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MICROWAVE SPECTRUM OF CHLOROMETHYLGERMANE

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Microwave spectra of five isotopic species of chloromethylgermane were studied in the 8000-34000 MHz region. The barrier height of the internal rotation was determined to be 1733 ± 30 cal/mole from the observed A-E splittings of the torsional excited state. The quadrupole coupling constants were obtained from the hyperfine structures.

We studied microwave spectra of chloromethylgermane, $ClCH_2GeH_3$, and its deuterated compound, $ClCH_2GeD_3$, in order to determine molecular structure, quadrupole coupling constants and barrier height of internal rotation. The microwave spectrometer used was a conventional 100 KHz Stark modulated type at National Chemical Laboratory. All the spectra were measured at dry ice temperature on recording chart.

About twenty of a-type R branch and b-type Q branch transitions were assigned for each of five isotopic species shown in Table 1. The assignment was done by considering the hyperfine splitting patterns and finally assured by the double resonance technique using $7_{0,7} \leftarrow 6_{1,6}$ and $7_{0,7} \leftarrow 6_{0,6}$ as pumping and signal transitions, respectively.

Table 1. Observed Rotational and Quadrupole Coupling Constants (in MHz)a)

Species b)	(35,74)-H_3	(35,72)-H_3	(35,70)-H_3	(37,74)-H_3	(35,74)-D_3
A	20655.77(46)	20665.75(52)	20676.58(47)	20581.30(53)	16705.07(41)
B	2086.54(4)	2105.33(6)	2125.04(5)	2018.46(3)	2004.01(3)
C	1964.04(4)	1980.75(5)	1998.30(4)	1902.96(3)	1894.59(3)
d_J	-0.0010(11)	-0.0010(10)	-0.0009(9)	-0.0013(10)	-0.0007(8)
χ_{aa}	-29.7(4)	-29.2(5)	-29.2(5)	-23.5(6)	-29.7(7)
$\eta_a\chi_{aa}$	-45.0(4)	-45.1(4)	-45.3(5)	-35.0(4)	-44.9(4)
χ_{zz} c)	-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} d)	-74.7	-74.3	-74.5	-58.5	-74.6

a) Numbers in parentheses represent the standard errors to be attached to the last significant figures.

b) The symbol (35,74)-H_3 indicates $^{35}ClCH_2{}^{74}GeH_3$ species, and so on.

c) The θ_{za} angle between the a- and z-axes was assumed from the structure.

d) The cylindrical symmetry about the z-axis was assumed, so that $\eta_z\chi_{zz} = 0$.

The quadrupole coupling constants, χ_{aa} and $\eta_a\chi_{aa}$, were determined from several transitions which exhibited large hyperfine splittings. The principal χ_{zz} and $\eta_z\chi_{zz}$ values were calculated with an assumption of either (1) the coincidence of the z-axis and C-Cl bond or (2) the cylindrical symmetry about the z-axis. These values given in Table 1 were essentially equal within experimental uncertainties. The isotopic ratio of χ_{zz} between ^{35}Cl and ^{37}Cl was 1.29 which agreed with the reported value 1.2688.$^{1)}$

The rotational constants and centrifugal distortion constant d_J shown in Table 1 were obtained by a least squares method using hypothetical unsplit frequencies evaluated from the observed frequencies and quadrupole coupling constants. The r_0 structure was determined, so as to reproduce the 15 rotational constants in Table 1, as $r_{C-Ge} = 1.961$ Å, $r_{Ge-H} = 1.517$ Å, α(ClCGe) = 110.2°, and α(CGeH) = 107.7°. In this calculation, the C_{3v} symmetry of GeH_3 group about C-Ge bond was assumed and the values of $r_{C-Cl} = 1.788$ Å, $r_{C-H} = 1.096$ Å, α(HCH) = 107.5°, and α(GeCH) = 109.3° were transferred from $ClCH_2SiH_3$.$^{2)}$ These parameters reproduce the rotational constants within the errors of 0.03 %.

Transitions in the first excited torsional state were observed and rotational constants were obtained as A = 20634.71, B = 2078.25, and C = 1958.63 MHz for $^{35}ClCH_2{}^{74}GeH_3$. These transitions showed the identical eqQ patterns as those in the ground state and K_a = 1 ← 0 transitions had further splittings of about 4 MHz due to the internal rotation. From these A-E splittings and the structure given above, the barrier height of the internal rotation was calculated. Using 6.3133 amu·Å^2 for the moment of inertia of the top, we arrived at $V_3 = 1733 \pm 30$ cal/mole. Comparison of the barriers of FCH_2GeH_3 (1.39 Kcal/mole)$^{3)}$, CH_3GeH_3 (1.24)$^{4)}$ and CH_3GeH_2F (0.94)$^{5)}$ indicates that the barrier increases when the hydrogen on the carbon of methylgermane is replaced by a fluorine whereas it decreases when the hydrogen on the germanium is replaced by a fluorine. The barrier value of $ClCH_2GeH_3$ indicates that the similar tendency may be expected for chlorides. In order to confirm the tendency, works for CH_3GeH_2Cl are under consideration.

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