MatrixIsolation Studies of the Infrared Spectra of the Free Radicals CCl3 and CBr3

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Matrix-Isolation Studies of the Infrared Spectra of the Free Radicals CCl₃ and CBr₃

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CCl₃ has been stabilized both by the reaction of lithium atoms with CCl₄ in an argon matrix at 20°K and by the vacuum-ultraviolet photolysis of HCCl₃ or of DCCl₃ in an argon or a nitrogen matrix at 14°K. The analogous techniques have been found to lead to the stabilization of CBr₃. The product spectra obtained in the lithium-atom experiments are considerably simpler than those obtained in the previous studies of the reaction of lithium atoms with matrix-isolated CX₄. In the vacuum-ultraviolet photolysis experiments, DCCl₂, HCBr₂, and CBr₂ have also been observed. The absorption frequencies and contours obtained for ν_3 of CCl₃ and of CBr₃ are independent of the method used to produce these species, suggesting that lithium atoms and their reaction products do not appreciably perturb the degenerate stretching mode of either CCl₃ or CBr₃. Despite yields of these species comparable to those previously reported, absorptions at 674 and at 582 cm⁻¹, previously attributed to ν_1 of CCl₃ and CBr₃, respectively, are completely missing from the present experiments. No other absorption attributable to ν_1 of either species has been detected. It is concluded that a pyramidal (C_{3v}) structure for CCl₃ and for CBr₃ has not been established.

INTRODUCTION

Recently, the infrared spectrum of the free radical CCl₃ has been reported by Andrews[1,2] and the infrared spectrum of the free radical CBr₃ by Andrews and Carver,[3] who studied the reaction of lithium atoms with the corresponding tetrahalomethane isolated in an argon matrix at cryogenic temperatures. Since two absorptions were attributed to stretching fundamentals of each of these species, it was inferred that both CCl₃ and CBr₃ are nonplanar, as has been established[4–6] for the related molecule CF₃.

Nevertheless, there remain problems regarding the proposed assignment of the stretching fundamentals of CCl₃ and CBr₃. Although the degenerate stretching fundamental ν_3 of these species is extremely prominent, the absorption attributed to the nondegenerate stretching fundamental ν_1 is weak. A 7-cm⁻¹ discrepancy was reported[2] between the observed and calculated values for ν_1 of ¹³CCl₃, assuming tetrahedral valence angles for CCl₃. Since the infrared spectra recorded in these experiments are quite complicated, with several other products stabilized in appreciable concentration, it is possible that the weak absorption attributed to ν_1 of the CX₃ radical may in fact be contributed by some other product species. Of still further interest is the electron spin resonance study of CCl₃ by Magat, Leray, and Roncin,[7] whose data are consistent with a planar structure. For a planar molecule, ν_1 would, of course, be infrared inactive.

In the light of these difficulties, it would be desirable to study the infrared spectra of CCl₃ and of CBr₃ produced under experimental conditions different from those heretofore reported. Two such approaches are described in the following discussion. The first of these, as in the earlier studies, involves the reaction of lithium atoms with the tetrahalomethane isolated in an argon matrix, but under conditions such that the complexity of the product spectrum is greatly reduced. The second approach involves the vacuum-ultraviolet photolysis of chloroform and bromoform isolated in an argon or a nitrogen matrix, a technique analogous to that by which it has previously been found that CF₃ can be stabilized in significant concentration.[5]

EXPERIMENTAL DETAILS[8]

CCl₄ and CBr₄ (Fisher Scientific Company) used in the lithium-atom reaction experiments were freed of dissolved gases by pumping on the sample condensed at 77°K. Ar:CCl₄ and Ar:CBr₄ mole ratios of approximately 100 and 200, respectively, were employed. After having been washed with hexane, a sample enriched to greater than 99% lithium-7 was loaded into a stainless-

