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The gas phase i.r. spectra of some perhalonitrosomethanes

N. P. Ernsting* and J. Pfab
Department of Chemistry, Heriot-Watt University, Edinburgh, U.K.

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Abstract—The gas phase i.r. spectra of the nitrosomethanes $CClF_2NO$, CCl_2FNO, CCl_3NO, $CBrCl_2NO$, CBr_2ClNO and CBr_3NO in the 3300–200 cm^{-1} region have been examined. It is concluded that CBr_2ClNO exists in two stable isomeric forms with a *cis* and *gauche* conformation respectively. For CCl_3NO and its heavier derivatives, the spectral region between 1000 and 500 cm^{-1} is likely to contain more fundamental vibrations than can be inferred from the related aldehydes. The spectra are compared and assignments are suggested for the observed bands.

INTRODUCTION

The spectroscopy of nitrosomethane is limited by chemical complications which arise whenever this compound is generated by the thermal dissociation of dimeric nitrosomethane. Incomplete dissociation, isomerization of the dimers, and particularly the rapid thermal rearrangement of the monomer to formaldoxime have hampered previous spectroscopic work [1–3] so that matrix isolation at low temperatures was required for an i.r. study of nitrosomethane [4].

In contrast, the perhalogenated nitrosomethanes do not dimerise and are known as deep blue gases or liquids at room temperature. Trifluoronitrosomethane in particular is readily available, and its vibrational behaviour is now well understood [5, 6]. The other perhalonitrosomethanes, however, have been neglected by spectroscopists, with the exception of a brief i.r. study of trichloronitrosomethane [7]. As a first step towards an understanding of these compounds, we have examined the gas phase i.r. spectra of $CClF_2NO$, CCl_2FNO, CCl_3NO, $CBrCl_2NO$, CBr_2ClNO and CBr_3NO, with an emphasis on practical and empirical aspects.

EXPERIMENTAL

Synthesis. Chlorodifluoronitrosomethane was prepared by the addition of NO_2/N_2O_4 to tetrafluoroethylene in the gas phase. Subsequent hydrolysis of the addition products gave an aqueous solution of difluoronitroacetic acid which provided the crude nitroso compound on decarboxylation in concentrated hydrochloric acid [8]. Dichlorofluoronitrosomethane was obtained similarly from chlorofluoronitroacetic acid [9], which in turn was prepared by nitration of 1,2-dichlorodifluoroethylene [10]. Trichloronitrosomethane was obtained by the nitrosation of sodium trichloromethylsulfinate [11–13].

The bromine containing nitrosomethanes were obtained from mercuric fulminate [14]. The explosive nature of this compound has probably prevented further work on these molecules so that only few of their physical properties are known. The mercuric fulminate was first converted into an aqueous solution of the sodium salt [15]. This was halogenated giving dichloroformoxime or dibromoformoxime [16]. Bromination of the former provided bromodichloronitrosomethane while the latter gave tribromonitrosomethane [17]. In order to obtain the dibromochloro compound, the mixed bromochloroformoxime was prepared followed by bromination [17].

Purification. Purification of all the compounds was achieved by trap-to-trap distillation. The various fractions were examined by i.r. spectroscopy and an optimal purification procedure could thus be established for each of the perhalonitrosomethanes.

Common impurities were nitrosyl chloride and nitrosyl bromide since they are produced by the thermal or photolytic decomposition of the perhalonitrosomethanes. Their strongest i.r. features occur in the 1800 cm^{-1} region. This spectral region was used to gauge the purity of the sample. It could be compared to the first overtone of the N—O stretching vibration which appears at *ca.* 3200 cm^{-1} with an absorbance of *ca.* 4 % relative to its fundamental. In all cases, the initial absorbance of the nitrosyl halides could be reduced to less than a quarter of the 3200 cm^{-1} overtone absorbance.

The crude gaseous chlorofluoronitrosomethanes were quickly washed with cold and slightly alkaline milk of lime and their middle fractions were collected. For spectroscopy, a small amount was condensed as a blue film in a trap at 77 K. Volatile impurities were removed by pumping the sample film at a temperature just above the melting point. The sample was then repeatedly refluxed and the higher fractions were removed until the corresponding i.r. spectra remained consistent. For trichloronitrosomethane and the bromine containing compounds, the middle fractions were also collected. It was found that the very last amount of any further fraction was quite pure. This sample was then condensed into the spectroscopic cell where a final purification was achieved by further pumping.

The synthesis and manipulation of all perhalonitrosomethanes was carried out in the dark as far as possible to prevent photochemical decomposition. The presence of oxygen was carefully excluded, and the products were stored at 77 K in the dark.

Recording of the i.r. spectra. The i.r. spectra were recorded on a Perkin–Elmer Model 580 spectrometer which was calibrated using the standard reference spectra of HCl, HBr, CO_2, CO, NH_3 and H_2O [18]. Spectroscopic cells with optical path lengths of 8 and 20 cm were used, and the window materials included CaF_2, KBr, and CsI.

The spectra were recorded in absorbance for various pressures and under a variety of scanning conditions. The spectra of the stable compounds $CClF_2NO$ and CCl_2FNO were scanned at a resolution of typically 0.6 cm^{-1} for the

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* Present address: Department of Chemistry, The University of Western Ontario, London, Canada.

high and medium energy region, and 2.5 cm^{-1} for the region below 300 cm^{-1}. The instability of the other compounds demanded a gain in scanning time and consequently a loss of resolution, but the important, sharper spectral features could all be recorded at resolutions below 2 cm^{-1} with the exception of the low energy region where the resolution was typically 10 cm^{-1}.

In order to gain some information on the effect of impurities from decomposition, each compound was photolyzed for various periods of time and the changes in the spectra were noted. Photolysis was carried out both in the absence and presence of dry oxygen. For CBr_3NO, the effect of added bromine was also investigated.

