

The infrared and Raman spectra of 2,4- and 2,5-dimethylbenzaldehydes

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Abstract. The vibrational frequencies of 2,4- and 2,5-dimethylbenzaldehydes have been reported from the study of IR absorption and Raman spectra of these molecules recorded in liquid phase. The probable assignments for all the frequencies are presented in terms of the fundamentals, overtones or combinations.

Keywords. Infrared spectrum; Raman spectrum; vibrational frequencies; dimethylbenzaldehydes.

1. Introduction

As a part of the general programme to obtain the vibrational frequencies pertaining to the (a) ground electronic state from the IR absorption, Raman and emission spectra and (b) excited electronic state from the near UV absorption spectra of polysubstituted benzenes and also with a view to apply them to the study of molecular force fields, mean square amplitudes of vibration, centrifugal distortion constants etc., the present paper deals with the recording of the IR and Raman spectra of 2,4- and 2,5-dimethylbenzaldehydes and the identification of the observed frequencies, in the ground electronic state, which have not been investigated so far.

2. Experimental

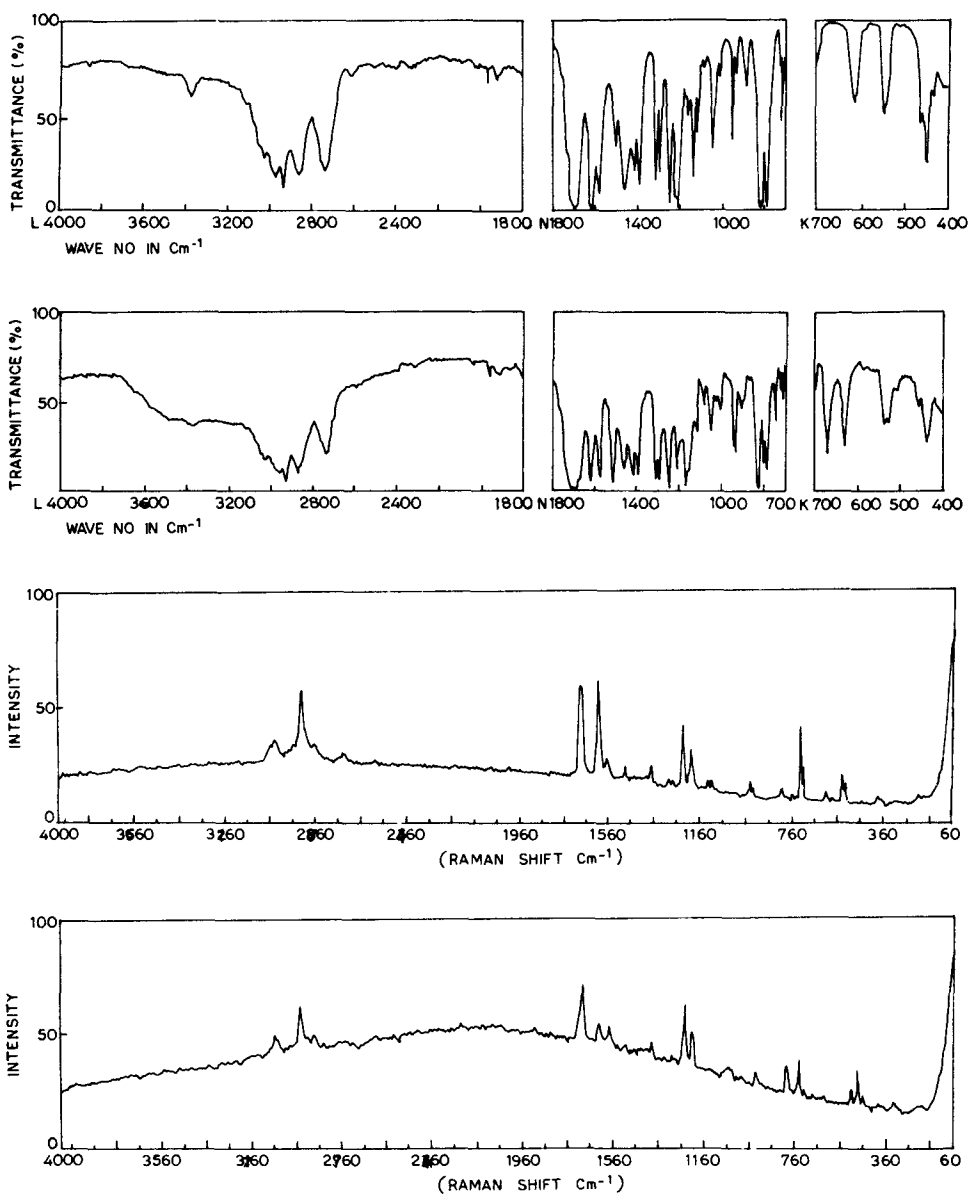
The IR absorption spectra of both the molecules are recorded in the liquid phase on a UR 10 spectrophotometer in the region $400\text{--}4000\text{ cm}^{-1}$. The Raman spectra are recorded on a Cary 82 spectrophotometer with Argon-Ion laser source. The traces of these spectra are shown in figures 1 to 4.

