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Molecular Structure and IR Vibrational Analysis of 3-Acetamidophenol Using Hartree-Fock and Density Functional Theory Calculations

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The molecular structure and infrared vibrational spectra of 3-Acetamidophenol molecule in the solid phase was download from the references 1 and 2. The molecular structure of 3-acetamidophenol in the ground state (in vacuum) are optimized by Hartree-Fock (HF) and density functional theory (DFT) (BLYP and B3LYP with the 6-311G(dp) basis set. All the calculated vibrational frequencies are scaled by 0,9085 for HF/6-311G(dp) and 0,9669 for BLYP/6-311G(dp). Molecular geometry is not restricted and all the calculations are performed by using Gauss view molecular visualization program and GAUSSIAN09 program package on the personal computer. The calculated frequencies has been scaled which have been compared with experimental infrared 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.

Keywords: 3-Acetamidophenol, Hartree-Fock, Density functional theory.

INTRODUCTION

In organic chemistry, phenol is very important and many valuable product which is wide spread use in industry[3,4]. Phenols have highly toxic and aromatic flavor which have already been black-listed as priority control pollutants by Environmental Protection Agency (EPA) by most of the countries[5]. Due to the binding of phenolic hydroxyl group, phenol derivatives are weak acids and can be easily oxidized in the environment[6,7]. 4-Acetamidophenol is capable of causing methemoglobinemia and widely used as analgesic drug[8,9]. 3-Acetamidophenol is a non-hepatotoxic regioisomer[10]. Infrared spectra and structures of *p*-chlorophenol and *p*-bromophenol molecules were studied both theoretically and experimentally[11]. Theoretical calculations of the thermo-chemical reactions of phenol molecules was calculated using density functional theory[12]. Rotational isomers and (FT-IR, FT-Raman) of 2,4,6-*tris*(dimethylaminomethyl)phenol molecule were calculated using quantum chemical calculations[13]. Bardakçi[14] studied vibrational frequencies of monochlorophenols and effects of symmetry. Infrared and Raman spectra of 4-hydroxy-3-methylacetophenone, 4-hydroxy-3-methoxyacetophenone and 2,4-dichloro-6-nitrophenol molecules were studied both theoretically density functional theory and experimentally[15,16]. A complete vibrational assignment of phenol and phenol-OD has been given by Green[17].

Although 3-acetamidophenol molecule has been studied by IR spectroscopy, the band assignments, Hartree-Fock (HF) and density functional theory theoretical calculations are not available in literature. Therefore, the present investigation was undertaken to study the vibrational spectra of the molecule completely and to identify the various normal modes with greater wave numbers accurately. *ab initio* Hartree-Fock (HF) and density functional theory (DFT) calculations have been performed to support our wave number assignments.

EXPERIMENTAL

The infrared vibrational spectra of 3-acetamidophenol in the solid phase is shown in Fig. 1.

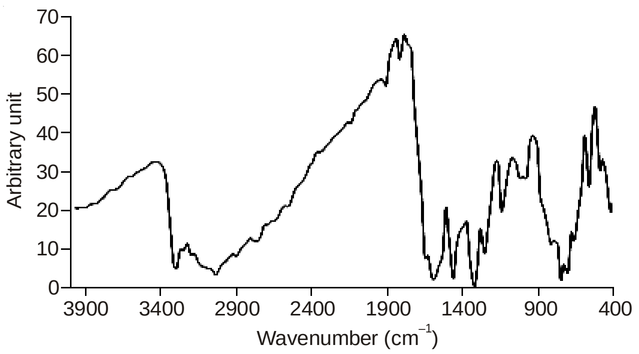


Fig. 1. IR spectra of 3-acetamidophenol molecule [Refs. 1 and 2]

Computational details: The molecular structure of 3-acetamidophenol in the ground state is optimized by Hartree-Fock (HF) and DFT/B3LYP with the 6-311G(dp) basis set. The optimized structural parameters were used in the vibrational frequency calculations at Hartree-Fock (HF) and density functional theory levels.

Density functional theory for all studies reported in this paper has the following from

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

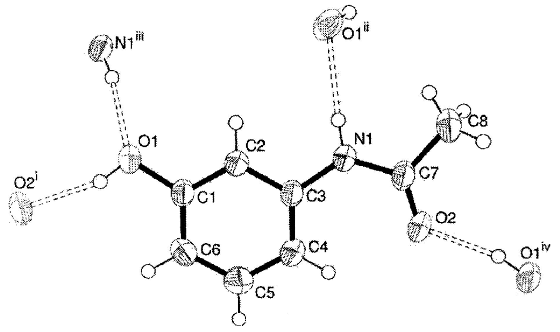
where, the energy terms are the Slater exchange, the Hartree-Fock exchange, Becke's exchange functional correlation, the gradient correlated correlation functional of Lee, Yang and Parr and the local correlation functional of Vosko, Wilk and Nusair[18]. HF/6-311G(dp) and DFT/B3LYP/6-311G(dp) levels of theory with the optimized geometries have been used to calculate infrared vibrations of the 3-acetamidophenol molecule.

All the calculated vibrational frequencies are scaled by 0,9085 for HF/6-311G(dp) and 0,9669 for BLYP/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].

