

Theoretical and experimental studies of vibrational spectra and thermodynamical analysis of 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone

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Abstract Quantum chemical calculations of molecular geometries, vibrational wavenumbers and thermodynamical properties of 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone were carried out using Hartree-Fock (HF) and density functional theory (DFT) using hybrid functional B3LYP with 6-31 G (d,p) as basis set. The optimized geometrical parameters obtained by HF and DFT calculations are in good agreement with the experimental FTIR and FT Raman spectral data. 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 Ab initio and DFT · 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone · FTIR and FT Raman spectra · Vibrational analysis

Introduction

Substituted propiophenones have tremendous pharmaceutical applications. A derivative, 3'-bromopropiophenone

thiosemicarbazone, inhibited cruzain and could cure mammalian cell cultures infected with *Trypanosoma cruzi* [1]. Chemically 3'-bromopropiophenone is called 1-(3-bromophenyl)-1-propanone. Certain special ethyl esters used as intermediate to prepare novel pyrazole derivatives which are antagonists of CCR-2 receptor and/or CCR-5 (Chemokine Receptor 2/Monocyte chemotactic protein 1 receptor Chemokine Receptor 5) and can be used as medicament have been synthesized from 3'-bromopropiophenone [2, 3]. 3'-bromopropiophenone is used to prepare α -Bromo-3'-bromopropiophenone an intermediate compound for the invention of N-aminoimidazole and N-aminoimidazole thione derivatives. The compound has Human Immunodeficiency Virus (HIV) replication inhibiting properties. It is also used in the manufacture of a medicament useful for the treatment of subjects suffering from HIV infection, as well as for treatment of other viral, retroviral or lentiviral infections [4]. Similarly the other compound 4'-bromo-3-chloropropiophenone is chemically called 1-(4-bromophenyl)-3-chloro-1-oxopropane. It is used to prepare macrocyclic compounds for diagnostic, research, and therapeutic use [5]. It is also used to invent nitrogenous compounds and combinations thereof, that have a central aromatic, alicyclic, or heterocyclic ring system that is substituted with at least two linear groups, and which contain a plurality of nitrogenous moieties which are useful inter alia for antibacterial pharmaceutical use. They are also useful for identifying metal chelating species for "heavy metal" therapy, as well as for industrial application [6]. 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 [7, 8] have shown promising conformity with experimental results. Therefore, in this present investigation ab initio and

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DFT techniques are employed to study the complete vibrational spectra of the title compounds and to identify the various normal modes with greater wave number accuracy.

Several other investigations have been carried out on the title compounds and its derivatives [9–12]. Literature survey reveals that to the best of our knowledge no ab initio HF/DFT frequency calculations of 1-(3-bromophenyl)-1-propanone and 1-(4-bromophenyl)-3-chloro-1-oxopropane has 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 vapor 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 on 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone have been performed to support our wave number assignments.

Experimental details

The compounds 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone were purchased from Sigma-Aldrich Chemical Company, USA with more than 98% purity and were used as such without further purification to record FTIR and FT Raman spectra. A projection of 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone are shown in Figs. 1, 2. The FTIR spectra of the compounds are recorded in the region $4000 - 400 \text{ cm}^{-1}$ in evacuation mode on Bruker IFS 66 V 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 $3500 - 100 \text{ cm}^{-1}$ on Bruker IFS 66 V 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'-bromopropiophenone and 4'-bromo-3-chloropropiophenone are presented in Figs. 3, 4, 5 and 6.

Method of calculation

The Hartree-Fock (HF) and DFT calculations were performed on a Pentium IV personal computer using the Gaussian 03 W package [13] program together with the 6-

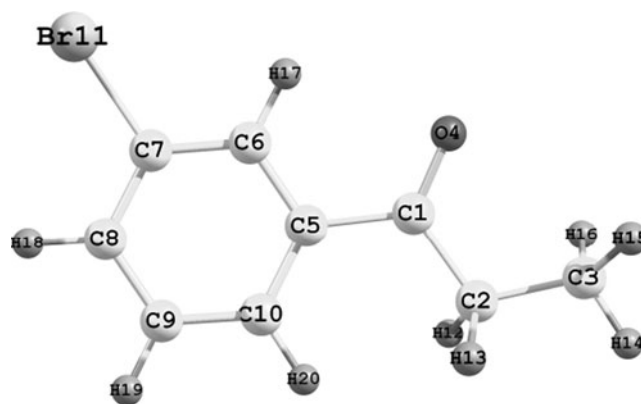


Fig. 1 The atom numbering for 3'-bromopropiophenone molecule

31 G(d,p) basis set function of the density functional theory (DFT) utilizing gradient geometry optimization [14]. The geometries were first determined at the Hartree Fock level of theory employing 6-31 G(d,p) basis set. All the geometries were then optimized using 6-31 G(d,p) basis sets using density functional theory (DFT) [15] employing the Becke's three-parameter hybrid functional [16] combined with Lee-Yang-Parr correlation [17] 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 [18]. 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'-bromopropiophenone and 4'-bromo-3-chloropropiophenone were used for harmonic vibrational frequency calculations resulting in IR and Raman frequencies. The DFT hybrid B3LYP functional also tends to overestimate the fundamental modes in

