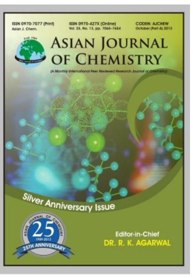
Asian Journal of Chemistry; *Vol. 25, No. 13 (2013), 7106-7114*

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.14453



Infrared Spectra, Density Functional Theory and Hartree-Fock Theoretical Calculations of 2-Methyl-8-quinolinol

K. ARICI[1,*] and R. YILMAZ[2]

[1]Department of Physics, Faculty of Science and Arts, Kilis 7 Aralik University, 79100 Kilis, Turkey
[2]Department of Physics, Faculty of Science and Arts, Yüzüncü Yil University, 65100 Van, Turkey

*Corresponding author: Fax: +90 348 8222351; Tel: +90 348 8202350; E-mail: arici@kilis.edu.tr

(*Received*: 17 August 2012; *Accepted*: 14 June 2013) AJC-13652

The Fourier transform infrared and Raman spectra of 2-methyl-8-quinolinol have been recorded at solid phase and in the region 4000-400 cm^{-1}. The molecular geometry, vibrational frequency, infrared intensities bands of 2-methyl-8-quinolinol in ground state have been calculated by Hartree-Fock and density functional theory with the B3LYP, BLYP and B3PW91 functional and 6-311G(dp) basis set, respectively. The calculated frequencies has been scaled which compared with experimental infrared and Raman spectra. The geometry and normal modes of vibration obtained from the Hartree-Fock and density functional theory methods are in good agreement with the experimental data.

Key Words: 2-Methyl-8-quinolinol, FTIR, FT-Raman Hartree-Fock, Density functional theory.

INTRODUCTION

Quinoline and its substituted derivatives are well known for antifungal, antibacterial, antiamoebic and antimicrobial activities[1,2]. These molecules are widely employed as good fluorogenic ligand binding with many metal cations due to its low quantum yield in aqueous and in some organic solutions. Quinolines have been extensively used for the extraction and analytical determination of metal ions[3,4]. Important applications of quinoline and derivatives are use as antimalarial drugs, in manufacturing dyes, as food colorant and a pH indicator[5,6].

X-Ray crystallographic structure of 2-methyl-8-hydroxy quinoline[7] and infrared spectra of hydroxyquinoline was determined[8]. Hydroxquinoline and its mercury(II) complexes[9], DFT calculations of isoquinoline and 8-hydroxyquinoline[10], infrared spectra and DFT of 8-hydroxyquinoline and its halogen derivatives[11], fundamental vibrational of 6-hydroxyquinoline[12], *ab initio* and DFT theoretical calculations[13] were studied. Infrared absorption spectra 2-methyl-8-quinolinol were also observed[14]. *Ab initio* calculations on 2-, 3- and 4-substituted quinoline are carried out in a search for a relationship between the molecular properties of these compounds[15]. *Ab initio*, density functional theory and structural studies were performed on 4-amino-2-methylquinoline[16]. Infrared and Raman spectra of the 2,4-diaminoquinazoline and 4-amino-2-methylquinoline were studied by density functional theory[17].

Although 2-methyl-8-quinolinol has been studied by IR spectroscopy, but band assignments are not available in literature. Here, we studied 2-methyl-8-quinolinol from the vibrational point of view. The HF and DFT(B3LYP, BLYP and B3PW91) theoretical calculations were calculated with the 6-311G(dp) basis set. This aim of the study is to make reasonably reliable first assignments of absorbance bands.

EXPERIMENTAL

The compound 2-methyl-8-quinolinol was purchased from the Sigma-Aldrich Chemical company. The infrared spectrum of 2-methyl-8-quinolinol has been recorded in the region 4000-400 cm^{-1}, Bruker FTIR IFS 66/S spectrophotometer using KBr pellet technique and the FT-Raman spectrum of the sample was recorded between 3500-80 cm^{-1} regions on FRA-106/S spectrometer at METU, Ankara/Turkey. The observed infrared and Raman spectra of 2-methyl-8-quinolinol are shown in Fig. 1.

Computational details: The molecular structure of 2-methyl-8-quinolinol in the ground state (*in vacuo*) are optimized by HF and DFT(B3LYP, BLYP and B3PW91) with the 6-311G(dp) basis set. The optimized structural parameters were used in the vibrational frequency calculations at HF and DFT levels.

DFT for all studies reported in this paper has the following from

$$E_{xc} = (1-a_0)E_x^{LSDA} + a_0E_x^{HF} + a_x\Delta E_x^{B88} + a_cE_c^{LYP} + (1 - a_c)E_c^{VWN}$$

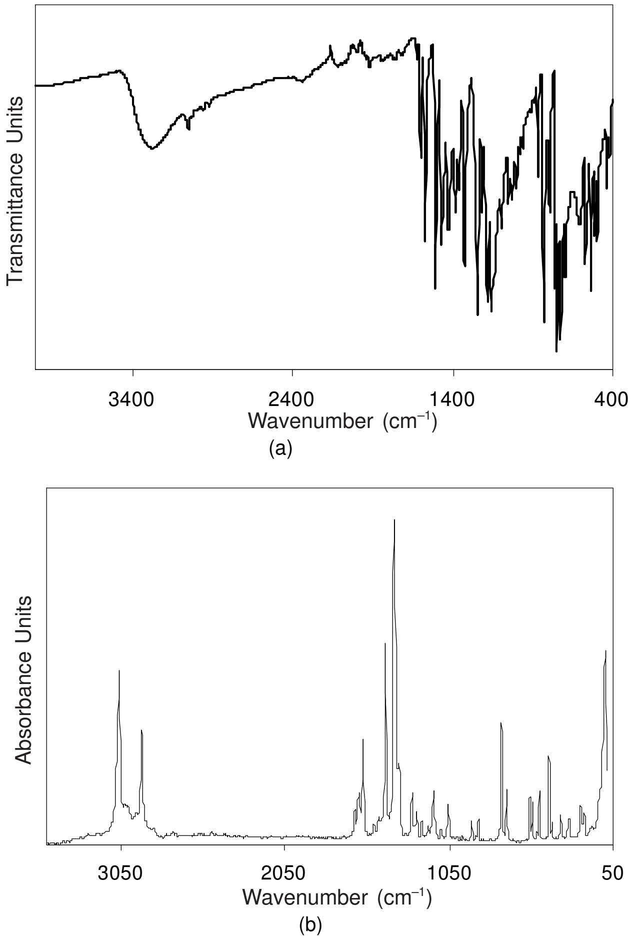


Fig. 1. (a) IR spectra and (b) Raman spectra of 2-methyl-8-quinolinol

where, the energy terms are the Slater exchange, the Hartree-Fock exchange, Becke's exchange functional correlation, the gradient correlated correlation functional of Lee, Yang and Parr and the local correlation functional of Vosko, Wilk and Nusair[18]. HF/6-311G(dp), B3LYP/6-311G(dp), BLYP/6-311G(dp) and B3PW91/6-311G(dp) levels of theory with the optimized geometries have been used to calculate all parameters of the 2-methyl-8-quinolinol.

