403. *Vibrational Spectra and Assignments of Chloropicrin and Bromopicrin; Some Corrections and Additions.*

By MRS. J. MASON (BANUS), J. DUNDERDALE, and A. H. CASTELLI.

The assignments of two of the fundamental frequencies of the chloropicrin molecule have been altered, since the expected band contour types were derived from calculated moments of inertia, two of which have been shown by recent measurements of the molecular dimensions to be in the wrong order. This has necessitated alterations in two corresponding bromopicrin assignments.

Improved spectra of chloropicrin are presented.

RECALCULATION of the moments of inertia of the chloropicrin molecule, by use of recent measurements [2] on the electron diffraction of chloropicrin vapour, as well as those [3] on the microwave spectrum of chloroform, shows that the least moment is I_z, about the axis parallel to the C–N bond, and the intermediate one is I_y, about an axis in the ONO plane. In our assignment [1] of the vibrational spectrum of chloropicrin, for comparison with that of fluoropicrin, this relationship was reversed, and certain revisions are therefore necessary. Improved spectra of chloropicrin (Fig. 1) are now available.

Table 1 shows the moments of inertia, the symmetry factors,[4] the contour type for the

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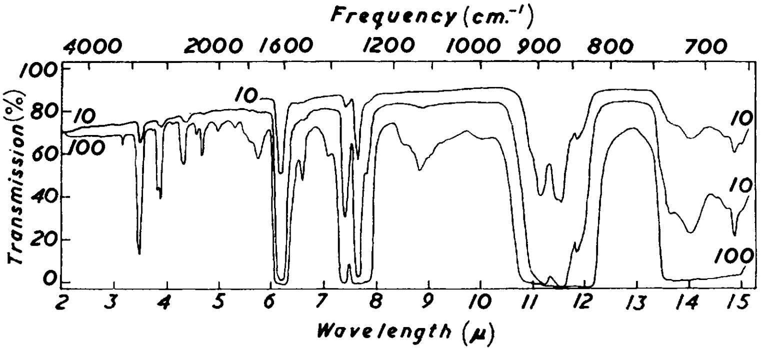
[1] Mason and Dunderdale, *J.*, 1956, 759.
[2] Barss, *J. Chem. Phys.*, 1957, **27**, 1260.
[3] Ghosh, Trambarulo, and Gordy, *J. Chem. Phys.*, 1952, **20**, 605.
[4] Badger and Zumwalt, *J. Chem. Phys.*, 1938, **6**, 711.

different symmetry species, and the separations of the *P* and *R* branch maxima for chloropicrin and also for bromopicrin, on the basis of the following " best values " for the dimensions (Å): CCl 1·76, CBr 1·92, CN (chloropicrin) 1·59, CN (bromopicrin) 1·62, NO 1·21; ∠ClCCl 110° 48′, ∠BrCBr 111°, ∠ONO 127°.

The order of the moments of inertia is unaltered for the new bromopicrin dimensions, so that the earlier band-envelope conclusions for that molecule can stand; the alterations in the *PR* separations are unimportant.

The most important consequence of the interchange of the A_1 and B_1 contour types in the chloropicrin spectrum is that the band at 677 cm.$^{-1}$ may now be assigned to the missing A_1 NO_2 deformation mode. This was previously ruled out because of the *A* type contour, and because it was thought unlikely that the frequency should be so high: the corresponding frequencies chosen for fluoropicrin and bromopicrin were 604 and 617 cm.$^{-1}$ respectively, and the correlation diagram for the $CX_3{\cdot}NO_2$ fundamentals [1] (X = H, D, F, Cl, Br) shows that the interaction between the two halves of the molecule is usually small. In addition, the NO_2 symmetric deformation frequencies are 658 cm.$^{-1}$ for nitromethane [5] and 632 cm.$^{-1}$ for trideuteronitromethane,[5] and all the other vibrations (except the NO asymmetric stretching mode) have lower frequencies for the halogenopicrin molecules than for their lighter analogues, as one might expect. As a further argument against the assignment to the A_1 deformation mode, the 673 cm.$^{-1}$ Raman line [6] is depolarised, as for non-totally symmetric vibrations.

FIG. 1. *Infrared spectrum of chloropicrin gas.*



Numerals are absorbing paths (10 or 100 cm.).

