

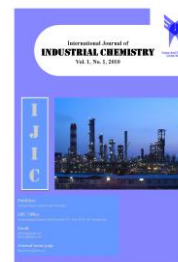


Islamic Azad University  
Quchan Branch

Int. J. Ind. Chem., Vol. 2, No. 4, 2011, pp. 223-234

**International Journal of Industrial Chemistry**

www.ijichem.org



ISSN (online): 2228-5547  
ISSN (print): 2228-5970

## Molecular Vibrational Spectroscopic Studies on “5-Chloro-7-Iodoquinolin-8-ol” by Density Functional Theory and HF method

Muthu Sambantham<sup>a,\*</sup>, Uma Maheswari Jawahar<sup>b</sup>, Sampath Krishnan Sadasivam<sup>a</sup>

<sup>a</sup>Department of Physics, Sri Venkateswara College of Engineering, Pennalur, Tamil Nadu, India.

<sup>b</sup>Department of Physics, Arignar Anna Institute of Science and Technology, Pennalur, Tamil Nadu, India.

\*Email: muthu@svce.ac.in

Received: 9 May 2011; Accepted: 2 July 2011

### Abstract

Quantum chemical calculations of energy, geometrical structure and vibration wavenumbers of 5-Chloro-7-Iodoquinolin-8-ol were carried out by Ab initio HF and DFT (B3LYP) method with 3-21G (d) and LANL2MB as the basis set. The Fourier-Transform Infrared and Fourier-Transform Raman spectra of 5-Chloro-7-Iodoquinolin-8-ol were recorded in the region 4000-400 cm<sup>-1</sup> and 3500-100cm<sup>-1</sup>. The thermodynamic functions of the title compound have been computed. A detailed interpretation of the vibration spectra of this compound has been made on the basis of the calculated potential energy distribution (PED). The calculated HOMO and LUMO energies show that charge transfer occurs within the molecule. Natural bond order analysis of the title molecule was also carried out. Comparison of the stimulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the vibration mode.

**Keywords:** DFT; FTIR; FT-Raman; HOMO; LUMO; NBO analysis.

### 1. Introduction

5-Chloro-7-Iodoquinolin-8-ol is used as a topical antifungal and antibacterial in the treatment of skin infections. Extensive work has been carried out on the title compound and derivatives in recent years [1-5]. The vibration frequencies of this drug have been identified and assigned on the basis of their relative intensity, characteristic positions and correlation of vibration bands [6] in related compounds.

Quantum chemical computational methods have proved to be an essential tool for interpreting and predicting vibration spectra [7, 8]. Now-a-days, sophisticated electron

correlation and density functional theory calculations are increasingly available and they deliver force field of high accuracy even for large polyatomic molecules [9, 10]. DFT calculations of the vibration spectra of many organic systems [11-15] have shown promising conformity with experimental results and they provide excellent vibration frequencies of organic compounds if the calculated frequencies are scaled to compensate for the approximate treatment of electron correlation in the basis set deficiencies and the anharmonicity [16-18]. Literature survey reveals that neither the complete Raman IR.

spectra nor the quantum chemical calculations for 5-Chloro-7-Iodoquinolin-8-ol have been reported so far. The aim of the present study is to give a complete description of the molecule geometry and molecular vibrations of the title molecule. For that purpose, quantum chemical computations were carried out for 5-Chloro-7-Iodoquinolin-8-ol using DFT and HF method. The calculated HOMO (highest occupied molecular orbitals) and LUMO (lowest unoccupied molecular orbitals) energies show that charge transfer occurs in the title molecule. These calculations are valuable for providing insight into the vibration spectrum and molecular parameters.

## 2. Experimental

The pure sample of 5-Chloro-7-Iodoquinolin-8-ol was obtained from sigma chemical company, USA and used as such. The FT-IR and FT-Raman spectra of the sample were recorded in the region 4000-400  $\text{cm}^{-1}$  and 3500-100  $\text{cm}^{-1}$  respectively using BRUCKER IFS 66V FT-IR spectrometer with a resolution of 0.5  $\text{cm}^{-1}$  at RSIC, Chennai, India. All the sharp bands of the spectrum have an accuracy of  $\pm 1\text{cm}^{-1}$ . The observed experimental and stimulated FT-IR and FT-Raman spectra are presented in Figs. 1 & 2.

### 2.1. Computational Details

All calculations were performed using the G03W [19-20] package of program. Initial geometry generated from standard geometrical parameters [21] and full optimizations were carried out. The vibration wavenumbers, geometric parameters, and other molecular properties were carried out using Ab initio HF and DFT (B3LYP) method with 3-21G (d) and LANL2MB levels. To compensate for the errors arising from the basis set incompleteness and neglect of vibration anharmonicity, we have scaled the wavenumbers with scaling

factors. By using the Gauss view program with symmetry considerations, vibration frequency assignments were made with a high degree of accuracy. The Raman activities ( $S_i$ ) calculated with Gaussian 03 were converted to relative Raman intensity using RaInt program [22] by the expression:

$$I_i = 10^{-12}(\nu_0 - \nu_i)^4 (1/\nu_i) S_i$$

Where  $I_i$  is the relative Raman intensity,  $S_i$ , the Raman activities,  $\nu_i$  is the wavenumber of normal modes and  $\nu_0$  denotes the wavenumber of the excitation laser. The vibration frequency assignment has been carried out by combining the result of the Gauss view program, symmetry consideration and the VEDA 4 program [23]. The last column of the table 4 shows the detailed vibration assignment obtained from the calculated potential energy distribution (PED).

