

Substituted Methanes

Part XXXIV. Raman and Infrared Spectral Data and Calculated Thermodynamic Properties for CH_2Cl_2 , CHDCl_2 , and CD_2Cl_2 * †

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Raman displacements, semiquantitative relative intensities, and approximate depolarization ratios were obtained for liquid CH_2Cl_2 , CHDCl_2 , and CD_2Cl_2 ; and wave numbers and estimated relative intensities for the infrared bands from 400 to 4000 cycles/cm were obtained for both the liquid and the gas. Vibrational assignments for the deuteriated compounds were made by comparison with the results for CH_2Cl_2 , and by application of the complete isotopic substitution rules of Brodersen and Langseth. The results confirm the infrared work of Shimanouchi and Suzuki for these compounds, except for the σ_2 fundamental of CD_2Cl_2 which was assigned to the 1052 cycles/cm Raman line. Thermodynamic properties (heat content function, free energy function, entropy, and heat capacity) were calculated for twelve temperatures from 100 to 1000°K to a rigid-rotor, harmonic-oscillator approximation.

INTRODUCTION

Vibrational spectral data for CH_2Cl_2 in the Raman (1-11) and infrared (12-15) have been reported and the assignment of the fundamentals made by Plyler and Benedict (14) has been confirmed by Welsh *et al.* (11) from a study of the band contours in the Raman spectrum of the vapor. Since pure samples of CHDCl_2 and CD_2Cl_2 have become available, the present investigation was undertaken in order to obtain spectral data for all these three molecules.

During the course of the present work, Shimanouchi and Suzuki (16) reported wave numbers for the infrared, made assignments for the fundamentals of these molecules, and calculated modified Urey-Bradley, and general quadratic valence

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force, potential energy constants. The present Raman work confirmed their results, except for the assignment of the σ_2 fundamental for CD_2Cl_2 .

EXPERIMENTAL PROCEDURES

The deuteriated compounds were obtained from the Merck, Sharp, and Dohme Company, Montreal, Canada. The Raman displacements were recorded on Eastman 103a-J photographic plates by the use of a Hilger E-612, two-prism spectrograph having a reciprocal linear dispersion of $100 \text{ cm}^{-1}/\text{mm}$ at 4358 \AA .

TABLE I
RAMAN SPECTRAL DATA FOR CH_2Cl_2^a

PR	$\Delta\sigma_l$			I	Depolarization ratio					$\Delta\sigma_g$	I_1
	PV	N	AD		PR	CR	T	W	PR ^b		
285	284	10	1.2	75	...	0.25	0.43	0.11	P	281.5	69 ^c
703	701	10	1.9	1000	...	0.07	0.09	P	P	712.9	137
742	737	7	2.0	10	...	0.84	0.79	0.70	D	748	38
895	896	4	2.5	vw	...	(D)	893	...
988	988 ^d	2	8.0	vw
1156	1153	6	3.5	2	...	0.87	0.89	0.75	D	1153	7
1220	vw
1265	1260	2	5.0	vw
1423	1419	9	2.9	6	0.6	0.83	0.88	0.71	P ^e	1430.1	22
1475	1470	3	4.3	vw
2001	vw
2306	vw
2365	vw
....	2854	5
2986	2986	11	1.4	181	0.2	0.05	0.27	P	P	2995.7	108
3053	3048	7	4.3	7	6/7	0.9	D	0.66	D	3040	98

^a $\Delta\sigma_l$ and $\Delta\sigma_g$ = Raman displacements in cycles/cm for the liquid and gas, respectively; I = semiquantitative relative intensity obtained from microphotometer measurements (vw = very weak); PR = present results; PV = probable value from the data of references 1-10; N = number of times the line has been observed in independent investigations; AD = average deviation from the mean; CR = Cabannes and Rousset (4); T = Trumpy (5); W = Wagner (7); PS = polarization state (P = polarized, D = depolarized); WCTL = Welsh *et al.* (11); and parentheses enclose values in regard to which there is some uncertainty.

