150. *Perfluoroalkyl Compounds of Nitrogen. Part III.* The Vibrational Assignment of Fluoropicrin, Chloropicrin, and Bromopicrin.*

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The infrared spectrum of gaseous fluoropicrin has been examined in the region 3000—420 cm.$^{-1}$. Ten of the observed bands have been assigned to twelve fundamental modes, two further modes have been assigned to a frequency beyond the range of this investigation on the evidence of combination bands and overtones, and the frequency of the infrared forbidden CN torsional vibration has been inferred from overtone evidence.

These assignments are supported by correlation of the fundamental frequencies of the molecules $CX_3{\cdot}NO_2$, where X is H, D, F, Cl, Br. The infrared spectra of liquid and gaseous chloropicrin and bromopicrin have been observed in the region 1800—450 cm.$^{-1}$, and some corrections have been made to previous assignments.

THE preparation of fluoropicrin has been described in Part I of this series.[1] Infrared spectra were taken at various gas pressures in a 10 cm. cell with a Hilger D 209 spectrometer (single beam), or with a 12C single-beam Perkin-Elmer recording spectrophotometer, with fluorite, rock-salt, and potassium bromide prisms. The gas cell was heated electrically for the spectra of chloropicrin and bromopicrin in the vapour state, and for liquid-phase spectra a sandwich cell was used.

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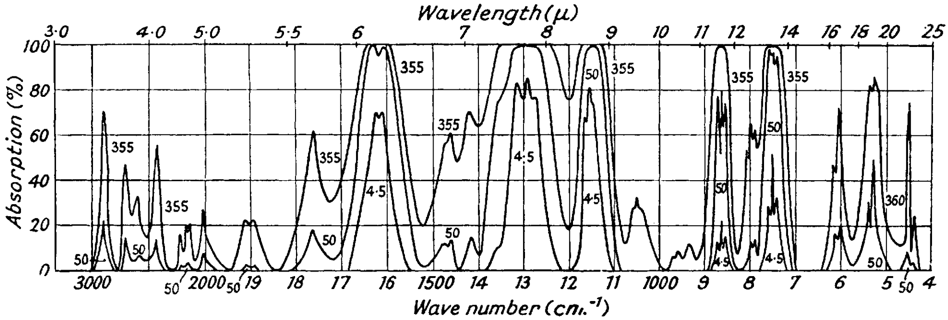
* Part II, preceding paper.

[1] Banus, *J.*, 1953, 3755.

Assigment of the Vibrational Frequencies of Fluoropicrin.—Molecules of the type $CX_3 \cdot NO_2$, *e.g.*, halogenopicrins, have effectively the symmetry of the C_{2v} point group, *i.e.*, the symmetry of the NO_2 group, as shown by Wells and Wilson [2] for nitromethane. The fifteen fundamental modes are distributed between the four symmetry classes A_1, A_2, B_1, and B_2, and all should be Raman active. With the exception of the CN torsional vibration, the sole member of the symmetry class A_2, all the fundamental modes are also allowed in the infrared spectrum.

However, fourteen distinct fundamental frequencies will not necessarily be observed, since the interaction between the CF_3 group and the less symmetrical NO_2 group may not be sufficient to split the frequencies corresponding to the degenerate CF_3 modes [cf. the CH unsymmetrical stretching vibrations in nitromethane [2,3] and the A' CF deformation vibrations in $CF_3 \cdot NO$ (Part II)].

FIG. 1. *Infrared spectrum of fluoropicrin.*



Numerals are gas pressures (mm.).

The frequencies observed (Fig. 1) for gaseous fluoropicrin, $CF_3 \cdot NO_2$, in the region 3000—420 cm.$^{-1}$ are listed in Table 1, together with an approximate description of the bands, and their assignment. A spectrum of fluoropicrin was published by Jander and Haszeldine [5] after the present results were obtained. There is general agreement between this spectrum, which covered only the NaCl region, and ours, except that weak bands observed at *ca.* 1000 and 1500 cm.$^{-1}$ were not found by us, and we observed additional weak bands at 936, 961, and 969 cm.$^{-1}$.

