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Scaled Quantum Chemical Studies of the Structure and Vibrational Spectra of 2-Chloro-1-Fluoro-4-Nitrobenzene and 2,4-Dibromo-1-Fluorobenzene

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ABSTRACT

The FTIR and FT-Raman spectra of 2-Chloro-1-Fluoro-4-Nitrobenzene (CFNB) and 2,4-Dibromo-1-Fluorobenzene (DBFB) 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 were calculated by using density functional theory (DFT) employing B3LYP 6-311++G and 6-311++G(d,p) basis set. The geometry of the molecule was fully optimized, vibrational spectra were calculated and fundamental vibration were assigned on the basis of total energy distribution (TED) of the vibrational modes calculated with scaled quantum mechanical (SQM) method.

Introduction

Benzene and its derivates have been investigated extensively using vibrational spectroscopy. Electronic spectra and vibrational spectra of some trisubstituted benzene have been studied and reported in the literature. Chloro,bromo, fluorobenzene and its derivatives are used to control carbon content in steel manufacturing [1]. It is also an intermediate for pharmaceutical pesticides and other organic compounds.

Literature survey reveals that to the best of my knowledge no DFT frequency calculations of 2-Chloro-1-fluoro-4-nitrobenzene (CFNB) and 2,4-dibromo-1-fluorobenzene (DBFB) have been reported so far. Therefore, we have undertaken the detailed theoretical and experimental investigation of the vibrational spectra of the title molecules.

2. Experimental methods

The compounds CFNB and DBFB in the solid form were purchased from Lancaster chemical company, UK and used as such without any further purification. The FT-Raman spectrum of CFNB and DBFB has been recorded using 1064nm line of Nd:YAG laser as excitation wavelength in the region 100-3500cm^{-1} on a BRUKER model IFS 66V spectrophotometer equipped with FRA 106 FT-Raman module accessory. The FTIR spectrum of CFNB and DBFB was recorded in the region 400-4000cm^{-1} at a resolution of ± 1 cm^{-1} using BRUKER on IFS 66V model FTIR spectrophotometer using KBr pellet technique.

3. Computational Details

The entire calculations were performed at B3LYP levels using GAUSSIAN 03 Window [2] program package involving gradient geometry optimization [3].

Initial geometry generated from standard geometrical parameters was minimized without any constraint in the potential energy surface at B3LYP levels adopting the standard 6-311++G basis set. This geometry was then re-optimized again at B3LYP level, using basis set 6-311++G(d,p). The optimized structural parameters were used in the vibrational frequency calculations at the DFT levels to characterize all stationary points as minima. We have utilized the gradient corrected density functional theory (DFT) [4] with the three parameters hybrid functional (B3) [5] for the exchange part and Lee-Yang-Parr (LYP) correlation function [6], accepted as a cost-effective approach, for the computation of molecular structure, vibrational frequencies and energies of optimized structures. Vibrational frequencies computed at DFT level have been adjudicated to be more reliable than those obtained by the computationally demanding Moller-Plesset perturbation methods. Density functional theory offers electron correlation frequently comparable to second-order Moller-Plesset theory (MP2). Finally, the calculated normal mode vibrational frequencies provide thermodynamic properties also through the principle of statistical mechanics.

By combining the results of the GAUSSVIEW program [7] with symmetry considerations vibrational frequency assignments were made with a high degree of accuracy. There is always some ambiguity in defining internal coordination.However, the defined coordinate form complete set and matches quite well with the motions observed using the GAUSSVIEW program. Raman intensities (Ii) using the following relationship derived from the basis theory of Raman scattering [8,9].

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$$I_i = \frac{f(\nu_0 - \nu_i)^4 S_i}{\nu_i \left[1 - \exp\left(\frac{hc\nu_i}{kT}\right)\right]} \quad \ldots (5.1)$$

Where $\nu_o$is the exciting frequency (in cm^{-1} units), ν_i is the vibrational wavenumber for the i^{th} normal modes, h, c, k are fundamental constants and f is a suitable chosen common normalization factor for all peak intensities.

4. Results and Discussion

4.1. Molecular geometry

The optimized molecular structure of CFNB and DBFB both having C^s symmetry are shown in Fig. 1 and 2 respectively. The global minimum energy obtained by the DFT structure optimization for CFNB are calculated as -995.58645926Hartrees and -995.75777428 Hartrees, from 6-311++G and 6-311++G(d,p) basis sets , respectively. The global minimum energy obtained by the DFT structure optimization for DBFB is calculated as -5478.47944501 Hartrees and -5478.65826417 Hartrees, from 6-311++G and 6-311++G(d,p) basis sets, respectively.

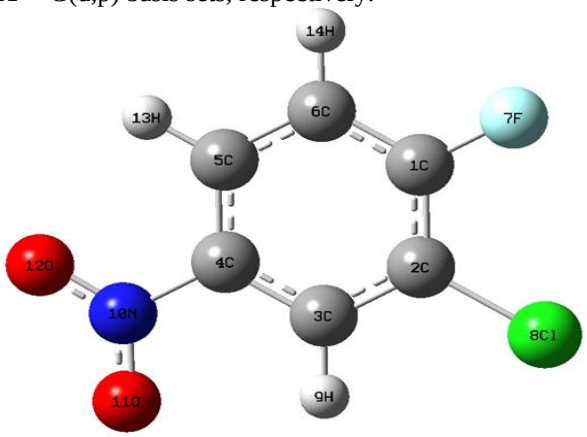

Fig. 1.Molecular Structure of 2-chloro-1-fluoro-4-nitrobenzene.

