

Vibrational spectroscopy investigation using *ab initio* and density functional theory analysis on the structure of 6-bromo-2-methylquinoline

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(Acceptance Date 11th July, 2012)

Abstract

The Fourier transform infrared (FT-IR) and FT-Raman spectra of 6-bromo-2-methylquinoline (6B2MQ) have been recorded in the range 4000-400 and 3500-100 cm^{-1} , respectively. The experimental vibrational frequency was compared with the wavenumbers obtained theoretically by *ab initio* HF and DFT/B3LYP gradient calculations employing the standard 6-31+G (d, p) and high level 6-311++G (d, p) basis sets for optimised geometry of the compound. The complete vibrational assignment and analysis of the fundamental modes of the compounds were carried out using the experimental FT-IR and FT-Raman data, and quantum mechanical studies. The geometry and normal modes of vibration obtained from the HF and DFT methods are in good agreement with the experimental data.

Key words: Vibrational investigation; *ab initio* and DFT; 6-bromo-2-methylquinoline.

Introduction

Quinoline derivatives are biologically and pharmaceutically important compounds¹⁻¹³. Quinoline derivatives are widely used as a parent compound to make drugs (cancer¹⁴, especially anti-malarial medicines), fungicides, biocides, alkaloids, rubber chemicals, flavoring agents¹⁵, catalyst, corrosion inhibitor, preservative, solvent for resins and terpenes. 2-, 4-, 6-methylquinoline {abbreviated henceforth

2-mq (quinaldine), 4- or 6-mq} are derivatives of quinoline and resemble naphthalene. Notable examples of the quinoline compounds include the 4-aminoquinoline chlorequine, the 8-aminoquinoline primaquine and quinolin-methanols mefloquine and quinine. Until the emergence of drug-resistant parasites, these drugs were the more effective means to treat malaria, a disease that claims 1 to 3 million lives annually (Foley and Tilley, 1998). In addition to malaria, quinoline-Containing and structurally related compounds have been used

in the treatment of lupus erythematosus (Van Beek and Piette, 2001), arthrititis (Fox, 1993), and HIV (Savarino *et al.*, 2001) and have been shown to exhibit antiprion activity (Korth *et al.*, 2001). Remarkably, there is no clear mechanism known for the therapeutic action of these drugs in any of these diseases. The most accepted theory for the action of the quinoline drugs in the treatment of malaria interference with hemo detoxification within red blood cell (Foley and Tilley, 1997). However, the heme detoxification mechanism cannot explain the action of the quinoline compounds in the treatment of arthritis, lupus or HIV. The 2-(aryl) quinolin-4 amine is used as inhibitors of human immunodeficiency virus (HIV)¹⁶. Quinolium derivatives have been widely used as novel inhibitors, *i.e.*, DHA topoisomerase II inhibitor¹⁷, topoisomerase inhibitor¹⁸, lipoxigenase inhibitor¹⁹, and kinase inhibitor²⁰. The infrared and Raman spectra of quinoline were discussed in detail^{21,22}. The absorption spectra of 2-mq in the near ultraviolet region were recorded by Shashidhar and Rao^{23,24}. In such type of molecule, the role of substituent is very important. Owing to the low symmetry and also because of the limited information about the molecular parameters, reliable theoretical calculations (DFT) for such molecules are not possible or tedious too. Thus, it is difficult to understand the role of the substituent by experimental and theoretical methods.

Recent spectroscopic studies of the quinoline and their derivatives have been motivated because the vibrational spectra are very useful for the understanding of the specific biological process and in the analysis of relatively complex systems. In the present study, we

extend a probing into the application of the HF/6-31+G (d, p), B3LYP/6-31+G (d, p) small basis sets and HF/6-311++G (d, p), B3LYP/6-311++G (d, p) large basis sets based on SQM method for Vibrational spectra. Based on these calculations, the simulated FT-IR and FT-Raman spectra were obtained. The observed and the simulated spectra agree well. The theoretical HF and density functional theory analysis give information regarding the nature of structure, the functional groups and orbital interactions and mixing of skeletal frequencies. The introduction of one or more substituent in quinoline ring leads to the variation of charge distribution in the molecule, and consequently, this greatly affects the structural and vibrational parameters. Though there are few studies on quinoline compounds²⁵⁻³⁹, the structural characteristics and vibrational spectroscopic analysis of 6-bromo-2-methylquinoline by the quantum mechanical HF and DFT methods have not been studied. Thus, considering the industrial and biological importance of 6-bromo-2-methylquinoline, an extensive experimental and theoretical study on 6B2MQ to obtain a complete reliable and accurate vibrational assignments and structural characteristics of the compound has been made. The density functional theory (DFT) is a popular post-HF approach for the calculation of molecular structures, Vibrational frequencies of molecules^{40,41}. The DFT calculations with the hybrid exchange-correlation functional B3LYP [Becke's three parameter (B3) exchange in conjunction with the Lee-Yang-Parr's (LYP) correlation functional] which are especially important in systems containing extensive electron conjugation and/or electron lone pairs⁴²⁻⁴⁷.

Experimental

The compound 6-bromo-2-methylquinoline in the solid form was purchased from the Sigma-Aldrich Chemical Company (Bangalore) with a stated purity of greater than 97%, and it was used as such without further purification to record FT-IR and FT-Raman spectra. The FT-IR spectrum has been recorded by KBr pellet technique in the region between 4400-400 cm^{-1} using Perkin Elmer RX-1 (Spectra 2000) FT-IR Spectrometer. The frequencies for all sharp bands are accurate to $\pm 1\text{cm}^{-1}$. The FT-Raman spectrum was also recorded in the range between 3500-100 cm^{-1} by the Renishaw Invia Raman microscope laser source with 220mW power operating and the spectral resolution is $\pm 2\text{cm}^{-1}$. The observed FT-IR and FT-Raman spectra are shown in Figs. 2 and 3.

