

# LASER RAMAN AND INFRARED ABSORPTION SPECTRA OF 2,4-DICHLORONITROBENZENE

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The laser Raman and infrared absorption spectra of 2,4-dichloronitrobenzene have been recorded in pure liquid state. The vibrational spectra have been analysed assuming  $C_s$  point group for the molecule. The assignments for fundamental vibrations, combination and overtone frequencies and internal modes of vibrations of  $\text{NO}_2$  group have been proposed.

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## 1. Introduction

The infrared spectral studies gained an unexpected momentum because of various reasons. A detailed assignment of the fundamental frequencies is useful for the characterisation and identification of the compounds and also for evaluating the force fields and thermodynamic functions of the molecules. The vibrational spectra of monohalogenonitrobenzenes have been studied by several workers [1-14]. Recently the studies on few dihalogenated nitrobenzenes have also been reported [15-16], but so far no work seems to have been done on vibrational spectra of pure liquid 2,4-dichloronitrobenzene. In the present investigation we report the IR and laser Raman spectra of 2,4-dichloronitrobenzene in liquid state. The observed bands have been analysed in terms of fundamentals, combination and difference frequencies. Probable modes of vibrations of the fundamental bands have been assigned.

## 2. Experimental

The spectrally pure 2,4-dichloronitrobenzene was purchased from M/S Aldrich Chemicals Co, USA in liquid form and was used without further purification. The infrared spectrum was recorded in the region of  $200\text{--}4600\text{ cm}^{-1}$  on Nicolet DX spectrophotometer with thin film specimen. The wavenumber scale was calibrated using the spectrum of a thin sheet of polystyrene. The Raman spectrum ( $50\text{--}3400\text{ cm}^{-1}$ ) was excited by the  $4880\text{ \AA}$  line of an argon ion laser of 100 mW power and was recorded on Jasco K 500 Raman spectrophotometer. The slit width at the entrance was  $380\text{ }\mu\text{m}$ , the time constant was 0.5 s, and the scanning speed was 5. Polarization measurements were made by recording the spectra at two perpendicular polarizations. The spectra are shown in Figs. 2-5.

## 3. Results and discussion

Figure 1 shows the structures of nitrobenzene and 2,4-dichloronitrobenzene with classical numbering of the atoms. The present molecule probably belongs to

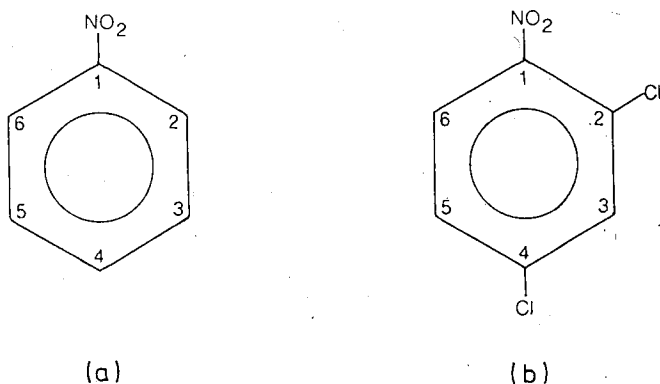


Fig. 1. Structures of benzene (a) and 2,4-dichloronitrobenzene (b).

the  $C_s$  point group as the  $\text{NO}_2$  group lies in the plane of the benzene ring. The 36 normal vibrations may be classified as 25  $a'$  (planar) and 11  $a''$  (non-planar) ones.  $a'$  vibrations are totally symmetric and give rise to polarized Raman lines, whereas  $a''$  vibrations are antisymmetric and give rise to depolarized Raman lines. The frequencies of the observed fundamental lines in IR and Raman spectra, their intensities and depolarization factor (in Raman spectrum) and assignments along with vibration numbers in Wilson's notation of the compound under consideration are given in Table I. The internal vibrations of  $\text{NO}_2$  group are listed in Table II. The combination and overtone bands for the same compound are listed in Table III.

