

Scaled Quantum chemical studies of the structure and vibrational spectra of 4-bromo-1,2(methylenedioxy)benzene

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Abstract

The FTIR and FT-Raman vibrational spectra of 4-bromo-1,2(methylenedioxy) benzene (BMDB) have been recorded using Bruker IFS 66V Spectrometer in the range $3600\text{--}10\text{cm}^{-1}$ in the solid phase. A detailed vibrational spectral analysis has been carried out and assignments of the observed fundamental bands have been proposed on the basis of peak positions and relative intensities. The Optimized molecular geometry, harmonic frequencies, electronic polarizability, atomic charges, dipole moment, rotational constants and several thermodynamic parameters in the ground state were calculated using *ab initio* Hartree Fock (HF) and density functional B3LYP methods (DFT) with 6-311++ G(d) basis set. With the help of different scaling factors, the observed vibrational wave numbers in FTIR and FT Raman spectra were analyzed and assigned to different normal modes of the molecule. Most of the modes have wave numbers in the expected range.

Keywords: BMDB, FT-IR, FT-Raman, DFT calculations

Introduction

Benzene is an important raw material in the manufacturing of therapeutic chemicals, dyes, shoes, explosives, detergents, linoleum and artificial leather. It helps to dissolve fats, waxes, paints, resins and inks to dry them fast. It is an important element in the production of phenol, styrene and rubber. It is an important industrial solvent and precursor in the production of drugs, plastics, synthetic rubber and dyes [1]. Benzene and its derivatives 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 [2]. It is also an intermediate for pharmaceutical, pesticides and other organic compounds. Owing to these applications, an attempt has been made in this study to interpret the vibrational spectra of 4-bromo-1,2-(methylenedioxy) benzene (BMDB).

The assignments of bands in the vibrational spectra of molecules are an essential step in the application of vibrational spectroscopy for solving various structural and chemical problems. The philosophy of computational methods of vibrational spectroscopy [3,4] changed significantly after the introduction

of scaled quantum mechanical (SQM) calculations. In SQM approach, the systematic errors of the computed harmonic force fields are corrected by a few scale factors which are found to be well transferable between chemically related molecules [5-7] and were recommended for general use.

Recently, computational methods based on density functional theory (DFT) are becoming widely used. These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules (typically normal modes exceeding 50) the DFT methods lead to the prediction of more accurate molecular structure and vibrational frequencies than the conventional *ab initio* Restricted Hartree-Fock (RHF) and Moller-pleuset second order perturbation theory (MP2) calculations [8-11]. In order to understand a full description of the vibrational spectra of BMDB, especially for the assignment of the vibrational modes, DFT calculations were carried out using B3LYP functional with the standard 6-311 ++ G (d,p) basis set.

Experimental details

Pure chemicals of BMDB were obtained from Lancaster Chemical Company, UK and used as such without any further purification. The FTIR spectra of the title compound were recorded in the region 4000 – 400 cm^{-1} using KBr pellet. The BRUKER IFS 66V model FTIR spectrometer was used for the spectral measurements. The global and mercury are sources, KBr beam splitters are used while recording FTIR spectra of the title compound.

The FT-Raman spectra of BMDB were recorded on a BRUKER IFS-66V model interferometer equipped with an FRA-106 FT-Raman accessory. The spectra were recorded in the Stokes region 3500 - 100 cm^{-1} using the 1064 nm line of an Nd: YAG

laser for excitation operating at 200 mW of power.

Computational details

Quantum chemical density functional calculations were carried out for BMDB with the 2009 Window version of the GAUSSIAN suite program [12] using Becke-3-Lee-Yang-Parr (B3LYP) functional [13,14] supplemented with the standard 6-311++G (d,p) basis set (referred to as DFT calculations). 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 in the wave number calculations. The Cartesian representation of the theoretical force constants have been computed at the fully optimized geometry. The transformation of force field from Cartesian to internal local symmetry coordinates, the scaling, the subsequent normal coordinate analysis (NCA) and the calculation of total energy distribution (TED) were done by MOLVIB program written by Sundius [15-17]. To achieve a close agreement between the observed and calculated frequencies, least-square fit refinement algorithm was used.