All the calculated vibrational frequencies are scaled by 0,9085 for HF/6-311G(dp), 0,9669 for B3LYP/6-311G(dp), 0,9962 for BLYP/6-311G(dp) and 0,9631 for B3PW91/6-311G(dp)[19]. Molecular geometry is not restricted and all the calculations are performed by using GaussView molecular visualization program[20] and GAUSSIAN09 program package on the personal computer[21].

RESULTS AND DISCUSSION

The molecule of 2-methyl-8-quinolinol consist of 21 atoms, so it has 57 normal vibrational modes. The geometry of the molecule under investigation is considered by possessing C_s point group symmetry. In this case, OH and $-CH_3$ molecules groups as point masses are present within the molecular plane. Fifty seven fundamental modes of vibrations of the compound are distributed into the irreducible representations under C_s symmetry as 38 in-plane vibrations of a' species and 19 out of plane vibrations of a" species, *i.e.*, $\Gamma_{vib} = 19a'' + 38a'$. All vibrations are active in both IR and Raman spectra. All the frequencies are assigned in terms of fundamental, overtone and combination bands.

The molecular structure and numbering of the atoms of 2-methyl-8-quinolinol l is shown in Fig. 2.

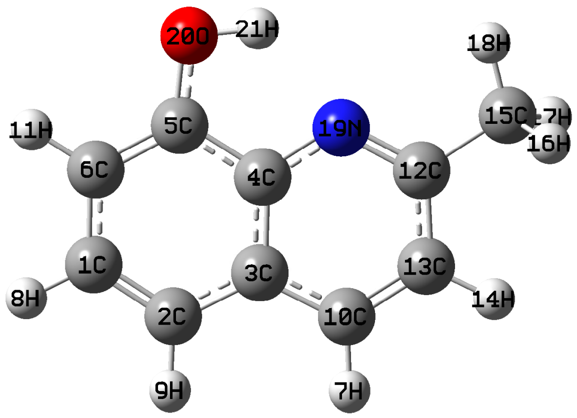


Fig. 2. 2-Methyl-8-quinolinol structure and atoms numbering

Geometrical structure: The optimized bond lengths and angles for 2-methyl-8-quinolinol at HF(6-311G**), DFT/B3LYP(6-311G**), DFT/BLYP(6-311G**) and DFT/B3PW91(6-311G**) levels are represented in Table-1 along with available experimental crystal data[7].

As discussed in previous papers[9-13] and their work[11,22,23], it is well known that HF methods underestimate for bond lengths. BLYP methods predict bond lengths which are systematically long, particularly C-H bond lengths. Since large deviation from experimental C-H bond lengths may arise from the low scattering factors of hydrogen atoms in the X-ray diffractions experiment so we did not discuss C-H bond lengths.

From the structural data given in Table-1 it is observed that the influence of the substituent on the molecular structure, particularly in C-C bond distance of ring carbon atoms seems to negligibly small except that C4-C5 and C12-C13 bonds lengths are longer than others quinoline rings, where the hydroxyl and methyl groups depends on C5 and C12 atoms, respectively. X-ray data of these bonds lengths are 1.417 and 1.415 Å, respectively[7]. The C4-C5 bond distance have been calculated at the 6-311G** level to be 1.422(HF), 1.418(B3LYP), 1.427(BLYP) and 1.425(B3PW91). This bond length was calculated as 1,433(B3LYP)[10], 1.425(HF), 1.430(B3LYP) and 1.440(BLYP)[9] with 6-31G* level for 8-hydroxyquinoline. The C12-C13 bond length have been calculated as 1.427(HF), 1.412(B3LYP), 1.423(BLYP) and 1.421(B3PW91) with 6-31G** level. The C12-C13 bond length was calculated as 1.42(HF,B3LYP) with 6-31G** and 6-311++D**levels for 4-amino-2-methylquinoline[16]. The C10-C13 and N19-C12 bond distances are shorter than other C-C and C-N bond lengths. These C10-C13 and N19-C12 bond distances are 1.352 and 1.319 Å, respectively. The N19-C12 bond distance was calculated as 1.32(B3LYP) with 6-31G** level and 1.29(HF) with 6-311++G** level for 4-amino-2-methylquinoline[16], 1.293(HF), 1.320(B3LYP) and 1.318(B3PW91) with 6-31G* level for 5,7-dichloro-8-hydroxyquinaldine[13]. All other in the quinoline ring C-C bond distances are calculated in the range 1.352-1.427 Å.

