Vibration Properties of ZnS nanostructure
Wurtzoids: ADFT Study
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Abstract. In this work, ZnS structure change from the molecular size of ZnS Wurtzite to obtain on longitudinal mode vibrational properties for both IR and Raman intensities and other features of vibration like forces constant and reduced masses for bare and H-passivation to ZnS Wurtzoids nanostructures. The vibrational modes represented by Longitudinal optical (LO) of structures as nanoscale with H-passivated (Hp) shifted to red shift inverse the bare of ZnS shift to blue with respect to ZnS bulk. The theoretical study of ZnS as nanotubes using Ab-initio density functional theory (ADFT) and comparison with experimental results, all calculations done in program Gaussian 09. At nanoscale properties, the nanostructure of ZnS different from at bulk or molecule limit to there are dangling bonds in the clusters at their surface.

1. Introduction
Depending on the previous studies whether the theoretical or experimental considered the ZnS is the most important material in the binary semiconductor as n-type, according to its applications widely in optical fields, especially when was as nanocrystals due to have some physical features like high refractive index and other parameters as absorption coefficients were low in spectrum regions the visible and infrared, for this there are academic applications or industrial of ZnS material such as sensors, UV-LED, etc. also direct band gap (3.66, 3.78) eV for cubic zinc blend and wurtzite [1-3], and in order to obtain information about lattice dynamics use Raman effect for a specific crystal. Many studies for Raman spectrum began from 1969 and till now for first and second -orders of Raman scattering for both polyforms of ZnS: zinc blende or wurtzite nevertheless stay some ambiguous about them, where magnitude of $A_1$(TO)=E$_1$(TO) =273 cm$^{-1}$ while A1(LO)=E1(LO) is about 353cm$^{-1}$ found experimentally by Cheng et. al. [4] whereas other researchers confirm that A1(To)=272cm$^{-1}$ E1(To)=276 cm$^{-1}$ &E1(LO)=351 cm$^{-1}$ but don’t appear value of A1(LO) [5]. According to previous studies found that Raman frequencies for wurzite ZnS for two orders there is controversy [6].

Currently, in this paper the theoretical study focused on the vibrational properties for ZnS wurtzoids as nanotubes after geometrical optimization of molecules using DFT and BL3YP as a basis set used 6-311G**, IR and Raman spectrum, forces constants and reduce masses, all vibrational modes of these nanotubes of ZnS are invest aged at the nanoscale limit .

2. Theory
Theoretical approximations are utilized in this work, one of this approximations methods represent by Density functional theory (DFT) that includes all electrons in the molecules at generalized gradient approximation GGA can be computed, this method considers as a framework to investigate the electronics characterizes at ground state of the molecules and other materials in solid state. These calculations have been performed by Gaussian program 09 and use the B3LYP (Becke, three-parameter, Lee-Yang-Parr) and basis set 6-311G** used this basis because the molecules ZnS contain on d,p orbitals in its configuration electronics...
and the double star on \( G(d,p) \) denotes to orbitals as a function polarization. The molecules of ZnS have heavy atoms Zn and light S and adding H-atom. as well known that ZnS bulk involves prototypes such as zinc blend, wurtzite, and other structure rock salt, in our study focused on ZnS Wurtzi to be the seed for formation the nanotubes of ZnS as wurtzoids at nanoscale limited. The vibrational calculations have been completed by use 0.967 as a scale factor to give the corrections on the frequencies, this scale associated with 3-611G**. All forms the nanotubes that built from molecules via variation size include wurtzi, wurtzoids 2c and triwurtzoids are studied their the vibration proprieties of molecules ZnS once as bare and again with H-atom - passivated. The geometry optimization of ZnS wurtzoids bare and H-passivated as shown in Fig (1).

3. Results and discussion

In Fig (2) demonstrates the relation between longitudinal optical frequencies of ZnS molecules at variation sizes (molecular –nanoscale limited) of bare and with H-passivation with the total number of Zn and S, it can be seen the bare of ZnS are nearer or higher from the experimental line than H-passivation that has values are low, note that at nanoscale limited decrease values of vibrational frequencies modes (LO), reason the values low of the bare molecules there the dangling bonds on their surfaces that effect on the forces constants for them and then lead to increase these constants to be high.

