

# Spectroscopic (FT-IR & FT-Raman), First Order Hyperpolarizability, NLO Analysis and Homo-Lumo Analysis of Metronidazole

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**Abstract-** The FT-IR, FT-Raman and UV-Visible spectra of Metronidazole were recorded for the interpretation of physical, chemical, thermal and toxic property. The spectroscopic data of the molecule in the ground state were calculated by performing computational calculations. The vibrational assignments for fundamental modes were assigned and their presence was keenly monitored to evaluate the internal parts whether it is active or not. The arrangement of the molecular polarizability and hyper activity for ensuring drug activity for the compound was studied.

**Keywords-** FTIR, Frontier molecular orbital energies, HOMO-LUMO, Hyper Polarizability.

## I. INTRODUCTION

Metronidazole (MNZ), marketed under the brand name Flagyl among others is an antibiotic and medication. It is used either alone or with other antibiotics to treat pelvic inflammatory disease, endocarditic, and bacterial vaginosis. It is effective for dracunculiasis, giardiasis, trichomoniasis, and amebiasis. It is the drug of choice for a first episode of mild-to-moderate Clostridium difficile colitis. Metronidazole is available by mouth, as a cream, and intravenously. Common side effects include nausea, a metallic taste, loss of appetite, and headaches. Occasionally seizures or allergies to the medication may occur. Metronidazole should not be used in early pregnancy but appears to be safe later in pregnancy. It should not be used when breastfeeding.

## II. EXPERIMENTAL

Metronidazole with >99% purity was obtained from Chennai reputed company, Chennai and was used without further treatments. The FTIR spectrum of the powder sample was recorded in KBr in the range 4000 – 400 cm<sup>-1</sup> using a Perkin Elmer spectrometer with a resolution of  $\pm 1$  cm<sup>-1</sup>. FT-Raman spectrum of the powder sample was recorded using 1064 nm line in Nd:YAG laser as the excitation wavelength in the region 4000-50 cm<sup>-1</sup> using Bruker RFS 27 spectrometer.

The UV–V is spectrum was recorded in the range 200-900nm using a Varian Cary 5E-UV-NIR spectrophotometer.

## III. COMPUTATIONAL DETAILS

The density functional theory treated according to hybrid Becke's three parameter and the Lee–Yang–Parr functional (B3LYP) functional were used to carry out analysis with the standard 6-311++G (d,p) basis sets to study the molecule Metronidazole . All calculations were carried out using Gaussian 09 package [9]. All these calculations have been carried out using Gaussian 09W [9] program package on Pentium IV processor in personal computer.

The mean polarizability properties of tested molecule were obtained from the theoretical calculations to show the NLO property of the molecules. The energy of highest occupied molecular orbit (EHOMO) and the energy of Lowest unoccupied Molecular Orbital (ELUMO) the dipole moment ( $\mu$ ), the ionization potential (I), the electron affinity (A), the electro negativity (X), the global hardness ( $\eta$ ) were calculated for both the molecules and the comparison also discussed . The electronic absorption spectrum requires calculation. The optimized molecular structure of the molecule is obtained from Gaussian 09 and Gauss view program and is show in figure.

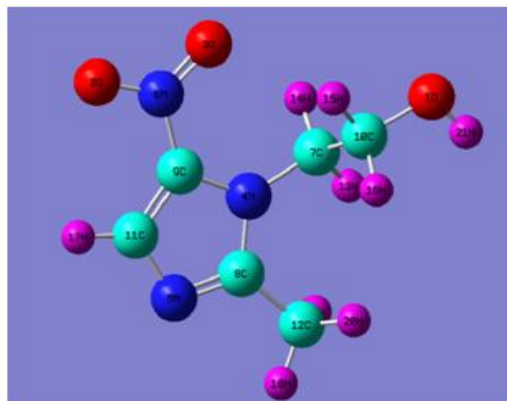


Fig.1. Optimized molecular structure and atomic numbering of Metronidazole.

