

Ab initio study of thermodynamic properties, IR spectra and electrical properties of $\text{Cu}_4\text{O}_3\text{H}_2$ nanosemiconductor

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Abstract. Cupric oxide is a p-type semiconductor has received a considerable attention due to their interesting properties, such as high-temperature superconductors, optical switch and anode electrodes for batteries. In this theoretical study thermodynamic properties and hyperfine spectroscopic parameters of this novel compound are carried out within a density functional methods (B3LYP, B1LYP and B3P86) employing 6-31G+ (d) basis set. All calculations were performed using GAUSSIAN 98 packages of program. Thermodynamic properties of $\text{Cu}_4\text{O}_3\text{H}_2$ nanocluster as well as IR data and spectra were obtained. In addition we are carrying out more detailed studies of the electronic and chemical properties of this compound such as HOMO and LUMO energies which have been used to explicate data regarding charge transfer within the molecule. HOMO and LUMO gap revealed that $\text{Cu}_4\text{O}_3\text{H}_2$ has obvious delocalization, making it have good stability, high voltage differences and its semiconductors property. [Elham Pournamdari, Majid Monajjemi and Karim Zare. **Ab initio study of thermodynamic properties, IR spectra and electrical properties of $\text{Cu}_4\text{O}_3\text{H}_2$ nanosemiconductor.** Life Sci J 2012;9(4):1729-1738] (ISSN:1097-8135). <http://www.lifesciencesite.com>. 264

Keywords: Ab initio, HOMO and LUMO, IR spectra, nanosemiconductor, Thermodynamic property, hyperfine spectroscopic parameters.

1 Introduction

Copper oxide (CuO) is p-type narrow band gap semiconductor substances which have inimitable physical properties and great potential for various photonic and electronic applications that need superconductivity, colossal magnetoresistivity, and piezoelectricity. CuO has widespread usage in lithium-copper oxide electrochemical cells, magnetic storage media, gas sensor, solar energy transformations, etc. Due to unique physical and electronic properties, [1–4] CuO Nanoscale materials have received a great significant attention in recent years both experimentally and theoretically as long as some new characteristics have been explored for them which are different from the bulk materials. For example, UV-visible absorption spectrum studies reveal that CuO band gap in bulk ($E_g = 1.85$ eV) is much smaller than that in nanoparticles CuO ($E_g = 2.18$ eV) [5]. Therefore, different morphologies with and without using surfactants or templates have been gained for the CuO , such as nanorods [6], nanowires [7, 8], nanowhiskers [9], nanoplatelets [10–12], nanoribbons [13, 14], feather-like [15], urchin-like

[16, 17], and plates-like [18]. CuO has been prepared by different synthetic methods such as hydrothermal [19–23], hydrothermal reduction [24], simple solution [25, 26], simple hydrolysis [27], self-catalytic mechanism [28], solvothermal [29] microwave heating using ionic liquids [30] and microwave irradiation [31]. However studies about CuO nanosemiconductor are still limited and it has been a serious problem to obtain single crystals of CuO suitable for quantitative infrared studies. Therefore theoretical investigation on these systems has been extensively used. In this theoretical research Vibrational studies as well as NBO analysis combined with ab initio and we have been reported an ab initio-based numerical method of obtaining infrared spectroscopic data for $\text{Cu}_4\text{O}_3\text{H}_2$ molecules that allows calculation of complete IR data, IR spectra and thermodynamic properties of this system. In the present paper, by using quantum methods the structure, stability, and electrical dipole moments of $\text{Cu}_4\text{O}_3\text{H}_2$ molecules have been investigated.

2 Calculation method

DFT calculations were done using the B3LYP, B1LYP and B3P86 functionals for studying

thermodynamic properties, IR data and NBO analysis. The first job for the computational work was to reveal the optimized geometry of the compound. Molecular structure of $\text{Cu}_4\text{O}_3\text{H}_2$ was optimized using B3LYP model with 6-31G (d) basis set. The B3LYP density functional model indicates good performance on electron affinities, vibrational frequencies, bond energies and geometries of inorganic compounds [32]. It is well known that in the quantum chemical literature the hybrid B3LYP [33, 34] method based on Becke's three parameter functional of density functional theory (DFT) yields a good description of harmonic vibrational wavenumbers for small and medium sized molecules [35]. Another factor which causes to choose the DFT methods is their capability to reproduce geometries and dipole moments of these molecules with quite high accuracy. All calculations were performed using the Gaussian 98 program package. The optimized geometric structure of $\text{Cu}_4\text{O}_3\text{H}_2$ with Cs symmetry is shown in Fig.1.