Results and discussion

Molecular geometry

The molecular structure of BMDB is shown in Fig.1. The global minimum energy obtained by the HF and DFT structure optimization for BMDB are calculated as – 2989.93443769 and –2994.25323779 Hartrees, respectively. The optimized geometrical parameters obtained by the large basis set calculations for BMDB are presented in Table 1.

Normal coordinate analysis was carried out for the molecule to provide a complete assignment of the fundamental vibrational frequencies [18-20]. For this purpose, the full set of 56 standard internal coordinates

(containing 17 redundancies) for BMDB are defined as given in Table 2, respectively. From these, a non-redundant set of local symmetry coordinates were constructed by suitable linear combinations of internal coordinates following the recommendations of Fogarasi and Pulay [21,22] are summarized in Table 3. The theoretically calculated DFT force fields were

transformed to this later set of vibrational coordinates and used in all subsequent calculations. The total energy distribution (TED) for each normal mode among the symmetry coordinates of the molecule was calculated. The complete assignment of the fundamentals was proposed based on the calculated TED values.

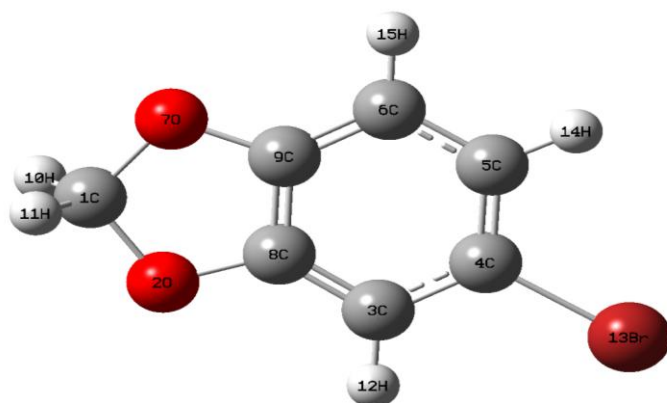


Figure 1: Molecular structure of 4-bromo-1,2-(methylenedioxy) benzene.

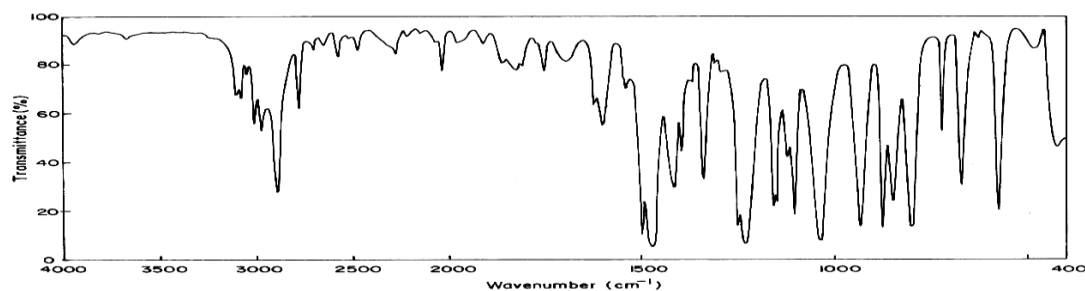


Figure 2: FTIR spectrum of 4-bromo-1,2-(methylenedioxy) benzene.

