INFRA-RED SPECTRAL STUDIES OF CHF_2–$CHCl_2$ AND $CBrCl_2$–$CBrCl$

BY V. B. KARTHA, SANTHA B. KARTHA AND N. A. NARASIMHAM, F.A.SC.

(Spectroscopy Division, Atomic Energy Establishment, Trombay, 414 A, Cadell Road, Bombay-28)

Received May 16, 1966

ABSTRACT

The infra-red spectra of two polyhalogenated ethanes, 1, 1-difluoro-2, 2-dichloro ethane and 1, 2-dibromo-1, 1, 2, 2-tetrachloro ethane were obtained in the region of 2·5–38 microns. The spectra of CHF_2-$CHCl_2$ were obtained in gas, liquid and solid states and also in solvents of widely varying dielectric constants.

These spectral studies showed that the molecule exists in the form of two rotational isomers. The fundamental modes of the two isomers were identified on the basis of intensity changes from gas to liquid to solid and in solvents of different dielectric constants. The observed infra-red absorption bands have been assigned in terms of the fundamental absorption bands.

Spectra of $CBrCl_2$–$CBrCl_2$ were obtained in the solid and vapour phase and in various solvents. These spectra showed that $CBrCl_2$–$CBrCl_2$ exists only in the trans form. The infra-red spectra, combined with Raman data available from literature was used for complete assignment of the observed absorption bands.

INTRODUCTION

SPECTROSCOPIC investigations of rotational isomerism have been so far confined largely to dihalogenated ethanes and to a few only of polyhalogenated ethanes. The ethanes, CHF_2–$CHCl_2$ and $CBrCl_2$–$CBrCl_2$ which belong to the latter category, have therefore been chosen for a spectroscopic study of rotational isomerism. From dipole moment measurement studies, the first is known to exist in two isomeric forms with an energy difference of 0·5–0·7 K. cal./mol. (Armand Di Giacomo and C. P. Smyth, 1955). The second is known to exist in a trans configuration, its dipole moment being zero (Kojima and Mizushima, 1937). A study of the vibration spectra of these two ethanes will, therefore, be helpful in establishing the existence of the isomeric forms. Whereas the Raman spectrum of $CBrCl_2$–$CBrCl_2$ is recorded by Kojima and

Mizushima (1937), no infra-red or Raman spectra are available for CHF_2–$CHCl_2$. In the present investigations, therefore, infra-red spectra of the two ethanes are obtained and discussed.

EXPERIMENTAL

A sample of 1, 1-difluoro-2, 2-dichloro ethane was obtained from K and K Laboratories, New York and was used as such without further purification. The substance is a liquid at room temperature and is highly volatile. It is soluble in common organic solvents such as carbon tetrachloride, cyclohexane and acetone. The second ethane, $CBrCl_2$–$CBrCl_2$ was synthesised by mixing bromine with tetrachloro ethylene in the ratio 1 : 2 by volume. The reaction flask containing the mixture was cooled by liquid nitrogen, evacuated to remove the last traces of oxygen present and sealed off. When the mixture was exposed to visible radiations of a hundred watt electric bulb for two hours $C_2Br_2Cl_4$ was obtained. This was purified by crystallisation from CCl_4 followed by vacuum sublimation.

Infra-red spectra of both the ethanes were obtained on a Perkin-Elmer Model 21 double beam spectrophotometer equipped with LiF, CaF_2, NaCl, KBr and CsBr prisms. Spectral slit widths of about 2 $cm.^{-1}$ and 5–10 $cm.^{-1}$ were used in the wavelength regions 6–38 microns and 2·5–6 microns respectively. Spectra of CHF_2–$CHCl_2$ were obtained in the solid state using a liquid-nitrogen cooled low temperature cell. Thin films of the sample were deposited on a cooled alkali halide window in vacuum, and the window was then rotated in position into the sample beam for recording spectra. In the case of $CBrCl_2$–$CBrCl_2$, solid state spectra were obtained in nujol mull and in KBr pellets. For its spectra in vapour phase, a high temperature cell with teflon gaskets was used.

Spectra of both the ethanes in solutions were obtained using cells of various thicknesses. Solvent compensation was carried out whenever necessary by using a variable thickness cell in the reference beam.

RESULTS AND DISCUSSION

A. CHF_2–$CHCl_2$

(i) *Possible forms of rotational isomers of the ethane and their normal modes of vibration.*—The CHF_2–$CHCl_2$ molecule could exist in two isomeric forms, the trans and the gauche. The molecule in the trans form possesses a plane of symmetry and belongs to point group Cs. Of the 18 fundamentals of the ethane, 11 are symmetric, of type (*a'*), and 7 are antisymmetric, of type

(*a''*), with respect to reflection in the plane of symmetry. In the gauche form, this distinction disappears as the molecule has no plane of symmetry and belongs to point group C_1. All the fundamental modes are active in the infra-red and Raman spectra of the molecule in both the configurations.

The infra-red spectra obtained for the ethane already show 23 strong absorption bands in the region 250–4000 cm.$^{-1}$ (Figs. 1 and 2 and Table I). The torsional modes and some of the skeletal modes are expected to lie below 250 cm.$^{-1}$ (Luff, 1955; Kagarise and Rank, 1952). If these vibrations are also included it will mean that more than the 18 fundamental modes of a single isomeric form of CHF_2–$CHCl_2$ are obtained in the infra-red absorption.

(ii) *Variation of relative intensities of bands from gas to liquid to solid states.*—A study of the variation of relative intensities of the bands of the

