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## A quantum chemical exploration on structural stability and electronic properties of CdZnO nanostructures

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### ABSTRACT

The realistic CdZnO nanostructures such as CdZnO ring, CdZnO sheet, CdZnO cube and CdZnO cage are optimized and simulated successfully using B3LYP/LanL2DZ basis set. Structural stability of CdZnO nanostructures are studied in term of calculated energy, chemical hardness, chemical potential and vibrational studies. Using HOMO-LUMO gap, ionization potential and electron affinity, electronic properties of CdZnO are discussed. CdZnO nanostructures point symmetry group and dipole moment are also reported. The current work explores the details about optimized CdZnO nanostructures which are most applicable to window material, solar cells and other optoelectronic devices.

**Keywords:** CdZnO, nanostructures, chemical potential, HOMO-LUMO, chemical hardness

### INTRODUCTION

Zinc oxide (ZnO) and Cadmium oxide (CdO) are the most suitable materials for window material and solar cells buffer layers application due to their marvelous transparency in the range of visible region [1, 2]. The resistivity of CdO is low with band-gap value of 2.29 – 2.73 eV and it belongs to n-type semiconductor. In contrast ZnO has high resistivity with band-gap of 3.3 eV. Therefore, homogeneous alloying of both materials compromise in between electrical and optical properties of intermediate pure ZnO and CdO which is much suitable for application in solar cells buffer layers.

ZnO and CdO have much attracted in both electronic and optoelectronic device applications [3-8]. ZnO plays a vital role, since due to its owing superior electrical properties and high transparency, particularly in thin film transistors adopting best current ratios and high mobility in the range of  $10^6$ – $10^7$  and 5–100  $\text{cm}^2/\text{Vs}$  respectively [9-17]. Ternary cadmium zinc oxide (CdZnO) semiconductor find potential application in high frequency optoelectronic devices and in laser diodes & light emitting diodes due to their band gap around 2.3 eV and 3.37 eV for CdO and ZnO respectively [18-20].

Incorporation of cadmium with ZnO prove that it results in narrow band gap, since the band-gap value is low for CdO in the order of 2.3 eV compared to ZnO with 3.3 eV. Resistivity of CdZnO is decreased with increasing cadmium concentration. Maiti et al. reported optical and structural properties of CdZnO [21]. Synthesis of CdZnO can be carried out by many methods such as pulsed laser deposition (PLD) [22-24], thermal evaporation [25,26], sol-gel method [27], r.f. sputtering [28] and MOVPE [29]. The inspiration behind the work is to fine-tune the structural stability linked with electronic properties of CdZnO nanostructures which enhances electronic

conductivity leading to many electronics and optoelectronics. In the present work, density functional theory (DFT) is adopted to study CdZnO nanostructures [30].

### MATERIALS AND METHODS

The ternary compound CdZnO nanostructures are optimized successfully by NWChem package [31] combined with Becke's three-parameter hybrid function method (B3LYP) and LanL2DZ basis set [32-36]. Atomic number of Cadmium, Zinc and Oxygen are forty eight, thirty and eight respectively. LanL2DZ gives precise output with pseudo potential approximation [37]. Structural stability and electronic properties of nanostructures can be calculated by the method of DFT. In this present work four different CdZnO nanostructures are simulated and optimized by NWChem package.

### RESULTS AND DISCUSSION

The present work mainly concentrates on calculated energy, ionization potential (IP), chemical potential, electron affinity (EA), HOMO-LUMO gap, dipole moment (DM) and vibrational studies of CdZnO nanostructures. The four different possible CdZnO nanostructures such as CdZnO ring, CdZnO sheet, CdZnO cube and CdZnO cage are constructed & studied and are shown in Figure 1(a) – 1(d). CdZnO ring structure consists of two Cd atoms, two Zn atoms and two O atoms to form ring like structure. Combination of each three Cd, Zn and O atoms forms CdZnO sheet nanostructures. The remaining CdZnO cube and cage has four Cd, Zn and O atoms each to form cube and cage like nanostructures respectively.

