



Computational study of electronic, spectroscopic and chemical properties of $(\text{CdO})_n$ ($n=1-7$) nanoclusters as a transparent conducting oxide

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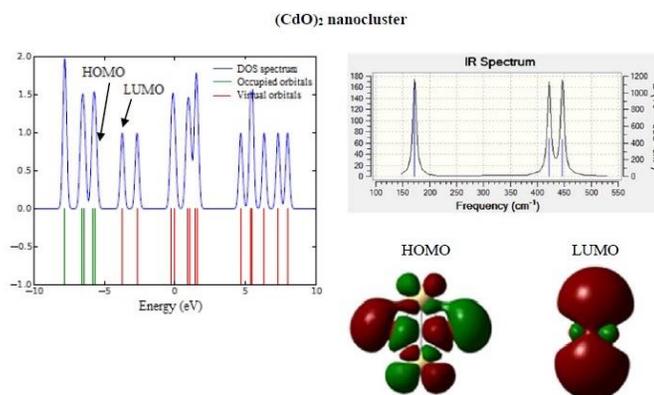
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HIGHLIGHTS

- The stable structures of $(\text{CdO})_n$ ($n=1-7$) nanoclusters were fully optimized using B3LYP level of theory.
- The harmonic vibrational frequencies of the clusters were calculated to announce dynamical stability.
- The highest vibrational frequencies of the nanoclusters arise from asymmetrical stretching vibrations.
- The lower frequencies correspond twisting, bending and the out-of-plane vibrations of Cd and O atoms.

GRAPHICAL ABSTRACT



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ABSTRACT

An ab initio study has been performed for the electronic, spectroscopic, and chemical properties of the most stable configuration of the $(\text{CdO})_n$ nanoclusters by employing B3LYP-DFT/LanL2DZ method. Different isomers were optimized to obtain structural stability and numerous chemical parameters such as dipole moment, ionization potential, etc. We report here the vibrational frequencies of the most stable configuration of $(\text{CdO})_n$ nanoclusters. We found that, the highest vibrational frequencies of each $(\text{CdO})_n$ nanoclusters arise from the asymmetrical stretching vibrations while the lower frequencies correspond twisting, bending and the out-of-plane vibrations of Cd and O atoms. Our results show that, the $(\text{CdO})_2$ nanocluster with the ring structure and the smallest HOMO-LUMO gap (HLG = 1.897) has the smallest hardness ($\eta = 0.95$) and consequently is expected to have the highest chemical reactivity.

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1. Introduction

Cadmium oxide (CdO) is a famous II–VI semiconductor with a direct band gap of 2.2 eV (520 nm). It has interesting properties like large band gap, high electrical conductivity and high transmission in the visible [1, 2]. Therefore, it possess band gap of energies corresponding to the wavelength which are shorter than that of the visible range of 400–700 nm. CdO has developed numerous applications such as its use in solar cells, electrochemical capacitors, photodiodes, nonlinear optics, thermo electricity, catalyst, electrodes for storage batteries, ceramic glazes, electroplating baths, liquid crystal displays, IR detectors, and gas sensors [3-7].

There are several reported methods for the preparation of the CdO nanoparticles. Pan et al. [8] reported a formation of several nanobelts at high temperatures from a number of metal oxides; one of them being CdO. The formation of CdO nanowires has been reported by Peng et al. [9]. Lately, Ristic et al. [10] reported the formation of CdO nano-particles using the thermal treatment of cadmium. Fundamental understanding or predicting the properties of materials at nanoscale levels is essential to their preparation and modification for device performance [11,12].

There are several research works have been carried out by different researchers in the field of CdO nanocluster using quantum mechanical calculations [13-15]. Nanometric CdO as particle or thin film forms creates attention in scientific community because of its significant electronic, spectroscopic and chemical properties. However, a few workers have informed the stability of small CdO nanoclusters [16, 17]. Among the Quantum mechanical studies, there have been investigations for the structural stabilities and vibrational modes of stable CdO nanoclusters. Nevertheless, other physical and chemical properties like hardness, ionization potential, electron affinity, and density of states have not been reported. Seshadri et al. [18] have performed a DFT calculation on CdO clusters stability, which show a strong dependence on the geometry of nanoclusters. Jeyakumaran et al. [19] have synthesized and characterized CdO nanoparticles by precipitation method and

observed good antimicrobial activity by inhibiting their growth.framework.

