

## Vibrational spectra of zirconium chelate of 1, 2-naphthoquinone dioxime by DFT and HF

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**ABSTRACT:** The infra red wave numbers of zirconium chelate of 1,2-naphthoquinone dioxime, were calculated using Gaussian 09 software code, employing RHF / SDD 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 ( $\eta$ ), chemical potential ( $\mu$ ) and global electrophilicity ( $\omega$ ). The calculated HOMO-LUMO energies show the charge transfer occurs in the molecule.

**Keywords:** 1-2 naphthoquinone dioxime, IR, HF and DFT, Energy gap, Zirconium dioximate

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### I. INTRODUCTION

The specific action of the grouping towards nickel ions has been attributed to the anti isomers of the compounds. A major aim to study such compounds originated from the fact that these types of ligand showed biological importance [1-7]. Oximes and dioximes have often been used as chelating ligand in the field of coordination chemistry and their metal complexes have been of great interest for many years. The presence of mildly acidic hydroxyl groups and slightly basic nitrogen atoms makes oximes, dioximes amphoteric ligands, which form square planar, square-pyramidal or octahedral complexes with transition metal ions such as Co (III) and Ni (II) as the central atom (8). The structure of 1-2 naphthoquinone dioxime is examined by use of the HF (6 -31 G\*level), density functional theory DFT (6 -31 G\* level) & hybrid functional B3LYP. Using the optimized structure of the titled compound IR, NMR, and ultraviolet data is calculated and compared with experimental data. It shows good relation between theoretically calculated IR wave numbers & observed values for Mid – Far IR data (9). Al, Zn, Cu (II), Ni (II) and alkali metal salts of dioximes were reported and the authors concluded that the colour of the quinone oximes is not related to quinone oxime structure (10). The polarographic behavior of the 1, 2-naphthoquinone has been investigated in the pH range 3 to 14. All of the compounds produce well defined polarographic reduction waves which can be used for analytical purposes. Polarographic evidence indicates that the monoximes and the dioximes exhibit tautomerism (11).

This paper describes synthesis and vibrational spectra of zirconium chelate of 1, 2-naphthoquinone dioxime calculated by HF and DFT level and SDD basis set the data is compared with experimental values. Geometrical parameters, Mulliken atomic charges and HOMO – LUMO energy gap of the chelate is reported.

### II. Materials and Methods

The ligand 1, 2-naphthoquinone dioxime is synthesized in laboratory as per the reported method (12). A stock solution of zirconium oxychloride ( $ZrOCl_2$ ) is prepared by using AR grade chemicals. Deionised water is used during synthesis.

#### 2.1 Preparation of metal chelates.

The chelates were prepared by mixing metal salt solution and ligand in 1: 1 proportion for silver chelate and 1: 2 for other metals. 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. Warm the mixture on water bath for about 15 minutes. On cooling it was filtered and found to be coloured.

#### 2.2 Instrumental Analysis.

Elemental analysis was carried out with a Perkin Elmer 2400 series for C, H, and O & N. The IR spectra are recorded on a Thermo Fischer FTIR spectrophotometer iS5 model in a KBr matrix and in the range of  $4000 - 400 \text{ cm}^{-1}$  as well as in the range of  $1000 - 300 \text{ cm}^{-1}$ .

##### 2.2.1 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. (13,14). All the geometries were optimised using SDD basis set using density functional theory (DFT) employing the Beeke’s three parameters hybrid functional (15) combined with Lee- Yang –Parr Correlation (16). 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 (17).

