



MatrixIsolation Study of the VacuumUltraviolet Photolysis of Methyl Chloride and Methylene Chloride. Infrared and Ultraviolet Spectra of the Free Radicals CCI, H2CCI, and CCI2

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Citation: The Journal of Chemical Physics **53**, 2688 (1970); doi: 10.1063/1.1674392 View online: http://dx.doi.org/10.1063/1.1674392 View Table of Contents: http://scitation.aip.org/content/aip/journal/jcp/53/7?ver=pdfcov Published by the AIP Publishing

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Matrix-Isolation Study of the Vacuum-Ultraviolet Photolysis of Methyl Chloride and Methylene Chloride. Infrared and Ultraviolet Spectra of the Free Radicals CCl, H₂CCl, and CCl₂

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Infrared and ultraviolet spectroscopic studies have been conducted on the products of the vacuumultraviolet photolysis of normal and isotopically substituted methyl chloride and methylene chloride isolated in argon and nitrogen matrices at 14°K. The cage effect has been found to inhibit halogen detachment processes in these systems. Infrared absorptions attributable to CCl, HCCl, and H₂CCl and the 2800-Å ultraviolet absorption of CCl appear in the methyl chloride photolysis studies. Observation of a "negative anharmonicity" for the lowest-frequency infrared absorption of H₂CCl can be explained by postulating that the molecule is planar. The C-Cl stretching force constant of H₂CCl is exceptionally high. The implications of $(p-d)\pi$ bonding, which may account for the large C-Cl stretching force constant, are explored. An absorption near 2300 Å behaves appropriately for assignment to a second electronic transition of CCl, providing support for the previous tentative assignment of a group of emission bands to such a transition. Photolysis of methylene chloride in a matrix environment leads principally to the stabilization of CCl₂. A revised estimate of the force constants of CCl₂ is given.

INTRODUCTION

In studies of the vacuum-ultraviolet photolysis of the partially fluorinated methanes isolated in inert matrices at 14°K, we have found that several fluorinecontaining free radical species are stabilized in sufficient concentration for infrared and ultraviolet spectroscopic detection. CF, HCF, and H₂CF have been observed in photolyzed samples of matrix-isolated methyl fluoride,¹ and a large concentration of CF₂, together with a smaller but appreciable concentration of HCF₂, has been observed in the corresponding study of the photolysis products of methylene fluoride.²

The results of these experiments suggest that the vacuum-ultraviolet photolysis of the partially chlorinated methanes isolated in inert matrices may lead to the stabilization of the chlorine analogs of these radicals in concentration sufficient for infrared and ultraviolet spectroscopic study. Although spectroscopic data have been reported for several of these species, there is much room for further work.

For many years an emission band system appearing between 2700 and 2900 Å in discharges through species containing carbon and chlorine has been attributed to the species CCl. The detailed analyses of this band system by Gordon and King³ and by Verma and Mulliken⁴ have confirmed this identification and have determined that the bands result from a ${}^{2}\Delta$ (case b)- ${}^{2}\Pi$ (case a) transition. The lower state has been presumed to be the ground state of CCl. Molecular constants have been derived for both states. A second band system, consisting of weak, red-degraded bands between 2360 and 2440 Å which appeared in low-current density discharges through a number of carbon-chlorine species, has been tentatively attributed to CCl by Barrow, Drummond, and Walker.⁵

The two stretching fundamentals of CCl_2 and an electronic transition of this species between 5600 and

4450 Å were first reported by Milligan and Jacox.6 In these studies, CCl₂ was formed by the reaction of photolytically produced carbon atoms with Cl₂ isolated in an argon or a nitrogen matrix. The most prominent infrared absorption of CCl₂, at 748 cm⁻¹, was sufficiently broad that the individual chlorine-isotopic contributions were not resolved. However, in this system two nitrogen molecules were produced for each carbon atom available for reaction, and slight perturbations due to this nitrogen may have broadened the CCl₂ absorption. The presence of nitrogen was avoided in the subsequent studies of Andrews,⁷ who reported the production of CCl₂ by the reaction of lithium atoms with carbon tetrachloride in an argon matrix. Splittings were resolved which were attributed to the individual chlorine-isotopic contributions to the CCl₂ absorption, and calculations based upon the detailed structure of the absorption were presented. However, it is possible that the resolved structure may have resulted not from the chlorine-isotopic splitting but from site perturbations due to the presence of lithium atoms and lithium chloride in the matrix. Moreover, the force constants obtained by Andrews are dependent on the validity of the high-frequency approximation used to remove from consideration the heretofore unobserved ground-state bending fundamental.

An electronic transition of HCCl appearing in absorption between 5500 and 8200 Å has been analyzed in detail by Merer and Travis,⁸ who were able to deduce the geometry of the molecule in the ${}^{1}A'$ lower state of the transition. Confirmation that this state is the ground state of the molecule was afforded by observation of this electronic transition in the matrix-isolation experiments of Jacox and Milligan,⁹ in which photolytically produced carbon atoms were found to react with HCl isolated in argon and nitrogen matrices. Two vibrational fundamentals of ground-state HCCl were also observed in the matrix-isolation study.



FIG. 1. Regions of especial interest in the spectrum of typical sample of CH_3Cl isolated in an argon matrix, before and after photolysis by radiation from a microwave discharge through hydrogen. —, Ar : $CH_3Cl = 500$. 14°K. 5.1 μ mol CH_3Cl , deposited without photolysis. - -, 55.2 μ mol additional CH_3Cl , deposited over period of 316 min, with simultaneous photolysis.

Relatively little is known about the structure and spectrum of H₂CCl and of HCCl₂. The electron spin resonance observations of Fessenden and Schuler¹⁰ are consistent with a planar or nearly planar structure for H₂CF, but indicate that HCF₂ is pyramidal. Molecular orbital theory provides some basis for predicting similar structures for H₂CCl and HCCl₂, respectively. Several infrared absorptions have been assigned to HCCl₂ as a result of the lithium-atom reaction studies of Carver and Andrews,¹¹ and their assignment for DCCl₂ has been confirmed in studies of the vacuum-ultraviolet photolysis of DCCl₃ conducted in this laboratory.¹²

The results of matrix-isolation experiments involving the vacuum-ultraviolet photolysis of methyl chloride and methylene chloride and of their deuterium-substituted counterparts are presented in the following discussion. All of the predicted free radical species have been stabilized in these experiments, and new information has been obtained on several of them.

EXPERIMENTAL DETAILS¹³

CH₃Cl (Matheson Company, Incorporated) and CH₂Cl₂ (Fisher Scientific Company) were used without further purification, except for condensation at 77°K and pumping on the condensed sample to remove traces of more volatile impurity. Samples of CD₃Cl and CD₂Cl₂ (Merck, Sharp & Dohme of Canada, Ltd.) were similarly treated. The infrared spectra of the resulting materials in the gas phase showed no evidence of impurity absorptions, nor were there detectable impurities other than traces of H₂O and CO₂ in unphotolyzed deposits of these materials in argon and nitrogen matrices in which the amount of halomethane was comparable to that deposited in a typical photolysis experiment. A