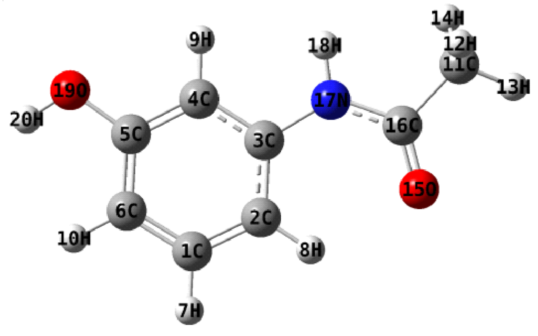
RESULTS AND DISCUSSION

Molecule of 3-acetamidophenol consist of 20 atoms: The 54 normal vibrational modes of 3-acetamidophenol, which span in the irreducible representation as 54 A under the C_1 point group symmetry, have been assigned according to the detailed motion of the individual atoms. All vibrations are active in IR spectra and assigned in terms of fundamental bands.

Molecular structure and numbering of atoms of 3-acetamidophenol is shown in Fig. 2.



(a) Experimental in solid phase [Ref. 22]



(b) Calculated in gas phase

Fig. 2. Structure of 3-acetamidophenol

Geometrical structure: The optimized bond lengths and angles for 3-acetamidophenol at HF/6-311G(dp) and DFT/B3LYP(6-311G(dp) levels are represented in Table-1 along with available experimental crystal data[22].

As discussed previously[23] and their work[24,25], it is well known that HF methods underestimate for bond lengths. DFT/B3LYP methods predict bond lengths which are systematically long, particularly C-H bond lengths. For example, C-H bond lengths values in the experiment are 0.93 and 0.96 Å but the values in the theoretical result are bigger than 1 Å. Since large deviation from experimental C-H bond lengths may arise from the low scattering factors of hydrogen atoms in the X-ray diffractions experimental we have not discussed the C-H bond lengths in the ring. As shown in Fig. 2a, 3-acetamidophenol molecule with other molecules has been linked with O-H…O and N-H…O bonds. Thus, the calculated O15-C16, N17-H18 and O19-H20 bond lengths are quite different from the experimental values (Table-1). The reason for this is theoretical calculations belong to isolated in gaseous phase and the experimental results belong to molecules in solid state. In the experimental data the C5-O19 bond length is 1,367Å which is calculated at the 6-311G(dp) level to be 1,3491 Å (HF) and 1,3670 Å (DFT). The experimental bond length value is equal to theoretical value by using DFT/B3LYP/6-311G(dp) level. This C5-O19 bond length was calculated as 1.370 Å at B3LYP/6-31++G(d,p) for paracetamol molecule[26], 1.3696 Å at DFT/B3LYP level for paracetamol[27] and 1.364 Å DFT/B3PW91/6-31G(d) for N(4-hydroxyphenyl)-acetamide molecule [28]. Table-1 showed that the experimental bond length of C3-N17 is 1.417 Å and is longer than the theoretical calculations. The calculated C3-N17 bond length ranges from 1.4052 Å to 1.4106 Å for all methods which are found to be almost the same with X-ray data. The corresponding bond length was calculated as 1.397 Å at B3LYP/6-31++G(d,p) for paracetamol molecule[26], 1.4253 Å at DFT/B3LYP level for paracetamol[27] 1.409 Å DFT/B3PW91/6-31G(d) for N(4-hydroxy-phenyl)acetamide molecule[28].

The C16-N17 bond length is 1.346 Å in the experimental data. This bond length have been calculated at the 6-311G(dp) level to be 1.3673 Å (HF) and 1.3785 Å (DFT). These calculated the C16-17N bond length which is larger about 0.026 Ao up from the experimental value. This C16-N17 bond length was calculated as 1.397 Å at B3LYP/6-31++G(d,p) for paracetamol molecule[26], 1.3792 Å at DFT/B3LYP level for paracetamol[27] and 1.372Å DFT/ B3PW91/6-31G(d) for N(4-hydroxyphenyl)acetamide molecule[28].

The C16-C11 bond length is 1.499 Å in the experimental data. This bond length have been calculated at the 6-311G(dp) level to be 1.5145 Å (HF) and 1.5217 Å (DFT). This C16-C11 bond length was calculated as 1.5173 Å at DFT/B3LYP level for paracetamol[27] and 1.519 Å DFT/B3PW91/6-31G(d) for N(4-hydroxyphenyl)acetamide[28]. The optimized bond length of C-C in phenol ring of phenol fall in the range: 1.3824-1.3925 Å at HF/6-311G(d,p) and 1.3911-1.4021 Å at B3LYP/6-311G(d,p) methods which are almost the same with the experimental data. The experimental C3-C4 bond length is equal to theoretical value with HF6-311G(dp) level. As seen from Table-1, the calculated C-C-C bond angles at the phenol ring are in good agreement with the crystal data of 3-aceta-

