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# The Vibrational Assignment and Force Constants of Halogenomethylsilanes and Their Germanium Analogues: $ClCH_2SiH_3$, $ClCH_2SiD_3$, $BrCH_2SiH_3$, $BrCH_2SiD_3$, $ClCH_2GeH_3$, and $ClCH_2GeD_3$

Keiichi OHNO and Hiromu MURATA

*Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima*

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The infrared spectra of $ClCH_2SiH_3$, $ClCH_2SiD_3$, $BrCH_2SiH_3$, $BrCH_2SiD_3$, $ClCH_2GeH_3$, and $ClCH_2GeD_3$ for both the gaseous and solid states in the 250—4000 $cm^{-1}$ region have been obtained. All the fundamental vibrations except for the skeletal bending and $YH_3(-D_3)$ (Y=Si, Ge) torsional vibrations have been observed and assigned. The normal vibration calculation has been carried out using a modified Urey-Bradley force field. The transferability of the force constants has also been investigated.

In order to get information about the vibrational assignments and the molecular forms of the rotational isomerism from normal vibration calculations, a set of force constants in a modified Urey-Bradley force field for the group of molecules containing silicon or germanium atoms will be obtained.

The force constants of $X_nYH_{4-n}$ (X=Cl, Br; Y=Si, Ge; $n$=1—4)[1] and $(CH_3)_4Si$[2] in an Urey-Bradley force field have been reported. Vibrational assignments for

1) D. E. Freeman and M. K. Wilson, *Spectrochim. Acta*, **21**, 1825 (1965).

2) N. Ishii and T. Shimanouchi, Annual Meeting of Chemical Society of Japan, Osaka (1965).

Table 1. Principal moments of inertia, Ray's asymmetry parameters, and P–R spacings of parallel bands of halogenomethylsilanes and their germanium compounds

| | Principal moments of inertia (amu-Å$^2$) | | | $\kappa$ | P–R (cm$^{-1}$) |
|---|---|---|---|---|---|
| | $I_a$ | $I_b$ | $I_c$ | | |
| $Cl^{35}CH_2Si^{28}H_3$ | 23.27 | 157.51 | 171.69 | −0.9718 | 14.7 |
| $Cl^{35}CH_2Si^{28}D_3$ | 28.86 | 172.55 | 186.38 | −0.9706 | 14.3 |
| $Br^{79}CH_2Si^{28}H_3$ | 25.19 | 236.21 | 252.31 | −0.9849 | 11.8 |
| $Br^{79}CH_2Si^{28}D_3$ | 30.74 | 258.96 | 274.68 | −0.9847 | 11.3 |
| $Cl^{35}CH_2Ge^{74}H_3$ | 24.76 | 237.84 | 253.08 | −0.9861 | 11.8 |
| $Cl^{35}CH_2Ge^{74}D_3$ | 30.59 | 247.92 | 262.63 | −0.9839 | 11.6 |

$CH_3YH_3$,[3] $CH_3CH_2YH_3$,[4] and $(CH_3)_2SiH_2$[5] (Y=Si, Ge) have also been made.

We will now report the vibrational assignment and force constants of $ClCH_2SiH_3$, $ClCH_2SiD_3$, $BrCH_2SiH_3$, $BrCH_2SiD_3$, $ClCH_2GeH_3$, and $ClCH_2GeD_3$.

These assignments and force constants will be compared with those of the corresponding ethyl halides. These force constants will be transferred to the molecules concerning the rotational isomerism, such as chloromethylmethylsilane.

## Experimental

The samples were prepared from tetrahalogenosilanes. The tetrahalogenosilanes were treated by diazomethane, and the resultant halogenomethyltrihalogenosilanes were reduced by $LiAlH_4$ or $LiAlD_4$ in *n*-butyl ether in a vacuum.[6] The crude samples were purified by repeated distillation in a vacuum. The germanium samples were prepared by a similar procedure.

The infrared spectra for the gaseous and solid states were recorded on a Perkin-Elmer model 621 infrared spectrophotometer. 10 cm and 1 m gas cells fitted with KBr or CsI windows were used for the gas measurements. The spectra for the solid states were obtained by condensing the gaseous samples on a CsI window cooled with liquid nitrogen.