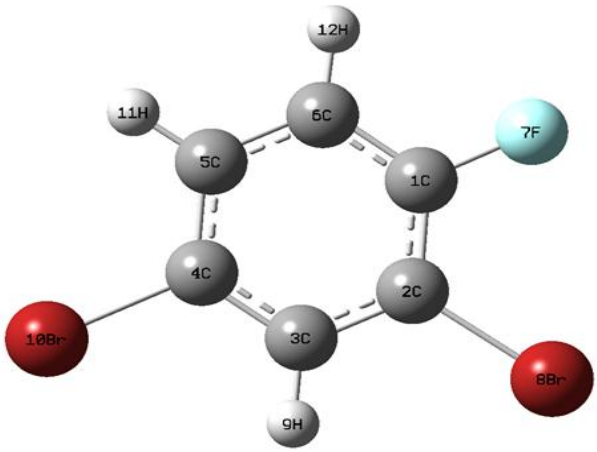

Fig. 2.Molecular Structure of 2,4-dibromo-1-fluorobenzene.

Detailed description of vibrational modes is given by means of normal coordinate analysis (NCA). For this purpose, the full set of 48 and 42 standard internal coordinates for CFNB and DBFB are defined as given in Table 1 and 2 respectively. The local symmetry coordinates are summarized in Tables 3 and 4 for CFNB and DBFB respectively. The optimized geometrical parameters obtained by the large basis set calculations in this study for CFNB and DBFB are presented in Tables 5 and 6 respectively. The detailed vibrational band assignments of CFNB and DBFB calculated by the DFT calculations based on B3LYP level with 6-311++G and 6-311++G(d,p) basis set along with the calculated IR intensities, Raman activities, Reduced masses, force constant and normal mode descriptions (characterized by TED) are reported in Table 7 and 8.

Table.1.Definition of Internal Coordinates of 2-chloro-1-fluoro-4-nitrobenzene.

No. (i)	Symbol	Type	Definition
Stretching			
1	S_i	C – F	C1 – F7
2	q_i	C - Cl	C2 – Cl8
3	Q_i	C – N	C4 – N10
4, 5	r_i	N – O	N10 – O11, N10 – O12
6 – 8	R_i	C – H	C3 – H9, C5 – H13, C6 – H14
9 – 14	T_i	C – C	C1 – C2, C2 – C3, C3 – C4, C4 – C5,C5 – C6, C6 – C1
In-plane bending			
15 – 20	α_i	ring	C1 – C2 – C3, C2 – C3 – C4, C3 – C4 – C5, C4 – C5 – C6, C5 – C6 – C1, C6 – C1 – C2
21 – 26	β_i	C – C – H	C2 – C3 – H9, C4 – C3 – H9, C4 – C5 – H13, C6 – C5 – H13,C5 – C6 – H14, C1 – C6 – H14
27 – 28	γ_i	C – C – Cl	C1 – C2 – Cl8, C3 – C2 – Cl8
29 – 30	θ_i	C – C – F	C6 – C1 – F7, C2 – C1 – F7
31 – 32	π_i	C – C – N	C3 – C4 – N10, C5 – C4 – N10
33 – 34	σ_i	C – N – O	C4 – N10 – O11, C4 – N10 – O12
35	ϕ_i	O – N – O	O11 – N10 – O12
Out-of- plane bending			
36 – 38	ω_i	C – H	H9 – C3 – C4 – C2, H13 – C5 – C6 – C4, H14 – C6 – C1 – C5
39	ψ_i	C – F	F7 – C1 – C2 – C6
40	λ_i	C - Cl	Cl8 – C2 – C3 – C2
41	η_i	C – N	N10 – C4 – C5 – C3
Torsion			
42 – 47	τ_i	ring	C1 – C2 – C3 – C4, C2 – C3 – C4 – C5, C3 – C4 – C5 – C6, C4 – C5 – C6 – C1, C5 – C6 – C1 – C2, C6 – C1 – C2 – C3
48	τ_i	C – NO_2	(C3, C5) – C4 – N10 – (O11, O12)

Table 2.Definition of Internal Coordinates of 2,4-dibromo-1-fluorobenzene.

No. (i)	Symbol	Type	Definition
Stretching			
1	r_i	C – F	C1 – f7
2 – 3	r_i	c – br	c2 – br8, c4 – br10
4 – 6	q_i	C – H	C3 – H9, C5 – H11, C6 – H12
7 – 12	Q_i	C – C	C1 – C2, C2 – c3, c3 – c4, c4 – c5, c5 – c6, c6 – c1
In-Plane Bending			
13 – 18	α	ring	c1 – c2 – c3, c2 – c3 – c4, c3 – c4 – c5, c4 – c5 – c6
19 – 20	β_i	C – c – f	c6 – c1 – f7, c2 – c1 – f7
21 – 24	γ_i	c – c - br	c1 – c2 – br8, c3 – c2, br8, c3 – c4 – br10, c5 – c4 – br10
25 – 30	θ_i	c- c – h	c2 – c3 – h9, c4 – c3 – h9, c4 – c5 – H11, c6 – c5 – h11, c5 – c6 – h12, c1 – c6 – h12
Out-of-plane bending			
31	ω_i	C – F	f7 – c1 – c2 – c6
32 – 33	ψ_i	C - Br	Br8 – C2 – C3 – C1, Br10 – c4 – c5 – c3

34 – 36	μ_i	c – h	h9 – c3 – c4 – c2, h11 – c5 – c6 – c4, h12, c6 – C1 – C5
Torsion			
37 – 42		ring	c1 – c2 – c3 – c4, c2 – c3 – c4 –c5, c3 – c4 – c5 – c6, c4 – c5 – c6 –c1, c5 – c6 – c1 – cl, c6 – c1 – c2 – c3

Table 3.Definition of Local Symmetry Coordinates of 2-chloro-1-fluoro-4-nitrobenzene.