TABLE-1
GEOMETRIC PARAMETERS BOND LENGTHS (Å) AND BOND ANGLES (°) OPTIMIZED FOR 3-ACETAMIDOPHENOL

	Bond lengths (Å)	Calculation HF 6-311G(dp)	Calculation DFT/B3LYP 6-311G(dp)	Experimental X-Ray [Ref. 22]
R1	C1-C2	1.3824	1.3911	1.386
R2	C1-C6	1.3833	1.3918	1.377
R3	C1-H7	1.0756	1.0842	0.930
R4	C2-C3	1.3925	1.4021	1.388
R5	C2-H8	1.0675	1.0777	0.930
R6	C3-C4	1.3890	1.3994	1.389
R7	C3-N17	1.4052	1.4106	1.417
R8	C4-C5	1.3824	1.3915	1.375
R9	C4-H9	1.0754	1.0847	0.930
R10	C5-C6	1.3851	1.3960	1.390
R11	C5-O19	1.3491	1.3670	1.367
R12	C6-H10	1.0764	1.0856	0.930
R13	C11-H12	1.0862	1.0918	0.960
R14	C11-H13	1.0798	1.0917	0.960
R15	C11-H14	1.0850	1.0920	0.960
R16	C11-C16	1.5145	1.5217	1.499
R17	O15-C16	1.1904	1.2155	1.228
R18	C16-N17	1.3673	1.3785	1.346
R19	N17-H18	0.9924	1.0079	0.860
R20	O19-H20	0.9404	0.9625	0.820
		Bond angle (°)		
A1	C2-C1-C6	122.2390	121.9107	122.00
A2	C2-C1-H7	118.6854	118.8722	119.00
A3	C6-C1-H7	119.0757	119.2121	119.00
A4	C1-C2-C3	118.4741	118.6643	118.76
A5	C1-C2-H8	120.9913	121.5615	120.60
A6	C3-C2-H8	120.5346	119.7741	120.60
A7	C2-C3-C4	119.9714	119.9945	119.56
A8	C2-C3-N17	123.6347	123.2549	124.70
A9	C4-C3-N17	116.3938	116.7506	115.74
A10	C3-C4-C5	120.3721	120.3158	120.90
A11	C3-C4-H9	121.1899	121.2478	119.50
A12	C5-C4- H9	118.4380	118.4371	119.60
A13	C4-C5-C6	120.3498	120.1857	120.05
A14	C4-C5-O19	117.0738	116.9920	116.60
A15	C6-C5-O19	122.5763	122.8223	123.40
A16	C1-C6-C5	118.5935	118.9291	118.70
A17	C1-C6-H10	120.7979	120.7263	120.70
A18	C5-C6-H10	120.6086	120.3446	120.70
A19	H12-C11-H13	108.9385	107.4037	109.50
A20	H12-C11-H14	108.3601	108.9973	109.50
A21	H12-C11-C16	109.2828	108.3773	109.50
A22	H13-C11-H14	109.7379	109.0029	109.50
A23	H13-C11-C16	108.5988	108.3470	109.50
A24	H14-C11-C16	111.8793	114.4597	116.50
A25	C11-C16-O15	121.9896	121.3778	121.76
A26	C11-C16-N17	113.4515	114.2852	114.90
A27	O15-C16-N17	124.4599	124.3370	123.40
A28	C3-N17-C16	129.3122	129.1383	129.27
A29	C3-N17-H18	114.7389	114.7870	115.40
A30	C16-N17-H18	115.9352	116.0747	115.40
A31	C5-O19-H20	110.5298	109.0199	109.50

midophenol. With the electron donating substituent on the phenol ring, the symmetry of the ring is distorted. As a result, ring angles smaller than 120° at the point of substitution. The O15-C16-N17 bond angle have been calculated at the 6-311G(dp) level to be 124.4599° (HF) and 124.3370° (DFT). This bond angle is 123.40° in the experimental data which is shorter about 1° from the calculated values. Danten *et al.*[28] have calculated 124.2° DFT/ B3PW91/6-31G(d) for N(4-hydroxyphenyl)acetamide. From Table-1, calculated C11-C16-N17 bond angle at HF6-311G(dp) level is seen to be smaller than both the DFT/B3LYP6-311G(dp) level and experimental values. The C11-C16-N17 bond angle is calculated by Danten *et al.*[28] to be 121.3° at the DFT/ B3PW-91/6-31G(d) for N(4-hydroxyphenyl)acetamide molecule.