TABLE-1
GEOMETRIC PARAMETERS BOND LENGTHS (Å) AND BOND ANGLES (^{O}) OPTIMIZED FOR 2-METHYL-8-QUINOLINOL

	Bond lengths (Å)	HF 6-311G(dp)	DFT/B3LYP 6-311G(dp)	DFT/BLYP 6-311G(dp)	DFT/B3PW91 6-311G(dp)	X-Ray Ref.[7]
R1	C1-C2	1.359	1.374	1.375	1.375	1.361
R2	C1-C6	1.411	1.402	1.411	1.409	1.397
R3	C1-H8	1.075	1.093	1.083	1.085	0.930
R4	C2-C3	1.415	1.405	1.416	1.413	1.412
R5	C2-H9	1.075	1.093	1.083	1.084	0.930
R6	C3-C4	1.397	1.411	1.419	1.416	1.409
R7	C3-C10	1.420	1.406	1.418	1.415	1.413
R8	C4-C5	1.422	1.418	1.427	1.425	1.417
R9	C4-N19	1.357	1.345	1.360	1.356	1.367
R10	C5-C6	1.361	1.375	1.377	1.377	1.364
R11	C5-O20	1.337	1.327	1.348	1.342	1.355
R12	C6-H11	1.074	1.092	1.082	1.083	0.930
R13	C10-H7	1.076	1.095	1.084	1.086	0.930
R14	C10-C13	1.352	1.368	1.369	1.369	1.352
R15	C12-C13	1.427	1.412	1.423	1.421	1.415
R16	C12-C15	1.505	1.482	1.506	1.500	1.494
R17	C12-N19	1.290	1.316	1.316	1.316	1.319
R18	C13-H14	1.074	1.093	1.083	1.085	0.930
R19	C15-H16	1.086	1.102	1.093	1.094	0.960
R20	C15-H17	1.086	1.102	1.093	1.094	0.960
R21	C15-H18	1.080	1.097	1.088	1.089	0.960
R22	O20-H21	0.946	1.001	0.972	0.975	0.860
			Bond angle (°)			
A1	C2-C1-C6	121.37	122.28	121.69	121.85	121.40
A2	C2-C1-H8	119.96	119.37	119.73	119.64	119.30
A3	C6-C1-H8	118.65	118.34	118.56	118.50	119.30
A4	C1-C2-C3	119.31	119.30	119.48	119.40	119.38
A5	C1-C2-H9	121.07	121.10	120.94	120.95	120.30
A6	C3-C2-H9	119.61	119.59	119.57	119.64	120.30
A7	C2-C3-C4	119.84	118.86	119.35	119.30	119.80
A8	C2-C3-C10	124.04	125.66	124.77	124.94	123.90
A9	C4-C3-C10	116.10	115.47	115.87	115.75	116.30
A10	C3-C4-C5	119.55	120.78	119.80	119.98	118.79
A11	C3-C4-N19	123.43	124.38	123.71	123.95	123.48
A12	C5-C4-N19	117.01	114.83	116.48	116.05	117.72
A13	C4-C5-C6	119.76	119.17	119.70	119.58	120.04
A14	C4-C5-O20	119.20	116.53	118.60	118.19	121.06
A15	C6-C5-O20	121.02	124.29	121.69	122.22	118.90
A16	C1-C6-C5	120.13	119.59	119.69	119.87	120.50
A17	C1-C6-H11	120.70	121.14	120.89	120.90	119.80
A18	C5-C6-H11	119.15	119.26	119.13	119.22	119.80
A19	C3-C10-H7	119.44	119.33	119.43	119.47	120.00
A20	C3-C10-C13	119.76	119.85	119.87	119.85	119.93
A21	H7-C10-C13	120.78	120.81	120.68	120.67	120.00
A22	C13-C12-C15	119.65	120.67	120.32	120.41	120.53
A23	C13-C12-N19	121.70	120.91	121.47	121.40	121.96
A24	C15-C12-N19	118.64	118.40	118.19	118.18	117.50
A25	C10-C13-C12	119.55	120.34	119.99	120.04	120.10
A26	C10-C13-H14	121.07	120.77	120.74	120.69	120.00
A27	C12-C13-H14	119.36	118.88	119.25	119.25	120.00
A28	C12-C15-H16	110.60	111.18	110.98	110.98	109.50
A29	C12-C15-H17	110.60	111.18	110.98	110.98	109.50
A30	C12-C15-H18	109.98	109.84	109.93	109.95	109.50
A31	H16-C15-H17	107.58	106.89	107.23	107.22	109.50
A32	H16-C15-H18	109.00	108.81	108.81	108.81	109.50
A33	H17-C15-H18	109.00	108.81	108.81	108.80	109.50
A34	C4-N19-C12	119.42	119.03	119.06	118.98	118.15
A35	C5-O20-H21	107.98	102.25	105.40	104.57	113.00

The O-H bond distance have been calculated at the 6-311G** level to be 0.964(HF), 1.001(B3LYP), 0.972(BLYP) and 0.975 Å (B3PW91). In previous work, this O-H bond is calculated as 0.948(HF), 0.974(B3LYP) and 0.860(B3PW91) with 6-31G** level for 5,7-dichloro-8-hydroxyquinaldine[13]. Also, this bond length was calculated as 0.949(HF) and 0.980(B3LYP) with 6-31G** level for 7-bromo-5-chloro-8-hydroxyquinoline[24].

The C12-C15 bond distance have been calculated at the 6-311G** level to be 1.505(HF), 1.482(B3LYP), 1.506(BLYP) and 1.500 Å (B3PW91). Previous results are 1.506(HF), 1.508(B3LYP), 1.503(B3PW91) for 5,7-dichloro-8-hydroxyquinaldine[13]. This bond length was calculated as 1.51(HF, B3LYP) for 4-amino-2-methylquinoline[16], 1.54(B3LYP)[17] and 1.5063(HF), 1.5085(B3LYP) for 2-methylquinoline[25] and 1.507 Å (HF, B3LYP) for lepidine[22]. This bond is quite longer than other experimental and theoretical calculations. The C12-C15 bond distance is longer than other bond is due to the steric repulsion between C12 atom and methyl group.

Table-1 showed that the C5-O20 bond distance have been calculated at the 6-311G** level to be 1.337(HF), 1.327(B3LYP), 1.348(BLYP) and 1.342 Å (B3PW91). This C5-O20 bond distance was calculated as 1.350 (B3LYP)[11], 1.333 (HF), 1.348 (B3LYP) and 1.342 (B3PW91)[13], 1.349 (BLYP)[26] and 1.328(HF), 1.342 (B3LYP)[24]. The experimental C5-O20 bond distance is longer than the theoretical calculations.

The calculated bond angles are close to each other except for the CCC bond angle at the point of methyl group substitution. With the electron donating substituent on the benzene ring, the symmetry of the ring is distorted, yielding ring angles smaller than 120º at the point of substitution and slightly larger than 120º at the *ortho* and *meta* positions[27]. Similar trend is not observed in 2-methyl-8-quinolinol. The C13-C12-N19 angle at the point of methyl group substitution is around 121.37º while at *meta* C10-C13-C12 and *para*, C3-C10-C13 positions the angles are found to be around 119.98 and 119.83º, respectively. The C13-C12-N19 angle was calculated as 123.28(HF) and 123.33(B3LYP) with 6-31G** level[16], 120.47(B3LYP) with 6-311+G** level[17], 121.9(HF), 122.1(B3LYP) and 122.1(B3PW91) with 6-31G* level[13]. Introduction of methyl group leads to significant perturbations in the substituted of pyridine ring, although the geometry of the benzene ring is seen to be relatively unperturbed.

The correlations graphics between the experimental and calculated bond lengths obtained by the several methods is shown in Fig. 3. According to our calculations, DFT/BLYP method correlates well for the bond length compared with the other HF, DFT/B3LYP and DFT/B3PW91 methods for 2-methyl-8-quinolinol molecule. Also, the HF method correlates well for the bond angle compared with other DFT/B3LYP, DFT/BLYP and DFT/B3PW91 methods for 2-methyl-8-quinolinol molecule (Fig. 4).

Vibrational assignments: The observed and theoretical FTIR and FT-Raman spectra of 2-methyl-8-quinolinol are given in Fig. 5. The observed and calculated frequencies using ab initio HF/6-311G**, B3LYP/6-311G**, BLYP/6-311G** and B3PW91/6-311G** along with their relative intensities, probable assignments in Table-2.

