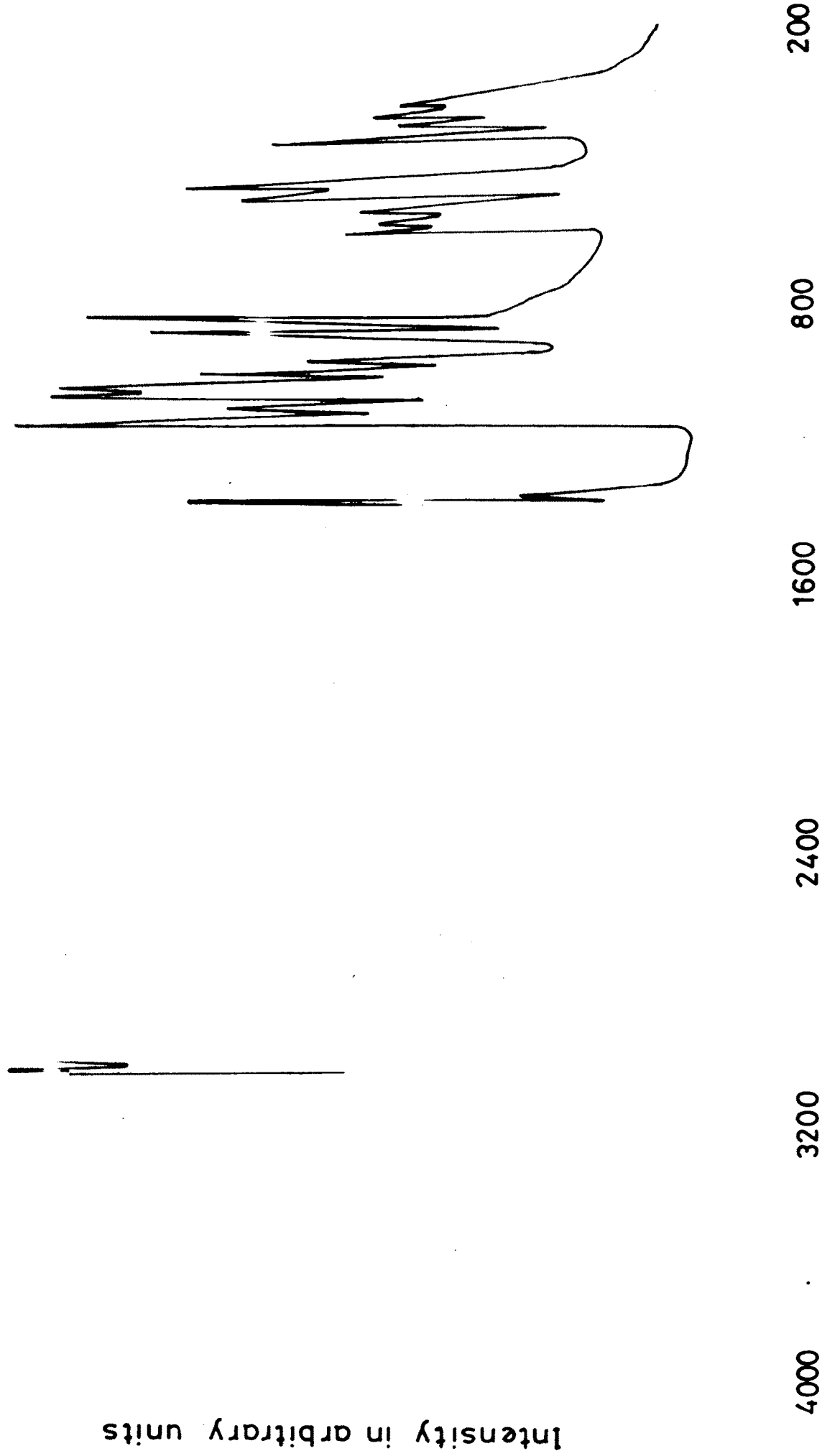


PART - II

EXPERIMENTAL VIBRATIONAL SPECTROSCOPY

CHAPTER - 7LASER RAMAN SPECTRUM OF  $\alpha$  - BROMOTOLUENEABSTRACT

The laser Raman Spectrum of  $\alpha$  - bromotoluene has been recorded in liquid phase in the region  $100-4000\text{ cm}^{-1}$  grating spectrophotometer with an argon laser source. The observed frequencies have been assigned to various modes of vibrations in terms of fundamentals, overtones and combinations assuming  $C_s$  point group symmetry.