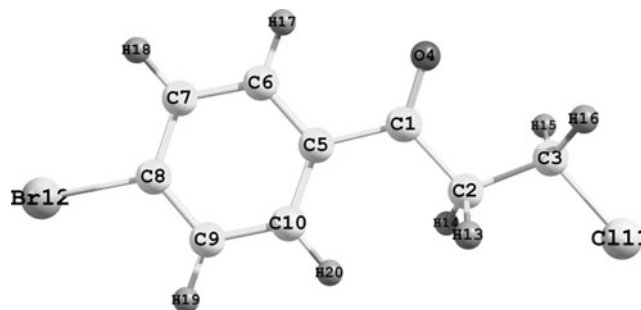
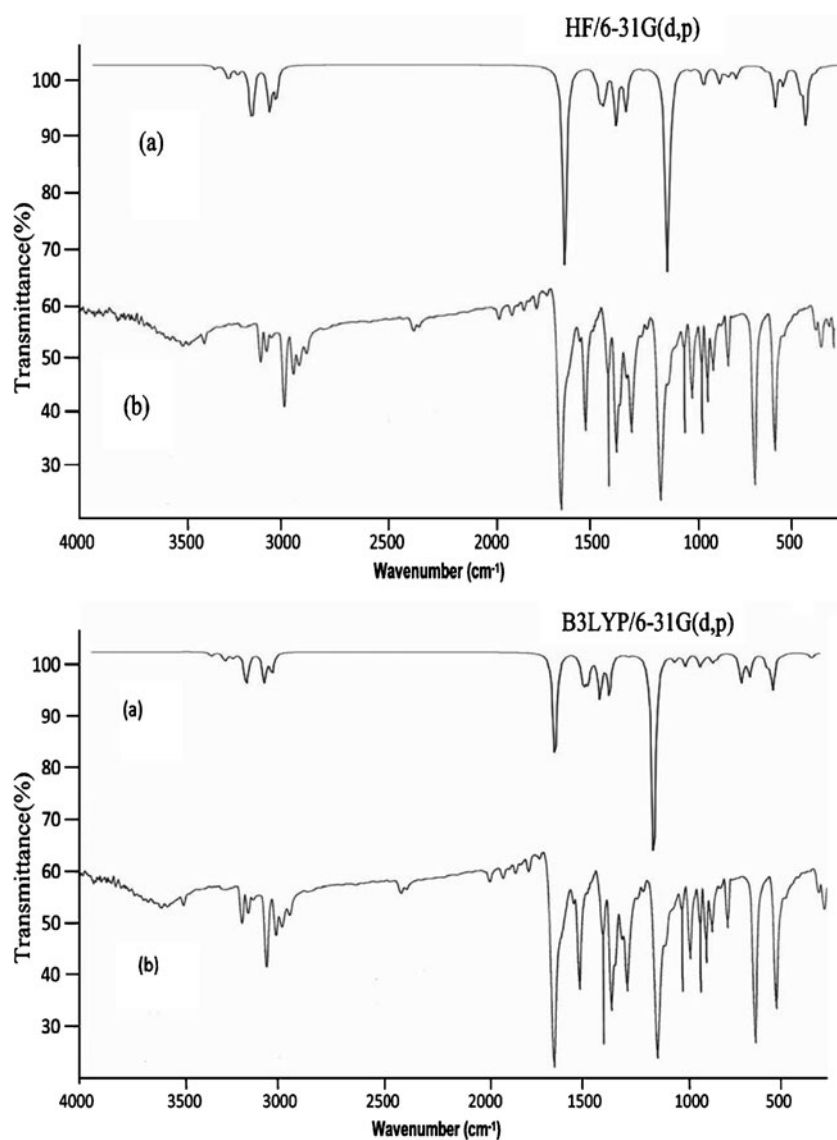


Fig. 2 The atom numbering for 4'-bromo-3-chloropropiophenone molecule

Fig. 3 FTIR Spectra of 3'-bromopropiophenone (a) Calculated and (b) Observed



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 [19], a scaling factor of 0.963 has been uniformly applied to the B3LYP calculated wave numbers. Similarly, the vibrational modes studies through HF method were scaled by a value of 0.891 [20]. 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 [21] with symmetry considerations, vibrational frequency assignments were made with a high degree of accuracy. There is always some ambiguity in defining internal coordination. However, the defined coordinate forms a complete set and matches quite well with the

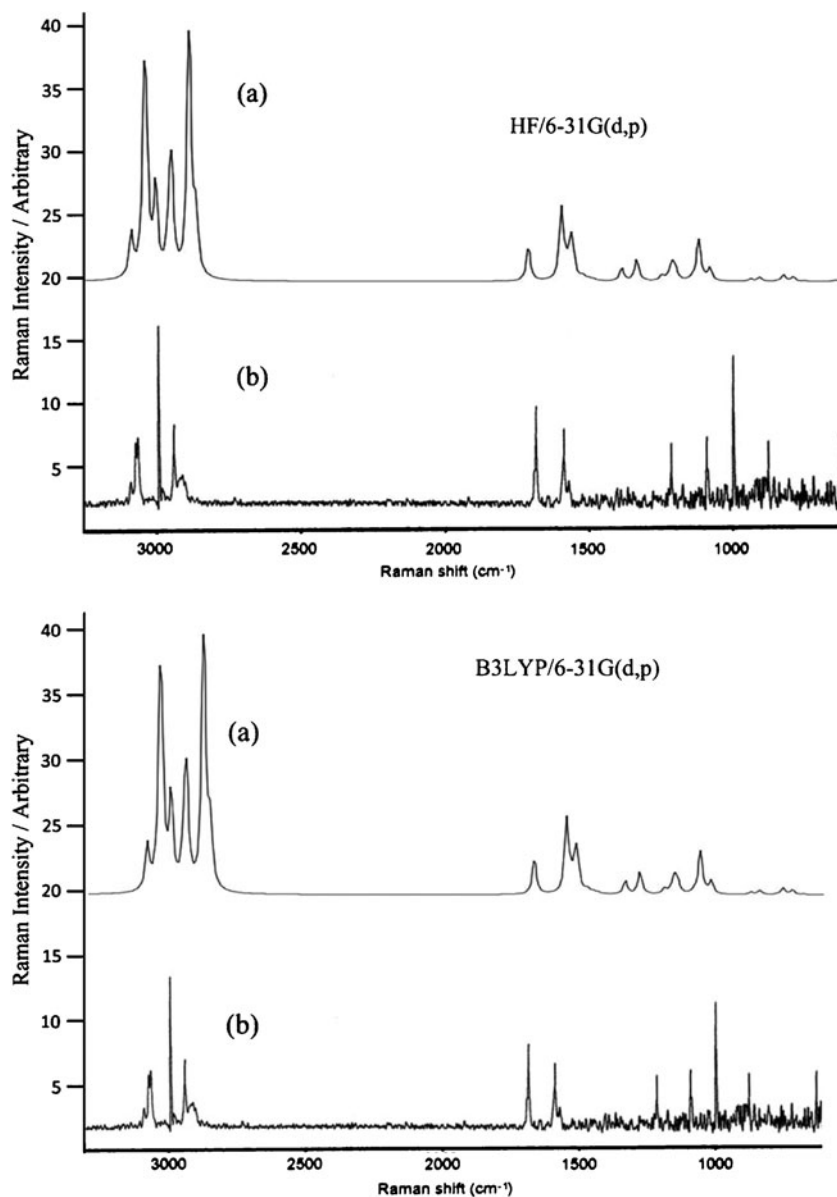
motions observed using the Gaussview program. To achieve a close agreement between observed and calculated frequencies, the least square fit refinement algorithm was used. For the plots of simulated IR and Raman spectrum, pure Lorentzian band shapes were used with a bandwidth of 10 cm^{-1} .