Attempts were also made to observe the far i.r. spectra of $CClF_2NO$ and CCl_3NO in the 180–20 cm^{-1} region using a Beckman RIIC FS-720 interferometer. Vapour pressures of 50 torr and an optical path length of 3 m [19] were used giving an integrated absorption of *ca.* 5 % for both cases. However, this weak absorption could not be located because of the shape and pronounced structure of the spectral background. No Raman signals could be recorded from liquid CCl_3NO using several visible exciting lines of the argon and krypton ion lasers.

RESULTS

The i.r. absorbance spectra of the perhalonitrosomethanes are shown in Figs. 1, 3 and 5. The corresponding relative maxima of absorbance, and the accuracy with which they could be located, are listed in Tables 1–6 together with their assignments which will be discussed later. For $CClF_2NO$ and CCl_2FNO, the bandshapes of the important features are also shown in Figs. 2 and 4.

Obviously, the scrutiny with which a particular compound could be examined depends on the thermal stability of that compound. Therefore, a number of very weak spectral features which were observed for the less stable bromonitrosomethanes are not listed here because they could not be assigned conclusively to the nitroso compound. This applied particularly to the nitrosyl halide region as well as to the spectral gap between the N—O and C–halogen stretching vibrations.

GENERAL ASPECTS OF THE VIBRATIONAL ANALYSIS

For an assignment of the observed spectra, a comparison with the related aldehydes where assignments are already available may seem useful. It is therefore instructive to summarize the corresponding comparison of trifluoronitrosomethane [6] to the isoelectronic aldehyde fluoral [20–22].

Both molecules are assumed to have an eclipsed conformation with respect to the oxygen atom. This leads to $8a'+4a''$ vibrational modes for the nitrosomethane and to $10a'+5a''$ modes for the aldehyde. The asymmetric vibrations of fluoral are sufficiently characterized by one symmetry coordinate alone. Their description is not changed when the nitroso group is substituted for the aldehyde group. This substitution increases the corresponding frequencies, particularly for the asymmetric rocking mode. The symmetric vibrations of trifluoronitrosomethane, however, could not be defined adequately by a single coordinate. They

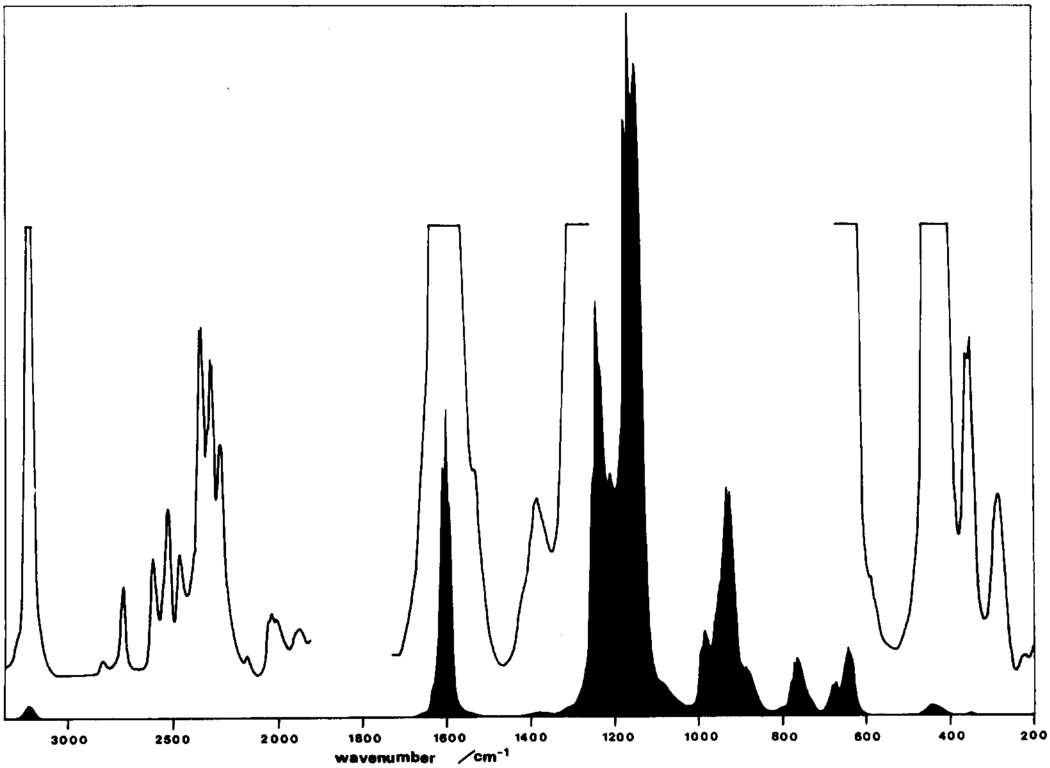

Fig. 1. Infrared absorbance spectrum of $CClF_2NO$ gas (6 and 440 torr at 30°C in 20 cm cell).