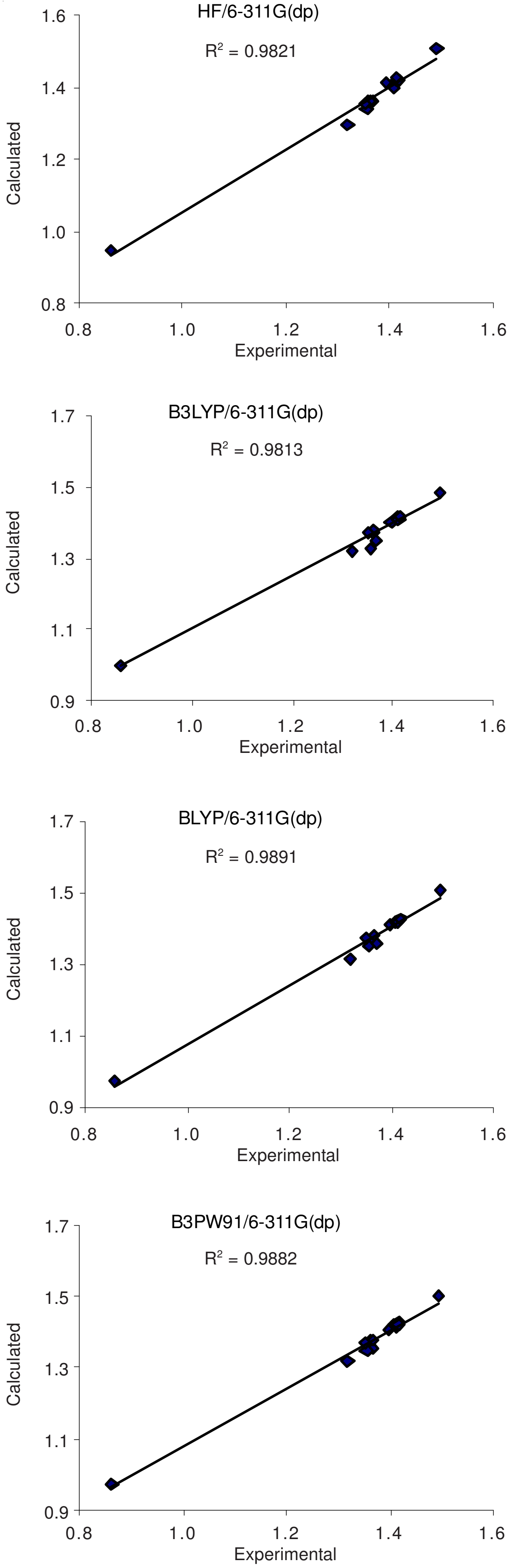


Fig. 3. Correlations graphics of bond lengths for 2-methyl-8-quinolinol molecule

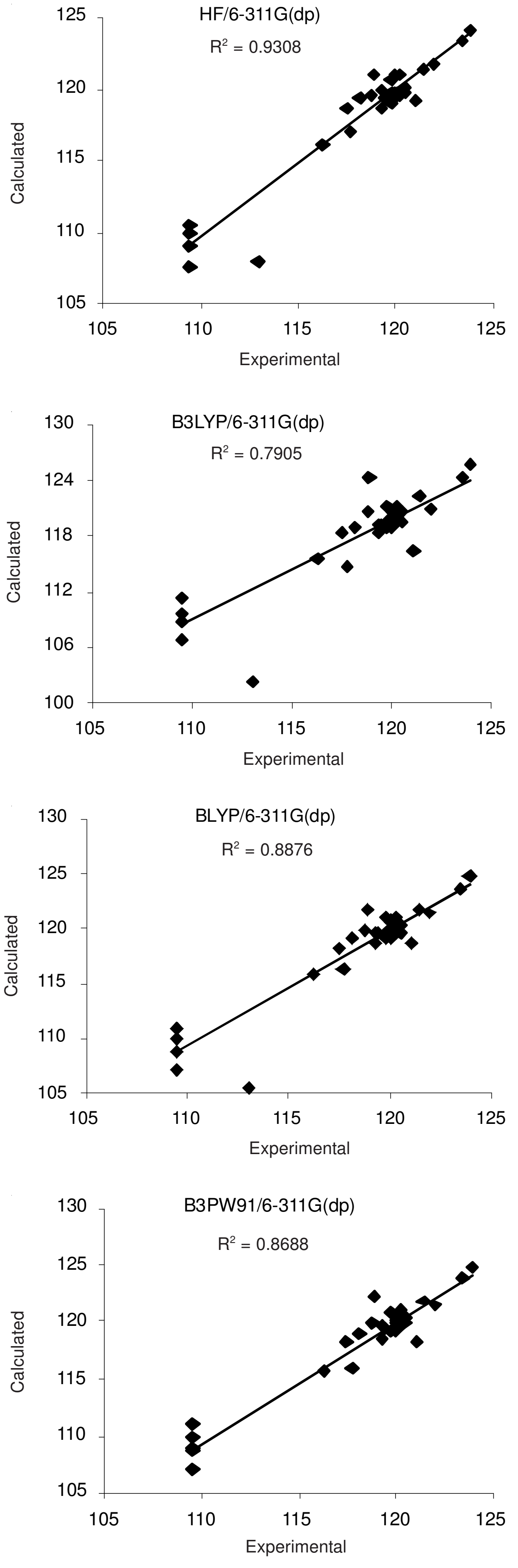


Fig. 4. Correlations graphics of bond angle for 2-methyl-8-quinolinol molecule

OH vibrations: The O-H stretching vibrations are sensitive to hydrogen bonding. The non-hydrogen bonded or free hydroxyl group absorbed strongly and sharp in 3670-3580 cm^{-1}. But in Raman spectra the O-H band is generally week. For solids, liquids and concentrated solutions a broad band of less intensity is normal observed[28-30]. Inter-molecular hydrogen bonding if present would reduce the O-H stretching band to 3550-3200 cm^{-1} region[31]. In the present study, medium broad is observed at 3272 cm^{-1} to O-H stretching vibration, which show that 2-methyl-8-quinolinol molecule possesses an inter-molecular hydrogen bond in solid state. This band is not observed in the Raman spectra. The theoretical scaled O-H stretching frequencies are (3713)HF, (3150)B3LYP, (3655)BLYP and (3489)B3PW91 with 6-311G** set. The O-H in-plane bending vibration is observed in the region 1440-1260 cm^{-1} [32]. The O-H in-plane bending vibration is observed at 1381 and 1382 cm^{-1} to be medium strong band in infrared and wery strong in Raman spectra, respectively. The 1381 cm^{-1} band is calculated to be (1393)HF, (1356)B3LYP, (1435)BLYP and (1394)B3PW91 with 6-311G** set. The out-of-plane bending of O-H is observed at 609 cm^{-1} in the infrared spectra to be medium strong. The out-of-plane bending band is calculated at (588)HF, (643)B3LYP, (631)BLYP and (637)B3PW91 with 6-311G**. The C-(OH) stretching band is observed at 1244 cm^{-1} (strong) and at 1247 cm^{-1} (weak) in infrared and Raman spectra, respectively of 2-methyl-8-quinolinol molecule. The 321 and 225 cm^{-1} in Raman bands can be attributed to C-(OH) in-plane-bending vibration and C-(OH) out-of-plane bending vibration, respectively[10,13,24].