steel tube with an i.d. of $\frac{3}{16}$ in. This tube was mounted in a furnace affixed to the base of the cryostat, with the open end approximately $4\frac{1}{2}$ in. from the center of the cryostat sample window. With the lithium furnace oriented perpendicular to the radiation shield, the lithium sample tube was heated by a coaxial filament winding to temperatures suitable for later sample deposition. Typically, temperatures between 440 and 460°C were measured by a thermocouple attached to the end of the heating filament. The temperature of the lithium sample is, of course, somewhat lower. When sufficient time had elapsed for outgassing of the lithium, the base of the cryostat was rotated, bringing the lithium tube into a position coaxial with the cryostat sample window. The Ar:CX₄ sample was codeposited with the lithium through a jet oriented obliquely to the sample window. The lithium temperature and the rate of deposition of the Ar:CX₄ sample were adjusted to yield rather small amounts of secondary reaction products such as CCl₂[9,10] and CBr₂.[3] Under these conditions, in contrast to those of the previous experiments, little or no LiX dimer was found to be present.

HCCl₃ and HCBr₃ (Fisher Scientific Company) and DCCl₃ (Merck, Sharp, and Dohme of Canada, Ltd.) used for the vacuum-ultraviolet photolysis studies were also subjected to a preliminary outgassing by repeated condensation at 77°K and pumping. Argon and nitrogen used as matrix gases were dried by passage through a column packed with P₂O₅. Samples were prepared with mole ratios ranging from 400 to 1500. Relatively nonvolatile trace impurities were removed from the samples containing HCCl₃ or DCCl₃ by passing the gas mixture through a trap cooled to −70°C prior to deposition on the cold sample window. The photolysis techniques employed in these experiments have previously been described.[11]

The cryostats used in all of the experiments were of conventional design, with a cesium iodide sample window. The lithium-atom studies were conducted at 20°K, the boiling point of hydrogen, and the vacuum-ultraviolet photolysis studies at 14°K, the triple point of hydrogen.

A Beckman IR-7 spectrophotometer equipped with sodium chloride and cesium iodide interchanges, which permit observations between 250 and 4000 cm⁻¹, was used for the lithium-atom experiments. A Beckman IR-9 spectrophotometer was used for the vacuum-ultraviolet photolysis experiments. In typical experiments, the resolution and absolute frequency accuracy are estimated to be 1 cm⁻¹. The separations of peaks less than about 100 cm⁻¹ apart could be determined with an accuracy of approximately 0.5 cm⁻¹.

OBSERVATIONS

The 500–920-cm⁻¹ spectral region observed in a typical study of the reaction of lithium atoms with CCl₄ is shown in Fig. 1. Traces A show the results of a tenfold
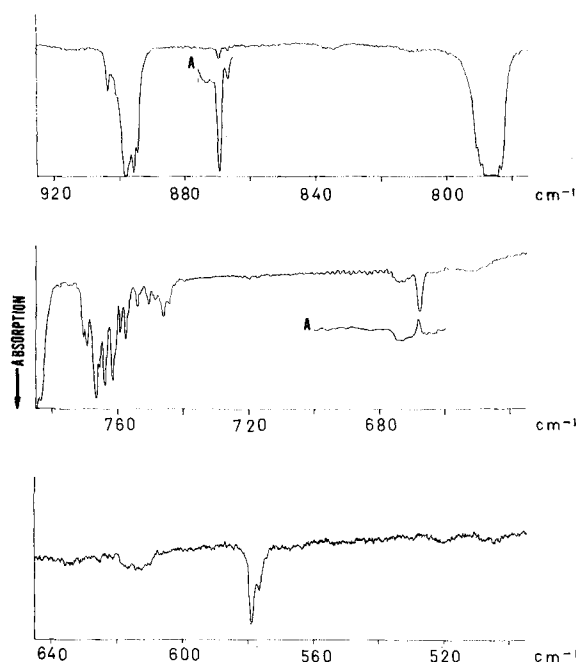

FIG. 1. Ar:CCl₄ = 100, 20°K, 320 μM CCl₄, codeposited with lithium atomic beam over period of 540 min (Traces A, tenfold ordinate expansion).