Results and discussion

Molecular geometry

The optimized structure parameters of 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone calculated by ab initio HF and DFT-B3LYP levels with the 6-31 G(d,p) basis set are listed in the Table 1 in accordance with the atom

Fig. 4 FT Raman Spectra of 3'-bromopropiophenone (a) calculated and (b) observed



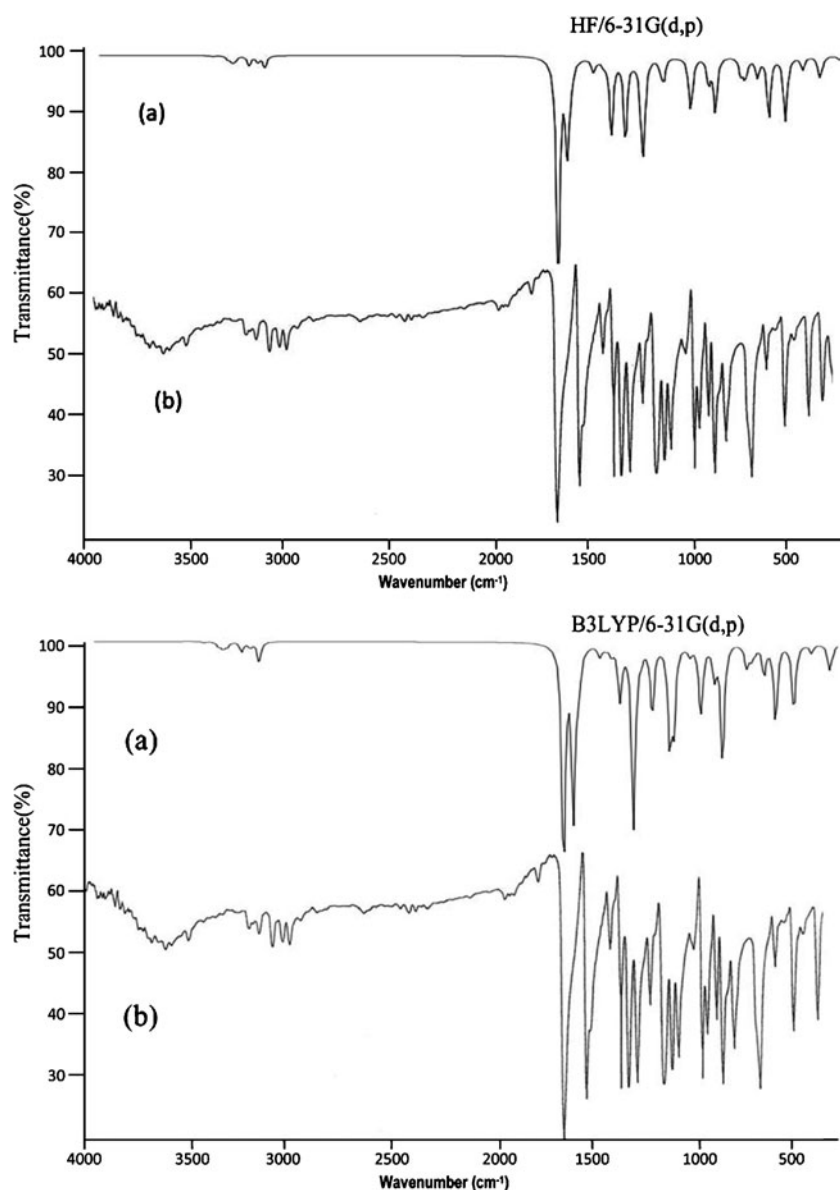
numbering scheme given in Figs.1, 2. The molecular structure, XRD studies have been studied for the compounds *m*-chloroacetophenone and *m*-nitroacetophenone. Since the compounds chosen for the present study has close structural relation with the above-mentioned compounds, the molecular parameters have been taken from *m*-chloroacetophenone and *m*-nitroacetophenone [22, 23]. Table 1 compares the calculated bond lengths and angles for 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone with those experimentally available from X-ray diffraction data [22, 23]. From the theoretical values, we can find that most of the optimized bond angles slightly vary from the experimental values, since 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 the higher side than the latter and the HF calculated values correlate 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'-bromopropiophenone and 4'-bromo-3-chloropropiophenone are performed on the basis

Fig. 5 FTIR Spectra of 4'-bromo-3-chloropropiophenone (a) calculated and (b) observed