TABLE I

Fundamental frequencies ( $\text{cm}^{-1}$ ) of 2,4-dichloronitrobenzene  
 (s = strong, vs = very strong, vvs = very very strong, m = medium,  
 w = weak,  $\nu$  = stretching,  $\beta$  and  $\delta$  = in-plane-bending,  
 $\gamma$  and  $\phi$  = out-of-plane bending).

	Symmetry	Wavenumber		Dep. ratio	Vib.No.	Assignments
		IR	Raman			
1	a'	3107(s)	-	-	2	$\nu$ (C-H)
2		-	3070(vs)	0.54	20a	$\nu$ (C-H)
3		3018(w)	-	-	7a	$\nu$ (C-H)
4		1574(vs)	1565(s)	0.48	8b	$\nu$ (C-C)
5		1542(vvs)	-	-	8a	$\nu$ (C-C)
6		1468(vs)	1462(w)	0.39	19b	$\nu$ (C-C)
7		1427(m)	-	-	19a	$\nu$ (C-C)
8		1311(m)	-	-	3	$\beta$ (C-H)
9		1267(w)	-	-	14	$\nu$ (C-C) Kekule Vib.
10		1159(s)	-	-	13	$\beta$ (C-NO <sub>2</sub> )
11		1134(vs)	1132(vs)	0.19	15	$\beta$ (C-H)
12		1100(s)	1105(w)	0.31	18b	$\beta$ (C-H)
13		1025(vw)	1035(m)	0.28	12	$\delta$ (C-C-C)
14		865(vs)	860(s)	0.20	1	$\nu$ (C-C) ring breath
15		591(m)	-	-	6b	$\delta$ (C-C-C)
16		444(w)	-	-	20b	$\nu$ (C-Cl)
17		430(w)	428(w)	0.31	7b	$\nu$ (C-Cl)
18		415(w)	410(m)	0.31	6a	$\delta$ (C-C-C)
19		360(w)	-	-	9b	$\beta$ (C-NO <sub>2</sub> )
20		338(w)	-	-	9a	$\beta$ (C-Cl)
21		310(vw)	305(m)	0.26	18a	$\beta$ (C-Cl)
22	a''	-	-	-	5	$\gamma$ (C-H)
23		800(s)	-	-	17b	$\gamma$ (C-H)
24		751(vs)	-	-	11	$\gamma$ (C-H)
25		675(m)	665(m)	-	4	$\phi$ (C-C-C)
26		387(w)	-	-	16a	$\phi$ (C-C-C)
27		302(m)	-	-	16b	$\phi$ (C-C-C)
28		284(m)	-	-	10a	$\gamma$ (C-NO <sub>2</sub> )
29		253(s)	250(w)	0.71	10b	$\gamma$ (C-Cl)
30		-	198(m)	0.71	17a	$\gamma$ (C-Cl)

TABLE II

Internal modes of vibration of the NO<sub>2</sub> group in  
2,4-dichloronitrobenzene.

	IR	Raman	
$\nu_1$	1525(vvs)	1525(w)	$\nu_{\text{asym}}(\text{NO}_2)$
$\nu_2$	1350(vs)	1340(vvs)	$\nu_{\text{sym}}(\text{NO}_2)$
$\nu_3$	836(vs)	-	$\nu_s(\text{NO}_2)$ scissoring
$\nu_4$	547(s)	-	$\nu_s(\text{NO}_2)$ rocking
$\nu_5$	693(w)	-	$\nu_{\text{asym}}(\text{NO}_2)$ wagging

