Infrared Spectra of the Germanium, Tin, and Lead Dichloride Molecules in Solid Argon

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Abstract: The vapors effusing from a Knudsen cell containing solid germanium, tin, and lead dichlorides have been condensed at 15°K with a stream of argon. Two new doublet infrared absorptions are observed which show splittings appropriate to natural chlorine isotopes for molecules containing two equivalent chlorine atoms. These two absorptions are assigned to the symmetric and antisymmetric metal–chlorine stretching vibrations of the covalent molecular dichlorides, which indicates that these molecules have the bent structure. Force constants calculated for the dichlorides are lower than those for their respective tetrachlorides. This observation suggests weaker bonds in the dichlorides, which is likely due to increased p character in the metal–chlorine bonds of the dichlorides relative to the tetrachlorides.

Bonding and structure of the group IV dichloride molecules have been of interest to numerous investigators. Early electron diffraction studies of Lister and Sutton[1] on the gas phase dichlorides of tin and lead suggested that the molecules are probably acutely bent with valence angles near 95°. Some time later Naegeli and Palmer[2] obtained chemiluminescent emission spectra of $SnCl_2$ from flames produced by the reaction of potassium vapor and $SnCl_4$ at 300°. From the analysis of the observed band system, these workers found intervals of 350 and 120 cm^{-1}, which they attributed to the symmetric stretching and bending frequencies of ground state $SnCl_2$. Further electric deflection of mass spectrometrically detected molecular beams[3] indicates that lead dichloride is bent and not linear like $HgCl_2$.

Recent advances in matrix isolation spectroscopy have contributed to the stabilization of unassociated molecules of the group IV dichlorides as well as some transition metal dichlorides. Milligan and Jacox[4] identified the reactive intermediate dichlorocarbene following the reaction of photolytically produced carbon atoms with chlorine molecules in solid argon. Concurrently, Andrews[5] stabilized dichlorocarbene as a secondary reaction product of alkali metals and carbon tetrachloride in an argon matrix, and observed frequencies in excellent agreement with those of Milligan and Jacox. These independent workers observed a symmetric carbon–chlorine stretch indicating a bent molecule. Later, photolysis of H_2SiCl_2 in solid argon by Milligan and Jacox[6] produced two absorptions which these workers assigned to a bent $SiCl_2$ species. The purpose of this work was to complete the group IV dichloride series by obtaining infrared spectra of the $GeCl_2$, $SnCl_2$, and $PbCl_2$ molecules.

The early evaporative work of Linevsky[7] produced molecular LiF for matrix study using a high-temperature Knudsen cell containing crystalline LiF as a source. Hastie, Hauge, and Margrave[8] have recently observed gas phase and matrix spectra of molecular GeF_2 vapor in equilibrium with solid GeF_2 at 150°. Later work of Jacox and Milligan[9] employed as effusion cell as well as the reaction of chlorine with the hot transition metal surface to produce transition metal dichlorides for spectral observation. Owing to the success of the Knudsen effusion technique, it was decided to evaporate the heavier group IV dichlorides from the solid state.

Experimental Section

The vacuum vessel, refrigeration system, and resistance-wire heater used in these studies have been described earlier.[10] The effusion cell was a screw-capped stainless steel bottle 1 in. long × 0.75 in. o.d. with a 2-mm orifice. Tin dichloride (Research Organic/Inorganic Chemical Corp., 99%) and lead dichloride (Alfa Inorganics, Inc., 99.99%) were used directly as obtained. Several grams of the solid dichloride were transferred to the Knudsen cell, which was positioned in the heater inside of the vacuum vessel. Following evacuation to 10^{-6} Torr, the CsI window was cooled to 15°K and deposition of argon (Air Products, 99.995%) at the rate of 2 mmol/hr was started. After approximately an hour of argon deposition, the Knudsen cell was slowly warmed to the temperature required for 1 μ of vapor pressure for the solid.[11] The temperature was monitored with a chromel–alumel thermocouple. Infrared spectra were recorded every 2 or 3 hr on a Beckman IR-12 filter-grating spectrophotometer. Frequency accuracy is ± 0.5 cm^{-1} and spectral slit widths were 2.4 cm^{-1} at 500 cm^{-1} and 4.0 cm^{-1} at 300 cm^{-1}.