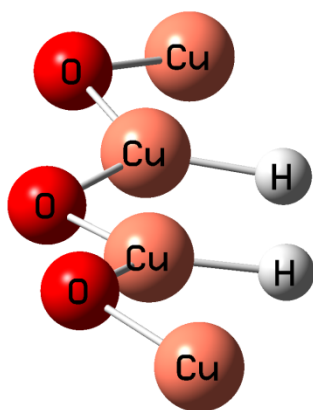


Figure1 Geometry optimized (6-31G+ (d)) structures for $\text{Cu}_4\text{O}_3\text{H}_2$ nanosemiconductor.

3 Results and Discussion

3.1 Thermodynamic properties

The energies and thermo chemical parameters can give valuable information about structures and relative stabilities of these systems. The relative stability, relative energy $\Delta(E)$, enthalpy $\Delta(H)$, Gibbs free energy $\Delta(G)$ and entropies(S) of $\text{Cu}_4\text{O}_3\text{H}_2$ nanosemiconductor are computed in DFT methods using B3LYP, B1LYP and B3P86 levels of theory and comparison of these different levels with 6-31G (d) basis set are listed in table 1. Since the Gibbs free energy controlling the structure stability by analyzing the data from Table 1, we have found that Gibbs free energy $\Delta(G)$ in B3P86 method is more negative than those of the other two methods. The entire trend observed for enthalpy $\Delta(H)$ and thermal energy $\Delta(E)$ which can be seen in Table 1 and fig. 1 though B3P86 shows the best results for $\text{Cu}_4\text{O}_3\text{H}_2$ systems among these methods for this structure stability at the point of thermodynamic properties. This effect is probably due to the large dipole moments of the Cu-O bonds, which preferentially enhance the structures stability. These results suggest that for a given increase of the dipole moment there is certain degree of stabilization.

Table1 Relative thermodynamic data for $\text{Cu}_4\text{O}_3\text{H}_2$ system in kcal/mol and antropy in cal/mol.kelvin

Basis set		6-31G+(d)			
Method	E(scF)	$\Delta(E)$	$\Delta(H)$	$\Delta(G)$	S
B3LYP	3.01	-1874.67	-1881.25	-1883.32	109.06
B1LYP	3.23	-2021.45	-2021.45	-2020.40	119.50
B3P86	0.00	0.00	0.00	0.00	116.00