Computational details :

The entire calculations were performed at density functional theory (DFT) levels on a HP Pavilion dv4/Intel(R)Core(TM) Duo CPU T6600 @ 2.20GHz personal computer using⁴⁸ Gaussian 03W program package, invoking gradient geometry optimization⁴⁹ using Hartree-Fock (HF) and Becke's three parameter hybrid functional (B3)⁴³ model using the Lee-Yang-Parr (LYP) correlation functional⁴⁴ (B3LYP) methods combined with standard 6-31+G (d, p) and 6-311++G (d, p) basis sets (referred to as small and large basis sets respectively). The Cartesian representation of the theoretical force constants have been computed at optimized geometry by assuming Cs point group symmetry. To satisfactorily describe the conformation and orientation of the bromo and methyl groups, a

fully polarized 6-31+G (d, p) and 6-311++G (d, p) basis sets are required and considered to be a complete basis sets. The optimized structural parameters were used in the Vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. The DFT hybrid B3LYP functional tends also to overestimate the fundamental modes; therefore scaling factors have to be used for obtaining a considerably better agreement with experimental data. Therefore, the scaling factors of 0.91 and 0.93 were uniformly applied to the HF for the C-H stretching mode and others mode of vibrations respectively and also the scaling factors 0.96 and 0.99 were uniformly applied to the B3LYP for the C-H stretching mode and others mode of vibrations respectively calculated wavenumbers^{50, 51}.

Results and Discussion

Molecular geometry :

The structure and the scheme of numbering the atom of 6-bromo-2-methylquinoline are represented in Fig. 1. The geometry of the molecules under investigation is considered by possessing Cs point group symmetry. The molecule has 20 atoms and 54 normal modes of fundamental vibrations distributed into the irreducible representations under Cs symmetry as 36 in-plane vibrations of A' species and 18 out-of-plane vibrations A" species *i.e.*

$$\Gamma_{\text{vib}} = 36 A' + 18 A''$$

All the frequencies are assigned in terms of fundamental, overtone and combination bands.

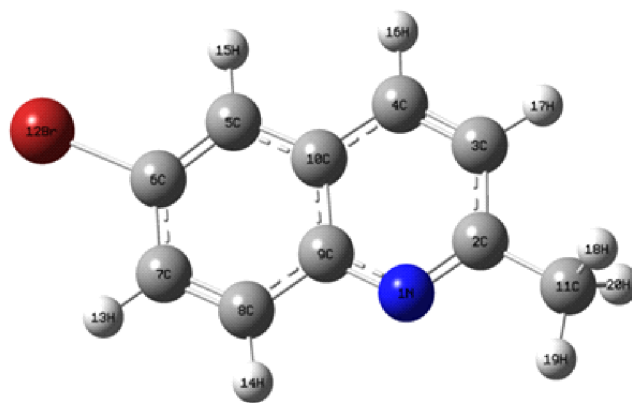


Fig. 1. Molecular structure of 6B2MQ

Structural properties :

The optimized bond lengths and angles for the thermodynamically preferred geometry of 6-bromo-2-methylquinoline determined at HF/6-31+G (d, p), B3LYP/6-31+G (d, p), HF/6-311++G (d, p) and B3LYP/6-311++G (d, p) levels are represented in Table 1 in accordance with the atom numbering scheme of the molecule shown in Fig. 1. From the structural data presented in Table 1 it is observed that the internuclear distance of the rings atoms N1-C2 is smaller than N1-C9 because the methyl group is attached with C2. The C-C-C bond angles are approximately same. From theoretical values we can find that most of the optimized bond lengths and bond angles are slightly longer and shorter than experimental values. Comparing bond angles and bond lengths of 6B2MQ molecule at B3LYP/6-311++G (d, p) method leads to geometrical parameters which are much closer to experimental values⁵³.

Vibrational analysis :

The observed Vibrational assignments and

analysis of 6-bromo-2-methylquinoline are discussed in terms of fundamental bands, overtones and combination bands. The experimental FT-IR and FT-Raman spectra of 6B2MQ are shown in Figs. 2 and 3 respectively. Due to the fluorescent nature of the compound, the peaks in FT-Raman spectra are not observed. The computational theoretical FT-IR and FT-Raman spectra of 6B2MQ are shown in Figs. 4-7. The observed and calculated unscaled and scaled vibrational frequencies using HF and DFT/B3LYP levels using the singlet split valence basis set along with diffused and polarization functions, standard small basis set 6-31+G (d, p) force field along with their relative species are collected in Table 2. Furthermore the observed and calculated unscaled and scaled vibrational frequencies along with their relative species, IR Intensity, Raman activity, reduced mass, force constants along with the depolarization ratios and most probable assignments with standard higher basis set 6-311++G (d, p) force field are collected in Table 3. Comparison of the frequencies calculated at B3LYP with the experimental values (in Tables 2 and 3) reveals the overestimation of the calculated vibrational

modes, due to neglect of anharmonicity in real system. Inclusion of electron correlation in density functional theory to a certain extent makes the frequency values smaller in comparison with the HF frequency data. Reduction in the computed harmonic vibrations, though basis set sensitive are marginal as observed in the DFT values using 6-311++G (d, p).

