FT-IR, FT-Raman vibrational spectra and molecular structure investigation of 2-chloro-4-methylaniline: A combined experimental and theoretical study

Mehmet Karabacak [a,*], Dilek Karagöz [a], Mustafa Kurt [b]

[a] Department of Physics, Afyon Kocatepe University, 03040 Afyonkarahisar, Turkey
[b] Department of Physics, Ahi Evran University, 40100 Kırşehir, Turkey

ARTICLE INFO

ABSTRACT

In this work, the experimental and theoretical vibrational spectra of 2-chloro-4-methylaniline (2Cl4MA, C_7H_8NCl) were studied. FT-IR and FT-Raman spectra of 2Cl4MA in the liquid phase have been recorded in the region 4000–400 cm^{-1} and 3500–50 cm^{-1}, respectively. The structural and spectroscopic data of the molecule in the ground state have been calculated by using Hartree-Fock (HF) and density functional method (B3LYP) with the 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p) and 6-311G(d), 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p) basis sets. The vibrational frequencies have been calculated and scaled values have been compared with experimental FT-IR and FT-Raman spectra. The observed and calculated frequencies are found to be in good agreement. The complete assignments were performed on the basis of the total energy distribution (TED) of the vibrational modes, calculated with scaled quantum mechanics (SQM) method. The DFT-B3LYP/6-311++G(d,p) calculations have been found more reliable than the ab initio HF/6-311++G(d,p) calculations for the vibrational study of 2Cl4MA. The optimized geometric parameters (bond lengths and bond angles) were compared with experimental values of aniline and *p*-methylaniline molecules.

1. Introduction

Aniline is a molecular archetype of the aromatic amine. Aniline and its derivatives have been subjected to many different types of scientific studies up to now. They have been widely used for pharmaceutical manufacturing, electro-optical, chemical dye industries and for other commercial and industrial purposes, and have been studied extensively [1–3]. Some of the *para*-substituted derivatives of aniline are commonly used local anesthetics, and among these molecules the amino group plays an important role in the interactions with the receptor. Therefore, understanding of aniline and its derivative properties as well as the nature of reaction mechanics, extensive experimental [4] and theoretical investigations have focused on elucidating the structure and normal vibrations of aniline and its methyl derivatives [1–8]. Molecular geometry changes due to enhanced interaction between the amino group and the aromatic ring. The inclusion of a substituent group in aniline also leads to the variation of charge distribution in the molecule, and consequently this greatly affects the electronic, structural and vibrational parameters [9].

Vibrational assignment based FT-IR in the vapor, solution and liquid phases and the Raman spectra in the liquid state have been reported for aniline [10]. It is also known in the gas phase from microwave spectroscopy [11,12] and in the solid state from X-ray crystallography [13]. Its structure has been reported theoretically using semi-empirical [14,15], ab initio methods [14,16,17]. Extensive recent studies on vibrational spectra of substituted anilines assigned [1,5,8,18–20] complete vibrational mode and frequency analyses. Assignments of some bands observed in the infrared spectrum of *p*-methylaniline are given in literature [4,21–25]. Vibrational modes and frequency analyses of *m*-methylaniline have been studied by Altun et al. [1]. The vibrational spectra of fluoromethylaniline [26,27] and chloromethylaniline [27,28] have been reported. Shanker et al. [29] studied 2-chloro-6-methylaniline (2Cl6MA) with polarized Raman and infrared spectra.

In spite of recent studies on vibrational spectra of aniline and a number of substituted anilines, neither IR and Raman spectra nor the quantum mechanical calculations for 2Cl4MA molecule have been reported, so far. Therefore, we have undertaken the detailed theoretical and experimental investigation of the vibrational spectra of this molecule. Ab initio HF and density functional B3LYP calculations have been performed to support our assignment. A detailed interpretation of the vibrational spectra of 2Cl4MA has been made on the basis of the total energy distribution (TED).

* Corresponding author. Tel.: +90 272 2281311; fax: +90 272 2281235.
E-mail address: karabacak@aku.edu.tr (M. Karabacak).

Table 1
Calculated energies and energy difference for 2Cl4MA by HF and DFT (B3LYP) methods.

Basis set levels	HF		B3LYP	
	Energy (Hartree)	Energy differences[a] (kcal/mol)	Energy (Hartree)	Energy differences[a] (kcal/mol)
6-311++G(d,p)	−783.77493123	0.000	−786.63802693	0.000
6-311+G(d,p)	−783.77478208	0.094	−786.63792790	0.062
6-311G(d,p)	−783.76801875	4.338	−786.63088021	4.485
6-311G(d)	−783.75144863	14.736	−786.61517055	14.343
6-31++G(d,p)	−783.69473519	50.324	−786.54624631	57.593
6-31+G(d,p)	−783.69458208	50.420	−786.54610097	57.684
6-31G(d,p)	−783.68568689	56.002	−786.53167078	66.739
6-31G(d)	−783.66761116	67.344	−786.51585917	76.661

[a] Energies of the other basis sets relative to 6-311++G(d,p).

2. Experimental

The compound 2Cl4MA molecule was purchased from Acros Organics Company with a stated purity of 99%. The FT-IR spectrum of title molecule, being liquid at room temperature, was recorded between 4000 cm^{-1} and 400 cm^{-1} on a PerkinElmer FT-IR System Spectrum BX spectrometer calibrated using polystyrene bands. The spectrum was recorded with a scanning speed of 10 cm^{-1} min^{-1} and the spectral resolution of 4.0 cm^{-1}. FT-Raman spectra of the sample were recorded on a Bruker RFS 100/S FT-Raman instrument using 1064 nm excitation from an Nd:YAG laser. The detector is a liquid nitrogen cooled Ge detector. Five hundred scans were accumulated at 4 cm^{-1} resolution using a laser power of 100 mW.

3. Calculations

The molecular structure of 2Cl4MA in the ground state (*in vacuo*) is computed by performing both ab initio-HF and DFT/B3LYP with 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), and 6-311G(d), 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p) basis sets. The optimized structural parameters were used in the vibrational frequency calculations at HF and DFT levels. The minimum energy of geometrical structure is obtained by using level 6-311++G(d,p) basis sets. Therefore, we had discussion on calculated values by using these sets. The calculated vibrational frequencies are scaled by 0.9050 for HF [30]. For B3LYP with 6-311++G(d,p) basis set, the wavenumbers in the ranges from 4000 to 1700 cm^{-1} and lower than 1700 cm^{-1} are scaled with 0.958 and 0.983, respectively [31]. The total energy distribution was calculated by using the SQM program and the fundamental vibrational modes were characterized by their TED.