^bApproximate values.

^cReduced integrated intensities I_1 are given. A few Raman bands for the gas were reported by Nielsen and Ward (8) at 281, 712, and 3002; and by Rao (10) at 276, 708, and 2988 c/cm.

^dPresent value taken as most probable. Wagner reports 972 c/cm which is much lower than the average observed infrared value of 987 c/cm.

^eThe presence of overtones and combinations of C-Cl stretching vibrations may account for the high depolarization ratio measured for this line.

TABLE II
 INFRARED SPECTRAL DATA FOR CH₂Cl₂^a

PR	σ_l	N	AD	I_e	SS	σ_g	PR	I_e
	PV			PR		PR		
452	448	2	4.0	vw	
530	w	
706	707	5	2.6	m	707.5	706	vw	
					727.5	725		
					749.6	750 ^b		
					755.6			
740	739	6	1.7	vs	758.8		vs	
					763.5	764		
896	896	5	2.0	s	897.7	897	vw	
986	987	3	2.3	vw	
1018	vw	
1154	1156	4	1.8	w	
					1260.6	1259		
1265	1265	4	1.0	vs	1268.1	1266	vs	
					1275.1	1275		
1276	w	
1424	1426	6	2.2	s	1462	1463	w	
					1473?	1472		
1442	w	
1550	1553	3	5.7	w	
1602	1612	3	7.0	vw	
2054	2055	3	2.0	vw	
2126	2132	3	3.7	vw	
2152	2154	2	1.5	vw	
2305	2308	3	4.7	w	
2409	2411	3	2.3	vw	
2520	2523	3	2.3	vw	
2691	2684	3	8.0	vw	
2826	2836	3	8.3	vw	
					2991	2986		
2983	2986	5	2.0	m	3007	3005	w	
3056	3049	5	2.6	s	
3688	3693	4	5.5	vw	
3941	3940	4	5.5	vw	

^a σ_l and σ_g = wave numbers in c/cm for the liquid and gas, respectively; I_e = estimated relative intensity (w = weak, m = medium, s = strong, v = very); PV = probable value from the data of references 12-16; SS = Shimanouchi and Suzuki (16); and other symbols have the same meaning as in Table I. A few bands reported by Kaye (18) between 2800 and 4000 c/cm were included in obtaining the average values.

^bBreitman and Steacie (15) reported vapor bands at 747, 762 and 1262, 1277 c/cm.

TABLE III
 ASSIGNMENTS FOR THE RAMAN AND INFRARED BANDS OF CH_2Cl_2^a

$\Delta\sigma_1$	I	PS	σ_1	I_e	σ_c	Assignment	Type
285	75	P	<u>285</u> ^b	σ_4	a_1
...	448	vvw	453	$\sigma_9 - \sigma_4$	B_2
...	530	w	525	$\sigma_8 - \sigma_9$	A_1
701	1000	P	707	m	<u>704</u>	σ_3	a_1
737	10	D	739	vs	<u>738</u>	σ_9	b_2
896	vw	.	896	s	<u>896</u>	σ_7	b_1
988	vw	.	987	vw	989	$\sigma_3 + \sigma_4$	A_1
....	1018	vvw	1023	$\sigma_4 + \sigma_9$	B_2
1153	2	D	1156	w	<u>1155</u>	σ_5	a_2
1220	vw	1229	$\sigma_3 + \sigma_8 - \sigma_9$	A_1
1260	vw	.	1265	vs	<u>1263</u>	σ_8	b_2
....	1276	w	1274	$\sigma_3 + 2\sigma_4$	A_1
1419	6	P	1426	s	<u>1422</u>	σ_2	a_1
....	1442	w	1442	$\sigma_3 + \sigma_9$	B_2
1470	vw	1476	$2\sigma_9$	A_1
....	1553	w	1548	$\sigma_4 + \sigma_8$	B_2
....	1612	vvw	1600	$\sigma_3 + \sigma_7$	B_1
2001	vw	2001	$\sigma_8 + \sigma_9$	A_1
....	2055	vvw	2051	$\sigma_5 + \sigma_7$	B_2
....	2132	vvw	2126	$\sigma_2 + \sigma_3$	A_1
....	2154	vvw	2160	$\sigma_2 + \sigma_9$	B_2
2306	vw	.	2308	w	2310	$2\sigma_5$	A_1
2365	vw	2344	$\sigma_6 - \sigma_3$	B_1
....	2411	vw	2418	$\sigma_5 + \sigma_8$	B_1
....	2523	vvw	2526	$2\sigma_8$	A_1
....	2684	vw	2685	$\sigma_2 + \sigma_8$	B_2
....	2836	vvw	2844	$2\sigma_2$	A_1
2986	181	P	2986	m	<u>2986</u>	σ_1	a_1
3048	7	D	3049	s	<u>3048</u>	σ_6	b_1
....	3693	vvw	3690	$\sigma_1 + \sigma_3$	A_1
....	3940	vw	3944	$\sigma_6 + \sigma_7$	A_1