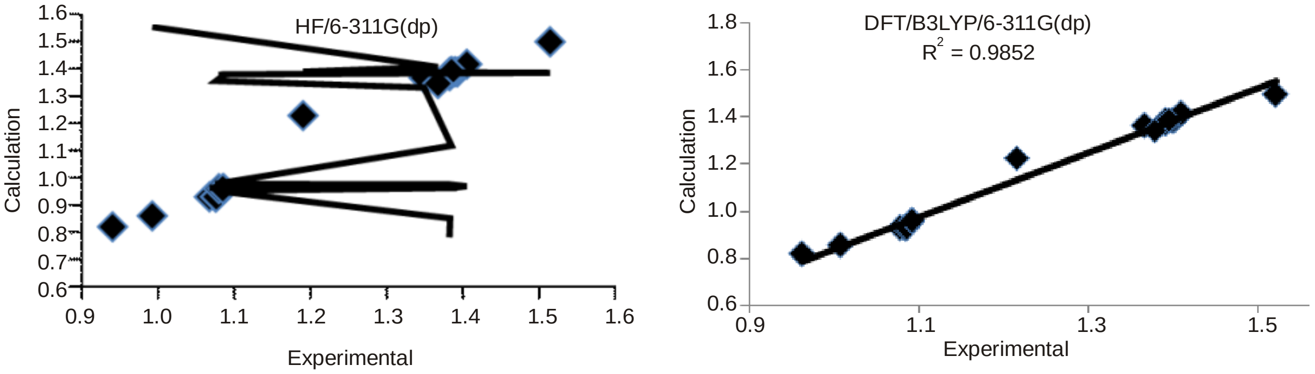


Fig. 3. Correlations graphics of bond lengths for 3-acetamidophenol molecule

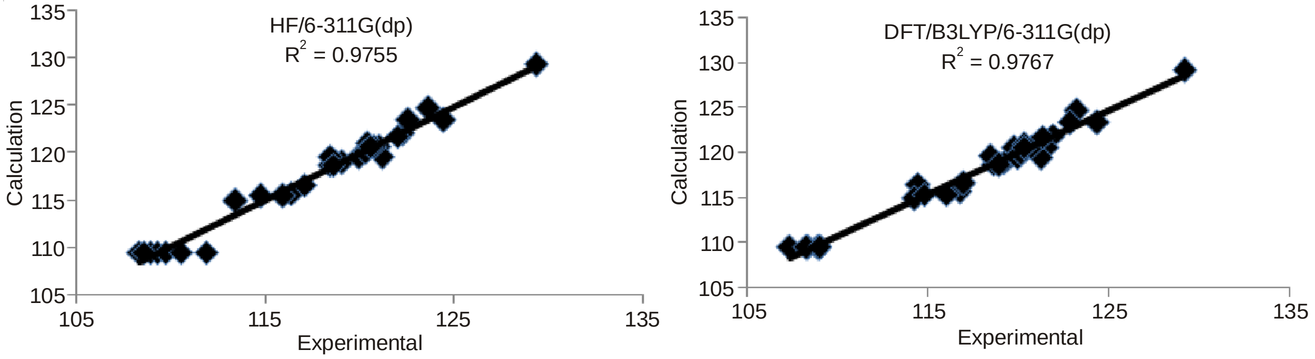


Fig. 4. Correlations graphics of bond angle for 3-acetamidophenol

To make comparison, the correlations graphics between the experimental and calculated bond lengths and bond angle obtained by the HF and DFT methods are shown in Figs. 3 and 4, respectively. As can be seen from Fig. 3 and 4, experimental bond lengths and bond angle are in better agreement with the calculated bond lengths and bond angle and are found to have a good correlation for DFT/B3LYP than HF method for 3-acetamidophenol.

Vibrational assignments: The observed and calculated frequencies using HF/6-311G(dp) and DFT/B3LYP/6-311G(dp) along with their relative intensities, probable assignments are given in Table-2.

O-H Vibrations: The O-H stretching vibrations are sensitive to hydrogen bonding. The non-hydrogen bonded or free hydroxyl group as absorbed strongly and sharp in 3670-3580 cm^{-1}. For solids, liquids and concentrated solutions a broad band of less intensity is normal observed[29-31]. The crystal structure of 3-acetamidophenol molecule possesses a three-dimensional hydrogen-bond network in solid state. Hence, the O-H stretching frequency was not observed. But, this band have been calculated at the 6-311G(dp) level to be 3804 cm^{-1} (HF) and 3708 cm^{-1} (DFT). The corresponding band is observed at 3594 cm^{-1} and calculated at the B3PW91 level 4049.3 (HF), 3791.1 (DFT1), 3788.3 (DFT2) and 3867.5 cm^{-1} (DFT3) for acetaminophen monomer molecule[28]. The in-plane bending of O-H vibration is in the region 1440-1260 cm^{-1} [32] which observed at 1254 cm^{-1} to be medium strong band in infrared spectra. The O-H in-plane bending vibration is calculated as (1229 cm^{-1}) HF and (1215 cm^{-1}) DFT/B3LYP with 6-311G(dp) set. The free out-of-plane bending O-H vibrations are observed in the region 320-290 cm^{-1} for phenols and in the region 710-517 cm^{-1} for associated O-H[33]. In both intermolecular and intramolecular associations, the frequency is at a higher value than in free OH. The frequency increase with hydrogen bond strength because of the larger amount of energy required to twist the O-H bond out-of-plane[34]. In the IR spectrum of solid *p*-nitrophenol this band is shifted to higher wave numbers (668 cm^{-1}) due to intermolecular hydrogen bonding[35]. The corresponding band frequencies is not observed at the infrared spectra of 3-acetamidophenol molecule but is calculated at (287 cm^{-1}) HF and (325 cm^{-1}) B3LYP with 6-311G(dp) level. The out-of-plane bending of O-H values calculated for 3-acetamidophenol molecule seems to be quite small according to the literature.Karthick *et al.*[36] have observed at 314 cm^{-1} in Raman spectra and calculated as 315 cm^{-1} with B3LYP/6-311++G(d,p) level for 2,4,6-*tris*(dimethylaminomethyl) molecule[36]. The (C-OH) frequency of 3-acetamidophenol is assigned at 1283 cm^{-1} in Table-2. This mode have been calculated at the 6-311G(dp) level to be 1298 (HF) and 1291 cm^{-1} DFT, respectively. The in-plane and out-of-plane bending of (C-OH) vibration are not observed in the 3-acetamidophenol spectrum because these appear at very low frequency but calculated at HF and density functional theory. Also a weak band is observed at 220 cm^{-1} for out-of-plane bending of (C-OH) vibration[37].

