

## Vibrational spectra of 2, 3 and 2, 6 dichloro anilines

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**Abstract.** The infrared and laser Raman spectra of 2, 3 dichloro aniline and 2, 6 dichloro aniline have been recorded. The vibrational spectra have been analysed assuming  $C_s$  and  $C_{2v}$  point groups for 2, 3 dichloro aniline and 2, 6 dichloro aniline respectively. Assignments for fundamental vibrations, combination and overtone frequencies and internal modes of vibration of amino group have been proposed.

**Keywords.** Raman spectra; infrared spectra; dichloro anilines; stretching; bending.

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### 1. Introduction

Infrared spectra of 2, 4 and 2, 5 dichloro anilines have been reported earlier (Srivastava 1967; Singh and Singh 1968; Singh and Singh 1983). IR spectra of 2, 6 dichloro aniline have been reported by Singh and Singh (1969). However, the Raman spectra of the same compound have not been investigated so far. The spectra of 2, 3 dichloro aniline have also not been reported so far. The aim of this work is to obtain all the vibrational frequencies and propose assignments for 2, 3 and 2, 6 dichloro anilines.

### 2. Experimental

The compounds 2, 3 dichloro aniline (in liquid state at room temperature) and 2, 6 dichloro aniline (in solid state at room temperature) were obtained from Fluka AG, Switzerland. These compounds were in pure state and used without further purification. The IR spectra were recorded on a double beam grating spectrophotometer (Pye-Unicam SP, model 2000) in the range of  $200\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ . The Raman spectra have been recorded on argon ion laser Raman or HG-2S (Jobin-Yvon, France) in the range of  $10\text{ cm}^{-1}$  to  $4000\text{ cm}^{-1}$ . The accuracy of measurements was  $\pm 5\text{ cm}^{-1}$ . The Raman spectrum was recorded with the incident beam parallel and perpendicular to the plane of polarization separately, so that the intensity ratios in the two types of traces for each band could give the nature of polarization of each band.

### 3. Results and discussion

As the local symmetry of the benzene ring is not much affected by the substituents, we assume  $\text{NH}_2$  group as a mass point (Randle and Whiffen 1956) and the total number of

fundamental vibrations will remain as 30, in addition to the internal modes of vibration of the substituent ( $\text{NH}_2$  in the present cases) and combination and overtone frequencies. The compounds 2,3 dichloro aniline and 2,6 dichloro aniline are termed as A and B respectively hereafter. Assuming that molecule A as a planar it would belong to  $C_s$  point group. Out of 30 normal modes of vibrations, 21 will be planar ( $a'$ ) and 9 will be non-planar ( $a''$ ). The molecule B belongs to  $C_{2v}$  point group. The fundamental frequencies have been divided into four species  $a_1, a_2, b_1$  and  $b_2$ . The  $11a_1 + 10b_2$  modes of vibrations are planar, whereas  $3a_2 + 6b_1$  are non-planar. The frequencies of non-planar vibrations must be below  $1000 \text{ cm}^{-1}$  and they are depolarized (Varsanyi 1969).

Assignments of the fundamental frequencies of Benzene are given in table 1. The frequencies of the observed fundamental bands, their intensities and assignments along with vibration number in Wilson's notations of compounds A and B are given in tables 2 and 3 respectively. The internal vibrations of  $\text{NH}_2$  group of compounds A and B are listed in table 4. The combination and overtone bands for these compounds are listed in table 5.

The various observed frequencies have been assigned on the basis of intensity of IR bands, the nature of polarization of Raman bands and the frequency range for different modes of similar molecules. All the modes of vibrations of compounds A and B are both infrared and Raman-active. The fundamental vibrations can be classified into the following three main groups.

