RESEARCH ARTICLE

SCALED QUANTUM CHEMICAL STUDIES OF THE STRUCTURE, VIBRATIONAL SPECTRA AND FIRST-ORDER HYPERPOLARIZABILITY OF 4-CHLORO-2-FLUROANILINE

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ABSTRACT

FT-IR and FT-Raman spectra of 4-Chloro-2-Fluroaniline (4C2FA) have been recorded. The spectra were interpreted with the aid of normal coordinate analysis following full structure optimizations and force field calculations based on density functional theory (DFT) using standard B3LYP/6-311+G** method. Normal coordinate calculations were performed with the DFT force field corrected by a recommended set of scaling factors yielding fairly good agreement between observed and calculated frequencies. The effects of the chloro, fluro and nitro substituents on vibrational frequencies have been investigated. Further, density functional theory (DFT) combined with quantum chemical calculations to determine the first-order hyperpolarizability

INTRODUCTION

One of the most successful selective scaling schemes, developed with deep understanding of the nature of molecular vibrations, is the so-called scaled quantum mechanical (SQM) force field method (Pulay et al., 1983; Rauhut et al., 1995 and Baker et al., 1998). It requires transformation of the QM force field to internal co-ordinates and applies a limited number of independent scaling that is common within groups of similar internal co-ordinates. Ideally, the number of scale factors applied is kept to a possible minimum to safeguard against arbitrariness in the effective force field produced. Uniform scaling (or frequency scaling) has been criticized by Pulay et al. (1990) pointing out that no scaling and uniform scaling of the force field may often lead to misassignments in case of large molecules, since proper correction for systematic errors of theory is impossible by a single factor. To enhance the utility of the SQM force field method, a set of 11 transferable scaling factors have been proposed for use with the B3LYP/6-311+G** density functional (DFT) force field that seem to be transferable within a wide range of organic molecules containing the atoms C, N, and H (Rauhut et al., 1995 and Baker et al., 1998).

The aim of this work is to check the performance of the B3LYP density functional force field for simulation of the FT-IR and FT-Raman spectra of 4C2FA (that have not been subjected to vibrational analysis before) with the use of the large B3LYP/6-311+G** basis sets, and comparing the effect of simpler and more elaborate versions of scaling, while paying attention to ensuring correct band assignments.

MATERIALS AND METHODS

The fine samples of 4C2FA were obtained from Lancaster Chemical Company, U.K. and used as such for the spectral measurements. The room temperature Fourier transform infrared spectra of the title compounds were measured in the region 4000-400 cm^{-1} at a resolution of ±1 cm^{-1}, using BRUKER IFS 66V vacuum Fourier transform spectrometer, equipped with an MCT detector, a KBr beam splitter and globar source. The FT-Raman spectra were recorded on the same instrument with FRA 106 Raman accessories in the region 3500-100 cm^{-1}. Nd:YAG laser operating at 200 mw power with 1064 nm excitation was used as source.

Computational details

Quantum chemical calculations for 4C2FA were performed with the GAUSSIAN 98W program (Frisch et al., 2002) using the Becke-3–Lee–Yang–Parr (B3LYP)

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functionals (Becke, 1993 and Lee et al., 1998) supplemented with the 6-311+G** basis sets (referred large basis sets), for the Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry by assuming C_s point group symmetry. Scaling of the force field was performed according to the SQM procedure (Pulay et al., 1983 and Rahght et al., 1995) using selective (multiple) scaling in the natural internal coordinate representation (Fogarasi et al., 1992). Transformations of the force field and the subsequent normal coordinate analysis including the least squares refinement of the scaling factors, calculation of total energy distribution (TED) and IR and Raman intensities were done on a PC with the MOLVIB program (Version V7.0-G77) written by Sundius (1990 and 2002). The TED elements provide a measure of each internal coordinate's contribution to the normal coordinate. For the plots of simulated IR and Raman spectra, pure Lorentzian band shapes were used with a band width (FWHM) of 10 cm^{-1}.

