Microwave Spectrum of (Chloromethyl)germane

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In order to determine the molecular structure and barrier to internal rotation of the GeH_3 group, the microwave spectra of (chloromethyl)germane and its deuterated species $ClCH_2GeD_3$ have been investigated. From splittings of the spectra due to the first excited GeH_3 torsional state, the barrier to internal rotation was determined to be 1740±30 cal/mol. Assuming the cylindrical symmetry of the C–Cl bond, the quadrupole coupling constant was determined to be $\chi_{zz}=-74.7$ MHz for the $^{35}ClCH_2{}^{74}GeH_3$ species.

Several papers have been published on a series of molecules containing germanium atom. In particular, the papers on (fluoromethyl)germane by Krisher *et al.*[1] and on fluoromethylgermane by Roberts[2] called our attention because of the remarkable difference of barrier heights to internal rotation between these molecules. For a comparison of the results, we dealt with (chloromethyl)germane and chloromethylgermane, two chlorine-substituted molecules of (fluoromethyl)germane and fluoromethylgermane. In the present paper, we report the results of (chloromethyl)-germane obtained by microwave spectroscopy.

Experimental

Samples of (chloromethyl)germane and its deuterated species $ClCH_2GeD_3$ were prepared by the reaction of germanium tetrachloride with diazomethane in diethyl ether and by reducing the resulting $ClCH_2GeCl_3$ with $LiAlH_4$ or $LiAlD_4$ in dibutyl ether.[3]

The sample contained ^{74}Ge, ^{72}Ge and ^{70}Ge nuclei (37, 27 and 21%) and ^{35}Cl and ^{37}Cl nuclei (75 and 25%) in natural isotopic abundance ratio.

Microwave spectra were measured with a conventional 100 kHz Stark modulation spectrometer at the National Chemical Loboratory for Industry, Tokyo. All the spectra were measured at dry ice temperature on a recording chart. The spectra of five different isotopic species could be assinged. For the sake of simplicity, we denote the species by symbols such as (35, 74)-H_3 and (35, 74)-D_3, *etc.* for $^{35}ClCH_2{}^{74}GeH_3$ and $^{35}ClCH_2{}^{74}GeD_3$, *etc.*

Microwave Spectra

(Chloromethyl)germane has a form of a nearly prolate symmetric top with an asymmetry parameter κ of about −0.987. Both *a*- and *b*-type transitions were observed. Due to the quadrupolar coupling effect, the spectra exhibit multiplet structures which can be predicted by the first order perturbation theory. Measurements of the spectra were carried out for comparatively intense hyperfine components which satisfy the relation $\Delta F=\Delta J$. The assignment was made by first considering the hyperfine splitting pattern and finally confirming it by the double resonance technique using $7_{07}\leftarrow 6_{16}$ and $7_{07}\leftarrow 6_{06}$ transitions as pumping and signal transitions, respectively. The frequencies observed are given in Table 1.

First, the quadrupole coupling constants χ_{aa} and $\eta_a\chi_{aa}$ and rough values of the rotational constants were determined by a least squares technique from several low J transitions with relatively large splittings. Frequencies of transitions were then calculated with use of the values of the quadrupole coupling constants and rotational constants. Since the observed quadrupolar splittings were predicted by these calculations (Table 2), the hypothetical unsplit frequencies were determined by comparing the observed and calculated frequencies. From the hypothetical unsplit frequencies (Table 3), the accurate rotational constants were determined by a least squares analysis so as to fit in with a modified rigid rotor expression including only the $D_J[J(J+1)]^2$ term of the centrifugal distortion formula. The rotational constants and the quadrupole coupling constants are given in Table 4.

Molecular Structure

The data of the present work are not sufficient to determine the r_s structural parameters of (chloromethyl)germane by the substitution method. For this molecule, if C_3 symmetry of the GeH_3 group around the C–Ge bond is assumed, there are eight independent structural parameters, four of which are related to the $ClCH_2$ part of the molecule and independent of the germanium atom. Schwendeman and Jacobs[4] reported the r_s structure of (chloromethyl)-silane. Thus four parameters related to the $ClCH_2$ part were assumed to be identical to those of (chloromethyl)silane. The other four parameters were so determined as to reproduce fifteen observed rotational constants by a least squares technique. The differences between the observed and calculated rotational constants are given in Table 4. The root mean square deviation of fifteen rotational constants is smaller than 0.03 %.