C-H vibrations: The aromatic C-H stretching vibrations are normally observed between 3050 and 3000 cm^{-1}. The C-H stretching of 2-methyl-8-quinolinol molecule gives bands at 3049, 3027 and 3002 cm^{-1} in infrared spectra to be weak and at 3058 (strong), 3028, 3019 and 3004 cm^{-1} in Raman spectra to be weak. The aromatic C-H stretching vibrations are generally highly pure modes. The C-H in-plane bending modes are observed in region 1200-1000 cm^{-1}. These modes are observed at 1160, 1140, 1094, 1051 and 1028 cm^{-1} in the infrared spectra and the corresponding frequencies are obtained in the Raman at 1142 and 1096 cm^{-1} in Table-2. The C-H out-of-plane bending modes are observed in the region 1100-760 cm^{-1}. The aromatic C-H out-of plane bending vibrations of 2-methyl-8-quinolinol are assigned to the bands observed at 970, 959, 887, 830 and 759 cm^{-1} in the infrared spectrum[10]. These bands not observed in Raman spectra of 2-methyl-8-quinolinol molecule. C-H vibrational frequencies calculated are given in Table-2.

Methyl group vibrations: There are nine basic methyl group vibrations. These are ν_sCH_3 symmetric stretch, two ν_aCH_3 asymmetric stretch, two ν_aCH_3 asymmetric bending, ν_sCH_3 symmetric bending CH_3 rocking, CH_3 wagging and CH_3 torsion. The ν_sCH_3 frequency is not observed in the infrared but asymmetric deformation modes ν_aCH_3 are assigned at 2918 and 2954 cm^{-1} under a'' and a' species of 2-methyl-8-quinolinol molecule, respectively. The ν_aCH_3 asymmetric bending deformation modes are obtained at 1426 and 1469 cm^{-1} a' species. The symmetrical bending methyl deformational mode ν_aCH_3 is not observed. The methyl deformational modes

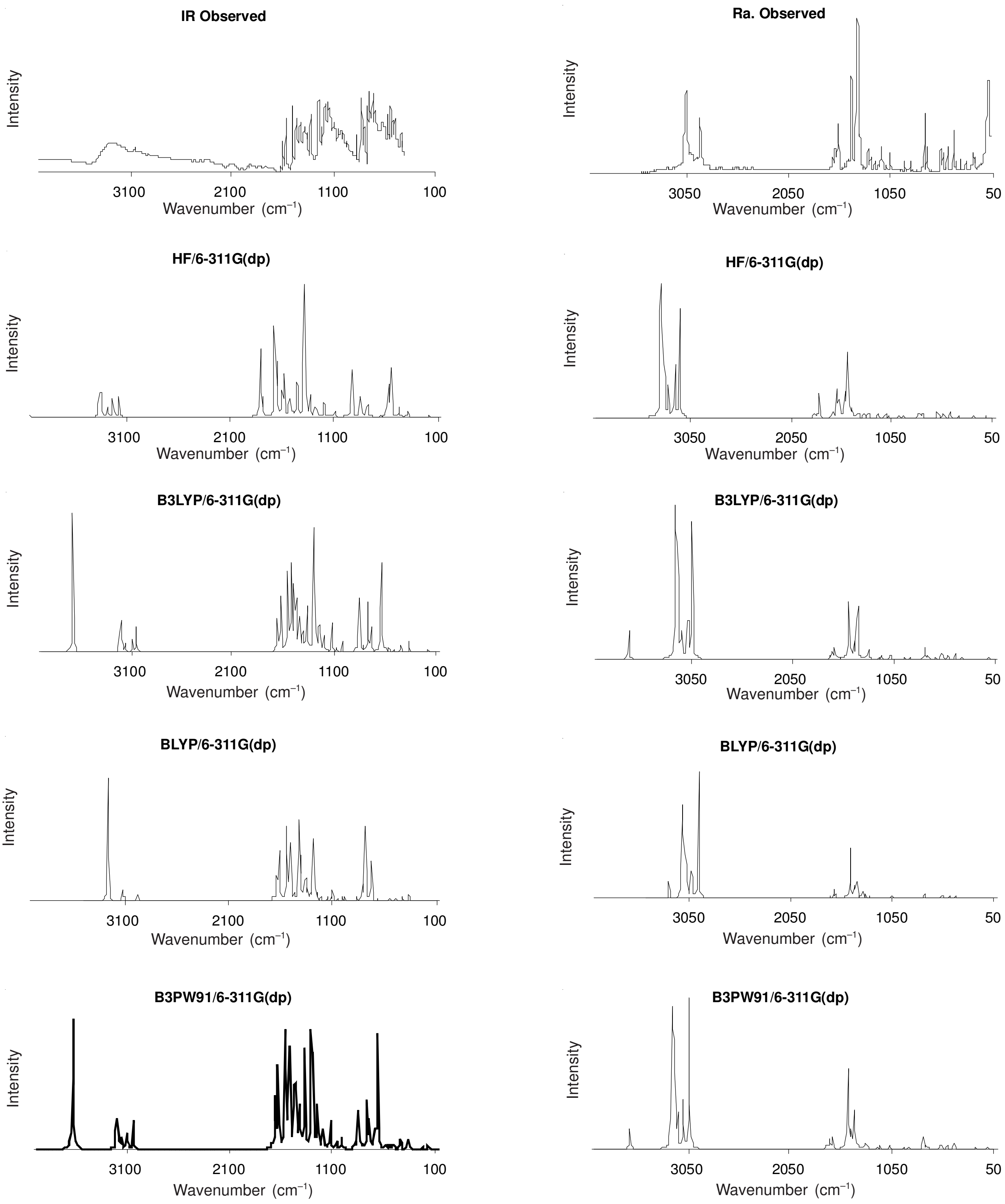
TABLE-2

OBSERVED FTIR, FT-RAMAN AND CALCULATED FREQUENCIES USING HF/6-311G**, B3LYP/6-311G**, BLYP/6-311G** AND B3PW91/6-311G** WITH SCALED FREQUENCIES, THEIR INTENSITIES AND PROBABLE ASSIGNMENTS OF 2M8Q