Table1. Optimized geometrical parameters for SFAP computed at various basis sets of Metronidazole

Geometrical Parameter	Methods				
	HF	B3LYP		B3PW91	
	6-311+G	6-31+G	6-311++G(d,p)	6-31+G	6-311++G(d,p)
<b>Bond length(R)</b>					
O1-C10	1.4	1.4212	1.4277	1.4133	1.412
O1-H21	0.9399	0.9659	0.9615	0.9637	0.9606
O2-N6	1.1884	1.2357	1.2288	1.2294	1.2218
O3-N6	1.1946	1.2418	1.238	1.2354	1.2285
N4-C8	1.4642	1.4699	1.4696	1.462	1.4617
N4-C9	1.3465	1.3682	1.3653	1.3642	1.363
N5-C8	1.3846	1.394	1.3935	1.3883	1.3869
N5-C11	1.3057	1.3336	1.332	1.3309	1.327
N6-C9	1.348	1.3563	1.3528	1.3526	1.3511
C7-C10	1.418	1.4196	1.4193	1.4164	1.4199
C7-H13	1.5214	1.5379	1.5216	1.5335	1.5315
C7-H14	1.0798	1.0932	1.0901	1.0939	1.0927
C8-C12	1.0765	1.0887	1.0872	1.0895	1.088
C9-C11	1.4951	1.4935	1.4901	1.4887	1.4867
C10-H15	1.3532	1.3816	1.3788	1.3796	1.3757
C10-H16	1.0839	1.0916	1.0977	1.0922	1.0909
C11-H17	1.0884	1.0995	1.0936	1.1002	1.0989
C12-H18	1.0688	1.0796	1.078	1.0802	1.079
C12-H19	1.0802	1.0906	1.0888	1.0906	1.0893
C12-H20	1.0855	1.0964	1.095	1.0962	1.095
C12-H21	1.0844	1.0954	1.0919	1.0951	1.0939
<b>Bond angle(Å)</b>					
C10-O1-H21	110.5853	109.7622	109.2819	109.5407	109.3047
C7-N4-C8	125.3348	125.3157	25.6143	125.2607	125.275
C7-N4-C9	130.1352	129.5789	29.1388	129.5849	129.5972
C8-N4-C9	104.5297	105.0995	05.2318	105.1395	105.0999
C8-N5-C11	106.1944	106.1072	106.3056	105.997	106.1031
O2-N6-O3	124.7479	124.4308	24.227	124.6384	124.7666
O2-N6-C9	116.8964	116.9303	17.12	116.822	116.7915
O3-N6-C9	118.3554	118.6386	18.6525	118.5394	118.4419
N4-C7-C10	112.4115	112.401	113.3286	112.3299	112.4112
N4-C7-H13	107.4201	106.8404	106.9387	106.8474	106.7965
N4-C7-H14	109.3938	109.1655	108.7095	109.2537	109.2874
C10-C7-H13	109.1381	110.1672	109.4586	110.2204	110.1847
C10-C7-H14	110.1575	109.5919	109.4952	109.5903	109.6157
H13-C7-H14	108.1956	108.5723	108.7971	108.4961	108.4361
N4-C8-N5	112.7686	112.2538	112.0339	112.3185	112.2574
N4-C8-C12	124.0519	124.1288	124.0768	124.0303	123.9633
N5-C8-C12	123.1751	123.6107	123.889	123.644	123.7721
N4-C9-N6	125.723	125.583	125.6811	125.5776	125.5211
N4-C9-C11	107.185	106.8021	106.7043	106.7907	106.8319
N6-C9-C11	127.0913	127.6148	127.6145	127.6307	127.6454
O1-C10-C7	106.1349	110.7423	108.1471	110.8851	110.9601
O1-C10-H15	111.4214	106.2885	110.9164	106.4258	106.4435
O1-C10-H16	110.8678	111.6398	111.5871	111.8451	111.8093

