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Quantum chemical vibrational study, molecular property and HOMO-LUMO energies of 3-bromoacetophenone for Pharmaceutical application

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ABSTRACT

Quantum chemical calculations of energies, geometries and vibrational wave numbers of 3-bromoacetophenone were carried out by ab initio and DFT levels of theory with complete relaxation in the potential energy surface using 6-31G (d,p) basis set. The study is extended to calculate the HOMO- LUMO energy gap, ionization potential, electron affinity, global hardness ,chemical potential and global electrophilicity, polarizability, Mulliken charges and thermodynamic properties of 3-bromoacetophenone . The FTIR and FT Raman spectra of 3-bromoacetophenone have been recorded in the regions 4000 – 400 cm^{-1} and 3500 – 100 cm^{-1}, respectively. A complete vibrational assignment aided by the theoretical harmonic frequency analysis has been proposed. The calculated HOMO and LUMO energies show the charge transfer occurs in the molecule. The harmonic vibrational frequencies calculated have been compared with experimental FTIR and FT Raman spectra. The observed and the calculated frequencies are found to be in good agreement. The experimental spectra also coincide satisfactorily with those of theoretically constructed simulated spectrograms.

Keywords: FTIR and FT Raman spectra; ab initio and DFT; 3-bromoacetophenone; vibrational analysis; HOMO-LUMO energy.

INTRODUCTION

Aromatic ketones such as acetophenone, propiophenone and their derivatives have great analytical and pharmaceutical applications. 3-bromoacetophenone is used as an intermediate product for the preparation of fenoprofen which is an anti-inflammatory, analgesic and anti-pyretic drug [1,2]. Chemically it is called as 1-(3-bromophenyl)-ethanone. Alzheimer's disease (progressive form of presenile dementia) is treated with the drug which was invented from 3-bromoacetophenonone [3]. It is used as a reaction initiator with organopolysiloxane, which is the base polymer to prepare silicone rubber [4]. It is also used as a coupling partner in microwave accelerated cross- coupling of a range of aryl boronic acids with aryl chlorides [5]. Substituted bromoacetophenone are used to synthesis dicationic diarylpyridines which are used as nucleic acid binding agents [6].

The title compound is used as an antibacterial agent [7]. It is also used as a photo radical polymerization initiator to provide a cross linkable silyl group terminated vinyl polymer [8]. Density functional theory (DFT), accepted by the ab initio quantum chemistry community is a cost-effective general procedure for studying physical properties of the molecules. DFT calculations of vibrational spectra of many organic systems [9,10], have shown promising conformity with experimental results. Therefore, in this present investigation ab initio and DFT techniques are employed to study the complete vibrational spectra of the title compound and to identify the various normal modes with greater wave number accuracy.

Several other investigations have been carried out on the title compound and its derivatives [11-15]. Literature survey reveals that to the best of our knowledge no ab initio HF/DFT frequency calculations of 3-bromoacetophenone have been reported so far. It may be due to difficulty in interpreting the spectra of these molecules because of their complexity and low symmetry. Due to the absence of Raman spectra and vapour phase infrared spectra, a complete vibrational assignment is not available in the literature.

Hence the present investigation was undertaken to study the vibrational spectra of this molecule completely and to identify the various normal modes with greater wave number accuracy. Assuming C_1 point group symmetry the band assignments have made.

Ab initio HF and Density Functional Theory (DFT) calculations have been performed to support our wave number assignments. The theoretically predicted IR and Raman intensities are well in agreement with that of experimental spectral data.

EXPERIMENTAL SECTION

The compound 3-bromoacetophenone was purchased from Sigma-Aldrich Chemical Company, USA with more than 98 % purity and was used as such without further purification to record FTIR and FT Raman spectra. A projection of 3-bromoacetophenone is shown in the Fig.1. The FTIR spectra of the compound is recorded in the region 4000 – 400 cm^{-1} in evacuation mode on Bruker IFS 66V spectrophotometer using KBr pellet technique (solid phase) with 4.0 cm^{-1} resolutions. The FT Raman spectra are recorded using 1064 nm line of Nd: YAG laser as excitation wavelength in the region 3500 – 100 cm^{-1} on Bruker IFS 66V spectrometer equipped with FRA 106 FT Raman module accessory. The spectral measurements were carried out at Sophisticated Instrumentation Analysis Facility, IIT, Chennai, India. The experimental FTIR and FT Raman spectra of 3-bromoacetophenone is presented in the Figs. 3 & 4.

Computational details

The entire calculations conducted in the present work were performed at Hartree-Fock (HF) and B3LYP levels included in the Gaussian 03W package [16] program together with the 6-31G basis set function of the density functional theory (DFT) utilizing gradient geometry optimization [17]. The geometries were first determined at the Hartree Fock level of theory employing 6-31G (d,p) basis set. All the geometries were then optimized using 6-31G (d,p) basis sets using density functional theory (DFT) [18] employing the Becke's three-parameter hybrid functional [19] combined with Lee-Yang-Parr correlation [20] functional (B3LYP) method. The DFT partitions the electronic energy as $E = E_T+E_V+E_J+E_{XC}$, where E_T, E_V, and E_J are the electronic kinetic energy, the electron nuclear attraction and the electron-electron repulsion terms respectively. The electron correlation is taken into account in DFT via the exchange correlation term E_{XC}, which includes the exchange energy arising from the antisymmetry of the quantum mechanical wavefunction and the dynamic correlation in the motion of individual electrons; it makes DFT dominant over the conventional HF procedure [21].

