

INFRARED AND RAMAN STUDY OF PARA-  
CHLORONITROBENZENE

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Plate III

**ABSTRACT.** The infrared absorption spectrum in the 4000–630  $\text{cm}^{-1}$  region in the solid state at 26°C and in solution in carbon tetrachloride and the Raman spectrum in the liquid state at 90°C have been reported for *para*-chloronitrobenzene. A complete assignment of the observed frequencies is given.

## I N T R O D U C T I O N

In a previous paper (Medhi, 1964) the infrared and Raman spectra of the three isomers of fluoronitrobenzene were presented and a complete assignment of the vibrational frequencies given. In continuation of that work the investigation has been extended to *para*-chloronitrobenzene. The infrared spectrum of this compound was studied previously by Lecomte (1938) over the limited range 1400–500  $\text{cm}^{-1}$  and by Mooney (1964). Earlier works on the Raman spectrum of this molecule relate to those of High (1931), Manzoni-Ansidei (1935), Reitz and Stockmair (1936) and Wittek (1942), and only a partial assignment of some of the fundamentals is given in Landolt-Börnstein Table (1951).

In the present investigation a detailed study of the infrared and the Raman spectrum of *para*-chloronitrobenzene has been made. Several new Raman lines which were not detected by the earlier workers have been observed. Essentially complete vibrational assignments, based largely on comparison with those proposed for *para*-fluoronitrobenzene (Medhi, 1964) are given.

## E X P E R I M E N T A L

The pure sample of *para*-chloronitrobenzene was supplied by Riedel-de Haen A. G. It was purified by fractional distillation. The fractions boiling at 242°C were collected and distilled again under reduced pressure before use.

A Perkin-Elmer Model 21 spectrophotometer equipped with sodium chloride prism was used to record the infrared absorption spectrum in the region 4000–630  $\text{cm}^{-1}$ . The instrument was calibrated with the standard atmospheric water vapour and carbon dioxide bands. The spectrum was obtained using a thin polycrystalline film grown by melting the substance between two NaCl

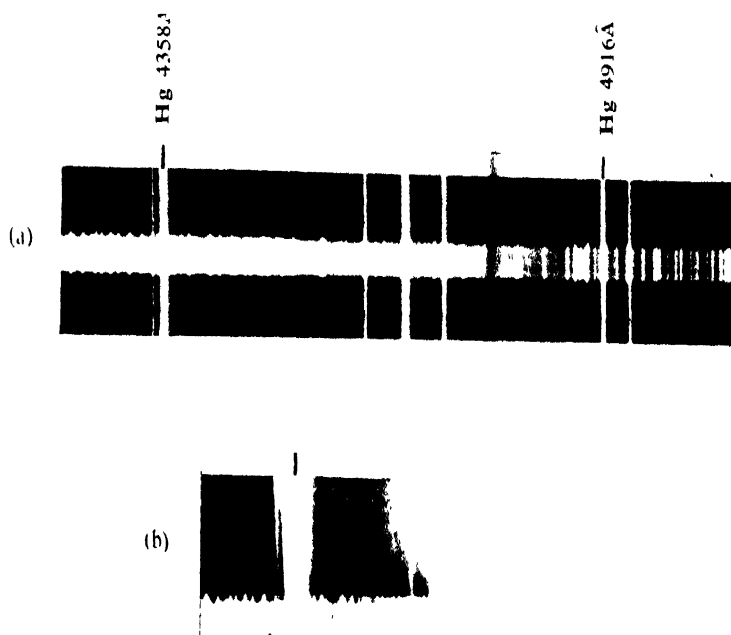


Fig. 2.—Raman Spectrum of Para-chloronitrobenzene.

(a) Short exposure.

(b) Long exposure.

plates and cooling the specimen slowly to room temperature. The infrared spectrum in the frequency region 3400-1600  $\text{cm}^{-1}$  was also measured in solution in carbon tetrachloride.

The Raman spectrum was recorded photographically using a Fuess glass spectrograph (dispersion 19 Å/mm in the 4358 Å region) in the liquid state at 90°C (i.e. at a temperature slightly above the melting point). The spectrum was excited by the Hg 4358 Å line. The compound being slightly yellowish in colour there is strong absorption in the region near 4358 Å. A fairly long exposure was necessary to record the low-lying Raman frequencies. The study of the polarisation of the Raman lines was also made by the method described elsewhere (Medhi, 1964).