Spc.	Ob. wavenumber (cm^{-1})		Cal. HF/6-311G**			Cal. B3LYP/6-311G**			Cal. BLYP/6-311G**			Cal. B3PW91/6-311G**			Probable assignment
	FTIR	FTRa	Scaled[a] (cm^{-1})	Ir. int.	Ra. act.	Scaled[b] (cm^{-1})	Ir. int.	Ra. act.	Scaled[c] (cm^{-1})	Ir. int.	Ra. act.	Scaled[d] (cm^{-1})	Ir. int.	Ra. act.	
A"	–	101 s	80	0.34	0.07	59	0.57	0.31	65	0.33	0.16	62	0.38	0.20	t (CH_3)
A"	–	–	107	0.32	0.75	103	0.54	1.65	108	0.29	1.80	103	0.34	1.75	t ring
A"	–	–	170	2.88	0.75	161	2.99	0.08	172	2.67	0.10	165	2.91	0.08	Butterfly
A'	–	–	218	0.14	026	214	0.86	1.53	224	0.46	0.55	214	0.57	0.54	δ ring
A"	–	225 w	222	0.64	1.79	214	0.75	0.62	225	0.69	1.55	216	0.90	1.56	γ (C-H_3)+ γ(C-OH)
A"	–		317	0.02	1.05	302	0.02	0.33	321	0.01	0.51	308	0.02	0.52	Fluctuation
A'	–	321w	356	8.30	1.36	353	14.64	1.91	366	10.10	1.85	352	11.28	1.71	δ(C-OH)+ δ(C-H_3)
A"	421 ms	423 w	425	5.61	7.97	407	2.33	1.87	434	2.38	2.17	415	2.48	2.05	γCCC
A'	438 ms	441 m	429	9.57	2.86	419	5.44	8.98	440	4.94	9.18	424	5.13	9.00	ν ring
A'	495ms	497 w	478	3.22	4.94	476	2.29	7.54	504	2.96	6.31	483	2.91	6.67	δ CNC
A"	509 ms		500	56.77	1.39	483	2.44	0.42	519	0.67	0.24	497	1.23	0.22	γCCC
A'	540 s	543 w	532	57.39	0.65	532	3.48	6.34	555	3.55	5.59	532	3.74	5.52	δ CCN
A'	572 w		538	4.44	4.55	544	0.59	9.56	566	0.47	9.83	545	0.65	9.49	δ CNC
A"	–	558 m	544	1.04	7.25	561	0.69	1.17	593	2.37	0.90	570	0.65	9.40	γCCC
A"	609 br		588	0.51	0.72	643	3.48	0.06	631	92.57	1.82	637	76.85	1.03	γOH
A"	695 s	697 m	672	0.71	0.66	677	0.60	5.47	682	2.01	0.51	660	16.22	1.00	γCCN
A'	722 vs	728 ms	676	0.78	7.40	705	38.90	0.69	705	0.93	7.07	680	0.89	6.97	δ CCC
A'	747vs	–	712	23.91	13.99	710	12.81	23.29	737	16.92	19.31	712	16.01	20.67	δ CCC
A"	759 ms	–	767	46.02	0.06	757	23.19	1.57	766	36.21	0.45	734	37.94	0.30	γCH
A"	795 ms	–	805	3.70	0.80	764	79.81	0.75	807	3.31	0.53	776	3.50	0.42	γ CNC
A"	830 vs	–	845	54.27	0.11	786	24.40	0.49	848	43.44	0.28	814	44.58	0.19	γCH
A'	867 ms	869 w	849	4.62	2.27	825	0.20	1.04	882	4.88	1.73	849	40.74	1.94	δ CCC
A"	887 w	–	888	1.11	1.92	839	5.35	1.44	893	0.45	1.14	856	0.30	0.93	γCH
A'	910w	909 w	900	1.91	1.90	891	0.12	3.48	929	0.31	2.76	898	0.12	2.99	δ CCC
A"	959 w	–	989	0.63	0.82	902	0.25	0.25	976	0.29	0.27	938	0.28	0.24	γCH
A"	970 w	–	991	5.83	1.46	929	0.52	0.10	999	0.35	0.13	959	0.38	0.14	γCH
A'	981 m	–	1013	0.23	0.81	948	5.99	0.85	1016	7.66	0.88	975	7.52	0.90	Wagging $CH_3)$
A"	1002 ms	–	1020	3.26	8.29	972	7.16	0.22	1060	3.32	0.16	1012	4.36	0.14	Rocking (CH_3)
A'	1028 ms	–	1050	3.25	0.42	1014	3.40	11.01	1071	1.83	11.18	1034	2.25	11.17	δCH
A'	1051 ms	1056 w	1080	0.22	3.19	1061	16.42	0.78	1116	21.73	0.95	1077	18.80	0.88	δCH
A'	1094 ms	1096 vw	1086	29.46	2.81	1085	4.36	6.39	1164	0.81	5.38	1120	1084	5.48	δCH
A'	1140 s	1142 w	1159	21.13	10.36	1114	7.54	2.87	1195	11.58	2.09	1147	11.47	2.37	δCH
A'	1160 vs	–	1173	2.22	4.64	1172	7.05	0.77	1231	27.49	0.35	1192	28.99	0.21	δCH
A'	1183 ms	1175 vw	1209	24.48	5.80	1207	10.73	1.59	1247	14.00	0.52	1210	5.12	0.75	νCC
A'	1215 ms	1216 w	1255	155.58	4.96	1239	78.89	6.79	1291	147.46	24.07	1248	128.55	15.35	νCC
A'	1244 vs	1247 w	1259	36.00	4.88	1270	11.66	15.77	1303	8.95	3.66	1265	10.85	8.08	ν (C-OH)
A'	1325 s	–	1322	75.06	22.41	1298	16.46	25.50	1359	61.92	1.74	1319	61.80	1.42	νCN
A'	–	–	1359	9.11	211.15	1319	45.45	7.37	1398	21.48	150.10	1347	6.56	25.11	$\delta_s(CH_3)$
A'	1357 ms	1352 w	1381	20.27	37.95	1355	41.13	44.48	1412	3.46	15.66	1365	30.30	88.51	νCC
A'	1381 ms	1382 vs	1393	12.33	1.74	1356	11.84	13.28	1435	23.98	27.07	1394	33.98	35.23	δOH+ νCC
A'	1426 ms	1438 s	1435	48.86	27.93	1375	105.24	36.12	1468	51.69	20.30	1411	61.47	6.30	$\delta_a(CH_3)$
A'	1469 s	–	1450	27.56	48.53	1382	27.78	18.92	1484	39.04	89.69	1422	8.61	12.63	$\delta_a(CH_3)$
A"	–	–	1455	7.02	11.81	1432	7.83	174.01	1488	7.59	13.19	1424	12.93	145.73	νCC
A'	1506 s	1507 vw	1492	69.82	8.83	1459	70.27	7.00	1516	65.96	4.07	1466	74.12	5.49	νCC
A'	1570 s	1571 ms	1513	170.48	1.72	1485	136.06	4.69	1549	102.18	2.21	1499	116.28	2.40	νCC
A'	1599 ms	1596 w	1616	23.19	43.65	1559	71.36	11.36	1616	45.76	25.71	1568	52.23	22.27	νCN+ νCC
A'	1624 w	1624 w	1642	94.40	6.47	1580	35.98	35.15	1648	41.04	20.31	1596	40.74	23.37	νCC
A'	–	–	1665	7.92	6.85	1611	7.54	9.20	1676	2.95	7.75	1624	3.18	8.36	νCC
A'	–	–	2878	27.36	221.18	2872	8.24	394.93	3026	22.16	300.61	2926	18.74	312.42	$\nu_s(CH_3)$
A"	2918 w	2921 ms	2924	25.83	105.72	2935	3.84	137.76	3073	17.24	122.60	2938	12.80	120.23	$\nu_a(CH_3)$
A'	2954 w	–	2978	13.99	61.03	2983	2.70	69.37	3132	9.54	62.27	3035	7.46	62.28	$\nu_a(CH_3)$
A'	3002 w	3004 w	3018	3.78	21.63	2993	3.13	85.48	3163	5.16	49.55	3058	4.68	60.40	νCH