The theoretical results have enabled us to make the detailed assignments of the experimental IR and Raman spectra of title molecule. All the calculations are performed by using GaussView molecular visualisation program [32] and *GAUSSSIAN 03* program package on the personal computer [33].

4. Results and discussion

The molecule of 2Cl4MA, which has three substituents such that the chloro atom and methyl group are at *ortho-* and *para*-position, respectively, with respect to amino group attached to a planar benzene ring, consists of 17 atoms, so it has 45 normal vibrational modes. Its molecular structure has not been studied by any diffraction technique; therefore we have taken into account two different symmetries depending on the conformation of the NH$_2$ and CH$_3$ groups. In earlier theoretical studies of *p*-methylaniline, the existence of different rotamers with respect to torsion around C—CH$_3$ bond is possible due to small energy barrier between such rotamers, so two geometries have been completely optimized at different levels of calculations [6,25], two methyl hydrogen on the same side of the lone pair electrons of N (staggered form) and two methyl hydrogens on the same side of amino hydrogens (eclipsed form). The

energy difference as well as other geometry differences was found negligible. Recently, Tzeng and Narayanan [4] and Ballesteros et al. [6] have studied the conformations of aniline derivatives and they have concluded that the amino group has a negligible effect on the relative stability among the rotamers in the ground state. But our results are not similar to this conclusion due to chloro substitution. In the staggered and eclipsed form, 2Cl4MA molecule has imaginary frequencies.

On the basis of C$_s$ symmetry the 45 fundamental vibrations of 2Cl4MA can be distributed as 31A′ + 14A″. The vibrations of the A′ species are in-plane and those of the A″ species are out-of-plane. If we take into account C$_s$ symmetry of this molecule, there are two imaginary frequencies corresponding to NH$_2$ wagging and methyl rotation perpendicular to the ring plane (CH$_3$ torsion). NH$_2$ plane is also parallel to the ring plane. The structure at any level was not a minimum energy structure. Two possessed imaginary frequencies of irreducible representation belong to A″. But if the molecule was C$_1$ there would not be any relevant distribution and the molecule has true minimum energy (for example, E(HF) = −783.77311944 a.u., E(B3LYP) = −786.63764480 a.u. for C$_s$ symmetry and E(HF) = −783.77493123 a.u., E(B3LYP) = −786.63802693 a.u. for C$_1$ symmetry by using 6-311++G(d,p)). By using the same methods and the basis sets, it was seen that all the vibrational frequencies of 2Cl4MA were positive. Therefore, we were confident that a definite absolute minimum energy in the potential energy was found. The C$_1$ symmetry structure was the lowest in energy at all levels. The calculated energies and energy difference for title molecule, determined by HF and B3LYP level 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p) and 6-311G(d), 6-311G(d,p), 6-311+G(d,p), 6-311++G(d,p) basis sets are presented in Table 1. As clearly seen from the values given in Table 1, on the calculated energies, there is little difference between basis sets for 6-311 (or 6-31), use of the basis sets of larger sizes gives rise to increase
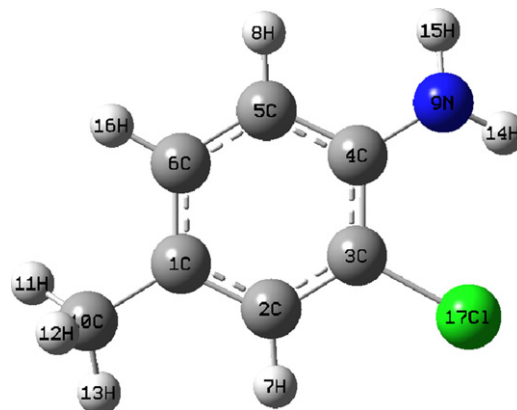

Fig. 1. Optimized geometry of 2Cl4MA structure and atoms numbering.

in the differences between the calculated energies of the title molecule. However, when we compared the 6-31 and 6-311 basis sets the difference was large.

The molecular structure and numbering of the atoms of 2Cl4MA molecule are shown in Fig. 1. The geometric parameters are compared with the aniline and *p*-methylaniline [4,12,20,25,34] bond lengths and bond angles. The calculated vibrational frequencies are compared with the experimental FT-IR and FT-Raman spectra of title molecule.

4.1. Geometrical structure

The first task for a computational work was to determine the optimized geometry of 2Cl4MA molecule. The optimized structure parameters calculated ab initio HF and DFT (B3LYP) with 6-31++G(d,p) and 6-311++G(d,p) basis sets are listed in Table 2 in accordance with the atom numbering scheme given in Fig. 1. As seen from the values given in Table 2, the increase in the basis set leads to a slight shortening of their values. Our calculated results show that the aromatic ring in 2Cl4MA is distorted from regular hexagon due to steric and electronic effects of electron donating and electron withdrawing substituted aniline.

To the best of our knowledge, experimental data on the geometric structure of 2Cl4MA are not available in the literature. Therefore, we could not compare the calculation results given in Table 2 with the experimental data. Only optimized geometric parameters of 2Cl4MA are compared to those of aniline and *p*-methylaniline [4,20,25,34].

Several authors [35,36] have explained the changes in frequency or bond length of the C—H bond on substitution due to a change in the charge distribution on the carbon atom of the benzene ring. The substituents may be either of the electron withdrawing type (F, Cl, and Br...) or of the electron donating type (CH$_3$, C$_2$H$_5$...). The carbon atoms are bonded to the hydrogen atoms with a σ bond in benzene and the substitution of a halogen for hydrogen reduces the electron density at the ring carbon atom. The ring carbon atoms in substituted benzenes exert a larger attraction on the valence electron cloud of the hydrogen atom resulting in an increase in the C—H force constant and a decrease in the corresponding bond length. The reverse holds well on substitution with electron donating groups. The actual change in the C—H bond length would be influenced by the combined effects of the inductive–mesomeric interaction and the electric dipole field of the polar substituent.

The equilibrium structure for the ground state shows that one of the methyl C—H bonds is parallel to the ring plane. In amino group, the nitrogen atom is slightly out-of-plane, with a torsional angle C2—C3—C4—N9 and C6—C5—C4—N9 in the ca. 177 (or ca. 3°). A measure of this displacement is defined as the tilt angle [20]. Existence of this angle has been interpreted to be caused by asymmetric interaction between the NH$_2$ group and benzene ring plane [17]. However, the X-ray angle value for this angle in aniline, 4.6° [13], is bigger than the theoretical value. This interaction is common to all aniline derivatives [4,19].

