Computational studies on the structure, first-order hyperpolarizability, homo-lumo analyses of 3, 4-dichlorobenzaldehyde and 4-methoxy-3-methyl benzaldehyde based on density functional theory studies

P.Anbarasu[1], N.K.Kandasamy[2], M. Arivazhagan[3] and N.Saravanan[4]

[1]Department of Electronics, Government Arts College, Kulithalai, Karur - 639120 Tamil Nadu, India.
[2]Department of Physics, Government Arts College, Karur- 639005,Tamil Nadu India.
[3]Department of Physics, Government Arts College, Tiruverumbur, Tiruchirappalli 620022,Tamil Nadu, India .
[4]Department of Chemistry, A.A. Government Arts College, Musiri-621211, Trichy, Tamilnadu, India.

ARTICLE INFO	ABSTRACT
	The FT-IR and FT Raman spectra of 3,4-dichlorobenzaldehyde (DCB) and 4-methoxy- 3-methyl benzaldehyde (MMB) molecules have been recorded in the region 4000-400cm^{-1} and 3500-50cm^{-1} respectively. Optimized geometrical parameters, harmonic vibrational frequencies and depolarization ratio have been computed by density functional theory (DFT) using B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) method and basis sets. The observed FT-IR and FT-Raman vibrational frequencies are analysed and compared with theoretically predicted vibrational frequencies. The geometries and normal modes of vibration obtained from DFT method are in good agreement with the experimental data. The first-order hyperpolarizability (β_0) of the investigated molecule were computed using DFT calculations. The calculated HOMO and LUMO energies shows that charge transfer occur within molecule. Unambiguous vibrational assignments of all the fundamentals was made using the total energy distribution (TED). © 2015 Elixir All rights reserved.

Introduction

Benzaldehyde and its derivatives are currently finding increasing applications for several reasons. We will concentrate on this work on benzaldehydes, containing benzene ring with an aldehyde substituent. It is the simplest representative of the aromatic aldehydes. Benzaldehyde derivatives are among the most interesting carbonyl containing system and they are used chiefly in the synthesis of other organic compounds, ranging from pharmaceuticals to plastic additives, Due to the highly interesting nature of the aldehyde group with the surrounding media and conjugation of the aldehydic group with the surrounding media and conjugation of the phenyl ring, they are important intermediates for the processing of perfume and flavouring compounds and in the preparation of certain aniline dyes [1-3]. They also exhibit an important role on the rate of hydrogen evolution in lead acid batteries, as the rate of hydrogen evolution depends on the polarity of the environment [4]. Benzaldehyde is used in perfumes, soaps, foods, drinks and other products as a solvent for oils, grains, some cellulose ethers. Cellulose acetate and cellulose nitrate in the production of derivates are employed in the perfume and flavor industries in photo chemistry; as a corrosion inhibitor and dyeing auxiliary in the electroplating industry and in the production of agricultural chemicals [5-7]. Benzaldehyde existing nature is occurring in combined and uncombined forms in many plants. The best known natural source of benzaldehyde is amygdaline. Benzaldehyde is also the main constitute of the essential oils obtained by processing the kernel's of peaches, cherries, apricots and other fruits [8]. Recent spectroscopic studies of the benzaldehyde and their derivatives have been motivated because the vibrational spectra are very useful for the understanding of specific biological process and for the analysis of relatively complex systems. Many important compounds are aromatic in part, including the steroidal hormone estone and the analgesic ibuprofen [5].

The vibrational studies of the 3,4-dichlorobenzaldehyde (DCB) and 4-methoxy- 3-methyl benzaldehyde (MMB) would be helpful in understanding the various types of bonding and normal modes of vibrations involved in the system. The computational methods of vibrational spectroscopy [8-10] changed significantly when quantum mechanical programs for optimization of the geometry of a molecule and for analytical determination of its force field appeared. Harmonic force fields derived from quantum mechanics are widely used for the calculation of frequencies and the modes of normal vibrations.

Indeed, applying current quantum mechanical methods have opened up the way for calculating the frequencies and intensities of spectral bands with a minimum degree of arbitrariness (although the degree depends on the level of the quantum mechanical treatment) and finding rational explanation for a number of chemical and physical properties of the substance.

However, for a proper understanding of IR and Raman spectra, reliable assignments of all vibrational bands are essential. Recently, computational methods based on density functional theory are becoming widely used. These methods predict relatively accurate molecular structure and vibrational spectra with moderate computational effort. In particular, for polyatomic molecules the DFT methods lead to the prediction of more accurate molecular structure and vibrational frequencies than the conventional *ab initio* restricted Hartree – Fock (HF) and Moller – Plesset second order perturbation theory (MP$_2$) calculations [11-14].

Table 1. Optimized geometrical parameters of 3,4-dichlorobenzaldehyde obtained by B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) method and basis set calculations

Bond length	Values (Å)		Bond angles	Values (°)		Dihedral angles (°)	Values (°)	
	B3LYP			B3LYP			B3LYP	
	6-311+G(d,p)	6-311++G(d,p)		6-311+G(d,p)	6-311++G(d,p)		6-311+G(d,p)	6-311++G(d,p)
C1 – C2	1.398	1.3951	C1 – C2 – C6	119.8466	119.8262	C6– C1– C2– C3	0.0	0.0
C1 – C6	1.3973	1.4004	C2 – C1 – C7	120.1940	119.2712	C6– C1– C2– H10	180.0	−180.0
C1 – C7	1.4824	1.4831	C6 – C1 – C7	119.963	120.9026	C7– C1– C2– C3	−180.0	−180.0
C2 – C3	1.3873	1.3917	C1 – C2 – C3	120.2054	120.4985	C7– C1– C2– H10	0.0	0.0
C2 – H10	1.0828	1.0841	C1 – C2 – H10	119.3516	120.3237	C2– C1– C6– C5	−0.0002	0.0
C3 – C4	1.4046	1.3995	C3 – C2 – H10	120.443	119.1778	C2– C1– C6– H14	−179.9999	180
C3 – Cl11	1.7451	1.7457	C2 – C3 – C4	119.7361	119.4529	C7– C1– C6– C5	179.9998	180.0
C4 – C5	1.3944	1.3991	C2 – C3 – Cl11	119.0271	118.9645	C7– C1– C6– H14	0.0	0.0
C4 – Cl12	1.7417	1.7414	C4– C3– Cl11	121.2368	121.5826	C2– C1– C7– O8	−0.0036	180.0
C5 – C6	1.3885	1.3845	C3 – C4 – C5	120.0714	120.0455	C2– C1– C7– H9	179.9971	0.0
C5 – H13	1.0822	1.0826	C3 – C4 – Cl12	121.2561	121.2951	C6– C1– C7– O8	179.9964	0.0
C6 – H14	1.0849	1.0831	C5– C4– Cl12	118.6725	118.6594	C6– C1– C7– H9	−0.0029	180.0
C7 – O8	1.2095	1.2095	C4 – C5 – C6	119.9451	120.2855	C1– C2– C3– C4	0.0002	0.0
C7 – H9	1.11	1.1097	C4 – C5–H13	119.0679	118.8305	C1– C2– C3– Cl11	−180.0	−180.0
			C6 – C5– H13	120.987	120.8839	H10– C2– C3– C4	180.0001	180
			C1 – C6– C5	120.1955	119.8913	H10– C2– C3– Cl11	0.0	0.0
			C1 – C6– H14	120.0036	119.14	C2– C3– C4– C5	−0.0001	0.0
			C5 – C6– H14	119.8009	120.90687	C2– C3– C4– Cl12	−180.0001	−180.0
			C1 – C7– O8	124.7165	124.4891	Cl11– C3– C4– C5	180.0	180.0
			C1 – C7– H9	114.5147	114.7359	Cl11– C3– C4– Cl12	0.0001	0.0
			O8 – C7– H9	120.7688	120.775	C3– C4– C5 –C6	−0.0001	0.0
						C3– C4– C5 – H13	180.0	−180.0
						Cl12– C4– C5 – C6	179.9999	−180.0
						Cl12– C4– C5 – H13	0.0	0.0
						C4– C5 –C6– C1	0.0003	0.0
						C4– C5 –C6– H14	−179.9999	180.0
						H13– C5 –C6– C1	180.0001	180.0
						H13– C5 –C6– H14	0.0	0.0