TABLE III

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

226	=	1574 - 1350	=	224 (A')
272	=	1134 - 865	=	269 (A')
298	=	1134 - 836	=	298 (A')
1676	=	2 × 836	=	1672(A')
1711	=	1159 + 547	=	1706(A')
1729	=	2 × 865	=	1730(A')
1747	=	1159 + 591	=	1750(A')
1760	=	1468 + 284	=	1752(A'')
1808	=	1525 + 284	=	1809(A'')
1826	=	1574 + 253	=	1827(A'')
1867	=	1574 + 284	=	1858(A'')
1913	=	1159 + 751	=	1910(A'')
1953	=	1159 + 800	=	1959(A'')
2337	=	1525 + 800	=	2325(A'')
2520	=	1427 + 1100	=	2527(A')
2671	=	1574 + 1100	=	2674(A')
2773	=	1468 + 1311	=	2779(A')
2858	=	3107 - 253	=	2854(A'')
2929	=	1574 + 1350	=	2924(A')
3155	=	2 × 1574	=	3148(A')
3782	=	3107 + 675	=	3782(A'')
3897	=	3107 + 800	=	3907(A'')

Assignments for the observed frequencies have been made on the basis of intensity of IR bands and the nature of polarization of Raman bands.

### 3.1. Ring vibrations

In substituted benzenes, four bands are usually observed in the region of 1400–1650 cm<sup>-1</sup>. These bands arise from the degenerate e<sub>2g</sub>(1595 cm<sup>-1</sup>) and the e<sub>1u</sub>(1485 cm<sup>-1</sup>) C–C stretching vibrations of benzene, i.e. vibrations 8 and 19, according to Wilson's notation, respectively. The fundamental bands  $\nu_4$ – $\nu_7$  observed

at 1574, 1542, 1468 and 1427  $\text{cm}^{-1}$  in the IR spectrum of the present molecule have been assigned to these modes. In the Raman spectrum two polarized bands

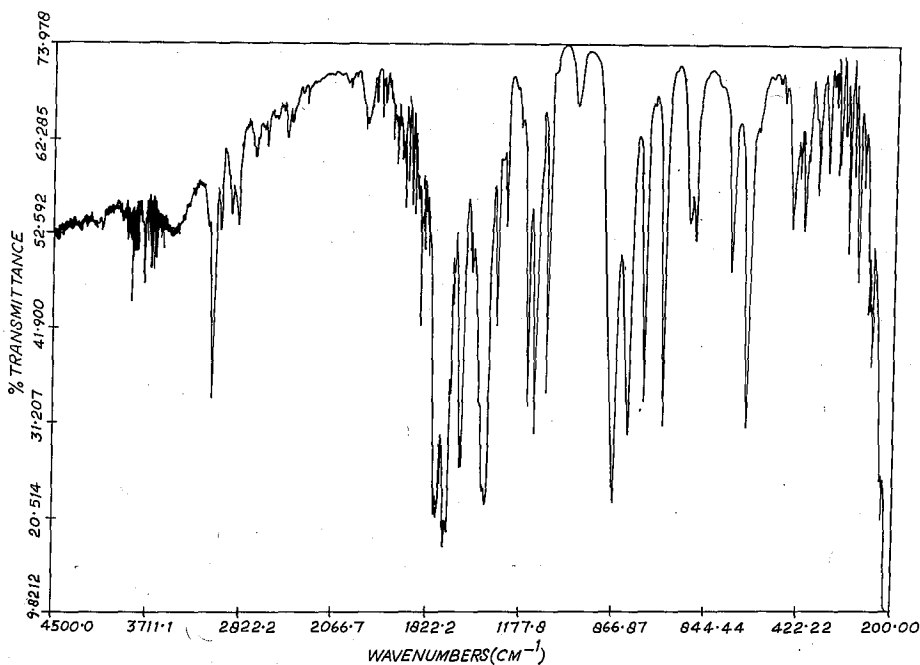


Fig. 2. Infrared spectra of 2,4-dichloronitrobenzene.