C-H Vibrations: The C-H stretching vibrations[38-41] occur as a series of weak bands in the region 3200 and 3000 cm^{-1}. The C-H stretching of 3-acetamidophenol molecule gives bands at 3272, 3212, 3162 and 3060 cm^{-1} in infrared spectra in Table-2. However, 3272 and 3212 cm^{-1} bands seem to slide

TABLE-2
OBSERVED INFRARED WAVE NUMBERS AND CALCULATED FREQUENCIES USING HF/6-311G(dp) AND DFT/B3LYP/6-311G(dp) WITH SCALED FREQUENCIES, THEIR INTENSITIES AND PROBABLE ASSIGNMENTS OF 3-ACETAMIDOPHENOL

No	Calculation HF/6-311G(dp)			Calculation BLYP/6-311G(dp)			Exp. wavenumber (cm^{-1})[19]	Approximate description
	Unscaled (cm^{-1})	Scaled[a] (cm^{-1})	Infrared int.	Unscaled (cm^{-1})	Scaled[b] (cm^{-1})	Infrared int.		
1	32.6212	30	1.232	21.7698	21	0.863	-	Torsion CH_3)
2	40.8067	37	4.744	50.4968	49	6.323	-	Torsion Molecule
3	87.1580	79	7.110	90.39.22	87	3.528	-	γ (CH_3)
4	170.9071	155	9.794	158.7979	154	8.310	-	δ Molecule
5	253.2271	230	4.983	232.8216	225	1.029	-	γ (CCC)
6	270.6766	246	1.593	257.0514	249	2.987	-	γ (CCC)
7	310.2445	282	1.915	289.8002	280	1.534	-	δ (C=O)
8	315.7605	287	120.882	336.1770	325	105.727	-	γ (O-H)
9	360.5757	328	0.596	343.2181	332	0.543	-	δ (CH_3)
10	487.6768	443	8.129	450.3182	435	7.639	-	δ (C-OH)
11	506.7323	460	1.626	462.7634	447	2.201	459 s	γ (CCC)
12	552.4248	502	83.061	526.5623	509	6.976	490 w	γ (N-H)
13	567.7182	516	5.507	536.8504	519	53.532	526 m	δ (CCC)
14	597.4547	543	20.322	550.7810	533	13.143	555 w	δ (CCC)
15	660.6136	600	0.319	618.6285	598	11.874	592 m	γ (CCC)
16	698.7793	635	3.747	635.8268	612	0.201	630 m	γ (CCC)
17	726.8544	660	4.256	674.0528	652	1.241	667 br	δ(CCC) + ν(C-CH_3)
18	762.3820	693	17.194	695.6094	673	17.648	686 s	γ (CCC)
19	864.3077	769	2.323	773.3632	748	4.557	736 vs	δ (CCC)
20	862.9320	784	55.935	794.4871	768	3.665	775 vs	γ (C-H)
21	940.8366	855	56.059	841.1476	813	32.540	802 br	γ (C-H)
22	978.4880	889	6.227	881.1527	852	7.090	848 s	γ (C-H)
23	985.4279	895	11.070	917.1481	887	12.702	871 m	δ (CCC)
24	1069.4006	972	2.924	982.7439	950	0.769	917 m	γ (CCC)
25	1077.3337	979	2.440	997.2844	964	5.032	967 w	Rocking (CH_3)
26	1101.2959	1001	1.042	1008.5498	975	8.513	999 m	γ (C-H)
27	1114.1403	1012	56.719	1027.4229	993	40.307	-.	Rocking (CH_3)
28	1153.8092	1048	8.783	1052.7712	1018	8.105	1037 m	Rocking (CH_3)
29	1190.5667	1082	9.023	1109.9979	1073	12.135	1080 m	δ (C-H)
30	1196.4463	1087	9.690	1177.8723	1139	117.177	-.	Ring ν(C-C)
31	1274.2692	1158	103.881	1188.9356	1150	28.166	1160 m	δ (C-H)
32	1310.5502	1191	19.897	1219.5998	1179	89.159	1176 m	δ (C-H)
33	1352.4714	1229	36.880	1256.3349	1215	82.335	1254 m	δ (O-H)
34	1376.8836	1251	385.548	1315.3213	1272	102.301	-	Ring ν(C-C)
35	1428.8425	1298	51.061	1334.8093	1291	133.510	1283 s	ν (C-OH) + ν (C-N)
36	1450.5234	1318	128.279	1355.9134	1311	76.421	1347 vs	ν (C-H)
37	152.8468	1385	42.006	1401.5099	1355	40.399	1380 s	Umbrella (CH_3)
38	1583.5957	1439	39.382	1470.1563	1421	8.266	1429 m	Sym. bend (CH_3)
39	1602.5596	1456	56.622	1474.5222	1426	80.603	-	Asy.bend (CH_3) + Ring ν(C-)
40	1604.5223	1458	8.680	1490.7782	1441	15.153	1457 br	Asy.bend (CH_3)
41	1652.9949	1502	258.273	1523.6671	1473	210.021	1491 vs	Ring ν(C-C)
42	1715.9309	1559	231.550	1568.0288	1516	172.796	-	δ (N-H)
43	1790.9872	1627	178.586	1639.8372	1586	132.995	1572 s	Ring ν(C-C)
44	1805.5500	1640	239.668	1661.7913	1607	142.181	1615 vs	Ring ν(C-C)
45	1964.5627	1785	300.152	1772.8622	1714	219.647	1661 s	ν(C=O)
46	3177.6527	2887	7.766	3041.9962	2941	9.737	2806 m	$ν_s$(CH_3)
47	3237.7839	2942	20.118	3115.7094	3013	18.106	2925 m	$ν_a$(CH_3)
48	3295.6560	2994	11.344	3116.9351	3014	5.703	-	$ν_a$(CH_3)
49	3312.9232	3010	13.534	3154.4522	3050	13.150	3060 m	ν (C-H)
50	3331.5554	3028	12.053	3171.1939	3066	8.620	3162 m	ν (C-H)
51	3338.2387	3033	16.376	3179.9826	3075	13.129	3212 m	ν (C-H)
52	3430.6518	3117	3.962	3254.7863	3147	6.869	3272 s	ν (C-H)
53	3877.2320	3522	33.179	3627.3992	3507	18.823	3325 s	ν (N-H)
54	4186.6196	3804	103.533	3843.5034	3708	64.445	-	ν (O-H)

