

InfraRed and Raman Spectra of Fluorinated Ethylenes II. 1,1Difluoro-2,2 Dichloroethylene

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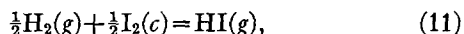
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consideration of the data of Taylor and Crist, Wagman arrives at the following constants for the reaction



$$\Delta H_f^0_{298.16} = 6.28 \text{ kcal.},$$

$$\Delta F_f^0_{298.16} = 0.39 \text{ kcal.},$$

$$\log_{10} K_f = -0.286.$$

These constants together with the heat of vaporization of iodine, the vapor pressure of iodine and the free energy functions for $\text{H}_2(\text{g})$, $\text{I}_2(\text{g})$, and $\text{HI}(\text{g})$ (all from the National Bureau of Standards tables) yield -1007 ± 10 cal. mole⁻¹ for the heat of formation of $\text{HI}(\text{g})$ at absolute zero. The values of K_7 used for HI were calculated from this ΔH_f^0 and the $(F^0 - H_0^0)$ tables of

the National Bureau of Standards.⁴ A plot of $\log K_7$ vs. $1/T$ is shown in Fig. 1 together with the experimental data of Taylor and Crist,⁹ Bodenstein,⁸ Bright and Hagerty,¹¹ and Rittenberg and Urey.¹² Finally, the equilibrium data of Taylor and Crist and of Bright and Hagerty on DI are combined with the theoretical values⁵ of K_{10} to give K_7 . It is seen that both the data of Taylor and Crist and Bright and Hagerty on DI are consistent with their respective HI data. Furthermore, the data of Taylor and Crist on HI are in good agreement with those calculated from spectroscopic data and the value of $\Delta H_f^0 - 1007$ cal. mole⁻¹.

¹² D. Rittenberg and H. C. Urey, *J. Chem. Phys.* **1**, 137 (1933); *J. Am. Chem. Soc.* **56**, 1885 (1934).

Infra-Red and Raman Spectra of Fluorinated Ethylenes II. 1,1-Difluoro-2,2-Dichloroethylene*

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The infra-red absorption spectrum of gaseous 1,1-difluoro-2,2-dichloroethylene between 2 and 22.6μ has been investigated with a prism spectrometer of high resolution. The Raman spectrum of $\text{CF}_2:\text{CCl}_2$ in the liquid state has been photographed with a three-prism glass spectrograph of linear dispersion 15A/mm at 4358A. Quantitative polarization measurements have been made. The 12 fundamental vibration frequencies have been assigned, and the observed vibration spectra have been interpreted in detail.

INTRODUCTION

THE Raman spectrum of liquid 1,1-difluoro-2,2-dichloroethylene has been studied by Hatcher and Yost.¹ The infra-red spectrum of the compound in the gaseous state has been investigated by Torkington and Thompson² who made an assignment of ten of the twelve fundamental vibration frequencies. In the present paper more accurate experimental data, a complete assignment of fundamentals and a detailed interpretation of the infra-red and Raman spectra of $\text{CF}_2:\text{CCl}_2$ will be given.

EXPERIMENTAL

The sample of $\text{CF}_2:\text{CCl}_2$ was prepared and purified in the Jackson Laboratory of E. I. du Pont de Nemours and Company. No information was available about its purity. However, the infra-red spectrum showed that it contained certain amounts of carbon dioxide and carbon monoxide as impurities.

* This work has been supported by the ONR under Contract N7-onr-398, Task Order I.

¹ J. B. Hatcher and D. M. Yost, *J. Chem. Phys.* **5**, 992 (1937).

² P. Torkington and H. W. Thompson, *Trans. Faraday Soc.* **41**, 236 (1945).