Prediction of Raman intensities

The Raman activities (Si) calculated with the GAUSSIAN 98W program and adjusted during the scaling procedure with MOLVIB were subsequently converted to relative Raman intensities (Ii) using the following relationship derived from the basic theory of Raman scattering (Polavarapu, 1990; Keresztury et al., 2007 and Keresztury, 2002).

$$I_i = \frac{f(v_o - v_i)^4 S_i}{v_i[1 - \exp(-hcv_i/KT)]} \text{--------------(1)}$$

Where υ_0 is the exciting frequency (in cm^{-1}), υ_i is the vibrational wavenumber of the ith normal mode; h, c and k are fundamental constants, and f is a suitably chosen common normalization factor for all peak intensities.

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:

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

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 98W output is given as follows (Frisch et al., 2002):

$$\beta_{tot} = [(\beta_{xxx} + \beta_{xyy} + \beta_{xzz})^2 + (\beta_{yyy} + \beta_{yzz} + \beta_{yxx})^2 + (\beta_{zzz} + \beta_{zxx} + \beta_{zyy})^2]^{1/2}$$

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 (Becke, 1993). 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 (Cohen et al., 1964). 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.

RESULTS

Molecular geometry

The optimized molecular structure of 4C2FA 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.

Detailed description of vibrational modes can be given by means of normal coordinate analysis (NCA). For this purpose, the 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 recommendations of Fogarasi et al., (1985 and 1992) are summarized in Table 4. The theoretically calculated DFT force fields were transformed in this later set of vibrational coordinates and used in all subsequent calculations.

Table 1. Total energies of 4C2FA, calculated at DFT (B3LYP)/6-31G* and (B3LYP)/6-311+G level**

Method	Energies (Hartrees)
6-31G*	-846.419315
6-311+G**	-846.430762

Analysis of vibrational spectra

The 36 normal modes of 4C2FA are distributed among the symmetry species as Γ_{3N-6}= 25 A' (in-plane) + 11 A″ (out-of-plane), and in agreement with C_s symmetry. All the vibrations were active both in Raman scattering and infrared absorption. In the Raman spectrum the in-plane vibrations (A') give rise to polarized bands while the out-of-plane ones (A″) to depolarized band.

Table 2. Optimized geometrical parameters of 4C2FA obtained by B3LYP/ 6–311+G** density functional calculations

Bond length	Value(Å)	Bond angle	Value(Å)	Dihedral angle	Value(Å)
C2-C1	1.402	C3-C2-C1	123.377	C4-C3-C2-C1	0.016
C3-C2	1.383	C4-C3-C2	118.208	C5-C4-C3-C2	-0.159
C4-C3	1.395	C5-C4-C3	120.627	C6-C5-C4-C3	0.197
C5-C4	1.392	C6-C5-C4	119.719	N7-C1-C2-C3	-177.001
C6-C5	1.395	N7-C1-C2	120.001	H8-N7-C1-C2	-21.696
N7-C1	1.392	H8-N7-C1	114.222	H9-N7-C1-C2	-153.783
H8-N7	1.012	H9-N7-C1	115.113	F10-C2-C3-C4	179.263
H9-N7	1.012	F10-C2-C3	119.366	H11-C3-C4-C5	179.569
F10-C2	1.358	H11-C3-C4	121.978	Cl12-C4-C5-C6	-179.985
H11-C3	1.083	Cl12-C4-C5	120.021	H13-C5-C6-C1	-179.996
Cl12-C4	1.759	H13-C5-C6	120.188	H14-C6-C1-C2	-179.657
H13-C5	1.084	H14-C6-C1	119.086		
H14-C6	1.087				