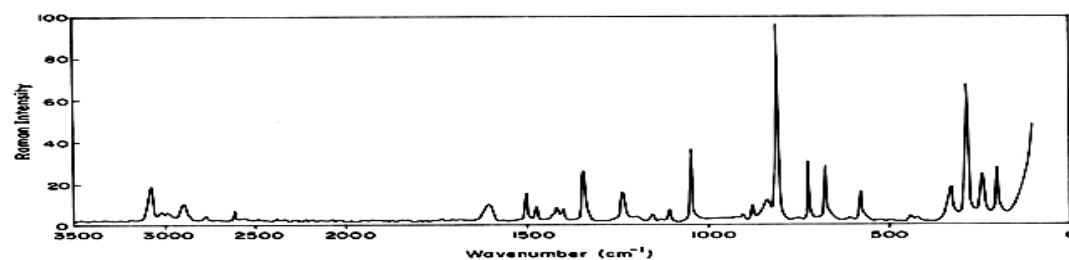


Figure 3: FT-Raman spectrum of 4-bromo-1,2-(methylenedioxy) benzene.

Table 1: Optimized geometrical parameters of 4-bromo-1,2-(methylenedioxy) benzene obtained by HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) calculations.

Parameter Bond length	Value (Å)		Bond angle	Value (Å)		Dihedral Angle	Value (Å)	
	HF	B3LYP		HF	B3LYP		HF	B3LYP
C1 – O2	1.4435	1.4756	O2 – C1 – O7	105.7018	106.5071	O7 – C1 – O2 – C8	-0.0309	-9.0342
C1 – O7	1.4428	1.474	O2 – C1 – Br13	109.5162	109.1517	Br13 – C1 – O2 – C8	117.9218	108.8325
C1 – Br13	1.0732	1.0881	O2 – C1 – H14	109.5161	109.1515	H14 – C1 – O2 – C8	-117.9837	-126.8624
C1 – H14	1.0732	1.0842	O7 – C1 – Br13	109.5673	109.2768	O2 – C1 – O7 – C9	0.0306	9.0617
O2 – C8	1.3822	1.4049	O7 – C1 – H14	109.5675	109.2441	Br13 – C1 – O7 – C9	-117.8878	-108.7224
C3 – C4	1.3948	1.4036	Br13 – C1 – H14	112.7304	113.2854	H14 – C1 – O7 – C9	117.949	126.8286
C3 – C8	1.3637	1.3799	C1 – O2 – C8	107.6267	106.0507	C1 – O2 – C8 – C3	-179.9838	-175.3742
C3 – H10	1.0671	1.078	C4 – C3 – C8	116.1371	116.0507	C1 – O2 – C8 – C9	0.02	5.7174
C4 – C5	1.379	1.392	C4 – C3 – H10	122.0892	122.1359	C8 – C3 – C4 – C5	0.0008	0.1406
C4 – H15	1.9319	1.9527	C8 – C3 – H10	121.7737	121.8134	C8 – C3 – C4 – H15	180.0006	-179.7899
C5 – C6	1.4001	1.4091	C3 – C4 – C5	122.1767	122.4209	H10 – C3 – C4 – C5	180.0011	-179.7672
C5 – H11	1.0682	1.079	C3 – C4 – H15	118.4142	118.3094	H10 – C3 – C4 – H15	0.0009	0.3023
C6 – C9	1.365	1.3788	C5 – C4 – H15	119.4091	119.2696	C4 – C3 – C8 – O2	180.0036	-178.8963
C6 – H12	1.0686	1.0796	C4 – C5 – C6	120.3653	120.2657	C4 – C3 – C8 – C9	-0.0007	-0.1072
O7 – C9	1.3828	1.4064	C4 – C5 – H11	119.9893	120.0279	H10 – C3 – C8 – O2	0.0032	1.0118
C8 – C9	1.3777	1.3912	C6 C5 – H11	119.6454	119.7064	H10 – C3 – C8 – C9	179.9989	179.8009
			C5 – C6 – C9	117.0797	117.1776	C3 – C4 – C5 – C6	-0.0002	-0.0265
			C5 – C6 – H12	121.3416	121.2692	C3 – C4 – C5 – H11	179.9998	-179.9581
			C9 – C6 – H12	121.5788	121.5531	H15 – C4 – C5 – C6	-180.0	179.9034
			C1 – O7 – C9	107.6738	106.1008	H15 – C4 – C5 – H11	0.0	-0.0283
			O2 – C8 – C3	128.1109	127.4169	C4 – C5 – C6 – C9	-0.0005	-0.1236
			O2 – C8 – C9	109.5442	110.2994	C4 – C5 – C6 – H12	179.999	179.7703

