Vibrational Spectral Analysis on P-Chloroaniline based on Scaled Quantum Chemical Calculation

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ABSTRACT

The FT-IR and FT-Raman spectra of P-Chloroaniline (PCA) have been recorded and analyzed. The optimized geometry, and harmonic vibrational wave numbers of PCA have been investigated with the help of B3LYP scaled quantum mechanical (SQM) method supplemented with 6-311++G** basis set. The infrared and Raman spectra were predicted theoretically from the calculated intensities. The observed and simulated spectra were found to be well comparable. In the investigation, we adopted density functional theory (DFT) combined with quantum chemical calculations to determine the first-order hyperpolarizability.

Introduction

P-Chloroaniline (PCA) is an important building block used in the chemical industry for the production of pesticides, drugs, and dyestuffs. It is a precursor to the widely used antimicrobial and bacteriocide Chlorhexidine and is used in the manufacture of pesticides, including pyraclostrobin, anilofos, monolinuron and chlorphthalim. Some benzodiazepine drugs use PCA in their manufacture. The vibrational spectra of substituted aniline have been the subject of several investigations. Literature survey reveals that to the best of our knowledge, the results based on quantum chemical calculations, FT-IR and FT-Raman spectral analyses on PCA have no reports. Herein, we reported detailed interpretations of the infrared and Raman spectra based on the experimental and theoretical results, which are acceptable and supportable to each other. In the present work, we have attempted to interpret the vibrational spectra of PCA by using B3LYP level of theory throughout with the 6-311++G** basis set implemented in the Gaussian 03 program suite.

Methodology

Experimental Details

The fine sample of PCA was obtained from Lancaster Chemical Company, UK and used as such for the spectral measurements. The FT-Raman spectrum of PCA was recorded using 1064 nm line of Nd:YAG laser as excitation wave length in the region 3500–100 cm^{-1} on thermo electron corporation model Nexus 670 spectrometer equipped with FT-Raman module accessory. The FT-IR spectrum of the title compound was recorded in the region 4000–400 cm^{-1} on Perkin Elmer Spectrophotometer in KBr pellet technique.

Computational methods

Quantum chemical calculations were used for PCA to carry out the optimized geometry and vibrational wavenumbers with the 2003 version of the Gaussian suite of program using the Becke–3–Lee–Yang–Parr (B3LYP) [1,2] functional supplemented with standard 6-311++G** basis set. The vibrational modes were assigned by means of visual inspection using the GAUSSVIEW program. The symmetry of the

molecule was also helpful in making vibrational assignments. The symmetries of the vibrational modes were determined by using standard procedure of decomposing the traces of the symmetry operations into irreducible representations. From the basic theory of Raman scattering Raman activities (S_i) calculated by Gaussian 03 program have been converted to relative Raman intensities (li) using the following relationship:

$$I_i = \frac{f\,(\gamma_0 - \gamma_i)^4\ S_i}{\gamma_i \left[1 - exp\left(\frac{-hc\gamma_i}{KT}\right)\right]} \qquad (1)$$

where γ_o is the exciting wave number (in cm^{-1} units), γ_i is the vibrational wave number of the in *ith* normal mode, *h, c,* and *k* are universal constant and *f* is the suitably chosen common scaling factor for all the peak intensities.

The analysis for the vibrational modes of PCA was presented in some detail in order to better describe the basis for the assignments. All the parameters were allowed to relax and all the calculations converged to an optimized geometry which corresponds to a true energy minimum, as revealed by the lack of imaginary values with wavenumber calculations. The Cartesian representation of the theoretical force constant has been computed at the fully optimized geometry by assuming the molecule belongs to C_s point group symmetry. The transformation force field from Cartesian to internal local symmetry coordinates, scaling the subsequent normal coordinate analysis (NCA), calculation of Potential Energy Distribution (PED) were done on a PC with the version V7.0–G77 of the MOLVIB program written by Sundius [3-10].

The optimized molecular structure of PCA was shown in Fig.1. The global minimum energy obtained by the DFT structure optimization was presented in Table 1. The optimized geometrical parameters obtained by the large basis set calculation were presented in Table 2. A detailed description of vibrational modes can be given by means of normal coordinate analysis. For this purpose, a full set of 49 standard

internal coordinates containing 13 redundancies were defined as given in Table. 3. From these, a non–redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendation of Pulay *et al* [11] and they are presented in Table .4. The theoretically calculated SQM force fields were transformed to this later set of vibrational coordinates and used in all subsequent calculations.