*for numbering of atom refer Fig. 1

Table 3. Definition of internal coordinates of 4C2FA

Definition No(i)	symbol	Type	Definition
Stretching			
1 -3			
	r_i	C-H	C3-H11,C5-H13,C6-H14.
4	R_i	C-Cl	C4-Cl2
5	q_i	C-F	C2-F10
6-7	Q_i	N-H	N7-H8,N7-H9
8	P_i	C-N	C1-N7
9-14	p_i	C-C	C1-C2,C2-C3,C3-C4,C4-C5, C5-C6,C6-C1
Bending			
15-20	β_i	C-C-H	C2-C3-H11,C4-C3-H11,C4-C5-H13, C6-C5-H13,C5-C6-H14,C1-C6-H14.
21-22	θ_i	C-C-Cl	C3-C4-Cl12,C5-C4-Cl12
23-24	φ_i	C-C-F	C1-C2-F10,C3-C2-F10
25-26	λ_i	C-C-N	C2-C1-N7,C6-C1-N7
27	γ_i	H-N-H	H8-N7-H9
28-29	Π_i	C-N-H	C1-N7-H8,C1-N7-H9
30-35	α_i	Ring	C1-C2-C3,C2-C3-C4,C3-C4-C5, C4-C5-C6,C5-C6-C1,C6-C1-C2
Out-of-plane bending			
36-38			
	ω_i	ωC-H	H11-C3-C2-C4,H13-C5-C4-C6, H14-C6-C5-C1
39	ω_i	ωC-Cl	Cl12-C4-C3-C5
40	ω_i	ωC-F	F10-C2-C1-C3
41	ω_i	ωC-N	N7-C1-C6-C2
42	ω_i	ωN-H	C1-N7-H8-H9
Torison			
43-48	τ_i	τRing	C1-C2-C3-C4,C2-C3-C4-C5,C3-C4-C5-C6,C4-C5-C6-C1,C5-C6-C1-C2,C6-C1-C2-C3
49	τ_i	τC-N	C2(C6)-C1-N7-H8(H9)

*for numbering of atom refer Fig. 1

The detailed vibrational assignments of fundamental modes of 4C2FA along with calculated IR, Raman intensities and normal mode descriptions (characterized by TED) were reported in Table 5. For visual comparison, the observed and simulated FT-IR and FT-Raman spectra of 4C2FA are produced in a common frequency scales in Fig. 2 and Fig. 3.

DISCUSSION

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

$$ \text{RMS} = \sqrt{\frac{1}{n-1}\sum_{i}^{n}\left(\upsilon_i^{calc} - \upsilon_i^{exp}\right)^2} $$

The RMS error of the observed and calculated frequencies (unscaled / B3LYP/6-311+G**) of 4C2FA was found to be 105 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 7.54 cm^{-1} between the experimental and scaled frequencies of the title compound.

Table 4. Definiton of local symmetry coordinates and the value corresponding scale factors used to correct the force fields for 4C2FA

No.(i)	Symbol[a]	Definition[b]	Scale factors used in calculation
1-3	C-H	r1,r2,r3	0.918
4	C-Cl	R4	0.913
5	C-F	q5	0.913
6	NH2(ss)	(Q6+Q7)/ /√2	0.904
7	NH2(as)	(Q6-Q7)/ /√2	0.904
8	C-N	P8	0.992
9-14	C-C	p9,p10,p11,p12,p13,p14	0.918
15-17	C-C-H	(β15- β16) /√2,(β17-β18) /√2,(β19- β 20) /√2	0.991
18	C-C-Cl	(θ21- θ 22) /√2	0.981
19	C-C-F	(φ23- φ24) /√2	0.991
20	C-C-N	(λ25- λ26) /√2.	0.959
21	NH2(sciss)	(2γ27-Π28- Π29) /√6	0.990
22	NH2(rock)	(Π28- Π29) /√2.	0.980
23	bring	(α30-α31+α32-α33+α34-α35)/ √6	0.979
24	bring	(2α30-α31-α32+2α33-α34-α35) √12	0.979
25	bring	(α31-α32+α34-α35)/2	0.979
26-28	ωC-H	ω36, ω37, ω38	0.993
29	ωC-Cl	ω39	0.990
30	ωC-F	ω40	0.990
31	ωC-N	ω41	0.993
32	ωN-H	ω42	0.961
33	tring	(τ43-τ44+τ45-τ46+τ47-τ48) √6	0.978
34	tring	(τ43-τ45+τ46-τ48)/2	0.978
35	tring	(-τ43+2τ44-τ45-τ46+2τ47-τ48) √12	0.978
36	τN-H	(τ49)/4	0.961