TABLE 1. *Moments of inertia and band-envelope calculations.*

p	*S*	Axis	Moment of inertia (10^{-40} g. cm.^{2})	Contour type for vibns. parallel to axis	Symmetry species	*PR* separation at 70° (cm.$^{-1}$)
			Chloropicrin			
0·16	0·18	*x*	654 (648)	*C*	B_2	13·5
		y	591 (586)	*B*	B_1	14·6
		z	554 (551)	*A*	A_1	12·6
			Bromopicrin			
0·21	0·56	*x*	1161	*B*	B_2	10·8
		y	1097	*A*	B_1	9·1
		z	1391	*C*	A_1	10·0

The moments of inertia in parentheses are calculated from the electron diffraction figures for the chloropicrin dimensions; the calculated band envelopes are the same for these as for the " best values " given above.

However, it is much more unlikely that the symmetric NO_2 deformation mode should

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[5] Smith, Pan, and Nielsen, *J. Chem. Phys.*, 1950, **18**, 706.

[6] Wittek, *Z. physikal. Chem.*, 1942, **51**, *B*, 103.

be inactive than that its frequency should be " high," and a high depolarisation factor of the 673 cm.$^{-1}$ Raman line (which was so weak that the polarisation factor was not measured) would not exclude the possibility that the vibration is totally symmetric.[7] We must therefore assume that this mode has a frequency of 677 cm.$^{-1}$ in the chloropicrin molecule, and examine the possibility that the frequencies chosen for fluoropicrin and bromopicrin (604 and 617 cm.$^{-1}$) are too low. In the fluoropicrin spectrum, however, there is no absorption between the 604 and the 750 cm.$^{-1}$ band system, and the assignment of the asymmetric NO$_2$ deformation mode to the latter is precluded by the much higher frequency, the demands of the CF symmetric deformation mode, and the good contour, which suggests that only one fundamental is involved.

In the bromopicrin spectrum there is a band at 669 cm.$^{-1}$, which was assigned to the

TABLE 2. *Frequency assignment of the vibrational spectrum of chloropicrin.*

IR, gas (cm.$^{-1}$)	IR, liq. (cm.$^{-1}$)	Raman,^{a} liq. (cm.$^{-1}$)	DP^{a}	Assignment		
3236 ^{c}w	—	—	—	2 × 1625 = 3250		A_1
2916 ^{c}s	—	—	—	1625 + 1311 = 2936		B_1
2703 ^{c}vw	—	—	—	1625 + 677 + 412 = 2714	A_1	[A_2]
2646 ^{c}m	—	—	—	{ 1625 + 1311 − 287 = 2649	A_1	[A_2]
				1625 + 717 + 296 = 2638	A_1	[A_2]
2611 ^{c}m	—	—	—	2 × 1311 = 2622		A_1
2462 ^{c}vw	—	—	—	1625 + 846 = 2471		B_1
2336 ^{c}m	—	—	—	1625 + 717 = 2342	A_1	[A_2]
2208 ^{c}w	—	—	—	{ 1625 + 2 × 296 = 2217		B_1
				1625 + 296 + 287 = 2208	A_1	[A_2]
				1625 + 2 × 287 = 2199	B_1	B_2
2160 ^{c}w	—	—	—	1311 + 846 = 2157		A_1
2119 ^{c}w	—	—	—	1625 + 296 + 202 = 2123	A_1	[A_2]
2028 ^{c}w	—	—	—	1625 + 412 = 2037	A_1	[A_2]
1905 ^{c}w	—	—	—	1625 + 287 = 1912	A_1	[A_2]
1835 ^{c} 1802 ^{c} } w	—	—	—	1625 + 202 = 1827	A_1	[A_2]
1754 ^{c}w	—	—	—	1311 + 439 = 1750		A_1
1701 ^{c}vw	—	—	—	2 × 846 = 1694		A_1
1632 1617 } vs	1610 vs	1607 m	0·79	NO asym. str.	•	B_1
1520 ^{c}m	—	—	—	846 + 677 = 1523		A_1
1500 ^{c}w	—	—	—	1311 + 202 = 1513	B_1	B_2
1484 ^{c}w	—	—	—	846 + 439 + 202 = 1487	B_1	B_2
1410 ^{c}w	—	—	—	{ 1625 − 202 = 1423	A_1	[A_2]
				717 + 412 + 287 = 1416	B_1	B_2
1387 w	—	—	—	{ 717 + 677 = 1394	B_1	B_2
				677 + 412 + 296 = 1385	B_1	B_2
1361 1355 } m 1349	1350 m	1345 m	—	2 × 677 = 1354		A_1
1311 vs	1307 s	1310 s	0·49	NO sym. str.		A_1
1286 w	1277 w	1275 vw	—	846 + 439 = 1285		A_1
1243 1235 } w	—	—	—	846 + 412 = 1258	B_1	B_2
1179 ^{c}w	—	—	—	1625 − 439 = 1186		B_1
1155 ^{c}w	—	—	—	717 + 439 = 1156	B_1	B_2
1133 w	—	—	—	{ 846 + 296 = 1142		A_1
				846 + 287 = 1133	B_1	B_2
				717 + 412 = 1129	A_1	[A_2]
1116 ^{c}w	—	1105 vw	—	677 + 439 = 1116		A_1
1070 vw	—	—	—	677 + 2 × 202 = 1081		A_1
1057 w	—	—	—	846 + 202 = 1048	B_1	B_2
1038 vw	—	1025 vw	—	{ 846 + 202 = 1048	B_1	B_2
				1311 − 287 = 1024	B_1	B_2
1007 vw	—	—	—	{ 1311 − 296 = 1015		A_1
				717 + 287 = 1004	A_1	[A_2]
1003 ^{c}w	—	—	—	717 + 287 = 1004	A_1	[A_2]