If the following molecular dimensions are assumed: [6] CF 1·33 Å; ∠FCF 108° 30′; CN 1·44 Å; NO 1·21 Å; ∠ONO 127°, then the moments of inertia are 209×10^{-40}, 303×10^{-40}, and 366×10^{-40} g. cm.^{2}. The axis of smallest moment of inertia is coincident with the CN bond, and the axis of intermediate moment lies in the plane of the NO_2 group irrespective of the position of the oxygen relatively to the fluorine atoms. The values of Badger and Zumwalt's symmetry factors [7] ρ and S are 0·62 and —0·45 respectively. The values calculated from these for the separation of the P and the R branch maxima for each of the contour types A, B, and C, are given, together with the observed values, in Table 2.

Three of the class A_1 bands, those centred at 863, 751, and 1154 cm.$^{-1}$, are readily recognised from their type A contour. Of these, the second and third can immediately be assigned as they are close to the frequencies suggested by Edgell and May,[8] namely, 700 and 1100 cm.$^{-1}$, for the "natural" CF symmetrical deformation and stretching vibration respectively. Similarly, the frequencies of the NO_2 symmetrical stretching and deformation modes are well established,[3,9] and the bands centred at 1315 and 604 cm.$^{-1}$

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[2] Wells and E. B. Wilson, *J. Chem. Phys.*, 1941, **9**, 314.
[3] Smith, Pan, and Nielson, *J. Chem. Phys.*, 1950, **18**, 706.
[4] Mason and Dunderdale, preceding paper.
[5] Jander and Haszeldine, *J.*, 1954, 912.
[6] (CF and ∠FCF) Bowen, *Trans. Faraday Soc.*, 1954, **50**, 444; (others) ref. 3.
[7] Badger and Zumwalt, *J. Chem. Phys.*, 1938, **6**, 711.
[8] Edgell and May, *ibid.*, 1954, **22**, 1808.
[9] Wittek, *Z. phys. Chem.*, 1942, **51**, *B*, (*a*) 103, (*b*) 187.

TABLE 1. *Description and assignment of* $CF_3·NO_2$ *spectrum.*

Band (cm.$^{-1}$) *		Assignment	
220 †		CN torsion	$[A_2]$
400 †		NO_2 rocking	$B_1 + B_2$
438·5	m	2 × 220 = 440	A_1
450·2	s	CF_3 rocking	$B_1 + B_2$
520	s		
529		CF asym. deformation	$B_1 + B_2$
538·5			
—	s		
604		NO sym. deformation	A_1
616		400 + 220 = 620	$B_1 + B_2$
744·5	vs		
751		CF sym. deformation	A_1
757		529 + 220 = 749	$B_1 + B_2$
790·5	m		
797·5		2 × 400 = 800	A_1
802		400 + 400 = 800	$[A_2]$
855	m	400 + 450 = 850	A_1 $[A_2]$
863		CN stretching	A_1
871			
936·5	vw	400 + 529 = 929	A_1 $[A_2]$
961	vw	220 + 751 = 971	$[A_2]$
969	vw	450 + 529 = 979	A_1 $[A_2]$
1042	m	450 + 604 = 1054	$B_1 + B_2$
1049		2 × 529 = 1058	A_1
1056		529 + 529 = 1058	$[A_2]$
1148			
1154	vs	CF sym. stretching	A_1
—	sh	751 + 400 = 1151	$B_1 + B_2$
1165			

