Ab initio, Hartree- Fock and Density Functional Theoretical study of vibrational spectra of zirconium chelate of 1,2-naphthoquinone -2, oxime

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Abstract: *The vibrational frequencies of trans zirconium chelate of 1,2-naphthoquinone -2, oxime , were calculated using Gaussian 09 software code, employing RHF / Lanl2DZ and DFT (B3LYP) level and SDD basis set to predict the molecular structure. The fundamental modes are assigned by using animation software. The calculated frequencies are in good agreement with the experimental values. The calculated geometrical parameters are also given. The study is extended to calculate the HOMO-LUMO energy gap, Ionization potential (I), Electron affinity (A), Global hardness (η), chemical potential (μ) and global electrophilicity (ω). The calculated HOMO-LUMO energies show the charge transfer occurs in the molecule.*
Keywords: *1-2 naphthoquinone -1, oxime, IR, HF and DFT, Energy gap, Zirconium 1-oximate*

I. Introduction

The interest to organic nitroso naphthoquinone molecules is provoked by their high toxic properties as well as mutagenic and carcinogenic ones (1). To understand the influence of nitroso compounds on human organism, it is useful to study the nature of their intramolecular hydrogen bonds that play a significant role in barious biochemical processes including metabolism. The importance of intramolecular hydrogen bonds is supported by a wealth of physical and chemical data (2, 3). Avdeenko A.P. et.al. (4) reported metal complexes of metals such as aluminium, zinc, copper and nickel of 1,2-naphthoquinone -2, oxime and studied the solid state existence in the quinone oxime form. IR absorption studies have been reported by S. Gurriari and G. Siracus (5) for metal complexes of manganese, iron , cobalt, nickel, copper, zinc, cadmium and lead with 1,2-naphthoquinone -2, oxime. Molecular structure of 1,2-naphthoquinone -2, oxime was studied by A.E. Shchavlev et.al. (6) and reported ab initio and DFT level calculations concerning to intramolecular hydrogen bonding along with tautomerism. They have reported selected bond lengths and bond angles of 1,2-naphthoquinone -2, oxime or 2-nitroso 1- naphthol was calculated by using SPARTAN 08 and the results of RHF level and 6-31*G basis have been reported (7). The complexes formed between 2-nitroso-1- naphthol and zirconium (IV) have been investigated in the mixture of water & ethanol and water & chloroform. They have reported that it gave two complexes of zirconium to ligand ratio of 1:1 and 1: 4 (8). The complexes Ni (NQO) $_2$ where NQO = 1-nitroso-2-naphthol or 2-nitroso-1-naphthol, have been prepared. The magnetic susceptibilities and electronic and mass spectra of the complexes have been investigated. The complexes Ni (NQO) $_2$ show some degree of association the extent of which depends on the method used for their preparation (9). This paper describes synthesis and vibrational spectra of zirconium chelate of 1, 2-naphthoquinone -2, oxime calculated by HF and DFT level and SDD basis set the data is compared with experimental values. Geometrical parameters and HOMO – LUMO energy gap of the chelate is reported.

II. Experimental

Materials and methods:

The ligand 1, 2-naphthoquinone-2-oxime or 2-nitroso-1-naphthol is used as it is supplied by Thomas Baker chemicals (AR grade). $ZrOCl_2$ was used as it is which is supplied by Fluka chemicals with 98.3% purity. Deionised water is used during synthesis.

Preparation of metal chelates:

The chelate was prepared by mixing metal salt solution and ligand in 1: 2 proportions. The mixture was constantly stirred for one hour on magnetic stirrer. The pH of the mixture was maintained, in between $5.0 - 6.0$ by adding ammonia solution to it. The mixture was warmed on water bath for about 15 minutes. On cooling it was filtered and the precipitate was found to be colored.

Instrumental Analysis:

Elemental analysis is carried out with a Perkin Elmer 2400 series for C, H, O and N.

The IR spectra are recorded on a Thermo Fischer FTIR spectrophotometer iS5 model in a KBr matrix and in the range of 4000 – 400 cm^{-1} as well as in the range of 1000 – 300 cm^{-1}.