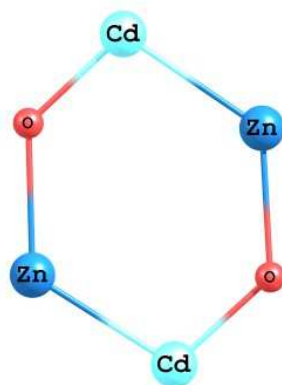


Figure. 1(a). CdZnO ring

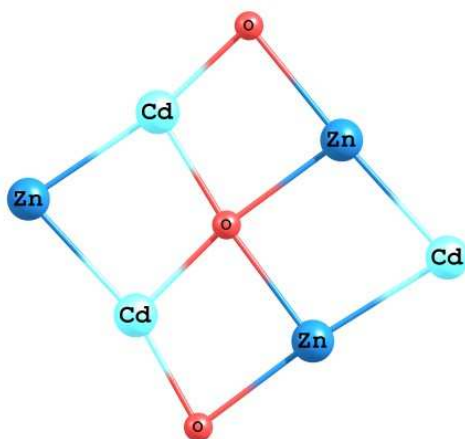


Figure. 1(b). CdZnO sheet

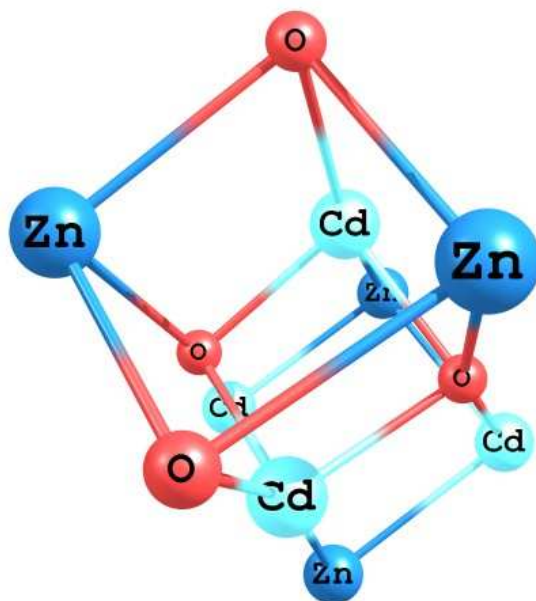


Figure. 1(c). CdZnO cube

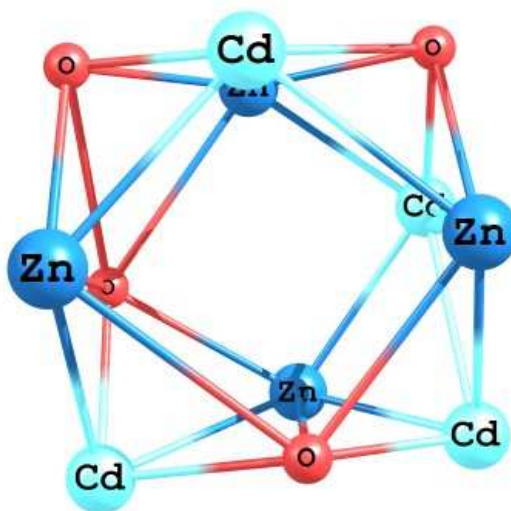


Figure. 1(d). CdZnO cage

Table 1. Energy, point symmetry and dipole moment of CdZnO nanostructures

Nanostructures	Energy(Hartrees)	Dipole moment (Debye)	Point symmetry
CdZnO ring	-377.68	0.21	C <sub>s</sub>
CdZnO sheet	-566.55	1.8	C <sub>s</sub>
CdZnO cube	-755.51	4.46	C <sub>1</sub>
CdZnO cage	-755.34	5.28	C <sub>1</sub>

