Vibrational Spectroscopic Studies, Homo-Lumo Analysis of 1-Methyl Isoquinoline

V.Tamilselvi[a]   M. Arivazhagan[a*]

[a]Department of Physics, pioneer kumaraswamy college ,
Nagercoil 629003 , kanyakumari (Dt)Tamil nadu, India
[a*]Department of Physics,. Govt. Arts College, (Affiliated to Bharathidasan
University,Tiruchirappalli 620 024),Trichy -022,Tamil nadu, India
[*] Corresponding author. Tel.:+91 9443189328.
*E-mail address:arivu.m3008@*gmail.com (M. Arivazhagan).

Abstract

The Fourier transform infrared (FTIR) and (FT-Raman spectra of 1-methylisoquinoline (1-MIQ) have been recorded in the region 4000-400cm^{-1}and3500-50cm^{-1}, respectively Utilizing the observed FTIR and FT-Raman data, a complete vibrational assignment and analysis of fundamental modes of the compound have been carried out. The optimum molecular geometry, harmonic vibrational frequency ,infrared intensity and Raman scattering activities, have been calculated by density functional theory (DFT/HF)methods with 6-31+G(d,p) and 6-311++G(d,p) basis set. The difference between the observed and scaled wave number values of most of the fundamentals is very small. A detailed interpretation of the infrared and Raman spectra of 1-MIQ is also reported based on total energy distribution (TED). The calculated HOMO and LUMO energies show that charge transfer occur within the molecule.

Key Words: HOMO-LUMO;. FTIR, FT-Raman, 1-METHYL ISOQUINOLINE

1. INTRODUCTION

line analogues are more potent and better tolerated local anasthetics than common local anasthetics. The anasthetic activity is similar to those of procaine or cocaine when injected. However it is seQuinoline and isoquinoline are heterocyclic compounds. Many drugs are heterocycles, pharmacological activity requires chemical reaction and reaction requires functionality. Quinoline and isoquinoveral times more potent than procaine when injected subcutaneously and about five times more toxic than cocaine when injected intravenously [1-3]. Quinoline and isoquinoline molecules are made up of two aromatic six membered rings. Benzene and pyridine rings are fused in these systems. Like naphthalene

both quinoline and isoquinoline undergo aromatic substitution at an α-position in the over all carbon ring. There are several syntheses of quinolines and isoquinolines, which are composed series of familiar reaction mechanisms [4].

Consideration of these factors motivated to undertake the vibrational spectroscopic studies of the brand new compound 1-methylisoquinoline (1-MIQ). The title compound 1-MIQ is used in the manufacture of pharmaceutical dyes, insecticides, rubber accelerator and in organic synthesis. They are soluble in non-polar solvents, insoluble in water and toxic by ingestion.

The assignments of band in the vibrational spectra of molecule is an essential step in the application of vibrational spectroscopy for solving various structural chemical problems. The philosophy of computational methods of vibrational spectroscopy [5-6] is changed significantly after the introduction of scaled quantum mechanical (SQM) calculations. In the SQM approach, the systematic, errors of the computed harmonic force field are corrected by a few scale factors which are found to be well transferable between chemically related molecules [7-9] and were recommended for general use. In the present study, the detailed vibrational analysis of the title compound was performed by combining the experimental and theoretical information using Pulay's density functional theory (DFT) based on SQM approach [10].

2. EXPERIMENTATION

A fine sample of 1-MIQ was purchased from Lancaster Chemical Company, UK and used as such for spectral measurements. The room temperature Fourier transform infrared spectrum of the title compound is measured in the 4000-400 cm^{-1} region at a resolution of $\pm$ 1 cm^{-1} using KBr pellets on BRUKER IFS-66V FT-IR spectrophotometer equipped with a cooled MCT detector. Boxcar apodization was used for the 250 averaged interferogrames collected for the sample.

The FT-Raman spectrum is recorded on a computer interfaced BRUKER IFS model interferometer equipped with FRA 106 FT-Raman accessory in the 3500-50 cm^{-1} Stokes region using the 1064 nm line of a Nd:YAG laser for excitation operating at 200 mw power. The reported wave numbers are believed to be accurate within $\pm$ 1 cm^{-1}.

3. QUANTUM CHEMICAL CALCULATIONS

The molecular geometry optimization, energy and vibrational frequency calculations were carried out for 1-MIQ with GAUSSIAN 09W software package [11] using the Becke-3-Lee-Yang-Parr (B3LYP) functionals [12-13] combined with the standard 6-311++G(d,p) basis set. The Cartesian representation of the theoretical force constants are computed at optimized geometry by assuming C_s point group symmetry. Scaling of the force field was performed according to the SQM procedure [14-15] using selective scaling in the natural internal coordinate representation. Transformations of the force field and subsequent normal coordinate analysis including the least square refinement of the scaling factors and calculation of the total energy distribution (TED) were done on a PC with the MOLVIB program (Version 7.0 – G77) written by Sundius [16-18].

The symmetries of the vibrational modes were determined by using the standard procedure [19] of decomposing the traces of the symmetry operation into irreducible representation. By combining the results of GAUSSVIEW program [20] with symmetry considerations, vibrational frequency assignments were made and presented in some detail for the title compound.

3.1. Prediction of Raman intensities

The Raman activities (S_i) calculated with the GAUSSIAN 09W program are subsequently converted to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering [21-23].

