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Hartree-Fock and Density Functional Studies on Vibrational Frequencies of 6-Hydroxyquinoline

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The vibrational frequency of 6-hydroxyquinoline in the ground state have been calculated by using Hartree-Fock and density functional methods (B3LYP, BLYP and B3PW91) with 6-31G** as the basis set. Comparison of observed fundamental vibrational frequencies of 6-hydroxyquinoline and calculated results by Hartree-Fock and density functional methods indicates that these methods give good results for molecular vibrational problems. Hartree-Fock method calculated vibrational frequencies of the lowest energy conformer are in good agreement with those observed experimentally.

Key Words: Hartree-Fock, Density, Vibrational frequencies, 6-Hydroxyquinoline.

INTRODUCTION

Quinoline and derivatives are great interest in pharmacy and some of them are used as antimalarial drug[1]. They are functional constituents of several biochemical systems or they act as defensive compound and are dyes[2]. Ochao *et al.*[3] have reported the absorption and emission spectra of 6-hydroxyquinoline in ethylene glycol and glycerol. Bech *et al.*[4] have reported the combined experimental (supersonic jet) and *ab initio* theoretical study of hydrogen bonded 6-hydroxyquinoline:water complex. Excited-state intra- and intramolecular proton transfer reactions have received considerable attention both experimentally and theoretically[5-9]. Mehata *et al.*[10,11] have also recorded the absorption, fluoresence and excitation spectra on the excited-state proton transfer reaction of 6-hydroxyquinoline in methanol and methanol containing water solution. To the best of our knowledge, no normal mode analysis and IR spectra have been reported in literature on 6-hydroxyquinoline yet. And as far as we know, there are no complete theoretical results of 6-hydroxyquinoline.

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In this study, by using HF and DFT (B3LYP and B3PW91) methods, the vibrational frequencies of 6-hydroxyquinoline were calculated in ground state to distinguish the fundamentals from the many experimental vibrational frequencies. These calculations are valuable for providing insight into the vibration spectrum.

EXPERIMENTAL

6-Hydroxyquinoline was obtained from Aldrich Chemical Co. Infrared spectra of 6-hydroxyquinoline was recorded between 4000-400 cm^{-1} on Perkin-Elmer1330 and Mattson 1000 FTIR spectrometers which were calibrated using polystyrene bands. The resolution of IR spectrometers is 0.2 cm^{-1} and the number of scan is 20. The sample was prepared as a KBr disc.

Calculations: The computations were performed using the Gaussian03 program package[12] and also Gauss-View molecular visualization program[13] was used on the personal computer. The full vibtarional frequency calculations were performed at HF and DFT (B3LYP and B3PW91) methods and with 6-31G** basis set. Then scaled by 0.8929, 0.9613 and 0.9970, respectively. The assignment of the experimentals frequencies are based on the observed bond frequencies and intensity changes in the infrared spectra and confirmed by establishing one to one correlation between observed and theoretically calculated frequencies.

RESULTS AND DISCUSSION

The molecular structure and infrared spectrum of 6-hydroxyquinoline are given in Figs. 1 and 2, respectively.