			C3 – C8 – C9	122.3449	122.2745	H11 – C5 – C6 – C9	179.9995	179.8082
			C6 – C9 – O7	128.6501	128.0115	H11 – C5 – C6 – H12	-0.001	-0.2978
			C6 – C9 – C8	121.8963	121.8104	C5 – C6 – C9 – O7	179.9968	178.8345
			O7 – C9 – C8	109.4536	110.1672	C5 – C6 – C9 – C8	0.0005	0.1584
						H12 – C6 – C9 – O7	-0.0027	-1.0592
						H12 – C6 – C9 – C8	-179.9989	-179.7352
						C1 – O7 – C9 – C6	179.984	175.4062
						C1 – O7 – C9 – C8	-0.0194	-5.7924
						O2 – C8 – C9 – C6	-180.0035	178.932
						O2 – C8 – C9 – O7	-0.0004	0.0432
						C3 – C8 – C9 – C6	0.0001	-0.0426
						C3 – C8 – C9 – O7	180.0032	-178.9316

For numbering of atoms refer Fig.1.

Table 2: Definition of Internal Coordinates of 4-bromo-1,2-(methylenedioxy) benzene.

No (i)	Symbol	Type	Definition ^a
Stretching			
1 – 4	r_i	C – O	C1 – O2, C8 – O2, C1 – O7, C9 – O7
5 – 7	R_i	C – H	C3 – H12, C5 – H14, C6 – H15
8	q_i	C – Br	C4 – Br13
9 – 10	Q_i	C – H	C1 – H10, C1 – H11
11 – 16	T_i	C – C	C3 – C4, C4 – C5, C5 – C6, C6 – C9, C9 – C8, C8 – C3
In- plane bending			
17 – 22	β_i	Ring1	C3 – C4 – C5, C4 – C5 – C6, C5 – C6 – C9, C6 – C9 – C8, C9 – C8 – C3, C8 – C2 – C7
23 – 27	α_i	Ring2	C1 – O2 – C8, O2 – C8 – C9, C8 – C9 – O7, C9 – O7 – C1, C7 – C1 – O2

28 – 33	θ_i	C – C – H	C 8 – C3 – H12, C4 – C3 – H12, C4 – C5 – H14, C6 – C5 – H14, C5 – C6 – H15, C9 – C6 – H15
34 – 35	π_i	C – C – Br	C5 – C4 – Br13, C3 – C4 – Br13
36 – 39	ϕ_i	O – C – H	O2 – C1 – H10, O7 – C1 – H11, O2 – C1 – H10, O2 – C1 – H11
Out-of-plane bending			
40 – 42	ω_i	C – H	H12 – C3 – C4 – C8, H14 – C5 – C6 – C4, H15 – C6 – C9 – C5
43	ψ_i	C – Br	Br13 – C4 – C5 – C3
Torsion			
44 – 49	τ_i	Ring 1	C3 – C4 – C5 – C6, C4 – C5 – C6 – C9, C5 – C6 – C9 – C8, C6 – C9 – C8 – C3, C9 – C8 – C3 – C4, C8 – C3 – C4 – C5
50 – 54	τ_i	Ring2	C1 – O2 – C8 – C9, O2 – C8 – C9 – O7, C8 – C9 – O7 – C1, C9 – O7 – C1 – O2 , O7 – C1 – O2 – C8
55 – 56	τ_i	Butterfly	O2 – C8 – C9 – C6, C3 – C8 – C9 – O7

^a For numbering of atoms refer Fig.1.

Table 3: Definition of Local symmetry coordinates of 4-bromo-1,2-(methylenedioxy) benzene.