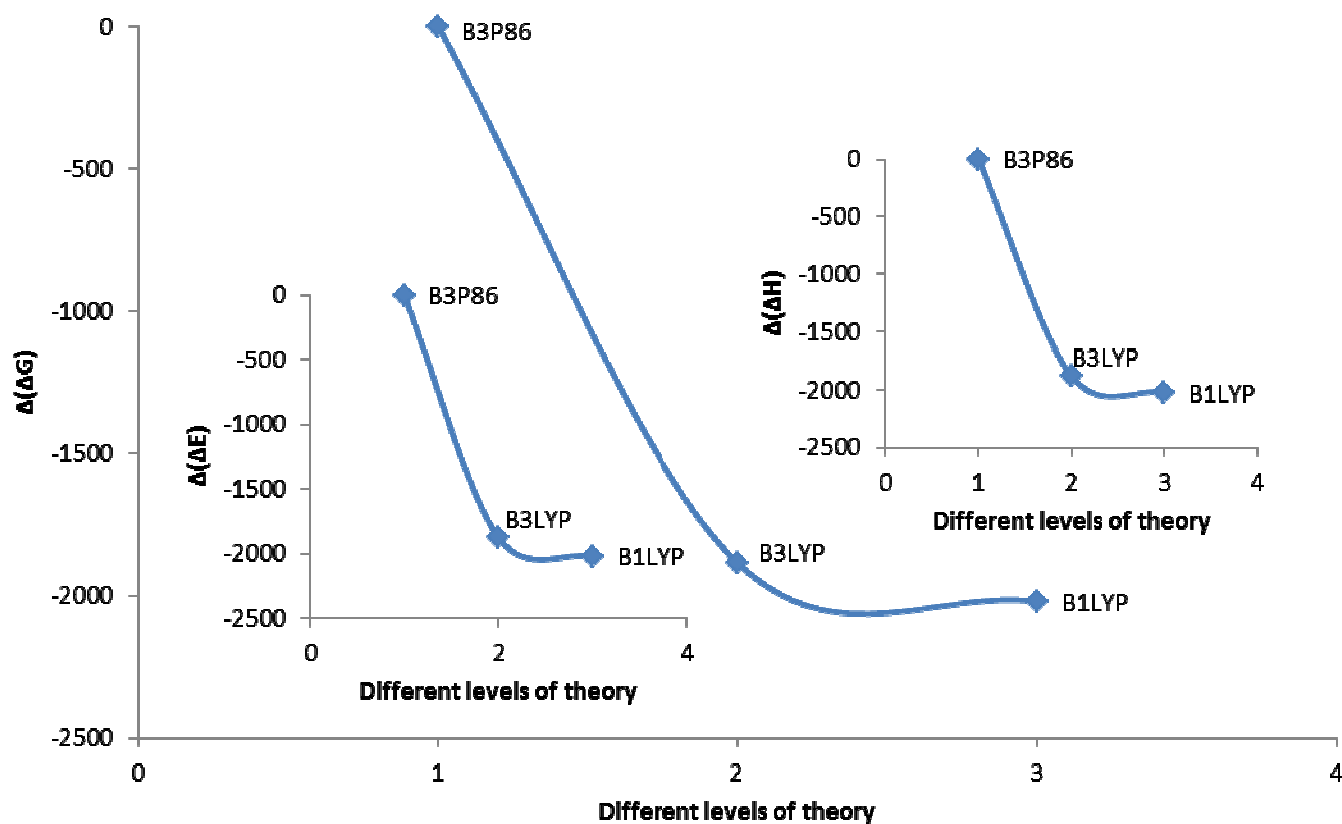


Figure 2 Different levels of theory as a function of Δ (ΔG), Δ (ΔH), Δ (ΔE) in kcal/mol in Cu₄O₃H₂ structure.

3.2 IR spectroscopy

Vibrational spectroscopy (infrared spectroscopy) has been recognized as an important tool for the characterization and understanding of molecular structures and dynamics for a long time [36]. DFT method yield very accurate infrared spectra of inorganic molecules in terms of band positions, band shapes, and band intensities [37, 38]. Absorption intensities and vibrational spectra serve as “fingerprints” to identify a known molecule, or determine the geometry of one that has not been defined before. Infrared measurements are generally complemented with theoretical calculations. These are usually carried out using quantum chemistry calculations where equilibrium conformations of lowest energies are calculated. In this work, geometry optimizations are implemented, and vibrational analyses are subsequently done for this structure. There have been efforts to carry out a detailed analysis of the vibrations based on vibrational spectroscopy data for Cu₄O₃H₂ molecules [8]. The studied compound

consists of 9 atoms, and so it has 21 normal vibrational modes. The numerical harmonic vibrational analysis was done for the optimized geometry, the absence of negative frequencies emphasizing that this structure correspond to real minimum which emphasized structural stability. We describe DFT numerical method of obtaining infrared spectroscopic data of Cu₄O₃H₂ molecules that allows calculation of complete sets of Vibrational modes, frequency and IR intensity which are calculated with B3LYP, B1LYP and B3P86 methods using 6-31G (d) basis sets that are represented in table 2 and comparison between them can be seen and IR spectrum of this nanocluster shown in figure 3, 4 and 5 for B3LYP, B1LYP and B3P86 methods of density functional theory (DFT), respectively. In each of three IR spectrums which are calculated with DFT methods 2 sharp frequency modes with high intensities could be observed. As can be seen in table 2 the maximum intensity in B3LYP levels of theory is at frequencies of 542.16 cm⁻¹ with 367.94 intensities,

