Harmonic Analysis of Vibrations of 4-Chloro-2-Fluroaniline: A Scaled Quantum Mechanical Approach

G. RAJA[1]* and K. SARAVANAN[2]

[1]Department of Chemistry,Paavai Engineering College, Namakkal - 637 018,India.
[2]Department of Chemistry, Thiruvalluvar Government Arts College,Rasipuram -637 401, India.
*Corresponding author E-mail: genuineraja@gmail.com

ABSTRACT

The FT-IR and Raman spectra of 4-Chloro-2-Fluroaniline (4C2FA) were measured. The fundamental vibrational frequencies and intensity of vibrational bands were evaluated using density functional theory (DFT) and standard B3LYP/6-311+G** basis set combination. The vibrational spectra were interpreted, with the aid of normal coordinate analysis based on a scaled quantum mechanical (SQM) force field. The infrared and Raman spectra were also predicted from the calculated intensities. Comparison of simulated spectra with the experimental spectra provides important information about the ability of the computational method to describe the vibrational modes. Unambiguous vibrational assignment of all the fundamentals was made using the total energy distribution (TED).

Key words: Normal coordinate analysis; FT-IR and FT-Raman spectra; Density functional theory.

INTRODUCTION

Quantum chemical computational methods have proved to be an essential tool for interpreting and predicting the vibrational spectra[1-3]. A significant advancement in this area was made by combining semi empirical quantum mechanical method; ab initio quantum mechanical method and density functional theory (DFT), each method having its own advantage. In scaled quantum mechanical (SQM) approach, the systematic errors of the computed harmonic force field are corrected by a few scale factors which are found to be well transferable between chemically related molecules and were recommended for general use. 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.

Experimental details

The fine samples of 4C2FA were obtained from Lancaster Chemical Company, UK, and used as such for the spectral measurements. The room temperature Fourier trans-form 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 GAUS-SIAN 98W program[4] using the Becke-3–Lee–Yang–Parr (B3LYP) functionals [5,6] 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 opti-mized geometry by assuming C_s point group symmetry.

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 [7,8] 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.

Analysis of vibrational spectra

The 36 normal modes of 4C2FA are distributed among the symmetry species as Γ_{3N-6}= 25 A' (in-plane) + $^{11}A^2$ (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^{11}) to depolarized band. The

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

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

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 & Fig. 3.

C-F Vibrations

The vibrations belonging to the bond between the ring and the halogen atoms are worth to discuss here, since mix-ing of vibrations are possible due to the presence of heavy atoms on the periphery of the molecule [9]. 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 signifi-cantly 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.

Table 3: Definition of internal coordinates of 4C2FA

No(i)	symbol	Type	Definition
Streching1 -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
Bending15-20	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	θ_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	Γ_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 bending36-38	w_i	wC-H	H11-C3-C2-C4,H13-C5-C4-C6,H14-C6-C5-C1
39	ω_i	τC-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
Torison43-48	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

Strong characteristic absorptions due to the C-F stretch-ing vibrations are observed in this study. In the organic halogen compounds the band due to C-F stretch-ing 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 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[10]. 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 pla-nar 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[11] the stretching, scissoring and rocking deformation of amino group appeared around 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,

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)	$(Q6+Q7)/\sqrt{2}$	0.904
7	NH2(as)	$(Q6-Q7)/\sqrt{2}$	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	$(\beta15-\beta16)/\sqrt{2},(\beta17-\beta18)/\sqrt{2},(\beta19-\beta20)/\sqrt{2}$	0.991
18	C-C-Cl	$(\theta21-\theta22)/\sqrt{2}$	0.981
19	C-C-F	$(\phi23-\phi24)/\sqrt{2}$	0.991
20	C-C-N	$(\lambda25-\lambda26)/\sqrt{2}.$	0.959
21	NH2(sciss)	$(2\gamma27-\Pi28-\Pi29)/\sqrt{6}$	0.990
22	NH2(rock)	$(\Pi28-\Pi29)/\sqrt{2}.$	0.980
23	bring	$(\alpha30-\alpha31+\alpha32-\alpha33+\alpha34-\alpha35)/\sqrt{6}$	0.979
24	bring	$(2\alpha30-\alpha31-\alpha32+2\alpha33-\alpha34-\alpha35)\sqrt{12}$	0.979
25	bring	$(\alpha31-\alpha32+\alpha34-\alpha35)/2$	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	τring	$(\tau43-\tau44+\tau45-\tau46+\tau47-\tau48)\sqrt{6}$	0.978
34	τring	$(\tau43-\tau45+\tau46-\tau48)/2$	0.978
35	τring	$(-\tau43+2\tau44-\tau45-\tau46+2\tau47-\tau48)\sqrt{12}$	0.978
36	τN-H	$(t49)/4$	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.