3. Analysis

Both the molecules belong to 1,2,4-trisubstituted benzene class on the basis of Varsányi's classification of the molecules (Varsányi 1974).

These molecules are expected to give rise to 30 fundamental vibrations characteristic of the phenyl ring and 24 fundamental vibrations characteristic of the internal vibrations of the substituent groups.

The identification of the 30 phenyl ring vibrations is based on (i) the procedure adopted by Varsányi (1974) in classifying the molecules and the identification of the



Figures 1-4. 1, 2. IR spectrum of 1. 2,4-dimethyl benzaldehyde 2. 2,5-dimethyl benzaldehyde
3, 4. Raman spectrum of 3. 2,4-dimethyl benzaldehyde 4. 2,5-dimethyl benzaldehyde.

fundamental modes of vibrations in such substituted benzenes together with the expected ranges for the modes of vibrations, (ii) a comparison of the spectra of benzaldehyde, isomers of methyl benzaldehyde, and other related molecules investigated by earlier workers [Padhye and Viladkar (1960); Dwivedi (1968); Singh and Singh (1968, 1978); Srivastava *et al* (1968, 1972); Green *et al* (1971); Green and Harrison (1976), Lal *et al* (1973); Varsányi (1974), Varsányi *et al* (1979); Sanyal *et al* (1981)], (iii) a

Table 1. Observed frequencies and their proposed assignments.