Band (cm.$^{-1}$) *		Assignment	
1277	vs	CF asym. stretching	B_2
		751 + 529 = 1280	$B_1 + B_2$
1288	vs	CF asym. stretching	B_1
1315	vs	NO sym. stretching	A_1
		863 + 450 = 1313	$B_1 + B_2$
1330	sh	529 + 2 × 400 = 1329	$B_1 + B_2$
1353	sh	604 + 751 = 1355	A_1
1418	w	604 + 2 × 400 = 1404	A_1
		604 + 400 + 400 = 1404	$[A_2]$
1461	w	604 + 863 = 1467	A_1
1476	w		
1614	s	NO asym. stretching	B_1
1626		863 + 751 = 1614	A_1
1754	w	604 + 1154 = 1758	A_1
1869	vw	604 + 1277 = 1881	B_2
1913	vw	604 + 1315 = 1919	A_1
		751 + 1154 = 1905	A_1
2020	vw	1154 + 863 = 2017	A_1
		1620 + 400 = 2020	A_1 $[A_2]$
2145	vw	529 + 1620 = 2149	A_1 $[A_2]$
		863 + 1277 = 2140	B_2
2160	vw	1288 + 863 = 2151	B_1
2220	vw	604 + 1620 = 2224	B_1
2430	w	1154 + 1288 = 2442	B_1
		1154 + 1277 = 2431	B_2
2595	vw	1277 + 1315 = 2592	B_2
		1288 + 1315 = 2603	B_1
2704	w	220 + 863 + 1620 = 2703	B_2
2902	w	1288 + 1620 = 2908	A_1

* w = weak; m = medium; s = strong; sh = shoulder; v = very.

† Not observed; postulated from combination bands and overtones. [ ] = Forbidden species.

TABLE 2. *The fundamental vibrations of fluoropicrin, chloropicrin, and bromopicrin,* C_{2v}.

Symmetry class	Vibrational mode	$CF_3·NO_2$				$CCl_3·NO_2$			$CBr_3·NO_2$		
				PR sepn. (cm.$^{-1}$)				*PR* sepn. (cm.$^{-1}$)			*PR* sepn. (cm.$^{-1}$)
		Cm.$^{-1}$	*CT* [b]	calc.	obs.	Cm.$^{-1}$	*CT* [b]	obs.	Cm.$^{-1}$	*CT* [b]	obs.
A_1	NO sym. str.	1315 [d]	A	12·4	—	1311	B	—	1311	C	—
Totally sym.	CN sym. str.	863 [d]			16	848		18	840		9
Raman active	NO sym. def.	604			12	—		—	617·5		15
Infrared active	CX sym. str.	1154 [d]			12	439 [a]		—	302 [a]	—	
Polarised	CX sym. def.	751 [d]			12·5	296 [a]		—	212 [a]	—	
A_2	CN torsion	[220] [c]	—	—	—	—	—	—	—	—	—
Asym.											
Raman active											
Infrared inactive											
Depolarised											
B_1	NO asym. str.	1620 [d]	B	14·6	12	1625	A	15	1606	A	—
In NO_2 plane	CX asym. str.	1288			—	677		12	617·5		15
Raman active	CX asym. def.	529			18·5	202 [a]		—	138 [a]		—
Infrared active	CX_3 rocking	450			—	287 [a]		—	190 [a]		—
Depolarised	NO_2 rocking	400 [c]			—	412 [a]		—	394 [a]		—
B_2	CX asym. str.	1277	C	19·8	—	717	C	—	669	B	—
Perp. to NO_2 plane	CX asym. def.	529			18·5	202 [a]		—	138 [a]		—
Raman active	CX_3 rocking	450			—	287 [a]		—	190 [a]		—
Infrared active	NO_2 rocking	400 [c]			—	412 [a]		—	394 [a]		—
Depolarised											

[a] Liquid-phase Raman frequencies observed by Wittek.[9a] [b] Contour type (Badger and Zumwalt [7]). [c] Postulated from combination bands and overtones. [d] In general agreement with Jander and Haszeldine,[5] who, however, assign the triplet 1310, 1285, 1270 cm.$^{-1}$ to the NO symmetric deformation mode, and do not state whether the CF stretching vibration at 1151 cm.$^{-1}$ is symmetric or asymmetric. [ ] = Forbidden species.

