

## Laser Raman spectra of 2,4- and 2,2'-dibromophenols

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**Abstract.** The laser Raman spectra of 2,4- and 2,2'-dibromophenols have been recorded in the region  $200\text{--}4000\text{ cm}^{-1}$  on a Cary Model 82 grating spectrophotometer with an argon laser source. The observed frequencies have been assigned to the various modes of vibrations in terms of fundamentals assuming  $C_s$  and  $C_{2v}$  point group symmetry.

**Keywords.** Laser Raman spectra; 2,4-dibromophenol; 2,2'-dibromophenols.

### 1. Introduction

Several workers (Evans 1960; Bist *et al* 1967; Dwivedi *et al* 1974; Goel *et al* 1979) have studied the vibrational spectra of phenols and its derivatives. The infrared spectra of these compounds have also been reported by Dwivedi *et al* (1974). In the spectra important bands like the C–H stretching are missing. Further they have also studied the spectra in the range  $900\text{--}4000\text{ cm}^{-1}$ . Hence the present investigation is aimed at studying the vibrational spectra of 2,4- and 2,2'-dibromophenols through laser Raman studies and to arrive at a satisfactory vibrational analysis for these molecules.

### 2. Experimental

Spectroscopically pure chemicals 2,4-dibromophenol (2,4-DBP – liquid at room temperature) and 2,2'-dibromophenol (2,2'-DBP – solid) obtained from Fluka A G, Switzerland and were used as such. The polarised laser Raman spectra of 2,4-DBP and 2,2'-DBP have been recorded using the 514.5 nm line of an Ar<sup>+</sup> laser of power 1.5 W for excitation in the region  $200\text{--}4000\text{ cm}^{-1}$  on a Cary model 82 grating spectrophotometer. The frequencies for all sharp bands are accurate to  $\pm\text{ cm}^{-1}$ .

### 3. Results and discussion

The observed frequencies with their relative intensities and assignments of the molecule 2,4-DBP and 2,2'-DBP are reported in table 1. All the assignments have been made assuming that the molecules 2,4-DBP and 2,2'-DBP belong to the  $C_s$  and the  $C_{2v}$  point groups, respectively, and considering the OH group as a point mass.  $C_s$  symmetry leads to two types of vibrations distributed as

$$\Gamma = 21a'(\text{planar}) + 9a''(\text{non-planar}),$$

in which  $a'$  gives rise to polarised lines whereas  $a''$  gives depolarized lines in the

**Table 1.** Assignment of fundamental frequencies of 2,4- and 2,2'-dibromophenols.

Freq 2,4-DBP (int)	Freq 2,2'-DBP (int)	Assignments
3576 <i>vs</i>	3561 <i>vs</i>	$\nu(\text{O-H})$ stretching
3130 <i>s</i>	3125 <i>s</i>	$\nu(\text{C-H})$ stretching
3040 <i>s</i>	3041 <i>s</i>	$\nu(\text{C-H})$ stretching
2980 <i>m</i>	2994 <i>m</i>	$\nu(\text{C-H})$ stretching
1605 <i>vs(p)</i>	1610 <i>s(p)</i>	$\nu(\text{C-C})$ stretching
1581 <i>s(p)</i>	1582 <i>s(p)</i>	$\nu(\text{C-C})$ stretching
1488 <i>vs</i>	1476 <i>s</i>	$\nu(\text{C-C})$ stretching
1400 <i>w</i>	1394 <i>m</i>	$\nu(\text{C-C})$ stretching
1290 <i>vs</i>	1269 <i>s</i>	$\beta(\text{C-H})$ in-plane bending
1180 <i>s</i>	1170 <i>s</i>	$\beta(\text{O-H})$ in-plane bending
1051 <i>s</i>	1059 <i>s</i>	C-C-C trigonal bending
815 <i>vs</i>	789 <i>vs</i>	$\nu(\text{C-C})$ ring breathing
738 <i>w</i>	729 <i>w</i>	$\nu(\text{O-H})$ stretching
705 <i>m</i>	708 <i>m</i>	$\delta(\text{C-C-C})$ out-of-plane bending
681 <i>vs(p)</i>	671 <i>vs(p)</i>	$\nu(\text{C-Br})$ stretching
541 <i>s(p)</i>	555 <i>s(p)</i>	$\nu(\text{C-Br})$ stretching
381 <i>w</i>	386 <i>m</i>	$\beta(\text{C-Br})$ in-plane bending
—	361 <i>m</i>	$\beta(\text{C-Br})$ in-plane bending
—	321 <i>w</i>	$\delta(\text{C-OH})$ out-of-plane bending

Abbreviations: Freq – frequency; int – intensity; *v* – very; *s* – strong; *m* – medium; *p* – polarized; *w* – weak

Raman spectrum.  $C_{2v}$  symmetry gives rise to 4 types of vibrations distributed as

$$\Gamma = 11a_1 + 10b_2 + 3a_2 + 6b_1.$$

Here, the vibrations are divided into two groups: (1) phenyl ring vibrations (2) OH group vibrations.

