

## **Laser Raman, infrared and far infrared spectra of 3,4,5-trimethoxybenzaldehyde**

Shabbir Ahmad and P K Verma

Department of Physics, Aligarh Muslim University, Aligarh-202 002, India

Received 9 March 1989, accepted 20 June 1989

**Abstract:** The infrared, far infrared and Laser Raman spectra are recorded in the region  $4000-200\text{ cm}^{-1}$ ,  $500-50\text{ cm}^{-1}$  and  $4000-100\text{ cm}^{-1}$  respectively. The vibrational analysis is carried out and assignments of the bands are made in terms of fundamental, combination and difference frequencies.

**Keywords:** Raman spectra, infrared spectra, far infrared spectra, 3,4,5-trimethoxybenzaldehyde, assignments.

**PACS Nos :** 33.10, 33.20.

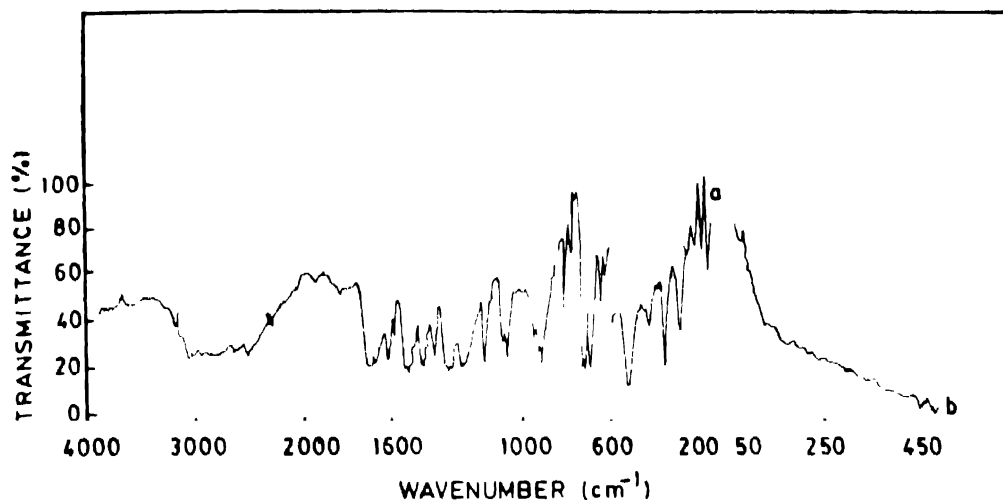
### **1. Introduction**

The vibrational spectra of benzaldehyde, monosubstituted benzaldehydes and disubstituted benzaldehydes have been extensively investigated by many earlier workers (Garg 1954, Scrocco and Liberti 1954, Heinert and Martell 1959, Padhey and Viladker 1960, Singh *et al* 1967, Dwivedi 1968, Singh and Singh 1968, Srivastava *et al* 1968, 1969 and 1972, Singh and Sanyal 1972, Lal *et al* 1973 Green and Harrison 1976, Singh and Singh 1978, Sanyal *et al* 1981, Tariq *et al* 1982, Yadav *et al* 1982, Shashidhar *et al* 1984, Venkoji 1984, 1986). Isomeric monomethoxybenzaldehyde were reported by only few workers (Purvis 1914, Morton and Stubbs 1940, Dwivedi 1968 and Kahovec and Kohlrausch 1937). Singh and Singh (1978) have reported the infrared spectra of isomeric dimethoxybenzaldehydes. The infrared and Raman spectra of 3,4,5-trimethoxybenzaldehyde (3,4,5-TMB) were reported by Gupta *et al* (1988). But only thirteen fundamental vibrations have been observed. In the present investigation laser Raman, infrared and Fourier's transform far infrared spectra of 3,4,5-TMB are recorded and forty four fundamentals are reported. Rest of the bands are assigned in terms of combinational and difference frequencies. The depolarisation ratio of Raman bands are measured which ascertain the symmetry of the vibrations.