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. 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 summarized 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 numbers and Raman activity of Zirconium dioximate by HF and DFT

Sr. No.	HF $cm^{-1}$	INT	RAMA N	DFT $cm^{-1}$	INT	RAMAN	EXPT $cm^{-1}$	INT	ASSIGNMENTS
1	29.7527	0.4007	53.434	31.6057	2.8636	--	--	--	Ring Deformation
2	114.565	6.3914	90.1987	121.700	3.7723	23.5585	--	--	Ring Deformation
3	131.1499	19.0213	1337.90	139.317	1.0778	28.1348	--	--	O-H Bending
4	149.9146	6.2577	146.461	--	--	6.6711	--	--	Zr-O Bending
5	159.0288	7.4029	524.582	159.251	3.7906	18.1044	--	--	C-H Bending O.P.
6	164.5611	5.3309	1864.01	168.933	5.1713	68.8341	--	--	C-H Bending O.P.
7	172.2742	4.731	3698.99	174.810	9.5175	44.0818	--	--	O-H Bending
8	190.6035	2.3713	1289.52	183.003	3.1234	2.9385	--	--	Zr-O Bending
9	199.5158	36.4123	288.484	202.474	2.9431	24.2735	--	--	Zr-O Bending
10	202.7255	15.7859	44.8111	211.941	2.6768	79.8584	--	--	Zr-N Bending
11	207.2752	33.1063	1509.84	215.351	6.3968	7.3505	--	--	O-H Bending
12	230.3664	0.2615	69.3882	220.184	17.633	8.2938	--	--	N-O Bending
13	241.5932	0.1357	39.8566	244.713	21.268	8.766	--	--	O-H Bending
14	286.0018	0.3714	24.1117	256.639	14.211	11.9832	--	--	M-N Bending
15	296.679	34.8353	275.909	303.814	10.201	1.2227	--	--	O-H Bending

16	314.1386	119.053	886.945	315.156	22.742	37.3497	304.59	0.385	O-H Bending
17	330.0174	12.1979	204.076	333.703	1.8312	3.0225	315.48	0.754	O-H Bending
18	336.1247	67.2512	9.7667	350.571	11.066	4.088	328.69	0.345	O-H Bending
19	360.6692	5.8064	1943.91	357.058	6.0936	2.4045	335.64	0.372	O-H Bending
20	364.7025	311.687	624.290	383.131	11.883	12.4811	341.99	0.293	C-N Bending
21	389.2486	22.048	302.492	387.416	5.543	5.6629	--	--	O-H Bending
22	392.436	30.6557	565.899	413.491	10.974	6.7166	--	--	O-H Bending
23	402.1219	2.8124	21.7013	416.877	3.2037	6.5963	--	--	C-H Bending O.P.
24	413.8066	212.097	301.226	427.166	2.2254	2.7023	--	--	C-H Bending O.P.
25	428.1456	50.6774	94.1221	439.578	0.5911	9.4254	--	--	N-O Bending
26	434.9284	280.806	389.647	454.810	6.3865	4.8584	--	--	C-H Bending O.P.
27	440.0996	1326.33	2329.03	462.015	10.383	5.3833	--	--	O-H Bending
28	481.9732	1106.92	2096.60	467.509	9.4679	1.2463	--	--	O-H Bending
29	502.4359	14.7018	67.5987	511.990	14.202	20.4301	--	--	N-O Stretching
30	514.229	915.863	1375.72	533.727	11.507	19.7085	496.5	33.91	O-H Bending
31	534.1212	97.383	967.096	546.255	30.853	11.6435	--	--	C-H Bending O.P.
32	538.1556	304.034	135.471	567.386	27.768	40.1517	--	--	C-H Bending O.P.
33	565.1754	4.6503	578.952	571.672	54.085	5.9588	548.4	40.58	Deformation
34	589.6131	398.363	1950.77	600.374	0.8577	26.0206	--	--	C-H Bending O.P.
35	600.8201	122.343	399.267	626.334	21.063	2.8306	--	--	C-H Bending O.P.
36	624.3243	2288.63	4057.57	638.239	9.2102	5.4433	595.2	42.07	Zr-N Stretching
37	650.3438	30.579	681.305	663.207	33.030	6.504	--	--	Zr-N Stretching
38	681.2596	4070.41	7392.50	690.847	24.314	3.4143	646.9	57.39	Deformation
39	705.2185	12.3982	84.2366	723.688	33.222	2.075	669.6	46.38	C-H Bending O.P.
40	708.4999	15.8835	14.581	749.139	18.631	2.3254	677.8	56.01	C-H Bending O.P.
41	727.6691	107.978	91.8232	752.625	29.352	3.1452	684.5	46.47	C-H Bending