^aThese are the present most probable values of the Raman and infrared wave numbers in c/cm .

^bThe underlined values are the observed wave numbers of the fundamentals for the liquid state; the other values are the wave numbers (σ_c) calculated for the overtones and combinations from these observed fundamentals. The other symbols have the same meaning as in the previous tables.

The optical densities of the Raman lines were measured with a Leeds and Northrup recording microphotometer and from these the semiquantitative relative intensities and depolarization ratios were determined by methods previously described (17). The infrared records were obtained with a Perkin-Elmer, model 21, double-beam recording spectrophotometer. KBr optics were used from 400 to 1000, NaCl from 1000 to 2000, and CaF₂ from 2000 to 4000 cycles/cm. The cells used for the liquid had a thickness of 100 μm . For wave-number measurements in regions of strong absorption, a drop of the liquid was pressed between two KBr plates to form a thin film. A 10-cm cell with KBr windows was used for the spectra of gaseous specimens.

SPECTRAL DATA AND ASSIGNMENTS

CH₂Cl₂

A summary of the present and previous data and assignments for CH₂Cl₂ is given in Tables I-III. The assignment is essentially the same as that of Plyler and Benedict (14), although a few additional combination bands have been observed and assigned.

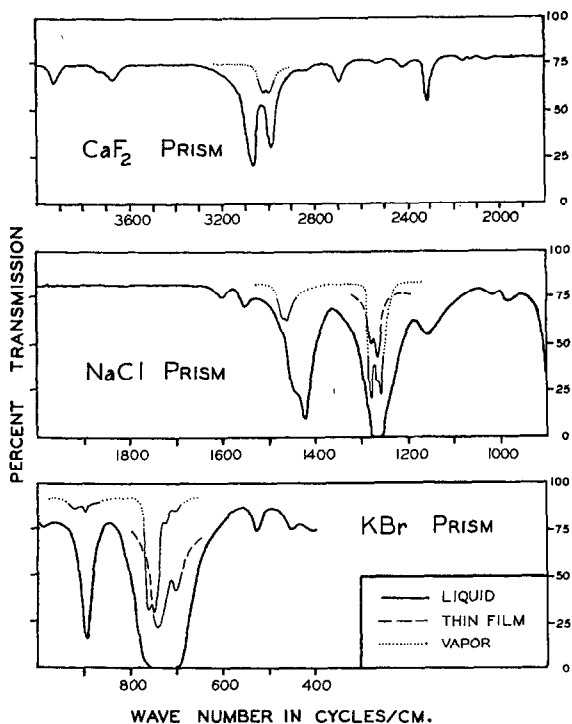
FIG. 1. Infrared spectrum of CH₂Cl₂

TABLE IV
 RAMAN AND INFRARED SPECTRAL DATA AND ASSIGNMENTS FOR CD₂Cl₂^a

$\Delta\sigma_1$	I	ρ^b	σ_g		σ_1		I_e	σ_c	Assignment	Type
PR	PR	PR	SS	PR	SS	PR	PR			
282	494	0.09	<u>282</u>	σ_4	A ₁
429	vw	428	vw	429	$\sigma_9 - \sigma_4$	B ₂
533	vw	564	2 σ_4	A ₁
677	1000	P	679	677	679	678	m	<u>678</u>	σ_3	A ₁
			695	695						
			721.7	719						
			726.8							
716	10	0.66	729.1		704	712	vs	<u>711</u>	σ_9	B ₂
			735.4	734						
...		<u>712^c</u>	σ_7	B ₁
826	vw	0.83	827	vw	<u>826</u>	σ_5	A ₂