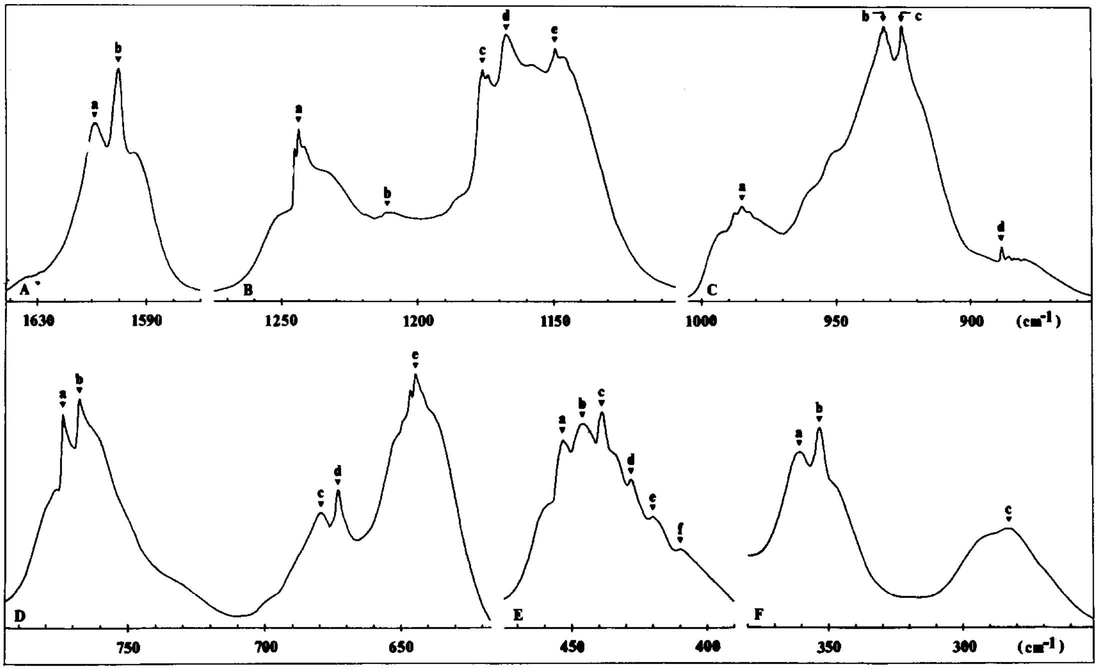

Fig. 2. Infrared band contours of $CClF_2NO$ gas (at 30°C: (A) 15 torr in 8 cm cell; (B) 8 torr, 8 cm; (C) 25 torr, 8 cm; (D) 90 torr, 8 cm; (E) 110 torr, 20 cm; (F) 400 torr, 20 cm).

also appear to have changed their character upon substitution. Therefore we conclude that at present it would be premature [23] to locate and assign the symmetric modes of the trihalonitrosomethanes CCl_3NO and CBr_3NO by transferring the available force constants from the corresponding aldehydes.

However, the similarity of the spectra of the heavier nitroso compounds is instructive. Mainly in order to emphasise this similarity, one vibrational label will be assigned to each set of vibrational features.

Nitrosomethane [24] and trifluoronitrosomethane [25] prefer an eclipsed conformation of the methyl group. Assuming that halogen substitution does not change the attractive character of the torsional potential and that it merely modifies the rotational barriers, an eclipsed conformation can be expected for the perhalonitrosomethanes. For the compounds CYX_2NO, there are then one *cis* conformation possessing a plane of symmetry and two equivalent *gauche* conformations which are completely unsymmetric. In case the various potential barriers are high, the *cis* and *gauche* conformers may coexist as two different, harmonically vibrating molecular species. Yet the internal rotation barrier in CF_3NO [26] and the first torsional frequency in

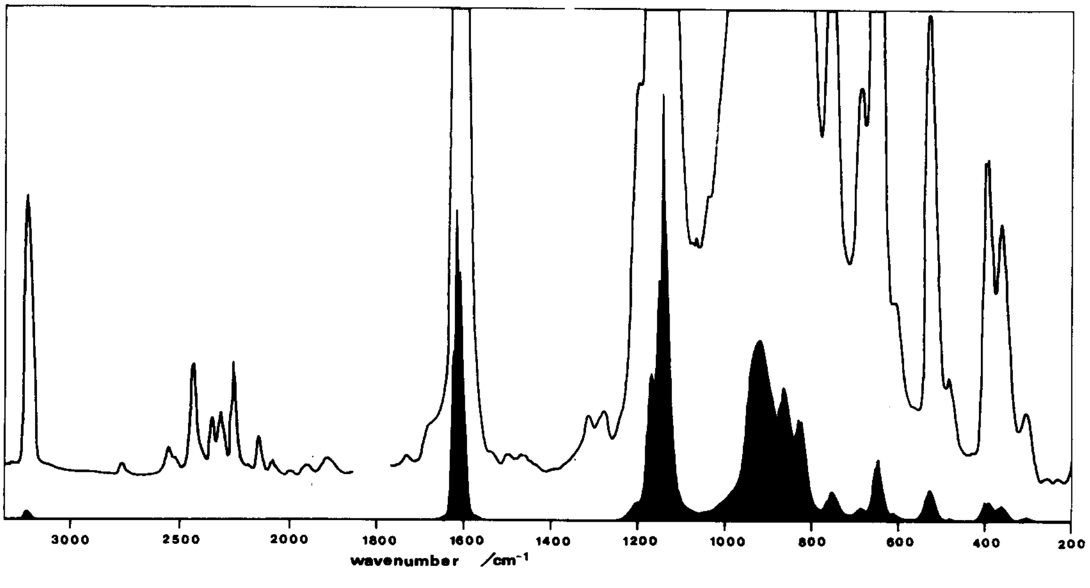

Fig. 3. Infrared absorbance spectrum of CCl_2FNO gas (6 and 151 torr at 30°C in 20 cm cell).