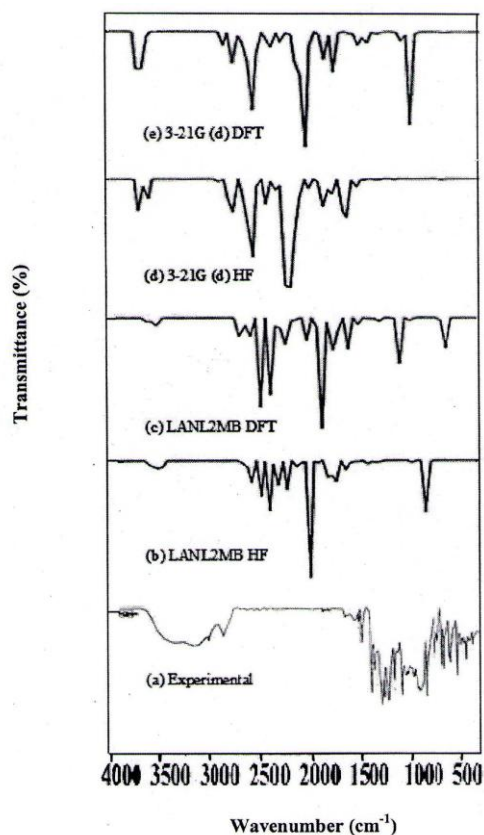


Fig. 1. Experimental (a), calculated (b), (c), (d) and (e), FT-IR spectra of 5-Chloro-7-Iodoquinolin-8-ol.

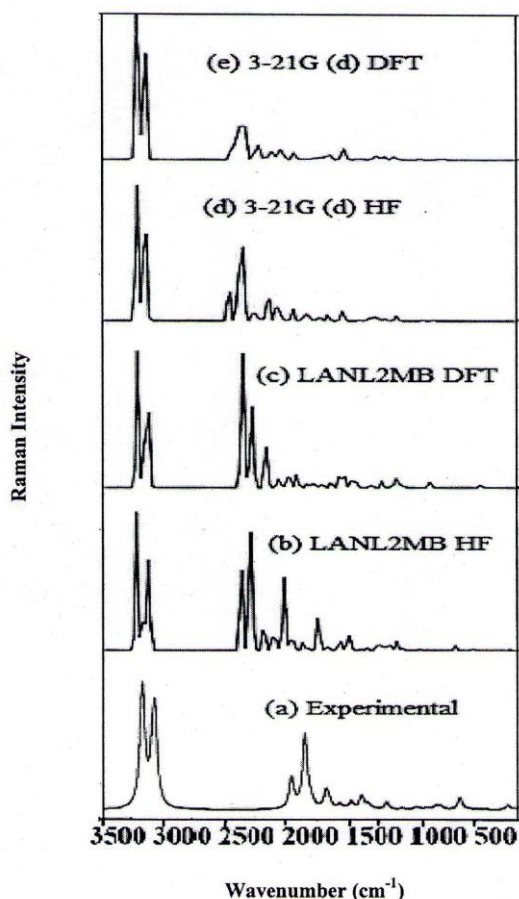


Fig. 2. Experimental (a), calculated (b), (c), (d) and (e) FT-Raman spectra of 5-Chloro-7-Iodoquinolin-8-ol.

### 3. Results and Discussion

#### 3.1. Geometrical structure

The optimized structure parameters of 5-Chloro-7-Iodoquinolin-8-ol were calculated by Ab initio (HF) and DFT (B3LYP) levels with the 3-21G (d) and LANL2MB basis set. The labeling of atoms in 5-Chloro-7-Iodoquinolin-8-ol is given in Fig. 3. Comparison table for the calculated bond lengths and angles for 5-Chloro-7-Iodoquinolin-8-ol with those of experimentally [24] available x-ray diffraction data are listed in the Table 1.

From the theoretical values, we can find that most of the optimized bond angles are slightly larger than the experimental values due to the theoretical calculations of the molecules in gaseous phase and the experimental results of the molecules in solid phase. When comparing bond angles and lengths of B3LYP with those

of HF as a whole, the values of B3LYP correlate well with the experimental results. In spite of the differences, calculated geometric parameters represent a good approximation and they are the basis for calculating other parameters such as vibration frequencies and thermodynamic properties.

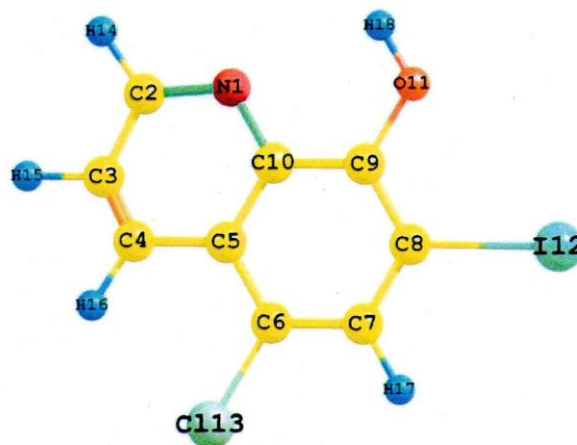


Fig. 3. Numbering system adopted in this study (5-Chloro-7-Iodoquinolin-8-ol).