The optimized structural parameters were used in the vibrational frequency calculations at the HF and DFT levels to characterize all stationary points as minima. Then vibrationally averaged nuclear positions of 3-bromoacetophenone is used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies together with intensities and Raman depolarization ratios. The DFT hybrid B3LYP functional also tends to overestimate the fundamental modes in comparison to the other DFT methods; therefore, scaling factors have to be used to obtain considerably better agreement with experimental data. Thus according to the work of Rauhut and Pulay [22], a scaling factor of 0.963 has been uniformly applied to the B3LYP calculated wavenumbers. Similarly, the vibrational modes studies through HF method were scaled by a value of 0.891 [23]. Finally, calculated normal mode vibrational frequencies, provide thermodynamic properties by way of statistical mechanics. Zero point vibrational energy was also calculated in the present work. By combining the results of the Gaussview program [24] with symmetry considerations, vibrational frequency assignments were made with high degree of accuracy. There is always some ambiguity in defining internal coordination. However, the defined coordinate form complete set and matches quite well with the motions observed using the Gaussview program. To achieve a close agreement between observed and calculated frequencies, the least square fit refinement algorithm was used. For the plots of simulated IR and Raman spectrum, pure Lorentzian band shapes were used with a bandwidth of 10 cm^{-1}. HOMO-LUMO energy gaps has been computed and other related molecular properties are calculated.

RESULTS AND DISCUSSION

Molecular geometry

The optimized structure parameters of 3-bromoacetophenone calculated by ab initio HF and DFT-B3LYP levels with the 6-31G(d,p) basis set are listed in the Table 1 in accordance with the atom numbering scheme given in Fig.1. The molecular structure, XRD studies have been studied for the compound m-chloroacetophenone and m-nitroacetophenone. Since the compound chosen for the present study has close structural relation with the above-mentioned compounds, the molecular parameters have been taken from m-chloroacetophenone and m-nitroacetophenone

[25,26]. Table 1 compares the calculated bond lengths and angles for 3-bromoacetophenone with those experimentally available from X-ray diffraction data [25, 26].

From the theoretical values, we can find that most of the optimized bond angles are slightly larger than the experimental values, due to the theoretical calculations belong to isolated molecules in gaseous phase and the experimental results belong to molecules in solid state. Comparing bond angles and lengths of B3LYP with those of HF, as a whole the formers are on higher side than the latter and the HF calculated values correlates well compared with the experimental results. In spite of the differences, calculated geometric parameters represent a good approximation and they are the bases for calculating other parameters, such as vibrational frequencies and thermodynamic properties.

Vibrational assignments

The vibrational analysis of 3-bromoacetophenone is performed on the basis of the characteristic vibrations of carbonyl,bromo, methyl, and phenyl ring modes. The computed vibrational wavenumbers, their IR and Raman activities, depolarization ratios and the force constants corresponding to the different normal modes are used for identifying the vibrational modes unambiguously. The harmonic vibrational frequencies calculated for 3-bromoacetophenone at HF and B3LYP levels using the 6-31G(d,p) basis set along with polarization functions have been summarized in Table 2 and 3. It can be noted that the calculated results are harmonic frequencies while the observed frequencies contain anharmonic contribution. The later is generally lower than the former due to anharmonicity. The reproductions of observed fundamental frequencies are more desirable because they are directly observable in a vibrational spectrum. Comparison between the calculated and the observed vibrational spectra helps us to understand the observed spectral features. Inclusion of electron correlation in density functional theory to a certain extend makes the frequency values smaller in comparison with the HF frequency data. For visual comparison, the observed and calculated (simulated) FTIR and FT Raman spectra of 3-bromoacetophenone is presented in a common wavenumber scale in Table 3.

C-H Vibrations

The aromatic structure shows the presence of C-H stretching vibrations in the region 3250 cm^{-1} - 2950 cm^{-1} which is characteristic region for the ready identification of C-H stretching vibrations and particularly the regions 3250 cm^{-1} - 3100 cm^{-1} for asymmetric stretching and 3100 cm^{-1} - 2950 cm^{-1} for symmetric stretching modes of vibration [27]. For most cases, the aromatic compound C-H vibration absorption bands are usually weak; in many cases it is too weak for detection. In this region, the bands are not affected, appreciably by the nature of substituents. In the present work, for the compound 3-bromoacetophenone, the FTIR bands observed at 3238 cm^{-1} ,3228 cm^{-1}, 3220 cm^{-1} and 3197 cm^{-1} have been assigned to C-H stretching vibration.

The B3LYP level at 6-31G(d,p) gives the same frequency values at 3236 cm^{-1}, 3225 cm^{-1} ,3216 cm^{-1} and 3195 cm^{-1} as indicated in Table 3. For the same vibration the HF/6-31G(d,p) gives a slightly decreased value when compared to experimental data. In general the aromatic C-H stretching vibrations calculated theoretically are in good agreement with the experimentally reported values [28-30] for di substituted benzene in the region 3200 - 2900 cm^{-1}.

The title compound 3-bromoacetophenone has both out-of-plane and in-plane aromatic C-H bending vibrations. The out of plane bending mode of C-H vibration of 3-bromoacetophenone is found well in agreement with the experimentally predicted in the region 1000-600 cm^{-1} [31]. At B3LYP/6-31G(d,p), 995 and 807 cm^{-1} , is calculated . The observed FTIR value of 996 cm^{-1} is in excellent agreement with 995 cm^{-1} of B3LYP/6-31G(d,p) results. The out of plane C-H deformation vibrations of 3-bromoacetophenone is experimentally predicted in the region 636 and 996 cm^{-1} coincides satisfactorily with the calculated values in the same region. The aromatic C-H in-plane bending modes of benzene and its derivatives are observed in the region 1300-1000 cm^{-1} [32]. The C-H in plane bending vibrations assigned even though found to be contaminated by C-CH_3 stretch are found in literature [33,34], while the experimentally observed values for 3-bromoacetophenone is at 1268 cm^{-1} . The C-H in-plane bending vibration of 3-bromoacetophenone coincides satisfactorily with the experimentally observed values in this region.