## Results and Discussion

*Band Contours.* Chloromethylsilane has been shown by microwave study to have the $C_s$ symmetry and to have a slightly prolate asymmetric top.[7] For $XCH_2YH_3(-D_3)$ (X=Cl, Br; Y=Si, Ge), the principal moments of inertia and Ray's asymmetry parameters given in Table 1 were calculated from the following parameters: C–Cl=1.788 Å, C–Br=1.950 Å, C–Si=1.889 Å, C–Ge=1.945 Å, C–H=1.096 Å, Si–H=1.477 Å, Ge–H=1.529 Å, Y–C–X=109.3°, Y–C–H=109.3°, H–Y–H=110.6°, and H–C–H=107.5°. The bond angles given above have been assumed to be equal to the values for chloromethylsilane. Ray's asymmetry parameters indicate that these molecules may be approximated as a prolate symmetric top. The expected P–R spacing of parallel bands given in Table 1 was calculated by the use of the formulae of Gerhard and Dennison, using $(I_b+I_c)/2$ for $I_x$.[8] The observed P–R spacing is given in Tables 8—10.

*Vibrational Assignments.* Halogenomethylsilanes and halogenomethylgermane may have the $C_s$ symmetry. The 18 normal vibrations are reduced to 11 vibrations of the A′ species and 7 of A″, both of which are infrared active. The *a* and *b* internal axes are in the plane of symmetry, while the *c* axis is perpendicular to it. The A′ vibrations may have either *a*-, *b*-, or *ab*-type infrared band contours in the asymmetric top case. The A″ vibrations, on the other hand, have *c*-type infrared band contours. Vibrational assignments of the $CH_2$ group may be made with reference to the band contours and assignments for $CH_2Cl_2$,[9] which has magnitudes of rotational constants and asymmetry parameters similar to those for $XCH_2YH_3(-D_3)$. Also, vibrational assignments are made with reference to those of $CH_3YH_3(-D_3)$[3] and $CH_3CH_2YH_3(-D_3)$.[4] The observed frequencies and their assignments are summarized in Tables 2—7. The fundamental vibrations are given in Tables 8—10, together with the intensities, band types, and P–R spacings.

Table 2. Infrared spectra of chloromethylsilane-$d_0$

| Vapor | | | Solid | | Assignments |
|---|---|---|---|---|---|
| cm$^{-1}$ | Type | Int. | cm$^{-1}$ | Int. | |
| 3116 | | vw | | | 2168+950=3118 |
| 2989 | C | s | 2997 | vw | $CH_2$ antisym. str. |
| 2954, 2948, 2939 | AB | s | 2943 | w | $CH_2$ sym. str. |
| 2810 | | vw | | | |
| 2801b | | vw | | | |
| 2795sh | | vw | | | |
| 2599, 2584 | B | vw | | | 1410+1182=2592 |
| 2326b | | vw | | | |
| | | | 2192sh | vs | |
| 2197 | C | vs | 2186 | vs | $SiH_3$ asym. str. (A′, A″) |

3) J. L. Duncan, *Spectrochim. Acta*, **20**, 1807 (1964), J. E. Griffiths, *J. Chem. Phys.*, **38**, 2879 (1963), and E. A. Clark and A. Weber, *ibid.*, **45**, 1759 (1966).

4) K. M. Mackay and R. Watt, *Spectrochim. Acta*, **23A**, 2761 (1967).

5) D. F. Ball, P. L. Goggin, D. C. McKean, and L. A. Woodward, *ibid.*, **16**, 1358 (1960).

6) D. Seyferth and E. G. Rochow, *J. Amer. Chem. Soc.*, **77**, 907 (1955).

7) R. H. Schwendeman and G. D. Jacobs, *J. Chem. Phys.*, **36**. 1251 (1962).

8) S. L. Gerhard and D. M. Dennison, *Phys. Rev.*, **43**, 197 (1933).

9) T. Shimanouchi and I. Suzuki, *J. Mol. Spectrosc.*, **8**, 222 (1962).