The atom coordinates for the chlorine and germanium atoms can be obtained by solving the Kraitchman equations with the data for suitable pairs of the species. The x_c coordinate of the out of plane hydrogen atom in the GeH_3 group can also be obtained from the data for the (35, 74)-H_3 and (35, 74)-D_3 species. The coordinates solved are given in Table 4 with the differences from the calculated coordinates from the structural parameters adjusted. The agreement between these two coordinate values is satisfactory. The structural parameters (Table 5) are compared with the reported parameters of similar molecules such as $ClCH_2SiH_3$, CH_3SiH_3[5] and CH_3GeH_3[6]. A comparison of the adjusted structural parameters of (chloromethyl)germane with those of similar molecules indicates several interesting facts.

r(CX), (X=Si or Ge) becomes longer by replacing a hydrogen atom in the methyl group with a chlorine atom, while r(XH) becomes shorter and α(HXC)

TABLE 1. OBSERVED FREQUENCIES OF (CHLOROMETHYL)GERMANE (MHz)[a)]

	F	(35, 74)-H_3	(35, 72)-H_3	(35, 70)-H_3	(37, 74)-H_3	(35, 74)-D_3
$3_{03} \leftarrow 2_{02}$	7/2, 5/2	12149.48	12255.88	12367.66	11762.17	11693.63
	3/2, 1/2	12147.70	12254.07	12365.84	11760.73	11691.79
$3_{12} \leftarrow 2_{12}$	7/2	11968.68	12072.04	12180.64	11591.44	11532.37
	5/2	11966.80	12070.14	12178.75	11589.96	11530.59
	3/2	11965.37	12068.74	12177.36	11588.94	11529.14
	1/2	11967.12	12070.50	12179.28	—	11531.00
$3_{12} \leftarrow 2_{11}$	7/2	12335.48			11937.46	11859.77
	5/2	12333.55			11935.87	11857.90
	3/2	12334.92			11937.07	—
	1/2	12336.63			11938.57	11861.19
$4_{04} \leftarrow 3_{03}$	9/2, 7/2	16196.12	16337.89	16486.75	15680.06	15588.50
	5/2, 3/2	16195.23	16336.97	16485.89	15679.39	15587.63
$4_{14} \leftarrow 3_{13}$	9/2	15956.55	16094.30	16239.07	15453.89	
	7/2	15955.77	16093.50	16238.22	15453.26	
	5/2	15954.73	16092.53	16237.28	15452.41	
	3/2	15955.55	16093.29	16238.00	15453.00	
$4_{13} \leftarrow 3_{12}$	9/2	16445.94	16592.01	16745.44	15915.30	—
	7/2, 5/2	16445.34	16591.37	16744.81	15914.75	15811.44
	3/2	16446.35	16592.33	16745.81	15915.30	—
$5_{05} \leftarrow 4_{04}$	11/2, 9/2	20240.43	20417.58	20603.52	19595.96	19480.66
	7/2, 5/2	20239.91	20416.98	20602.93	19595.52	19480.00
$5_{15} \leftarrow 4_{14}$	11/2	19944.10	20116.34	20297.22		19217.03
	9/2	19943.74	20115.95	20296.86		19216.62
	7/2	19942.98	20115.24	20296.15		19215.93
	5/2	19943.39	20115.61	20296.56		19216.31
$5_{14} \leftarrow 4_{13}$	11/2	20556.21	20738.74	20930.17		19763.70
	9/2, 7/2	20555.82	20738.40	—		19763.32
	5/2	20556.21	20738.74	20930.17		19763.70
$5_{24} \leftarrow 4_{23}$	11/2	20252.38	20429.84	20616.17	19606.59	
	9/2, 7/2	20250.88	20428.26	20614.64	19605.35	
	5/2	20252.38	20429.84	20616.17	19606.59	
$5_{23} \leftarrow 4_{22}$	11/2	20264.22	20442.24	20628.89	19617.18	
	9/2, 7/2	20262.84	20440.83	20627.53	19616.09	
	5/2	20264.22	20442.24	20628.89	19617.18	
$6_{06} \leftarrow 5_{05}$	13/2, 11/2	24281.40	24493.62	24716.65	23508.53	23369.80
	9/2, 7/2	24281.12	24493.36	24716.36		23369.48
$1_{11} \leftarrow 0_{00}$	5/2—3/2	22619.82	22646.74			
	3/2—3/2	22618.15	22644.88			
	1/2—3/2	22621.37	22648.50			
$2_{12} \leftarrow 1_{01}$	5/2					22389.94
	3/2					22388.02
$3_{13} \leftarrow 2_{02}$	7/2	30416.40				
	5/2, 3/2	30412.66				
	1/2	30416.40				
$4_{14} \leftarrow 3_{03}$	9/2	34223.46				
	7/2	34219.04				
	5/2	34219.70				
	3/2	34224.20				
$2_{11} \leftarrow 2_{02}$	7/2	18812.22	18807.45	18802.97		
	5/2	18821.64	18816.56	18812.22		
$3_{12} \leftarrow 3_{03}$	9/2	18998.04	18996.69	18995.16		15084.02
	7/2	19005.56	19004.32	19003.01		15091.79
	5/2	19002.10	19000.75	18999.43		15088.12
	3/2	18994.50	18993.22	18991.90		15080.77

Table 1. (Continued)