Computational details:
The entire calculations conducted in the present work were performed at Hartree – Fock (HF/ SDD) and Density Functional Theory (DFT) at B3LYP / SDD basis set in the Gaussian 09 software code. The geometries were first determined at the Hartree – Fock level of employing SDD basis set. (10,11). All the geometries were optimised using SDD basis set using density functional theory (DFT) employing the Beeke's three parameters hybrid functional (12) combined with Lee- Yang –Parr Correlation (13). The electron correlation is taken into account in DFT via the exchange energy arising from the anti symmetry of the quantum mechanical wave function and the dynamic correlation in the motion of individual electron; it makes DFT dominant over the HF calculation procedure (14).

The DFT hybrid leads to overestimate the fundamental modes in comparison to the other DFT Method. So the scaling factors have to be used to obtain considerably better agreement with experimental data. The wave number value computed theoretically contains known systematic error due to the negligence of electron correlation (15). We have used the scaling factor value of 0.8929 for HF /SDD basic set and 0.9613 for B3LYP/SDD Basic set. The absence of imaginary wave number on the calculated Vibrating Spectrum conform that the structure corresponds to minimum energy. HOMO-LUMO energy gap and other related molecular parameters are calculated.

III.   Results and Discussion:-
The vibrational analysis of ZrO (NQO)2 is performed on the basic of the characteristics vibration of hydroxyl, Carbonyl, C=N, N-O, Zr-N, and Zr = O modes. The computed vibrational wave numbers of IR with intensity used for identifying modes unambiguously. The harmonics vibrational frequencies calculated for ZrO(NQO)2 at HF and DFT levels using the SDD basis set have been symmetrised Table -1. It can be noted that calculated results are harmonics frequencies while the observed contains unharmonic contribution also. The value of the wave number is lower than the former due to anharmonicity. Comparison between the calculated and the observed vibration spectra help us to understand the observed spectral frequency.

Table 1 WAVE NUMBER OF ZrO (NQO)2 AT HF AND DFT LEVEL

Sr.No	HF cm^{-1}	INT.	DFT cm^{-1}	INT.	EXP cm^{-1}	INT.	ASSIGNMENT
1.	26.706	36.752	30.127	1.491	--	--	deformation
2.	53.377	7.748	--	--	--	--	deformation
3.	77.843	0.354	70.297	4.758	--	--	deformation
4.	111.889	4.711	112.984	2.14	--	--	deformation
5.	122.630	2.045	124.074	11.822	--	--	deformation
6.	138.417	0.09	138.922	2.244	--	--	41Zr-42O bending
7.	141.667	15.727	--	--	--	--	37O-38H Bending
8.	165.311	43.494	--	--	--	--	41Zr -40O bending
9.	171.606	39.63	170.808	1.5	--	--	37O-38H Bending
10.	182.392	54.55	184.242	5.566	--	--	35O-36H Bending
11.	196.848	5.131	--	--	--	--	37O-38H Bending
12.	212.920	42.849	209.882	34.474	--	--	33N-35O Bending
13.	222.948	73.89	--	--	--	--	C-H Bending o.p.
14.	226.010	4.634	--	--	--	--	C-H Bending o.p.
15.	236.154	42.854	244.055	10.234	--	--	35O-36H Bending
16.	273.807	76.854	269.070	4.788	--	--	41Zr -34N bending
17.	276.075	14.717	--	--	302.63	675.9	35O-36H Bending
18.	325.069	1045.164	--	--	308.80	674.2	37O-38H Bending
19.	345.329	359.71	--	--	330.29	38.4	37O-38H Bending
20.	357.168	24.24	359.462	1.902	--	--	14C-33N Bending
21.	362.963	181.621	363.776	5.216	--	--	41Z -33N Bending
22.	387.563	1661.201	393.500	7.736	--	--	41Zr-34N Bending
23.	409.341	769.053	411.865	14.003	--	--	C-H Bending o.p.
24.	420.091	26.322	--	--	--	--	41Zr-40O Bending
25.	435.717	8.111	--	--	--	--	C-H Bending o.p.