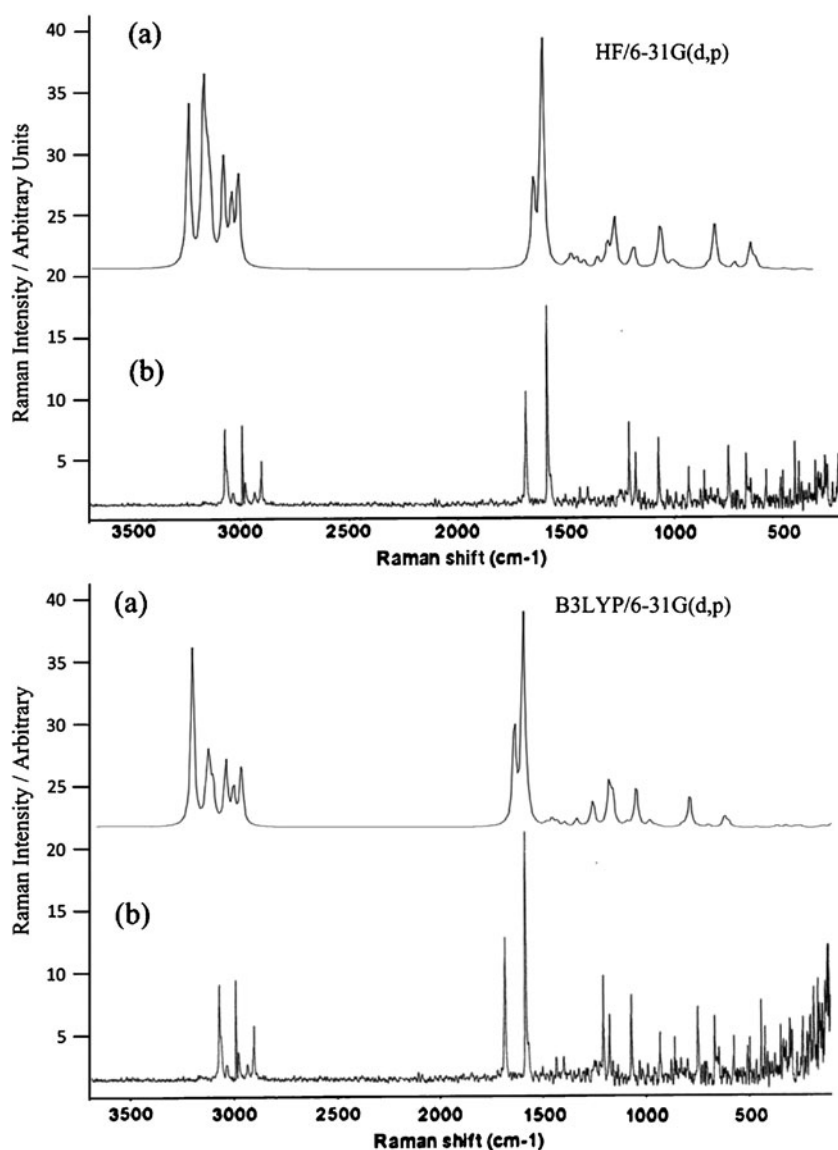
of the characteristic vibrations of carbonyl, methyl, bromo and chloro modes. The computed vibrational wavenumbers, their IR and Raman activities, corresponding to the different normal modes are used for identifying the vibrational modes unambiguously. The harmonic vibrational frequencies calculated for 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone at HF and B3LYP levels using the 6-31 G(d,p) basis set have been summarized in Table 2. 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 extent 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'-bromopropiophenone and 4'-bromo-3-chloropropiophenone

are presented in a common wavenumber scale in Figs. 3, 4, 5 and 6.

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 the 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 [24]. 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'-bromopropiophenone, the FTIR

Fig. 6 FT Raman spectra of 4'-bromo-3-chloropropiophenone (a) calculated and (b) observed



bands observed at 3212 cm^{-1} , 3194 cm^{-1} and FT Raman bands at 3224 cm^{-1} , 3195 cm^{-1} have been assigned to C-H asymmetric stretching vibration. Similarly the FTIR bands observed at 3031 cm^{-1} and FT Raman bands at 3027 cm^{-1} have been assigned to C-H symmetric stretching vibration.

The B3LYP level at 6-31 G(d,p) gives the same frequency values at $3227, 3195$ and 3029 cm^{-1} of Table 2. For the same vibration the HF/6-31 G(d,p) gives a slightly varying 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 [25–27] for di substituted benzene in the region $3200 - 2900\text{ cm}^{-1}$.

The other compound 4'-bromo-3-chloropropiophenone shows FTIR bands at 3220 and 3204 cm^{-1} and FT Raman bands at 3216 and 3210 cm^{-1} for C-H asymmetric stretching vibration.

The title compound 4'-bromo-3-chloropropiophenone has both out-of-plane and in-plane aromatic C-H bending vibrations. The out-of-plane bending mode of C-H vibration of 4'-bromo-3-chloropropiophenone is found well in agreement with the experimentally predicted [28] in the region $1000\text{--}600\text{ cm}^{-1}$. At B3LYP/6-31 G(d,p), it is observed in 979 and 866 cm^{-1} . The observed FTIR value of 978 cm^{-1} is in excellent agreement with 979 cm^{-1} of B3LYP/6-31 G(d,p) results. The out-of-plane C-H deformation vibrations of 3'-bromopropiophenone is experimentally predicted in the region 879 and 774 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 $1300\text{--}1000\text{ cm}^{-1}$ [29]. The C-H in plane bending vibrations assigned even though found to be contaminated by C-CH₃ stretch are found in literature [30, 31], while the experimentally

Table 1 Optimized geometrical parameters of 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone bond length(Å), Interaxial angles(°)