A'	–	3019 w	3021	2.34	90.21	3001	1.04	61.52	3167	1.45	81.58	3062	1.50	69.95	νCH
A'	–	–	3036	23.31	114.35	3012	6.06	193.68	3182	14.23	124.94	3076	11.14	138.18	νCH
A'	3027 w	3028 w	3041	23.27	150.29	3015	9.64	161.44	3183	27.02	202.45	3077	22.60	181.70	νCH
A'	3049 w	3058 s	3050	13.43	235.89	3029	1.19	247.90	3196	10.15	252.38	3090	7.48	242.14	νCH
A'	3272 br	–	3713	134.45	35.96	3150	178.01	61.88	3655	105.52	53.23	3489	116.52	53.95	νOH

[a]Scaling factor (s.f.): 0.9085, [b]s.f.: 0.9669, [c]s.f.: 0.9962, [d]s.f.: 0.9631, act.: activity, cal.: calculated, def.: deformation, int.: intensity, m.: medium, ob.: observed, spc.: species, s.: strong, ν:stretching, δ:in-plane bending, δ_s: symmetric bending, δ_a: asymmetric bending, ν_a: asymmetric stretching, ν_s: symmetric stretching, γ:out of plane, τ :torsion, w.: weak, v.: very.



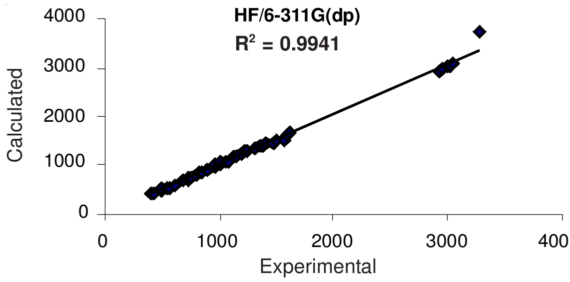
I: Column is infrared spectra II: Column is Raman spectra

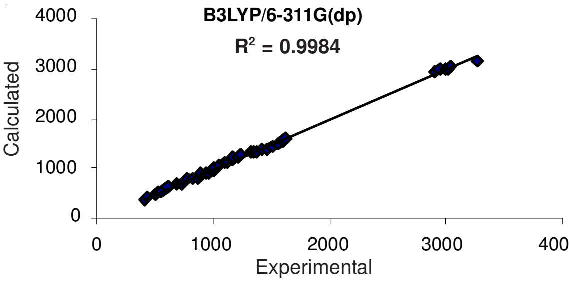
Fig. 5. Observed and calculated the spectra for 2-methyl-8-quinolinol molecule

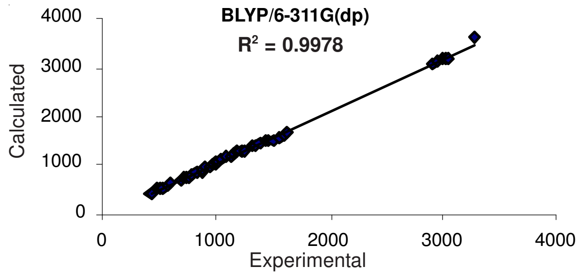
mainly coupled with the C-C in-plane bending vibrations. The CH_3 rocking and CH_3 wagging modes of 2-methyl-8-quinolinol are determined at 1002 and 981 cm^{-1} in infrared spectra. The 101 cm^{-1} strong band in Raman spectra is attributed CH_3 torsion mode. These assignments are substantiated by the reported literature[25].

Skeletal vibrations: The identification of vibrational modes in 1600-1300 cm^{-1} region is difficult task since the mixing of several bands are possible in this region. The C-C stretching bands appeared in the infrared spectrum are assigned at 1624, 1599, 1570, 1506, 1381, 1357, 1215 and 1185 cm^{-1} in the 2-methyl-8-quinolinol molecule under C_s symmetry. The 1599 and 1325 cm^{-1} bands are assigned to the ring CN stretching vibrations. The corresponding CC and CN stretching modes observed in the Raman spectrum are given in Table-1. The bands occurring at 910, 867, 747, 722, 572, 540 and 495 cm^{-1} in the infrared are assigned to be in-plane bending modes. The 795, 695, 509 and 421 cm^{-1} bands can be attributed the out-of-plane bending ring vibrations of 2-methyl-8-quinolinol. The results are in good agreement with the literature values[16,33-35]. The vibrational assignments of the fundamental modes are also supported by Gaussview molecular visualization program[20].

To make comparison with experimental, we present correlation graphics the frequencies for 2-methyl-8-quinolinol molecule in Fig. 6 based on the calculations. As can be seen from Fig. 6 experimental fundamentals are in better agreement with the scaled fundamentals and are found to have a good correlation for DFT/B3LYP than HF, DFT/BLYP and DFT/B3PW91 for 2-methyl-8-quinolinol molecule.







