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# Computational Study for the Electronic and Molecular Properties of $Zn_3Se_3$ Clusters

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Low affinity energy thresholds were precisely tailored into the $Zn_3Se_3$ cluster's molecular geometry configurations. The structu ral and electronic characteristics of the $Zn_3Se_3$ composite were examined using the 6-113G (d, p) basis set for density functional theory calculations (DFT/B3LYP). Comprehensive vibrational mode frequencies were methodically examined using potential energy distribution as a basis for analysis. The energy band gap ($E_{\boldsymbol{g}}$) for the $Zn_3Se_3$ structured was computed and plotted HOMO and LUMO, or high occupied and low unoccupied molecular orbitals, are frontier values. The result is the value of $E_{\boldsymbol{g}}$ (0.0383) eV. The molecular electrostatic potential as well as surface and contour diagram of $Zn_3S_3$ were determined, along with electronic properties of the stated structures. These include IP, EA, Ef, $E_{\boldsymbol{g}}$, $Cp$, $\chi$, $\eta$, S, and $\omega$.

## 1. INTRODUCTION

Zinc selenide (ZnSe) is a light-yellow binary compound (II–VI) semiconductor that has a wide band gap (2.7 eV). The low resistivity, and great photosensitivity are just a few of the extremely desirable properties of this semiconducting material. There are two crystalline forms of zinc selenium: wurtzite (a hexagonal form) and zinc blende (a cubic form), with the cubic phase being thought to be stable. The electron affinity of ZnSe is 4.09 eV. ZnSe is often manufactured as an-type semiconductor, like the majority of II-VI group 7 semiconductors, although producing a p-type is challenging [1].

Owing to its large and direct band gap, it can be used as both emitters and detectors in optoelectronic devices. It is beneficial for optical parts of windows with high strength lasers. Because of its broad transmission wavelength range of 600 nm to 2000 nm, it is also employed as an infrared optical material. It is frequently utilized as a transmission window in ATR prisms, night vision applications, and infrared spectroscopy. Electronic structure can be found in chemical and physical systems through the use of Density Functional Theory (DFT), a quantum mechanical modeling tool [2]. Additionally, ZnSe can be employed in high resolution thermal imaging systems to rectify color distortion that is frequently present in other lenses that are part of the system. To validate the results of experiments, DFT has shown to be an invaluable research tool [3].

Chemical interactions can be studied at better scales recognitions to combinatorial phenomena, in especially the low cost (DFT) technique, which theoretically gives material design predictions through geometrical structures [4].

Furthermore, when theoretical research is “confirmed" for a particular experiment, the more quantitative predictions of events the more broadly accepted the entire theory which is made and validated by experiment [5]. However, a number of theoretical investigations have been cited and considered in real-world applications as gas sensors [6].

Recently, the ZnSe molecules' electrical and structural properties as nanotubes with varying amounts of ZnSe atoms have been studied using DFT theory [7, 8].

This paper demonstrates that the ground state (GS) and other characteristics of a many-electron system may be determined using DFT.

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## 2. COMPUTATIONAL DETAILS

Density functional theory (DFT) has been applied to many-electron systems to study their electronic structure and behavior, and it has influenced the quantum mechanical approach. The electron density distribution is understood in physics and chemical sciences through the application of functional analysis. DFT is by far the most popular and adaptable computational method chemistry and physics. It has also demonstrated effectiveness ins simulating the ground state properties of materials. Utilizing DFT theory and a basis set comprising 6-311G**, this study employs a modified Lee-Yang-Parr (Becke, three-parameters, Lee-Parr) strategy. The heavy-atom polarization set d-function is represented by the first asterisk above basis G. But the second symbol, which sometimes needs to be expressed as 6-311G (d, p), shows the polarization of the hydrogen atoms' p-functions [9, 10]. These formulas and theories were all part of Gaussian 09 and Gaussian View 6.0 [11]. Precise molecular geometries optimization was necessary to provide reliable results and reduce the thresholds for convergence. The frequency of typical vibrations were also determined the self-consistent field (SCF) that can solve equation, which validated the decreased energy at geometric optimization. Three Zn and three Se atoms make up the chemical structure of the $Zn_3Se_3$ cluster, as illustrated in Figure (1).