Skeletal Vibrations :

C-C and C-N Vibrations :

The carbon-carbon stretching modes of the phenyl group are expected in the range from 1650 to 1200 cm^{-1} . The actual position of these mode are determined not so much by the nature of the substituent but by the form of

substitution around the ring⁵⁴, although heavy halogens cause the frequency to diminish undoubtedly⁵⁵. In 6B2MQ under CS symmetry the carbon-carbon stretching bands appearing in the infrared spectrum at 1620, 1558, 1505, 1370, 1337 and 1315 cm^{-1} are assigned to skeletal C-C bonds while the bands at 1620, 1558, 1370, 1315 and 1229 cm^{-1} have been also assigned to the ring C-N stretching vibrations with C-C vibrations but no bands are observed in the Raman spectra. The corresponding C-C and C-N stretching modes observed in the FT-IR spectrum are given in Table 3. The bands occurring at 948, 633 and 445 cm^{-1} in the infrared but no bands are observed in the Raman spectra are assigned to the skeletal C-C/C-N-C in-plane bending modes of 6B2MQ.

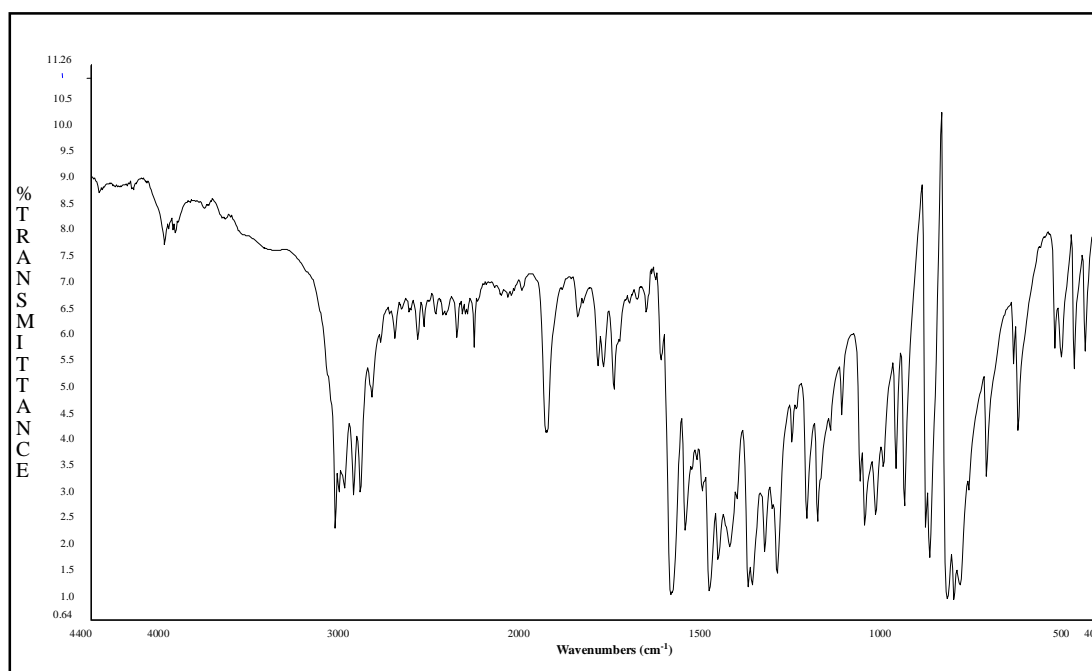


Fig. 2. Experimental FT-IR Spectra (region 4400-400 cm^{-1}) of 6B2MQ

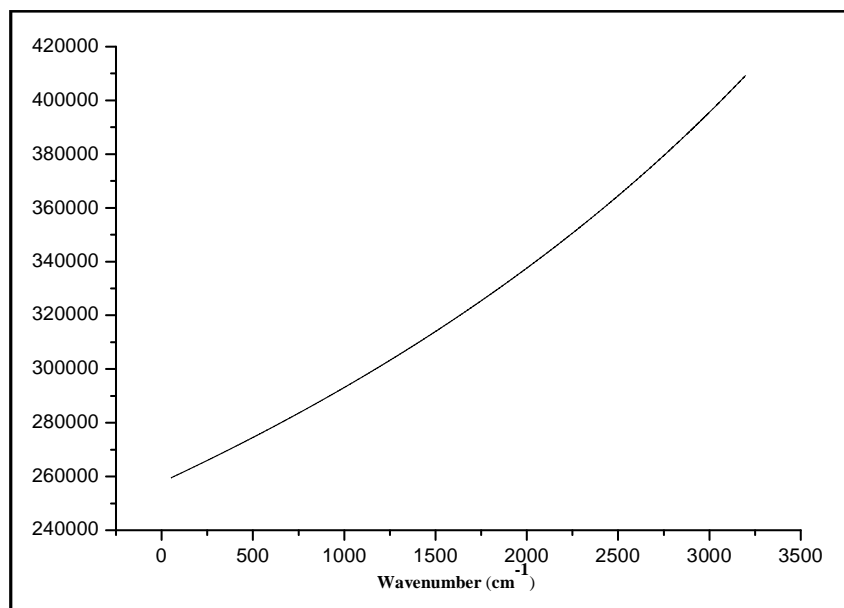


Fig. 3. Experimental Laser Raman Spectra (region 100-3500 cm⁻¹) of 6B2MQ

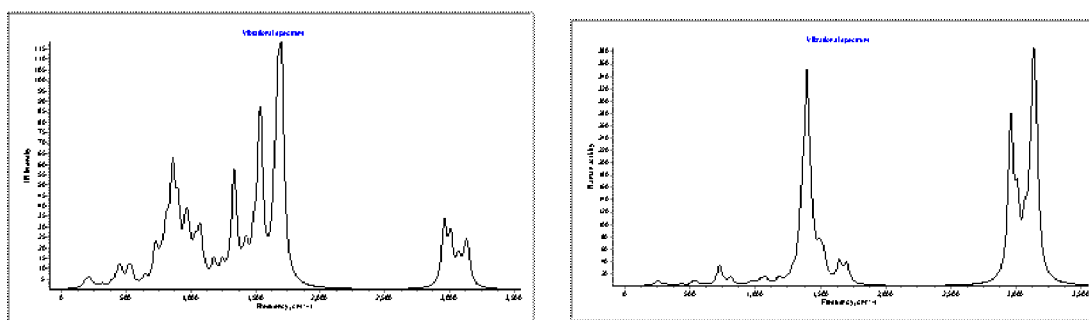


Fig. 4. Computed FT-IR/ FT-Raman spectra of 6B2MQ HF/6-31+G (d, p)