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i \left[1 - \exp\left(\frac{-hcv}{kT} \right) \right]}$$

where v_0 is the exciting frequency in cm^{-1}, v_i is the vibrational wave number of the ith normal mode, h, c, k are the fundamental constants and f is a suitably chosen common normalization factor for all the peak intensities.

4. RESULTS AND DISCUSSION
4.1. Molecular geometry

The molecular structure of 1-MIQ having C_s symmetry is shown in Fig. 1. The global minimum energy obtained by *ab initio* / HF and DFT / B3LYP methods is calculated as -438.484 and -441.359 Hartrees. The calculated optimized geometrical parameters of the title compound is presented in Table 1.

5. VIBRATIONAL SPECTRA

The title compound 1-MIQ, consists of 20 atoms and its 54 normal modes are distributed amongst the symmetry species as

$$\Gamma_{3N-6} = 37A' \text{ (in-plane)} + 17 A'' \text{ (out-of-plane)}$$

The detailed vibrational assignments of fundamental modes of 1-MIQ along with the observed and calculated frequencies and normal mode descriptions (characterized by TED) are reported in Table 2. Also, the IR intensity, Raman activity and force constants with calculated frequencies of the title compound are presented in Table 3. For visual comparison, the observed and calculated FT-IR and FT-Raman spectra of 1-MIQ at HF and DFT-B3LYP level using 6-311++G(d,p) basis set are shown in Figs. 2 and 3, respectively.
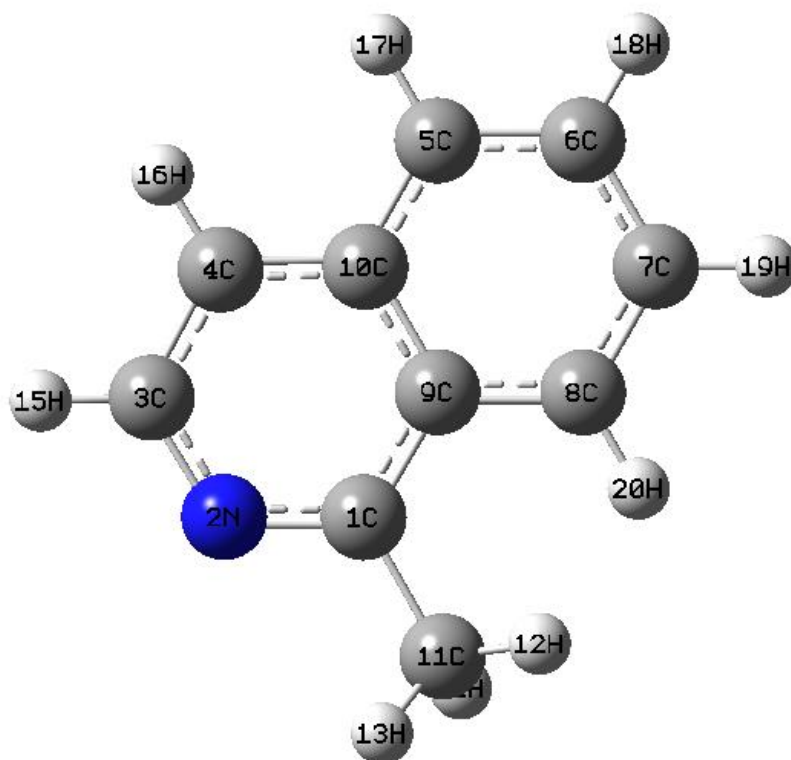
Fig. 1: Molecular structure of 1-methylisoquinoline

C-H vibrations

The C-H stretching vibrations of aromatic and hetero aromatic structure are normally appear in the region 3100-3000 cm^{-1} [24-25]. The bands due to C-H in-plane ring bending vibrations, interact marginally C-C stretching vibrations, are observed as a number of sharp bands in the region 1300-1000 cm^{-1}. The C-H out-of-plane bending vibrations are strongly coupled vibrations and occur in the region 900-667 cm^{-1}. Accordingly, in the present study, the C-H vibrations of the title compound are observed at 3060 and 3052 and 3020 cm^{-1} in the FT-IR spectrum and the Raman bands are observed at 3067, 3039 and 3028 cm^{-1}. The C-H in-plane and out-of-plane bending vibrations are also identified and listed in Table 2.

C-C vibrations

The bands between 1400 cm^{-1} and 1650 cm^{-1} in the aromatic and hetero aromatic compounds are assigned to C-C stretching vibrations [24]. Therefore, the carbon-carbon stretching vibrations [26-27] of the title compound are observed at 1623, 1584, 1564, 1502, 1358, 1302, 1198 and 1066 cm^{-1} in FT-IR and 1624, 1585, 1565, 1501, 1391, 1389, 1360, 1068 and 1022 cm^{-1} in FT-Raman. The in-plane and out-of-plane bending vibrations of carbon-carbon group are presented in Table 2. These assignments are in good agreement with the literature [28-29].

