

RAMAN AND INFRARED SPECTRA OF 1-FLUORO-
2, 4-DINITROBENZENE AND 1-CHLORO-
2, 4-DINITROBENZENE*

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Plate XIII

ABSTRACT. The Raman and infrared spectra of 1-fluoro-2,4-dinitrobenzene and 1-chloro-2,4-dinitrobenzene have been investigated and the observed frequencies have been assigned to different modes of vibration of the ring, by assuming C_2 symmetry for the molecules. Some of the vibrational frequencies due to vibrations within the NO_2 group have also been identified. It is observed that some of the modes of the skeleton C-C ring which are forbidden in infrared and *vice versa* in the case of benzene, appear in the spectra and it is concluded that the symmetry of the skeleton ring is disturbed by the substituents.

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

The assignment of vibrational frequencies of some trisubstituted benzene compounds was made recently by Deb and Banerjee (1960) by studying the Raman and infrared spectra of the compounds. Such assignment was not made by any previous worker in the case of 1-fluoro-2, 4-dinitrobenzene and 1-chloro-2, 4-dinitrobenzene. In fact, the infrared spectra of these two compounds and the Raman spectra of the fluoro compound were not known. The present investigation was undertaken to study the infrared spectra of these two compounds and the Raman spectrum of 1-fluoro-2, 4-dinitrobenzene and to identify the frequencies of different modes of vibration of the molecules. The fluorine and chlorine substituted compounds have been chosen, because by comparing the spectra it might be possible to get some results which would help accurate assignment of the frequencies.

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

The compounds supplied by E. Merck were of guaranteed reagent quality. The liquid 1-fluoro-2, 4-dinitrobenzene was distilled under reduced pressure before use while the chloro compound was purified by crystallization from benzene. The infrared spectra were recorded with a Perkin Elmer Model 21 spectrophotometer with rocksalt optics, the resolution dial being set at 927. The absorption

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spectra of very thin films of the substances enclosed between NaCl plates were recorded. In the case of 1-chloro-2,4-dinitrobenzene the molten compound was poured on a hot NaCl plate and a similar hot plate was placed on it so that a thin film of the pure substance was enclosed between the plates. The spectrum of the solidified film was recorded. The Raman spectra of both the compounds were recorded on Ilford Zenith plates using a Fuess Glass Spectrograph of large dispersion. Iron arc spectrum was also photographed on the plate for

TABLE I.

Raman and infrared frequencies of 1-fluoro-2,4-dinitrobenzene

Infrared bands ν in cm^{-1} & strength	Raman shift (cm^{-1}) & Intensity	Assignment
	164 (2b)	a" fundamental
	300 (0)	a' "
	513 (1b)	a' "
630 (w)	634 (3)	
672 (w)		a" "
706 (s)		a' "
743 (s)	742 (1b)	a" "
813 (w)	811 (1)	a" "
840 (vs)	835 (3)	a' "
917 (s)	925 (2)	a" "
973 (wb)		
1008 (vwb)		
1072 (s)	1070 (2)	a' "
1129 (ms)	1129 (1)	a' "
1153 (w)	1151 (5)	a' "
1244 (m)	1241 (2)	a' "
1272 (vs)	1269 (6)	a' "
	1296 (0)	
	1323 (2)	a' "
1347 (vs)	1346 (10)	a' "
1418 (ms)	1415 (3)	a' "
1490 (s)	1490 (2)	a' "
1525 (vs)		a' "
1551 (s)	1546 (6)	a' "
1606 (vs)	1616 (5)	a' "
1805 (w)		743 + 1072
1939 (w)		[706 + 1244 813 + 1129]
2082 (w)		917 + 1153 840 + 1244]
2877 (w)		1272 + 1606 1347 + 1525]
2962 (w)		1551 + 1418
3100 (s)	3102 (2b)	a' fundamental

TABLE II
Raman and infrared frequencies of 1-chloro-2,4-dinitrobenzene.