For numbering of atoms refer Fig 1

Table 2. Optimized geometrical parameters of 4-methoxy-3-methylbenzaldehyde obtained by B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) method and basis set calculations

| Bond length | Values (Å) B3LYP | | Bond angles | Values (°) B3LYP | | Dihedral angles | Values (°) B3LYP | |
	6-311+G(d,p)	6-311++G(d,p)		6-311+G(d,p)	6-311++G(d,p)		6-311+G(d,p)	6-311++G(d,p)
C1 – C2	1.4099	1.4099	C1 – C2 – C6	119.1606	119.1571	C6– C1 –C2–C3	0.0043	−0.0013
C1 – C6	1.4008	1.4009	C2 – C1 – C7	121.0564	121.0767	C6– C1 –C2–H10	−179.9986	180.0009
C1 – C7	1.4645	1.4646	C6 – C1 – C7	119.783	119.7662	C7– C1 –C2–C3	−179.9981	179.9941
C2 – C3	1.3895	1.3896	C1 – C2 – C3	121.7778	121.7744	C7– C1 –C2–H10	−0.0047	−0.0037
C2 – H10	1.0822	1.0822	C1 – C2 – H10	118.2455	118.2526	C2– C1 –C6–C5	−0.0057	0.0017
C3 – C4	1.4167	1.4166	C3 – C2 – H10	119.9768	119.9729	C2– C1 –C6–H21	179.993	180.0026
C3 – Cl11	1.5069	1.5067	C2 – C3 – C4	117.696	117.704	C7– C1 –C6–C5	−179.9996	−179.9937
C4 – C5	1.3994	1.3995	C2 – C3 – C11	122.2228	122.2106	C7– C1 –C6–H21	−0.0009	0.0071
C4 – C115	1.3867	1.3868	C4 – C3 – C11	120.01812	120.854	C2– C1 –C7–H8	0.033	−180.0342
C5 – C6	1.3947	1.3947	C3 – C4 – C5	121.5399	121.5377	C2– C1 –C7–O9	−179.9685	−0.029
C5 – H20	1.0796	1.0797	C3 – C4 – O15	114.91111	124.9242	C6– C1 –C7–H8	−179.9732	−0.0388
C6 – H21	1.0836	1.0837	C5 – C4 – O15	123.549	123.5381	C6– C1 –C7–O9	0.0254	−180.0336
C7 – H8	1.2437	1.1027	C4 – C5 –C6	119.3714	119.369	C1– C2 –C3–C4	0.0011	−0.0033
C7 – O9	1.1027	1.2437	C4 – C5 –H20	120.9128	120.9072	C1– C2 –C3–C11	179.984	−180.0047
C11 – H12	1.0921	1.0922	C6 – C5 –H20	119.7158	119.7238	H10– C2 –C3–C4	−179.996	179.9945
C11 – H13	1.0897	1.0922	C1 – C6 –C5	120.4543	120.4527	H10– C2 –C3–C11	−0.0132	−0.0069
C11 – H14	1.0921	1.0898	C1 – C6 –H21	119.8502	119.837	C2 –C3–C4 –C5	−0.0052	0.0076
O15 – C16	1.4555	1.4553	C5 – C6 –H21	119.6955	119.7053	C2 –C3–C4 –O15	−179.9801	−179.9939
C16 – H17	1.0916	1.0849	C1 – C7 –H8	125.0095	115.4299	C11 –C3–C4 –C5	−179.9884	480.009
C16 – H18	1.0916	1.0917	C1 – C7 –O9	115.422	125.0269	C11 –C3–C4 –O15	0.00366	0.0075
C16 – H19	1.0849	1.0916	H8 – C7 –O9	119.5686	119.5432	C2 –C3–C11 –H12	−120.5977	120.6937
			C3 – C11 –H12	111.2802	111.2937	C2 –C3–C11 –H13	0.0475	−120.6365
			C3 – C11 –H13	110.6555	111.2885	C2 –C3–C11 –H14	120.7186	0.0301
			C3 – C11 –H14	111.3058	110.6469	H14 –C3–C11 –H12	59.3848	−59.3077
			H12– C11 –H13	108.4461	106.5385	C4 –C3–C11 –H13	−179.79	59.3621
			H12– C11 –H14	106.5476	108.4581	C4 –C3–C11 –H14	−59.2989	−179.9714
			H13– C11 –H14	108.453	108.4631	C3 –C4–C5 –C6	0.0038	−0.0073
			C4– C5 –C16	119.8676	119.8537	C3 –C4–C5 –H20	−179.9809	179.9912
			O15– C16 –H17	110.9532	104.9164	O15 –C4–C5 –C6	179.9765	179.9944
			O15– C16 –H18	110.9779	110.9729	O15 –C4–C5 –H20	−0.0081	−0.0071
			O15– C16 –H19	104.9244	110.9731	C3 –C4–O15 –C16	179.9624	179.9869
			H17– C16 –H18	110.1662	109.8466	C5 –C4–O15 –C16	−0.012	−0.0147
			H17– C16 –H19	109.8451	109.8492	C4 –C5–C6 –C1	0.0018	0.0025
			H18– C16 –H19	109.8533	110.1635	C4 –C5–C6 –H21	−179.9969	−179.9984
						H20 –C5–C6 –C1	179.9866	−179.9961
						H20 –C5–C6 –H21	−0.0121	0.003
						C4 –O15–C16 –H17	−61.3875	−179.9824
						C4 –O15–C16 –H18	61.445	−61.4026
						C4 –O15–C16 –H19	−179.96	61.4335

For numbering of atoms refer Fig 2

Table 3. Definition of internal coordinates of 3,4-dichlorobenzaldehyde

No (i)	Symbol	Type	Definition[a]
			Stretching
1 – 4	r_i	C–H	C2–H10, C5–H13, C6–H14, C7–H9
5 – 11	R_i	C–C	C1–C2, C2–C3, C3–C4, C4–C5, C5–C6, C6–C1, C1–C7
12 – 13	q_i	C–Cl	C3–Cl11, C4–Cl12
14	Q_i	C=0	C7–O8
			In-plane bending
15 – 20	γ_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	C1–C2–H10, C3–C2–H10, C4–C5–H13, C6–C5–H13, C5–C6–H14, C1–C6–H14
27	γ_i	C–C–H	C1–C7–H9
28	σ_i	C–C–O	C1–C7–O8
29 – 32	ϕ_i	C–C–Cl	C2–C3–Cl17, C4–C3–Cl11, C3–C1–Cl12, C5–C4–Cl12
			Out-of-plane bending
33 – 35	ω_i	C–H	H10–C2–C3–C1, H13–C5–C6–C4, H14–C6–C4–C5,
36	ψ_i	C–C	C7–C1–C2–C6
37-38	η_i	C–Cl	Cl11–C3–C4–C2, Cl12–C4–C5–C3
			Torsion
39 – 44	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
45	τ_i	τ C–CO	(C6–C2) – C1–C7–O8
46	τ_i	τ C–OH	(C2, C6) – C1–C7–H9
47	τ_i	CH	C1–C7–O8–H9

[a] For numbering of atom refer Fig. 1.