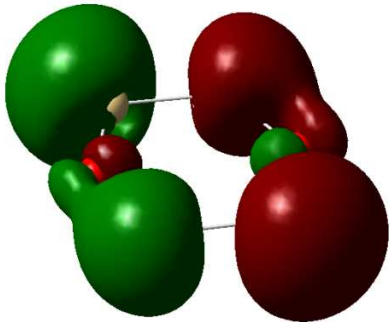
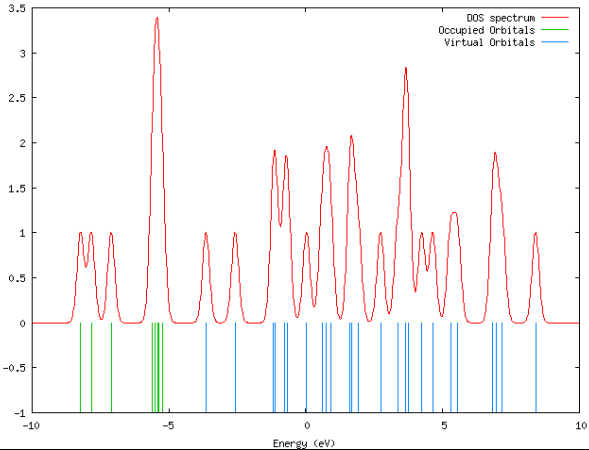
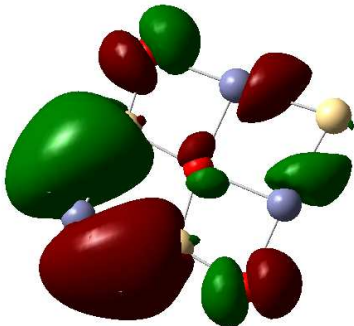
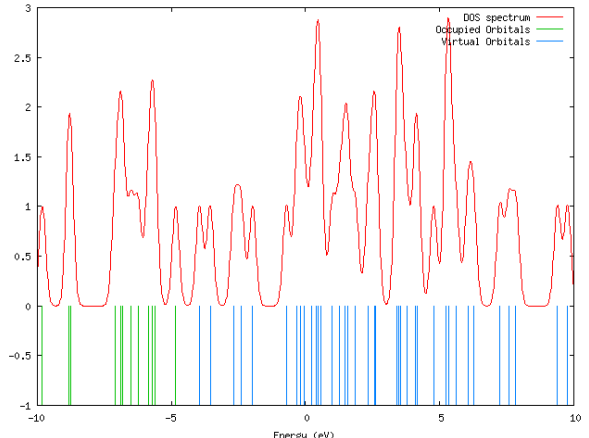
The calculated energy of all the four different CdZnO is tabulated in Table 1. Since the stability of optimized CdZnO nanostructures can be described by calculated energy. The energy of CdZnO has found to be -377.68 Hartrees. The calculated energy of CdZnO sheet, cube and cage are found to be -566.55, -755.51 and -755.34 Hartrees respectively. From the result the stability of CdZnO nanostructures gets increased due to addition of more