Infrared bands ν in cm^{-1} & strength	Raman shifts (cm^{-1}) & intensity (Harrand, 1953)	Assignment
	152 (1b)*	a'' fundamental
	205 (0)*	a' "
658 (w)	666 (1)	a'' "
687 (m)		a' "
730 (s)		a' "
745 (m)		a'' "
832 (ms)		a'' "
847 (m)	841 (1)	a' "
900 (s)		a'' "
912 (m)		
980 (vw)		
1040 (s)	1050 (1)	a' "
1080 (vwh)		
1099 (vw)	1109 (1)	a' "
1138 (m)		a' "
1151 (m)	1160 (2)	a' "
1210 (vw)		
1247 (w)	1255 (1)	a' "
1302 (wh)	1301 (2)	a' "
1346 (vs)	1358 (10)	a' "
	1396 (1)	
1421 (mh)		a' "
1459 (m)		a' "
	1472 (0)	
	1494 (0)	
1525 (vs)	1538-50 (1b)	a' "
1550 (s)		
1590 (vs)	1593 (3)	a' "
	1628 ?	
1698 (vw)		658 + 1040
1742 (vwh)		832 + 900
1785 (vw)		745 + 1040
1820 (vwh)		2 \times 900
1967 (w)		832 + 1138
2873 (wh)		1421 + 1459
3053 (w)		1459 + 1590
3100 (s)		a' fundamental

*Observed in the reinvestigated Raman spectrum by the present author.

comparison. The Hg line 4358 Å was first used to excite the Raman spectra but it was found that in the case of 1-chloro-2, 4-dinitrobenzene the absorption in the neighbourhood of the 4358 Å line was very strong and no line with Raman shift less than 666 cm^{-1} was observed. Hence the Hg line 5461 Å was used as the exciting line and Agfa Isopan plates were used to photograph the spectra.

RESULTS AND DISCUSSION

The spectrograms showing Raman lines of 1-fluoro-2, 4-dinitrobenzene and 1-chloro-2, 4-dinitrobenzene are given in Figs. 1 and 2, Plate XIII and the infrared absorption curves are reproduced in Figs. 3(a) & (b) and 4(a) & (b). The

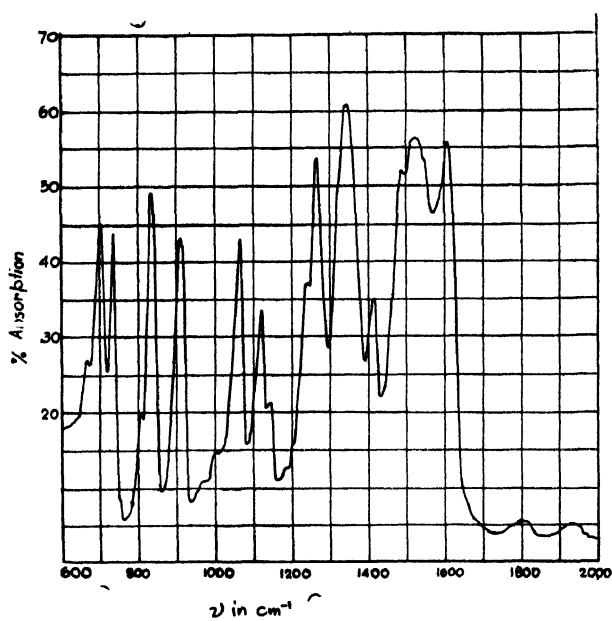


Fig. 3(a). Infrared spectrum of 1-fluoro-2,4 dinitrobenzene (liquid at 26°C)

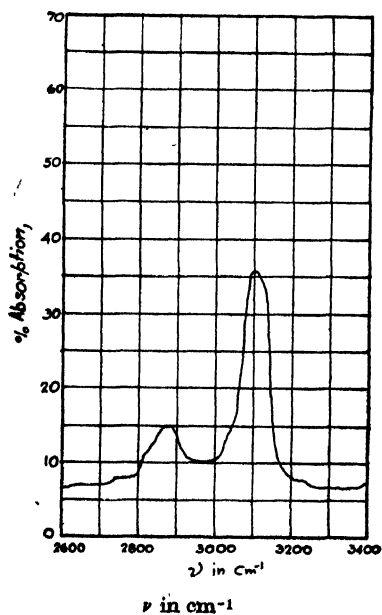


Fig. 3(b). Infrared spectrum of 1-fluoro-2,4 dinitrobenzene (liquid at 26°C)



Fig. 1. Raman spectrum of 1-fluoro-2,4-dinitrobenzene (liquid at 30°C).

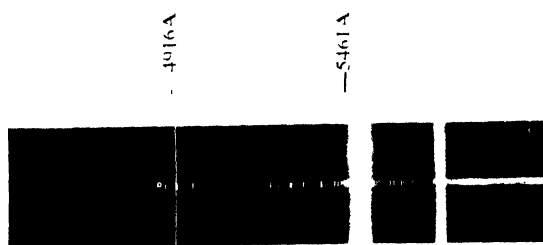


Fig. 2. Raman spectrum of 1-chloro-2,4-dinitrobenzene (solid at 30°C).