The infra-red absorption spectrum of gaseous $\text{CF}_2:\text{CCl}_2$ was measured from 2 to 22.6μ in the manner described in the first paper of this series.³ The Raman spectrum of liquid $\text{CF}_2:\text{CCl}_2$ was photographed by means of a Lane-Wells spectrograph.³ Quantitative measurements of the depolarization ratios of the Raman bands were made with an apparatus similar to that described by Crawford and Horwitz,⁴ except for the use of mercury lamps with internally water-cooled electrodes. The Type H polaroid sheets were given a permanent cylindrical shape by bending them tightly around a glass tube of appropriate diameter, wrapping a string around them along the whole length and heating them in an oven for one to two hours at 75°C.

In order to make the two exposures accurately equivalent, an intensity integrator was used. It consists of a glow tube relaxation circuit in which the resistance in series with the condenser is furnished by a 929 photo-cell and depends on the intensity of the light falling on the cell. The condenser charges at a rate determined by

³ Smith, Nielsen, and Claassen, *J. Chem. Phys.* **18**, 326 (1950).

⁴ B. L. Crawford, Jr. and W. Horwitz, *J. Chem. Phys.* **15**, 882 (1947).

TABLE I. Infra-red spectrum of CF₂:CCl₂ (gas).*

Wave number	Description	Interpretation
459 cm ⁻¹	vw	B ₁ Fundamental
556 564 573	s	Type C B ₂ Fundamental
~617 622 ~629 635 640 ~647	m	Type A A ₁ Fundamental
758	vs	Type A A ₁ Fundamental
805	vw	993 - (188) = 805(A ₁); (188) + 622 = 810(B ₁)
838	vvw	1032 - (188) = 844(B ₁)
881	m	sh (258) + 622 = 880(B ₂)
884 887	m	(434) + 459 = 893(B ₁)
989 996	vs	Type B B ₁ Fundamental
1027 1032 1037	vs	Type A A ₁ Fundamental
~1051 1056 1060	vw	Type A? (434) + 622 = 1056(A ₁)
1125 1131 1136	s	Type A 2 × 564 = 1128(A ₁)
1171	s	Type C? 564 + 622 = 1186(B ₂); (188) + 993 = 1181(A ₁)
1214 1221	m	Type B (188) + 1032 = 1220(B ₁)
1250	vvw	2 × 622 = 1244(A ₁)
1281	w	2 × 640 = 1280(A ₁); (258) + 1032 = 1290(B ₂)
1323 1330	vs	Type B B ₁ Fundamental
1427	m	(434) + 993 = 1427(B ₁)

the applied voltage and the intensity of the light. When the condenser voltage becomes equal to the breakdown voltage of the glow tube the condenser discharges through a sensitive relay that activates a mechanical counter. When the voltage has fallen to the extinction voltage of the glow tube the discharge stops, and the condenser begins to charge again. The photo-cell is mounted, with appropriate shielding, above the reflector in the polarization apparatus, and suitable holes in the reflector transmit light equally from the two mercury lamps to the photo-cell.⁵ The two exposures,

⁵ This intensity integrator was designed by Dr. Russell L. Hudson and will be described by him elsewhere.

TABLE I.—Continued.

Wave number	Description	Interpretation
1477 cm ⁻¹ 1485	m m	459 + 1032 = 1491(B ₁)
1543	w	1749 - (188) = 1561(B ₁)?
1575 1585	vvw vvw	2 × 564 + 459 = 1587(B ₁)? 264 + 1032 = 1596(B ₂)?
1627 1636	vw	Type B? 640 + 993 = 1633(B ₁)
1745 1749 1752	vs	Type A A ₁ Fundamental
1798 1878 1894	vvw vvw vvw	459 + 1327 = 1786(A ₁) (188) + 640 + 1032 = 1860(B ₁)? 2 × 459 + 993 = 1911(B ₁)?
1936	vw	(188) + 1749 = 1937(B ₁); 622 + 1327 = 1949(B ₁)
1978	m	2 × 993 = 1986(A ₁); 640 + 1327 = 1967(B ₁)
1998	vvw	(258) + 1749 = 2007(B ₂)
2058	m	2 × 1032 = 2064(A ₁)
2175**	m	(434) + 1749 = 2183(A ₁)
2296	vvw	564 + 1749 = 2313(B ₂)
2375	vvw	622 + 1749 = 2371(A ₁)
2441	vvw	(258) + (434) + 1749 = 2441(B ₂)
2500	vvw	(188) + 993 + 1327 = 2508(B ₁)
2563	vvw	258 + 564 + 1749 = 2571(A ₁)
2636	s	2 × 1327 = 2654(A ₁)
2732	w	993 + 1749 = 2742(B ₁)
2770	s	1032 + 1749 = 2781(A ₁)
2841	m	(188) + 2 × 1327 = 2842(B ₁); 459 + 640 + 1749 = 2848(B ₁)
3062	m	1327 + 1749 = 3076(B ₁)
3470	w	2 × 1749 = 3498(A ₁)
3620	w	2 × 1327 + 993 = 3629(B ₁)