Table 4. Definition of internal coordinates of 4-methoxy-3-methyl benzaldehyde

No (i)	Symbol	Type	Definition[a]
Stretching			
1 – 4	r_i	C–H	C2–H10, C5–H20, C6–H21, C7–H9
5 – 7	q_i	C–O	O7–O8, C4–O15, C16–O15
8 – 15	Q_i	C–C	C1–C2, C2–C3, C3–C4, C4–C5, C5–C6, C6–C1, C1–C7, C3–C11
16 – 21	R_i	C–H (Methyl)	C11–H12, C11–H13, C11–H14, C16–H17, C16–H18, C16–H19,
In-plane bending			
22 – 27	γ_i	ring	C1–C2–C3, C2–C3–C4, C3–C4–C5, C4–C5–C6, C5–C6–C4, C6–C1–C2,
28 – 33	β_i	C–C–H	C1–C2–H10, C3–C2–H10, C4–C5–H20, C6–C5–H20, C5–C6–H21, C1–C6–H21,
34	β_i	C–C–H	C1–C7–H9
35	σ_i	C–C–O	C1–C7–O8
36 – 37	δ_i	C–C–O	C5–C4–O15, C3–C4–O15
38	ϕ_i	C–O–C	C4–O15–C16
39 – 42	ϕ_i	C–C–C	C6–C1–C7, C2–C1–C7, C2–C3–C11, C4–C3–C11
43 – 45	β_i	O–C–H (Methyl)	O15–C16–H17, O15–C16–H18, O15–C16–H19
46 – 48	Σ_i	H–C–H	H17–C16–H18, H17–C16–H19, H18–C16–H19
49 – 51	β_i	C–C–H (Methyl)	C3–C11–H12, C3–C11–H13, C3–C11–H14
52 – 54	Σ_i	H–C–H	H12–C11–H13, H12–C11–H14, H13–C11–H14
Out-of-plane bending			
55 – 57	ω_i	C–H	H10–C2–C3–C1, H20–C5–C6–C4, H21–C6–C1–C5
58	ω_i	C–H	H9–C7–C1–C1(C6, C1)
59 – 60	ψ_i	C–C	C11–C3–C4–C2, C7–C1–C2–C6
61	η_i	C–O	O15–C4–C5–C3
Torsion			
62 – 67	τ_i	ring	C1–C2–C3–C4, C2–C3–C2–C5, C3–C4–C5–C6, C4–C5–C6–C1, C5–C6–C1–C2, C6–C1–C2–C3
68	τ_i	t O–CH$_3$	C4–O15–C16– (H17, H18, H19)
69	τ_i	t C–CH$_3$	(C2, C4) –C3–C11– (H12, H13, H14)
70		t CO	(C6–C2) –C1–C7–O8
71	τ_i	t CH	H9–C7–O11–C1

[a] For numbering of atom refer Fig. 2.

Table 5. Definition of local symmetry coordinates of 3,4-dichlorobenzaldehyde

No (i)	Type[a]	Definitions[b]
1 – 4	CH	r_1, r_2, r_3, r_4
5 – 11	CC	$R_5, R_6, R_7, R_8, R_9, R_{11}$
12 – 13	CCl	q_{12}, q_{13}
14	CO	Q_{14}
15	R trigd	$(\gamma_{15} - \gamma_{16} + \gamma_{17} - \gamma_{18} + \gamma_{19} - \gamma_{20}) / \sqrt{6}$
16	R symd	$(-\gamma_{15} - \gamma_{16} + 2\gamma_{17} - \gamma_{18} - \gamma_{19} + 2\gamma_{20}) / \sqrt{12}$
17	R asymd	$(\gamma_{15} - \gamma_{16} + \gamma_{18} - \gamma_{19}) / 2$
18 – 20	bCH	$(\beta_{21} - \beta_{22}) / \sqrt{2}$, $(\beta_{23} - \beta_{24}) / \sqrt{2}$, $(\beta_{25} - \beta_{26}) / \sqrt{2}$
21	bCH	γ_{27}
22	bCO	σ_{28}
23 – 24	bCCl	$(\theta_{29} - \theta_{30}) / \sqrt{2}$, $(\theta_{31} - \theta_{32}) / \sqrt{2}$
25 – 27	ωCH	$\omega_{33}, \omega_{34}, \omega_{35}$
28	ψCC	ψ_{36}
29 – 30	ηCCl	η_{37}, η_{38}
31	tR tridg	$(\tau_{39} - \tau_{40} + \tau_{41} - \tau_{42} + \tau_{43} - \tau_{44}) / \sqrt{6}$
32	tR symd	$(\tau_{39} - \tau_{41} + \tau_{42} - \tau_{44}) / \sqrt{2}$
33	tR asymd	$(-\tau_{39} + 2\tau_{40} - \tau_{41} - \tau_{42} + 2\tau_{43} - \tau_{44}) / \sqrt{12}$
34	tCO	τ_{45}
35	tOH	τ_{46}
36	τCH	τ_{47}

[a] These symbols are used for description of the normal modes by assignment in Table 7.
[b] The internal coordinates used here are defined in Table 3.

Table 6. Definition of local symmetry coordinates of 4-methoxy-3-methyl benzaldehyde

No (i)	Type[a]	Definition[b]
1 – 4	CH	r_1, r_2, r_3, r_4
5 – 7	CO	q_5, q_6, q_7
8 – 15	CC	$Q_8, Q_9, Q_{10}, Q_{11}, Q_{12}, Q_{13}, Q_{14}, Q_{15}$
16, 17	CH₃ ss	$(R_{16} + R_{17} + R_{18})/\sqrt{3}$, $(R_{19} + R_{20} + R_{21})/\sqrt{3}$,
18, 19	CH₃ ips	$(2R_{16} + R_{17} + R_{18})/\sqrt{6}$, $(2R_{19} + R_{20} + R_{21})/\sqrt{6}$,
20, 21	CH₃ ips	$(R_{17} + R_{18})/\sqrt{2}$, $(R_{20} + R_{21})/\sqrt{2}$,
22	R trigd	$(\gamma_{22} - \gamma_{23} + \gamma_{24} - \gamma_{25} + \gamma_{26} - \gamma_{27})/\sqrt{6}$
23	R symd	$(-\gamma_{22} - \gamma_{23} + 2\gamma_{24} - \gamma_{25} - \gamma_{26} + 2\gamma_{27})/\sqrt{12}$
24	R asymd	$(\gamma_{22} - \gamma_{23} + \gamma_{25} - \gamma_{26})/2$
25 – 27	bCH	$(\beta_{28} - \beta_{29})/\sqrt{2}$, $(\beta_{30} - \beta_{31})/\sqrt{2}$, $(\beta_{32} - \beta_{33})/\sqrt{2}$
28	bCH	β_{34}
29	bCO	σ_{35}
30	bCO	$(\delta_{36} - \delta_{37})/\sqrt{2}$
31	bOC	θ_{38}
32 – 33	bCC	$(\phi_{39} - \phi_{40})/\sqrt{2}$, $(\phi_{41} - \phi_{42})/\sqrt{2}$,
34, 35	CH₃ ipb	$(-\beta_{43} - \beta_{44} - \beta_{45} + \Sigma_{46} + \Sigma_{47} + \Sigma_{48})/\sqrt{6}$ $(-\beta_{49} - \beta_{50} - \beta_{51} + \Sigma_{52} + \Sigma_{53} + \Sigma_{54})/\sqrt{6}$
36, 37	CH₃ ipb	$(\Sigma_{46} - \Sigma_{47} - 2\Sigma_{48})/\sqrt{6}$, $(\Sigma_{52} - \Sigma_{53} - 2\Sigma_{54})/\sqrt{6}$
38, 39	CH₃ ipb	$(\Sigma_{46} - \Sigma_{47})/\sqrt{2}$, $(\Sigma_{52} - \Sigma_{53})/\sqrt{2}$
40, 41	CH₃ ipr	$(2\beta_{43} - \beta_{44} - \beta_{45})/\sqrt{6}$, $(2\beta_{49} - \beta_{50} - \beta_{51})/\sqrt{6}$
42, 43	CH₃ ipr	$(\beta_{44} - \beta_{45})/\sqrt{2}$, $(\beta_{50} - \beta_{51})/\sqrt{2}$
44 – 46	ωCH	$\omega_{55}, \omega_{56}, \omega_{57}$
47	ψCH	ψ_{58}
48 – 49	ψCC	ϕ_{59}, ϕ_{60},
50	ηCO	η_{61}

51	tR trigd	$(\tau_{62} - \tau_{63} + \tau_{64} - \tau_{65} + \tau_{66} - \tau_{67})/\sqrt{6}$
52	tR symd	$(\tau_{62} - \tau_{64} + \tau_{65} - \tau_{67})/\sqrt{2}$
53	tR asymd	$(-\tau_{62} - 2\tau_{63} - \tau_{64} - \tau_{65} + 2\tau_{66} - \tau_{67})/\sqrt{12}$
54	t OCH$_3$	τ_{68}
55	t C-CH$_3$	τ_{69}
56	t C-OC	τ_{70}
57	t OH	τ_{71}

[a]These symbols are used for description of the normal modes by assignment in Table 8.
[b]The internal coordinates used here are defined in Table 4.