Essentials of nonlinear optics related to β

The nonlinear response of an isolated molecule in an electric field $E_i(\omega)$ can be represented as a Taylor expansion of the total dipole moment μ_t induced by the field:

$$\mu_t = \mu_0 + \alpha_{ij}E_i + \beta_{ijk}E_iE_j + ...$$

Where α is linear polarizability, μ_0 the permanent dipole moment and β_{ijk} are the first-order hyperpolarizability tensor components.

The components of first-order hyperpolarizability can be determined using the relation

$$\beta_i = \beta_{iii} + \frac{1}{3}\sum_{i \neq j}(\beta_{ijj} + \beta_{jij} + \beta_{jji})$$

Using the x, y and z components the magnitude of the total static dipole moment (μ), isotropic polarizability (α_0), first-order hyperpolarizability (β_{total}) tensor, can be calculated by the following equations:

$$\mu_1^0 = (\mu_x^2 + \mu_y^2 + \mu_z^2)^{1/2}$$

$$\beta_{tot} = (\beta_x^2 + \beta_y^2 + \beta_z^2)^{1/2}$$

The complete equation for calculating the first-order hyperpolarizability from GAUSSIAN 03W output is given as follows [12]:

$$\beta_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]$$

The β components of GAUSSIAN 98W output are reported in atomic units, the calculated values have to be converted into electrostatic units (1 a.u= 8.3693 x10^{-33} esu).

Before calculating the hyperpolarizability for the investigated compound, the optimization has been carried out in the UHF (unrestricted open-shell Hartree-Fock) level. Molecular geometries were fully optimized by Berny's optimization algorithm using redundant internal coordinates. All optimized structures were confirmed to be minimum energy conformations. An optimization is complete when it has converged. i.e., when it has reached a minimum on the potential energy surface, thereby predicting the equilibrium structures of the molecules.

This criterion is very important in geometry optimization. The inclusion of d polarization and double zeta function in the split valence basis set is expected to produce a marked improvement in the calculated geometry.

At the optimized structure, no imaginary frequency modes were obtained proving that a true minimum on the potential energy surface was found. The electric dipole moment and dispersion free first-order hyperpolarizibility were calculated using finite field method. The finite field method offers a straight forward approach to the calculation of hyperpolarizabilities. All the calculations were carried out at the DFT level using the three-parameter hybrid density functional B3LYP and a 3-21 G (d, p) basis set.

Result and Discussion
Structure and Symmetry

The optimized structural parameters and global minimum energy of PCA were calculated by C_s point group symmetry with B3LYP/6-311++G** level. In accordance with the atom numbering scheme is given in Fig. 1. The global minimum energy of PCA is -747.19885835 hartrees. The optimized structure of the title compound was compared with other similar systems for which the crystal structures have been solved. From the theoretical values we can find that most of the optimized bond lengths are slightly longer and shorter than experimental values. The computed bond length and bond angles show satisfactory agreement with experimental observation.
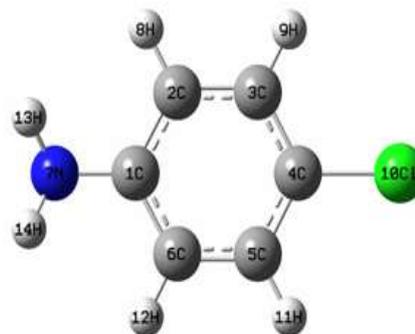

Fig.1. The optimized molecular structure of PCA

Table 1. Total energies of PCA, calculated at DFT (B3LYP)/6-31G* and (B3LYP)/6-311+G level**

Method	Energies (Hartrees)
6-31G*	-747.17532541
6-311+G**	-747.19885835

Vibrational assignments

The 36 normal modes of PCA are distributed among the symmetry species as $\Gamma_{3N-6} = 25\ A'$ (in-plane) $+ 11\ A''$ (out-of-plane) by assuming C_s point group symmetry. The detailed vibrational assignments of fundamental modes of PCA along with observed and calculated frequencies, IR intensities, Raman scattering activities and normal mode descriptions have been reported in Table 5. The observed and simulated FT-IR and FT-Raman spectra of PCA are produced in a common frequency scales in Fig. 2 & Fig. 3.