3'-bromopropiophenone				4'-bromo-3-chloropropiophenone			
Parameters	Experimental	HF/6-31 G (d,p)	B3LYP/6-31 G (d,p)	Parameters	Experimental	HF/6-31 G (d,p)	B3LYP/6-31 G (d,p)
C ₁₀ -H ₂₀	1.100	1.074	1.084	C ₁₀ -H ₂₀	1.100	1.074	1.085
C ₉ -H ₁₉	1.100	1.075	1.086	C ₉ -H ₁₉	1.100	1.073	1.084
C ₈ -H ₁₈	1.100	1.074	1.084	C ₇ -H ₁₈	1.100	1.073	1.084
C ₆ -H ₁₇	1.100	1.072	1.083	C ₆ -H ₁₇	1.100	1.073	1.085
C ₃ -H ₁₆	1.113	1.083	1.093	C ₃ -H ₁₆	1.113	1.077	1.089
C ₃ -H ₁₅	1.113	1.083	1.093	C ₃ -H ₁₅	1.113	1.077	1.089
C ₃ -H ₁₄	1.113	1.085	1.094	C ₂ -H ₁₄	1.113	1.086	1.097
C ₂ -H ₁₃	1.113	1.088	1.099	C ₂ -H ₁₃	1.113	1.086	1.097
C ₂ -H ₁₂	1.113	1.088	1.099	C ₅ -C ₁₀	1.394	1.390	1.403
C ₅ -C ₁₀	1.394	1.389	1.402	C ₉ -C ₁₀	1.394	1.385	1.393
C ₉ -C ₁₀	1.394	1.386	1.395	C ₈ -C ₉	1.394	1.381	1.394
C ₈ -C ₉	1.394	1.383	1.395	C ₇ -C ₈	1.394	1.385	1.396
C ₇ -C ₈	1.398	1.385	1.396	C ₆ -C ₇	1.394	1.381	1.390
C ₆ -C ₇	1.394	1.378	1.388	C ₅ -C ₆	1.394	1.392	1.404
C ₅ -C ₆	1.394	1.393	1.403	C ₈ -Br ₁₂	1.881	1.894	1.907
C ₇ -Br ₁₁	1.881	1.898	1.913	C ₃ -Cl ₁₁	1.795	1.797	1.817
C ₁ -C ₅	1.351	1.506	1.505	C ₁ -C ₅	1.351	1.499	1.496
C ₁ -O ₄	1.208	1.195	1.221	C ₁ -O ₄	1.208	1.196	1.223
C ₂ -C ₃	1.523	1.524	1.527	C ₂ -C ₃	1.523	1.519	1.521
C ₁ -C ₂	1.500	1.518	1.524	C ₁ -C ₂	1.509	1.519	1.526
H ₂₀ -C ₁₀ -C ₅	120.0	120.7	120.5	H ₂₀ -C ₁₀ -C ₅	120.0	120.9	120.7
H ₂₀ -C ₁₀ -C ₉	120.0	119.0	119.3	H ₂₀ -C ₁₀ -C ₉	120.0	118.4	118.6
C ₅ -C ₁₀ -C ₉	119.9	120.3	120.2	C ₅ -C ₁₀ -C ₉	119.9	120.7	120.7
H ₁₉ -C ₉ -C ₁₀	120.0	120.0	120.1	H ₁₉ -C ₉ -C ₁₀	120.0	120.6	120.8
H ₁₉ -C ₉ -C ₈	120.0	119.6	119.5	H ₁₉ -C ₉ -C ₈	120.0	120.3	120.2
C ₁₀ -C ₉ -C ₈	119.9	120.3	120.5	C ₁₀ -C ₉ -C ₈	119.9	119.1	119.1
H ₁₈ -C ₈ -C ₉	119.9	120.7	120.9	C ₉ -C ₈ -C ₇	120.0	121.3	121.3
H ₁₈ -C ₈ -C ₇	119.9	120.2	120.2	C ₉ -C ₈ -Br ₁₂	119.9	119.3	119.3
C ₉ -C ₈ -C ₇	120.0	119.1	119.0	C ₇ -C ₈ -Br ₁₂	119.9	119.3	119.4
C ₈ -C ₇ -C ₆	120.0	121.3	121.4	H ₁₈ -C ₇ -C ₈	119.9	120.2	120.1
C ₈ -C ₇ -Br ₁₁	119.9	119.2	119.1	H ₁₈ -C ₇ -C ₆	119.9	120.7	120.9
C ₆ -C ₇ -Br ₁₁	119.9	119.5	119.5	C ₈ -C ₇ -C ₆	120.0	119.0	119.0
H ₁₇ -C ₆ -C ₇	120.0	121.1	121.7	H ₁₇ -C ₆ -C ₇	120.0	120.3	120.8
H ₁₇ -C ₆ -C ₅	120.0	119.3	118.8	H ₁₇ -C ₆ -C ₅	120.0	118.9	118.3
C ₇ -C ₆ -C ₅	119.9	119.6	119.6	C ₇ -C ₆ -C ₅	119.9	120.8	120.9
C ₁₀ -C ₅ -C ₆	120.0	119.4	119.5	C ₁₀ -C ₅ -C ₆	120.0	119.1	119.0
C ₁₀ -C ₅ -C ₁	119.9	123.1	123.1	C ₁₀ -C ₅ -C ₁	119.9	122.9	123.0
C ₆ -C ₅ -C ₁	119.9	117.5	117.4	C ₆ -C ₅ -C ₁	119.9	118.0	118.0
H ₁₆ -C ₃ -H ₁₅	109.5	107.6	107.2	H ₁₆ -C ₃ -H ₁₅	109.5	108.9	108.6
H ₁₆ -C ₃ -H ₁₄	109.4	108.5	108.5	H ₁₆ -C ₃ -Cl ₁₁	109.4	106.9	107.0
H ₁₆ -C ₃ -C ₂	109.4	111.0	111.0	H ₁₆ -C ₃ -C ₂	109.4	111.8	111.7
H ₁₅ -C ₃ -H ₁₄	109.4	108.5	108.5	H ₁₅ -C ₃ -Cl ₁₁	109.4	106.9	107.0
H ₁₅ -C ₃ -C ₂	109.4	111.0	111.0	H ₁₅ -C ₃ -C ₂	109.4	111.8	111.7
H ₁₄ -C ₃ -C ₂	109.5	110.1	110.5	Cl ₁₁ -C ₃ -C ₂	109.5	110.3	110.6
H ₁₃ -C ₂ -H ₁₂	109.5	106.1	105.4	H ₁₄ -C ₂ -H ₁₃	109.5	106.7	106.1
H ₁₃ -C ₂ -C ₃	109.4	110.5	110.8	H ₁₄ -C ₂ -C ₃	109.4	110.1	110.2