			952.8	952						
			957.4							
...	960.7	962	955	957	vs	<u>955</u>	σ_8	B ₂
			967.4	968						
			998.4	998						
992	vw	1004.3	1004	995	994	s	993 ^d	$\sigma_4 + \sigma_9$	B ₂
			1009.9	1010						
			1017.2	1014						
1052	6	0.23	<u>1052</u>	σ_2	A ₁
...	1137	w	1140	2 $\sigma_9 - \sigma_4$	A ₁
...	1173	vw	1167	$\sigma_2 + \sigma_5 - \sigma_9$	B ₁
...	1408	1390	m	1389	$\sigma_3 + \sigma_9$	B ₂
1419 ^e	vw	1422	2 σ_9	A ₁
...	1537	vw	1538	$\sigma_5 + \sigma_7$	B ₂
...	1634	vw	1626	$\sigma_6 - \sigma_3$	B ₁
1655	vw	1652	2 σ_5	A ₁
...	1695	w	1730	$\sigma_2 + \sigma_3$	A ₁
...	1755	m	1763	$\sigma_2 + \sigma_9$	B ₂
1896	vw	1910	2 σ_8	A ₁
...	2005	vw	2007	$\sigma_2 + \sigma_8$	B ₂
2095	vw	2094	vw	2104	2 σ_2	A ₁
2198	199	0.07	2198.7	2199	2198	2199	m	<u>2198</u>	σ_1	A ₁
			2212.4	2214						
2304	4	0.80	2304	2305	m	<u>2304</u>	σ_6	B ₁
...	2876	vw	2876	$\sigma_1 + \sigma_3$	A ₁
...	2910	vw	2909	$\sigma_1 + \sigma_9$	B ₂
...	3011	vw	3016	$\sigma_6 + \sigma_7$	A ₁
...	3117	w	3130	$\sigma_5 + \sigma_6$	B ₂
...	3354	3333	w	3356	$\sigma_2 + \sigma_6$	B ₁

^aThe symbols have the same meanings as in the previous tables.

^bApproximate values.

^cCalculated from the complete isotope rule.

^dShimanouchi and Suzuki (16) assigned this band as the fundamental σ_2 .

^eThis band might at first thought be ascribed to a trace of CH₂Cl₂ remaining in the specimen. However, even in the pure CH₂Cl₂, this was a weak band and as only a trace it would probably be unobservable. Besides, the overtone 2 σ_9 was observed in CH₂Cl₂ and therefore would also be expected in CD₂Cl₂.

The assignment of the apparently depolarized Raman line $\sigma_2 = 1419$ cycles/cm to the a_1 vibrational species (symmetric CH_2 deformation) has been discussed by Welsh *et al.* (11). They found that the band contour for the gas had the strong Q -branch characteristic of an a_1 vibration, but with a comparatively high intensity in the rotational wings, indicating that the depolarization ratio is large.