**Table 1.** Normal vibrations of benzene.

Species	Frequency ( $\text{cm}^{-1}$ )	Vibration No.	Mode of vibration
$e_{1u}$	3080	20(a, b)	$\nu(\text{C}-\text{H})$
$a_{1g}$	3062	2	$\nu(\text{C}-\text{H})$
$b_{1u}$	3060*	13	$\nu(\text{C}-\text{H})$
$e_{2g}$	3046	7(a, b)	$\nu(\text{C}-\text{H})$
$e_{2g}$	1585	8(a, b)	$\nu(\text{C}-\text{C})$
$e_{1u}$	1485	19(a, b)	$\nu(\text{C}-\text{C})$
$a_{2g}$	1326*	3	$\delta(\text{C}-\text{H})$
$b_{2g}$	1310*	14	$\nu(\text{C}-\text{C})$
$e_{2g}$	1178	9(a, b)	$\delta(\text{C}-\text{H})$
$b_{2u}$	1150*	15	$\delta(\text{C}-\text{H})$
$e_{1u}$	1033	18(a, b)	$\delta(\text{C}-\text{H})$
$b_{1u}$	1010*	12	$\delta(\text{C}-\text{C}-\text{C})$
$a_{1g}$	992	1	$\nu(\text{C}-\text{C})$
$b_{2g}$	985*	5	$\gamma(\text{C}-\text{H})$
$e_{2u}$	970*	17(a, b)	$\gamma(\text{C}-\text{H})$
$e_{1g}$	850	10(a, b)	$\gamma(\text{C}-\text{H})$
$b_{2g}$	703*	4	$\gamma(\text{C}-\text{C}-\text{C})$
$a_{2u}$	671	11	$\gamma(\text{C}-\text{H})$
$e_{2g}$	606	6(a, b)	$\delta(\text{C}-\text{C}-\text{C})$
$e_{2u}$	404	16(a, b)	$\gamma(\text{C}-\text{C}-\text{C})$

\* = calculated values;  $\nu$  = stretching vibrations;  $\delta$  = in-plane bending vibrations;  $\gamma$  = out-of-plane bending vibrations.

**Table 2.** Fundamental frequencies ( $\text{cm}^{-1}$ ) of (A) 2, 3 dichloro aniline.

	IR	Raman	Vibration No.	Assignment
<i>a'</i>				
$\nu_1$	3080(2.5)	3080(3.54)	2	$\nu(\text{C—H})$
$\nu_2$	—	3060(3.5)P	20a	$\nu(\text{C—H})$
$\nu_3$	3032(2.18)	3042(3.58)	20b	$\nu(\text{C—H})$
$\nu_4$	1618(9.0)	1612(2.8)	8b	$\nu(\text{C—C})$
$\nu_5$	1575(7.11)	1585(2.84)	8a	$\nu(\text{C—C})$
$\nu_6$	1480(9.0)	1480(2.9)	19b	$\nu(\text{C—C})$
$\nu_7$	1451(9.0)	1450(2.8)	19a	$\nu(\text{C—C})$
$\nu_8$	1302(7.2)	1298(2.66)P	3	$\delta(\text{C—H})$
$\nu_9$	—	1280(2.65)	14	$\nu(\text{C—C})$ Kekule vibration
$\nu_{10}$	1210(5.8)	1215(2.62)	13	$\nu(\text{C—NH}_2)$
$\nu_{11}$	1165(3.8)	1167(2.57)	15	$\delta(\text{C—H})$
$\nu_{12}$	—	1084(2.57)	18b	$\delta(\text{C—H})$
$\nu_{13}$	—	1049(2.65)P	1	$\nu(\text{C—C})$ Ring breathing
$\nu_{14}$	770(9.0)	764(2.36)	6b	$\delta(\text{C—C—C})$
$\nu_{15}$	741(8.0)	746(2.36)	6a	$\delta(\text{C—C—C})$
$\nu_{16}$	720(4.32)	719(2.35)	12	$\delta(\text{C—C—C})$
$\nu_{17}$	442(6.7)	440(2.25)	7b	$\nu(\text{C—Cl})$
$\nu_{18}$	421(5.72)	425(2.35)	7a	$\nu(\text{C—Cl})$
$\nu_{19}$	230(7.8)	224(2.25)	9b	$\delta(\text{C—NH}_2)$
$\nu_{20}$	—	195(2.19)	18a	$\delta(\text{C—Cl})$
$\nu_{21}$	n.i.	187(2.20)	9a	$\delta(\text{C—Cl})$
<i>a''</i>				
$\nu_{22}$	945(2.05)	943(2.45)	5	$\gamma(\text{C—H})$
$\nu_{23}$	870(4.0)	877(2.45)dp	17b	$\gamma(\text{C—H})$
$\nu_{24}$	775(9.0)	785(2.4)dp	11	$\gamma(\text{C—H})$
$\nu_{25}$	708(8.2)	705(2.32)dp	4	$\gamma(\text{C—C—C})$
$\nu_{26}$	582(3.9)	575(2.2)dp	16a	$\gamma(\text{C—C—C})$
$\nu_{27}$	—	456(2.28)dp	16b	$\gamma(\text{C—C—C})$
$\nu_{28}$	270(9.0)	270(2.2)	10a	$\gamma(\text{C—NH}_2)$
$\nu_{29}$	n.i.	180(2.1)	10b	$\gamma(\text{C—Cl})$
$\nu_{30}$	n.i.	132(2.2)dp	17a	$\gamma(\text{C—Cl})$

$\nu$ , stretching;  $\delta$ , in-plane bending;  $\gamma$ , out-of-plane bending; n.i., not investigated; P, polarised; dp, depolarised. The figures in the bracket indicate intensity in the scale of 0 to 10.