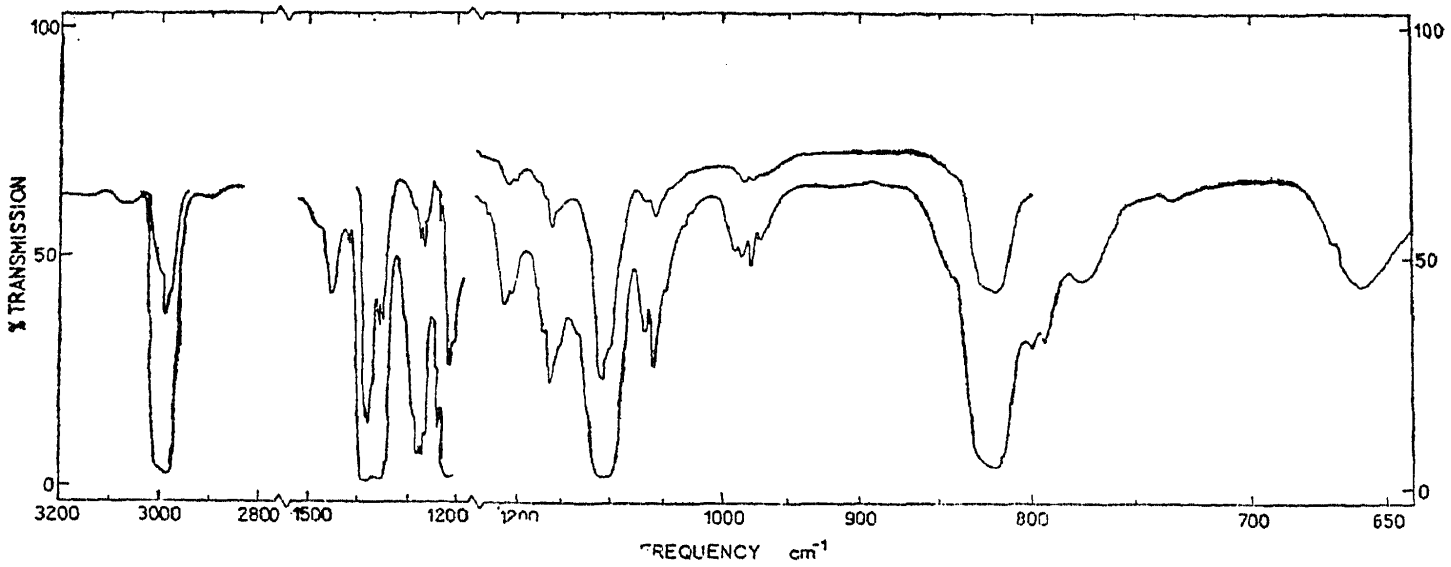

FIG. 1. (*a*) Infra-red spectra of CHF_2–$CHCl_2$ gas.

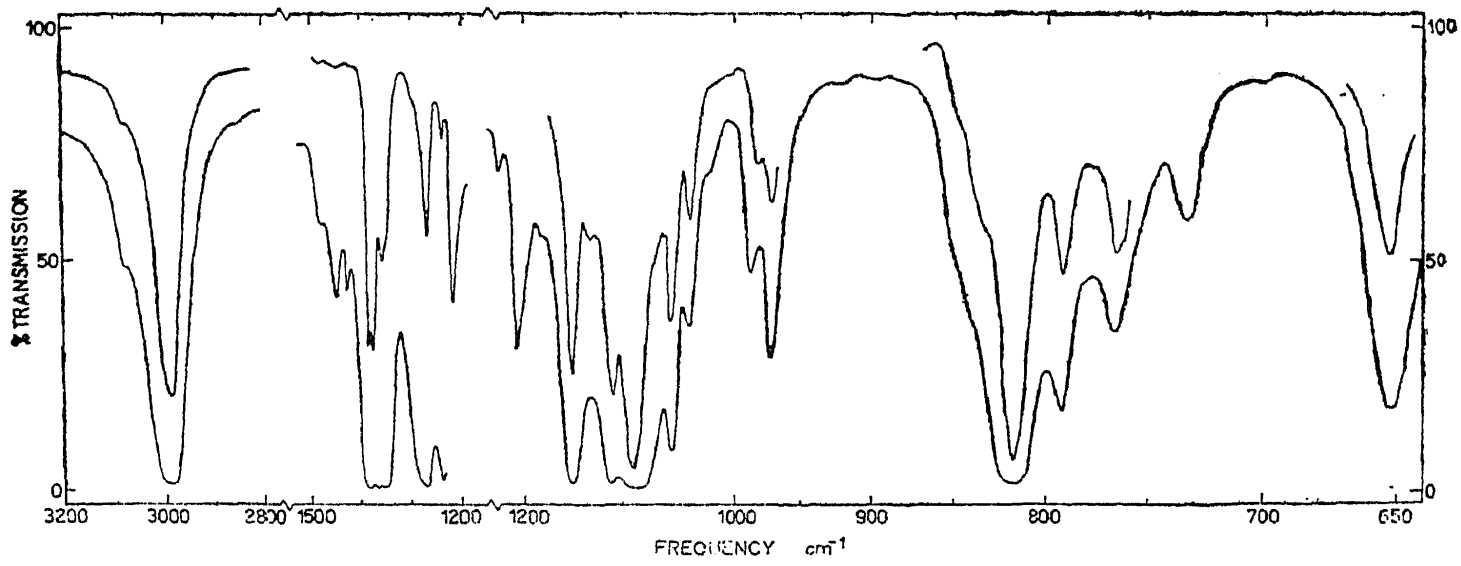

FIG. 1. (*b*) Infra-red spectra of CHF_2–$CHCl_2$ liquid.

