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Theoretical study for Vibration, Energy gap and Thermodynamic of Tetrahydrofuran (THF) pure and its Derivatives in Gas Phase Base on DFT

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The spectroscopic, vibrational and electronic properties of Tetrahydrofuran (THF) pure and its derivatives (THF amino, THF diamino, THF Cu, THF 2Cu), Density functional theory was used to perform of calculation the gas phase. Energy gap, and thermodynamic properties we have plotted frontier orbital HOMO-LUMO surface to explain the reactive nature of THF and its derivatives. It was observed to have $E_{LUMO} - E_{HOMO}$ energy gap of THF Cu (2.085eV), THF 2Cu (0.987eV) with LDA, Moreover, The Thermodynamic properties parameters such as thermal energy, entropy(S), Enthalpy, Gibbs free energy and molar heat Capacity(Cp) of this compound in the gas phase in different temperatures were determined by DFT Tetrahydrofuran and its derivatives are an excellent candidate for future studies of semiconductor and optoelectronic materials.

Keywords: DFT, Vibration, Energy gap, Thermodynamic

1 Introduction

Tetrahydrofuran (THF), or oxolane, is an organic compound with the formula $(CH_2)_4O$. The compound is classified as heterocyclic compound, specifically a cyclic ether. It is a colorless, water-miscible organic liquid with low viscosity. It is mainly used as a precursor to polymers[1]. its Molecular Weight 72.11 g/mol and Boiling point 151 F at 760 mm Hg , Melting Point163.3 F/ -108.5 C [2,3]. The discovery of ‘‘organic semiconductors’’ dates back to the 1940s[4]. Organic semiconductors have been investigated for about a century. These materials have entirely different properties to their inorganic counterparts: they are formed of organic molecules which are bound by the van der Waals interaction. The main difference is that the electronic coupling due to the van der Waals interaction is much weaker than the covalent coupling. Therefore, organic semiconductors are characterized by a typically much lower electron or hole mobility than inorganic semiconductors[5].

Nevertheless, Organic molecular semiconductors have attracted considerable attention because of the prospect of utilizing properties inherent in organic molecules, such as low cost, ease of manufacturing, flexibility, and freedom of design, for creating a new class of electronic devices. Indeed, organic semiconductors have been demonstrated to yield important (opto) electronic devices[6], organic light emitting diodes (OLED), displays, transistors, and solar cells[7] .Current and future applications of organic semiconductors range from commercially available OLED displays, and infrared applications. Compared to inorganic materials, the use of organic semiconductors are attractive because these materials offer many advantages, for example, low cost and the ability to form thin films, which enable the fabrication of large-area and flexible devices. Organic semiconductors include both small molecules and polymers, small molecules have advantages such as easier synthetic procedures, purification methods, and characterization in view of their small size and well-defined structure[8]. Within the last 30 years, density-functional theory (DFT) has been applied to computational studies of a large variety of properties both for crystalline systems and molecules[9]. Density functional theory (DFT) description of electronic structure and related properties offer significant accuracy with low cost. Unfortunately, most of these calculations based on LDA and GGA Exchange-Correlation (XC) functionals are underestimating the energy band gap[10]. density functional theory (DFT) has become a popular approach for the computation of molecular structures, vibrational frequencies and energies of chemical reactions[11]. In this paper ,This study's aim is to investigate (CH2)4O vibration spectrum and electronic structure in the IR region,

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using DFT with the Local-density Approximations (LDA) and Generalized Gradient Approximations (GGA) functional. One important characteristics that have been studied are for the thermodynamic principles which is concerned with the energy transformation of the substance in the empty space that the substance occupies (system) and the subsequent shift in its energy level the internal energy is a type of potential energy in the system which plays a role in many concepts, including heat capacity its unit cal.mol-1 deg-1[12]. The enthalpy of all materials is dependent on pressure, temperature, and internal energy, except for gases that behave ideally or almost ideally[13]. The distinctive characteristic that relates to the stability of the compound is either the heat of formation or the enthalpy of formation. If it is positive, the compound is unstable, and if it is negative, it is stable. Entropy (S), which is a measure of the resulting randomness of a compound due to the change in temperature degrees, is another function[14]. Additionally, free Gibbs energies were calculated using Materials Studio 2017.

2 Calculation Methods

This study used density functional theory (DFT) with GGA and LDA approximations in (Material Studio 2017) to computationally investigate the spectroscopic and thermodynamic properties[15]. The calculations have been carried DFT out using the Dmol3 module in material studio2017 program package[16]. The Generalized Gradient Approximations (GGA) and Local –density Approximations (LDA) were gradient performed to optimize the conformation of the molecular structure of THF. Calculating the IR spectrum in the ground state. In addition, computation the electronic properties such as total energy, highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) and energy gap between the (HOMO) and (LUMO) Levels

$E_g = E_{LUMO} - E_{HOMO}$[17,18].

The HOMO and LUMO energies were used to determine:

Ionization Potential (I)

Ionization potential refers to the ability of a molecule or ion to donate electrons or, in simpler terms, the energy required to remove electrons from the system. The energy of the highest occupied molecular orbital (HOMO) is directly connected to the ionization potential, as depicted in the following equation[19,20].

$$I = |-E_{HOMO}| \qquad \text{... (1)}$$

Electronic Affinity (A)

Electron affinity refers to the capacity of a molecule or ion to attract and capture electrons from other species. It characterizes the energy variation that takes place when electrons are introduced to a neutral atom, leading to the creation of a negatively charged ion[21]. The energy of the lowest unoccupied molecular orbital (LUMO) is closely associated with electron affinity, and this connection is expressed through equation[19].

$$A = |-E_{LUMO}| \qquad \text{... (2)}$$

Chemical Hardness(η)

Hardness is a qualitative assessment of the polarizability of an atom, ion, or molecule, indicating the degree to which its electron cloud is distorted by an electric field.The stability of interacting molecules is influenced by their hardness, which can be assessed using the following mathematical representation[22,23].

$$\eta = \frac{(1-A)}{2} \qquad \text{... (3)}$$

Electronegativity (χ)