### 3.1 Stretching vibrations ( $\nu$ )

**3.1a  $\nu(\text{C—H})$  and  $\nu(\text{C—X})$ :** In the case of trisubstituted benzene derivatives, out of six  $\nu(\text{C—H})$  of benzene (table 1), the three  $\nu(\text{C—H})$  frequencies do not change due to substitution and lie in the range of  $3000\text{--}3100\text{ cm}^{-1}$  (Varsanyi 1969) while the remaining three  $\nu(\text{C—X})$  frequencies ( $X = \text{substitution for H atom}$ ) are mass-dependent and decrease considerably. Corresponding to light substituents (atomic mass  $< 25$ ) these frequencies will remain above  $1000\text{ cm}^{-1}$  and for heavy substituents (atomic mass  $> 25$ ) these frequencies are found below  $500\text{ cm}^{-1}$  (Varsanyi 1969). The frequencies  $\nu_1, \nu_2, \nu_3$  for compound A (table 2) and  $\nu_1, \nu_2, \nu_{21}$  for compound B (table 3) have been assigned as  $\nu(\text{C—H})$  corresponding to the modes 2, 20a, 20b respectively. The frequencies  $\nu_{10}, \nu_{17}, \nu_{18}$  for compound A and  $\nu_5, \nu_{28}, \nu_{10}$  for compound B have been

**Table 3.** Fundamental frequencies ( $\text{cm}^{-1}$ ) of (B) 2,6 dichloro aniline.

	IR	Raman	Vibration No.	Assignment
<i>a</i> <sub>1</sub> type				
<i>v</i> <sub>1</sub>	—	3088(2.16)P	2	$\nu(\text{C—H})$
<i>v</i> <sub>2</sub>	3060(6.8)	—	20a	$\nu(\text{C—H})$
<i>v</i> <sub>3</sub>	1575(6.75)	1584(5.28)	8a	$\nu(\text{C—C})$
<i>v</i> <sub>4</sub>	1450(6.8)	1452(1.84)	19a	$\nu(\text{C—C})$
<i>v</i> <sub>5</sub>	1251(2.7)	1253(1.92)	13	$\nu(\text{C—NH}_2)$
<i>v</i> <sub>6</sub>	1168(1.72)	1162(1.85)	9a	$\delta(\text{C—H})$
<i>v</i> <sub>7</sub>	1012(2.28)	1006(1.91)	12	$\delta(\text{C—C—C})$
<i>v</i> <sub>8</sub>	735(3.68)	730(1.81)	6a	$\delta(\text{C—C—C})$
<i>v</i> <sub>9</sub>	625(4.2)	620(1.95)P	1	$\nu(\text{C—C})$ Ring breathing
<i>v</i> <sub>10</sub>	433(2.9)	427(1.86)	7a	$\nu(\text{C—Cl})$
<i>v</i> <sub>11</sub>	—	200(1.86)	18a	$\delta(\text{C—Cl})$
<i>a</i> <sub>2</sub> type				
<i>v</i> <sub>12</sub>	890(0.7)	855(1.88)dp	17a	$\gamma(\text{C—H})$
<i>v</i> <sub>13</sub>	570(3.52)	561(1.97)dp	16a	$\gamma(\text{C—C—C})$
<i>v</i> <sub>14</sub>	—	182(1.82)dp	10a	$\gamma(\text{C—Cl})$
<i>b</i> <sub>1</sub> type				
<i>v</i> <sub>15</sub>	949(2.78)	955(1.84)	17b	$\gamma(\text{C—H})$
<i>v</i> <sub>16</sub>	760(7.0)	762(1.92)dp	11	$\gamma(\text{C—H})$
<i>v</i> <sub>17</sub>	715(6.82)	710(1.84)dp	4	$\gamma(\text{C—C—C})$
<i>v</i> <sub>18</sub>	552(3.4)	555(1.96)dp	16b	$\gamma(\text{C—C—C})$
<i>v</i> <sub>19</sub>	—	272(2.72)dp	10b	$\gamma(\text{C—NH}_2)$
<i>v</i> <sub>20</sub>	n.i.	142(1.84)dp	5	$\gamma(\text{C—Cl})$
<i>b</i> <sub>2</sub> type				
<i>v</i> <sub>21</sub>	3030(6.82)	3020(1.94)	20b	$\nu(\text{C—H})$
<i>v</i> <sub>22</sub>	1625(8.9)	1627(1.89)	8b	$\nu(\text{C—C})$
<i>v</i> <sub>23</sub>	1477(9.2)	1480(1.88)	19b	$\nu(\text{C—C})$
<i>v</i> <sub>24</sub>	1302(4.23)	1292(2.0)	3	$\delta(\text{C—H})$
<i>v</i> <sub>25</sub>	1280(4.0)	1271(1.86)	14	$\nu(\text{C—C})$ Kekule vibration
<i>v</i> <sub>26</sub>	1090(5.84)	1082(1.9)	9b	$\delta(\text{C—H})$
<i>v</i> <sub>27</sub>	789(3.6)	784(1.82)	6b	$\delta(\text{C—C—C})$
<i>v</i> <sub>28</sub>	433(2.9)	435(1.85)	7b	$\nu(\text{C—Cl})$
<i>v</i> <sub>29</sub>	405(3.6)	405(1.88)	18b	$\delta(\text{C—NH}_2)$
<i>v</i> <sub>30</sub>	n.i.	189(1.82)	15	$\delta(\text{C—Cl})$