The infrared spectrum is shown in Fig. 1. The absorption band near 1400 cycles/cm has a peculiar shape both for the liquid and the gas. The combination $\sigma_3 + \sigma_9 = 1442$ cycles/cm (B_2) appears as a shoulder, and it is possible that the overtones $2\sigma_3 = 1414$ (A_1), and $2\sigma_9 = 1478$ cycles/cm (A_1) contribute to the absorption. Welsh *et al.* (11) observed this line at 1430 cycles/cm in the Raman spectrum of the gas. This is a shift of 11 cycles/cm from the wave number for the liquid, as might be expected. In the infrared spectrum of the gas there is an absorption near 1467 cycles/cm, a shift of more than 40 cycles/cm from the infrared value of σ_2 in the liquid. This is a much larger shift than might be expected. Perhaps in the gas as well as in the liquid, the absorption in this region is due principally to the combinations and overtones of the C—Cl stretching vibrations, and not to the CH_2 deformation vibration.

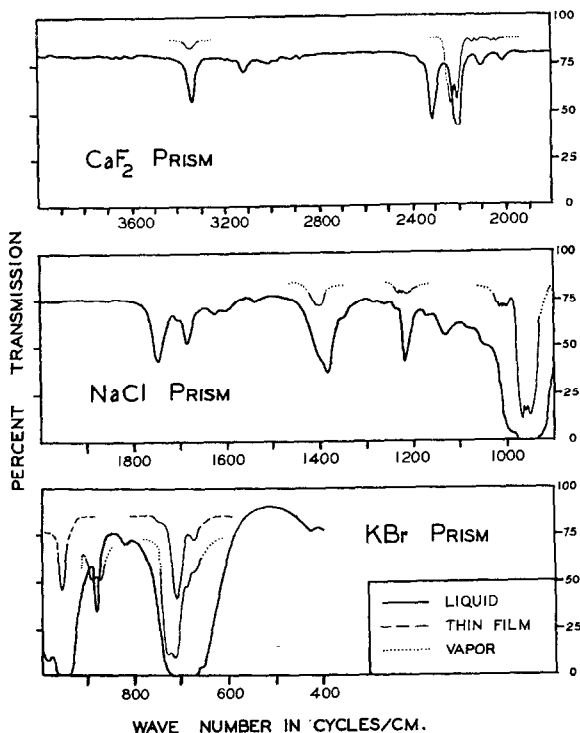


FIG. 2. Infrared spectrum of CD_2Cl_2

TABLE V
RAMAN AND INFRARED SPECTRAL DATA AND ASSIGNMENTS FOR CHDCl₂^a

$\Delta\sigma_1$ PR	I PR	ρ^b PR	σ_g SS	PR	σ_l SS	PR	I_e PR	σ_c	Assignment	Type
283	136	P	<u>283</u>	σ_6	a'
...	433	vw	440	$\sigma_9 - \sigma_6$	A''
477	vw	495	$\sigma_4 - \sigma_6$	A'
...	600	w	602	$\sigma_8 - \sigma_6$	A''
650	vw	653	$\sigma_7 - 2\sigma_6$	A''
682	1000	P	684 701 729.4 737.1 739.3 745.0	684 700 729	684	681	m	<u>683</u>	σ_5	a'
725	20	0.67	745.0	743	725	719	vs	<u>723</u>	σ_9	a''
779	16	0.02	787	790	778	778	m	<u>778</u>	σ_4	a'
886	vw	0.73	881.6 889.8 896.6	880 888 895	885	885	vs	<u>885</u>	σ_8	a''
....	1168	w	1168	$\sigma_6 + \sigma_8$	A''
1221	vw	0.69	1215.6 1222.9 1230.0	1216 1222 1230	1218	1218	vs	<u>1219</u>	σ_7	a''
1253	vw	1259	$\sigma_7 + \sigma_9 - \sigma_5$	A'
1276	1	0.50	1294	1277 1287	1283	1275	s	<u>1278</u>	σ_3	a'
....	1361	vw	1366	$2\sigma_5$	A'
....	1404	m	1406	$\sigma_5 + \sigma_9$	A''
1443	vw	1446	$2\sigma_9$	A'