Table 7. Vibrational assignment of fundamental observed (FT-IR and FT-Raman) and calculated (Unscaled and scaled) frequencies of 3,4-dichlorobenzaldehyde using B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) level [wave number cm^{-1}; IR intensities (Km mol^{-1}); Raman intensity (Å^4 amu^{-1}); Force constant (m dyne A^{-1})]

Species C$_1$	Observed frequencies (cm^{-1})		Calculated frequencies (cm^{-1})				Force constant		^{a}IR intensity		^{b}Raman intensity		Assignments with TED (%) among types of internal co-ordinates
			B3LYP				B3LYP		B3LYP		B3LYP		
	FT-IR	FT-Raman	6-311+G(d,p)		6-311++G(d,p)		6-311+G(d,p)	6-311++G(d,p)	6-311+G(d,p)	6-311++G(d,p)	6-311+G(d,p)	6-311++G(d,p)	
			Unscaled	Scaled	Unscaled	Scaled							
A	-	3196	3206	3185	3205	3192	6.6359	6.6174	1.1560	2.7812	63.4474	80.1439	νCH (98)
A	-	3182	3194	3168	3203	3178	6.5410	6.6030	0.1730	2.1574	20.9179	1.1768	νCH (96)
A	3094	-	3183	3074	3172	3088	6.5133	6.4587	0.2604	3.0739	27.6651	35.8367	νCH (95)
A	2853	2852	2901	2847	2898	2849	5.3741	5.3528	104.2778	115.8065	89.1438	99.7048	νCH (92)
A	1702	-	1773	1685	1772	1696	19.1272	19.1403	331.1489	309.0518	99.1211	97.3167	νC=O (89)
A	1696	1697	1622	1676	1619	1692	8.9434	9.0233	69.4319	90.6398	98.0771	79.9047	νCC (87)
A	1686	1683	1592	1675	1595	1680	11.0346	10.4493	56.5314	19.5967	53.5768	29.7447	νCHC(86)
A	1588	1586	1496	1578	1490	1583	3.4658	3.5028	25.2766	28.4725	9.5806	0.9616	νCC (87)
A	1563	-	1433	1552	1435	1558	1.8902	1.9780	8.8035	11.2846	16.4889	5.8308	νCC (85)
A	1462	-	1389	1450	1396	1458	2.4218	2.4473	38.1549	52.3172	20.9818	1.9474	νCC (84)
A	1408	1406	1317	1396	1316	1402	10.6929	10.3996	1.3130	15.8424	11.7810	21.7731	νCC (82)
A	1372	-	1283	1360	1274	1375	1.4898	1.3385	13.0115	1.4407	4.4611	3.3163	bCC (80)
A	1366	-	1212	1350	1206	1360	2.5880	2.6532	159.5401	173.2974	98.8735	92.2191	bCH (78)
A	1286	1288	1158	1272	1162	1281	1.0169	1.1523	6.3453	4.4088	15.6474	4.2323	bCH (79)
A	1269	-	1139	1259	1134	1265	1.8175	1.6045	40.3152	30.8417	67.4232	63.3605	bCH (81)
A	1196	1195	1043	1184	1043	1192	3.0900	2.9683	38.8846	37.9547	72.1396	67.2665	bCH (75)
A	1152	1150	1027	1141	1028	1148	1.1133	1.1349	1.7335	2.2210	12.4178	17.0874	R trigd (72)
A	1126	-	991	1118	971	1120	0.7767	0.7451	0.2421	0.8938	1.6023	0.7917	R symd (71)
A	1033	1030	899	1021	920	1030	0.6543	0.6650	11.2663	9.7832	1.7560	1.4277	R asymd (70)
A	1005	1008	886	998	916	1001	2.5335	2.7957	65.2773	55.8971	47.2350	26.7485	νCCl (68)
A	917	915	844	902	830	915	0.5564	0.5334	31.412	32.9850	0.1015	1.0053	νCCl (69)
A	892	-	749	881	716	888	2.2004	1.8797	38.2337	26.6490	35.4277	8.2665	bCO (66)
A	744	741	715	735	701	740	1.3119	1.3178	0.636	0.7475	5.9035	0.2261	bCC (64)
A	706	-	675	691	687	702	1.8232	2.0664	6.6869	12.6373	67.3503	19.7371	bCCl (62)
A	696	695	581	685	560	695	1.5762	0.8287	15.5989	3.7092	7.5638	6.1298	bCCl (60)
A	680	-	555	670	553	678	0.7833	1.4358	4.4006	23.4151	1.2089	24.7778	ωCH (55)
A	555	552	456	543	449	553	1.0370	0.3678	5.7331	6.1655	99.3744	0.0271	ωCH (56)
A	542	540	450	530	445	539	0.3805	1.935	3.4914	1.7276	2.5078	98.3406	ωCH (52)
A	-	447	353	435	418	442	0.7242	0.6514	8.9557	15.3355	30.8467	100	ωCH (56)
A	420	417	338	411	328	416	0.7768	0.2591	0.7556	0.6120	28.3252	9.7510	t R trigd (52)
A	-	320	309	312	316	318	0.2267	0.8688	1.0924	0.1385	12.9250	62.7988	t R symd (50)
A	-	210	222	198	205	205	0.1047	0.6701	7.2022	0.1387	22.9627	50.1383	t R asy (52)
A	-	192	201	180	175	190	0.7265	0.0647	0.2148	3.8293	71.6041	90.5833	ωCC (53)
A	-	175	172	168	167	171	0.1687	0.680	6.9645	3.5933	9.1428	19.6958	ωCCl (54)
A	-	170	121	165	161	168	0.0380	0.1801	3.5731	5.3026	81.7671	69.6848	ωCCl (52)
A	-	102	85	98	76	100	0.0454	0.0407	4.7541	4.4873	4.2577	78.0807	ωCO (51)

Abbreviations: ν - stretching; b - in-plane bending; ω - out-of-plane bending; asymd - asymmetric; symd - symmetric; t - torsion; trig - trigonal; ss - symmetric stretching; ass - asymmetric stretching; ips - in-plane stretching.; ops - out-of-plane stretching; sb - symmetric bending; ipr - in-plane rocking; opr - out-of-plane rocking; opb - out-of-plane bending.

[a] Relative absorption intensities normalized with highest peak absorption equal to 1.0
[b] Relative Raman intensities calculated by Eq. (5.1) and normalized to 100.

Table 8. Vibrational assignment of fundamental observed (FT-IR and FT-Raman) and calculated (Unscaled and scaled) frequencies of 4-methoxy-3-methylbenzaldehyde using B3LYP 6-311+G(d,p) and B3LYP/6-311++G(d,p) level [wave number cm⁻¹; IR intensities (Km mol⁻¹); Raman intensity (Å⁴ amu⁻¹); Force constant (m dyne A⁻¹)]