CH₃ group vibrations

The 1-MIQ under consideration possesses a CH_3 group in the benzene ring. For the assignments of CH_3 group frequencies, one can expect that nine fundamentals can be associated to each CH_3 group. Three stretching, three bending, two rocking modes and a single torsional mode describes the motion of methyl group. Hence, in the present investigation, the FT-IR and FT-Raman bands observed at 2861 and 2858 cm⁻¹ are designated to CH_3 symmetric stretching vibrations, respectively. The CH_3 in-plane stretching frequency is assigned at 2919 cm⁻¹ in IR and CH_3 out-of-plane stretch frequency appeers at 2970 cm⁻¹ in Raman. These assignments are also supported by the literature [30] in addition to TED output. The two in-plane methyl hydrogen deformation modes are also well established. The symmetrical methyl deformation mode is observed at 1331 cm⁻¹ in IR and 1332 cm⁻¹ in Raman spectrum. The bands at 1438 cm⁻¹ in IR and 1421 cm⁻¹ in Raman are attributed to CH_3 out-of-plane bending and in-plane bending modes, respectively. The methyl deformation modes are mainly coupled with in-plane bending vibrations. The IR bands are obtained at 1020 cm⁻¹   940 cm⁻¹ in CH_3 in-plane and out-of-plane rocking modes. The assignment of the band is found at 141 cm⁻¹ in Raman that is attributed to methyl twisting mode.
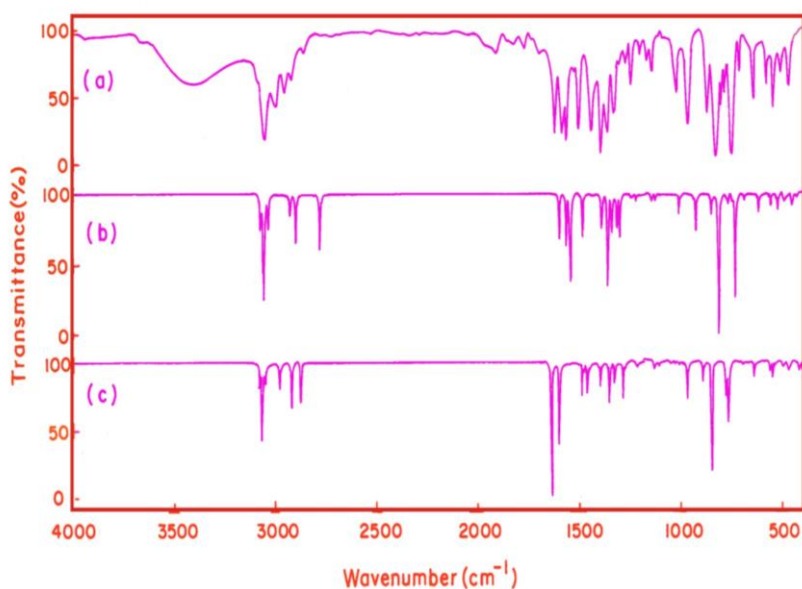

Fig. 2: Comparison of observed and calculated FT-IR Spectra of 1-methylisoquinoline (a) Observed in solid phase (b) calculated with B3LYP/6-311++G(d,p) and (c) calculated with HF/6-311++G(d,p)
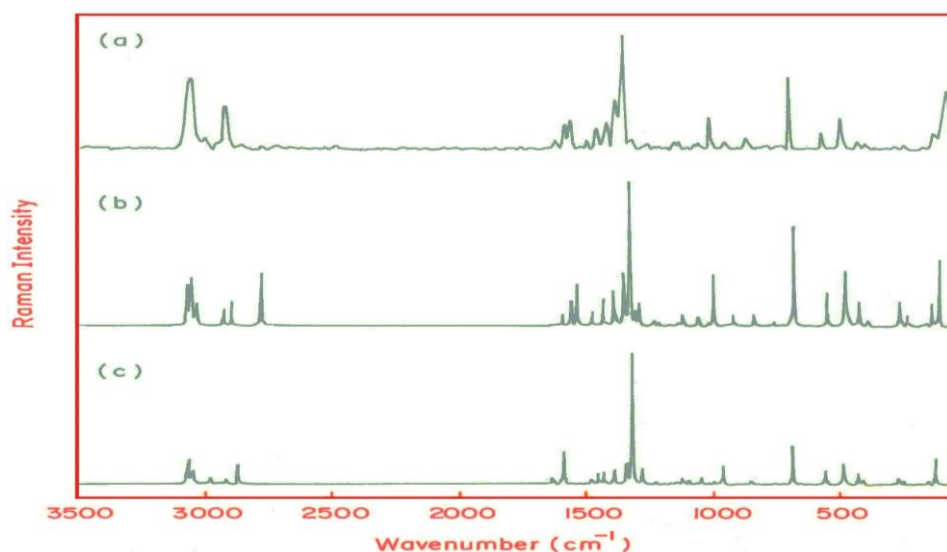
Fig. 3: Comparison of observed and calculated FT-Raman Spectra of 1-methylisoquinoline (a) Observed in solid phase (b) calculated with B3LYP/6-311++G(d,p) and (c) calculated with HF/6-311++G(d,p)

6. HOMO-LUMO ANALYSIS

Many organic molecules, containing conjugated π electrons are characterized by large values of molecular and analyzed by means of vibrational spectroscopy [31]. In most of the cases, even in the absence of inversion symmetry, the strongest band in the Raman spectrum is weak in the IR spectrum and vice-versa. But the intramolecular charge from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment making IR and Raman activity strong at the same time. The experimental spectroscopic behavior described above is well accounted for DFT calculations in π conjugated systems that predict exceptionally on infrared intensities for the same normal modes. It is also observed in our 1-MIQ the strong bands at 3052, 1623, 1584, 1564, 1502, 1267, 963, 799 and 642 cm^{-1} in IR have their counterparts in Raman at 3067, 1462, 1068, 731 and 502 cm^{-1} so that the relative intensities in IR and Raman spectra are comparable resulting from the electron cloud movement through a π conjugated frame work from electron donor to electron acceptor groups.

