

Infrared Studies of 1,2-Dibromo-2,2-difluoroethane

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The infrared spectra of 1,2-dibromo-2,2-difluoroethane as a vapour, as a liquid, and as a solid were recorded in the region 4000–250 cm^{-1} . Moreover, the compound was crystallized at room temperature under high pressure, and the infrared spectra of a polycrystalline sample and of a single crystal were obtained. The dichroic ratio of the stronger bands were registered. From the spectra it is clear that the same conformer is present in the low temperature and in the high pressure solids.

The vibrational spectra of 1,2-dibromo-2,2-difluoroethane were reported a long time ago by Kagarise.¹ He observed a considerable simplification of the infrared spectrum in the solid state compared to the liquid. In agreement with the results for other halogenated ethanes,² this molecule therefore exists as a mixture between conformers in the liquid, but only one conformer is present in the crystal.¹ Since this molecule has the general formula $\text{CX}_2\text{Y}-\text{CX}_2'\text{Y}'$, two of the staggered conformations are spectroscopically identical (mirror images) and we expect a single *trans* form (C_s symmetry) and two enantiomorphous *gauche* forms (C_1 symmetry).

We were primarily interested in studying this compound under high pressure and determining which conformer was present in the high pressure solid. In addition the vapour spectrum was recorded with the aid of a 10 m path length cell, and the low temperature spectrum was extended down to 250 cm^{-1} .

EXPERIMENTAL

The sample of $\text{CH}_2\text{Br}-\text{CF}_2\text{Br}$ was received from Kagarise and had been used in his study.¹ It was redistilled under reduced pressure and the purity was checked by gas chromatography.

The infrared spectra were recorded with a Perkin-Elmer model 621 spectrometer equipped with a gold grid polarizer. A 10 m folded cell from Beckman with CsBr windows was employed for the vapour spectrum. The low temperature solid was studied as a capillary in a conventional low-temperature cell, using liquid nitrogen or dry ice as refrigerants. For the high pressure experiments, a cell³ with type II diamonds was used with a 6 \times beam condenser. Spacers of stainless steel were used between the diamonds, and the sample was situated in a hole of approximately 0.3 mm diameter. Because of

Table 1. Infrared spectral data^a of 1,2-dibromo-2,2-difluoroethane.

Vapour	Liquid	Solid (-170°)	Solid (25 kbar)	
3056 s ^b	3052 vs			
3007 vs } A ^c				
3003 vs } A ^c	2992 vs			
3000 vs } A ^c				
2988 w } A				
2985 w } A	2975 s			
2982 w } A				
2838 w	2836 m			
1427 m } B				
1429 s } B	1415 vs	1418 s	1422 s a ^e	I II ^d
1425 s } B				
1423 m } B				
1375 m				
1350 w } B				
1345 w } B				
1303 w } B	1299 w	1295 m	1303 m a	I
1297 w } B				
		1273 m		
1256 vs	1257 s	1255 vs	1259 vs a	I II
1249 vs	1241 vs	1227 vs	1236 vs	I
1225 m, sd	1219 vs	1210 w		II
1218 vs	1209 vs	1195 vs	1210 vs	I
1173 s } B				
1167 s } B	1167 s	1177 w		II
1162 s	1159 m, sd	1165 w	1170 w, sd	I?
1097 s	1083 vs	1078 vw	1085 vw	II
1077 s } C				
1074 vs } C	1066 vs	1055 vs } B	1058 vs	I
1071 s } C		1050 vs } B		
		1037 w		
987 vs	979 vs	975 vw		II
961 m } A				
956 m } A	943 w, sd	960 m	970 vw	I ?
933 vs } A				
928 vs } A	924 vs	925 vs	932 vs	I
925 vs } A				
		902 vw		
868 m } A				
865 m } A	864 m	861 m	866 s b	I
861 m } A				
840 vw				
782 w	779 w, sd	781 w	790 vw	I
758 s } B				
752 s } B	756 m	750 vs	758 vs	I
737 m } A				
733 m } A	729 m	720 vw	727 vw a	II
728 m } A				
677 w } B				
672 w } B	682 w, sd	681 w		
654 s	649 w, sd	650 w	655 w	
648 s } B				
638 s } B	641 s	636 vs	644 vs b	I
618 w } B		628 m, sd	633 m, sd	II
612 w } B	611 m	614 vw	614 vw a	II

Table 1. Continued.