Since $GeCl_2$ is known to be unstable, it was synthesized immediately before use. Germanium dichloride can be prepared by the reaction[12,13] of Ge and $GeCl_4$ at 350° or from the decomposition[14,15] of trichlorogermane to germanium dichloride and hydrogen chloride. The germanium dichloride used here was prepared from trichlorogermane (Alfa Inorganics, Inc.) by trap-to-trap distillation. Liquid trichlorogermane with six Pyrex beads was held in a finger at $-22°$ with a carbon tetrachloride slush and an argon overpressure of 4 mm. The volatile materials HCl and $HGeCl_3$ were condensed in a finger cooled to liquid nitrogen temperature over a period of several hours, leaving a thin coating of $GeCl_2$ in the finger at $-22°$.

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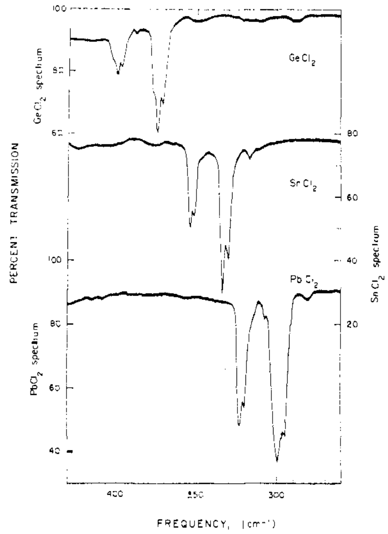

Figure 1. Infrared spectra of the vapors effusing from a Knudsen cell containing solid germanium, tin, and lead dichloride deposited in argon at 15°K.

The HCl and $HGeCl_3$ were separated using an acetone slush (−95°) and the $HGeCl_3$ was returned to the −22° finger, where the whole process was repeated. The six Pyrex beads coated with canary yellow solid $GeCl_2$ were placed directly from the vacuum line into the Knudsen cell for use as described above. This reaction is exceedingly slow with a very low yield of $GeCl_2$.

Results

Infrared spectra of germanium, tin, and lead dichloride, produced by evaporation from the solid state into an argon matrix at 15°K, are illustrated in Figure 1. The observed frequencies are recorded in Table I along with those for carbon dichloride (dichlorocarbene) and silicon dichloride.

Table I. Chlorine Stretching Frequencies and Chlorine Isotopic Splittings for the Group IV Dichloride Molecules

Molecule	Frequency, cm^{-1}	Splitting, cm^{-1}	Ref
$^{12}CCl_2$	745.7	2.0	*a*
	743.7		
	719.5	2.8	
	716.7		
$^{13}CCl_2$	723.2	2.0	*a*
	721.2		
	698.5	3.0	
	695.5		
$^{28}SiCl_2$	512.7	2.4	*b*
	510.3		
	502.0	3.3	
	498.7		
$^{74}GeCl_2$	399.7	3.1	*c*
	396.6		
	374.5	3.0	
	371.5		
$SnCl_2$	354.8	2.5	*c*
	352.3		
	334.6	3.9	
	330.7		
$PbCl_2$	322.3	2.8	*c*
	319.5		
	299.3	3.8	
	295.5		

[a] Reference 5. [b] Reference 6. [c] This work.

Two experiments were run with germanium dichloride. In the first experiment, bands at 399 and 374 cm^{-1} appeared when the Knudsen cell was warmed to 80°. The $GeCl_2$ sample was slowly warmed to 235° over a period of 16 hr, which produced a marked growth in the 399 and 374 cm^{-1} absorptions with no detectable absorption at 460 cm^{-1}, where $GeCl_4$ has been observed in an argon matrix.[16] This heating apparently expended the $GeCl_2$ sample, since in a following experiment the sample was heated to 250° for 2 hr, producing no absorptions. Subsequent examination of the Knudsen cell showed no canary yellow solid but a thin metallic gray coating (presumably elemental germanium) on the Pyrex beads. The second experiment using a fresh sample of $GeCl_2$ evaporated the material for 6 hr at temperatures of 80–120° and deposited it with an increased argon flow of 3.0 mmol/hr. The splittings on the 399- and 374-cm^{-1} bands were more clearly resolved in this experiment, which is illustrated in Figure 1.