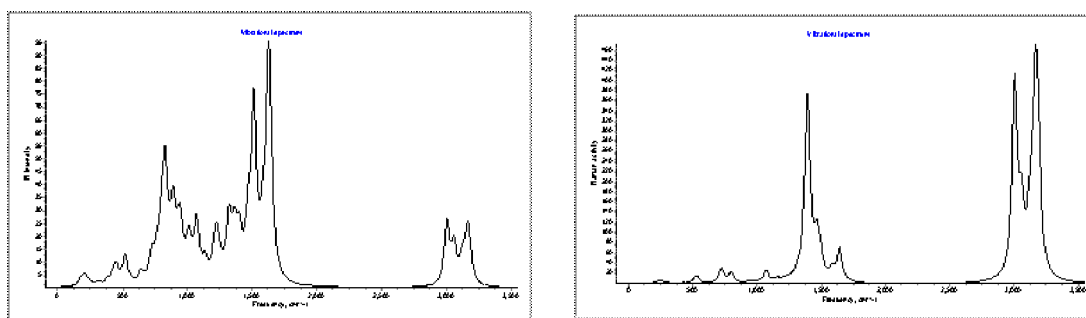


Fig. 5. Computed FT-IR/ FT-Raman spectra of 6B2MQ B3LYP/631+G (d, p)

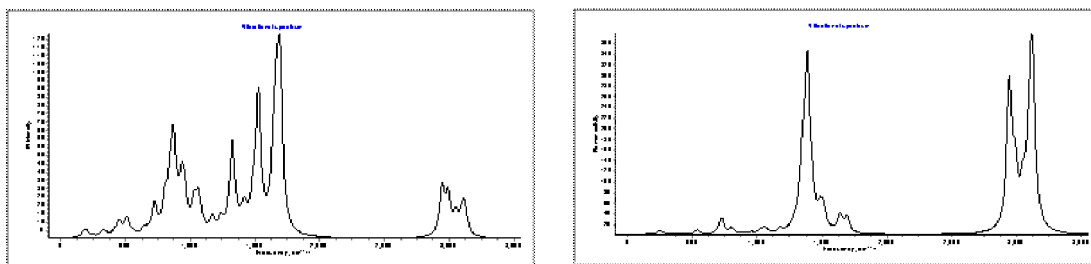


Fig. 6. Computed FT-IR/ FT-Raman spectra of 6B2MQ HF/6-311++G (d, p)

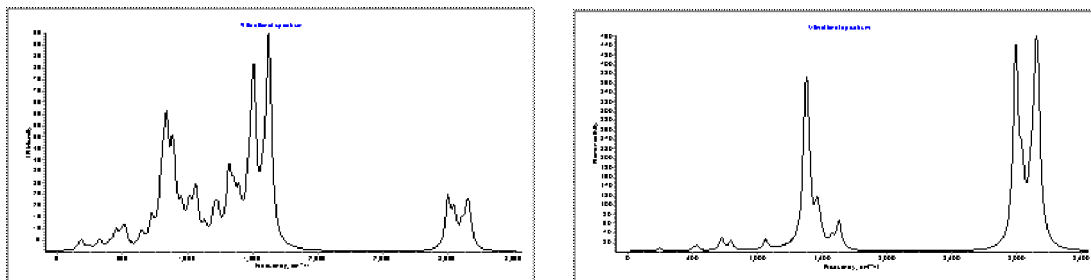


Fig. 7. Computed FT-IR/ FT-Raman spectra of 6B2MQ B3LYP/6311++G (d, p)

The other in-plane bending vibrations of the ring modes are calculated through HF and DFT methods. The out-of-plane bending ring vibrations under CS symmetry are assigned to the bands at 647, 531 and 478 cm^{-1} and the other out of plane bending vibrations of the ring modes are calculated through HF and DFT methods. The results are in good agreement with the literature values⁵⁶⁻⁵⁹. The density functional theory analysis shows that significant mixing of skeletal in-plane bending with C-H in-plane bending and vice versa occurs. In benzene the ring breathing (a_{1g}) vibrations exhibit the characteristic frequencies at 995 cm^{-1} ⁵⁵. In 6B2MQ the ring breathing mode is observed at 793, 721 and 513 cm^{-1} in the infrared. The shorter internuclear distance of N1-C2 indicates that the benzene ring exerts larger attraction on valence electron cloud of nitrogen atom resulting in easy delocalization

of lone pair of electrons into the ring and thereby increase in force constant and decrease in internuclear distance. The internuclear distance of the ring carbons atoms C2-C3 and C9-C10 are very close to each other at all levels of calculations but the others C-C of the ring seems to be slightly differ to each other's and C2-C11 is much longer than others. The internuclear distance C6-Br12 is much longer than the others like N-C, C-C and C-H. The internuclear distance of C-H atoms of methyl group is longer than the others C-H atoms.