553 s	550 m, sd	542 vvw		II
547 vs	542 s	537 s	544 s a	I
543 s				
463 vw				
395 w	397 m	395 w	396 w b	I
379 w	373 w		373 vw	II
	332 w	326 w	323 w	I
	320 w			
	297 vs	300 w	299 m	II
	275 s		275 s	
	252 vs		243 vs	

^a Only bands in the fundamental regions 3000–2800 and below 1500 cm^{-1} are included.

^b The following abbreviations have been used: s, strong; m, medium; w, weak; v, very and sd, shoulder.

^c A, B, and C denote band contours.

^d I and II are the two conformers.

^e a and b are bands which are more intense in Fig. 2 and Fig. 3, respectively.

the small sample size in the diamond cell, wide slits, high gain, and slow recording speeds were necessary. We recorded quite satisfactory spectra down to 300 cm^{-1} , but unavoidable moisture around the beam condenser unit obscured the spectra in the low frequency region.

INTERPRETATION

Vapour, liquid and solution. The infrared absorption frequencies observed in the vapour, in the liquid, in the low temperature and in the high pressure solids are listed in Table 1. Our absorption bands from the liquid agree well with the older values.¹ Undoubtedly because of our higher resolution, additional bands at 1215, 1155, 939, and 775 cm^{-1} were recorded. To all the stronger liquid bands we observed bands in the vapour spectrum. Only a few of these had well resolved band contours. Therefore no classification of the vibrational bands into one or the other conformer can be based upon the infrared vapour contours. Nor can the bands characteristic of the *trans* conformer be divided into the species *A'* or *A''* from the infrared vapour data. The resolved doublet situated at 1253 and 1237 cm^{-1} in the liquid overlapped completely in the vapour. This was also true for the doublets at 1215 and 1205 cm^{-1} and those at 1163 and 1155 cm^{-1} . On the other hand a faint shoulder at 939 cm^{-1} in the liquid appeared as a distinct *B*-type vapour band at 958 cm^{-1} .

A close inspection of the relative band intensities in the vapour spectrum compared to that of the liquid indicated some significant variations. Thus, the vapour band at 1097 cm^{-1} had a higher intensity relative to the one at 1074 cm^{-1} in comparison with the intensity ratio of the two corresponding bands in the liquid. Analogous conclusions can be drawn from the band pairs at 615 cm^{-1} and 643 cm^{-1} , and at 733 cm^{-1} and 755 cm^{-1} . In agreement with Kagarise¹ we assign the 1097, 733, and 615 cm^{-1} bands to one conformer and those at 1074, 755, and 643 cm^{-1} to the other, based upon the solid state spectra. The molar absorbance of an infrared band can vary considerably from the vapour phase to the liquid. However, since the observed intensity variations were observed for three pairs of bands, there are good reasons

to conclude that the *trans-gauche* ratio is different in the liquid compared to the vapour. As discussed by numerous authors² and based upon the Onsager dielectric theory⁴ the more polar conformer should be more stabilized in the liquid. Although there might be reasons to assume¹ a higher bond moment for the C—Br than for the C—F bonds, these values are very similar.⁵ We shall therefore make no commitment regarding which conformer is more stable in the liquid than in the vapour, but designate the 1074, 775, and 643 cm^{-1} as conformer I and those at 1097, 733, and 615 cm^{-1} as conformer II.