No. (i)	Symbol ^a	Definition ^b
1 – 4	CO	r_1, r_2, r_3, r_4
5 – 7	CH	R_5, R_6, R_7
8	CBr	q_8
9	CH ₂ ss	$(Q_9 + Q_{10})/\sqrt{2}$
10	CH ₂ ass	$(Q_9 - Q_{11})/\sqrt{2}$
11 – 16	CC	$T_{11}, T_{12}, T_{13}, T_{14}, T_{15}, T_{16}$

17	R1trigd	$(\beta_{17} - \beta_{18} + \beta_{19} - \beta_{20} - \beta_{21} + \beta_{22})/\sqrt{6}$
18	R1 symd	$(-\beta_{12} - \beta_{18} + 2\beta_{19} - \beta_{20} - \beta_{21} + 2\beta_{22})/\sqrt{12}$
19	R1asymd	$(\beta_{12} - \beta_{18} + \beta_{20} - \beta_{21})/2$
20	R2 bend1	$\beta_{23} + a(\beta_{24} + \beta_{27}) + b(\beta_{25} + \beta_{26})$
21	R2 bend2	$(a - b)(\beta_{24} - \beta_{27}) + (1 - a)(\beta_{25} - \beta_{26})$
22 – 24	bCH	$(Q_{28} - Q_{29})/\sqrt{2}, (Q_{30} - Q_{31})/\sqrt{2}, (Q_{32} - Q_{33})/\sqrt{2}$
25	bCBr	$(\pi_{34} - \pi_{35})/\sqrt{2}$
26	CH ₂ sciss	$(Q_{36} + Q_{37} + Q_{38} + Q_{39})$
27	CH ₂ wag	
28	CH ₂ rock	$\phi_{36} + \phi_{37} - \phi_{38} - \phi_{39}$
29	CH ₂ twist	$\phi_{36} - \phi_{37} - \phi_{38} + \phi_{39}$
30 – 32	ω CH	$\omega_{40}, \omega_{41}, \omega_{42}$
33	φ CBr	ψ_{43}
34	tR1trigd	$(\tau_{44} - \tau_{45} + \tau_{46} - \tau_{42} + \tau_{48} - \tau_{49})/\sqrt{6}$
35	tR1symd	$(\tau_{44} - \tau_{46} + \tau_{48} - \tau_{49})/\sqrt{2}$
36	tR1 asymd	$(-\tau_{44} + 2\tau_{45} - \tau_{46} - \tau_{47} + 2\tau_{48} - \tau_{49})/\sqrt{6}$
37	torsion 1	$b(\tau_{50} + \tau_{54}) + a(\tau_{51} + \tau_{53}) + \tau_{52}$
38	torsion 2	$(a-b)(\tau_{54} - \tau_{50}) + (1-a)(\tau_{53} - \tau_{51})$
39	Butterfly	$(\tau_{55} - \tau_{56})/\sqrt{2}$

^a These symbols are used for description of normal modes by TED in Table 4.

^b The internal coordinates used here are defined in Table 2.

Table 4: The observed FTIR, FT-Raman and calculated (unscaled and Scaled) frequencies (cm^{-1}) IR intensity (Km mol^{-1}), Raman Activity ($\text{\AA}^4 \text{amu}^{-1}$), Reduced masses (amu) and force constant (m dyne \AA^{-1}) and probable assignments (characterized by TED) of 4-bromo-1,2-(methylenedioxy) benzene using HF/6-311++G(d,p) and B3LYP/6-311++G(d,p) calculations.