The HOMO is located over isoquinoline and CH$_3$ group, and the HOMO-LUMO transition implies an electron density transfer to methyl group from the isoquinoline ring. Moreover, these orbitals significantly overlap in their positions of 1-MIQ. The atomic orbital compositions of the frontier molecular orbital are sketched in Fig.4.

The HOMO-LUMO energy gap of 1-MIQ was calculated at the B3LYP/6-311++G(d,p), which reveals that the energy gap reflects the chemical activity of the molecule. The LUMO, as an electron acceptor represents the ability to obtain an electron, and HOMO represents the ability to donate an electron.

426

The calculated self-consistent field (SCF) energy of 1-MIQ is -441.359 Hartree. Moreover, a lower HOMO-LUMO energy gap explains the fact that eventual charge transfer interaction takes place within the molecule.

$$E_{HOMO} = -0.260731 \text{ a.u.}$$
$$E_{LUMO} = -0.229826 \text{ a.u.}$$
$$E_{GAP} = -0.030905 \text{ a.u.}$$

LUMO PLOT
(First excited state)

$$E_{LUMO} = -0.229826 \text{ a.u.}$$

$$\Delta E = -0.030905 \text{ a. u.}$$

$$E_{HOMO} = -0.260731 \text{ a.u.}$$

HOMO PLOT
(Ground state)
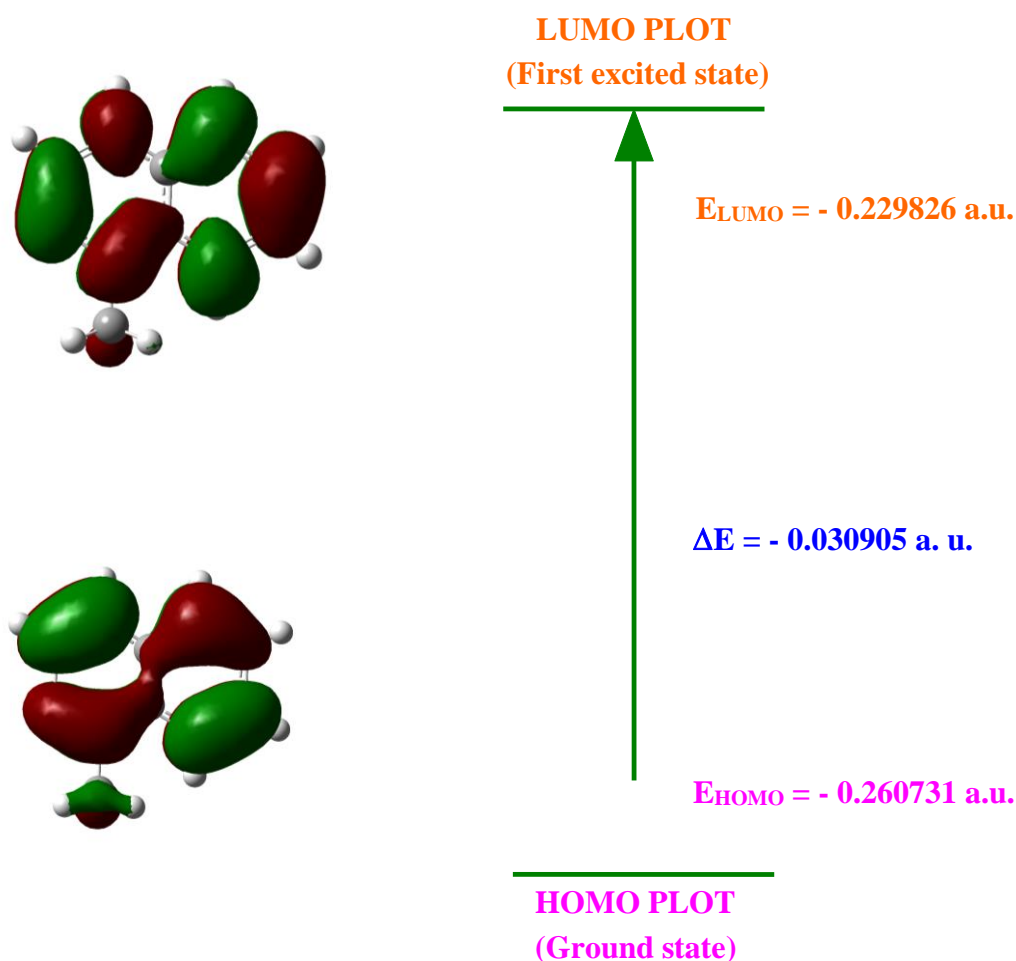
Fig. 4: The atomic orbital compositions of the frontier molecular orbital for 1-methylisoquinoline

7. CONCLUSION

The optimized geometrical parameters and vibrational frequencies of the fundamental models of 1-MIQ are obtained from *ab initio* and DFT methods. The theoretical results were compared with the experimental vibrations. Both type of calculations are useful to explain vibrational spectra of 1-MIQ. However, *ab initio* calculations at HF/6-311++G(d,p) level is found little poorer than DFT-B3LYP/6-311++G(d,p) level calculations. The close agreement established between the experimental and scaled frequencies obtained using large basis set (6-

311++G(d,p)) calculation is proved to be more reliable and accurate than the calculations of semi-empirical methods. The TED calculation regarding the normal modes of vibration provides a strong support for the frequency assignment. Therefore, the assignments proposed at higher level of theory with higher basis set with only reasonable deviations from the experiment values seem to be correct. The HOMO-LUMO energy gap explains the eventual charge transfer taking place within the molecule.