Electronegativity refers to the ability of a molecule to attract electrons towards itself. This property can be measured by taking the negative average energy value of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), as represented below.

$$\chi = \frac{(1+A)}{2} \qquad \text{... (4)}$$

Softness (S)

Softness is a quantitative measure reflecting the extent of charge transfer occurring within a molecule. Molecules with a narrow HOMO-LUMO energy gap are considered soft because they demand minimal energy to undergo excitation. Reactivity-wise, molecules possessing a high softness value exhibit greater reactivity but lower stability compared to hard molecules. Put simply, the softness of a molecule can be expressed as the inverse of its hardness [22,24].

$$S = \frac{1}{2\eta} \qquad \text{... (5)}$$

Electrophilicity Index (ω)

The electrophilicity index (ω) quantifies the decrease in energy experienced by a molecule as a result of the flow of electrons between a donor and an acceptor. It can be computed using the following mathematical expression [25].

$$\omega = \frac{\chi^2}{2\eta} \qquad \text{... (6)}$$

Some thermal (thermodynamic) properties of a molecule were also calculated, including entropy, enthalpy, heat capacity, and free energy of compression at standard temperature (289K), and compared with previous studies.

3 Results and Discussion

3.1 Molecular Geometry

The structural diagram of the THF molecule was drawn using the (Materials Studio 2017) program, and the geometric optimization of the molecule was performed to obtain a stable and balanced shape, After drawing the molecule, the bond length of the optimized structural parameters of THF calculated by the GGA and LDA approximations The THF molecule was obtained in equilibrium (lowest energy level) after engineering optimization of the molecule and we calculated some of the properties and energies involved in the molecule (total energy, binding energy, some of atomic energies, kinetic energy, electrostatic energy, spin polarization, exchange-correlation , Zero point energy, molecular weight using the(Dmol3) program by (LDA and GGA) approximation as in Table 1.

3.2 Vibrational Frequencies and Patterns

The vibrational frequencies of the THF molecule were calculated under the study of the DFT method using the dmol3 program with the LDA and GGA

Table 1 — shows the results of some properties and energies of the THF molecul

Quantum	Calculated Value		Unit
	THF pure		
	LDA	GGA	
Total Energy	-6280.226059922	-6327.004000915	eV
Sum of atomic energy	-6217.5773442513	-6270.664718193	eV
Kinetic Energy	-55.102338350394	-52.96386413658	eV
Electrostatic	-43.82010577226	-41.31835531962	eV
Spin Polarization	14.484871061344	16.**436943148775**	eV
Binding Energy	-62.64870	-56.33927	eV
Exchange-correlation	21.787865554098	21.505999028448	eV
Zero point vibration energy	71.326	71.814	Kcal/mol
Molecular weight	72.106600	72.10660	amu
	THF Amino		
	LDA	GGA	
Total Energy	-7776.84609851962	-7833.836449268	eV
Sum of atomic energy	-7705.1708266889	-7769.778509814	eV
Kinetic Energy	-60.3094063683250	-58.79650172413	eV
Electrostatic	-55.627748084848	-51.49736036507	eV
Spin Polarization	18.538480651096	20.806462062495	eV
Binding Energy	-71.67527	-64.05794	eV
Exchange-correlation	25.722388531599	25.429	eV
Zero point vibration energy	82.069	82.569	Kcal/mol
Molecular weight	87.121200	87.121200	amu
	THF Diamino		
	LDA	GGA	
Total Energy	-9273.32335892179	-9340.471478921	eV
Sum of atomic energy	-9192.7643064053	-9268.89230415687	eV
Kinetic Energy	-65.840378418405	-64.32092012136	eV
Electrostatic	-67.0938632176091	-61.87938963703	eV
Spin Polarization	22.59408751970902	25.175980976215	eV
Binding Energy	-80.55905	-71.51916	eV

(*Contd.*)

Table 1 — shows the results of some properties and energies of the THF molecul (*Contd.*)

Exchange-correlation	29.7811043210271	29.444839493379	eV
Zero point vibration energy	92.722	93.562	Kcal/mol
Molecular weight	102.135800	102.135800	amu
	THF Cu		
	LDA	GGA	
Total Energy	-51072.94947147	-51188.84027691	eV
Sum of atomic energy	-51007.23925332	-51130.38984428	eV
Kinetic Energy	-150.8591529055	-151.8446272220	eV
Electrostatic	48.42734616369	54.23972486682	eV
Spin Polarization	14.9477940534078	17.17900064231	eV
Binding Energy	-65.70908	-58.44967	eV
Exchange-correlation	21.77378909888	21.97547996697	eV
Zero point vibration energy	73.341	73.521	Kcal/mol
Molecular weight	136.6605	136.6605	amu
	THF 2Cu		
	LDA	GGA	
Total Energy	-95834.374063079	-96018.85385918	eV
Sum of atomic energy	-95770.686661207	-95962.73704867	eV
Kinetic Energy	-181.78570734089	-181.2306084655	eV
Electrostatic	82.92626710545	87.48490250112	eV
Spin Polarization	14.353216884598	16.41672508145	eV
Binding Energy	-63.65381	-56.08455	eV
Exchange-correlation	20.818821478616	21.21217037306	eV
Zero point vibration energy	66.890	66.80	Kcal/mol
Molecular weight	199.1986	199.198	amu

approximations in the infrared region through the wavenumber in (cm^{-1}) and the intensity in (km/mol). According to the relationship for nonlinear molecules (3N-6), there were THF pure(33) mode, THF amino(39) mode, THF diamino(44) mode, THF Cu(45) mode, THF 2Cu GGA(45) mode - THF 2Cu LDA(39) mode, in the molecule. The results in Table (2-7) respectively, show that the vibrational frequencies of the particle are close to the theoretical and practical results in the literature.