26.	438.101	4.497	--	--	337.38	57.7	C-H Bending o.p.
27.	486.094	38.099	488.2	1.05	--	--	41Zr-33N Stretching
28.	489.210	70716	489.571	6.356	497.3	54.87	41Zr-34N Stretching
29.	517.783	0.822	--	--	--	--	C-H Bending o.p.
30.	521.694	4.947	--	--	524.4	63.85	C-H Bending o.p.
31.	527.552	11.286	528.886	24.303	--	--	41Zr-39O Stretching
32.	566.821	557.895	--	--	--	--	21C-40O Stretching
33.	577.617	27.382	--	--	575.6	58.31	C-H Bending o.p.
34.	578.634	59.35	--	--			C-H Bending o.p.
35.	587.135	10.471	590.765	32.821	583.5	61.11	41Zr-40O Stretching
36.	633.441	1419.887	634.087	16.049	--	--	41Zr-39O Stretching
37.	651.433	69.201	650.789	18.823	643.4	71.07	41Zr-42O Stretching
38.	671.978	69.019	--	--	--	--	C-H Bending o.p.
39.	679.586	53.384	--	--	675.9	63.56	C-H Bending o.p.
40.	689.122	203.325	688.431	22.06	683.4	50.13	C-H Bending o.p.
41.	703.926	2920.366	704.528	41.602	--	--	41Zr-40O Stretching
42.	705.337	26.3.946	--	--	--	--	41Zr-39O Stretching
43.	720.498	324.651	719.702	4.102	731.43	39.9	C-H Bending o.p.
44.	776.412	29.678	--	--	757.59	54.00	C-H Bending i.p.
45.	785.430	33.357	787.059	146.662	783.2	82.48	C-H Bending i.p.
46.	798.824	107.509	798.120	10.920	796.23	56.20	Zr -N Stretching
47.	803.940	0.156	--	--	806.2	75.65	C-H Bending o.p.
48.	809.101	1.459	--	--	--	--	C-H Bending o.p.
49.	819.575	172.838	--	--	818.7	55.39	C-H Bending o.p.
50.	831.147	3993.509	--	--	--	--	21C-40O Stretching
51.	848.031	93.954	843.200	0.308	851.7	91.75	C-H Bending o.p.
52.	870.970	30.83	873.020	19.052	--	--	21C-40O Stretching
53.	881.167	180.836	880.660	23.633	--	--	39O-11C Stretching
54.	913.204	1.245	--	--	--	--	C-H Bending o.p.
55.	924.464	7.447	923.790	4.100	922.7	54.28	C-H Bending o.p.
56.	940.973	517.099	939.185	1.036	950.9	66.79	C-C Stretching
57.	965.653	1483.604	968.726	0.023	969.7	33.96	C-C Stretching
58.	976.028	10.64	979.432	32.68	--	--	C-H Bending o.p.
59.	993.324	5.142	--	--	--	--	C-H Bending o.p.
60.	1006.061	37.633	--	--	1007.5	90.67	C-H Bending o.p.
61.	1008.637	96.825	--	--	--	--	C-H Bending i.p.
62.	1011.271	0.963	--	--	--	--	C-H Bending o.p.
63.	1019.263	594.58	1019.65	29.822	--	--	C-C Stretching
64.	1030.049	1.394	1027.991	24.219	--	--	C-H Bending o.p.
65.	1035.710	0.624	--	-	1033.6	76.06	C-H Bending o.p.
66.	1073.596	35.282	--	--	--	--	C-H Bending i.p.
67.	1077.739	24.491	1076.32	104.719	1076.2	80.86	C-H Bending i.p.
68.	1106.320	18.521	1106.37	41.206	1103.9	78.44	C-H Bending i.p.
69.	1112.937	72.824	--	--	--	--	C-H Bending i.p.
70.	1123.161	290.701	1134.576	5.758	--	--	C-C Stretching