Stannous chloride was deposited in three separate experiments. During Knudsen cell warming in the first experiment, an absorption appeared at 410 cm^{-1} where $SnCl_4$ has been observed in solid argon,[16] but this feature did not continue its growth throughout the experiment, as did new bands at 354 and 334 cm^{-1}. In the second experiment the same sample, which had been thoroughly outgassed in the first run, yielded the 354- and 334-cm^{-1} bands after evaporation for 6 hr at approximately 190° with no absorption at 410 cm^{-1}. It appears from these results that the $SnCl_2$ sample had either disproportionated since its manufacture or been contaminated with a trace of $SnCl_4$. The authors do not believe that the $SnCl_2$ disproportionated in the Knudsen cell at 190°, since no absorption for $SnCl_4$ was observed in the second experiment. A third experiment with the same sample heated to 160° produced similar results.

Two lead dichloride experiments produced the absorptions at 322 and 299 cm^{-1} illustrated in Figure 1. Using an evaporation temperature of 355°, these bands appeared over a deposition period of 6 hr. Particular notice was given to the 348-cm^{-1} region[17] where $PbCl_4$ is expected, but no absorption was observed.

Discussion

Identification of Absorptions. Each of the present experiments produced two sharp doublet absorptions which can be attributed to the monomeric dichloride. No significant additional features were observed which could be assigned to polymeric species. As a result of the gradual warming of the Knudsen cell to relatively low temperatures for Knudsen effusion experiments, with the resulting low vapor pressure and slow deposition rate, isolation of the monomer in the argon matrix with no observable molecular aggregates of the same species was successful. Furthermore, from electron diffraction studies, Lister and Sutton[1] concluded that in the vapor pressure range of the Knudsen effusion reported here, no appreciable amount of dimer is present in the vapor of $SnCl_2$ and $PbCl_2$. The two absorption bands of each molecular species are partially resolved doublets. In each case the relative intensities

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Table II. Force Constant and Chlorine Isotopic Splitting Calculations

Assignment	Assumed valence angle, deg	$F_{\mathrm{M-Cl}}$[a]	$F_{\mathrm{M-Cl,M-Cl}}$[a]	Splitting[b] ν_1	ν_3
$GeCl_2$	90	2.09	0.14	3.6	3.4
$\nu_1 > \nu_3$	100	2.10	0.26	3.8	3.2
$GeCl_2$	90	2.09	−0.14	3.4	3.6
$\nu_3 > \nu_1$	100	2.09	−0.02	3.6	3.4
$SnCl_2$	90	1.86	0.14	3.7	3.5
$\nu_1 > \nu_3$	100	1.90	0.19	3.8	3.4
$SnCl_2$	90	1.86	−0.14	3.5	3.7
$\nu_3 > \nu_1$	100	1.89	−0.04	3.6	3.5
$PbCl_2$	90	1.71	0.12	3.8	3.4
$\nu_1 > \nu_3$	100	1.71	0.17	3.9	3.3
$PbCl_2$	90	1.71	−0.12	3.4	3.8
$\nu_3 > \nu_1$	100	1.70	−0.08	3.5	3.7

[a] Units, mdyn/Å. [b] One-half ($M^{35}Cl_2 - M^{37}Cl_2$). ^{74}Ge isotopic mass and atomic weights of Sn and Pb used in the calculations.

of the observed doublets agree well with the expected intensities of a molecular species containing two equivalent chlorine atoms exhibiting natural isotopic abundance. The unresolved shoulder on the high-frequency side of the $GeCl_2$ absorptions may be due to the lighter isotopes of germanium. The authors conclude that the observed doublets are due to the germanium, tin, and lead dichloride molecules.[17a]