3.3 Electronic Properties

Calculating the energy values for the highest occupied molecular orbital, E_{HOMO} and the lowest unoccupied molecular orbital, E_{LUMO}, using the DFT method in the dmol3 program with the LDA and GGA approximations. The energy difference between HOMO and LUMO is called the energy gap. Shows the interaction of that molecules with other species. Frontier orbital energy gap helps to differentiate the chemical reactivity of the molecules. In case of tetrahydrofuran and its derivatives, frontier orbital energy gaps is THFpure (6.478eV), THF amino(4.131eV), THF diamino(6.035eV), THF Cu (2.085eV), THF2Cu(0.981eV),with the LDA approximation and its value is THFpure (6.664eV), THF amino (3,947eV), THF diamino(6.164eV), THF Cu (2.227eV), THF 2Cu (1.769eV), with the GGA approximation, respectively, and is given in Table (8). So it can be concluded that THF 2Cu (LDA) is the most reactive compound among all. The picture of HOMO, LUMO, for tetrahydrofuran and its derivatives are shown in Fig. 2.

Table 8 shows the energy gap between HOMO and LUMO. It can be calculated. Through ($Egap = E_{LUMO} - E_{HOMO}$) its value is THFpure (6.478), THF amino(4.131), THF diamino(6.035), THF Cu(2.085), THF2Cu(0.981), (1.49 eV) with the LDA approximation and its value is THFpure (6.664), THF amino (3,947), THF diamino(6.164), THF Cu (2.227), THF 2Cu (1.769), (1.5 eV) with the GGA approximation and the results are compared with the theoretical and experimental values of previous studies shown in the Table 8.

After obtaining the values of HOMO and LOMO in the THF Pure, THF Amino , THF Diamino, THF Cu, THF 2Cu, molecule, some electronic properties were calculated (Ionization potential (I), electronic affinity (A) Chemical hardness(η), Electronegativity (χ), Softness (S) and electrophilic(ω)) using the equation 1,2,3,4 and 5 respectively as shown in Table 9.

Table 2 — The vibrational frequencies of the THF, molecule are calculated using LDA and GGA approximations and compared with practical and theoretical values

Vib. Mode	THF Pure LDA		THF Pure GGA		Exp[26]
	Wave number cm-	Intensity Km/mol	Wave number cm-	Intensity Km/mol	Wave number cm-
1	47.6	4.32	78.4	4.63	
2	268.8	0.00	263.9	0.01	281
3	559.8	1.10	575.1	1.10	
4	663.8	3.79	657.9	3.12	644
5	832.7	4.33	831.9	10.96	
6	872.8	4.52	867.1	11.25	866
7	899.6	3.78	880.1	18.89	
8	920.7	35.88	890.2	5.37	901
9	941.9	0.81	912.8	6.32	941
10	951.5	0.19	949.7	0.06	959
11	1025.9	3.57	1012.4	3.29	1046
12	1099.6	102.66	1042.2	107.11	1097
13	1133.1	0.17	1139.9	0.25	
14	1143.0	21.09	1144.3	4.60	
15	1166.3	7.15	1156.6	5.47	
16	1219.7	0.46	1221.9	4.13	1214
17	1226.7	8.40	1236.2	3.27	
18	1261.2	2.87	1277.1	0.86	1261
19	1291.8	1.67	1304.5	0.43	1268
20	1312.6	0.62	1322.7	0.56	
21	1340.1	0.51	1364.3	1.52	1395
22	1413.3	10.67	1452.7	5.59	
23	1422.6	12.27	1461.2	6.66	
24	1454.5	1.66	1480.3	0.78	
25	1467.8	0.00	1494.9	0.11	1506
26	2916.7	147.28	2951.8	152.26	2958
27	2923.8	1.69	2958.8	5.16	2968
28	2988.0	14.06	3016.6	17.34	
29	2993.5	4.45	3028.2	15.90	
30	3008.4	87.97	3037.8	61.44	
31	3008.7	2.13	3053.5	45.41	
32	3057.7	9.84	3077.4	22.18	3052
33	3064.1	22.39	3092.1	33.88	3062

Table 3 — The vibrational frequencies of the THF Amino, molecule are calculated using LDA and GGA approximations and compared with practical and theoretical values

Vib. Mode	AminoTHF LDA		Amino THF GGA		Exp[26]
	Wave number cm-	Intensity Km/mol	Wave number cm-	Intensity Km/mol	Wave number cm-
1	70.5	2.66	99.5	5.08	
2	242.9	32.02	190.9	35.71	197
3	253.3	14.15	252.6	5.85	
4	417.0	2.41	405.6	4.90	
5	520.2	7.75	508.3	6.90	
6	588.4	1.71	599.8	1.59	
7	719.4	46.05	715.3	17.71	
8	775.2	96.58	792.0	114.10	778
9	825.6	7.17	824.1	1.02	
10	852.8	4.41	844.1	19.77	877
11	905.5	21.76	884.7	30.58	
12	932.6	6.85	916.8	4.78	
13	954.7	26.84	932.3	23.85	957
14	1021.6	11.36	1002.5	27.45	
15	1027.9	9.46	1012.6	12.40	

(*Contd.*)

Table 3 — The vibrational frequencies of the THF Amino, molecule are calculated using LDA and GGA approximations and compared with practical and theoretical values (*Contd.*)

Vib. Mode	AminoTHF LDA		Amino THF GGA		Exp[26]
	Wave number cm-	Intensity Km/mol	Wave number cm-	Intensity Km/mol	Wave number cm-
16	1078.8	110.99	1057.0	100.45	1067
17	1109.2	16.51	1101.1	12.04	
18	1158.0	13.49	1166.9	6.72	1133
19	1183.7	12.07	1193.7	8.10	
20	1192.0	9.64	1200.1	8.37	
21	1226.4	1.56	1233.2	0.46	
22	1260.2	10.09	1274.5	7.70	
23	1271.1	4.35	1290.6	1.46	
24	1310.4	3.87	1332.7	0.90	
25	1331.0	27.09	1349.1	28.64	
26	1346.5	6.87	1376.5	8.88	
27	1405.8	3.05	1445.3	2.17	
28	1423.6	15.82	1461.0	7.04	
29	1440.8	9.50	1476.6	5.26	1443
30	1570.8	52.84	1583.9	36.09	1647
31	2920.7	77.62	2966.2	85.25	
32	2944.6	37.36	2986.2	46.29	2971
33	2998.3	21.91	3035.1	26.60	2993
34	3005.3	20.01	3043.1	31.62	
35	3053.2	6.39	3086.1	1.30	3023
36	3057.6	18.80	3099.1	26.15	3058
37	3068.4	25.21	3108.8	46.97	3095
38	3423.5	0.54	3417.0	0.41	
39	3520.6	7.31	3510.5	1.59	3595