	F	(35, 74)-H_3	(35, 72)-H_3	(35, 70)-H_3	(37, 74)-H_3	(35, 74)-D_3
$4_{13} \leftarrow 4_{04}$	11/2	19247.88	19250.85	19254.06		
	9/2	19254.93	19257.85	19260.92		
	7/2	19252.27	19255.24	19258.49		
	5/2	19245.68	19248.62	—		
$5_{14} \leftarrow 5_{05}$	13/2	19563.65	19572.05	19581.04	19499.80	15590.95
	11/2	19570.06	19578.58	19587.58	19504.79	15597.46
	9/2	19568.31	19576.78	19585.80	19503.50	15595.62
	7/2	19561.70	19570.06	19579.03	19498.18	15589.00
$6_{15} \leftarrow 6_{06}$	15/2	19947.32	19962.55	19978.61	19860.88	15935.41
	13/2	19953.80	19968.99	19985.02	19865.84	15941.89
	11/2	19952.30	19967.43	19983.53	19864.60	15940.22
	9/2	19945.91	19961.04	19977.10	19859.70	15933.80
$7_{16} \leftarrow 7_{07}$	17/2	20401.90	20425.09	20449.77	20288.00	16344.21
	15/2	20408.31	20431.45	20456.13	20293.08	16350.62
	13/2	20407.00	20430.09	20454.76	20292.02	16349.32
	11/2	20400.57	20423.74	20448.37	20287.00	16342.84
$8_{17} \leftarrow 8_{08}$	19/2	20930.17			20783.97	16820.29
	17/2	20936.57			20789.00	16826.74
	15/2	20935.40			20788.12	16825.61
	13/2	20928.91			20783.06	16819.12
$9_{18} \leftarrow 9_{09}$	21/2	21535.64			21352.03	
	19/2	21542.14			21357.07	
	17/2	21541.08			21356.22	
	15/2	21534.58			21351.23	

a) Since the measured components of the multiplets satisfy the rule of $\Delta F = \Delta J$, they can be labeled by the F quantum number of the lower level of the transitions shown in the table except for the components of the $1_{11} \leftarrow 0_{00}$ transitions. For the symbols for the species, see the text.

Table 2. Observed quadrupolar splittings of transitions from hypothetical unsplit frequencies (MHz)[a)]

	F	(35, 74)-H_3	(35, 72)-H_3	(35, 70)-H_3	(37, 74)-H_3	(35, 74)-D_3
$3_{03} \leftarrow 2_{02}$	7/2	0.32 (−5)	0.34 (−3)	0.34 (−3)	0.27 (−2)	0.35 (−3)
	5/2	(0)	(3)	(3)	(2)	(4)
	3/2	−1.46 (4)	−1.47 (1)	−1.48 (0)	−1.17 (2)	−1.49 (2)
	1/2	(−1)	(−4)	(−6)	(−2)	(−4)
$3_{13} \leftarrow 2_{12}$	7/2	1.07 (0)	1.08 (2)	1.07 (1)	0.82 (−2)	1.02 (−5)
	5/2	−0.81 (−1)	−0.82 (−4)	−0.82 (−4)	−0.66 (−2)	−0.76 (4)
	3/2	−2.24 (0)	−2.22 (0)	−2.21 (2)	−1.68 (8)	−2.21 (3)
	1/2	−0.49 (−11)	−0.46 (−7)	−0.29 (10)	—	−0.35 (2)
$3_{12} \leftarrow 2_{11}$	7/2	0.58 (5)			0.45 (2)	0.51 (−2)
	5/2	−1.35 (−1)			−1.14 (−9)	−1.36 (−2)
	3/2	0.02 (1)			0.06 (7)	—
	1/2	1.73 (14)			1.56 (9)	1.93 (5)
$4_{04} \leftarrow 3_{03}$	9/2	0.24 (−1)	0.25 (0)	0.23 (−2)	0.17 (−3)	0.23 (−3)
	7/2	(6)	(7)	(5)	(2)	(5)
	5/2	−0.65 (2)	−0.67 (−1)	−0.63 (2)	−0.50 (2)	−0.64 (3)
	3/2	(−6)	(−8)	(−5)	(−3)	(−5)
$4_{14} \leftarrow 3_{13}$	9/2	0.63 (1)	0.62 (1)	0.65 (4)	0.51 (3)	
	7/2	−0.15 (0)	−0.18 (−4)	−0.20 (−6)	−0.12 (0)	
	5/2	−1.19 (−1)	−1.15 (2)	−1.14 (3)	−0.97 (−4)	
	3/2	−0.37 (5)	−0.39 (3)	−0.42 (0)	−0.38 (−6)	
$4_{13} \leftarrow 3_{12}$	9/2	0.26 (−2)	0.29 (2)	0.28 (1)	0.30 (8)	—
	7/2	−0.34 (14)	−0.35 (13)	−0.35 (13)	−0.25 (13)	−0.35 (13)
	5/2	(−12)	(−15)	(−15)	(−8)	(−13)
	3/2	0.67 (−12)	0.61 (6)	0.65 (10)	0.30 (−13)	—
$5_{05} \leftarrow 4_{04}$	11/2	0.16 (−4)	0.20 (1)	0.20 (1)	0.14 (−1)	0.28 (8)
	9/2	(6)	(10)	(10)	(6)	(18)
	7/2	−0.36 (3)	−0.40 (−1)	−0.39 (1)	−0.30 (1)	−0.38 (2)
	5/2	(−6)	(−11)	(−10)	(−6)	(−9)
$5_{15} \leftarrow 4_{14}$	11/2	0.40 (0)	0.40 (0)	0.37 (−3)		0.41 (1)
	9/2	0.04 (3)	0.01 (0)	0.01 (0)		0.00 (−1)
	7/2	−0.72 (−2)	−0.70 (0)	−0.70 (0)		−0.69 (1)
	5/2	−0.31 (0)	−0.33 (−2)	−0.29 (2)		−0.31 (0)