RESULTS AND DISCUSSION

The observed infrared and Raman frequencies of para-chloronitrobenzene and their approximate intensities are given in Table I. The assignment of the fundamental frequencies is given in the fourth column of the table. Fig. 1 shows the infrared spectrum in the range 1800-630  $\text{cm}^{-1}$ . The Raman spectrum is reproduced in Fig. 2, Plate III.

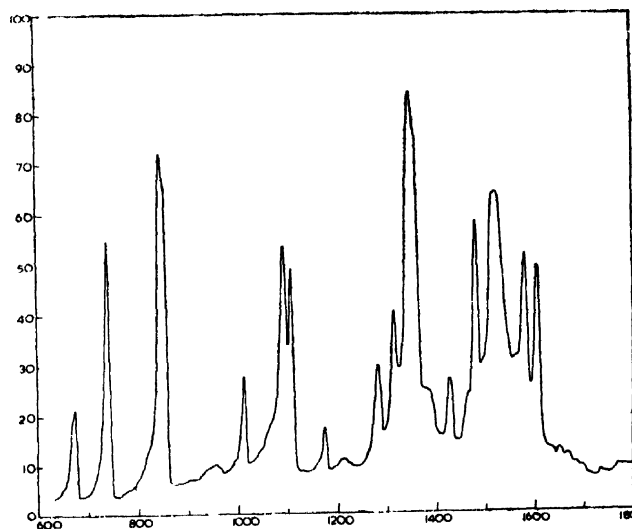


Fig. 1. Infrared spectrum of parachloronitrobenzene

The parachloronitrobenzene molecule is assumed to have  $C_{2v}$  symmetry. It should thus have thirty-six fundamental modes of vibration which are distributed over the four symmetry species as follows

In-plane vibrations

13  $a_1$  (infrared and Raman active) + 12  $b_1$  (infrared and Raman active).

Out-of-plane vibrations

TABLE I  
Infrared and Raman frequencies of *p*-chloronitrobenzene

Infrared, $\nu$ in cm <sup>-1</sup> . Solid at 26°C	Raman, $\Delta\nu$ in cm <sup>-1</sup> . Liquid at 90°C	Assignment		Remarks
		Species	Corresponding modes of benzene	
	212 (0b)	b <sub>2</sub>	16B	
	276 (2) dp	b <sub>2</sub>	11	
	314 (1)	a <sub>1</sub>	6A	
	367 (0) ?	b <sub>2</sub>	4	
	415 (0)	a <sub>2</sub>	16A	
	444 (0)	b <sub>1</sub>		NO <sub>2</sub> rocking
467†		b <sub>1</sub>	18B	
535†	530 (1)	b <sub>2</sub>		NO <sub>2</sub> out of plane rocking.
	569 (0)	b <sub>2</sub>	10B	
	597 (0)	b <sub>2</sub>	17B	
645 (sh)	623 (3) dp	b <sub>1</sub>	6B	
670 (sh)				
674 (m)	677 (0)	a <sub>1</sub>		NO <sub>2</sub> bending
740 (vs)	734 (2) dp	b <sub>1</sub> , a <sub>1</sub>	9B, 18A	
	790 (0)	b <sub>2</sub>	5	
820 (sh)	826 (0)			
846 (vs)		a <sub>1</sub>	12	
854 (vs)	855 (5) p	a <sub>1</sub> , a <sub>2</sub>	1, 10A	
935 (w)				
955 (w)	960 (1)			
1013 (m)	1015 (0)	a <sub>2</sub>	17A	
1045 (sh)				
1065 (sh)	1056 (2b) dp ?	b <sub>1</sub>	15	
1093 (s)	1095 (3) p	a <sub>1</sub>	19A	
1109 (s)	1110 (6) p	a <sub>1</sub>	2	
	1148 (0)			
1174 (w)	1174 (2) p	a <sub>1</sub>	9A	
1213 (vw)	1214 (0)			
1231 (vw)	1249 (0)			
1283 (m)	1290 (2)	b <sub>1</sub>	3	
1314 (m)		b <sub>1</sub>	14	
1347 (vs)	1347 (10) p	a <sub>1</sub>		NO <sub>2</sub> stretching
1355 (sh)				
1380 (sh)	1387 (2) dp			
1426 (m)	1426 (3) p	a <sub>1</sub>	20A	
1464 (sh)		a <sub>1</sub>	13	
1481 (vs)	1480 (3) p	a <sub>1</sub>	7A	
1514 (sh)		b <sub>1</sub>	19B	
1526 (vs)	1523 (3) dp	b <sub>1</sub>		NO <sub>2</sub> asymmetric stretching
1564 (vw)				

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TABLE I (contd.)