Species C$_1$	Observed frequencies (cm^{-1})		Calculate frequencies (cm^{-1}) B3LYP				Force constant B3LYP		[a]IR intensity B3LYP		[b]Raman intensity B3LYP		Assignments with TED (%) among types of internal co-ordinates
			6-311+G(d,p)		6-311++G(d,p)								
	FT-IR	FT-Raman	Unscaled	Scaled	Unscaled	Scaled	6-311+G(d,p)	6-311++G(d,p)	6-311+G(d,p)	6-311++G(d,p)	6-311+G(d,p)	6-311++G(d,p)	
A	-	3028	3207	3012	3205	3025	6.6165	6.6104	12.7926	12.4356	49.4745	49.2152	vCH (99)
A	3010	-	3183	3000	3182	3008	6.5124	6.5081	3.8010	3.8027	22.6189	22.4824	vCH (98)
A	2950	-	3161	2940	3160	2948	6.4167	6.4096	10.2676	9.8145	34.9003	34.6780	vCH (96)
A	2926	2925	3151	2906	3150	2925	6.4310	6.4293	18.4231	18.3674	55.7341	54.8105	vCH (94)
A	-	2850	3105	2835	3105	2952	6.2509	6.2496	17.8943	17.9642	28.7147	28.4525	CH$_3$ ops(75)
A	2841	-	3084	2828	3084	2838	6.1969	6.1952	35.5941	35.4710	30.1953	30.9412	CH$_3$ ops(70)
A	2824	-	3076	2814	3075	2820	6.1185	6.1151	16.2012	16.4251	41.7972	43.0687	CH$_3$ ss(90)
A	-	2768	3022	2775	3021	2765	5.5721	5.5694	26.2296	26.2302	58.3641	24.6457	CH$_3$ ss(91)
A	2754	-	3010	2748	3010	2753	5.5122	5.5102	53.7286	54.3955	83.2114	86.6396	CH$_3$ ips(93)
A	2722	-	2933	2718	2932	2720	5.4963	5.4920	121.1936	121.6798	95.5592	98.2665	CH$_3$ ips(90)
A	1717	-	1662	1710	1661	1712	10.5005	10.4892	79.2433	76.3962	96.5955	96.4726	vCC(89)
A	1686	-	1632	1675	1632	1685	7.7807	7.7995	316.2930	318.1289	98.9577	83.7003	vCC (88)
A	1682	1681	1605	1672	1605	1680	10.4796	10.5163	86.8043	87.6056	80.2569	62.5728	vCC (86)
A	1606	-	1544	1710	1544	1606	2.1963	2.2019	45.8835	45.7161	3.9618	4.2731	vCHC(87)
A	-	1602	1530	1592	1530	1600	1.4724	1.4724	20.6806	20.2674	16.2723	17.1841	vCC (88)
A	-	1584	1524	1574	1523	1580	1.4386	1.4368	12.3404	10.9515	45.3289	49.2933	vCC (85)
A	1504	1502	1520	1490	1520	1502	1.4224	1.4216	11.7217	12.4376	25.8863	27.3589	vCC (84)
A	1466	-	1517	1456	1517	1462	1.9975	1.9935	88.3753	89.1237	51.1338	51.3611	vCC (83)
A	1462	1460	1484	1442	1483	1465	1.5354	1.5335	8.4931	8.1349	18.0230	18.4146	CH$_3$ ipb(80)
A	1442	1445	1460	1430	1460	1440	2.0228	2.0299	21.3350	21.1996	66.6019	64.2717	CH$_3$ ipb(81)
A	1422	1419	1457	1410	1457	1420	1.9795	1.9869	31.011	31.0112	85.1220	87.2681	CH$_3$ sb(78)
A	1395	1392	1428	1381	1427	1393	2.0176	2.0004	9.6241	9.6727	8.6769	9.2385	CH$_3$ sb(80)
A	1380	-	1363	1365	1463	1375	7.6227	7.6096	1.2458	1.2108	20.7807	17.8621	vCO (76)
A	-	1331	1328	1320	1328	1334	1.4494	1.4482	0.4485	0.4851	5.3437	5.4953	vCO (77)
A	1327	-	1268	1318	1268	1325	4.4625	4.4425	347.2009	345.0405	6.2864	6.9258	vCO (75)
A	1292	-	1256	1285	1256	1290	2.5036	2.5005	24.0133	25.0766	26.0352	24.5111	bCH (70)
A	1260	1260	1206	1247	1206	1258	1.2310	1.2317	3.1424	3.1782	11.4219	11.6251	bCH (72)
A	1227	1226	1182	1221	1181	1225	1.2226	1.2212	3.9712	4.0309	13.5181	13.5157	bCH (74)
A	1162	-	1160	1150	1160	1160	1.6838	1.6838	161.4566	161.9617	54.7112	55.0098	bCH (71)
A	1125	1127	1156	1115	1155	1120	0.9909	0.9878	0.6408	0.6077	14.5405	18.8037	CH$_3$ opb(65)
A	1028	-	1096	1018	1097	1025	1.0574	1.0666	3.5487	3.9059	0.5146	0.5538	CH$_3$ opb(64)
A	-	1005	1047	998	1047	1000	1.0386	1.0380	0.8107	0.8125	2.6906	2.4595	R trigd (68)
A	-	986	1031	975	1035	984	1.1109	1.1300	5.1848	5.4996	10.2944	13.3583	R symd (69)
A	968	-	1011	950	1011	965	4.9720	4.9686	10.8799	60.9962	13.5232	13.8671	R asymd (66)
A	-	959	976	947	974	952	0.7645	1.8728	1.5958	8.1650	0.1371	37.3817	CH$_3$ ipr(67)
A	938	-	974	928	970	935	1.8735	0.7497	8.1497	2.1555	37.3388	0.4614	CH$_3$ ipr(65)
A	900	-	947	882	947	902	0.6873	0.6861	9.1163	8.5927	3.2427	4.2577	CH$_3$ opr(59)
A	815	-	840	800	837	812	0.5945	0.5876	48.7709	49.7190	3.3309	1.4430	CH$_3$ opr(60)
A	-	788	758	762	758	785	1.7060	1.7077	17.8592	18.1744	5.7187	6.3535	bCC (65)
A	781	-	754	770	754	780	1.7270	1.7242	5.0430	4.6499	98.5810	3.2603	bCC (64)
A	-	761	740	750	745	759	1.2200	1.2203	0.4863	0.6790	2.3666	3.9688	bCO (62)
A	740	-	646	731	646	742	1.4111	1.4109	37.6614	37.6303	85.2688	85.8779	bCO (60)
A	640	641	572	730	571	641	0.6106	0.6098	3.1458	3.0378	1.1152	0.1627	bCO (58)
A	615	614	548	600	548	612	1.0069	1.0067	7.1715	7.1431	69.3423	69.9359	ωCH (55)
A	552	-	501	540	501	554	0.5711	0.5709	0.5273	0.5114	72.0287	72.3582	ωCH (56)
A	-	547	463	535	464	545	0.3553	0.3603	0.5353	4.1357	61.1580	4.7584	ωCH (53)
A	529	-	435	519	435	524	0.5943	0.5939	10.9130	10.8720	21.4966	21.3384	ωCH (54)
A	-	524	369	518	368	520	0.2982	0.2972	2.6707	2.6143	8.3750	7.5828	t R trigd (52)
A	496	-	312	480	312	494	0.2124	0.2126	0.9907	0.9728	55.6109	56.1383	t Rsymd (51)
A	-	489	230	470	228	485	0.2452	0.0457	0.1837	0.2304	10.9374	18.8258	t R asymd (50)
A	424	-	219	414	219	420	2.0912	0.0912	8.0042	8.0053	82.1947	82.4383	ωCC (54)
A	-	428	204	418	204	425	0.0582	0.0568	5.1024	4.8704	89.6689	14.9940	ωCC (51)
A	-	388	181	375	181	385	0.0373	0.0363	0.2419	0.2686	31.0200	34.1547	ωCC (53)
A	-	312	173	307	173	310	0.0991	0.0991	3.1400	3.1122	12.0337	12.1216	ωCC (52)
A	-	235	147	225	151	232	0.0145	0.0152	3.6384	3.1928	5.0532	6.1991	ωCC (50)
A	-	208	121	200	121	205	0.0286	0.0305	12.9669	13.4203	18.6801	19.8692	t CH$_3$ (51)
A	-	185	66	180	66	182	0.0110	0.0109	0.0334	0.0238	82.2466	88.5331	t CH$_3$ (52)

Abbreviations:v - stretching; b - in-plane bending; ω - out-of-plane bending; asymd - asymmetric; symd - symmetric; t - torsion; trig - trigonal; ss - symmetric stretching; ass - asymmetric stretching; ips - in-plane stretching,; ops - out-of-plane stretching; sb - symmetric bending; ipr - in-plane rocking; opr - out-of-plane rocking; opb - out-of-plane bending.
[a] Relative absorption intensities normalized with highest peak absorption equal to 1.0.
[b] Relative Raman intensities calculated by Eq. (5.1) and normalized to 100.