Table 1: Optimized geometrical parameters of 1-methylisoquinoline using obtained by HF and B3LYP methods with 6-311++G(d,p) basis set

Bond Length	Value (Å)		Bond Angle	Value (°)	
	HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)		HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)
C1-N2	1.2923	1.3185	N2-C1-C9	122.2433	122.320
N2-C3	1.3549	1.3596	N2-C1-C11	116.9153	116.633
C3-C4	1.3514	1.3696	C9-C1-C11	120.8413	121.0465
C4-C10	1.4200	1.4175	C1-N2-C3	119.4304	119.0686
C10-C5	1.4179	1.4186	N2-C3-C4	123.8061	123.8221
C5-C6	1.3591	1.3744	N2-C3-H15	115.2549	115.3310
C6-C7	1.4139	1.4136	C4-C3-H15	120.9390	120.8469
C7-C8	1.3603	1.3759	C3-C4-C10	118.6447	118.9667
C8-C9	1.4184	1.4189	C3-C4-H16	120.8966	120.7801
C9-C10	1.4030	1.4267	C10-C4-H16	120.4587	120.2531
C1-C9	1.4374	1.4361	C6-C5-C10	120.3669	120.5535
C1-C11	1.5081	1.5080	C6-C5-H17	120.5878	120.5354
C11-H12	1.0863	1.0945	C10-C5-H17	119.0452	118.9111
C11-H13	1.0803	1.0888	C5-C6-C7	120.4338	120.3288
C11-H14	1.0863	1.0946	C5-C6-H18	120.0976	120.0879
C3-C15	1.0753	1.0855	C7-C6-H18	119.4686	119.5833
C4-H16	1.0747	1.0844	C6-C7-C8	120.1836	120.3593
C5-H17	1.0756	1.0849	C6-C7-H19	119.6253	119.623
C6-H18	1.0756	1.0843	C8-C7-H19	120.1911	120.0177
C7-H19	1.0751	1.0841	C7-C8-C9	120.6384	120.7279

Bond Length	Value (Å)		Bond Angle	Value (°)	
	HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)		HF/ 6-311++G(d,p)	B3LYP/ 6-311++G(d,p)
C8-H20	1.0735	1.0829	C7-C8-H20	119.5380	119.6417
			C9-C8-H20	119.8236	119.6304
			C1-C9-C8	123.0565	123.2137
			C1-C9-C10	117.9584	118.0213
			C8-C9-C10	118.9851	118.765
			C4-C10-C5	122.6908	122.9337
			C4-C10-C9	117.9170	117.8009
			C5-C10-C9	119.3922	119.2655
			C1-C11-H12	108.8413	111.5133
			C1-C11-H13	111.1767	108.8600
			C1-C11-H14	111.1766	111.5134
			H12-C11-H14	107.8702	107.3862
			H13-C11-H14	108.8912	108.7468
			H12-C11-H13	108.8912	108.7461

For numbering of atoms refer Fig. 1.

Table 2: The observed FT-IR, FT-Raman and calculated (Unscaled and Scaled) frequencies (cm^{-1}) and probable assignments (characterized by TED) of 1-methylisoquinoline using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) methods and basis set

No.	Symmetry species	Observed frequency (cm^{-1})		Calculated frequency (cm^{-1})				Assignment with TED (%)
		FT-IR	FT-Raman	HF/6-311++G(d,p)		B3LYP/6-311++G(d,p)		
				Unscaled	Scaled	Unscaled	Scaled	
1	A′	-	3067(ms)	3364	3073	3197	3070	CH(99)
2	A′	3060	-	3351	3062	3185	3060	CH(99)