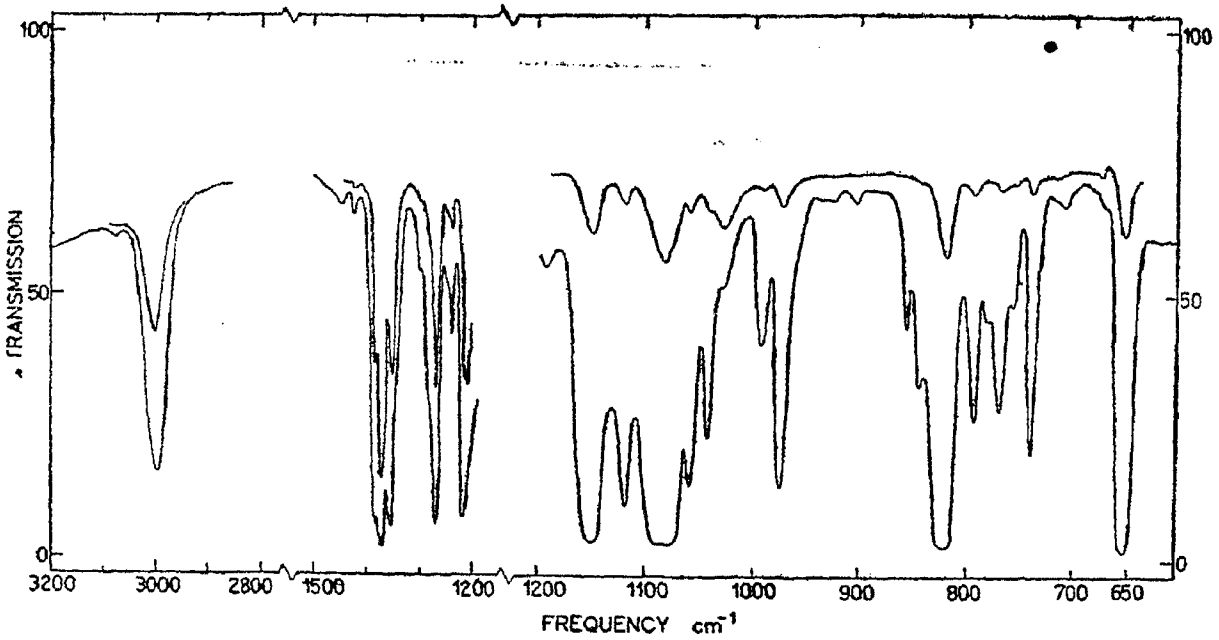

FIG. 1. (*c*) Infra-red spectra of CHF_2–$CHCl_2$ solid.

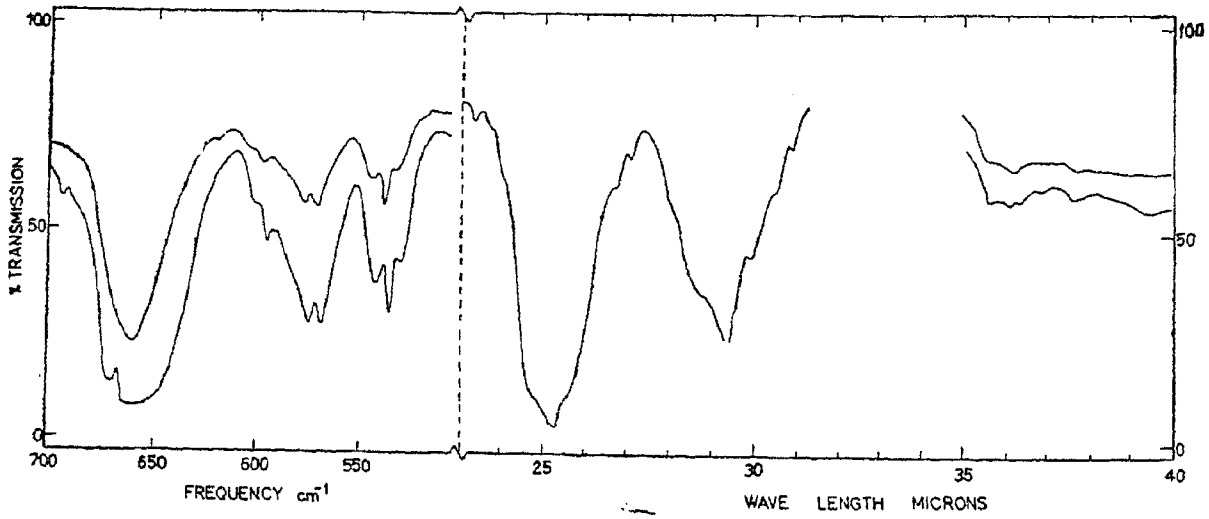

FIG. 2. (*a*) Infra-red spectra of CHF_2–$CHCl_2$ gas.

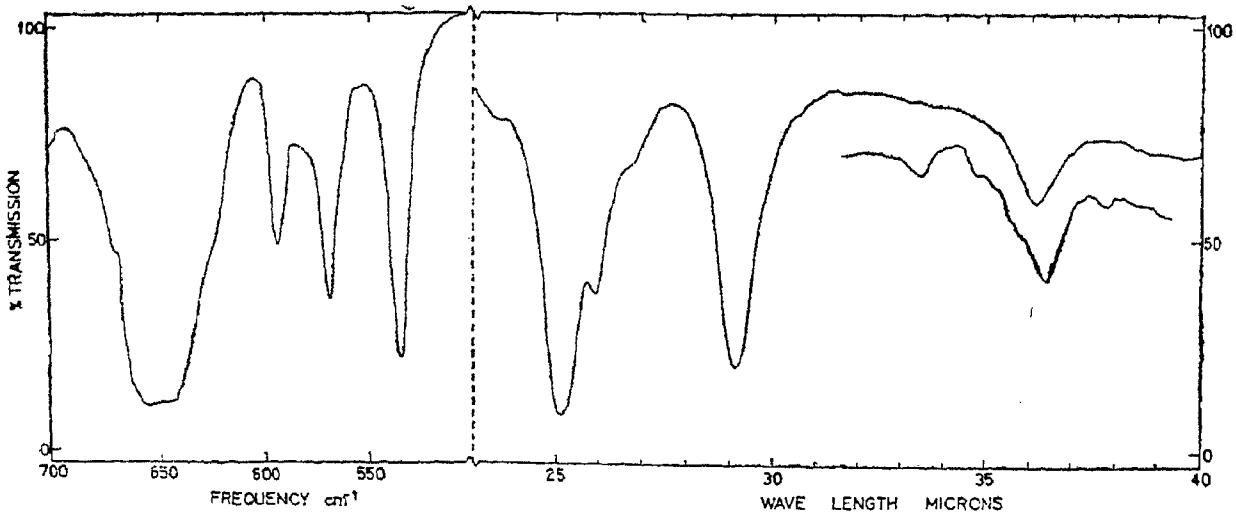

FIG. 2. (*b*) Infra-red spectra of CHF_2–$CHCl_2$ liquid.