[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

C-C Vibrations:

The bands between 1650-1400 cm^{-1} in benzene derivatives are assigned to C–C stretching modes (Sathyanarayana, 2004). Accordingly in the present study, the carbon–carbon vibrations are observed in 4C2FA at 1630, 1602, 1587,1500,1457,1423 cm^{-1} in the FT-IR spectrum and in the FT-Raman at 1631 cm^{-1}.

C-H Vibrations:

Hetroaromatic structure shows the presence of C-H. Stretching vibration in the region 3100–3000 cm^{-1}. This is the characteristic region for the ready identification of C-H stretching vibration (Varsanyi, 1973). In this region, the bands are not affected appreciably by the nature of the substituents. In the present investigation, the bands observed at 3088,3069 cm^{-1} in FT-IR and at FT-Raman at 3065 cm^{-1} has been designated to C-H stretching vibration. The C-H bending vibrations are expected to interact a little around 1300–1600 cm^{-1} with ring vibrations. The band at 810 cm^{-1} is associated with C-H out-of-plane binding mode.

C-N Vibrations:

The identification of C-N vibration is a difficult task, since the mixing of vibrations is possible in this region. However, with the help of force field calculations, the C-N vibrations were identified and assigned in this study. The FT-IR and FT-Raman bands observed at 1154, 1147, 1077 and 1075 cm^{-1}, in the title compounds have been assigned to C-N stretching vibrations. The in-plane and out-of-plane bending vibrations assigned in this study are also supported by the literature (Krishnakumar et al., 2003 and Peet et al., 1988).

N-H Vibrations:

It has been observed that the presence of N-H in various molecules may be correlated with a constant occurrence of absorption bands whose positions are only slightly altered from one compound to another, this is because the atomic group vibrates independently of the other groups in the molecule and has its own frequency. Normally in all the hetrocyclic compounds, the N-H stretching vibration (Socrates, 2001) occurs in the region 3500-3000 cm^{-1}. The FT-IR and FT-Raman bands appearing at 3466,3382,3099 and 3077 cm^{-1} is assigned to N-H stretching modes of vibration. The N-H in-plane bending and out-of-plane bending vibrations are found at 575,564 cm^{-1} in FT-IR and at 560 cm^{-1} in FT-Raman.

C-F Vibrations:

The vibrations belonging to the bond between the ring and the halogen atoms are worth to discuss here, since mixing of vibrations are possible due to the presence of heavy atoms on the periphery of the molecule (Bakiler et al., 1999). C–F bond show lower absorption frequencies as compared to C–H bond due to the decreased force constant and increase in reduced mass. F cause redistribution of charges in the ring. In 4C2FA, the C–F stretching and out-of-plane bending vibrations appeared at 1246,1210 and 1247,1212 cm^{-1} in FT-IR and FT-Raman, respectively. The C–F in-plane bending vibration was found at 564 and 560 cm^{-1} in FT-IR and FT-Raman spectrum and second position of aniline ring significantly changes the normal modes. Finally, the charge on the F and its variation during vibration significantly contribute to many of the IR lines, due to heavy atoms substituent in 4C2FA. The very similar behaviour in the IR intensities of vC-Cl and vC-F were also observed. In 4C2FA, the very strong and the medium strong FT-IR bands observed at 1246, 1210, 689, 683 cm^{-1} and Raman bands are observed at 1247, 1212, 668 cm^{-1} are assigned to vC-F. The very strong IR bands obtained at 810 and 783 cm^{-1} and Raman bands at 786 cm^{-1} in the observed spectra are assigned to vC-Cl. Strong characteristic absorptions due to the C-F stretching vibrations are observed in this study. In the organic halogen compounds the band due to C-F stretching vibrations may be found over a wide frequency range, 1360–1000 cm^{-1}, since the vibration is easily influenced by adjacent atoms or groups. The C-Cl stretching