*v*, stretching;  $\delta$ , in-plane bending;  $\gamma$ , out-of-plane bending; n.i., not investigated; P, polarised; dp, depolarised. The figures in the bracket indicate intensity in the scale 0 to 10.

assigned as  $\nu(\text{C—NH}_2)$ ,  $\nu(\text{C—Cl})$ ,  $\nu(\text{C—Cl})$  corresponding to the modes 13, 7b and 7a respectively.

**3.1b (C—C) stretching vibrations:** Out of six (C—C) stretching vibrations of benzene, the frequencies of five modes remain unchanged but the frequency of vibration 1 (ring breathing) for compound A will appear above  $1000\text{ cm}^{-1}$  and for compound B it will appear below  $1000\text{ cm}^{-1}$  or even below  $700\text{ cm}^{-1}$  (Varsanyi 1969, 1974). The frequencies  $\nu_5, \nu_4, \nu_7, \nu_6, \nu_9, \nu_{13}$  for compound A and  $\nu_3, \nu_{22}, \nu_4, \nu_{23}, \nu_{25}, \nu_9$  for compound B have been assigned as  $\nu(\text{C—C})$  corresponding to modes 8a, 8b, 19a, 19b, 14 and 1 respectively. These assignments are in good agreement with those reported earlier (Srivastava 1967; Singh and Singh 1969, 1983; Sharma and Dwivedi 1976).

**Table 4.** Internal modes of vibration of NH<sub>2</sub> group.

	Compound A		Compound B		Mode of vibration
	IR	Raman	IR	Raman	
$\nu_1$	—	3445	3450	3454	$\nu_{as}(\text{NH}_2)$
$\nu_2$	—	3356	3355	3360	$\nu_s(\text{NH}_2)$
$\nu_3$	1625	1629	1620	1618	$\delta_s(\text{NH}_2)$ Scissoring
$\nu_4$	1037	1032	—	1042	$\delta_{as}(\text{NH}_2)$ Rocking
$\nu_5$	675	670	672	673	$\gamma_s(\text{NH}_2)$ Wagging

$\nu$ , stretching;  $\delta$ , in-plane bending;  $\gamma$ , out-of-plane bending; s, symmetric; as, antisymmetric.