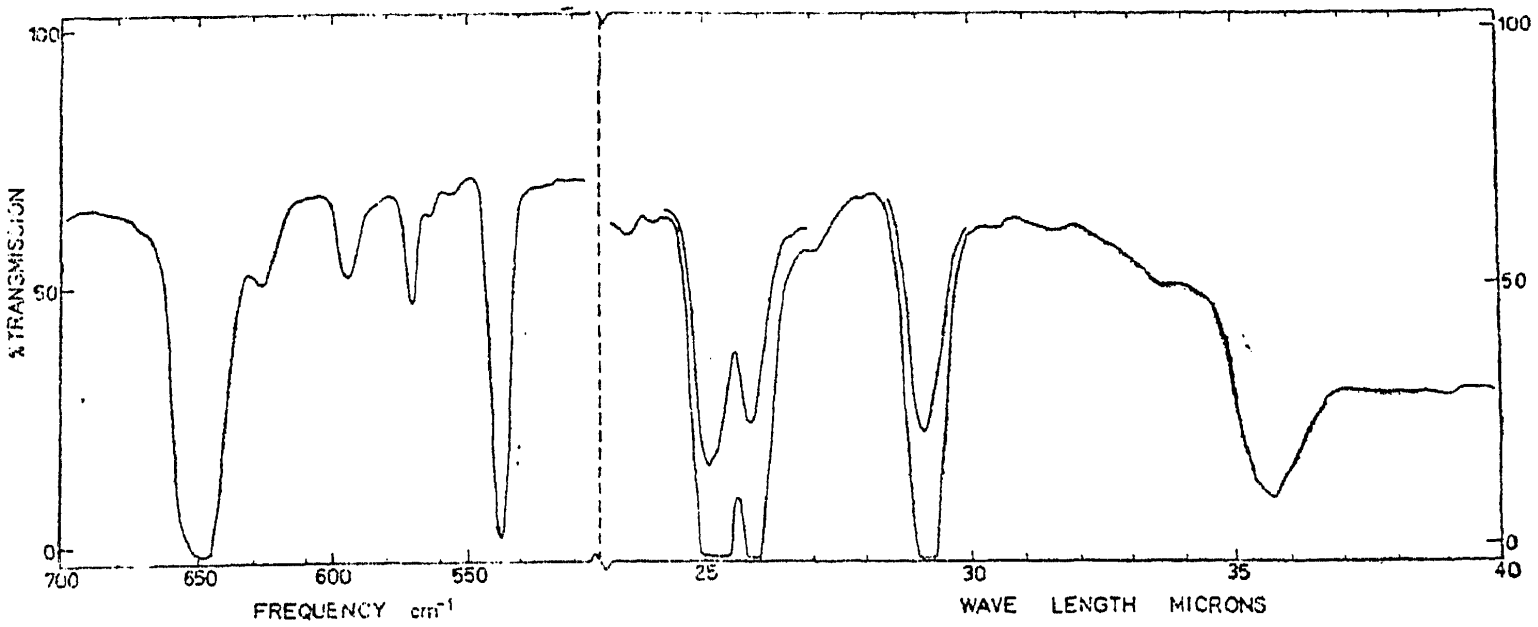

FIG. 2. (*c*) Infra-red spectra of CHF_2–$CHCl_2$ solid.

TABLE I

Frequencies of observed bands ($cm.^{-1}$) of CHF_2–$CHCl_2$ in the gaseous, liquid and solid state with a tentative assignment

Gas	Liquid	Solid	Assignment
279 m	276 s	281 s	Fundamental
	301 m	299 m	90+215 = 305
335 341 s 348	344 vs	344 vs	Fundamental
	378 sh	371 w	90+281 = 371
	388 w	388 s	Fundamental
397 vs	399 vs	399 vs	Fundamental
	424 w	426 w	344+90 = 434
530 536 w 543	535 m	538 vs	Fundamental
		555 w	344+215 = 559
	565 w	565 w	281×2 = 562

TABLE I (*Contd.*)

Gas	Liquid	Solid	Assignment
568 575 w	568 m	571 m	Fundamental
	580 sh	585 sh	399+194 = 593
595 600 w	593 m	595 m	Fundamental
	624 sh	626 m	538 + 90 = 628
659 663 s	653 s	651 vvs	Fundamental
694 w	700 w	711 w	90+281+344 = 715
734 w	732 m	737 s	Fundamental
750 vw		754 w	538+215 = 753
775 m	765 s	768 s	Fundamental
		778 w	388+399 = 787
795 800 m	790 s	791 s	Fundamental
821 s	816 vvs	819 vvs	Fundamental
844 sh	847 sh	842 m	651+194 = 845
		857 m	651+215 = 866
		903 w	816+90 = 906
		926 w	737+194=931
971 978 w	972 m	973 s	Fundamental
985 990 w	986 s	991 s	Fundamental
	1037 s	1041 s	651+399 = 1050
1050 1060 m 1068	1055 s	1058 s	Fundamental

TABLE I (*Contd.*)

Gas	Liquid	Solid	Assignment
	1089 vs	1082 s	Fundamental
1109 vvs	1110 vs	1117 s	Fundamental
1151 1162 m 1170	1153 s	1149 vs	Fundamental
	1183 w	1191 w	535+653 = 1188
1218 m	1214 s	1221 s	Fundamental
1242 m	1239 m	1239 m	1058+194=1252
1269 1276 w 1281	1271 m	1269 s	Fundamental
1291 w	1280 sh	1280 sh	1089 + 194 = 1283
1354 1364 s	1359 s	1553 s	972 + 388 = 1360 1271 + 90 = 1361 1153 + 215 = 1368 816 + 538 = 1354
1380 s	1379 s	1373 vs	Fundamental
	1386 s	1385 sh	Fundamental
	1429 w	1424 w	1214 + 215 = 1429
1458 w	1451 w	1450 w	1110 + 344 = 1454 1271 + 194 = 1465 1055 + 399 = 1454
1485 b, w			1276 + 215 = 1491
	1589 w	1589 w	1055 + 537 = 1592 1379 + 215 = 1594
1600 b, w	1612 w	1615 vw	1218 + 399 = 1617 1272 + 344 = 1616
1685 w	1682 w	1675 vs	1109 + 574 = 1680 1162 + 537 = 1699

TABLE I (*Contd.*)

Gas	Liquid	Solid	Assignment
	1735 vw	1741 vw	986 + 765 = 1751
	1785 vw		1214 + 569 = 1783
	1890 w	1885 w	1110 + 790 = 1900
1949 vvw			1380 + 571 = 1951
	1967 vw	1960 vvw	1153 + 816 = 1969
2030 vvw	2029 vw	2045 vw	1379 + 653 = 2032 1055 + 972 = 2027
	2058 vw		2 × 986 + 90 = 2062
2080 vvw			1110 + 974 = 2084
	2120 sh	2110 b, w	2 × 1055 = 2110 1153 + 972 = 2125
2167 m	2156 m	2140 w	1380 + 775 = 2155
	2182 sh		2 × 1089 = 2178
2198 m			1380 + 821 = 2201
2208 m			1218 + 988 = 2206
		2215 m	2 × 1109 = 2218
	2231 m		1271 + 972 = 2243
2262 b, w			2 × 1089 + 90 = 2268
	2292 vw	2280 w	2 × 1153 = 2306
2339 b, m	2335 m		1379 + 972 = 2351
2409 w	2412 m	2410 m	1155 + 1271 = 2426
2442 vw			1380 + 1061 = 2441
2486 w	2484 vw	2480 vw	1386 + 1110 = 2496
2530 vw	2525 w	2520 w	1379 + 1153 = 2532