									O.P.
42	730.3951	358.194	790.565	772.988	4.3688	3.8898	--	--	Ring deformation
43	756.3237	291.048	2114.69	775.884	16.078	6.0622	727.3	74.18	Ring deformation
44	789.7738	7.3282	697.112	803.427	45.741	33.3891	--	--	Zr-N Stretching
45	794.5616	486.194	955.865	838.961	116.78	123.5284	755.5	47.32	Zr-N Bending
46	819.0505	15.5893	14.2859	844.047	10.206	7.2283	--	--	C-H Bending O.P.
47	820.2879	9.3114	3.7057	870.061	100.78	5.7844	783.1	74.06	C-H Bending O.P.
48	842.5587	1.6344	509.679	871.375	96.881	18.7441	796.5	51.35	C-H Bending O.P.
49	870.8041	140.689	66.8034	895.033	32.357	11.8108	803.3	59.86	C-H Bending O.P.
50	902.5422	5101.15	9502.58	925.038	35.184	6.4397	815.9	41.25	N-O Stretching
51	933.076	28.2937	90.5803	958.752	1.1665	2.3485	848.04	0.458	C-H Bending O.P.
52	934.6576	236.086	563.802	991.188	8.8246	11.143	--	--	C-H Bending O.P.
53	962.3587	12.6936	0.8047	992.868	4.2209	13.5506	--	--	C-H Bending O.P.
54	970.4663	1.9084	3.0468	1022.29	0.1121	15.7604	--	--	C-H Bending O.P.
55	1033.375	4.0387	229.982	1030.90	0.6481	19.9095	--	--	C-H Bending O.P.
56	1040.818	3.6149	140.794	1097.73	0.984	1.2569	942.51	0.489	C-H Bending O.P.
57	1046.258	134.766	1021.04	1105.64	1.9393	0.889	970.04	0.744	C-H Bending I.P.
58	1048.67	644.636	346.812	1111.41	82.290	7.0857	--	--	C-C Stretching
59	1073.835	7.4977	1558.83	1113.98	12.273	1.6219	--	--	C-H Bending O.P.
60	1077.34	1.4547	5.0661	1140.71	7.4049	4.3635	--	--	C-H Bending O.P.
61	1095.158	10.646	19.682	1144.43	55.610	56.1176	1033.87	0.433	C-H Bending O.P.
62	1103.254	35.1567	1558.53	1163.36	90.665	55.9496	--	--	C-C Stretching
63	1110.015	65.9137	177.385	1171.96	58.975	194.3655	--	--	C-H Bending