C7-C10-H15	109.8919	109.4632	107.9025	109.3147	109.3115
C7-C10-H16	109.9188	110.234	109.899	110.1257	110.0811
H15-C10-H16	108.5896	108.3504	108.3224	108.1125	108.1039
N5-C11-C9	109.3222	109.7369	109.7234	109.7538	109.707
N5-C11-H17	123.1473	123.1253	123.2196	123.1732	123.253
C9-C11-H17	127.5304	127.1376	127.057	127.073	127.04
C8-C12-H18	107.8509	107.7651	107.9214	107.686	107.7761
C8-C12-H19	111.0952	111.8904	111.6674	111.9104	111.8147
C8-C12-H20	111.7871	112.2784	111.1203	112.3374	112.2618
H18-C12-H19	108.7194	108.3005	108.2852	108.2441	108.2938
H18-C12-H20	109.0557	108.5165	109.5232	108.4791	108.5146
H19-C12-H20	108.2728	107.9723	108.27	108.059	108.0632
<b>Dihedral Angles(Å)</b>					
H21-O1-C10-C7	164.8776	-76.2761	-166.4099	-75.7771	-74.3901
H21-O1-C10-H15	45.275	164.9172	75.4534	165.435	166.7744
H21-O1-C10-H16	-75.7923	46.9616	-45.4203	47.5715	48.9298
C8-N4-C7-C10	-97.4603	-96.5428	-97.5001	-96.445	-96.507
C8-N4-C7-H13	22.6111	24.4127	23.2024	24.5383	24.4472
C8-N4-C7-H14	139.8316	141.6387	140.51	141.724	141.5518
C9-N4-C7-C10	82.3056	82.4326	80.8685	81.938	81.276
C9-N4-C7-H13	-157.623	-156.6119	-158.4289	-157.0787	-157.7698
C9-N4-C7-H14	-40.4025	-39.3859	-41.1214	-39.893	-40.6652
C7-N4-C8-N5	179.7858	179.2955	179.0113	178.866	178.4449
C7-N4-C8-C12	-0.9507	-1.6134	-1.1963	-2.0806	-2.4966
C9-N4-C8-N5	-0.0293	0.1134	0.3226	0.157	0.2141
C9-N4-C8-C12	179.2341	179.2045	-179.885	179.2103	179.2727
C7-N4-C9-N6	-0.1347	0.7669	1.1654	1.4855	2.0514
C7-N4-9-C11	-179.8555	-179.3198	-178.9248	-178.851	-178.3803
C8-N4-C9-N6	179.6681	179.901	179.791	-179.8823	-179.8231
C8-N4-C9-C11	-0.0528	-0.1857	-0.2993	-0.2188	-0.2549
C11-N5-C8-N4	0.0992	0.0078	-0.211	-0.0276	-0.0823
C11-N5-C8-C12	-179.1717	-179.0888	179.9962	-179.0853	-179.143
C8-N5-C11-C9	-0.1308	-0.1301	0.0086	-0.1172	-0.0877
C8-N5-C11-H17	179.9603	-179.9647	-179.9792	179.9694	179.9388
O2-N6-C9-N4	178.1477	177.8117	178.7428	178.111	178.3732
O2-N6-C9-C11	-2.1866	-2.0835	-1.1481	-1.4822	-1.1049
O3-N6-C9-N4	-2.036	-2.3643	-1.4808	-2.0156	-1.7062
O3-N6-C9-C11	177.6297	177.7405	178.6284	178.3911	178.8157
N4-C7-C10-O1	172.6054	177.1116	65.6714	177.1459	177.2205
N4-C7-C10-H15	-66.7973	-66.0211	-174.2831	-65.8251	-65.6866
N4-C7-C10-H16	52.6553	53.0655	-56.3611	52.8136	52.913
H13-C7-C10-O1	53.5342	58.0855	-53.5951	58.1213	58.2314
H13-C7-C10-H15	174.1315	174.9529	66.4504	175.1503	175.3243
H13-C7-C10-H16	-66.4159	-65.9605	-175.6276	-66.211	-66.0762
H14-C7-C10-O1	-65.1176	-61.3128	-172.7781	--61.215	-61.025
H14-C7-C10-H15	55.4797	55.5546	-52.7326	55.814	56.0679
H14-C7-C10-H16	174.9323	174.6412	65.1894	174.4527	174.6675
N4-C8-C12-H18	175.4448	177.2933	176.9268	177.137	177.6196
N4-C8-C12-H19	-65.5022	-63.7545	-64.172	-64.0187	-63.474
N4-C8-C12-H20	55.5697	57.8446	56.831	57.7507	58.1761
N5-C8-C12-H18	-5.3667	-3.7168	-3.3051	-3.915	-3.4286
N5-C8-C12-H19	113.6864	115.2354	115.5961	114.9294	115.4778