at 1565 and 1462  $\text{cm}^{-1}$  could be identified as C-C stretching vibrations  $\nu_4$  and  $\nu_6$ . The C-C vibration 14,  $b_{2u}$  (1310  $\text{cm}^{-1}$ ), known as the Kekule mode, occurs in the region of 1240–1290  $\text{cm}^{-1}$  in asymmetric vicinal trisubstituted benzenes [17]. This mode has been identified at 1267  $\text{cm}^{-1}$  in the present molecule. The frequency of the ring breathing vibration 1,  $a_{1g}$  (992  $\text{cm}^{-1}$ ) of benzene is quite reduced in the  $C_s$  symmetry due to the interaction with the closely lying  $b_{1u}$  (1010  $\text{cm}^{-1}$ ) vibration of benzene, since under  $C_s$  symmetry both these vibrations belong to the same symmetry type,  $a'$ . In the present case the ring breathing vibration has been identified at 865  $\text{cm}^{-1}$  in the IR spectrum. Corresponding to this mode of vibration a strong and polarized band at 860  $\text{cm}^{-1}$  has been observed in the Raman spectrum.

There are three modes associated with ring in-plane deformations which correspond to vibrations 12,  $b_{1u}$  (1010  $\text{cm}^{-1}$ ) and 6,  $e_{2g}$  (608  $\text{cm}^{-1}$ ) of benzene. The observed bands  $\nu_{15}$  and  $\nu_{18}$  have been assigned as corresponding to  $e_{2g}$  (608  $\text{cm}^{-1}$ ) mode of benzene. The third in-plane bending vibration is thought to remain virtually undisplaced at nearly 1010  $\text{cm}^{-1}$  and has been observed at 1025  $\text{cm}^{-1}$  in the IR spectrum. Corresponding to these vibrations only two bands at 410 and 1035  $\text{cm}^{-1}$  could be observed in the Raman spectrum and have been assigned

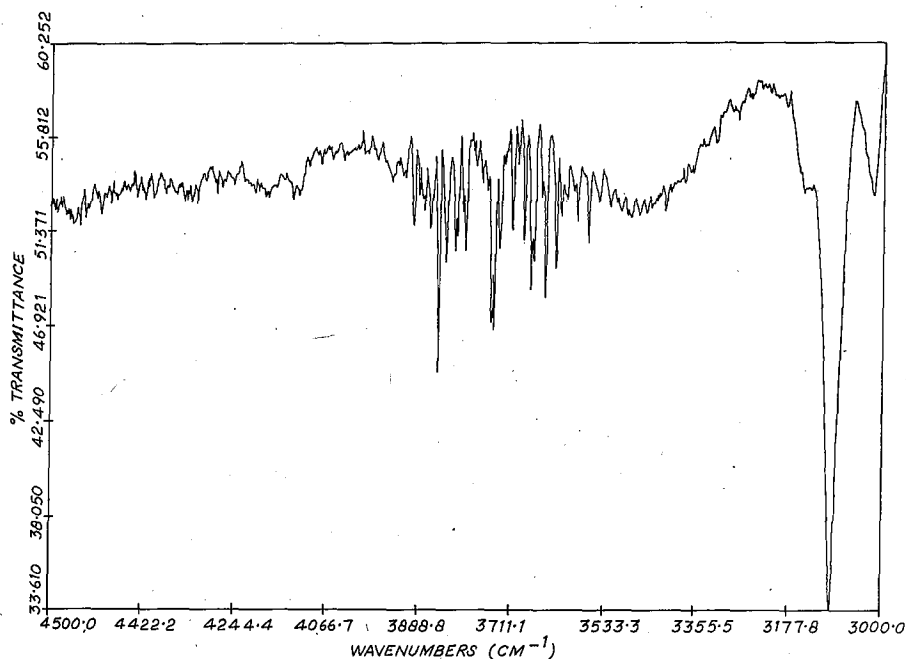


Fig. 3. Infrared spectra of 2,4-dichloronitrobenzene.

to the modes 6a and 12, respectively, of benzene. The ring out-of-plane bending vibrations in substituted benzenes owe their origin to the non-degenerate 4,  $b_{2g}$  ( $703\text{ cm}^{-1}$ ) and the degenerate 16,  $e_{2u}$  ( $404\text{ cm}^{-1}$ ) modes of benzene. The IR bands  $\nu_{25}$ ,  $\nu_{26}$  and  $\nu_{27}$  in the present molecule have been assigned to these three C-C out-of-plane bending vibrations. In the Raman spectrum only the non-degenerate mode 4 could be observed at  $665\text{ cm}^{-1}$ .