C-H Vibrations :

The aromatic C-H stretching vibrations are normally found between 3100 and 3000 cm^{-1} . The C-H stretching of 6B2MQ gives bands at 3050 and 3029 cm^{-1} in FT-IR but no bands are observed in the FT-Raman spectra.

Table 1. Optimized geometrical Parameters of 6B2MQ obtained by HF and DFT/B3LYP calculations with the basis sets 6-31+G (d, p) and 6-311++G (d, p)

Bond length (Å)	Basis set 6-31+G (d, p)		Basis set 6-311++G (d, p)		Experimental Value
	HF	B3LYP	HF	B3LYP	
N1-C2	1.294	1.321	1.291	1.317	1.393
N1-C9	1.358	1.366	1.358	1.364	1.331
C2-C3	1.429	1.429	1.429	1.426	1.365
C2-C11	1.506	1.508	1.506	1.507	-
C3-C4	1.353	1.372	1.351	1.368	1.427
C3-H17	1.075	1.086	1.075	1.084	-
C4-C10	1.421	1.421	1.420	1.418	1.393
C4-H16	1.076	1.087	1.076	1.085	-
C5-C6	1.357	1.376	1.355	1.372	1.374
C5-C10	1.417	1.419	1.417	1.417	1.410
C5-H15	1.074	1.085	1.074	1.083	-
C6-C7	1.413	1.415	1.413	1.413	1.389
C6-Br12	1.895	1.909	1.901	1.918	-
C7-C8	1.361	1.378	1.359	1.375	1.393
C7-H13	1.073	1.084	1.073	1.082	-
C8-C9	1.417	1.420	1.417	1.417	1.402
C8-H14	1.074	1.085	1.074	1.083	-
C9-C10	1.403	1.429	1.401	1.426	1.428
C11-H18	1.086	1.097	1.087	1.095	-
C11-H19	1.081	1.091	1.081	1.089	-
C11-H20	1.086	1.097	1.087	1.095	-
Bond angle (deg.)					
C2-N1-C9	119.3	118.9	119.3	118.9	117.5
N1-C2-C3	122.3	122.3	122.3	122.3	123.8
N1-C2-C11	118.3	117.8	118.4	117.9	-
N1-C9-C8	118.5	118.5	118.5	118.6	-

Table 1 Contd.					
N1-C9-C10	122.6	122.7	122.7	122.7	121.6
C3-C2-C11	119.4	119.9	119.3	119.9	-
C2-C3-C4	119.4	119.7	119.4	119.7	117.8
C2-C3-H17	119.5	119.5	119.5	119.4	-
C2-C11-H18	110.7	111.0	110.5	110.9	-
C2-C11-H19	109.9	109.9	109.9	109.9	-
C2-C11-H20	110.7	111.0	110.5	110.9	-
C4-C3-H17	121.2	120.8	121.2	120.8	-
C3-C4-C10	119.3	119.4	119.2	119.3	121.4
C3-C4-H16	121.0	121.0	121.0	121.0	-
C10-C4-H16	119.7	119.6	119.7	119.6	-
C4-C10-C5	122.9	123.1	122.9	123.1	117.7
C4-C10-C9	117.1	117.0	117.1	117.1	118.8
C6-C5-C10	119.4	119.3	119.5	119.4	119.6
C6-C5-H15	120.9	120.9	120.9	120.9	-
C5-C6-C7	121.4	121.7	121.3	121.7	121.4
C5-C6-Br12	120.1	119.8	120.1	119.8	-
C10-C5-H15	119.7	119.8	119.6	119.7	-
C5-C10-C9	120.0	119.8	120.0	119.8	-
C7-C6-Br12	118.5	118.6	118.6	118.6	-
C6-C7-C8	119.7	119.6	119.7	119.6	-
C6-C7-H13	119.6	119.7	119.6	119.7	-
C8-C7-H13	120.7	120.7	120.7	120.7	-
C7-C8-C9	120.6	120.8	120.7	120.9	119.6
C7-C8-H14	121.2	121.2	121.1	121.1	-
C9-C8-H14	118.2	118.0	118.2	118.0	-
C8-C9-C10	118.9	118.8	118.9	118.7	121.4
H18-C11-H19	109.0	108.9	109.1	108.9	-
H18-C11-H20	107.5	107.2	107.6	107.2	-
H19-C11-H20	109.0	108.9	109.1	108.9	-

Table 2. Assignment of fundamental vibrations of 6-bromo-2-methylquinoline calculations using from HF and DFT/B3LYP basis set 6-31+ G (d, p)

S.No.	Species	Observed Wave		Calculated Wave No.(cm ⁻¹)			
		No.(cm ⁻¹)		HF/6-31+G (d, p)		B3LYP/6-31+G (d, p)	
		FT-IR	FT-Raman	Unscaled	Scaled	Unscaled	Scaled
1	A'	-	-	3393	3088	3222	3093
2	A'	-	-	3376	3072	3207	3079
3	A'	-	-	3375	3071	3206	3078
4	A'	-	-	3370	3067	3199	3071
5	A'	3050 s	-	3348	3047	3180	3053
6	A'	3029 s	-	3303	3006	3152	3026
7	A''	2953 s	-	3237	2946	3091	2967
8	A'	2905 s	-	3184	2897	3037	2916
9	A'	-	-	1831	1703	1660	1643
10	A'	1620 m	-	1800	1674	1644	1628
11	A'	1596 w	-	1769	1645	1600	1584
12	A'	1519 s	-	1652	1536	1530	1515
13	A'	1489 vs	-	1635	1521	1507	1492
14	A''	-	-	1606	1494	1489	1474
15	A'	1466 vs	-	1599	1487	1480	1465
16	A'	1411 s	-	1541	1433	1419	1405
17	A'	-	-	1532	1425	1412	1398
18	A'	1381 vs	-	1502	1397	1405	1391
19	A'	1370 vs	-	1463	1361	1378	1364
20	A'	1337 s	-	1434	1334	1336	1323
21	A'	1262 m	-	1383	1286	1284	1271
22	A'	1238 m	-	1336	1243	1247	1235
23	A'	1215 s	-	1270	1181	1226	1214
24	A'	1161 m	-	1266	1177	1175	1163
25	A'	1120 m	-	1193	1110	1147	1136
26	A'	-	-	1173	1091	1083	1072
27	A''	1058 s	-	1152	1071	1073	1062
28	A'	1018 s	-	1130	1051	1026	1016
29	A''	1003 s	-	1123	1044	1011	1001
30	A''	971 s	-	1110	1032	1003	993

