FORCE CONSTANTS FOR SUBSTITUTED GERMANES*

PART II. GeCl₃H and GeCl₄.

BY S. L. N. G. KRISHNAMACHARI

PHYSICS DEPARTMENT, ANDHRA UNIVERSITY, WALTAIR.

ABSTRACT. Force constants are calculated for $GeCl_3H$ and $GeCl_4$ using the Wilson F-G matrix method. A comparison is made between the force constants which are common for the three molecules GeH_3Cl, $GeCl_3H$ and $GeCl_4$. The agreement between $GeCl_3H$ and $GeCl_4$ is found to be better than that between $GeCl_3H$ and GeH_3Cl.

In continuation of the work on GeH_3Cl and GeD_3Cl (author, 1955), the force constants for the molecules $GeCl_3H$ and $GeCl_4$ are calculated and reported in the present paper. The Raman frequency data used in the calculations are taken from the recent investigations by Delwaulle (1952).

$GeCl_3H$: The molecule $GeCl_3H$ belongs to the C_{3v} point group. The normal coordinates are similar to those for GeH_3Cl and the G-matrices are the same as those for CF_3H (Pace, 1950) excepting that in this case μ_{Ge} replaces μ_C and μ_{Cl} replaces μ_F. The F-matrices that are employed are

$$
A_1 \quad
\begin{vmatrix}
f_d & 0 & 0 \\
 & f_D + 2f_{DD} & D/\sqrt{2}\,(2f_{D\eta} + f_{D\eta}') \\
 & & D^2/2\left\{ f_\eta + 2f_{\eta\eta} - 4f_{\beta\eta} + \dfrac{d^2}{D^2}(f_x + 2f_{\beta\beta}) \right\}
\end{vmatrix}
$$

$$
E \quad
\begin{vmatrix}
f_D - f_{DD} & -Df_{D\eta} & \\
 & 0 & 0 \\
d^2(f_\beta - f_{\beta\beta}) & D^2(f_x - f_{\eta\eta}) &
\end{vmatrix}
$$

in which

d = Ge—H bond distance and
D = Ge—Cl bond distance.

The bond distances (Venkateswarlu, Mockler and Gordy, 1953) used in the calculations are,

d = 1.55 A.U.
D = 2.114 A.U.

Tetrahedral angles are assumed in these calculations.

---

* Communicated by Prof. K. R. Rao.

The nature of these force constants is shown in the first column of Table I. The values of the force constants are so adjusted as to reproduce the observed frequencies accurately. The final set so obtained is shown in the third column of Table I. The agreement between the observed and calculated frequencies is shown in Table II.

TABLE I

Force constants for $GeCl_3H$.

Nature of the force constant	Representation	Value $(10^5$ dynes/cm)
Ge-Cl bond stretching -	f_D	2.622
Ge-H bond stretching	f_d	2.731
Ge-Cl, Ge-Cl interaction	f_{DD}	0.193
H-Ge-Cl bending and H-Ge-Cl, H-Ge-Cl interaction	$f_\beta - f_{\beta\beta}$	0.188
Cl-Ge-Cl bending and Cl-Ge-Cl, Cl-Ge-Cl interaction	$f_\eta - f_{\eta\eta}$	0.143
Ge-Cl, Cl-Ge-Cl interaction with a common bond	$f_{D\eta}$	0.028
Ge-Cl, Cl-Ge-Cl interaction with a common atom	$f_{D\eta}'$	0.008
Cl-Ge-Cl, Cl-Ge-Cl interaction and H-Ge-Cl, H-Ge-Cl interaction	$f_{\eta\eta} + \dfrac{d^2}{D^2} f_{\beta\beta}$	0.028

TABLE II

Calculated and observed frequencies of $GeCl_3H.(cm^{-1})$

		Calculated	Observed
A_1	ν_1	2159	2159
	ν_2	409	409
	ν_3	181	181
E	ν_4	707	699
	ν_5	433	438
	ν_6	149	149

$GeCl_4$:

The molecule $GeCl_4$ belongs to T_D point group. The force constants for this molecule were calculated previously by using approximate methods. (Hertz berg, 1945). In the present work a more general potential function containing all the interaction terms is made use of.