### 3.2. C-H and C-X vibrations

The C-H stretching frequencies in benzene derivatives arise from two non-degenerate  $a_{1g}$  ( $3073\text{ cm}^{-1}$ ) and  $b_{1u}$  ( $3060\text{ cm}^{-1}$ ) and two degenerate modes  $e_{2g}$  ( $3046\text{ cm}^{-1}$ ) and  $e_{1u}$  ( $3080\text{ cm}^{-1}$ ), i.e. vibrations 2, 13, 7 and 20, respectively. In trisubstituted benzenes, three of these modes would give rise to three C-H stretching frequencies which almost retain the frequencies of benzene and lie in the region of  $3000\text{--}3100\text{ cm}^{-1}$ , while the other three frequencies would depend on the mass and nature of substituents and decrease considerably below  $1200\text{ cm}^{-1}$  [18]. In the present investigation only two bands at  $3107$  and  $3018\text{ cm}^{-1}$  could be observed due to C-H stretching vibrations in the IR spectrum, whereas in the Raman spectrum, only one band was observed at  $3070\text{ cm}^{-1}$ . The substituent sensitive stretching vibrations have been identified at  $1159$ ,  $444$  and  $430\text{ cm}^{-1}$  in

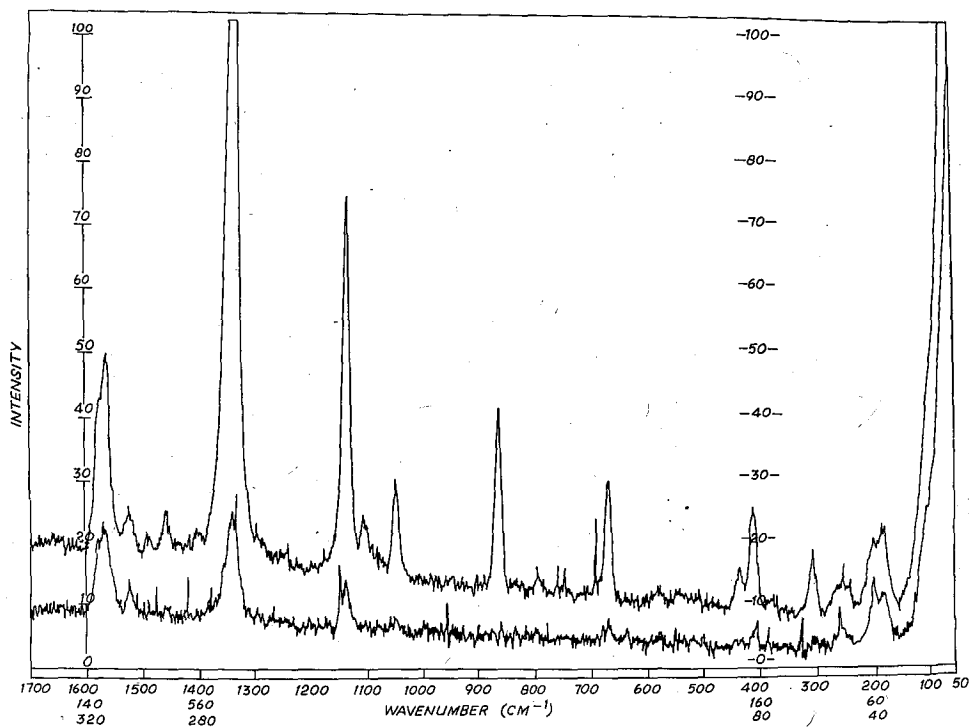


Fig. 4. Raman spectra of 2,4-dichloronitrobenzene.

the IR spectrum, whereas in the Raman spectrum only one of these vibrations has been observed at  $428\text{ cm}^{-1}$ .