The optimized N—H bond length by HF and DFT with 6-311++G(d,p) method is 0.995 and 1.009 Å, respectively. By comparing these values with experimental value of 1.02 Å for *p*-methylaniline (1.07, 1.001, 1.021 Å for aniline), it is observed that B3LYP estimate the N—H bond length better than HF, which underestimate this bond than experimental values.

The optimized bond lengths of C—C in the ring in the range from 1.376 to 1.397 Å for HF, 1.387 to 1.405 Å for B3LYP with 6-311++G(d,p) methods which are in good agreement with *p*-methylaniline (1.36–1.40 Å) and 1.380–1.404 Å for aniline. The C4—N9 bond distance of ca. 1.39 Å is just 0.04 Å lower than the reported experimental value of 1.43 Å for *p*-methylaniline [4]. The C—CH$_3$ bond length is calculated underestimate for experimen-

tal value for the title molecule at all the levels. This bond length (C1—C10) the calculated value of ca. 1.51 Å is also found to deviate negatively only by 0.04 Å in comparison with the corresponding value in *p*-methylaniline [4].

The C—Cl bond length indicates a considerable increase when substituted in place of C—H. This has been observed even in benzene derivatives [37]. The C—Cl bond length is found to be 1.767 Å (B3LYP) and 1.752 Å (HF) by using 6-311++G(d,p). Bakiler et al. [38] calculated this bond length 1.746 Å for 3-Cl-pyridine and 1.748 Å for 2-Cl-pyridine by using force field calculations. Kurt et al. [39] calculated C—Cl bond length at 1.767 Å (B3LYP), 1.75 (HF) and 1.789 Å (BLYP) for 3-Cl-4MA. This bond length was also observed 1.735–1.744 Å range for similar molecules [40,41–44].

The asymmetry of the benzene ring is also evident from the negative deviation of C3—C4—C5 and C2—C1—C6 angles which are calculated ca. 116° and 117° (HF and B3LYP) and positive deviation of the remaining angles from the normal value of 120° (for example the C4–C5–C6 angle found to be bigger than ca. 2° hexagonal angles). Similar values were found to be other aniline derivatives which are *m*-methylaniline [1], *o*-methylaniline [7], *p*-methylaniline [4] and 3-Cl-4MA [39]. As discussed Ballesteros et al. [6] for *p*-methylaniline C2—C1—C10 is equal to the C6—C1—C10 angle, and C3—C4—N9 is equal to C5—C4—N9, and therefore no significant interaction between the methyl group and amino group exists as it occurs in the *m*-methylaniline and contrary to *o*-methylaniline where interaction exists between both groups. Our calculated values are 121.2° and 121.3° for C2—C1—C10 and C6—C1—C10, or 121.15° and 122.36° for C5—C4—N9 and C3—C4—N9, by using B3LYP/6-311++G(d,p), respectively. This clearly shows that the substitution of Cl group in place of hydrogen appreciably affects the C2—C1—C10, C6—C1—C10, C5—C4—N9 and C3—C4—N9 bond angles.

4.2. Vibrational spectra

In order to obtain the spectroscopic signature of 2Cl4MA molecule, we performed a frequency calculation analysis. Calculations were made for a free molecule in vacuum, while experiments were performed for liquid sample, so there are disagreements between calculated and observed vibrational wavenumbers.

Experimental FT-IR and FT-Raman spectra are shown in Fig. 2. The calculated IR spectra are shown in Fig. 3 for comparative purposes, where the calculated intensity is plotted against the harmonic vibrational frequencies and the calculated Raman spectra are shown in Fig. 3 for comparative purposes, where the calculated activity is plotted against the harmonic vibrational frequencies. The experimental wavenumbers are tabulated in Table 3 together with the calculated wavenumbers of studied molecule. The resulting vibrational frequencies for the optimized geometries and the proposed vibrational assignments as well as IR intensities and Raman scattering activities are given in Table 3. The descriptions concerning the assignments have also been showed in the last column of Table 3. All of the calculated modes are numbered from the biggest to the smallest frequency within each fundamental wave numbers, *vn*, in the first column of the table. In the last column a detailed description of the normal modes based on the total energy distribution is given.

For 2Cl4MA group, the vibrational modes are N—H stretching, C—H stretching, C—Cl stretching, C—N stretching, C—C—H bending, C—C—C bending, C—C—N bending, C—N—H bending, ring bending, ring breathing, NH$_2$ scissoring, NH$_2$ wagging, NH$_2$ rocking, and ring torsion modes.

The fundamental modes involving the amino group are stretching and bending of NH bonds and torsion. Varsanyi [24] expressed that the frequencies of the amino group appear around 3500–3300 cm^{-1} for the NH$_2$ stretching, 1630–1610 cm^{-1} for

Table 2
Optimized geometry of 2Cl4MA in the ground state.