31	A'	948 s	-	1054	980	962	952
32	A''	-	-	1031	959	945	936
33	A'	882 s	-	967	899	905	896
34	A''	878 vs	-	966	898	889	880
35	A''	829 vs	-	923	858	838	830
36	A'	810 vs	-	883	821	809	801
37	A''	-	-	869	808	808	800
38	A''	769 s	-	830	772	773	765
39	A'	721 s	-	781	726	732	725
40	A'	647 s	-	688	640	647	641
41	A''	-	-	659	613	610	604
42	A'	531 w	-	579	538	541	536
43	A''	-	-	578	538	531	526
44	A'	513 m	-	556	517	521	516
45	A'	445 m	-	487	453	455	450
46	A''	-	-	462	430	429	425
47	A''	-	-	412	383	385	381
48	A'	-	-	337	313	316	313
49	A'	-	-	268	249	250	248
50	A''	-	-	229	213	212	210
51	A''	-	-	196	182	180	178
52	A'	-	-	173	161	161	159
53	A''	-	-	88	82	76	75
54	A''	-	-	74	69	62	61

The potential energy distribution contribution of the aromatic stretching modes indicates that these are also highly pure modes as carbon-carbon stretching. The C-H in-plane bending modes are normally observed in the region 1350-950 cm^{-1} . These modes are observed in 6B2MQ at 1489, 1337, 1315, 1262 and 1229 cm^{-1} . The C-H out of plane bending modes is observed in the region 950-600 cm^{-1} . The aromatic C-H out of plane bending vibrations of 6B2MQ is assigned to the bands observed

at 971, 882, 829, 810 and 769 cm^{-1} and these bands occurred in the said region^{50,51,52,59-61}. The density functional theory analysis reveals that the aromatic C-H in-plane and out of plane bending vibrations have substantial overlapping with the ring C-C-C in-plane and out-of-plane bending modes, respectively. All these C-H in-plane and out-of-plane bending modes of the compound are also assigned within the said region and are presented in Table 3.

Table 3. Assignment of fundamental vibrations of 6-bromo-2-methylquinoline calculations using From HF and DFT/B3LYP basis set 6-311++ G (d, p)

S. No.	Species	Observed Wave No. (cm ⁻¹)		Calculated Wave No. (cm ⁻¹)				IR Intensity	Raman Activity	Red. Mass	Force Constant	Depolarisation ratio	Assignment
		FT-IR	FT-R	HF/6-311++G (d, p)	B3LYP/6-311++G (d, p)	Unscaled	Scaled						
1	A'	-	-	3369	3066	3205	3077	2.39	158.10	1.10	6.63	0.18	v C-H
2	A'	-	-	3352	3050	3190	3062	0.19	75.11	1.09	6.52	0.55	v C-H
3	A'	-	-	3351	3049	3187	3060	3.04	66.08	1.09	6.53	0.17	v C-H
4	A'	3050 s	-	3347	3046	3182	3055	13.64	171.34	1.10	6.54	0.21	v C-H
5	A'	3029 s	-	3325	3026	3163	3036	4.02	64.75	1.09	6.41	0.74	v C-H
6	A'	2998 s	-	3281	2986	3135	3010	7.36	65.00	1.10	6.36	0.73	v _a CH ₃
7	A''	2953 s	-	3217	2928	3074	2951	14.09	121.77	1.10	6.12	0.75	v _a CH ₃
8	A'	2905 s	-	3168	2883	3026	2905	21.08	405.62	1.04	5.60	0.10	v _s CH ₃
9	A'	1620 m	-	1820	1693	1649	1633	26.06	57.90	6.62	10.61	0.65	v C-C + v C-N
10	A'	-	-	1789	1664	1634	1618	67.99	2.17	6.29	9.90	0.75	v C-C
11	A'	1558 s	-	1762	1639	1591	1575	14.80	19.43	6.97	10.39	0.69	v C-C + v C-N
12	A'	1505 s	-	1643	1528	1521	1506	67.61	1.85	3.43	4.67	0.32	v C-C
13	A'	1489 vs	-	1625	1511	1499	1484	4.30	29.06	2.36	3.12	0.32	β C-H + Sci in CH ₃
14	A''	1466 vs	-	1602	1490	1485	1470	8.48	10.41	1.04	1.36	0.75	ρ CH ₃
15	A'	1458 s	-	1594	1482	1475	1460	9.76	58.31	1.20	1.53	0.41	Sci in CH ₃
16	A'	-	-	1532	1425	1410	1396	7.97	43.17	2.96	3.46	0.16	β C-H + v C-C
17	A'	1381 vs	-	1522	1416	1406	1392	8.47	27.46	1.33	1.55	0.34	ω CH ₃
18	A'	1370 vs	-	1490	1386	1391	1377	0.02	317.22	5.97	6.80	0.22	v C-C + v C-N
19	A'	1337 s	-	1452	1350	1367	1353	16.11	2.88	3.56	3.91	0.73	v C-C + β C-H
20	A'	1315 vs	-	1424	1324	1329	1316	27.72	8.40	2.92	3.04	0.13	β C-H + v C-C + v C-N
21	A'	1262 m	-	1375	1279	1279	1266	0.87	3.78	1.72	1.66	0.41	β C-H
22	A'	1229 m	-	1329	1236	1243	1231	10.86	3.28	2.20	2.00	0.09	β C-H + v C-C(H ₃)
23	A'	-	-	1264	1176	1216	1204	11.60	2.62	2.60	2.27	0.46	β C-H + v C-C
24	A'	1151 s	-	1258	1170	1172	1160	0.25	3.85	1.17	0.95	0.40	β C-H
25	A'	1120 m	-	1183	1100	1143	1132	6.65	2.45	1.53	1.18	0.19	β C-H
26	A'	1058 s	-	1155	1074	1075	1064	21.04	22.49	2.30	1.57	0.15	v C-Br
27	A''	-	-	1141	1061	1055	1044	2.29	0.18	1.59	1.04	0.75	γ C-C(H ₃)
28	A'	1018 s	-	1109	1031	1024	1014	13.92	0.91	1.85	1.14	0.68	β C-C(H ₃)