C-Br Vibration

The compound under consideration 3-bromoacetophenone has a bromine substitution in m-position. The heavier mass of bromine obviously makes the C-Br stretching mode to appear in longer wavelength region. Bellamy has assigned the region 700-600 cm^{-1} for the C-Br stretching [35,36]. Based on this, the band observed at 660 cm^{-1}in FTIR is assigned to C-Br stretching. The theoretically calculated value 670 $cm\text{-}^{1}$ is well agreed with the experimental value. The C-Br in-plane bending and out-of-plane bending vibrations are assigned to 305 and 267 cm^{-1} respectively in the FT-Raman spectrum. These values agree very well with the literature values [37,38,39].

Methyl group vibrations

The compound under consideration 3-bromoacetophenone possess a CH_3 group in the side substitution chain. There are nine fundamentals one can expect to a CH_3 group, namely the symmetrical stretching in CH_3 (CH_3 sym.stretch)and asymmetrical stretching(in plane hydrogen stretching mode); the symmetrical(CH_3 sym.deform) and asymmetrical(CH_3 asym.deform) deformation modes; in-plane rocking, out-of-plane rocking, twisting and bending modes [40]. Each methyl group has three stretching vibrations, one being symmetric and other two asymmetric. The frequencies of asymmetric vibrations are higher than the symmetric one [41]. The theoretically computed values 3050 for CH_3 symmetric stretching and 3114, 3171 for CH3 asymmetric stretching shows an excellent agreement with the range allotted by Williams and Fleming [42]. CH_3 asymmetric and symmetric in-plane bending are observed at 1470 and 1315 cm^{-1} in FTIR and corresponding Raman values are 1474 and 1312 cm^{-1}, respectively [43]. The torsion vibrations are not observed in the FTIR and FT Raman spectrum because these appear at very low frequency. The observations at 52 cm^{-1} in 3-bromoacetophenone is in agreement with theoretical results of similar compounds.

C=O vibrations

The C=O stretching vibration in 3-bromoacetophenone has a main contribution in the mode, with B3LYP/6-31G(d,p) predicted frequencies at 1642 cm^{-1} (Table 3) for 3-bromoacetophenone. This is in agreement with the very strong experimental frequencies at 1635 cm^{-1} in FTIR spectrum of 3-bromoacetophenone. The FT Raman spectrum of 3-bromoacetophenone shows a band at 1639 cm^{-1} and thus confirms the presence of C=O stretching vibrations. The C=O stretching vibration calculated with HF level shows slightly higher range of frequencies than the experimental results. The out of plane C=O bending vibration mode of 3-bromoacetophenone with the experimental frequency of 149 cm^{-1} found to be in excellent agreement with the calculated values at HF and B3LYP levels. The above conclusions are in agreement with the literature value [44].

Table 1 Optimized geometrical parameters of 3-bromoacetophenone, bond length(Å), Interaxial angles(°)

Parameters	Expt	HF/6-31 G(d,p)	B3LYP/6-31 G(d,p)
C_9-H_{17}	1.100	1.074	1.085
C_8-H_{16}	1.100	1.075	1.086
C_7-H_{15}	1.100	1.074	1.084
C_5-H_{14}	1.100	1.072	1.083
C_2-H_{13}	1.113	1.080	1.090
C_2-H_{12}	1.113	1.085	1.096
C_2-H_{11}	1.113	1.085	1.096
C_4-C_9	1.395	1.388	1.402
C_8-C_9	1.395	1.386	1.395
C_7-C_8	1.395	1.383	1.395
C_6-C_7	1.395	1.385	1.396
C_5-C_6	1.395	1.377	1.388
C_4-C_5	1.395	1.393	1.403
C_6-Br_{10}	1.881	1.898	1.913
C_1-C_4	1.351	1.504	1.504
C_1-O_3	1.208	1.194	1.221
C_1-C_2	1.512	1.513	1.518
H_{17}-C_9-C_4	120.0	120.7	120.4
H_{17}-C_9-C_8	120.0	119.1	119.4
C_4-C_9-C_8	120.0	120.3	120.2
H_{16}-C_8-C_9	120.0	120.1	120.1
H_{16}-C_8-C_7	120.0	119.7	119.5
C_9-C_8-C_7	120.0	120.3	120.4
H_{15}-C_7-C_8	120.0	120.7	120.9
H_{15}-C_7-C_6	120.0	120.1	120.1
C_8-C_7-C_6	120.0	119.1	119.0
C_7-C_6-C_5	120.0	121.2	121.3
C_7-C_6-Br_{10}	120.0	119.2	119.1
C_5-C_6-Br_{10}	120.0	119.6	119.6
H_{14}-C_5-C_6	120.0	121.1	121.7
H_{14}-C_5-C_4	120.0	119.3	118.8
C_6-C_5-C_4	120.0	119.5	119.5
C_9-C_4-C_5	120.0	119.5	119.5
C_9-C_4-C_1	120.0	122.8	123.0
C_5-C_4-C_1	120.0	117.7	117.5
H_{13}-C_2-H_{12}	109.5	109.4	109.4
H_{13}-C_2-H_{11}	109.4	109.4	109.4
H_{13}-C_2-C_1	109.4	108.5	108.6
H_{12}-C_2-H_{11}	109.4	107.9	107.4
H_{12}-C_2-C_1	109.4	110.8	111.0
H_{11}-C_2-C_1	109.5	110.8	111.0
C_4-C_1-O_3	120.0	120.2	120.4
C_4-C_1-C_2	120.0	119.1	118.8
O_3-C_1-C_2	120.0	120.7	120.8