No. (i)	Type	Definition
1	CF	S1
2	CCl	q2
3	CN	Q3
4	NO_2ss	(r4 + r5) / $\sqrt{2}$
5	NO_2ass	(r4 – r5) / $\sqrt{2}$
6 – 8	CH	R6, R7, R8
9 – 14	CC	T9, T10, T11, T12, T13, T14
15	R trigd	(α15 - α16 + α17 - α18 + α19 - α20) / $\sqrt{6}$
16	R symd	(-α15 - α16 + 2α17 - α18 - α19 + 2α20) $\sqrt{12}$
17	R asymd	(α15 - α16 + α18 - α19) / 2
18 – 20	bCH	(β21 - β22) / $\sqrt{2}$, (β23 - β24) / $\sqrt{2}$, (β25 - β26) / $\sqrt{2}$
21	bCCl	(γ27 - γ28) / $\sqrt{2}$
22	bCF	(θ29 - θ30) / $\sqrt{2}$
23	bCN	(π31 - π32) / $\sqrt{2}$
24	NO_2 rock	(σ33 - σ34) / $\sqrt{2}$
25	NO_2 twist	(σ33 + σ34) / $\sqrt{2}$
26	NO_2sciss	(2ϕ35 - σ33 - σ34) / $\sqrt{6}$
27 – 29	ωCH	ω36, ω37, ω38
30	ψCF	ψ39
31	λCCl	λ40
32	ΩCN	Ω41
33	tR trige	(τ42 - τ43 + τ44 - τ45 + τ46 - τ47) / $\sqrt{6}$
34	tR symd	(τ42 - τ44 + τ45 - τ46) / $\sqrt{2}$
35	tRasynd	(-τ42 + 2τ43 - τ44 - τ45 + 2τ46 - τ47) / $\sqrt{2}$
36	tNO_2 wag	τ48

Table 4.Definition of Local Symmetry Coordinates of 2,4-dibromo-1-fluorobenzene.

No. (i)	Type	Definition
1	CF	r1
2, 3	cBr	R2, R3
4 – 6	CH	q4, q5, q6
7 – 12	CC	Q7, Q8, Q9, Q10, Q11, Q12
13	R trigd	(α13 - α14 + α15 - α16 - α17 - α18) / $\sqrt{6}$
14	R symd	(-α13 - α14 + 2α15 - α16 - α17 + 2α18) / $\sqrt{12}$
15	R asymd	(α13 - α14 + α16 - α17) / $\sqrt{2}$
16	bCF	(β19 - β20) / $\sqrt{2}$
17 – 18	bCBr	(γ21 - γ22) / $\sqrt{2}$, (γ23 - γ24) / $\sqrt{2}$
19 – 21	bCH	(θ25 - θ26) / $\sqrt{2}$, (θ27 - θ28) / $\sqrt{2}$, (θ29 - θ30) / $\sqrt{2}$
22	ωCF	ω31
23 – 24	ψCBr	ψ32, ψ33
25 – 27	μCH	μ34, μ35, μ36
28	t R trigd	(τ37 - τ38 + τ39 - τ40 + τ41 - τ42) / $\sqrt{6}$
29	t R symd	(τ37 - τ39 + τ40 - τ42) / $\sqrt{2}$
30	t R asymd	(-τ37 + 2τ38 - τ39 - τ40 + 2τ41 - τ42) / $\sqrt{12}$

4.2. Vibrational Spectra

The 36 and 30 normal modes of CFNB and DBFB are distributed amongst the symmetry species as:

Γ_{3N-6} = 25 A' (in-plane) + 11 A" (out-of-plane)

Γ_{3N-6} = 21 A' (in-plane) + 9 A" (out-of-plane) respectively,

in agreement with C_s symmetry. All the vibrations are active both in the Raman scattering and infrared absorption.

The observed and calculated frequencies of CFNB and DBFB are summarized in Tables 7 and 8 respectively. The detailed vibrational assignment of fundamental modes of CFNB and DBFB along with the calculated IR and Raman intensities and normal mode description (characterized) by TED are reported in tables. The FTIR and FT-Raman spectra of CFNB and DBFB are shown in Figs. 3 – 6.

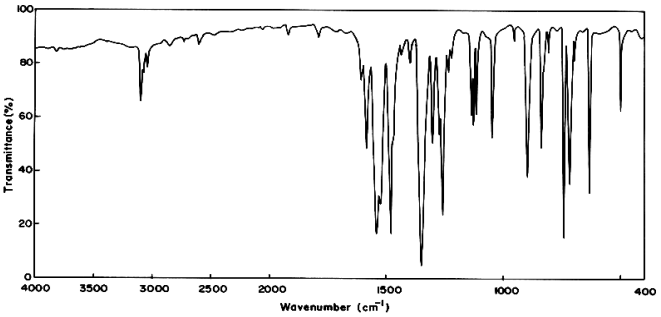

Fig 3. FTIR Spectrum of 2-chloro-1-fluoro-4-nitrobenzene.