ordinate expansion (full scale = 10% absorption) of selected regions of this spectrum. To minimize problems due to residual carbon dioxide absorption in the 660–700-cm⁻¹ spectral region, more stringent efforts at purging the spectrometer were employed for the ordinate-expansion scan. The success of these efforts is demonstrated by the absence of the 667-cm⁻¹ CO₂ peak and of the R-branch structure at higher frequencies from the ordinate-expansion scan. It is apparent from Fig. 1 that the spectrum which was observed was much simpler than that of the earlier work. Nevertheless, an extremely high yield of CCl₃, which contributes the absorption near 900 cm⁻¹, was obtained. Conditions were adjusted so that infrared absorptions due to (LiCl)₂ did not appear, although the 579-cm⁻¹ absorption of ⁷LiCl was prominent. The 870-cm⁻¹ absorption of ¹³CCl₃ present in natural abundance was readily detected in these experiments and, as is shown in trace A, was extremely prominent in the scale-expansion scans. The absorption due to CCl₂, near 745 cm⁻¹, was more intense than the 870-cm⁻¹ absorption of ¹³CCl₃, but not so prominent as in the experiments of Andrews.[2] In the earlier experiments, the absorption attributed to ν_1 of CCl₃, at 674 cm⁻¹, was approximately twice as intense as the 870-cm⁻¹ ¹³CCl₃ absorption. As is shown in trace A of Fig. 1, in the present experiments the 870-cm⁻¹ absorption was several times stronger than any absorption near 674 cm⁻¹. The broad, unstructed absorption between about 670 and 680 cm⁻¹ in Fig. 1 has also been observed in experiments in which lithium atoms were not present. It is estimated that the in-
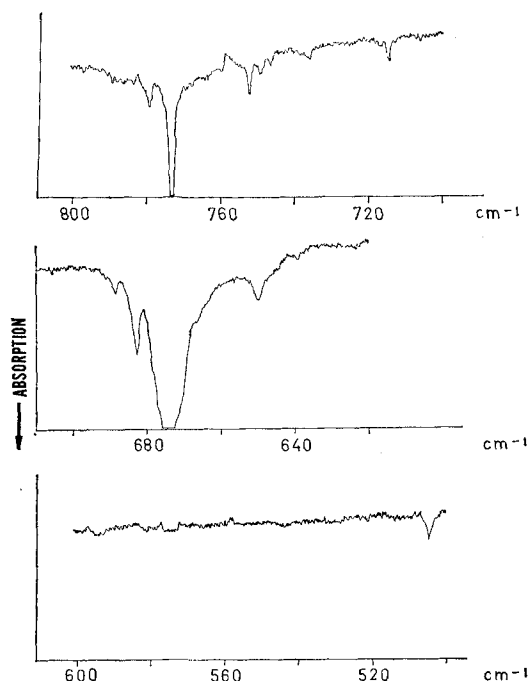
FIG. 2. Ar:CBr$_4$=200, 20°K, 240 μM CBr$_4$, codeposited with lithium atomic beam over period of 960 min.

tectable absorption due to (LiBr)$_2$, and any CBr$_2$ absorption at 641 cm^{-1} was too weak to be resolved from the rather broad ^{13}CBr$_4$ absorption.

The frequencies and approximate relative intensities of the absorptions which appeared upon vacuum-ultraviolet photolysis of HCCl$_3$ in argon and nitrogen matrices are summarized in Table I, and regions of especial interest in the spectra observed in a typical nitrogen-matrix study of HCCl$_3$ are shown in Fig. 3(a). The most prominent product absorption in both the argon- and the nitrogen-matrix experiments was that near 900 cm^{-1}. In the argon-matrix experiments, the intensity pattern and the peak absorption frequencies in the region near 900 cm^{-1} agreed within experimental error with those observed in the lithium-atom experiments, assigned to ν_3 of CCl$_3$. In a nitrogen matrix, the absorption pattern was somewhat more complicated. However, there was a separation of about 2.4 cm^{-1} between the two highest-frequency components of the absorption pattern (excluding the weak high-frequency shoulder absorptions) in both argon- and nitrogen-matrix observations, suggesting that the splitting is in-

tensity of the 674-cm^{-1} absorption, if indeed it is present, must be some 200–500 times less than that of the 900-cm^{-1} absorption of CCl$_3$.