#### 3.2. Vibration assignments

IR and Raman spectra contain a number of bands at specific wavenumbers. The aim of the vibration analysis is to decide which of the vibration modes give rise to each of these observed bands. According to the theoretical calculations, 5-Chloro-7-Iodoquinolin-8-ol has a structure of  $C_1$  point group, 18 atoms and 48 modes of fundamental vibrations. Almost all the 48 fundamental vibrations are active in both IR absorption and Raman scattering. The reduced mass and force constants along with the depolarization ratios of the calculated frequencies have been included in Tables 2 and 3 to have rational basis for the assignments. Table 4 shows FT-IR and FT-Raman frequencies assignments for 5-Chloro-7-Iodoquinolin-8-ol. The potential energy distribution is also supporting the present study. The relative intensities were obtained by dividing the computed value by the intensity of the strongest line. The computed intensities show marked deviations from the observed

**Table 1.** Optimized parameters for 5-Chloro-7-Iodoquinolin-8-ol B3LYP and RHF with 3-21G (d)

Parameters	Experimental	B3LYP/3-21G(d)	RHF/3-21G(d)
<b>Bond length</b>			
N(1)-C(2)	1.3580	1.3281	1.3008
N(1)-C(10)	1.3580	1.3665	1.3558
C(2)-C(3)	1.4200	1.4154	1.4114
C(2)-H(14)	1.1000	1.0840	1.0706
C(3)-C(4)	1.4200	1.3792	1.3582
C(3)-H(15)	1.1000	1.0823	1.0699
C(4)-C(5)	1.4200	1.4189	1.4162
C(4)-H(16)	1.1000	1.0822	1.0693
C(5)-C(6)	1.4200	1.4212	1.4162
C(5)-C(10)	1.4200	1.4207	1.3970
C(6)-C(7)	1.4200	1.3770	1.3539
C(6)-Cl(13)	1.7190	1.7622	1.7482
C(7)-C(8)	1.4200	1.4147	1.4128
C(7)-H(17)	1.1000	1.0812	1.0689
C(8)-C(9)	1.4200	1.3791	1.3566
C(8)-I(12)	2.1490	2.1249	2.1159
C(9)-C(10)	1.4200	1.4278	1.4199
C(9)-O(11)	1.3350	1.3591	1.3507
O(11)-H(18)	0.9720	1.0120	0.9722
<b>Bond Angle</b>			
C10-N1-C2	114.999	118.4955	119.5746
C3-C2-N1	123.5000	122.3419	122.0277
H14-C2-N1	116.5000	117.3389	117.6472
C5-C10-N1	120.0000	123.3261	122.6020
H14-C2-C3	120.0000	120.3191	120.3252
C4-C3-C2	129.3823	119.6281	119.3574
H15-C3-C2	120.0000	119.5311	119.6132
H15-C3-C4	120.0000	120.8407	121.0294
C5-C4-C3	115.6177	119.6424	119.6535
H16-C4-C3	122.1908	121.1481	121.0111
H16-C4-C5	122.1915	119.2095	119.3354
C6-C5-C4	119.9988	125.9652	125.3202
C10-C5-C4	120.0002	116.566	116.7848
C10-C5-C6	119.9985	117.4688	117.8949
C7-C6-C5	120.0002	120.8078	120.5368
C5-C10-C9	119.9989	121.5402	121.2000
Cl13-C6-C7	120.0000	119.3604	119.4681
C8-C7-C6	119.9966	120.4847	121.0412
H17-C7-C6	120.0019	119.7328	119.8380
H17-C7-C8	120.0015	119.2755	119.1208
C9-C8-C7	119.9965	120.4847	120.2967
I12-C8-C7	120.0019	120.5402	119.7304
I12-C8-C9	120.0016	118.9751	119.9729
C8-C9-C10	119.9999	118.7068	119.0304
O11-C9-C8	124.3000	123.6280	122.5033
O11-C9-C10	124.3000	117.6651	118.4664
H18-O11-C9	108.0000	104.8345	109.8695

**Table 2.** Vibrational wavenumbers obtained for 5-Chloro-7-Iodoquinolin-8-ol HF/B3LYP/3-21G(d) [harmonic frequency ( $\text{cm}^{-1}$ ), IR intensities (K/mmol), Raman scattering activities ( $\text{A}^4\text{amu}^{-1}$ ), Raman depolarization ratio, reduced mass (amu) and force constants ( $\text{m dyne A}^{-1}$ )]

