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Quantum chemical vibrational study, molecular property and HOMO-LUMO gap energies of zirconium chelate of 1, 2 naphthoquinone – 1, oxime

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Abstract

The vibrational frequencies of $ZrO(NQO)_2$ where $NQO = 1, 2$ naphthoquinone – 1, oxime, were calculated using Gaussian 09 software code, employing RHF / Lanl2DZ and DFT (B3LYP) 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

Interest in Naphthoquinone of the 1, 4-naphthoquinone and 1, 2- Naphthoquinone arise from the chemical properties and biological importance. They play significant roles in the dye industry and medicinal chemistry (1). The conjugated structure of naphthoquinones is also common in numerous natural products associated with antifungal, antibacterial, antiviral and anti tumour activities (2). Naphthoquinones possess a biological function in cell metabolism as electron carriers, other compounds of this class have been found active against bacteria and fungi (3). A DFT study on the structures and absorption spectra of the M-1-nitroso-2- naphthol compounds (M = Ni, Cu, Cr, Cd, Pb) have been reported by Tugba Tugsuz and Fatma Serin (4). They have reported HOMO and LUMO localized on the ligand with $\pi(C=C)$ character. They have calculated lowest energy absorptions of studied complexes in water and chloroform. A systematic theoretical study concerning the tautomerism of O-nitronaphthols have been reported by Krazan et. al. (5). The nitroso-oxime tautomeric equilibrium was studied by ab initio molecular orbital calculations using HF method. In the present investigation this work was undertaken to study the vibrational wave numbers of $ZrO(NQO)_2$ molecule completely and to identify the various normal modes with greater wave number accuracy. C_{1v} point group symmetry is assumed for the assignment of the bands. Hartree –Fock and Density Functional Theory levels were used to calculate parameters using Gaussian 09 computer code to support our wave number assignments.

II. Experimental

A. Materials and methods

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

B. Preparation of metal chelates

The chelates was prepared by mixing metal salt solution and ligand in 1 : 2 proportion. 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.

C. 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 $4000 - 400\text{ cm}^{-1}$ and $1000 - 300\text{ cm}^{-1}$.

D. 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. (6,7). All the geometries were optimised using SDD basis set using density functional theory (DFT) employing the Beeke's three parameters hybrid

functional (8) combined with Lee- Yang –Parr Correlation (9). 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 (10). 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 (11). 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. Result 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 number of IR with intensity used for identifying modes unambiguously. The harmonics vibrational Frequencies Calculated for ZrO(NQO)2 at HF/DFT levels using the SDD basis have been symmetrised i.e. Table 1. It can be noted that calculated result are harmonics frequencies while the observed contains harmonic contribution. The wave 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 (ngo) 2 at HF AND DFT Level