**Table 5.** Combination and overtone frequencies (cm<sup>-1</sup>).

Compound A	Compound B
3303 = 3080 + 224 = 3304(A')	3260 = 1627 × 2 = 3254(A <sub>1</sub> )
3091 = 1612 + 1480 = 3092(A')	3220 = 3080 + 142 = 3222(B <sub>1</sub> )
2900 = 1450 × 2 = 2900(A')	3160 = 1584 × 2 = 3168(A <sub>1</sub> )
2595 = 1298 × 2 = 2596(A')	2880 = 1584 + 1288 = 2872(B <sub>2</sub> )
2581 = 1298 + 1280 = 2578(A')	2666 = 1584 + 1082 = 2666(B <sub>2</sub> )
2491 = 1612 + 877 = 2489(A'')	2290 = 1584 + 710 = 2294(B <sub>1</sub> )
2393 = 1612 + 785 = 2397(A'')	2165 = 1082 × 2 = 2164(A <sub>1</sub> )
2354 = 1612 + 746 = 2358(A')	2020 = 1452 + 561 = 2013(A <sub>2</sub> )
2181 = 1612 + 575 = 2187(A'')	2006 = 1006 × 2 = 2012(A <sub>1</sub> )
1956 = 1215 + 746 = 1961(A')	1928 = 762 + 1162 = 1924(B <sub>1</sub> )
1941 = 1480 + 456 = 1936(A'')	1906 = 955 × 2 = 1910(A <sub>1</sub> )
1693 = 943 + 746 = 1689(A'')	1854 = 1584 + 272 = 1856(B <sub>1</sub> )
1682 = 943 + 746 = 1689(A'')	1730 = 1162 + 561 = 1723(A <sub>2</sub> )
1531 = 764 × 2 = 1528(A')	1566 = 784 × 2 = 1568(A <sub>1</sub> )

### 3.2 In-plane bending vibrations ( $\delta$ )

**3.2a  $\delta(\text{C—H})$  and  $\delta(\text{C—X})$ :** The three  $\delta(\text{C—H})$  and three  $\delta(\text{C—X})$  modes of trisubstituted benzene are derived from the six  $\delta(\text{C—H})$  of benzene. The  $\delta(\text{C—H})$  frequencies remain almost unaltered upon substitution but the  $\delta(\text{C—X})$  frequencies change considerably. Modes 3, 15, 18b for compound A and 3, 9a, 9b for compound B are regarded as  $\delta(\text{C—H})$  while modes 9a, 9b, 18a for compound A and 15, 18a, 18b for compound B become  $\delta(\text{C—X})$ . The frequency for mode 9b for compound A and  $\nu_{18b}$  for compound B will be the highest among all the  $\delta(\text{C—X})$  frequencies (Varsanyi 1969). For compound A the frequencies  $\nu_8, \nu_{11}, \nu_{12}$  corresponding to modes 3, 15, 18b and for compound B the frequencies  $\nu_{24}, \nu_6, \nu_{26}$  corresponding to modes 3, 9a, 9b respectively have been assigned as  $\delta(\text{C—H})$ . For compound A the frequencies  $\nu_{19}, \nu_{20}, \nu_{21}$  corresponding to modes 9b, 18a, 9a and for compound B the frequencies  $\nu_{29}, \nu_{11}, \nu_{30}$  corresponding to modes 18b, 18a, 15 have been assigned as  $\delta(\text{C—NH}_2)$ ,  $\delta(\text{C—Cl})$  and  $\delta(\text{C—Cl})$  respectively. For trichloro benzene the frequency for modes 18b is nearly 400 cm<sup>-1</sup>. Further our assignments agree with the observations of Srivastava (1967), Singh and Singh (1969, 1983).

3.2b ( $C-C-C$ ) *In-plane bending vibrations*: The normal modes 6a, 6b and 12 are regarded as  $\delta(C-C-C)$ . For both compounds the frequencies for both the components of vibrational pair 6 are found above  $700\text{ cm}^{-1}$  (Varsanyi 1969, 1974) but the frequency of mode 12 for compound A is  $< 800\text{ cm}^{-1}$  and it is  $> 1000\text{ cm}^{-1}$  for compound B. The frequencies  $\nu_{15}, \nu_{14}, \nu_{16}$  for compound A and  $\nu_8, \nu_{27}, \nu_7$  for compound B have been identified as  $\delta(C-C-C)$  corresponding to the modes 6a, 6b and 12 respectively. The above assignments are within the frequency range given by Varsanyi (1969) and find support from Srivastava (1967), Singh and Prasad (1978) and Singh and Singh (1983).