for B1LYP is at frequencies of 548.89 cm^{-1} with 469.71 intensities and for B3P86 levels of theory is at frequencies of 540.55 cm^{-1} with 362.87 intensities which are shown that there is a slightly increase in intensity for B1LYP methods in comparison of B3LYP and B3P86 levels of theory. These three frequencies are the strongest signals in $\text{Cu}_4\text{O}_3\text{H}_2$ molecules. Obviously, the low intensity mode for B3LYP levels of theory is at 142.88 cm^{-1} with 0.05 intensities, for B1LYP levels of theory is at frequencies of 150.56 cm^{-1} with 0.30 intensities

and for B3P86 levels of theory is at frequencies of 158.91 cm^{-1} with 0.42 intensities in spectrum of $\text{Cu}_4\text{O}_3\text{H}_2$ molecules is the A' mode in all three levels of theory. B3P86 method has largest blue shift in comparison of B3LYP and B1LYP levels of theory which implies different applications of this novel nanosemiconductor molecule. The present spectroscopic analysis shows that all DFT methods have nearly identical spectral characteristics and they are in good agreement with each other's.

Table 1 Vibrational mode, harmonic frequency (cm^{-1}) and IR intensity (KM/Mole) with B3LYP, B1LYP and B3P86 with 6-31G+ (d) basis set.

Basis set	6-31G(d)							
Method	B3LYP		B1LYP			B3P86		
Vibrational modes	Frequency	IR intensity	Vibrational modes	Frequency	IR intensity	Vibrational modes	Frequency	IR intensity
A'	755.54	5.14	A'	717.76	3.38	A'	762.75	4.43
A''	542.16	367.94	A''	548.89	469.71	A''	540.55	362.87
A''	87.33	12.04	A'	26.3211	1.55	A'	24.35	0.71
A'	26.77	1.43	A''	37.08	4.05	A''	6.15	7.53
A'	54.75	3.49	A'	57.28	3.49	A'	65.25	2.26
A'	63.27	2.47	A'	65.22	1.879	A'	67.89	1.85
A''	71.61	7.03	A''	69.85	7.62	A''	76.59	8.30
A'	81.62	97.37	A'	82.62	5.29	A'	99.08	7.38
A''	97.37	2.68	A''	103.51	3.37	A''	106.38	2.50
A''	122.07	0.50	A''	145.16	3.03	A''	145.84	3.17
A'	142.88	0.05	A'	150.56	0.30	A'	158.91	0.42
A''	191.70	2.34	A''	209.11	5.87	A''	211.30	4.80
A'	226.08	23.25	A'	250.92	27.51	A'	256.14	22.94
A'	400.14	38.53	A'	401.12	38.10	A'	398.31	38.69
A''	443.21	14.01	A''	444.81	14.10	A''	439.90	15.19
A'	473.34	5.08	A'	475.38	5.384	A'	468.35	5.36
A''	588.18	271.16	A''	592.21	311.19	A''	579.53	275.06
A'	598.45	4.04	A'	603.19	4.30	A'	590.24	4.31
A''	648.66	232.31	A''	653.90	235.90	A''	640.46	219.23
A'	1893.12	19.60	A'	1892.95	23.79	A'	1886.80	17.45
A''	1894.64	9.48	A''	1893.15	12.72	A''	1889.94	10.92