* Frequencies observed as fundamentals only in the Raman spectrum of liquid CF₂:CCl₂ are enclosed in parentheses, since they may differ somewhat from the corresponding frequencies for the gas.

** Coincides with the maximum in the R branch of the CO band.

with the two different polaroid cylinders, are made equal by extending them to the same number of counts. For film calibration two step-sectored spectra of a continuous source were made on another spectrograph. The four films were cut from the same sheet and were developed together in a plastic holder. Their blackening was measured by means of a Leeds and Northrup Knorr-Albers microphotometer.

RESULTS

The infra-red absorption spectrum of gaseous 1,1-difluoro-2,2-dichloroethylene from 2.5 to 22.6 μ is shown in Fig. 1. The infra-red absorption maxima at 668, 720, 2346, and 2355 cm^{-1} are caused by an admixture of carbon dioxide. The rotational structure appearing around 2150 cm^{-1} is caused by a small admixture of carbon monoxide. The wave numbers for the observed absorption maxima (or "shoulders") are given in the first column of Table I. In the second column the relative intensities are indicated as well as the type of the band contours in Badger and Zumwalt's notation.⁶

The observed Raman shifts of liquid CF_2CCl_2 are listed in the first column of Table II. In the second column are given rough estimates of the relative intensities of the bands and, for some bands, information about exceptionally sharp or diffuse appearance. The measured depolarization ratios are listed in the third column.

The infra-red spectrum, as observed in the present work, includes many bands not found by Torkington and Thompson, and the wave number measurements are considerably more accurate. The Raman shift of 883 cm^{-1} reported by Hatcher and Yost was not observed