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) withB3LYP/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	0.612	0.35	gCF(41),bNH2(21), tring(19),gCN(11)
27	A'		471 w	475	0.582	5.12	bCN(25),bCF(22),bring(20),CC(10),bCCl(9)
28	A'		467 s	470	0.442	0.59	bring(48),bCF(22),CC(9),CCl(6),bCCl(5)
29	A'		453 w	458	0.416	16.47	tring(60),gCF(23),gCN(6),gCH(5)
30	A"		373 vs	383	0.621	0.45	bring(78),CCl(9),CC(7)
31	A"		344 w	356	0.081	11.34	gCN(27),gCF(19),tring(17),gCCl(16),gCH(11),tNH(8)
32	A"		303 w	324	0.008	6.13	tNH(43),bCN(26),bCF(10)
33	A"		297 w	315	0.011	6.26	tNH(41),bCN(24),bCF(13),bring(10)
34	A"		235 vw	272	0.567	0.32	bCCl(78),CC(9),bCN(5)
35	A"		225 s	243	0.434	2.14	tring(47),gCCl(21),gCF(17),gCH(13)
36	A"		128 w	179	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.
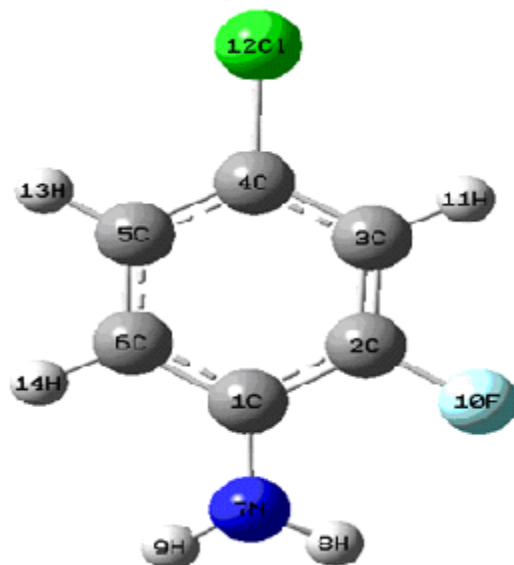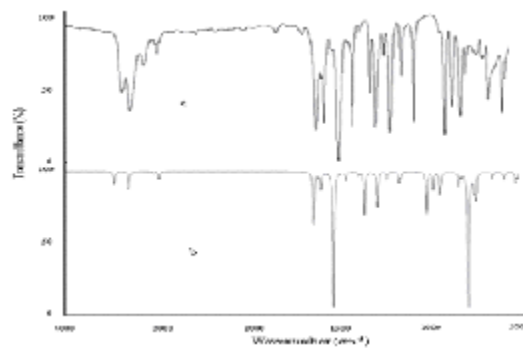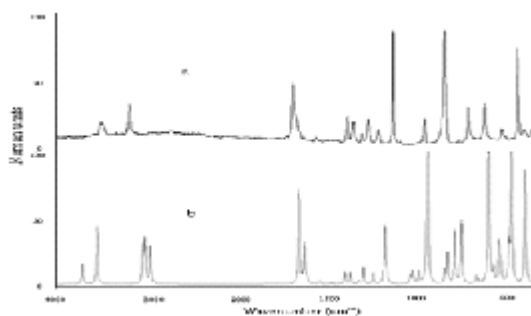
[c] For the notations used see Table 4.

Fig. 1: The optimized molecular structure of 4C2FA

(a)Observed (b) Calculated with B3LYP/6-311+G**

Fig. 2: FT-IR spectra of 4C2FA

(a) Observed (b) Calculated with B3LYP/6-311+G**

Fig. 3: FT-Raman spectra of 4C2FA

1630 cm^{-1} in FT-IR and 3077, 1631 cm^{-1} in FT-Raman respectively.

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 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.

REFERENCES

1. P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs, A. Vargha, *J. Am. Chem. Soc.* **105**: 7037 (1983).
2. G. Rauhut, P. Pulay, *J. Phys. Chem.* **99**: 3093 (1995).
3. J. Baker, A.A. Jarzecki, P. Pulay, *J. Phys. Chem.,* **A102**: 1412 (1998).
4. M.J. Frisch, G.W. Trucks, H.B. Schlega, G.E. Scuseria, M.A. Robb, J.R. Cheesman, V.G. Zakrzewski, J.A. Montgomery Jr., R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, N. Roga, P. Salvador, J.J. Dannenberg, D.K. Malick, A.D. Rabuck, K. Rahavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Penng, A.
Nanayakkara, M. Challa-Combe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle and J.A. Pople, Gaussian 98, Revision A 11.4, Gaussian Inc., Pittsburgh, PA (2002).
5. A.D. Becke, *J. Chem. Phys.*, **98**: 5648 (1993).
6. C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B.* 37: 785 (1998).
7. G. Fogarasi and P. Pulay In: J.R. Durig, Editor, Vibrational Spectra and Structure vol. 14, Elsevier, *Amsterdam*, pp. 125 (Chapter 3) (1985).
8. G. Fogarasi, X. Xhov, P.W. Taylor and P. Pulay, *J. Am. Chem. Soc.* **114**: 8191 (1992).
9. M. Bakiler, I.V. Maslov, S. Akyiiz, *J. Mol. Struct.* **475**: 83 (1999).
10. B. Lakshmaiah, G. Ramana Rao, *J. Raman Spectrosc.* **20**: 439 (1989).
11. G. Socrates, Infrared and Raman characteristic group frequencies, tables and charts, third ed., Wiley, Chichester (2001).