Table 4 — The vibrational frequencies of the THF Diamino, molecule are calculated using LDA and GGA approximations and compared with practical and theoretical values

Vib. Mode	DiaminoTHF LDA		DiaminoTHF GGA		Exp[26]
	Wave number cm-	Intensity Km/mol	Wave number cm-	Intensity Km/mol	Wave number cm-
1	94.5	1.66	108.3	1.25	
2	192.1	10.69	183.2	9.89	
3	229.3	18.26	260.2	18.38	257
4	308.7	2.95	291.8	7.14	
5	359.0	17.77	359.9	10.58	
6	389.8	25.14	388.5	22.90	424
7	513.7	26.92	508.7	23.09	
8	549.1	3.97	540.3	10.11	
9	662.4	13.40	651.7	4.66	
10	708.6	18.37	706.8	8.50	
11	764.0	150.40	807.3	137.20	753
12	795.1	58.55	812.3	16.02	
13	858.0	30.70	848.1	91.93	
14	871.2	31.79	881.4	42.33	
15	933.5	3.20	906.2	7.61	921
16	967.6	18.69	939.4	17.96	
17	995.8	7.30	982.7	9.44	954
18	1004.9	7.55	992.8	28.86	1029
19	1078.0	113.87	1048.3	123.96	1068
20	1097.3	17.91	1089.6	2.29	
21	1132.8	7.57	1105.1	11.42	
22	1145.7	19.87	1160.1	6.53	1164
23	1183.0	10.29	1192.2	4.88	
24	1205.6	1.89	1221.4	6.92	
25	1220.8	4.32	1226.8	0.70	

(*Contd.*)

Table 4 — The vibrational frequencies of the THF Diamino, molecule are calculated using LDA and GGA approximations and compared with practical and theoretical values (*Contd.*)

Vib. Mode	DiaminoTHF LDA		DiaminoTHF GGA		Exp[26]
	Wave number cm-	Intensity Km/mol	Wave number cm-	Intensity Km/mol	Wave number cm-
26	1256.4	16.34	1283.0	5.64	
27	1278.1	4.98	1318.3	1.67	
28	1314.3	25.83	1337.1	7.51	
29	1329.9	1.33	1344.4	14.69	
30	1339.1	13.27	1364.6	16.92	
31	1354.5	3.67	1382.6	1.86	
32	1412.6	6.41	1448.5	4.50	
33	1437.2	10.53	1474.3	3.52	1446
34	1552.1	78.79	1592.1	53.27	
35	1581.9	51.32	1617.3	35.99	1669
36	2928.4	35.10	2969.2	21.48	
37	2944.8	73.73	2988.3	107.35	
38	2966.2	48.18	3001.5	52.12	2974
39	2990.9	21.54	3035.5	27.18	3034
40	3030.9	10.96	3079.5	18.68	3044
41	3053.3	27.53	3098.4	37.46	3074
42	3343.7	68.01	3410.3	30.00	
43	3427.4	0.77	3425.4	1.22	
44	3517.4	11.14	3513.5	3.71	3578

Table 5 — The vibrational frequencies of the THF Cu, molecule are calculated using LDA and GGA approximations and compared with practical and theoretical values

Vib, Mode	THF Cu LDA		THF Cu GGA	
	Wave number cm-	Intensity Km/mol	Wave number cm-	Intensity Km/mol
1	-72.0	0.22	-26.5	0.38
2	-0.0	0.00	-0.0	0.47
3	-0.0	0.42	-0.0	0.62
4	-0.0	0.53	-0.0	0.53
5	-0.0	0.64	0.0	0.42
6	0.0	1.57	0.0	0.61
7	0.0	0.37	0.0	0.75
8	115.6	42.62	120.5	13.51
9	143.7	4.12	139.5	16.29
10	214.9	1.54	204.5	1.93
11	296.2	20.95	270.1	14.69
12	376.4	33.96	352.0	61.94
13	561.2	68.83	532.1	67.60
14	668.8	2.39	663.9	2.24
15	713.4	73.19	711.7	74.50
16	738.5	10.56	734.9	13.07
17	781.8	11.47	776.9	7.69
18	843.5	146.22	829.0	198.20
19	871.7	68.55	873.2	46.54
20	915.2	20.91	899.8	24.75
21	930.9	28.77	913.5	8.16
22	941.2	9.90	926.3	59.09
23	975.3	16.70	957.8	9.27
24	1044.1	27.09	1041.9	6.25
25	1058.3	21.34	1063.1	68.45
26	1152.5	46.08	1156.5	25.87
27	1185.1	84.08	1162.8	123.68

(*Contd.*)

Table 5 — The vibrational frequencies of the THF Cu, molecule are calculated using LDA and GGA approximations and compared with practical and theoretical values (*Contd.*)

Vib, Mode	THF Cu LDA		THF Cu GGA	
	Wave number cm-	Intensity Km/mol	Wave number cm-	Intensity Km/mol
28	1202.7	13.08	1202.3	9.06
29	1217.5	30.42	1213.4	12.89
30	1243.6	10.26	1252.7	8.88
31	1257.0	7.24	1274.5	3.50
32	1299.8	3.48	1322.3	1.67
33	1352.2	13.81	1365.3	8.73
34	1393.7	61.29	1430.6	31.07
35	1399.4	5.01	1432.4	5.87
36	1433.8	33.23	1471.7	18.66
37	1821.5	324.28	1757.4	400.01
38	1917.5	44.40	1858.9	35.65
39	2916.7	4.07	2991.8	14.40
40	2978.5	8.33	3003.9	10.35
41	3021.8	18.88	3044.6	24.53
42	3058.2	4.86	3098.2	7.61
43	3067.2	9.91	3121.1	24.26
44	3079.5	8.51	3126.0	2.17
45	3113.7	6.52	3131.7	8.43

Table 6 — The vibrational frequencies of the THF 2Cu, molecule are calculated using GGA approximations and compared with practical and theoretical values