Species	Observed wave numbers (cm^{-1})		HF/6-311++G(d,p)						B3LYP/6-311++G(d,p)						TED% among types of coordinates
	FTIR	FT Raman	Unscaled	Scaled	Reduced mass	Force Constants	IR intensity	Raman active	Unscaled	Scaled	Reduced mass	Force Constants	IR intensity	Raman active	
A	3102 (ms)	3100 (ms)	3393	3105	1.0957	7.4349	0.8068	75.6349	3227	3105	1.0936	6.7135	0.5036	83.9255	vCH (99)
A	3078 (ms)	3081 (w)	3385	3083	1.0977	7.4112	3.0725	118.2146	3219	3084	1.0959	6.6923	2.5408	125.8376	vCH (98)
A	3050 (ms)	3052 (w)	3367	3053	1.0917	7.2943	1.2850	41.0136	3203	303	1.0898	6.5902	1.5335	49.3389	vCH (96)
A	3010 (ms)	-	3328	3007	1.1199	7.3089	28.4760	99.7463	3150	3007	1.1150	6.5197	23.3449	141.8603	CH ₂ ss(92)
A	2974 (s)	2970 (w)	3254	2979	1.0547	6.5836	80.3144	192.8746	3059	2980	1.0576	5.8319	80.3872	246.7834	CH ₂ ass (90)
A	1829 (ms)	-	1793	1835	7.9507	15.0713	3.9004	9.7076	1650	1835	8.3167	13.3445	4.7500	6.0022	vCC (89)
A	1753 (s)	-	1788	1750	7.3158	13.7009	5.3864	13.1204	1630	1750	7.2937	11.4306	8.1889	17.6502	vCC (87)
A	1626 (s)	1620 (ms)	1693	1629	1.1032	1.8638	0.6363	15.7545	1549	1630	1.1062	1.5648	0.1063	19.6080	vCC (86)
A	1599 (s)	-	1638	1596	2.8178	4.4574	294.2357	4.3238	1504	1595	2.5957	3.4602	241.5680	2.3437	vCC (82)
A	1492(s)	1498 (w)	1563	1495	3.1232	4.4980	26.6873	2.6439	1444	1495	3.2415	3.9828	19.8790	3.2945	vCC (84)
A	1476(vw)	1470 (w)	1538	1472	1.3003	1.8122	7.0046	9.8068	1405	1475	1.2652	1.4723	3.3069	16.9850	vCC (80)
A	1417 (s)	1415 (w)	1439	1421	2.5297	3.0891	84.7535	10.4902	1369	1422	5.8948	6.5124	7.4448	5.4498	vCO (79)

A	1310 (s)	1315 (w)	1392	1307	1.6948	1.9371	34.9810	3.4026	1298	1307	1.4176	1.4080	13.5764	0.3856	vCO (76)
A	1261(ms)	1264 (ms)	1296	1265	3.5486	3.5136	118.3436	4.9802	1241	1265	3.9942	3.6300	212.3251	15.1016	vCO (75)
A	1214 (vs)	1210 (ms)	1289	1210	1.0387	1.0169	0.0008	7.7724	1174	1211	1.5065	1.2239	9.2780	2.0265	vCO (74)
A	1159 (s)	-	1266	1164	2.4806	2.3436	78.1206	4.3084	1166	1163	1.0560	0.8466	0.3770	7.7570	CH ₂ sciss (72)
A	1152(w)	1150 (ms)	1224	1155	1.4469	1.2782	18.2650	0.8507	1115	1155	3.6853	2.7009	42.1382	5.7931	CH ₂ rock (71)
A	1123 (vw)	-	1216	1120	2.5008	2.1794	18.8096	4.4820	1112	1120	1.4648	1.0688	9.5104	0.9600	bCH (70)
A	1105 (ms)	1106 (ms)	1144	1110	2.1391	1.6499	14.5781	9.4898	1065	1110	2.0994	1.4038	3.8754	12.4783	bCH (72)
A	1039 (s)	1040 (ms)	1120	1035	7.1838	5.3095	158.7172	2.8447	1003	1036	6.6463	3.9450	159.435	1.3641	bCH (70)
A	936(w)	-	1097	940	1.3692	0.9714	1.4983	0.3524	970	940	1.3401	0.7444	1.2518	0.3085	Rtrigd (69)
A	876 (vw)	-	1047	872	9.6676	6.2546	68.0386	1.2533	888	872	1.2913	0.6001	22.9899	0.1981	Rsymd (68)
A	857 (vw)	862 (w)	1007	860	1.3280	0.7938	27.5321	0.1233	878	861	10.2896	4.6770	37.0480	1.3585	Rasynd (66)
A	848 (ms)	840 (vs)	952	845	1.3345	0.7127	50.2413	0.2919	858	845	6.4386	2.7982	39.2022	1.9366	R bend 1 (69)
A	806 (ms)	811 (ms)	940	810	6.4838	3.3785	33.5561	5.6426	838	811	1.3341	0.5531	46.4910	0.2369	R bend 2 (70)
A	799 (s)	-	873	794	7.2886	3.2803	11.2166	30.5351	800	795	6.6953	2.5268	10.4176	32.0048	ω CH (64)
A	721 (s)	724 (ms)	791	725	8.6011	3.1784	0.8782	2.8108	712	725	9.6886	2.9019	1.4998	4.4920	ω CH (63)
A	675 (ms)	675 (ms)	753	672	6.2164	1.9724	1.2686	0.3681	669	675	8.6918	2.2922	14.7704	3.9306	ω CH (60)

