Infrared and Raman spectral studies and evaluation of force fields for the three isomeric methoxy benzaldehydes

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Abstract · Infrared and Raman spectra of three isomeric methoxy benzaldehydes have been studied and vibrational assignments to different infrared and Raman wavenumbers have been proposed In order to check the proposed vibrational assignments, force field calculations using the Wilson's FG-matrix method were carried out It could be possible to assign all the 48 normal modes and determine consistent force fields for all the three molecules

Keywords · Force fields IR and Raman spectra, vibrational spectra

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1. Introduction

Vibrational spectra of anisole [1,2] and its derivatives have received considerable attention as the former is a representative model compound for a number of chemically and biologically interesting systems. For example, the wood constituent lignin contains units of the methoxyphenyl type [3]. Structure activity relationship of one-ring psychotomimetics depend on the number of methoxy substituents [4] and their orientation is known to be of importance for their pharmacological properties [5]. Horak *et al* [6] investigated infrared and Raman spectra of para-halogenated anisoles and Josefi *et al* [7] studied vibrational and NMR spectra of meta-halogenated anisoles. Mooney [8] reported the infrared spectra of *o*- and *p*-chloro and *o*- and *p*-bromo anisoles. Infrared spectra of *m*-fluoro [9], *p*-fluoro and *p*-chloro anisoles [10] and some nitro-anisoles [11] have also been reported. UV absorption spectra of anisole and some of its mono-halogenated derivatives were studied by Dearden and Forbes [12]. Electrical nature of the OCH₃ group was investigated using Raman spectroscopy by Venkateswarlu and Radhakrishnan [13]. Vibrational spectra of *m*- and *p*-methyl anisoles were reported

in literature [14,15]. Molecular interactions in anisidines have been investigated using dipole moments [16], electronic spectra [17] and infrared spectra and heat of dilution [18]. Similarly, vibrational spectra of CHO substituted benzenes have been extensively studied by a large number of workers (Ref. [19] and Refs. cited therein). The earlier spectroscopic studies were confined to anisoles, substituted anisoles, and substituted benzaldehydes and their substituted counter parts received little attention. Therefore, we have undertaken a systematic vibrational spectroscopic investigation of some aldehydes substituted anisoles. The present paper deals with the recording and analysis of the Raman and the infrared spectra, proposing consistent vibrational assignments and evaluation of the force fields for the three isomeric methoxy benzaldehydes (MBDs).

2. Experimental

Pure grade *o*- and *m*-isomers were purchased from Fluka, A.G. (Switzerland) and *p*-isomer was purchased from Sigma Chemical Co., (USA). All the three isomers form colourless liquids at room temperature and were used as purchased for recording the infrared spectra. However, prior to recording

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the Raman spectra, these compounds were vacuum-distilled twice to minimize the fluorescence background.

The infrared spectra of the three compounds were recorded at room temperature in pure liquid and CCl_4 solution phases at different concentrations in the region 200–4000 cm^{-1} on a Perkin Elmer-621 spectrometer by placing the liquid between two CsI plates. The spectrometer was calibrated with the spectrum of polystyrene thin film.

The Raman spectra were recorded on a Jobin Yuvon Ramanor HG.2S spectrometer. The samples were placed in a quartz cell. The *o*- and *m*-isomers were excited by the 5145 A line and the *p*-isomer with the 4880 A line of an Ar$^+$ laser with 100–300 mW power at the samples. The depolarization ratios were measured using a half wave plate. The spectrometer was calibrated with the spectra of $CHCl_3$, CCl_4 and CS_2. The accuracy of the measurements was estimated to be within ± 3 cm^{-1} and the resolution was better than 3 cm^{-1} throughout the entire range under the experimental conditions employed for recording the infrared and the Raman spectra.

3. Force field calculation

It has been argued [20] that in the anisole molecule ($C_6H_5.OCH_3$), all the atoms excepting the H atoms of CH_3 group, are in the same plane. During force field calculations, Zwarich *et al* [21] took the benzaldehyde molecule ($C_6H_5.CHO$) to be planar. To the best of authors' information, the structures of the three isomeric MBDs have not been reported so far. Therefore, in the present study, the CHO group, the O and C atoms of the OCH_3 group and one of the H atoms of the CH_3 group were taken to be in the plane of the phenyl ring. With this assumed structural model, the three isomers belong to the C_s point group and the 48 normal modes of vibration are distributed between the two species *a'* and *a"* of the C_s point group as :

   (i)   phenyl ring : 21*a'* + 9*a"*,

   (ii) OCH_3 group : 7*a'* + 5*a"*,

   (iii)   CHO group : 7*a'* + 2*a"*.

The following were the structural parameters for the OCH_3 moeity [22] used for the calculation of the *G* matrix elements : r(C–OCH_3) = 1.356 Å, r(C'–H) = 1.10 Å, r(O–CH_3) = 1.435 Å, α(C–O–C') = 118.1°, α(O–C'–H) = 109.5°, where C'denotes the carbon atoms of the OCH_3 group. The structural parameters for benzaldehyde part are same as in Ref. [21].

The vibrational problem was set up in terms of the internal coordinates and from these the symmetry coordinates were constructed assuming C_{3v} local symmetry for the CH_3 group. Here, all the planar bending internal coordinates are of β-type as used in Ref. [19]. The symmetry coordinates for

the phenyl ring and for the OCH_3 and the CHO groups were constructed as earlier [19]. It may also be noted here that each of the ring, torsional internal coordinates have been taken to be the average of the two internal coordinates, $\Delta\Phi_{CCCC}$ and $\Delta\Phi_{XCCY}$ (X, Y = H/OCH_3/CHO) and the torsional internal coordinates for the CH_3 group about the O–CH_3 bond was formed by averaging the three dihedral angle deformations and similarly, for the CHO group, by averaging all the four dihedral angle deformations.