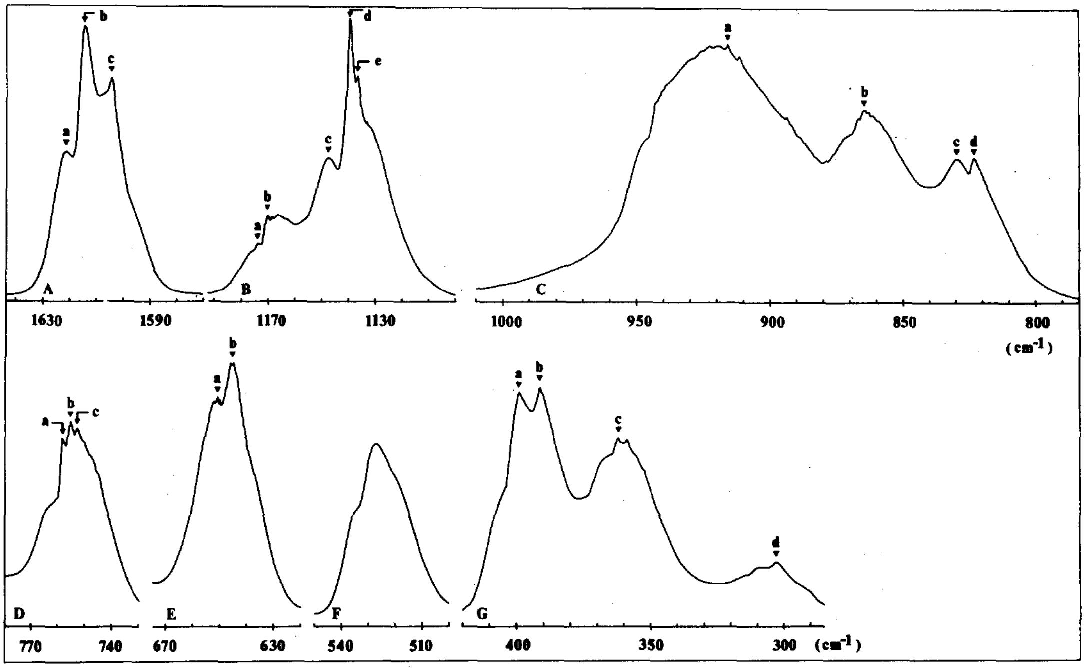

Fig. 4. Infrared band contours of CCl_2FNO gas at 30°C: (A) 15 torr in 8 cm cell, (B) 11 torr, 8 cm; (C) 26 torr, 8 cm; (D) 163 torr, 8 cm; (E) 86 torr, 8 cm; (F) 163 torr, 8 cm; (G) 88 torr, 20 cm).

chloral [22] suggests that the torsional states in $CClF_2NO$ and CCl_2FNO encompass the two conformations. The general anharmonicity induced by internal rotation may also influence the higher spectral energies giving rise to combination tones which would otherwise be weak, or even shifting some i.r. bands.

Substitution of a different halogen atom in a trihalonitrosomethane reduces the local C_{3v} symmetry of the substituted methyl group whereby the locally symmetric and asymmetric parts of an ideally degenerate mode are further divided. If the substitution takes place in the plane of symmetry, the overall molecular symmetry remains unchanged and the resulting infrared spectrum should largely resemble the original one. Large spectral changes are to be expected if an unsymmetric *gauche* conformation is preferred since all vibrational motions can then mix freely.

The choice of symmetry (if any) may be inferred from the shape of the band in question [27] and from its Raman depolarization. Because of the increasing moments of inertia, only the lighter compounds $CClF_2NO$ and CCl_2FNO show informative bandshapes. For a Raman study, the sensitivity of the nitrosomethanes to visible light requires that near u.v. exciting lines be used which were not available to us.

DISCUSSION OF THE i.r. SPECTRA OF CCl_3NO, $CBrCl_2NO$, CBr_2ClNO AND CBr_3NO

The i.r. spectrum of trichloronitrosomethane has already been reported by Briden *et al.* [7]. Their frequencies differ from our values, and they also found two medium absorptions at 1159 and 1150 cm^{-1} which we could not verify. The series of i.r. spectra from trichloro- to tribromonitrosomethane is shown in Fig. 5. The spectra are generally characterized by a band at 1600 cm^{-1} and by a succession of a very strong, a medium strong, and again a very strong absorption band in the 1000–500 cm^{-1} region.

For CBr_2ClNO, the spectrum below 1000 cm^{-1} is clearly more complicated. The characteristic strong bands appear to be split and reduced in their intensity relative to the band at 1600 cm^{-1}. Yet the integrated absorbance in this region is comparable to the other compounds. On account of the synthesis of CBr_2ClNO, traces of $CBrCl_2NO$ and CBr_3NO might be suspected as impurities. However, a detailed comparison of the spectra shows that this is not the reason for the apparent complexity. Hence we conclude that CBr_2ClNO exists as two separate conformers, *cis* and *gauche*, resulting in two superimposed i.r. spectra.

The torsional barriers must be high in this case, and it is likely that they are also high for $CBrCl_2NO$ which may therefore possess distinct conformations. The resemblance of its spectrum to that of CCl_3NO then indicates that bromine substitution of the latter preserves the molecular symmetry, i.e. that $CBrCl_2NO$ prefers the *cis* conformation.

For $CBrCl_2NO$, photo-oxidation experiments showed that a strong band of an impurity may be generated at 680 cm^{-1}. The shoulder in that spectral position could not be removed by distillation. It is therefore not clear whether this feature relates to the pure compound.