Table 9. Thermodynamic properties of 3,4-dichlorobenzaldehyde and 4-methoxy-3-methylbenzaldehyde

Parameters	3,4-dichlorobenzaldehyde		4-methoxy-3-methylbenzaldehyde	
	B3LYP		B3LYP	
	6-311+G(d,p)	6-311++G(d,p)	6-311+G(d,p)	6-311++G(d,p)
Self Consistent Field energy (a.u)	-1264.90787	-1264.90780	-499.39869	-499.40810
Zero -point vibrational energy (Kcal/Mol)	56.56842	56.51874	106.6079	106.5898
Rotational constants (GHz)				
A	1.81509	1.71826	2.3666	2.3667
B	0.60145	0.63746	0.6701	0.6701
C	0.45176	0.46496	0.5257	0.5256
Entropy (Cal/Mol-Kelvin)	93.760	93.787	100.047	100.065
Specific heat capacity at constant volume (Cal/Mol-Kelvin)	31.584	31.613	38.726	38.959
Translational Energy KCal/Mol-Kelvin	0.889	0.889	0.889	0.889
Rotational energy (KCal/Mol-Kelvin)	0.889	0.889	0.889	0.889
Vibrational energy (KCal/Mol-Kelvin)	60.261	60.213	111.488	111.430
Dipole moment (Debye)	3.0344	3.1213	5.4567	5.7665
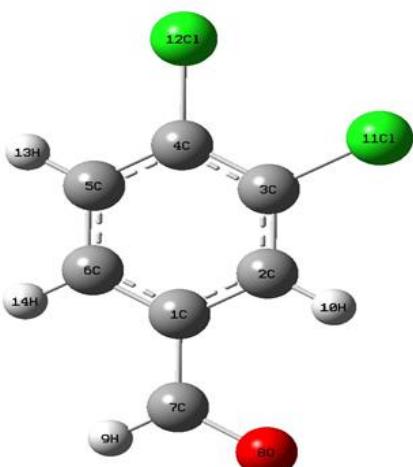
Fig 1. Molecular structure of 3,4-dichlorobenzaldehyde
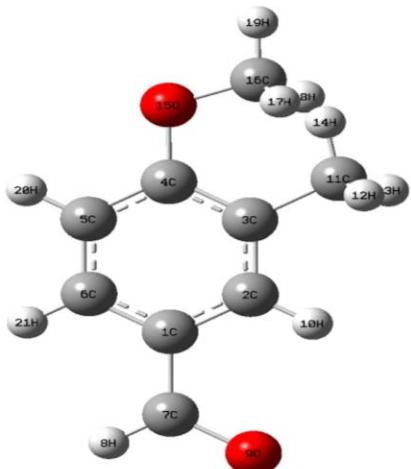
Fig 2. Molecular structure of 4-methoxy-3-methylbenzaldehyde
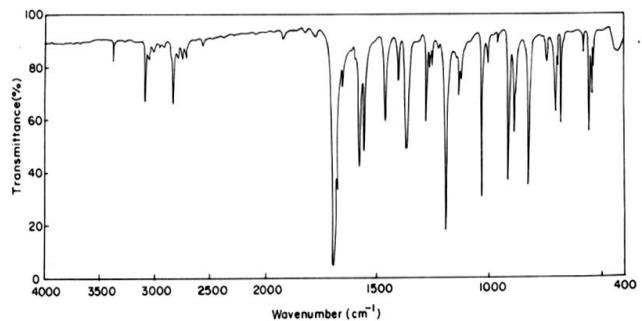
Fig. 3. FT-IR spectrum of 3,4-dichlorobenzaldehyde
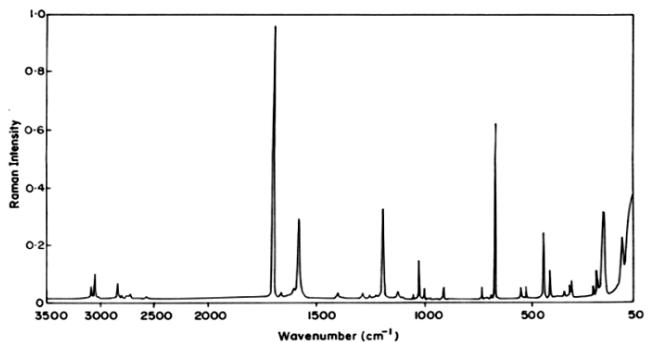
Fig. 4. FT-Raman spectrum of 3,4-dichlorobenzaldehyde
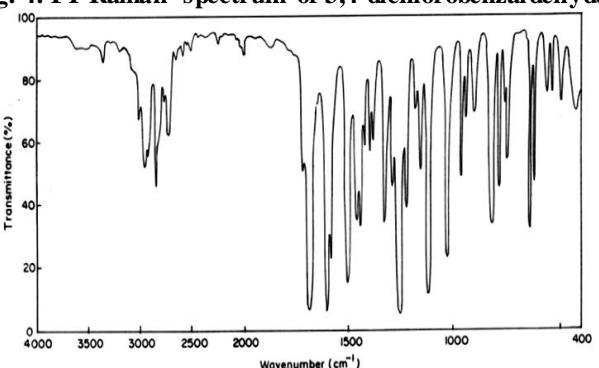
Fig. 5. FT-IR spectrum of 4-methoxy-3-methylbenzaldehyde
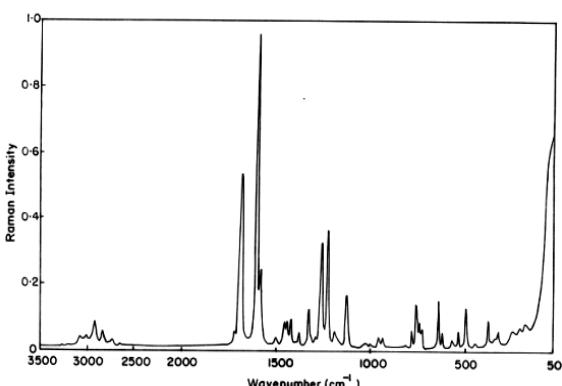
Fig. 6. FT-Raman spectrum of 4-methoxy-3-methylbenzaldehyde
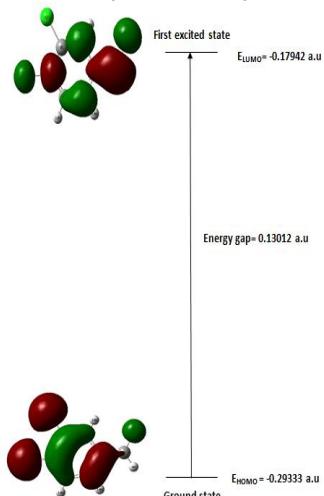
Fig. 7. The atomic orbital HOMO-LUMO composition of the frontier molecular orbital for 3,4-dichlorobenzaldehyde
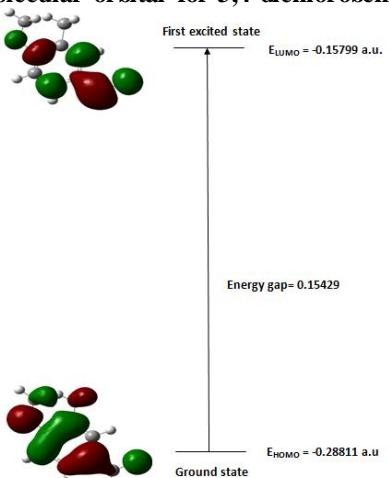

Fig. 8. The atomic orbital HOMO-LUMO composition of the frontier molecular orbital for 4-methoxy-3-methylbenzaldehyde

To the best of our knowledge, there have been no theoretical calculations to understand the structure and the fundamental vibrational frequencies of DCB and MMB

In order to present a full description of the vibrational spectra of the title compounds, we carried out DFT calculations using B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) to obtain the geometries, vibrational frequencies, IR intensities and Raman intensities.

Experimental Analysis

Pure chemicals of 3,4-dichlorobenzaldehyde (DCB) and 4-methoxy -3-methyl benzaldehyde (MMB) were obtained from Lancaster chemical company, UK and used as such without any further purification. The FT-IR spectra of the title compounds were recorded in the region of 4000 – 400 cm^{-1} using KBr pellet.

The FT-Raman spectra of DCB and MMB were recorded on a BRUKER IFS 66V model interferometer equipped with an FRA-106 FT-Raman accessories. The spectra were recorded in the stokes region 3500 – 50 cm^{-1} using the 1064 nm line of Nd:YAG laser for excitation operating at 200 mW of power.

Methods of Computation

The molecular geometry optimizations, energy and vibrational frequency calculations are carried out for DCB and MMB with the GAUSSIAN 09W software package [15] using the B3LYP functions combined with the standard 6-311+G(d,p) and 6-311++G(d,p) basis sets. The Cartesian representation of the theoretical force constants has been computed at optimized geometry by assuming C$_1$ point group symmetry. Scaling of the force field is performed according to the SQM procedure [16,17] using selective scaling in the natural internal coordinate representation [18,19]. Transformations of the force field and the subsequent normal coordinate analysis including the least square refinement of the scaling factors, calculation of the total energy distribution (TED), are done on a PC with MOLVIB program (version V7.0 - G77) written by Sundius [20,21]. The symmetry of the molecule is also helpful in making vibrational assignments. The symmetries of the vibrational mode are determined by using the standard procedure [22] of decomposing the traces of the symmetry operation into the irreducible representations. The symmetry analysis for the vibrational modes of DCB and MMB are presented in some details in order to describe the basis for the assignments.