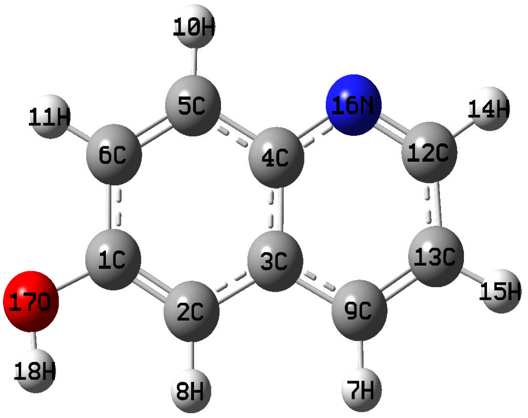


Fig. 1. 6-Hydroxyquinoline structure and atom numbering

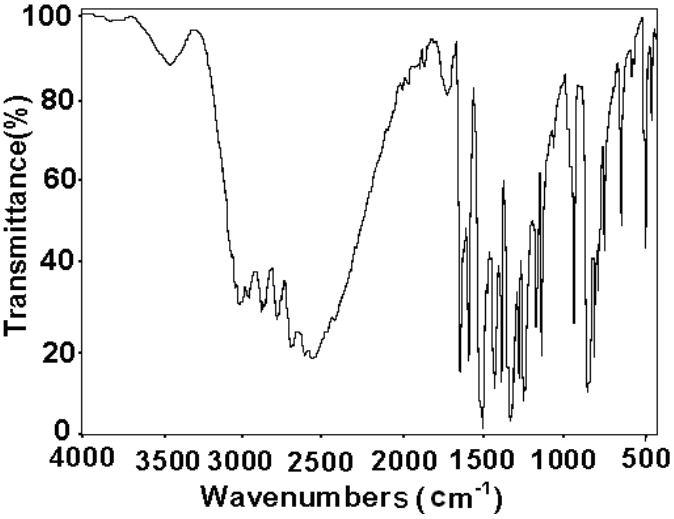


Fig.2. IR spectrum of 6-hydroxyquinoline (in KBr)

The substitution of the -OH group at position six in quinoline does not destroy the plane of symmetry if one ignores the hydrogen atom. Consequently, the C_s point group can be ascribed to this molecule. Excluding the vibrations pertaining to the -OH group, there will be in all 42 modes of vibrations which are disdributed in the a' and a'' symmetry species[14]. The fundamentals vibrations of a' and a'' were attributed to the plane-in and plane-out modes, respectively. All vibrations are both infrared and Raman active.

As one can see in Fig. 2, experimental description of fundamentals vibration in the region above 2000 cm^{-1} is not straight forward:one problems is the weakness of the -CH streching and appearing of the overtones in this region. The broadness of -OH streching is characteristic.

As seen in Table-1, the broad band at 3475 cm^{-1} has been attributed to ν(OH) streching vibration. This band is assigned by Thube *et al.*[15] 3280 cm^{-1} (strong), Rostkowska *et al.*[16] 3419 cm^{-1} (strong) in Ar matrix and Thube *et al.*[17] 3125 cm^{-1} (broad). Srivastava *et al.*[14] and Arici *et al.*[18] did not observed this band. The fundamental vibration at 3475 cm^{-1} is correlated with the calculated values of 3743 (HF), 3672 (B3LYP) and 3842 (B3PW91), respectively. Infrared intensities of this band are middle strong computering with the other fundamentals. The observed experimental values of vibration at 3475 cm^{-1} show great deviation in the HF, B3LYP and B3PW91 calculations.

The spectra in the 3050-2500 cm^{-1} region show six broad bands at 3018, 2963, 2875, 2782, 2694 and 2569 cm^{-1} which are assigned solely to ν(CH) stretching vibrations. The bands at 2963 and 3018 cm^{-1} in the spectra are assigned[14] by at 2992 and 3007 cm^{-1}, respectively, to be ν(CH) streching bands. The theoretical intensities of the 2963 and 3018 cm^{-1} bands are very low while the experimental intensities of these bands are high.

Nine strong and sharp bands at 1637, 1607, 1580,1501, 1460, 1432, 1376, 1340 and 1320 cm^{-1} have been observed in the 1700-1200 cm^{-1} region. The former eight bands are assigned to ν(CC) + δ(CH) + δ(OH) vibrational bands. The 1340 and 1320 cm^{-1} bands are assigned to ν(CC) + δ(CH) and ν(CC) + ν(CN) + δ(CH), respectively. The 1501 cm^{-1} band is assigned[14] by 1500 cm^{-1} to ring streching[15] 1500 cm^{-1} to ν(CC) + δ(CH) + ν(CN) and 1508 cm^{-1} to νring + δ(CH) + δ(OH)[18]. The 1320 cm^{-1} band is assigned[14] by 1327 cm^{-1} to ring streching[15]. While infrared intensities from experimental fundamentals at 1501 and 1320 cm^{-1} are very strong, the calculated at HF, B3LYP and B3PW91 intensities of these bands are not in the same order.