are assigned accordingly. The unusual contour of the latter may be due to merging of the P and the Q branch, since the resolving power of the spectrometer is less good in this region. The only remaining fundamental belonging to symmetry species A_1 is the symmetrical CN stretching mode, which must be represented by the band centred at 863 cm.$^{-1}$; this is found between 800 and 920 cm.$^{-1}$ in the lower nitroalkanes.[3]

There is only one band which can be said to possess a type B contour [7] and that is the doublet at 1613 and 1626 cm.$^{-1}$. This must represent the NO_2 asymmetric stretching frequency. The group of bands at *ca.* 1280 cm.$^{-1}$ will contain the CF asymmetric stretching frequencies. The bands at 1277 and 1288 cm.$^{-1}$ have been chosen for these fundamentals, and on the evidence of combination bands the band at the higher frequency has been assigned to the B_1 mode. Although the band at 542 cm.$^{-1}$ seems to have the contour of a type C band, it has been chosen to represent both the B_1 and the B_2 CF asymmetric deformation modes, as in the cases of chloropicrin and bromopicrin [9a] and trifluoronitrosomethane.[4]

The band envelope in the neighbourhood of 440 cm.$^{-1}$ is not as one would expect for branches of the same band, and is probably due to two different vibrations. It is unlikely that the frequencies of the CX_3 rocking modes will be split in fluoropicrin, since they are not split in chloropicrin or bromopicrin,[9a] and are split only to a very small extent in nitromethane.[3] In view of the relative intensities of the two shoulders, it is suggested that the band at 438·5 cm.$^{-1}$ is the first overtone of the inactive CN torsional vibration. The CN fundamental should thus occur at *ca.* 220 cm.$^{-1}$. Some combination bands appear to suggest such a value for this frequency, although they can all be explained otherwise, *e.g.*, 2704 cm^{-1}. may be a difference frequency ($2 \times 1620 - 529$). The band at 450 cm.$^{-1}$ is then assigned to the B_1 and the B_2 CF_3 rocking mode.

An alternative possibility is that one of the bands in the region of 440 cm.$^{-1}$ may arise from one of the NO_2 rocking modes, but in view of the apparent degeneracy of these modes in chloro- and bromo-picrin we prefer to assign both the NO_2 rocking modes in fluoropicrin to a possible band at *ca.* 400 cm.$^{-1}$, with the band centred at 797·5 cm.$^{-1}$ as its first overtone. This band has a type A contour, and is therefore of symmetry class A_1, and does not appear to be due to a fundamental vibration or to a combination of these. Such a frequency would meet the requirements of several combination bands. Since the combination bands provide no evidence of another fundamental frequency, it is suggested that both the B_1 and the B_2 rocking mode would give rise to a band at 400 cm.$^{-1}$.

This assignment is further supported by a consideration of the series $CX_3{\cdot}NO_2$, where X is H, D, F, Cl, or Br.

Correlation of the $CX_3{\cdot}NO_2$ *Fundamentals.*—For nitromethane and trideuteronitromethane the assignments by Smith *et al.*[3] and Wilson,[10] respectively, have been adopted without change, except that the symmetric CH deformation and the symmetric NO stretching frequencies in nitromethane have been interchanged, to give better sequences. This alternative interpretation was mentioned by Smith *et al.*

The Raman spectra of liquid chloropicrin and bromopicrin have been reported by Wittek [9a] and by Pendl, Reitz, and Sabathy,[11] the Raman and infrared spectra by Mathieu and Massignon,[12] and the infrared spectra (sodium chloride region) by Haszeldine.[13] No vapour-phase spectra have been published. Wittek [9] has given the only complete assignment, assuming C_s symmetry, but more recent work shows several changes to be necessary. Spectra were accordingly observed for both compounds, in the vapour state at various pressures, and in the liquid state, for the region 1800—450 cm.$^{-1}$. The frequencies are listed in Tables 3 and 4, together with the Raman and infrared frequencies observed for these compounds in the liquid phase by Wittek.