TABLE I. Absorptions ^a (cm ⁻¹) app	pearing on vacuum-ultraviole	et photolysis of CH ₈ Cl ir	argon and nitrogen matrices.
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Ar∶CH₃Cl	Ar∶CH ₃ Cl (54% ¹³ C)	N₂:CH₃Cl	N ₂ :CH ₃ Cl (54% ¹³ C)	Assignment
 			402 s	H ₂ ¹³ CCl
402 s	402 s	405 s	405 s	$H_2^{12}CCl$
570 w-m				CICO
			607 m	¹³ CH ₃
606 w-m				¹² CH ₃
617 w-m		611 m–s	611 m	$^{12}CH_{3}$
649 w				
700 w				
717 vw				
736 m	737 m, br			
741 s	741 m			
747 w				
751 m		750 m, br		CH_2Cl_2
763 w-m	774			
	774 VW			
	780 w-m		707	112001
	788 w-m 701		181 W	HIGH
709	791 w-m 708			
190 W	802 A unu			
	$805.2 \text{ w}_{}\text{m}$		813 m	H-13CC)
804 m	005.2 W III	805 yw	015 m	112 001
807 w		808 sh		
810 sh	808 vw	000 54		
812 m	811 w-m	810 w-m	810 w	$H^{12}(\mathbb{C})$
815 m	814 w-m	814 w	010 11	n ool
010 111	818 w			H ₃ 13CCl
	820 sh			172
821 w-m		828 m	829 vw, sh	
827 m-s	826.0 w	834 m-s	834 m	$H_2^{12}CCl$
	828 vw			-
835 w				
	835.0 w-m			
840 m	838.6 m			$H_2^{12}CCl$
			844 w	¹³ C ³⁷ Cl
	841.2 w-m			
	844.8 w-m		850 m	¹³ C ³⁵ Cl
855 w	853 vw			
861 m–s	860 w-m	868 sh		
864 sh	864 sh	870 m	870 sh	15C34Cl
866 s	866.0 w-m	874 sh	874 sh	107 105 2 11
870 m–s	870.0 w-m	8/0 s	870 m	
	<u> </u>	882 w		
	009 V W		803 w-m	
000	808 mm br		895 w-m	
090 VW	090 vw, Di		902 w-m	HCCl
905 w 011 ww			<i>y</i> 02 w m	110 012
J 11 VW			920 w	
	992 vw			
	995 w			
	1020.8 w			
1027 s	1026.0 w			
1197 vw				
1201 w				HCCl
1266 vw				
1269 w				
	1297 w		1298 m	¹³ CH ₄

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Ar:CH₃Cl	Ar:CH₃Cl (54% ¹³ C)	N2:CH3Cl	N ₂ :CH ₃ Cl (54% ¹³ C)	Assignment	
 1305 s	1305 w	1306 s	1307 m	¹² CH ₄	
1356 w-m					
1400 w					
1429 w					
		1479 w			
		1875 w			
1878 s		1879 w		CICO	
1886 w					
		2098 w-m			
		2104 m		CH_2N_2	
2140 w-m		2142 m		CO	
2158 m					
2712 w-m					
2792 m, br					
2800 w					
2808 m		2812 w			
2820 m					
		2854 m–s		HCl	
2858 w-m					
2870 m				HCl	
3032 w		3020 m, br		CH_4	
3040 m					
3045 m					
3274 m					
3282 sh					
3338 vw					

TABLE I (Continued)

^a vw. very weak, peak optical density less than 0.015; w. weak, peak optical density between 0.03 and 0.07; s, strong, peak optical density greater than 0.07; optical density between 0.015 and 0.03; m. medium, peak optical density br, broad; sh, shoulder.

sample of methyl chloride enriched in carbon-13 was prepared by the reaction of a gas mixture consisting of 10 parts of methane (54% ¹³C) and one part chlorine, contained in a Pyrex bulb and exposed to the radiation of a medium-pressure mercury arc for approximately 30 min. The reaction product was purified by passing through a trap cooled to 90°K, to remove unreacted methane, and by passing through a column packed with Ascarite, to remove hydrogen chloride. The infrared spectrum of the resulting material corresponded well with that anticipated for the isotopic mixture of methyl chloride. A small but significant concentration of methylene chloride was also present in the sample.

Argon and nitrogen used as matrix materials were dried by passage through a column packed with P_2O_5 . Mole ratios of the matrix gas to the species of interest from 250 to 2000 were employed. Prior to deposition on the cold cryostat window, the samples were passed through a trap cooled to -70° C to remove relatively nonvolatile trace impurities.

The cryostats, photolysis procedures, and spectroscopic equipment used in these experiments have previously been described.¹⁴ All observations were at 14°K. Typical scanning conditions used for the 400–4000-cm⁻¹ spectral range permitted a resolution and absolute wavenumber accuracy of 1 cm⁻¹ between 400 and 2000 cm^{-1} and of 2 cm^{-1} between 2000 and 4000 cm^{-1} . Selected regions of the spectrum were more intensively studied, using smaller slits and slower scanning speeds. Absorptions studied in this way have been cited to the nearest tenth of a wavenumber in the tables. The relative separations of two such peaks falling within an interval of approximately 50 cm⁻¹ could be determined with an accuracy of 0.5 cm⁻¹. The 250–450-cm⁻¹ spectral region was also studied for several of the samples, using the cesium iodide interchange for the Beckman IR-9 infrared spectrophotometer. Under the conditions of the present experiments, the resolution and frequency accuracy between 250 and 450 cm⁻¹ have been estimated to be 2 cm⁻¹. The separation of closely spaced peaks could be determined with an accuracy of approximately 1 cm⁻¹. Ultraviolet absorption studies covered the 2000–5400-Å spectral range.

OBSERVATIONS

Photolysis of Methyl Chloride

The spectrum observed in a typical study of the vacuum-ultraviolet photolysis of CH₃Cl in an argon matrix is shown in Fig. 1, and the frequencies of the absorptions which appear on photolysis of the sample are summarized in the first column of Table I. A promi-



FIG. 2. 775–900-cm⁻¹ spectral region compared for samples of isotopically substituted CH₃Cl isolated in an argon matrix at 14°K and subjected to photolysis by radiation from a microwave discharge through hydrogen. (a) Ar:CH₃Cl=250. 125 μ mol CH₃Cl, deposited over period of 263 min, with simultaneous photolysis. (b) Ar:CH₃Cl (54% ¹³C)=250. 53.9 μ mol CH₃Cl, deposited over period of 290 min, with simultaneous photolysis. Fourfold ordinate expansion. (c) Ar:CD₃Cl=500. 62.9 μ mol CD₃Cl, deposited over period of 298 min, with simultaneous photolysis.

nent absorption appears at 402 cm⁻¹, prominent, structured absorptions near 740 and 750 cm⁻¹, a very complex product spectrum between 800 and 880 cm⁻¹, and a single sharp peak at 1027 cm⁻¹. The weak to moderately intense 1197-1201-cm⁻¹ absorptions have been assigned to the expected product HCCl,9 which also contributes to the prominent absorption pattern between about 800 and 820 cm⁻¹. In the earlier study, HCCl was always produced in an environment in which appreciable nitrogen was present, since for each carbon atom available for reaction to form HCCl two nitrogen molecules were also formed. The strong, relatively broad absorption at 1305 cm⁻¹ is readily assigned to CH₄ produced in the reactions following photolysis. Not shown in the figure, but present in several of the experiments, are absorptions at 570 and 1878 cm⁻¹, which may be assigned to CICO.¹⁵ Trace impurities of oxygen and carbon dioxide in the sample and the desorption of water from the walls of the deposition line may account for the stabilization of this species. The complicated pattern of absorptions between 2700 and 2900 cm⁻¹ has been tentatively assigned to HCl, which has a series of absorptions that are extremely sensitive to the nature of the matrix environment in this spectral region.¹⁶

All of the product absorptions between 400 and 1200 cm⁻¹ except that at 750 cm⁻¹ disappear when the sample is warmed to a temperature above about 32°K, permitting the onset of molecular diffusion through the argon matrix. The relatively stable species responsible for the 750-cm⁻¹ absorption is readily identified as CH_2Cl_2 , which has its most prominent infrared absorption at

this frequency. The 1305-cm⁻¹ peak, assigned to CH₄, also persists as the sample is warmed. Peaks appearing at higher frequencies were somewhat too weak for a definitive study of their behavior on warmup of the sample.

Absorptions observed after photolysis of samples of methyl chloride enriched to 54% in the carbon-13 species and isolated in an argon matrix are summarized in the second column of Table I. Only the 400–2000-cm⁻¹ spectral region has been studied in the argon-matrix carbon-13 enrichment experiments. A weak absorption at 750 cm⁻¹ in the initial sample is contributed by traces of $^{12}CH_2Cl_2$. The corresponding absorption of $^{13}CH_2Cl_2$ is overlapped by the absorption of $^{12}CH_3Cl$ near 725 cm⁻¹.