By combining the results of the GAUSSVIEW program [23] with symmetry considerations, vibrational frequency assignments are made with a high degree of confidence. There is always some ambiguity in defending internal coordinate form complete set and matches quite well with the motions observed using the GAUSSVIEW program.

Results and discussion

Molecular geometry

The molecular structures of DCB and MMB are shown in Figs. 1 and 2, respectively. The global minimum energy obtained by using the B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) method and basis set for DCB are calculated as −1264.90787 and −1264.90780 Hartrees, respectively. The global minimum energy obtained by using the B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) method and basis set for MMB are calculated as −499.39869 and −499.40810 Hartrees, respectively. The optimized geometrical parameters obtained by the large basis set calculations for DCB and MMB are presented in Tables 1 and 2, respectively.

Normal coordinate analysis is carried out for the molecules to provide a complete assignment of the fundamental vibrational frequencies [24-26]. For this purpose, the full set of 47 and 71 standard internal coordinates (containing 11 and 14 redundancies) for DCB and MMB, respectively, are defined as given in Tables 3 and 4 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 [18,19] are summarized in Tables 5 and 6. The theoretically calculated DFT force fields are 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 molecules are calculated.

The complete assignment of the fundamentals is proposed based on the calculated TED values. The FT-IR and FT-Raman spectra of the title compounds are shown in Figs 3 - 6.

Prediction of Raman intensities

The Raman activities (S_i) calculated with the GAUSSSIAN 09W program and adjusted during the scaling procedure with MOLVIB are subsequently converted in to relative Raman intensities (I_i) using the following relationship derived from the basic theory of Raman scattering,

$$I_i = \frac{f(v_0 - v_i)^4 S_i}{v_i\left[1 - \exp\left(\frac{hcv_i}{kT}\right)\right]} \qquad \dots (1)$$

where v_o is the exciting frequency (in cm^{-1} units), v_i is the vibrational wavenumber for the ith normal modes, h, c, k are fundamental constants and f is a suitable chosen common normalization factor for all peak intensities.

C–H Vibrations

The substituted benzene gives rise to C–H stretching. C–H in-plane bending and C–H out-of-plane deformations. The heteroaromatic structure shows the presence of C–H stretching vibrations in the region $3000 - 3100\ cm^{-1}$ which is the characteristic region for the ready identification of such stretching vibrations [27,28]. Accordingly in this study the C-H vibrations of the DCB are observed at 3094, 2853 cm^{-1} in FT-IR and 3196, 3182, 2852 cm^{-1} in FT-Raman spectrum and the MMB is observed at 3010, 2950, 2926 cm^{-1} in FT-IR and in FT-Raman at 3028, 2925 cm^{-1}. The C-H in-plane and out-of-plane bending vibrations have also identified and listed in Tables. 7 and 8.

C–C Vibrations

The bands between $1400 - 1650\ cm^{-1}$ in benzene derivatives are due to C–C stretching vibrations [29]. Therefore, the C–C stretching vibrations are found at 1696, 1686, 1588, 1563, 1462, 1408, 1372 cm^{-1} and 1697, 1683, 1586, 1406 cm^{-1} in FT-IR and FT-Raman spectra of DCB respectively. In the MMB these vibrations are found at 1717, 1686, 1682, 1606, 1504, 1466 cm^{-1} in FT-IR and 1681, 1602, 1584, 1502 cm^{-1} in FT-Raman spectrum. In the present investigation the ring in-plane and out-of-plane bending vibrations are made for the title compounds by careful consideration of their qualitative descriptions.

C–Cl Vibrations

The vibrations belong to the band between the ring and the halogen atoms are worth to discuss here, since mixing of vibrations are possible due to the lowering of the molecular symmetry and the presence of heavy atoms on the periphery of molecule [30]. The assignments of C–Cl stretching and deformation vibrations have been made by comparison with similar molecules, para-bromophenol [31] and the halogen–substituted benzene derivatives[32] and Mooney [33,34] assigned vibrations of C–X group (X=Cl, Br and I) in the frequency range of $1129 - 480\ cm^{-1}$. In the present investigation, the FT-IR bands observed at 1005, 917 cm^{-1} and the FT-Raman bands at 1008, 915 cm^{-1} have been assigned to C–Cl stretching mode of DCB. The C–Cl in-plane bending and out-of-plane bending vibrations are also summarized in Table-7.

C=O Vibrations

The carbonyl bonds are the most characteristic bands of infrared spectrum. Both the carbon and oxygen atoms of the carbonyl group move during vibration and they have nearly equal amplitudes. The carbonyl frequencies can be altered by intermolecular hydrogen bonding. A great deal of structural information can be derived from the exact position of the carbonyl stretching absorption peaks. Normally carbonyl group vibrations [35] occur in the region $1800 - 1700\ cm^{-1}$. Accordingly in the present investigation the FT-IR band appearing at 1702 cm^{-1} and 1380 cm^{-1} are assigned as C=O stretching vibration. The C=O in-plane bending and out-of-plane bending vibration are also identified for DCB and MMB listed in Tables 7 and 8.

CH$_3$ vibrations

For the assignments of CH_3 group frequencies nine fundamental vibrations can be associated to each CH_3 group. Three stretching, three bending, two rocking modes and a single torsional mode describe the motion of the methyl group. The above modes are defined in Table 8. The CH_3 symmetric stretching vibration is identified at 2824 cm^{-1} and 2768 cm^{-1} in FT-IR and FT-Raman spectrum, respectively and in plane stretching vibrations are identified at 2754, 2722 cm^{-1} in FT-IR spectrum. The CH_3 symmetric bending frequencies are identified at 1422, 1395 cm^{-1} in FT-IR and in FT-Raman 1419, 1362 cm^{-1}. The CH_3 in-plane bending frequencies are identified at 1462, 1442 cm^{-1} in FT-IR and 1460, 1445 cm^{-1} in FT-Raman. These assignments are also supported by the literatures [29,36]. The in-plane rocking and out-of-plane rocking modes of the CH_3 group are found at 938 cm^{-1} in FT-IR and in FT-Raman 959 cm^{-1} and 900, 815 cm^{-1} in FT-IR respectively. The FT-IR band obtained at 2841cm^{-1} and 2850 cm^{-1} are assigned to CH_3 out-of-plan stretching and CH_3 out-of -plane bending modes are observed at 1125, 1028 cm^{-1} in FT-IR and 1127 cm^{-1} in FT-Raman. The assignments of the bands at $208 - 185\ cm^{-1}$ in FT-Raman are assigned to torsion modes.

Homo-Lumo Analysis

The electronic absorption corresponds to the transitions from the ground state to the first excited state and is mainly described by one electron excitation from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

The HOMO-LUMO energy gaps of the title molecules are calculated at B3LYP/6-311++G(d,p) level, which reveals that the energy gap reflects the chemical activity of the molecule. The strong charge transfer interaction through π-conjugated bridge results in substantial ground state donor-acceptor mixing and the appearance of a charge transfer band in the electron absorption spectrum. The corresponding orbitals are shown in Figs. 7 and 8 respectively.

The HOMO of DCB is mainly localized on chlorine atoms and benzene ring as LUMO is spread over C=O group. The HOMO of MMB is localized on ring atoms, methyl and methoxy hydrogen atoms as LUMO is populated on the molecule except methyl and methoxy group hydrogen atoms.

For DCB

HOMO energy	=	−0.29333 a.u
LUMO energy	=	−0.17942 a.u
HOMO-LUMO energy gap	=	0.11391 a.u

For MMB

HOMO energy	=	−0.28811 a.u
LUMO energy	=	−0.15799 a.u
HOMO-LUMO energy gap	=	0.13012 a.u

The Rmodynamic Properties

Several calculated thermodynamical parameters, rotational constants, and dipole moment have been presented in Table 9. The zero-point vibration energies, the entropy and the molar capacity at constant volume are calculated. The variations in the zero-point vibration energies seem to be insignificant. The total energies and the change in the total entropy of DCB and MMB at room temperature at different methods are only marginal.