Sr.No	HF cm ⁻¹	INTE.	DFT B3LYP cm ⁻¹	INT.	EXP cm ⁻¹	INTE.	ASSIGNMENT
1.	53.931	0.755	60.0332	3.2701	--	--	39Zr-38O
2.	79.343	6.534	--	--	--	--	ring deformation
3.	105.732	14.195	106.633	9.490	--	--	14C-37O Bending
4.	112.282	21.021	--	--	--	--	C-H Bending o. p.
5.	122.059	2.992	142.678	3.223	--	--	C-H Bending o.p.
6.	140.328	7.325	153.386	8.6222	--	--	35O-36H Bending
7.	195.062	1.891	211.08	12.907	--	--	C-H Bending o.p.
8.	196.982	7.636	--	--	--	--	C-H Bending o.p.
9.	209.376	2.44	234.895	9.2414	--	--	C-H Bending o.p.
10.	216.528	25.116	--	--	--	--	C-H Bending o.p.
11.	225.903	17.258	--	--	--	--	39Zr-34N Bending
12.	255.601	154.302	263.305	4.547	--	--	39Zr-33N Bending
13.	261.351	125.357	269.38	8.528	--	--	39Zr-42O Bending
14.	291.281	323.404	319.956	7.947	303.12	0.885	33N-40O Bending
15.	323.167	4.008	328.700	23.094	314.12	1.177	34N-35O Bending
16.	330.855	279.339	380.365	11.1136	326.15	6.508	35O-36H Bending
17.	345.195	1.003	--	--	352.51	0.544	40O-41H Bending
18.	368.687	922.969	--	--	--	--	C-H Bending o.p.
19.	377.223	430.313	397.006	17.1408	--	--	35O-36H Bending
20.	398.894	279.019	419.1072	11.609	--	--	35O-36H Bending
21.	410.332	311.095	--	--	--	--	C-H Bending o.p.
22.	414.984	18.707	--	--	--	--	C-H Bending o.p.
23.	421.100	91.883	456.654	2.222	--	--	C-H Bending o.p.
24.	448.075	147.257	458.628	8.590	--	--	35O-36H Bending
25.	457.164	29.779	472.207	40.941	--	--	35O-36H Bending
26.	472.094	13.594	493.450	1.063	--	--	35O-36H Bending
27.	527.284	3.653	534.686	35.0912	528.00	65.26	Ring Vibration
28.	534.070	1.175	--	--	--	--	C-H Bending o.p.
29.	534.498	0.523	--	--	--	--	C-H Bending o.p.
30.	544.892	99.056	--	--	--	--	C-H Bending o.p.
31.	553.499	377.114	--	--	--	--	C-H Bending o.p.
32.	564.000	137.506	614.326	68.213	571.9	77.33	35O-36H Bending
33.	605.913	366.088	620.846	9.2776	--	--	39Zr-37O Bending
34.	626.271	44.573	638.228	14.532	626.8	81.73	39Zr-33N Stretching
35.	637.655	661.803	652.933	79.067	--	--	39Zr-34N Stretching
36.	647.763	154.404	666.434	82.651	652.3	60.81	39Zr-42O Stretching
37.	678.505	174.783	680.773	38.724	--	--	C-H Bending o.p.
38.	690.363	15.191	707.516	47.162	--	--	C-H Bending o.p.
39.	697.194	342.639	727.700	103.682	--	--	39Zr-42O Stretching
40.	718.436	279.567	747.653	2.341	717.6	90.90	C-H Bending o.p.
41.	731.106	15.503	748.954	110.844	--	--	C-H Bending o.p.
42.	732.276	204.518	754.760	--	--	--	40O-41H Bending
43.	745.366	--	759.662	47.314	--	--	C-H Bending o.p.
44.	753.036	133.611	764.862	61.494	15.843	73.52	C-H Bending o.p.
45.	772.653	39.853	--	--	--	--	C-H Bending o.p.