TABLE 2. (Continued)

	F	(35, 74)-H_3	(35, 72)-H_3	(35, 70)-H_3	(37, 74)-H_3	(35, 74)-D_3
$5_{14} \leftarrow 4_{13}$	11/2	0.19(2)	0.17(1)			0.19(2)
	9/2	−0.20(3)	−0.17(5)			−0.19(3)
	7/2	(−3)	(−1)			(−2)
	5/2	0.19(−3)	0.17(−6)			0.19(−4)
$5_{24} \leftarrow 4_{23}$	11/2	0.76(12)	0.79(15)	0.77(13)	0.62(11)	
	9/2	−0.74(−11)	−0.79(−16)	−0.76(−13)	−0.62(6)	
	7/2	(10)	(5)	(8)	(−11)	
	5/2	0.67(−10)	0.79(−7)	0.77(−9)	0.62(−5)	
$5_{23} \leftarrow 4_{22}$	11/2	0.69(9)	0.70(10)	0.68(8)	0.55(8)	
	9/2	−0.69(10)	−0.71(8)	−0.68(11)	−0.54(9)	
	7/2	(−9)	(−11)	(−8)	(−7)	
	5/2	0.69(−10)	0.70(−9)	0.68(−11)	0.55(−8)	
$6_{06} \leftarrow 5_{05}$	13/2	0.08(−8)	0.07(−9)	0.09(−7)		0.10(−6)
	11/2	(3)	(2)	(4)		(6)
	9/2	−0.20(7)	−0.19(8)	−0.20(7)		−0.22(6)
	7/2	(−4)	(−3)	(−4)		(−6)
$1_{11} \leftarrow 0_{00}$	5/2—3/2	0.30(−8)	0.29(−10)			
	3/2—3/2	−1.37(15)	−1.57(1)			
	1/2—3/2	1.85(−5)	2.05(7)			
$2_{12} \leftarrow 1_{01}$	5/2					1.18(0)
	3/2					−0.74(−2)
$3_{13} \leftarrow 2_{02}$	7/2	1.58(−2)				
	5/2	−2.16(−3)				
	3/2	(8)				
	1/2	1.58(8)				
$4_{14} \leftarrow 3_{03}$	9/2	1.82(−2)				
	7/2	−2.60(0)				
	5/2	−1.94(−3)				
	3/2	2.56(3)				
$2_{11} \leftarrow 2_{02}$	7/2	−2.70(−2)	−2.55(11)	−2.61(6)		
	5/2	6.72(3)	6.56(−9)	6.64(−4)		
$3_{12} \leftarrow 3_{03}$	9/2	−2.52(0)	−2.56(−5)	−2.79(−26)		−2.65(−13)
	7/2	5.00(−4)	5.07(4)	5.06(1)		5.12(8)
	5/2	1.54(3)	1.50(−1)	1.48(−3)		1.45(−6)
	3/2	−6.06(−1)	−6.03(0)	−6.05(1)		−5.90(14)
$4_{13} \leftarrow 4_{04}$	11/2	−2.56(−6)	−2.56(−6)	−2.48(3)		
	9/2	4.49(12)	4.44(7)	4.38(−2)		
	7/2	1.83(−13)	1.83(−13)	1.95(−2)		
	5/2	−4.76(14)	−4.79(11)	—		
$5_{14} \leftarrow 5_{05}$	13/2	−2.45(7)	−2.52(1)	−2.53(1)	−1.91(6)	−2.48(5)
	11/2	3.96(−8)	4.01(−4)	4.01(−6)	3.08(−6)	4.03(−2)
	9/2	2.21(2)	2.21(2)	2.23(2)	1.79(8)	2.19(−1)
	7/2	−4.40(−2)	−4.51(−13)	−4.54(−13)	−3.53(−12)	−4.43(−4)
$6_{15} \leftarrow 6_{06}$	15/2	−2.63(−5)	−2.57(1)	−2.57(3)	−1.97(3)	−2.54(5)
	13/2	3.85(1)	3.87(0)	3.84(−6)	2.99(−1)	3.94(6)
	11/2	2.35(1)	2.31(−4)	2.35(−1)	1.75(−7)	2.27(−8)
	9/2	−4.04(6)	−4.08(2)	−4.08(5)	−3.15(4)	−4.15(−4)
$7_{16} \leftarrow 7_{07}$	17/2	−2.63(0)	−2.59(5)	−2.57(9)	−2.09(−4)	−2.62(3)
	15/2	3.78(1)	3.77(0)	3.79(−1)	2.99(6)	3.79(0)
	13/2	2.47(1)	2.41(−6)	2.42(−6)	1.93(2)	2.49(1)
	11/2	−3.96(−2)	−3.94(1)	−3.97(1)	−3.09(−3)	−3.99(−3)
$8_{17} \leftarrow 8_{08}$	19/2	−2.64(−6)			−2.12(−2)	−2.72(0)
	17/2	3.76(4)			2.91(3)	3.73(−2)
	15/2	2.59(2)			2.03(4)	2.60(1)
	13/2	−3.90(−5)			−3.03(−4)	−3.89(0)
$9_{18} \leftarrow 9_{09}$	21/2	−2.78(0)			−2.15(0)	
	19/2	3.72(2)			2.89(2)	
	17/2	2.66(1)			2.04(−3)	
	15/2	−3.84(−3)			−2.95(0)	