N5-C8-C12-H20	-125.2417	-123.1654	-123.4008	-123.3012	-122.8721
N4-C9-C11-N5	0.1147	0.2002	0.1863	0.2136	0.2183
N4-C9-C11-H17	-179.9815	-179.9735	-179.8265	-179.8773	-179.8094
N6-C9-C11-N5	-179.6012	-179.8888	-179.9062	179.868	179.7745
N6-C9-C11-H17	0.3026	-0.0626	0.081	-0.2229	-0.2533

**Table 2: Observed and HF and DFT (B3LYP & B3PW91) with 6-31++G (d,p) & 6-311++G (d,p) level calculated vibrational frequencies of Metronidazole.**

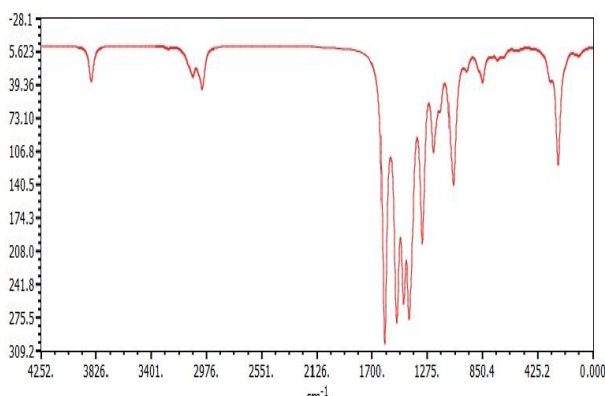
S. No.	Symmetry Species $C_s$	Observed frequency ( $\text{cm}^{-1}$ )		Methods					Vibrational Assignments
				HF			B3LYP		
		FT-IR	FT-Raman	6-311++G (d,p)	6-311++G (d,p)	6-311++G (d,p)	6-31++G (d,p)	6-311++G (d,p)	
1	A	3460 m	3460w	3460	3451	3436	3460	3433	(N-H) $\nu$
2	A	3310 m	-	3163	3286	3263	3295	3272	(N-H) $\nu$
3	A	2940 m	-	3071	3174	3153	3183	3165	(C-H) $\nu$
4	A	2920 vs	-	2963	3161	3145	3179	3160	(C-H) $\nu$
5	A	2840 vs	-	2940	3136	3098	3144	3126	(C-H) $\nu$
6	A	1670 s	-	2840	3099	3095	3120	3101	(C=O) $\nu$
7	A	1650 s	-	1657	3091	3066	3097	3084	(C=N) $\nu$
8	A	1590s	1590 w	1657	3043	3032	3055	3042	(C=N) $\nu$
9	A	1570 m	-	1620	3018	3004	3025	3012	(C=C) $\nu$
10	A	1560 m	-	1590	1583	1562	1623	1609	(N-H) $\delta$
11	A	1460 vs	1540 w	1570	1551	1540	1569	1562	(N-H) $\delta$
12	A	1340 vs	1490 w	1560	1514	1516	1526	1521	(C-N) $\nu$
13	A	1330 vs	1460 w	1540	1509	1501	1516	1509	(C-N) $\nu$
14	A	1160 st	1380 s	1490	1505	1499	1509	1503	(C-N) $\nu$
15	A	1080 w	1370 s	1460	1490	1485	1485	1479	(C-C) $\nu$
16	A	1040 w	1330 s	1460	1481	1473	1476s	1470	(C-C) $\nu$
17	A	980 m	1320 vs	1380	1461	1453	1468	1461	(N-H) $\gamma$
18	A	970 m	1160 w	1370	1426	1440	1434	1422	(N-H) $\gamma$
19	A	870 v	1040 w	1340	1420	1413	1424	1421	(C-H) $\gamma$
20	A	850 s	870 s	1330	1401	1396	1411	1405	(C-H) $\gamma$
21	A	830 s	850 s	1330	1392	1388	1398	1391	(C-H) $\gamma$
22	A	800 s	-	1320	1380	1381	1384	1386	(C-H) $\gamma$