The 500- to 800-cm^{-1} spectral region observed in a typical study of the reaction of lithium atoms with CBr$_4$, illustrated in Fig. 2, showed even less evidence for the occurrence of secondary reactions. The very prominent 675-cm^{-1} absorption is, of course, contributed by CBr$_4$. The moderately intense absorption at 650 cm^{-1} was also present in samples in which lithium atoms were not present, and is readily assigned to ^{13}CBr$_4$ present in natural abundance; the calculated position of the ^{13}CBr$_4$ absorption is 649 cm^{-1}. Moderately intense absorptions at 712, 748, 753, and 778 cm^{-1} were also present in experiments in which lithium atoms were not present and are attributed to traces of impurity in the CBr$_4$ sample. The 773-cm^{-1} absorption previously assigned to ν_3 of ^{12}CBr$_3$ was very prominent in all of the experiments, and the 746-cm^{-1} absorption of ^{13}CBr$_3$ present in natural abundance was readily detectable. In the experiments of Andrews and Carver,[3] the 582-cm^{-1} absorption attributed to ν_1 of CBr$_3$ was of intensity comparable to that of the 746-cm^{-1} absorption which they assigned to ν_3 of ^{13}CBr$_3$ present in natural abundance. In the present experiments, any absorption at or near 582 cm^{-1} must be much weaker than the absorption due to ν_3 of ^{13}CBr$_3$ and must be several hundred times weaker than the 773-cm^{-1} absorption of CBr$_3$. The only other product absorption was that due to ^{7}LiBr at 504 cm^{-1}. There was no de-

TABLE I. Absorptions[a] (cm^{-1}) appearing in 400–4000-cm^{-1} spectral region on vacuum-ultraviolet photolysis of matrix-isolated HCCl$_3$.

Ar Matrix	N$_2$ Matrix	Assignment
	663 w-m	CO$_2$
706 vw		
	742 sh	
	746 s	DCCl$_3$
	754 m	CH$_2$Cl$_2$ (?)
793 vw	791 m	CCl$_4$, C$_2$Cl$_6$
835 sh		
838 w-m		
	894.5 sh	
892.6 w	896.2 s	
894.7 m	898.2 w, sh	
896.0 s	899.5 s	
898.4 vs	901.8 vs	CCl$_3$
904 w, sh	905.6 w, sh	
	916 m–s	DCCl$_3$
	926 w	
	938 w	
	943 w	
	993 vw	
1035 sh		
1038 s		
	1243 w	
1272 w	1272 vw	
	2812 w	
	2845 s	
	2854 sh	HCl
	3453 w	

[a] vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder.

deed attributable to different chlorine-isotopic species rather than to the occurrence of different types of site in the matrix.

Several other absorptions also appeared upon photolysis of HCCl₃ in a matrix environment. The only prominent additional absorption in the argon-matrix experiments was that at 1038 cm⁻¹, with a low-frequency satellite at 1035 cm⁻¹. Since this absorption did not appear in the nitrogen-matrix experiments, it cannot be attributed to CCl₃. The prominent product absorptions at 746 and 916 cm⁻¹ shown in Fig. 3(a) were peculiar to this experiment. Desorption from the walls of the deposition line of traces of deuterium-containing materials used in the preceding experiments apparently provided a photolytic source of deuterium atoms, which reacted with CCl₃ to produce DCCl₃, the species responsible for these two absorptions. Of the remaining absorptions, only that at 2845 cm⁻¹, with a shoulder at 2854 cm⁻¹, was prominent. The 2854-cm⁻¹ absorption is readily assigned to HCl trapped in a nitrogen matrix.[12] Quite possibly the 2845-cm⁻¹ absorption is also contributed by HCl, perturbed by the presence of another species, such as HCCl₃, trapped in a nearby site. The moderately intense absorption at 754 cm⁻¹ in the nitrogen-matrix experiments is tentatively attributed to CH₂Cl₂, which has its strongest absorption at this frequency. In studies of the vacuum-ultraviolet photolysis of matrix-isolated methyl chloride, Milligan and Jacox[13] have detected appreciable concentrations of both CH₃ and CH₄ among the photolysis products, indicating that photolytic rupture of the C–Cl bond and diffusion of the chlorine atom from the site of its

TABLE II. Absorptions[a] (cm⁻¹) appearing in 400–4000-cm⁻¹ spectral region on vacuum-ultraviolet photolysis of matrix-isolated DCCl₃.