Despite the extremely complicated absorption pattern, it has been possible to sort virtually all of the absorptions observed in the carbon-13 enrichment experiments into pairs, with one member of each pair contributed by the carbon-12 molecule and the other by its carbon-13 counterpart. Thus, in the carbon-13 enrichment studies an absorption of intensity comparable to that of the 402-cm⁻¹ peak appears on its low-frequency side. Unfortunately, the peak of this absorption is slightly outside the range of the instrument. The nitrogen-matrix observations, to receive subsequent discussion, included scans of the 250-450cm⁻¹ spectral region and have confirmed the appearance of a peak assigned to the carbon-13 species 3 cm⁻¹ below the peak assigned to the carbon-12 species. The 741-cm⁻¹ peak is relatively weak in the carbon-13 enrichment experiments, and the 737-cm⁻¹ absorption is of approximately equal intensity and is somewhat broadened, suggesting that the carbon-13 counterpart of the 741-cm⁻¹ absorption contributes to the 737-cm⁻¹ absorption. Of especial interest are the absorptions between 775 and 900 cm⁻¹, shown in trace (a) of Fig. 2 for a photolyzed Ar: CH₃Cl sample and in trace (b) for an Ar:CH₃Cl sample enriched to 54% in carbon-13. Because only a small sample was available, it was necessary to scan the spectrum shown in trace (b) with fourfold ordinate expansion; for this one trace, the "10% absorption" spacing corresponds to approximately 2.5% absorption. In the experiment of trace (b), the absorptions of H13CCl between 774 and 791 cm⁻¹ were relatively weak, as were the absorptions of H¹²CCl between 808 and 814 cm⁻¹, and the 805.2-cm⁻¹ absorption was much too prominent to be attributable to H¹²CCl. It is necessary to conclude that the carbon-13 counterpart of the species responsible for the 827-cm⁻¹ absorption contributes to this 805-cm⁻¹ absorption. The 818-cm⁻¹ absorption of the carbon-13 substituted species appears 22 cm⁻¹ lower than the corresponding absorption of the carbon-12 species at 840 cm⁻¹, just as the 805-cm⁻¹ absorption of the carbon-13 experiment appears 22 cm⁻¹ lower than the 827 cm⁻¹ absorption of the ordinary samples. The rather prominent absorption at 838.6 cm⁻¹ may be correlated with the moderately

intense 840-cm⁻¹ absorption of the unenriched samples. Except for this one absorption, the pattern of absorptions between 835 and 847 cm⁻¹ is of appropriate spacing and relative intensity for assignment to the carbon-13 counterpart of the species contributing the 860-870cm⁻¹ absorptions; the 835-cm⁻¹ absorption is much too prominent to be contributed entirely by the species which contributes the weak 835-cm⁻¹ absorption of the unenriched samples. In the place of the prominent 1027-cm⁻¹ absorption of the unenriched samples, a pair of relatively weak, equally intense absorptions appears at 1020.8 and 1026.0 cm⁻¹ in the experiments on carbon-13 enriched samples. Absorptions at 1297 and 1305 cm⁻¹ may be assigned to ¹³CH₄ and to ¹²CH₄, respectively. In summary, all of the absorptions observed in the 400-2000-cm⁻¹ spectral region for photolyzed samples of carbon-13 enriched CH₃Cl isolated in an argon matrix behave appropriately for assignment to species containing a single carbon atom.

The detailed assignment of the species which contribute to the spectrum of photolyzed methyl chloride samples isolated in an argon matrix has been somewhat clarified by the corresponding nitrogen-matrix studies. The absorptions which appear upon vacuumultraviolet photolysis of CH₃Cl isolated in a nitrogen matrix are summarized in the third column of Table I. The 402-cm⁻¹ absorption of the argon-matrix experiments is shifted upward to 405 cm⁻¹ in a nitrogen matrix. The weak-to-medium intensity absorptions at 606 and 617 cm⁻¹ in an argon matrix have their nitrogen-matrix counterpart at 611 cm⁻¹, in agreement with the previously reported absorption of CH₃.¹⁴ The prominent absorptions at 736 and 741 cm⁻¹ do not appear in the nitrogen matrix, or are shifted into the region of nearby prominent absorption due to the parent molecule. The 800-900-cm⁻¹ region of the spectrum of a typical photolyzed N₂:CH₃Cl sample is shown in trace (a) of Fig. 3. The relative simplicity of the absorption pattern in this spectral region for nitrogen-matrix samples is apparent. The contribution of HCCl is clearly separated from the higher-frequency absorption pattern and, in Fig. 3(a), is relatively weak. The frequencies and relative intensities of the HCCl absorptions in a nitrogen matrix agree within experimental error with those previously reported.9 Instead of two prominent absorption pairs between 820 and 850 cm⁻¹, only a single pair of absorptions, at 828 and 834 cm⁻¹, is observed. Their relative intensities and the 6-cm⁻¹ separation between them suggest that these absorptions are contributed by the C-Cl stretching mode of a species containing a single chlorine atom. Similarly, only two prominent absorptions, each with a partially resolved low-frequency shoulder, appear near 870 cm⁻¹. Like the 736-741-cm⁻¹ pair of absorptions, the 1027-cm⁻¹ absorption of the argon-matrix experiments has no counterpart in the nitrogen-matrix observations, or is obscured by a nearby parent molecule absorption. Methane is also identified, and the appearance of



FIG. 3. 775-900-cm⁻¹ spectral region compared for samples of isotopically substituted CH₃Cl isolated in a nitrogen matrix at 14°K and subjected to photolysis by radiation from a microwave discharge through hydrogen. (a) N₂:CH₃Cl = 500. 42.4 μ mol CH₃Cl, deposited over period of 238 min, with simultaneous photolysis. (b) N₂:CH₃Cl (54% ¹³C) = 500. 34.2 μ mol CH₃Cl, deposited over period of 272 min, with simultaneous photolysis. (c) N₂:CD₃Cl = 500. 56.7 μ mol CD₃Cl, deposited over period of 291 min, with simultaneous photolysis.

moderately intense absorptions at 2098 and 2104 cm⁻¹, assigned to CH₂N₂, indicates that a small concentration of CH₂, which reacts with the nitrogen matrix, is formed on photolysis. In the nitrogen-matrix experiments, only one prominent absorption, at 2854 cm⁻¹, appears between 2700 and 2900 cm⁻¹. This absorption corresponds within experimental error with the absorption observed by Bowers and Flygare¹⁶ for HCl isolated in a nitrogen matrix.

The positions and approximate relative intensities of absorptions which appear upon photolysis of a N₂: CH₃Cl sample enriched to 54% in carbon-13 are summarized in the fourth column of Table I, and the 775–900-cm⁻¹ spectral region observed for a photolyzed sample is shown in trace (b) of Fig. 3. The $3-cm^{-1}$ separation of the pair of absorptions observed near 400 cm⁻¹, previously mentioned, has been determined not only with the KBr interchange, but also with the CsI interchange for the infrared spectrophotometer. The 607-cm⁻¹ absorption is readily assigned to ¹³CH₃, known from previous studies to have an absorption at 606.5 cm⁻¹ in a nitrogen matrix.¹⁴ Because the sample used for the nitrogen-matrix study contained considerable CH₂Cl₂, the 750-cm⁻¹ spectral region was obscured. However, as will later be shown, the products of the photolysis of CH₂Cl₂ have their most prominent absorptions near 750 and 900 cm⁻¹, resulting in very little spectral interference with the absorptions presently of interest. Only a small concentration of HCCl, evidenced by the weak H¹³CCl absorption at 787 cm⁻¹ and by the weak H¹²CCl absorption at 810 cm⁻¹, was present in

Ar:CD ₃ Cl	N ₂ :CD ₃ Cl	Assignment
291 m		D ₂ CCl
	462 w-m	CD_3
544 w-m		C_2D_2
554 vw		
563 vw		
570 w		CICO
703 w		
710 m		
747 vw		
766 m		
774 vw		
782 w		
	787 vw, sh	
788 m	789 w	
795 m	796 m-s	D_2CCl
799 sh		
801 m	801 m	DCCl
805 w-m	804 vw	
855 vw		
	862 vw	
861 m	868 sh	
864 w	870 m	$^{12}C^{37}Cl$
866 m–s	$874 \mathrm{sh}$	
870 m	876 s	¹² C ³⁵ Cl
957 m	962 w	_
994 m	994 m	CD_4
1028 m		
1045 m	1044 m–s	
1048 w-m		
	1875 m	0100
1878 s	1878 m	CICO
1886 w	1881 m	
1965 w, br		
2020 w, br	2020	
2026 w	2030 m	
2040 w-m	2036 w	
	2058 vw	DO
2070	2008 m-s	DCi
2070 VW		
2082 VW 2000		
2090 w 2000 m		
2099 III 2140 w		CO
2140 w 2420 w m br		C ₂ D ₂
2450 w~III, DI		$C_2 D_2$

TABLE II. Absorptions^a (cm⁻¹) appearing on vacuum-ultraviolet photolysis of CD₃Cl in argon and nitrogen matrices.