The moments of inertia, the symmetry factors,[7] and the separations of the P and the R branch maxima were calculated for chloropicrin and bromopicrin. The CN bond is coincident with the z axis, and the y axis lies in the plane of the NO_2 group; the following

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[10] T. P. Wilson, *J. Chem. Phys.*, 1943, **11**, 361.
[11] Pendl, Reitz, and Sabathy, *Proc. Indian Acad. Sci.*, 1938, **8**, *A*, 508.
[12] Mathieu and Massignon, *Ann. Physique*, 1941, **16**, 5.
[13] Haszeldine, *J.*, 1953, 2525.

molecular dimensions were assumed:[14] (*a*) CCl 1·76; CBr 1·92; CN 1·46; (*b*) NO 1·21; ∠ONO 127°; (*c*) ∠ClCCl 112°; ∠BrCBr 111°. The results of the band envelope calculations are given in Table 5. The contours of several bands are distinctive for particular symmetry species, and this has been helpful in deciding assignments.

The intensity distribution in each spectrum is unusual, for many of the combination bands or overtones are stronger than the fundamentals; *e.g.*, the doublet at *ca.* 870 cm.$^{-1}$ is the strongest band in the spectrum of chloropicrin, and the band at 810 cm.$^{-1}$ is the strongest in the spectrum of bromopicrin, and neither can be assigned as a fundamental. Wittek sought a special explanation for the high intensity of the band at 1345 cm.$^{-1}$ in the spectrum of chloropicrin, but in view of the other peculiarities of the intensity distribution, this is hardly necessary.

TABLE 3. *Frequency assignment of the vibrational spectrum of chloropicrin.*

Infrared, vapour (cm.$^{-1}$)	Infrared, liquid (cm.$^{-1}$)	Raman,[a] liquid (cm.$^{-1}$)	DP †	Assignment *	
1632 1617 vs	1610 vs	1607 [b] m	0·79	NO asym. str.	B_1
1387 w	—	—	—	296 + 412 + 677 = 1385 677 + 717 = 1394	A_1 $[A_2]$ $[A_2]$
1361 1355 m 1349	1350 m	1345 m	—	2 × 677 = 1354	A_1
1311 vs	1307 s	1310 [b] s	0·49	NO sym. str.	A_1
1286 w	1277 w	1275 vw	—	439 + 846 = 1285	A_1
1243 1235 w	—	—	—	412 + 846 = 1258	B_1 B_2
1133 w	—	1105 vw	—	287 + 846 = 1133 296 + 846 = 1142 412 + 717 = 1129	B_1 B_2 A_1 A_1 $[A_2]$
1070 vw	—	—	—	202 + 202 + 667 = 1071	B_1 B_2
1038 vw	—	1025 vw	—	202 + 846 = 1048	B_1 B_2
1007 vw	—	—	—	287 + 717 = 1004	A_1 $[A_2]$
916 900 s —	895 s	910 w	—	202 + 717 = 919	A_1 $[A_2]$
876 868 vs	858 s	865 vw	—	2 × 439 = 878 202 + 677 = 879	A_1 A_1 $[A_2]$
— 853 846 m 840	842 m	843 [b] s	0·27	CN stretching	A_1
746·5 741 738 m —	733 w	—	—	296 + 439 = 735	A_1
717 s	707 m	710 s	0·70	CCl asym. str.	B_2
682·5 677 m 670·5	670 m	673 w	dp	CCl asym. str.	B_1
	523 w	516 w	—	202 + 296 = 498	$B_1 + B_2$
	445 m	439 [b] vs	0·09	CCl sym. str.	A_1
		412 vw	—	NO_2 rocking	$\mathrm{B}_1 + B_2$
		296 s	0·66	CCl sym. deformation	A_1
		287 s	dp	CCl_3 rocking	$B_1 + B_2$
		202 [b] vs	0·81	CCl asym. deformation	$B_1 + B_2$

[a] Wittek.[9a] [b] Assignment by Wittek.[9]

* If the frequency 610 cm.$^{-1}$ is assumed for the NO symmetric deformation mode, then the following combination bands are possible: 610 + 677 = 1287 B_1; 2 × 610 = 1220 A_1; 610 + 439 = 1049 A_1; 610 + 296 = 906 A_1; 610 + 287 = 897 B_1; B_2.