46.	789.966	8.619	--	--	--	--	C-H Bending o.p.
47.	797.975	8.844	813.1668	22.9998	798.7	95.50	C-H Bending o.p.
48.	823.691	82.14	--	--	817.2	83.44	22C-38O Stretching
49.	830.664	27.22	840.544	7.4393	826.1	86.64	C-H Bending o.p.
50.	836.254	205.735	877.6108	6.1192	839.6	67.17	C-H Bending o.p.
51.	877.979	7.264	881.896	4.892	871.5	92.46	C-H Bending i.p.
52.	879.899	338.78	--	--	--	--	C-H Bending o.p.
53.	884.069	181.795	904.834	0.584	--	--	C-H Bending o.p.
54.	913.579	6.708	951.434	0.810	917.1	92.46	C-H Bending o.p.
55.	959.135	1.565	--	--	957.2	81.85	C-H Bending o.p.
56.	972.028	0.695	--	--	--	--	C-H Bending o.p.
57.	975.350	27.195	--	--	974.7	84.69	22C-38O Stretching
58.	975.457	8.032	--	--	--	--	C-H Bending o.p.
59.	1002.24	4.079	1003.562	70.536	1002.8	85.36	C-H Bending o.p.
60.	1002.40	12.093	1027.646	11.526	--	--	C-H Bending o.p.
61.	1013.88	0.5811	1042.149	150.644	--	--	C-H Bending o.p.
62.	1023.29	4.339	1048.649	4.1727	1022.7	78.31	C-H Bending o.p.
63.	1033.52	7.059	1065.194	72.6314	--	--	C-C Stretching
64.	1041.67	138.679	1081.285	81.568	1045.7	8087	C-C Stretching
65.	1083.69	55.425	1095.335	355.298	--	--	C-H Bending i.p.
66.	1084.77	20.523	1109.472	58.6842	1091.2	63.30	C-H Bending i.p.
67.	1118.96	3.115	1120.73	7.0346	1115.5	73.12	C-H Bending i.p.
68.	1121.90	11.699	1126.248	11.703	--	--	C-H Bending i.p.
69.	1141.33	253.632	1165.047	4.3142	1145.1	65.54	33N-40O stretching
70.	1159.12	272.532	1189.594	108.125	1158.9	44.81	C-H Bending i.p.
71.	1184.95	1583.27	1205.763	73.705	1175.2	46.53	C-H Bending i.p.
72.	1197.80	199.322	1221.989	19.6889	1198.	74.58	C-H Bending i.p.
73.	1220.00	34.94	1233.189	273.778	1215.5	49.52	C-H Bending i.p.
74.	1238.67	478.708	--	--	1242.	38.05	C-H Bending i.p.
75.	1249.03	587.881	--	--	--	--	C-H Bending i.p.
76.	1260.65	5.388	1284.7	596.374	--	--	C-C Stretching
77.	1281.17	73.291	1295.948	11.6637	1277.9	71.99	C-C Stretching
78.	1293.73	43.005	1299.029	76.4903	--	--	C-C Stretching
79.	1296.73	103.836	1312.165	38.4634	1304.2	48.24	C-C Stretching
80.	1316.69	56.791	1344.309	284.278	--	--	O-H Bending