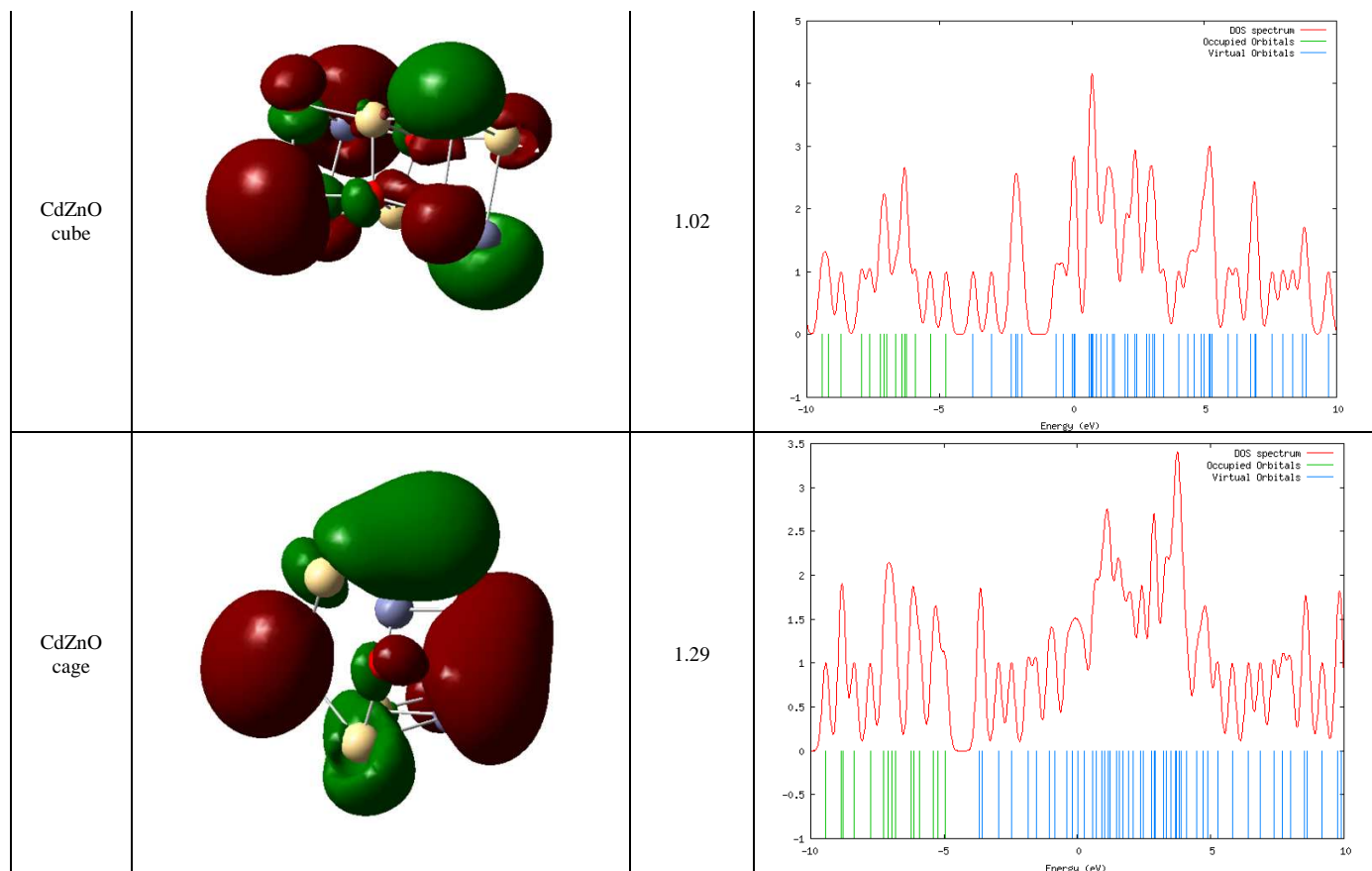
number of atoms in nanostructure as shown in Table 1. Dipole moment (DP) of CdZnO nanostructures are also reported in Table 1. DP of CdZnO ring, sheet, cube and cage are 0.21, 1.8, 4.46 and 5.28 Debye respectively. CdZnO ring and sheet has low DP value, since the atoms are tightly bounded and charges are evenly distributed in these nanostructures. Point symmetry group of all the discussed nanostructures shows asymmetry which is either  $C_s$  or  $C_1$ .

#### HOMO-LUMO gap of CdZnO nanostructures

Electronic properties of CdZnO can be delivered by lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) [38,39]. The energy gap of optimized CdZnO nanostructures has low value in the range 0.88 – 1.58 eV. These CdZnO nanostructures show a narrow gap semiconducting property. Due to this narrow energy gap the electrons in HOMO level can easily move to LUMO level by applying small external energy. The localization of charge in CdZnO nanostructures are more in LUMO level rather than in HOMO level which is visualized by density of states (DOS) spectrum as shown in Table 2.