Table 1 (continued)

3'-bromopropiophenone				4'-bromo-3-chloropropiophenone			
Parameters	Experimental	HF/6-31G (d,p)	B3LYP/6-31G (d,p)	Parameters	Experimental	HF/6-31G (d,p)	B3LYP/6-31G (d,p)
H ₁₃ -C ₂ -C ₁	109.4	108.3	108.2	H ₁₄ -C ₂ -C ₁	109.4	109.2	109.4
H ₁₂ -C ₂ -C ₃	109.4	110.5	110.8	H ₁₃ -C ₂ -C ₃	109.4	110.1	110.2
H ₁₂ -C ₂ -C ₁	109.4	108.2	108.2	H ₁₃ -C ₂ -C ₁	109.4	109.3	109.4
C ₃ -C ₂ -C ₁	109.5	112.9	113.0	C ₃ -C ₂ -C ₁	109.5	111.2	111.3
C ₅ -C ₁ -O ₄	120.0	119.9	120.2	C ₅ -C ₁ -O ₄	120.0	120.6	120.9
C ₅ -C ₁ -C ₂	120.0	118.9	118.8	C ₅ -C ₁ -C ₂	120.0	118.9	118.8
O ₄ -C ₁ -C ₂	120.0	121.2	121.0	O ₄ -C ₁ -C ₂	120.0	120.5	120.3

observed values for 3'-bromopropiophenone is at 1247 cm⁻¹. The C-H in-plane bending vibration of 3'-bromopropiophenone coincides satisfactorily with the experimentally observed values in this region.

C-Br Vibration

The compound under consideration 3'-bromopropiophenone has a bromine substitution in the meta position and the compound 4'-bromo-3-chloropropiophenone has a bromine substitution in the para position. The heavier mass of bromine obviously makes the C-Br stretching mode appear in the longer wavelength region. In 3'-bromopropiophenone the assigned 401 cm⁻¹ is in agreement with the range 200–400 cm⁻¹ as reported by Kurt et al. [32]. Sundaraganesan et al. has assigned 511 cm⁻¹ for C-Br stretching [33]. In view of the above 507 cm⁻¹ has been assigned for 4'-bromo-3-chloropropiophenone as C-Br stretching. Varsanyi assigned [34] the C-Br in-plane bending mode at 275 cm⁻¹. Based on the above the C-Br in-plane bending is assigned at 293 cm⁻¹ for 4'-bromo-3-chloropropiophenone. Sundaraganesan et al. has assigned C-Br in-plane bending at 330 cm⁻¹ and at 208 cm⁻¹ out-of-plane bending [33]. In the above view 312 cm⁻¹ has been assigned as in-plane bending for 3'-bromopropiophenone and 205 cm⁻¹ as out-of-plane bending for 4'-bromo-3-chloropropiophenone. All the above vibrations agree well with the experimental results.

Methyl group vibrations

The compound under consideration 3'-bromopropiophenone possess a CH₃ group in the side substitution chain. There are nine fundamentals one can expect to a CH₃ group, namely the symmetrical stretching in CH₃ (CH₃ sym.stretch) and asymmetrical stretching (in plane hydrogen stretching mode); the symmetrical (CH₃ sym.deform) and asymmetrical (CH₃ asym.deform) deformation modes; in-plane rocking, out-of-plane rocking,

twisting and bending modes [35]. 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 [36]. The theoretically computed values 3063 cm⁻¹ for CH₃ symmetric stretching and 3143, 3136 cm⁻¹ for CH₃ asymmetric stretching shows an excellent agreement with the range allotted by Williams and Fleming [37]. CH₃ in-plane-bending and out-of plane bending observed at 1616 and 1545 cm⁻¹ in FTIR and 1612 and 1542 cm⁻¹ in Raman agree well with theoretically computed values. The torsion vibrations are not observed in the FTIR and FT Raman spectrum because these appear at very low frequency. The observations at 38 cm⁻¹ in 3'-bromopropiophenone is in agreement with theoretical results of similar compounds.

C = O vibrations

The characteristic infrared absorption frequencies of carbonyl group in ketones are normally strong in intensities and found in the region 1685 – 1660 cm⁻¹. The carbon-oxygen double bond formed by p_π - p_π between carbon and oxygen. Because of the different electronegativity of carbon and oxygen atom, the bonding electrons are not equally distributed between the two atoms. The lone pair of electrons on oxygen also determine the nature of carbonyl group [38]. The C-O stretching vibration has been assigned as 1620 cm⁻¹ by Gunasekaran et al. [35]. Based on the above the C-O stretching vibration in 4'-bromo-3-chloropropiophenone has been assigned a computed frequency of 1683 cm⁻¹. This is in agreement with strong experimental frequency in FTIR spectrum at 1684 cm⁻¹ and 1682 cm⁻¹ in Raman spectrum. The C-O out-of-plane bending mode with the theoretical frequency of 155 cm⁻¹ agrees well with the experimental Raman value. Sang Yeon Lee assigned 1721 cm⁻¹ for the C-O stretching [39]. Hence 1777 cm⁻¹ has been assigned as C-O stretching for 3'-bromopropiophenone.