Vib. Mode	THF 2Cu GGA	
	Wave number cm-	Intensity Km/mol
1	-8.5	1.75
2	-0.0	1.62
3	-0.0	1.70
4	-0.0	0.63
5	0.0	0.14
6	0.0	1.75
7	0.0	1.51
8	49.6	0.87
9	110.8	4.04
10	157.8	15.99
11	171.5	11.35
12	206.6	26.02
13	252.3	9.04
14	379.0	17.97
15	406.7	134.80
16	489.8	27.27
17	563.5	57.03
18	647.7	1.72
19	769.5	4.53
20	810.3	8.06
21	816.6	20.09
22	864.7	60.92
23	902.6	14.00
24	925.9	6.78
25	978.0	4.99
26	1028.0	11.33
27	1073.5	65.63
28	1145.5	55.53
29	1160.4	14.87
30	1192.7	41.78
31	1248.6	216.88
32	1259.5	50.14
33	1286.0	12.36
34	1354.3	5.63
35	1442.2	3.98
36	1459.7	10.08
37	1477.2	31.31
38	1513.8	38.86
39	1910.4	104.29
40	3002.6	33.24
41	3029.4	24.83
42	3089.6	7.19
43	3121.8	18.50
44	3193.5	1.45
45	3235.4	7.07

Table 7 — The vibrational frequencies of the THF 2Cu, molecule are calculated using LDA approximations and compared with practical and theoretical values

Vib. Mode	THF 2Cu LDA	
	Wave number cm-	Intensity Km/mol
1	25.8	1.64
2	49.3	0.09
3	122.7	3.34
4	183.3	24.42
5	197.2	21.51
6	217.1	10.21

(*Contd.*)

Table 7 — The vibrational frequencies of the THF 2Cu, molecule are calculated using LDA approximations and compared with practical and theoretical values (*Contd.*)

Vib. Mode	THF 2Cu LDA	
	Wave number cm-	Intensity Km/mol
7	267.5	10.52
8	414.3	146.46
9	418.2	1.30
10	511.1	27.98
11	572.5	44.91
12	639.2	1.56
13	754.3	10.64
14	823.7	18.14
15	835.9	14.93
16	873.3	34.75
17	930.3	14.79
18	943.4	11.62
19	991.7	6.69
20	1019.0	4.51
21	1063.8	33.24
22	1147.2	37.25
23	1178.1	63.54
24	1201.1	28.91
25	1252.0	7.16
26	1282.3	19.35
27	1230.2	241.94
28	1347.5	7.50
29	1408.4	7.75
30	1424.0	18.68
31	1496.3	56.80
32	1557.2	9.73
33	1991.4	75.44
34	2938.8	13.65
35	2959.3	27.88
36	3052.8	2.90
37	3084.9	12.07
38	3124.2	4.47
39	3171.5	7.82

3.4 Thermodynamic Properties

3.4.1 Entropy (S)

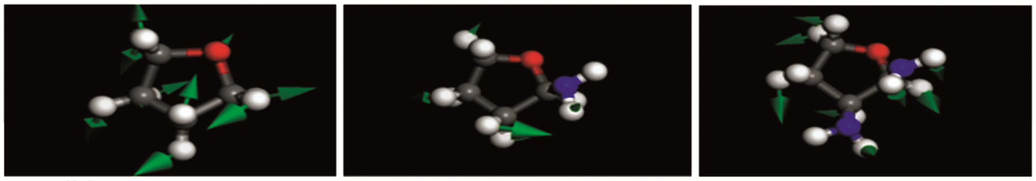
The entropy was calculated to describe the randomness of the compound at different temperatures extending from (25^0K -$1000\ ^0$K) which includes the standard temperature (298 ºK). A graph of the entropy values with temperature was drawn as in the Fig. 3. It was shown that the entropy values (the randomness of the molecule) increased with increasing temperature, and the entropy value at the standard temperature was equal to these values as shown in Table 10. which is close to the theoretical value obtained from previous studie ((THF pure (67.259 cal/k.mol)), (THFAmino(78.055 cal/k.mol). THF Diamino(81.513 cal/k.mol))[26].

3.4.2 Heat Capacity (Cp)

The heat capacity is the total energy required to raise the temperature of the substance and is symbolized by the symbol Cp. The heat capacity was calculated at different temperatures starting from (25^0K-1000^0K) and at room temperature 298ºK and the pressure 1 atm equals to these values as shown in Table 11. which is close to the theoretical value obtained from previous studies ((THF pure (14.943 cal/k.mol),THF Amino(22.356 cal/k.mol). THF Diamino (26.632 cal/k.mol))[26]. Figure 4 shows the relationship between temperature and heat capacity. As the temperature rises, the population of particles in higher vibrational energy levels increases, leading to an increase in the heat capacity at constant pressure.

3.4.3 Enthalpy

The enthalpy function represents the combined internal and external energy of a system. It is



(1a): THF Pure (Mode: 5)
Frequency (LDA):832.7cm^{-1}
Frequency(GGA):831.9cm^{-1}

(1b): THF Amino (Mode: 12)
Frequency (LDA):932.6cm^{-1}
Frequency(GGA):916.8cm^{-1}

(1c) · THF Diamino (Mode:20)
Frequency (LDA):1097.3cm^{-1}
Frequency (GGA):1089.6cm^{-1}

(1d): THF CU(Mode:24)
Frequency (LDA):1044.1cm^{-1}
Frequency (GGA):1041.9cm^{-1}

(1e): THF 2CU (Mode:|30)
Frequency (LDA):1496.3cm^{-1}
Frequency (GGA):1192.7cm^{-1}

Fig. 1 — (a-e) shows a description of some vibrational modes of the THF molecule using the dmol3 program by indicating the directions of vibration of the atoms with arrows and indicating the intensity of each mode