TABLE 2. (continued)

| Vapor | | | Solid | | Assignments |
|---|---|---|---|---|---|
| $cm^{-1}$ | Type | Int. | $cm^{-1}$ | Int. | |
| 2175 | | | | | |
| 2168 | AB | vs | 2177 | vs | $SiH_3$ sym. str. |
| 2160 | | | | | |
| 2040b | | vw | | | 1110+925=2035 |
| 1978b | | vw | | | |
| 1738b | | vw | | | 1182+557=1739 |
| 1637b | | vw | | | 925+719=1644 |
| 1441sh | | vw | | | |
| | | | 1442 | vvw | 719×2=1438 |
| 1417 | | | | | |
| 1410 | AB | m | 1399 | ms | $CH_2$ sci. |
| 1402 | | | | | |
| 1384sh | | vw | | | |
| 1330 | B | w | 1327 | vw | |
| 1316 | | | | | |
| 1281 | B | w | 1269b | vw | 719+557=1276 |
| 1265 | | | | | |
| | | | 1234b | vw | |
| 1189 | B | wm | 1181 | m | $CH_2$ wag. |
| 1174 | | | 1178 | | |
| | | | 1152 | vw | |
| 1110 | C | m | 1116 | m | $CH_2$ twist. |
| 1096b | | m | | | |
| 1065 | | vw | 1078 | vw | |
| | | | 1046b | vw | |
| 950sh | | s | 941 | vs | $SiH_3$ asym. def. (A″) |
| 930 | B | vs | 926sh | vs | |
| 920 | | | 920 | vs | $SiH_3$ asym. def. (A′) |
| | | | 911sh | vs | $SiH_3$ sym. def. |
| | | | 908 | vs | |
| | | | 894 | vs | |
| 880 | | vw | | | |
| | | | 870b | vw | |
| 815 | C | s | 811 | s | $CH_2$ rock. |
| 811sh | | s | 806sh | m | |
| 773 | B | m | 756 | s | C–Cl str. |
| 756 | | | | | |
| | | | 738 | vw | |
| 725 | B | m | 714 | ms | C–Si str. |
| 713 | | | | | |
| 684 | | vw | | | |
| 674 | C | vw | | | |
| 662 | | vw | | | |
| | | | 643b | vvw | |
| | | | 585 | vvw | |
| 562 | | | | | |
| 557 | AB | s | 552 | s | $SiH_3$ rock. (A′) |
| 548 | | | | | |
| 522 | | | 521 | w | |
| 513 | | | | | |
| 509 | C | mw | 516 | w | $SiH_3$ rock. (A″) |
| 498 | | | | | |
| | | | 276? | vw | Cl–C–Si bend. ? |
| | | | 264? | vw | |

Int.=intensity; s, m, w=strong, medium, weak; v=very; sh=shoulder; b=broad; A, B, C=*a*-type, *b*-type, and *c*-type infrared band contours in the asymmetric top case, respectively.