a) Figures in parentheses indicate the difference between observed and calculated values.

Table 3. Hypothetical unsplit frequencies of (chloromethyl)germane (MHz)[a)]

Species	(35, 74)-H_3	(35, 72)-H_3	(35, 70)-H_3	(37, 74)-H_3	(35, 74)-D_3
$3_{03} \leftarrow 2_{02}$	12149.16(−5)	12255.54(−6)	12367.32(−3)	11761.90(−5)	11693.28(0)
$3_{13} \leftarrow 2_{12}$	11967.61(12)	12070.96(−11)	12179.57(14)	11590.62(11)	11531.35(13)
$3_{12} \leftarrow 2_{11}$	12334.90(−11)			11937.01(0)	11859.26(−20)
$4_{04} \leftarrow 3_{03}$	16195.88(−13)	16337.64(−13)	16486.52(−15)	15679.89(−6)	15588.27(13)
$4_{14} \leftarrow 3_{13}$	15955.92(9)	16093.68(6)	16238.42(4)	15453.38(13)	
$4_{13} \leftarrow 3_{12}$	16445.68(−17)	16591.72(−20)	16745.16(−16)	15915.00(−24)	15811.79(−3)
$5_{05} \leftarrow 4_{04}$	20240.27(−3)	20417.38(4)	20603.32(0)	19595.82(14)	19480.38(−11)
$4_{15} \leftarrow 4_{14}$	19943.70(21)	20115.94(26)	20296.85(24)		19216.62(14)
$5_{14} \leftarrow 4_{13}$	20556.02(4)	20738.57(4)			19763.51(0)
$6_{06} \leftarrow 5_{05}$	24281.32(−13)	24493.55(−12)	24716.56(−7)	23508.53(−4)	23369.70(−4)
$2_{11} \leftarrow 2_{22}$	18814.92(8)	18810.00(−20)	18805.58(−8)		
$3_{12} \leftarrow 3_{03}$	19000.56(−8)	18999.25(7)	18997.95(0)		15086.67(0)
$4_{13} \leftarrow 4_{04}$	19250.44(−4)	19253.41(8)	19256.54(−6)		—
$5_{14} \leftarrow 5_{05}$	19566.10(−6)	19574.57(5)	19583.57(4)	19501.71(−15)	15593.43(5)
$6_{15} \leftarrow 6_{06}$	19949.95(2)	19965.12(7)	19981.18(4)	19862.85(3)	15937.95(−2)
$7_{16} \leftarrow 7_{07}$	20404.53(9)	20427.68(−2)	20452.34(5)	20290.09(12)	16346.83(2)
$8_{17} \leftarrow 8_{08}$	20932.81(4)			20786.09(2)	16823.01(2)
$9_{18} \leftarrow 9_{09}$	21538.42(3)			21354.18(−2)	
$1_{11} \leftarrow 0_{00}$	22619.52(−28)	22646.45(−4)			
$2_{12} \leftarrow 1_{01}$					22388.76(−6)
$3_{13} \leftarrow 2_{02}$	30414.82(1)				
$4_{14} \leftarrow 3_{03}$	34221.64(20)				

a) Figures in parentheses indicate the difference between observed and calculated values.

