnSe)_5$ clusters. As it was mentioned among $n \leq 10$ clusters, $(ZnSe)_6$ is the first one having three-dimensional ground state geometry and its hardness cannot be compared with ring-like structure of $(ZnSe)_5$. Figure 5 shows that there is remarkable similarity in the computed pattern of hardness for ZnSe and ZnS clusters [36]. Thus, the hardness can be used as a useful parameter to establish the stability of clusters with almost similar structures.
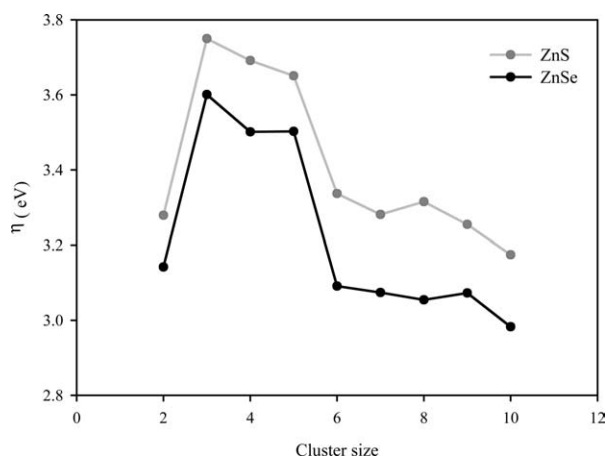
**FIGURE 5.** Chemical hardness as a function of cluster size.
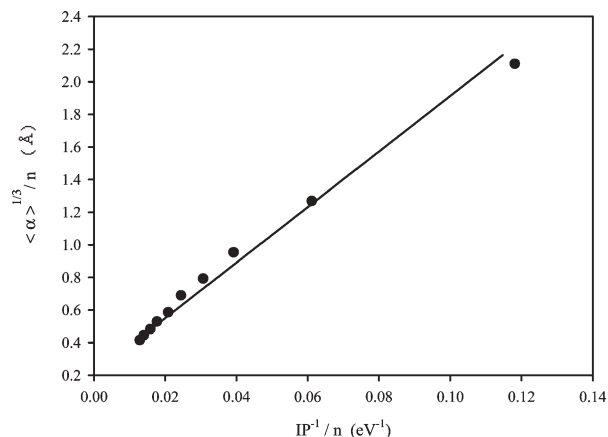
FIGURE 6. The correlation between the cube root of mean polarizabilities per ZnSe unit and the inverse of the vertical ionization potential for $(ZnSe)_n$ clusters ($n \leq 10$).

4.5. CORRELATIONS OF THE STATIC DIPOLE POLARIZABILITY AND SOME ELECTRONIC PROPERTIES

The static dipole polarizability is a measure of the distortion of the electronic density and the information about the response of the system under the effect of an external static electric field. However, the ionization potential reveals how tightly an electron is bound within the nuclear attractive field of the systems. Dmitrieva and Plindov [72] were the first to obtain a relationship between the polarizability and the ionization potential for atomic systems using a statistical model. In recent works, a correlation between the cube root of polarizability and the inverse of the ionization potential was found for atomic systems such as gold, sodium, lithium, and yttrium clusters [73–75] and also for ZnS as molecular cluster [36]. In this work, we have checked the validity of this correlation for ZnSe clusters. Figure 6 displays that the cube root of mean polarizability per ZnSe unit increases linearly with increasing the inverse of vertical ionization potential per ZnSe unit. The corresponding linear correlation coefficient is found to be 0.993, indicating the reliability of the correlation. This is an important observation that can provide a way to calculate the polarizability of the larger clusters from the values of their ionization potentials.

Finally, let us analyze the relationship between the global softness and polarizability in these clusters. Although the global softness parameter is directly related to the polarizability of the systems, this relation is reported to be valid for
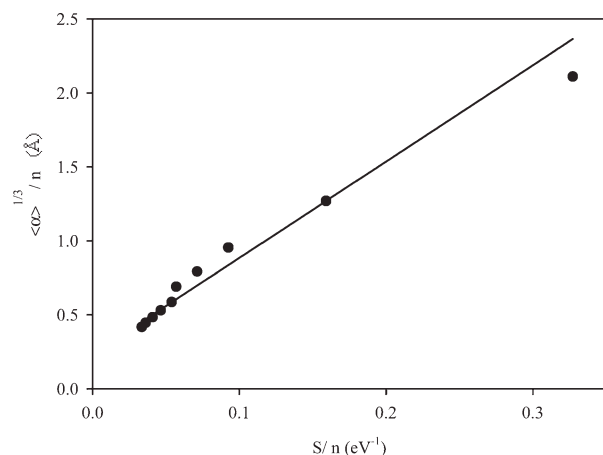
FIGURE 7. The correlation between the cube root of mean polarizabilities per ZnSe unit and the global softness for (ZnSe)$_n$ clusters ($n \leq 10$).

atomic systems [74]. Here, we have shown that this relationship can be validated for the ZnSe clusters as well. It is evident from Figure 7, where the cube root of mean polarizability is plotted against softness, that there exists almost linear relation between these two quantities for ZnSe clusters. Despite the linear correlation of 0.980 does not show an excellent fit, a preliminary estimation of the polarizability of the large size clusters can also be achieved from the value of their global softness.

5. Summary

Various properties for stoichiometric (ZnSe)$_n$ clusters ($n \leq 10$) as a function of cluster size are investigated systematically at the B3LYP level of theory. The similarity function has been used to investigate the extent that the clusters are similar to the pure ZnSe. Although ring-like structures with $n \leq 5$ exhibit similar structural behavior, a distinct mismatch has been found for $n = 6$. In addition, clusters with $7 \leq n \leq 10$ which are all containing four- and six-membered rings have structures that are more similar to each other. The size evolution of reactivity descriptors such as static dipole polarizability and chemical hardness has been determined for ZnSe clusters. As measured by second-order difference in total energy among small studied clusters, (ZnSe)$_3$ and (ZnSe)$_6$ show enhanced stability. The MPP and PMH can be also used to characterize the stability of these two types of clusters. The most important new

feature of this work, however, lies in the observation that the size-dependent polarizability and ionization potential of the ZnSe clusters strongly correlate with each other. We have also found a rather good linear correlation between the polarizability and global softness of the clusters. These results will have some important implications in calculating the polarizability of these clusters in terms of the ionization potentials and softness. By comparing the obtained results for ZnSe clusters to what we previously found for ZnS clusters, we observed similar pattern in both structural and electronic properties for these two types of II–VI nanoclusters.

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