TABLE I (*Contd.*)

Gas	Liquid	Solid	Assignment
	2565 vw		$2 \times 986 + 593 = 2565$
2591 vw	2598 vw		$1386 + 1214 = 2600$
2614 w	2612 m	2610 vw	$1379 + 1153 + 90 = 2622$
2687 w	2679 vw	2678 vvw	$1386 + 1089 + 215 = 2690$
2735 w	2728 m	2724 w	$1379 + 1271 + 90 = 2740$
2755 w			$1380 \times 2 = 2760$
2905 w			$2991 - 90 = 2901$
2982 2991 s 3000	2992 s	2999 s	Fundamental
3080 b, w	3080 sh	3080 vw	$2992 + 90 = 3082$
	3609 w		$2992 + 344 + 275 = 3611$
	3700 m		$2992 + 733 = 3725$
	3790 b, w		$2992 + 790 = 3782$
3800 w			$2992 + 816 = 3808$
3950 vw	3950 w	3950 vw	$2992 + 972 = 3964$

vvw = very very weak, vw = very weak, w = weak, b = broad, m = medium, s = strong, vs = very strong, vvs = very very strong, sh = shoulder.

ethane from gas to liquid to solid states will be useful to ascertain which of the isomeric forms is more stable in the solid state and at lower temperatures. For purposes of such comparison, the intensities of the absorption bands are normalised on an arbitrary scale giving a value of 100 for the intensity of the C–H band, at 3000 cm.$^{-1}$ Figure 3 shows the bands which are drawn on such a relative intensity scale (Table II).

TABLE II

Relative intensities of the fundamental frequencies of the two isomeric forms of CHF_2–$CHCl_2$

Gas		Liquid		Solid	
Frequency cm.$^{-1}$	Intensity	Frequency cm.$^{-1}$	Intensity	Frequency cm.$^{-1}$	Intensity
279	m	276	s	281	s
335 341 348	s	344	vs	344	vs
		388	w	388	s
397	vs	399	vs	399	vs
530 536 543	41	535	145	538	1048
568 575	38	568	82	571	94
595 600	15	593	47	595	63
659 663	125 sh	653	379	651	1223
734	12	732	94	737	398
775	86	765	340	768	251
795 800	182	790	371	791	09
821	698	816	1737	819	1653
971 978	67	972	233	973	437
985 990	60	986	125	991	106
1050 1060 1068	254	1055	410	1058	410
		1089	2146	1082	1771

TABLE II (*Contd.*)

Gas		Liquid		Solid	
Frequency cm.$^{-1}$	Intensity	Frequency cm.$^{-1}$	Intensity	Frequenay cm.$^{-1}$	Intensity
1109	1426	1110	723	1117	543
1152 1162 1170	278	1153	669	1149	1152
1218	119	1214	223	1221	208
1269 1276 1281	44	1271	140	1269	223
		1379		1373	437
1380	285		363		
		1386		1385 sh	
2982 2991 3000	100	2992	100	2999	100

Intensity of CH vibration is taken as 100 and with respect to this value, the intensities of the remaining vibrational frequencies are computed. Such a normalisation is not done for frequencies below 400 cm.$^{-1}$ They are however marked vs =very strong, s = strong, m = medium, w = weak.

A close study of Fig. 3 shows the following prominent variations in the relative intensities of bands. One group of bands (Group I) at 1271, 1153, 972, 732, 653 and 535 cm.$^{-1}$ shows considerable increase in intensity from the gas to liquid to solid states, while the bands at 1214, 790, 765, 593 and 568 cm.$^{-1}$ (Group II) decrease in intensity. A few bands, however, do not show any appreciable change in intensity and they are at 816, 399, 344 and 276 cm.$^{-1}$ It may therefore be inferred that there exist two rotational isomers, I and II, one form of which (I) has a larger concentration in the solid state as manifested by an increase in intensity of one set of bands. Those bands that decrease in intensity belong to the less abundant isomer (II) in the solid state. The bands that remain unchanged in their intensities may be taken to belong to both isomers. There is yet another category of bands like the one at 1380 cm.$^{-1}$ which in the liquid and solid states shows up as two bands

at 1373 and 1383 cm.$^{-1}$ The former shows an increase in intensity in the solid state and belongs to form I. The latter at 1383 cm.$^{-1}$ decreases in intensity and hence belongs to form II. A similar situation is obtained for the band at 1109 cm.$^{-1}$ in gas. In the liquid state, two bands are observed, both of which decrease in intensity in solid indicating that they belong to isomeric form II.