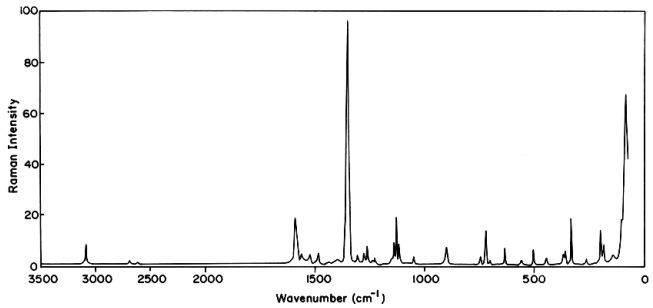

Fig. 4.FT-Raman Spectrum of 2-chloro-1-fluoro-4-nitrobenzene.

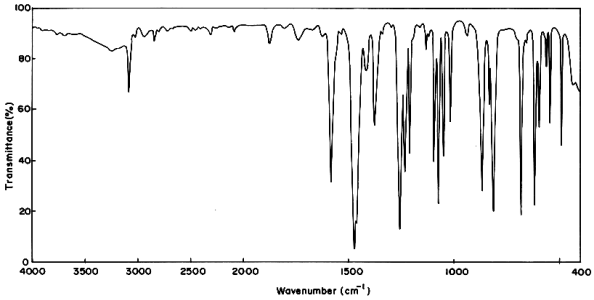

Fig. 5.FTIR Spectrum of 2,4-dibromo-1-fluorobenzene.

Table 5.Optimized geometrical parameters of 2-Chloro-1-fluoro-4-Nitrobenzene obtained by B3LYP/6-311++G and B3LYP/6-311++G(d,p) density functional calculations.

Parameter	Value (Å)		Bond angle	Value (°)		Dihedral Angle	Value (°)	
Bond length	B3LYP/ 6-311++G	B3LYP/ 6-311++G(d,p)		B3LYP/ 6-311++G	B3LYP/6-311++G(d,p)		B3LYP/6-311++G	B3LYP/ 6-311++G(d,p)
C1 – C2	1.3927	1.3967	C1 – C2 – C3	119.4795	119.1925	C1 – C2 – C3 C4	-0	0.0028
C2 – C3	1.3881	1.3886	C2 – C3 – C4	118.3913	118.7041	C2 – C3 – C4 –C5	0.0086	-0.0034
C3 – C4	1.3961	1.3906	C3 – C4 – C5	122.392	122.4182	C3 – C4 – c5 – c6	-0.0107	0.0017
c4 – c5	1.396	1.391	c4 – c5 – c6	118.6502	118.5976	c4 – c5 – c6 – c1	0.0062	0.0005
c5 – c6	1.3926	1.3886	c5 – c6 – c1	119.0937	119.4899	c6 – c1 – c2 – c3	0.0	-0.0007
c6 – c1	1.3891	1.3881	c6 – c1 – c3	121.9933	121.5978	c6 – c1 – c2 – cl8	-180.0016	-180.0002
c1 – c7	1.3869	1.3384	c6 – c1 –f7	118.4499	118.9133	c1 – c2 – c3 – h9	17.9981	180.0018
c2 – cl8	1.8017	1.7394	c2 – c1 – f7	119.5568	119.4889	c2 – c3 – c4 – n10	-180.0091	180.0022
c3 – h9	1.0782	1.0807	c1 – c2 – cl8	120.2882	120.1073	c3 – c4 – n10 – o11	180.0079	0.0215
c4 – n10	1.4652	1.4791	c3 – c2 – cl8	120.2323	120.7001	c3 – c4 – n10 – o12	0.0154	180.0173
n10 – o11	1.2671	1.2237	c2 – c3 – h9	121.2955	121.037	c5 – c4 – n10 – o11	-0.0093	180.0269
n10 – o12	1.267	1.2238	c4 – c3 – h9	120.3132	120.259	c5 – c4 – n10 – o12	-180.0017	0.0227
c5 – h13	1.0783	1.0807	c3 – c4 – n10	118.4909	118.4809	c3 – c4 – c5 – h13	179.9962	-179.9989
c6 – h14	1.0795	1.0825	c5 – c4 – n10	119.1171	119.1009	c4 – c5 – c6 – h14	180.0042	-179.9997
			c4 – n10 – o11	118.0653	117.6029	c5 – c6 – c1 – f7	-180.001	179.999
			c4 – n10 – o12	118.2218	117.4277	c1 – c6 – f7 – h14	0.001	-0.0008
			c4 – c5 – h13	119.9095	119.8788			
			c6 – c5 – h13	121.4403	121.5237			
			c5 – c6 – h14	121.6161	121.5544			
			c1 – c6 – h14	119.2902	118.9557			

Table 6.Optimized geometrical parameters of 2,4-dibromo-1-fluorobenzene obtained by B3LYP/6-311++G and B3LYP/6-311++G(d,p) density functional calculations.