The various i.r. spectra will now be related in

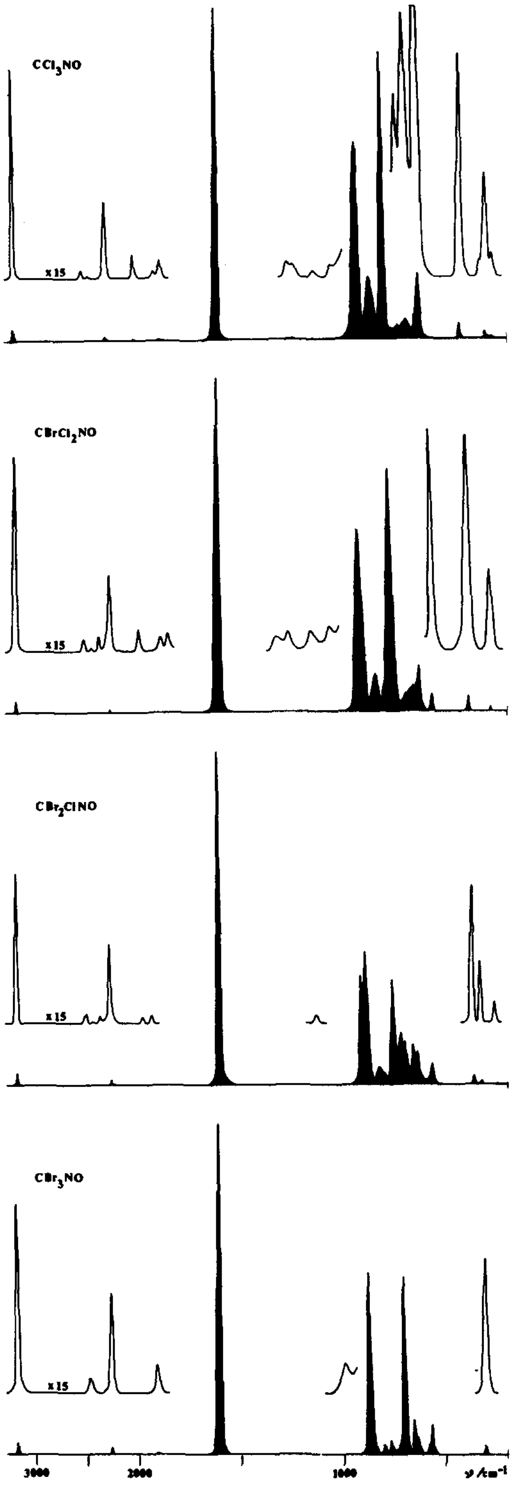

Fig. 5. Infrared absorbance spectra of gaseous CCl_3NO, $CBrCl_2NO$, CBr_2ClNO, and CBr_3NO (at 30°C; from several runs at various pressures, 20 cm).

Table 1. Observed frequencies ν and tentative band descriptions of chlorodifluoronitrosomethane

Ref.*	ν	$\pm\ \Delta\nu$ /cm^{-1}		description†
	225	3	vw	
Fc	283	2	w	rock ?
Fb	353	0.5	w	(a') δ(CNO)
Fa	361	1		
Ef	410	1	m	(a') δ(ClCF$_2$), and (a") δ(FCF)
Ee	420	1		
Ed	428	0.7		
Ec	439	0.5		
Eb	446	1		
Ea	453	0.7		
De	644	0.6	s	(a') δ(CF$_2$Cl)
Dd	673	0.5	m	(439 + 225 = 664)
Dc	679	0.8		
Db	768	0.5	s	(a') ν(CN)
Da	774	0.2		
Cd	888	0.2		impurity
Cc	925	0.5	vs	(a') ν(ClCF$_2$)
Cb	932	0.5		
Ca	985	0.5	s	?
	1087		sh	
Be	1149	0.5	vs	(a") ν(FCF)
Bd	1167.5	1		
Bc	1176	0.3		?
Bb	1211	1.3	m	(985 + 225 = 1210)
Ba	1243.5	0.5	vs	(a') ν(CF$_2$Cl)
	1386	4	w	(1149 + 225 = 1374)
	1538	0.5	vwsh	768 + 768 = 1536
Ab	1600.5	0.6	vs	(a') ν(NO)
Aa	1609	0.7		
	1952	1.5	vw	1600 + 353 = 1953
	2041	2	vw	1600 + 439 = 2039
	2152	1.5	vw	1168 + 985 = 2153
	2158	1.5		
	2282	3	w	1149 + 1149 = 2298
	2289	1		
	2320	2	w	1168 + 1168 = 2336
	2328	0.7		
	2376	2	w	(1600 + 768 = 2368, or 1244 + 1149 = 2393)
	2382	0.7		
	2474	3	vw	1244 + 1244 = 2488
	2531	3	w	1600 + 925 = 2525
	2604	1.5	vw	(1600 + 985 = 2585)
	2745	2	vw	1600 + 1149 = 2749
	2842	2	vw	1600 + 1244 = 2844
	3176	0.7	m	1600 + 1600 = 3200

* Reference to indices in Fig. 2.

† See reference [5] for the corresponding coordinates.

Table 2. Observed frequencies ν and tentative band descriptions of dichlorofluoronitrosomethane

Ref.*	ν	$\pm\ \Delta\nu$ /cm^{-1}		description†
	232	2	vw	
	260	2	vw	
Gd	306	3	vw	rock
Gc	362	0.7	m	(a") δ(ClCCl)
Gb	391	0.7	m	(a') δ(FCCl$_2$)
Ga	399	0.7		
	481	1	vw	
	484.5	0.5		
F	527	1.5	m	(a') δ(CCl$_2$F)
	605	3	vw	
Eb	646	1	s	(a') ν(CCl$_2$F)
Ea	651	1.5		
	685	3	w	
Dc	753.5	0.5	m	(a') δ(CNO)
Db	756	0.2		
Da	759	0.2		
Cd	823	0.5	s	(a") ν(ClCCl)
Cc	829	0.7		
Cb	864.5	1.5	(vs)	(1170 − 306 = 864)
Ca	916		vs	(527 + 399 = 926, or 646 + 260 = 906, or 1170 − 260 = 910, or 1140 − 232 = 908)
	(943)			(a') ν(CN), from combination.
	1041	1	vw	uncertain
	1067	1	vw	uncertain
Be	1137	0.3	vs	(a') ν(FCCl$_2$)
Bd	1139.5	0.2		
Bc	1147.5	1		
Bb	1170	0.5		(864 + 306 = 1170, or 940 + 232 = 1172, or 646 + 527 = 1173, or 916 + 260 = 1176)
Ba	1174	0.5		
	1280	2	vw	(756 + 527 = 1283, or 646 + 646 = 1292)
	1314	2	vw	916 + 399 = 1315
	1465	5	vw	940 + 527 = 1467
	1500	5	vw	1140 + 362 = 1502
Ac	1604	0.5	vs	(a') ν(NO)
Ab	1614	0.5		
Aa	1621	1		
	1734	2	vw	uncertain, (864 + 864 = 1728)
	1916	3	vw	1614 + 306 = 1926
	1963	3	vw	1140 + 823 = 1963
	2002	2	vvw	1140 + 864 = 2004
	2078	3	vw	1140 + 940 = 2080
	2143	2	vw	1614 + 527 = 2141
	2262	0.7	w	(1614 + 646 = 2260, or 1140 + 1140 = 2280)

Table 2. (*Contd*)

2317	3	vw		1170 + 1140 = 2310
2360	3	vw		1614 + 756 = 2370
2440	1.5	w		1614 + 823 = 2437
2526	4	sh		1614 + 916 = 2530
2557	2	vw		1614 + 940 = 2554
2770	4	vw		1140 + 1140 = 2280
3182	1.5	m		
3202	2			1614 + 1614 = 3228

* Reference to indices in Fig. 4.