Parameters	Exp. [4] *p*-methylaniline	Exp.[a,b,c] aniline	6-31++G(d,p)		6-311++G(d,p)	
			HF	B3LYP	HF	B3LYP
Bond lengths (Å)						
C1—C2	1.39	1.380, 1.394, 1.3933	1.383	1.399	1.381	1.395
C1—C6	1.39	1.404, 1.397, 1.403	1.395	1.404	1.394	1.400
C1—C10	1.55		1.511	1.512	1.511	1.510
C2—C3	1.40	1.386, 1.396, 1.3955	1.389	1.394	1.387	1.391
C2—H7	1.08	1.03, 1.082, 1.099	1.075	1.086	1.075	1.084
C3—C4	1.36		1.387	1.405	1.385	1.402
C3—Cl17		1.744, 1.745, 1.739[d]	1.751	1.767	1.752	1.767
C4—C5	1.39	1.404, 1.397, 1.403	1.399	1.408	1.397	1.405
C4—N9	1.43	1.398, 1.402, 1.4057	1.388	1.391	1.390	1.390
C5—C6	1.40	1.380, 1.394, 1.3933	1.378	1.391	1.376	1.387
C5—H8	1.08	1.05, 1.08, 1.099	1.076	1.087	1.076	1.085
C6—H16	1.08	0.95, 1.083, 1.099	1.077	1.087	1.077	1.085
N9—H14	1.02	1.07, 1.001, 1.021	0.995	1.011	0.995	1.009
N9—H15	1.02	1.07, 1.001, 1.021	0.995	1.010	0.995	1.009
C10—H11	1.09		1.086	1.095	1.086	1.094
C10—H12	1.09		1.086	1.098	1.086	1.096
C10—H13	1.09		1.084	1.094	1.084	1.092
Bond angles (°)						
C2—C1—C6	117.8	117.6, 118.92, 119.03	117.28	117.41	117.29	117.42
C2—C1—C10			121.62	121.19	121.59	121.25
C6—C1—C10			121.11	121.40	121.12	121.33
C1—C2—C3	121.5	122.1, 120.70, 120.69	121.17	120.97	121.13	120.94
C1—C2—H7			120.37	120.31	120.40	120.34
C3—C2—H7			118.46	118.72	118.47	118.72
C2—C3—C4	120.5		121.89	122.10	121.96	122.17
C2—C3—Cl17			118.40	118.86	118.33	118.80
C4—C3—Cl17			119.72	119.04	119.72	119.03
C3—C4—C5	120.3	117.9, 119.43, 119.01	116.70	116.50	116.64	116.43
C3—C4—N9		124.0, 120.28, 120.45	122.80	122.31	122.86	122.36
C5—C4—N9			120.45	121.14	120.44	121.15
C4—C5—C6	120.5		121.43	121.49	121.45	121.51
C4—C5—H8			118.78	118.66	118.75	118.63
C6—C5—H8			119.79	119.85	119.79	119.85
C1—C6—C5	119.2	119.7, 120.12, 120.28	121.54	121.54	121.53	121.53
C1—C6—H16			119.61	119.55	119.62	119.56
C5—C6—H16			118.84	118.91	118.85	118.91
C4—N9—H14		119.0, 115.94, –	115.83	116.16	115.52	116.08
C4—N9—H15		119.0, 115.94, –	114.82	115.83	114.48	115.74
H14—N9—H15	113	113.1, –, –	112.45	113.48	112.17	113.43
C1—C10—H11			111.20	111.35	111.15	111.33
C1—C10—H12			111.19	111.42	111.14	111.34
C1—C10—H13			111.10	111.38	111.11	111.34
H11—C10—H12	109.5		107.64	107.26	107.66	107.30
H11—C10—H13	109.5		107.78	107.80	107.82	107.82
H12—C10—H13	109.5		107.76	107.42	107.80	107.50
C6—C5—C4—N9			−177.54	−177.35	−177.53	−177.33
C2—C3—C4—N9			177.39	177.22	177.36	177.20
C5—C4—N9—H15			−26.67	−24.99	−27.33	−25.16
C3—C4—N9—H14			22.55	20.72	22.79	20.81

[a] From Ref. [13,20], [b] From Ref. [12], [c] From Ref. [25], [d] From Ref. [41].

the NH$_2$ scissoring deformation, and 1090–1060 cm^{-1} for the NH$_2$ rocking deformation. The mode ν_{as}(NH$_2$) has higher frequency compared to the ν_s(NH$_2$) mode. In addition, the ν_s(NH$_2$) mode occurs with greater infrared intensity compared to the ν_{as}(NH$_2$) mode (see Fig. 2). Also, the N—H bond length in aniline (1.07 Å) is bigger than the disubstituted benzene (for example *p*-methylaniline). Therefore, the asymmetric and symmetric NH$_2$ stretching vibrations in aniline are higher than those of them. In aniline, these modes are assigned at 3500 and 3418 cm^{-1} antisymmetric and symmetric stretching vibrations, respectively. In this study, the NH$_2$ asymmetric and symmetric stretches (ν1 and ν2) at 3463 and 3375 cm^{-1} FT-IR are in agreement with the calculated values. As expected these two modes are pure stretching modes as it is evident from TED column, they are almost contributing 100%. In the Raman spectrum this absorption (NH$_2$ stretching) is absent. The NH$_2$ asymmetric and symmetric stretching modes are assigned 3435 and 3354 cm^{-1} for *m*-methylaniline [1], 3416 and 3333 cm^{-1}

for *p*-methylaniline [25] and 3485 and 3396 cm^{-1} for 2Cl6MA [29]. About 1625 cm^{-1} value is observed for the amino scissoring band for aniline [27], *o*-methylaniline [7], *m*-methylaniline [1] and *p*-methylaniline [4,25]. We assigned this band (ν9) at 1625 cm^{-1} both FT-IR and FT-Raman. The computed value of NH$_2$ scissoring is at 1636 cm^{-1} and deviates positively by 11 cm^{-1} from experimental value. In the present investigation, the amino rocking band (ν22) is calculated 1078 cm^{-1} with DFT exactly coincides with experimental value which is assigned at 1075 cm^{-1}. In the literature, the amino rocking band is observed 1077 cm^{-1} for *m*-methylaniline [1], 1074 cm^{-1} for *p*-methylaniline [25] and 1079 for 2Cl6MA [29].

Because of the mixing of several bands, the identification of C—N vibrations is a very difficult task. Silverstein et al. [45] assigned C—N stretching absorption in the region 1382–1266 cm^{-1} for aromatic amines. The C—N stretching is observed at 1293 cm^{-1} [21]. Hence the band at 1298 cm^{-1} in FT-IR (and FT-Raman) spectrum is assigned to C—N stretching vibration. After scaled down computed

Table 3
Comparison of the calculated and experimental (FT-IR and FT-Raman) vibrational spectra of 2Cl4MA.