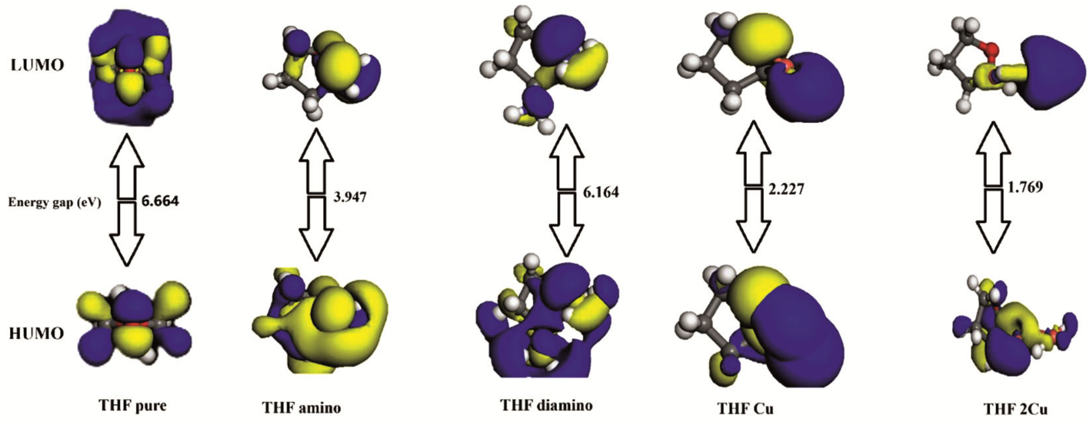


Fig. 2 — The HOMO, LUMO for THF molecule GGA Approximation

Table 8 — The HOMO, LUMO and energy gap for the THF Pure,THFAmino,THFDiamino molecule using the LDA and GGA approximations

parameters	THF Pure LDA	THF Pure GGA	Exp work[26]	THF Amino LDA	THF Amino GGA	Exp work[26]	THF Diamino LDA	THF Diamino GGA	Exp work[26]
HOMO(eV)	-5.535	-5.375	-0.255	-4.501	-4.315	-0.233	-5.428	-5.315	-0.222
LUMO(eV)	0.943	1.289	-0.036	-0.370	-0.368	0.020	0.607	0.845	0.028
Eg(eV)	6.478	6.664	7.040	4.131	3.947	6.906	6.035	6.164	6.831

Parameters	THF Cu LDA	THF Cu GGA	THF 2Cu LDA	THF 2Cu GGA
HOMO(eV)	-5.543	-5.469	-4.834	-4.583
LUMO(eV)	-3.458	-3.242	-3.853	-2.814
Eg(eV)	2.085	2.227	0.981	1.769

Table 9 — The electronic molecular properties of the THF Pure, THF Amino,THFDiamino using LDA and GGA approximation

Parameters	THF Pure LDA	THF Pure GGA	Exp work[26]	THF Amino LDA	THF Amino GGA	Exp wor[26]	THF Diamin LDA	THF Diamin GGA	Exp work[26]
Ionization potential (I.P) (eV)	5.353	5.375	---	4.501	4.315	---	5.428	5.315	---
Electronic affinity (E.A)(eV)	-0.943	-1.289	---	0.370	0.368	---	-0.607	-0.845	---
Chemical hardness (η)(eV)	3.239	3.332	0.145	2.0655	1.9735	0.134	3.0175	3.08	0.133
Electronegativity (χ)(eV)	2.296	2.043	0.109	2.4355	2.3415	0.100	2.4104	2.235	0.101
Softness (S)(eV)	0.1501	0.1500	3.425	0.1883	0.253	3.706	0.1657	0.1623	3.731
Electrophilic (ω)(eV)	0.7718	0.6262	0.04	1.435	1.389	0.037	0.962	0.8109	0.038

Parameters	THF Cu LDA	THF Cu GGA	THF 2Cu LDA	THF 2Cu GGA
Ionization potential (I.P)(eV)	5.543	5.469	4.834	4.583
Electronic affinity (E.A)(eV)	3.458	3.242	3.853	2.814
Chemical hardness (η)(eV)	1.0425	1.1135	0.4905	0.8845
Electronegativity (χ)(eV)	4.5005	4.3555	4.343	3.698
Softness (S)(eV)	0.4796	0.449	1.019	0.565
Electrophilic (ω)(eV)	9.714	8.518	19.226	7.730

evaluated at various temperatures. Its value was calculated at standard temperature $298^0$and is equal to these values as shown in Table 12. The plot in Fig. 5 illustrates the correlation between the temperature of the THF molecule and its corresponding enthalpy values. The direct relationship observed indicates that enthalpy is dependent on temperature.

3.4.4 Gibbs Free Energy

The entropy and enthalpy changes were analyzed for the temperature range of (25^0K-1000^0K) of the THF molecule. These values were used to calculate the Gibbs free energy, employing the equation $\Delta G = \Delta E - T\Delta S$, at the standard temperature of these values as shown in Table 13. A graphical representation, as shown in Fig. 6, depicted an inverse relationship