71.	1140.161	101.767	1142.446	16.293	1137.9	60.79	C-H Bending i.p.
72.	1149.055	159.293	--	--	1147.6	67.94	34N-37O Stretching
73.	1185.405	1438.875	--	--	--	--	33N-35O Stretching
74.	1213.156	8.71	1208.832	137.945	1204.6	30.68	C-C Stretching
75.	1219.656	1.311	1222.767	15.76	--	--	C-C Stretching
76.	1247.497	51.646	1250.833	228.271	--	--	C-H Bending i.p.
77.	1263.489	468.993	--	--	1257.4	34.55	C-H Bending i.p.
78.	1269.176	21.227	1269.414	30.805			C-H Bending i.p.
79.	1275.721	26.026	--	--	1274.2	62.1	C-H Bending i.p.
80.	1288.945	42.934	1295.044	443.578	1291.9	44.25	C-H Bending i.p.
81.	1307.160	627.882	1309.555	34.045	--	--	C-C Stretching
82.	1320.179	51.317	--	--	--	--	35O-36H Bending
83.	1360.252	1964.23	--	--	--	--	37O-38H Bending
84.	1382.575	193.316	1382.158	741.62	741.62	--	22C-34N Stretching
85.	1390.289	414.955	1394.401	120.321	1388	36.15	37O-38H Bending
86.	1397.808	108.306	1400.523	65.009	--	--	C-C Stretching
87.	1413.549	120.499	1411.651	125.429	--	--	C-H Bending i.p.
88.	1416.996	7.301	1417.033	91.464	1415.7	67.92	C-H Bending i.p.
89.	1433.827	26.344			1448.4	26.48	C-H Bending i.p.
90.	1440.837	335.604	1449.159	61.837	--	--	21C-40O Stretching
91.	1464.266	479.284	1475.298	160.418	1470.1	57.15	11C-39O Stretching
92.	1496.536	42.617	--	--	1493.9	84.23	C-C Stretching
93.	1502.652	498.604	--	--	--	--	C-C Stretching
94.	1509.126	97.592	1511.893	338.979	1508.1	74.55	C-C Stretching
95.	1537.814	57.775	1535.13	48.168	--	--	C-C Stretching
96.	1566.360	842.612	1569.617	151.486	1560.1	29.65	C-C Stretching
97.	1579.977	82.173	1575.348	23.216	1581.2	56.84	C-C Stretching
98.	1583.192	413.08	--	--	--	--	C-C Stretching
99.	1608.809	67.594	1612.241	311.222	1606.8	39.66	C-C Stretching
100.	1681.982	86.681	1700.374	19.934	1692.6	95.36	14C-33N Stretching
101.	2994.554	50.903	3173.875	7.417	--	--	C-H Stretching
102.	3004.671	136.64	3183.197	8.934	--	--	C-H Stretching
103.	3005.537	3.284	3184.754	0.242	--	--	C-H Stretching
104.	3007.867	71.749	3188.973	21.038	--	--	C-H Stretching
105.	3017.769	19.644	3199.169	15.264	--	--	C-H Stretching
106.	3029.984	6.293	3209.798	0.3829	--	--	C-H Stretching
107.	3031.493	227.598	3215.074	80.134	--	--	C-H Stretching
108.	3045.351	6.866	3228.355	7.836	--	--	C-H Stretching
109.	3049.458	173.685	3228.97	23.602	--	--	C-H Stretching
110.	3063.780	188.455	3250.092	64.138	3057.2	43.03	C-H Stretching
111.	3074.495	3.876	3256.262	5.426	--	--	C-H Stretching
112.	3093.514	75.137	3277.635	17.173	--	--	C-H Stretching
113.	3553.081	355.822	3802.927	20.075	3561.8	57.21	37O-38H Stretching
114.	3586.064	1856.253	3848.92	38.603	3582.1	58.86	35O-36H Stretching

C-H vibration:

The Naphthalene structure show the presence of structural vibration in the region 3250-2950 cm^{-1} which is characteristics for the zero identification of C-H stretching vibration .The region 3250-3100 cm^{-1} is for symmetric stretching. And the region 3100-2950 cm^{-1} is for asymmetric stretching modes of vibration (16).

For most cases, the naphtholic C-H vibration absorption bands are usually weak and it is too weak for detection. In the present work, for the ZrO $(NQO)_2$ the FTIR band is observed at 3357.2 cm have been assigned to C-H stretching vibration. The HF level gives 2994.554, 3004.671, 3005.537, 3007.867, 3017.769, 3029.984, 3031.493, 3045.351, 3049.458, 3063.780, 3074.495 and 3093.514 cm^{-1} while DFI. B3LYP level gives values at 3173.875, 3183.197, 3184.754, 3188.973, 3199.169, 3209.798, 3215.074, 3228.97, 3250.092, 3256.262 and 3277.635 cm^{-1}

The title compound has both C-H out of plane and in plane bending vibration. The out of plane bending mode of C-H vibration of ZrO$(NQO)_2$ is found well is agreement with the experimental predicted in the region 1030-650 cm^{-1} HF and DFT levels and SDD basis shows this region which gives number of vibration and case comparable with experimental results as shown in fig 1. The in plane C-H deformation vibration of ZrO $(NQO)_2$ is experimentally practiced in the region 1250-1080 cm^{-1} which is supported week by the vibration values practiced by HF and DFT levels.

The other region for C-H bending out of plane are practiced by HF in the region 521 to 435 cm^{-1}, 4409cm^{-1}, 226 to 171 cm^{-1} which DFT has predicted at 411 cm^{-1} only and very few vibration modes.