Mode no.	HF/6311++G(d,p)				B3LYP/6311++G(d,p)				Experimental		TED[c]
	Unscaled frequency	Scaled frequency[a]	$I^{infrared}$	S^{Raman}	Unscaled frequency	Scaled frequency[b]	$I^{infrared}$	S^{Raman}	FT-IR	FT-Raman	
$\nu1$	3898	3527	29.3	36.5	3676	3521	27.5	44.6	3463		νNH(100) asym.
$\nu2$	3797	3436	33.0	128.2	3573	3423	28.8	183.4	3375		νNH(100) sym.
$\nu3$	3347	3029	3.7	75.1	3184	3050	2.4	89.7		3051	νCH(99) ring
$\nu4$	3331	3014	20.7	139.1	3170	3037	17.2	158.2			νCH(99) ring
$\nu5$	3311	2996	12.1	55.7	3153	3021	11.3	64.0	3025		νCH(100) ring
$\nu6$	3240	2932	24.5	59.1	3099	2969	16.9	64.5			νCH$_2$ of CH$_3$(98) asym.
$\nu7$	3212	2907	27.8	90.3	3070	2941	19.7	103.4	2921	2921	νCH$_3$(100) asym.
$\nu8$	3164	2863	48.6	220.5	3019	2892	42.7	311.6	2860		νCH$_3$(100) sym.
$\nu9$	1816	1643	116.0	44.7	1664	1636	115.3	57.3	1625	1625	ρNH$_2$(40) + νCC(33) ring + δCNH(13) + νCN(6)
$\nu10$	1790	1620	17.0	13.5	1640	1612	22.4	11.6	1605		νCC(35) ring + ρNH$_2$(33) + δCNH(20)
$\nu11$	1755	1588	10.1	4.2	1602	1575	6.7	3.8	1581		νCC(67) ring + δCCC(5) + δCCH(4) + NH$_2$(4) rock
$\nu12$	1662	1504	117.0	2.4	1537	1511	124.3	2.0	1508		δCCH(41) ring + νCC(31) ring + νCN(10) + νC—CH$_3$(4)
$\nu13$	1617	1463	18.0	7.4	1499	1473	17.1	8.1			CH of CH$_3$ asym. bend(51) + τHCCC(24) + δCCH(10)
$\nu14$	1604	1452	6.1	10.2	1488	1463	6.9	11.7	1455		CH of CH$_3$ asym. bend(57) + τHCCC(27) + δCCH(12)
$\nu15$	1546	1399	8.7	2.2	1435	1410	5.4	2.5	1408		νCC(37) ring + δCCH(19) ring + δCCN(3) + δCCC(3)
$\nu16$	1539	1393	5.3	11.2	1417	1393	0.1	24.9	1380	1380	CH$_3$ sym. bend(52) + δCCH(45)
$\nu17$	1432	1296	17.0	2.1	1341	1318	9.2	5.1	1309		νCC(60) ring + δCNH(18) + δCCH(13)
$\nu18$	1391	1259	45.6	19.9	1327	1304	49.8	13.1	1298	1298	δCH(35) ring + νCN(29) + νCC(19)
$\nu19$	1323	1197	16.2	6.6	1287	1265	14.2	8.1	1258	1259	νCC(36) ring + δCCH(30) + νC—NH$_2$(15) + νC—CH$_3$(4)
$\nu20$	1309	1185	0.9	2.7	1230	1209	11.0	11.7	1212	1212	νC—CH$_3$(34) + δCCH(27) + νCC(16) ring + δCCC(3)
$\nu21$	1222	1106	12.4	4.7	1180	1160	10.3	1.5	1155		δCH(65) + NH$_2$(30) rock + νCC(18) ring
$\nu22$	1187	1075	34.4	1.7	1096	1078	12.9	2.5	1075		NH$_2$(47) rock + νCC(18) ring + δCCH(9) + νCC(4) + δCCC(4)
$\nu23$	1164	1054	2.4	0.0	1062	1044	5.8	2.0	1046		CH$_3$(57) rock + γCCC(20) + γCH(3)
$\nu24$	1138	1030	12.2	1.6	1056	1038	13.6	0.7			δCCC(26) ring + νCC(24) ring + δCCH(23) + NH$_2$(7) rock + νCCl(4)
$\nu25$	1076	974	1.4	0.2	1012	994	14.9	1.4	996		CH$_3$(54) rock + τCCCH(19) + νCC(12) asym. ring
$\nu26$	1074	972	28.7	4.5	950	934	0.5	0.3	941		γCH(75) + γCCC(10)
$\nu27$	998	904	6.4	0.4	892	877	17.6	26.1	888	890	νCC(42) ring breath + νC—CH$_3$(13) + νCCl(13) + νC—NH$_2$(8) + δCCC(9)
$\nu28$	954	864	14.8	22.7	884	869	8.1	1.0	871		γCH(58) + γCCC(22)
$\nu29$	917	830	54.8	0.5	822	808	38.6	0.1	812		γCH(80) + γCCC(10)
$\nu30$	830	751	11.6	3.4	780	767	13.5	4.8	770	772	νC—CH$_3$(19) + νC—NH$_2$(19) + δCCC(16) ring + νCC(12) ring + νCCl(5)
$\nu31$	808	731	6.7	3.6	729	716	1.0	2.0	714		γCCCC(44) ring + γCH(26) + γCCN(13)
$\nu32$	744	673	13.6	9.7	695	684	9.7	9.0	686	685	δCCC(50) ring def. + νCC(15) ring + νCCl(11) + νC—CH$_3$(4)
$\nu33$	664	601	204.6	3.1	576	566	27.6	0.6	554		γCCC(20) ring + ωNH$_2$(19) + τCCCH(19) + ωCH$_3$(7) + τNCCCl(7)
$\nu34$	614	556	91.0	1.3	538	529	258.4	3.3			ωNH$_2$(75) + τCCC(13) ring
$\nu35$	530	479	1.7	6.2	490	482	4.4	5.8	494	493	δC—NH$_2$(47) + νCCl(17) + δC—CH$_3$(11) + νCC(6) + δCCCl(4)
$\nu36$	508	460	2.2	11.9	477	469	4.1	10.6	473	476	δCCC(45) + δC—CH$_3$(17) + νCC(11) + δC—NH$_2$(8)
$\nu37$	496	449	15.2	0.2	447	439	14.7	0.3	437		τCCCC(48) ring + τCCCH(17) + τCCCN(9) + τCCCCl(7)
$\nu38$	432	391	0.9	4.6	402	395	0.9	4.1	401	400	νCCl(29) + δCCC(23) ring + δC-CH$_3$(18) + δCCCl(11)
$\nu39$	367	332	4.0	1.5	344	338	7.6	0.5		337	NH$_2$ twist(70) + τCCCN(16) + τCCCC(6)
$\nu40$	319	288	7.9	0.8	320	314	16.9	1.1			NH$_2$ twist(57) + τCCCN(10) + τCCCC(10) + τHCCN(4)
$\nu41$	290	262	17.8	0.3	296	291	3.4	0.7		296	δC—CH$_3$(36) + δC—NH$_2$(33) + δCCCl(8) + νCCl(7)
$\nu42$	247	224	0.7	1.5	232	228	0.2	2.0		234	δCCl(64) + δC—CH$_3$(21)
$\nu43$	198	180	2.5	1.0	180	177	2.4	1.0		190	o.o.p. torsion (C—Cl(44) + C—C(17) + C—N(9))
$\nu44$	147	133	2.7	0.5	133	131	2.5	0.7		126	τCCCC(24) ring + τCCCCl(19) + τCCC—NH$_2$(19) + τCCC—CH$_3$(18)
$\nu45$	48	43	0.1	0.3	19	19	0.2	0.6		82	τCH$_3$(99)
σ (RMS)		27.432				16.132					
R^2		0.9990				0.9999					

ν; stretching, δ; in-plane bending, γ; out-of-plane (o.o.p.) bending, ρ; scissoring, ω; wagging, τ; torsion.
[Frequency (cm^{-1}), IR intensities; $I^{infrared}$ (Km/mol), Raman scattering activities; S^{Raman} (Å amu^{-1})].

[a] Scale factor of 0.9050 was used for HF/6-311++G(d,p) basis set [30].