No.	Symmetry species	Observed frequency (cm⁻¹)		Calculated frequency (cm⁻¹)				Assignment with TED (%)
		FT-IR	FT-Raman	HF/6-311++G(d,p)		B3LYP/6-311++G(d,p)		
				Unscaled	Scaled	Unscaled	Scaled	
		ms						
3	A′	3052 ms	-	3346	3057	3178	3057	CH(99)
4	A′	-	3039(ms)	3334	3046	3173	3042	CH(99)
5	A′	-	3028 (w)	3329	3032	3162	3031	CH(99)
6	A′	3020 w	-	3320	3024	3156	3026	CH(99)
7	A″	-	2970w	3284	2992	3137	2977	CH₃ops(50), CH3ss(45)
8	A′	2919 w	-	3220	2934	3073	2917	CH₃ips(75), CH3ops(25)
9	A′	2861 w	2858w	3170	2888	3025	2871	CH₃ss(50), CH3ips(49)
10	A′	1623s	1624w	1820	1641	1659	1618	CC(65), bCH(16),Ring2(10),Ring1(6)
11	A′	1584s	1585w	1780	1605	1623	1583	CC(63), bCH(19),CN(8),Ring1(6)
12	A′	1564s	1565w	1771	1599	1604	1565	CC(50),CN(26),bCH(8),Ring1(7),Ring2(6)
13	A′	1502s	1501w	1660	1500	1537	1497	CC(47),bCH(39),CN(10)
14	A′		1462vs	1615	1467	1496	1450	bCH(52),CC(29),CN(12)
15	A′	1438 w	-	1607	1464	1487	1427	CH₃opb(95)
16	A″	-	1421w	1598	1453	1476	1422	CH₃ipb(43), CC(23), bCH(19), CH₃opr(6)
17	A′	1391 w	-	1563	1418	1450	1407	CC(51), Ring2(35), Ring1(6)
18	A′	-	1389w	1539	1398	1415	1376	CC(72),bCH(13),Ring1(7)
19	A′	1358 w	1360w	1501	1360	1397	1355	CC(54),CN(32),bCH(11)
20	A′	1331 w	1332w	1474	1326	1386	1345	CH₃sb(38),CC(20),CH₃ipr(16),CH₃ipb(15)
21	A′	1302 w	-	1433	1295	1352	1319	CC(44),bCH(23),CN(9),CH₃ipb(7),Ring2(5),bCC(5)
22	A′	1267 w	1266s	1385	1255	1294	1254	bCH(45),Ring1(23),CC(23)
23	A′	1242 w	1238w	1385	1229	1268	1232	bCH(50),CC(30),CN(10),Ring2(6)
24	A′	1198 w	-	1292	1173	1224	1192	CC(46),bCH(34),CN(14)
25	A′	-	1146w	1265	1145	1186	1151	bCH(65),CC(25)

No.	Symmetry species	Observed frequency (cm⁻¹)		Calculated frequency (cm⁻¹)				Assignment with TED (%)
				HF/6-311++G(d,p)		B3LYP/6-311++G(d,p)		
		FT-IR	FT-Raman	Unscaled	Scaled	Unscaled	Scaled	
26	A′	1141 w	-	1231	1114	1168	1134	bCH(61),CC(34)
27	A′	1081 w	1083w	1163	1053	1107	1080	CN(33) bCH(30),CC(25)
28	A′	1066 w	1068ms	1154	1048	1080	1047	CC(39), Ring2(33), bCH(10), CH₃opr(8), Ring1(5)
29	A′	-	1022w	1144	1031	1054	1018	CC(76), bCH(14)
30	A′	1020 w	-	1113	996	1042	1008	CH₃ipr(42), CH3opr(22), gCN(15), tRing1(8), CH₃opb(7)
31	A″	963ms	963w	1099	984	1000	959	gCH(86), tRing2(14)
32	A″	-	951w	1091	976	983	943	gCH(88), tRing1(10)
33	A″	940w	-	1073	968	980	943	CH₃opr(38), CN(18), Ring1(13), Ring2(10), CC(9), CH₃ipr(9)
34	A″	-	878w	1064	963	974	936	gCH(93)
35	A′	867vs	-	969	867	889	860	Ring1(37), CC(34), Ring2(21)
36	A′	824w	-	951	859	880	850	gCH(71), tRing2(20), tRing1(8)
37	A″	799vs	801w	920	824	841	810	gCH(93)
38	A′	782w	-	861	778	810	782	Ring2(38), Ring1(37), CC(21)
39	A″	747w	-	859	771	793	777	tRing2(42), tRing1(38), gCH(11), gCN(6)
40	A″	-	731s	835	747	759	731	gCH(92)
41	A′	708w	709w	765	690	720	700	bCH(54), CC(19), CH₃ipb(18)
42	A″	642ms	604w	708	634	658	647	tRing2(47), tRing1(28), gCH(13), gCN(11)
43	A′	576w	576w	620	562	586	567	Ring2(43), Ring1(34), CC(16)
44	A″	541w	-	604	543	550	535	tRing1(31), gCN(21), Butter(20), gCH(13), tRing2(10)
45	A′	505w	-	542	491	511	495	Ring1(40), Ring2(26), CC(24), bCC(5)
46	A′	-	502ms	536	486	504	487	Ring1(40), Ring2(40), CC(14)
47	A″	465ms	-	521	466	477	470	tRing2(57), tRing1(32), gCH(11)
48	A′	-	442w	473	430	446	443	bCC(44), Ring1(24), CC(13), Ring2(10)
49	A″	-	410w	459	411	419	411	tRing2(53),gCH(17),gCN(11), tRing1(10), Butter(8)
50	A′	-	295w	298	271	279	277	bCC (49), Ring2(19), Ring1(16), CC(11)
51	A″	-	261w	278	249	252	246	tRing2(44), tRing1(27), gCN(12), Butter(7)
52	A″	-	183w	192	173	174	169	Butter(34), tRing2(19), tRing1(18), gCH(17), gCN(7)

N o.	Symme try species	Observed frequency (cm⁻¹)		Calculated frequency (cm⁻¹)				Assignment with TED (%)
		FT-IR	FT-Raman	HF/6-311++G(d,p)		B3LYP/6-311++G(d,p)		
				Unscaled	Scaled	Unscaled	Scaled	
53	A″	-	141w	176	158	148	143	tCH₃(80)
54	A″	-	88w	136	122	122	119	tRing1(51), tRing2(36), gCN(5)

Abbreviations: b-bending; g-out-of-plane bending; t-torsion; R-ring; ss-symmetric stretching; ops-out-plane stretching; ips-in-plane stretching; sb-symmetric bending; ipr-in-plane rocking; opr-out-plane rocking; asym-assymetic; sym-symmetric; Butter-butterfly; s-strong; vs-very strong; ms-medium strong; w-weak.