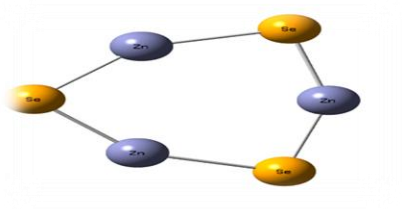


**Figure 1.** Using basis set 6-311G**, the DFT approach optimized the structures of ($Zn_3Se_3$).

Calculations were performed on the compounds' ionization potential (IP), which is the energy required to break the structural unit of the weakest electron attachment to the nucleus, Fermi level energy (Ef), and energy of bandgap ($E\boldsymbol{g}$). Electron energy is the energy generated when an electron is introduced to a gaseous atom, affinity (EA), and it may be calculated after determining the following equations to find the Lowest Unoccupied Molecular Orbital (LUMO) and Highest Occupied Molecular Orbital (HOMO) energies. [12, 13].

Electron extraction is more difficult at higher ionization energies.

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$$E\boldsymbol{g} = ELUMO - EHOMO \quad (1)$$

$$IP = - EHOMO \quad (2)$$

$$EA = - ELUMO \quad (3)$$

$$Ef = (EHOM + ELUMO) / 2 \quad (4)$$

Moreover, the identities of the quantum molecules are ($Cp$, $\chi$, $\eta$, S, and $\omega$). Typically, these descriptors look like this: the following metrics are provided by [14, 15]: electronegativity ($\chi$), which measures an atom's capacity to draw electrons into chemical bonds; Softness (s), global hardness ($\eta$), and electrophilicity index ($\omega$). Bonds in a semiconductor, the energy that can be absorbed or released due to a change in the number of particles is called the ferry energy when the electron system is at absolute zero temperature. This energy is also known as the chemical potential (Eq.).

$$Cp = -\chi \quad (5)$$

$$\chi = IP+EA / 2 \quad (6)$$

$$\eta = IP-EA /2 \quad (7)$$

$$S = 1/\eta \quad (9)$$

$$\omega = - \chi^2 / 2\eta \quad (10)$$

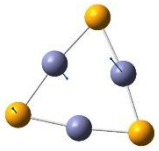
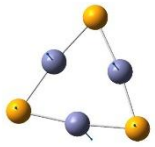
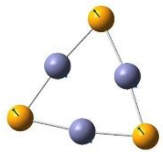
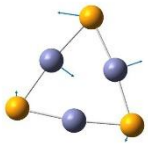
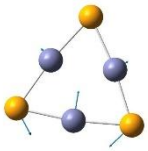
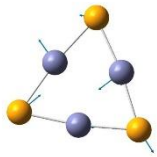
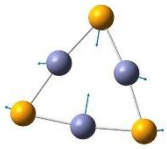
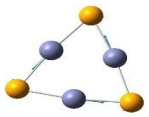
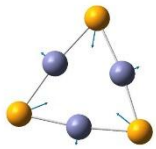
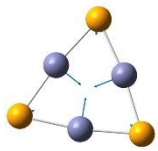
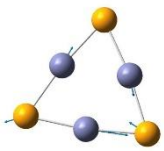
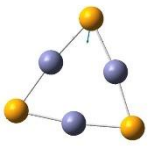
## 3. RESULTS and DISCUSSION

### 3.1 Vibrational Frequencies & FTIR spectra

The number of normal vibration modes of non-linear molecules can be computed using the equation ($3N^{-6}$), where N is the number of atoms. As a result, the six-atom $Zn_3Se_3$ molecule, twelve vibrational modes were found from the pattern's lowest frequency to its highest mode. These frequencies are shown in Table 1. In the range (290.94_291.62) $cm^{-1}$, the highest frequency modes are (11and 12).

Conversely, the DFT-B3LYP levels with the 6-311G** basis set were used to compute the IR spectra of the investigated structure in the region of 0–4000 $cm^{-1}$. Figure 2 depicts the $Zn_3Se_3$ FT-IR spectrum.