[b] Wavenumbers in the ranges from 4000 to 1700 cm^{-1} and lower than 1700 cm^{-1} are scaled with 0.958 and 0.983 for B3LYP/6-311++G(d,p) basis set, respectively [31].
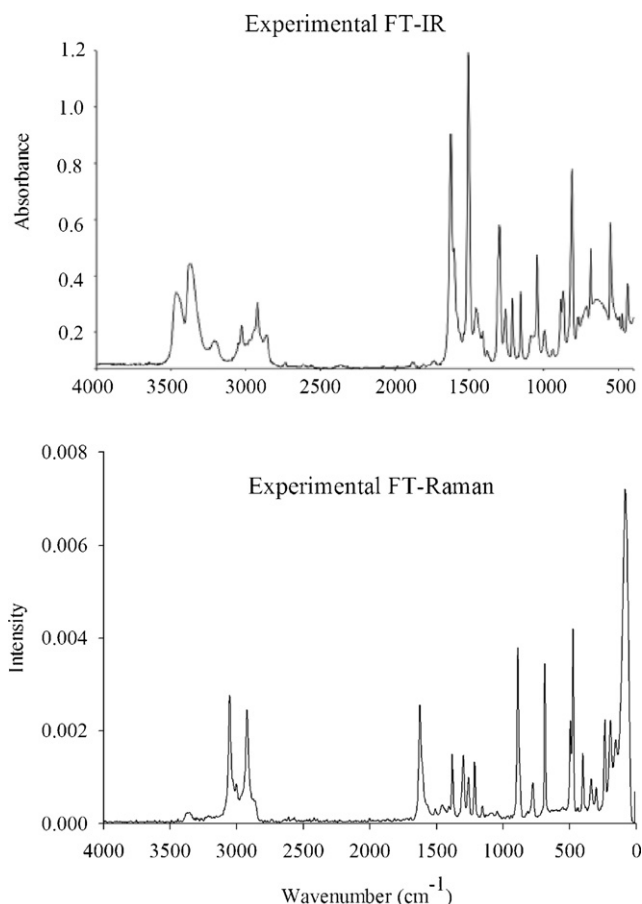
[c] Total energy distribution.

Fig. 2. Experimental FT-IR and FT-Raman spectra of 2Cl4MA.

The heteroaromatic structure shows the presence of C—H and N—H stretching vibrations above 3000 cm^{-1} which is the characteristic region for ready identification of this structure [45,46]. These are usual range of appearance for NH$_2$, CH$_3$ and ring C—H stretching vibrations. Accordingly, in the present study, the three adjacent hydrogen atoms left around the ring of the 2Cl4MA give rise to three C—H stretching modes (ν3–ν5), three C—H in-plane bending (ν18, ν20, ν21) and three C—H out-of-plane bending (ν26, ν28, ν29) vibrations which correspond to modes of C2—H7, C5—H8, and C6—H16 units. The vibrations ν3–ν5 assigned to C—H stretching are in agreement with the literature [45]. The C—H stretching band assigned 3015 and 3034 cm^{-1} for *m*-methylaniline [1] and 3008, 3020, and 3056 cm^{-1} for *p*-methylaniline [25]. In this work, we calculated B3LYP frequencies to be 3021, 3037, and 3050 cm^{-1} (ring C—H str.) for benzene ring. The C—H in-plane bending frequencies appear in the range of 1000–1300 cm^{-1} and C—H out-of-plane bending vibration in the range 750–1000 cm^{-1} [47]. Hence the CH in-plane bends is assigned to the FT-IR bands at 1298, 1212 and 1155 cm^{-1} (modes 18, 20, and 21), the calculated values 1304, 1209 and 1160 cm^{-1} show excellent agreement with the experimental values. The CH out-of-plane bends are assigned to the FT-IR bands in the range from 941 to 812 cm^{-1}. Both the in-plane and out-of-plane bending vibrations are described as mixed modes. In general the aromatic C—H vibrations (stretching, in-plane and out-of-plane vibrations) calculated theoretically are in good agreement with experimentally accepted values [1,24–26,45–48]. The calculated mode (ν45) is CH$_3$ torsional mode, and it is to be noted here that this is a pure mode.

A major coincidence of theoretical values with that of experimental evaluations is found in the symmetric and asymmetric vibrations of the CH$_3$ moiety (ν8 and ν7). The asymmetric stretching for the NH$_2$, CH$_2$ and CH$_3$ has the magnitude higher than the symmetric stretching [48]. For benzene derivates containing a CH$_3$ group two bands, which antisymmetrical and symmetrical stretching occurs about 2900 and 2850 cm^{-1}, respectively [29]. The symmetric stretching of CH$_3$ observed in FT-IR at 2860 cm^{-1} was calculated (ν8) at about 2863 cm^{-1} at HF level, while DFT estimates it at 2892 cm^{-1}. The asymmetric CH$_3$ stretch (ν7) calculated at HF after scaling down gives the value of 2907 cm^{-1} that is nearer to the observed value of 2921 cm^{-1} in both FT-IR and FT-Raman. But
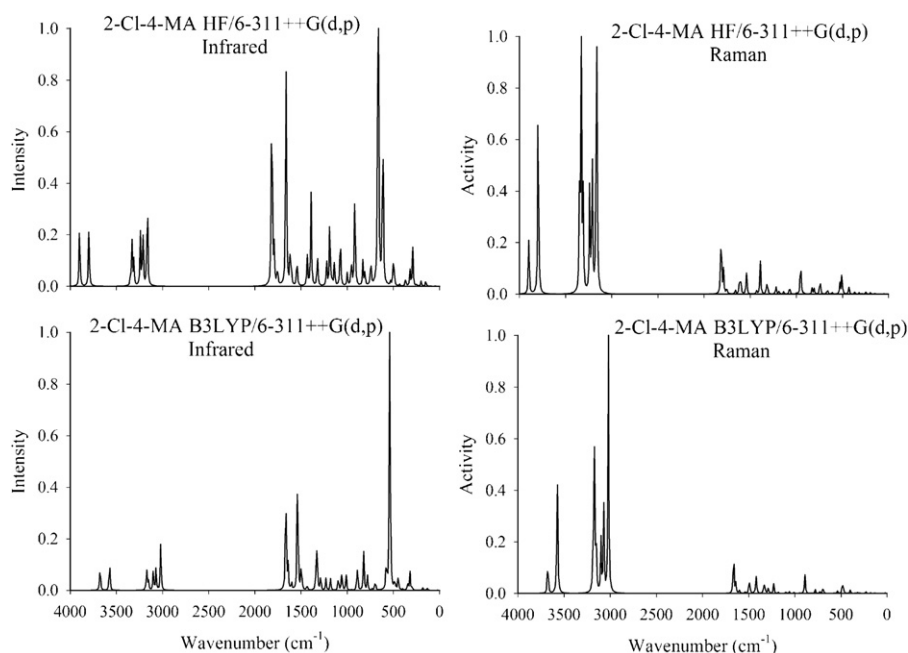
value (ν18) of C—N stretching vibration also is 1304 cm^{-1} nearer to the observed value. The TED for this mode suggests that this is a mixed mode. For *p*-methylaniline, Altun et al. [25] assigned this band at 1267 cm^{-1} FT-IR (1271 cm^{-1} FT-Raman).