Table 3: Calculated fundamental harmonic frequencies (cm⁻¹), force constant (mdyn A⁻¹), infrared - intensity (km/mol) and Raman activity (Å amu⁻¹) of 1-methylisoquinoline are analysed based on SQM force calculation using B3LYP/6-311++G(d,p) and HF/6-311++G(d,p) methods and basis set

HF/6-311++G(d,p)				B3LYP/6-311++G(d,p)			
Frequency	Force constants	IR Intensity	Raman Activity	Frequency	Force constants	IR Intensity	Raman Activity
3364	7.307	10.702	137.091	3197	6.594	10.545	192.547
3351	7.273	34.329	210.992	3185	6.539	20.436	177.004
3346	7.238	23.946	107.208	3178	6.521	29.828	186.984
3334	7.148	6.137	118.628	3173	6.462	4.58	107.106
3329	7.104	8.005	40.751	3162	6.399	0.076	44.434
3320	7.061	0.987	45.587	3156	6.382	10.423	93.539
3284	6.989	13.196	77.168	3137	6.368	7.823	75.46
3220	6.726	23.191	61.870	3073	6.119	15.117	73.895
3170	6.16	21.328	165.000	3025	5.604	17.313	215.219
1820	12.104	57.040	19.912	1659	9.695	15.271	12.541
1780	9.588	13.078	30.942	1623	8.241	15.563	26.25
1772	14.032	56.650	57.874	1604	10.741	29.497	41.048

HF/6-311++G(d,p)				B3LYP/6-311++G(d,p)			
Frequency	Force constants	IR Intensity	Raman Activity	Frequency	Force constants	IR Intensity	Raman Activity
1660	4.807	18.715	10.178	1537	4.176	12.993	13.54
1616	2.646	2.485	29.144	1496	2.086	2.363	27.872
1607	1.591	9.155	9.288	1487	1.362	9.87	9.439
1598	1.868	7.996	3.570	1476	1.74	9.901	3.857
1563	2.687	3.111	23.920	1450	2.378	0.657	26.161
1539	2.255	14.991	1.817	1415	3.218	33.011	26.262
1501	3.025	19.572	18.471	1397	1.91	3.094	10.591
1474	6.746	7.335	259.943	1386	6.32	9.416	142.084
1433	3	19.400	28.756	1352	3.002	18.506	10.101
1385	2.268	0.827	3.664	1294	1.897	1.008	5.019
1357	1.836	3.218	2.279	1268	1.589	2.244	1.853
1293	1.227	0.502	5.677	1224	1.66	0.59	0.561
1265	1.397	4.087	9.903	1186	1.07	2.416	2.494
1231	1.373	3.430	4.243	1168	1.063	2.705	6.382
1163	2.448	0.183	9.263	1107	1.52	0.411	4.665
1154	1.26	0.880	0.186	1080	1.929	0.096	4.906
1144	1.691	1.023	2.134	1054	1.047	1.258	0.008
1113	0.967	0.124	1.179	1042	1.715	5.954	25.771
1100	0.975	0.087	1.585	1000	0.765	0.024	0.359
1091	0.941	1.355	2.666	983	0.772	0.139	0.334
1073	2.344	6.325	21.021	980	1.114	12.872	4.92
1064	1.475	15.113	2.221	974	0.754	1.394	0.958
969	0.867	9.732	0.210	889	1.98	0.214	4.673
951	2.301	0.123	3.348	880	0.719	6.57	0.014
920	0.668	55.750	0.026	841	0.552	44.979	0.001
861	1.44	0.766	0.348	810	2.364	2.881	1.021
859	2.668	5.049	0.903	794	1.226	1.078	0.16
835	0.519	41.240	0.698	759	0.425	34.79	0.316
765	1.768	1.515	24.805	720	1.553	1.376	29.083

HF/6-311++G(d,p)				B3LYP/6-311++G(d,p)			
Frequency	Force constants	IR Intensity	Raman Activity	Frequency	Force constants	IR Intensity	Raman Activity
708	1.045	7.697	0.157	658	0.964	5.445	0.108
620	1.294	5.372	5.808	586	1.151	3.761	8.131
604	0.579	9.113	0.171	550	0.481	6.783	0.082
542	1.163	2.432	7.783	511	1.062	2.006	9.475
536	0.978	0.879	5.998	504	0.861	0.837	7.04
521	0.586	5.282	0.347	477	0.51	3.761	0.196
473	0.459	1.632	2.804	446	0.403	1.356	3.079
459	0.373	4.475	1.530	419	0.309	3.382	0.963
298	0.165	0.811	1.274	279	0.143	0.687	1.9
279	0.144	6.136	0.649	252	0.122	5.396	0.579
192	0.064	0.370	0.065	174	0.079	0.095	0.089
176	0.022	0.291	0.329	148	0.014	0.431	0.544
136	0.036	0.192	1.144	121	0.029	0.227	1.165

Referencs

[1]   Takman B H and Adams H J, "Local anaesthetics In: Medicinal Chemistry (Ed) (ME Wolff, Fourth Edn, New York, Wiley Interscience) 1980.