Parameter Bond length	Value (Å)		Bond angle	Value (°)		Dihedral Angle	Value (°)	
	B3LYP/ 6-311++G	B3LYP/6-311++G(d,p)		B3LYP/ 6-311++G	B3LYP/6-311++G(d,p)		B3LYP/6-311++G	B3LYP/6-311++G(d,p)
C1 – C2	1.3886	1.3917	C1 – C2 – C3	118.9433	119.5908	C1 – C2 – C3 – C4	-0.0033	0.0
C2 – C3	1.3954	1.3936	C2 – C3 – C4	119.3431	119.1149	C2 – C3 – C4 – C5	-0.0013	0.0
C3 – C4	1.393	1.3913	C3 – C4 – C5	121.4113	121.3699	C3 – C4 – C5 – C6	0.0056	0.0
C4 – C5	1.3935	1.392	C4 – C5 – C6	119.129	119.1518	C4 – C5 – C6 – C1	-0.0012	0.0
C5 – C6	1.3962	1.3917	C5 – C6 – C1	118.1532	119.7529	C5 – C6 – C1 – C2	-0.0035	0
C6 – C1	1.3865	1.3863	C6 – C1 – C2	122.0201	121.0197	C6 – C1 – C2 – C3	0.0057	0
C1 – F7	1.395	1.3446	C1 – C2 – Br8	120.6925	120.1945	C5 – C6 – C1 – F7	-180.0032	180.0
C2 – Br8	1.931	1.9023	C3 – C2 – Br8	120.3642	120.2147	C6 – C1 – C2 – Br8	180.061	180.0
C3 – H9	1.0782	1.0807	C2 – C3 – H9	119.832	119.9517	C1 – C2 – C3 –	-180.034	180

						H9		
C4 – Br10	1.9486	1.9143	C4 – C3 – H9	120.8249	120.9334	C2 – C3 – C4 – Br10	179.9979	180
C5 – H11	1.076	1.0812	C3 – C4 – Br10	11.0511	119.0932	C3 – C4 – C5 – H11	-179.996	180
C6 – H12	1.0801	1.0825	C5 – C4 – Br10	119.5376	119.537	C4 – C5 – C6 – H12	179.9989	180
			C4 – C5 – H11	120.577	120.5854	C5 – C6 – C1 – H11	179.9984	180
			C6 – C5 – H11	120.294	120.2628	C1 – C2 – C3 – F7	180.0055	180
			C5 – C6 – H12	121.4499	121.2137	C2 – C3 – C4 – Br8	-180.0036	180
			C1 – C6 – H12	119.3969	119.0335	C3 – C4 – C5 – H9	179.9988	180
			C6 – C1 – F7	118.2305	118.8977	C4 – C5 – C6 – Br10	180.0044	180
			C2 – C1 – F7	119.7434	120.0826			

Table 7.The observed FTIR, FT Raman and calculated (Unscaled and Scaled) frequencies (cm^{-1}) using B3LYP/6-311++G and B3LYP/6-311++G(d,p), IR intensity (kM mol^{-1}), Raman activity (Å amu^{-1}), Reduced masses (amu) and force constant (mdyne $Å^{-1}$) and probable assignments (characterized by TED) of 2-chloro-1-fluoro-4-nitrobenzene.

Symmetry species Cs	Observed wave numbers (cm^{-1})		B3LYP/6-311++G						B3LYP/6-311++G (d,p)						TED% among types of coordinates
	FTIR	FT Raman	Unscaled Frequency cm^{-1}	Scaled Frequency cm^{-1}	Reduced masses	Force Constants	IR Intensity	Raman activity	Unscaled Frequency cm^{-1}	Scaled Frequency cm^{-1}	Reduced masses	Force Constants	IR Intensity	Raman activity	
A'	3104ms	-	3235	3106	1.0954	6.7532	5.2311	102.9497	3230	3105	1.0921	6.7124	11.3415	39.9041	νCH(99)
A'	3081vw	3075w	3233	3080	1.0926	6.7297	10.5012	26.4336	3230	3081	1.0938	6.7221	6.5901	87.1536	νCH(96)
A'	3061w	-	3213	3065	1.0912	6.6391	0.0287	83.3937	3205	3062	1.0912	6.6029	0.0241	102.9619	νCH(98)
A'	-	1662ms	1631	1665	8.3000	13.0082	1.5692	2.4397	1647	1663	9.0007	14.3892	29.4029	3.4268	νCC(91)
A'	1612vs	1620w	1620	1615	6.2580	9.6708	40.6855	117.7151	1622	1618	6.8834	10.6721	50.8810	70.8472	νCC(90)
A'	1545vs	-	1514	1550	2.5923	3.5000	85.0191	6.7341	1586	1548	12.6856	18.7929	253.3521	22.4630	νCC(88)
A'	1482s	1480vw	1465	1480	6.6494	8.4130	161.2302	12.3607	1509	1483	3.0152	4.0449	125.4113	4.2392	νCC(87)
A'	1441vs	1450vs	1411	1445	4.6072	5.4025	29.6152	7.6763	1428	1443	4.3948	5.2765	3.0310	0.4929	NO_2ass(82)
A'	-	1363w	1354	1365	11.3742	12.2907	24.4955	2.3726	1370	1364	14.0238	15.4995	312.9419	197.0291	νCC(81)
A'	1306vs	-	1293	1310	1.5809	1.5565	15.7637	43.2035	1344	1309	10.9083	11.6022	22.6811	6.0392	νCC(80)
A'	1275ms	1277w	1267	1278	6.9393	6.5644	362.8251	288.0965	1279	1276	2.6602	2.5620	123.3151	20.9250	νCN(79)
A'	1238s	-	1241	1240	3.6655	3.3241	25.0738	4.2907	1255	1240	1.6412	1.5234	17.2313	11.0225	NO_2ss(80)
A'	-	1150w	1166	1155	1.3326	1.0668	29.9308	8.4559	1145	1153	1.3254	1.0240	37.3303	10.1049	bCH(78)
A'	1138ms	1136ms	1134	1140	4.2233	3.2020	23.8990	12.8055	1130	1140	3.8262	2.8762	46.1122	29.7657	bCH(74)
A'	1118s	-	1071	1120	2.6299	1.7763	23.4061	6.4100	1067	1120	2.2343	1.4975	27.1719	3.6569	bCH(76)
A"	1049s	-	1007	1050	1.3183	0.7871	0.0366	0.0622	975	1050	1.3033	0.7297	0.0198	0.0492	νCF(73)
A"	-	1050vw	948	1058	1.3517	0.71457	34.0492	0.3063	918	1054	1.3593	0.6742	24.6269	0.1061	νCCl(72)
	899w	-	882	905	8.5099	3.8996	24.5893	16.5539	911	901	8.7997	4.2994	37.6766	16.6106	bCN(71)
	839ms	836ms	864	845	1.3875	0.6105	38.9084	0.0612	845	842	1.4951	0.6295	25.9739	0.0191	R symd(74)
	811vs	815w	785	816	9.7936	3.5570	1.2385	0.3389	825	814	8.5104	3.4147	4.7015	1.2241	R asymd(70)
	745vs	-	710	752	8.1587	2.4228	46.7336	15.5392	725	741	8.2090	2.5391	55.6993	13.7204	R trigd (69)