A	650 (ms)	-	726	655	8.5996	2.6774	16.5062	6.6079	646	655	6.8936	1.6975	0.8273	0.4098	vCBr (68)
A	-	585 (w)	654	588	4.7325	1.1949	11.0871	0.0906	582	567	5.2691	1.0548	8.1723	0.3082	CH ₂ wagg (62)
A	580 (vs)	-	624	576	6.9062	1.5871	11.8960	6.6552	577	577	6.8961	1.3542	12.6228	6.4908	CH ₂ twist (61)
A	492 (w)	-	490	495	2.8162	0.3997	6.0679	0.4310	443	495	2.8747	0.3331	5.9725	0.2792	tRtrigd (60)
A	418 (vw)	415 (w)	466	420	5.0506	0.6473	6.4746	0.7986	429	420	5.0963	0.5542	6.8904	0.4484	tRsymd (59)
A	-	325 (w)	362	329	7.7784	0.6018	1.4419	1.3812	319	328	8.1113	0.4876	0.5725	1.4309	bCBr(67)
A	-	283 (s)	292	288	15.2714	0.7700	0.6792	12.4556	269	287	15.3004	0.6562	0.9305	9.2914	t Rasymd (61)
A	-	241 (ms)	259	245	6.1562	0.2434	0.0185	1.6958	230	246	6.2110	0.1949	0.1135	1.5596	t R bend 1 (58)
A	-	201 (w)	203	198	8.5873	0.2104	0.0421	1.6380	188	201	8.6206	0.1801	0.1319	1.7015	t R bend 2 (59)
A	-	-	134	-	8.5921	0.0918	3.6833	0.0371	118	-	8.9327	0.0745	2.2617	0.0190	ωCBr (57)
A	-	-	68	-	0.4343	0.0067	16.2753	0.4988	65	-	2.4107	0.0060	14.1715	0.9977	Butterfly (56)

Abbreviations: γ -stretching; b-bending; ω -out-of-plane bending; R-ring; trigd-trigonal deformation; symd-symmetric deformation; asymd-antisymmetric deformation; t-torsion; s-strong; vs-very strong; ms-medium strong; w-weak; vw-very weak.

Vibrational Spectra

The optimized structural parameters were used to compute the vibrational frequencies of BMDB at the HF and B3LYP level with 6-311++G (d,p) basis set. From the structural point of view, the molecule is assumed to have C_1 point group symmetry and hence, all the calculated frequency transforming to the same symmetry species (A). The molecule BMDB consists of 15 atoms and expected to have 39 normal modes of vibrations. All the vibrations are active both in the Raman Scattering and infrared absorption.