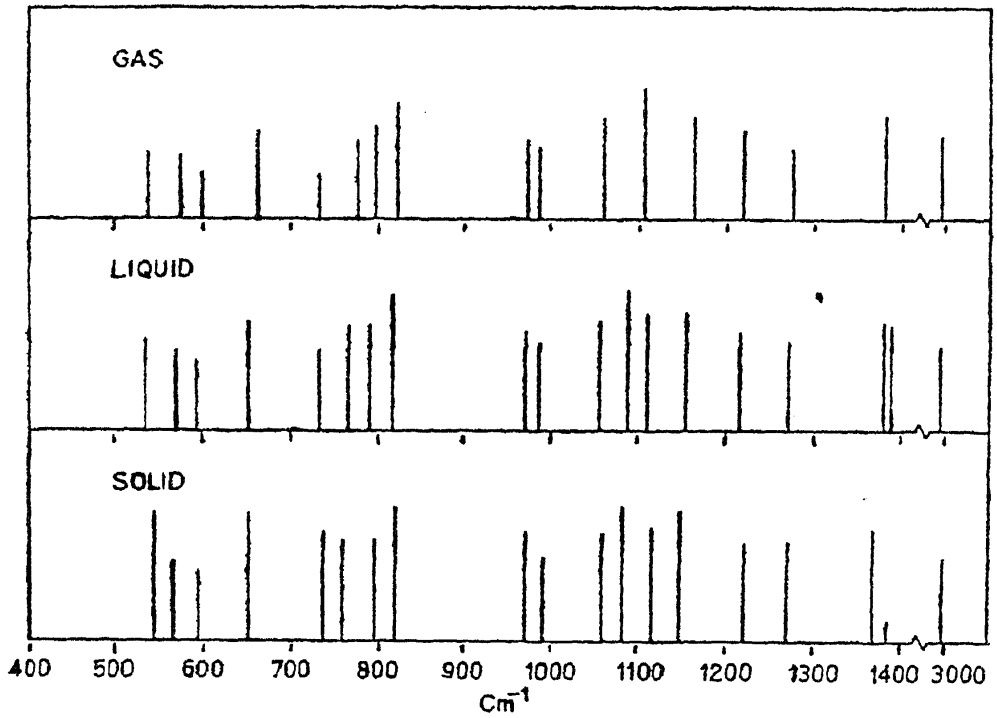

FIG. 3. Infra-red bands of CHF_2–$CHCl_2$.

(iii) *Solvent effect studies.*—Further confirmation of the existence of two isomeric forms is obtained from studies of the spectra of CHF_2–$CHCl_2$ in solvents of high and low dielectric constants. Carbon tetrachloride, dichloro ethylene, acetonitrile, cyclohexane and nitromethane which have dielectric constants of 2·24, 10·5, 1·87, 38·8, 2·05 and 39·4 respectively at 20° C. are chosen as suitable solvents. The intensities of the bands are dependent on the solvents chosen, as is evident from the extent of the absorption peaks of the bands in Fig. 4. The bands at 1379, 1153, 971, 654, 537 and 388 cm.$^{-1}$ are relatively stronger in solvents of high dielectric constants. These are also the bands of the isomeric form I that show an increase in intensity from gas to liquid to solid states (Fig. 3). The bands at 1386, 1214, 1110, 1089, 982, 792 and 763 cm.$^{-1}$ are more intense in solvents of low dielectric constants and are also the bands of isomeric form II that are less abundant in the solid state.

The two configurations of CHF_2–$CHCl_2$, the trans and the gauche, will possess different dipole moments and hence differ in their behaviour in

solvents of widely differing dielectric constants. The one of higher dipole moment is usually the more stable in solvents of higher dielectric constant. This indicates that form I has a larger dipole moment compared to form II. In the case of other polyhalogenated ethanes a similar result has been observed (Hallam and Ray, 1964).

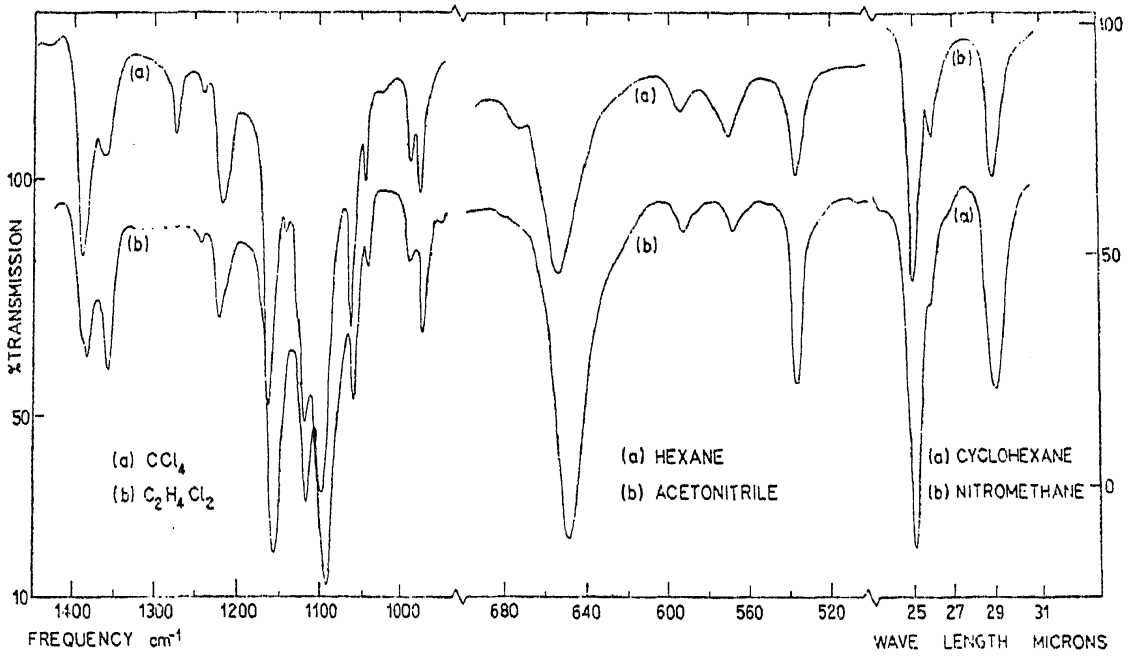

FIG. 4. Infra-red spectra of CHF_2-$CHCl_2$ solution.

(iv) *Assignment of vibrational frequencies.*—Each isomeric form of the ethane, CHF_2–$CHCl_2$ has 18 non-degenerate modes of fundamental vibrations. A calculation of moments of inertia of the molecule, using values of bond lengths and bond angles borrowed from similar molecules (Bucker and Nielsen, 1963) gives the following values for the trans (I) and gauche (II) forms:

(Trans) Form I	(Gauche) Form II
$I_a = 337{\cdot}4 \times 10^{-40}$ gm. cm.^{2}	$309{\cdot}5 \times 10^{-40}$ gm. cm.^{2}
$I_b = 407{\cdot}2 \times 10^{-40}$ gm. cm.^{2}	$441{\cdot}3 \times 10^{-40}$ gm. cm.^{2}
$I_c = 719{\cdot}3 \times 10^{-40}$ gm. cm.^{2}	$612{\cdot}2 \times 10^{-40}$ gm. cm.^{2}

The trans form approximates to a symmetric top which gives rise to parallel and perpendicular type infra-red bands. If the alternating dipole moment lies along the top axis or perpendicular to it, parallel and perpendicular bands result. Under the resolution employed in the present studies, these bands do not show any fine structure, but only band envelopes of unresolved PQR branches. For a parallel band of the trans form of CHF_2–$CHCl_2$, approximated to a symmetric top, the expected PR separation

is about 17 cm.$^{-1}$ (Gerhard and Dennison, 1933), while for a perpendicular band it is much less. The spectra in the gaseous state do show certain bands with a PR separation of 13–18 cm.$^{-1}$, and are accordingly assigned to the trans form. These are also the bands that increase in intensity in the solid state and in solvents of high dielectric constants. The molecule in the gauche configuration is an asymmetric top. The bands corresponding to it show more complex structure. In the present studies none of the bands could be assigned with certainty to the asymmetric top form solely on the basis of band contours.