In this study, the geometry, binding energy, vibrational frequency, density of states, HOMO-LUMO energies and quantum chemical parameters of CdO nanoclusters are considered using DFT method with B3LYP [20] as basis set of LanL2DZ level [21]. We have compared our obtained results with the former calculated and experimental results anywhere available.

2. Theoretical details

In this report, the CdO nanoclusters were computed using the density functional theory (DFT). DFT methods, which attempt to contain electron correlation effects, have been widely described to be an applied and effective computational tool for metallic clusters. The B3LYP exchange-correlation hybrid functional was selected and appears to give reliable results for the considered systems. In the present investigation, the standard LanL2DZ basis set is used for all cadmium and oxygen atoms. Since the atomic number of cadmium and oxygen were 48 and 8, respectively, LanL2DZ is appropriate basis set [22, 23] and therefore all the parameters were calculated using this basis set. The frequency calculations have been done at the identical level of theory and it was established that the structures are at their energy minima. The ionization potential (IP), electron affinity (EA), electronegativity (χ), hardness (η), and softness (σ) have been calculated using the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energies [24]. These quantum chemical parameters were measured using Equations (1)-(3):

$$IP = -E_{\text{HOMO}} \quad EA = -E_{\text{LUMO}} \quad (1)$$

$$\chi = \left(\frac{IP + EA}{2} \right) \quad \eta = \left(\frac{IP - EA}{2} \right) \quad (2)$$

$$\sigma = 1/\eta \quad (3)$$

All the calculations have been implemented in GAUSSIAN 09 [25].

3. Results and discussion

Initially, the structures of $(\text{CdO})_n$ ($n=1-7$) nanoclusters were generated and optimized by careful consideration of the previously reported stable geometries [18]. All these initial structures were completely optimized by relaxing the atomic positions by minimizing the total energy until the force acting on each atom became negligible. The relative stabilities of the clusters are significant parameters for finding the most stable structures. The binding energy (E_b) equation can be defined as: $E_b = [nE(\text{Cd}) + mE(\text{O}) - E(\text{CdO})_n]/(n + m + 1)$. The calculated E_b for the stable clusters are shown in Table 1. Among all the different atomic arrangement of $(\text{CdO})_n$ nanoclusters, the structure which possesses maximum binding energy is named as most stable structures and reported. Minimum energy structures and HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital) pictures of all these nanoclusters are shown in Fig.1.

According to Table 1, one can note that the $(\text{CdO})_5$ nanocluster with the ring structure has the greatest HLG (3.651) and the highest hardness, and therefore is expected to have the lowest chemical reactivity. On the other hand, the $(\text{CdO})_2$ nanocluster with the ring structure and the smallest HLG (1.897) has the smallest hardness (0.95) and consequently is expected to have the highest chemical reactivity.

The vibrational calculations of the most stable $(\text{CdO})_n$ nanoclusters are examined and the obtained IR spectra are presented in Fig. 2. We obtain the stretching mode frequency of 584 cm^{-1} for CdO nanocluster, while Seshadri et al. [18] have obtained it as 553 cm^{-1} . For the $(\text{CdO})_2$ with rhombus structure, we find three normal modes of vibrational frequencies. The highest frequency of 445 cm^{-1} corresponds to the breathing vibrations of Cd and O atoms while the lowest frequency of 170 cm^{-1} arises due to out of plane vibration of Cd and O atoms. Asymmetric stretching vibration appears at the frequency of 410 cm^{-1} . For the $(\text{CdO})_3$ with planer configuration, there are five normal modes of vibrational frequencies. The highest