Fig. 3. Comparison of calculated frequencies in cm^{-1} normalized IR intensities and Raman activities at each level of theory considered for 2Cl4MA. These theoretical spectra were obtained by using HF and DFT (B3LYP) methods with 6-311++G(d,p).

DFT gives high estimate of this frequency at 2941 cm^{-1}. The TED of these modes is 100%. Altun et al. [1] assigned these bands at 2919 and 2857 cm^{-1} for *m*-methylaniline. These bands were observed at 2984 (also 2935) and 2886 cm^{-1} for 2Cl6MA by Shanker et al. [29]. In the present investigation, the methyl CH$_3$ bending mode observed at 1455 cm^{-1}. These vibration frequencies were calculated to be 1452 and 1463 cm^{-1} and assigned modes ν13 and ν14. The CH$_3$ rocking mode is observed at 1045 and 1059 cm^{-1} for 2Cl6MA by Shanker et al. [29]. We assigned this band at 1046 cm^{-1} FT-IR. This ν23 mode calculated to be 1044 cm^{-1} with DFT method is in agreement with experimental value. The methyl group assignments proposed in this study are also in agreement with the literature values [1,8,12,25,29,39,45,48].

The ring stretching vibrations are very much important in the spectrum of benzene and its derivatives are highly characteristic of the aromatic ring itself. When the ring modes in toluene [49] and aniline [7,20], which contain one substituent group attached to an aromatic ring, are compared to each other, it is seen that most of the aniline modes are found slightly higher in frequency than that of the toluene modes. However, most of the ring modes of toluene or aniline are found to have significantly lower frequencies in 2Cl4MA, which is disubstituted in benzene. For example, the ring modes labeled ν3, ν5, ν11, ν15, ν26 and ν36 downshift, respectively, from 3079 cm^{-1} (3084 cm^{-1}), 3072 cm^{-1} (3074 cm^{-1}), 1587 cm^{-1} (1590 cm^{-1}), 1445 cm^{-1} (1468 cm^{-1}), 961 cm^{-1} (996 cm^{-1}) and 522 cm^{-1} (526 cm^{-1}) in toluene [49] (aniline) [7,20] to 3051, 3025, 1581, 1408, 941 and 476 cm^{-1} in 2Cl4MA. The frequency changes in the modes ν11, ν15, ν26, and ν36 are due to the changes in the force constant-reduced mass ratio resulting mainly from different extents of mixing between vibrations of the ring and substituent groups. The frequency reduction seen in the pure ring modes (ν3 and ν5) with the inclusion of a substituent group to aniline or toluene can be explained based on the corresponding changes in the reduced masses and force constants. Vibrations between 1400 and 1650 cm^{-1} in benzene derivates are assigned ring carbon–carbon stretching modes. In the present investigation, the CC stretching modes are calculated at 1612 and 1575 cm^{-1} which were observed at 1605 and 1581 cm^{-1} (ν10–ν11) in the FT-IR spectrum. As revealed by TED, the ring-breathing mode at 888 cm^{-1} coincides satisfactorily with the very strong FT-Raman band at 861 cm^{-1} [50]. The ring assignments proposed in this study are also in agreement with literature values [1,8,20,25,29,39,49,50].

Some vibrational modes were shown to be Cl-sensitive modes whereas others were calculated in a narrow frequency range for methylanilines. Involving the ring-halogen modes is related partially to Cl—C stretching and bending modes. These modes are in 200–600 cm^{-1} frequency range as reported by Varsanyi [24]. We may, therefore, assign the band 401 cm^{-1} FT-IR (400 cm^{-1} FT-Raman) to the ν(C—Cl) and calculated 395 cm^{-1} this mode (ν38). According to the calculated TED, our calculations show that there is no pure ν(C—Cl) band in this range. The bending C—Cl mode was located at 280–294 cm^{-1} for chloro derivatives [42]. However, the calculated bending modes are 228 cm^{-1} (i.p.) and 177 cm^{-1} (o.o.p.) for B3LYP. The remainder of the observed and calculated frequencies is shown in Table 3.

The infrared intensity for the title molecule from experimental fundamentals at 1508 cm^{-1} is very strong, secondly, theoretical intensity of these fundamentals is very strong fundamentals for HF and B3LYP methods. This fundamental's intensity is 117.0 and 124.3 km mol^{-1} for HF and B3LYP methods, respectively (see Table 3).

We present RMS (σ) and correlation values to make comparison with experimental data, based on the calculations at the bottom of Table 3. After scaling, the RMS errors between the observed and scaled frequencies of the molecule are found to be 27.432 and 16.132 cm^{-1} and the plots are linear with a unit slope and the cor-

relation (R^2) values are found to be 0.9990 and 0.9999 for HF and B3LYP methods, respectively. It is noticed that this means that the experimental fundamentals are in better agreement with the scaled fundamentals and the B3LYP/6-311++G(d,p) calculation is better than HF/6-311++G(d,p) method.

5. Conclusion

In the present work, we have performed the experimental and theoretical vibrational analysis of 2Cl4MA, for the first time. The molecular geometry, vibrational frequencies, infrared intensities and Raman scattering activities of the molecule in the ground state have been calculated by using ab initio HF and DFT (B3LYP) methods with 6-31G(d), 6-31G(d,p), 6-31+G(d,p), 6-31++G(d,p), 6-311G(d), 6-311G(d,p), 6-311+G(d,p), and 6-311++G(d,p) basis sets. The vibrational frequencies were calculated and scaled values (6-311++G(d,p) basis set) have been compared with the experimental FT-IR and FT-Raman spectra. The observed and the calculated frequencies are found to be in good agreement.