Ar Matrix	N₂ Matrix	Assignment
603 vw		
614 vw		
644 m–s		
662 vw	663 w	CO₂
683 sh		
686 vw		C₂Cl₆
	726 w	
	730 w	
	755 m	
766 sh	767 m	HCCl₃, CCl₄
768 s	769 m	
794 m	790 m, broad	CCl₄, C₂Cl₆
814 w–m	813 m	DCCl₂
838 w		
864 vw		
867 sh		
870 w		¹³CCl₃
881 vw	881 vw	
885 vw		
	894.5 m	
	896.4 s	
	898.3 w, sh	
896 s	899.6 sh	
899 vs	902.0 vs	¹²CCl₃
	926 w	
967 m	969.4 sh	
973 m–s	973.0 s	DCCl₂
1035 m		
1038 s		
	2062 m, broad	DCl

[a] vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder.

production can occur to at least a limited extent under the conditions of these experiments. The assignment of the absorption near 790 cm⁻¹ is somewhat uncertain; both CCl₄ and C₂Cl₆[2] absorb near this frequency.

The experiments on the photolysis of HCCl₃ provide no information on the 674-cm⁻¹ absorption previously assigned to ν_1 of CCl₃ since HCCl₃ also has an absorption at this frequency.

Regions of especial interest in the spectrum of a N₂:DCCl₃ sample are shown in Fig. 3(b), and the frequencies of absorptions which appear on vacuum-ultraviolet photolysis of DCCl₃ in argon and nitrogen matrices are summarized in Table II. Once again, the most prominent absorptions were those near 900 cm⁻¹, which, as is apparent from the comparison of the dotted traces in Figs. 3(a) and 3(b) and of the frequencies in Tables I and II, were independent of the presence of hydrogen or deuterium in the parent molecule.

The assignment of several other absorptions is

FIG. 3. (a) N₂:HCCl₃=500, 14°K, —, 5.8 μM HCCl₃, unphotolyzed. - - -, 46.9 μM additional HCCl₃, deposited over period of 320 min, with simultaneous photolysis by microwave discharge through H₂:He=1:9. (b) N₂:DCCl₃=500, 14°K. —, 5.8 μM DCCl₃, unphotolyzed. - - -, 45.8 μM additional DCCl₃, deposited over period of 341 min, with simultaneous photolysis by microwave discharge through H₂:He=1:9.
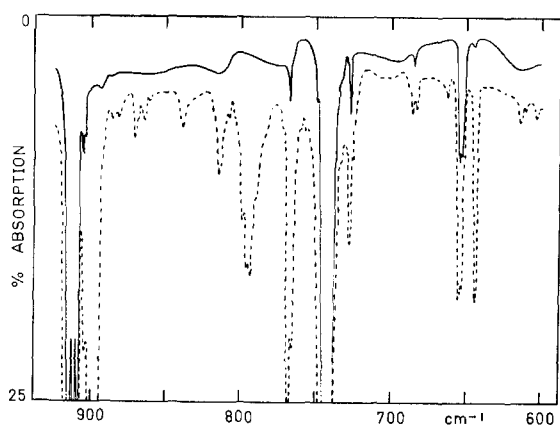
FIG. 4. Ar:$DCCl_3$ = 500, 14°K. —, 12.2 μM $DCCl_3$, unphotolyzed. - - -, 36.8 μM additional $DCCl_3$, deposited over period of 270 min, with simultaneous photolysis by microwave discharge through H_2:He = 1:9.