Table 4. Rotational constants (MHz), quadrupole coupling constants (MHz) and atom coordinates (Å)

	(35, 74)-H_3	(35, 72)-H_3	(35, 70)-H_3	(37, 74)-H_3	(35, 74)-D_3
A[a)]	20655.77(46)	20665.75(52)	20676.58(47)	20581.30(53)	16705.07(41)
B[a)]	2086.54(4)	2105.33(6)	2125.04(5)	2018.46(3)	2004.01(3)
C[a)]	1964.04(4)	1980.75(5)	1998.30(4)	1902.96(3)	1894.59(3)
D_J[a)]	0.0010(11)	0.0010(10)	0.0009(9)	0.0013(10)	0.0007(8)
ΔA[b)]	2.22(0.01)	1.80(0.01)	1.68(0.01)	1.09(0.01)	−2.51(−0.02)
ΔB[b)]	0.39(0.02)	0.36(0.02)	0.31(0.02)	0.51(0.03)	0.52(0.03)
ΔC[b)]	−0.44(−0.02)	−0.50(−0.03)	−0.54(−0.03)	−0.30(−0.02)	−0.14(−0.01)
χ_{aa}[c)]	−29.7(4)	−29.2(5)	−29.2(5)	−23.5(6)	−29.7(7)
$\eta_a\chi_{aa}$[c)]	−45.0(4)	−45.1(4)	−45.3(5)	−35.0(4)	−44.9(4)
χ_{zz}[d)]	−74.5	−72.0	−71.1	−57.7	−74.4
$\eta_z\chi_{zz}$[d)]	−0.2	−2.2	−3.4	−0.9	−0.2
χ_{zz}[e)]	−74.7(6)	−74.3(6)	−74.5(7)	−58.5(7)	−74.6(8)
θ_{za}(st.)[f)]	39°18′	39°15′	39°12′	39° 5′	39°17′
$\theta_{za}(\chi)$[f)]	39°19′	39°28′	39°34′	39°11′	39°17′

Atom coordinate (Å)[g)]

Atom	Used species	$\lvert x_a \rvert$	$\lvert x_b \rvert$	$\lvert x_c \rvert$
Cl	(35, 74)-H_3, (37, 74)-H_3	2.0382(−21)	0.2161(16)	0
Ge	(35, 74)-H_3, (35, 72)-H_3	1.0313	0.0758	0
	(35, 74)-H_3, (35, 70)-H_3	1.0311	0.0784	0
	average	1.0312(−11)	0.0771(−3)	0
H_a(Ge)	(35, 74)-H_3, (35, 74)-D_3	—	—	1.2540(34)

a) Figures in parentheses indicate the uncertainties calculated from 2.5 times the standard deviation attached to the last significant figures. b) These indicate the difference in the observed and calculated rotational constants. Figures in parentheses indicate quantities such as $100\times\Delta A/A$. c) Figures in parentheses indicate the experimental uncertainties attached to the last significant figures. d) Calculated from χ_{aa} and $\eta_a\chi_{aa}$ under the assumption of the coincidence of the z-axis and the C-Cl bond. e) Calculated from χ_{aa} and $\eta_a\chi_{aa}$ under the assumption of the cylindrical symmetry of the tensor ($\eta_z=0$). f) θ_{za}(st.), the angle between the z- and a-axis obtained from the structure. $\theta_{za}(\chi)$, the θ_{za} angle obtained from the χ values. g) Figures in parentheses indicate the difference of the values obtained from the solution of the Kraitchman equations and from the structure.

becomes smaller. The ratio of the changes of the parameters from CH_3XH_3 to $ClCH_2XH_3$ is close to each other for organosilane and germane. On the other hand, for α(XCCl) the germane has a larger value than the silane.

Quadrupole Coupling Constants

The principal value χ_{zz} and the asymmetry parameter $\eta_z(=\chi_{xx}-\chi_{yy})/\chi_{zz})$ of the quadrupole coupling tensor can be obtained if both the diagonal and off-diagonal values of the tensor in the principal inertial axis system are available. However, because of the lack of off-diagonal values, χ_{zz} and η_z values were calculated under an assumption of either 1) the coincidence of the z-axis and C–Cl bond or 2) the cylindrical symmetry of the tensor along the z-axis. In the former case, the angle θ_{za} between the z- and a-axes was taken as that from the structure described in the preceding section. The asymmetry parameter η_z was found to be fairly small for every species (Table 4). In the latter case where $\eta_z=0$, the angle θ_{za} can be calculated from the χ values. The calculated θ_{za} is in good agreement with that from the structure. This indicates that the structure given in the preceding section is a plausible one and the electric charge distribution around the Cl nucleus has nearly cylindrical symmetry along the C–Cl bond.

TABLE 5. STRUCTURAL PARAMETERS

X=Si, Ge	$ClCH_2GeH_3$[a]	CH_3GeH_3[b]	$ClCH_2SiH_3$[c]	CH_3SiH_3[d]
r(CX) Å	1.961	1.945	1.889	1.867
r(XH) Å	1.517	1.529	1.477	1.485
α(HXC)	107°43′	109°41′	108°20′	110°41′
α(XCCl)	110°11′	—	109°18′	—
r(CCl) Å	1.788 (assumed)	—	1.788	—
r(CH) Å	1.096 (assumed)	1.083	1.096	1.093
α(HCH)	107°30′ (assumed)	108°25′	107°30′	107°40′
α(HCX)	109°18′ (assumed)	110°31′	109°18′	111°16′

a) This work. b) Ref. 6. c) Ref. 4. d) Ref. 5.