Vibrational Assignment. Two metal–chlorine stretching frequencies have been observed for each of the dichloride molecules. This fact alone indicates that the molecules are bent, since the linear molecule would have only a single infrared active metal–chlorine stretching vibration. These triatomic molecules possess C_{2v} symmetry with three normal modes of vibration: ν_1 (a_1, symmetric M–Cl stretch), ν_2 (a_1, symmetric valence angle bend), and ν_3 (b_1, antisymmetric M–Cl stretch). Since the analogous valence angle bending modes of $GeCl_4$ and $SnCl_4$ are reported at 172 and 126 cm^{-1}, respectively,[18] the bending modes of $GeCl_2$ and $SnCl_2$ are expected to absorb below 200 cm^{-1}, which is the low frequency limit of the spectrophotometer in this laboratory. This is in agreement with the 120 ± 5 cm^{-1} interval in the electronic spectrum of $SnCl_2$ vapor which is attributed to the valence angle bending mode of the ground state molecule.[2]

It is difficult to deduce the correct vibrational assignment $\nu_3 > \nu_1$ or $\nu_1 > \nu_3$ for the two absorptions observed for the germanium, tin, and lead dichloride molecules. Table II lists force constant calculations described below which were done for the two possible assignments along with the calculated chlorine isotopic splittings for assumed bond angles of 90 and 100°. The doublet splitting ($M^{35}Cl_2 - M^{35}Cl^{37}Cl$) is calculated by assuming that the mixed isotopic frequency lies halfway between the $M^{35}Cl_2$ and $M^{37}Cl_2$ frequencies. Comparison of the calculated chlorine isotope splittings with the observed splittings contained in Table I shows little preference for either assignment. The expected difference in chlorine isotope splittings for ν_1 and ν_3 decreases as the cosine of the valence angle and the reduced mass of the central atom approach zero. However, there is uncertainty in the measurement of chlorine isotopic splittings due to the incomplete resolution of these absorptions.

The Raman spectrum[19] of Et_2GeCl_2 shows that the antisymmetric germanium–chlorine stretch is the higher of the two Ge–Cl stretching modes. Rochkind and Pimentel[20] observed the antisymmetric O–Cl stretching vibration of OCl_2 to be the higher of the two stretching frequencies; however, the symmetric stretch was the more intense absorption. Dropping down one element in group VI, the Raman spectrum[21] of SCl_2 shows that ν_3 is the higher frequency than ν_1. Andrews[5] has assigned the more intense and higher C–Cl stretching frequency for dichlorocarbene to ν_3. However, the spectra of Milligan and Jacox[6] for $SiCl_2$ show that the lower Si–Cl stretching frequency is more intense, and these workers prefer the assignment $\nu_3 > \nu_1$ for $SiCl_2$. Spectra illustrated in Figure 1 show that the lower stretching frequency is the more intense absorption. The fact that the antisymmetric stretch is assigned to the higher stretching frequency for CCl_2, $SiCl_2$, OCl_2, SCl_2, and Et_2GeCl_2 suggests the assignment $\nu_3 > \nu_1$ for the dichlorides of germanium, tin, and lead. However, the electronic spectrum[2] of $SnCl_2$ provides a 350 ± 5 cm^{-1} assignment to ν_1 since vibronic selection rules only allow progressions of the totally symmetric vibrational modes. If the argon matrix shifts for $SnCl_2$ are small, as is the case for $SnCl_4$ (ν_3 = 408 cm^{-1} gas,[18] 410 cm^{-1} argon matrix[16]), the electronic spectrum indicates the vibrational assignments ν_1 = 354 cm^{-1} and ν_3 = 334 cm^{-1} for $SnCl_2$ in an argon matrix. The authors believe that the excellent agreement between ν_1 deduced from the electronic spectrum for $SnCl_2$ and the higher band observed here confirms the observation of the $SnCl_2$ molecule and provides sound basis for preference of the assignments $\nu_1 > \nu_3$ for the $GeCl_2$, $SnCl_2$, and $PbCl_2$ molecules.

It is interesting to note the general increase in chlorine isotopic splittings in Table I as the mass of the central atom increases. This is attributed to the fact that the chlorine atom contributes progressively more to the reduced mass of the M–Cl vibration. The decreasing frequencies in the series $GeCl_2$, $SnCl_2$, and $PbCl_2$ are also expected as the mass of the central atom increases.