23	A	790 s	680 w	1160	1346	1301	1342	1343	(C-H) $\gamma$
24	A	740 w	340 w	1160	1308	1293	1325	1316	(C-H) $\gamma$
25	A	680 w	170 w	1080	1303	1262	1310	1309	(CNC) $\gamma$
26	A	650 m	100 w	1040	1221	1221	1234	1230	(CCN) $\gamma$
27	A	550 w	80 w	1040	1205	1213	1206	1205	(NCC) $\gamma$
28	A	530 s	-	980	1177	1175	1182	1176	(C-N) $\delta$
29	A	520 s	-	970	1087	1089	1105	1099	(C-C) $\gamma$
30	A	510 s	-	870	1065	1083	1075	1077	(CNC) $\gamma$
31	A	500 s	-	870	1062	1064	1056	1054	(CCN) $\gamma$
32	A	480 w	-	850	1038	1013	1047	1046	(NCC) $\gamma$
33	A	470 s	-	850	1005	980	1003	1001	(C-N) $\gamma$
34	A	450 s	-	830	970	955	975	974	(C-C) $\gamma$
35	A	440 w	-	800	893	889	891	887	(CCN) $\tau$
36	A	430 s	-	790	831	876	841	852	(N-H) $\tau$
37	A	420 s	-	740	801	839	805	804	(C=N) $\nu$
38	A	410 w	-	680	776	746	777	777	(C=O) $\nu$
39	A	400 w	-	680	740	732	750	737	(C=N) $\gamma$
40	A	390 s	-	650	698	689	702	703	(C=C) $\gamma$
41	A	380 s	-	550	681	651	683	684	(C-N) $\gamma$
42	A	370 w	-	530	605	607	608	608	(C-C) $\gamma$
43	A	360 s	-	530	575	564	577	578	(CNC) $\gamma$

44	A <sup>''</sup>	350 w	-	520	454	499	456	455	(CCN) $\gamma$
45	A <sup>''</sup>	340 w	-	500	393	418	396	395	(NCC) $\gamma$
46	A <sup>''</sup>	330 s	-	480	345	394	348	347	(C-N) $\gamma$
47	A <sup>''</sup>	320 s	-	430	337	347	337	336	(C-C) $\gamma$
48	A <sup>''</sup>	310 w	-	420	319	288	320	318	(CCN) $\gamma$
49	A <sup>''</sup>	300 s	-	380	286	268	286	281	(N-H) $\gamma$
50	A <sup>''</sup>	290 w	-	340	269	247	275	270	(C-H) $\gamma$
51	A <sup>''</sup>	280 w	-	320	214	218	213	213	(CNC) $\gamma$
52	A <sup>''</sup>	270 s	-	310	148	164	149	146	(C-H) $\gamma$
53	A <sup>''</sup>	260 w	-	300	142	147	142	139	(C-H) $\gamma$
54	A <sup>''</sup>	250 w	-	280	111	117	111	112	(N-H) $\gamma$
55	A <sup>''</sup>	240 w	-	170	95	88	95	94	(CNC) $\gamma$
56	A <sup>''</sup>	230 w	-	100	69	82	69	69	(CCN) $\gamma$
57	A <sup>''</sup>	220w	-	80	47	43	48	45	(N-H) $\gamma$