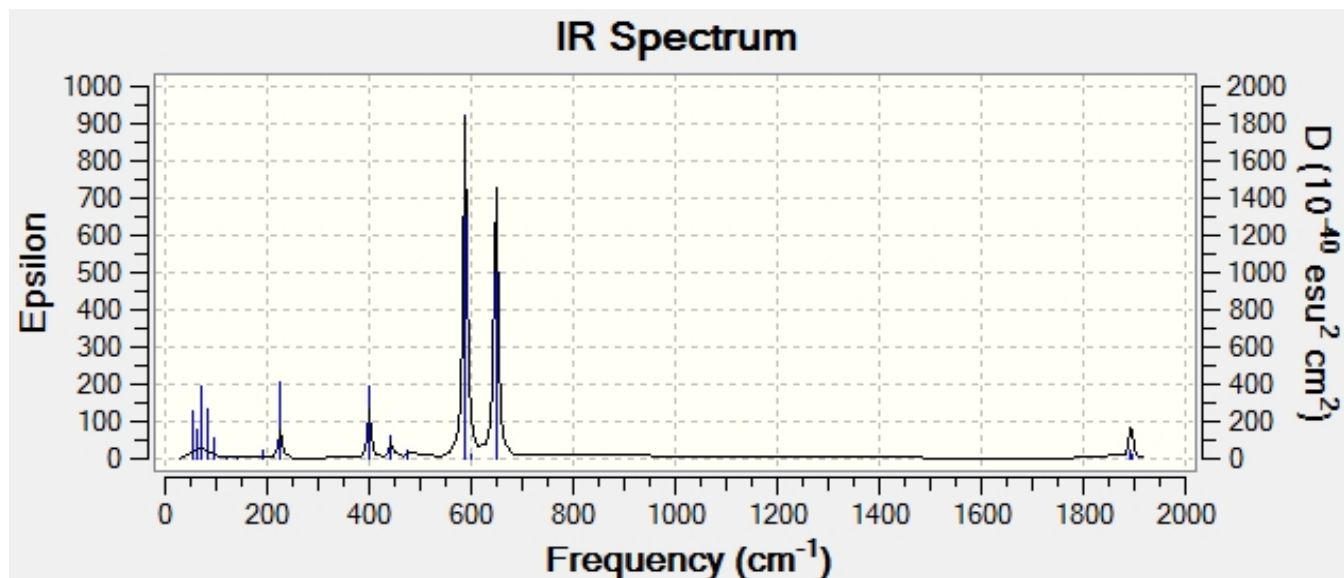


Figure 3 IR spectrum of $\text{Cu}_4\text{O}_3\text{H}_2$ system obtained from B3LYP/6-31G+ (d) methods.

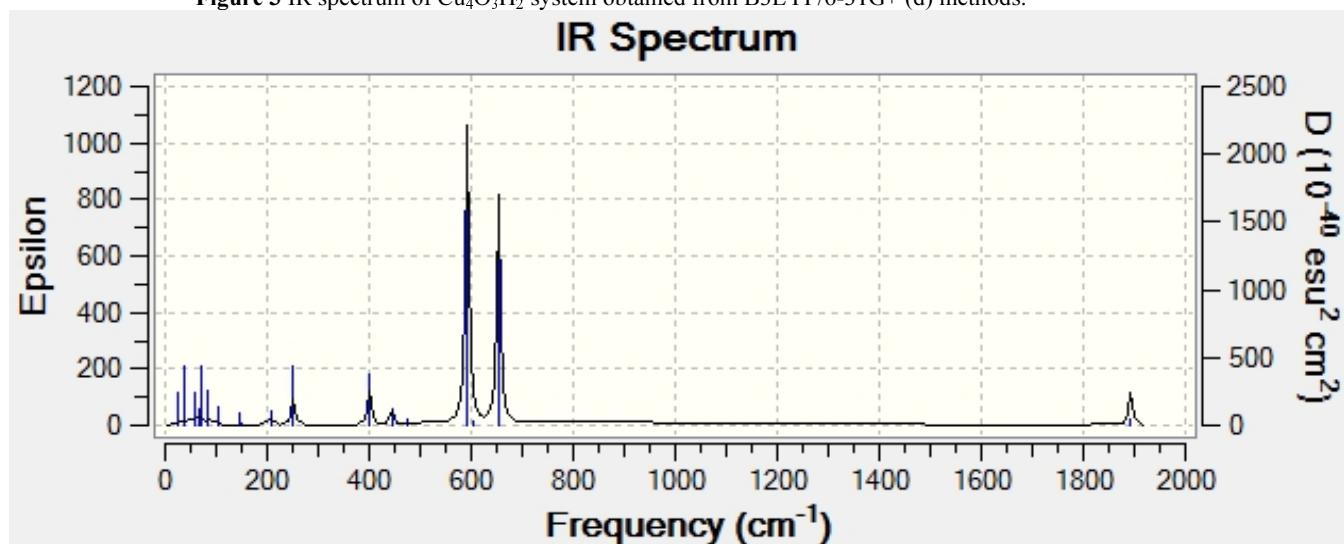


Figure 4 IR spectrum of $\text{Cu}_4\text{O}_3\text{H}_2$ system obtained from B1LYP/6-31G+ (d) methods.