In constructing the *F* matrix elements, the total number of force constants considered were 78, 78 and 77 for the *o*-, *m*- and *p*-isomers respectively. The starting set of force constants were transferred from the work on benzaldehyde [21,23] for benzaldehyde part and from Refs. [2,24–28] for the methoxy group. The interaction constants for which no values were available in literature were taken as zero to start with. Six force constants, namely, ν(C–OCH_3)/ν(C–CHO), α(H–C'–O)/α(H–C'–O), α(H–C'–H)/α(H–C'–H), α(C–O C')/ν(O–CH_3), ν(O–CH_3)/α(H–C'–O) and τ(C–OCH_3)/τ(C–CHO) were kept fixed with zero values due to the fact that these have either small contributions to the potential energy distributions (PEDs) or large uncertainties. After 2 3 iterations, a good fit between the observed and the calculated fundamentals have been obtained. All the force constants, their descriptions, numerical values and dispersions are given in Table 1.

4. Results and discussion

For vibrational assignments, assistance has also been taken from the vibrational assignments made for benzene derivatives containing OCH_3 [1,2,24–28] and CHO [19,21,29,30] groups. All the observed infrared and Raman wavenumbers alongwith the calculated wavenumbers, PEDs and the proposed assignments are collected in Tables 2–4. The discussion of the normal mode assignments can be divided into the following four groups :

   (i)   the phenyl ring modes,

   (ii)   the CHO group modes,

   (iii)   the O–CH_3 group modes and

   (iv)   the CH_3 group modes.

4.1. Phenyl ring modes :

Since many of the phenyl ring modes are well established only some important and controversial modes would be discussed in the following. Some of the phenyl ring modes are substituent sensitive [31]. Amongst such modes are the ring breathing mode-1, the trigonal planar ring bending mode-12, the Kekule C=C stretching mode-14 and the umbrella C–H non-planar bending mode-11.

For *m*-substituted benzenes the ring breathing mode is assigned at 1000 cm^{-1} owing to its characteristic intensity

Table 1. Valence force constants for isomeric MBDs.

# S.N and Description	@,* o-MBD		@,* m-MBD		@,* p-MBD	
Planar principal force constants						
1. ν(C–C) (R)	6.4845	0.1358	6 4850	0.3809	6.4924	0.1184
2. ν(C–OCH₃) (r_1)	5.7476	0.1841	5.7477	0.0	5.7492	0.1651
3 ν(C–CHO) (r_2)	4 6681	0 9291	4 6677	0 1181	4 6676	0 5013
4. ν(C–H) (r_i, i = 3–6)	5 0874	0.0169	5.0878	0 0330	5 0922	0 0215
5 ν(C=O) (r_s)	9.636-1	0.1238	9.6358	0.1275	9.6358	0.7173
6. ν(C'–H) (r_7)	4.1125	0 0305	4.1103	0 0511	4 1072	0 0388
7 α(C–C–C) (α)	1.4104	0.1299	1.4098	0 3264	1.4104	0.0620
8. β(C–OCH₃) (β_1)	1 7320	0.1844	1.7322	0 1061	1.7356	0.9809
9. β(C–CHO) (β_2)	1.5893	0.1259	1.5893	0.0	1.5925	0.1393
10 β(C–H) (β_i, i = 3, . 6)	1 0179	0.0165	1.0245	0 0280	1.0284	0.0193
11. β(C=O) (θ_2)	1.8699	0 0	1.8699	0 0	1.8699	0.0
12. β(C'–H) (θ_1)	1.2426	0.1258	1.2425	0.0971	1.2524	0.0644
13. α(C–O–CH₃) (θ_9)	1.2870	0.2408	1 2868	0.8925	1.2917	0 4090
14. ν(O–CH₃) (r_9)	5.2647	0.8953	5.2647	0.1258	5.2647	0 0
15 ν(C''–H) (r_i, i = 10–12)	4.6398	0 8953	4 6391	0 0314	4.6384	0 0236
16 α(O–C''–H) (θ_i, i = 3–5)	0 6727	0 2373	0.6697	0 0448	0.6726	0.0
17 α(H–C''–H) (θ_i, i = 6–8)	0.5795	0.3490	0 5790	0.0225	0.5739	0 0174
Non-planar principal force constants						
18 ϕ(C–C–C–C) (ϕ)	0.0633	0 0088	0.0603	0.0267	0 0710	0 0149
19 γ(C–OCH₃) (δ_1)	0 2061	0 0757	0 2060	0 0504	0 2172	0 2007
20 γ(C–CHO) (δ_2)	0 3170	0.0508	0.3165	0.1434	0.3188	0.3401
21 γ(C–H) (δ_i, i = 3 -6)	0 3359	0.0116	0 3360	0.0373	0 3213	0.0207
22 τ(C–CHO) (τ)	0 0090	0 0	0 0083	0 0	0.0085	0.0
23. ω(CHO) (ω)	0 4044	0 1227	0.4027	0.0657	0.4042	0.0423
24 τ(C–OCH₃) (τ_1)	0 0238	0 0015	0 0237	0.0863	0 0246	0.0
25. τ(O–CH₃) (τ_2)	0 0061	0.0060	0.0062	0.0047	0.0071	0.0
Planar interaction force constants						
26. $(RR)^o$	0 7781	0.0	0.7781	0.0	0.7781	0.0
27 $(RR)^m$	−0.3492	0.0	−0.3492	0.0	−0.3492	0.0
28 $(RR)^p$	0.2717	0 0	0.2717	0.0	0.2717	0.0
29. $(\alpha\alpha)^o$	−0.0135	0.0	−0.0135	0.0	−0.0135	0.0
30. $(R\alpha)^p$	0.4968	0.0	0.4968	0.0	0.4968	0.0
31. $(r_2\beta_3)^o$	0 0653	0.0	0.0653	0.0	0.0653	0.0
32. $r_2\beta_4 = -r_2\beta_6$	0.0582	0.0	0.0582	0.0	0.0582	0.0
33. $r_s\theta_1$	−0.3332	0.0	−0.3332	0.0	−0.3332	0.0
34. $-\beta_i\alpha_{i+1} = \beta_i\alpha_{i-1}$ (i = 3, 4.., 6)	0.0700	0.0	0.0700	0.0	0.0700	0.0
35. $R_1r_1 = R_6r_1$	0.4534	0.3376	0.4535	0.9317	0.4504	0.6917
36. $R_2r_1 = R_5r_1$	−0.0704	0.8560	−0.0705	0.1029	−0.0678	0.4976
37. $R_3r_1 = R_4r_1$	−0.1233	0.1019	−0.1231	0.1630	−0.1251	0.4559
38. $R_1r_2 = R_2r_2$	0.6738	0.0	0.6738	0.0	0.6738	0.0
39. $R_6r_2 = R_3r_2$	0 1919	0.0	0.1919	0.0	0.1919	0.0
40. $R_5r_2 = R_4r_2$	0.2352	0.0	0.2352	0.0	0.2352	0.0