Table 2 Vibrational wavenumbers obtained for 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone at HF/6-31 G(d,p), B3LYP/6-31 G(d,p) and observed IR and Raman wavenumbers [harmonic frequency (cm^{-1})]

3'-bromopropiophenone				4'-bromo-3-chloropropiophenone					
Calculated wavenumbers (cm^{-1})		Observed wavenumbers (cm^{-1})		Assignment	Calculated wavenumbers (cm^{-1})		Observed wavenumbers (cm^{-1})		Assignment
HF	B3lyp	IR	Raman		HF	B3lyp	IR	Raman	
35	38			CH ₃ torsion	32	32			γ ring
93	92		102	β C-H	63	65			ρ CH ₂
120	122		120	Lattice vibration	67	68			LatticeVibration
158	155		159	γ C = O + β C-H	84	85			γ C = O + γ CH ₂
203	202		204	CH ₃ torsion + γ C-H	101	104		103	ρ CH ₂
229	228		221	CH ₃ torsion	179	183		183	γ C-Cl + β C-Br
244	244		251	γ C-Br	210	205		203	γ C-Br
314	312		310	β C-Br	247	252		248	γ ring + ρ CH ₂
342	343		343	lattice vibration	293	293		291	β C-Br
399	401	403	406	ν C-Br	298	297		301	β C- Cl + γ C-Br
464	464	460	469	γ C-H	422	421	425	424	Lattice vibration
524	524	521	526	CH ₂ rocking	452	452	449	452	γ C-H
527	530	534	532	β C-C-C	496	492	496	490	γ C-H + ρ CH ₂
655	661	654	659	CH ₂ rocking	510	507	520	497	ν C-Br
699	700		701	ring breathing	586	584	558	584	ρ CH ₂ + γ C = O
738	739	731	732	Lattice vibrat + γ C-Br	640	642	640	647	β C-C
763	764	774	764	γ C-H	664	661	664	667	ν C-Cl + ν C-C
836	837	836	838	τ ring	738	734	727	728	ρ CH ₂
871	873	879	876	γ C-H	742	740	748	738	ν C-Cl
912	914	897	915	CH ₂ rocking	789	790	772	798	ρ CH ₂
1039	1034	1041	1039	γ C-H	831	830	814	830	ν C-C
1056	1061	1065	1069	γ C-H	844	847	836	847	γ C-H + β CH ₂
1071	1079	1083	1076	ν C-C	863	866	858	862	γ C-H
1085	1084	1091	1089	γ C-H	977	979	978	970	γ C-H
1112	1114	1103	1117	ring breathing	998	994	988	991	ν C-C
1124	1132	1139	1136	γ C-H	1006	1005	1006	1004	γ C-H + ρ CH ₂
1179	1181	1182	1184	CH ₂ twisting	1022	1023	1024	1020	ρ CH ₂
1192	1193	1189	1189	β C-H	1033	1028	1028	1030	γ C-C
1194	1197	1192	1197	ν C-C + CH ₃ wagging	1080	1084	1068	1086	ν C-C
1207	1211	1215	1213	β C-H	1089	1091	1096	1099	ν C-C
1236	1240	1247	1249	β C-H	1135	1135	1137	1136	β C-H
1322	1329	1325	1327	γ C-H	1156	1153	1172	1159	CH ₂ twisting
1338	1338	1350	1339	CH ₂ twisting	1208	1205	1203	1205	δ C-H
1399	1400	1403	1402	β C-H	1223	1223	1239	1225	ν C-C + γ CH ₂
1439	1436	1422	1433	ν C-C	1299	1299	1284	1291	CH ₂ wagging
1514	1518	1520	1516	CH ₂ wagging	1309	1306	1303	1301	CH ₂ twisting
1535	1540	1545	1542	CH ₃ wagging	1332	1331	1329	1336	β C-H
1558	1559	1564	1554	β C-H	1346	1348	1357	1350	ν C-C
1597	1598	1590	1594	δ CH ₂	1379	1380	1395	1382	CH ₂ wagging
1605	1607	1604	1605	CH ₃ twisting	1442	1438	1431	1435	ν C- C + β C-H
1610	1610	1611	1611	β C-H	1476	1476	1480	1465	δ CH ₂
1614	1612	1616	1612	δ CH ₃	1502	1501	1502	1502	δ CH ₂
1627	1627	1624	1620	ν C-C	1523	1526	1526	1529	ρ C-H

Table 2 (continued)

3'-bromopropiophenone				4'-bromo-3-chloropropiophenone					
Calculated wavenumbers (cm ⁻¹)		Observed wavenumbers (cm ⁻¹)		Assignment	Calculated wavenumbers (cm ⁻¹)		Observed wavenumbers (cm ⁻¹)		Assignment
HF	B3lyp	IR	Raman		HF	B3lyp	IR	Raman	
1644	1642	1639	1638	ν C-C	1620	1616	1596	1606	ν C-C
1779	1777	1774	1770	ν C = O	1639	1641	1646	1643	ν C-C
3029	3029	3031	3027	ν_s CH ₂	1680	1683	1684	1682	ν C = O
3056	3061	3049	3060	ν_{as} CH ₂	3059	3052	3062	3058	ν_s CH ₂
3061	3063	3063	3068	ν_s CH ₃	3091	3090	3087	3104	ν_{as} CH ₂
3129	3136	3135	3137	ν_{as} CH ₃	3129	3127	3120	3122	ν_s CH ₂
3140	3143	3144	3149	ν_{as} CH ₃	3191	3189	3192	3182	ν_{as} CH ₂
3194	3195	3194	3195	ν C-H	3204	3209	3204	3210	ν CH
3229	3227	3212	3224	ν C-H	3218	3217	3220	3216	ν CH
3240	3234	3237	3233	ν C-H	3224	3228	3231	3229	ν CH
3294	3287	3305	3285	ν C-H	3292	3290	3281	3288	ν CH