Table 2. HOMO-LUMO Gap of CdZnO nanostructures

Nano Structures	HOMO – LUMO Visualization	Eg(eV)	HOMO, LUMO and DOS Spectrum
CdZnO ring		1.58	
CdZnO sheet		0.88	



### Ionization potential, Electron affinity, chemical potential and chemical hardness of CdZnTe nanostructures

Electron affinity (EA) and Ionization potential (IP) are the key parameter to deliver the electronic properties of CdZnO nanostructures as shown in Figure 2. EA and IP are mainly related to energy released due to adding of electron and energy required for removing the electron from nanostructures respectively [40]. EA values of CdZnO nanostructures are observed to be low in the range of 3.65 – 3.96 eV followed by IP values of 4.74 – 5.23 eV which is highly applicable to window material and solar cells buffer layer applications. The stability of CdZnO nanostructures can also be defined by chemical hardness (CH) and chemical potential (CP).  $\mu = -(IP+EA)/2$  and  $\eta = (IP-EA)/2$  are the significant formula to predict CP and CH respectively. Almost same CP values of around -4.2 to -4.4 eV are observed for all the CdZnO nanostructures. Meanwhile not much difference is observed in CH as shown in the Table 3.

Table 3. Chemical potential and Chemical hardness of CdZnO nanostructures

Nano Structures	Chemical potential (eV)	Chemical hardness (eV)
CdZnO ring	-4.44	0.79
CdZnO sheet	-4.40	0.44
CdZnO cube	-4.23	0.51
CdZnO cage	-4.325	0.64

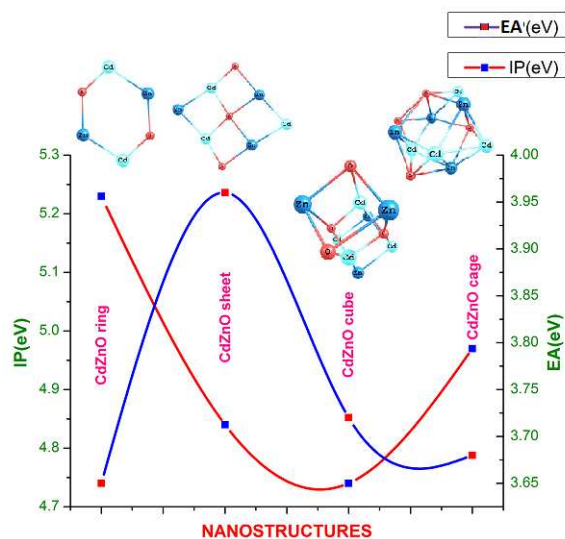


Figure. 2. IP and EA of CdZnO nanostructures

### Vibrational Studies of CdZnO nanostructures

The stability of CdZnO nanostructures can be explained by vibrational studies. CdZnO nanostructures are stable if and only if the imaginary frequency do not exist [41]. Vibrational frequency and IR intensity of CdZnTe are reported in Table 4. CdZnO ring has the vibrational frequency at 433.98 and 146.51  $\text{cm}^{-1}$  with IR intensity 151.13 and 12.14  $\text{km/mole}$  respectively. CdZnO sheet has vibrational frequency at 207.21 and 328.89  $\text{cm}^{-1}$  with corresponding IR intensity of 37.56 and 17.58  $\text{km/mole}$  respectively. The prominent IR intensity of CdZnO cube has 27.48 and 11.02  $\text{km/mole}$  with vibration frequency of 106.73 and 357.85  $\text{cm}^{-1}$  respectively followed by CdZnO cage vibrational frequency noticed at 460.24 and 173.08  $\text{cm}^{-1}$  along with IR intensity of 24.68 and 24.51  $\text{km/mole}$  respectively. Molecular stretching mode has been observed for all the optimized CdZnO nanostructures and the vibrational spectrum are shown in Figure 3(a) – 3(d).