....	1505	vw	1501	$\sigma_4 + \sigma_9$	A''
....	1608	vw	1502	$\sigma_6 + \sigma_7$	A''
....	1608	vw	1608	$\sigma_8 + \sigma_9$	A'
....	1668	vw	1663	$\sigma_4 + \sigma_8$	A''
....	1713	vw	1714	$\sigma_4 + \sigma_7 - \sigma_6$	A''
....	1766	vw	1770	$2\sigma_8$	A'
....	1965	vw	1961	$\sigma_3 + \sigma_5$	A'
....	1997	vw	1964	$\sigma_2 - \sigma_6$	A'
....	1997	vw	1997	$\sigma_4 + \sigma_7$	A''
....	2047	vw	2056	$\sigma_3 + \sigma_4$	A'
2246	59	P	2243.2 2259.5	2243 2260	2248	2246	m	<u>2247</u>	σ_2	a'
....	2426	w	2438	$2\sigma_7$	A'
....	2494	vw	2497	$\sigma_3 + \sigma_7$	A''
....	2542	vw	2530	$\sigma_2 + \sigma_6$	A'
3019	66	P	3015.9 3031.7	3015 3035	3019	3021	s	<u>3020</u>	σ_1	a'
....	3118	vw	3132	$\sigma_2 + \sigma_8$	A''

^aThe symbols have the same meanings as in the previous tables.

^bApproximate values.

The 1156 cycles/cm line, assigned as the torsional vibration $\sigma_5(a_2)$, is allowed only in the Raman spectrum, but also appears weakly in the infrared. The selection rules may break down for liquids due to molecular interactions, and we find that there are similar coincidences for CH_2D_2 (19), CH_2Br_2 (20), CH_2F_2 , and CH_2I_2 (14); and for CD_2Cl_2 .

CD_2Cl_2

The Raman and infrared data and assignments for CD_2Cl_2 are summarized in Table IV, and the infrared spectrum is shown in Fig. 2. The assignment of the fundamentals was made after consideration of the Raman and infrared intensities, the depolarization ratios, and a comparison with the results for CH_2Cl_2 .

The polarized Raman line at 1052 cycles/cm, which has nearly the same intensity as the 1419 cycles/cm line of CH_2Cl_2 , was assigned as $\sigma_2(a_1)$, the CD_2 symmetric deformation vibration. Shimanouchi and Suzuki (16) assigned this vibration to the strong infrared band at 995 cycles/cm. However, this infrared band can be assigned as the B_2 combination $\sigma_4 + \sigma_9 = 993$ cycles/cm. In Fig. 2, a small amount of infrared absorption can be observed near 1050 cycles/cm,