† See reference [5] for the corresponding coordinates.

Table 3. Observed frequencies ν and tentative band descriptions of trichloronitrosomethane

ν	$\pm\Delta\nu$ /cm^{-1}		description‡	
207	4	vw		uncertain
272.5	2.5	vw	a"(e)	δ(ClCCl)
305	1	w	a'(e)	δ(ClCCl$_2$)
336	3	vwsh		
431.5	1	m	a'(a1)	δ(CCl$_3$)
637.5	0.5	s	a'(a1)	ν(CCl$_3$)
643.5	0.5	sh		
696	1	m	a'	δ(CNO)
734	1	w		812 − 78 ?
812.5	1.5	vs	a"(e)	ν(ClCCl)
880		s	a'(e)	ν(ClCCl$_2$)
936	0.8	vs	a'(a1)	ν(CN)
942	1			
1058	3	vw		uncertain
1148	4	vw		
1245	3	vw	A'	942 + 305 = 1247
1270	3	vw	A'	637 + 637 = 1274
1502	4	vw		uncertain
1619.5	0.5	vs	a'	ν(NO)
1895	1	vw	A"	1619 + 272 = 1891
1927	2	vw	A'	1619 + 305 = 1924
2053	2	vw	A'	1619 + 431 = 2050
2232	6	vvw		uncertain
2318	2	w	A'	1619 + 696 = 2315
2500	3	vvw	A'	1619 + 880 = 2499
2552	1	vw	A'	1619 + 936 = 2555
2558	1			1619 + 942 = 2561
3213.5	1	m	A'	1619 + 1619 = 3238

‡ See reference [5] for the corresponding symmetry coordinates.

Table 4. Observed frequencies ν and tentative band descriptions of bromodichloronitrosomethane

ν	$\pm\Delta\nu$ /cm^{-1}		description‡	
281.5	2	w	a'(e)	δ(BrCCl$_2$)
391	1.5	m	a'(a1)	δ(CCl$_2$Br)
572.5	1	m	a'(a1)	ν(CCl$_2$Br)
638	1.5	s		?
663	2		a'	δ(CNO)
680	7	sh		uncertain
774.5	1.5	vs	a"(e)	ν(ClCCl)
849	3	ms	a'(e)	ν(BrCCl$_2$)
928	1.5	vs	a'(a1)	ν(CN)
1072	5	vw		uncertain
1165	3	vw		
1272	5	vw		
1335	5	vw		
1614	1	vs	a'	ν(NO)
1859.5	1	vw		1614 + 245 ?
1895	2	vw	A'	1614 + 281 = 1895
2004	2	vw	A'	1614 + 391 = 2005
2182	4	vvw	A'	1614 + 572 = 2186
2281	2	w	A'	1614 + 663 = 2277
2388	2	vw	A"	1614 + 774 = 2388
2462	4	vvw	A'	1614 + 849 = 2463
2538	3	vw	A'	1614 + 928 = 2542
3199	1	m	A'	1614 + 1614 = 3228

‡ See reference [5] for the corresponding symmetry coordinates.

Table 5. Observed frequencies ν and tentative band descriptions of dibromochloronitrosomethane

ν	$\pm\Delta\nu$ /cm^{-1}		description†	
255	4	vw	(a')	δ(ClCBr$_2$)
327	2	w	(a')	δ(CBr$_2$Cl)
366	1.5	w		
568	1	m	(a')	ν(CBr$_2$Cl)
642	1	sm	(a')	δ(CNO)
647	1.5			
666	1			
702	1.5	s		?
723	1.5		(a")	ν(BrCBr)
761	1	s		
826		m	(a')	ν(ClCBr$_2$)
893	1	vs	(a')	ν(CN)
914	1.5			
1131	4	vw		
1610.5	1	vs	(a')	ν(NO)
1936	2	vw		1610 + 327 = 1937
1980	2	vw		1610 + 366 = 1976
2281	2	w		1610 + 666 = 2276
2374	3	vw		1610 + 761 = 2371
2503	3	vw		1610 + 893 = 2503
2523	3			1610 + 914 = 2524
3195	1	wm		1610 + 1610 = 3220

† See reference [5] for the corresponding coordinates.

Table 6. Observed frequencies ν and tentative band descriptions of tribromonitrosomethane

ν	$\pm\Delta\nu$ /cm^{-1}		description‡	
303	1	w	a'(a1)	$\delta(CBr_3)$
563.5	1.5	sm	a'(a1)	$\nu(CBr_3)$
588	4	sh		
627	4	sh		
655.5	1.5	s	a'	$\delta(CNO)$
701.5	1	vs	a"(e)	$\nu(BrCBr)$
768	1	m	a'(e)	$\nu(BrCBr_2)$
800	2	w		873 - 73 ?
873	1	vs	a'(a1)	$\nu(CN)$
996	2	vw		
1604.5	0.5	vs	a'	$\nu(NO)$
1910	3	vw	A'	1604 + 303 = 1907
2269	3	w	A'	1604 + 656 = 2260
2476	3	vw	A'	1604 + 873 = 2477
3184	2	m	A'	1604 + 1604 = 3208

‡ See reference [5] for the corresponding symmetry coordinates.

detail. In particular, some bands recurring throughout the series may be grouped together and they may be labelled a vibrational mode. Frequencies will be mentioned in the order from CBr_3NO to CCl_3NO.