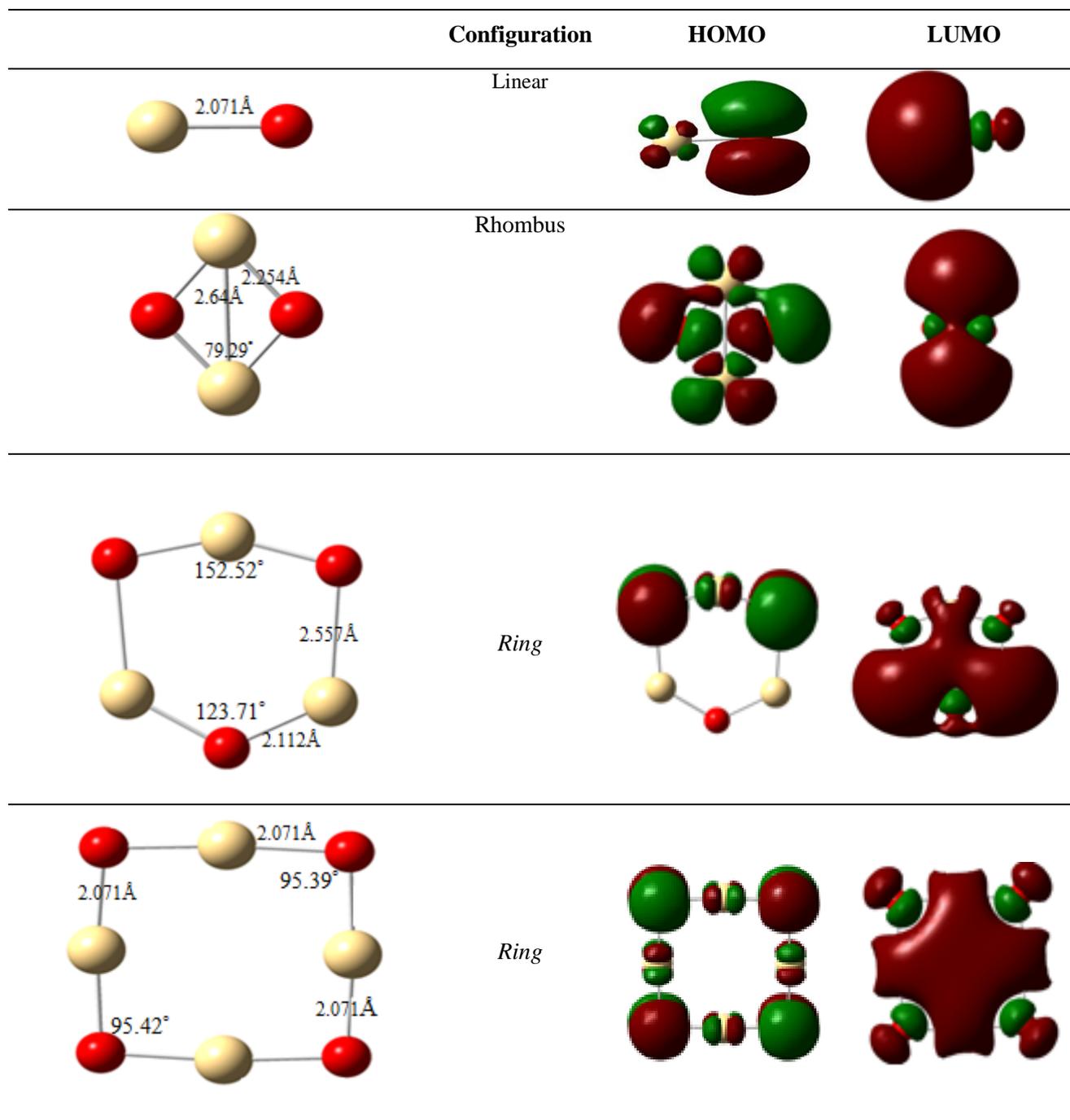
frequency of 540 cm^{-1} comes from asymmetric stretching vibration. The frequencies, 80 and 90 cm^{-1} correspond to the twisting of Cd and O atoms. The frequency of 160 cm^{-1} arise due to the out of plane vibrations of Cd and O atoms. The frequency of 460 cm^{-1} corresponds to the bending vibration. For $(\text{CdO})_4$ nanocluster, we find four normal modes of vibrational frequencies. Asymmetric stretching vibration appears at the highest frequency of 620 cm^{-1} . Bending vibration appears at the frequency of 440 cm^{-1} . The frequencies 110 and 150 cm^{-1} arise due to the out of plane vibrations of Cd and O atoms. The planar $(\text{CdO})_5$ structure has four normal modes of vibrational frequencies. The frequencies of 110 and 160 cm^{-1} originates from the out of plane vibrations of Cd and O atoms. Bending vibration appears at the frequency of 400 cm^{-1} . Asymmetric stretching vibration appears at the highest frequency of 680 cm^{-1} . The $(\text{CdO})_6$ nanocluster with 3D structure has six normal modes of vibrational frequencies. The twisting mode of Cd and O atoms appears at the frequencies of 80 and 150 cm^{-1} . The frequencies of 330, 360, and 370 cm^{-1} arise due to the bending vibration. Asymmetric stretching vibration, also appears at the highest frequency of 520 cm^{-1} . There are several normal modes of vibrational frequencies in range of $80-150 \text{ cm}^{-1}$ for $(\text{CdO})_7$ nanocluster that originate from the twisting of Cd and O atoms. Bending vibrations appear at the range of $200-450 \text{ cm}^{-1}$ and the frequencies 540, 560 and 570 cm^{-1} arise due to asymmetric stretching vibration.