D N Singh, I D Singh and R A Yadav

Table 1. *(Cont'd)*

# S.N and Description	$\langle i \rangle$.* o-MBD		$\langle i \rangle$.* m-MBD		$\langle i \rangle$.* p-MBD	
41. $R_i\beta_i = -R_{i-1}\beta_i$ $(i = 3, .6)$	-0 2853	0 0	-0.2853	0.0	-0.2853	0 0
42. $R_{i+1}\beta_i = -R_{i-2}\beta_i$ $(i = 3, . 6)$	-0 0092	0 0	-0 0092	0.0	-0.0092	0.0
43. $\beta_i, _2R_i = -\beta_{i+3}R_i$ $(i = 3, 6)$	0 0186	0.0	0 0186	0 0	0.0186	0 0
44. $r_1\theta_9$	-0 2003	0 4765	-0 2001	0.7740	-0 1989	0 5709
45. r_1r_9	-0 9246	0 5128	-0.9248	0 7069	-0.9251	0 1001
46. $r_2\theta_1$	-0 0643	0.0	-0.0643	0.0	-0 0643	0.0
47. r_ir_{i+1} $(i = 3, .6)$	0 0337	0 0	0 0337	0.0	0.0337	0 0
48. r_ir_{i+2} $(i = 3, 6)$	0.0275	0 0	0.0275	0.0	0.0275	0 0
49. r_ir_{i+3} $(i = 3, ..6)$	-0 1452	0 0	-0.1452	0 0	-0 1452	0.0
50. $\beta_1\beta_2$	-0.4380	0.9129	-0 4378	0.4728	-0.4322	0 4674
51. $\beta_i\beta_{i+1}$ $(i = 3, ...6)$	-0 0206	0.0	-0 0206	0.0	-0 0206	0 0
52. $\beta_i\beta_{i+2}$ $(i = 3, ...6)$	-0 0549	0 0	-0.0549	0 0	-0.0549	0 0
53. $\beta_i\beta_{i+3}$ $(i = 3, ..6)$	-0 0158	0 0	-0 0158	0.0	-0 0158	0 0
54. $\theta_1\theta_2$	-0.5510	0 0	-0.5510	0 0	-0.5510	0.0
55. r_ir_{i+1} $(i = 10, 11, 12)$	0.0093	0.0120	0.0074	0 0225	0 0103	0.0170
56. $\theta_3\theta_7 = \theta_3\theta_8 = \theta_4\theta_6 = \theta_4\theta_8 = \theta_5\theta_6 = \theta_5\theta_7$	0.0721	0.1260	0 0726	0 0472	0 0673	0 0431
57. $\beta_2\theta_1$	0.0049	0 0	0 0049	0 0	0 0049	0 0
58. $\beta_2\theta_2$	0.2682	0 0	0.2682	0 0	0 2682	0 0

Non-planar interaction force constants

# S.N and Description	o-MBD		m-MBD		p-MBD	
59. $\phi_i\phi_{i+1}$ $(i = 1, . 6)$	-0 0204	0.0	-0 0354	0 0	-0 0354	0 0
60. $\delta_i\delta_{i+1}$ $(i = 3, 6)$	0 0092	0.0	0.0092	0 0	0 0092	0 0
61. $\delta_i\delta_{i+2}$ $(i = 3, 6)$	-0 0213	0.0	-0.0213	0 0	-0.0213	0 0
62. $\delta_i\delta_{i+3}$ $(i = 3, ...6)$	-0.0045	0.0	-0 0045	0.0	-0 0045	0.0
63. $\delta_i\phi_i = -\delta_i\phi_{i-1}$ $(i = 3, ..6)$	-0 0204	0.0	-0 0335	0 0	-0 0335	0 0
64. $\delta_2\phi_2 = -\phi_1\delta_2$	0.0104	0.0	0.0104	0.0	0.0104	0 0
65. $\delta_2\delta_1$	0.0096	0.0	0.0096	0 0	0.0096	0 0
66. $\delta_2\delta_4 = \delta_2\delta_6$	-0 0103	0 0	-0.0103	0.0	0 0103	0 0
67. $\delta_2\delta_5$	0.0185	0.0	0 0185	0 0	–	–
68. $\delta_2\omega$	0 0359	0.0	0.0359	0.0	0 0359	0.0
69. $\phi_1\tau = \phi_2\tau$	0.0062	0 0	0.0062	0 0	0 0062	0.0
70. $\omega\phi_2 = -\phi_1\omega$	0.0137	0.0	0 0137	0.0	0 0137	0.0
71. $\phi_1\tau_1 = \phi_6\tau_1$	-0 0080	0 0480	-0.0076	0 0571	-0 0041	0.0380
72. $\tau_1\tau_2$	0.0033	0 0040	0 0039	0 0179	-0.0008	0 0

: o, m and p stand for ortho, meta and para respectively : R_i ($i = 1, 2, 3...6$) is bond $C_i - C_{i-1}$ where C1 is the carbon atom of the phenyl ring to which the OCH_3 group is attached. R_i, t_i, and t are internal coordinates from the atom C_i in a clockwise sense. C'' aldehyde group carbon C'' CH_3 group carbon.

@ : Units of force constants are as follows : mdyne/A for stretch and stretch-stretch interaction, mdyne/rad for stretch-bond interaction and mdyne A/rad² for the remaining force constants.

* : The force constants for which dispersions are zero were kept fixed.

and depolarization features in the Raman spectrum. In the present case too the Raman frequency at 996 cm⁻¹ for the m-isomer is assigned to this mode. For a number of mono-, o- and p-substituted benzenes the ring breathing mode is assigned at ~1040 and ~800 cm⁻¹ respectively [29,32,33]. In the present case, for the o-isomer there are two Raman frequencies 1044 and 786 cm⁻¹ having identical features which could be correlated to the ring breathing mode-1. However, the higher frequency is better assigned to the mode C–H in-plane bending and hence, the lower one is assigned to the mode-1. For the p-MBD the ring breathing mode is assigned at 860 cm⁻¹.