**TABLE 1.** The frequency range of $Zn_3Se_3$ 's typical vibrational modes, in order of lowest to highest

| No. Mode | Frequency/ $cm^{-1}$ | Structure |
|---|---|---|
| MODE 1 | 61.27 |  |
| MODE2 | 61.35 |  |
| MODE3 | 85.42 |  |
| MODE4 | 85.42 |  |
| MODE5 | 93.55 |  |
| MODE6 | 152.67 |  |
| MODE7 | 169.10 |  |
| MODE8 | 169.64 |  |
| MODE9 | 174.18 |  |
| MODE10 | 271.59 |  |
| MODE11 | 290.94 |  |
| MODE12 | 291.62 |  |

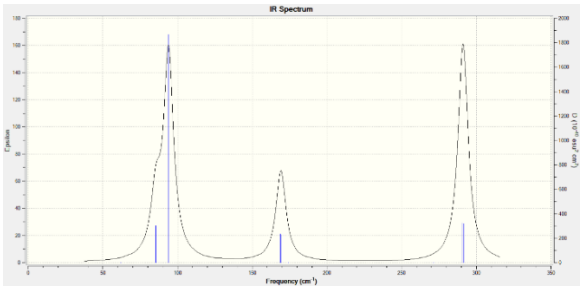



**Figure 2.** The FTIR spectrum for Zn3Se3

Additional peaks with signs at (1800, 800, and 1800) cm-1 correspond to the $Zn_3Se_3$ (DFT), ZnSe, and they are ascribed to the Zn-Se bond's stretching vibrations [16, 17].

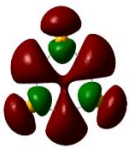
### 3.2 Electronic Properties

A significant amount of complexity has been added to the model known as molecular orbital theory (MOTs), which addresses many different facets of orbital bonding, energy, chemical processes, and characterization. The highest occupied molecular orbitals (HOMOs), which have the highest energy, are those that have electrons occupying them. The second is known as the lowest energy unoccupied molecular orbital, or LUMO that is devoid of electrons. The DFT method with the 6-113G** basis set was used to calculate the values of the molecular orbitals for Zn3Se3 . The (1–10) Equations were used to a useful index of the interaction system which is the HOMO, LUMO, and HOMO-LUMO (E$\boldsymbol{g}$). It can be used to calculate the electronic characteristics IP, EA, Ef, Eg, $Cp$, χ, η, S, and ω. $Zn_3Se_3$ 's electrical characteristics are shown in **Table 2**.

**Figure 2** demonstrates the $Zn_3Se_3$ cluster's electronic properties and makes the HOMO and LUMO MOs for the molecules in question be clear. The energy gap (E$\boldsymbol{g}$) rises as more polymer is added, indicating that the $Zn_3Se_3$ particles are affected, strongly supporting the idea of quantum confinement, and the larger value for the band gap (the smallest nano particle diameter) [18].

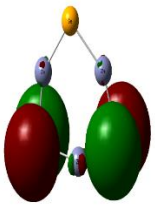
**Table 2.** Demonstrates the electronic properties of $Zn_3Se_3$

| Properties | Zn3Se3 (DFT) |
|---|---|
| $E_{HOMO}$ | - 0.23784 |
| $E_{LUMO}$ | -0.19951 |
| *Ef* / eV | - 0.218675 |
| *Eg*/ eV | 0.03833 |
| *IP* / eV | 0.23784 |
| *EA* / eV | 0.19951 |
| *Cp* / eV | - 0.21867 |
| χ / eV | 0.21867 |
| η / eV | 0.01917 |
| *S* / (eV)$^{-1}$ | 52.164 |
| *ω* / ev | -1.247 |



**LUMO**

Eg= 0.0383 E$\boldsymbol{g}$ = ELUMO – EHOMO



**HOMO**

**Figure 2.** Frontier molecular Zn3Se3 features: E$\boldsymbol{g}$ and HOMO/LUMO orbitals

### 3.3 Molecular Electrostatic Potential

In order to assess the relationships and non-covalent interactions between molecules at a distance from one another and to look into repulsive or attractive interactions, density of the electron with charge, the molecular electrostatic potential (MEP) diagram, B3LYP calculations using basis set 6-311G(d,p), and nonlocalized dispersion among the structure's reactions were used [19]. Figure provided a description of these interaction zones for the molecule to depict three areas of contacts based on the electron density function. Blue zones illustrate the nature of hydrogen bonding. Green zones denote the Van der Waals bonding (VdW), while red areas represent repulsive interactions [20]. Moreover, the benefit of the molecular electrostatic potential scheme is a helpful instrument to look into how responsive the systems under study are to either nucleophilic or electrophilic assaults, depending on the charge distribution. The color-coded system for two regions is represented by the colored line in Fig. (4)'s upper border: the red and blue regions between -$8.065\times10^{-2}$ and $8.065\times10^{-2}$, and the $Zn_3Se_3$ cluster's range from -4.036×10-4 to $4.036\times10^{-4}$. The red-colored negative charge concentrations indicate the acceptor of an H-bonding molecule. In contrast, the second zone shows the donor of the H-bonding's positive charge densities in the blue ruler [21].