To gain an overall view of the electronic structures of $(\text{CdO})_n$ nanoclusters, the density of states (DOSs) of $(\text{CdO})_n$ nanoclusters along with the HOMO, and LUMO levels are shown in Figure 3. These pictures have helped us to recognize the areas where electron density is concentrated. The positive and negative phases are represented in red and green colors, respectively. The HOMO-LUMO gap (HLG) is a useful measure for examining the stability of clusters. It is observed that systems with greater HLG's are, in general, less reactive. In other words, the gap reflects the ability of electrons to jump from the occupied orbital to the unoccupied orbital; it also represents the ability

for the molecular participates to produce chemical reactions to some degree.

Table 1. HOMO-LUMO energy gap, dipole moment, ionization potential, electron affinity, electronegativity, hardness, and softness of Cu_n clusters.

	$\Delta E_{\text{HOMO-LUMO}}$	E_b	μ (Debye)	IP	EA	χ	η	σ
CdO	2.226	1.067	5.6175	6.44	4.22	5.33	1.11	0.90
(CdO) ₂	1.897	1.992	0.0005	5.63	3.73	4.68	0.95	1.05
(CdO) ₃	3.227	2.573	0.0057	6.46	3.23	4.84	1.61	0.62
(CdO) ₄	3.466	2.843	0.0212	6.52	3.06	4.79	1.73	0.58
(CdO) ₅	3.651	2.976	0.0654	6.66	3.01	4.83	1.82	0.55
(CdO) ₆	2.688	3.154	0.0096	5.98	3.30	4.64	1.34	0.74
(CdO) ₇	2.827	3.184	2.716	5.84	3.43	4.63	1.20	0.83

Fig. 1. Minimum energy structures and HOMO, LUMO pictures of $(\text{CdO})_n$ nanoclusters

