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Rotational Isomers of the 1-Fluoro-2-haloethanes

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The infrared spectra of 1-chloro-2-fluoroethane, 1-bromo-2-fluoroethane, and 1-fluoro-2-iodoethane have been obtained in the solid, liquid, and vapor states. Raman spectra of the liquids are also presented. A complete vibrational-frequency assignment has been made for each of the molecules. The results indicate that the *gauche* isomer is the more stable in the liquid state whereas the *trans* form is more stable in the vapor. Enthalpy differences have been determined for each of the molecules in the liquid and vapor states except for gaseous 1-fluoro-2-iodoethane.

INTRODUCTION

The vibrational spectra of 1,2-disubstituted ethanes have been extensively studied with particular reference to the problem of hindered internal rotation.[1,2] Normally these investigations have shown that the molecules exist in the gaseous and liquid states as equilibrium mixtures of the *gauche* and *trans* isomers. However in the solid state it is usually found that only the more stable isomer, i.e., the form of lower potential energy, remains.

In all studies which have been made of 1,2-dihaloethanes of the type $X\cdot CH_2\cdot CH_2\cdot X$ or $X\cdot CH_2\cdot CH_2\cdot Y$ it has been found that the *gauche* form is less stable than, or approximately equally stable with the *trans* form in the liquid and gaseous states, except in the case of 1-chloro-2-fluoroethane where the *gauche* form was found to be the more stable in the liquid phase.[3] Apart from the above study, a comprehensive study of 1,2-difluoroethane,[4] and a partial one of 1-bromo-2-fluoroethane,[5] no detailed vibrational spectroscopic investigations of this series of molecules appear to have been made.

The present investigation was therefore undertaken in an attempt to detect the presence of rotational isomers and to measure enthalpy differences between the isomers in both the liquid and vapor phases. It was also hoped to make a vibrational-frequency assignment for each of the molecules since it was felt that only by studying such a series as this can one hope to make a reasonable vibrational-frequency assignment for any member of the series.

EXPERIMENTAL

The infrared spectra of the compounds were obtained on a Grubb–Parsons G.S. 2A infrared spectrometer over the range 4000–425 cm^{-1}.

Spectra of the liquids were obtained using capillary films between potassium bromide plates. Solid-state spectra were obtained by condensing the vapor from the volatile liquids on to a potassium bromide plate cooled to approximately −170°C. Care was taken to avoid fast condensation which in some cases may lead to freezing out of a mixture of two isomers.[6] Room-temperature vapor-phase spectra were obtained using the equilibrium vapor pressure of the appropriate liquid in a 10-cm glass cell. Vapor spectra at higher temperatures were obtained using a similar but insulated cell which was heated by means of Nichrome wire. The temperature was controlled to ±1°C by means of an Ether 12-91 anticipatory potentiometric controller and an iron–constantan thermocouple.

Temperature-dependence studies of the liquids were more difficult than is usual owing to the high volatility of this series of compounds. Room temperature was the highest which could conveniently be used. The studies were made using a standard R.I.I.C. cold cell, the temperature of which was varied with dry-ice–acetone mixtures. In practice it proved possible to maintain temperatures to an accuracy of ±1°C over the studied range by the occasional addition of small amounts of dry ice. Care was taken to ensure that the spectral bandwidth was less than $\frac{1}{5}$ of the band half-width in each case.[7] Each band was run at least five times at each temperature and the mean value was taken. A minimum of five runs was also made for the vapor studies.

The Raman spectra of the liquids were recorded in the region 2700–70 cm^{-1} using a Cary Laser Raman Model 81 photoelectric recording spectrometer. Unfortunately this spectrometer was not equipped for obtaining Raman spectra at higher than 2700 cm^{-1} but this is not a region where rotational isomers are expected to show unique spectra.

1-Chloro-2-fluoroethane was prepared by the method of Saunders, Stacey, and Wilding[8] from thionyl chloride and 2-fluoroethanol. The boiling point after fractionation was 53°C (lit bp 51°–53°C).

1-Bromo-2-fluoroethane was prepared from potassium fluoride and 1,2-dibromoethane using Hoffman's

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[5] D. Simpson and E. K. Plyler, J. Res. Natl. Bur. Std. **50**, 223 (1953).

[6] V. A. Pozdyskhev, Y. A. Pentin, and V. M. Tatevskii, Dokl. Akad. Nauk SSSR **114**, 583 (1957).