Frequencies		IR Intensity		Raman Activity		Depolar (P)	Reduced masses	Force constant
Scaled DFT	Scaled HF	Rel	Abs	Rel	Abs			
3646	3484	16	8	2	1	0.73	9.24	81.00
3634	3462	190	100	110	59	0.28	1.07	9.24
2935	2801	2	1	46	25	0.29	1.10	6.22
2922	2791	39	21	187	100	0.24	1.10	6.22
2858	2728	1	0	56	30	0.28	1.09	5.87
2839	2706	67	35	150	80	0.37	1.07	5.68
1895	1864	9	5	63	34	0.26	10.49	26.33
1808	1775	25	13	42	22	0.75	8.38	19.08
1801	1741	4	2	119	64	0.29	8.46	18.52
1761	1724	40	21	22	12	0.14	6.80	14.60
1658	1625	20	11	19	10	0.17	3.02	5.75
1636	1571	58	31	6	3	0.67	1.79	3.18
1563	1517	78	41	3	2	0.43	1.76	2.93
1532	1496	43	23	2	1	0.75	2.00	3.24
1485	1472	12	6	50	27	0.33	3.59	5.63
1413	1386	0	0	29	16	0.28	3.35	4.65
1367	1355	18	9	8	4	0.57	2.00	2.65
1329	1332	33	18	3	2	0.59	1.62	2.08
1242	1224	0	0	1	1	0.73	1.10	1.20
1137	1220	49	26	18	10	0.15	2.67	2.87
1135	1132	147	77	1	1	0.56	2.79	2.58
1043	1124	1	1	4	2	0.75	1.35	1.23
1041	1105	13	7	3	1	0.75	1.39	1.22
1013	1083	132	70	11	6	0.69	1.75	1.48
965	1038	81	43	2	1	0.48	9.11	7.10
937	996	40	21	2	1	0.74	1.90	1.36
902	960	8	4	6	3	0.75	2.36	1.57
868	880	15	8	10	5	0.19	6.90	3.86
737	741	5	3	2	1	0.22	7.65	3.04
733	727	40	21	15	8	0.18	8.99	3.44
674	720	13	7	2	1	0.74	7.33	2.75
609	648	16	8	0	0	0.75	4.76	1.44
586	619	30	16	0	0	0.49	6.39	1.77
553	560	1	0	1	1	0.31	8.85	2.01
407	472	171	90	5	3	0.75	1.22	0.20
399	462	24	13	1	1	0.75	2.92	0.45
335	415	5	3	8	4	0.29	7.38	0.92
306	360	2	1	3	2	0.64	8.35	0.78
289	337	9	5	0	0	0.75	8.97	0.73
207	305	4	2	4	2	0.14	9.18	0.62
194	251	2	1	1	0	0.75	5.65	0.26
134	195	0	0	9	5	0.33	18.37	0.51
76	147	0	0	1	1	0.71	15.83	0.25
53	97	2	1	0	0	0.75	10.55	0.07
45	91	1	1	1	0	0.75	9.77	0.04
38	83	0	0	1	1	0.75	5.31	0.13
27	71	1	0	1	0	0.71	5.77	1.57
14	55	0	0	3	1	0.75	6.47	5.14

**Table 3.** Vibrational wavenumbers obtained for 5-Chloro-7-Iodoquinolin-8-ol HF/B3LYP LANL2MB [harmonic frequency ( $\text{cm}^{-1}$ ), IR intensities ( $\text{K}/\text{mmol}$ ), Raman scattering activities ( $\text{A}^4 \text{amu}^{-1}$ ), Raman depolarization ratio, reduced mass ( $\text{amu}$ ) and force constants ( $\text{m dyne A}^{-1}$ )]

Frequencies		IR Intensity		Raman Activity		Depolar (P)	Reduced mass	Force constant
Scaled DFT	Scaled HF	Rel	Abs	Rel	Abs			
4186	4300	54	31	99	85	0.29	1.07	12.39
3873	3940	1	0	3	3	0.56	5.79	56.25
3353	3489	9	5	116	100	0.31	1.11	8.43
3350	3484	50	29	20	17	0.48	1.10	8.39
3267	3399	14	8	47	40	0.67	1.07	7.74
3219	3334	12	7	96	83	0.22	1.20	8.33
2080	2175	9	5	103	89	0.24	11.10	32.88
2001	2078	13	7	36	31	0.71	9.45	25.55
1967	2057	9	5	103	89	0.36	10.00	26.51
1934	2026	37	21	22	19	0.26	8.42	21.64
1806	1889	63	36	31	27	0.23	5.42	12.11
1781	1778	94	54	7	6	0.38	1.92	3.80
1659	1738	75	43	19	16	0.45	3.76	7.12
1631	1664	6	3	3	2	0.44	1.30	2.26
1562	1632	41	24	17	15	0.21	5.24	8.74
1515	1610	2	1	64	55	0.55	3.23	5.24
1420	1519	62	35	16	14	0.46	1.78	2.57
1374	1487	15	9	2	2	0.61	1.42	1.97
1302	1383	12	7	7	6	0.11	2.00	2.40
1231	1378	0	0	2	1	0.74	1.08	1.28
1193	1317	5	3	2	2	0.75	3.73	4.05
1122	1196	79	45	17	15	0.74	2.34	2.10
1018	1192	10	6	6	5	0.75	1.29	1.15
983	1189	174	100	18	15	0.43	2.45	2.17
903	1166	6	3	2	2	0.75	1.26	1.07
901	1076	12	7	5	4	0.75	1.19	0.86
851	922	28	16	12	10	0.16	7.28	3.88
763	836	3	1	2	2	0.75	9.56	4.19
715	834	45	26	4	3	0.69	7.90	3.44
674	797	41	23	14	12	0.24	8.30	3.30
556	666	2	1	1	1	0.75	6.77	1.88
529	641	25	14	1	1	0.52	5.97	1.54
525	577	6	3	3	2	0.18	8.81	1.83
407	557	5	3	0	0	0.74	5.39	1.05
404	447	2	1	9	7	0.25	8.92	1.12
277	392	0	0	3	3	0.75	5.13	0.49
245	360	4	2	2	2	0.75	5.91	0.48
214	311	9	5	2	1	0.74	4.99	0.30
147	297	3	2	6	5	0.16	8.75	0.48
106	207	1	1	9	7	0.42	15.93	0.43
97	176	7	4	0	0	0.75	5.60	0.11
86	127	1	1	2	2	0.75	15.96	0.16
79	117	0	0	1	1	0.75	7.19	0.04
76	105	0	0	0	0	0.75	7.21	0.16
64	90	6	3	0	0	0.75	6.06	0.33
58	74	127	73	4	4	0.75	1.40	0.24
41	49	2	1	1	0	0.70	5.83	2.03
20	35	0	0	1	1	0.75	6.92	6.53