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[7] Herzberg, " Infrared and Raman Spectra," Van Nostrand, New York, 1945, p. 270.

TABLE 2. (*Continued.*)

IR, gas (cm.$^{-1}$)	IR, liq. (cm.$^{-1}$)	Raman,[a] liq. (cm.$^{-1}$)	DP[a]	Assignment	
916 909[c] 898 888 } s	895 s	910 w	—	717 + 202 = 919 1311 − 412 = 899	A_1 $[A_2]$ B_1 B_2
876 868 } vs	858 s	865 vw	—	677 + 202 = 879 2 × 439 = 878 1311 − 439 = 872	B_1 B_2 A_1 A_1
— 853 846 840 } m	842 m	843 s	0·27	CN str.	A_1
746·5 741 738 — } m	733 w	—	—	439 + 296 = 735	A_1
725[c] s	—	—	—	439 + 287 = 726	B_1 B_2
717 s	707m	710s	0·70	CCl asym. str.	$B_1 + B_2$
689[c] m	—	—	—	412 + 287 = 699	A_1 $[A_2]$
682·5 677 670·5 } m	670 m	673 w	dp	NO_2 sym. def.	A_1
	523 w	516 w	—	296 + 202 = 498 717 − 202 = 515	B_1 B_2 A_1 $[A_2]$
	445 m	439 vs	0·09	CCl sym. str.	A_1
		422 vw	—	NO_2 rocking	$B_1 + B_2$
		296 s	0·66	CCl sym. def.	A_1
		287 s	dp	CCl_3 rocking	$B_1 + B_2$
		202 vs	0·81	CCl asym. def.	$B_1 + B_2$

[a] Wittek.[6] [c] New bands (see Experimental section). [ ] = Forbidden species.

CBr B_2 stretching mode (contour type B). The observed contour is, however, structureless, and might just as well be type A as type B, so that in view of the chloropicrin assignment this higher frequency must be considered preferable for the NO_2 symmetric deformation vibration in bromopicrin, particularly since the Raman line is polarised (DP = 0·75).

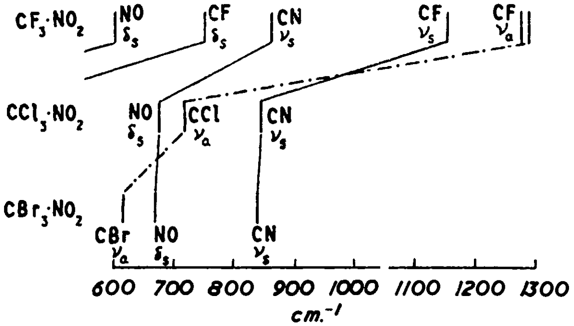
The descriptions of some of these vibrations, such as the NO_2 symmetric deformation and the CN stretching vibration, are only approximate, since it is likely that these two (for example) are coupled with each other and with lower A_1 frequencies in the chloro- and bromo-picrins; the CN stretching vibration for fluoropicrin, at 863 cm.$^{-1}$, is probably coupled with the CF symmetric deformation at 751 cm.$^{-1}$, which in turn may mix with the NO_2 symmetric deformation vibration at 604 cm.$^{-1}$.