#### IV. RESULT AND DISCUSSION

The geometrical structure along with numbering of atoms of Metronidazole is obtained from Gaussian 09 and GAUSSVIEW programs are shown in Fig.1. The optimized geometrical parameters of metronidazole obtained by DFT–B3LYP/6-311++G (d,p) and HF/6-311++G(d,p) levels are listed in Table 1. From the structural data given in it is observed that the various bond lengths are found to be almost same at HF and B3LYP levels. However, the B3LYP/6-311++G (d,p) level of theory, in general slightly over estimates bond lengths but it yields bond angles in excellent agreement with the HF method. The calculated geometric parameters can be used as origin to calculate the other parameters for the compound. The calculated C–C bond lengths of the ring vary from 1.418 to 1.4164 Å.

In this study the C-H bond lengths were studied as 1.0962 Å. The density functional calculation gives almost same bond angles in tested molecule. The dihedral angles of our title molecule show that our tested molecule was planar. In generally the optimized bond length and bond angles are slightly smaller than the experimental values. This is due to the fact that all the theoretical calculations belongs to isolated molecule were done in gaseous state and the experimental results were belongs to molecule is in solid state.



Theoretical value of infrared spectrum

#### V. VIBRATIONAL ANALYSIS

The vibrational spectrum is mainly determined by the modes of free molecule observed at higher wave numbers, together with the lattice (translational and vibrational) modes in the low wave number region. In our present study, we have performed a frequency calculation analysis to obtain the spectroscopic signature of Metronidazole. The Metronidazole molecule consists of 21 atoms therefore they have 57 vibrational normal modes. All the frequencies are assigned. The measured (FTIR and FT-Raman) wave numbers and assigned wave numbers of the some selected intense vibrational modes calculated at the B3LYP and HF levels using basis set 6-311++G(d,p) basis set and they are listed in Table 2. For B3LYP and HF with 6-311++G(d,p) basis set, the wave numbers are scaled with 0.99 and 0.98 respectively.

##### N-H Vibrations

Generally, the NH group vibrations are very dominative and no way have their vibrational bands not affected. Here the mono amine group was substituted along with the chain of ethyl-methyl group. When the NH group placed between chain and aromatic ring, the secondary N-H stretching vibrational frequencies are observed in the region 3360-3310  $\text{cm}^{-1}$ .

##### C-N Vibrations

Due to the favoring of charge levels in amino group, the bending mode only were active. The C-N stretching vibrations, in plane bending and out of plane bending vibrations are generally observed in the region 1650-1590  $\text{cm}^{-1}$ . In this title compound, the C-N stretching vibration is calculated, due to the lees energy availability and moved in far infrared region.

### C-H Vibrations

C-H stretching vibrations are normally observed in the region 3100-3000 $\text{cm}^{-1}$  for aromatic benzene structure which shows their uniqueness of the skeletal vibrations. The band appeared at 1070,820  $\text{cm}^{-1}$  in the metronidazole has been assigned to C-H stretching vibrations.

The C-H in out plane bending vibrations is normally occurred a number of strong to weak intensity bands in the region 870 to 340  $\text{cm}^{-1}$ . According to the literature, the inplane & out of plane bending vibrational frequencies are found to be well within the characteristic region.

## VI. FRONTIER MOLECULAR ORBITAL ANALYSIS

The HOMO represents the ability to donate an electron, LUMO as an electron acceptor represents the ability to obtain an electron. The electronic absorption corresponds to the transition from the ground to the first excited state and is mainly described by one electron excitation from the HOMO to the LUMO. Chemical hardness ( $\eta$ ) and softness ( $s$ ) can be used as harmonizing tools to describe the thermodynamic aspects of chemical reactivity. The Frontier orbital gap helps to characterize the chemical reactivity kinetic stability, chemical reactivity, optical polarizability, chemical hardness, softness of a molecule. The investigations of FT-IR, FT-Raman, UV-Visible, FT-NMR Spectra and Quantum Chemical Computations of metronidazole molecule calculated HOMO and LUMO energy and the energy values of the frontier orbitals by B3LYP/6-311++G (d,p) are presented in Table 3.