Table 5. Detailed assignments of fundamental vibrations of 4C2FA by normal mode analysis based on SQM force field calculation

No.	Symmetry species Cs	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'	3466 s		3665	3465	0.006	20.11	NH(100)
2	A'	3382 s		3484	3380	0.004	22.11	NH(100)
3	A'	3099 w	3077 s	3263	3105	0.052	25.38	NH(99)
4	A'	3088 w		3165	3080	0.109	1.36	CH(99)
5	A'	3069 w	3065 s	3127	3051	0.108	10.24	CH(99)
6	A'	1712 w		1822	1710	0.581	6.11	bNH2(79),CN(9),CC(8)
7	A'	1630 w	1631 w	1764	1656	0.781	15.62	CC(65),bCH(11), bNH2(8),bring(7)
8	A'	1602 s		1675	1625	0.610	27.92	CC(70),bring(8),bCH(8)
9	A'	1587 s		1615	1583	0.620	0.64	CC(42),bCH(37),CN(11),CF(5)
10	A'	1500 s		1570	1466	0.116	17.92	CC(55),bCH(21),CF(7),bCF(5)
11	A'	1457 w		1496	1450	0.117	18.33	CC(56),bCH(15),CN(11),bNH(11)
12	A'	1423 s		1447	1415	0.523	18.99	CC(66),CN(13),bCH(11)
13	A'	1295 w		1380	1295	0.539	1.44	CC(62), bCH(23)
14	A'	1246 s	1247 s	1367	1247	0.03	7.96	CF(31),bring(18),CN(16),bCH(12),CC(10),bNH(6)
15	A"	1210 s	1212 vs	1291	1209	0.147	16.27	CF (56),CN(21),bNH(8),CC(7)
16	A'	1147 s	1154 w	1205	1152	0.314	20.22	CN(35),CCl(25),bCH(21),CF(7),CC(5)
17	A'	1075 vs	1077 vs	1143	1069	0.520	1.71	CN(44),bNH(30),CC(10),bCH(6)
18	A"	858 s		990	860	0.103	0.77	CCl(52), gCH(12),bring(12),CC(8),tring(6)
19	A'	810 s		964	822	0.082	8.34	CCl(52),bring(12),gCH(12),CC(8),tring(6)
20	A'	783 vs	786 s	858	790	0.085	0.59	CCl(81),tring(13)
21	A"	689 vs		772	692	0.084	0.64	gCF(76),tring(9),gCN(7)
22	A'	683 s		749	680	0.712	2.71	gCF(42),bring(20),CN(14),gCH(11)
23	A'		668 w	724	686	0.432	2.12	gCF(57),gCN(15),tring(11),gCCl(5)
24	A"		580 s	682	597	0.578	0.42	bring(35),tring(22),gNH2(8),CCl(8),CC(7)
25	A'	575 s		628	571	0.098	0.36	gNH2(51),bNH2(17),CN(10),tring(9)
26	A'	564 s	560 s	594	558	0.612	0.35	gCF(41),bNH2(21), tring(19),gCN(11)
27	A'		471 w	475	473	0.582	5.12	bCN(25),bCF(22),bring(20),CC(10),bCCl(9)
28	A'		467 s	470	468	0.442	0.59	bring(48),bCF(22),CC(9),CCl(6),bCCl(5)
29	A'		453 w	458	453	0.416	16.47	tring(60),gCF(23),gCN(6),gCH(5)
30	A"		373 vs	383	374	0.621	0.45	bring(78),CCl(9),CC(7)
31	A"		344 w	356	345	0.081	11.34	gCN(27),gCF(19),tring(17),gCCl(16),gCH(11),tNH(8)
32	A"		303 w	324	304	0.008	6.13	tNH(43),bCN(26),bCF(10)
33	A"		297 w	315	298	0.011	6.26	tNH(41),bCN(24),bCF(13),bring(10)
34	A"		235 vw	272	235	0.567	0.32	bCCl(78),CC(9),bCN(5)
35	A"		225 s	243	225	0.434	2.14	tring(47),gCCl(21),gCF(17),gCH(13)
36	A"		128 w	179	128	0.218	22.36	tring(68),gCCl(12),gCH(11),gCF(6)

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.