Taking into consideration, the band contours in the gaseous state, the variation of relative intensities of bands from gas to liquid to solid states as well as in solvents of widely varying dielectric constants and finally, from a comparison of spectra of similar polyhalogenated ethanes, an assignment of fundamental frequencies of the two isomeric forms of CHF_2–$CHCl_2$ is made as given in Table III. The observed infra-red spectra are interpreted (Table I) in terms of these fundamentals.

TABLE III

Fundamental frequencies of the two isomeric forms of CHF_2–$CHCl_2$

Form I (Trans) cm.$^{-1}$	Form II (Gauche) cm.$^{-1}$	Approximate character
90*	90*	Torsion
194*	194*	
215*	215*	CCl_2 skeletal modes
281	281	
344	344	
388	399	
399	571	CF_2 skeletal modes
538	595	
651	768	
737	791	C–Cl stretch symmetric
819	819	C–Cl stretch antisymmetric
973	991	C–C stretch
1058	1117	H–C–C–bend
1269	1221	
1149	1082	C–F stretch symmetric
1373	1385	C–F stretch antisymmetric
2999	2999	C–H stretch symmetric
2999	2999	C–H stretch antisymmetric

* Estimated frequency values from combination and overtone bands.

B. $CBrCl_2$–$CBrCl_2$

(i) *Infra-red spectra of the trans form of* $CBrCl_2$–$CBrCl_2$.—The $CBrCl_2$–$CBrCl_2$ molecule in its trans configuration belongs to point group C_{2h}. Because of the centre of inversion the totally symmetric vibrations, a_g and b_g are active in the Raman spectrum only, while the vibrations which are not symmetric with respect to inversion, a_u and b_u are active in the infra-red only. In the Raman spectrum of $CBrCl_2$–$CBrCl_2$ only 10 bands were recorded by Mizushima all of them lying below 965 cm.$^{-1}$ No further studies of Raman or infra-red spectra of the ethane are known till the present investigations are undertaken.

Figure 5 shows the spectrum in the region 1000–500 cm.$^{-1}$. Since no absorption bands have been observed above 1000 cm.$^{-1}$ and in the region between 500 and 250 cm.$^{-1}$, only the absorption spectrum between 1000–500 cm.$^{-1}$, is shown in Fig. 5. The frequencies of the absorption bands are given in Table IV. For comparison, the Raman frequencies recorded by Mizushima are also noted alongside the infra-red frequencies. It is readily seen that the infra-red and Raman bands are mutually exclusive. Further, the infra-red spectra of $CBrCl_2$–$CBrCl_2$ in the solid state at — 186° C. and 29° C., and the gas at 150° C. and 175° C. did not show any significant changes either in the position of the bands or their relative intensities (Fig. 5). This meant that the ethane exists only in one configuration.

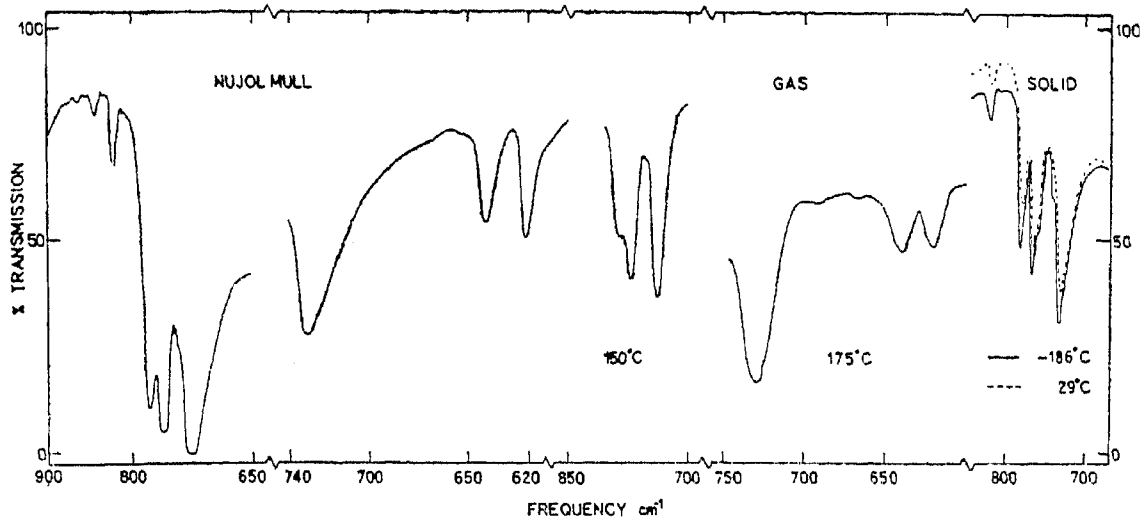

FIG. 5. Infra-red spectra of $C_2Br_2Cl_4$.

(ii) *Solvent effect studies.*—The spectra of $CBrCl_2$–$CBrCl_2$ in acetone, acetonitrile and cyclohexane have been taken. Figure 6 shows three of the absorption bands observed in the region 700–800 cm.$^{-1}$ in these solvents.