The Ionization potential (I.P) values suggest how tightly an electron is bound within the nuclear attractive field of the systems. It is linearly related with the chemical hardness ( $\eta$ ). By using HOMO and LUMO energy values for a molecule,

The Ionization potential and chemical hardness of the molecule were calculated using Koopmans' theorem and are given by  $\eta = (IP - EA)/2$

Where  $IP \sim E(\text{HOMO})$ ,  $EA \sim E(\text{LUMO})$ ;  $IP =$  Ionization potential (eV);  $EA =$  electron affinity (eV).  
 $\eta = \frac{1}{2} (\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}})$ .

The hardness has been associated with the stability of chemical system. Considering the chemical hardness, large

HOMO–LUMO gap means a hard molecule and small HOMO–LUMO gap means a soft molecule.

One can also relate the stability of molecule to hardness, which means that the molecule with least HOMO–LUMO gap means, it is more reactive. The hard molecules are not more polarizable than soft ones because they need big energy to excitation 3D plots of the HOMO, LUMO, orbitals computed at the B3LYP/6-311++G (d,p) level for the tested molecule are illustrated in fig.1.

The electron affinity can be used in combination with ionization energy to give electronic chemical potential,  $\mu = \frac{1}{2} (\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}})$ .

Chemical softness ( $S$ ) =  $1/\eta$  describes the capacity of an atom or group of atoms to receive electrons and is the inverse of the global hardness.

The soft molecules are more polarizable than the hard ones because they need small energy to excitation. A molecule with a low energy gap is more polarizable and is generally associated with the high chemical activity and low kinetic stability and is termed soft molecule. A hard molecule has a large energy gap and a soft molecule has a small energy gap.

It is shown from the calculations that Metronidazole has the least value of global hardness and the highest value of global softness is expected to have the highest inhibition efficiency.

The global electrophilicity index,  $\omega = \mu^2/2\eta$ ,  $\eta$  is also calculated and these values are listed in Table 3.

**Table 3: Calculated energies, chemical hardness, electro negativity, Chemical potential, Electrophilicity index of Metrodinazole.**

Parameter	B3LYP
	6311++G(d,p)
$E_{\text{total}}$ (Hartree)	-624.0610
$E_{\text{HOMO}}$ (eV)	-8.334301
$E_{\text{LUMO}}$ (eV)	-4.38429
$\Delta E_{\text{HOMO-LUMO gap}}$ (eV)	-3.950011
$E_{\text{HOMO-1}}$ (eV)	-9.334301
$E_{\text{LUMO+1}}$ (eV)	-3.38429
$\Delta E_{\text{HOMO-1-LUMO+1 gap}}$ (eV)	-5.950011
Chemical hardness ( $\eta$ )	-1.975005
Electro negativity ( $\gamma$ )	-6.359295
Chemical potential ( $\mu$ )	-6.359295
Chemical softness ( $S$ )	7.900022
Electrophilicity index ( $\omega$ )	10.23810
Dipole moment	4.8355

## VII. NLO PROPERTIES

Nonlinear optical (NLO) effects arise from the interactions of electromagnetic fields in various media to produce new fields altered in phase, frequency, amplitude or other propagation characteristics from the incident fields. The first hyper polarizability ( $\beta_0$ ) of this novel molecular system and related properties ( $\beta_{tot}$ ,  $\alpha$ ,  $\Delta\alpha$ ) of Metronidazole are calculated using DFT/B3LYP method at 6-311G++ (d,p) basis set based on the finite field approach.