Raman shifts of the two substances and the infrared frequencies are given in Tables I and II respectively. The Raman frequencies of 1-chloro-2, 4-dinitrobenzene reported by Harrand (1953) have also been included in Table II. Tentative assignments of the lines are given in the third column of Tables I and II. The numbering of the modes of the vibrations has been made following that for the benzene ring made by Pitzer and Scott (1943).

The molecules of both the compounds belong to C_2 point group, if the NO_2 group lies in the plane of the molecule. There are four modes of types a_{1g} , b_{1u} , e^+_g and e^-_u in the benzene molecule giving rise to a' type C—H valence oscillations in these two molecules. The infrared frequency 3100 cm^{-1} observed in the case of both the compounds represent such a' -type C—H vibrational frequency and they may be identified with e^-_u mode in benzene (Mode No. 20) in which the two diametrically opposite C—H vibrate in opposite phases against the ring, the other substituents remaining almost stationary.

In the spectrum of 1-fluoro, 2, 4-dinitrobenzene a characteristic frequency 1272 cm^{-1} is observed while in the spectrum of 1-chloro-2, 4-dinitrobenzene there is a characteristic frequency 730 cm^{-1} . These two frequencies approximate to C—F and C—Cl vibrational frequencies respectively and they are to be assigned to a' -type mode arising from e^-_u type C—H stretching mode in benzene discussed above.

The degenerate e^+_g mode of C—C vibration of frequency 1596 cm^{-1} (No. 8A, B) in benzene will split up into two components with reduction of symmetry to C_2 , one of the components being slightly reduced in frequency and the other remaining almost unaffected. These two components have been identified with the strong infrared bands 1606 and 1551 cm^{-1} of 1-fluoro-2, 4-dinitrobenzene and 1590 and 1550 cm^{-1} of 1-chloro-2, 4-dinitrobenzene. The e^-_u mode (No. 19A, B) in benzene similarly becomes a' -type vibration giving rise to the frequencies 1490 and 1418 cm^{-1} of 1-fluoro-2, 4-dinitrobenzene and 1459 and 1421 cm^{-1} of 1-chloro-2, 4-dinitrobenzene. These assignments are in agreement with those proposed for other 1, 2, 4-trisubstituted benzenes (Plyler *et al.*, 1957, Deb and Banerjee, 1960). These lines appear strongly in the Raman effect owing to the lack of centre of symmetry. The Raman frequency 513 cm^{-1} of 1-fluoro-2, 4-dinitrobenzene might be a component of the e^+_g vibration of benzene (No. 6A, B), which splits up into two frequencies with lowering of symmetry, the other component having a still lower frequency may be identified with the Raman line 300 cm^{-1} . This mode may give the Raman line 205 cm^{-1} in the 1-chloro compound, the other component being too weak to be recorded.

The a' -components of in-plane CH bending modes of the two molecules may be derived from similar modes a_{2g} (No. 3), b_{2u} (No. 15), e^+_g (No. 9) and e^-_u (No. 18) of benzene. Superposition of modes a_{2g} and e^+_g of benzene may give rise to the mode of frequency 1244 cm^{-1} and 1247 cm^{-1} in the fluoro and chloro com-

pound respectively. Similar superposition of modes e^-_u and e^+_g , may give rise to the frequencies 1153 and 1151 cm^{-1} in the two compounds. The frequencies 1129 and 1138 cm^{-1} of the two respective compounds may be similarly produced by the interaction of b_{2u} and e^-_u modes of benzene. The observed frequencies 706

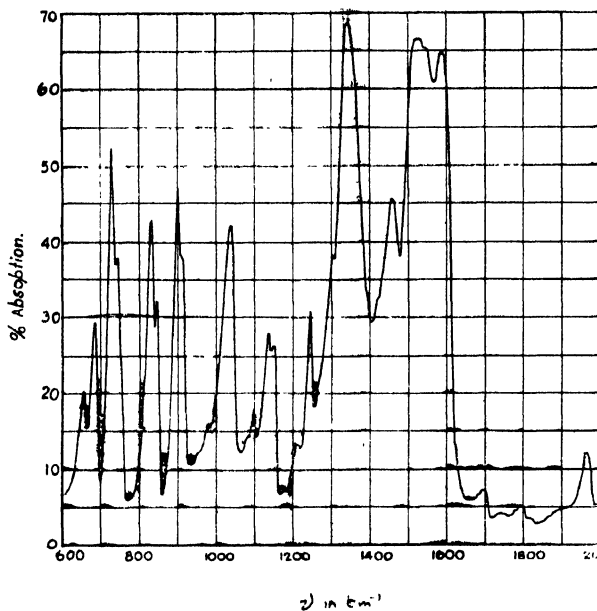


Fig. 4(a). Infrared spectrum of 1-chloro-2,4-dinitrobenzene (solid at 26°C).