 $^{\rm a}$ vw, very weak; w, weak; m, medium; s, strong; sh, shoulder; br, broad. For key to approximate optical densities, see footnote to Table I.

this experiment. However, moderately intense absorptions appeared both at 813 and at 834 cm⁻¹. The 834-cm⁻¹ absorption lies 7 cm⁻¹ above the most prominent argon-matrix absorption in this region, that at 827 cm⁻¹, and the 813-cm⁻¹ absorption lies 8 cm⁻¹ above the anomalously intense 805-cm⁻¹ absorption of the Ar:CH₃Cl (54% ¹³C) experiments, supporting the previous assignment of the 805-cm⁻¹ absorption to the carbon-13 counterpart of the species which contributes

the 827-cm⁻¹ absorption. The 844–850-cm⁻¹ absorption pair of the N₂: CH₃Cl (54% ¹³C) study is very readily assigned to the carbon-13 counterpart of the species which contributes the 870–876-cm⁻¹ pair of absorptions in the N₂: CH₃Cl experiments. A group of moderately intense absorptions between 893 and 902 cm⁻¹ may be assigned to H¹²CCl₂, for which Carver and Andrews¹¹ have observed a rather complicated absorption pattern near 900 cm⁻¹. Broad, unresolved absorption underlying the 870–876-cm⁻¹ absorptions shown in trace (b) of Fig. 3 may be attributed to H¹³CCl₂. Finally, absorptions of both ¹³CH₄ and ¹²CH₄ appear near 1300 cm⁻¹. The 2000–4000-cm⁻¹ spectral region was not scanned.

Positions and approximate relative intensities of all of the product absorptions resulting on vacuum-ultraviolet photolysis of CD₃Cl isolated in an argon matrix are summarized in the first column of Table II, and the 775-900-cm⁻¹ spectral region of a typical photolyzed sample is shown in trace (c) of Fig. 2. Of especial interest is the moderately intense absorption at 291 cm^{-1} , which disappears as the sample is warmed. It is likely that this peak is the counterpart of the 402-cm⁻¹ peak of the Ar:CH₃Cl experiments. The 710-cm⁻¹ absorption may be contributed by the same species which contributes the 741-cm⁻¹ absorption to the Ar:CH₃Cl experiments. A rather complicated pattern of absorptions appears between 785 and 805 cm⁻¹. The assignment of these absorptions will be considered in the discussion of the nitrogen-matrix observations. Comparison of all three traces of Fig. 2 shows that the absorption pattern near 870 cm⁻¹ is identical in position and contour in all three systems, providing strong evidence that the species responsible for this absorption contains a single carbon atom but no hydrogen. Evidence for the formation of CD₂Cl₂ on photolysis is relatively uncertain. The moderately intense 957-cm⁻¹ absorption appears at the appropriate frequency for assignment to CD₂Cl₂ and persists when the sample is warmed, indicating that it is contributed by a relatively unreactive species. However, the equally intense absorption of CD_2Cl_2 at 723 cm⁻¹ has not been observed in these experiments. Finally, CD₃, CD₄, and a small concentration of C_2D_2 have been identified in the Ar: CD_3Cl experiments, and the complicated pattern of absorptions between about 2000 and 2100 cm⁻¹ may reasonably be attributed to DCl produced upon photolysis.

Results of analogous experiments on N₂: CD₃Cl samples are summarized in the second column of Table II, and the spectrum observed between 775 and 900 cm⁻¹ is shown in trace (c) of Fig. 3. The 250–400-cm⁻¹ spectral region has not been studied for N₂: CD₃Cl samples. The 703–710-cm⁻¹ pair of absorptions of the argon-matrix experiments does not appear in the nitrogen-matrix studies. The moderately intense peak at 801 cm⁻¹ and the weak peak at 804 cm⁻¹ in the N₂: CD₃Cl experiments correspond within experimental error with the two most prominent absorptions previously reported⁹ for DCCl in a nitrogen matrix, permit-

ting the inference that the lower-frequency peaks, the most prominent of which lies at 796 cm⁻¹, are contributed by the deuterium-substituted analog of the species responsible for the 834-cm⁻¹ absorption in the N₂: CH₃Cl experiments, rather than by DCCl. As in the argon-matrix experiments, the absorption pattern near 870 cm⁻¹ is unchanged upon substitution of deuterium in the molecule. The absorption at 2068 cm⁻¹ agrees, within experimental error, with the ab-

TABLE III. Absorptions^a (cm⁻¹) appearing on vacuum-ultraviolet photolysis of CH_2Cl_2 in argon and nitrogen matrices.

Ar:CH ₂ Cl ₂	N ₂ :CH ₂ Cl ₂	Assignment
402 w-m		H ₂ CCl
715 w~m	718 vw	
718 w	723 w	
721 w-m	726 m	CCl_2
	729 sh	
747.5 sh		CCl_2
	761 s	
766 sh	765 m	
769 w	769 sh	HCCl ₃
831 vw	830 m	
838 w		
	870 w	C ³⁷ Cl
	876 m	$C^{35}Cl$
	894 w~m	
895 m	896 m	
898 m	898 sh	
901 w-m	900 m	$HCCl_2$
903 sh	903 sh	
	913 sh	
	919 s	
1043 vw		
1046 w		
1269 sh	1272 sh	
	1432 w-m	
1877 w	1878 m, br	CICO
2140 w-m	2140 m-s	CO
2808 m	2812 w-m	
	2836 m–s, br	
	2853 m-s	HCl

^a vw, very weak; w, weak; m, medium; s, strong; sh, shoulder; br, broad. For key to approximate optical densities, see footnote to Table I.

sorption previously reported¹⁴ for DCl in a nitrogen matrix.

The 2200–3000-Å spectral region of a typical photolyzed Ar: CH₃Cl sample is shown in Fig. 4. The most prominent absorption, at 2798 Å(35 730 cm⁻¹), has a sharp high-frequency satellite peak at 2782 Å (35 935 cm⁻¹). The only other prominent absorption observed between 2000 and 5400 Å in photolyzed samples is that at 2313 Å (43 220 cm⁻¹), with a high-frequency shoulder at 2305 Å (43 370 cm⁻¹). There may also be some diffuse absorption near 2400 A, but at least part of the apparent absorption shown in this region in Fig. 4 is characteristic of the background. The relative in-



FIG. 4. Absorptions appearing in 3000-2200-Å spectral region for a typical sample of CH₃Cl isolated in an argon matrix at 14°K and subjected to photolysis by radiation from a microwave discharge through hydrogen. Ar:CH₃Cl=1000. 9.2 μ mol CH₃Cl, deposited over period of 309 min, with simultaneous photolysis.

tensities of the 2800- and 2300-Å peaks are approximately constant in all of the observations, suggesting, but not proving, that the two absorptions are contributed by the same species. The only other absorption is a very weak band near 4300 Å, most likely contributed by the A-X transition of CH.¹⁴

Photolysis of Methylene Chloride

Positions and approximate relative intensities of the absorptions which have been observed on vacuumultraviolet photolysis of methylene chloride in argon and nitrogen matrices are summarized in Table III. No product absorptions have been detected between 250 and 400 cm⁻¹ for photolyzed Ar: CH₂Cl₂ samples. A pair of weak to moderately intense absorptions at 718 and 721 cm⁻¹ in the argon-matrix experiments may be assigned either to the strongest absorptions of CH₃Cl or to CCl₂.⁶ The appearance of the counterparts of these absorptions at 723 and at 726 cm⁻¹ in

FIG. 5. Contour of CCl₂ absorption between 740 and 750 cm⁻¹ resulting in a typical sample of CD₂Cl₂ isolated in an argon matrix at 14°K and subjected to photolysis by radiation from a microwave discharge through hydrogen. Ar:CD₂Cl₂=2000. 12.5 μ mol CD₂Cl₂, deposited over period of 409 min, with simultaneous photolysis.