[a]Scaling factor (s.f.): 0.9085, [b](s.f.): 0.9669

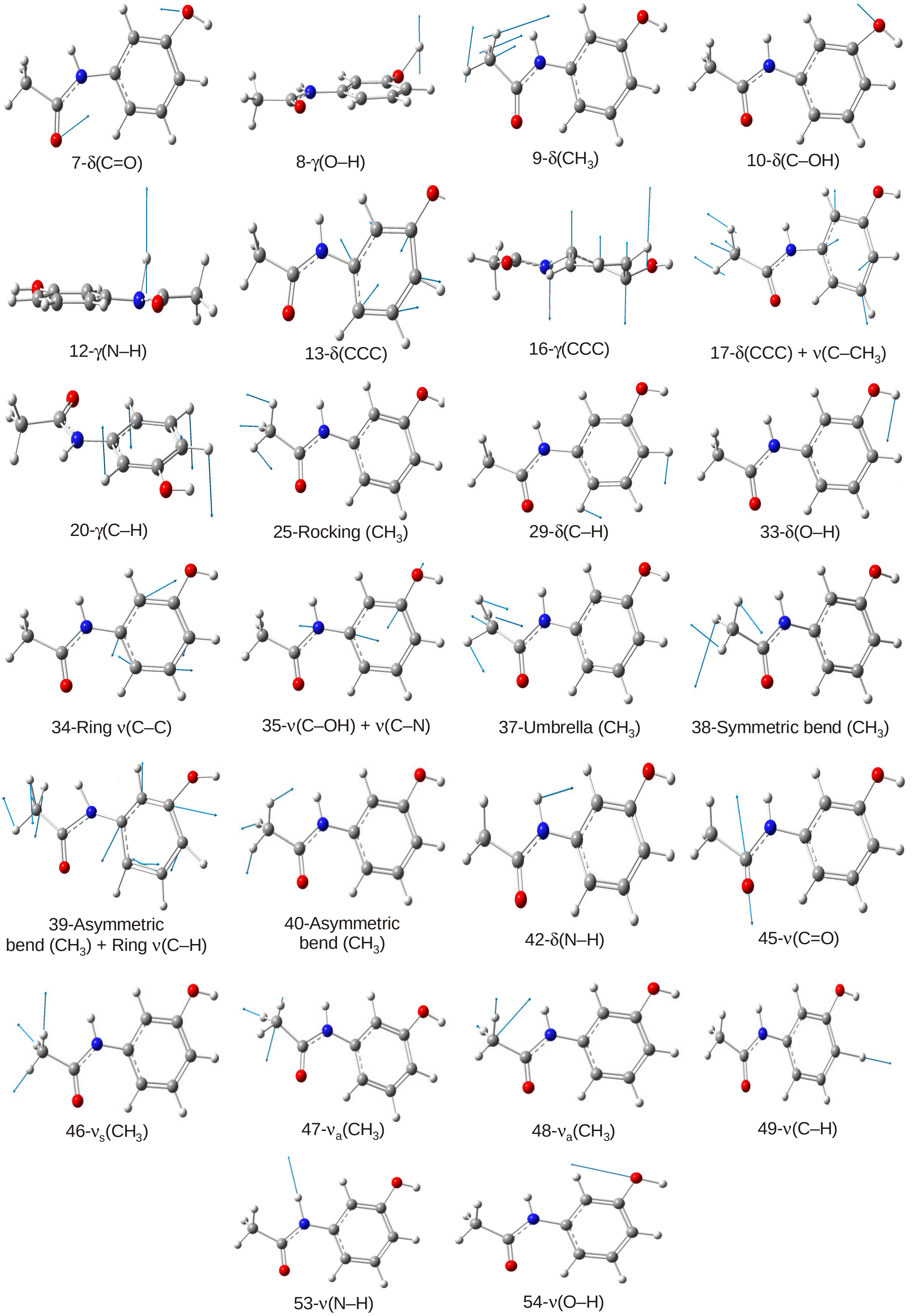
up from the 3100 cm^{-1} band. The corresponding bands frequencies have been calculated at the 6-311G(dp) level to be 3117, 3033, 3028 and 3010 cm^{-1} (HF), respectively and 3114, 3075, 3066 and 3050 cm^{-1} (DFT), respectively. Dante *et al.*[28] have observed aromatic C-H stretching vibrations between 3160 and 2960 cm^{-1} and calculated between 3460.2 and 3156.8 using HF and DFT methods for acetaminophen molecule. The C-H in-plane bending modes are usually observed in region 1300-1000 cm^{-1} in infrared spectra[42]. The corresponding frequencies are obtained at 1347, 1176, 1160 and 1080 cm^{-1} in the infrared spectra (Table-2). The C-H in-plane bending modes have been calculated at the 6-311G(dp) level to be 1318, 1191, 1158 and 1082 cm^{-1} (HF), respectively and 1311, 1179, 1150 and 1073 cm^{-1} (DFT), respectively. The C-H out-of-plane bending modes are observed[43] in the region 1100-750 cm^{-1}. The aromatic C-H out-of plane bending vibrations of 3-acetamidophenol are observed at 775, 802, 848 and 999 cm^{-1} (Table-2). These modes have been calculated at the 6-311G(dp) level to be 1001, 889, 855 and 784 cm^{-1} (HF), respectively and 975, 852, 813 and 768 cm^{-1} (DFT), respectively.