† DP = depolarisation factor. dp = depolarised.

Another curious feature of the chloropicrin spectrum is the absence of a band that can be assigned to the A_1 NO_2 symmetric deformation mode. The frequency would be expected to be about 600 cm.$^{-1}$, as for the lower alkanes,[3, 9b] and in the case of bromopicrin the band

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[14] Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, New York, 1945, p. 164; ref. 3; ref. 14*a*, p. 84.

is at 617 cm.$^{-1}$. However there is no absorption in this region in any of the reported spectra of chloropicrin, although a fundamental at *ca.* 610 cm.$^{-1}$ would allow several further interpretations of combination bands, as shown at the end of Table 3. Wittek reports weak bands at 519 and 516 cm.$^{-1}$ in the spectra of chloropicrin and bromopicrin respectively, which were not observed by us. The former cannot be assigned as a combination band or as an overtone, and on the evidence of some of the bands at higher frequencies in each spectrum each of these frequencies could represent a fundamental. It is possible that these bands are due to the A_1 symmetric NO_2 deformation modes in chloropicrin and bromopicrin, but as the frequencies are so low, for no obvious reason, the matter must be left open.

TABLE 4. *Frequency assignment of the vibrational spectrum of bromopicrin.*

Infrared, vapour (cm.$^{-1}$)	Infrared, liquid (cm.$^{-1}$)	Raman,[a] liquid (cm.$^{-1}$)	DP	Assignment	
1606 m	1595 vs	1591 [b] s	0·74	NO asym. str.	B_1
	1540 w				
1385 m	1395 w	—	—	?	
1311 m	1307 s	1306 [b] s	0·32	NO sym. str.	A_1
845 840 } s 834	840 m	840 [b] s	0·28	CN sym. str.	A_1
810 vs	805 795 } vs	799 m	—	617·5 + 190 = 807·5 669 + 138 = 807	A_1 B_1 B_2 [A_2] A_1 [A_2]
669 m	669 w	669 m	0·75	CBr asym. str.	B_2
625 617·5 } m 609·5	613 m	613 m	0·82	NO sym. bending CBr asym. str.	A_1 B_1
589 m	587 m	—	—	394 + 190 = 584	A_1 [A_2]
		516 vw	—	212 + 302 = 514	A_1
		394 [b] s	0·91	NO_2 rocking	B_1 + B_2
		324 vw	—	190 + 138 = 328	A_1 [A_2]
		302 [b] vs	0·03	CBr sym. str.	A_1
		272 vw	—	138 + 138 = 276	A_1 [A_2]
		212 [b] s	0·50	CBr sym. deformation	A_1
		190 s	0·77	CBr_3 rocking	B_1 + B_2
		138 [b] s	0·76	CBr asym. deformation	B_1 + B_2

[a] Wittek.[9a] [b] Assignment by Wittek.[9a]

TABLE 5. *Band envelope calculations.*

Axis	Moment of inertia about axis g.cm.^{2} × 10^{40}	Contour type for vibns. parallel to axis	Symmetry species	*PR* separation at 70°
Chloropicrin	ρ = 0·104; S = 0·49.			
x	611	C	B_2	13
y	550	A	B_1	14
z	564	B	A_1	18·5
Bromopicrin	ρ = 0·26; S = 0·54.			
x	1110	B	B_2	10
y	1047	A	B_1	8·5
z	1391	C	A_1	9·7

The nearest band to the position in which the NO_2 symmetric deformation frequency would be expected is the band at 677 cm.$^{-1}$, but this has an A type contour, and must be correlated with a vibration of species B_1; in any case the frequency of the NO_2 symmetric deformation mode would not be expected to be so high. The assignment of the 617 cm.$^{-1}$ band in the bromopicrin spectrum is in accord with the expected C type contour, and to account for the high depolarisation factor we may assign the B_1 CBr asymmetric stretching mode to this frequency as well.