As seen in Table-1, the 1267 between 1047 cm^{-1} bands are assigned solely to δ(CH) + δ(OH) but the 1125 cm^{-1} belong to δ(CH) band is except. The very strong band at 1239 cm^{-1} is assigned[14] by 1220 cm^{-1} to δ(CH) and at1245 cm^{-1} to δ(CCH)[15]. Among calculated frequencies, the biggest difference for 1125 cm^{-1} between experimental and calculated frequencies is 68 cm^{-1} for B3PW91. Experimental fundamental at 125 cm^{-1} is very strong, theoretical intensities of this fundamental is not in the same order except HF. The calculted value of the 1158 cm^{-1} band both spectra and intensities are agreement with experimental.

The strong band at 729 cm^{-1} is assigned to ν(C-OH) + ring def. This band have been observed[14] by at 710 cm^{-1} assigned to skeletal in-plane bending, at 727 cm^{-1} to CCC bending[15] and at 708 cm^{-1} to δ(CH) + ring breat. + ν(ring) to be assigned[18].

It is shown in the Table-1, while experimental value is strong for 835 cm^{-1} mode, calculated intensities of B3LYP and B3PW91 (except HF) for this band deviate very much from experimental values.

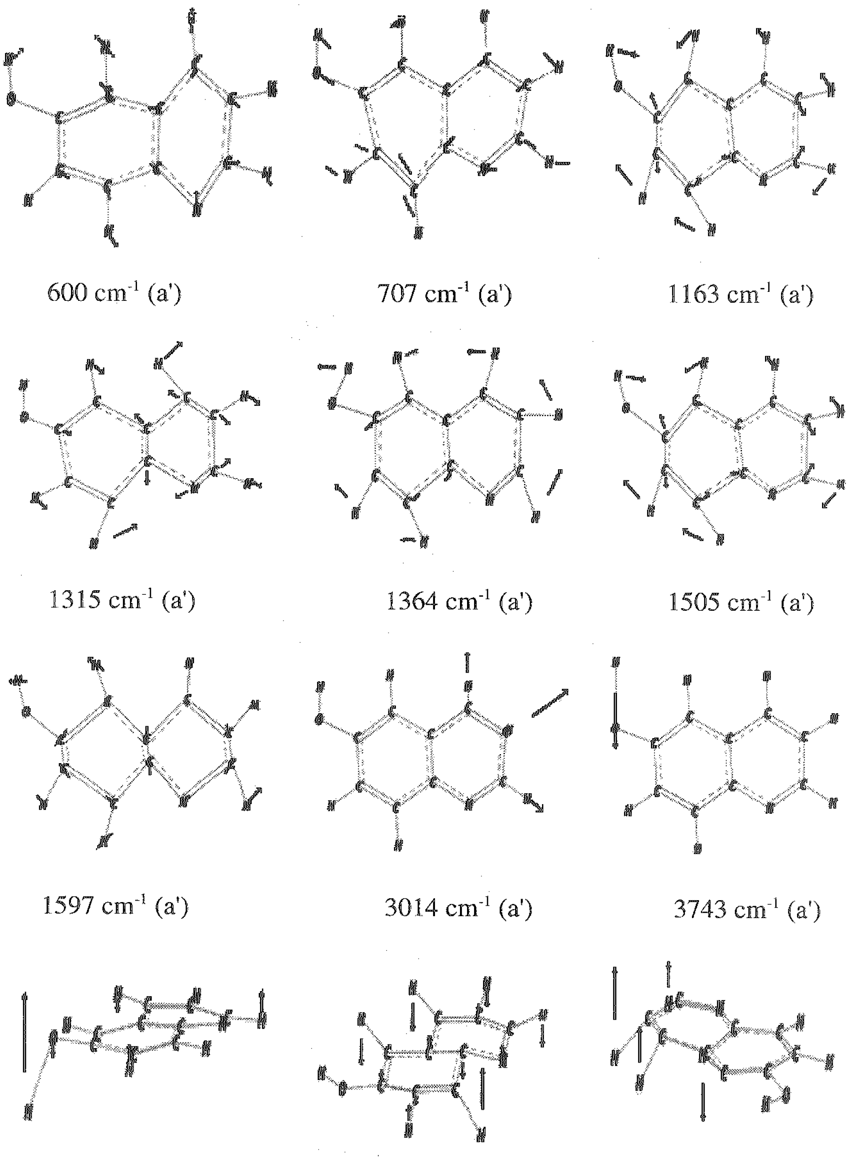
In present observations, infrared intensities are high according to our calculations and nearly the same as those 8-hydroxyquinoline[14]. Among the calculated fundamental the best value betveen experimental and calculated intensities are in low frequency region. The theoretical and experimental low intensities may lead to the wrong identification in the assignment fundamentals[19] or *vice-versa*, especially in the lowest frequency region. As known previously, because of reasons, such as anharmonic effect, vibrational intensitiy could not be estimated very accuratly using quantum chemistry software till now.