Root mean square (RMS) values of frequencies were obtained in the study using the following expression,

$$RMS = \sqrt{\frac{1}{n-1}\sum_i^n (\upsilon_i^{calc} - \upsilon_i^{exp})^2}$$

The RMS error of the observed and calculated frequencies (unscaled / B3LYP/6-311+G**) of PCA was found to be 103 cm^{-1}. This is quite obvious; since the frequencies calculated on the basis of quantum mechanical force fields usually differ appreciably from observed frequencies. This is partly due to the neglect of anharmonicity and partly due to the approximate nature of the quantum mechanical methods. In order to reduce the overall deviation between the unscaled and observed fundamental frequencies, scale factors were applied in the normal coordinate analysis and the subsequent least square fit refinement algorithm resulted into a very close agreement between the observed fundamentals and the scaled frequencies. Refinement of the scaling factors applied in this study achieved a weighted mean deviation of 9.32 cm^{-1} between the experimental and scaled frequencies of the title compound. It is

convenient to discuss the vibrational spectra of PCA in terms of characteristic spectral region as describe below.

Table 2. Optimized geometrical parameters of PCA obtained by B3LYP/ 6–311+G** density functional calculations

Bond length	Value(Å)	Bond angle	Value(Å)	Dihedral angle	Value(Å)
C2-C1	1.38599	C3-C2-C1	120.00023	C4-C3-C2-C1	0.00000
C3-C2	1.38600	C4-C3-C2	120.00023	C5-C4-C3-C2	0.00000
C4-C3	1.38599	C5-C4-C3	119.99953	C6-C1-C2-C3	0.00000
C5-C4	1.38599	C6-C1-C2	119.99953	N7-C1-C2-C3	179.42810
C6-C1	1.38599	N7-C1-C2	119.99899	H8-C2-C1-N7	-1.14384
N7-C1	1.44605	H8-C2-C1	119.99903	H9-C3-C4-C5	-179.42805
H8-C2	1.12205	H9-C3-C4	119.99903	Cl10-C4-C5-C6	-179.42484
H9-C3	1.12205	Cl10-C4-C5	119.99898	H11-C5-C6-C1	-179.42806
Cl10-C4	1.75996	H11-C5-C6	119.99826	H12-C6-C1-N7	1.14384
H11-C5	1.12205	H12-C6-C1	119.99903	H13-N7-C1-C2	-59.42751
H12-C6	1.12205	H13-N7-C1	119.99759	H14-N7-C1-C2	121.14692
H13-N7	1.02800	H14-N7-C1	119.99426		
H14-N7	1.02800				

*for numbering of atom refer Fig. 1.

Table 3. Definition of internal coordinates of PCA

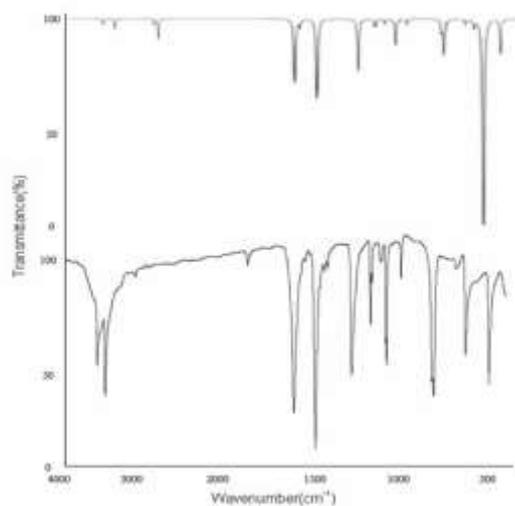| No(i)	Symbol	Type	Definition
Streching			
1-4	r_i	C-H(aro)	C2-H8,C3-H9,C5-H11,C6-H12
5	R_i	C-Cl(aro)	C4-Cl10
6	n_i	C-N (sub)	C1-N7
7-8	p_i	N-H(sub)	N7-H13,N7-H14
9-14	P_i	C-C(ring)	C1-C2,C2-C3,C3-C4,C4-C5,C5-C6,C6-C1
Bending			
15-20	α_i	C-C-C(ring)	C1-C2-C3,C2-C3-C4,C3-C4-C5, C4-C5-C6,C5-C6-C1,C6-C1-C2
21-28	θ_i	C-C-H	C1-C2-H8,C3-C2-H8, C2-C3-H9,C4-C3-H9,C4-C5-H11, C6-C5-H11,C1-C6-H12,C5-C6-H12
29	Φ_i	H-N-H	H13-N7-H14
30-31	β_i	C-C-Cl	C3-C4-Cl10,C5-C4-Cl10
32-33	μ_i	C-C-N	C6-C1-N7,C2-C1-N7
34-35	γ_i	C-N-H	C1-N7-H13,C1-N7-H14
Out-of-plane			
36-39	ω_i	C-H	H8-C2-C1-C3,H9-C3-C2-C4, H11-C5-C4-C6,H12-C6-C5-C1
40	ν_i	C-Cl	Cl10-C4-C3-C5
41	φ_i	C-N	N7-C1-C6-C2
42	ξ_i	C-N-H	C1-N7-H13-H14
Torison	τ_i	C-C-C	C1-C2-C3-C4,C2-C3-C4-C5,
43-48			C3-C4-C5-C6,C4-C5-C6-C1, C5-C6-C1-C2,C6-C1-C2-C3
49	τ_i	C-N	C2(C6)-C1-N7-H13(H14)