### **2. Experimental**

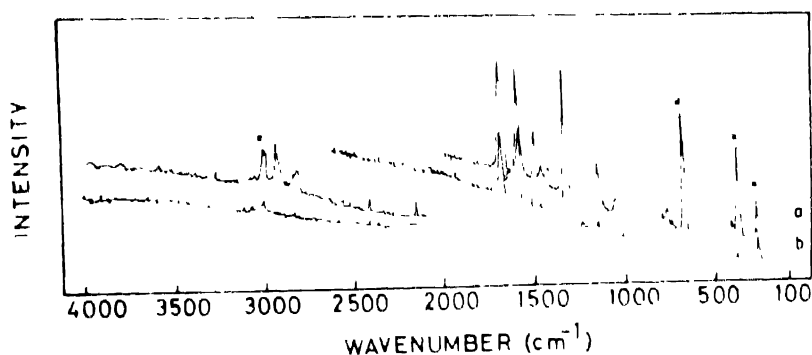
3,4,5-Trimethoxybenzaldehyde was obtained in pure solid form from M/S K-Light Labs and used without further purification. The infrared spectrum was recorded

in the region  $200-4000\text{ cm}^{-1}$  on PE-983 spectrophotometer using KBr pellet technique. The FT far infrared spectrum was recorded in the region  $50-500\text{ cm}^{-1}$  on Polytech FIR 30 spectrophotometer. The polarized and depolarized Raman



**Figure 1.** Infrared and far infrared spectra of 3,4,5-trimethoxybenzaldehyde: (a) infrared, (b) far infrared.

spectra were recorded, in  $\text{CHCl}_3$  solution, in the region  $100-4000\text{ cm}^{-1}$ , on Cary-82 Laser Raman spectrometer using  $5145\text{ \AA}$  line of Argon-ion laser as the



**Figure 2.** Raman spectra of 3,4,5-trimethoxybenzaldehyde: (a) parallel and (b) perpendicular polarization.  
\*Raman band of solvent.

source of excitation. The bands observed at  $265$ ,  $370$ ,  $670$  and  $3071\text{ cm}^{-1}$  are due to  $\text{CHCl}_3$ . The traces of infrared, far infrared and Raman spectra are shown in Figures 1-2.

### 3. Results and discussion

The molecule under present investigation is tetrasubstituted benzene. If we assume each of the substituent groups as a single mass point, it may belong to  $C_s$  point group. There will be only two types of vibrations that are  $a'$  (planar) and  $a''$  (non-planar). For analysis of the spectra, particularly for assigning the fundamentals to different modes of vibration, assistance are taken from the studies made in the similar molecules by earlier workers and the depolarization ratio of Raman bands. Observed frequencies and probable assignments for 3,4,5-TMB are presented in Table 1.

#### 3.1. $C-X$ ( $X$ =substituent) stretching and bending vibration :

Earlier reports on substituted benzaldehydes (Padhey and Viladker 1960, Garg 1954, Dwivedi 1968, Singh and Singh 1978) show that  $C-CHO$  stretching frequency, which generally gives rise to strong band, appears at  $1175\text{ cm}^{-1}$  in 3,4,5-TMB. Out of three expected  $C-OCH_3$  stretching vibrations, only two at  $928$  and  $944\text{ cm}^{-1}$  are observed in 3,4,5-TMB. These assignments are based on the studies made by Syam Sunder (1986) in 3,5-dimethoxyphenol. A very strong band appears at  $525\text{ cm}^{-1}$  in the infrared spectrum of 3,4,5-TMB which may be assigned to  $C-OCH_3$  in-plane bending vibration. This frequency was identified at  $520$  and  $425\text{ cm}^{-1}$  in 3,4-DMB and 2,3-DMB by Singh and Singh (1978). A review of the earlier studies on substituted benzaldehydes (Venkoji 1986, Srivastava *et al* 1968 and Tariq *et al* 1982) shows that the frequency at  $445\text{ cm}^{-1}$  appearing in the infrared and far infrared corresponds to  $C-CHO$  planar bending vibration and the frequency at  $240\text{ cm}^{-1}$  to  $C-CHO$  out-of-plane-bending vibration.