Prediction of First Hyperpolarizability

The first hyperepolarizability (β_0) of molecular system and the related properties (β_0, α_0) of DCB and MMB are calculated using B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) basis set, based on the finite field approach. In the presence of an applied electric field, the energy of a system is a function of the electric field. The first hyperpolarizability is a third-rank tensor that can be described by a $3 \times 3 \times 3$ matrix. The 27 components of the 3D matrix can be reduced to 10 components due to the Kleinman symmetry . It can be given in the lower tetrahedral. The components of β are defined as the coefficients in the Taylor series expansion of the energy in the external electric field. When the external electric field is weak and homogenous, this expansion becomes

$$E = E^0 - \mu_\alpha F_\alpha - \frac{1}{2}\alpha_{\alpha\beta}F_\alpha F_\beta - \frac{1}{6}\beta_{\alpha\beta\gamma}F_\alpha F_\beta F_\gamma + ... \qquad ... (5.2)$$

where E^0 is the energy of the unpertubed molecules, F_α the field at the origin and μ_α, $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first hyperpolarizabilities, respectively. The total static dipole moment μ, the mean polarizability α_0 and the mean first hyperpolarizability β_0, using the x, y, z components are defined as follows,

$$\mu = \left(\mu_x{}^2 + \mu_y{}^2 + \mu_z{}^2\right)^{1/2}$$

$$\alpha = \frac{\alpha_{xx} + \alpha_{yy} + \alpha_{zz}}{3}$$

$$\alpha = 2^{-1/2}\left[\left(\alpha_{xx} - \alpha_{yy}\right)^2 + \left(\alpha_{yy} - \alpha_{zz}\right)^2 + \left(\alpha_{zz} - \alpha_{xx}\right)^2 + 6\alpha^2 xx\right]^{1/2}$$

$$\beta_0 = \left(\beta_x{}^2 + \beta_y{}^2 + \beta_z{}^2\right)^{1/2}$$

where

$$\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$$
$$\beta_y = \beta_{yyy} + \beta_{xxy} + \beta_{yzz}$$
$$\beta_z = \beta_{zzz} + \beta_{xxz} + \beta_{yyz}$$

Theoretically calculated values of first hyperpolarizability of DCB and MMB are 8.60761×10^{-30} esu and 1.07344×10^{-30} esu, respectively. The dipole moment of DCB and MMB are 3.1213 and 5.7665 Debye, respectively. One can conclude that, the title molecules are an attractive object for future studies of non-linear optical properties.

Conclusion

A complete vibrational analysis of 3, 4-dichlorobenzaldehyde and 4-methoxy-3-methyl benzaldehyde are performed based on DFT calculation at the B3LYP/6-311+G(d,p) and B3LYP/6-311++G(d,p) and their frequencies are compared. The influences of benzaldehyde group and methyl group to the vibrational frequencies of 3,4-dichlorobenzaldehyde and 4-methoxy-3-methyl benzaldehyde are discussed. Any discrepancy noted between the observed and the calculated frequencies may be due to the fact that the calculations have been actually done on a single molecule contrary to the experiment values recorded in the presence of intermolecular interactions. Furthermore, the first hyperpolarizabilities and total dipole moments of the compounds have been calculated in order to get insight into the compounds. Also HOMO and LUMO energy gap explains the eventual charge transfer interaction taking place within the molecule.

References

1. R. Narukula, D.E.G. Shukur, Y.Z. Xu, Nucleic Acids 33 Res (2005) 1767−1778.
2. D. Barcevic, S.Sosa, R.D.Loggia, A. Tubaro, B. Simonovska, A. Krana, A.Zupanicic, Journal of Ethropharm 75 (2001) 125.
3. C.A. Liberko, J. Shearer, Journal of Chemical Education 77 (2000) 1204−1205.
4. Yu. Kamenev, A.V. Kiselevich, E.I. Ostapenko, V.N.Varypaev, Russian Journal of Applied Chemistry 77 (2004)1455−1459.
5. N. Georgieva, V. Gadjeva , Tolakova Dimitrov D. Pharmazie ,60 (2005) 138.
6. R. J. Lewis Sr. Hawlay's Condensed Chemical Dictionary,(14th edn) John Wiley & Sons, (2002).
7. R.G. Parr, W. Yang, *Density Functional Theory of Atoms and Molecules*, Oxford University Press, New York, 1989.
8. F. Bruhne et al., Benzaldehyde. In Ullmann's Encyclopedia of Industrial Chemistry (7th edn). John Wiley & Sons (2005).
9. M.V.Volkenstein, M.A.Elyshevitch, B.I.Stepanov, Kolebaniya *Molecule (Molecula Vibrations)*, Vols. I/II, GITTL, Moscow, 1949 (in Russian).
10. S.J.Cyrin, *Molecular Vibrations and Mean Square Amplitudes, Eleseiver,* Amsterdam, 1968.
11. L.A. Gribov, M.J. Orille – Thomas, *Theory and Methods of Calculation of Molecular Spectra*, Wiley, Chichester, 1988.
12. P. Pulay, G. Forgarasi, X. Zhou, P.W. Taylor, *Vib. Spectro* SC.1 (1990) 159.
13. H.A. Kramers, W. Heisenberg, *J. Phys.* 31 (1925) 681.
14. J.M.L Martin, C.V. Alsenoy, *J. Phys. Chem.* 100 (1996) 6973.
15. M.J. Frisch, G.W. Trucks, H.B. Schlegal, G.E. Scuseria, M.A. Robb, J.R. Cheesman, V.G. Zakrzewski, J.A. Montgomerg, 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. Rega, P. Salvador, J.J. Dannenberg, D.K. Malich, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, A.G. Baboul, B.B. Stetanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, M. Challacombe, 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, 2009.
16. P. Pulay, G. Fogarasi, G. Pongor, J.E. Boggs, A. Vargha, *J. Am. Chem. Soc.* 105 (1983) 7037.
17. J.M.L. Martin, J.E.I. Yazal, J.P. Francis, *J. Phys. Chem.* 100 (1996) 15358.
18. G. Fogarasi, P. Pulay in During J R (Ed.), *Vibrational Spectra and Structure*, Vol. 14, Elsevier, Amsterdam, Chapter 3, pp. 1985, 125 - 219.
19. G. Rauhut, P. Pulay, *J. Phys. Chem* 99 (1995) 3093.
20. T. Shimanouchi, I. Nakagawa, J. Hiraishi and M. Ishil, *J. Mol. Spectry.*, 19, 78 (1966).
21. G.Fogarasi, X.Zhou, P.W.Taylor, P.Pulay, *J. Am. Chem. Soc.* 114 (1992) 819.
22. T.Sundius, *Vibr. Spectrosc.* 29 (2002) 89
23. A Frisch, A.B.Nielson, A.J.Holder, *GAUSSVIEW Users Manual, Gaussion Inc., Wallingford CT*, 2009.
24. W.D. Gwinn, *J. Chem. Phys.* 55, (1977) 477.
25. F.A.Cotton, *Chemical Applications of Group Theory*, Wiley/Interscience, New York, 1971.
26. P.R. Griffiths, *Chemical Infrared Fourier Transform Spectroscopy*, J. Wiley, New York, 1975.
27. A.El. Rayyes, *J.Mol. Struct.* (*Theo. Chem.*) 617 (2002) 17.
28. D.A. Kleiman phys Rev. 126(1962) 1977

29. D.N. Sathyanarayana, *Vibrational Spectroscopy - Theory and Applications,* second ed., New Age International (P) Limited Publishers, New Delhi, 2004.

30. J. Karpagam, N. Sundaraganesan, S. Sebastin, S. Monoharan, M. Kurat, *J. Raman Spectroscopy* 41(2010)53.

31. B.S. Yadav, Israt Ali, Pradeep Kumar & Preeti Yadav, Indian *j. Pure & App. Phys., 5(2007)979*

32. W. Zierkiewiez, D. Michalska, Th. Zeegors – Huyskens, *J. Phys. Chem.* A 104 (2000) 11685.

33. N. Sundaraganesan , saleem II, S. mohan, spectrochimica Acta, 59A (2003) 1113.

34. S. Gunasekaran, R. Rajkumar, Indian pure & Appl Phys. 41 (2003) 839.

35. V. Virendra Kumar, Y. Panikar, M. A. Palafox, J. K. Vats, I.Kostova, K. Lang and V. K. Rastogi, *Indian J Pure & Appl. Phys*., 48 (2010) 85.

36. M. Arivazhagan, V. Krishnakumar , India J. pure & Appl phys, 41(2003) 341.