

## LASER RAMAN SPECTRUM AND VIBRATIONAL ASSIGNMENT OF *META* BROMO BENZALDEHYDE

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(Received 24 August 1987; Accepted 11 September 1987)

The laser Raman spectrum of *m*-bromobenzaldehyde has been recorded in liquid phase. About 50 Raman frequencies have been observed in the present molecule between 100 and 4000  $\text{cm}^{-1}$ . Out of these 32 have been taken as fundamentals while the rest are considered as the summation frequencies. The vibrational frequencies identified in the analysis of this spectrum have been assigned to specific modes of vibration.

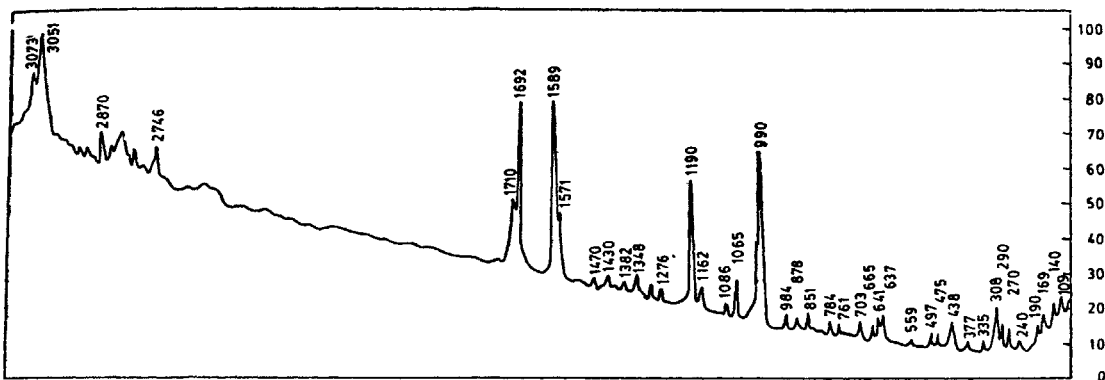
**Key Words :** Laser Raman Spectrum; Metabromobenzaldehyde; Vibrational Assignment

### INTRODUCTION

THE knowledge of vibrational analysis of the benzene molecule is very important since it can be applied to many compounds of similar structure. Because of the simplicity and highly symmetrical nature of this molecule, it is very suitable as a model in methodological research work and structural studies. Whiffen<sup>1</sup> and Varsanyi<sup>2</sup> in their study of different monosubstituted benzenes viz.,  $\text{C}_6\text{H}_5\text{X}$  have been shown that out of thirty fundamental vibrations of the aromatic ring, twenty-four frequencies do not change much when the *X*-group is changed. The remaining six frequencies alone are sensitive to the *X*-group. They have also concluded that two of the frequencies occur at fairly high frequency region and the other four at lower frequency region. Scherer and Overand<sup>3</sup> have studied twenty-one chlorinated benzenes and three isotopes of benzene spectroscopically. Recently, the infrared spectra of parafluoro, *meta* and *para*-chlorotoluene in the vapour and liquid states and in solution have been recorded by Mukherjee *et al.*<sup>4</sup> The present investigation presents the laser Raman spectrum of *m*-bromobenzaldehyde.

### EXPERIMENTAL

*Meta*-bromobenzaldehyde is obtained from Fluka AG Chemische Fabrik, Schmeiz. The laser Raman spectrum of this molecule has been recorded in Carry model 82 Laser Raman spectrophotometer in the region 100-4000 $\text{cm}^{-1}$  and is presented in Fig. 1. The observed frequencies are listed in Table I. The frequencies for all sharp bands are expected to be accurate to  $\pm 1\text{cm}^{-1}$ .

FIG 1 Laser Raman spectrum of *m*-bromobenzaldehyde

### RESULTS AND DISCUSSION

Table I shows the fundamental frequencies identified from the analysis of the laser Raman spectrum of this molecule. The assignment to specific modes of vibration in terms of the corresponding modes of benzene is discussed in the present investigation.