	-	724ms	693	730	5.7359	1.6208	1.0477	0.5185	723	723	8.2084	2.5281	19.2524	1.0435	ωCH(65)
	718s	-	677	726	8.7861	2.3733	11.3790	2.1990	698	720	4.6019	1.3197	0.4014	0.7770	ωCH(64)
	634s	644w	642	639	9.3865	2.2783	28.8596	2.9006	644	635	8.6046	2.1005	13.2969	3.0512	NO_2sciss(63)
	603s	604ms	552	615	5.8527	1.0509	1.8028	2.0312	559	604	5.5581	1.0233	1.1894	1.5291	ωCH(62)
	-	533w	536	540	4.5416	0.7673	0.2295	0.6752	533	534	4.4347	0.7429	0.7157	0.3442	t R trigd(61)
	-	475vw	485	482	9.8044	1.3576	8.2848	4.8586	502	478	10.3007	1.5310	6.6661	3.0601	NO_2wag(60)
	-	441w	457	450	3.1555	0.3887	4.1566	0.0219	452	444	3.2834	0.3843	3.5724	0.0321	R symd(67)
	-	427ms	364	436	13.2349	1.0352	0.0195	2.6123	369	430	13.0950	1.0478	0.1091	4.0813	t R asymd(66)
	-	387ms	348	394	14.4991	1.0338	0.5398	9.2982	351	391	13.9615	1.0104	0.2893	4.7721	NO_2 rock(67)
	-	306w	327	316	8.1880	0.5153	0.2165	0.7757	329	309	8.0742	0.5142	0.2388	1.0377	ωCN(62)
	-	260ms	243	266	15.2510	0.5283	3.1840	0.9616	252	264	15.1102	0.5635	2.1035	0.6677	bCF(67)
	-	238s	172	247	16.5168	0.2869	2.1944	1.3534	176	239	16.1200	0.2944	1.6590	1.1181	bCCl(69)
	-	220ms	168	226	5.8022	0.0967	0.0452	0.7598	170	225	5.8092	0.0985	0.0143	0.9599	ωCF(62)
	-	140w	116	147	10.5954	0.0834	6.8979	0.2371	115	142	10.6037	0.0821	4.7474	0.2440	ωCCl(61)
	-	120vw	48	128	15.3359	0.0212	0.0788	0.8514	46	126	15.3064	0.0191	0.0610	0.5686	NO_2 twist(59)

Abbreviations: t, torsion; R1 trigd, Ring 1 trigonal deformation; R2 trigd, Ring 2 trigonal deformation; asym, asymmetric; s, symmetric; ω, bending out-of-plane; asymd,asymmetric deformation; symd, symmetric deformation; b, bending in-plane; s, strong; w, weak; m, medium; vs, very weak; ms, medium strong, Harmonic Frequencies in cm^{-1}. The absolute IR intensity in Km mol^{-1}.Raman scattering activity in A^4 amu^{-1}. Depolarization rations for plane and unpolarised in amu. Reduced masses in AMU Force constants in m Dyne A.

Table 8.The observed FTIR, FT Raman and calculated (Unscaled and Scaled) frequencies (cm^{-1}) using B3LYP/6-311++G and B3LYP/6-311++G(d,p), IR intensity (kM mol^{-1}), Raman activity (Å amu^{-1}), Reduced masses (amu) and force constant (mdyne $Å^{-1}$) and probable assignments (characterized by TED) of 2,4-dibromo-1-fluorobenzene.