References

[1] A. Altun, K. Gölcük, M. Kumru, J. Mol. Struct. (Theochem.) 625 (2003) 17.
[2] J. Whysner, L. Vera, G.M. Williams, Pharmacol. Ther. 71 (1996) 107.
[3] M. Kanungo, A. Kumar, A.Q. Contractor, J. Electroanal. Chem. 528 (2002) 46.
[4] W.B. Tzeng, K. Narayanan, J. Mol. Struct. 446 (1998) 93;
    W.B. Tzeng, K. Narayanan, J. Mol. Struct. (Theochem.) 434 (1998) 247.
[5] Ş. Yurdakul, A.I. Sen, Vib. Spectrosc. 20 (1999) 27.
[6] B. Ballesteros, E. Marinez, L. Sontos, J. Sanchez-Marin, J. Mol. Struct. 605 (2002) 225.
[7] W.B. Tzeng, K. Narayanan, J.L. Lin, C.C. Tung, Spectrochim. Acta 55A (1999) 153.
[8] M. Karabacak, D. Karagöz, M. Kurt, J. Mol. Struct. 892 (2008) 25.
[9] P. Hohenberg, W. Kohn, Phys. Rev. B 136 (1964) 864.
[10] J.C. Evans, Spectrochim. Acta 16 (1960) 428.
[11] G. Roussy, A. Nonat, J. Mol. Spectrosc. 118 (1986) 180.
[12] G.D. Lister, J.K. Tyler, J.H. Hog, N.W. Larsen, J. Mol. Struct. 23 (1974) 253.
[13] M. Fukuyo, K. Hirotsu, T. Higuchi, Acta Crystallogr. 38B (2) (1982) 640.
[14] M. Castellá-Ventura, E. Kassab, Spectrochim. Acta 50A (1) (1994) 69.
[15] A.D. Gorse, M. Pesquer, J. Mol. Struct. (Theochem.) 281 (1993) 21.
[16] C.W. Bock, P. George, M. Trachtman, Theor. Chim. Acta 69 (1986) 235.
[17] Y. Wang, S. Saebø, C.U. Pittman, J. Mol. Struct. (Theochem.) 281 (1993) 91.
[18] I. López-Tocón, M. Becucci, G. Pietraperzia, E. Castelluchi, J.C. Otero, J. Mol. Struct. 565/566 (2001) 421.
[19] M.E. Vaschetto, B.A. Retamal, A.P. Monkman, J. Mol. Struct. (Theochem.) 468 (1999) 209.
[20] M.A. Palafox, J.L. Nunez, M. Gil, J. Mol. Struct. (Theochem.) 593 (2002) 101.
[21] C. Engelter, D.A. Thornton, M.R. Ziman, J. Mol. Struct. 49 (1978) 7.
[22] C. Engelter, D.A. Thornton, M.R. Ziman, J. Mol. Struct. 33 (1976) 119.
[23] P.R. Johnson, D.A. Thornton, Chimia 28 (7) (1974) 345.
[24] G. Varsanyi, Assignments of Vibrational Spectra of 700 Benzene Derivatives, Wiley, New York, 1974.
[25] A. Altun, K. Gölcük, M. Kumru, J. Mol. Struct. (Theochem.) 637 (2003) 155.
[26] S.J. Simgh, S.M. Pandey, Indian J. Pure Appl. Phys. 12 (1974) 300.
[27] S.N. Sharma, C.P.D. Dwivedi, Indian J. Pure Appl. Phys. 13 (1975) 570.
[28] G. Wolf, J.S. Almeida, C. Pinheiro, V. Correia, C. Rodrigues, M.A.M. Reis, J.G. Crespo, Biotech. Bioeng. 72 (3) (2001) 297.
[29] R. Shanker, R.A. Yadav, I.S. Singh, O.N. Singh, Indian J. Pure Appl. Phys. 23 (1985) 339.
[30] D.C. Young, Computational Chemistry: A Practical Guide for Applying Techniques to Real World Problems (Electronic), John Wiley & Sons Inc., New York, 2001.
[31] N. Sundaraganesan, S. Ilakiamani, H. Saleem, P.M. Wojciechowski, D. Michalska, Spectrochim. Acta A 61 (2005) 2995.
[32] A. Frisch, A.B. Nielsen, A.J. Holder, Gaussview Users Manual, Gaussian Inc., Pittsburg, PA, 2000.
[33] M.J. Frisch, et al., Gaussian 03, Revision B.4, Gaussian Inc., Pittsburgh, PA, 2003.
[34] G. Pongor, P. Pulay, G. Fogarasi, J.E. Boggs, J. Am. Chem. Soc. 106 (1984) 2765.
[35] J.V. Prasad, S.B. Rai, S.N. Thakur, Chem. Phys. Lett. 164 (6) (1989) 629.
[36] M.K. Ahmed, B.R. Henry, J. Phys. Chem. 90 (1986) 1737.

[37] J.R. Durig, T.S. Little, T.K. Gounev, Gargner FJ.K. Jr., J.F. Sullivan, J. Mol. Struct. 375 (1996) 83.
[38] M. Bakiler, I.V. Maslov, S. Akyüz, J. Mol. Struct. 475 (1999) 83.
[39] M. Kurt, M. Yurdakul, Ş. Yurdakul, J. Mol. Struct. (Theochem.) 711 (2004) 25.
[40] M. Karabacak, M. Çınar, M. Kurt, J. Mol. Struct. 885 (2008) 28.
[41] A.K. Hermetet, L.J. Ackerman, K.K. Eilts, T.K. Johnson, J.K. Swearingen, J.M. Giesen, K.I. Goldberg, W. Kaminsky, D.X. West, J. Mol. Struct. 605 (2002) 241.
[42] J. Hanuza, M. Maczka, A. Waslowska, W. Oganowski, M. Andruszkiewicz, H.B. Ogonowska, B. Lutz, V. der-Maas, J. Mol. Struct. 404 (1997) 33.
[43] N. Sundaraganesan, et al., Spectrochim. Acta A 65 (2006) 1053.
[44] M. Karabacak, M. Kurt, Spectrochim. Acta A 71 (2008) 876.
[45] M. Silverstein, G. Clayton Basseler, C. Morill, Spectrometric Identification of Organic Compounds, Wiley, New York, 1981.
[46] V. Krishnakumar, R. Ramasamy, Spectrochim. Acta A 62 (2005) 570.
[47] N. Sundaraganesan, S. Ilakiamani, B.D. Joshua, Spectrochim. Acta A 67 (2007) 287.
[48] D. Lin-Vien, N.B. Colthup, W.G. Fateley, J.G. Grasselli, The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules, Academic Press, Boston, MA, 1991.
[49] H.F. Hameka, J.O. Jensen, J. Mol. Struct. (Theochem.) 362 (1996) 325.
[50] N.P. Sing, R.A. Yadav, Indian J. Phys. B 75 (4) (2001) 347.