Infrared, $\nu$ in $\text{cm}^{-1}$ . Solid at $26^\circ\text{C}$	Raman, $\Delta\nu$ in $\text{cm}^{-1}$ . Liquid at $90^\circ\text{C}$	Assignment		Remarks
		Species	Corresponding modes of benzene	
1581 (s)	1577 (8) dp	$a_1$	8A	
1607 (s)	1605 (2) dp	$b_1$	8B	
1630 (w)				
1660 (w)*				
1690 (sh)*				
1705 (sh)*				
1730 (vww)*				
1780 (w)*				
1828 (vw)*				
1840 (vw)*				
1880 (sh)*				
1920 (w)*				
1974 (vw)*				
2030 (vww)*				
2090 (vww)*				
2135 (vww)				
2215 (sh)*				
2228 (vw)*				
2291 (w)*				
2454 (w)*				
2570 (sh)*				
2595 (vw)*				
2630 (vww)*				
2690 (vw)*				
2757 (vw)*				
2855 (w)*				
2930 (vw)*				
3050 (sh)*		$b_1$	7B	
3085 (sh)*	3087 (3) p			
3110 (m)*		$b_1$	20B	
3157 (sh)*				
3205 (sh)*				
3300 (sh)*				
3580 (vww)*				
3665 (sh)*				
3690 (vww)*				
3718 (sh)*				
3825 (vww)*				
3920 (vww)*				

(s)=strong; (m)=medium; (w)=weak; (vw)=very weak (sh)=shoulder; (b)=broad; p=polarised; dp=depolarised.

†Taken from Mooney (1964).

\*Frequency observed in  $\text{CCl}_4$  solution.

4  $a_2$ (Raman active) | 7 $b_2$  (infrared and Raman active).

The species  $a_1$  would give rise to polarised Raman lines and the remaining species to depolarised Raman lines

*Species  $a_1$*  The eleven  $a_1$  modes taking  $\text{NO}_2$  as a single group are derived from the modes 1, 2, 6A, 7A, 8A, 9A, 12, 13, 18A, 19A and 20A of benzene (Wilson, 1934). In the disubstituted benzenes with the substituents in the para positions, the frequencies of the Modes 1, 6A, 7A, 8A, 12, 13, 18A, 19A and 20A are expected to be lowered considerably due to the presence of the heavy atoms in the para positions. The probable values of the frequencies which can be assigned to these modes are shown in the last but one column of Table I. The intense polarised Raman line  $855 \text{ cm}^{-1}$  has been assigned to  $\nu_1$ . Its appearance also as a strong infrared band may be due to the difference in the two substituents. The polarised line  $1480 \text{ cm}^{-1}$  is assigned to  $\nu_{7A}$  and the strong infrared band at  $1481 \text{ cm}^{-1}$  may be due to superposition of the bands due to modes  $\nu_{7A}$  and  $\nu_{10B}$ . The other polarised line  $1426 \text{ cm}^{-1}$  is assigned to  $\nu_{20A}$  and the infrared frequency  $1964 \text{ cm}^{-1}$  may be due to  $\nu_{13}$ . The intense depolarised Raman line  $1577 \text{ cm}^{-1}$  is evidently due to  $\nu_{8A}$  and the weak line  $314 \text{ cm}^{-1}$  is due to  $\nu_{6A}$ , as suggested by Mocke-Korkhof (1951). The strong polarised line  $1110 \text{ cm}^{-1}$  is assigned to  $\nu_2$  and the polarised Raman line  $1174 \text{ cm}^{-1}$  to  $\nu_{9A}$ , because this latter mode is not affected by the substitution in the para position. The strong infrared band at  $846 \text{ cm}^{-1}$  is assigned to  $\nu_{12}$  and it may have also appeared feebly as a weak unresolved companion of the line  $855 \text{ cm}^{-1}$  in the Raman spectrum. The strong infrared band at  $740 \text{ cm}^{-1}$  may be due to  $\nu_{18A}$  and the polarised line  $1095 \text{ cm}^{-1}$  is probably due to  $\nu_{19A}$  as suggested by Mocke-Kherkhof (1951). The other two modes of this species are the symmetric stretching and bending vibrations of  $\text{NO}_2$  group giving the Raman lines  $1347 \text{ cm}^{-1}$  and  $677 \text{ cm}^{-1}$  respectively.