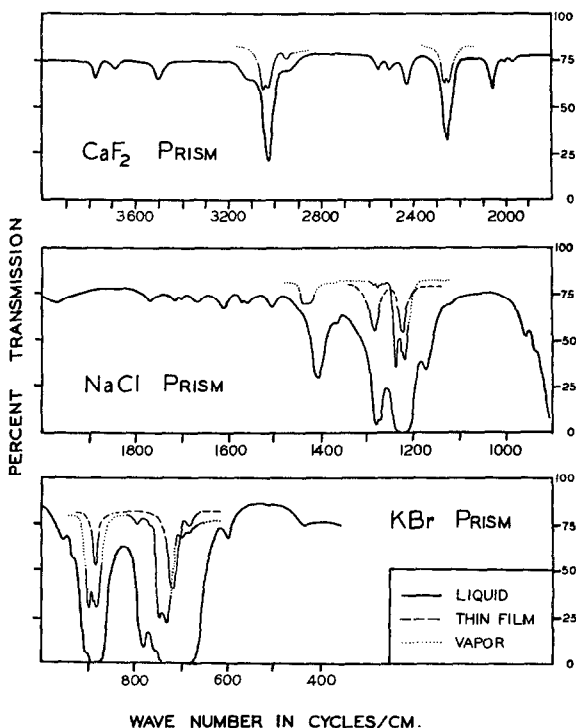


FIG. 3. Infrared spectrum of CHDCl_2

but for the cell thickness used here, there is no measurable peak. The fact that the corresponding vibration in CH_2Cl_2 is observed as a fairly strong band in the infrared can be partly explained by attributing much of the absorption to C—Cl stretching combinations and overtones, as we have stated above.

The 827 cycles/cm band assigned as $\sigma_5(a_2)$, forbidden in the infrared for the gaseous state, was observed as a weak band for the liquid, as was the a_2 fundamental of CH_2Cl_2 . One of the b_1 fundamentals, expected to appear near 700 cycles/cm, was not observed because of the strong C—Cl stretching bands in this region. The infrared bands at 885 and 1218 cycles/cm are due to traces of CHDCl_2 in the sample.

CHDCl_2

The assignments for the fundamentals were easily made for CHDCl_2 with the help of the complete isotopic substitution rules of Brodersen and Langseth (21). The observed Raman displacements for CH_2Cl_2 and CD_2Cl_2 were used for these calculations. For the one b_1 fundamental for CD_2Cl_2 which was not observed, a tentative value of 704 cycles/cm was first used; this was the average of the calculated values of Decius (22) and Shimanouchi (23). After the observed wave numbers for CHDCl_2 had been assigned, the observed fundamentals for CHDCl_2 and CH_2Cl_2 were used with the Brodersen—Langseth rule to calculate a better

TABLE VI
WAVE NUMBERS FOR THE FUNDAMENTALS^a

ν	CH_2Cl_2			CD_2Cl_2			ν	CHDCl_2			
	σ_1	σ_g	D	σ_1	σ_g	D		σ_1	σ_g	D	σ_{ci}
$\nu_1(a_1)$	2986	2996	10	2198	2207	9	$\nu_1(a')$	3020	3024	4	3038
$\nu_2(a_1)$	1422	1430	8	1052	1060 ^b	..	$\nu_2(a')$	2247	2251	4	2252
$\nu_3(a_1)$	704	713	9	678	687	9	$\nu_3(a')$	1278	1282	4	1277
$\nu_4(a_1)$	285	282	-3	282	279 ^b	..	$\nu_4(a')$	778	789	11	773
$\nu_5(a_2)$	1155	1153	-2	826	824 ^b	..	$\nu_5(a')$	683	692	9	681
$\nu_6(b_1)$	3048	3040	-8	2304	2296 ^b	..	$\nu_6(a')$	283	280 ^c	-3	284
$\nu_7(b_1)$	896	897	1	712 ^d	713 ^b	..	$\nu_7(a'')$	1219	1222	3	1220
$\nu_8(b_2)$	1263	1267	4	955	961	6	$\nu_8(a'')$	885	889	4	884
$\nu_9(b_2)$	738	757	19	711	728	17	$\nu_9(a'')$	723	738	15	725

^a ν = frequency; D = $\sigma_g - \sigma_1$; σ_{ci} = wave number calculated by the complete isotope rule from the observed $\Delta\sigma_1$ values of CH_2Cl_2 and CD_2Cl_2 ; other symbols have the same meanings as in the previous tables.

^bEstimated value obtained by adding to σ_1 the value of D for the corresponding fundamental of CH_2Cl_2 .

^cEstimated by comparison of the observed CCl_2 deformation wave numbers for all three molecules in the liquid state, and interpolation between the corresponding gas values for CH_2Cl_2 and CD_2Cl_2 .

^dCalculated from the complete isotope rule.