Table 2. Observed and calculated frequencies for o-MBD*.

Observed			Calculated		Proposed assignments*	Species
Raman (liquid) cm⁻¹ Rel. Int & Dep	Infrared (liquid) cm⁻¹ Rel. Int	CCl₄ Sol cm⁻¹ Rel Int	cm⁻¹	Potential energy distribution'ᶜ		
–	3100 sh	–	3105	4(96)	C–H stretch (20a)	a'
3077 (1, 42)	3075 (8)	–	3077	4(98)	C–H stretch (2)	a'
3057 (1, 25)	–	–	3052	4(100)	C–H stretch (20b)	a'
3012 (0, p)	3010 (8)	∿	3012	4(102)	C–H stretch (7b)	a'
–	2965 (8)	–	2953	15(100)	CH₃ asym stretch	a"
2947 (1, p)	2945 (9)	–	2955	15(99)	CH₃ asym stretch	a'
2847 (1, .35)	2853 (9)	2840 (7)	2847	15(99)	CH₃ sym stretch	a'
2752 (0, p)	2755 (8)	–	2755	6(99)	C–H stretch CHO group	a'
1687 (10, .29)	1700 (10)	1680 (9)	1679	5(49), 3(23), 12(21), 1(10), 11(7)	FR between 1677, C=O stretch and 2 × 856	a'
1667 (3, 29)	1650 (10)	1658 (8)				
1602 (9, 46)	1588 (9, br)	1594 (10)	1614	1(57), 2(19), 7(14), 10(6)	C=C stretch (8b)	a'
1584 (2, .38)	1570 sh	1570 sh	1566	1(70), 10(13), 7(11), 5(10), 2(5)	C=C stretch (8a)	a'
1484 (3, .36)	1485 sh	1470 (9)	1499	1(44), 10(39), 2(7), 7(5)	C=C stretch (19b)	a'
	–	–	1467	17(100)	CH₃ asym deform	a"
1463 (1, 38)	1461 (10)	1461 (9)	1465	17(98)	CH₃ asym deform	a'
1440 (1, 33)	1428 (9)	1436 (9)	1449	10(41), 1(29), 5(8), 17(6), 16(5)	C=C stretch (19a)	a'
.	.		1425	10(19), 11(18), 12(18), 1(14), 14(11), 16(10), 17(9)	CH₃ sym. deform	a'
1397 (2, .34)	1395 (10)	1398 (8)	1378	12(37), 10(22), 11(21), 1(15), 5(11)	C–H i p b CHO group	a'
1304 (1, 65)	1298 (10)	1298 sh	1313	1(41), 10(21), 16(19), 2(16), 17(15), 7(9)	C–OCH₃ stretch (7a)	a'
	1288 (10)	1280 (9)	1286	1(117), 10(16), 7(6)	C–C steretch (14)	a'
1248 (10, .17)	1236 (9)	1241 (10)	1243	10(80), 1(12)	C–C i p b. (3)	a'
1192 (6, 23)	1178 (9)	1183 (9)	1193	10(76), 1(13)	C–H i p b (9a)	a'
1163 (5, .23)	1156 (10)	1157 (9)	1163	3(26), 7(24), 10(19), 1(18), 12(11).	C–CHO stretch (13)	a'
1104 (3, 36)	1098 (9)	1098 (8)	1109	1(39), 10(28), 7(10), 16(7)	C–H i.p.b, (18a)	a'
–	.	–	1059	16(71), 1(14), 10(5)	CH₃ parallel rock	a'
–	–	.–	1040	16(97)	CH₃ perpendicular rock	a"
1044 (6, .14)	1039 (10)	1038 (10)	1026	1(64), 10(16), 7(6)	C–H i p b. (18b)	a'
1026 (1, .26)	1020 (10)	1020 (10)	1005	14(38), 1(21), 16(17), 17(12), 7(12)	O–CH₃ stretch	a'
1009 (0, .10)	–	–	1004	21(85), 18(23), 23(12)	C–H o.p.b. (5)	a"
–	–	–	992	21(58), 23(33), 18(17)	C–H o.p b. (17b)	a"
–	944 (6)	940 (5)	962	23(43), 21(50), 18(14)	CHO wagging	a"
–	856 (8)	853 (6)	866	21(85), 18(19)	C–H o p b (17a)	a"
837 (1, .44)	831 (10)	830 (9)	841	7(47), 3(18), 1(12), 12(6)	C–C–C i.p.b. (12)	a'
786 (6, .13)	790 (9)	790 (9)	810	1(27), 7(27), 2(14)	C=C stretch (1)	a'

Table 2. *(Cont'd)*

Observed			Calculated		Proposed assignments*	S p e c t e s
Raman (liquid) cm^{-1} Rel. Int & Dep.	Infrared					
	(liquid) cm^{-1} Rel Int	CCl$_4$ Sol cm^{-1} Rel Int	cm^{-1}	Potential energy distribution$^{@}$		
756 (0, dp)	758 (10)	754 (10)	750	21(91), 18(12)	C–H o.p b (11)	a"
726 (0, .63)	720 (7)	718 (6)	713	18(33),21(18), 20(14), 19(9)	C–C–C–C torsion (4)	a"
640 (1, .36)	641 (9)	643 (7)	621	7(55), 1(11), 12(6)	C–C–C i p.b (6a)	a'
583 (2, .71)	580 (7)	580 (3)	582	7(27), 13(24), 11(12), 1(8), 8(7)	C–O i p b.	a'
529 (0, ?)	526 (6)	521 (2)			436 + 92	A'
480 (1, .70)	480 (8)	480 (4)	494	20 (43), 18 (19), 19(15), 21(10)	C–C–C–C torsion (16a)	a'
436 (0, 1.0)	428 (7)	430 (2)	426	18(39), 19(29), 21(6)	C–OCH$_3$ o.p b. (10a)	a"
402 (4, .18)	400 (3)	-	420	7(33), 8(19), 9(19), 2(13), 3(11), 1(6)	C–C–C i p b (6b)	a'
–	341 (1)	–	349	11(21), 13(21), 1(13), 2(8), 3(8), 7(7)	C–O–C angle bending	a'
277 (1, .67)	275 (3)	–	272	18(24), 19(19), 25(15), 20(15), 24(9), 21(9)	C–CHO o p b (10b)	a"
...	230 (4)	–	221	18(35), 22(35) 25(10)	C–C–C–C torsion (16b)	a"
201 (1, 65)	-	–	203	9(37), 8(30), 13(21), 11(14), 7(8)	C–OCH$_3$ i p b (9b)	a"
–	–	–	164	9(30), 8(28), 13(12) 11(9)	C–CHO i p b (15)	i
166 (0, dp)	–	-	163	25(70), 19(8)	O–CH$_3$ torsion	a'
128 (0, dp)	–	–	133	22(44), 18(32), 24(5), 25(5)	C–CHO torsion	a"
–	–	–	92	24(85), 19(9), 28(8), 22(5)	C–OCH$_3$ torsion	a"