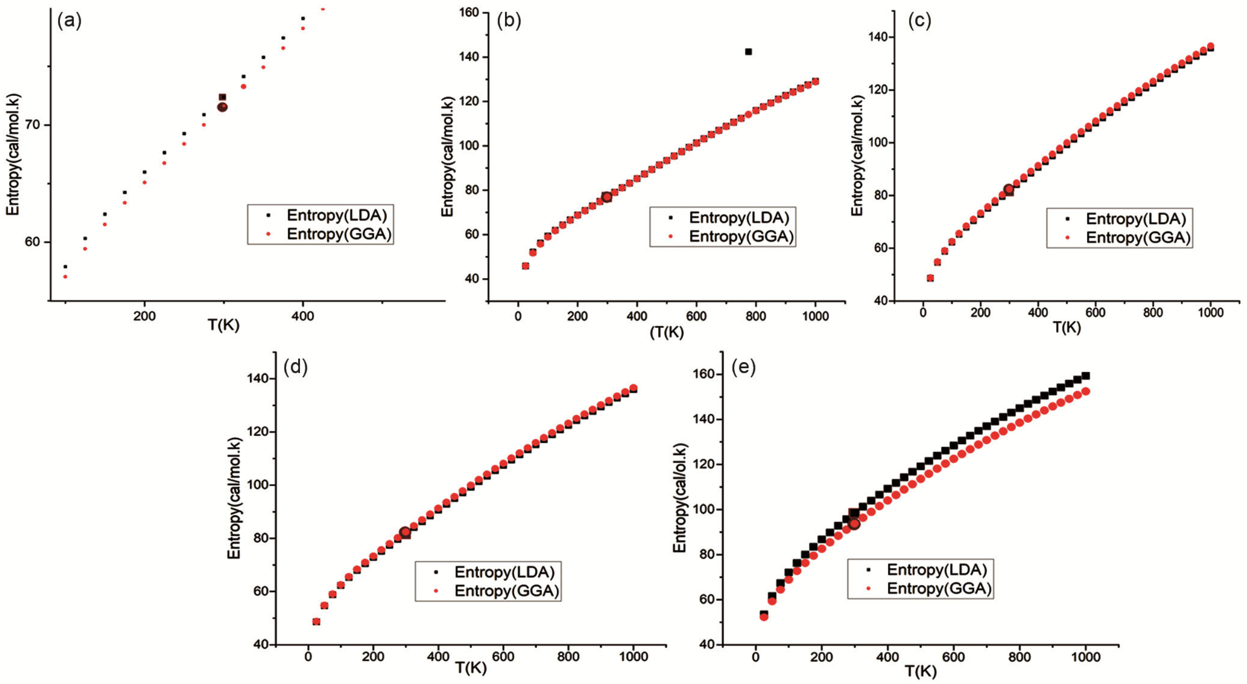


Fig. 3 — (a-e) The relation between the Entropy and temperature of the THF molecule

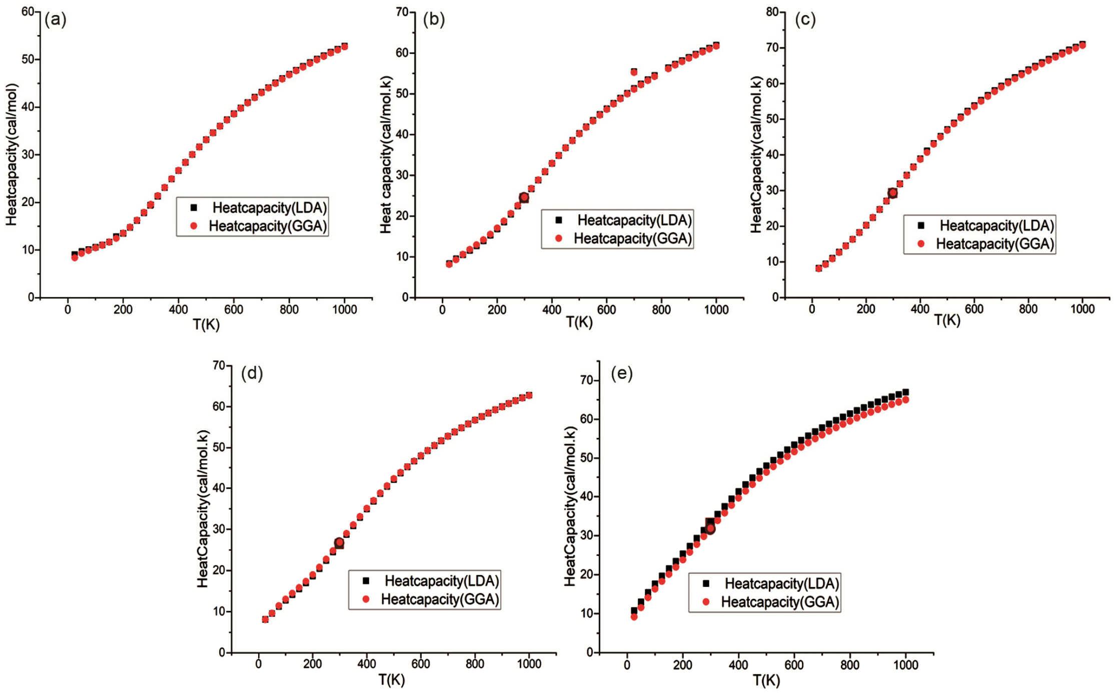


Fig. 4 — (a-e) The relationship between the Heat Capacity and temperature of the THF molecule

Table 10 — The Entropy of the THF molecule in the standard temperature298^0 K

Parameter	THF pure		THF amino		THF diamino		THF Cu		THF 2Cu	
	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA
Entropy (S) Cal/ mol.k	72.380	71.513	76.896	76.819	81.580	81.391	81.685	82.244	98.319	93.546

Table 11 — The Heat Capacity of the THF molecule in the standard temperature298^0K.

Parameter	THF pure		THF amino		THF diamino		THF Cu		THF 2Cu	
	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA
Heat Capacity (Cp) Kcal/mol	19.369	19.445	24.394	24.506	29.287	29.238	26.442	26.707	33.275	31.694

Table 12 — The Heat Enthalpy of the THF molecule in the standards temperature 298^0K

Parameter	THF pure		THF amino		THF diamino		THF Cu		THF 2Cu	
	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA
Enthalpy (H) Kcal/mol	75.051	75.510	86.434	86.988	97.754	97.924	78.075	78.324	73.210	72.704

Table 13 — The Free energy of the THF molecule in the standard temperature 298^0K

Parameter	THF pure		THF amino		THF diamino		THF Cu		THF 2Cu	
	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA	LDA	GGA
GibbsFree Energy(G) Kcal/mol	53.471	54.188	63.508	64.084	73.431	74.309	53.720	53.803	43.896	44.813