LASER RAMAN SPECTRUM OF  $\alpha$ -BROMOTOLUENE

## INTRODUCTION

The vibrational spectra of some mono - and di - halogenated toluenes have been studied by several workers(1-6). But no work so far has been reported on the Raman Spectra of  $\alpha$  - mono halogenated toluenes. In the present investigation, we present the results and analysis of the laser Raman Spectrum of  $\alpha$  - bromotoluene.

## EXPERIMENTAL

Spectroscopically pure chemical (liquid at room temperature) was obtained from Tokyo Kasei Kogyo Co. Ltd., Japan and it was used as such. The polarised laser Raman Spectra of  $\alpha$  - bromotoluene has been recorded using 488 nm line of  $\text{Ar}^{+1}$  for excitation in the region  $100\text{-}4000\text{ cm}^{-1}$  at Indian Institute of Technology, Madras on Cary Model 82 grating spectrophotometer and a 4W argon laser. The frequencies for all the sharp bands are accurate to  $\pm 1\text{ cm}^{-1}$ .

## RESULTS AND DISCUSSIONS

The observed frequencies for  $\alpha$  - bromotoluene along with their relative intensities and the probable assignments are presented in Table-1. The observed spectrum is explained on the basis of  $C_s$  point group symmetry for  $\alpha$  - bromotoluene by

assuming  $\text{CH}_2\text{Br}$  group as a point mass.  $C_s$  symmetry leads to 30 normal vibrations distributed as  $\Gamma = 21A'$  (planar) and  $9A''$  (non-planar). All the vibrations are active in both Raman and infrared. The species  $A'$  gives rise to polarised lines while  $A''$  species gives depolarised lines in Raman Spectrum. In addition to these vibrations, 9 group vibrations (6 internal and 3 external) due to  $\text{CH}_2\text{Br}$  group also appear. Assignments have been made on the basis of relative intensity magnitudes of frequencies and the depolarisation of Raman lines. In addition to this the assignments are made on the basis of spectra of molecules of similar structure. The vibration of the molecules under consideration are clearly divided into two groups. (1) Phenyl ring vibrations and (2)  $\text{CH}_2\text{Br}$  group vibrations.

#### Phenyl Ring Vibrations:

##### (a) Carbon Vibrations:

Benzene has two doubly degenerate modes  $e_{2g}$  ( $1596\text{ cm}^{-1}$ ) and  $e_{1u}$  ( $1485\text{ cm}^{-1}$ ) and two non degenerate modes  $b_{2u}$  ( $1319\text{ cm}^{-1}$ ) and  $a_{1g}$  ( $995\text{ cm}^{-1}$ ) due to skeleton stretching of C-C bonds. Hence bands between  $1400\text{-}1650\text{ cm}^{-1}$  in benzene derivatives are assigned to these modes. The actual positions are determined not so much by the nature of the substituents but by the form

of the substitution around the ring (7). The two doubly degenerate frequencies split up into four totally symmetric components under  $C_s$  symmetry. Four bands observed at 1621, 1580, 1511 and 1398  $\text{cm}^{-1}$  in  $\alpha$ -bromotoluene have been assigned to these two degenerate vibrations of benzene. The  $b_{2u}$  carbon vibration of benzene changes appreciably in the substitution and the 1345  $\text{cm}^{-1}$  band has been assigned to this mode.