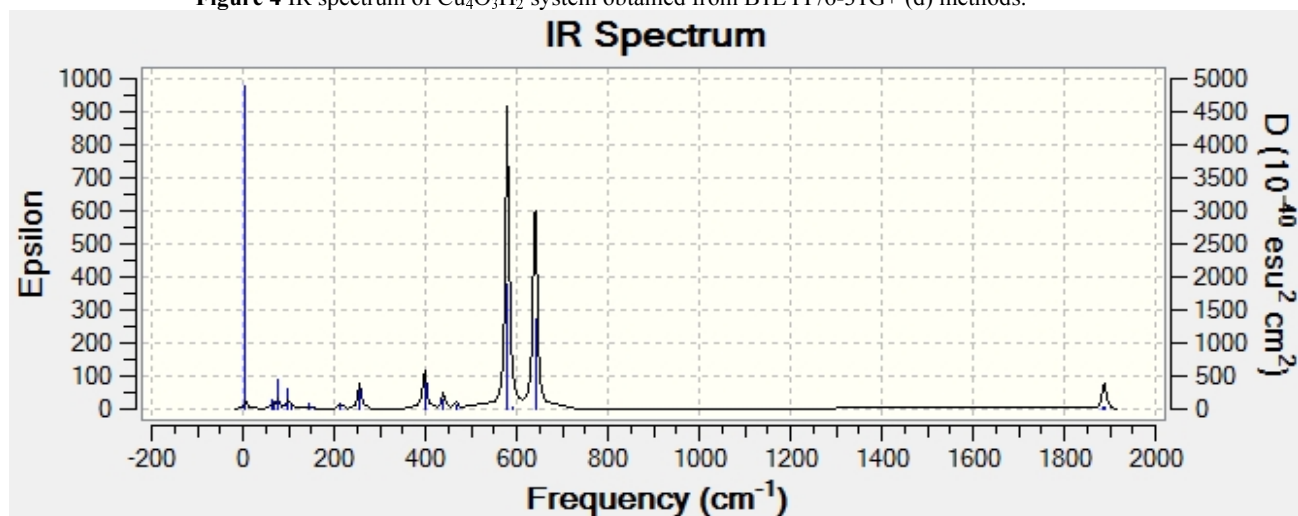


Figure 5 IR spectrum of $\text{Cu}_4\text{O}_3\text{H}_2$ system obtained from B3P86/6-31G+ (d) methods.

3.3 HOMO-LUMO Gap of the System

The HOMO-LUMO band gap is a gap between the LUMO (the lowest unoccupied molecular orbital) and HOMO (the highest occupied molecular orbital). The large LUMO-HOMO gap is often concerned as a molecule stability condition [39]. Both (LUMO) and (HOMO) are the main orbital accompanied in chemical reaction. The HOMO energy describes the ability of electron giving, LUMO describes the ability of electron accepting, and the gap between them describes the molecular chemical stability [40]. A critical parameter in determining molecular electrical transport property is the energy gap between the highest occupied and

the lowest unoccupied molecular orbitals, because it shows a measure of electron conductivity. Table 2 represented the band gap and dipole moment of $\text{Cu}_4\text{O}_3\text{H}_2$ molecule which are calculated in B3LYP, B1LYP and B3P86 levels of DFT theory. According to table 2 the obtained result for B3LYP levels of theory are in good agreement with reported experimental values [5]. Moreover, it could be observed that between B3LYP, B1LYP and B3P86 the largest band gap energy calculated for B3P86 levels of theory which caused the blue shift for $\text{Cu}_4\text{O}_3\text{H}_2$ nanosemiconductors molecule and the highest stability for this structure.