There are two degenerate  $e_{2g}$  ( $1178\text{ cm}^{-1}$ ) and  $e_{1u}$  ( $1033\text{ cm}^{-1}$ ) and two non-degenerate  $b_{2u}$  ( $1150\text{ cm}^{-1}$ ) and  $a_{2g}$  ( $1326\text{ cm}^{-1}$ ) modes of vibrations, i.e. vibrations 9, 18, 15 and 3 in benzene, which involve C-H in-plane bending vibrations. In trisubstituted benzenes, these modes should give rise to three planar bending vibrations involving the substituents and three involving the three hydrogen atoms. In asymmetric trisubstitution, the normal modes 3, 15 and 18b are regarded as C-H in-plane bending vibrations and the normal modes 9a, 9b and 18a are regarded as C-X in-plane bending vibrations [17]. In the present molecule the observed fundamental frequencies  $\nu_8$ ,  $\nu_{11}$ ,  $\nu_{12}$  in the IR/Raman spectra have been assigned to C-H in-plane bending vibrations and  $\nu_{19}$ ,  $\nu_{20}$  and  $\nu_{21}$  to the C-X in-plane bending vibrations.

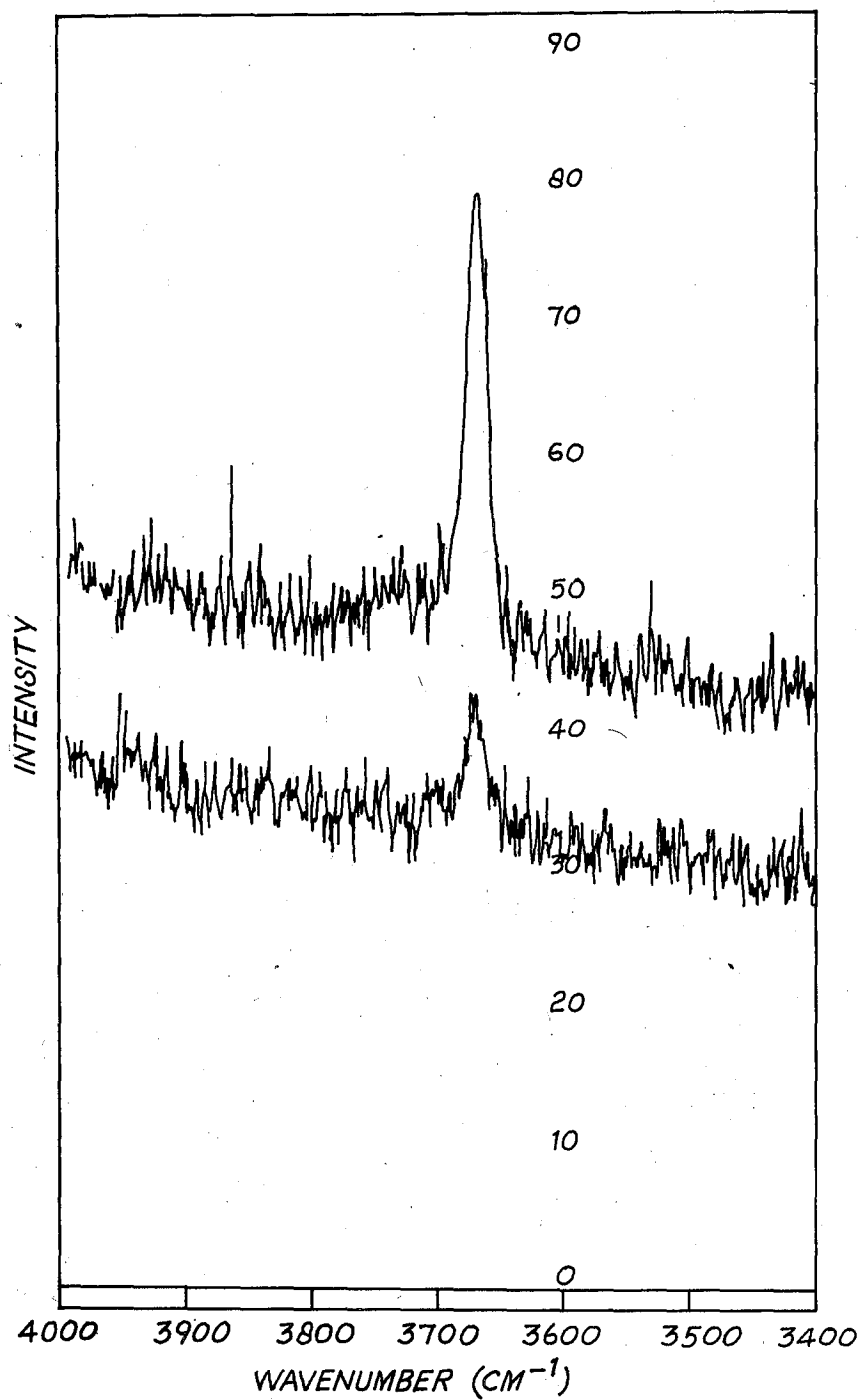


Fig. 5. Raman spectra of 2,4-dichloronitrobenzene.



The three  $\gamma(\text{C-H})$  and three  $\gamma(\text{C-X})$  modes of vibrations of trisubstituted derivatives are derived from the six (C-H) modes of benzene. The vibrational modes 5, 17b and 11 for compound under consideration correspond to (C-H) and the remaining three modes 17a, 10a and 10b correspond to (C-X) [17]. The IR frequencies  $\nu_{22}$ ,  $\nu_{23}$  and  $\nu_{24}$  have been identified as  $\gamma(\text{C-H})$  corresponding to the modes 5, 17b and 11, respectively. Frequencies below  $350\text{ cm}^{-1}$  are to be assigned as  $\gamma(\text{C-X})$ . The IR/Raman frequencies  $\nu_{28}$ ,  $\nu_{29}$  and  $\nu_{30}$  have been assigned as the three C-X out-of-plane bending vibrations 10a, 10b and 17a, respectively.