**Table 4.** Experimental, computed frequencies ( $\text{cm}^{-1}$ ) and PED with assignments of 5-Chloro-7-Iodoquinolin-8-ol with 3-21G (d)

MODE No.	IR	RAMAN	RHF	B3LYP	Assignments	PED%
1	-	3496	3484	3646	C-H Stretching	100
2	3456w	-	3462	3634	C-H Stretching	97
3	2801vw	2815m	2801	2935	C-H Stretching	95
4	-	-	2791	2922	C-H Symm Stretching	95
5	2750m	-	2728	2858	C H Symm Stretching	99
6	-	-	2706	2839	C- H Symm Stretching	92
7	1857w	-	1864	1895	N-C Stretching	84
8	-	1760	1775	1808	C-C symm stretching	54
9	-	-	1741	1801	C-O Stretching	39
10	-	-	1724	1761	C-C Stretching	54
11	1632s	-	1625	1658	C-N- C Ring Deformation	53
12	1581vs	1581vs	1571	1636	C-C Stretching	56
13	1507m	1517m	1517	1563	C-C Stretching	31
14	1489m	-	1496	1532	Aromatic C- N Assym Stretching	61
15	1461vvs	-	1472	1485	C-C stretching	57
16	1381w	1382vw	1386	1413	C-C Stretching	80
17	1355vw	1352w	1355	1367	O-C Stretching	84
18	1330vw	1330vw	1332	1329	C-C-H In Plane Bending	48
19	1225w	1229m	1224	1242	O-H out of plane bending	27
20	-	1182w	1220	1137	C-O Stretching	70
21	-	1130m	1132	1135	In Plane Bending C-N-H	78
22	-	-	1124	1043	In Plane Bending C-H	73
23	1100w	1112w	1105	1041	In Plane Bending C-N-C	75
24	1078w	1080w	1083	1013	In Plane Bending C-N-H	68
25	1030s	1035vw	1038	965	C-C out of bending	62
26	-	980m	996	937	H-C-C In Plane Bending	37
27	953vs	950w	960	902	C-C-H Bending	52
28	890w	888m	880	868	C-O-C In Plane Bending	34
29	735m	-	741	737	Out Of Plane Bending N-C-C	30
30	730w	730w	727	733	Ring Deformation	50
31	693m	719w	720	674	Out Of Plane Bending C-C-C	71
32	649vs	-	648	609	C-Cl Stretching	76
33	620w	615m	619	586	C-C-O Asym Bending	73
34	563s	566w	560	553	C- I Stretching	87
35	470w	475m	472	407	C-C-C Symm Stretching	66
36	462w	460m	462	399	C- C- Cl Symm Bending	93
37	420w	415m	415	335	C-N-C Symm Bending	85
38	-	362s	360	306	Out Of Plane Bending N-C-N	74
39	-	333w	337	289	C-C-C Bending	78
40	-	312w	305	207	In Plane Bending C-C-O-H	93
41	-	260vs	251	194	N-C-C-C Torsion	53
42	-	216m	195	134	Out Of Plane Bending C -N	75
43	-	150w	147	76	Lattice Vibrations	54
44	-	-	97	53	Torsion	86
45	-	-	91	45	C-C Torsion	86
46	-	-	83	38	C-C Torsion	58
47	-	-	71	27	C-C Torsion	67
48	-	-	55	14	Torsion	62

values. One may note that the computed wavenumbers correspond to the isolated molecular state, whereas the observed wavenumbers correspond to the solid state spectra. We have assigned the fundamental mode of 5-Chloro-7-Iodoquinolin-8-ol on the basis of a group vibration concept and calculated vibration wavenumbers. Chem craft, which is a graphical interface, was used to assign the calculated harmonic wavenumbers using displacement vectors to identify the motion of modes. On the whole, the predicted vibration wavenumbers were in agreement with the experimental results.

### 3.2.1. C-H Stretching

The heterocyclic aromatic compounds and its derivatives are structurally very close to benzene. The C-H stretching vibrations [25] of aromatic and hetero aromatic occur in the region of 3100-3000  $\text{cm}^{-1}$ . This permits the ready identification of the structure. Accordingly, in the present study the C-H vibrations of the title compound are observed at 3456  $\text{cm}^{-1}$ , 2801  $\text{cm}^{-1}$ , 2750  $\text{cm}^{-1}$  in the FT-IR spectrum and at 3496  $\text{cm}^{-1}$ , 2815  $\text{cm}^{-1}$  in the FT-Raman spectrum respectively. The in-plane and out-of-plane bending vibrations of C-H group were found well within the characteristic region [26-27] and are presented in the Table 4.