C=O Vibration:

The C=O stretching vibration of ZrO$(NQO)_2$ has a main contribution in the mode with B3LYP /SDD predicted frequency at 1475 cm^{-1} & 1449 cm^{-1} and HF/SDD predicted at 1549.76 cm^{-1}. In the FTIR spectra, we observed then peak at 1470.1 cm^{-1}, which is in good agreement with predicted data. The other C=O frequencies are observed at 1494.1, 1477, 974, 817 cm^{-1}, which are also in good agreement with the data predicted by HF/SDD.

C=N Vibrations:

The frequency of C=N bond is observed at 1692.6 cm^{-1} in the FTIR spectra of ZrO$(NQO)_2$ while it is predicted at 1700.37 cm^{-1} by DFT/SDD and at 1681.98 cm^{-1} by HF/ SDD is predicted. The V(C=N) in chelates shows lower frequency owing to elongation of these bands on co-ordination.

N-O Vibration:

The observation of γ (N-O) is observed at 1147.6 cm^{-1} in the FTIR spectrum which is predicted at 1149.05 cm^{-1} by HF/SDD but DFT/SDD has not predicted for the band. This band is in good agreement with observed data. The absorption of this γ (N-O) at higher wave number indicates that this bond is significantly shorter in the chelates. The higher wave length of the N-O indicates that nitroso atoms of the oxime group coordinate to the centre (17, 18).

Zr-O Stretching Vibration:

The wave number of Zr-O stretching in the chelate ZrO$(NQO)_2$ are predicted at 705.33 and 703.92 cm^{-1} by HF theory and 704.528 cm^{-1} by DFT theory but we do not observed this peak. This Frequency is lower which suggests that it is attached to central atom.

Zr-O bending Vibration:

Zr-O bending vibration is predicted at 138.41, 165.31, 420.09, and 527.55 cm^{-1} by the HF level and 138.41 and 528.88 cm^{-1} by DFT/B3LYP theory. In the FTIR spectra, this frequency is not found.

Zr-N Stretching:

The frequencies of Zr-N is observed in the FTIR spectrum at 626 cm^{-1} but the predicted IR values are at 626 and 637 cm^{-1} by HF level as well as at 637 and 652 cm^{-1} by DFT level. These values are in good agreement with experimental data.

Zr-N bending vibration:

The IR absorption frequencies of Zr- N bending are predicted at 273.80, 362.96 and 387.56 cm^{-1} with HF level and 269.07, 363.77and 393.5 cm^{-1} with DFT level. Experimental values are not recorded.

Molecular geometry:

The optimized structure parameters of ZrO $(NQO)_2$ calculated by ab initio, HF/SDD and DFT/B3LYP/SDD basis set are listed in Table 2 in accordance with the atom numbering scheme given in Fig -1. The values of bond length in A^0 and bond angles in degree are given in Table 2.

Table No: 2 Bond Lengths and Bong Angles of ZrO $(NQO)_2$

Bond length	A^o	Bond angle	(o)
C1-C2	1.402	C3-C2-C1	120.073
C2-C3	1.405	C4-C3-C2	119.529
C3-C4	1.404	C5-C4-C3	120.304
C4-C5	1.396	C6-C1-C2	119.529
C5-C6	1.399	H8-C1-C6	119.976
H9-C2	1.074	H9-C2-C1	120.032
H8-C1	1.074	C10-C3-C2	119.887