Abbreviations used . Rel. int = Relative intensity, Dep = depolarization ratio, br = broad, sh = shoulder, i p b – in-plane bend, o p.b – out-of-plane bend, sym. = symmetric, asym. = asymmetric, deform = deformation, sol. = solution FR – Fermi resonance

@ : The numbers out side the brackets are the force constants number defined in Table 1 and those within the brackets are the corresponding contributions

* . The modes corresponding to the benzene modes as given by Wilson are given within the brackets following each assignments

The modes 1 and 12 of *m*-substituted benzenes give rise to two frequencies in the neighbourhood of 1000 cm^{-1} and 750 cm^{-1}. As the ring breathing mode-1 for the *m*-isomer has already been assigned at 996 cm^{-1}, the mode-12 is assigned at the frequency 760 cm^{-1} which is in a Fermi resonance with the first overtone of the fundamental at 382 cm^{-1}. For the *p*-MBD the trigonal bending mode 12 is assigned at 720 cm^{-1}, whereas for the *o*-MBD the frequency 837 cm^{-1} is assigned to this mode.

In the present case, the NCA suggests that the C=C stretching and C–H planar bending force constants give rise to two frequencies in the region 1240–1300 cm^{-1}. For all the three isomers, the lower frequency is assigned to the C–H planar bending mode-3 and the higher one to the Kekule C–C stretching mode-14. From Tables 2–4, it is obvious that the mode 3 is a pure C–H bending mode for the *p*-isomer whereas it shows a weak and a substantial mixings with the

C–C stretching for the *o*- and *m*-isomers respectively. Similarly, the Kekule mode-14 appears to be a pure C=C stretching mode having a little mixing with the C–H planar bending mode for the *o*- and *p*-isomers. For the *m*-isomer it remains almost a pure mode having mixing with several other planar modes.

The C–H non-planar bending mode-11 (umbrella mode) is expected to appear in the regions 735–770, 770–795 and 795–820 cm^{-1} for *o*-, *m*- and *p*-substituted benzenes [34]. In the present case, this mode is assigned at the frequencies 756, 742 and 771 cm^{-1} for the *o*-, *m*- and *p*-isomers respectively. The PED for this mode indicates that this is largely a pure C–H non-planar bending mode, having a small mixing with the ring C–C–C–C torsion.

The C–OCH$_3$ stretching mode is assigned at 1200 cm^{-1} for anisole by Balfour [1] whereas Ramana Rao and co-workers [2,24,26,28] assigned this mode for the same

Table 3. Observed and calculated frequencies for m-MBD[#]

Observed			Calculated		Proposed assignments*	Species
Raman (liquid) cm⁻¹ Rel Int & Dep.	Infrared (liquid) cm⁻¹ Rel. Int	CCl₄ Sol cm⁻¹ Rel Int	cm⁻¹	Potential energy distribution[a]		
3200 (0, p)	--	--			2*1602	A'
3181 (0, p)	-	--			2*1593	A'
-	-	-	3105	4(96)	C–H stretch (20b)	a'
3080 (2, 42)	3075 (5)	-	3079	4(98)	C–H stretch (2)	a'
3040 (0, p)	·	--	3050	4(100)	C–H stretch (20a)	a'
3020 (1, p)	3013 (6)	-	3012	4(102)	C–H stretch (7a)	a'
2960 (0, dp)	2965 (7)	–	2953	15(100)	CH₃ asym stretch	a"
2945 (1, p)	2951 (7)		2955	15(99)	CH₃ asym stretch	a'
2839 (1, 35)	2845 (9)	2841 (7)	2846	15(99)	CH₃ sym stretch	a'
2740 (0, p)	2738 (6)	2741 (7)	2750	6(99)	C–H stretch CHO group	a'
1703 (10, 29)	1701 (10)	1700 (10)	1716	5(46), 12(26), 3(17), 1(11), 11(7)	FR between 1691, C=O stretch and 1041 + 650	a'
1685 (3, 29)	1681 (10)	1681 (9)				
1607 (2, 59)	·	·	1604	1(54), 2(21), 7(14), 10(18)	C=C stretch (8b)	a'
1602 (2, 44)	1599 sh	1600 sh			FR between 1597	a'
1593 (2, 44)	1586 (10)	1580 (10)	1570	1(72), 7(10), 5(8), 10(7), 8(7)	C–C stretch (8a) and 1196 + 399	
	·		1513	1(40), 10(22), 2(9), 7(8), 3(6)	C–C stretch (19b)	a'
1491 (1, 37)	1480 (10)	1480 (9)	1475	1(38), 10(38), 17(15), 5(6)	C–C stretch (19a)	a'
	--		1464	17(101)	CH₃ asym deform	a"
1462 (1, 32)	1460 (10)	1459 (10)	1464	17(85), 10(8), 1(7)	CH₃ asym deform	a'
1435 (1, 41)	1431 (9)	1430 (9)	1425	10(40), 1(17), 16(13), 17(11), 14(13)	CH₃ sym deform	a'
1389 (1, 35)	1385 (9)	1380 (9)	1370	12(54), 11(36), 5(24), 10(6), 1(5)	C–H i p b CHO group	a'
1329 (3, 16)	1329 (9)	1322 (10)	1334	1(41), 16(19), 10(15), 17(15), 2(12), 7(10)	C–OCH₃ stretch (13)	a'
1291 (2, 18)	1286 (10)	1288 (9)	1288	1(85), 10(13), 16(11), 17(9), 2(8), 11(6), 7(5) ·	C=C stretch (14)	a'
1269 (10, 12)	1266 (10)	1260 (9)	1240	10(90), 1(39)	C–H i p.b. (3)	a'
1258 (sh, p)					1041 + 209	A'
1196 (3, .21)	1188 (8)	1190 (9)	1197	10(84), 1(10)	C–H i p b (9b)	a'
1167 (1, p)	1161 (10)	1160 (10)			FR between 1161,	a'
1154 (2, 33)	1150 (10)	1148 (9)	1146	3(23), 7(24), 10(21), 1(10), 12(9), 16(8)	C–CHO stretch (7b) and 1038 + 127	
1076 (1, p)	1076 (6)	1080 (8)	1089	1(40), 10(25), 7(12)	C–H i.p.b. (18b)	a'
1040 (1, .23)	1041 (10)	1040 (10)	1050	16(73), 1(10)	CH₃ parallel rock	a'
-	-	-	1038	16(98)	CH₃ perpendicular rock	a"
-	-	-	1025	1(42), 10(15), 14(16), 7(10), 16(9), 17(6)	C–H i p.b (18a)	a'