The bands at 296 and 190 cm.$^{-1}$ in the spectra of chloropicrin and bromopicrin respectively were assigned by Wittek to CX A' and A'' stretching modes (C_s symmetry having been assumed) as doubly degenerate vibrations. However, these frequencies are obviously far too low, when compared with values observed in other CX_3 compounds, such

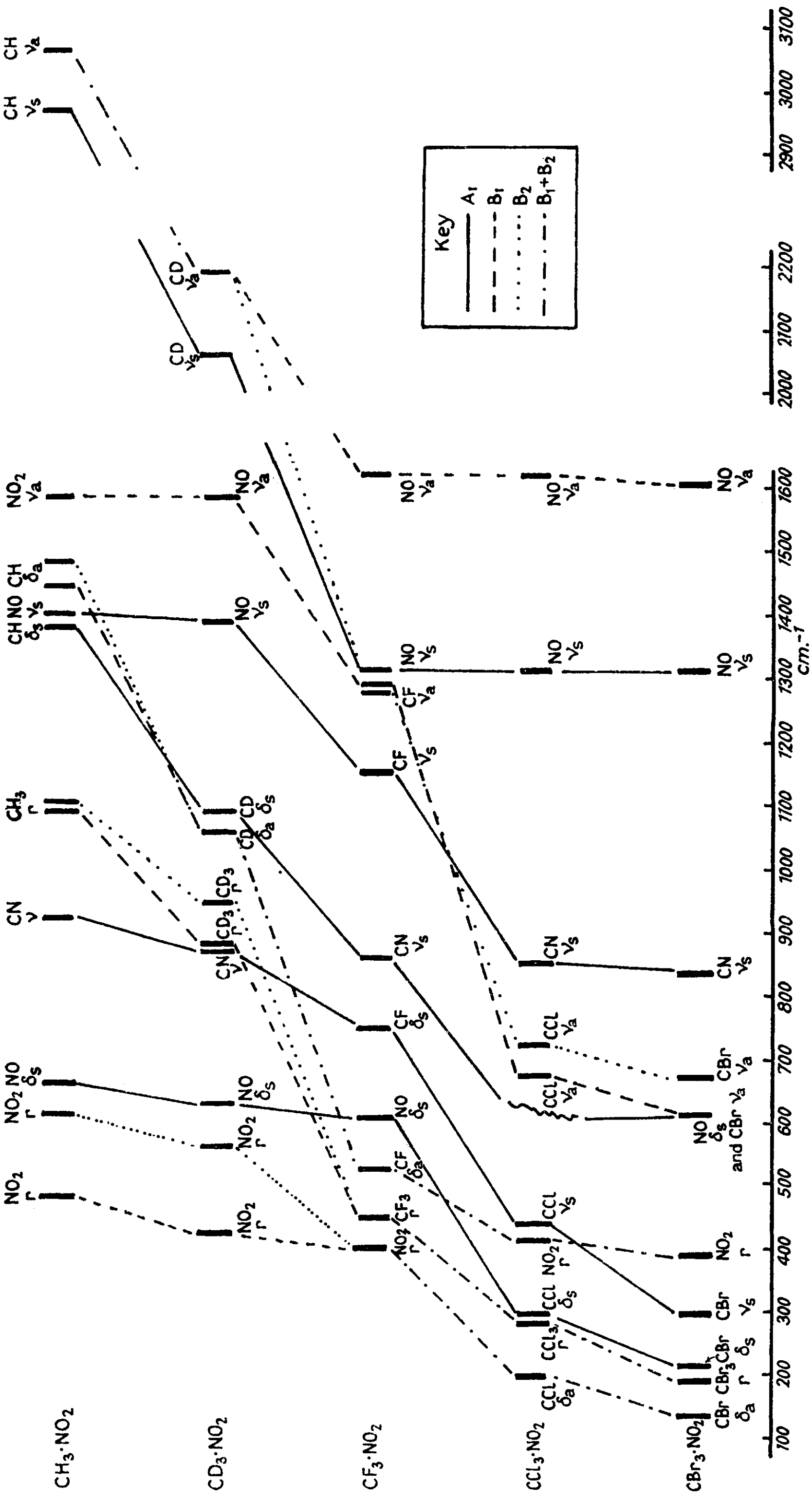

FIG. 2. *Correlation diagram of the* $CX_3{\cdot}NO_2$ *fundamental frequencies.*