In order to get more information about the *trans-gauche* equilibrium, the compound was dissolved in an unpolar solvent, carbon tetrachloride, and in a moderately polar solvent, dichloromethane. We recorded the infrared spectra of these solutions between 1400 and 400 cm^{-1} . In the transparent regions it was observed that the bands at 1062 and 921 cm^{-1} were enhanced relative to those at 1079 and 976 cm^{-1} in dichloromethane compared to carbon tetrachloride. The more polar conformer should be stabilized in the former solvent. Therefore, the absorbance values in the vapour compared to the liquid as well as the data in solution agree with the assumption¹ that the I conformer is more stable and persists in the crystal.

Low temperature and high pressure solids. The infrared spectrum of the solid 1,2-dibromo-2,2-difluoroethane at liquid nitrogen temperature is shown in Fig. 1. Compared with the vapour and liquid spectra a number of bands

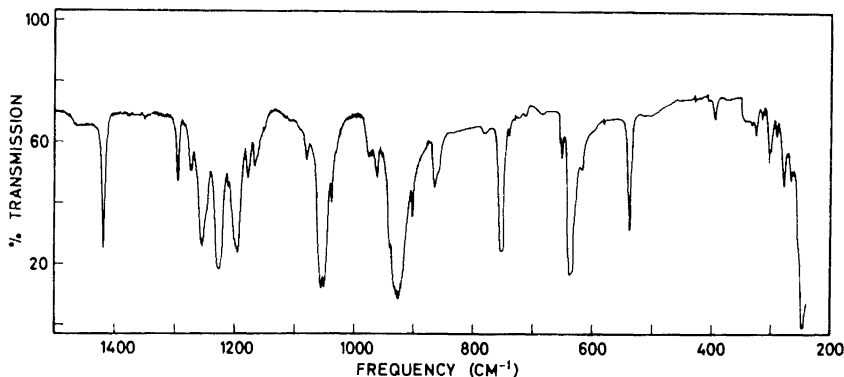


Fig. 1. The infrared spectrum of solid $\text{CH}_2\text{Br}-\text{CF}_2\text{Br}$ at -170° .

are greatly reduced in intensity. These bands are marked with II in Table I and are assigned to the conformer which is absent in the crystal. Other bands are enhanced in the crystal, and these are marked with I. The sample was crystallized several times under different conditions, it was annealed just below the freezing point *etc.* However, in no case did the II-bands disappear completely, indicating that a small amount of this conformer was present in the solid, probably as an amorphous glass. These measurements down to 240 cm^{-1} extended considerably the earlier low temperature study¹ which was recorded in the rock salt region only. In the region of overlapping investiga-

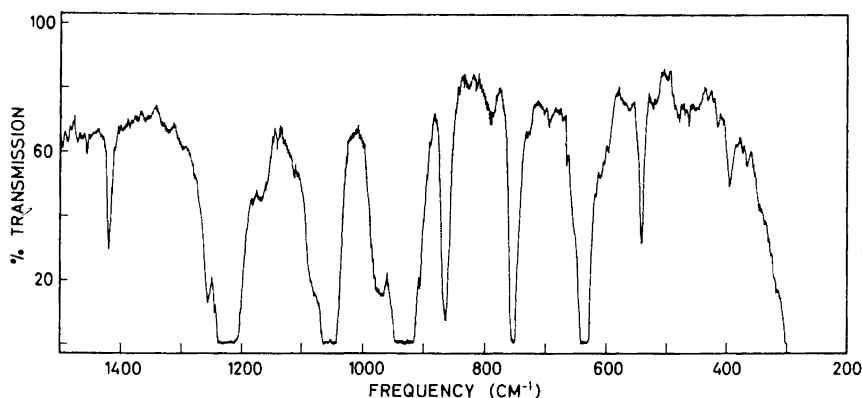


Fig. 2. The infrared spectrum of a single crystal of $\text{CH}_2\text{Br}-\text{CF}_2\text{Br}$ at ambient temperature using polarized radiation; pressure approximately 25 kbar.