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Species	Observeda	Calculated	
¹² C ³⁵ Cl	876	(876.0)	
$^{12}C^{37}Cl$	870	870.0	
$^{13}C^{35}Cl$	850	850.7	
¹³ C ³⁷ Cl	844	844.5	

TABLE IV. Absorptions (cm⁻¹) of isotopically substituted CCl.

^a Nitrogen-matrix values.

the nitrogen-matrix experiments has dictated their assignment to CCl₂, for which the frequency agreement is exact, rather than to CH₃Cl, for which the most prominent absorption has been observed at 734 cm⁻¹ in a nitrogen matrix. The absorption of CCl₂ near 750 cm^{-1} is obscured by the very intense CH_2Cl_2 absorption. However, in the argon-matrix experiments a shoulder grows in at 747.5 cm⁻¹, on the low-frequency side of the CH₂Cl₂ absorption, as the sample is photolyzed. The absorption near 770 cm⁻¹, which is most prominent for relatively concentrated samples, may be contributed by a small concentration of HCCl₃ produced on photolysis. The appearance of weak to moderately intense absorptions near 400 and 840 cm⁻¹ suggests that a species is produced which is common to the Ar: CH₃Cl experiments. A rather complicated absorption pattern has been observed in both matrices between 895 and 905 cm⁻¹. A strong absorption near 919 cm⁻¹ is present in nitrogen-matrix experiments, but not in argon-matrix ones. The 1269-cm⁻¹ shoulder on the CH_2Cl_2 absorption appears to grow more rapidly than the parent molecule peak as the sample is photolyzed. However, it is not entirely certain whether this absorption should be attributed to a photolysis product. The appearance of a prominent absorption at 2853 cm⁻¹ in the nitrogen-matrix experiments indicates that HCl is present in this system.

Only argon-matrix studies of the photolysis of CD₂Cl₂ have been conducted. Once again, evidence has been obtained for the stabilization of CCl₂ in photolyzed samples. The prominent CD_2Cl_2 absorption at 722 cm⁻¹ obscures the absorption due to the 721-cm⁻¹ CCl_2 fundamental. Unphotolyzed samples show no absorption in the 740–750-cm⁻¹ spectral region, whereas photolyzed samples show the very prominent absorption pattern illustrated in Fig. 5. Of especial interest are the resolution of absorption maxima at 746.6 and 744.6 cm⁻¹ and the observation of a weak shoulder at 742.8 cm⁻¹, with separations and approximate relative intensities appropriate for assignment to the three chlorine-isotopic species of CCl₂. The absorptions near 900 cm⁻¹ are not present in Ar: CD₂Cl₂ photolysis experiments, suggesting that they are contributed by a species containing one or more hydrogen atoms. A moderately intense absorption due to DCCl₂¹¹ has been observed at 974 cm⁻¹.

Only the 3650–5400-Å spectral region was scanned

in studies of the visible-ultraviolet spectrum of photolyzed samples of methylene chloride in an argon matrix. The positions of the weak absorptions which appear between 4600 and 5300 Å correspond, within experimental error, with those previously reported⁶ for the most strongly absorbing bands of the electronic transition of CCl₂. No other absorptions have been detected in the spectral region studied.

DISCUSSION

Spectrum of CCl

The studies of Gordon and King³ and of Verma and Mulliken⁴ have established a value of $36\ 002\pm2\ \mathrm{cm}^{-1}$ for the band origin of the transition between the ground ${}^{2}\Pi_{1/2}$ state of CCl and the upper ${}^{2}\Delta$ state, and $\Delta G''(\frac{1}{2})$ has been found to be 866.7 cm⁻¹ for this transition. In the matrix experiments on vacuum-ultraviolet photolysis of methyl chloride, a prominent absorption appears at 35 730 cm⁻¹, sufficiently close to the band origin for the CCl transition to suggest the presence of CCl. The red shift of 270 cm⁻¹ in the band origin of CCl trapped in an argon matrix is quite reasonable; red shifts of 200 or 300 cm⁻¹ are commonly observed for the band origins of electronic transitions of small molecules trapped in an argon matrix.

The infrared spectroscopic data are also consistent with the identification of CCI in the methyl chloride photolysis experiments. As is apparent from Figs. 2 and 3, the contour and positions of the absorptions near 870 cm⁻¹, while strongly dependent on the nature of the matrix material, are unchanged upon substitution of deuterium in the parent molecule. In studies of the photolysis of methyl chloride enriched to 54% in carbon-13, an approximately equally intense group of absorptions, with similar contour, appears near 845 cm⁻¹. The disappearance of these absorptions as the sample is warmed dictates their assignment to a reactive species. The band contour observed in the argonmatrix experiments is sufficiently complex to suggest that the 860-, 866-, and 870-cm⁻¹ absorptions must all be contributed by ¹²C³⁵Cl, presumably trapped in different types of site in the argon matrix. A similar splitting in the C-Cl stretching modes of HCCl has already been noted. In a nitrogen matrix, the band contour is much simpler; two prominent peaks having the appropriate 3:1 intensity ratio and a separation of 6 cm⁻¹ are observed. Each of these peaks has a low-frequency shoulder, suggesting the trapping of CCl in at least two different types of site in the nitrogen matrix, as well. Considering the rather complicated band contour, the position of the CCl absorption in an argon matrix is in reasonable agreement with the $\Delta G(\frac{1}{2})$ value of 866.7 cm⁻¹ observed for the ground ${}^{2}\Pi_{1/2}$ state of CCl in the gas-phase studies. As is indicated in Table IV, the isotopic shifts observed for the absorptions assigned to CCI in a nitrogen matrix agree within experimental error

with the calculated values. Similar shifts, previously discussed in considerable detail, have also been observed for the various absorptions assigned to CCl isolated in an argon matrix.

In summary, all of the spectroscopic data support the assignment of the 2798-Å ultraviolet absorption and of the pattern of infrared absorptions near 870 cm⁻¹ to CCl trapped in a matrix environment. The close correspondence between the positions observed for these absorptions and those derived from analysis of the gasphase data support the assignment of the ${}^{2}\Pi_{1/2}$ state of CCl as the ground state.

The 2313-Å absorption of the argon-matrix experiments also behaves appropriately for assignment to CCl, and its position is close to that expected for the absorption counterpart of the emission bands tentatively assigned to CCl by Barrow, Drummond, and Walker.⁵ Still further support for the identification of this absorption with a second electronic transition of CCl has been obtained in studies in our laboratory of the vacuum-ultraviolet photolysis of CH₂ClF isolated in an argon matrix.¹⁷ Both the 2798- and the 2313-Å absorptions appear weakly and with similar relative intensities in these experiments, consistent with the assignment of both absorptions to CCl.

Spectrum of H₂CCl

In both the argon- and the nitrogen-matrix studies of the photolysis of the various isotopically substituted species of methyl chloride, three groups of absorptions appear between 775 and 875 cm⁻¹ which must be assigned to the C-Cl stretching mode of reactive species containing a single carbon atom. The identification of the absorptions of CCl and of HCCl in this spectral region leaves unassigned the prominent pair of absorptions at 821 and 827 cm⁻¹ and the weaker pair of absorptions at 835 and 840 cm⁻¹ in the argon-matrix experiments and the prominent pair of absorptions at 828 and 834 cm^{-1} in the nitrogen-matrix experiments. The relative intensities of the two peaks in each of these pairs are in approximately the 1:3 ratio expected for a vibrational mode involving appreciable motion of a single chlorine atom. Since the C-Cl stretching modes of both CCl and HCCl undergo significant site perturbations in an argon matrix, and since identical isotopic shifts have been observed for the 827- and 840-cm⁻¹ peaks of the argon-matrix experiments and the 834 cm^{-1} peak of the nitrogen-matrix experiments, it is reasonable to assume that the pairs of absorptions at 835-840 and 821-827-cm⁻¹ in the argon-matrix experiments are contributed by the C-Cl stretching mode of a single species which is trapped in several different types of site in the argon lattice. The appearance in a nitrogen matrix of a single absorption pair at a position approximately midway between the positions of the argon-matrix absorption pairs also suggests assignment of these absorptions to a single species. It is reasonable also to infer that the species which contributes these peaks is the free radical H_2CCl .