H7-C10	1.069	C11-C4-C3	119.615
C3-C10	1.408	H7-O10-C15	119.854
C4-C11	1.401	H12-C5-C4	120.109
H12-C5	1.069	H13-C6-C1	120.091
H13-C6	1.076	C14-C11-C4	119.304
C11-C14	1.430	C15-C14-C11	120.745
C14-C15	1.391	H16-C15-C14	119.884
H16-C15	1.076	C19-C18-C17	120.459
C10-C15	1.401	C20-C19-C18	120.459
C17-C18	1.407	C21-C20-C19	120.553
C18-C19	1.411	H23-C26-C19	119.985
C19-C20	1.407	H24-C17-C18	119.565
C20-C21	1.396	H25-C18-C17	119.830
C21-C22	1.468	C26-C19-C18	119.830
H23-C26	1.075	C27-C20-C19	120.494
H24-C17	1.070	C28-C27-C20	119.980
H25-C18	1.077	C29-C26-C19	119.790
C19-C26	1.402	H30-C27-C20	119.803
C20-C27	1.396	H31-C28-C27	119.473
C27-C28	1.396	H32-C29-C26	119.725
C28-C29	1.406	N33-C14-C11	117.869
H30-C27	1.073	N34-C22-C17	121.982
H31-C28	1.071	O35-N33-C14	123.689
H32-C29	1.070	H36-O35-N33	109.763
N33-C14	1.298	N34-C22-C17	121.982
N34-C22	1.321	O37-N34-C22	125.946
O35-N33	1.395	N33-C14-C15	121.385
H36-O35	0.955	H38-O37-N34	109.875
N34-O37	1.363	O39-C11-C4	121.098
H38-O37	0.957	O40-C21-C22	121.849
O39-C11	1.286	O40-C21-C20	119.144
O40-C21	1.307	Zr41-O40-C21	107.578
Zr41-O40	1.864	O42-Zr41-O40	106.586
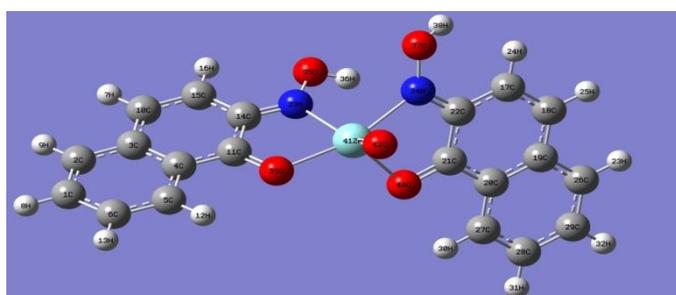
Fig.1. Molecular Structure of ZrO(NQO)$_2$

Mulliken Charges:

Mulliken charges arise from the Mulliken population analysis (19,20) and provide a means of estimating partial atomic charges from calculations carried out by the methods of computational chemistry, particularly those based on the linear combination of atomic orbitals molecular orbital method, and are routinely used as variables in linear regression QSAR(21) procedures(22).

In the application of quantum mechanical calculation to molecular system, the calculation of effective atomic charges plays an important role. The electron distribution of ZrO (NQO)$_2$ is compared in the two different mechanical methods and the sensitivity of the calculated charges to charge in choice of methods is studied. By determining electron population of each atom in the defined basis function, the Mulliken charges are calculated by HF/SDD and DFT/B3LYP/ SDD level. The results are presented in Table-3 which the values of atomic charges of each atom of the concerned molecule. Fig. 2 shows atomic charge against atoms of the said molecule.