TABLE 6. OBSERVED AND HYPOTHETICAL UNSPLIT FREQUENCIES OF THE (35, 74)-H_3 AND (35, 72)-H_3 SPECIES OF (CHLOROMETHYL)GERMANE IN THE EXCITED TORSIONAL STATE (MHz)[a]

		(35, 74)-H_3 Species					
	F =	$J+3/2$	$J+1/2$	$J-1/2$	$J-3/2$	ν_0[b]	$\Delta\nu$[c]
$3_{13} \leftarrow 2_{12}$	A	11932.10	11930.23	11928.83	11930.64	11931.04(20)	
	E						
$4_{04} \leftarrow 3_{03}$	A	16141.86		16140.97		16141.62(−10)	
	E						
$4_{14} \leftarrow 3_{13}$	A	15907.82	15906.97	15905.97	—	15907.15(5)	
	E						
$5_{13} \leftarrow 3_{12}$	A	16385.69	16385.09		16386.08	16385.43(−14)	
	E						
$5_{05} \leftarrow 4_{04}$	A	20172.91		20172.37		20172.74(−5)	
	E						
$5_{15} \leftarrow 4_{14}$	A	19883.20	19882.86	19882.14	19882.56	19882.84(7)	
	E						
$5_{14} \leftarrow 4_{13}$	A	20481.06		20480.70		20480.88(5)	
	E						
$3_{13} \leftarrow 2_{02}$	A	30369.81	30366.03		30369.81	30368.21(−5)	
	E	30373.40	30369.81		30373.40		−3.69(−5)
$4_{14} \leftarrow 3_{03}$	A	34168.89	34164.53	34165.08	34169.46	34167.02(−1)	
	E	34172.57	34168.25	—	34173.25		−3.74(−4)
$5_{14} \leftarrow 5_{05}$	A	19526.89	19533.43	19531.41	19524.96	19529.34(−19)	
	E	19530.97	19537.44	19535.52	19528.87		−4.03(4)
$6_{15} \leftarrow 6_{06}$	A	19901.43	19907.77	19906.30	19899.86	19903.96(7)	
	E	19905.48	19911.88	19910.38	19903.92		−4.07(6)
$7_{16} \leftarrow 7_{07}$	A	20344.67	20351.00	—	20343.36	20347.28(16)	
	E	20348.85	20355.05	20353.76	20347.44		−4.07(1)
$8_{17} \leftarrow 8_{08}$	A	20859.67	20865.92	20864.76	20858.45	20862.29(13)	
	E	20863.74	20870.04	20868.96	20862.59		−4.13(3)
$9_{18} \leftarrow 9_{09}$	A	21449.57	21455.96	—	21448.60	21452.34(2)	
	E	—	21460.19	21459.15	21452.79		−4.18(1)
$10_{19} \leftarrow 10_{010}$	A	22118.33	22124.78	22123.82	22117.36	22121.12(−13)	
	E	22122.57	22128.96	22128.05	22121.60		−4.22(−1)
$11_{110} \leftarrow 11_{011}$	A	22869.53	22876.13	22875.27	22868.68	22872.44(−19)	
	E	22873.80	22880.39	22879.48	22872.96		−4.26(−5)

Table 6. (Continued)

				(35, 72)-H_3 Species			
$4_{04} \leftarrow 3_{03}$	A	16283.21		16282.27		16282.94(0)	
	E						−4.14(4)
$5_{15} \leftarrow 4_{14}$	A	20054.96	20054.50	20053.81	20054.29	20054.52(−8)	
	E						−4.18(3)
$5_{14} \leftarrow 4_{13}$	A	20662.73		20662.47		20662.60(8)	
	E						−4.24(2)
$8_{17} \leftarrow 8_{08}$	A	20891.86	20898.17	20897.05	20890.69	20894.51(−12)	
	E	20896.00	20902.31	20901.18	20894.85		−4.29(−1)
$9_{18} \leftarrow 9_{09}$	A	21492.68	21499.06	21498.03	21491.70	21495.42(3)	
	E	21496.88	21503.21	21502.20	21495.89		−4.33(−5)
$10_{19} \leftarrow 10_{010}$	A	22173.89	22180.32	22179.38	22172.97	22176.69(16)	
	E	22178.11	22184.49	22183.68	22177.23		
$11_{110} \leftarrow 11_{011}$	A	22939.30	22945.80	22944.94	22938.46	22942.17(6)	
	E	22943.58	22950.10	22949.27	22942.73		
$12_{111} \leftarrow 12_{012}$	A	23793.36	23800.02	23799.29	23792.54	23796.34(−14)	
	E	—	23804.36	23803.58	23796.91		

a) Components of the quadrupolar multiplets are labeled F quantum number of the lower level; components of the internal rotation doublet are labeled A or E. b) Hypothetical unsplit frequencies. Figures in parentheses indicate the difference between the observed and calculated frequencies. c) Spacing of the internal rotation doublet, $\nu_A - \nu_E$. Figures in parentheses indicate the difference between the observed and calculated values.