straightforward. The product absorption in both matrices near 768 cm^{-1} is contributed by $HCCl_3$. Traces of water desorbed from the walls of the deposition line provide a likely source of H atoms for reaction with CCl_3. Either CCl_4 or C_2Cl_6 may contribute the absorption near 790 cm^{-1}, which persists and sometimes grows as the sample is warmed. The very weak absorption at 686 cm^{-1} may also be contributed by C_2Cl_6. The prominent 644-cm^{-1} absorption of the argon-matrix experiments has been observed in a variety of other systems in which a deuterium-containing substance isolated in an argon matrix is subjected to vacuum-ultraviolet photolysis. It is believed to result from the reaction of deuterium atoms with the cesium iodide sample window.[14] The H-atom counterpart of this absorption, at 904 cm^{-1}, would be obscured by CCl_3. The 973-cm^{-1} absorption has also been observed on vacuum-ultraviolet photolysis of CD_2Cl_2,[13] and its appearance is consistent with its assignment to $DCCl_2$, for which Carver and Andrews[15] have recently reported absorptions at 974 and at 814–816 cm^{-1}. The most prominent absorption reported by these workers for $HCCl_2$ is near 900 cm^{-1}, and apparently any such absorption in the present series of experiments is sufficiently weak compared to the 900-cm^{-1} absorption of CCl_3 that it does not alter the band contour of the very strong CCl_3 absorption. The 1035- and 1038-cm^{-1} absorptions again appeared, unshifted, in an argon-matrix experiments, but were absent from the nitrogen-matrix experiments. On the other hand, the 2062-cm^{-1} absorption of the nitrogen-matrix experiments may be attributed to DCl,[12] not identified in the argon-matrix studies.

The absence of any product absorption near 674 cm^{-1} in the studies of the vacuum-ultraviolet photolysis of $DCCl_3$ is illustrated by Fig. 4, in which are shown the spectra of an unphotolyzed and a photolyzed Ar:$DCCl_3$ sample, observed using a fourfold ordinate expansion. Under these scanning conditions, the 870-cm^{-1} absorp-

tion of $^{13}CCl_3$ present in natural abundance was readily detectable, again providing a reference intensity for comparison with the observations of Andrews.[2] There was no detectable absorption within 10 cm^{-1} of the 674-cm^{-1} absorption previously attributed to ν_1 of CCl_3.

The previous report of the persistence of the CCl_3 absorption at temperatures somewhat above those at which most small free radical species disappear has been confirmed in these studies. This observation may indicate either that CCl_3 is relatively stable or that its mass is sufficiently great to slow down the onset of its diffusion through the matrix.

The 575–800-cm^{-1} spectral region observed for unphotolyzed and photolyzed samples of $HCBr_3$ in an argon matrix is shown in Fig. 5, and the frequencies of the absorptions which appear on photolysis are summarized in Table III. The most prominent product absorption, at 774 cm^{-1}, corresponds very well with the 773-cm^{-1} absorption attributed in the lithium-atom

TABLE III. Absorptions[a] (cm^{-1}) appearing in 400–4000-cm^{-1} spectral region on vacuum-ultraviolet photolysis of matrix-isolated $HCBr_3$.

Ar Matrix	N$_2$ Matrix	Assignment
565 w–m		
571 w		
580 w	580 w	CH_2Br_2
595 w		CBr_2
640 s		CBr_2
645 w–m	646 s	CH_2Br_2
648 w–m		
653 w–m		
735 m		
747 w		$^{13}CBr_3$
	772 m	
774 vs	776 s	$^{12}CBr_3$
780 m, sh		$HCBr_2$
783 w		
787 w–m		
838 w		
852 w		
874 s		
898 w		
901 w–m		
938 w–m		
	1023 w	
	1043 w	
1148 s	1144 m	
1166 w		$HCBr_2$
1195 sh		
1198 m	1200 m–s	
1205 m		
	2545 w–m	HBr
2728 s		
	3378 m	
	3418 m	

[a] vw, very weak; w, weak; m, medium; s, strong; vs, very strong; sh, shoulder.

studies to CBr₃. In a nitrogen matrix, the ν_3 absorption of CBr₃, like that of CCl₃, was doubled. Sufficient CBr₃ was stabilized in the photolysis experiments for detection of the 747-cm⁻¹ absorption of ^{13}CBr₃ present in natural abundance. A weak absorption also appeared at 580 cm⁻¹, close to the 582-cm⁻¹ absorption assigned by Andrews and Carver[3] to ν_1 of CBr₃. Both the 774- and the 580-cm⁻¹ absorptions persisted as the sample was warmed. Moreover, a strong absorption at 640 cm⁻¹ and a weak absorption at 595 cm⁻¹ correspond with the absorptions previously attributed to CBr₂. The 640-cm⁻¹ absorption disappeared quite readily as the sample was warmed, consistent with its assignment to CBr₂. The 595-cm⁻¹ absorption was too weak for a definitive determination of its behavior on warm-up.