Table 3 cont.

29	A''	-	-	1105	1028	989	979	1.15	0.41	1.31	0.76	0.75	γ C-H
30	A''	971 s	-	1096	1019	981	971	0.45	0.42	1.31	0.74	0.75	γ C-H
31	A'	948 s	-	1025	953	961	951	12.37	2.75	3.18	1.73	0.05	β C-C-C
32	A'	-	-	1003	933	903	894	16.98	0.64	4.55	2.18	0.52	β C-C-C + ν C-Br
33	A''	882 s	-	961	894	890	881	22.63	0.16	1.46	0.68	0.75	γ C-H
34	A''	829 vs	-	934	869	845	837	42.94	0.13	1.84	0.77	0.75	γ C-H
35	A''	810 vs	-	906	843	821	813	9.34	0.03	1.35	0.54	0.75	γ C-H
36	A'	793 vs	-	865	804	806	798	15.91	19.65	5.29	2.03	0.07	ring breathing
37	A''	769 s	-	852	792	777	769	0.62	0.16	2.54	0.90	0.75	γ C-H
38	A'	721 s	-	778	724	730	723	10.55	27.00	5.96	1.87	0.07	ring breathing
39	A''	647 s	-	718	668	657	650	1.89	0.15	3.59	0.92	0.75	γ C-C-C
40	A'	633 m	-	686	638	648	642	4.33	0.58	7.79	1.93	0.11	β C-C-C + ν C-Br
41	A'	-	-	592	551	540	535	0.14	10.80	6.92	1.19	0.43	β C-C-C + β C-N-C
42	A''	531 w	-	576	536	538	533	1.00	0.18	3.26	0.56	0.75	γ C-C-C
43	A'	513 m	-	553	514	519	514	7.80	4.09	5.56	0.88	0.27	ring breathing + ν C-Br
44	A''	478 m	-	544	506	492	487	2.99	0.16	3.33	0.48	0.75	γ C-C-C
45	A'	445 m	-	485	451	455	450	6.82	0.03	3.55	0.43	0.29	β C-C-C
46	A''	-	-	442	411	405	401	2.40	1.48	3.62	0.35	0.75	γ C-C-C
47	A''	-	-	362	337	333	330	2.92	0.14	4.25	0.28	0.75	γ C-C-C
48	A'	-	-	335	312	315	312	1.74	1.80	3.62	0.21	0.06	β C-C(H ₃)
49	A'	-	-	266	247	247	245	1.40	7.08	9.20	0.33	0.25	ν C-Br
50	A''	-	-	207	193	188	186	4.08	0.71	4.96	0.10	0.75	γ C-C-C
51	A''	-	-	184	171	164	162	0.86	0.58	3.85	0.06	0.75	γ C-C-C
52	A'	-	-	171	159	160	158	0.28	0.94	6.32	0.10	0.59	β C-Br
53	A''	-	-	86	80	68	67	0.02	0.21	2.65	0.01	0.75	τ CH ₃
54	A''	-	-	70	65	56	55	0.23	1.39	1.28	0.00	0.75	τ CH ₃

Where

s - strong, vs - very strong, m - medium, w- weak, vw - very weak, ν - stretching, ν_s - symmetric stretching, ν_a - anti symmetric stretching, β - in plane bending, γ - out of plane bending, τ - torsion/twisting, ω - wagging, ρ - rocking, wavenumbers (cm^{-1}), IR intensities (KM/mole), Raman activities (A^0)^{4/} (a.m.u.), reduced mass (a.m.u.), force constant (mdyn/ A^0)

*Group Vibrations :**C-Br Vibrations :*

According to Colthup *et al.*⁶² in aryl halides no band is comparable to the aliphatic C-X stretching bands due to interaction with ring vibration. It has been pointed out by Arjunan V *et al.*⁵⁹ that the most aromatic bromo compounds absorb strongly in the region 650-395 cm^{-1} due to C-Br stretching vibrations, although when there is more than one bromine atoms on the same carbon atom. In the present investigation the vibration observed at 633 and 513 cm^{-1} has been assigned to C-Br stretching mode in infrared spectrum and it is also finding only theoretically at 245 cm^{-1} . Vipin⁶³ suggested that the C- Br in-plane bending mode at 500-400 cm^{-1} and out-of-plane bending mode at 210 cm^{-1} in the FT-IR and FT-Raman spectrum of tri-substituted phenols, but in case of quinoline, the FT-IR band observed at 490 cm^{-1} has been assigned to C-Br in-plane bending mode. The C-Br out-of-plane bending modes are not possible in case of FT-IR spectra. In the present study the in-plane and out-of-plane bending mode of vibrations are not observed experimentally in the infrared region but theoretically in-plane bending is assigned at 158 cm^{-1} .