Abbreviations used τ - torsion; γ - out of plane bending; β - in plane bending; ρ - rocking; δ - scissoring; ν - stretching; ν_s , symmetric stretching; ν_{as} - asymmetric stretching

C-Cl vibrations

The title compound 4'-bromo-3-chloropropiophenone has a chloro group in the side substitution chain. The C-Cl stretching vibrations give generally strong bands in the region 710-505 cm⁻¹ [40]. Dong Jin Pyo et al. observed C-Cl vibrations in the range 800-600 cm⁻¹ [41]. The C-Cl stretching vibration of 4'-bromo-3-chloropropiophenone observed at 740 cm⁻¹ is in agreement with the literature [42]. The C-Cl out-of-plane and in-plane bending vibrations, vibrationally coupled with other groups observed at

183 cm⁻¹ and 297 cm⁻¹ agree well with experimental values and are found in literature [40].

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 [43–45]. The IR bands are 1646, 1596, 1431 cm⁻¹ ; the Raman bands are 1643, 1606 and 1435 cm⁻¹ for 4'-bromo-3-chloropropiophenone. Similarly the other compound 3'-

Table 3 Theoretically computed energies (a.u.), zero-point vibrational energies (kcalmol⁻¹), rotational constants (GHz), entropies (calmol⁻¹ K⁻¹) and Dipole moment (D) of 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone

3'-bromopropiophenone			4'-bromo-3-chloropropiophenone	
Parameters	HF / 6-31 G(d,p)	B3LYP/6-31 G(d,p)	HF / 6-31 G(d,p)	B3LYP/6-31 G(d,p)
Total energy	-2990.83257950	-2995.3276610	-3449.7329360	-3454.9210791
Zero point energy	105.11791	98.25465	99.69037	92.90420
Rotational constants	1.93466	1.90190	2.26379	2.21547
	0.34424	0.34061	0.16498	0.16315
	0.29328	0.28990	0.15406	0.15225
Entropy				
Total	102.072	104.584	109.244	112.389
Translational	41.958	41.958	42.401	42.401
Rotational	31.776	31.815	32.991	33.035
Vibrational	28.338	30.811	33.852	36.953
Dipole moment	4.2233	3.7152	1.7243	1.9766

bromopropiophenone shows bands at 1639, 1624, 1422 cm^{-1} in IR and 1638, 1620 and 1433 cm^{-1} in Raman. Of these bands, 1620 in 3'-bromopropiophenone and 1641 cm^{-1} in 4'-bromo-3-chloropropiophenone 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 both in FTIR and FT Raman spectra of both title compounds. As is seen from Table 2 the predicted frequencies by both RHF and B3LYP agree well with the observed ones.

Other molecular properties

On the basis of vibrational analysis at B3LYP/6-31 G(d,p) and HF/6-31 G(d,p) levels, several thermodynamic parameters are calculated and are presented in Table 3. The zero point vibration energies (ZPVE) and the entropy, $S_{\text{vib}}(T)$ are calculated to the extent of accuracy and the variations in ZPVEs seem to be insignificant. The total energies and the change in the total entropy of 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone at room temperature at different methods are only marginal.

Thermodynamic properties

The prediction of thermodynamic and physical properties for organic compounds is vital for the design of chemical and petrochemical plants. Therefore, on the basis of HF/6-31 G(d,p) and B3LYP/6-31 G(d,p) vibrational analyses and statistical thermodynamics, the thermodynamic functions like translational, rotational, vibrational entropies, dipole moment, zero point energy, rotational constants of the compounds were obtained and are listed in Table 3. The prediction of zero point energy goes in accordance with Heisenberg's uncertainty principle. The translational entropy 41.958 $\text{cal mol}^{-1}\text{K}^{-1}$ in 3'-bromopropiophenone and 42.401 $\text{cal mol}^{-1}\text{K}^{-1}$ in 4'-bromo-3-chloropropiophenone indicates the fact that the translational entropy is directly proportional to the molecular weight of the compounds. Lighter hydrogen atom leads to lower vibrational entropy, which is indicated by 30.811 $\text{cal mol}^{-1}\text{K}^{-1}$ of B3LYP/6-31 G(d,p) in 3'-bromopropiophenone compared to 36.953 $\text{cal mol}^{-1}\text{K}^{-1}$ in 4'-bromo-3-chloropropiophenone where the lighter hydrogen is replaced by a chlorine atom. The total entropy increases with the size of a molecule, because the number of degrees of freedom increases with the number of atoms. Weakly bound solids have a larger total entropy than strongly bound solids as in accordance with the total entropy of 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone. It is evident from the melting point of 4'-bromo-3-chloropropiophenone which is greater than the

melting point of 3'-bromopropiophenone, the total entropy increases drastically with the increase in the melting point. The charge asymmetry is obtained as the dipole moment of the molecule and the greater dipole moment of 3'-bromopropiophenone is in accordance with the greater polarity of the bond.

Conclusions

Attempts have been made in the present work for the proper frequency assignments for the 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone from the FTIR and FT Raman spectra. The equilibrium geometries and harmonic frequencies of 3'-bromopropiophenone and 4'-bromo-3-chloropropiophenone were determined and analyzed both at HF and DFT levels of theories utilizing 6-31 G(d, p) basis set. The difference between observed and calculated wavenumber values of most of the fundamental modes is very small. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations have been actually done on a single molecule in the gaseous state contrary to the experimental values recorded in the presence of intermolecular interactions. Therefore, the assignments made at higher levels of theory with only reasonable deviations from the experimental values seem to be correct.

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