Table-3 : Atomic Charges of ZrO(NQO)2

HF		DFT	
Atom	Atomic charge	Atom	Atomic charge
1 C	-0.214068	1 C	-0.226669
2 C	-0.385366	2 C	-0.429771
3 C	0.406674	3 C	0.463266
4 C	0.161673	4 C	0.181366
5 C	-0.287999	5 C	-0.344136
6 C	-0.253799	6 C	-0.240694
7 H	0.235250	7 H	0.246638
8 H	0.224583	8 H	0.231699
9 H	0.227246	9 H	0.245116
10 C	-0.405894	10 C	-0.437521
11 C	0.378174	11 C	0.150448
12 H	0.281528	12 H	0.287683
13 H	0.228511	13 H	0.235632
14 C	0.346016	14 C	0.213530
15 C	-0.436899	15 C	-0.408224
16 H	0.267228	16 H	0.267498
17 C	-0.498550	17 C	-0.468967
18 C	-0.429911	18 C	-0.458534
19 C	0.386522	19 C	0.460859
20 C	0.161504	20 C	0.151962
21 C	0.363155	21 C	0.170208
22 C	0.465611	22 C	0.350010
23 H	0.223671	23 H	0.244879
24 H	0.200868	24 H	0.213212
25 H	0.225775	25 H	0.240302
26 C	-0.388579	26 C	-0.432665
27 C	-0.310483	27 C	-0.346469
28 C	-0.252870	28 C	-0.245699
29 C	-0.234821	29 C	-0.232777
30 H	0.270406	30 H	0.281394
31 H	0.222789	31 H	0.236536
32 H	0.220753	32 H	0.232946
33 N	-0.520184	33 N	-0.353271
34 N	-0.521696	34 N	-0.351792
35 O	-0.504315	35 O	-0.396511
36 H	0.442200	36 H	0.398414
37 O	-0.457275	37 O	-0.344281
38 H	0.392498	38 H	0.350423
39 O	-0.671718	39 O	-0.433746
40 O	-0.746823	40 O	-0.484140
41 Zr	1.909363	41 Zr	1.247433
42 O	-0.720749	42 O	-0.465589
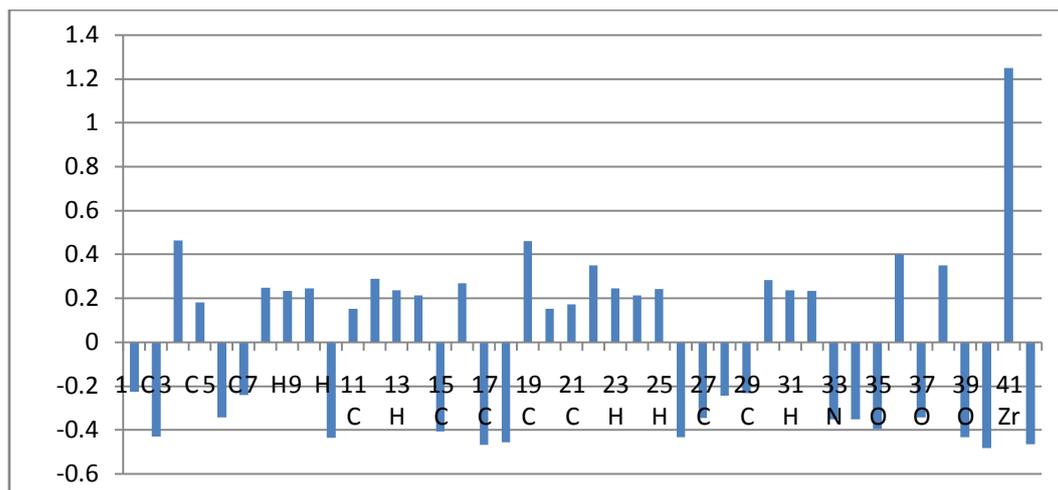
Fig 2 Atomic charge against atoms

HOMO-LUMO energy gap and related molecular properties:

The HOMO-LUMO energy gap of the molecule ZrO(NQO)$_2$ in the HF and DFT/B3LYP level and SDD basis set has been calculated. The HOMO-LUMO energy gap is constant in both methods. It is known that the value of EHOMO is often associated with the electron donating ability of inhibitor molecule, higher values of EHOMO is an indication of the greater ease of donating electrons to the unoccupied d orbital of the receptor. The value of ELUMO is related to the ability of the molecule to accept electrons, lower values of ELUMO shows the receptor would accept electrons. Consequently, the value of *Egap* provides a measure for the stability of the formed complex on the metal surface. The frame work of SCF MO theory, the ionization energy and electron affinity can be expressed through HOMO and LUMO energies AS I= -E $_{HOMO}$, A= -E $_{LUMO}$. The hardness compounds to the gap between the HOMO and LUMO orbital energies. If the gap energy is higher than the Hardness is also larger. The global hardness η= ½ (E $_{HOMO}$-E $_{LUMO}$). The hardness is associated with the stability of chemical potential (μ) can be expressed in combination of electron affinity and ionization potential. The global electrophilicity index ($_ω$) is also calculated and listed in table- 4.

Table No: - 4 Comparison of HOMO-LUMO, Energy gap and related Molecular Properties of ZrO (NQO)$_2$

Molecular Properties	HF/SDD	DFT/B3LYP/SDD
HOMO eV	-0.20379	-0.17774
LUMO eV	-0.09716	-0.15014
Energy gap	0.10663	0.0276
Ionisation Potential (I)	0.20379	0.17774
Electron Affinity(A)	0.09716	0.15014
Global Hardness (η)	0.021326	0.0138
Chemical Potential (μ)	0.053315	0.0138
Global Electrophilicity (ω)	0.06110	0.0069

Table 5 Theoretically computed Energies (a.u.), Zero point Energy (Kcal / mol) Rotational Constants (GHz), Entropy (cal mlo^{-1}K^{-1}) and Dipole moment D (Kcal/ mlo^{-1}K^{-1})