The detailed vibrational assignments of fundamental modes of BMDB along with the calculated Reduced mass, Force constants IR intensity, Raman activity and normal mode descriptions (characterized by TED) are reported in Table 4. The FTIR and FT-Raman spectra of BMDB are shown in Figs.2.and 3, respectively.

C-H Vibrations

The C-H stretching vibrations of benzene derivatives generally appear in the region 3100 - 3000 cm^{-1} [23]. In this region, the bands are not affected appreciably by the nature of the substituent. Hence, in the present investigation, the C-H vibrations have been found at 3102, 3078 and 3050 cm^{-1} in IR and 3100, 3081 and 3052 cm^{-1} in Raman for BMDB. The C-H in-plane and out-of-plane bending vibrations have also been identified and presented in Table 4. For BMDB.

C-C Vibrations

The bands between 1400 and 1650 cm^{-1} , in benzene derivatives are due to C-C stretching vibrations [24]. Therefore, the C-C stretching vibrations of BMDB are found at 1829, 1753, 1626, 1599, 1492 and 1476 cm^{-1} in the FTIR spectrum and at 1620, 1498, 1470 cm^{-1} in the FT-Raman spectrum. The in-plane and out-of-plane bending

vibrations of Carbon-Carbon group are presented in Table 4. for the title compound.

C - O Vibrations

The interaction of carbonyl group with other groups present in the system did not produce such a drastic and characteristic change in the frequency of c-o stretch as did by interaction of N-H stretch. The c-o stretching vibrations of BMDB are identified at 1417, 1310, 1261 and 1214 cm^{-1} in IR and 1415, 1315, 1264 and 1210 cm^{-1} in the Raman band. The in-plane and out-of-plane bending vibrations of C-O group are also found well within the characteristic region [25].

CH₂ Group Vibrations

For the assignments of CH₂ group frequencies, basically six fundamentals can be associated to each CH₂ group namely, CH₂ss-symmetric stretch; CH₂ ass-antisymmetric stretch; CH₂ sciss-scissoring and CH₂ rock-rocking which are belongs to in-plane (A') vibrations. In addition to that, CH₂ wag-wagging and CH₂ twist - twisting modes of CH₂ group would be expected to be depolarized for out-of-plane (A'') symmetry species.

The antisymmetric CH₂ stretching vibrations are generally observed in the region 3100-3000 cm^{-1} , while the symmetric stretch will appear between 3000 and 2900 cm^{-1} . The CH₂ antisymmetric vibrations were observed in IR and Raman spectra at 2974 and 2970 cm^{-1} , respectively, for BMDB. The symmetric stretching was also identified in IR spectra at 3010 cm^{-1} for BMDB. The bands corresponding to scissoring, wagging, rocking and twisting vibrations of CH₂ group are summarized in Table 4. These assignments are also supported by TED output.

C-Br Vibrations

Bromine compounds absorb strongly in the region 650-485 cm^{-1} due to the C-Br

stretching vibrations [26]. In the observed spectra the bands identified at 650 cm^{-1} in FTIR for BMDB have been assigned to C-Br stretching vibrations. The bending vibrations arising from C-Br bands were observed in their respective characteristic regions and they were listed in Table 4.

Conclusion

Complete vibrational analysis of 4-bromo-1,2(methylenedioxy) benzene were performed on the basis of HF and B3LYP level with 6-311++G(d,p) basis set of calculations. Although both types of calculations are useful to explain vibrational spectra of BMDB, *ab initio* calculation at HF/6-311++G(d,p) level is found little poorer than DFT-B3LYP/6-311++G(d,p) level calculations. The close agreement established between the experimental and scaled frequencies obtained using the large basis set 6-311++G(d,p) calculation is proved to be more reliable and accurate than the calculation of semi-empirical methods. The role of methyl and carbonyl groups in the vibrational frequencies of the title compound are discussed. The various modes of vibrations were unambiguously assigned based on the results of the TED output obtained from normal coordinate analysis.

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