Table 2 Vibrational wavenumbers obtained for 3-bromoacetophenone at HF/ 6-31G(d,p) [harmonic frequency (cm^{-1}) IR intensities(km mol^{-1}), Raman scattering activities (Å amu $^{-1}$), Raman depolarization ratio, reduced mass (amu) and force constants (m dyn Å $^{-1}$)]

ν_{cal}	IR intensity		Raman	Intensity	Depolarisation	Reduced	Force
(cm^{-1})	Rel	Abs	Rel	Abs	ratio	mass	Constant
52	3.973	2	0.017	0	0.750	4.180	0.016
139	1.562	1	1.212	1	0.665	8.895	0.113
147	0.230	0	2.220	2	0.750	5.409	0.079
175	0.100	0	0.695	0	0.750	1.100	0.022
189	0.022	0	2.996	2	0.750	3.374	0.086
269	4.769	2	3.824	3	0.330	4.129	0.199
309	0.726	0	5.251	4	0.210	7.251	0.467
385	2.954	1	2.076	1	0.633	6.343	0.630
427	0.071	0	0.042	0	0.750	3.146	0.402
485	1.747	1	1.895	1	0.163	4.256	0.665
532	6.525	3	0.445	0	0.750	3.840	0.639
594	43.516	18	2.649	2	0.583	4.378	1.057
624	2.638	1	1.131	1	0.750	2.976	0.812
670	24.489	10	7.670	5	0.174	6.842	2.092
706	26.694	11	0.548	0	0.750	2.123	0.734
780	18.544	8	1.400	31	0.123	6.121	2.544
806	30.356	13	0.769	1	0.750	1.392	0.658
935	0.116	0	0.458	0	0.750	1.355	0.888
956	12.063	5	7.800	5	0.161	2.165	1.422
967	10.449	4	1.027	1	0.750	1.413	0.948
997	4.885	2	30.823	21	0.110	5.844	4.066
1013	0.002	0	0.148	0	0.750	1.364	1.017
1052	0.945	0	3.013	2	0.750	1.895	1.482
1095	11.319	5	9.319	6	0.231	3.452	2.810
1103	7.391	3	1.885	1	0.681	1.767	1.457
1127	0.604	0	5.213	4	0.561	1.682	1.467
1197	2.857	1	2.911	2	0.732	2.581	2.328
1273	7.372	3	0.032	0	0.310	1.510	1.557
1314	240.264	100	19.684	14	0.200	3.037	3.426
1359	0.678	0	0.157	0	0.203	1.306	1.593
1391	29.791	12	2.490	2	0.425	1.380	1.905
1459	66.859	28	2.924	2	0.732	2.946	4.327
1480	6.751	3	10.572	7	0.716	1.052	1.586
1494	9.769	4	20.062	14	0.750	1.047	1.597
1510	11.708	5	0.751	1	0.190	2.255	3.572
1562	24.093	10	7.273	5	0.750	5.454	10.09
1595	5.681	2	55.555	38	0.563	5.591	10.62
1643	235.172	98	30.308	21	0.321	11.69	27.35
3056	4.066	2	102.011	70	0.011	1.039	6.254
3110	14.892	6	48.610	33	0.750	1.101	6.897
3175	14.054	6	101.550	70	0.563	1.103	7.139
3199	6.363	3	68.269	47	0.611	1.089	7.242
3213	8.709	4	67.488	46	0.489	1.093	7.370
3224	7.505	3	145.322	100	0.119	1.097	7.432
3234	3.247	1	36.376	25	0.247	1.093	7.509

Table 3 Vibrational wavenumbers obtained for 3-bromoacetophenone at B3LYP/ 6-31G(d,p) [harmonic frequency (cm^{-1}) IRintensities (km mol^{-1}), Raman scattering activities (Å amu $^{-1}$), Raman depolarization ratio, reduced mass (amu) and force constants (m dyn Å ^{1})]