χ_{zz} values obtained from the above two cases are nearly equal to each other. They are -74.7 ± 0.6 and -58.5 ± 0.7 MHz, for the $^{35}ClCH_2{}^{74}GeH_3$ and $^{37}ClCH_2{}^{74}GeH_3$ species, respectively, when $\eta_z=0$ is assumed and the ratio between the ^{35}Cl and ^{37}Cl species is 1.28 which is close to the ratio of quadrupole moments of the ^{35}Cl and ^{37}Cl nuclei (1.2688).[7]

The χ_{zz} values for ethyl chloride ($^{35}ClCH_2CH_3$) and (chloromethyl)silane ($^{35}ClCH_2SiH_3$) were reported by Schwendeman and Jacobs,[4,8] to be -71.24 ± 0.19 and -72.0 ± 0.6 MHz under the same assumption as in the present work. It should be noted that the χ_{zz} value for (chloromethyl)germane is about 4% larger than that of ethyl chloride and (chloromethyl)-silane beyond experimental error.

Internal Rotation of the GeH_3 Group

Weak spectra attributed to the excited vibrational state exist around the ground state spectra. Some of them exhibit doublet structures besides the hyperfine structures due to the quadrupolar coupling effect. The assignments of the excited state spectra were made for the (34, 74)-H_3 and (35, 72)-H_3 species. They are presumably the spectra due to the first excited GeH_3 torsional state from the spacings of the doublet structures found for the b-type transitions. The observed frequencies of these spectra are given in Table 6. The χ_{aa} and $\eta_a\chi_{aa}$ values for the excited state are essentially equal to those for the ground state (Table 7).

From the splittings of the doublet structures, the barrier to internal rotation of the GeH_3 group was calculated by the principal axis method using the structure given in the preceding section. The barrier height is $V_3=1740\ \pm30$ cal/mol[10] which is much higher than that for (fluoromethyl)germane (1390 ± 40),[1] fluoromethylgermane (941 ± 5)[2] and methylgermane (1239 ± 25).[6] The ratio of the barriers for (chloromethyl)germane and (fluoromethyl)germane is calculated to be 1.25, while that for ethyl chloride (3685 ± 12)[8] and ethyl fluoride (3306 ± 100)[9] is 1.11. The increase in the barrier from the fluoride to the chloride for the germane is much larger than for the ethyl halides.

Table 7. Torsional excited state and internal rotation barrier of the GeH_3 group[a,b]

	(35, 74)-H_3	(35, 72)-H_3
A (MHz)	20634.71(46)	20646.26(45)
B (MHz)	2078.25(2)	2096.90(1)
C (MHz)	1958.63(2)	1975.31(1)
D_J (MHz)	0.0003(12)	−0.0002(13)
χ_{aa} (MHz)	−29.7(15)	−29.7(20)
$\eta_a\chi_{aa}$ (MHz)	−44.3(8)	−44.2(10)
I_α amu Å^2	6.3133	6.3133
F (GHz)	99.819	99.820
λ_a	0.86162	0.86123
λ_b	0.50759	0.50821
s	81.255	81.301
V_3 (cal/mol)	1740(30)	1741(30)

a) Figures in parentheses indicate the uncertainties calculated from 2.5 times the standard deviation attached to the last significant figures. b) I_α; Moment of inertia of the GeH_3 group about the internal rotation axis, λ_a and λ_b; direction cosine of the internal rotation axis against the a- and b-inertial axes, F; $\hbar/2rI_\alpha$, $r=1-\lambda_a{}^2I_\alpha/I_a-\lambda_b{}^2I_\alpha/I_b$, s; Reduced barrier.

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References

1) L. C. Krisher, W. A. Watson, and J. A. Morrison, *J. Chem. Phys.*, **60**, 3417 (1974).
2) R. F. Roberts, Thesis, New York University (1972).

3) D. Seyferth and E. G. Rochow, *J. Am. Chem. Soc.*, **77**, 907 (1955).
4) R. H. Schwendeman and G. D. Jacobs, *J. Chem. Phys.*, **36**, 1251 (1962).
5) R. W. Kilb and L. Pierce, *J. Chem. Phys.*, **27**, 108 (1957).
6) V. W. Laurie, *J. Chem. Phys.*, **30**, 1210 (1959).
7) C. H. Townes and A. L. Schawlow, "Microwave Spectroscopy," McGraw-Hill, New York (1955), Appendix VII.
8) R. H. Schwendeman and G. D. Jacobs, *J. Chem. Phys.*, **36**, 1245 (1962).
9) D. R. Herschbach, *J. Chem. Phys.*, **25**, 358 (1956).
10) The barrier height slightly differs from the one reported but is essentially equal within experimental error. (J. Nakagawa and M. Hayashi; *Chem. Lett.*, **1974**, 1379).