Although a number of other absorptions remain unassigned in the studies of the photolysis of CH₃Cl in an argon matrix, only the absorption near 402 cm⁻¹ is common to both the argon- and the nitrogen-matrix experiments. Since H₂CCl has been found to be stabilized in both matrices, it seems reasonable to attribute the 402-cm⁻¹ absorption to H₂CCl, as well. The position of this absorption suggests its assignment to the out-ofplane deformation of the planar structure or to the symmetric HCCl deformation of the pyramidal structure. In the studies of the photolysis of CD₃Cl, a moderately intense absorption appears near 1045 cm⁻¹ in both argon- and nitrogen-matrix experiments. Such an absorption might be contributed either by the symmetric CD₂ deformation ("scissors") mode or by the antisymmetric DCCl deformation (CD₂ "wag") of D_2 CCl. Since no absorption of comparable intensity has been observed which can be attributed to the corresponding motion of the CH_2 group of H_2CCl , it is inferred that the intensification of the CD₂ absorption results from the interaction of this mode with the CCl stretching mode of D₂CCl. Such an interaction would be possible for the CD_2 "scissors" mode, but not for the "wag" mode. The appreciable shift in the position of the C-Cl stretching mode, from 834 to 796 cm⁻¹, when deuterium is substituted in the molecule confirms the occurrence of interaction between the C-Cl stretching and the symmetric CD_2 deformation modes; the much lower frequency of the DCCl symmetric deformation (291 cm⁻¹) excludes the possibility of a significant interaction between this mode of a pyramidal structure and the C-Cl stretching mode. It is concluded that the 1045-cm⁻¹ absorption may most reasonably be assigned to the symmetric CD_2 deformation of D_2CCl . The symmetric CH_2 deformation mode might then be expected to lie in the 1300-1400-cm⁻¹ spectral region. A rather weak absorption does appear at 1356 cm⁻¹ in photolyzed samples of CH₃Cl isolated in an argon matrix, but the corresponding absorption has not been identified in the nitrogen-matrix experiments. Since the position of the 1045-cm⁻¹ absorption of the CD₃Cl experiments is shifted relatively little in going from an argon to a nitrogen matrix, it might be expected that, if the 1356-cm⁻¹ absorption is contributed by the CH₂ symmetric deformation, it would also be relatively unshifted in a nitrogen matrix. However, in a nitrogen matrix a rather prominent CH₃Cl absorption appears at 1355 cm⁻¹ and would obscure any product absorption near 1356 cm⁻¹.

Unfortunately, the structure of H₂CCl, which would be necessary for a rigorous normal coordinate analysis, has not been determined. However, Fessenden and Schuler¹⁰ have estimated that the related species H₂CF deviates from planarity by less than 5°. An approximate set of force constants has been derived for H₂CCl by assuming that the molecule is planar, with 120°

	$ u_{ m CH_2}$		$\nu_{\rm CC1}$		ν_Δ	
Species	Obs	Calc	Obs	Calc	Obs	Calc
$H_2^{12}C^{35}Cl$	1356	1356.0	834	834.2	402	402.0
$H_{2}^{12}C^{37}Cl$	•••	1355.9	828	827.8	•••	402.0
$H_{2}^{13}C^{35}Cl$	•••	1352.8	813	813.0	399	398.5
$D_2^{12}C^{35}Cl$	1045	1001.4	796	795.9	291	314.9
$D_2^{12}C^{37}Cl$	•••	1001.3	789	789.1	•••	314.8

TABLE V. Comparison of absorptions (cm⁻¹) observed for H2CCl with those calculated for a planar structure,
assuming r_{CC1} =1.781 Å, r_{CH} =1.096 Å, HCCl angles=120°

^a F_{CH} fixed at 5.30×10² N m⁻¹; F_{HCC1} fixed at 0.85×10⁻¹⁸ N ·m.

bond angles. The C-Cl and C-H bond lengths have been assumed to be 1.781 and 1.096 Å, respectively, the values determined by Costain¹⁸ for methyl chloride. In the absence of data on either of the C-H stretching fundamentals of H₂CCl, a value of 5.3×10^2 N m⁻¹ has been assumed for the C-H stretching force constant. The dependence of the values of the remaining force constants on that of the C-H stretching force constants is expected to be small. The HCCl bending force constant has been fixed at 0.85×10^{-18} N m, consistent with a value close to 1200 cm⁻¹ for the unobserved antisymmetric HCCl deformation vibration. The HCCl bending vibration of HCCl appears at 1201 $\text{cm}^{-1,9}$ and that of HCCl₃ at 1224 cm⁻¹, in an argon matrix. With these assumptions, the valence-force potential constants for H₂CCl have been adjusted using the program FADJ, developed by Schachtschneider,¹⁹ to give the best fit to the observed vibrational frequencies of all of the isotopic species of H₂CCl. The extent to which the observed vibrational frequencies of H₂CCl could be fitted using this procedure is shown in Table V. Because of the complexity of the pattern observed for the C-Cl stretching absorption in argon-matrix experiments, the values observed for this mode in nitrogen-matrix experiments have been used for the calculation. The average of the two peaks assigned to the C-Cl stretching vibration of H₂¹²C³⁵Cl in an argon matrix is 833.5 cm⁻¹, very close to the 834-cm⁻¹ value observed for the single absorption of the nitrogen-matrix experiments. Except for the 291- and 1045-cm⁻¹ peaks of D₂CCl, all of the absorptions of the various isotopic species of H₂CCl are fitted within experimental error. The 1045-cm⁻¹ absorption of D₂CCl, contributed by the CD₂ deformation mode, lies at a frequency appreciably higher than the calculated value, in accord with the usual deviation due to anharmonicity. On the other hand, the 291-cm⁻¹ absorption lies considerably lower than the calculated value. The position calculated for this absorption has been found to be quite insensitive to the bond lengths assumed for the planar structure; a change of less than 1 cm^{-1} results if a C-Cl bond length of 1.70 Å is used in the calculation. For a planar structure, the out-ofplane deformation vibration is separable from all of the other vibrational modes. Since this low-frequency

vibration is nontotally symmetric, only quartic terms can contribute to its anharmonicity, and these, unlike the cubic terms, can be of either sign. Such a "negative anharmonicity" has also been observed for the out-of-plane deformation vibration of CH₃.¹⁴ On the other hand, if H₂CCl is pyramidal, the low-frequency vibration possesses the full symmetry of the molecule, and the cubic contribution to the anharmonicity must predominate, precluding such a "negative anharmonicity." It appears reasonable to assume that a small deviation ($<5^{\circ}$) of H₂CCl from the planar structure would lead to only a small shift in the position of the symmetric "umbrella" deformation, as has been found for the corresponding mode of CH₃, and would not reverse the sign of the large anharmonic correction. It is concluded that the shift in the low-frequency mode on deuterium substitution can most satisfactorily be explained by postulating a planar structure for H₂CCl. Nevertheless, proof of this hypothesis must await experimental determination of the structure of this molecule.

The force constants obtained for H₂CCl using the above procedure are compared with those calculated for CCl and for HCCl in Table VI. The force constant of CCl was calculated using a value of 876 cm⁻¹; ω_e = 875.9 cm⁻¹ for the ²H_{1/2} ground state of CCl. The values cited for HCCl differ slightly from those previously given for this species⁹; the force constants of HCCl were recalculated using the least-squares adjustment pro-

TABLE VI. Valence force constants of chlorine-containing free radicals derived from methyl chloride.

	CCl	HCCl	H ₂ CCl
F _{CC1} ^a	4.04	3.82	4.16
FHCCI ^b	•••	0.98	$(0.85)^{d}$
FHCHb	•••	•••	0.19
Feel Heel ^e		0.54	0.41
$F_{\Lambda^{\rm b}}$	•••	•••	0.045

^a mdyn/Å, or $\times 10^2$ N m⁻¹.

^b mdyn·Å, or $\times 10^{-18}$ N m.