Observed Wavenumbers		Calculated using B3LYP/6-31G(d,p)								
ν_{IR} cm^{-1}	ν_{Raman} cm^{-1}	ν_{cal} cm^{-1}	IR intensity		Raman intensity		Depolarization Ratio	Reduced Mass	Force constant	Characterisation of normal modes
			Rel	Abs	Rel	Abs				
		52	2.961	1	0.097	0	0.750	4.123	0.017	τCH_3 torsion
	135	136	1.364	1	1.474	1	0.672	8.955	0.098	lattice vibration
	149	145	0.123	0	2.269	2	0.750	5.522	0.068	γ C=O + γCH
	176	173	0.256	0	0.681	0	0.750	1.097	0.019	CH_3 torsion
	189	188	0.002	0	2.892	2	0.750	3.407	0.071	CH_3 torsion+ βCH
	265	267	4.563	2	4.025	3	0.334	4.179	0.175	γ C-Br
	305	305	0.773	0	4.102	3	0.199	7.165	0.394	β C-Br
	383	383	2.747	1	1.907	1	0.614	6.122	0.529	β C-H
430	422	428	0.103	0	0.055	0	0.750	3.191	0.345	γ C-H
460	484	481	1.826	1	1.951	1	0.165	4.131	0.563	γ C-H
538	536	532	3.949	1	0.416	0	0.750	3.893	0.545	γ C-C-C
590	598	593	28.950	11	1.933	1	0.663	4.401	0.913	β C-C-O
636	627	625	0.719	0	0.861	1	0.750	3.022	0.695	CH_3 CH_3 twisting
660	660	670	24.368	9	6.164	4	0.207	6.823	1.804	υ C-Br
683	710	706	15.917	6	0.444	0	0.750	2.168	0.637	ring breathing
785	786	781	22.408	8	2.477	2	0.155	6.196	2.228	β C-C-C
838	807	807	23.955	9	1.994	1	0.750	1.433	0.549	γ C-H
901	936	933	0.043	0	1.025	1	0.750	1.356	0.695	γ C-H
960	954	956	9.105	3	1.746	1	0.750	1.371	0.738	γ C-H
987	969	971	12.712	5	11.111	8	0.121	2.125	1.182	γ C-H
996	997	995	0.024	0	0.188	0	0.750	1.324	0.772	γ C-H
1020	1015	1012	4.405	2	26.321	19	0.117	5.581	3.369	δ ring + γC-H
1064	1044	1049	1.067	0	1.715	1	0.750	1.892	1.227	CH_3 twisting
1091	1094	1091	15.660	6	16.180	12	0.150	2.931	2.056	γ C-H + β C-C
1101	1098	1099	0.037	0	3.924	3	0.471	1.907	1.353	β C-H
1124	1124	1128	1.434	1	4.057	3	0.455	1.564	1.173	υ C-C+ β C-H
1186	1196	1199	7.031	3	2.280	2	0.749	1.120	0.949	δ C-H
1268	1277	1272	264.277	100	26.912	19	0.231	3.032	2.892	υ C-C+ βC-H
1315	1312	1310	4.514	2	2.095	1	0.163	1.519	1.536	ρ C-H
1357	1358	1356	2.791	1	1.277	1	0.726	5.448	5.906	γ C-C
1405	1399	1395	37.706	14	3.919	3	0.746	1.329	1.524	CH_3 wagging
1450	1456	1459	56.116	21	3.929	3	0.720	2.970	3.725	υ C-C
1470	1474	1483	8.249	3	9.835	7	0.748	1.060	1.373	δ C-H_3 δ CH_3
1494	1496	1493	9.612	4	21.998	16	0.750	1.048	1.376	υ C-C
1516	1508	1509	10.404	4	1.822	1	0.245	2.267	3.042	υ C-C
1566	1568	1560	30.842	12	12.596	9	0.683	5.901	9.130	υ C-C
1592	1591	1592	5.268	2	69.104	49	0.522	6.069	9.643	υ C-C
1635	1639	1642	146.307	55	40.364	29	0.260	10.99	20.563	υ C=O
3066	3068	3050	2.322	1	111.719	80	0.008	1.038	5.689	υ_s CH_3
3127	3108	3114	8.172	3	49.266	35	0.750	1.100	6.284	$\upsilon_{as}CH_3$
3153	3175	3171	9.724	4	101.785	73	0.567	1.102	6.527	υ_{as} CH_3
3197	3193	3195	5.744	2	78.175	56	0.560	1.088	6.543	υ C-H
3220	3212	3216	7.357	3	82.434	59	0.356	1.092	6.654	υ C-H
3228	3230	3225	3.868	2	140.233	100	0.148	1.095	6.711	υ C-H
3238	3236	3236	4.374	2	42.341	30	0.203	1.091	6.733	υ C-H

Abbrevations used τ- torsion; γ- out of plane bending; β- in plane bending; ρ- rocking; δ- scissoring; υ- stretching; υ_{s}- symmetric stretching; υ_{as}- asymmetric stretching

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C-C vibrations

The C-C aromatic stretching vibrations gives rise to characteristic bands in both the observed IR and Raman spectra, covering the spectral range from 1600 – 1400 cm^{-1} [45-48]. The IR bands are 1592,1566, 1516, 1494 cm^{-1} ; the Raman bands are 1591, 1568, 1508 and 1496 cm^{-1}. Of these bands, 1566 and 1591 cm^{-1} have appeared characteristically strong in the IR and Raman spectra, respectively. The calculated bands at B3LYP and HF levels in the same region are in excellent agreement with experimental observations of both in FTIR and FT Raman spectra of 3-bromoacetophenone. The ring in plane vibrations has given rise to weak bands across the low frequency region, that is to say, below 1000 cm$^{-1.}$ The bands at 781 cm^{-1} in 3-bromoacetophenone has been assigned to C-C in- plane bending vibrations [49]. As is seen from Table the predicted frequencies by both RHF and B3LYP agree well with the observed ones.

Table 4 Comparison of HOMO, LUMO, energy gaps (*e*HOMO –LUMO), and related molecular properties of 3-bromoacetophenone (eV)

Molecular properties	HF/6-31G(d,p)	B3LYP/6-31G(d,p)
ε_{HOMO} eV	-0.34100	-0.25185
ε_{LUMO} eV	0.07971	-0.06567
Energy gap	0.42071	0.18618
Ionisation Potential (I)	0.34100	0.25185
Electron affinity(A)	-0.07971	0.06567
Global Hardness (η)	0.21036	0.09309
Chemical potential (μ)	-0.13065	-0.15876
Global Electrophilicity (ω)	0.04057	0.13538

Table 5 Mulliken atomic charges of 3-bromoacetophenone for HF and B3LYP with 6-31G basis set

Atom with Numbering	HF 6-31G(d,p)	B3LYP 6-31G(d,p)
C_1	0.553987	0.399236
C_2	-0.431130	-0.400378
O_3	-0.567465	-0.446817
C_4	-0.134410	0.041401
C_5	-0.082045	-0.098974
C_6	-0.042867	0.046202
C_7	-0.107812	-0.076425
C_8	-0.158992	-0.091824
C_9	-0.134564	-0.117878
Br_{10}	-0.095419	-0.117878
H_{11}	0.142597	0.125452
H_{12}	0.142596	0.140293
H_{13}	0.168000	0.141834
H_{14}	0.223846	0.139955
H_{15}	0.184264	0.115530
H_{16}	0.167915	0.102392
H_{17}	0.171499	0.094878

The force constant values computed at HF and DFT levels of theories at basis set 6-31G(d,p) have been collected in Table 3 .