Table 6. The dipole moment (μ) and first-order hyperpolarizibility (β) of 4C2FA derived from DFT calculations

β_{xxx}	123.0254396
β_{xxy}	-23.5074574
β_{xyy}	-3.0073122
β_{yyy}	-2.058542
β_{zxx}	51.0205493
β_{xyz}	-12.2543771
β_{zyy}	0.3660359
β_{xzz}	39.0641505
β_{yzz}	-14.7386395
β_{zzz}	-42.362928
β_{total}	1.643564
μ_x	0.5246274
μ_y	-0.5576629
μ_z	-1.0567506
μ	1.304964

Dipole moment (μ) in Debye, hyperpolarizibility $\beta(-2\omega;\omega,\omega)$ 10^{-30} esu.
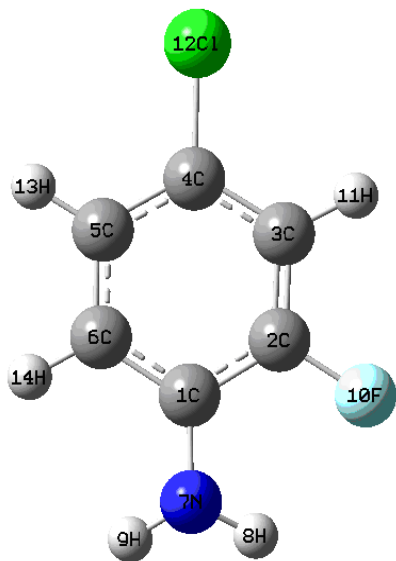
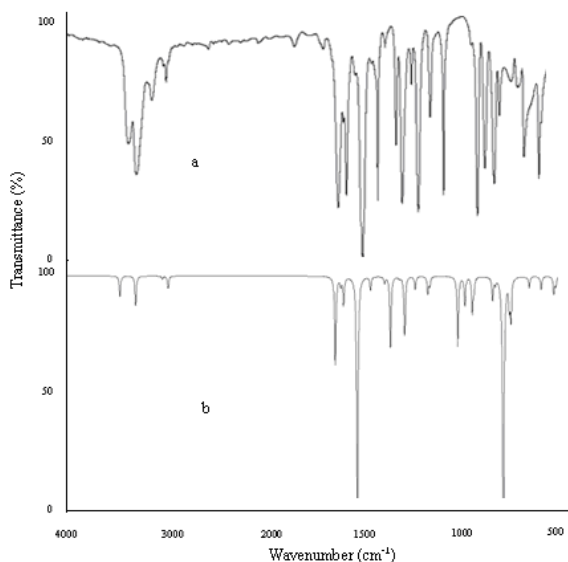**Fig. 1. The optimized molecular structure of 4C2FA**

Fig. 2   FT-IR spectra of 4C2FA (a)   Observed (b) Calculated with B3LYP/6-311+G**

vibrations give generally strong bonds in the region 760–505 cm^{-1}.

C-Cl Vibrations:

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 (Lakshmaiah et al., 1989). Based on this, the FT-IR and FT-Raman bands observed at 858,810,786 and 783 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 668 cm^{-1} and 580 cm^{-1} for IR and Raman, respectively.