Methyl group vibrations: Each methyl group has three stretching vibrations, one being symmetric and other two asymmetric. But, one of the asymmetric stretching vibrations was observed. Methyl group vibrations have shown that asymmetric and symmetric methyl stretching bands can be observed around 2846 and 2960 cm^{-1}, respectively[44-47]. The C-H asymmetric and symmetric stretching modes of methyl group are observed 2925 and 2806 cm^{-1} in the infrared spectra as medium in IR, respectively. These modes have been calculated at the 6-311G(dp) level to be 2942 and 2887 cm^{-1} (HF), respectively, 3013 and 2941 cm^{-1} (DFT), respectively (Table-2). For a methyl group, the electronic charge is back donated from the lone pair of oxygen atom to the δ^* orbital of C-H bonds causing the weakening of C-H bonds[48]. This is followed by the increase of C-H bond distance and the decrease of C-H force constants and can cause enhancement of infrared band intensities of C-H stretching modes. In 3-acetamidophenol the methoxy hydrogen atoms are cause the decrease of asymmetric methyl stretching wavenumbers and the enhancement of infrared intensities as reported in literature for similar molecular systems[48-50]. The asymmetric bending vibrations of methyl group normally appear around 1460 cm^{-1} [45]. The medium broad band at 1457 cm^{-1} in IR spectrum is assigned to the methyl group asymmetric bending modes. This have been calculated at the 6-311G(dp) level to be 1458 cm^{-1} (HF) and 1441 cm^{-1} (DFT) in (Table-2.). The symmetric bending vibrations of methyl group are assigned at 1429 cm^{-1} and the umbrella mode is assigned at 1380 cm^{-1} in infrared spectrum. The electronic effects must be responsible for the observed lowering of symmetric bending modes by about 3 cm^{-1} compared to the result[45]. The symmetric bending and umbrella modes in methyl group has been calculated at the 6-311G(dp) level to be 1439 and 1385 cm^{-1} (HF), respectively, 1421 and 1335 cm^{-1} (DFT), respectively (Table-2.). The rocking vibrations of the CH_3 group are appearing as mixed vibrations in 970-1040 cm^{-1} range[45]. The corresponding frequencies are obtained at 1037 and 967 cm^{-1} in the infrared spectra in Table-2. These bands have been calculated in 1018-964 cm^{-1} range at HF and DFT, respectively. The C-CH_3 stretching vibration is obtained at 667 cm^{-1}. The torsion and out-of-plane bending vibrations are not observed in the 3-acetamidophenol spectrum because these appear at very low frequency but calculated at HF and DFT. The observations in 3-acetamidophenol are in agreement with theoretical results of similar compounds[51-54].

Ring vibrations: The identification of vibrational modes around 1300-1650 cm^{-1} is very difficult task since the mixing of several bands are possible in this region. The phenyl ring has six C-C stretching vibrations. But three of the C-C stretching vibrations were observed in the infrared spectrum. The corresponding frequencies are 1615, 1572 and 1491 cm^{-1} and these has been calculated at the 6-311G(dp) level to be 1640, 1627 and 1502 cm^{-1} (HF), respectively, 1607, 1586 and 1473 cm^{-1} (DFT), respectively (Table-2.). The in-plane deformation vibration is at higher frequencies than the out-of-plane vibrations. The in-plane deformation vibration bands observed at 917, 871, 736, 667, 555 and 526 cm^{-1} are assigned to CCC in-plane deformations of phenyl ring. The theoretically computed values at 972, 895, 769, 660, 543 and 516 cm^{-1} by HF, respectively, 950, 887, 748, 652, 533 and 519 cm^{-1} by DFT method, respectively. The 686, 630, 592 and 459 cm^{-1} bands are assigned to be CCC out-of-plane bending modes. But, the other two bands are not observed at IR spectrum because these appear at very low frequency. The corresponding frequencies have been calculated by HF and DFT methods. The results are in good agreement with the literature values[54-57].