Symmetry species Cs	Observed wave number (cm^{-1})		B3LYP/6-311++G						B3LYP/6-311++G (d,p)						TED% among types of coordinates
	FTIR	FT Raman	Unscaled Frequency cm^{-1}	Scaled Frequency cm^{-1}	Reduced masses	Force Constants	IR Intensity	Raman activity	Unscaled Frequency cm^{-1}	Scaled Frequency cm^{-1}	Reduced masses	Force Constants	IR Intensity	Raman activity	
A'	3247s	-	3221	3245	1.0940	6.6888	0.9466	120.3642	3221	3245	1.0924	6.6764	1.7223	56.8068	νCH(99)
A'	3112vw	-	3219	3115	1.0952	6.6852	0.2774	82.5091	3216	3114	1.0950	6.6737	0.1533	127.6654	νCH(98)
A'	3081w	3079ms	3203	3085	1.0896	6.5857	0.5643	58.6919	3200	3084	1.0894	6.5740	0.4147	86.3941	νCH(96)
A'	1680ms	-	1617	1683	7.7772	11.9791	9.0511	17.1558	1613	1682	6.8726	10.5364	12.9324	21.0123	νCC(91)
A'	1663s	-	1605	1665	6.1661	9.3629	12.0172	12.8055	1610	1665	7.8930	12.0606	1.5274	8.2726	νCC(90)
A'	1584vs	1579ms	1508	1585	2.3444	2.1400	157.4857	1.2206	1498	1585	2.7026	3.5715	206.1099	3.7782	νCC(88)
A'	1471vs	1477w	1404	1475	2.7404	3.1835	13.3571	12.3939	1402	1474	3.3836	3.9193	13.3500	2.9672	νCC(86)
A'	-	1309w	1324	1310	9.4481	9.7546	0.5435	2.7978	1308	1310	11.1461	11.2294	1.2680	2.6308	νCC(89)
A'	1268vs	-	1297	1270	1.4484	1.4361	7.3060	0.6204	1277	1269	1.6294	1.5654	41.8324	4.3666	νCC(88)
A'	1234vs	-	1232	1235	3.2539	2.9092	72.5339	14.3890	1254	1235	2.4575	2.2775	53.1736	14.5406	νCF(79)
A'	-	1151ms	1169	1155	1.4447	1.1632	1.9213	4.2682	1152	1152	1.3340	1.0427	1.3510	5.5945	νCBr(73)
A'	1094vs	-	1095	1096	2.8064	1.9824	26.6207	9.1624	1089	1096	2.4308	1.6979	24.7821	12.1164	νCBr(73)
A'	1076vs	-	1075	1072	4.6509	3.1680	39.2761	8.5560	1060	1077	4.5304	2.9928	36.6043	2.7948	bCH(74)
A'	-	976s	1015	980	1.3846	0.8408	0.1127	0.1336	948	979	1.3158	0.6972	0.9239	0.0273	bCH(70)
A'	-	977vs	958	983	1.4514	0.7853	12.2636	0.4507	877	982	1.3354	0.6057	15.1523	0.1094	bCH(68)
A'	867s	-	866	871	1.4558	0.6439	50.4565	0.3303	841	870	7.2623	3.0299	6.2156	27.3086	R asymd(78)
A'	811s	-	830	815	7.6216	3.0944	8.1356	25.6467	824	830	1.4473	0.5790	35.3787	0.2210	R symd(74)
A'	-	715vs	754	720	3.5076	1.1751	0.2688	1.0182	689	718	8.1100	2.2694	36.5469	7.1576	R trigd(76)
A'	-	695ms	691	698	7.8318	2.2055	23.7786	8.2192	689	696	4.6824	1.3084	0.0115	0.8127	bCF(65)
A'	668s	662s	614	670	10.0871	2.2377	45.9884	1.0764	622	670	9.2095	2.1004	36.1619	1.6143	bCBr(62)

A'	596s	590w	580	610	4.0115	0.7945	5.4001	0.5229	550	598	4.0811	0.7278	4.4634	0.2054	bCBr(61)
A"	544s	550vw	478	551	6.0192	0.8145	7.2438	2.6547	491	550	6.0655	0.8615	5.8424	1.7438	ωCH(65)
A"	-	528w	469	534	3.0473	0.8945	6.0206	0.0029	425	533	3.2715	0.3817	3.9915	0.0073	ωCH(62)
A"	-	428s	333	436	7.8381	0.5125	0.6890	0.5681	332	434	9.6022	0.6232	0.6995	1.8626	ωCH(65)
A"	-	415s	330	425	9.9475	0.6392	1.2398	2.4314	330	422	8.0150	0.5153	0.4533	1.0731	tRasymd(62)
A"	-	400ms	271	406	15.6733	0.6768	0.9537	8.9298	279	404	15.5155	0.7109	0.6271	6.8574	tRsymd(67)
A"	-	365vs	213	372	17.9415	0.4773	0.8673	1.1254	218	369	17.3743	0.4854	0.5290	0.8957	tRtrigd(61)
A"	-	230s	152	236	5.2912	0.0719	0.7703	1.4542	147	235	5.3547	0.0682	0.5479	1.6127	ωCF(62)
A"	-	210ms	126	218	26.5654	0.2493	0.0315	3.2180	128	217	26.0207	0.2501	0.0239	2.5820	ωCBr(59)
A"	-	150w	112	157	10.2609	0.0760	1.3847	0.4331	110	156	10.1777	0.0732	0.7774	0.4748	ωCBr(58)

Abbreviations: t, torsion; R1 trigd, Ring 1 trigonal deformation; R2 trigd, Ring 2 trigonal deformation; asym, asymmetric; s, symmetric; ω, bending out-of-plane; asymd,asymmetric deformation; symd, symmetric deformation; b, bending in-plane; s, strong; w, weak; m, medium; vs, very weak; ms, medium strong, Harmonic Frequencies in cm^{-1}. The absolute IR intensity in Km mol^{-1}.Raman scattering activity in A^4 amu^{-1}. Depolarization rations for plane and unpolarised in amu. Reduced masses in AMU Force constants in m Dyne A.