TABLE-1
COMPARISON OF THE OBSERVED AND CALCULATED VIBRATIONAL SPECTRA OF 6-HYDROXYQUINOLINE

Sym.	HF 6-31G**		DFT B3LYP 6-31G**		DFT B3PW91 6-31G**		Exp.[d]	Present Exp.	Approx mod.[e]
	Freq.[a]	$I_{int.}$	Freq.[b]	$I_{int.}$	Freq.[c]	$I_{int.}$			
a’	288	0.82	290	0.93	302	0.97		–	δ(C-OH)+δ Ring
a’	416	7.24	416	6.71	430	7.67		–	Ring str.
a’	447	18.99	450	13.81	466	13.14		433 w	Ring Def.
a’	525	5.33	528	3.96	547	4.18	488	481 m	Ring str.
a’	600	12.85	606	7.55	625	7.37	–	–	Ring str.
a’	707	7.85	714	8.89	742	8.48	710	729 s	ν(C-OH)+Ring Def.
a’	753	1.49	753	1.46	786	1.15	740	761 s	Ring str.
a’	886	6.93	891	6.55	924	5.92	–	874 sh	δ(OH)+Ring Def.
a’	934	1.34	939	1.71	975	1.78	–	945 m	δ(OH)+Ring Def.
a’	980	22.05	1018	2.44	1062	1.82	1027	1009 sh	δ(CH)+ν(CC)
a’	1068	39.62	1096	20.77	1136	18.54	1066	1047 w	δ(CH)+δ(OH)
a’	1110	2.16	1117	8.59	1157	5.59	1100	1083 sh	δ(CH)+δ(OH)
a’	1125	0.74	1149	96.92	1193	108.21	–	1125 s	δ(CH)
a’	1163	141.31	1162	154.74	1211	137.72	1148	1158 s	δ(CH)+δ(OH)
a’	1206	11.56	1218	9.99	1265	20.12	1167	1180 m	δ(CH)+δ(OH)
a’	1219	15.23	1226	15.25	1275	10.75	1220	1239 vs	δ(CH)+δ(OH)
a’	1253	0.73	1270	8.82	1327	17.38	1267	1267 s	δ(CH)+δ(OH)
a’	1315	6.23	1330	19.96	1394	28.37	1327	1320 vs	ν(CC)+δ(CH)+ ν(CN)
a’	1341	72.51	1347	11.47	1402	4.45	–	1340 s	ν(CC)+δ(CH)
a’	1364	52.74	1373	4994	1431	41.70	1375	1376 s	ν(CC)+δ(CH)+δ(OH)
a’	1432	0.42	1427	0.05	1488	0.63	1427	1432 s	ν(CC)+δ(CH)+δ(OH)
a’	1464	34.99	1457	40.54	1517	47.26	1467	1460 s	ν(CC)+δ(CH)+δ(OH)
a’	1505	78.21	1502	48.52	1567	56.17	1500	1501 vs	ν(CC)+δ(CH)+δ(OH)
a’	1597	7.34	1559	3.39	1630	3.35	1560	1580 s	ν(CC)+δ(CH)+δ(OH)
a’	1623	76.88	1590	27.99	1660	34.48	1613	1607 s	ν(CC)+δ(CH)+δ(OH)