Other molecular properties

HOMO-LUMO energy gap and related molecular properties

The HOMO, LUMO and HOMO-LUMO energy gap of 3-bromoacetophenone in the HF and DFT level in 6-31G(d,p) basis set has been calculated. . The HOMO–LUMO energy gap is consistent for B3LYP method and varies erotically to HF method. Associated within the framework of SCF MO theory the ionization energy and electron affinity can be expressed through HOMO and LUMO orbital energies as $I = -E_{HOMO}$ and $A= -E_{LUMO}$ .The hardness corresponds to the gap between the HOMO and LUMO orbital energies. The larger the HOMO-LUMO energy gap the harder the molecule. The global hardness, $\eta = 1/2(E_{LUMO} - E_{HOMO})$. The hardness has been associated with the stability of chemical system. The electron affinity can be used in combination with ionization energy to give electronic chemical potential, $\mu = 1/2(E_{HOMO} + E_{LUMO})$. The global electrophilicity index, $\omega = \mu^2/2\eta$ is also calculated and listed in table 4.

Table 6 Theoretically computed energies (a,u), zero point vibrational energies (kcal mol^{-1}), rotational constants (GHz) entropies (cal mol^{-1} k^{-1}) and Dipole moment (D) (Kcal Mol^{-1} Kelvin^{-1}) of 3bromoacetophenone

Parameters	HF – 6-31G(d,p)	B3LYP – 6-31G(d,p)
Total energy	-2951.7942976	-2956.0104244
Zero point energy	86.01024	80.32412
Rotational constants	2.07781	2.03909
	0.47400	0.46883
	0.38687	0.38209
Entropy		
Total	95.190	97.127
Translational	41.754	41.754
Rotational	31.112	31.154
Vibrational	22.324	24.219
Dipole moment	4.3250	4.1260

Table 7 Calculated polarizabilities of 3-bromoacetophenone

Basis Set	α_{xx}	α_{xy}	α_{yy}	α_{xz}	α_{yz}	α_{zz}	$<\alpha>$
HF/ 6-31G(d,p)	130.060	2.722	104.523	0.032	0.016	45.330	93.304
B3LYP/ 6-31G(d,p)	144.838	1.343	110.942	0.011	0.034	45.949	100.576

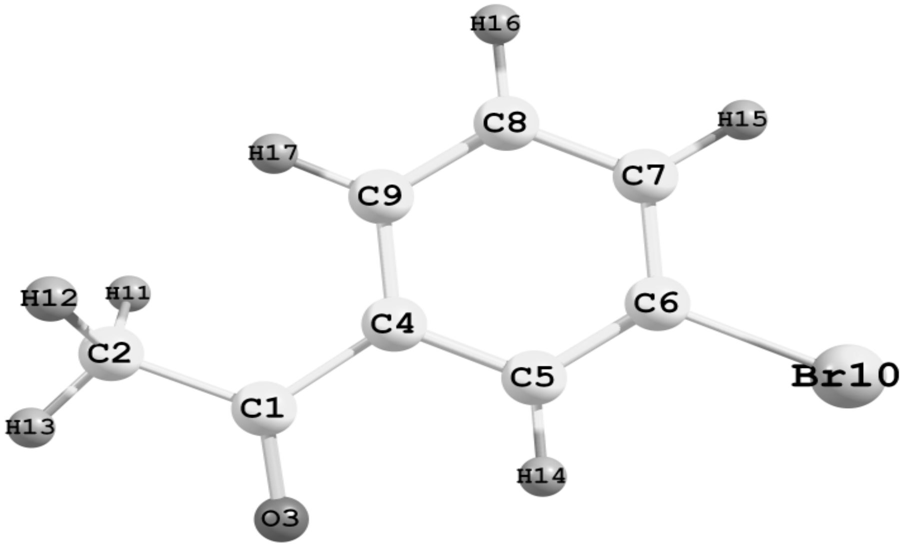
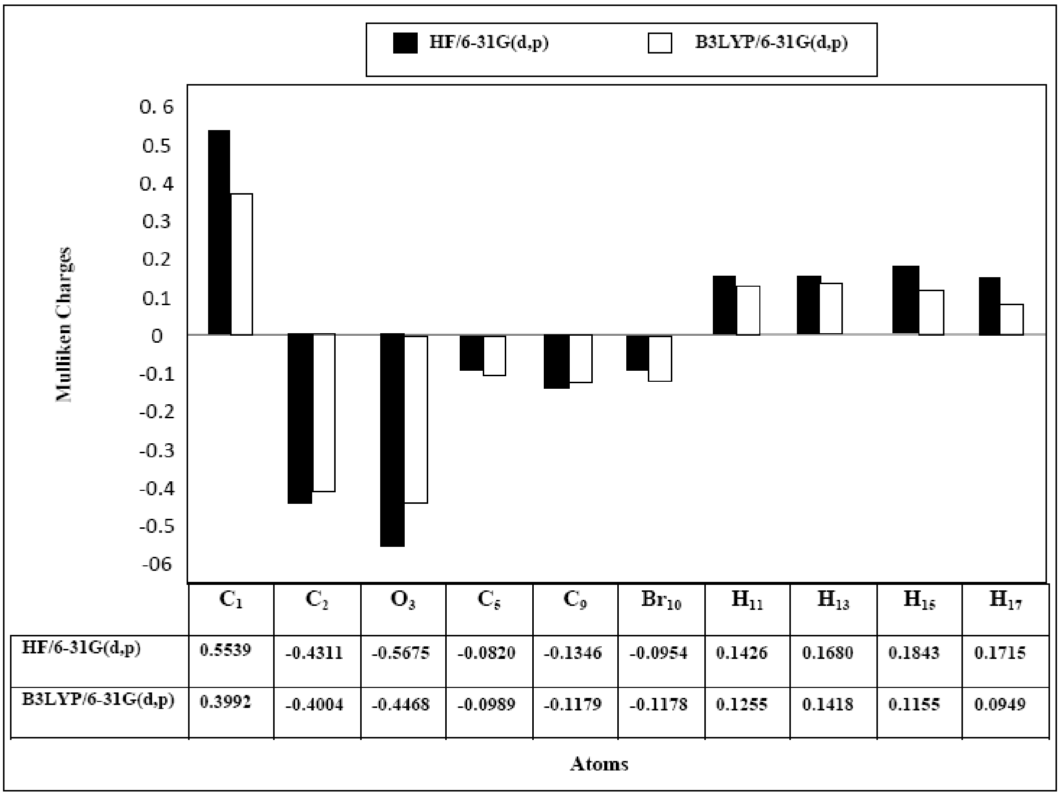