The in plane carbon bending vibrations are derived from non degenerate  $b_{1u}$  (1010  $\text{cm}^{-1}$ ) and degenerate  $e_{2g}$  (606  $\text{cm}^{-1}$ ) modes of benzene. The  $e_{2g}$  (606  $\text{cm}^{-1}$ ) degenerate frequency splits up into two totally symmetric components under  $C_s$  symmetry which have been observed at 631 and 562  $\text{cm}^{-1}$  in  $\alpha$ -bromotoluene. In the present compound, the breathing and trigonal modes due to  $a_{1u}$  and  $b_{1u}$  interaction modes of benzene have also been observed. According to Randal and Whiffen (8) the trigonal mode usually remains around 1000  $\text{cm}^{-1}$ . The breathing mode is sensitive to the substitution to the benzene molecules. The bands observed are 1005 and 872  $\text{cm}^{-1}$  have been assigned to C-C in plane trigonal mode and C-C stretching ring breath vibration respectively.

The carbon out of plane bending vibrations are derived from non degenerate  $b_{2g}$  (703  $\text{cm}^{-1}$ ) and degenerate  $e_{2u}$  (404  $\text{cm}^{-1}$ ) modes of benzene. In general the  $b_{2g}$  vibrations is found to be

constant in substituted benzene (6) and in the present case it is observed at  $690\text{ cm}^{-1}$  in  $\alpha$  - bromotoluene. The degenerate  $e_{2u}$  ( $404\text{ cm}^{-1}$ ) splits up into two non totally symmetric components and the bands observed are at  $415$  and  $375\text{ cm}^{-1}$  in  $\alpha$  - bromotoluene are assigned to these vibrations.

(b) C-H Vibrations:

The  $\alpha$  - bromotoluene which is the subject of present investigation gives rise to 4 C-H aromatic stretching, 5 C-H out of plane deformations and 5 C-H in plane bendings. The aromatic structures show the presence of C-H stretching vibrations in the region  $3000\text{-}3100\text{ cm}^{-1}$ , which is the characteristic region for ready identification of this structure. In this region the bands are not affected considerably by the nature of the substituents. In benzene derivatives the C-H stretching frequencies arise from the modes  $a_{1g}$  ( $3062\text{ cm}^{-1}$ ),  $e_{2g}$  ( $3047\text{ cm}^{-1}$ ),  $b_{1u}$  ( $3060\text{ cm}^{-1}$ ) and  $e_{1u}$  ( $3080\text{ cm}^{-1}$ ). It is known that in mono substituted benzene the above modes give rise to five C-H stretching frequencies while the sixth C-H stretching frequency mostly depends on the nature of the substituents and their masses. The bands at  $3044$ ,  $3075$ ,  $3091$  and  $3006\text{ cm}^{-1}$  in  $\alpha$  - bromotoluene have been assigned to C-H stretching modes.

Studies on the spectra of benzene show that there appears two

degenerate  $e_{2g}$  ( $1178 \text{ cm}^{-1}$ ) and  $e_{1u}$  ( $1037 \text{ cm}^{-1}$ ) and two non degenerate  $b_{2u}$  ( $1152 \text{ cm}^{-1}$ ) and  $a_{2g}$  ( $1340 \text{ cm}^{-1}$ ) vibrations involving C-H in plane bending. In the present work these modes yield five planar bending vibrations involving hydrogen atom. The frequencies 1327, 1285, 1250, 1161 and  $1046 \text{ cm}^{-1}$  in  $\alpha$  - bromotoluene are assigned to C-H in plane bending vibrations which belong to  $A'$  species. These assignments are in good agreement with literature values (2,3).