*for numbering of atom refer Fig. 1

Fig. 2. FT-IR spectra of PCA
(a) Observed (b) Calculated with B3LYP/6-311+G**

Table 4. Definition of local symmetry coordinates and the value corresponding scale factors used to correct the force fields for PCA

No.(i)	Symbol[a]	Definition[b]	Scale factors used in calculation
1-4	C-H(aro)	r1,r2,r3,r4	0.916
5	C-Cl(aro)	R5	0.953
6	C-N(sub)	n6	0.916
7-8	N-H(sub)	p7,p8	0.914
9-14	C-C(ring)	P9,P10,P11,P12,P13,P14	0.963
15	bring	$(\alpha15-\alpha16+\alpha17-\alpha18+\alpha19-\alpha20)/\sqrt{6}$	0.992
16	bring	$(2\alpha15-\alpha16-\alpha17+2\alpha18-\alpha19-\alpha20)/\sqrt{12}$	0.992
17	bring	$(\alpha16-\alpha17+\alpha19-\alpha20)/2$	0.992
18-21	C-C-H	$(\theta21-\theta22)/\sqrt{2},(\theta23-\theta24)/\sqrt{2},$ $(\theta25-\theta26)/\sqrt{2},(\theta27-\theta28)/\sqrt{2}$	0.990
22	H-N-H	$\Phi29$	0.918
23	C-C-Cl	$(\beta30-\beta31)/\sqrt{2}$	0.971
24	C-C-N	$(\mu32-\mu33)/\sqrt{2}$	0.967
25	C-N-H	$(\gamma34-\gamma35)/\sqrt{2}$	0.903
26-29	C-H	$\omega36,\omega37,\omega38,\omega39$	0.992
30	C-Cl	$\nu40$	0.964
31	C-N	$\varphi41$	0.962
32	C-N-H	$\xi42$	0.960
33	tring	$(\tau43-\tau44+\tau45-\tau46+\tau47-\tau48)/\sqrt{6}$	0.994
34	tring	$(\tau43-\tau45+\tau46-\tau48)/2$	0.994
35	tring	$(-\tau43+2\tau44-\tau45-\tau46+2\tau47-\tau48)/\sqrt{12}$	0.994
36	C-N	$\tau49/4$	0.830

a These symbols are used for description of the normal modes by TED in Table 5.

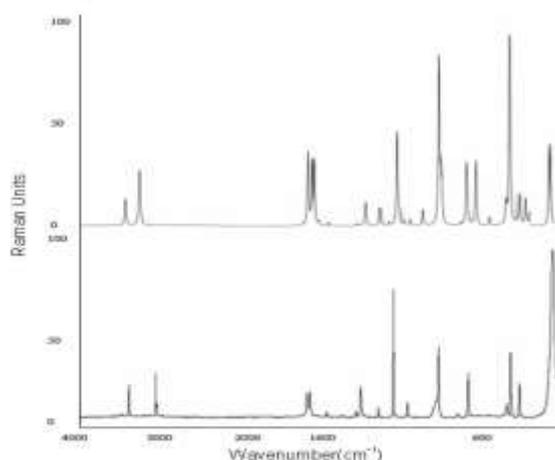b The internal coordinates used here are defined in Table 3.

Fig. 3. FT-Raman spectra of PCA
(a) Observed (b) Calculated with B3LYP/6-311+G**

C–H vibration

The presence of hetro-aromatic-type structure is best recognized by the presence of C–H stretching vibrations [13] near 3030 cm^{-1}. In this region, the absorption bands are little affected by the substitutional patterns and the presence of conjunction with double bonds of the ring. In PCA the band were observed at 3037 cm^{-1} and 3061 cm^{-1} in FTIR & FT Raman respectively.