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[8] B. C. Saunders, G. J. Stacey, and I. G. E. Wilding, J. Chem. Soc. **1949**, 773.

TABLE I. Vibrational frequencies and assignments of fundamental modes of vibration of the *gauche* isomers (cm^{-1}).

$Cl\cdot CH_2\cdot CH_2\cdot F$				$Br\cdot CH_2\cdot CH_2\cdot F$				$I\cdot CH_2\cdot CH_2\cdot F$				
Infrared			Raman	Infrared			Raman	Infrared			Raman	
Vapor	Liquid	Solid	Liquid	Vapor	Liquid	Solid	Liquid	Vapor	Liquid	Solid	Liquid	Assignment
2978 s	2962 m	2966 s		2978 s	2976 m	2980 s		2992 m	2973 m	2981 2971 m		$\nu_a(CH_2)$
		2918 wsh			2951 sh	2960 s			2948 sh	2948 m		$\nu_a(CH_2)$
2915 2894 m	2898 mw	2897 m		2898 m	2888 m	2895 s		2901 mw	2907 mw	2898 m		$\nu_s(CH_2)$
1459 w	1458 m	1458 m	1461 (1)	1457 1448 mw	1458 mw	1458 s	1462 (1)	1467 sh	1459 mw	1461 m	1462 (½)	$b(CH_2)$
1429 w	1428 s	1428 s	1429 (1)	1434 1429 1417 mw	1421 m	1419 vs	1424 (1)	1426 1416 w	1412 m	1409 s	1415 (½)	$b(CH_2)$
1390 w	1390 mw	1390 m	1394 (½)	1395 1383 1375 mw	1386 mw	1385 s	1399 (1)	1396 1386 mw	1382 m	1383 m	1383 (½)	$w(CH_2)$
1310 1305 1295 m	1299 vs	1299 vs	1301 (1)	1291 1284 1278 ms	1280 vs	1278 vs	1280 (2)	1277 1272 1265 s	1264 vs	1266 vs	1264 (2)	$w(CH_2)$
1263 1257 1250 w	1250 vw	1250 w	1252 (1)	1238 w	1229 mw	1226 m	1231 (2)	1206 1193 s	1193 ms	1196 1188 s	1195 (2)	$tw(CH_2)$
1197 vw	1194 m	1197 m	1196 (1)	1183 w	1180 w	1177 s	1181 (1)	1175 1167 s	1169 m	1167 m	1170 (2)	$tw(CH_2)$
1073 1056 m	1075 vs	1073 vs	1072 (1)	1073 1062 vs	1070 vs	1063 vs	1067 (1)	1063 1054 s	1063 vs brd	1052 vs	1060 (½)	$\nu(CC)$
1040 1026 vs	1030 vs	1032 vs	1028 (1)	1035 sh 1026 vs	1004 vs brd	994 vs	1004 (2)	1018 1009 vs	979 vs brd	978 s	980 (1)	$\nu(CF)$

TABLE I (*Continued*)

$Cl\cdot CH_2\cdot CH_2\cdot F$				$Br\cdot CH_2\cdot CH_2\cdot F$				$I\cdot CH_2\cdot CH_2\cdot F$				
Infrared			Raman	Infrared			Raman	Infrared			Raman	
Vapor	Liquid	Solid	Liquid	Vapor	Liquid	Solid	Liquid	Vapor	Liquid	Solid	Liquid	Assignment
963 vw	956 mw	955 m	958 (1)	959 952 } w 946	943 s	938 s	944 (1)	940 vw sh	930 m	922 vs	931 (½)	$r(CH_2)$
851 845 } w 838	839 s	837 s	840 (2)	821 vw	821 s	821 s	822 (1)	794 782 } w 769	789 mw	788 vs	790 (½)	$r(CH_2)$
693 685 } m 678	668 s	667 vs	668 (10)	593 588 } w 580	573 m	568 vs	573 (10)	526 } vw 513	517 m	517 s	517 (10)	$\nu(CX)$
469 464 } m 456	465 m	469 vs	468 (1)	451 s	449 s	454 vs	451 (3)	431 s	431 s	430 s	431 (7)	$b(CCF)$
			290 (2)				264 (2)				244 (2)	$b(CCX)$
			142 (1)				126 (½)				116 (½)	torsion

method.[9] After fractional distillation the boiling point was 73°–74°C (lit bp=71°–74°C).