The bands at 1604.5, 1610.5, 1614 and 1619.5 cm^{-1} clearly represent the N–O stretching vibration [1,5,7]. Another obvious series of bands is 303, 327 and 366, 391 and 431.5 cm^{-1}. The splitting for CBr_2ClNO suggests that the vibration is sensitive to conformational isomerism. In the high energy region above 1600 cm^{-1}, the binary combination tones must necessarily comprise ν(NO). The weak bands at 2269, 2281, 2281 and 2318 cm^{-1} are particularly remarkable for their relative intensity in this region. Since the character of a vibration is well reflected in the various combination bands, it is concluded that this series refers to some related features in the middle energy region. The bands in question would then be those at 655.5, 666, 663 and 696 cm^{-1}.

The number of fundamental vibrations which may be observed for the trihalonitrosomethanes can be inferred from the related aldehydes chloral and bromal [28]. Apart from the N–O stretching vibration, there should be four further fundamentals above 500 cm^{-1}, viz. the symmetric C–N, higher C–halogen stretching, and C–N–O bending modes, and the asymmetric C–halogen stretching mode. The other symmetric C–halogen stretching vibration should appear near 440 cm^{-1} for trichloronitrosomethane and near 320 cm^{-1} for the tribromo compound. Of the low energy vibrations, the asymmetric torsional mode and both components of the degenerate (in C_{3v}) rocking mode are not expected to fall in this spectral range, leaving the three deformation modes for the lowest observed spectral region.

A survey of the spectra from trichloro- to tribromonitrosomethane shows, however, that there are evidently more than four pronounced features in the 1000–500 cm^{-1} region. By comparison with chloral and bromal, some of these features would have to be explained as combinations, as for instance the bands of CCl_3NO at 696 and 734 cm^{-1}. Two reasons stand against this approach. Firstly, it would lead to ternary combinations for the series at 2280 cm^{-1} which we consider unlikely. Secondly, the latter bands are remarkably affected by bromine substitution: they gain intensity, and a new series of bands appears at 570 cm^{-1}. We therefore propose that the 1000–500 cm^{-1} region contains all C–halogen stretching vibrations.

The following assignment is suggested for CCl_3NO. Of the two higher C–Cl stretching modes, one must be symmetric and the other asymmetric [28]. If the molecular symmetry were C_{3v}, their energies would coincide and they may then be compared with the highest degenerate modes of CCl_3F or CCl_3Br [29]. On reduction to C_s, it is reasonable to assume that the asymmetric part will be affected least. The strong band at 812.5 cm^{-1} should then be identified as the asymmetric C–Cl stretching fundamental. Its symmetric equivalent is assigned to the broad and weaker band at 880 cm^{-1}. The C–N stretching vibration is located at 942 cm^{-1}. Then the medium band at 696 cm^{-1} is tentatively assigned to the C–N–O bending mode. Clearly the strong band at 637.5 cm^{-1} must now represent the other symmetric C–Cl stretching mode.

Of the methyl deformation modes, the one belonging to a_1 in C_{3v} should be the highest, and it is assigned to the lone medium band at 431.5 cm^{-1}. The large influence of the nitroso group on this vibration is demonstrated by the splitting of the corresponding vibration of CBr_2ClNO, and its comparatively high frequency may thus be explained. The next band down at 305 cm^{-1} must then be the symmetric part of the degenerate methyl deformation which is closely followed by the asymmetric component at 272.5 cm^{-1}. The observed spectrum of trichloronitrosomethane has now been labelled completely, and all of the expected fundamentals have been indicated.

Bromine substitution results in a new series of bands below 580 cm^{-1}. It may be concluded that these bands have a C–Br stretching character. This is in agreement with the assignment of the 637.5 cm^{-1} band in CCl_3NO to which the series may be related. In $CBrCl_2NO$, a strong feature next to the C–N–O bending mode remains. In this context it has to be explained as a superimposed combination band. Its strength emphasises the anharmonic influence of the torsional mode. This influence becomes quite dramatic for CBr_2ClNO as most spectral bands have been duplicated. It is interesting to note that the band at 568 cm^{-1} is not affected. This may indicate that the vibration is well contained in the perhalomethyl group. Finally, for CBr_3NO the central medium band now at 768 cm^{-1} clears the view on a weak feature at 800 cm^{-1} which is assigned to a torsional hot band.

DISCUSSION OF THE I.R. SPECTRA OF CCl_2FNO AND $CClF_2NO$

A survey of the i.r. spectra from CF_3NO [5] to CCl_3NO in Figs. 1, 3 and 5 shows a marked change of general appearance. This can be rationalized in two regions of the fundamental spectrum. In the 1400–600^{-1} region, a regrouping of the stretching and higher deformation modes leads to the familiar pattern of trichloronitrosomethane. The region below 600 cm^{-1} is characterized in CF_3NO by some accidental degeneracies [6]. It appears that these degeneracies have been removed in $CClF_2NO$ resulting in a rather more complex spectrum which is eventually shifted below 200 cm^{-1} upon complete chlorine substitution.

A particular aspect concerns the effect of torsional motion. As mentioned earlier, the torsional behaviour may be visualized between two extreme cases. Either it results in two different torsional conformers with their superimposed spectra. Or torsional motion will lead to enhanced combination bands or even to frequency shifts so that a combinational analysis becomes very difficult. If the rich structure in the spectra of $CClF_2NO$ and CCl_2FNO is examined in this context it is indeed not clear whether torsional isomerism, torsional interaction, or just the removal of accidental degeneracies is responsible. In consequence there is no evidence permitting an identification of preferred conformers or of the vibrational symmetries. No attempts will therefore be made to label the i.r. spectra in terms of symmetry representations, and symmetry descriptions refer to local symmetries only.