									O.P.
64	1143.707	5.6762	210.929	1179.14	23.746	13.1892	1092.97	0.490	C-H Bending I.P.
65	1189.157	43.8425	282.074	1214.93	880.59	136.1513	--	--	C-H Bending I.P.
66	1192.398	72.2482	611.16	1263.21	241.72	16.8869	1134.11	0.530	N-O Stretching
67	1222.991	94.8725	170.783	1266.66	3.7777	3.2641	--	--	N-O Stretching
68	1226.093	51.3024	172.577	1299.15	84.940	106.0597	--	--	C-H Bending I.P.
69	1228.004	60.6063	1144.00	1302.45	10.367	2.0209	1156.51	0.522	C-H Bending I.P.
70	1242.406	105.139	205.391	1304.48	55.915	3.11	--	--	N-O Stretching
71	1247.995	30.9401	458.552	1319.78	0.998	39.0163	--	--	N-O Stretching
72	1270.113	4.9355	282.377	1325.72	54.918	50.4725	1203.65	0.678	C-H Bending I.P.
73	1276.734	17.2659	386.269	1349.216	45.649	53.1565	--	--	C-H Bending I.P.
74	1293.022	693.287	71.916	1356.249	8.465	93.593	1233.4	68.43	C-H Bending I.P.
75	1303.579	37.3774	1500.24	1373.552	45.344	85.5305	--	--	C-H Bending I.P.
76	1354.344	1605.79	5632.56	1384.767	28.807	66.107	1290.4	48.81	O-H Bending
77	1370.795	86.2405	1713.39	1438.693	214.96	48.159	--	--	C-H Bending I.P.
78	1386.347	255.462	3933.57	1456.169	64.441	55.4942	--	--	O-H Bending
79	1395.445	85.284	7.4224	1472.689	82.821	106.9614	--	--	O-H Bending
80	1417.482	2869.95	4072.68	1482.354	5.7401	10.8621	1335.2	71.26	C-H Bending I.P.
81	1434.877	277.761	2710.68	1505.763	6.2708	37.1481	1358.3	45.06	O-H Bending
82	1444.086	85.284	7.4224	1524.242	17.365	33.4024	1372.2	50.51	O-H Bending
83	1460.125	53.7771	752.378	1534.025	5.2625	400.5176	1388.8	33.89	C-C Stretching
84	1470.581	75.6703	1844.46	1551.062	31.543	220.7149	--	--	O-H Bending
85	1478.739	88.854	442.179	1562.17	26.397	416.3041	1415.9	70.77	O-H Bending
86	1508.441	1282.29	24097.3	1570.836	43.896	240.7269	--	--	N-O Stretching
87	1518.235	58.9133	802.305	1602.388	9.209	380.4442	--	--	C-H Bending i.p.
88	1521.687	387.327	14875.3	1612.791	8.8732	2165.805	1448.	22.68	C-H Bending i.p.
89	1525.88	294.318	2660.43	1616.458	265.64	80.8937	--	--	C=N Stretching
90	1528.022	821.764	1990.25	1620.912	2.5508	396.3139	--	--	C=N Stretching
91	1557.105	558.028	105808.	1623.188	783.56	1861.426	1493.9	79.21	C-C Stretching
92	1581.838	343.683	46809.2	1654.082	13.093	637.4838	1503.8	83.04	C-C Stretching
93	1606.282	43.7053	1096.61	1680.355	147.73	10759.47	1512.7	74.62	C-C Stretching

94	1615.035	77.1387	7736.79	1706.322	114.34	185.3456	--	--	C-C Stretching
95	1661.207	23.9847	2196.46	1715.621	302.53	920.1873	1560.1	27.13	C-C Stretching
96	1665.794	117.810	1577.39	1764.668	34.908	449.457	1582.4	58.02	C-C Stretching
97	1679.666	120.629	1890.82	1769.54	39.173	134.45	--	--	C=N Stretching
98	1690.366	198.058	1397.24	1784.276	61.896	108.0503	1606.9	33.65	C=N Stretching
99	1705.886	39.7258	2600.98	1795.643	481.81	55.4335	1633.2	71.50	C=N Stretching
100	1768.159	14.5034	4444.99	1812.13	12.602	292.5579	--	--	C-C Stretching
101	1768.559	29.2015	1037.80	1878.281	76.521	127.9831	1681.7	94.32	C-C Stretching
102	1780.007	256.106	2350.67	1878.705	21.374	603.0195	1693.7	99.19	C=N Stretching
103	1786.381	52.8935	2015.73	1890.866	19.426	397.5908	1700.3	93.34	C=N Stretching
104	3191.02	3.2	196.858	1897.638	34.836	289.3088	--	--	C-H Stretching asym.
105	3193.974	4.5436	63.5135	3389.759	33.916	229.5086	--	--	C-H Stretching asym.
106	3194.668	32.1646	882.981	3392.896	30.101	21.182	--	--	C-H Stretching asym.
107	3197.759	41.391	358.760	3393.633	36.940	77.93	--	--	C-H Stretching asym.
108	3204.104	18.2258	379.234	3396.916	3.6803	54.3511	--	--	C-H Stretching asym.
109	3207.143	15.9793	250.577	3403.657	33.737	281.007	--	--	C-H Stretching asym.
110	3216.821	113.218	1056.02	3406.886	5.023	57.1708	--	--	C-H Stretching asym.
111	3219.367	90.6223	2374.79	3417.166	38.668	400.8238	--	--	C-H Stretching asym.
112	3221.384	153.337	1541.43	3419.87	16.451	105.9613	--	--	C-H Stretching asym.
112	3224.411	145.689	4510.56	3422.013	28.005	37.3493	--	--	C-H Stretching sym.
114	3231.114	105.021	892.86	3425.229	29.673	470.2592	3074.4	0.610	C-H Stretching asym.
115	3259.728	52.4522	357.322	3432.349	38.379	217.9491	--	--	C-H Stretching