C–Cl vibration

In present investigation, The C–Cl stretching frequency is generally observed in the region 800–600 cm^{-1} depending on the configuration and conformation of the compound [14]. Based on this, the FTIR and FT-Raman bands observed at 831,691,640 and 819, 636 cm^{-1} has been assigned to C–Cl stretching modes show strong mixing with several planar modes. However, the planar C–Cl bending modes appear to be relatively pure modes. The C–Cl out of plane bending modes were identified at 286 cm^{-1}and 327 cm^{-1} for IR and Raman, respectively.

C–N vibrations

The identification of C–N stretching frequency is a very difficult task, since the mixing of bands are possible in this region. Hence the FT-IR bands observed at 1334, 1369, 1428, 1554 cm^{-1} and the Raman bands at 1597, 1617 cm^{-1} in PCA are assigned to C–N stretching modes of vibrations. These assignments are made in accordance with the assignments proposed by Roy [15].

N–H vibrations

In all the heterocyclic compounds, the N–H stretching vibration [16] occur in the region 3500–3000 cm^{-1}. Hence the FT-IR band observed at 3037 cm^{-1} and Raman band at 3061 cm^{-1} in PCA have been designated to N–H stretching modes of vibrations.

C–C vibrations

The bands between 1400 and 1650 cm^{-1} in benzene derivatives are assigned to C–C stretching modes [17]. Accordingly in the present study, the carbon–carbon vibrations are observed in PCA at 1441 cm^{-1} in the FT-IR spectrum and 1478 cm^{-1} in the FT-Raman.

Ring vibrations

Many ring modes are affected by the substitutions in the ring of PCA. In the present study the bands identified at 1039, 843, 704, 418, 408 and 286 cm^{-1} for PCA have been designated to ring in-plane and out-of-plane bending modes, respectively by

careful consideration of their quantitative descriptions. A small change in frequencies observed for these modes are mainly due to the presence of Amino group in PCA and from different extents of mixing between ring and constituent group vibrations.

Hyperpolarizability calculations

The first-order hyperpolarizibility (β_{ijk}) of the novel molecular system of PNBC is calculated using 3-21 G (d,p) basis set based on finite field approach. Hyperpolarizibility is a third rank tensor that can be described by a 3 x 3 x 3 matrix. It strongly depends on the method and basis set used. The 27 components of 3D matrix can be reduced to 10 components due to Kleinman [18] symmetry. The calculated first-order hyperpolarizibility (β_{total}) of PCA is 0.251551x10^{-30} esu, which value is higher than that of urea (0.1947 x 10^{-30} esu). The calculated dipole moment (μ) and first-order hyperpolarizibility (β) are shown in Table 6. The theoretical calculation seems to be more helpful in determination of particular components of β tensor than in establishing the real values of β. Domination of particular components indicates on a substantial delocalization of charges in those directions. It is noticed that in β_{zxx} (which is the principal dipole moment axis and it is parallel to the charge transfer axis) direction, the biggest values of hyperpolarizability are noticed and subsequently delocalization of electron cloud is more in that direction.

Table 5. Detailed assignments of fundamental vibrations of PCA by normal mode analysis based on SQM force field calculation