The appearance of prominent absorptions between 1140 and 1210 cm⁻¹ indicates that products in which the hydrogen atom is retained in the molecule are present in appreciable concentration. One such product is HCBr₂, for which Carver and Andrews[16] have reported absorptions at 1166, 786, and 779 cm⁻¹, in satisfactory agreement with absorptions observed in the present experiments. The 2545-cm⁻¹ absorption of the nitrogen-matrix experiment corresponds very well with the absorption reported by Bowers and Flygare[12] for HBr isolated in a nitrogen matrix. The absorption between 645 and 650 cm⁻¹ is, quite possibly, contributed by CH₂Br₂, which also absorbs near 580 cm⁻¹. The 645-cm⁻¹ peak was especially prominent in the later stages of photolysis and increased somewhat in intensity as the sample was warmed, indicating that it is contributed by a stable species. The 580-cm⁻¹ absorption was too weak for defin-

TABLE IV. Absorption frequencies (cm⁻¹) and approximate relative intensities of peaks near 900 cm⁻¹ for isotopic species of CCl₃.[a]

Species	Approximate relative intensity	Observed[b]	Calculated	
			Planar	Tetrahedral
^{12}C^{35}Cl₃	54	898.4	(898.4)	(898.4)
^{12}C^{35}Cl₂^{37}Cl	27		898.4	898.4
	27	896.0	895.5	895.2
^{12}C^{35}Cl^{37}Cl₂	9		897.0	896.8
	9	894.7	893.9	893.4
^{12}C^{37}Cl₃	2		893.9	893.4
^{13}C^{35}Cl₃	1	870	869.9	870.6

[a] Assuming $\nu_1 = 750$ cm⁻¹ and equal intensity for each component when degeneracy is removed.
[b] Argon matrix.

itive warm-up observations, but may also have grown slightly as the sample was warmed.

DISCUSSION

The presently reported lithium-atom experiments and the vacuum-ultraviolet photolysis studies support the previous assignment of an absorption pattern near 900 cm⁻¹ to ν_3 of CCl₃. However, in both sets of experiments there is no evidence for the 674-cm⁻¹ absorption previously attributed to ν_1 of CCl₃. Since in the present lithium-atom experiments the only other product absorptions detected were those of CCl₂ and of LiCl, the possibility that the absorption due to ν_1 is obscured by absorptions of other products is rather small. It is, of course, possible that the ν_1 absorption is obscured by the strong parent molecule absorption, but the regions obscured in the experiments on HCCl₃ and DCCl₃ differ sufficiently from those obscured in the Li+CCl₄ system to permit the conclusion that any such absorption must be rather weak. In the absence of any absorption attributable to ν_1 of CCl₃, the possibility of a planar structure for this species cannot be excluded.

The close similarity of the absorption pattern observed for ν_3 of CCl₃ in both the lithium-atom and the photolysis experiments indicates that any perturbation of CCl₃ by lithium atoms or by other reaction products must be relatively insignificant.

A detailed analysis of the intensity pattern of the absorption near 900 cm⁻¹ has been conducted for the various isotopic species of CCl₃, using computation procedures similar to those previously employed in the analysis of the stretching vibrations of SiCl₃.[17] Unfortunately, the isotopic pattern of ν_3 has been found to be remarkably insensitive to either the frequency of ν_1 (for assumed values between 600 and 850 cm⁻¹) or the structure of the molecule, assuming Cl–C–Cl valence angles between 120° (planar) and 109.5° (tetrahedral, with missing apex atom). The values calculated assuming that ν_1 lies at 750 cm⁻¹ are summarized in Table IV.