NH$_2$ Vibrations:

According to Socrates, (2001) the stretching, scissoring and rocking deformation of amino group appeared around
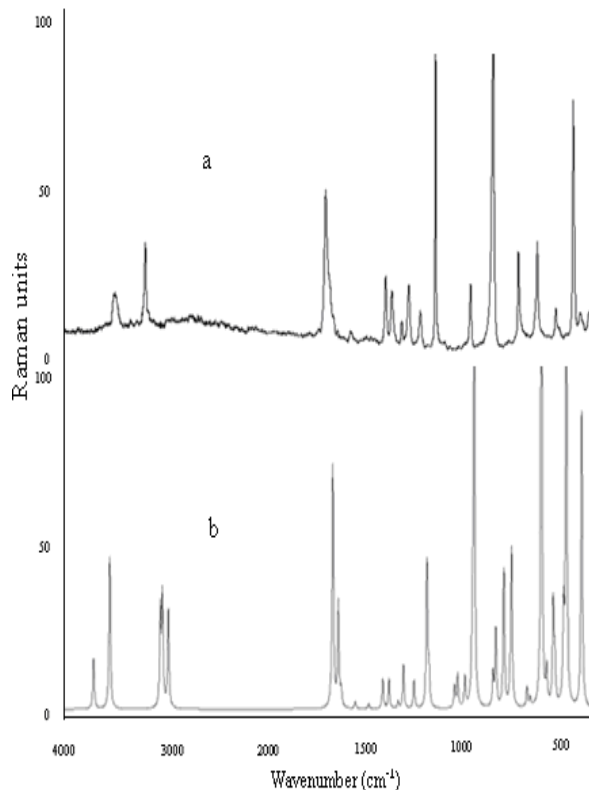

Fig. 3 FT-Raman spectra of 4C2FA (a) Observed (b) Calculated with B3LYP/6-311+G**

3500–3000, 1700–1600, 1150–900 cm^{-1}, respectively in absorption spectra. In 4C2FA, the antisymmetric, symmetric stretching modes of NH$_2$ group found at 3466, 3382, 1712, 1630 cm^{-1} in FT-IR and 3077, 1631 cm^{-1} in FT-Raman respectively.

Ring Vibrations:

Several ring modes are affected by the substitution to the aromatic ring of aniline. In the present study, the bands ascribed at 1246,858,810,786,783,689,668 and 580 cm^{-1} have been designated to ring in-plane and out-of-plane bending modes, respectively. The reduction in frequencies of these modes compared to aniline are due to the changes in the force constant, resulting mainly from addition of nitro group to aniline and from different extents of mixing between the ring and substituent groups vibration.

Hyperpolarizability calculations

The first-order hyperpolarizibility (β_{ijk}) of the novel molecular system of 4C2FA 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 symmetry (Kleinman, 1962). The calculated first-order hyperpolarizability (β_{total}) of 4C2FA is 1.643564×10^{-30} esu, which is nearly nine times that of urea (0.1947×10^{-30} esu). The calculated dipole moment (μ) and first-order hyperpolarizability (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_{xxx} (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. 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 (Prasad et al., 1991). 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.

Conclusion

Based on the SQM force field obtained by DFT calculations at B3LYP/6-311+G** levels, a complete vibrational properties of 4C2FA have been investigated by FT-IR and FT-Raman spectroscopies. The roles of chloro, fluro and nitro groups in the vibrational frequencies of the title compounds were discussed. Refinement of the scaling factors applied in this study achieved a weighted mean deviation of 7.54 cm^{-1} between the experimental and scaled frequencies of the title compound. The various modes of vibrations were unambiguously assigned based on the results of the TED output obtained from normal coordinate analysis. The assignment of the fundamentals is confirmed by the qualitative agreement between the calculated and observed band intensities and polarization properties as well and is believed to be unambiguous. The first-order hyperpolarizibility (β_{ijk}) of the novel molecular system of 4C2FA is calculated using 3-21 G (d,p) basis set based on finite field approach. The calculated first-order hyperpolarizability (β_{total}) of 4C2FA is 1.643564x10^{-30} esu, which is nearly nine times that of urea (0.1947 x 10^{-30} esu).

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