a’	1645	76.58	1616	101.52	1690	102.09	1633	1637 s	ν(CC)+δ(CH)+δ(OH)
a’	2972	21.06	3034	32.01	3157	28.92	–	2569 s	ν(CH)
a’	2976	21.93	3038	14.25	3163	15.77	–	2694 s	ν(CH)
a’	2988	20.85	3056	13.08	3181	11.00	–	2782 s	ν(CH)
a’	3010	1.79	3082	1.71	3208	1.07	–	2875 s	ν(CH)
a’	3014	25.13	3083	21.59	3210	18.98	2992	2963 s	ν(CH)
a’	3027	8.89	3097	6.61	3223	5.15	3007	3018 s	ν(CH)
a’	3743	85.89	3672	48.90	3842	56.99	–	3475 br	ν(OH)
a’’	124	0.22	122	0.12	125	0.18	–	–	Butterfly
a’’	176	1.09	171	0.85	176	1.01	–	–	Ring Tors.
a’’	295	34.14	295	0.41	305	0.32	–	–	γ(OH)+Ring Tors.
a’’	322	115.12	367	124.05	387	127.10	–	–	γ(OH)+Ring Tors.
a’’	403	1.22	400	0.07	413	0.04	–	405 vw	γ(CCH)
a’’	477	4.99	468	2.65	482	4.02	460	470 m	γ(CCH)
a’’	541	0.35	534	0.37	552	0.33	–	544 vw	γ(CCH)
a’’	639	0.81	628	0.11	652	0.05	–	623 m	γ(CCH)
a’’	762	3.41	748	1.76	775	1.92	782	772 s	γ(CCH)
a’’	792	5.43	766	1.00	792	1.45	804	792 s	γ(CH)
a’’	843	5.04	815	45.09	844	46.08	820	822 s	γ(CH)
a’’	849	107.17	823	28.31	852	39.64	–	835 s	γ(CH)
a’’	963	0.15	921	0.06	954	0.04	900	921 s	γ(CH)
a’’	989	0.07	944	0.08	978	0.15	–	964 w	γ(CH)
a’’	999	1.00	954	1.44	989	1.68	980	983 vw	γ(CH)

Vibrational frequencies (in cm^{-1}), I_{inf} = infrared intensities, [a]Scaling factor = 0.8929, [b]Scaling factor = 0.9613, [c]Scaling factor = 0.9970, [d]Ref. 14, [e] Our vibrational frequency assignment on the HF calculations, str: strecthing, def: deformation, tor: torsion.

The some sensitive modes characterized at HF/6-31G** level in 6-hydroxyquinoline molecule are plotted in Fig. 3. The vibrational motions are represented by the vector corresponding to the atomic displacement for each atom and computed wavenumbers. Displacements are indicated by dark arrow.