Fig. 1 The atom numbering for 3-bromoacetophenone molecule



	C_1	C_2	O_3	C_5	C_9	Br_{10}	H_{11}	H_{13}	H_{15}	H_{17}
HF/6-31G(d,p)	0.5539	-0.4311	-0.5675	-0.0820	-0.1346	-0.0954	0.1426	0.1680	0.1843	0.1715
B3LYP/6-31G(d,p)	0.3992	-0.4004	-0.4468	-0.0989	-0.1179	-0.1178	0.1255	0.1418	0.1155	0.0949

Fig. 2 Comparision of HF/6-31G(d,p) and B3LYP/6-31G(d,p) methods for calculated atomic charges

Mulliken charges

In the application of quantum mechanical calculations to molecular system, the calculation of effective atomic charges plays an important role. The electron distribution in 3-

bromoacetophenone are compared in two different quantum mechanical methods and the sensitivity of the calculated charges to change in the choice of methods are studied. By determining the electron population of each atom in the defined basis function, the Mulliken charges are calculated. The calculated Mulliken charges at different levels are listed in table 5. The results can be represented in graphical form as given in fig 2.

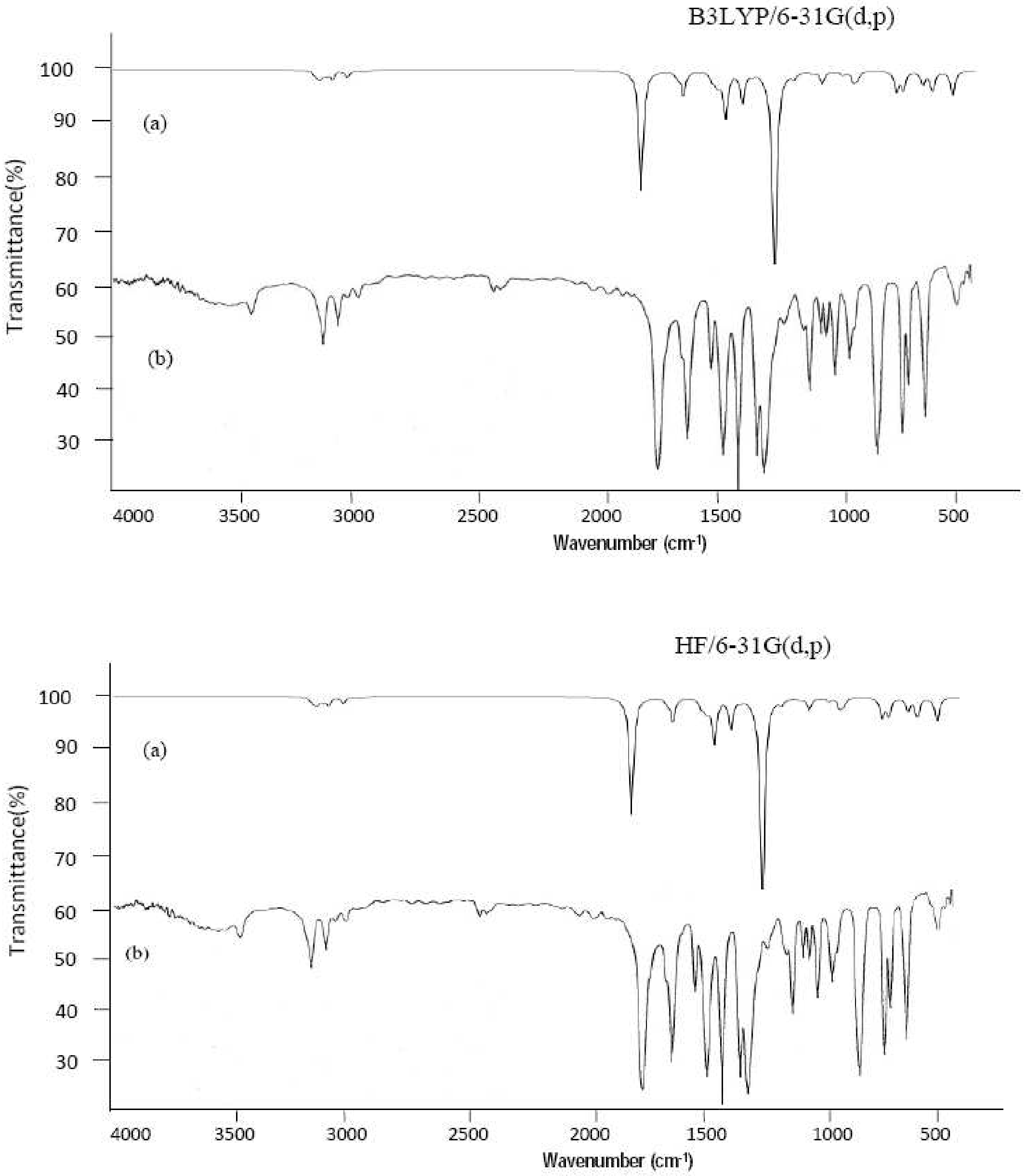


Fig.3 FTIR spectra of 3-bromoacetophenone (a) calculated and (b) observed

Thermodynamic properties

On the basis of vibrational analysis at B3LYP/ 6-31G(d,p) and HF/6-31G(d,p) levels, several thermodynamic parameters are calculated and are presented in Table 6 . The zero point vibration energy (ZPVE) and the entropy, S $_{vib}$ (T) are calculated to the extent of accuracy and the variations in ZPVE seem to be insignificant. The total energy and the change in the total entropy of 3-bromoacetophenone at room temperature at different methods are only marginal.