as halogeno-methanes and -ethanes.[15] Much closer agreement is obtained by assigning the bands at 677 and 717 cm.$^{-1}$ for chloropicrin and 617 and 669 cm.$^{-1}$ for bromopicrin to the CX asymmetric stretching vibrations. The band contours in each case indicate that the higher frequency corresponds to the B_2 mode, which suggests that the same may be true for fluoropicrin, where the choice of the higher of the two available frequencies for the B_1 mode was based on very limited evidence.

For the NO_2 in-plane rocking modes, the bands at 438 * and 390 cm.$^{-1}$ were chosen by Wittek for chloropicrin and bromopicrin respectively; however, 412 cm.$^{-1}$ is preferable for this mode in chloropicrin, for, although the band is weak, this frequency is necessary for the interpretation of the prominent band at 846 cm.$^{-1}$. Each of these bands, 412 and 390 cm.$^{-1}$, is now assigned to both B_1 and B_2 species, as in the case of fluoropicrin; only in the lighter molecules, proto- and deutero-nitromethane, are the B_1 and B_2 frequencies of the NO_2 or the CX_3 rocking modes separated, and only in nitromethane are the two CX asymmetric deformation modes separated (and then only by 40 cm.$^{-1}$).

The lowest frequency in each spectrum (chloropicrin and bromopicrin) has been assigned to the two CX asymmetric deformation vibrations, and the next lowest to the two CX_3 rocking modes, although it cannot be said with certainty which is which; it is also possible that the two frequencies in each molecule may arise from mixtures of the two types of motion.

The band in the chloropicrin spectrum at 296 cm.$^{-1}$, which was assigned by Wittek to one of the asymmetric CX stretching modes, is now assigned to the CCl symmetric deformation vibration. The remaining assignments agree with Wittek's. No indication of the magnitude of the inactive torsion frequencies can be obtained from the spectra.

Table 2 lists the fundamental frequencies of chloropicrin and bromopicrin, together with an approximate description of the vibrations. Complete assignments are given in Tables 3 and 4. Where combination bands have been obtained as the sum of a Raman liquid-phase frequency and an infrared vapour-phase frequency, the figure is probably about 5—10 cm.$^{-1}$ lower than if two vapour-phase frequencies had been added.

The frequencies of the fundamentals of the molecules $CX_3{\cdot}NO_2$ have been plotted to form the correlation diagram (Fig. 2). This is drawn so that series of the same symmetry species do not cross, although it should be emphasised that in general the type of vibration in a given series alters as the mass of X increases. The fundamental frequencies of fluoropicrin have been fitted into the series, and this has been very helpful in making the assignments.

The authors thank Delia M. Simpson (Mrs. J. N. Agar) for much useful advice. Some of the spectra were taken (by J. B.) at the Ohio State University, Columbus, Ohio, in 1953, and others by courtesy of Prof. A. Albert of the Australian National University (Perkin-Elmer instruments). We thank also Mr. D. Watson of University College for the spectra of chloropicrin and bromopicrin taken at elevated temperatures, in the vapour phase. One of us (J. D.) thanks the Ministry of Education for a grant under the Further Education and Training Scheme.

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[*Received, July 8th*, 1955.]

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* Wittek assigned this band to the CCl symmetrical stretching vibration as well; we agree with this.

[15] Claassen, *J. Chem. Phys.*, 1954, **22**, 50; Plyler and Benedict, *J. Res. Nat. Bur. Stand.*, 1951, **47**, 202; Infrared Spectra of Fluorinated Hydrocarbons, Naval Res. Lab., Rept. 3924. Washington, 1952.