4. IR and Raman intensities

In Fig (3) and Fig (4) show that IR and Raman intensities for ZnS wurtziod (bare and Hp), note that the value of experimental locates between bare and Hp of wurtziod, the bare of wurtziod has red shifted due to the phonon confinement quantum while the Hp has blue shifted, also same thing with respect to wurtziod 2c as shown in fig(5 & 6)

5. Force Constants and Reduced Masses

Elastic waves have three different modes of vibration: two perpendicular transverse modes and one longitudinal mode. The energy of a phonon can not have an arbitrary value but is quantized according to quantum mechanics.

In both Fig (7), Fig(8) illustrate the reduced masses of ZnS wurtzoids and force constant for two cases the bare and H-passivation as function of vibrational frequencies, we can notice that the experimental value of bulk ZnS of vibrational reduced mass locates between values the bare and Hp of ZnS wurtzoids, the bare of ZnS wurtziod has higher value of reduced mass than Hp of ZnS wurtzoids due to not passivation hydrogen atoms with dangling bonds of them. Also to discuss the Fig (7) notice same the section mentioned above, for the molecules that consist of two atoms one of them heavy mass and other light, if the heavy atoms vibrate and so the frequencies at boundary brillion zone depend on this equation as below, the frequencies [10]:

\[
u = \frac{1}{2\pi} \sqrt{\frac{k}{\mu}}
\]

where \( k \) and \( \mu \) is force constant and reduced mass of molecules, we can see the frequencies is proportional with force constant but inversely with the reduce mass, but the value of both them in this paper coincide with highest value of LO mode at last mode in the bare but before the vibrational frequencies of hydrogen atom at H-passivated of ZnS wurtzoids, the values modes for two cases bare and HP that shown in Fig (7) approximately 356cm\(^{-1}\) and 257.77cm\(^{-1}\) respectively if compared with experimental value of LO for ZnS wurtzite while
ZnS diamantane molecules that shown in Fig(9) have values of frequencies modes in the range 426 cm\(^{-1}\) and 398 cm\(^{-1}\) for the bare and Hp for diamantane and partial diamantane.

Fig (10 ), Fig(11) illustrate the reduced masses and force constant of ZnS wurtzoids2C for two cases the bare and H-passivation as function of vibrational frequencies

**Conclusion**

Through the theoretical study of ZnS nanostructures as results of variation sizes of ZnS molecule at Wurtzite structure using basis set of BL3YP and employed the approximation methods (ADFT), our results proved that the longitudinal frequencies modes of Raman spectrum of molecules with H-passivated be higher than bare, in addition to the experimental line located between the bare and H-p of molecules or nanostructures of ZnS wurtzoid, also increasing the intensities for both of IR and Raman with H–passivated more than bare of ZnS and shifted toward the red and the last mode of LO start H-vibrations.

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Figure 1. shows the wurtziods of ZnS nanotubes structure (a-bare and b- H-passivated ) after optimized

Figure 2. The vibrational longitudinal frequencies (LO) of ZnS bare and without hydrogen as function number of Zn and S, in addition to the experimental value of LO for ZnS bulk[5].
Figure 3. Raman of ZnS wurtziod bare and Hp as a function of frequencies compare with experimental bulk value

Figure 4. IR of ZnS wurtziod (bare and HP) as a function of Frequencies and experimental value of ZnS bulk
Figure 5. Raman of ZnS wurtziod 2c (Bare & HP) as function of Frequencies and experimental value of ZnS bulk

Figure 6. IR of wurtzoid 2c (B, HP) of ZnS using BLY3P base set 6-331G** of Frequencies and experimental value of ZnS bulk
Figure 7. Reduce mass of ZnS wurtzoid bare and Hp as function of frequencies and experimental value of LO mode of ZnS bulk [5]

Figure 8. The forces constants of bare and H-passivation of ZnS wurtzoid as a function of vibrational frequencies[5]
Figure 9. Reduce mass of ZnS diamantane bare and Hp as function of frequencies and experimental value of LO mode of ZnS bulk [5]

Figure 10. Reduce mass of ZnS wurtziod 2c bare and Hp as function of frequencies and experimental value of LO mode of ZnS bulk [5]
Figure 11. Force constant of ZnS wurtziod 2c (bare and HP) as a function of frequencies and