The preparation of 1-fluoro-2-iodoethane was carried out using the method of Hine and Ghirardelli[10] using sodium iodide and 1-bromo-2-fluoroethane. After purification by fractional distillation the boiling point was 94.5°–96.5°C (lit bp=96.5°–97°C).

RESULTS

Each isomer of the molecules in this series should possess 18 fundamental modes of vibration, each of which should be infrared and Raman active. Hence 36 distinct fundamental bands are theoretically possible. In practice this number of bands is never found since the corresponding vibrational modes in the two isomers usually have virtually identical frequencies which result in an infrared or Raman band common to both species. Hence it is usually found that the solid-state spectrum of a disubstituted ethane of the type $X\cdot CH_2\cdot CH_2\cdot X$ is simplified by the loss of perhaps three or four bands compared with the liquid-state spectrum.

A frequency assignment for the approximate modes of vibration for the *gauche* isomers is given in Table I and the bands unique to the *trans* isomers are given in Table II. Table II illustrates the above point that very little simplification of the spectra occurs on passing to the solid state. Overtone and combination tones are given in Table III.

Assignments such as these must be tentative particularly with reference to the modes of vibration involving the (CH_2) groups. We have adopted the usual scheme for assigning these vibrations in order of decreasing frequency, i.e., $\nu(CH_2) > d(CH_2) > w(CH_2) > tw(CH_2) > r(CH_2)$. The only previous attempt at a vibrational-frequency assignment for any of these molecules was that made for 1-bromo-2-fluoroethane.[5] However, that assignment was made without the aid of solid-state spectra and is considerably different from the present one. In particular many of the bands which were previously assigned to the *trans* isomer are now assigned as arising from both isomers since they did not disappear on solidification of the sample. The present assignment also has the advantage of having been made for three very similar molecules. One can see from Tables I and II that the assignments are internally consistent but since they must be to some extent arbitrary they will not be discussed in detail except for a few specific points.

All bands above 500 cm^{-1} which have been assigned to the *trans* molecule disappeared in the solid state and hence such assignments are not in doubt. Assignment of bands unique to the *gauche* isomer are less easy. Normally this has been accomplished by observing intensity changes in solvents of various polarities. The more polar isomer is favored in more polar solvents. This rule

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[10] J. Hine and R. G. Ghirardelli, J. Org. Chem. **23**, 1550 (1958).

TABLE II. Vibrational frequencies and assignments of fundamental modes of vibration unique to the *trans* isomer (cm^{-1}).

$\mathrm{Cl \cdot CH_2 \cdot CH_2 \cdot F}$				$\mathrm{Br \cdot CH_2 \cdot CH_2 \cdot F}$				$\mathrm{I \cdot CH_2 \cdot CH_2 \cdot F}$				
Infrared			Raman	Infrared			Raman	Infrared			Raman	
Vapor	Liquid	Solid	Liquid	Vapor	Liquid	Solid	Liquid	Vapor	Liquid	Solid	Liquid	Assignment
1469 w	1458* m	1458* m	1461* (1)		1458* mw	1458* s	1462* (1)	~1480 sh	1467 wsh		1462* (½)	$b(\mathrm{CH_2})$
1445 1438 w				1457 1448 mw *	1450 wsh			1452 1442 mw	1438 mw		1440 (<½)	$b(\mathrm{CH_2})$
1390 w[a]	1390* mw	1390* m	1368(<½)	1395 1383 1375 mw *	1386* mw	1385* s	1373(<½)	1371 1362 wsh	1367 vw		1372(<½)	$w(\mathrm{CH_2})$
1232 vw	1232 vw			1223 1211 m	1218 wsh		1222 sh (<½)	1206 1193 m *	1193* ms	1196 1188 s *	1195*(2)	$tw(\mathrm{CH_2})$
1092 sh	1075* vs	1073* vs	1072*(1)	1094 1081 msh	1070* vs	1063* vs	1067*(1)	1089 1076 msh	1063* vs	1052* vs	1060*(½)	$\nu(\mathrm{CF})$
1040 1026 vs *	1013 msh		1012 sh(½)	1035 sh 1026 vs *	1004* vs brd	994* vs	1004*(2)	1018 1009 vs *	979* vs brd	978* s	980*(1)	$r(\mathrm{CH_2})$
781 777 769 s	759 m		760 (1)	695 687 s	681 m		683 (3)	640 631 s	631 m		631 (3)	$\nu(\mathrm{CX})$
			383 (2)				338 (3)				313 (4)	$b(\mathrm{CCF})$
			262(<½)				226(<½)				204 (1)	$b(\mathrm{CCX})$

[a] Asterisks indicate bands which are also *gauche* fundamentals.