^e mdyn, or $\times 10^{-8}$ N.

d Assumed value.

cedure of Schachtschneider.¹⁹ The value obtained for the C–Cl stretching force constant of H₂CCl is in good agreement with the 4.09 mdyn/Å value cited for this molecule by Carver and Andrews,¹¹ based on experimental data and structural assumptions which have not heretofore appeared in the literature. of especial interest is the relatively high value obtained for the C–Cl stretching force constant of all three molecules. Further consideration of this point is deferred to the subsequent discussion.

Spectrum of CCl₂

The identification of CCl₂ in the studies of the vacuum-ultraviolet photolysis of matrix-isolated methylene chloride has provided still further support for the previous spectroscopic identification of CCl₂.⁶ The chlorine-isotopic splittings are in reasonable agreement with those reported by Andrews,⁷ indicating that CCl₂ is not significantly perturbed by the presence of lithium atoms or of a lithium halide in the matrix.

In the course of reanalysis of the vibration pattern of isotopically substituted CCl₂, we have found that the bending vibration of this molecule cannot be neglected. This conclusion is in accord with the analysis given by Herzberg,²⁰ who has shown that for a bent XY_2 molecule the symmetric stretching fundamental is separable from the bending fundamental if and only if the mass of the Y atoms is small compared to that of the X atom. For any value of the bending frequency above 200 cm⁻¹, the force constants obtained by Milligan and Jacox⁶ and by Andrews⁷ do not satisfactorily reproduce the observed pattern in the stretching absorption region, and it is necessary to use the most general four-constant valence-force potential to obtain a satisfactory fit. As has been found by Andrews,⁷ the pattern of isotopic shifts calculated for the antisymmetric stretching fundamental, which is unmixed with the bending vibration, is in most reasonable accord with a valence angle near 100° and with the assignment of the 747-cm⁻¹ absorption to this fundamental. The relatively great intensity of the 747-cm⁻¹ absorption is also consistent with this assignment. Moreover, in the present detailed analysis of the data, only sets of potential constants

TABLE VII. Valence force constants of CCl₂ for various values of ν_2 , assuming $r_{CCl} = 1.70$ Å, ClCCl angle = 100°.

ν ₂ (cm ⁻¹)	F _{CC1} ^a	F _{CC1,CC1} ^a	FCICCI ^b	F _{CCLCICCI} e
0	2.86	0.27	0	0
250	2.93	0.33	0.95	0.30
300	3.04	0.44	1.36	0.51
350	3.17	0.57	1.84	0.76

^a ×10² N m⁻¹.

° ×10^{-s} N.

TABLE VIII. Comparison of C-Cl bond length (in angstroms) and stretching force constant $(\times 10^2 \text{ N m}^{-1})$ for various small molecules.

Species	rcci	$F_{\rm CC1}$	$(F_{\rm CC1} - F_{\rm CC1, CC1})$
CCI	1.65*	4.04	•••
HCCl	1.69 ^b	3.82	•••
H ₂ CCl	•••	4.16	•••
CH ₃ Cl	1.78°	3.42 ^d	•••
CCl		3.17e	2.60
HCCl ₂	• • •	•••	3.60 ^f
CH ₂ Cl ₂	1.77 ≤	3.30 ^h	$2.80^{ m h}$
CCl ₃	•••	•••	3.10 ⁱ
HCCl ₃	1.76 ^g	3.23 ^j	2.65 ^j
CCL	1.77s	3.08f	2.63f
C_2Cl_4	1.72	3.86 ^k	3.44 ^k

^a References 3 and 4.

^b Reference 8.

^e Reference 18.

^d J. Aldous and I. M. Mills, Spectrochim. Acta 19, 1567 (1963).

^e If $\nu_2 = 350$ cm⁻¹. Smaller for lower values of ν_2 .

^f Reference 11.

^g Reference 24.

^h T. Shimanouchi and I. Suzuki, J. Chem. Phys. 42, 296 (1965).

ⁱ Assuming planar structure. 3.40 for tetrahedral angles.

^j V. Galasso, G. de Alti, and G. Costa, Spectrochim. Acta 21, 669 (1965).

^k G. de Alti, V. Galasso, and G. Costa, Spectrochim. Acta **21**, 649 (1965).

which correspond to this assignment have been found to give a satisfactory fit to the observed frequencies. In order to provide an exact fitting for the mixed chlorine-isotopic species, the unsymmetrized problem was considered. The behavior of the force constants of CCl₂ as the bending frequency increases is summarized in Table VII. For all three bending vibration frequencies, the average deviation of the observed from the calculated frequencies was 0.2 cm^{-1} , and none of the calculated frequencies deviated from the observed values by more than 0.5 cm⁻¹. Most significant is the approximately 10% increase in the value of the C-Cl stretching force constant as the bending frequency is increased. Since an upper-state band separation of 305 cm⁻¹ has been observed⁶ for the electronic transition of CCl₂, and since the analogous transition of CF_2 involves a decrease of approximately 160 cm^{-1} in the bending vibration spacing, it is likely that the bending fundamental of ground-state CCl₂ lies appreciably higher than 300 cm⁻¹. Recent studies of the fluorescence of CCl₂ by Shirk and Bass²¹ are consistent with a value near 340 cm⁻¹.

Bonding of the Chloromethyl Radicals

The C-Cl bond distances and stretching force constants for a number of simple compounds are summarized in Table VIII. It is immediately apparent that the C-Cl stretching force constants of CCl, HCCl, and H_2 CCl are appreciably greater than that for CH₃Cl. Furthermore, the C-Cl bond distances of CCl and HCCl are considerably shorter than that of CH₃Cl. A parallel may be drawn to the properties

2699

^b ×10⁻¹⁸ N m.

of the C-F bond in CF, HCF, H₂CF, and CH₃F. The force constant of CF itself is appreciably greater than that of any other C-F stretching mode, and the CF bond distance for ground-state CF is 1.27 Å.²² The C-F bond distance increases to 1.31 Å for groundstate HCF,23 and the C-F stretching force constant, while still somewhat greater than for most species with a C-F bond, is smaller than that of CF.¹ The C-F bond distance for CH₃F is 1.385 Å,²⁴ and the C-F stretching force constant is typical. The bond distance and force constant pattern for the series CCl, HCCl, CH₃Cl is similar to that for the series CF, HCF, CH₃F. Unfortunately, data available for H₂CF do not suffice for determination of the C-F stretching force constant, so that it is uncertain whether H₂CF resembles H₂CCl in having an anomalously large C-X stretching force constant.

If, as appears to be likely, the bending vibration of CCl₂ lies between 300 and 350 cm⁻¹, the C-Cl stretching force constant of CCl_2 is comparable in magnitude to that of CH₂Cl₂. For both of these species, and for all of the other compounds included in Table VIII for which both the stretching and the stretchinginteraction force constants have been determined, the stretching-interaction force constant is positive, with a magnitude between 0.4×10^2 and 0.6×10^2 N m⁻¹. On this basis, the C-Cl stretching force constant of HCCl₂ would be expected to be at least 4.0×10^2 N m⁻¹, and that of CCl₃ would be approximately 3.60×10^2 N m⁻¹, significantly greater than for more typical compounds. A short C-Cl bond distance and a large C-Cl stretching force constant have also been observed for C_2Cl_4 , in which the carbon atoms possess sp^2 hybridization. The parallel suggests, but does not prove, that the carbon atom in H₂CCl, HCCl₂, and CCl_3 may also possess sp^2 hybridization and that the C-Cl bonds in these species are somewhat shorter than those typical of the chlorine-substituted methanes.