### 3.3 *Out-of-plane bending vibrations ( $\gamma$ )*

3.3a  $\gamma(C-H)$  and  $\gamma(C-X)$ : The three  $\gamma(C-H)$  and three  $\gamma(C-X)$  modes of vibrations of trisubstituted derivatives are derived from the six  $\gamma(C-H)$  of benzene. Vibration modes 5, 17b, 11 for compound A and 17a, 17b, 11 for compound B will correspond to  $\gamma(C-H)$ . For compound A the modes 17a, 10a, 10b and for compound B the modes 5, 10a, 10b will correspond to  $\gamma(C-X)$  (Varsanyi 1969). The  $\gamma(C-H)$  frequencies for compound A have been assigned at  $\nu_{22}, \nu_{23}, \nu_{24}$  corresponding to the modes 5, 17b, 11 and for compound B these have been assigned at  $\nu_{12}, \nu_{15}, \nu_{16}$  corresponding to the modes 17a, 17b, 11 respectively. Frequencies below  $350\text{ cm}^{-1}$  are to be assigned to  $\gamma(C-X)$ . The  $\gamma(C-NH_2)$ ,  $\gamma(C-Cl)$  and  $\gamma(C-Cl)$  frequencies have been assigned at  $\nu_{28}, \nu_{29}, \nu_{30}$  corresponding to the modes 10a, 10b, 17a for compound A and at  $\nu_{19}, \nu_{14}, \nu_{20}$  corresponding to modes 10a, 10b, 5 respectively for compound B. The frequency intervals for  $\gamma(C-H)$  and  $\gamma(C-X)$  have been established by normal coordinate analysis by Whiffen (1955) and the assignments made here lie in the intervals established.

3.3b ( $C-C-C$ ) *out-of-plane bending vibrations*: Vibration modes 4, 16a, 16b of Benzene are regarded as  $\gamma(C-C-C)$ . The frequency  $\nu_{25}$  for compound A and  $\nu_{17}$  for compound B may be identified as the mode 4. As regards the degenerate pair 16, Bentley and Wolforth (1959) assigned the component 16a between  $530$  and  $590\text{ cm}^{-1}$  and 16b in the interval of  $450-440\text{ cm}^{-1}$  in the case of asymmetric trisubstitution. The frequency of vibration 16b is  $428-476\text{ cm}^{-1}$  for asymmetric trisubstituted benzenes and  $535-570\text{ cm}^{-1}$  for vicinal trisubstituted benzenes (Jakobsen and Bentley 1964). For compound A the frequencies  $\nu_{26}, \nu_{27}$  and for compound B the frequencies  $\nu_{13}, \nu_{18}$  have been identified as  $\gamma(C-C-C)$  corresponding to modes 16a and 16b respectively. Our assignments are thus in harmony with the studies made by other workers quoted above.

### 3.4 *Internal vibrations of $NH_2$ group*

The  $NH_2$  group has two ( $N-H$ ) stretching frequencies, one being symmetric and the other asymmetric. The frequency of asymmetric vibration is higher than that of symmetric one. The frequencies  $\nu_1, \nu_2$  (table 4) have been assigned as asymmetric and symmetric stretching frequencies respectively. The  $NH_2$  group has scissoring, rocking, wagging and twisting modes of bending vibrations. The frequencies  $\nu_3, \nu_4, \nu_5$  have been assigned as scissoring, rocking and wagging modes. These assignments are within the

frequency range given by Varsanyi (1969, 1974) and find support from the works of Singh and Singh (1968, 1983).

### 3.5 Combinations and overtones bands

The moderately strong and weak bands at frequencies that could not reasonably be assigned to fundamentals may be combinations and overtones of normal modes, whose assignments have been made according to the direct product rule for the point groups  $C_s$  and  $C_{2v}$  for compound A and compound B respectively.

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### References

- Bentley F F and Wolforth E F 1959 *Spectrochim. Acta* **15** 165  
Jakobsen R L and Bentley F F 1964 *Appl. Spectrosc.* **18** 88  
Randle R R and Whiffen D H 1956 *Molecular spectroscopy* (London: Institute of Petroleum)  
Sharma S N and Dwivedi C P D 1976 *Indian J. Phys.* **50** 25  
Singh R N and Prasad S C 1978 *Spectrochim. Acta* **34** 39  
Singh S K and Singh R N 1983 *Indian J. Pure Appl. Phys.* **21** 744  
Singh S N and Singh N L 1969 *Indian J. Pure Appl. Phys.* **7** 250  
Singh V B and Singh I S 1968 *Indian J. Pure and Appl. Phys.* **6** 81  
Srivastava S L 1967 *Indian J. Pure Appl. Phys.* **5** 189  
Varsanyi G 1969 *Vibrational spectra of benzene derivatives* (New York: Academic Press)  
Varsanyi G 1974 *Assignment for vibrational spectra of seven hundred benzene derivatives* (London: Adam Hilger)  
Whiffen D H 1955 *Spectrochim. Acta* **7** 253