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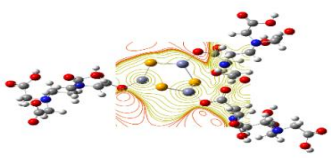
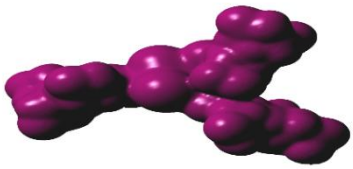


**2D**



**3D**

**Figure 4.** Charge MEP is the $Zn_3Se_3$ surface surfaces diagram; MEP contour surface of $Zn_3Se_3$; densities distribution as color-coded ruler in top adage (red color for negative charge and blue for positive charge).

The top surface, however, will be the only one visible if all $Zn_3Se_3$ Plots of surfaces are made using every isosurface value. To view the surfaces of all the molecules under study, just draw the contours of each surface surrounding the molecule, as
the $Zn_3Se_3$ cluster illustrates in **Figure 4.**

## 4. CONCLUSION

Here is a bullet-point summary of the information:

-DFT Calculations: Density Functional Theory (DFT) calculations were performed using the 6-311G(d, p) basis set and the B3LYP hybrid functional.

- $Zn_3Se_3$ Cluster: structural and electronic properties of a $Zn_3Se_3$ cluster (three Zn and three Se atoms) were theoretically calculated.

- Comparison: the same DFT calculations were performed for another similar molecule for comparison. Spectral lines such as FTIR spectra were examined.

- Spectral Agreement: The active peaks in the theoretical and experimental FTIR spectra aligned well, confirming the accuracy of the calculations.

- Vibrational Modes: Twelve vibrational modes were observed for the $Zn_3Se_3$ molecule, within a frequency range of 0 $cm^{-1}$.

- Energy Gap (Eg): The HOMO-LUMO energy gap (Eg) was calculated. The energy gap increased from 4.031 eV to 4.459 eV after adding a polymer to the ZnSe cluster.

- Quantum Confinement: the findings support the quantum confinement effect, demonstrated by a higher band gap value and minimum nanoparticle diameter in line with experimental results.

- MEP Analysis: Molecular electrostatic potential (MEP), surface and contour diagrams, and estimated charge densities were calculated, showing nucleophilic and electrophilic attack points.

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## Arabic Abstract

تم تصميم عتبات طاقة الألفة المنخفضة بدقة في التكوينات الهندسية الجزيئية لمجموعة $Zn_3Se_3$ . تم فحص الخصائص الهيكلية والإلكترونية لمركب $Zn_3Se_3$ باستخدام نظرية الكثافة الوظيفية (حسابات DFT/B3LYP باستخدام مجموعة الأساس G (d, p113-6). وتم فحص ترددات الوضع الاهتزازي الشامل بشكل منهجي باستخدام توزيع الطاقة المحتمل كأساس للتحليل. تم حساب فجوة نطاق الطاقة ($E\boldsymbol{g}$) لمركب $Zn_3Se_3$ ورسمها باستخدام المدارات الجزيئية العليا المشغولة والمنخفضة غير المشغولة (HOMO&LUMO). بالإضافة إلى ذلك، تم تحديد الإمكانات الكهروستاتيكية الجزيئية على السطح وتم تحديد مخطط كفاف لـ $Zn_3S_3$، إلى جانب الخصائص الإلكترونية. من الهياكل المذكورة، بما في ذلك جهد التأين (IP) والألفة الإلكترونية (EA) وعامل الإلكترون (Ef) والسعة الحرارية المولارية ($Cp$) والكهرسلبية ($\chi$) والصلابة العامة ($\eta$) والنعومة (S) ومؤشر الكهروفيلية ($\omega$).