Other vibrations: Normally in all the heterocyclic compounds, the N-H stretching vibration occurs strongly and broadly in the region 3500-3000 cm^{-1} [58]. For the title compound, the strong band at 3325 cm^{-1} in the IR spectrum is assigned as N-H stretching mode. The calculated values for this mode are 3522 cm^{-1} (HF) and 3507 cm^{-1} (DFT). The calculated N-H stretching wavenumbers are shifted in the IR spectrum with a strong intensity from the observed wavenumber. The shifting of the N-H stretching mode to lower wavenumber could be interpreted as N-H intermolecular interaction and the computations performed in the gas phase. For acetaminophen monomer was observed at 3440 cm^{-1} and calculated at 3876.9 cm^{-1} (HF) and cm^{-1} 3640.0 (DFT1-B3PW91)[28], observed at 3488 cm^{-1} for *p*-bromoacetanilide and calculated at 3488 cm^{-1} (HF) and cm^{-1} 3488 (B3LYP/6-311++G(d,p) methods[52]. N-H in-plane bending mode is not observed bat computed at 1559 cm^{-1} (HF) and 1516 cm^{-1} (DFT). N-H out of plane bending mode is observed as a weak intensity band in the infrared at 490 cm^{-1} which computed at 502 cm^{-1} (HF) and 509 cm^{-1} (DFT).

The carbonyl group shows a strong absorption band due to C=O stretching vibration and is observed in the region 1700-1660 cm^{-1} [59,60]. The carbonyl stretching mode is simultaneously influenced by the conjugation of C=O with amide nitrogen and the intermolecular hydrogen bonding. The conjugation and influence of intermolecular hydrogen bonding (C=O….H) type network in the crystal results in lowered C=O stretching wavenumber. In this instance, the conjugation of C=O (Fig. 2a-b) bond with aromatic ring, may increase its single bond character resulting in lowered values of carbonyl stretching wave numbers. The intense band in infrared spectrum at 1661 cm^{-1} is assigned to C=O stretching mode. This mode was calculated at 1785 cm^{-1} (HF) and 1714 cm^{-1} (DFT). The in-plane bending vibrations is not observed in the 3-acetamidophenol



7-δ(C=O) 8-γ(O–H) 9-δ(CH$_3$) 10-δ(C–OH)

12-γ(N–H) 13-δ(CCC) 16-γ(CCC) 17-δ(CCC) + ν(C–CH$_3$)

20-γ(C–H) 25-Rocking (CH$_3$) 29-δ(C–H) 33-δ(O–H)

34-Ring ν(C–C) 35-ν(C–OH) + ν(C–N) 37-Umbrella (CH$_3$) 38-Symmetric bend (CH$_3$)

39-Asymmetric bend (CH$_3$) + Ring ν(C–H) 40-Asymmetric bend (CH$_3$) 42-δ(N–H) 45-ν(C=O)

46-ν_s(CH$_3$) 47-ν_a(CH$_3$) 48-ν_a(CH$_3$) 49-ν(C–H)

53-ν(N–H) 54-ν(O–H)

Fig. 6. Atomic displacement vectors corresponding to some vibrational modes of 3-acetamidophenole

spectrum but calculated at HF and DFT. The C=O stretching band assigned at 1629 cm^{-1} in *p*-bromo acetanilide by Gnanasambandan *et al*.[52]. In the present investigation, the infrared band observed at 1283 is assigned to the C-N stretching mode. The calculated value at 1298 cm^{-1} (HF) and 1291 (DFT) are in agreement with the observed value for the corresponding mode of vibration.

Table-2 showed the observed infrared wavenumbers and calculated frequencies using HF/6-311G(dp) and density functional theory/B3LYP/6-311G(dp) with scaled frequencies, their intensities and probable assignments of 3-acetamidophenol. Atomic displacements vectors corresponding to some normal modes of 3-acetamidophenol molecule are shown in Fig. 6.

Conclusion

The molecular structural parameters and vibrational frequencies of the fundamental modes of the 3-acetamidophenol molecule have been obtained from quantum mechanical Hartree-Fock and density functional theory calculations. The geometry was optimized without any symmetry constraints using the Hartree-Fock and DFT(B3LYP) method with 6-311G(dp) basis set. The theoretical results were compared with the experimental structure parameters and observed vibrational wave numbers. The bond length and bond angle parameters of 3-acetamidophenol molecule computed by DFT/BLYP and Hartree-Fock are in reasonable agreement with the experimental data, respectively. The infrared absorption and intensities are also computed by Hartree-Fock and DFT(B3LYP) methods and in well agreement with experimental data. The results confirm the ability of the methodology applied for interrelation of the vibrational spectrum and geometric parameters of 3-acetamido-phenol in the solid state.

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