Carver and Andrews¹¹ have suggested that the participation of the chlorine d orbitals in the C-Cl bonding of HCCl₂ might lead to strengthening of these bonds, with a consequent increase in the C-Cl stretching force constant. It is quite possible that such $(p-d)\pi$ bonding may occur for H₂CCl, HCCl₂, and CCl_3 . However, it should be noted that the overlap between the chlorine d orbital and the unpaired electron on the chloromethyl radical would be greatest for a planar structure. Such $(p-d)\pi$ bonding has also been invoked to explain the relatively short Si-N bonds, the relatively high Si-N stretching force constant, and the planar or nearly planar skeletal structure of trisilvlamine.^{25,26} It has already been shown that the "negative anharmonicity" observed for the lowestfrequency fundamental of H₂CCl is constant with a planar structure. Furthermore, the recent studies of the infrared spectrum of CCl₃ by Rogers, Abramowitz, Jacox, and Milligan¹² have failed to confirm the previous identification of the symmetric stretching fundamental of CCl₃ by Andrews.²⁷ Since no absorption attributable to ν_1 of CCl₂ has been detected even in experiments in which ν_3 is sufficiently strongly absorbing for the observation of the absorption due to ν_3 of ¹³CCl₃ present in natural abundance, it is possible that the molecule possesses a planar structure, for which the appearance of ν_1 in the infrared spectrum would be forbidden. Should structural determinations confirm the planarity or near planarity of the three chloromethyl radicals, suggested by the presently available infrared data, the relatively high C–Cl stretching force constants and the planar or near-planar configuration could both be accounted for by the occurrence of $(p-d)\pi$ bonding.

Processes Occurring in the Matrix

In the gas phase, photolysis of methyl chloride, bromide, or iodide produces significant concentrations of the methyl radical and of the halogen atom. On the other hand, in the present studies of the vacuumultraviolet photolysis of methyl chloride isolated in a matrix, only a small concentration of CH_3 has been detected. The extent to which atomic diffusion may occur in a rare-gas or a nitrogen matrix is guite strongly dependent on the mass of the atom. Milligan and Jacox²⁸ have observed extremely strong absorption due to the violet system of CN in studies of the vacuumultraviolet photolysis of matrix-isolated HCN, strong absorption on photolysis of FCN, weak absorption on photolysis of ClCN, and little or no absorption on photolysis of BrCN, although in all of these systems the photolysis of XCN was evidenced by the appearance of prominent infrared absorptions assigned to the XNC isomer, formed on cage recombination of the X and CN fragments. Presumably, diffusion of a Cl atom from the site of its photoproduction in the matrix experiments is sufficiently inhibited that a large proportion of the CH₃ radicals undergo cage recombination with Cl atoms.

The photoproduction of $CH_2 + HCl$ might also be expected to occur to some extent. However, diatomic and polyatomic molecules are unable to diffuse through argon or nitrogen matrices, and, since CH_2 is highly reactive, it would be expected that CH_2 and HClwould recombine at the site of their photoproduction. A small concentration of CH_2N_2 has been detected in the nitrogen-matrix experiments. The production of only a small concentration of CH_2 could be accounted for either if this CH_2 results from the secondary photolysis of CH_3 or if an appreciable concentration of CH_2 results from a primary photolysis process but CH_2 reacts more readily with HCl than with N_2 .

The HCCl observed in the methyl chloride photolysis experiments could, of course, have resulted from the secondary photolysis of H_2 CCl. It is also possible that HCCl is formed by the elimination of H_2 from CH₃Cl. Whether cage recombination of H_2 with HCCl would occur is not known. Present data do not permit an assessment of the relative importance of these two processes in leading to the observed stabilization of HCCl. Similarly, CCl may result from the photolysis of either or both H₂CCl or HCCl in a matrix environment.

The identity of the species which contributes the absorptions near 740 and 1025 cm⁻¹, observed in the argon-matrix studies of the vacuum-ultraviolet photolysis of methyl chloride but not in the nitrogen-matrix studies, has not been ascertained.

The prominence of CCl_2 in the methylene chloride photolysis studies suggests that the primary photodetachment of H₂ plays an important role in this system. However, the detection of a small concentration of HCCl₂ in these experiments indicates that hydrogen-atom detachment also occurs. There is very little evidence for the occurrence of chlorine-atom detachment in the methylene chloride photolysis studies.

CONCLUSIONS

The cage effect plays an important role in restricting the products observed upon vacuum-ultraviolet photolysis of methyl chloride and of methylene chloride in a matrix environment; only species derived from the parent molecule by hydrogen-atom detachment have been observed in appreciable concentration.

The close correspondence with the gas-phase data observed for the position of both the 2800-Å electronic transition and the vibrational fundamental of matrixisolated CCl has confirmed the previous assumption that the ${}^{2}\Pi_{1/2}$ state is the ground state of the molecule. Furthermore, the appearance near 2300 Å of a second absorption attributable to CCl provides support for the previous tentative assignment of an emission band system between 2360 and 2440 Å to a second electronic transition of CCl. The previous infrared spectroscopic identifications of HCCl and of CCl₂ have been confirmed in these experiments. The valenceforce potential appropriate for CCl₂ has been reconsidered. For any reasonable value of the bending frequency, it is necessary to use the most general valence-force potential in order to obtain a satisfactory

fit to the isotopic data. The behavior of the lowest frequency absorption of H₂CCl is consistent with a planar structure. The exceptionally large C-Cl stretching force constant obtained for this molecule can be explained by the occurrence of $(p-d)\pi$ bonding, which would also favor a planar structure.

¹M. E. Jacox and D. E. Milligan, J. Chem. Phys. 50, 3252 (1969)

² D. E. Milligan and M. E. Jacox (unpublished data). ³ R. D. Gordon and G. W. King, Can. J. Phys. **39**, 252 (1961). ⁴ R. D. Verma and R. S. Mulliken, J. Mol. Spectry. 6, 419 (1961).

⁵ R. F. Barrow, G. Drummond, and S. Walker, Proc. Phys. Soc. (London) 67A, 186 (1954)

⁶ D. E. Milligan and M. E. Jacox, J. Chem. Phys. 47, 703 (1967)

⁷ L. Andrews, J. Chem. Phys. 48, 979 (1968).

⁸ A. J. Merer and D. N. Travis, Can. J. Phys. 44, 525 (1966). ⁹ M. E. Jacox and D. E. Milligan, J. Chem. Phys. 47, 1626 (1967)

¹⁰ R. W. Fessenden and R. H. Schuler, J. Chem. Phys. 43, 2704 (1965)

¹¹ T. G. Carver and L. Andrews, J. Chem. Phys. 50, 4235 (1969)

¹² E. E. Rogers, S. Abramowitz, M. E. Jacox, and D. E. Milligan, J. Chem. Phys. 52, 2198 (1970).

¹³ Certain commercial instruments and materials are identified in this paper in order adequately to specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the instruments or materials identified are necessarily the best available for the purpose.

¹⁴ D. E. Milligan and M. E. Jacox, J. Chem. Phys. 47, 5146 (1967)

¹⁵ M. E. Jacox and D. E. Milligan, J. Chem. Phys. 43, 866 (1965)

¹⁶ M. T. Bowers and W. H. Flygare, J. Chem. Phys. 44, 1389 (1966)

¹⁷C. E. Smith, D. E. Milligan, and M. E. Jacox (unpublished data).

¹⁸C. C. Costain, J. Chem. Phys. 29, 864 (1958).

¹⁹ J. H. Schachtschneider, "Vibrational Analysis of Polyatomic Molecules," Shell Development Co., Emeryville, Calif., 1964, Technical Repts. 231-64 and 57-65 (private communication).

²⁰ G. Herzberg, Molecular Spectra and Molecular Structure. II. Infrared and Raman Spectra of Polyatomic Moleculas Structure 11.
 Infrared and Raman Spectra of Polyatomic Molecules (Van Nostrand, Princeton, N.J., 1945), p. 197.
 ²¹ J. S. Shirk and A. M. Bass (private communication).
 ²² E. B. Andrews and R. F. Barrow, Proc. Phys. Soc. (London)

A64, 481 (1951).

²³ A. J. Merer and D. N. Travis, Can. J. Phys. 44, 1541 (1966). ²⁴ L. E. Sutton (Ed.), Chem. Soc. (London), Spec. Publ. 18, S17s (1965).

²⁵ H. Kriegsmann, Z. Anorg. Allgem. Chem. 299, 138 (1959).

²⁶ E. A. V. Ebsworth, Volatile Silicon Compounds (Pergamon, New York, 1963), pp. 105–109. ²⁷ L. Andrews, J. Chem. Phys. **48**, 972 (1968).

²⁸ D. E. Milligan and M. E. Jacox, J. Chem. Phys. 47, 278 (1967).