Table 3. *(Cont'd)*

Raman (liquid) cm⁻¹ Rel. Int & Dep	Infrared (liquid) cm⁻¹ Rel Int	CCl₄ Sol cm⁻¹ Rel Int	Calculated cm⁻¹	Potential energy distribution@	Proposed assignments*	Species
–	1001 sh	1000 sh	1005	23(80), 20(8), 21(8)	CHO wagging	a''
996 (9, 35)	991 (7)	990 (6)	999	1(60), 7(15), 14(8), 3(6)	C=C stretch (1)	a'
960 (0, dp)	960 (4)	965 (4)	977	21(97), 18(30)	C–H o p b (5)	a''
935 (0, dp)	928 (8)	925 (8)	900	21(95), 18(21)	C–H o.p b (17a)	a''
909 (0, p)	–	–	909	1(22), 14(20), 7(17), 3(12), 16(9), 2(7)	O–CH₃ stretch	a'
897 (0, dp)	899 (8)	890 (8)	885	21(91), 18(21), 23(5)	C–H o p b (17b)	a''
775 (2, 15)	776 (10)	770 (10)	761	7(44), 1(18), 2(8), 3(5)	FR between 760, C–C–C i p b (12) and 2*382	a'
742 (5, 08)	735 (8)	740 (8)				
759 (sh, dp)	759 (6)	750 (7)	756	21(36), 18(22), 19(6), 23(5)	C–C–C–C torsion (4)	a''
·	–	–	742	21(83), 18(19)	C–H o.p.b. (11)	a''
650 (2, .23)	650 (5)	650 (6)	620	7(45), 13(14), 1(9), 11(9)	C=O i p b	a'
–	634 (8)	630 (7)			420 + 209	A''
557 (2, 53)	552 (5)	550 (5)	580	7(43), 13(14), 1(13), 1(8)	C–C–C i p b (6a)	a'
455 (3, 44)	455 (2)	458 (1)	469	20(40), 18(27), 21(7)	FR between 452, C–C–C–C torsion (16a) and 233 + 207	a''
449 (4, .43)						
421 (1, dp)	420 (4)	420 (4)	436	19(48), 18(29), 20(7)	C–OCH₃ o p b (10a)	a''
–	–	· –	399	7(22), 9(22), 3(21), 11(19), 1(9), 8(7)	C–C–C i p b (6a)	a'
382 (2, 19)	–	–	386	7(20), 8(21), 2(20), 13(15), 14(12), 1(11)	C–O–C angle bending	a'
277 (0, 31)	270 (3)	··	277	18(32), 25(13), 22(13), 19(13), 21(11)	C–C–C–C torsion (16b)	a''
233 (0, .30)	250 (3)	–	241	18(22), 20(18), 22(14), 4(14), 25(11), 21(10)	C–CHO o p b (10b)	a''
209 (1, ?)	–	·	207	8(42), 13(32), 9(28)	C–OCH₃ i.p b (15)	a'
167 (1, .77)	–	–	165	25(74), 19(8)	O–CH₃ torsion	a''
·	–	–	158	9(39), 8(13), 11(9), 12(8)	C–CHO i p.b (9a)	a'
127 (1, .87)	–	–	135	22(64), 18(13), 20(9), 24(7)	C–CHO torsion	a''
–	·	–	84	24(84), 19(9), 25(7), 21(6), 20(5)	C–OCH₃ torsion	a''

#, *, @ : Symbols defined in Table 2

molecule in the region 1250–1325 cm⁻¹. In the present case this mode could be assigned at the frequencies 1304, 1329 and 1320 cm⁻¹ for *o*-, *m*- and *p*-isomers respectively. For all the three isomers it is a strongly mixed mode having mixing with the ring C–C stretching, phenyl C–H plane bending, ring angle bending and the CH₃ deformation and rocking modes.

The C–CHO stretching mode falls in the region where other planar modes are also expected to appear. Hence, this mode is likely to have strong interaction with the other

modes. In the present case this mode is assigned at the frequencies 1163 and 1164 cm⁻¹ for the *o*- and *p*-isomers respectively. For the *m*-MBD there are two frequencies 1167 and 1154 cm⁻¹ in the Raman and 1160 and 1148 cm⁻¹ in the IR spectra having identical features. These are explained in terms of Fermi resonance between the C–CHO stretching fundamental and combination band 1038 (a'', cal.) + 127 (a''). The PED for this mode suggests that this mode indeed appears to interact strongly with several planar modes for all the three isomers.

Table 4. Observed and calculated frequencies for p-MBD#.