TABLE III. Assignment of infrared bands other than to fundamental vibrations (cm^{-1}).

$Cl\cdot CH_2\cdot CH_2\cdot F$			$Br\cdot CH_2\cdot CH_2\cdot F$			$I\cdot CH_2\cdot CH_2\cdot F$			
Vapor	Liquid	Solid	Vapor	Liquid	Solid	Vapor	Liquid	Solid	Assignment
	2982 wsh	2992 sh						2993 vw	
2865 vw	2850 vwsh	2845 vwsh	2846 vwsh		2938 vw		2857 vwsh		$2\times b(CH_2)$
	2752 vw	2759 vw	2757 vw		2750 vw				$2\times w(CH_2)$
							2329 vw		$2\times w(CH_2)$
								2180 w	$w(CH_2)+r(CH_2)$
							1219 vw	1222 w	$r(CH_2)+b(CCF)$
								1032 msh	$2\times\nu(CI)$
							951 wsh	949 m	$\nu(CF)+b(CCF)$
				905 vwsh					$\nu(CBr)+b(CCBr)$
		522 w							$b(CCF)$ +torsion

is sufficiently reliable for frequency assignments to have been made on this basis.[11] The rule may also be used to determine which is the more stable isomer since in asymmetrically disubstituted ethanes of the type $X\cdot CH_2\cdot CH_2\cdot Y$, all vibrations should be infrared and Raman active and it is not obvious which bands belong to which isomer. Wyn-Jones and Orville-Thomas[12] have developed a novel method for distinguishing between the *gauche* and *trans* carbon–halogen stretching vibrations of 1,2-disubstituted ethanes based on product of the electronegativities of X and Y. We have reached similar conclusions using solvents of various polarities.[13] The solvent method is more generally applicable since it is not limited to carbon–halogen stretching vibrations. It is also particularly useful for bands which occur at frequencies below 500 cm^{-1}. The present assignments for this region have been made from a comparison of the Raman intensities in the pure liquid and in carbon disulfide solution. Since solid-state Raman spectra are not easy to obtain and because far-infrared spectrometers are still not generally available, this method would appear to be particularly useful in other similar cases.

The most difficult bands to assign were those arising from the carbon–fluorine stretching vibrations. These vibrations are likely to be coupled with other vibrations and also they occur in the 1000-cm^{-1} region where other bands may be present. For liquid 1-chloro-2-fluoroethane it was found that the infrared spectrum showed a broad, very strong band at 1075 cm^{-1} and another strong band at 1030 cm^{-1} with a low-frequency shoulder at 1013 cm^{-1}. In a carbon disulfide solution the higher-frequency band was partially resolved into a very strong band at 1078 cm^{-1} with a shoulder at 1066 cm^{-1}. Similarly the shoulder at 1013 cm^{-1} appeared as a band approximately equal in intensity to that at 1030 cm^{-1}. By use of this and other solvents of various dielectric constants for each of the 1-fluoro-2-haloethanes it was concluded that there were actually four bands in this spectral region. It is suggested that the higher-frequency band is composed of $\nu(CC)$ common to both isomers and $\nu(CF)$ of the *trans* isomer. The lower-frequency band has been assigned to $\nu(CF)$ of the *gauche* isomer and $r(CH_2)$ of the *trans* form. These assignments are consistent with the apparent abnormal sharpening of these bands in the solid state which may well be due to the loss of one component from each. The assignment of the *trans* $\nu(CF)$ at higher frequency than the corresponding *gauche* vibration is in agreement with the assignments for other 1,2-dihalogenoethanes with the exception of that made for 1,2-difluoroethane.[4] However this latter assignment could readily be altered to

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[11] S. Mizushima, T. Shimanouchi, T. Miyazawa, I. Ichishima, K. Kuratani, I. Nakagawa, and N. Shido, J. Chem. Phys. **21,** 815 (1953).

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TABLE IV. Sum rule agreement for the 1-fluoro-2-haloethanes using liquid-phase values.