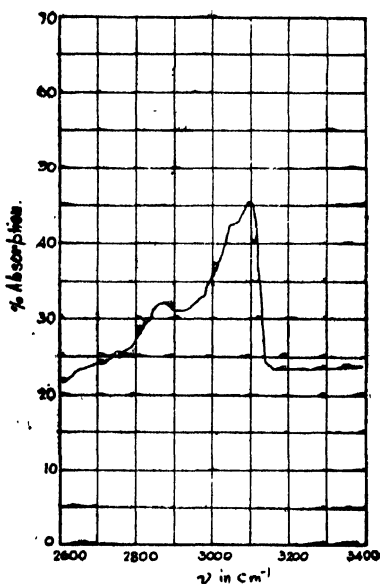


Fig. 4(b). Infrared spectrum of 1-chloro-2,4-dinitrobenzene (solid at 26°C).

and 1072 cm^{-1} in the case of the fluoro compound and 687 and 1040 cm^{-1} in the case of the chloro compound may represent components of the modes e^-_g and e^+_g .

The four out-of-plane CH bending modes of benzene (e^-_g , a_{2u} , e^+_u and b_{2g}) give such bending modes of type a'' in the case of these molecules assumed to belong to C_s point group. Superposition of modes b_{2g} (No. 5) and e^-_g (No. 10B) may give rise to a mode in which only the two diametrically opposite C—H bonds undergo out of plane bending. This frequency may be 917 cm^{-1} which appears both in Raman and infrared spectra of 1-fluoro-2, 4-dinitrobenzene (900 cm^{-1} in 1-chloro-2, 4-dinitrobenzene). The modes No. 10A and 17A of types e^-_g and e^-_u of benzene may similarly interact to produce frequencies 813 and 832 cm^{-1} observed in the spectra of the two compounds.

Norman Jones and Sandorfy (1956) discussed the occurrence of a C—H bending vibrational frequency at about 745 cm^{-1} in the case of 1, 2, 4-trisubstituted benzenes which is, according to them, known to be active only in Raman effect, but it should be noted that in the present work a strong frequency at 743 cm^{-1} in the case of 1-fluoro-2, 4-dinitrobenzene and a similar frequency at 745 cm^{-1} in the case of 1-chloro-2, 4-dinitrobenzene have been observed in the infrared. This can be obtained from superposition of the modes e^+_u (No 17A) and a_{2u} (No. 11).

The frequencies 672 and 658 cm^{-1} observed in 1-fluoro-2, 4-dinitrobenzene and 1-chloro-2, 4-dinitrobenzene respectively represent out-of-plane carbon bending vibration corresponding to the b_{2g} mode in benzene (No.4) which is expected to remain unaltered with substitution. The Raman frequency at 164 cm^{-1} observed in the case of the fluoro compound and 152 cm^{-1} in the case of the chloro compound may represent another such out-of-plane bending mode derived from e^+_u mode in benzene (No.16).

In the case of 1-fluoro-2, 4-dinitrobenzene and 1-chloro-2, 4-dinitrobenzene, frequencies at 840 and 847 cm^{-1} respectively have been observed. Similar frequencies were also observed in the spectra of 2, 4- and 3, 4-dichlorotoluene and 1, 2, 4-trichlorobenzene (Deb and Banerjee, 1960). As suggested in a previous paper (Deb and Banerjee, 1960) these frequencies may originate from superposition of a_{1g} and b_{1u} modes (No. 1 and 12) in benzene. The frequencies 1323 cm^{-1} of 1-fluoro-2, 4-dinitrobenzene and 1302 cm^{-1} of 1-chloro-2, 4-dinitrobenzene may be a component of the e^+_g mode of benzene.

Besides these molecular frequencies, the spectra of both the compounds should contain frequencies due to vibration in the NO_2 groups. The results for fluoronitro- and chloronitrobenzenes obtained by previous workers have been tabulated in Landolt-Börnstein's Tables (1951). On comparing these results the frequencies 1525 and 1347 cm^{-1} of 1-fluoro-2, 4-dinitrobenzene and 1525 and 1346 cm^{-1} of 1-chloro-2, 4-dinitrobenzene can be readily identified with asymmetric and symmetric stretching vibration in NO_2 groups.

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