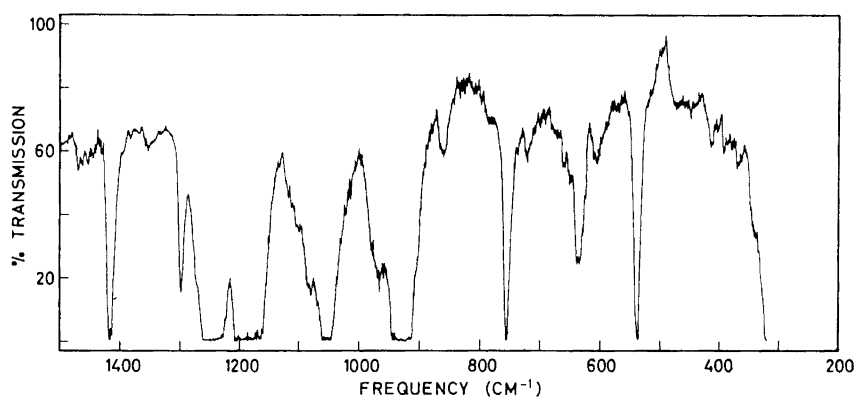


Fig. 3. The infrared spectrum of a single crystal of $\text{CH}_2\text{Br}-\text{CF}_2\text{Br}$ at ambient temperature using polarized radiation. The plane was rotated 90° compared with Fig. 2, pressure approximately 25 kbar.

tions there are discrepancies compared with the older data at 1256, 1225, 1205, 1162, and 958 cm^{-1} (vapour frequencies).

Infrared spectra of a polycrystalline sample and a single crystal under high pressure at ambient temperature were recorded. Negligible differences between the spectra of these samples, pressurized to *ca.* 25 kbar were observed. The method used in growing a single crystal in the diamond cell has been described.⁶

The high pressure and the low temperature spectra were closely related when allowance is made for the conditions of much lower resolution in the former. Particularly, the bands which diminish greatly in intensity upon crystallization at low temperature (II), practically disappear in the high

pressure solid. Thus, the same conformer (I) crystallizes at low temperatures and under high pressure as recently observed for the halogenocyclohexanes.⁷ Various combinations of pressurizing and cooling were tried simultaneously, but in no case did the II-bands persist in the solid. Brasch⁸ reported that other halogenated ethanes can crystallize as different conformers at low temperature and under high pressure. In the present molecule, however, the conformer I must be thermodynamically favoured in the crystal, inasmuch as this conformer is more stable¹ in the vapour and in the liquid at room temperature.

We recorded the absorption spectra of a single crystal, using polarized infrared radiation. The polarizer was first rotated to give the maximum absorption of the bands at 866 and 644 cm^{-1} (Fig. 2). Then the electric vector was rotated 90° and with unchanged instrument settings, the absorption curve in Fig. 3 was obtained. An inspection of the infrared curves reveal that several absorption bands displayed a large dichroic effect. Thus, the change in dipole moment during the normal vibration was closely parallel or perpendicular to the plane of the electric vector. Since the crystal structure of this substance has not been determined, we do not know the orientation of the neighbouring molecules in the unit cell. Until then the dichroism cannot be used as an aid for assigning the fundamental frequencies.

No attempts will be made to propose a complete assignment of the fundamental frequencies for this molecule. However, there are some bands which obviously can be assigned from the empirical group frequency relations. The vapour band at 1425 cm^{-1} must be the CH_2 deformation mode and the one at 1300 cm^{-1} the CH_2 wagging mode. We can confidently assign some of the strong bands between 1260 and 1100 cm^{-1} to the C—F stretching vibrations in the two conformers. The bands at 1097 and 1074 cm^{-1} may be the CH_2 rocking fundamental for each conformer and the bands at 987 and 928 cm^{-1} the C—C stretching modes. There are two C—Br stretching vibrations of conformer I at 643 (out-of-phase) and at 545 cm^{-1} (in-phase), for conformer II they are situated at 615 and 553 cm^{-1} , respectively. Moreover, the bands at 756 and 733 cm^{-1} might be connected with the CH_2 twisting vibration for the two conformers. The various skeletal deformation modes will be situated below 500 cm^{-1} , and some of them will be outside the spectral range of the present study.

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