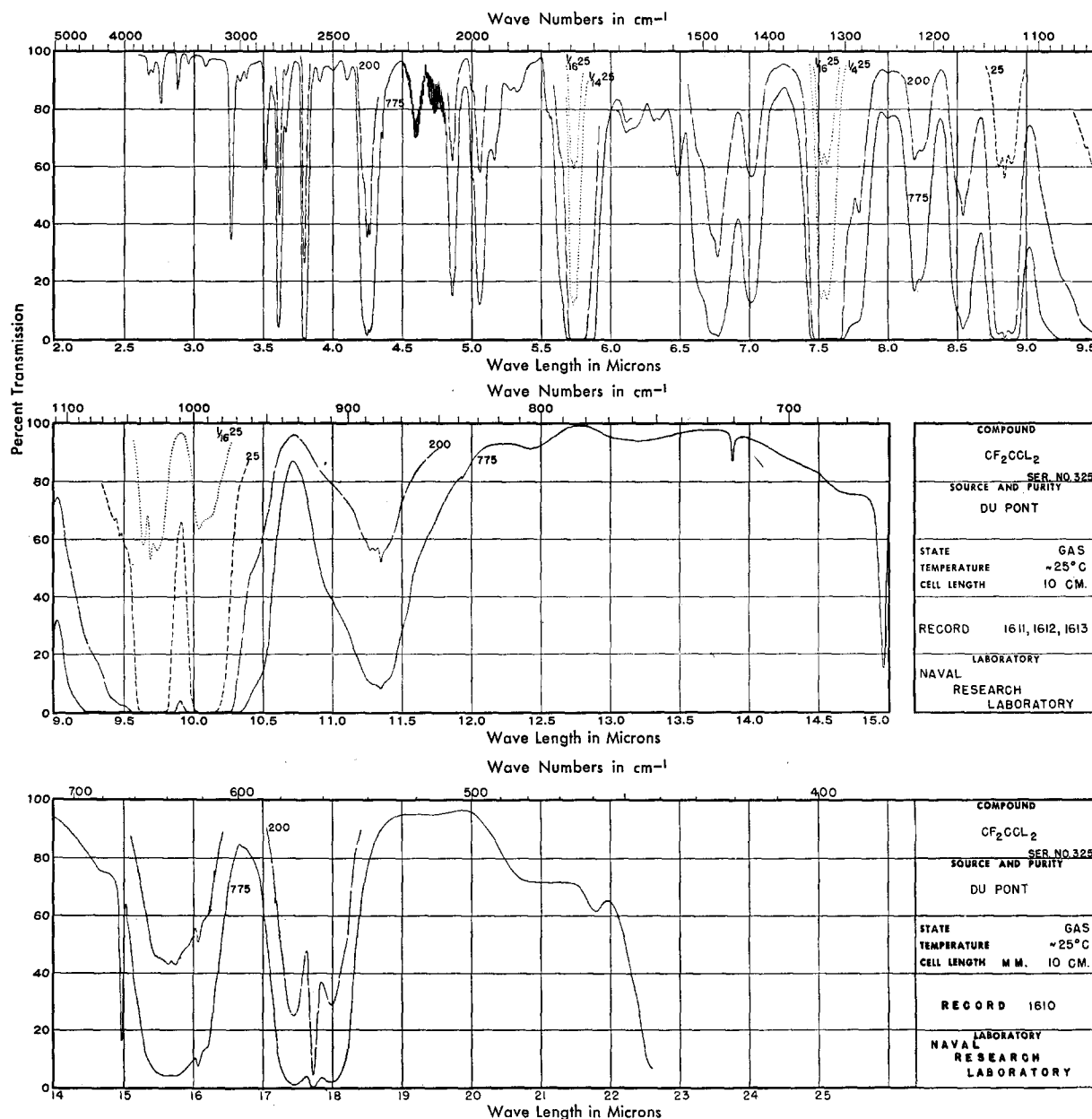


FIG. 1. Infra-red absorption spectrum of 1,1-difluoro-2,2-dichloroethylene.

⁶ R. M. Badger and L. R. Zumwalt, J. Chem. Phys. 6, 711 (1938).

TABLE II. Raman spectrum of $\text{CF}_2\text{:CCl}_2$ (liquid).

Wave number	Description	Depolarization	Interpretation
167* cm^{-1}	vw		A_2 Fundamental
187.8	w	0.88	B_1 Fundamental
258	vs	0.86	B_2 Fundamental
433.8	vs sh	0.07	A_1 Fundamental
454	w d	0.8	B_1 Fundamental
560.8	vs	0.83	B_2 Fundamental
623.0	s sh	0.12	A_1 Fundamental
646	w d	0.20	A_1 Fundamental
986	vw	~ 1	B_1 Fundamental
1027.6	m sh	0.35	A_1 Fundamental
1121.8	w sh	0.11	$2 \times 560.8 = 1121.6 (A_1)$
1313	vw		B_1 Fundamental
1738.8	s sh	0.27	A_1 Fundamental
1966	vw		$2 \times 986 = 1972 (A_1)$

* This faint band may be spurious, or it may be interpreted as $258 - 188 = 170 (A_2)$.

here. On the other hand, Table II contains four Raman bands at 1313, 986, 187.8 and 167 cm^{-1} , not found by Hatcher and Yost, and these authors made no polarization measurements. Except for the very faint band at 1966 cm^{-1} , which was observed by Hatcher and Yost at 1976 cm^{-1} , the agreement between the Raman shifts obtained in the present work and those reported by Hatcher and Yost is very good.