#### 3.2. Internal vibration of substituent groups :

$C=O$  stretching vibration gives rise to a strong absorption in the region  $1680-1815\text{ cm}^{-1}$ . The study of Morton and Stubbs (1940) shows that this frequency remain nearly the same on substitution of phenyl ring in place of hydrogen atom in formaldehyde. A review of earlier studies (Srivastava *et al* 1968, Sanyal *et al* 1981, Singh and Singh 1978 and Venkoji 1986) shows that the bands observed at  $1685\text{ cm}^{-1}$  in 3,4,5-TMB may be assigned to  $C-O$  stretching vibration. The  $C-H$  stretching mode of vibration in aldehyde group is expected in the region  $2730-2870\text{ cm}^{-1}$ . The weak band observed at  $2738\text{ cm}^{-1}$  is assigned to this vibration in 3,4,5-TMB. The strong band at  $620\text{ cm}^{-1}$  may be assigned to  $C=O$  out-of-plane bending vibration. Venkoji (1986) has identified this band at  $625\text{ cm}^{-1}$  in disubstituted benzaldehyde.

One  $CH_3$  asymmetric stretching vibration is assigned to the band observed at  $2990\text{ cm}^{-1}$  in the molecule presently investigated. The bands observed at  $2830$  and  $2940\text{ cm}^{-1}$  are assigned to  $CH_3$  symmetric stretching vibration.  $CH_3$

**Table 1.** Observed vibration frequencies (in  $\text{cm}^{-1}$ ) and their probable assignment for 3,4,5-trimethoxybenzaldehyde

IR Frequencies ( $\text{cm}^{-1}$ )	Laser Raman frequencies ( $\text{cm}^{-1}$ )	Assignment
—	3280 w	$A''$ 3062+220
3078 ms	—	$a'$ C-H stretching
3062 m	3062 m, p	$a'$ C-H stretching
2990 w	—	$a''$ $\text{CH}_2$ asymmetric stretching
2940 w	2940 s, p	$a'$ $\text{CH}_2$ symmetric stretching
2830 m	2832 ms, p	$a'$ $\text{CH}_2$ symmetric stretching
2738 w	2738 w, p	$a'$ C-H stretching in CHO group
2660 w	2660 m	$A'$ 1620+1040
2610 w	—	$A'$ 1680+928
2520 w	—	$A'$ 1578+944
2500 w	—	$A'$ 1578+928
2440 w	—	$A'$ 1402+1040
2310 m	—	$A''$ 1620+692
2320 m	—	$A'$ 1680+640
2290 w	—	$A'$ 1515+772
2270 w	—	$A''$ 1578+692
2258 w	—	$a''$ 1343+915
2210 w	—	$A''$ 1515+692
2180 w	—	$A'$ 1680+495
—	2155 m, p	$A'$ 1456+706
2115 w	—	$A'$ 1620+495
2075 w	—	$A'$ 1578+495
1955 w	—	$A''$ 1680+272
1932 w	1932 m, p	$A'$ 1410+525
1875 vw	—	$A'$ 1578+297
1855 sh	—	$A''$ 1578+272
1840 w	—	$A''$ 1620+220
1820 w	—	$A'$ 1295+525
1810 w	—	$A'$ 1515+297
1795 w	—	$A''$ 1578+220
1700 sh	—	$A'$ 1175+525
1685 b	1685 vs, p	$a'$ C=O stretching
1674 w	—	$A''$ 1402+272
1648 vw	1648 w	$A''$ 1402+240
1620 s	1620 w	$a'$ C-C stretching
1578 s	1580 vs, p	$a'$ C-C stretching
1550 sh	—	$A''$ 915+640
1535 w	—	$A''$ 1295+240

Table 1 (Contd.)