### 3.3. Internal vibrations of $\text{NO}_2$ group

The  $\text{NO}_2$  group has two stretching frequencies, one being symmetric and the other asymmetric. Randle and Whiffen [19] assigned the symmetric stretching frequency to a band lying between  $1333$  and  $1370\text{ cm}^{-1}$  and the antisymmetric frequency between  $1494$  and  $1539\text{ cm}^{-1}$  in the spectra of aromatic nitrobenzene derivatives. In the present case we have assigned the strong bands at  $1355$  and  $1525\text{ cm}^{-1}$  (Table II) to  $\text{NO}_2$  symmetric and asymmetric stretching vibrations, respectively, in accordance with the assignments made by Mooney [7], Kishore et al. [20] and Singh and Rai [21]. In the Raman spectrum the symmetric vibration has appeared very strongly at  $1340\text{ cm}^{-1}$  but asymmetric vibration has occurred weakly at  $1525\text{ cm}^{-1}$ . The bands observed at  $836$ ,  $693$  and  $547\text{ cm}^{-1}$  in the IR spectrum have been assigned to  $\text{NO}_2$  scissoring, wagging and rocking vibrations, respectively. These assignments find support from the work of Varsanyi et al. [22], Green and Harison [11] and Ahmad and Verma [8]. The band at  $180\text{ cm}^{-1}$  in the Raman spectrum may be the first overtone of  $\text{NO}_2$  torsion.

### 3.4. Combination and overtone bands

The moderately strong and weak bands at frequencies that could not be reasonably assigned to fundamentals, may be combinations and overtones of normal modes, whose assignments have been made in Table III according to the direct product rule for the point group  $C_s$ .

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