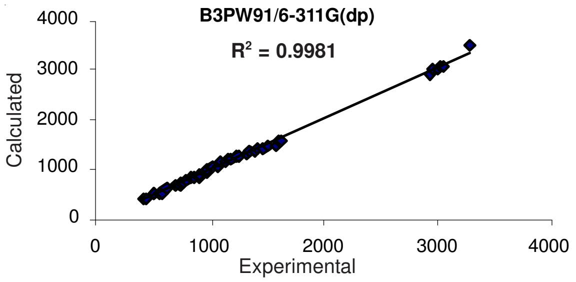


Fig. 6. Correlations graphics of frequencies for 2-methyl-8-quinolinol molecule

Conclusion

Infrared and Raman spectra have been obtained 2-methyl-8-quinolinol molecule. The molecular structural parameters and vibrational frequencies of the fundamental modes of the 2-methyl-8-quinolinol molecule have been obtained from quantum mechanical *ab initio* and DFT calculations. The geometry was optimized without any symmetry constraints using the HF and DFT(B3LYP, BLYP, B3PW91) method with 6-311G(dp) basis set. The theoretical results were compared with the experimental structure parameters and observed vibrational waven umbers. The bond length and bond angle parameters of 2-methyl-8-quinolinol molecule computed by DFT/BLYP and HF are in reasonable agreement with the experimental data, respectively. The infrared absorption and intensities computed by B3LYP method are agreement with experimental data. The results confirm the ability of the methodology applied for interpretation of the vibrational spectrum and geometric parameters of 2-methyl-8-quinolinol molecule in the solid state.

ACKNOWLEDGEMENTS

This work was supported by Kilis 7 Aralik University with BAP projects 2010/04 and 2010/02/08.

REFERENCES

1. R.E. Babry, In ed.: M.E. Wolf, Burger's Medicinal Chemistry, Part II, John Wiley, New York, pp. 41-81 (1979).
2. J.-H. Jeon, C.-H. Lee and H.-S. Lee , *J. Korean Soc. Appl. Biol. Chem.*, **52**, 202 (2009)
3. A.E. Martell and M. Calvin, Chemistry of Metal Chalete Compounds, Prentice Hall, Englewood Cliffs, Ch. 10 (1959).
4. (a) Z.J. Huang, X.G. Wang and J. Chang, *Asian J. Chem.*, **22**, 365 (2010); (b) B.S. Kumar, A. Abhilasha, W. Cyril and D. Sobhana, *Asian J. Chem.*, **23**, 889 (2011).
5. S. Mohan, N. Puviarasa and S. Bakkialakshmi, *Spectrochim. Acta A*, **55**, 2911 (1999).
6. J.R. Rodrigues, de NG. Bominguez and B. Plasmodium, *Exp. Parasitol*, **115**, 19 (2007).
7. F. Yousef, M.A. Mostafa, G. Shan and W.N. Seik, *Acta Cryst*., **E64**, 97 (2008).
8. S.L. Srivastava, M. Prasad and Rohitashava, *Spectrochim. Acta*, **40A**, 681 (1984).
9. K. Arici, M. Yurdakul and S. Yurdakul, *Spectrochim. Acta A*, **61**, 37 (2005).
10. V. Krishnakumar and R. Ramasany, *Spectrochim. Acta A*, **61**, 673 (2005).
11. K. Bahgat and A. Ganie Ragheb, *Central Eur. J. Chem.*, **5**, 201 (2007).
12. K. Arici and H. Köksal, *Asian J. Chem.*, **20**, 5653 (2008).
13. K. Arici and H. Köksal, *Asian J. Chem.*, **22**, 2898 (2010).
14. R.G. Charles, H. Freiser, R. Friedel, L.E. Hilliard and D. William, *Spectrochhim. Acta*, **8**, 1 (1965).

15. R. Zvaans and C. Thomson, *J. Mol. Struct.:Theochem.*, **362**, 51 (1996).
16. V. Arjunan, I. Saravanan, P. Ravindran and S. Mohan, *Spectrochhim. Acta*, **74**, 375 (2009).
17. V. Krishnakumar and R. John Xavier, *Chem. Phys.*, **312**, 227 (2005).
18. S.H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, **58**, 1200 (1980).
19. K.K. Irikura, D.R. Johnson III and N.R. Kacker, *J. Phys. Chem. A*, **109**, 8435 (2005).
20. A. Frisch, A.B. Nielsen and A.J. Holder, Gaussview Users Manuel, Gaussian Inc., Pittsburg (2003).
21. Gaussian 09, Revision A.1, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N.J. Millam, M. Klene, J.E. Knox, 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, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, Gaussian, Inc., Wallingford CT (2009).
22. M. Kurt and S. Yurdakul, *J. Mol. Struct. (Theochem.)*, **730**, 59 (2005).
23. M. Kurt and S. Yurdakul, *J. Mol. Struct. (Theochem.)*, **804**, 75 (2007).
24. V. Arjunan, S. Mohan, P. Ravindran and C.V. Mythill, *Spectrochim. Acta A*, **72**, 783 (2009).
25. E. Aysen Özel, K. Serda and A. Sevim, *Vibrational Spectrosc.*, **42**, 325 (2006).
26. T. Dzimbowska, M. Szafran, E. Jagodzinska, I. Natkaniec, A. Pawlukoje, J.S. Kwiatkowski and J. Baran, *Spectrochim. Acta A*, **59**, 2175 (2003).
27. Y. Wang, S. Saebar and C.U. Pittman Jr., *J. Mol. Struct.: Theochem.*, **28**, 91 (1993).
28. N.S. Sundra, *Spectrochim. Acta*, **42A**, 1449 (1985).
29. E.T.G. Lutz and J.H. Van der Mass, *Spectrochim. Acta*, **42A**, 755 (1986).
30. R.M. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric Identification of Organic Compounds, John Wiley & Sons. Inc., New York (1981).
31. A. Ragheb, A. Shalabi and E. Sawi, *J Serb. Chem. Soc.*, **52**, 679 (1987).
32. D.N. Sathyanarayana, Vibrational Spectroscopy-Theory and Applications, New Age International (P) Limited Publishers, New Delhi edn. 2 (2004).
33. A. Altun, K. Gölcük and M. Kumru, *J. Mol. Struct. (Theochem.)*, **637**, 155 (2003).
34. N. Puviarasan, V. Arjunan and S. Mohan, *Turk. J. Chem.*, **28**, 53 (2004).
35. V. Arjunan, S. Mohan, S. Subramanian and B.T. Gowda, *Spectrochim. Acta*, **60A**, 1141 (2004).