Observed Raman (liquid) cm⁻¹ Rel. Int. & Dep.	Observed Infrared (liquid) cm⁻¹ Rel. Int.	Observed Infrared CCl₄ Sol cm⁻¹ Rel. Int	Calculated cm⁻¹	Calculated Potential energy distribution@	Proposed assignments*	Species
3202 (0, p)					2*1603	A'
3160 (0, ?)					2*1581	A'
3104 (0, .16)	–	–	3103	4(96)	C–H stretch (20a)	a'
3082 (2, .19)	–	–	3082	4(98)	C–H stretch (2)	a'
3057 (1, .30)	–	–	3054	4(100)	C–H stretch (20b)	a'
3017 (1, .29)	–	–	3014	4(102)	C–H stretch (7b)	a'
2961 (0, dp)	2956 (6)	–	2952	15(100)	CH₃ asym stretch	a"
2944 (7, .0)	2945 (6)		2954	15(99)	CH₃ asym. stretch	a'
2915 (sh, p)					1699 + 1220	A'
2847 (10, .09)	2829 (7)	2830 (9)	2847	15(99)	CH₃ sym. stretch	a'
2744 (4, .20)	2732 (6)	2731 (8)	2753	6(99)	C–H stretch CHO group	a'
1699 (4, 32)	1693 (8)	1695 (7)	1714	5(48), 12(27), 3(18), 11(8), 1(7)	FR between 1696, C=O stretch and 2 × 860	a'
1683 (7, 25)	1680 (8)	1680 (0)				
1603 (10, .30)	1600 (9)	1600 (10)	1590	1(45), 2(27), 10(18), 7(14), 14(7)	C=C stretch (8a)	a'
1580 (4, .27)	1577 (8)	1570 (8)	1566	1(83), 7(12), 10(8), 8(6)	C=C stretch (8b)	a'
1515 (0, 60)	1510 (8)	–	1524	1(48), 10(38), 5(8), 7(8)	C=C stretch (19a)	a'
–	–	–	1463	17(79), 1(11)	CH₃ asym deform	a'
1464 (0, 43)	1461 (6)	–	1460	17(100)	CH₃ asym deform	a"
1446 (sh, p)	1442 (6)	–	1444	1(30), 17(29), 10(15), 14(12), 16(9)	CH₃ sym deform.	a'
1431 (2, .26)	1426 (6)	–	1432	1(33), 10(29), 16(9), 17(8), 14(7), 5(6)	C=C stretch (19b)	a'
1395 (0, .26)	1392 (5)	1390 (5)	1369	12(55), 11(40), 5(24)	C–H i p b. CHO group	a'
1320 (1, 14)	1316 (7)	1318 (8)	1319	16(25), 17(20), 10(20), 2(19), 1(16), 7(12)	C–OCH₃ stretch (7a)	a'
1307 (sh, p)	1302 (6)	1305 (8)	1289	1(121), 10(33)	C=C steretch (14)	a'
1264 (2, .14)	1260 (8)	1265 (8)	1270	10(100)	C–H i.p.b (3)	a'
1220 (3, 25)	1216 (7)	1215 (6)	1213	10(60), 1(22)	C–H i p.b. (9a)	a'
1184 (1, .12)	1182 (6)	1180 (4)			839 + 335; 945 + 240	A'
1164 (9, .07)	1161 (8)	1160 (8)	1167	7(28), 3(26), 1(21), 10(14), 12(10)	C–CHO stretch (13)	a'
1113 (0, .40)	–	–	1119	10(40), 1(37), 7(6)	C–H i.p.b. (18b)	a'
–	–	–	1057	16(77), 1(8)	CH₃ parallel rock	a'
–	–	–	1040	16(97)	CH₃ perpendicular rock	a"
1029 (0, .45)	1025 (7)	1020 (8)	1017	1(44), 7(28), 10(17)	C–H i.p.b. (18a)	a'
1009 (0, .50)	–	–	1006	23(81), 21(7), 20(7)	CHO wagging	a"
–	–	–	995	14(38), 1(32), 16(16), 17(10)	O–CH₃ stretch	a'
–	–	–	971	21(89), 18(33), 18(17)	C–H o.p.b. (17a)	a"
–	945 (4)	960 (6)	947	21(83), 18(35)	C–H o.p.b. (5)	a"
860 (2, .02)	857 (7)	858 (5)	870	1(43), 7(18), 3(6), 14(5)	C=C stretch (1)	a'

Table 4. *(Cont'd.)*

| Observed | | | Calculated | | Proposed assignments* | S p e c i e s |
| Raman (liquid) cm⁻¹ Rel. Int & Dep. | Infrared | | | | | |
	(liquid) cm⁻¹ Rel. Int	CCl₄ Sol. cm⁻¹ Rel. Int	cm⁻¹	Potential energy distribution$^{@}$		
839 (1, 02)	833 (7)	830 (5)	820	21(90), 18(28)	C–H o.p.b. (17b)	a"
771 (0, .18)	-	-	768	21(85), 18(27)	C–H o p.b. (11)	a"
762 (0, .14)	–	–	762	21(32), 18(21), 20(10), 19(8)	C–C–C–C torsion (4)	a"
720 (0, 50)	716 (3)	720 (6)	718	7(21), 1(18), 3(16), 2(13), 13(6), 12(5)	C–C–C i p b. (12)	a'
[646 (2, 28) 635 (2, .50)	653 (5) –	650 (6) –	670	7(84)]	FR between 640, C–C–C i.p.b. (6b) and 2*335	a'
611 (1, .11)	607 (5)	608 (8)	579	7(28), 11(17), 1(10), 9(8), 8(8), 13(5)	C=O i.p bend	a'
515 (0; p)	514 (5)				335 + 169	A'
491 (0, 45)	--	480 (7)	481	18(36), 21(17)	C–C–C –C torsion (16b)	a"
–	–	–	452	19(32), 20(36), 18(16)	C–OCH₃ o p.b. (10b)	a"
[424 (0, ?) 397 (0, .23)	- 392 (5)	430 (3) 390 (4)	422	13(22), 11(18), 1(15), 3(9), 2(8), 8(8), 7(6) 7(6)]	FR between α(C–O–C) and 240 + 169 cm⁻¹	a'
373 (1, .14)	-	--	359	7(31), 8(23), 9(19), 2(11), 3(10), 1(6), 11(5), 14(5)	C–C–C i p b. (6a)	a'
335 (0, 66)	-	--	330	18(24), 19(28), 20(21), 21(10), 22(5), 25(13), 24(7)	C–CHO o p.b. (10a)	a"
273 (1, .16)	283 (4)				2*133, lattice mode	A'
–	248 (4) ·ₜ	240 (3)	226	22(28), 25(24), 18(22), 21(8)	C–C–C–C torsion (16a)	a"
191 (1, 58)	–	–	200	9(34), 8(32), 13(23), 11(8), 7(8), 12(5)	C–OCH₃ i.p b. (9b)	a'
–	–	–	168	9(31), 8(19), 13(15), 1(9), 11(6), 12(6)	C–CHO i.p.b (15)	a'
–	–	–	169	25(54), 22(22), 19(12), 18(8)	O–CH₃ torsion	a"
			133	24(40), 22(28), 18(8), 20(8), 25(7)	C–CHO torsion	a"
--	–	78	24(48), 18(13), 22(13), 21(7), 19(6), 20(5)	C OCH₃ torsion	a"	

*, #, @ · Symbols defined in Table 2.