IR Frequen- cies (cm <sup>-1</sup> )	Laser Raman frequencies (cm <sup>-1</sup> )	Assignment
1525 b	—	A' 998+525
1500 sh	1498 vs, p	a' C-C stretching
1458 b	1456 m, dp	a'' CH <sub>2</sub> asymmetric bending
—	1435 w, sh	A'' 915+525
1410 s	1415 m, p	a' C-C stretching
—	1380 w	A' 625+755
1360 sh	—	A'' 445+915
1335 b	1330 vs, p	a' CH <sub>2</sub> symmetric deformation
1290 s	1292 m	a' C-C stretching
1280 w	—	A' 803+477
1270 w	—	A'' 998+273
1175 s	1178 m, p	a' C-CHO stretching
1150 sh	—	A'' 928+220
1135 w	1135 s	a' CH <sub>2</sub> rocking
1117 w	—	A' 640+477
1070 vs	—	a' C-H in-plane bending
1050 sh	—	A'' 772+272
1040 s	1040 s, p	a' O-CH <sub>2</sub> stretching
998 m	998 m, p	a' CH <sub>2</sub> rocking
—	970 m, p	A' 755+220
941 s	—	a' C-OCCH <sub>2</sub> stretching
928 m	925 w	a' C-OCCH <sub>2</sub> stretching
915 vs	915 w	a'' C-H out-of-plane bending
803 vs	—	a' Ring breathing
775 vs	780 m, p	a' CH <sub>2</sub> rocking
755 ms	755 m, dp	a'' C-C out-of-plane bending
725 sh	725 w	A'' 272+455
715 vs	720 w	a'' C-II out-of-plane bending
690 vs	690 w	a'' C-C out-of-plane bending
665 sh	—	A'' 445+220
640 vs	645 w, p	a' C-C in-plane bending
620 s	625 w	a'' C=O out-of-plane bending
525 vs	525 m, p	a' C-OCCH <sub>2</sub> in-plane bending
*495 sh	—	a' C-C in-plane bending
*495 s	—	
*485 w	—	A'' 325+160
*490 ms	—	
*465 w	—	A' 220+240
*165 w	—	

Table 1. (Contd.)

IR Frequencies (cm <sup>-1</sup> )	Laser Raman frequencies (cm <sup>-1</sup> )	Assignments
*445 s *445 w		a' C-CHO in-plane bending
*412 m *412 w	405 sh	A' 240+175
*385 vs *385 w	390 m, p	a'' C-C out-of-plane bending
325 vs	—	a' C-O-C in-plane bending
*316 sh *316 w	—	a' C-O-C in-plane bending
*300 s *300 w	300 w, p	a' C-O-C in-plane bending
272 s	—	a'' CH <sub>3</sub> torsion
*240 vs *230 w	240 w —	a'' C-CHO out-of-plane bending a'' CH <sub>3</sub> torsion
*220 vs *220 w	220 w	a'' CH <sub>3</sub> torsion
*180 sh	—	— 412-230
*175 w	—	a'' OCH <sub>3</sub> torsion
*160 w	160 m, dp	a'' OCH <sub>3</sub> torsion
*127 w		a'' C-OCH <sub>3</sub> torsion
*125 w		a'' C-CHO twisting
*120 sh		— 418-300
*75 m		— 465-385

\*=frequency observed in the far infrared spectrum; s=strong; vs=very strong; ms=medium strong, m=medium; w=weak; vw=very weak; sh=shoulder; p=polarized; dp=depolarized.

asymmetric and symmetric bending vibrations are identified at 1458 and 1335 cm<sup>-1</sup> in 3,4,5-TMB. The bands observed at 1135, 998 and 775 cm<sup>-1</sup> are assigned to CH<sub>3</sub> rocking vibrations in 3,4,5-TMB. These assignments are made on the basis of comparison with studies made by earlier workers (Srivastava *et al* 1968, Scherer and Evans 1963, Singh and Singh 1978, Gupta *et al* 1983, Syam Sunder 1986, Babu *et al* 1987 and Goel *et al* 1986). The strong band at 1040 cm<sup>-1</sup> may be assigned to O-CH<sub>3</sub> stretching vibration in 3,4,5-TMB. Singh and Singh (1978) have reported this vibration at 1035, 1025 and 1030 cm<sup>-1</sup> in three isomeric dimethoxybenzaldehydes. The weak bands at 175 and 160 cm<sup>-1</sup> may be assigned to OCH<sub>3</sub> torsion in 3,4,5-TMB. Nearly at the same frequency Sanyal *et al* (1981) have reported these vibrations. Goel *et al* (1986) have also reported these vibrations at 172 and 169 cm<sup>-1</sup> in 3,4,5-trimethoxytoluene and Goel and Agarwal (1982) have assigned at 155 cm<sup>-1</sup> in 4-methoxybenzotrile. The observed bands at 272, 230 and 220 cm<sup>-1</sup> are assigned to CH<sub>3</sub> torsional vibrations in 3,4,5-TMB. Goel *et al* (1986) have reported these vibrations at 259 and 223 cm<sup>-1</sup> in 3,4,5-trimethoxytoluene. The