Now that the 677 cm.$^{-1}$ frequency in the chloropicrin spectrum and the 669 cm.$^{-1}$ frequency in the bromopicrin spectrum are assigned to the NO_2 symmetric deformation modes, the other fundamentals previously assigned to these frequencies should probably be located elsewhere (the bands are of medium intensity only). These are the CCl B_1 and the CBr B_2 stretching modes. It is quite likely that for chloropicrin and for bromopicrin the B_1 and B_2 CX stretching modes are degenerate, or nearly so, for they are only split to the extent of 10 cm.$^{-1}$ in the fluoropicrin spectrum, and increase in weight of the atom X may well decrease the splitting. Thus both the CCl asymmetric stretching modes may be assigned to the very broad amorphous-looking band at 717 cm.$^{-1}$ in the chloropicrin spectrum, and both the CBr asymmetric stretching modes to the broad A- or C-type band at 617 cm.$^{-1}$ in the bromopicrin spectrum.

If the CN bond is significantly longer in chloropicrin and in bromopicrin than in fluoropicrin, the assignment of the CN stretching mode (863 cm.$^{-1}$ for fluoropicrin) should perhaps be transferred from 846 cm.$^{-1}$ (chloropicrin) and 840 cm.$^{-1}$ (bromopicrin) to lower frequencies. However, chloropicrin does not absorb in the region between the 846 and the 740 cm.$^{-1}$ band system, the 843 cm.$^{-1}$ Raman line is polarised, and this frequency cannot be assigned as a combination or difference tone, so the earlier assignment must stand. In the bromopicrin spectrum there is a band at 810 cm.$^{-1}$, the intensity of which is very high for a combination band, but there are several arguments against assigning this frequency to the CN stretching vibration, particularly in view of the chloropicrin value. One is that the greatest change in C–N bond length in the $CX_3{\cdot}NO_2$ series (change in mass seems less important in this connection) probably occurs between fluoropicrin and chloropicrin, so that one might expect the CN stretching frequencies to be closer for bromopicrin and chloropicrin than for chloropicrin and fluoropicrin. Another is that at least two combination tones and possibly two overtones may contribute to the high intensity of the 810 cm.$^{-1}$ band; in the spectrum of the liquid the band is a doublet, with peaks at 805—810 and at 790—795 cm.$^{-1}$, and the first overtones of the B_1 and B_2 rocking modes would absorb at 788 cm.$^{-1}$.

The high intensity of the chloropicrin doublet at *ca.* 870 cm.$^{-1}$ is not explained by the sum and difference frequencies that can be assigned to it; perhaps the results of a normal co-ordinate treatment (which is in hand) of the $CX_3{\cdot}NO_2$ series will help to explain some of the oddities of the intensity distribution in the chloropicrin and bromopicrin spectra.

FIG. 2. *Section of the* $CX_3{\cdot}NO_2$ *correlation diagram, showing the revised fundamental frequencies.*



——— A_1; —·—·— $B_1 + B_2$.

The frequency assignments for the vibrational bands of chloropicrin are shown in Table 2. Fig. 2 is a section of the halogenopicrin correlation diagram showing the revised chloropicrin and bromopicrin fundamentals, which agree with the non-crossing rule. A fuller account of the spectra, tables of fundamentals, and acknowledgment of previous work, is in the earlier paper.[1]

Experimental.—New measurements of the chloropicrin spectrum were made (by A. H. C.) with a Perkin-Elmer model 21 infrared spectrophotometer, with a sodium chloride prism. The chloropicrin (Eastman Kodak white label, re-distilled) was examined as a liquid in 0·254 mm. thickness, and as a vapour with an absorbing path of 10 or 100 cm. The new bands marked [c] in Table 2 were obtained with the 100 cm. absorbing path, in a multiple reflection cell.

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WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES,
UNIVERSITY COLLEGE, LONDON, W.C.1.
RESEARCH DEPARTMENT, BRITISH TITAN PRODUCTS LIMITED (J. D.).
SPECTROSCOPY LABORATORY, BUILDING 162-S, PICATINNY ARSENAL,
DOVER, NEW JERSEY (A. H. C.).
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