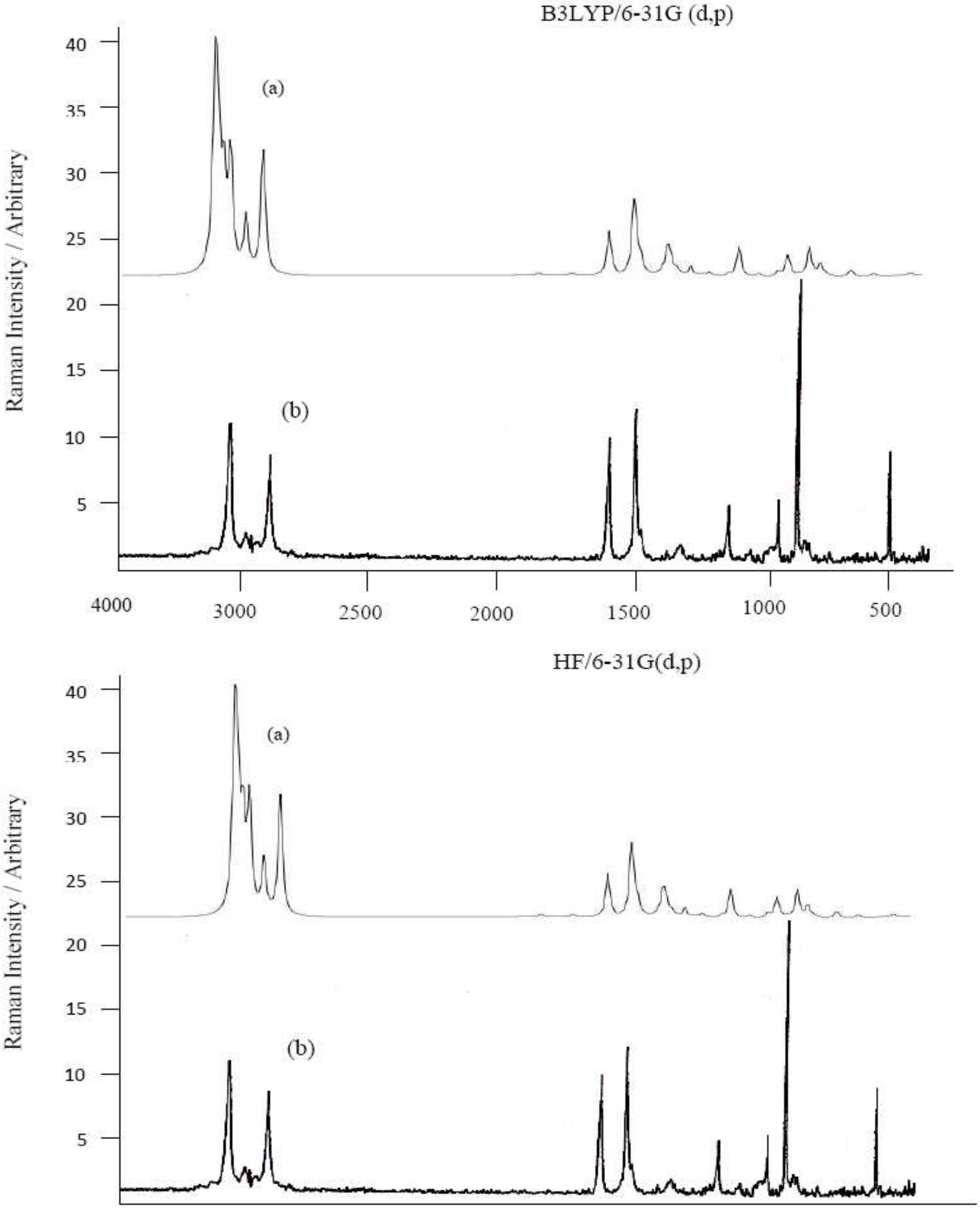


Fig.4 FTRaman spectra of 3-bromoacetophenone (a) calculated and (b) observed

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Molecular polarizability

One of the objectives of the present investigation is to study the effect of the basis sets B3LYP/6-31G(d,p) and HF/6-31G(d,p) levels on molecular polarizability of 3-bromo acetophenone using the Gaussian03W program. In this study, the computation of the molecular polarizability of 3-bromo acetophenone was reported. Here, α is a second-rank tensor property called the dipole polarizability and mean polarizability $< \alpha >$ is evaluated using the eqn. [50]

$$<\alpha>= 1/3\ (\alpha_{xx} + \alpha_{yy} + \alpha_{zz})$$

The calculated polarizabilities using HF and DFT methods for the 3-bromoacetophenone molecule are summarized in Table 7.

CONCLUSION

The results of the study lead to the following conclusions. (i) The proper frequency assignments for the compound 3-bromoacetophenone is performed for the first time from the FTIR and FT Raman spectra. The experimental FTIR and FT Raman spectra were compared with the theoretical ab initio and DFT calculations of the vibrational spectra of the molecule. (ii) The equilibrium geometries of 3-bromoacetophenone was determined and analyzed both at HF and DFT levels of theories utilizing 6-31G(d, p) basis set. The molecular geometry of 3-bromoacetophenone was best at the B3LYP level of DFT. (iii) The HOMO-LUMO energy gap and other related molecular properties were discussed and reported. (iv) Mulliken charges and molecular polarizability were calculated and the results were discussed.

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