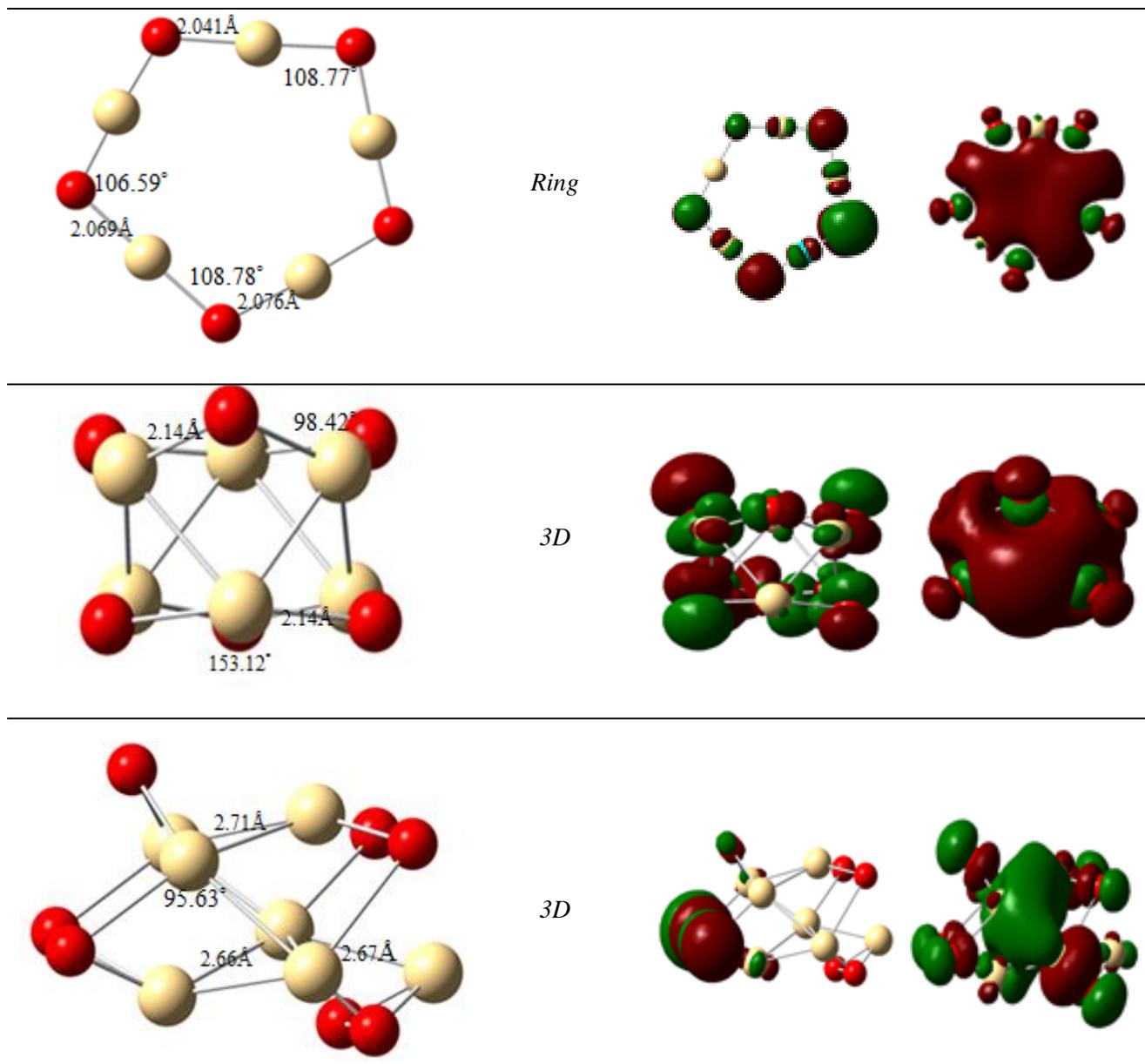


Fig. 1. (Continued)