									asym.
116	3689.395	466.660	675.638	3462.745	2.3134	823.0788	3629.1	0.521	O-H Stretching
117	3697.957	149.954	2876.28	3919.172	5.8859	814.0687	3675.6	0.472	O-H Stretching
118	3710.179	106.22	2480.85	3928.267	70.820	128.9466	3744.9	0.472	O-H Stretching
119	3714.066	108.425	1034.37	3941.251	147.42	35.5388	3854.4	0.491	O-H Stretching

### O-H vibrations

The hydroxyl OH group provides four normal vibrations,  $\nu$ OH,  $\delta$ OH and  $\gamma$ OH, of which not only the stretching vibration but also the out-of-plane deformation are good group vibrations (18). HF level calculations give the  $\nu$ OH mode at 3714.066, 3710.179, 3697.957 and 3689.395  $\text{cm}^{-1}$  while DFT/ B3LYP calculations give at 3941.251, 3928.267, 3919.172 and 3462.745  $\text{cm}^{-1}$ . We observed these values at 3629.1, 3675.6, 3744.9 and 3854.4  $\text{cm}^{-1}$ . The moderate to strong absorption at  $1350 \pm 40 \text{ cm}^{-1}$  in the spectrum of phenol is assigned to  $\delta$ OH mode (19). In the FTIR spectrum of title compound, the vibration at 1415.9, 1372.2, 1358.3 and 1290.4  $\text{cm}^{-1}$  are observed for  $\delta$ OH mode. This band is predicted by HF at 1478.739, 1470.581, 1434.877, 1395.445, 1386.347, and 1354.344  $\text{cm}^{-1}$  while DFT level predicted the same vibration at 1562.17, 1551.062, 1524.242, 1472.689, 1456.169 and 1384.767  $\text{cm}^{-1}$ . The  $\gamma$ OH mode is observed in the FTIR spectrum at 496.5, 335.64, 328.69, 315.48 and 304.59  $\text{cm}^{-1}$ . The vibration for  $\gamma$ OH are predicted by HF at 481.9732, 440.0996, 392.436, 389.2486, 360.6692, 336.1247, 330.0174, 296.679 and others which are not recorded and DFT/ B3LYP level predicted at 467.509, 462.015, 413.491, 387.416, 357.058, 357.058, 333.703, 315.156 and 303.814  $\text{cm}^{-1}$ .

### C-H vibration

The Naphthalene structure shows the presence of structural vibration in the region 3250-2950  $\text{cm}^{-1}$  which is characteristics for the zero identification of C-H stretching vibration. The region 3250-3100  $\text{cm}^{-1}$  is for symmetric stretching and 3100-2950  $\text{cm}^{-1}$  for asymmetric stretching modes are of vibration (20). 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  $\text{ZrO}(\text{NQO})_2$  the FTIR band is observed at 3074.488  $\text{cm}^{-1}$  have been assigned to C-H stretching vibration. The HF level predicted absorption at 3259.728, 3231.114, 3224.411, 3221.384, 3219.367, 3057.915, 3216.821, 3207.143, 3204.104, 3197.759, 3194.668, 3193.974 and 3191.02  $\text{cm}^{-1}$  while DFT/ B3LYP level gives values at 3432.349, 3425.229, 3422.013, 3419.87, 3417.166, 3406.886, 3403.657, 3396.916, 3393.633, 3392.896, 3389.759 and 1897.638  $\text{cm}^{-1}$ .