Table 2. Band gap in eV and dipole moment in Debye for $\text{Cu}_4\text{O}_3\text{H}_2$ molecule at different levels of theory with 6/31G+ (d) basis set.

Basis set	6-31G+(d)	
Method	band gap (HOMO-LUMO) (eV)	Dipole moment (Debye)
B3LYP	2.28	8.67
B1LYP	2.76	8.85
B3P86	2.32	8.82

3.4 Hyperfine spectroscopic parameters

Total atomic charge, electric potential, total atomic spin densities and voltage difference (a.u) at B3LYP, B1LYP, LSDA, B3P86 and B3PW91 levels of theory have been done and the results have been performed in table 3. As can be seen from table 3 and figure 6, Cu atoms has positive and oxygen has negative charge and the same trend have been found for all these levels of theory and all of them are in agreement with each other. Figure 7 represented Voltage of each atom versus atomic charge of $\text{Cu}_4\text{O}_3\text{H}_2$ molecule. Moreover, Voltage difference of this novel structure for each bond has been reported and maximum and minimum picks have been observed for all these levels of theory which performed that also they shows similar trend. The consequence exhibited electrical current go through all the atoms in the structure and the effluvium is not invariable and steady which emphasized the applications of this structure as a semiconductor.

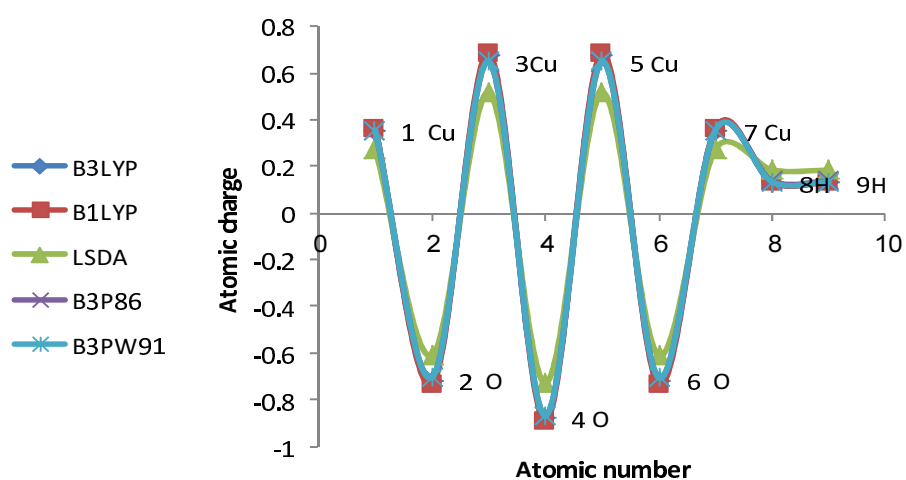


Figure 6 Atomic charges (a.u) of $\text{Cu}_4\text{O}_3\text{H}_2$ system as a function of atomic number at different levels of theory with 6-31G+ (d) basis set.