Table 4. Vibrational Frequency and IR Intensity of CdZnO nanostructures

Nano Structures	Frequency ( $\text{cm}^{-1}$ )		IR intensity ( $\text{km/mole}$ )	
CdZnO ring	433.98	146.51	151.13	12.14
CdZnO sheet	207.21	328.89	37.56	17.58
CdZnO cube	106.73	357.85	27.48	11.02
CdZnO cage	460.24	173.08	24.68	24.51

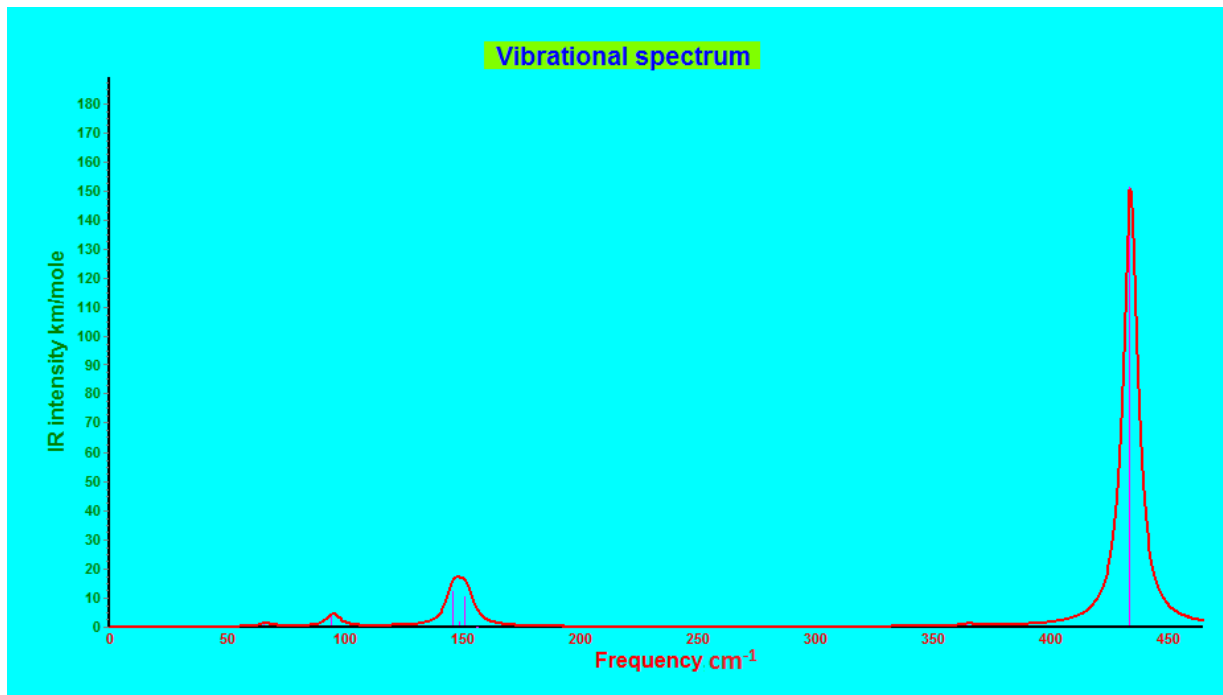


Figure 3(a). CdZnO ring

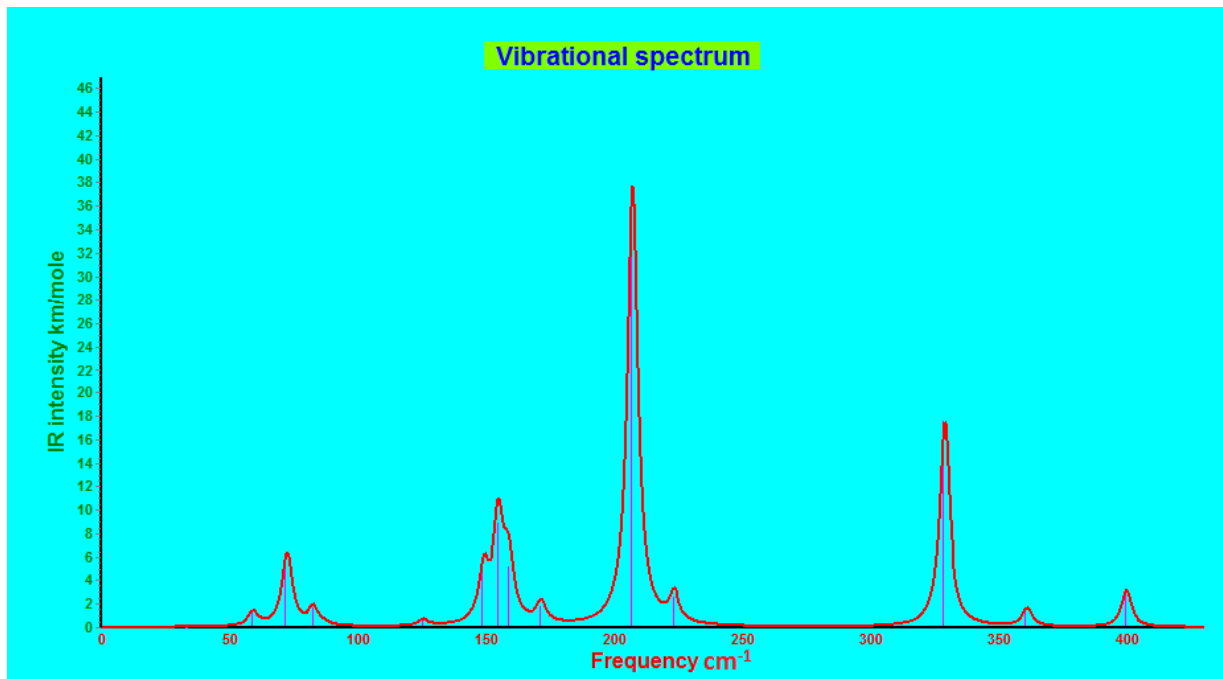


Figure 3(b). CdZnO sheet