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  $\text{ZrO}(\text{NQO})_2$  is found well in agreement with the experimental predicted in the region 1055-670  $\text{cm}^{-1}$  and 571-151  $\text{cm}^{-1}$ . HF and DFT levels and SDD basis shows this region which gives number of vibration and are comparable with experimental results as shown in Fig 1. In plane bending vibration, the region is 1450-1087  $\text{cm}^{-1}$ . Which are compared with the predicted data. The in plane C-H deformation vibration of  $\text{ZrO}(\text{NQO})_2$  is experimentally observed in the region 1250-1080  $\text{cm}^{-1}$  which is supported by the vibration values predicted by HF and DFT levels.

### C=N Vibrations.

The frequency of C=N bond is observed at 1700.3, 1693.7, 1633.2 and 1606.9  $\text{cm}^{-1}$  in the FTIR spectra of  $\text{ZrO}(\text{NQO})_2$  while these are predicted at 1765.586, 1747.876, 1703.0, 1673.884, 1532.136 and 1522.431  $\text{cm}^{-1}$  by DFT/SDD. HF/ SDD is predicted at 1698.137, 1692.077, 1621.618, 1606.865, 1596.693, 1492.54 and 1450.504  $\text{cm}^{-1}$ . The  $\nu(\text{C}=\text{N})$  in chelates shows lower frequency owing to elongation of these bonds on co-ordination.

### N-O Stretching Vibration.

The observation of  $\gamma(\text{N-O})$  wave number is observed at 1134.11 and 815.9  $\text{cm}^{-1}$  in the FTIR spectrum. HF/SDD predicted at 1433.927, 1186.346, 1181.033, 1162.577, 1133.495 and 857.958  $\text{cm}^{-1}$  while DFT/SDD predicted at 1448.53, 1168.509, 1164.455, 1146.902, 1117.546 and 837.2299  $\text{cm}^{-1}$ . The absorption of this  $\gamma(\text{N-O})$  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 (21, 22).

**Zr-N Stretching.**

The frequencies of Zr-N stretching are observed in the FTIR spectrum at 595.2 cm<sup>-1</sup> but the predicted IR values are at 750.7601, 618.2178 and 593.4837 cm<sup>-1</sup> by HF level as well as at 761.5026, 665.2667 and 633.3533 cm<sup>-1</sup> 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 192.7112, 271.8738, and 755.3114 cm<sup>-1</sup> with HF level and 176.3888, 244.7147 and 763.9222 cm<sup>-1</sup> with DFT level. Experimental value is recorded at 755.5 cm<sup>-1</sup> only.

**Zr-O bending vibration**

The IR absorption frequencies of Zr-O bending are predicted at 189.66, 181.188, 163.7641 and 142.5091 cm<sup>-1</sup> with HF level and 173.3336, 158.4055, 144.9019 and 105.5827 cm<sup>-1</sup> with DFT level. Experimental values are not obtained.

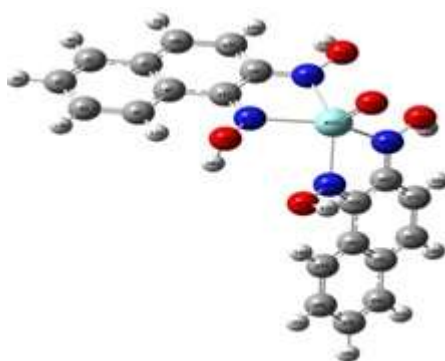


Fig.1 Molecular structure of zirconium dioximate

**Molecular geometry.**

The optimized structure parameters of ZrO (NQO)<sub>2</sub> 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 Å, bond angles and dihedral angles in degree are given in Table 2.

Table No:- 2 Bond Lengths, Bond Angles and dihedral angles of ZrO (NQO)<sub>2</sub>