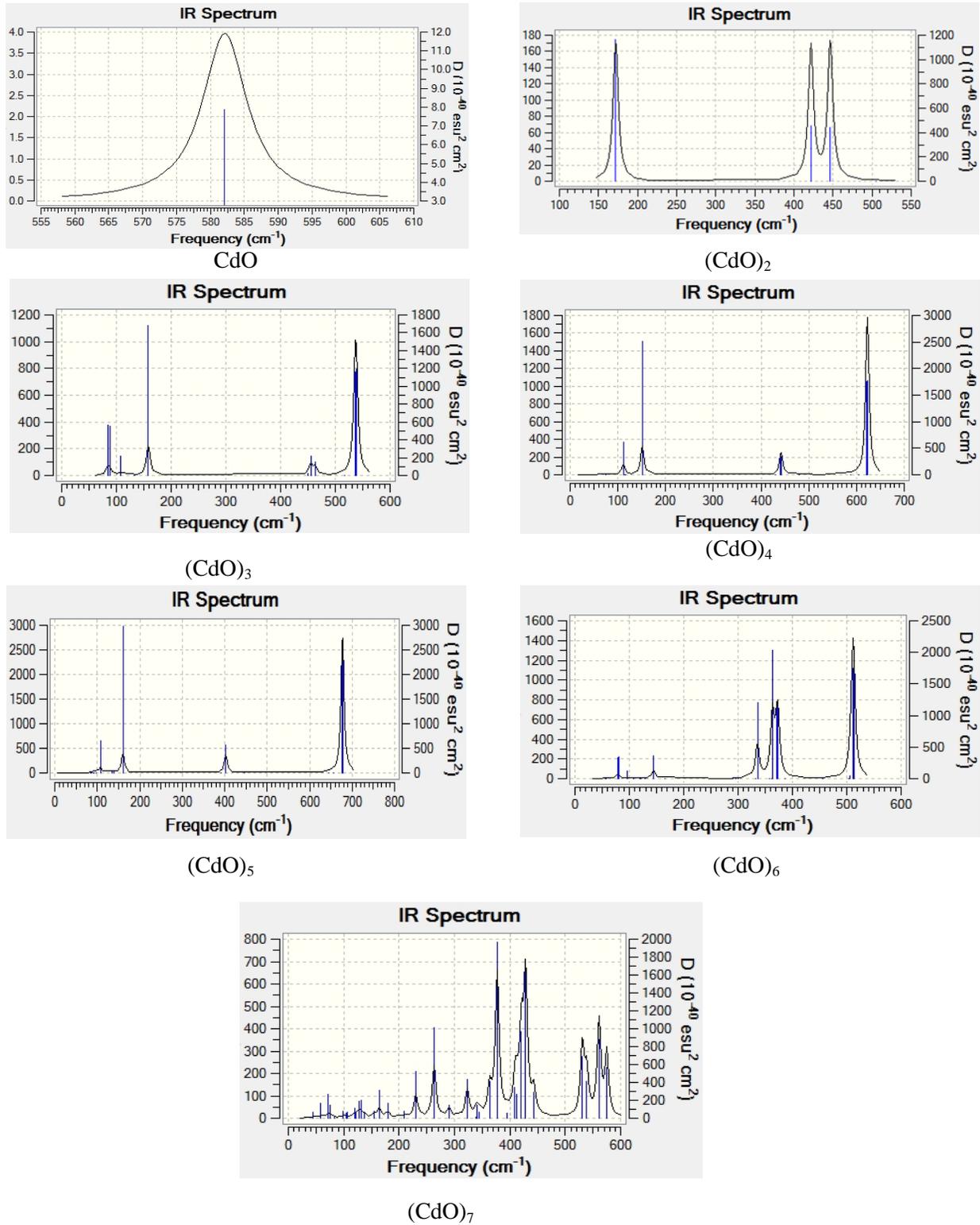
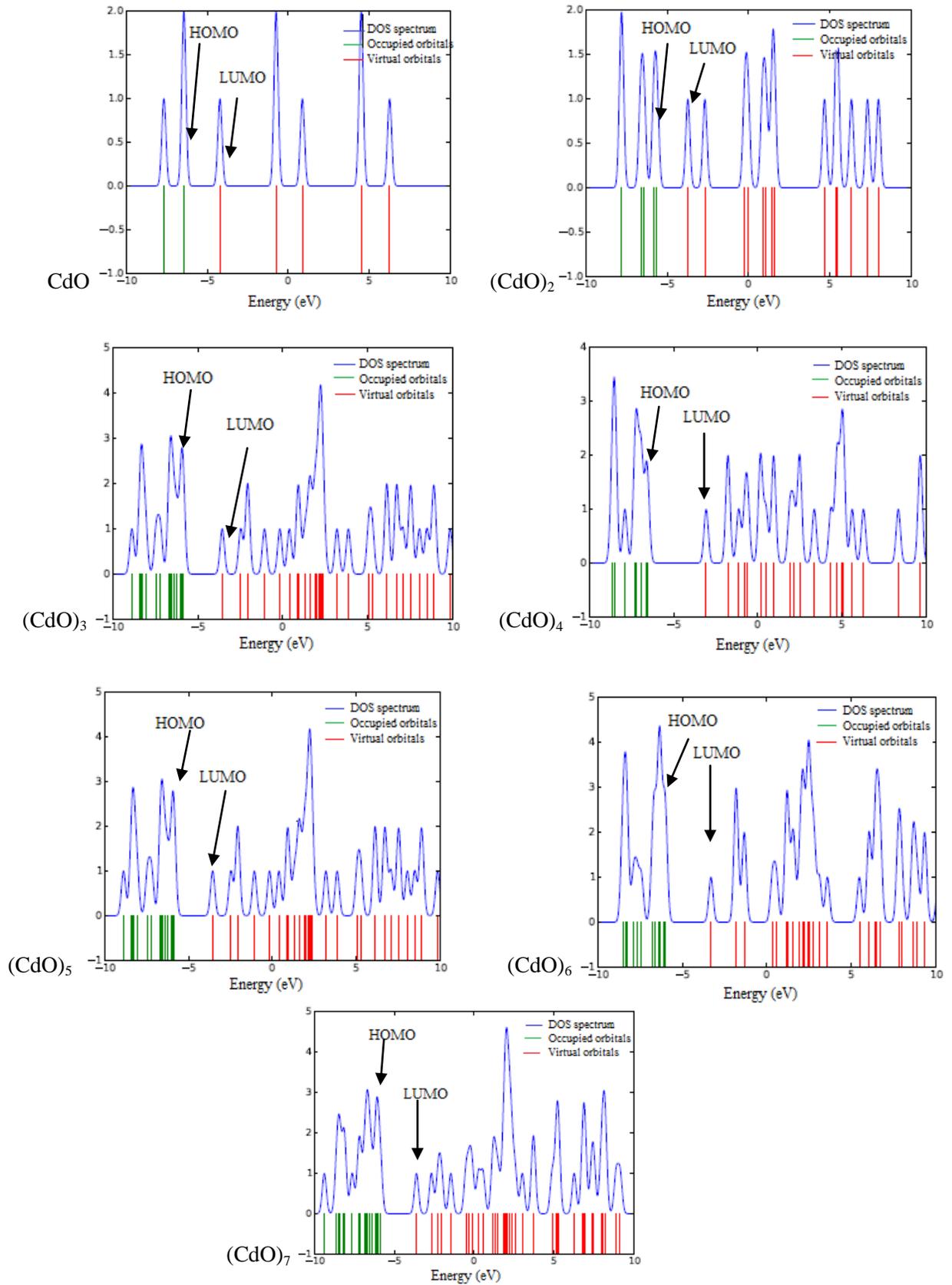


Fig. 2. Simulated IR of $(CdO)_n$ nanoclusters

Fig. 3. DOS of (CdO)_n nanoclusters

4. Conclusions

We have investigated the stable structures of the $(\text{CdO})_n$ ($n=1-7$) nanoclusters using B3LYP level of theory implementing LanL2DZ basis set with Gaussian 09 program package. The binding energy, dipole moment, vibrational frequency as well as the HOMO-LUMO energy gap and the electronic density of states (DOS) were obtained. The results are summarized as follows:

- For $n = 2-5$, the 2D structures is more stable, but for $n = 6$ and 7 , the 3D structures is more stable than the 2D structures.

- The highest vibrational frequencies of each $(\text{CdO})_n$ nanoclusters arise from the asymmetrical stretching vibrations while the lower frequencies correspond twisting, bending and the out-of-plane vibrations of Cd and O atoms.

- With increasing nanocluster size, the HOMO-LUMO energy gap expands gradually both for 2D structures and 3D structures.

- The $(\text{CdO})_2$ nanocluster with the ring structure and the smallest HOMO-LUMO gap (HLG=1.897) has the smallest hardness ($\eta=0.95$) and consequently is expected to has the highest chemical reactivity.

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