Force Constant Calculations. Using symmetry coordinates, the antisymmetric stretch is alone in its symme-

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[17a] NOTE ADDED IN PROOF. Recently Guillory (W. A. Guillory, private communication) has observed two intense bands at 397 and 372 cm^{-1} following the vacuum ultraviolet photolysis of H_2GeCl_2 in an argon matrix. These absorptions are attributed to the species $GeCl_2$.

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try class and the unobserved bending mode can be separated from the symmetric stretching vibration by the approximate separation of high and low frequencies. Force constant calculations were performed for both possible vibrational assignments and assumed bond angles of 90, 100, 110, and 120°. Table II lists the force constants and the calculated chlorine isotopic splittings for the 90 and 100° bond angles. Notice that the magnitude of the force constant is relatively insensitive to the bond angle or the choice of vibrational assignments. The stretching force constants of the group IV dichlorides and tetrachlorides are compared in Table III. Both compounds show a decrease in force constant descending the group, and the dichlorides have smaller force constants than the tetrachlorides, especially for the heaviest members of the group.

Table III. M–Cl Stretching Force Constants (mdyn/Å) for the Group IV Tetrachloride and Dichloride Molecules

Molecule	M–Cl force constant	Ref
CCl_4	3.1	*a*
CCl_2	2.9	*b*
$SiCl_4$	3.1	*c*
$SiCl_2$	2.3	*d*
$GeCl_4$	2.7	*c*
$GeCl_2$	2.1	*e*
$SnCl_4$	2.5	*c*
$SnCl_2$	1.9	*e*
$PbCl_4$	2.1	*f*
$PbCl_2$	1.7	*e*

[a] Reference 12. [b] Reference 5. [c] Calculated using approximate separation of frequencies and data of ref 18, where force constants were also determined. [d] Reference 6. [e] This work. [f] Same as *c*, using data from ref 17.

Conclusions

Chemistry. Germanium dichloride was synthesized in very small yields from the decomposition of trichlorogermane. No disproportionation was observed for the dichlorides studied here. The conclusion is that $GeCl_2$ is stable toward disproportionation up to 80°, at least under vacuum. Similar stability toward disproportionation was observed for $SnCl_2$ at 190° and $PbCl_2$ at 355°.

Structure and Bonding. The predominant vapor species over the solids at elevated temperatures have been identified as covalent molecular dichlorides of germanium, tin, and lead. These molecules exhibit two infrared active vibrations which characterize a bent species, in support of earlier electron diffraction and molecular beam studies. The force constants reported here indicate weaker M–Cl bonds descending the group and weaker bonds in a given dichloride relative to its tetrachloride counterpart.

This latter fact can be rationalized by considering hybridization about the central atom. Certainly in the covalent tetrahalides, the tetrahedral geometry indicates sp^3 hybridization of the group IV element. The group IV dichlorides possess two nonbonding electrons, probably localized in a single orbital. It is well known that nonbonding electrons assume increased s character descending groups V and VI of the periodic table, which causes the remaining bonds to have more p character and decreased bond angles. The valence angles in the group V trihydrides decrease from 107, 94, and 92, to 91° for N, P, As, and Sb; and in the group VI dihydrides a decrease from 105, 93, and 91 to 90° is found for O, S, Se, and Te, respectively.[22] Thus, increasing p character and decreasing bond angles are expected for the covalent dichlorides descending the group. The p character in the divalent germanium, tin, and lead bonds to chlorine surely exceeds sp^3, which suggests weaker bonds and accounts for lower force constants in the dichlorides relative to the tetrachlorides.

It has been suggested that the carbon–chlorine bonds in dichlorocarbene could have multiple bond character since the vacant p orbital on CCl_2 could form a π bond with one of the chlorine atoms.[23] The force constant comparison between CCl_2 and CCl_4 in Table III was used by Andrews[5] to conclude that no appreciable amount of multiple bond character is present in dichlorocarbene. Perhaps electron transfer leading to double bond formation is made unfavorable by increased electron–electron repulsions with the nonparticipating chlorine atom. In like manner, the force constant comparisons of Table III indicate that no multiple bonding of this type is present in the heaviest members of the group IV dichloride family.

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