2,4-dimethyl bzh		2,5-dimethyl bzh			Wilson's mode (5)	Proposed assignments (6)
IR Freq. (cm ⁻¹) (1)	Raman Freq. (cm ⁻¹) (2)	IR Freq. (cm ⁻¹) (3)	Raman Freq. (cm ⁻¹) (4)			
3376 w					441 + 2930	
3116 vw					1500 + 1615	
3043 sh	3057 w	3050 sh	3056 vw	2	C-H stretching	
3028 w	3038 w, p	3030 vw	3041 vw	20 b	C-H stretching	
2968 sh		2969 m			C-H asym. stretching in CH ₃ group	
2954 sh					C-H asym. stretching in CH ₃ group	
2930 ms	2919 vs, p	2935 s	2937 s		C-H sym. stretching in CH ₃ group	
2869 br	2865 w	2874 m	2875 m		2 × C-H asym. def.	
2738 s	2738 w	2735 br			C-H stretching in CHO group	
		2183 vw			939 + 1248	
		2115 vw			826 + 1291	
1961 vw					717 + 1246	
1913 vw					791 + 1117	
		1913 vw			826 + 1083	
		1800 vw			905 × 2	
1700 vs	1693 vs	1700 vs	1695 s		C=O stretching	
		1687 sh			783 + 905	
1615 vs	1609 vs, dp	1617 vs	1625 m	8 b	C-C stretching	
1577 vs	1571 w, p	1574 vs	1579 m	8 a	C-C stretching	
1500 ms	1489 w, p	1508 vs	1506 vw	19 b	C-C stretching	
1465 s		1461 s			CH ₃ asym. def.	
1409 ms	1400 vw	1417 s		19 a	C-C stretching	
1390 vs	1377 w	1391 vs	1391 vw		CH ₃ sym. def.	
1310 s	1300 s	1308 vs	1302 w		C-H i.p. bending (CHO group)	
1291 s	1281 vw	1291 s		14	C-C stretching	
1246 vs	1235 s, p	1248 vs	1248 vs	7 a	C-CH ₃ stretching	
1209 vs	1197 m	1209 s	1217 s	13	C-CHO stretching	
1175 vw					456 + 717	
		1165 vw	1145 vw	18 a	C-H i.p. bending	
1161 vw					441 + 717	
1138 vs	1127 w, p			18 a	C-H i.p. bending	
1117 m	1110 w, p	1117 mw	1118 vw	18 b	C-H i.p. bending	
1083 vw					545 × 2	
		1083 vw			535 × 2	
1045 s		1048 m	1050 vw		CH ₃ rocking	
1008 vw		1005 w	1002 vw		CH ₃ rocking	
950 ms	943 w, p			7 b	C-CH ₃ stretching	
938 vw	931 vs, dp	939 s	941 w	17 b	C-H o.p. bending	
		905 w		7 b	C-CH ₃ stretching	
888 w		869 vw		5	C-H o.p. bending	
817 s		826 vs		11	C-H o.p. bending	
800 sh	802 w, p	800 ms	802 w		C=O i.p. bending	
791 vs	785 vs	783 vs		12	C-C-C i.p. bending	
717 m	722 ms	743 m	745 s	1	ring breathing	
		718 vw	715 vw		333 + 393	
704 sh	712 m	709 w	710 vw	4	C-C-C o.p. bending	
		672 s	641 vw		C=O o.p. bending	
613 w	610 vw	630 s	595 vw	16 a	C-C-C o.p. bending	

Contd

Table 1. (Continued)

2,4-dimethyl bzh		2,5-dimethyl bzh			
IR Freq. (cm ⁻¹) (1)	Raman Freq. (cm ⁻¹) (2)	IR Freq. (cm ⁻¹) (3)	Raman Freq. (cm ⁻¹) (4)	Wilson's mode (5)	Proposed assignments (6)
545 m	537 w	535 w	517 w	6 a	C-C-C i.p. bending
456 m	452 vw	508 vw	491 m	6 b	C-C-C i.p. bending
441 s		458 w	468 w	16 b	C-C-C o.p. bending
425 vw	425 vw	437 ms		9 b	C-CHO i.p. bending
	383 vw		393 vw	10 a	C-CH ₃ o.p. bending
			333 w	9 a	C-CH ₃ i.p. bending
	210 vw		210 vw	10 b	C-CHO o.p. bending

bzh = benzaldehyde, v = very, s = strong, m = medium, w = weak, sh = shoulder, br = broad, p = polarized, dp = depolarized, sym = symmetric, asym = asymmetric, def = deformation, i.p = in-plane, o.p = out-of-plane.

general comparison of the frequencies identified by Green *et al* (1971) in the 1,2,4-trisubstituted benzenes, and also (iv) taking care to see that overlaps of the regions expected of different modes of vibrations are properly explained. The frequencies together with their visual intensities and modes thus identified are shown in table 1.

Regarding the 24 vibrational frequencies characteristic of the substituents, one expects 9 vibrations for a methyl group and 6 vibrations for the aldehyde group. As these internal frequencies are not expected to show any marked variations, in the substituted benzenes having these substituents, these internal frequencies could be identified with less ambiguity. In the present investigation seven internal frequencies—two asymmetric stretching, one symmetric stretching, one asymmetric deformation, one symmetric deformation and two rocking modes—due to methyl group, and five internal frequencies—C=O stretching, C=O in-plane-bending, C=O out-of-plane bending, C-H stretching and C-H in-plane bending—due to the aldehyde group could be identified.

The assignments, are well in agreement with those made in substituted toluenes (Singh and Singh 1968), xylenes (Varsányi 1974) and benzaldehydes (Padhye and Viladkar 1960; Varsányi 1974) and are shown in table 1.

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