In the presence of an applied electric field, the energy of a system is a function of the electric field. First order hyper polarizability is a third rank tensor that can be described by 3 x 3 x 3 matrices. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry. It can be given in the lower tetrahedral format. It is obvious that the lower part of the 3 x 3 x 3 matrices is a tetrahedral. The components of  $\beta$  are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogeneous, this expansion becomes:

$$E = E_0 - \mu\alpha F\alpha - 1/2\alpha\alpha\beta F\alpha F\beta - 1/6\beta\alpha\beta\gamma F\alpha F\beta F\gamma + \dots$$

Where  $E_0$  is the energy of the unperturbed molecules,  $F\alpha$  is the field at the origin,  $\mu\alpha$ ,  $\alpha\alpha\beta$  and  $\beta\alpha\beta\gamma$  are the components of dipole moment, polarizability and the first order hyperpolarizabilities, respectively.

DFT has been extensively used as an effective method to investigate the organic NLO materials.

The total static dipole moment ( $\mu$ ), the mean polarizability ( $\alpha_0$ ), the anisotropy of the polarizability ( $\Delta\alpha$ ) and the mean first order hyper polarizability ( $\beta_0$ ), using the x, y, z components they are defined as:

$$\alpha_{total} = \alpha_0 = 1/3 (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

$$\Delta\alpha = [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6\alpha_{2xz} + 6\alpha_{2xy} + 6\alpha_{2yz}]^{1/2}$$

$$\beta_0 = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{xxy} + \beta_{yzz})^2 + (\beta_{zzz} + \beta_{xxz} + \beta_{yyz})^2]^{1/2}$$

$$\Delta\alpha = [(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 / 2]^{1/2}$$

The total dipole moment can be calculated using the following equation.

$$\mu = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

Polarizability is the property of a species and it is minimum for most stable species and is maximum for least stable species like transition state.

The  $\alpha$  and  $\beta$  values of the Gaussian 05 output are in atomic units (a.u) and these calculated values converted into electrostatic unit (e.s.u).

( $\alpha$ : 1 a.u =  $0.1482 \times 10^{-24}$  esu; for  $\beta$ : 1 a.u =  $8.639 \times 10^{-33}$  esu;) and these above polarizability values of Metronidazole are listed in Table 4.

**Table 4: The Electronic Dipole moment, Polarizability and first hyperpolarizability of Metronidazole.**

Parameter	a.u	Parameter	a.u
$\alpha_{xx}$	-80.0137	$\beta_{xxx}$	38.7052
$\alpha_{xy}$	6.9692	$\beta_{xxy}$	-13.6578
$\alpha_{yy}$	-72.2032	$\beta_{xyy}$	9.9731
$\alpha_{xz}$	-0.9236	$\beta_{yyy}$	44.0127
$\alpha_{yz}$	4.1741	$\beta_{xxx}$	-0.0568
$\alpha_{zz}$	-65.7608	$\beta_{xyz}$	7.6274
$\alpha_{tot}$	131.809	$\beta_{yyz}$	8.0291
$\Delta\alpha$	190.061	$\beta_{zzz}$	5.8749
$\mu_x$	4.4598	$\beta_{yzz}$	15.6052
$\mu_y$	1.7981	$\beta_{zzz}$	7.6718
$\mu_z$	-0.5094	$\beta_{tot}$	199.736
$\mu_{tot}$	4.8355		

## VIII. CONCLUSION

The FTIR, FT-Raman, UV-Visible spectral measurements have been made for the metronidazole molecule. The complete vibrational analysis and first order hyperpolarizability, NLO properties, HOMO and LUMO analysis and thermodynamic properties of the title compound was performed on the basis of DFT and HF calculations at the 6-311++G(d,p) basis set. The consistency between the calculated and experimental FTIR and FT-Raman data indicates that the B3LYP and HF methods can generate reliable geometry and related properties of the title compound. The calculated dipole moment and first order hyperpolarizability results indicate that the title compound is a good candidate of NLO material. The calculated normal-mode vibrational frequencies provide thermodynamic properties by the way of statistical mechanics.

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