600 cm^{-1} (a') 707 cm^{-1} (a') 1163 cm^{-1} (a')

1315 cm^{-1} (a') 1364 cm^{-1} (a') 1505 cm^{-1} (a')

1597 cm^{-1} (a') 3014 cm^{-1} (a') 3743 cm^{-1} (a')

322 cm^{-1} (a'') 762 cm^{-1} (a'') 792 cm^{-1} (a'')

Fig. 3. Some sensitive a' and a'' vibrational modes for 6-hydroxyquinoline calculated at the HF/6-31G**

To make comparison with current experimental, the correlation graphics in Fig. 4 based on the calculations are presented. As can be observed from the correlation graphics in Fig. 4, experimental fundamentals are in better agreement with the scaled fundamentals and are found to have a good correlation for HF than B3LYP and B3PW91. Serious disagreement is, however, observed between the peak position of experimental frequencies and B3PW91 values. These are assigned to the ν(CH) vibrational modes.

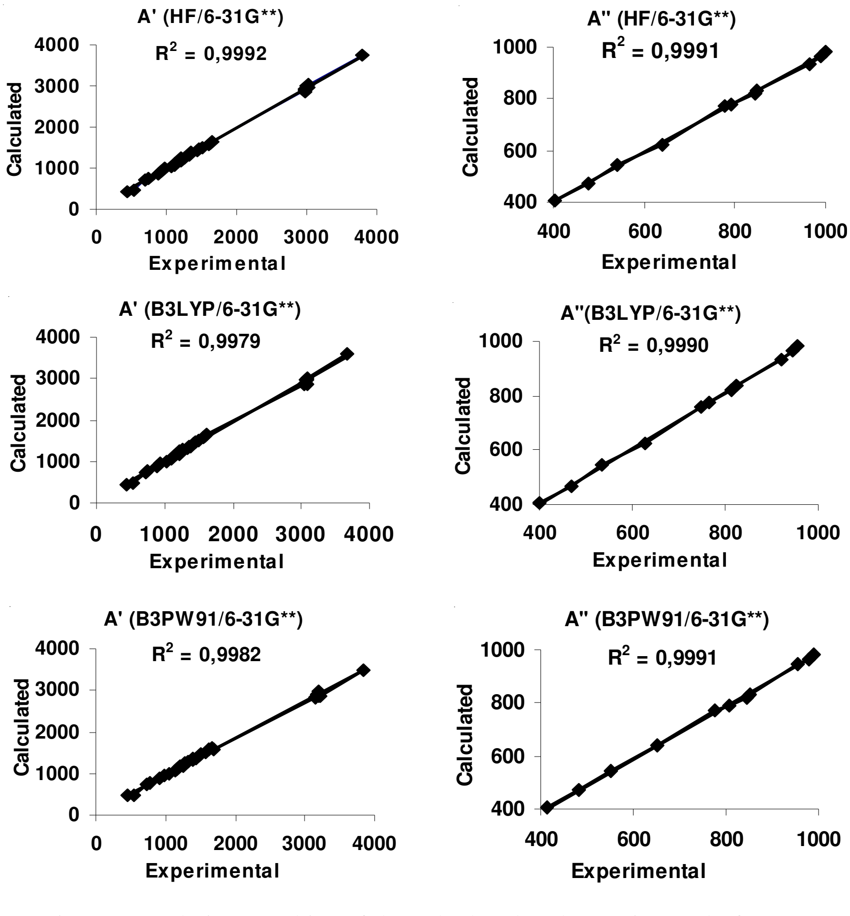


Fig. 4. Correlation graphics of the calculated and experimental of 6-hydroxyquinoline

Conclusion

Comparison of the observed fundamental vibrational frequencies of 6-hydroxyquinoline and the results calculated by Hartree-Fock and density functional B3LYP, B3PW91 methods indicates that the scaled HF is superior than B3LYP and B3PW91 for this molecule vibrational problems. On the basis of the calculated results, assignment of the fundamental vibrational frequencies given by Srivastava *et al.*[14] have been examined and some new vibrational modes are proposed. In this study, there is a good agreement between experimental and HF/6-31G** calculated values. This result indicate that the Hartree-Fock method is reliable and provides valuable information for understanding the vibrational spectra of 6-hydroxyquinoline molecule.

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