[2]   Edmices D L and Mitscher L A (Eds) "Local anaesthetics in the organic chemistry of drug synthesis", (John Wiley & Sons, New York) 1977.

[3]   Foye W O (Ed) "Principles of Medical Chemistry (Second Edition, Philadelphia Lea & Febiger) 1981.

[4]   Maitland Jones, Jr, "Organic chemistry" (Norton & Company, New York) 1997.

[5]   Gunasekaran S, Seshadri S, Muthu S, *Indian J. Pure Appl. Phys.*, 44 (2006) 581.

[6]   Pulay P, in: Schaefer H F III (Ed.), Application of Electronic structure Theory, Modern Theoretical Chemistry, Vol. 4, Plenum, New York (1977) 153.

[7]   Pulay P, Zhou X, Fogarasi G, in: R. Fransto (Ed.), NATO ASI series, Vol. C, 406, Kluwer, Dordrecht (1933) 99.

[8]   De Mare G R, Panchenko Y N, Bock C W, *J. Phys. Chem.*, 98 (1994) 1416.

[9]   Yamakita Y, Tasuni M, *J. Phys. Chem.*, 99 (1995) 8524.

[10]   Rauhut G, Pulay P, *J. Phys. Chem.*, 99 (1995) 3093.

[11]   M.J. Frisch, G.W. Trucks, H.B. Schlegal, G.E. Scuseria, M.A. Robb,J.R. Cheesman, .G. Zakrzewski, J.A. Montgomerg, Jr., R.E. Stratmann,J.C. Burant, S. Dapprich, J.M. illam, A.D. Daniels,K.N.Kudin,M.C.Strain,O.Farkas,J. Tomasi, V. Barone, M. Cossi, R. Cammi,B.

Mennucci,C.Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, N. Rega, P. Salvador, J.J. Dannenberg,D.K. Malich, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski,J.V. Ortiz, A.G. Baboul, B.B. Stetanov, G. Liu, A.Liashenko,P.Piskorz,I.Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham,C.Y.Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, B. Johnson,W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon,E.S. Replogle, J.A. Pople, GAUSSIAN 09, Revision A 11.4, Gaussian, Inc, Pittsburgh PA, 2009.

[12] A.D. Becke, Journal of Chemical Physics, 98 (1993) 5648.

[13] C. Lee, W. Yang, R.G. Parr, Phys. Rev., B37 (1988) 785.

[14] P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs, A. Vargha, Journal Am. Chem. Soc.105 (1983)7037.

[15] Rauhut G, Pulay P, *J. Phys. Chem.*, 99 (1995) 3093.

[16] T. Sundius, Journal of Molecular Spectroscopy,. 82 (1980) 138.

[17] T.Sundius, Journal of Molecular Structure., 218 (1990) 321.

[18] T. Sundius, Vibrational Spectroscopy, **29** (2002) 89.

[19] Cotton F A, Chemical Applications of Group Theory, Wiley Inter science, New York, 1963.

[20] Frisch, Nielson A B, Holder A J, Gauss view user's manual, Gaussian Inc., Pittsburgh, PA, 2009.

[21] G. Keresztury, S. Holly, J. Varga, G. Besenyei, A.Y. Wang, J.R. Durig, Spectrochim. Acta Part A, **49** (1993) 2007.

[22] G. Keresztury, Raman Spectroscopy: Theory in: J.M. Chalmers, P.R. Griffiths (Ed.), Handbook of Vibrational Spectroscopy, Wiley, **1** (2002).

[23] G. Fogarasi, P. Pulay, in: J.R. Durig (Ed.), *Vibrational Spectra and Structure*, Vol.14, Elsevier, Amsterdam, Chapter 3, 1985, 125.

[24] Kandasamy M, Velraj G, Kalaichelvan S, Mariappan G, *Spectrochim. Acta Part A*, 134 (2015) 191.

[25] Karpagam J, Sundaraganesan N, Sebatian S, Manoharan S, Kurt K, *J. Raman Spectrosc.*, 41 (2011) 53.

[26] James C, Amal Raj A, Reghunathan R, Jayakumar V S, Hubert Joe I, *J. Raman Spectrosc*, 37 (2006) 1381.

[27] Krishnan A R, Saleem H, Subaschandrabose S, Sundaraganesan N, Sebastian S, *Spectrochim. Acta* A 78 (2011) 582.

[28] Jag Mohan, *Organic Spectroscopy - Principles and Applications*, second ed., Narosa, Publishing House, New Delhi, 2001.

[29] Dani V R, Organic Spectroscopy, Tata-McGraw Hill Publishing Company, New Delhi, (1995) 139.

[30] Krishnakumar V. and Balachandran V, *Spectrochim, Acta*, Part A, 61 (2005) 2510.

[31] Ataly Y, Avci D, BaSoglu A, *Struct. Chem*. 19 (2008) 239.s