81.	1336.77	111.33	1357.897	53.033	--	--	O-H Bending
82.	1342.04	110.33	1385.844	137.931	1341.6	68.39	C-C Stretching
83.	1360.60	12.893	1398.873	477.865	1354.3	49.95	C-C Stretching
84.	1370.98	215.123	1403.948	176.244	1367.5	68.89	C-C Stretching
85.	1390.71	1411.04	1410.776	10.8081	--	--	C-H Bending i.p.
86.	1411.61	24.285	1421.311	103.893	1406.3	49.16	C-H Bending i.p.
87.	1422.79	529.144	1437.027	54.9068	1416.1	58.80	C-H Bending i.p.
88.	1445.38	20.58	1479.399	189.521	1450.7	65.32	C-C Stretching
89.	1474.37	453.06	1490.714	73.8506	1477.	63.37	14C-37O Stretching
90.	1499.59	358.001	1507.297	267.304	1494.1	76.89	22C-38O Stretching
91.	1501.45	209.698	1531.844	15.6124	1503.6	75.70	C-C Stretching
92.	1519.70	190.068	1539.461	3.3025	--	--	21C-34N Stretching
93.	1549.76	118.352	1573.802	392.952	1558.9	36.61	22C-38O Stretching
94.	1563.57	9.196	1595.373	701199	1574.	51.77	21C-34N Stretching
95.	1592.06	1427.58	16.8.345	4.3533	1594.9	32.50	C-C Stretching
96.	1600.57	48.832	1630.494	94.227	--	--	C-C Stretching
97.	1605.98	35.416	1654.347	222.045	--	--	C-C Stretching
98.	1618.26	270.556	1679.337	152.336	--	--	C-C Stretching
99.	1798.90	38.34	1778.237	26.6108	1713.15	59.20	C-H Bending i.p.
100	3043.42	4.038	3232.473	0.8686	2924.81	23.56	C-HStretching unsym.
101	3043.42	0.062	3240.177	0.8885	--	--	C-HStretching unsym
102	3051.56	31.115	3240.784	1.3976	--	--	C-H Stretching unsym
103	3053.72	6.483	3244.077	0.1749	--	--	C-H Stretching unsym
104	3055.79	24.402	3245.204	14.5313	--	--	C-H Stretching unsym
105	3056.31	21.971	3260.275	11.6762	--	--	C-H Stretching unsym
106	3067.92	190.022	3260.458	10.3109	--	--	C-H Stretching unsym
107	3069.10	25.725	3261.691	13.5713	--	--	C-H Stretching unsym
108	3069.54	547.508	3262.673	75.8257	--	--	C-H Stretching sym.
109	3070.49	73.661	3273.728	61.0205	--	--	C-H Stretching sym
110	3100.97	33.046	3305.873	50.8874	--	--	C-H Stretching
111	3150.08	127.608	3432.89	21.0747	3355.88	40.00	C-H Stretching
112	3448.59	1275.2	3682.242	260.118	--	--	400-41H Stretching
113	3502.89	571.565	3763.192	25.3799	--	--	350-36H Stretching