TABLE VII
HEAT CONTENT AND FREE ENERGY FUNCTIONS, ENTROPY, AND HEAT CAPACITY FOR CH₂Cl₂, CHDCl₂, and CD₂Cl₂^a

T	(H° - E ₀ °)/T		-(F° - E ₀ °)/T		S°		C _p °		
	CH ₂ Cl ₂	CHDCl ₂	CD ₂ Cl ₂	CH ₂ Cl ₂	CHDCl ₂	CD ₂ Cl ₂	CH ₂ Cl ₂	CHDCl ₂	CD ₂ Cl ₂
100	8.09	8.09	8.10	45.65	47.29	46.05	53.74	55.39	54.15
200	8.69	8.75	8.80	51.42	53.08	51.85	60.11	61.83	60.66
273.16	9.27	9.43	9.58	54.22	55.91	54.71	63.49	65.33	64.29
298.16	9.50	9.68	9.88	55.04	56.74	55.56	64.53	66.43	65.44
300	9.51	9.70	9.90	55.10	56.80	55.62	64.61	66.51	65.52
400	10.45	10.77	11.11	57.96	59.74	58.64	68.41	70.51	69.75
500	11.39	11.81	12.25	60.39	62.26	61.24	71.79	74.06	73.49
600	12.27	12.76	13.27	62.55	64.50	63.57	74.82	77.25	76.84
700	13.08	13.61	14.18	64.50	66.53	65.68	77.58	80.14	79.86
800	13.80	14.37	14.97	66.30	68.40	67.63	80.10	82.77	82.60
900	14.47	15.06	15.68	67.96	70.13	69.43	82.43	85.19	85.12
1000	15.06	15.67	16.31	69.52	71.75	71.12	84.58	87.42	87.43

^aThese values are for the ideal gaseous state at one atmosphere pressure, and are in cal deg⁻¹ mole⁻¹. T = temperature in degrees Kelvin, H = heat content, F = free energy, S = entropy, C_p = heat capacity at one atmosphere pressure, the superscript (°) indicates that the values are for the ideal gaseous state, and E₀° = energy of one mole of the ideal gas at 0°K.

value for this line, namely, 712 cycles/cm. The probable values of the wave numbers for the fundamentals of CHDCl_2 are given in Table V, along with the observed Raman and infrared spectral data and assignments. The infrared spectrum is shown in Fig. 3. The shoulders at 955 and 1265 cycles/cm are attributed to CD_2Cl_2 and CH_2Cl_2 , respectively.

The probable values of the fundamentals for the liquid and gas and the liquid to gas shifts in the wave numbers for CH_2Cl_2 , CD_2Cl_2 , and CHDCl_2 are given in Table VI. Also given, in the last column, are the wave numbers calculated for the fundamentals of CHDCl_2 by use of the Brodersen-Langseth complete isotopic rule.

THERMODYNAMIC PROPERTIES

The heat content function $(H^0 - E_0^0)/T$, free energy function $-(F^0 - E_0^0)/T$, entropy S^0 , and heat capacity C_p^0 at one atmosphere pressure were computed for all three molecules at twelve temperatures to the ideal gaseous state, rigid-rotor, harmonic-oscillator approximation. The wave numbers for the gaseous state, listed in Table VI, were used in these calculations. The symmetry number is 2 for CH_2Cl_2 and CD_2Cl_2 , and 1 for CHDCl_2 . The products of the principal moments of inertia, taken from Meyers and Gwinn (24), are 3.9645×10^5 (amu \AA^2)³ for CH_2Cl_2 , 5.5472×10^5 for CD_2Cl_2 , and 4.7456×10^5 for CHDCl_2 . The results are given in Table VII.

The thermodynamic properties for CH_2Cl_2 thus calculated differ slightly from those obtained from the wave numbers for the liquid by Gelles and Pitzer (25). The average deviation of their values from the present results is 0.03 cal deg⁻¹ mole⁻¹ for the heat content function, 0.05 for the free energy function, 0.08 for the entropy, and 0.07 for the heat capacity.

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