Parameter	DFT/B3LYP/SDD	HF/SDD
Total Energy e.u.	-1303.8238	-1294.83507
Zero Point Energy	192.24662	203.8663
Rotational constants	0.37756	0.44159
	0.08181	0.07949
	0.07767	0.07615
Entropy Total	137.430	133.239
Translational	44.215	44.215
Rotational	36.148	36.040
Vibrational	57.068	52.984
Dipole moment (D)	9.5808	6.915

IV. Conclusion:

The results of the study lead to the following conclusions,

1. The proper frequency assignment for the chelate ZrO $(NQO)_2$ is performed for time from the FTIR spectra. The experimental vibration frequencies are compared with HF and DFT theory.
2. The assignments were confirmed with the help of animation process which is available in Gaussian 09 computer code.
3. The molecular geometry of ZrO $(NQO)_2$ best at the DFT/ B3LYP/SDD level.
4. The HOMO- LUMO energy was calculated and other related molecular properties were also discussed.
5. The Mullikan atomic charges were calculated and the results were discussed
6. Thermodynamic parameters were calculated.

Reference.

[1] V.N. Maistrenko, R.Z. Hamitov and G.K. Budnikov, An ecological and analytical monitoring of superacotoxicants, Khimiya, Moskow, (1996).
[2] G.A. Jaffrey, An introduction to Hydrogen bonding, Oxford University press New York, (1997).
[3] F.Hibbert, J. Emesley, Advanced Phy. Org, Chem, 26, 255 (1990).
[4] A.P. Avdeenko, G.M.Glinyanaya and V.V. Pirozhenko, Russian Journal of Organic Chemistry, 35(10), 1480 – 1487 (1999).
[5] S. Gurriari and G. Siracus, Inorganica Chimica Acta, Vol.5, No.3, 650-954 (1971).
[6] A.E.Shchavlev, A.N. Pankratov and V. Enchav. J. Phys, Chem., A, 111, 7112-7123 (2007).
[7] N.R. Gonewar, V.B.Jadhav, K.D. Jadhav & R.G.Sarawadekar, Research in Pharmacy, 2(1), 18-25 (2012).
[8] H. B. Jonassen and Winston R. De Monsabert ,Inorganic Complex Compounds Containing Polydentate Groups. VIII. Zirconium(IV) Complexes with 2-Nitroso-1-naphthol, *J. Am. Chem. Soc.*, 1952, 74 (21), pp 5298–5301
[9] J. Charalambous, P. Maple, N.A. Nassef, and F.B. Taylor, Complexes of nickel(II) with 1-nitroso-2-naphthol and 2-nitroso-1-naphthol (Monooximes of 1,2-naphthoquinones), Inorganica Chimica Acta, Volume 26, 1978, Pages 107–111
[10] H. B. Schleqel, J. Comput. Chem. 3,124 (1982).
[11] P.Hohenberg and W.Kohn, Phy.Rev. 136, B 864 (1964)
[12] D. Beeke, J.Chem. Phys, 98, 5648 (1993)
[13] C.Lee, W.Yang and R.G. Parr, Phy. Rev., B37, 785(1998).
[14] J. B. Foresman and A. Frisch, exploring Chemistry with Electronics Structure Method, Seccrd edition, Gaussian Pittsburg USA, (1996).
[15] N.P.G. Roeqes, A Guide to the Complete Interpretation of Infra Red Spectra of Organics Structure, Willey, New York (1994).
[16] G.Varsayani, Assignment for Vibration Spectra of Seven number Benzene derivatives Vol. 1 & 2 Academic Kiqclo Budapest, (1973).
[17] V. R. Constantino, H.E.Toma, L.F.C.Oli venia and P. S. Santos, Raman Spectroscopy, 23,629(1992).
[18] C. Natrajan and A. Nazeer Hussain, Indian J. Chem. 22A, 527 (1983).
[19] Mulliken, R. S. "Electronic Population Analysis on LCAO-MO Molecular Wave Functions. I". *The Journal of Chemical Physics* **23** (10): 1833–1831(1955).
[20] G. Csizmadia, Theory and Practice of MO Calculations on Organic Molecules, Elsevier, Amsterdam, (1976).
[21] Leach, Andrew R., *Molecular modelling: principles and applications*. Englewood Cliffs, N.J. Prentice Hall. ISBN 0-582-38210-6. (2001).
[22] Ohlinger, William S.; Philip E. Klunzinger, Bernard J. Deppmeier, and Warren J. Hehre "Efficient Calculation of Heats of Formation". *The Journal of Physical Chemistry A,* **113** (10), 2165–2175 (2009).