CCl_2FNO

The most prominent feature which emerges from the substitution of a single fluorine atom in CCl_3NO is the very strong band at 1139.5 cm^{-1}. Clearly this band represents the larger part of the C–F stretching motion and it must therefore belong (at least locally) to the symmetric representation. The remaining strong and very strong bands above 600 cm^{-1} should ideally contain four further stretching vibrations. The broad band between 960 and 880 cm^{-1} reappears in combination with the 1614 cm^{-1} N–O stretching vibration at 2557 ($=1614+943$) cm^{-1} with a shoulder at 2530 cm^{-1}. The corresponding fundamental must therefore be located near the steep blue side of the broad band at 960–880 cm^{-1}. The strong band at 823 cm^{-1} is confirmed by the weak combination tone at 2440 ($1614+823=2437$) cm^{-1}. The intermediate band at 864.5 cm^{-1}, however, may be contained only in the extremely weak combination band at 2002 ($1140+864=2004$) cm^{-1} for which alternative combinations are also conceivable. It is therefore suggested that the 864.5 cm^{-1} band is a combination tone (e.g. $1140–306=864$). The spectrum can now be compared with that of trichloronitrosomethane resulting in the labels of Table 2. It must be emphasized that torsional effects may have altered the low energy region so that a comparative assignment is by no means conclusive.

$CClF_2NO$

Here, the very strong bands at roughly 1244, 1150 and 925 cm^{-1} plainly represent some stretching modes. Of these, the 925 cm^{-1} band can be recognised as containing the C–Cl motion and may be assigned to the (locally) symmetric representation. Since the locally asymmetric methyl stretching vibration will probably carry a greater dipole moment change than the symmetric one, the strongest band at 1150 cm^{-1} is labelled (a''). This band shows three well-defined features at 1176, 1167.5 and 1149 cm^{-1}, and the question arises which should be adopted for the Q-branch of the fundamental. Although all of these frequencies may be used to explain the higher combination region, the value of 1149 cm^{-1} appears more often, and most convincingly in the distinct 2745 ($1600+1149=2749$) cm^{-1} combination band, so that it may be used for the fundamental in question. The round feature at 1167.5 cm^{-1} would then represent the P-branch of a superimposed band at 1176 cm^{-1}. This band cannot be explained satisfactorily as a combination of the observed frequencies and must be attributed to torsional effects.

A particular feature of the CF_3NO i.r. spectrum is the superposition of two bands in the 540 cm^{-1} region. Of these, the one located at 551 cm^{-1} has been described [6] as a clearly defined asymmetric deformation mode. This should not be affected too strongly by symmetric chlorine substitution. Yet the 600–400 cm^{-1} region in the spectrum of $CClF_2NO$ is empty implying a strong influence of the torsional motion. For this reason the assignment given in Table 1 represents only one of a number of possibilities.

The various bandshapes can be used to relate the corresponding bands to each other. In conjunction with an estimate for the molecular geometry [30] which is shown in Fig. 6, the choice of vibrational symmetry (if any) may be suggested. The vibration at 353 cm^{-1} clearly resembles the N–O stretching band and it is therefore considered to take place in the same direction. Similarly, the 1243.5 cm^{-1} stretching vibration shows the same steep characteristic as the band at 768 cm^{-1}. Since it is unlikely that an asymmetric mode occurs in this region, it follows that both vibrations are of a symmetric character. The only vibration of a well-defined B-type is the band at 644 cm^{-1} indicating a contribution from the C–Cl stretching motion of a *cis* conformation. Finally, the spectral structure at 888

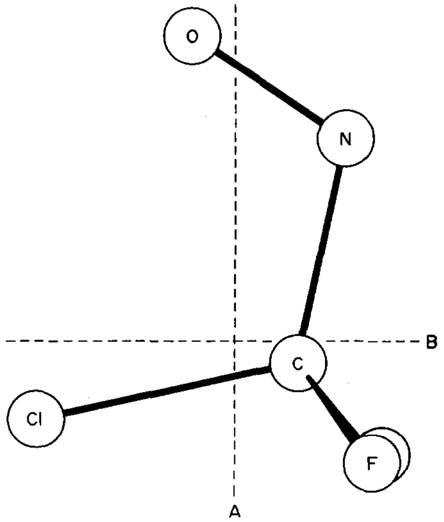

Fig. 6. Plausible structure of $CClF_2NO$ [30] in the *cis* conformation. (bond lengths: FC = 1.324 Å, ClC = 1.726 Å, CN = 1.51 Å, NO = 1.195 Å; angles: FCN = 113.9 °, ClCN = 113.9 °, all Newman projection angles = 120 °, and CNO = 112.4 °) The inferred moments of inertia are $I_A = 140.3$, $I_B = 164.3$, and $I_C = 221.1$ amu Å².

cm^{-1} is evidently too sharp in comparison. It is therefore assumed to belong to an impurity.

CONCLUSIONS

The gas phase i.r. spectra of the perhalonitrosomethanes have been obtained for the spectral region between 3300 and 200 cm^{-1}.

A comparison of the i.r. spectra of trichloronitrosomethane and its bromine derivatives showed that the spectrum of CBr_2ClNO is rather more complex than the other spectra. It was concluded that CBr_2ClNO exists in the form of two stable isomers, viz. in a *cis* and *gauche* conformation of the substituted methyl group with respect to the chlorine and oxygen atoms. For these compounds, the region between 1000 and 500 cm^{-1} probably contains more fundamental vibrations than can be inferred from the related aldehydes. The main i.r. bands were related for the various compounds and thus assigned.

The i.r. spectra of the fluoronitrosomethanes appeared to be strongly influenced by internal rotation. The spectrum of CCl_2FNO could be compared to that of CCl_3NO and was labelled correspondingly. Chlorine substitution of CF_3NO, however, leads to a drastically altered spectrum in the region below 600 cm^{-1}. Consequently, a vibrational assignment of $CClF_2NO$ requires more information on the torsional behaviour which may ultimately be obtained by a combination of microwave and far i.r. spectroscopy [31, 32].

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