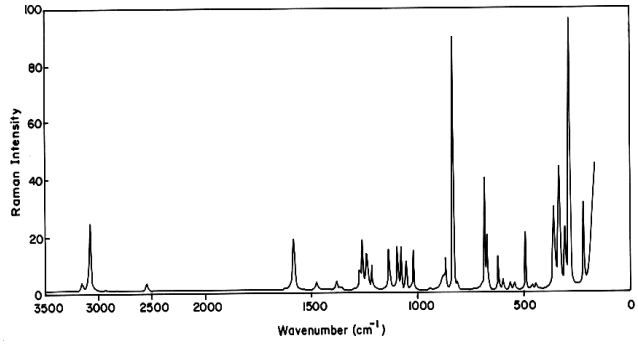

Fig. 6.FT-Raman Spectrum of 2,4-dibromo-1-fluorobenzene.

C - H Vibrations

The C-H stretching vibrations of aromatic and heteroaromatic structure [10,11] are normally appearing in the region 3000 - 3100 cm^{-1}. In this region, the bands are not affected appreciably by the nature of the substituent. Hence, in the present investigation, the C–H stretching vibrations of CFNB are observed at 3104, 3081, 3061 cm^{-1} in IR and Raman bands observed at 3075 cm^{-1}. The bands observed at 3247, 3112, 3081 cm^{-1} in IR and 3079 cm^{-1} in FT-Raman have been designated to C-H stretching vibrations for DBFB. The C-H in-plane and out-of-plane bending vibrations of the title compounds have also been identified and listed in Table 7 and 8.

C - C Vibrations

The bands between 1400 and 1650 cm^{-1} in benzene derivatives are due to C-C stretching vibrations [1]. Therefore, the C – C stretching vibrations of CFNB are observed at 1612, 1545, 1482, 1306 cm^{-1} in FTIR and 1662, 1620, 1480, 1363 cm^{-1} in FT-Raman spectrum. The C-C stretching vibrations of DBFB are observed at 1680, 1663, 1584, 1471, 1268 cm^{-1} in FTIR and in FT-Raman spectrum the bands observed at 1579, 1477, 1309 cm^{-1}. The in-plane and out-of-plane bending vibrations of carbon-carbon group are presented in Table 7 and 8 for the title compounds.

C - F Vibrations

In the vibrational spectra of related compounds, the bands due to C-F stretching vibrations [12]may be found over a wide frequency range 1360-1000 cm^{-1} since the vibration is easily affected by adjacent atoms or groups. In the present investigation, the bands observed at 1275 cm^{-1} in both IR and Raman and 1234 cm^{-1} in IR have been assigned to C-F stretching mode of vibration for CFNB and DBFB respectively.

C - Br Vibrations

The assignment of C - Br stretching and deformation modes have been made through comparison with assignments in other halogens substituted benzene derivatives [13]. Krishnakumar*et al.*, [14, 15]have assigned the C-Br vibrations in the frequency range 1300-550 cm^{-1}. In this study, the band observed at 1094 cm^{-1} in FTIR spectrum and 1151 cm^{-1} in Raman have been designated to C-Br stretching vibrations of DBFB.

NO_2 Group Vibrations

For molecules with an NO_2 group, the NO_2 asymmetric stretching vibration band range is 1625-1540 cm^{-1} and that of symmetric stretching vibration is 1400-1360 cm^{-1} [13]. In the present study, the asymmetric stretching modes of NO_2 group in CFNB is assigned at 1441 cm^{-1} in IR and 1450 cm^{-1} in Raman spectra, the band observed at 1238 cm^{-1} in the IR have been assigned to NO_2 symmetric stretching modes of CFNB. The bands appeared at 634 cm^{-1} in IR and 644 cm^{-1} in Raman have been assigned to scissoring modes of NO_2 group for CFNB.

The Rocking, wagging and twisting vibrational modes of NO_2 for the title compound are also presented in Table 7 and 8.

C-N Vibrations

The identification of C-N vibrations are a very difficult task, since the mixing of several modes are possible in the region. Silverstein et al. [16] assigned C-N stretching absorption in the region 1266-1382 cm^{-1} for aromatic compounds. In the present work, the bands observed at 1275 cm^{-1} in FT-IR spectrum have been assigned to C-N stretching vibrations. The same vibration which corresponds to Raman spectrum is at 1277 cm^{-1}. In our title molecule, the FTIR and FT Raman bands at 899 and 306 cm^{-1} are assigned to C-N in-plane and out-of-plane bending vibrations respectively.

5.5. Conclusion

The vibrational properties of CFNB and DBFB have been investigated by FTIR and FT-Raman spectroscopies and were based on DFT calculations at the B3LYP/6-311G and B3LYP/6-311++G(d,p) level. The assignments of the most of the fundamentals of the title compounds provided in this work are quite comparable and unambiguous. The close agreement obtained between the calculated, the observed frequencies and the TED calculations are also supporting the assignments made for various functional groups present in the molecules. The results confirm the ability of the methodology applied for interpretation of the vibrational spectra of the title compounds in the solid phase. The frequencies calculated with B3LYP/6-311++G(d,p) method which are in a better agreement with the experimental ones are superior to those calculated with B3LYP/6-311++G method.

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