		Mizushima sum rule			Bernstein and Pullin sum rule		
Molecules	State	*gauche* $\sum_i \nu_i^2\times10^{-7}$	*trans* $\sum_i \nu_i^2\times10^{-7}$	% Difference	*gauche* $\sum_i \nu_i\times10^{-4}$	*trans* $\sum_i \nu_i\times10^{-4}$	% Difference
$Cl\cdot CH_2\cdot CH_2\cdot F$	liquid	3.255	3.266	0.34	1.934	1.936	0.10
$Br\cdot CH_2\cdot CH_2\cdot F$	liquid	4.084	4.093	0.22	2.202	2.200	0.09
$I\cdot CH_2\cdot CH_2\cdot F$	liquid	4.050	4.058	0.20	2.178	2.175	0.14

be consistent with the others. One anticipates that the carbon–halogen stretching vibration of the *trans* isomer should occur at a higher frequency than that of the *gauche* form because this frequency in isomers of substituted ethanes has been found to increase as the electronegativity of the grouping which is *trans* to it increases.[12]

A check on the assignments may be made from the Mizushima sum rule[14] and also from the empirical sum rule derived by Bernstein and Pullin.[15] It can be seen from Table IV that the agreement is satisfactory. However it is worth pointing out that these sum rules are not particularly rigorous tests of assignments in these cases, since most of the bands unique to a particular isomer occur at low frequencies.

Enthalpy differences between the isomers have been calculated in the vapor and liquid states using the distinct carbon–halogen stretching vibrations. The enthalpy differences were calculated from the formula

$$\frac{\ln(\text{optical density of } \textit{trans} \text{ band})}{\ln(\text{optical density of } \textit{gauche} \text{ band})} = \text{constant}\ \exp(-\Delta H/RT). \quad (1)$$

In the case of the vapor measurements the area under the bands were used rather than the peak height optical densities used for the liquids. This procedure was adopted for the vapor measurements because there were some indications of structure on the bands which made it difficult to obtain accurate peak-height measurements. The measurements are given in Tables V and VI and the calculated enthalpy differences along with those for related molecules are given in Table VII. Unfortunately we were unable to measure the enthalpy difference of 1-fluoro-2-iodoethane in the vapor state because the ν(CI) band arising from the *gauche* isomer

TABLE V. Temperature dependence of the optical densities of the ν(C–X) bands (where X = Cl, Br, or I) for liquid 1-fluoro-2-haloethanes.

Compound	Temperature (°C)	Optical density of *trans* band	Optical density of *gauche* band	$\log_{10}\frac{\text{O.D. } trans}{\text{O.D. } gauche}$
$Cl\cdot CH_2\cdot CH_2\cdot F$	7	0.338	0.0550	0.789
	−12	0.361	0.0520	0.840
	−18	0.380	0.0499	0.882
	−29	0.444	0.0505	0.944
	−51	0.459	0.0476	0.984
$Br\cdot CH_2\cdot CH_2\cdot F$	22	0.395	0.344	0.0601
	6	0.455	0.351	0.113
	−11	0.519	0.353	0.168
	−28	0.392	0.249	0.196
	−44	0.452	0.248	0.266
$I\cdot CH_2\cdot CH_2\cdot F$	23	0.134	0.357	−0.426
	0	0.161	0.401	−0.396
	−16	0.186	0.431	−0.365
	−38	0.196	0.415	−0.325
	−53	0.206	0.392	−0.278
	−67	0.198	0.333	−0.225

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[14] S. Mizushima, T. Shimanouchi, I. Nakagawa, and A. Miyake, J. Chem. Phys. **21**, 215 (1953).

[15] H. J. Bernstein and A. D. A. Pullin, J. Chem. Phys. **21**, 2188 (1953).

TABLE VI. Temperature dependence of the areas of the ν(C–X) bands (where X = Cl or Br) for gaseous 1-chloro-2-fluoroethane and 1-bromo-2-fluoroethane.