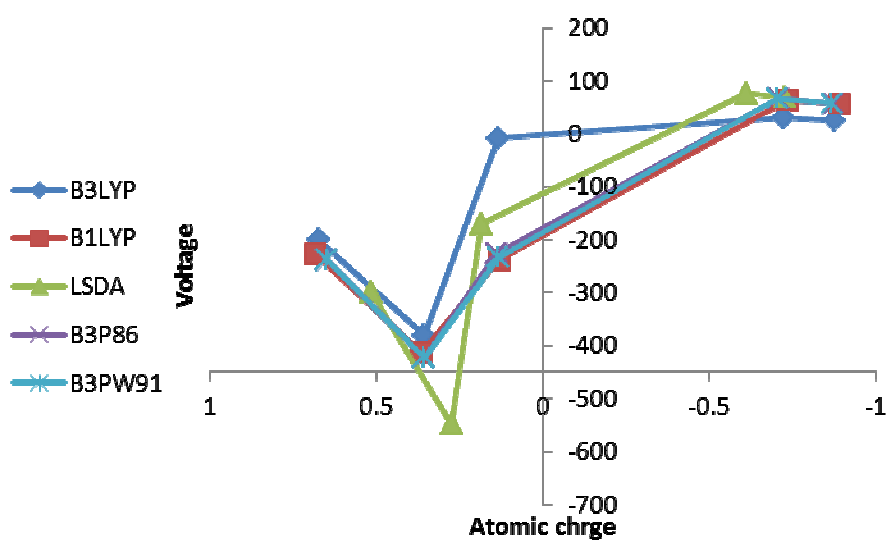


Figure 7 Voltage of $\text{Cu}_4\text{O}_3\text{H}_2$ systems as a function of atomic charge at different levels of theory with 6-31G+ (d) basis set.

Table 3. Total atomic charge (a. u), Electrical potential (a. u), total atomic spin densities and voltage difference (a. u) of Cu₄O₃H₂ molecule with EPR=6/31G+d at different levels of DFT theory.

EPR=6-31G+d												
Method	Total atomic charges	Electric potential	$\Delta V = V_2 - V_1$	Total atomic spin densities	Total atomic charges	Electric potential	$\Delta V = V_2 - V_1$	Total atomic spin densities	Total atomic charges	Electric potential	$\Delta V = V_2 - V_1$	Total atomic spin densities
B3LYP →												
1 Cu	0.36	-135.23	410.97	3.58	0.36	-150.76	477.12	3.58	0.27	-150.68	625.72	1.89
2 O	-0.72	-22.33	→	3.51	-0.74	-46.87	→	3.51	-0.61	-46.80	→	1.87
3 Cu	0.67	-135.21	226.41	1.83	0.69	-154.78	281.81	1.83	0.52	-154.71	368.38	1.35
4 O	-0.88	-22.35	→	1.31	-0.89	-50.00	→	1.31	-0.73	-49.91	→	1.14
5 Cu	0.67	-135.21	231.85	1.83	0.69	-154.78	289.61	1.83	0.52	-154.71	376.52	1.35
6 O	-0.72	-22.33	→	3.51	-0.74	-46.87	→	3.51	-0.61	-46.80	→	1.87
7 Cu	0.36	-135.23	372.45	3.58	0.36	-150.76	175.92	3.58	0.27	-150.68	379.23	1.89
8 H	0.13	-1.02	→	1.87	0.13	-31.35	→	1.87	0.18	-31.32	→	1.37
9 H	0.13	-1.02	372.45	1.87	0.13	-31.35	175.92	1.87	0.18	-31.32	379.23	1.37
B3P86 →												
1 Cu	0.36	-150.76	489.28	3.58	0.36	-150.76	489.60	1.89	-	-	-	-
2 O	-0.71	-46.86	→	3.51	-0.71	-46.86	→	1.87	-	-	-	-
3 Cu	0.65	-154.79	296.07	1.83	0.65	-154.79	295.62	1.35	-	-	-	-
4 O	-0.87	-49.99	→	1.31	-0.87	-49.99	→	1.14	-	-	-	-
5 Cu	0.65	-154.79	305.03	1.83	0.65	-154.79	304.42	1.35	-	-	-	-
6 O	-0.71	-46.86	→	3.51	-0.71	-46.86	→	1.87	-	-	-	-
7 Cu	0.36	-150.76	196.72	3.58	0.36	-150.76	188.68	1.89	-	-	-	-
8 H	0.14	-31.35	→	1.87	0.13	-31.35	→	1.37	-	-	-	-
9 H	0.14	-31.35	196.72	1.87	0.13	-31.35	188.68	1.37	-	-	-	-
B3PW91 →												
LSDA →												

Conclusion

In this paper we have been calculated thermodynamic properties, HOMO- LUMO gap which have shown molecular electrical transport property, dipole moment, vibrational frequencies, IR intensities and IR spectra of $\text{Cu}_4\text{O}_3\text{H}_2$ molecule with B3LYP, B1LYP and B3P86 levels of DFT theory and comparison between them have been done. The obtained results confirmed that these levels are in good agreement with each other's and implies this novel structure as a new semiconductor system. Comparison between theoretical and experimental result [5] indicant hybrid functional theory are capable of performing reliable molecular properties.

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10/23/2012