### 3.2.2. C-Cl Vibration

The vibration belonging to the bond between the ring and the halogen atom are worth discussing since mixing of vibrations is possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of the molecule [28]. Coupling with other groups may result in the shift of the absorption band as high as 840  $\text{cm}^{-1}$ . For simple chlorine containing organic compounds, C-Cl absorption is in the region 750-700  $\text{cm}^{-1}$ , whereas for the Trans- and Gauche- [29] forms it is near 650  $\text{cm}^{-1}$ . In the present study, the band observed at 649  $\text{cm}^{-1}$  in the IR spectrum

and the same band is observed in Gunasekaran et al [6], 650  $\text{cm}^{-1}$  in the IR and 652  $\text{cm}^{-1}$  in Raman spectrum in Sundaraganesan et al [37] which is identified as C-Cl stretching corresponding to theoretically calculated values 648  $\text{cm}^{-1}$  (3-21G(d)) and 666  $\text{cm}^{-1}$  (LANL2MB). This impure mode contains significant contribution from other modes (Table 4). The result is in agreement with reported values given by Varghese et al [30], George et al [31] and Palafox et al [32].

### 3.2.3. O-H Vibrations

The OH group gives rise to three vibrations (stretching, in-plane bending and out-of-plane bending vibrations). The O-H group vibrations are likely to be the most sensitive to the environment and hence show pronounced shifts in the spectra of the hydrogen-bonded species. The O-H in-plane bending vibration for phenols, in general, lies in the region 1150–1250  $\text{cm}^{-1}$  and is not affected much due to hydrogen bonding and the stretching, out-of-plane bending wave numbers. In almost all 5-Chloro-7-Iodoquinolin-8-ol derivatives with one OH, vibration was found in a narrow region of 1225–1252  $\text{cm}^{-1}$ [33]; but in our study the wave number corresponds to the O-H out-of-plane bending vibration at 1225  $\text{cm}^{-1}$  and 1229  $\text{cm}^{-1}$ . In both inter-molecular and intra-molecular associations, the wave number is at a higher value than in free OH. The wave number increases with hydrogen-bond strength because of the large amount of energy required to twist the OH bond. The O-H out-of-plane bending vibration computed by HF/3-21G (d) 1224  $\text{cm}^{-1}$  shows good agreement with the recorded FT-IR band at 1225  $\text{cm}^{-1}$ .

### 3.2.4. C-O Stretching

If the compound contains carbonyl group, the absorption caused by C-O stretching is generally among the strongest present [34].



Accordingly, the FTIR bands observed at 1313  $\text{cm}^{-1}$  and 1304  $\text{cm}^{-1}$  in 5-Chloro-7-Iodoquinolin-8-ol have been assigned to C-O stretching modes of vibrations. The assignments of C-O in-plane and out-of-plane bending vibrations made in this study are supported by the literature Ashdown and Kletz [35]; many such cases have been reported and the range of frequencies 1020-1110  $\text{cm}^{-1}$  is associated with the C-O linkage. In the present case, the experimental frequencies at 1182  $\text{cm}^{-1}$  in FT-Raman spectrum of 5-Chloro-7-Iodoquinolin-8-ol are assigned to C-O stretching vibrations, which are in excellent agreement with the predicted frequencies at 1220  $\text{cm}^{-1}$ .

### 3.3. Other Molecular properties

On the basis of vibration analysis at 3-21G (d) and LANL2MB levels, several thermodynamic parameters are calculated and presented in Table 5. Scale factors have been recommended [36] for an accurate prediction in

determining the zero-point vibration energies (ZPVE) and the entropy. The vibrations in the ZPVE seem to be insignificant. The total energy, entropy of 5-Chloro-7-Iodoquinolin-8-ol is also calculated. The analysis of the wave function indicates that the electron absorption corresponds to the transition from the ground to the first excited state. It is mainly described by one-electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The Atomic orbital HOMO – LUMO composition of the frontier molecular orbital for 5-Chloro-7-Iodoquinolin-8-ol is shown in Fig. 4. The HOMO-LUMO energy gap of 5-Chloro-7-Iodoquinolin-8-ol was calculated and presented in Table 6; it reveals that the energy gap reflects the chemical activity of the molecule. LUMO as an electron acceptor represents the ability to obtain an electron and HOMO represents the ability to donate an electron.

**Table 5.** Theoretically computed energies (a.u.), zero-point vibrational energies (kcal/mol), rotational constants (GHz), entropies (cal/mol.K), dipole moment (D).