Bond Length	Å	Bond Angle	(°)	Dihedral Angle	(°)
O46-Zr45	1.854	Zr45-N17-C14	112.501	O46- Zr45-N17-C14	-113.99
N17-C14	1.321	O46- Zr45-N17	106.979	Zr45-N17-C14-C11	7.077
Zr45-N17	2.125	H44-O43-N39	111.913	H44-O43-N39-C36	-90.821
H44-O43	0.969	O43-N39-C36	123.556	O43-N39-C36-C33	-177.706
H42-O41	0.981	H42-O41-N40	107.833	H42-O41-N40-C33	-87.127
O41-N40	1.349	N40-C33-C26	123.247	O41-N40-C33-C26	-6.784
N40-C33	1.302	N39-C36-C33	118.673	N40-C33-C26-C25	177.981
N39-C36	1.292	N17-C14-C11	118.231	N39-C36-C33-C26	-178.17
N18-C11	1.319	N18-C11-C4	122.707	N17-C14-C11-C4	-179.95
O19-N18	1.355	O19-N18-C11	124.126	N18-C11-C4-C3	177.841
H20-O19	0.957	O21-N17-C14	123.896	O19-N18-C11-C4	-8.523
O21-N17	1.373	H22-O21-N17	108.689	H20-O19-N18-C11	151.042
H22-O21	0.970	N18-C11-C14	123.896	O21-N17-C14-C11	-173.04
Zr45-N39	2.125	N17-C14-C15	122.349	H22-O21-N17-C14	152.203
Zr45-N18	2.129	N40-C33-C36	117.527	O46- Zr45-N40-C33	108.318
C1-C2	1.362	C3-C2-C1	120.460	C4-C3-C2-C1	0.062
C2-C3	1.398	C5-C4-C3	120.756	C6-C5-C4-C3	0.0667
C4-C3	1.401	H7-C10-C3	120.464	H8-C1-C2-C3	179.999
H7-C10	1.064	H9-C2-C1	119.845	C10-C3-C2-C1	-179.91



H9-C2	1.063	C11-C4-C3	119.727	C28-C27-C26-C25	-0.066
C14-C11	1.429	C15-C10-C3	120.321	C33-C26-C25-C24	-179.86
C23-C24	1.356	C11-C14-C15	119.705	H34-C27-C26-C25	179.939
C24-C25	1.415	C26-C33-C36	119.705	C36-C33-C26-C25	-0.135
C27-C26	1.370	C25-C32-C37	120.792	H13-C6-C5-C4	179.996
H34-C24	1.068	C28-C23-C24	120.084	C15-C10-C3-C2	179.948
C32-C25	1.416	H34-C27-C26	120.029	C26-C25-C24-C23	-0.062
C36-C33	1.411	C28-C27-C26	119.943	H30-C23-C28-C27	-179.97

### Mulliken Atomic Charges

Mulliken charges arise from the Mulliken population analysis (23,24) 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(23) procedures(25).

In the application of quantum mechanical calculation to molecular system, the calculation of effective atomic charges plays an important role. The electron distribution of  $ZrO(NQO)_2$  are compared in the two different mechanical methods and the sensitivity of the calculated charges to charge in choice of methods are 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.

Table-3 :- Atomic Charges of  $ZrO(NQO)_2$

Sr.No	HF/SDD		DFT/SDD	
	Atom	Atomic charge	Atom	Atomic charge
1.	1 C	-0.23321	1 C	-0.224178
2.	2 C	-0.38809	2 C	-0.440827
3.	3 C	0.407427	3 C	0.482793
4.	4 C	0.171305	4 C	0.112729
5.	5 C	-0.24858	5 C	-0.302175
6.	6 C	-0.31011	6 C	-0.297743
7.	7 H	0.231965	7 H	0.247963
8.	8 H	0.224871	8 H	0.225897
9.	9 H	0.226698	9 H	0.248306
10.	10 C	-0.45418	10 C	-0.435742
11.	11C	0.355973	11 C	0.186073
12.	12H	0.235520	12 H	0.322249
13.	13H	0.225191	13 H	0.232704
14.	14C	0.491805	14 C	0.260363
15.	15 C	-0.45441	15 C	-0.392859
16.	16 H	0.191793	16 H	0.273094
17.	17 N	-0.54352	17 N	-0.344885
18.	18 N	-0.54005	18 N	-0.332612
19.	19 O	-0.50601	19 O	-0.441151
20.	20 H	0.433900	20 H	0.416371
21.	21 O	-0.44612	21 O	-0.387745
22.	22 H	0.392445	22 H	0.403236
23.	23 C	-0.24302	23 C	-0.230695
24.	24 C	-0.39204	24 C	-0.437156
25.	25 C	0.403572	25 C	0.451782
26.	26 C	0.153920	26 C	0.166492
27.	27 C	-0.30701	27 C	-0.379012
28.	28 C	-0.29882	28 C	-0.313281
29.	29 H	0.225327	29 H	0.240378