4.2 CHO group modes

The C–H stretching mode is assigned at the frequencies 2752, 2740 and 2744 cm⁻¹ for the *o-*, *m-* and *p-*isomers respectively. In the C=O stretching region two frequencies have been observed for all the three isomers. Appearance of the doublet in each case is explained in terms of the Fermi resonance between the C=O stretching fundamental and a suitable combination/overtone frequencies. The C–H planar bending mode of the CHO group is observed near 1380 cm⁻¹ for benzaldehyde and its derivatives [19,21,29,30].

In the present case, it is assigned in a very narrow region 1380–1400 cm⁻¹.

The C=O in-plane bending mode is assigned in the region 600–620 cm⁻¹ for benzaldehyde and at 587 cm⁻¹ for benzaldehyde-d₆ [12]. In the present case, the frequencies 583, 650 and 611 cm⁻¹ are assigned to this mode in light of the PEDs. Out of the two CHO non-planar modes, one corresponds to the wagging mode and has a ₜmagnitude near 1000 cm⁻¹. The present force field calculations place this mode at 962, 1001 and 1009 cm⁻¹ for the *o-*, *m-* and

p-isomers respectively. Zwarich *et al* [21] and Compagnaro and Wood [35] have assigned the CHO torsional mode near 135 cm⁻¹. In the present case, the frequencies 128 and 127 cm⁻¹ observed for the *o*- and *m*-isomers respectively are assigned to the CHO torsional mode. For the *p*-isomer, no frequency is observed near 130 cm⁻¹. The force field calculation places this mode at 133 cm⁻¹ for the *p*-isomer. It is to be noted here that except the C–H stretching mode all the remaining five internal modes of the CHO group are coupled modes. However, it is to be noted that the C=O stretching and the C–H (CHO) planar bending modes are localized group modes as these two involve force constants of the CHO group only, except that the C=O stretching mode has very small contribution from the ring C=C stretching force constant. The C–H non-planar wagging mode also appears to be a pure mode for the *m*- and *p*-isomers whereas for the *o*-isomer it shows strong mixing with the ring C–H non-planar bending and the C–C–C–C torsional modes. The CHO torsional mode, is mixed with the ring C–C–C–C torsion for the *o*- and *p*-isomers whereas for the *p*-isomer this is mixed with the OCH₃ torsional mode.

4 3 O–CH₃ group modes :

The O–CH₃ mode is assigned at ~1040 cm⁻¹ for anisole [1] and in the region 1000–1100 cm⁻¹ for anisole and its derivatives [24,26,28]. This mode is assigned at 1026, 909 and 995 cm⁻¹ for the *o*-, *m*- and *p*-MBDs respectively. The present NCA suggests that this mode is strongly mixed with the CH₃ deformation and the ring C–C stretching modes for all the three isomers. Difference in magnitudes of this mode for the *o*-, *m*- and *p*-MBDs suggests that this mode is influenced by the substituent.

The C–O–CH₃ angle bending mode is assigned near 300 cm⁻¹ for anisole by Owen and Hester [20] and at 421 cm⁻¹ for *p*-MBD by Compagnaro and Wood [35]. Ramana Rao *et al* [2,24,26,28] have proposed assignment for this mode in the region 300–670 cm⁻¹ for anisole and its derivatives. As this mode lies in the region of the ring planar C–C–C angle bending modes 6 (*a,b*), a strong mixing amongst these two modes and other planar modes is expected. The C–O–CH₃ angle bending mode is assigned at 341, 382 and 430 cm⁻¹ for the *o*-, *m*- and *p*-isomers respectively. The PED for this mode suggests a strong mixing of this mode with other planar modes (Tables 2–4). The torsional mode of the OCH₃ group was observed for anisole at 100 cm⁻¹ by some workers [30,31]. Balfour [1] assigned this mode at 81.5 cm⁻¹ and Lakshmaiah and Ramana Rao [24] calculated this mode to be at 58 cm⁻¹ for anisole. This mode is expected to lie beyond the investigated range presently. The calculated frequencies for this mode for the three isomers *o*-, *m*- and *p*- are respectively 92, 84 and 78 cm⁻¹.

4.4. CH₃ group modes :

For the OCH₃ group compounds, the mode v_s appears in the range 2825–2870 cm⁻¹, lower in magnitude compared to its value in CH₃ compounds (2860–2935 cm⁻¹), whereas the two v_{as} modes for both the types of compounds lie in the same region 2925–2985 cm⁻¹. The PEDs for these modes suggest that these are pure CH₃ stretching modes.

The deformation mode δ_s of the CH₃ group lies in the region 1285–1370 cm⁻¹ in OCH₃ compounds [31]. However, the present force field calculations place this mode at 1440 cm⁻¹ for all the three isomers. It could be seen from Tables 2–4 that this is a strongly mixed mode for the three isomers. The two δ_{as} modes for the OCH₃ compounds also lie in the region of δ_{as} of the CH₃ compounds (1410–1470 cm⁻¹) and are substituent independent modes. In the present case, it could be seen from the PEDs that the two δ_{as} modes are pure CH₃ group modes. The two rocking modes $a' + a''$ of the CH₃ group lie in the range 990–1070 cm⁻¹ for OCH₃ and CH₃ compounds and the present assignments for three modes are also in the above region. It is interesting to note that these are also pure CH₃ group modes.

The CH₃ torsional mode could be assigned at ~165 cm⁻¹ in all the three cases. It is to be noted here that this is a pure mode for the *o*- and *m*-isomers whereas it shows a strong mixing with the CHO torsional mode and a weak mixing with other non-planar modes for the *p*-isomer.

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