*Species  $b_1$* . Out of the twelve modes of this species ten are derived from the modes 3, 6B, 7B, 8B, 9B, 14, 15, 18B, 19B and 20B of benzene respectively and the remaining two are contributed by the  $\text{NO}_2$  group. The frequencies of the modes 6B, 8B, 7B and 20B remain unchanged on substitution. So, the Raman lines  $623$  and  $1605 \text{ cm}^{-1}$  are assigned to  $\nu_{6B}$  and  $\nu_{8B}$  respectively and the infrared bands at  $3110 \text{ cm}^{-1}$  and  $3050 \text{ cm}^{-1}$  are assigned to the modes  $\nu_{20B}$  and  $\nu_{7B}$  respectively. The Raman line  $1290 \text{ cm}^{-1}$  may be due to  $\nu_3$ . The Raman line at  $3087 \text{ cm}^{-1}$  may be due to one of the two modes which can be derived from a superposition of  $\nu_2$  and  $\nu_{8B}$ . The depolarised Raman line  $734 \text{ cm}^{-1}$  is assigned to  $\nu_{9B}$  and the weak band at  $467 \text{ cm}^{-1}$  to  $\nu_{18B}$ . As mentioned earlier, the infrared band at  $1481 \text{ cm}^{-1}$  is due to  $\nu_{10B}$ . The infrared bands at  $1314 \text{ cm}^{-1}$  and  $1056 \text{ cm}^{-1}$  may be assigned tentatively to  $\nu_{14}$  and  $\nu_{15}$  respectively, as the destruction of centre of symmetry makes these modes weakly allowed in the infrared. The remaining two modes of this species are due to the asymmetric

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stretching and rocking vibrations of the  $\text{NO}_2$  group giving the depolarised line  $1523\text{ cm}^{-1}$  and the weak line  $444\text{ cm}^{-1}$  respectively.

*Species  $a_2$ .* There are three vibrations of this molecule belonging to species  $a_2$  corresponding to the modes  $\nu_{10A}$ ,  $\nu_{16A}$  and  $\nu_{17A}$  of benzene. The frequency of  $\nu_{10A}$  should be  $849\text{ cm}^{-1}$  as benzene gives a Raman line of this frequency but it is not possible to resolve this line from the strong line at  $855\text{ cm}^{-1}$ . The line  $415\text{ cm}^{-1}$  is given by the mode  $\nu_{16A}$  and probably the weak line  $1015\text{ cm}^{-1}$  is due to  $\nu_{17A}$ , the corresponding infrared band  $1013\text{ cm}^{-1}$  being of medium strength. The fourth vibration arises from  $\text{NO}_2$  twisting which has not appeared in the spectra.

*Species  $b_2$ .* Six modes of this species arise from the modes  $\nu_1$ ,  $\nu_5$ ,  $\nu_{10B}$ ,  $\nu_{11}$ ,  $\nu_{16B}$  and  $\nu_{17B}$  of benzene. All these modes are expected to have frequencies lower than the corresponding frequencies of benzene. The Raman lines  $212$ ,  $276$  and  $367\text{ cm}^{-1}$  can be assigned to  $\nu_{16B}$ ,  $\nu_{11}$  and  $\nu_1$  respectively. The Raman lines  $569$  and  $597\text{ cm}^{-1}$  may be assigned to  $\nu_{10B}$  and  $\nu_{17B}$  respectively and the line  $790\text{ cm}^{-1}$  may be due to  $\nu_5$ . The seventh vibration arises from  $\text{NO}_2$  out of plane rocking and is assigned to the frequency  $530\text{ cm}^{-1}$  appearing both in the Raman and infrared spectra.

Besides the frequencies mentioned above numerous bands, mostly very weak have been observed in the infrared spectrum of the solution in the region from  $1630\text{ cm}^{-1}$  to  $3920\text{ cm}^{-1}$ . The bands are evidently due to combinations of some of the fundamental modes mentioned above.

### ACKNOWLEDGMENT

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### REFERENCES

- High, M. E., 1931, *Phys. Rev.*, **38**, 1837.
- Lecomte, J., 1938, *J. Phys. Radium* **9**, 13.
- Manzoni-Ansidei, R., 1935, *Gazz. Chim. Ital.*, **65**, 871.
- Moock-Korkhof, 1951, Landolt-Bornstein Tables, Auflage 6, Band I.
- Medhi, K. C., 1964, *Spectrochim. Acta.*, **20**, 675.
- Moonoy, E. F., 1964, *Spectrochim. Acta.*, **20**, 1021.
- Reitz, A. W. and Stockmar, 1936, *Monatsh. Chem.*, **67**, 92.
- Wilson, E. B., 1934, *Phys. Rev.*, **45**, 706.
- Witteck, H., 1942, *Z. Physik. Chem. B* **52**, 153, 315.