C-H vibration

The Naphthalene structure show the presence of structural vibration in the region $3250\text{--}2950\text{ cm}^{-1}$ which is characteristics for the zero identification of C-H stretching vibration. The region $3250\text{--}3100\text{ cm}^{-1}$ is for symmetric stretching, and $3100\text{--}2950\text{ cm}^{-1}$ for symmetric stretching modes of vibration(12). 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 bands are observed at 3355.88 cm^{-1} and 2924.81 cm^{-1} have been assigned to C-H stretching vibration. The HF level gives $3043.42, 3043.42, 3051.56, 3053.72, 3055.79, 3056.31, 3067.42, 3069.10, 3069.54, 3070.49, 3100.97$ and 3150 cm^{-1} while DFT/B3LYP level gives values at $3232.473, 3240.177, 3240.784, 3244.077, 3245.204, 3260.274, 3260.458, 3261.691, 3262.673, 3273.728, 3305.873$ and 3432.89 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 is agreement with the experimental predicted in the region $1030\text{--}650\text{ cm}^{-1}$ 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 $\text{ZrO}(\text{NQO})_2$ is experimentally practiced in the region $1250\text{--}1080\text{ cm}^{-1}$ which is supported week by the vibration values practiced by HF and DFT levels.

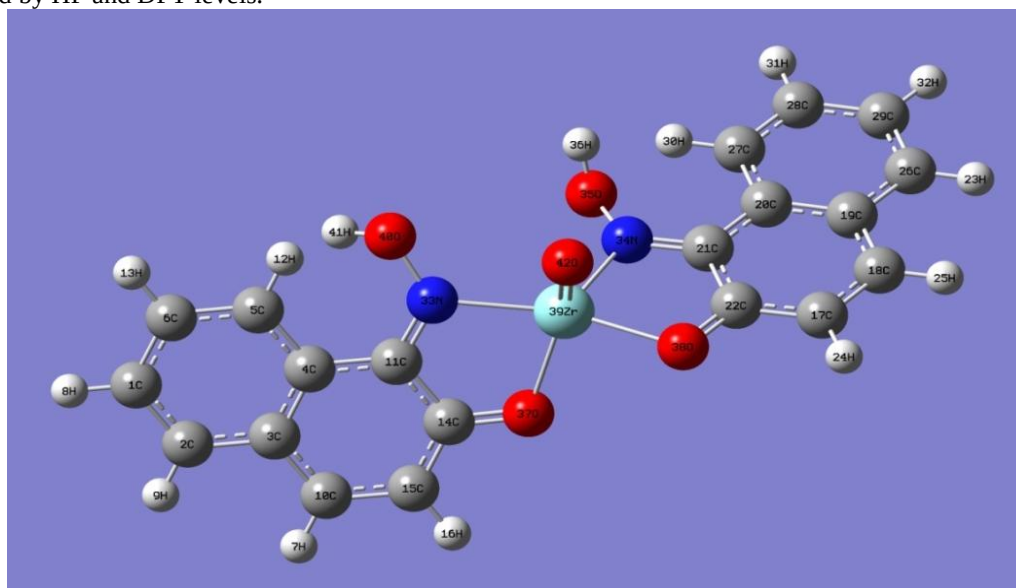


Fig.1. Molecular Structure of $\text{ZrO}(\text{NQO})_2$

The other region for C-H bending out of place are predicted by HF in the region $553\text{ to }534\text{ cm}^{-1}$, $421\text{ to }410\text{ cm}^{-1}$, $216\text{ to }195\text{ cm}^{-1}$ which DFT has predicted very few vibration modes.

C=O Vibration

The C=O stretching vibration of $\text{ZrO}(\text{NQO})_2$ has a main contribution in the mode with B3LYP/SDD predicted frequency at 1473.802 cm^{-1} and HF/SDD predicted at 1549.76 cm^{-1} . In the FTIR spectra, we observed then peak at 1558.9 cm^{-1} , which good agreement with predicted data. The other C=O frequencies are observed at $1494.1, 1477, 974, 817\text{ cm}^{-1}$, 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 1574 cm^{-1} in the FTIR spectra of $\text{ZrO}(\text{NQO})_2$ while it is predicted at 1745.373 cm^{-1} by DFT/SDD and at 1563.57 cm^{-1} by HFI/SDD is predicted but this is not observed in the FTIR spectra. The $\text{V}(\text{C}=\text{N})$ is chelates shows lower frequency owing to elongation of these bands on co-ordination.

N-O Vibration

The observation of $\gamma(\text{N-O})$ is observed at 1145.1 cm^{-1} in the FTIR spectrum which is predicted at 1165.04 cm^{-1} by DFT/SDD and at 1141.33 cm^{-1} by HF/SDD. These bands are good agreement with observed data. The absorption of this $\gamma(\text{N-O})$ at higher wave number indicates that THEIR Bond was significantly shorter in the chelates. The higher wave length of the N-O indicates that nitroso atoms of the oxime group coordinates to the centre (13, 14).

Zr-O Stretching Vibration

The wave number of Zr-O stretching in the chelate $\text{ZrO}(\text{NQO})_2$ are predicted at 647 and 697 by HF theory and 666 and 727 cm^{-1} by DFT theory but we observed a peak at 652 cm^{-1} . This Frequency is lower which suggests that it is attached to central atom.

Zr-O bending Vibration

Zr-O bending vibration is predicted at $53, 261$ and 605 cm^{-1} by the HF level and $60, 264$ and 620 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 225 cm^{-1} with HF level and 255 and 263 cm^{-1} with DFT level. Experimental values are not recorded.

Molecular geometry

The optimized structure parameters of $\text{ZrO}(\text{NQO})_2$ 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 $\text{\AA}$ and bond angles in degree are given in Table 3.