TABLE IV

Vibrational frequencies and assignments for $CBrCl_2$–$CBrCl_2$

Infra-red cm.$^{-1}$	Raman cm.$^{-1}$	Assignment	
80*		Torsion	
	190 (2)	Fundamental	CCl_2 skeletal modes
	245 (5)	Fundamental	
	267 (2)	Fundamental	
	303 (4)	Fundamental	
336 w		417 − 80 = 337	
347 m		267 + 80 = 347	
376 w		303 + 80 = 383	
	393 (6)	Fundamental.	CCl_2 deformation
	417 (2*b*)	Fundamental.	C–Br stretch
621 s		Fundamental.	C–Br stretch
641 s		Fundamental.	CCl_2 deformation
732 vs		Fundamental.	C–Cl stretch
742 w		824 − 80 = 744	
765 s		Fundamental.	C–Cl stretch
	803 (3)	Fundamental.	C–Cl stretch
820 m		641 + 190 = 831	
	824 (2)	Fundamental.	C–Cl stretch
	844 (2)	765 + 80 = 845	
864 vw		621 + 245 = 866	
902 vw		641 + 267 = 908	
919 vw		732 + 190 = 922	
		621 + 303 = 924	
942 vw		641 + 303 = 944	
964 vw		732 + 245 = 977	
	964 (2)	Fundamental.	C–C stretch
990 vw		732 + 267 = 999	

* Estimated frequency. m = medium, s = strong, w = weak, vs = very strong, vw = very weak.

As can be seen from this spectrogram, which is typical of the rest of the infra-red spectrum, no significant change in any of the bands is observed in spite of the widely varying dielectric constants of the solvents. The solvent spectra therefore indicate that the ethane $CBrCl_2$–$CBrCl_2$ does not possess any resultant dipole moment in any of these solvents. Further, the solvent spectra are not different from the infra-red spectrum of the solid ethane itself. These observations support that $CBrCl_2$–$CBrCl_2$ exists in the trans configuration.

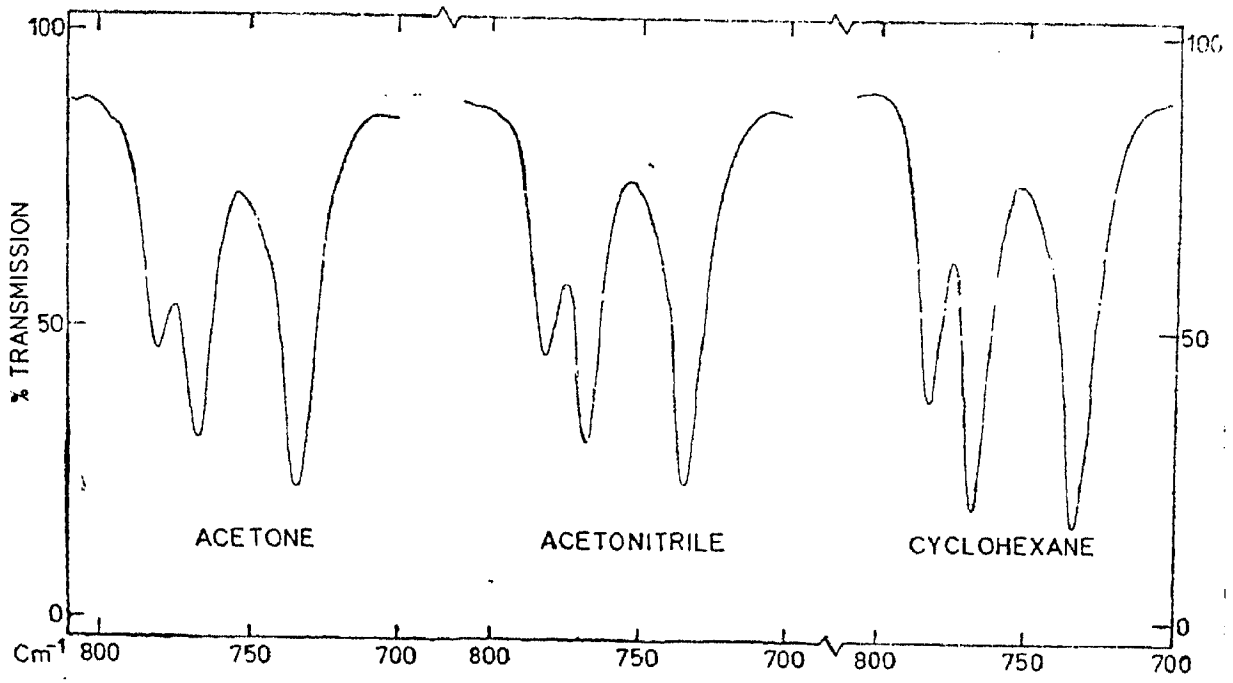

FIG. 6. Infra-red spectra of $C_2Br_2Cl_4$ solution.

(iii) *Assignment of the vibrational frequencies.*—The $CBrCl_2$–$CBrCl_2$ molecule is expected to have six carbon halogen stretching modes, four representing C–Cl vibration and two representing C–Br vibrations. To the former belong, the frequencies 732 (IR), 765 (IR), 803 (R) and 824 (R) and to the latter 417 (R) and 621 (IR), where IR and R in parentheses indicate that they are observed in infra-red and Raman spectra. The C–C stretch is totally symmetric and is represented by the Raman band at 964 cm.$^{-1}$ The C–Cl_2 skeletal modes and other low lying frequencies are assigned tentatively to certain characteristic group vibrations and given in Table IV. All the observed frequencies are explained as either fundamentals or combination bands. In the Raman spectrum bands appear below 300 cm.$^{-1}$ which region is inaccessible to us in the infra-red. The frequency at 80 cm.$^{-1}$ noted under the infra-red column in Table IV is taken to correspond to the torsional mode since several bands could be satisfactorily explained in combination with this frequency.

ACKNOWLEDGEMENTS

We are indeed grateful to Professor R. K. Asundi for a critical discussion of the manuscript and many helpful suggestions.

REFERENCES

Armand Di Giacomo and Charles P. Smyth	*J. Am. Chem. Soc.*, 1955, **77**, 1361.
Kojima, K. and San-Ichiro Mizushima	Science Papers Institute, *Phys. Chem. Research* (*Tokyo*), 1937, **31**, 296.
Luff, N. W. ..	*J. Phys. Chem.*, 1955, **59**, 92.
Kagarise, R. E. and Rank, D. H.	*Trans. Farad. Soc.*, 1952, **48**, 394.
Hallam, H. E. and Ray, T. C. ..	*Ibid.*, 1962, **58**, 1299.
Bucker, H. P. and Nielsen, J. R.	*J. Mol. Spec.*, 1963, **11**, 47.
Gerhard, S. L. and Dennison, D. M.	*Phys. Rev.*, 1933, **43**, 197.