### 3.1 Phenyl ring vibrations

3.1a *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  $b_{2u}$  ( $1310 \text{ cm}^{-1}$ ) and  $a_{1g}$  ( $995 \text{ cm}^{-1}$ ) due to skeletal stretching modes of C–C bonds. The two strong polarized bands observed at 1605, 1581, 1488 and  $1400 \text{ cm}^{-1}$  in 2,4-dibromophenol and the bands at 1610, 1582, 1476 and  $1394 \text{ cm}^{-1}$  in 2,2'-dibromophenol have been assigned to C–C stretching vibrations.

The carbon out-of-plane bending vibrations are derived from the non-degenerate  $b_{2g}$  ( $703 \text{ cm}^{-1}$ ) and degenerate  $e_{2u}$  ( $404 \text{ cm}^{-1}$ ) modes of benzene (the former is found to be constant in substituted benzenes) (Green 1963) and in the present case it is observed at  $705 \text{ cm}^{-1}$  in 2,4-dibromophenol and at  $708 \text{ cm}^{-1}$  in 2,2'-dibromophenol.

The C–C ring breathing  $a_{1g}$  ( $995 \text{ cm}^{-1}$ ) and C–C–C trigonal bending, non-degenerate  $b_{1u}$  ( $1010 \text{ cm}^{-1}$ ) vibrations of benzene under  $C_s$  symmetry give rise to combined modified modes. In trisubstituted benzene, one mode appears at about  $800 \text{ cm}^{-1}$  while the other appears at  $1000 \text{ cm}^{-1}$ . The C–C–C trigonal bending and

C–C ring breathing vibrations have been assigned to  $1051\text{ cm}^{-1}$  and  $815\text{ cm}^{-1}$  in 2,4-dibromophenol and the bands at  $1059$  and  $789\text{ cm}^{-1}$  in 2,2'-dibromophenol respectively.

3.1b *C–H vibrations*: The aromatic structure shows the presence of C–H stretching vibrations in the region  $3000\text{--}3100\text{ cm}^{-1}$  which affords a ready identification for this structure. The bands at  $3130$ ,  $3040$  and  $2980\text{ cm}^{-1}$  in 2,4-dibromophenol and the bands at  $3125$ ,  $3040$  and  $2994\text{ cm}^{-1}$  in 2,2'-dibromophenol have been assigned to C–H stretching modes. The bands at  $1290\text{ cm}^{-1}$  and  $1269\text{ cm}^{-1}$  in 2,4-dibromophenol and 2,2'-dibromophenol respectively have been identified as C–H in-plane bending vibrations. These observations are in good agreement with the literature values (Bellamy 1959, 1975).

3.1c *C–Br vibrations*: Szymansky (1964) and Green *et al* (1970) have assigned the C–Br stretching mode in the region  $700\text{--}500\text{ cm}^{-1}$ . In accordance with their assignments, we have assigned the strong polarised bands at  $681$  and  $541\text{ cm}^{-1}$  in 2,4-dibromophenol and the bands at  $671$  and  $555\text{ cm}^{-1}$  in 2,2'-dibromophenol have been assigned to the C–Br stretching vibrations respectively. The in-plane C–Br bending vibrations are assigned to  $381\text{ cm}^{-1}$  in 2,4-dibromophenol and  $386$  and  $361\text{ cm}^{-1}$  in 2,2'-dibromophenol.

### 3.2 *OH group vibrations*

Group vibrations are determined in terms of the motions that the nuclei in a structural group in the molecule undergo during vibrations and they appear in fairly constant regions in the spectrum.

The OH-group frequencies have been extensively studied by a number of workers. The bands at  $3576$  and  $738\text{ cm}^{-1}$  in 2,4-dibromophenol and at  $3561$  and  $729\text{ cm}^{-1}$  in 2,2'-dibromophenol have been assigned to the O–H stretching mode. This observation is in good agreement with the earlier work (Nakanishi and Solomon 1977). We have assigned the bands at  $1180$  and  $1170\text{ cm}^{-1}$  as O–H in-plane bending in 2,4-dibromophenol. The C–OH out-of-plane bending mode (the remaining one at  $321\text{ cm}^{-1}$ ) has been assigned to 2,2'-dibromophenol.

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