INTERPRETATION

If the $\text{CF}_2\text{:CCl}_2$ molecule has a planar structure of symmetry C_{2v} , the normal vibrations divide themselves into species in the same manner as for $\text{CF}_2\text{:CH}_2$, i.e., $5A_1 + 1A_2 + 4B_1 + 2B_2$, and the rules for finding the species of combination bands are the same.

Assuming the following dimensions for the $\text{CF}_2\text{:CCl}_2$ molecule: C=C distance = 1.27 \AA , C-F distance = 1.32 \AA , C-Cl distance = 1.7 \AA , and F-C-F angle = Cl-C-Cl angle = 110° , the following moments of inertia are obtained:

$$I_A = 298 \times 10^{-40}, \quad I_B = 392 \times 10^{-40}, \\ I_C = 690 \times 10^{-40} \text{ g cm}^2.$$

From these values Badger and Zumwalt's parameters are found to be $\rho = 0.74$ and $S = 0.16$. Using their curves for $\rho = \frac{2}{3}$ and $S = 0$, the values 5.8, 2.7 and 9.7 cm^{-1} for the separation $\nu - \nu_0$ of the rotational branches from the band center for Types A, B and C bands, respectively, are obtained.

Seven of the observed Raman bands are definitely polarized, namely 433.8, 623.0, 646, 1027.6, 1121.8, 1738.8, and 1966 cm^{-1} . The weak band at 1121.8 cm^{-1} and the very faint band at 1966 cm^{-1} are undoubtedly overtones, $2 \times 560.8 = 1121.6$ and $2 \times 986 = 1972$, respectively. The very strong Raman band at 433.8 cm^{-1} , which lies outside the range covered by the infra-red measurements, must be a fundamental of species A_1 . The frequencies 1027.6 and 1738.8 cm^{-1} occur, with small shifts because of the change in the state of aggregation, as intense Type A bands in the infra-red

spectrum. They must also be interpreted as A_1 fundamentals. The contours of the two partly overlapping infra-red bands at 622 and 640 cm^{-1} are not quite typical of Type A bands. This may be caused in part by the superposition of two A_1 combination bands, $188 + 434 = 622$ and $188 + 459 = 647 \text{ cm}^{-1}$. However, the intensities of the bands in question are so high that the bands must be interpreted as fundamentals, and since the corresponding Raman bands are polarized, they must belong to species A_1 . Thus, we have accounted for all of the five totally symmetrical fundamentals.

The strong infra-red band at 564 cm^{-1} is definitely of Type C, and its counterpart in the Raman spectrum, 560.8 cm^{-1} , is very strong and depolarized. There can be no doubt that these bands represent one of the two B_2 fundamentals. Another Raman band at 258 cm^{-1} is strikingly similar to 560.8 in appearance and intensity and is also depolarized. It is undoubtedly the other B_2 fundamental.

The very intense Type B infra-red band at 1327 cm^{-1} must be a fundamental of species B_1 . The corresponding Raman band for liquid $\text{CF}_2\text{:CCl}_2$, at 1313 cm^{-1} , is so weak that its polarization could not be ascertained. Another very strong infra-red band, at 993 cm^{-1} , appears rather definitely to be of Type B. Its counterpart in the Raman spectrum of the liquid is depolarized. It must also be a B_1 fundamental. Although the depolarization ratio for the weak and diffuse Raman band at 454 cm^{-1} is not measured with great accuracy, the band is fairly certainly depolarized. The corresponding band in the infra-red, at 459 cm^{-1} , does not have any clearly defined contour. Nevertheless, it appears rather certain that these bands represent a B_1 fundamental. The depolarized Raman band at 187.8 cm^{-1} must be the last B_1 fundamental.

There remains only the A_2 fundamental. A rough estimate, based on the values of the twisting frequency in C_2H_4 and $\text{CF}_2\text{:CH}_2$, indicates that this frequency should lie somewhere in the region between 100 and 150 cm^{-1} . Unfortunately, certain spurious light effects in the Raman spectrograph make this region difficult to observe and throw some doubt upon the reality of the observed Raman band at 167 cm^{-1} . Until this doubt can be removed, and the region close to the exciting mercury line investigated, it is tentatively assumed that 167 cm^{-1} is the A_2 fundamental.