The C-H out of plane deformation result from  $b_{2g}$  ( $985 \text{ cm}^{-1}$ ),  $e_{2u}$  ( $970 \text{ cm}^{-1}$ ),  $e_{1g}$  ( $850 \text{ cm}^{-1}$ ) and  $a_{2u}$  ( $671 \text{ cm}^{-1}$ ) modes of benzene and they are expected to occur in the region  $600\text{-}1000 \text{ cm}^{-1}$  (9). The changes in the frequencies of these deformation from the values in benzene are almost determined exclusively by the relative position of the substituents and almost independent of their nature (9, 10). Hence the bands at 975, 926, 853, 822 and  $665 \text{ cm}^{-1}$  have been assigned to five C-H out of plane bending vibration.

(c) C-Br Vibrations:

The C-Br stretching frequency usually occurs in the region  $500\text{-}700 \text{ cm}^{-1}$  (11). The band at  $605 \text{ cm}^{-1}$  in  $\alpha$  - bromotoluene is assigned to C-Br stretching vibration. This assignment is in good agreement with those made by Green (12) in the case of



p fluoro bromobenzene and p bromo methyl benzene molecules.

#### CH<sub>2</sub>Br Group Vibrations:

Group frequencies are described in terms of the motions that the nuclei in a structural group in the molecule undergo during the vibration and they appear in fairly constant region in the spectrum. In CH<sub>2</sub>Br group there exists two stretching vibrations distributed as one symmetric and one asymmetric vibrations. The symmetric and asymmetric vibrations in CH<sub>2</sub>Br group in  $\alpha$ -bromotoluene are assigned as 2910 and 2865 cm<sup>-1</sup> respectively. For one CH<sub>2</sub>Br group attached to the benzene ring two bending vibrations are expected. The bands at 1375 cm<sup>-1</sup> is assigned to C-H symmetric bending of CH<sub>2</sub>Br group while the band at 1500 cm<sup>-1</sup> is assigned to C-H asymmetric bend in CH<sub>2</sub>Br group.

TABLE - 1

ASSIGNMENT OF VIBRATIONAL FREQUENCIES OF ( $\text{cm}^{-1}$ ) OF  $\alpha$  - BROMOTOLUENE

Wave Number	Intensity	Assignment
3170	S	2865 + 306
3006	VS	C-H aromatic stretch
3091	VS	C-H aromatic stretch
3075	VS	C-H aromatic stretch
3044	VS	C-H aromatic stretch
2910	M	C-H Asymmetric stretch in $\text{CH}_2\text{Br}$ group
2865	W	C-H Symmetric stretch in $\text{CH}_2\text{Br}$ group
1914	S	1046 + 872
1626	S	926 + 690
1621	S	C-C Stretching
1580	M	C-C Stretching
1511	VS	C-C Stretching
1500	VS	C-H Asymmetric bend in $\text{CH}_2\text{Br}$ group
1398	S	C-C Stretching

Wave Number	Intensity	Assignment
1375	W	C-H Symmetric bend in CH <sub>2</sub> Br group
1345	VS	C-C Stretching
1327	S	C-H Inplane bending
1285	S	C-H Inplane bending
1250	VS	C-H Inplane bending
1161	VS	C-H Inplane bending
1110	M	CH <sub>2</sub> Br Rock
1068	VS	CH <sub>2</sub> Br Rock
1046	VS	C-H Inplane bending
1005	S	C-C Inplane (trigonal) bending
975	M	C-H out of plane bending
926	VS	C-H out of plane bending
872	S	C-C Stretching (ring breath)
853	M	C-H out of plane bending
822	S	C-H out of plane bending
690	M	C-H out of plane bending

Wave Number	Intensity	Assignment
665	M	C-H out of plane bending
631	M	C-H Inplane bending
605	S	C-Br Stretching
562	S	C-C Inplane bending
460	S	C-CH <sub>2</sub> Br Stretching
415	M	C-C out of plane bending
375	M	C-C out of plane bending
340	W	C-Br Inplane bending
319	M	C-CH <sub>2</sub> Br bending
306	M	C-Br out of plane bending
284	M	C-CH <sub>2</sub> Br out of plane bending

VS : Very Strong

S : Strong

M : Medium

W : Weak

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