-CH₃ (Methyl) group vibrations :

There are three C-H bands in methyl group so there will be three C-H stretching vibrations, out of which one is symmetric stretching vibration and the rest two are asymmetric stretching vibrations⁶². The asymmetric stretching and asymmetric deformation modes of the -CH₃ group would be expected to be

depolarized for A" symmetry species. The $\nu_s\text{CH}_3$ frequencies are established at 2953 cm^{-1} in the infrared and $\nu_a(\text{CH}_3)$ is assigned at 2905 cm^{-1} under A' and A" species of 6B2MQ, respectively. The symmetrical methyl deformational mode is obtained at 1498, 1458, 1466 and 1381 cm^{-1} in FT-IR. The methyl deformational modes are mainly coupled with the C-C in-plane bending vibrations. The -CH₃ scissoring, rocking and wagging modes of 6B2MQ are given in the table 3. Further Owen *et al.*⁶³ have assigned the CH₃ torsional modes in between 240-177 cm^{-1} , while Tylli *et al.* have assigned this mode around 280 cm^{-1} . In the present study, the -CH₃ torsion assignments are observed only theoretical assigned at 67 and 55 cm^{-1} . These assignments are substantiated by the reported literature^{28,60,64-66}. The vibrational assignments of the fundamental modes are also supported by Gauss view molecular visualization program⁶⁷.

Overtone of aryl ring vibrations :

According to Kalsi⁶⁸, usually intense overtones of aryl ring vibrations occur in the region 2000-1650 cm^{-1} . These bands are somewhat weaker than fundamentals and are most clearly seen in the spectra of moderately thick samples. In the present study, in the infrared bands observed in the region 1937, 1852, 1839, 1798, 1752 and 1663 cm^{-1} has been assigned to overtone of aryl ring vibrations are shown in Fig. 2. These assignments are further in agreement with the standard literature^{62,69}. But these vibrations could not be seen in the theoretically calculated FT-IR and FT-Raman spectra.

Computed IR intensity and Raman activity analysis :

Computed vibrational spectral FT-IR intensities and FT-Raman activities of the corresponding wave numbers by B3LYP/6-311++G (d, p) basis set have been collected in Table 3. The FT-IR intensities and FT-Raman activities calculated by B3LYP/6-311++G (d, p) level with experimental values exposes the variation of FT-IR intensities and FT-Raman activities. These variations may be due to the substitution of the methyl and electronegative atom.

Vibrational force constant :

The output files of the quantum mechanical calculations contain the force constants matrix in Cartesian co-ordinates and in mdyn/A^0 units. These force constants were transformed to the force fields in the internal local-symmetry co-ordinates. The force field determined was used to calculate the vibrational potential energy distribution among the normal co-ordinate. In both molecules the values show the variation due to the substitutions of the halogen and methyl groups. They are listed in Table 3.

A better agreement between the computed and experimental frequencies can be obtained by using different scale factors for different regions of vibrations. Initially, all scaling factors have been kept fixed at a value. The correction factors used to correlate the experimentally observed and theoretically computed frequencies for each Vibrational modes of 6B2MQ under HF and DFT/B3LYP methods are similar and an explanation of this approach was discussed previously⁷⁰⁻⁷⁷.

Subsequently, in HF method a scale factor of 0.91 rings C-H and methyl C-H stretching modes while 0.93 for the all other vibrations are used. In B3LYP level a scale factor of 0.96 for C-H and methyl C-H stretching vibrations and 0.99 for other fundamental modes have been utilized to obtain the scaled frequencies of the compound 6B2MQ with 6-31+G (d, p) and 6-311++G (d, p) basis sets. The scale factors used in this study minimized the deviations very much between the computed and experimental frequencies both at HF and DFT/B3LYP level of calculations. DFT/B3LYP correction factors are all much closer to unity than the HF correction factor, which means that the DFT/B3LYP frequencies are very much closer to the experimental values than the HF frequencies. Thus, vibrational frequencies calculated by using the B3LYP functional with 6-31+G (d, p) and 6-311++G (d, p) basis sets can be utilized to eliminate the uncertainties in the fundamental assignments in infrared vibrational spectra⁷⁷.

Conclusions

Attempts have been made in the present work for the proper frequency assignments for the compound 6B2MQ from the FT-IR and FT-Raman spectra. Comparison between the calculated vibrational frequencies and the experimental values indicates that both the methods of B3LYP/6-31+G (d, p), B3LYP/6-311++G (d, p), HF/6-31+G (d, p) and HF/6-311++G (d, p) can predict the IR and laser Raman spectra of the title compound well. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations have been actually

done on single molecules in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. The optimized geometry parameters calculated at B3LYP/6-311++G (d, p) are slightly larger than those calculated at HF/6-311++G (d, p) level and the HF calculated values coincides well compared with the experimental data on the whole. The difference between the observed and scaled wave number values of most of the fundamentals is very small. The observed and the calculated frequencies are found to be in good agreement.

Acknowledgement

Authors are thankful to Central Instruments Facility (CIF) - USIC, University of Delhi, for recording the FT-IR and FT-Raman spectra of the said compound.

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