The infra-red and Raman bands interpreted as fundamentals for $\text{CF}_2\text{:CCl}_2$ are listed in Table III. The terms given in the second column serve to indicate in a very rough manner the general nature of the vibrations but do not pretend to describe them with any accuracy.

As mentioned above, Torkington and Thompson,² on the basis of Hatcher and Yost's Raman data and their own infra-red observations, made an assignment of ten of the fundamentals for $\text{CF}_2\text{:CCl}_2$. Two of their assignments, 648 cm^{-1} to B_2 and 255 cm^{-1} to A_1 , must be interchanged, since the former is strongly polarized and the latter depolarized. They interpreted the Raman

TABLE III. Fundamental vibration frequencies for $\text{CF}_2\text{:CCl}_2$.

Symmetry species	Approximate character*	Infra-red (gas)			Raman (liquid)			Depolarization
		Wave number	Description		Wave number	Description		
A_1	C=C Stretching	1749 cm^{-1}	vs	Type A	1738.8 cm^{-1}	s	sh	0.27
A_1	CF Stretching	1032	vs	Type A	1027.6	m	sh	0.35
A_1	CCl Stretching	640	s		646	w	d	0.20
A_1	CF_2 Deformation	622	m	Type A	623.0	s	sh	0.12
A_1	CCl_2 Deformation				433.8	vs	sh	0.07
B_2	CF_2 Wagging	564	s	Type C	560.8	vs		0.83
B_2	CCl_2 Wagging				258	vs		0.86
A_2	Twisting				167	vw		
B_1	CF Stretching	1327	vs	Type B	1313	vw		
B_1	CCl Stretching	993	vs	Type B	986	vw		~ 1
B_1	CF_2 Rocking	459	vw		454	w	d	0.8
B_1	CCl_2 Rocking				187.8	w		0.88

* Only very rough meaning can be attached to the terms used in this column.

band at 883 cm^{-1} , which was not observed in the present work, as a B_1 fundamental. If this Raman band should be real, it must be very faint; hence it would be more natural to interpret it as a combination band, $434 + 454 = 888\text{ cm}^{-1}$. Torkington and Thompson left unassigned one of the B_1 fundamentals, as well as the A_2 twisting frequency.

On the basis of the fundamental vibration frequencies listed in Table III, it has been possible to interpret all of the observed infra-red and Raman bands. The interpretation of the infra-red bands is given in the third column of Table I and that of the Raman bands in the third column of Table II. In the former table, frequencies observed only as fundamentals in the Raman spectrum of liquid $\text{CF}_2\text{:CCl}_2$ are enclosed in parentheses, since these frequencies may be expected to differ somewhat from the corresponding frequencies for the gas.

DISCUSSION

The interpretation of the two Raman bands not regarded as fundamentals is entirely satisfactory. The majority of the infra-red bands are also interpreted satisfactorily. However, for many of the bands, especially at high wave numbers, alternative interpretations are possible. Except in cases where two assignments are about equally plausible, the alternatives are not listed

in the table. About half of the possible binary combination bands have been observed. A third of the missing combination bands may be masked by stronger bands, the others are apparently too weak for observation. Four bands have been interpreted as difference bands, and a number as ternary combination bands.

For some bands, the interpretation given is not quite satisfactory. Thus, the infra-red band at 1936 cm^{-1} is interpreted as a B_1 combination, although its contour more nearly resembles that of a B_2 or A_1 band. If the selection rules were disregarded, the faint infra-red band at 758 cm^{-1} could be interpreted as $1327 - 564 = 763(A_2)$, and the band at 1894 cm^{-1} could be interpreted as the corresponding sum band. Also, two or three other bands could be given alternative interpretations. This evidence, however, is hardly sufficient to warrant a serious consideration of the possibility that the $\text{CF}_2\text{:CCl}_2$ molecule is non-planar. In any case, the fact that both of the B_2 fundamentals give depolarized Raman bands indicates that a deviation from planar structure, if it exists, must be small.

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