Compound	Temperature (°C)	Area of *trans* band (arbitrary units)	Area of *gauche* band (arbitrary units)	$\log_{10}\frac{\text{Area}_{trans}}{\text{Area}_{gauche}}$
$Cl\cdot CH_2\cdot CH_2\cdot F$	28	1.84	1.38	0.124
	45	1.67	1.27	0.119
	63	1.51	1.17	0.109
	84	1.36	1.07	0.104
	103	1.19	0.95	0.099
$Br\cdot CH_2\cdot CH_2\cdot F$	28	3.62	0.87	0.618
	41	3.30	0.82	0.603
	62	3.06	0.79	0.589
	83	2.74	0.71	0.584
	103	2.47	0.66	0.572

was too weak to allow accurate measurements. However, by comparison of the ratio of the areas of the optical-density plots of the *trans* and *gauche* ν(CI) bands (15:1) in the vapor spectrum with the ratios for the corresponding bands for both liquid and vapor phases (Tables V and VI), it would appear that the vapor-phase enthalpy difference for 1-fluoro-2-iodoethane is greater than for the other two compounds.

It is interesting to observe from Table VII that in the case of each of the 1-fluoro-2-haloethane molecules there is a reversal in stability on passing from the liquid to the gaseous phase. To the best of our knowledge this is the only series of substituted ethanes for which there is experimental evidence for this type of behavior. It is true to say, however, that the ratio of the more polar isomer to the less polar isomer is always increased on passing from the vapor to the liquid phase. This has been accounted for experimentally in terms of an electrostatic effect[1] which may be described by the Onsager equation. According to this equation, when a molecule of dipole moment μ is transferred from a vacuum into a medium of dielectric constant ϵ, it loses potential energy by an amount E such that

$$E = (\epsilon - 1)/(2\epsilon + 1)(\mu^2/a^3), \qquad (2)$$

where a is the molecular radius. Obviously in the case of rotational isomers the loss of potential energy will be greater for the more polar form and consequently it will have an increased stability in the liquid phase. In the vapor phase the effects governing stability are likely to be a combination of electrostatic and steric effects. From Table VII it would appear that the predominating effect is that of steric repulsion since the enthalpy differences increase with increasing mass of the halogen atoms. Unless there is a specific intramolecular interaction such as hydrogen bonding in the gaseous phase as in the case of the 2-haloethanols[16] it would appear most unlikely that the *gauche* isomer will be the more stable form. However, in the liquid state, the intermolecular electrostatic forces will have a large effect on the relative stabilities and in extreme cases such as the 1-fluoro-2-haloethanes, they may even cause a reversal in the stability. These results indicate the limited value of enthalpy differences measured in the liquid state or in solution since the values obtained are unlikely to be indicative of the intramolecular forces.

TABLE VII. Enthalpy differences of 1,2-dihalogenoethanes.

Molecule	Phase	ΔH for *trans–gauche* equilibrium kcal/mole	Reference
$F\cdot CH_2\cdot CH_2\cdot F$	Gas	0.0 ± 0.2	4
$Cl\cdot CH_2\cdot CH_2\cdot F$	Gas	0.2 ± 0.08	present work
	Gas	0.06 ± 0.04	3
	Gas	0.48	a
$Br\cdot CH_2\cdot CH_2\cdot F$	Gas	0.3 ± 0.08	present work
$I\cdot CH_2\cdot CH_2\cdot F$	···	···	···
$Cl\cdot CH_2\cdot CH_2\cdot Cl$	Gas	1.24 ± 0.05	b
	Gas	1.15 ± 0.15	c
$Br\cdot CH_2\cdot CH_2\cdot Cl$	Gas	1.43 ± 0.1	d
$Br\cdot CH_2\cdot CH_2\cdot Br$	Gas	1.77 ± 0.15	e
$F\cdot CH_2\cdot CH_2\cdot F$	Liquid	~ -0.9	4
$Cl\cdot CH_2\cdot CH_2\cdot F$	Liquid	-1.01 ± 0.20	present work
	Liquid	-0.47 ± 0.06	3
$Br\cdot CH_2\cdot CH_2\cdot F$	Liquid	-0.92 ± 0.20	present work
$I\cdot CH_2\cdot CH_2\cdot F$	Liquid	-0.61 ± 0.15	present work
$Cl\cdot CH_2\cdot CH_2\cdot Cl$	Liquid	0[g]	1
$Br\cdot CH_2\cdot CH_2\cdot Cl$	Liquid	0.49 ± 0.10	f
$Br\cdot CH_2\cdot CH_2\cdot Br$	Liquid	0.72[g]	1

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[e] H. J. Bernstein, J. Chem. Phys. **18**, 897 (1950).
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[g] Average of what we consider the most reliable values.

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