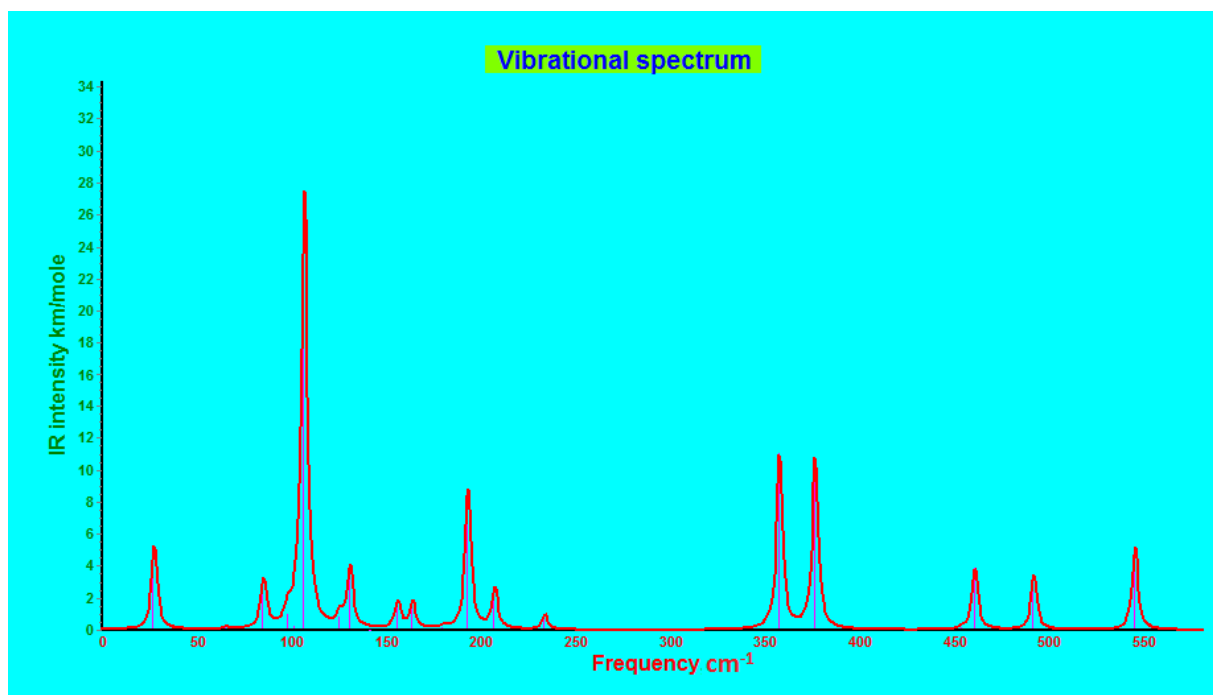


Figure 3(c). CdZnO cube

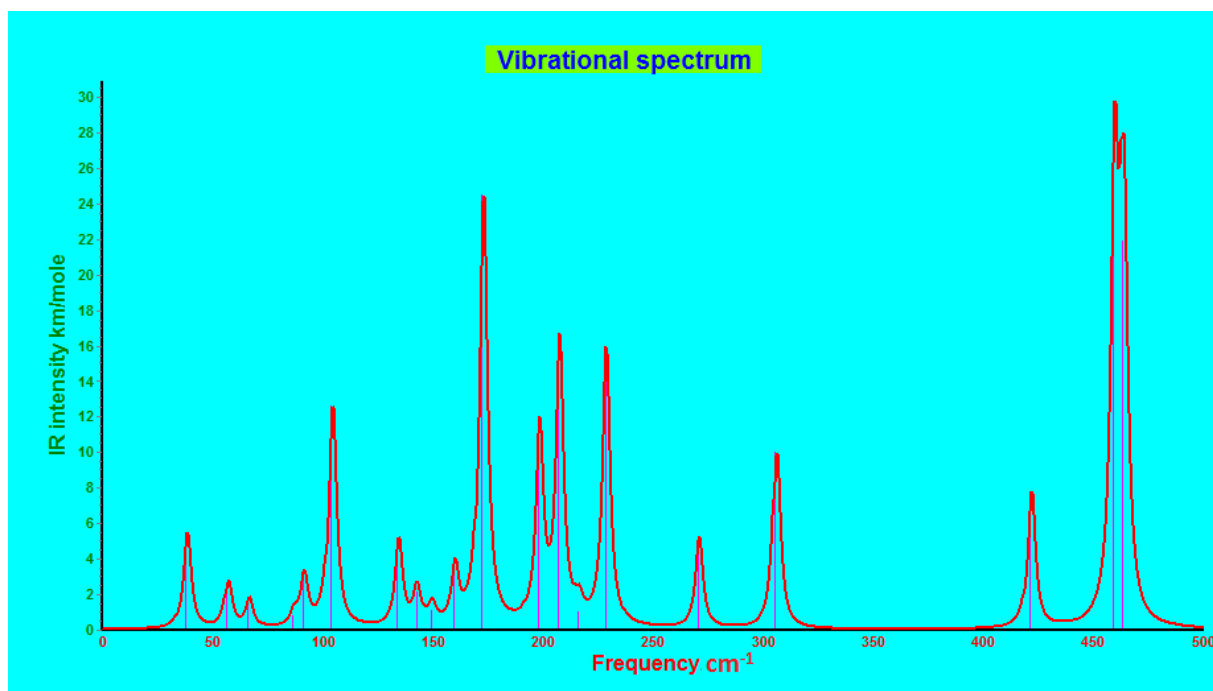


Figure 3(d). CdZnO cage

### CONCLUSION

In conclusion utilizing DFT method, CdZnO nanostructures are optimized and simulated precisely by using suitable basis set B3LYP/LanL2DZ. The stability of CdZnO nanostructures are scrutinized by calculated energy, chemical potential, chemical hardness and vibration studies. With the help of HOMO – LUMO gap, ionization potential and



electron affinity electronic properties of CdZnO are discussed. Dipole moment and point symmetry group of CdZnTe are also reported. The information provided in the report can be used to tailor proper CdZnO nanostructures with superior electronic properties which are much suitable for solar cells buffer layers and many optoelectronics devices.

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