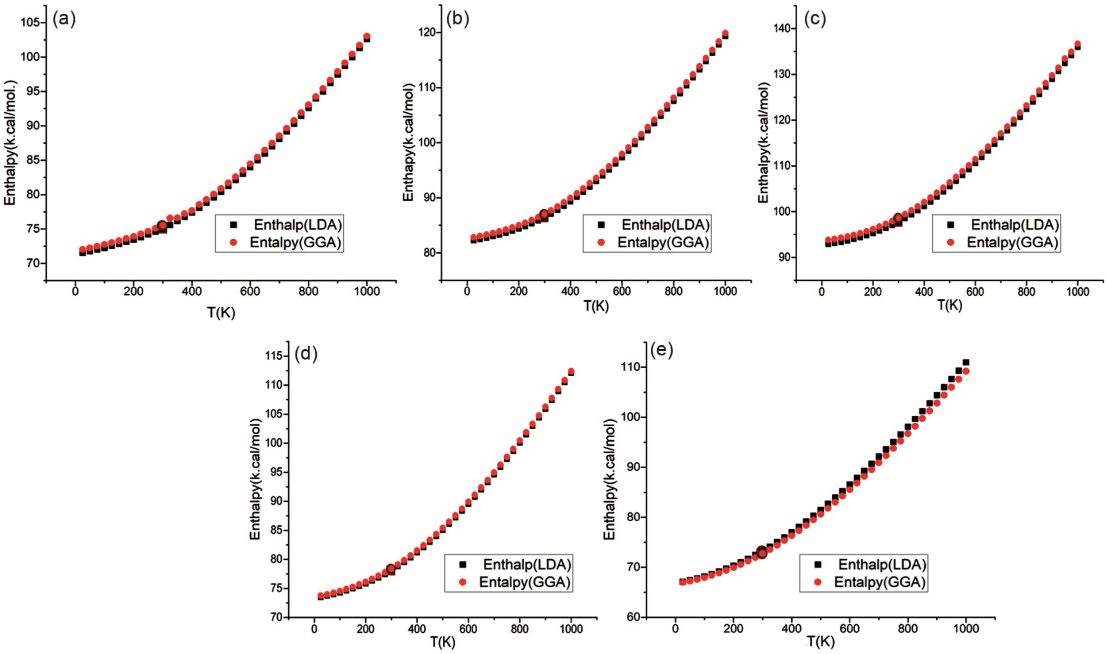
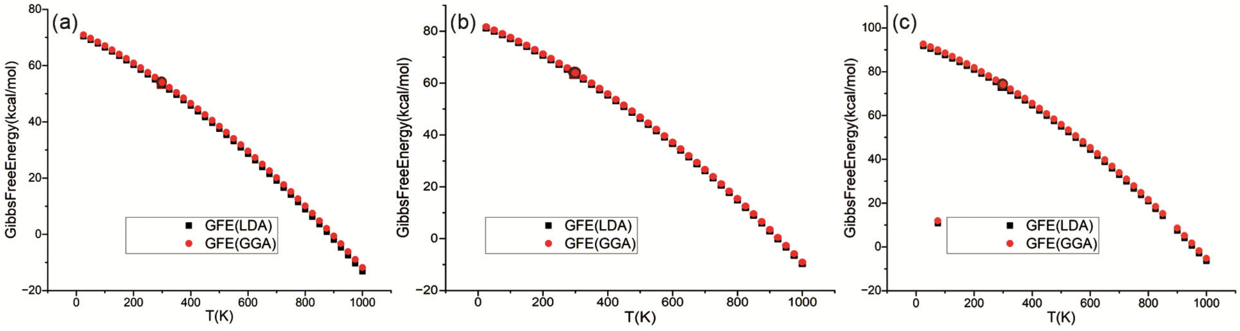


Fig. 5 — (a-e) The relationship between the Enthalpy and temperature of the THF molecule



(*Contd.*)

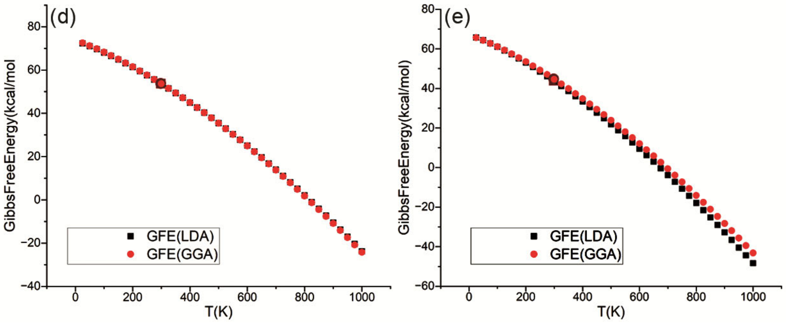


Fig. 6 — (a-e) The relationship between the Gibbs Free Energy and temperature of the THF molecule

between the Gibbs free energy and temperature. Specifically, as the temperature increased, the Gibbs free energy gradually decreased. This analysis aimed to determine the spontaneity of the reaction.

4 Conclusion

Tetrahydrofuran (THF) was among the first material systems studied in the field of organic electronics, and has remained a model system for studying, for example, transport or optical properties with minimal influence of structural disorder. The most important results calculated are the energy gap, ionization energy vibration frequencies and thermal properties when (Ni and Cu) are added to a THF molecule using DFT. The pure THF molecule contains a total of (20) mod, THF amino (24) mod,. , THF diamino (28), THF Cu (35), THF 2Cu (49) mod, occupied electron orbitals and pure THF (21) mod,, THF amino (25) mod,, THF diamino (29), THF Cu (36), THF 2Cu (50) unoccupied electron orbitals. Band gap regulation in organic semiconductors is of great concern due to its importance in various applications, including light-emitting diodes, organic photovoltaic devices, and photodynamic therapy as a photosensitizer.The calculation of the IR spectra is not only important in order to confirm the validity of the simnlations additional insight in to the molecular level of the system not accessible from experiment. The calculated band gap (E_gap) of The studied molecules for THF Cu and THF 2Cu were in the rang (2.085-2.224) eV and (0.981-1.769) eV respectively can be used as organic solar cells. It THF-Cu has a higher electronegativity, while it THF-pure has a lower electrophilicity. Correlations have been found between the electronegativity of different chemical compounds and the reaction rates in biochemical systems.When considering the thermal properties, it is observed that , Cp (heat capacity), H (enthalpy), and S (entropy) are directly proportional to temperature. This interpreted in the context of quantum mechanics, as thermal energies arising from translational, rotational, and vibrational motions of molecules are quantum energies, all of which exhibit direct proportionality to temperature.At higher temperatures, electronic movement becomes significant, leading to electronic transitions due to the increased energy levels. Furthermore, the increase in entropy values with rising temperature can be attributed to enhanced energy diffusion associated with rotational and vibrational energies.

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