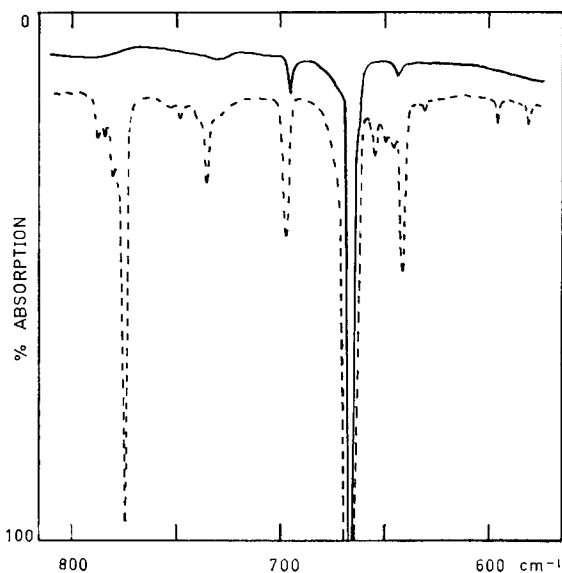Fig. 5. Ar:HCBr₃=500, 14°K. —, 7.1 μM HCBr₃, unphotolyzed. - - -, 59.7 μM additional HCBr₃, deposited over period of 316 min, with simultaneous photolysis by microwave discharge through H₂:He≈1:9.

In general, the values obtained for other assumed frequencies of ν_1 agree within 0.5 cm^{-1} with those reported in the table. There is slightly better agreement for a planar structure than for a pyramidal one, but this agreement can hardly provide a definitive case for a planar structure. The neglect of the unobserved bending frequencies of CCl$_3$ in this calculation tends to increase somewhat the calculated frequency separations of the various isotopic contributions to ν_3.

Andrews' conclusion that the C–Cl stretching force constant of CCl$_3$ is somewhat larger than that of more typical molecules appears to be borne out by these calculations. Both the stretching and the stretching-interaction constants become even larger as the molecule approaches planarity.

The present study of the reaction of lithium atoms with CBr$_4$ has demonstrated that the previously reported absorption at 582 cm^{-1} cannot be assigned to ν_1 of CBr$_3$. As has previously been indicated, the appearance of an absorption at 580 cm^{-1} in the Ar:HCBr$_3$ photolysis experiments is not inconsistent with this conclusion, since there is evidence for the stabilization of an appreciable concentration of CH$_2$Br$_2$, which also absorbs near 580 cm^{-1}, in this system.

In view of the somewhat higher concentrations of CCl$_4$ and of CBr$_4$ used in the present series of lithium-atom experiments, compared to those of Andrews,[1-3] and of the higher sample temperature, the relative simplicity of the product spectrum is at first glance surprising. The crucial factor in explaining the difference between the two sets of experiments appears to be the lithium-atom concentration. Because the distance between the sample window and the port of the lithium furnace is relatively great, only a small solid angle is subtended by the sample window. Although the temperature of the heating coil is somewhat greater than the lithium effusion temperature employed by Andrews, this temperature represents an upper limit on the temperature of the lithium furnace, which may actually have been lower than in the previous experiments.

There is evidence for the occurrence of processes other than the photodetachment of H atoms in the photolysis experiments. Photodetachment of a halogen atom from HCX$_3$ would, of course, account for the observation of the HCX$_2$ species. Secondary photolysis processes, such as the reaction of X with CX$_3$ and the photolysis of HCX$_2$ to produce CX$_2$, may also occur.

CONCLUSIONS

CCl$_3$ and CBr$_3$ are stabilized in excellent yield in inert solid matrices not only upon reaction of lithium atoms with the corresponding CX$_4$ species, but also upon vacuum-ultraviolet photolysis of the corresponding HCX$_3$ species. In the photolysis experiments, the HCX$_2$ radicals are also stabilized in appreciable concentration. The previous assignment of the absorption near 900 cm^{-1} to ν_3 of CCl$_3$ and of the 773-cm^{-1} absorption to ν_3 of CBr$_3$ has been confirmed. These absorptions show no evidence of significant perturbation by the presence of lithium in the experimental system. The previous assignment of an absorption at 674 cm^{-1} to ν_1 of CCl$_3$ and of an absorption at 582 cm^{-1} to ν_1 of CBr$_3$ is not supported by the present observations. In the absence of any other absorption attributable to ν_1 of either of these species, the possibility that CCl$_3$ and CBr$_3$ may be planar cannot be excluded.

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