bands appearing at 325, 316 and 300  $\text{cm}^{-1}$  are assigned to C—O—C in-plane bending vibration. These assignment are based on the report of Sanyal *et al* (1981) and Owen and Hester (1969) in substituted benzaldehyde and anisole respectively.

### Acknowledgments

We are thankful to the Chairman, Physics Department, A M U, Aligarh for the encouragement and help in the research work. The authors are grateful to the Head, RSIC, Madras for providing facilities to record the spectra and to the UGC, New Delhi for financial assistance.

### References

- Babu Ashok V, Lakshmiath B, Ramulu Shree K and Ramana Rao G 1987 *Indian J. Pure Appl. Phys.* **25** 58
- Dwivedi C P D 1968 *Indian J. Pure Appl. Phys.* **6** 440
- Garg S N 1954 *J. Sci. Res., Banaras Hindu Univ.* **4** 42
- Goel R K, Sharma S and Gupta A 1986 *Indian J. Phys.* **60B** 375
- Goel R K and Agarwal M L 1982 *Spectrochim. Acta* **38A** 583
- Green J H S and Harrison D J 1976 *Spectrochim. Acta* **32A** 1265
- Gupta S P, Sharma S K and Goel R K 1983 *Acta Phys. Pol.* **64A** 495
- Gupta S P, Gupta C, Miss Sema and Goel R K 1988 *Indian J. Phys.* **62B** 560
- Heinert Dietrich and Martell Arthur E 1959 *J. Am. Chem. Soc.* **81** 3933
- Kahovec R A and Kohlrausch K W F 1937 *Z. Phys. Chem.* **38B** 119
- Lal B B, Srivastava M P and Singh I S 1973 *Indian J. Pure Appl. Phys.* **11** 615
- Morton R A and Stubbs A L 1940 *J. Chem. Soc.* 1347
- Owen N L and Hester R E 1969 *Spectrochim. Acta* **25A** 243
- Padhey M R and Viladker B G 1960 *J. Sci. Ind. Res.* **19B** 45
- Purvis J E 1914 *J. Chem. Soc.* 2482
- Sanyal Nitish K, Goel R K and Agarwal M L 1981 *Indian J. Pure Appl. Phys.* **19** 480
- Scheer J R and Evans J C 1963 *Spectrochim. Acta* **19** 1739
- Serocco Marisa and Liberti Arnaldo 1954 *Reccerra Sci.* **24** 1687
- Saasthidar M A, Shanbhag P V, Ayachit N H and Rao Suryanarayana K 1984 *Indian J. Pure Appl. Phys.* **22** 433
- Singh V B and Singh I S 1968 *Indian J. Pure Appl. Phys.* **6** 81
- Singh O N, Srivastava M P and Singh I S 1967 *Curr. Sci. (India)* **36** 630
- Singh S J and Singh Ranjeet 1978 *Indian J. Pure Appl. Phys.* **16** 939
- Singh H S and Sanyal Nitish K 1972 *Indian J. Pure Appl. Phys.* **10** 545
- Srivastava, Lal B B and Singh I S 1972 *Indian J. Pure Appl. Phys.* **10** 570
- Srivastava M P, Singh O N and Singh S I 1968 *Curr. Sci. (India)* **37** 100
- 1969 *Indian J. Pure Appl. Phys.* **7** 504
- Syam Sunder N 1986 *Indian J. Phys.* **60B** 490
- Tariq S, Verma P K and Rashid A 1982 *Indian J. Pure Appl. Phys.* **20** 974
- Venkoji 1984 *Proc. Indian Acad. Sci. (Chem. Sci.)* **93** 105
- 1986 *Indian J. Pure Appl. Phys.* **24** 166
- Yadav R A, Ramakant, Mishra P C and Singh I S 1982 *Pramana* **18** 311