Table No: 2 Bond Length and Bond Angle of $\text{ZrO}(\text{NQO})_2$

Bond length	$\text{\AA}$	Bond angle	$^{\circ}$
C1-C2	1.401	C1-C2-C3	120.034
C2-C3	1.401	C2-C3-C4	119.822
C3-C4	1.403	C3-C4-C5	120.169
C4-C5	1.400	C4-C5-C6	119.927
C5-C6	1.401	H8-C1-C6	119.927
C3-C10	1.406	H7-C10-C3	119.795
C4-C11	1.398	C3-C2-H9	119.982
C10-C15	1.406	C5-C6-H12	120.36
C11-C14	1.426	H13-C6-C1	120.002
C15-C14	1.399	H8-C1-C2	119.795
C17-C18	1.405	H7-C10-C15	119.795
C18-C19	1.407	C1-C2-H9	119.983
C19-C20	1.403	C5-C6-H13	120.002
C20-C21	1.397	H12-C5-C4	120.030
C21-C22	1.399	H16-C15-C14	120.132
C26-C27	1.401	C10-C15-H16	120.132
C27-C28	1.401	C17-C18-C19	120.794
C28-C29	1.401	C18-C19-C20	120.612
C20-C27	1.401	C19-C20-C21	119.777
C19-C26	1.401	C20-C21-C22	119.835
O42-Zr39	1.856	C22-C17-C18	120.068
Zr39-O37	2.098	C19-C26-H23	119.952
O38-Zr39	2.070	C29-C26-H23	119.952
N33-Zr39	2.123	C17-C18-H25	119.60
O40-N33	1.360	H24-C17-C18	119.966
H41-O40	0.960	C26-C29-C28	120.042
Zr39-N34	2.091	C29-C28-C27	119.985
O35-N34	1.360	C20-C27-C28	119.980
H36-O35	0.960	H30-C27-C20	120.010
N34-C21	1.318	C28-C29-H32	119.979
O38-C22	1.306	H31-C28-C27	120.008
O37-C14	1.282	C28-C27-H30	120.010
N33-C11	1.298	H31-C28-C29	120.008
H12-C5	1.070	C26-C29-H32	119.976
H16-C15	1.070	H36-O35-N34	109.471
H24-C17	1.070	O42-Zr39-O38	83.752
H30-C27	1.070	N34-Zr39-O42	106.142
H31-C28	1.070	H41-O40-N33	109.471
H24-C17	1.070	C11-N33-O40	123.804
H8-C1	1.070	C14-O37-Zr39	112.956
H23-C26	1.070	Zr39-O38-C22	108.007
		O35-N34-C21	125.956

Mulliken Atomic Charges

Mulliken charges arise from the Mulliken population analysis (15,16) 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(17) procedures(18). In the application of quantum mechanical calculation to molecular system, the calculation of effective atomic charges plays an important role. The electron distribution of $\text{ZrO}(\text{NQO})_2$ are compared in the two different mechanical methods and the sensitivity of the calculated charges to change 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 barchart of atomic charge against atoms.

Table-3: Atomic Charges of ZrO(NQO)₂

Sr.No	HF/SDD		DFT/SDD	
	Atom	Atomic charge	Atom	Atomic charge
1.	1 C	-0.242543	1 C	-0.227643
2.	2 C	-0.386040	2 C	-0.438768
3.	3 C	0.428912	3 C	0.511356
4.	4 C	0.162745	4 C	0.136260
5.	5 C	-0.217951	5 C	-0.237328
6.	6 C	-0.310896	6 C	-0.324626
7.	7 H	0.228837	7 H	0.245440
8.	8 H	0.223726	8 H	0.235197
9.	9 H	0.228282	9 H	0.249135
10.	10 C	-0.418765	10 C	-0.449391
11.	11C	0.328530	11 C	0.159992
12.	12H	0.115357	12 H	0.120491
13.	13H	0.224510	13 H	0.238464
14.	14C	0.425438	14 C	0.258388
15.	15 C	-0.418534	15 C	-0.363342
16.	16 H	0.249451	16 H	0.258480
17.	17 C	-0.451455	17 C	-0.383307
18.	18 C	-0.397951	18 C	-0.451029
19.	19 C	0.403551	19 C	0.493177
20.	20 C	0.191841	20 C	0.156500
21.	21 C	0.368859	21 C	0.196496
22.	22 C	0.478294	22 C	0.297348
23.	23 H	0.228527	23 H	0.246403
24.	24 H	0.258162	24 H	0.261005
25.	25 H	0.233071	25 H	0.244328
26.	26 C	-0.387126	26 C	-0.442542
27.	27 C	-0.274875	27 C	-0.327089
28.	28 C	-0.295405	28 C	-0.297720
29.	29 C	-0.232564	29 C	-0.226248
30.	30 H	0.236716	30 H	0.245145
31.	31 H	0.223174	31 H	0.233098
32.	32 H	0.224286	32 H	0.232166
33.	33 N	-0.553398	33 N	-0.376732
34.	34 N	-0.560992	34 N	-0.384265
35.	35 O	-0.515484	35 O	-0.407975
36.	36 H	0.434482	36 H	0.391575
37.	37 O	-0.733673	37 O	-0.470950
38.	38 O	-0.653335	38 O	-0.422611
39.	39 Zr	1.954270	39 Zr	1.293926
40.	40 O	-0.442691	40 O	-0.323134
41.	41 H	0.379441	41 H	0.324967
42.	42 O	-0.736785	42 O	-0.474638