Parameters	HF/3-21G(d)	B3LYP/3-21G(d)	HF/LANL2MB	B3LYP/LANL2MB
Zero point energy	86.51767	81.14012	90.85364	84.07066
Dipole moment	3.7360	3.1141	4.7110	4.2483
Rotational constants				
	0.90805	0.90805	0.90805	0.90805
	0.28084	0.28084	0.28083	0.28083
	0.21450	0.21450	0.21450	0.21450
Entropy				
Total	91.338	86.311	95.434	88.708
Translational	0.889	0.889	0.889	0.889
Rotational	0.889	0.889	0.889	0.889
Vibrational	89.561	84.534	93.657	86.931

**Table 6.** Comparison of HOMO, LUMO and energy gaps of (B3LYP/3-21G (d)/LANL2MB) and (HF/3-21G (d)/LANL2MB)

Basis set	HOMO (eV)	LUMO (eV)	Energy Gap (eV)
HF/3-21G(d)	-8.5090	2.3619	10.8710
B3LYP/3-21G(d)	-6.0333	-1.2803	4.7530
HF/LANL2MB	-7.7210	4.4763	12.1973
B3LYP/LANL2MB	-5.0238	0.1077	5.1315

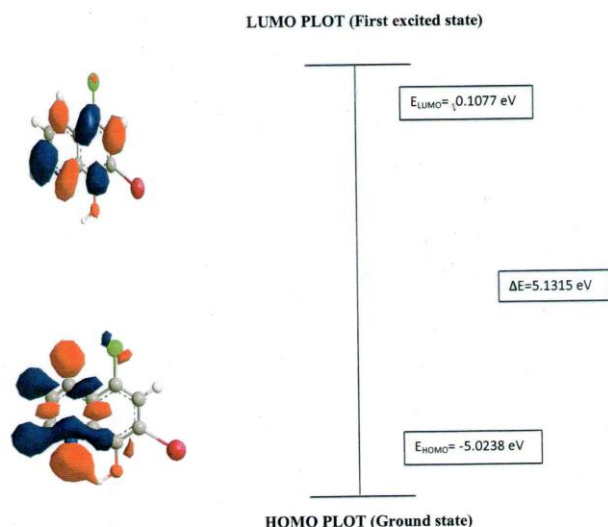


Fig. 4. Atomic orbital HOMO-LUMO composition of the frontier molecular orbital for 5-Chloro-7-Iodoquinolin-8-ol

### 3.4. Natural Population Analysis

The calculation of effective atomic charges plays an important role in the application of quantum mechanical calculations to molecular systems. Our interest here is in the comparison of different methods (RHF and DFT) to describe the electron distribution in 5-Chloro-7-Iodoquinolin-8-ol as broadly as possible, and to assess the sensitivity of the calculated

charges to changes in the choice of the quantum chemical method. The calculated natural atomic charge values from the natural population analysis (NPA) and Mulliken population analysis (MPA) procedures using the RHF and DFT methods are listed in Table 7. The NPA from the natural bonding orbital (NBO) method is better than the MPA scheme. Table 7 compares the atomic charge site of 5-Chloro-7-Iodoquinolin-8-ol with both MPA and NPA methods. The NPA of 5-Chloro-7-Iodoquinolin-8-ol shows that the presence of oxygen atom [ $O_{11}$  -0.7187(HF) and -0.6224(DFT)] imposes low negative charges on the hydrogen atoms, [ $H_{18}$  0.5153 (HF) and  $H_{18}$  0.4894 (DFT)]. However, the nitrogen atom  $N_1$  possesses low negative charges, resulting in the positive charges on the carbon atoms  $C_2$  and  $C_{10}$ . Moreover, there is no difference in charge distribution observed on all hydrogen atoms except the  $H_{18}$  hydrogen atom ( $H_{18}$  0.5153(HF) and  $H_{18}$  0.4894(DFT)]. The large positive charge on  $H_{18}$  is due to the low negative charge accumulated on the  $O_{11}$  atom.

Table 7. Natural atomic charges of 5-Chloro-7-Iodoquinolin-8-ol

Atom with numbering	MPA		NPA	
	RHF/3-21G(d)	B3LYP/3-21G(d)	RHF/3-21G(d)	B3LYP/3-21G(d)
$N_1$	-0.829360	-0.708149	-0.47391	-0.42887
$C_2$	0.180988	0.129493	0.11454	0.06791
$C_3$	-0.419553	-0.298029	-0.29123	-0.28042
$C_4$	0.034569	0.038509	-0.18604	-0.19187
$C_5$	-0.135418	-0.040878	-0.06256	-0.06948
$C_6$	-0.223758	-0.211098	-0.07400	-0.06937
$C_7$	-0.192622	-0.192744	-0.21270	-0.23382
$C_8$	-0.237708	-0.142029	-0.29338	-0.24782
$C_9$	0.511541	0.382938	0.39703	0.31956
$C_{10}$	0.309880	0.278531	0.08762	0.08793
$O_{11}$	-0.777002	-0.630447	-0.71879	-0.62242
$I_{12}$	0.158552	0.105619	0.19471	0.17282
$Cl_{13}$	0.073083	0.065485	0.00898	0.02361
$H_{14}$	0.263436	0.204274	0.23081	0.22710
$H_{15}$	0.242428	0.178507	0.22724	0.22873
$H_{16}$	0.311514	0.225589	0.25886	0.25253
$H_{17}$	0.295430	0.229415	0.27751	0.27442
$H_{18}$	0.433999	0.385014	0.51531	0.48948

## 4. Conclusions

Ab initio and density functional theory calculations have been carried out on the structure and vibration spectrum of 5-Chloro-7-Iodoquinolin-8-ol. The equilibrium geometry computed by DFT/HF level for both the bond angles and bond lengths show better performance. The vibration frequency analysis for some values of HF and DFT method in the basis set agrees satisfactorily with experimental results. On the basis of agreement between the calculated and experimental results, assignments of all the fundamental vibration results and the fundamental vibration modes of 5-Chloro-7-Iodoquinolin-8-ol were examined in this investigation. Any discrepancy noted between the observed and the calculated frequencies is due to the fact that the calculations have been actually done on the single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignments made with minimal basis set and reasonable deviations from the experimental values seem to be correct. The calculated HOMO and LUMO energies also show that charge transfer occurs within the molecule. The PED contributions to each of the observed frequencies show the reliability and accuracy of the spectral analysis. This study demonstrates that scaled DFT/B3LYP calculations are a powerful approach for understanding the vibration spectra of medium sized organic compounds. The Mulliken charges and natural atomic charges of the title molecule have been studied by both the HF and DFT methods. The calculated normal-mode vibration frequencies provide thermodynamic properties through statistical mechanics.