30.	30 H	0.219259	30 H	0.228010
31.	31 H	0.222756	31 H	0.246106
32.	32 C	-0.46754	32 C	-0.443925
33.	33 C	0.320900	33 C	0.144848
34.	34 H	0.303388	34 H	0.331665
35.	35 H	0.218681	35 H	0.238552
36.	36 C	0.481271	36 C	0.243289
37.	37 C	-0.45010	37 C	-0.408717
38.	38 H	0.184759	38 H	0.259562
39.	39 N	-0.57263	39 N	-0.367862
40.	40 N	-0.57757	40 N	-0.375437
41.	41 O	-0.57691	41 O	-0.450910
42.	42 H	0.442988	42 H	0.391452
43.	43 O	-0.46184	43 O	-0.472630
44.	44 O	0.387761	44 O	-0.472630
45.	45 Zr	2.099256	45 Zr	1.269437
46.	46 O	-0.780878	46 O	-0.537604

### 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  $E_{HOMO}$  is often associated with the electron donating ability of inhibitor molecule, higher values of  $E_{HOMO}$  is an indication of the greater ease of donating electrons to the unoccupied d orbital of the receptor. The value of  $E_{LUMO}$  is related to the ability of the molecule to accept electrons, lower values of  $E_{LUMO}$  shows the receptor would accept electrons. Consequently, the value of  $E_{gap}$  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  $\eta = \frac{1}{2} (E_{HOMO} - E_{LUMO})$ . The hardness is associated with the stability of chemical potential ( $\mu$ ) can be expressed in combination of electron affinity and ionization potential. The global electrophilicity index ( $\omega$ ) 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	-0.19677	-0.09676
LUMO eV	-0.06863	-0.1070
Energy gap	0.12814	0.01024
Ionisation Potential (I)	0.19677	0.09676
Electron Affinity(A)	0.06863	0.1070
Global Hardness ( $\eta$ )	0.06407	0.00512
Chemical Potential ( $\mu$ )	-0.1327	-0.10188
Global Electrophilicity ( $\omega$ )	0.1374	0.1013

### Thermodynamic Properties

Several thermodynamics properties are calculated on the basis of vibrational analysis at HF/SDD and DFT/B3LYP/SDD Level and the data in presented in Table-5 The Zero Point Vibration Energy and the entropy  $S_{vib}(T)$  are calculated to the extent of accuracy and variations in ZPVE seem to be insignificant the total energy and the change in the total entropy of  $ZrO(NQO)_2$  at room temperature at different method are only marginal. Dipole moment values are comparable.

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

Parameter	DFT/B3LYP/SDD	HF/SDD
Total Energy e.u.	-1413.6229	-1404.7137
Zero Point Energy	215.32832	229.83678
Rotational constants	0.2801231	0.23364
	0.0852041	0.09611
	0.0793167	0.08107
Entropy Total	138.189	136.564
Translational	44.406	44.406
Rotational	36.383	36.422
Vibrational	57.399	55.736
Dipole moment (D)	3.6416	3.8573

#### IV. Conclusions

The proper frequency assignment for the chelate ZrO (NQO)<sub>2</sub> is performed from the FTIR spectra. The experimental vibration frequencies are compared with HF and DFT theory and found most of them are in good agreement. The assignments were confirmed with the help of animation process which is available in Gaussian 09 computer code. The results suggest that it shows the formation of chelates. The molecular geometry of ZrO(NQO)<sub>2</sub> best at the DFT/ B3LYP/SDD level. The HOMO- LUMO energy was calculated and other related molecular properties were also discussed. The Mulliken atomic charges were calculated and the results were discussed. Thermodynamic parameters were calculated.

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