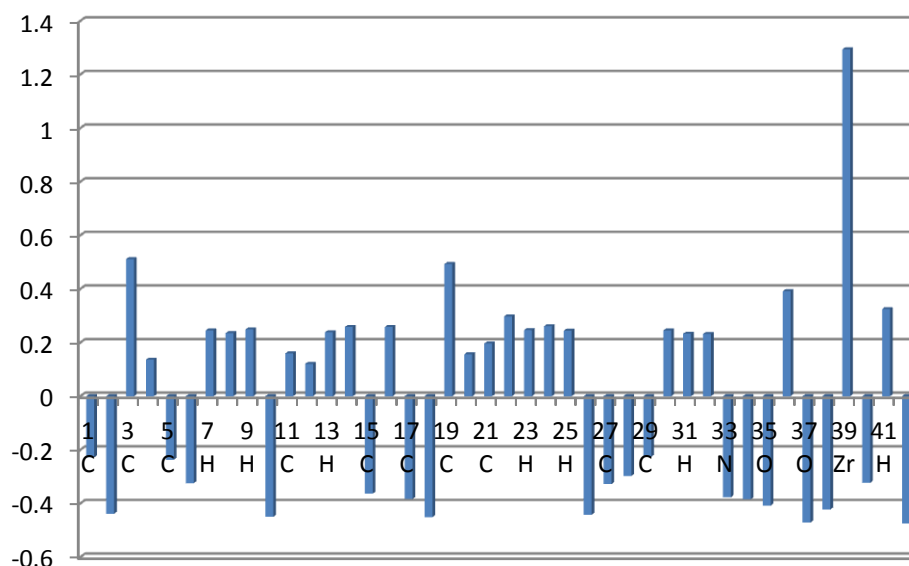


Fig. 2 Barchart of atomic charge against atoms.

HOMO-LUMO energy gap and related molecular properties

The HOMO-LUMO energy gap of the molecule $\text{ZrO}(\text{NQO})_2$ 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 $I = -E_{\text{HOMO}}$, $A = -E_{\text{LUMO}}$. 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 $\eta = \frac{1}{2} (E_{\text{HOMO}} - E_{\text{LUMO}})$. 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 $\text{ZrO}(\text{NQO})_2$

Molecular Properties	HF/SDD	DFT/B3LYP/SDD
HOMO eV	-0.19706	-0.17549
LUMO eV	-0.09668	-0.15030
Energy gap	0.10038	0.02519
Ionisation Potential (I)	0.19706	0.15030
Electron Affinity(A)	0.09668	0.17549
Global Hardness (η)	0.05019	0.0123
Chemical Potential (μ)	0.05019	0.012595
Global Electrophilicity (ω)	0.02509	0.0000793

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 $S_{\text{vib}}(T)$ 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 $\text{ZrO}(\text{NQO})_2$ at room temperature at different method are only marginal dipole moment value are comparable.

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

Parameter	HF/SDD	DFT/B3LYP/SDD
Total Energy e.u.	-1294.76217	-1303.01787
Zero Point Energy	205.89377	193.0492
Rotational constants	0.44159	0.44159
	0.07949	0.07949
	0.07615	0.07615
Entropy Total	131.136	133.239
Translational	44.215	44.215
Rotational	36.040	36.040
vibrational	50.881	52.984
Dipole movement (D)	8.5305	6.915

IV. Conclusions

The results of the study lead to the following conclusion.

1. The proper frequency assignment for the chelate $\text{ZrO}(\text{NQO})_2$ 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 $\text{ZrO}(\text{NQO})_2$ 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.

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