The *meta*-bromobenzaldehyde belongs to  $C_s$  point group and possesses 25 planar and 11 non-planar vibrations. All these modes are allowed in Raman as well as in the infrared spectra. Considering bromobenzaldehyde as a substituted benzene on one hand and a substituted formaldehyde on the other, the observed fundamental frequencies in the spectrum of this molecule can be discussed as the phenyl and aldehyde group frequencies as follows :—

#### *Phenyl Group Frequencies*

**C-C stretching frequencies :** The C-C stretching vibrations in substituted benzenes are derived from the four C-C stretching modes  $1595\text{cm}^{-1}$ ,  $1485\text{cm}^{-1}$ ,  $1311\text{cm}^{-1}$  and  $992\text{cm}^{-1}$  of benzene, of which the first two are doubly degenerate. Thus one would expect six C-C stretching vibrations in substituted benzenes.

Assignment of the frequency at  $1382\text{cm}^{-1}$  in the laser Raman spectrum of *m*-bromobenzaldehyde to C-C stretching mode is in good agreement with the assignment given by Garrigau-Lagrange *et al.*<sup>5</sup> and Chattopadhyaya and Jha<sup>6</sup> in benzaldehyde.

As pointed out by many previous workers, a frequency of the order of  $1008\text{cm}^{-1}$  is invariably observed in mono-substituted, *meta*-di-substituted and symmetrical tri-substituted benzenes. This frequency has been assigned by previous authors to the breathing mode of benzene ring in which the carbon atoms at positions 2, 4 and 6 only are displaced radially while the other three atoms remain at rest. This mode has been shown by Whiffen<sup>1</sup> as *p*-mode in case of monohalogenated benzenes. In the present case a very intense frequency at

TABLE I  
*Vibrational frequencies and assignments for m-bromobenzaldehyde*

Frequency $\text{cm}^{-1}$	Intensity <sup>+</sup>	Assignments
109	M	$270 - 169 = 101$
140	W	$308 - 169 = 139$
169	VW	O. P. bending
190	VW	$438 - 240 = 198$
240	VW	O. P. bending
270	W	O. P. bending
290	W	$784 - 497 = 287$
308	W	C-C-C i.p bending
335	VW	$641 - 308 = 333$
377	VW	$878 - 497 = 381$
438	W	C-C-C i. p. bending
475	VW	$2 \times 240 = 480$
497	VW	C-C-C i. p. bending
559	VW	$1000 - 438 = 562$
637	W	inplane hydrogen bending
641	W	C-C-C i. p. bending
665	MW	C-Br stretching
703	VW	C-C-C o. p. bending
761	VW	$497 + 270 = 767$
784	VW	C-H o. p. bending
851	VW	C-CHO stretching
878	VW	C-H o. p. bending
964	VW	C-H o. p. bending
990	S	C-C-str. (ring breathing)
1000	M	C-C-C i. P. bending
1065	M	C-H i. p. bending
1086	M	C-H i. p. bending
1162	W	C-H i. p. bending
1190	S	C-H str.
1276	VW	C-H i. p. bending (in CHO group)
1348	VW	C-C stretching
1382	VW	C-C stretching
1430	VW	$990 + 438 = 1428$
1470	VW	C-C stretching
1571	M	C-C stretching
1589	VS	C = C stretching
1698	VS	C = O stretching
1710	M	$1065 + 641 = 1706$
2746	M	C-H stretching (in CHO group)
2870	M	C-H stretching (formaldehyde)
3051	VS	C-H stretching
3075	S	C-H stretching

<sup>+</sup>VS-Very Strong; S-Strong; M-Medium; W-Weak; VW-Very Weak; i.p.-in-plane; o.p.-out of plane

$990 \text{ cm}^{-1}$  is observed in *meta*-bromobenzaldehyde and has been assigned to this mode.

### Ring Deformation Frequencies

As given in Table I, all the six ring deformation frequencies are observed in the laser Raman spectrum of bromobenzaldehyde. Of these, three come from inplane bending vibrations corresponding to  $606\text{cm}^{-1}$  and  $1010\text{cm}^{-1}$  modes of benzene and remaining three are derived from out of plane bending vibrations corresponding to  $404\text{cm}^{-1}$  and  $711\text{cm}^{-1}$  modes of benzene.