## References

[1] R. M. Acheson, An introduction to chemistry of heterocyclic compounds, Third Edition, John Wiley, New York, 1977.

[2] K. D. Tripathi, Medical pharmacology, 3E Jaypee Medical Publishers, New York, 1995.

[3] Indian Pharmacopeia, Vol. 1 & 2 Controller of publications civil lines, New Delhi, 1996.

[4] S. Gunasekaran, E. Sailatha, S. Seshadri, S. Kumaresan, Indian J Pure Appl Phys 47 (2009) 12.

[5] L. E. Sutton, The interatomic bond angles and bond distances in molecule and ions (Chemical society, London), 1956.

[6] S. Gunasekaran, U. Ponnambalam, S. Muthu, S. Anand, Indian J Pure Appl Phys 42 (2004) 162.

[7] B. A. Hess, J. Schaad, P. Carsky, R. Zahradnik Jr, Chem Rev 86 (1986) 709.

[8] P. Pulay, X. Zhon, G. Fogarasi, in NATO ASI Series, (Ed.:R Fransto), Kluwer: Dordrecht C 406 (1993) 99.

[9] J. Andzelm, E. Wimmer, J Chem Phys 96 (1992) 1280.

[10] A. D. Becke, J Chem phys 96 (1992) 2155.

[11] B. G. Jonhson, P. M. W. Gill, J. A. Pople, J Chem Phys 98 (1993) 5612.

[12] N. C. Handy, C. W. Murray, R. O. Amos, J Phys Chem 97 (1993) 4392.

[13] D. P. Chan, A. V. Ree, Chem Phys Lett 210 (1993) 443.

[14] A. Berces, T. Zeigler, J Chem Phys 98 (1993) 4793.

[15] F. Sim, A. St-Amat, D. R. Salahub, J Am Chem Soc 114 (1992) 4391.

[16] N. C. Handy, P. E. Masten, R. D. Amos, J. S. Andrews, C. W. Murray, G. Laming, Chem Phys Lett 197 (1992) 506.

[17] N. C. Handy, P. E. Masten, R. D. Amos, J Phys Chem 97 (1993) 4392.

[18] P. J. Stephens, F. J. Devlin, C. F. Chavalowski, M. Frish, J Phys Chem 99 (1995) 16883.

[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr, T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, Gaussian Inc., Waling ford, CT, 2004.

[20] H. B. Schlegel, J Comput Chem 3 (1982) 214.

[21] Carl Kemnity, Chemoffice Ultra 10, Academic Trial version, 2002.

[22] D. Michalska, Raint Program, Wroclaw University of Technology, 2003.

- [23] M. H. Jamroz, *Vibrational Energy Distribution Analysis: VEDA 4 program*, Warasaw, Poland, 2004.
- [24] A. Casini, G. De Simone, C. Pedone, J. Antel, A. Scozzafava, C. T. Supuran, *Acta Cryst A* 61 (2005) c242.
- [25] G. Ilango, M. Arivazhagan, J. Prince, V. Balachandran, *Indian J Pure Appl Phys* 46 (2008) 698.
- [26] S. Gunasekaran, R. K. Natarajan, D. Shyamala, R. Rathika, *Indian J Pure Appl Phys* 44 (2006) 315.
- [27] V. Krishnakumar, R. J. Xavier, *Chem Phys* 312 (2005) 227.
- [28] C. Lee, W. Yang, R. G. Parr, *Phys Rev B* 37 (1988) 785.
- [29] G. Socrates, *Infrared characteristics group frequencies*, John Wiley, New York, 1987.
- [30] H. T. Varghese, C. Y. Panicker, D. Philip, P. Pazdera, *Spectrochim Acta, Part A* 67 (2007) 1055.
- [31] W. O. George, S. McIntyre, *Introduction to spectroscopy*, John Wiley, New York, 1987.
- [32] M. A. Palafox, V. K. Rastogi, L. Mittal, *Int J Quantum Chem* 94 (2003) 189.
- [33] G. Varsanyi, *Assignments for vibrational spectra of seven hundred Benzene derivatives*, Wiley, New York, 1973.
- [34] D. N. Sathyanarayana, *Vibrational spectroscopy-Theory and applications* (New age International, New delhi), 2004.
- [35] A. Ashdown, T. A. Kletz, *J Chem Soc* 1039 (1948) 1454.
- [36] M. A. Palafox, *Int J Quantum Chem Chem* 77 (2000) 661.
- [37] N. Sundaraganesan, B. Dominic Joshua, M. Rajamoorthy, C. H. Gangadhar, *Indian J Pure Appl Phys* 45 (2007) 969.

Archive of SID