S. No.	Symmetry species C$_s$	Observed frequency (cm^{-1})		Calculated frequency (cm^{-1}) with B3LYP/6-311+G** force field				TED (%) among type of internal coordinates[c]
		Infrared	Raman	Unscaled	Scaled	IR[a] A$_i$	Raman[b] I$_i$	
1	A'			3654	3649	9.512	74.542	NH(100)
2	A'	3550	3560	3557	3551	15.439	197.349	NH(100)
3	A'			3229	3220	0.422	179.963	CH(99)
4	A'	3230		3225	3219	8.830	28.640	CH(99)
5	A'		3184	3189	3182	18.519	84.654	CH(99)
6	A'	3137		3190	3182	13.417	82.772	CH(99)
7	A'		1690	1695	1689	99.447	32.562	bHNH(76),CC(9),CN(8)
8	A'	1664		1667	1661	11.770	28.072	CC(56),bCH(21),bHNH(10),bring(10)
9	A'		1617	1635	1629	0.514	1.597	CC(70),bCH(11),bring(10)
10	A'	1545		1560	1554	123.828	1.287	bCH(57),CC(34),CN(6)
11	A'		1490	1483	1478	1.437	0.167	bCH(43),CC(43),bNH(6),bCN(5)
12	A'			1374	1369	1.097	0.672	bCH(55),CC(33),bNH(9)
13	A'	1338		1340	1334	5.634	0.793	CC(78),bCH(16)
14	A'		1322	1325	1320	81.281	6.686	CN(53),CC(17),bCH(16),bring(13)
15	A'			1227	1222	12.438	4.590	bCH(76),CC(22)
16	A'	1174		1172	1167	7.666	0.792	bCH(53),CC(28),bNH(17)
17	A'		1110	1114	1107	40.589	20.099	CC(54),CCl(25),bCH(13),bring(9)
18	A'	1089		1096	1091	1.266	2.326	bNH(50),CC(36),bCH(10)
19	A'	1037		1045	1039	8.872	1.202	bring(64),CC(25),bCH(7)
20	A''		950	947	941	0.375	2.635	gCH(92),tring(8)
21	A''	955		949	941	0.003	0.044	gCH(80),tring(17)
22	A'			850	843	18.248	23.598	CC(37),bring(24),CN(12),gCH(12)
23	A''	831		835	828	54.307	6.493	gCH(61),tring(14),gCN(13)
24	A''		819	822	816	0.130	6.625	gCH(100)
25	A''	691		709	704	8.024	0.338	tring(63),gCN(15),gCCl(11),gCH(7)
26	A'		661	670	664	0.000	5.788	bring(82),CC(9)
27	A'	640		665	658	13.239	1.494	bring(33),CCl(28),gCNH(17),CC(6),bHNH(5),tring(5)
28	A''			611	605	352.601	5.771	gCNH(54),bHNH(18),CN(13),tring(5)
29	A''	507	536	516	509	53.607	0.567	tring(39),gCCl(26),gCN(25),gCH(6)
30	A''		420	426	418	0.327	0.021	tring(80),gCH(19)
31	A'			415	408	0.279	1.004	bCN(61),bCCl(16),bring(15)
32	A'		381	390	383	3.557	9.599	bring(44),CCl(42),CC(10)
33	A''		327	333	326	4.418	1.074	gCCl(40),tring(34),gCH(13),gCN(11)
34	A''			295	286	21.749	0.767	tCN(91)
35	A'			265	258	0.057	0.308	bCCl(71),bCN(17),CC(9)
36	A''		125	134	126	1.260	0.584	tring(72),gCH(17),gCCl(9)

Abbreviations used: b, bending; g, wagging; t, torsion; s, strong; vs, very strong; w, weak; vw, very weak;
[a] Relative absorption intensities normalized with highest peak absorption
[b] Relative Raman intensities calculated by Eq.1 and normalized to 100.
[c] For the notations used see Table 4.

The higher dipole moment values are associated, in general, with even larger projection of β_{total} quantities. The electric dipoles may enhance, oppose or at least bring the dipoles out of the required net alignment necessary for NLO properties such as β_{total} values. The connection between the electric dipole moments of an organic molecule having donor–acceptor substituent and first hyperpolarizability is widely recognized in the literature [19]. The maximum β was due to the behavior of non-zero μ value. One of the conclusions obtained from this work is that non-zero μ value may enable the finding of a non-zero β value. Of course Hartee–Fock calculations depend on the mathematical method and basis set used for a polyatomic molecule.

Table 6. The dipole moment (μ) and first-order hyperpolarizibility (β) of PCA derived from DFT calculations

β_{xxx}	-0.04442
β_{xxy}	-0.08363
β_{xyy}	-0.15544
β_{yyy}	-0.00621
β_{zxx}	0.125724
β_{xyz}	0.05038
β_{zyy}	-0.08832
β_{xzz}	-0.01715
β_{yzz}	0.097021
β_{zzz}	-0.16441
β_{total}	0.251551
μ_x	0.975496967
μ_y	8.70489E-09
μ_z	0.331536658
μ	1.143255717

Dipole moment (μ) in Debye, hyperpolarizibility $\beta(-2\omega;\omega,\omega)$ 10^{-30}esu.

Conclusions

The vibrational properties of P-Chloroaniline (PCA) have been investigated by FT IR and FT–Raman spectroscopies and were performed on the basis of DFT–B3LYP calculations at 6–311+G** basis set level. The energy of the title compound has been calculated using the above mentioned basis sets. On the basis of the comparison between calculated and observed results, assignments of fundamental vibrational modes were examined using scaling procedure and found to be unambiguous. The simulated and observed IR and Raman spectra agree well with the better frequency fit and intensities. The calculated first-order hyperpolarizability (β_{total}) of PCA is 0.251551×10^{-30} esu, which value is higher than that of urea (0.1947×10^{-30} esu).

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