The inplane bending mode of benzene splits into two components in substituted benzenes; while both these components reduce heavily in metal isomers of di-substituted benzenes. The medium strong frequencies  $438$  and  $308\text{cm}^{-1}$  in *meta*-bromobenzaldehyde have been assigned to C-C-C inplane bending mode. These assignments are in good agreement with those given by Mukherjee.<sup>4</sup>

Medium weak frequency observed at  $665\text{cm}^{-1}$  in the Laser Raman spectrum of *m*-bromobenzaldehyde has been assigned to C-Br stretching mode. This is in good agreement with the assignment proposed by Mukherjee<sup>4</sup> in the case of isomeric chlorotoluene. The only frequency occurring weakly around  $703\text{cm}^{-1}$  in the laser Raman spectrum of the present molecule has been assigned to the mode of C-C-C out of plane bending.

### C-H Stretching Frequencies

Among  $3061\text{cm}^{-1}$ ,  $3063\text{cm}^{-1}$ ,  $3048\text{cm}^{-1}$  and  $3080\text{cm}^{-1}$  modes corresponding to C-H stretching vibrations of benzenes, the last two are degenerate and each of them gives rise to two components in substituted benzenes. In di-substituted benzenes while one component in each has remains around the original frequency, the order is Br-sensitive and is heavily reduced depending upon the substituents. Strong frequencies observed at  $3073\text{cm}^{-1}$  and  $3051\text{cm}^{-1}$  in the laser Raman spectrum of *m*-bromobenzaldehyde have been assigned to C-H stretching mode. Assignment of very strong Raman frequency at  $1190\text{cm}^{-1}$  in the present case to C-H stretching mode is in agreement with that in the case of benzaldehyde molecule.<sup>6</sup> Whiffen<sup>1</sup> has assigned a frequency of value  $673\text{cm}^{-1}$  which is a mixture of C-H and C-Br stretching. In the present case we have observed medium strong Raman frequency at  $641\text{cm}^{-1}$  and has been assigned to C-C-C i.p bending mode.

### C-H Deformation Frequencies

The C-H deformation vibrations in benzene derivative are expected to arise from  $1298\text{cm}^{-1}$ ,  $1178\text{cm}^{-1}$ ,  $1170\text{cm}^{-1}$  and  $1035\text{cm}^{-1}$  modes (in-plane hydrogen bending) and  $1016\text{cm}^{-1}$ ,  $849\text{cm}^{-1}$ ,  $671\text{cm}^{-1}$  and  $985\text{cm}^{-1}$  modes (out of plane hydrogen bending) of benzene. In the present case frequencies at  $637\text{cm}^{-1}$  and  $308\text{cm}^{-1}$  in *m*-benzaldehyde have been assigned as the in-plane hydrogen bending frequencies. Frequencies around  $1086\text{cm}^{-1}$  and  $1276\text{cm}^{-1}$  have been assigned to C-H in-plane bending modes. In the region  $160$ – $280\text{cm}^{-1}$  we have observed three medium weak frequencies in the present study. We have assigned the higher of the two frequencies at  $270\text{cm}^{-1}$  and  $240\text{cm}^{-1}$  in *meta* isomer to out-of-plane bending in which bromine atom remains at rest and the lower mode in which CHC group

remains at rest. Frequencies of similar intensity observed at  $169\text{cm}^{-1}$  and  $270\text{cm}^{-1}$  *m*-bromobenzaldehyde have been correlated with out-of-plane bending modes.

#### *Aldehyde Group Frequencies*

The laser Raman frequency at  $2870\text{cm}^{-1}$  observed in *meta*-bromobenzaldehyde has been assigned to C-H stretching mode. A frequency near  $1692\text{cm}^{-1}$  observed as one of the most intense bands has been assigned to C-O stretching mode. This is in good agreement with those given by several previous authors.

#### CONCLUSION

The vibrational frequencies identified in the analysis of laser Raman spectrum of *m*-bromobenzaldehyde have been assigned to specific modes of vibration.

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