TABLE 3. INFRARED SPECTRA OF CHLOROMETHYLSILANE-$d_3$

| Vapor | | | Solid | | Assignments |
|---|---|---|---|---|---|
| $cm^{-1}$ | Type | Int. | $cm^{-1}$ | Int. | |
| 2993 | C | w | 2996 | w | $CH_2$ antisym. str. |
| 2958 | | | | | |
| 2951 | AB | m | 2948 | m | $CH_2$ sym. str. |
| 2943 | | | | | |
| 2870b | | vw | | | |
| 2795b | | vw | | | 1405×2=2810 |
| 2575b | | w | | | 1405+1175=2580 |
| 2197 | | | | | |
| 2175 | B | w | 2186 | vw | $ClCH_2SiH_3$ |
| 2160 | | | | | |
| 1728b | | w | | | |
| | | | 1702 | vw | |
| 1603 | C | vs | 1598sh | vs | $SiD_3$ asym. str. (A″) |
| 1595 | | vs | 1593 | vs | $SiD_3$ asym. str. (A′) |
| 1584sh | | vs | | | |
| 1575 | | | | | |
| 1568 | AB | vs | 1565 | s | $SiD_3$ sym. str. |
| 1560 | | | 1559sh | m | |
| | | | 1525b | vw | 765×2=1530, 1113+413=1526 |
| 1465 | | vw | | | 765+700=1465 |
| 1413 | | | | | |
| 1405 | AB | m | 1393 | s | $CH_2$ sci. |
| 1398 | | | | | |
| 1365b | | vw | 1362b | vw | 696+676=1372, 682×2=1364 |
| | | | 1324 | vvw | |
| 1184 | | | | | |
| 1175 | AB | w | 1176 | m | $CH_2$ wag. |
| 1169 | | | | | |
| 1105 | C | w | 1113 | w | $CH_2$ twist. |
| 1083b | | w | | | 676+409=1085 |
| | | | 1064b | vvw | |
| | | | 876 | vvw | |
| 864sh | | w | | | 455+409=864 |
| 845 | | w | 851 | w | |
| 842 | | m | 835sh | w | |
| 834sh | | w | 833 | w | 413×2=826 |
| | | | 823 | w | |
| 779 | B | s | 765 | vs | C–Si str. |
| 765 | C | s | | | $CH_2$ rock. |
| 756sh | | m | 733 | w | |
| 704sh | | vs | | | |
| 700 | C | vs | 688 | vs | $SiD_3$ asym. def. (A″) |
| 689 | B | vs | 682 | vs | C–Cl str. |
| 676 | | s | 672 | vs | $SiD_3$ asym. def. (A′) |
| 650 | | | | | |
| 643 | A | s | 638 | s | $SiD_3$ sym. def. |
| 637 | | | | | |
| 536 | B | w | 520 | w | |
| 523 | | | | | |
| 459 | | | | | |
| 455 | AB | s | 457 | s | $SiD_3$ rock. (A′) |
| 445 | | | | | |
| 409 | C | m | 413 | m | $SiD_3$ rock. (A″) |

TABLE 4. INFRARED SPECTRA OF BROMOMETHYLSILANE-$d_0$

| Vapor | | | Solid | | Assignments |
|---|---|---|---|---|---|
| $cm^{-1}$ | Type | Int. | $cm^{-1}$ | Int. | |
| 3113 | | w | | | |
| 3005sh | | m | 3004 | w | $CH_2$ antisym. str. |
| 2988sh | | m | 2967b | vw | 2167+797=2964 |
| 2964, 2958, 2953 | AB | s | 2951 | w | $CH_2$ sym. str. |
| | | | 2931b | vw | |
| 2870 | | w | 2863b | vw | |
| 2787b | | vw | 2801 | vw | |
| 2532, 2521 | B | vw | | | 1398+1135=2533 |
| 2316b | | vw | | | |
| 2197 | C | vs | 2181 | vs | $SiH_3$ asym. str. (A′, A″) |
| 2171, 2164, 2158 | AB | vs | 2167 | vs | $SiH_3$ sym. str. |
| 2092 | | w | 2099 | w | |
| 2080 | | w | 2087 | vw | 1135+944=2079 |
| 2033b | | vw | | | |
| 1876b | | | | | 1135+739=1874 |
| | | | 1490 | vw | |
| 1431b | | vw | 1440b | vw | 925+504=1429 |
| | | | 1407b | vw | |
| 1404, 1398, 1392 | AB | m | 1385 | s | $CH_2$ sci. |
| 1359, 1347 | B | vw | 1344b | vw | 674×2=1348 |
| 1314, 1304, 1294b | AB | vw | 1314 | vw | |
| | | | | | 804+504=1308 |
| | | | 1298b | vw | 797+499=1296 |
| 1264, 1259, 1254 | AB | w | 1250 | vw | |
| | | | 1245 | w | |
| | | | 1168b | vw | 674+499=1173 |
| | | | 1155 | vw | |
| 1142, 1129 | B | m | 1131 | m | $CH_2$ wag. |
| | | | 1112b | w | |
| 1076b | | vw | | | |
| 1060 | C | m | 1066 | s | $CH_2$ twist. |
| | | | 1059sh | w | |
| 1016 | | vw | 1024 | vw | |
| | | | 997b | vw | 499×2=998 |
| 954sh | | s | | | |
| 944 | C | s | 939 | s | $SiH_3$ asym. def. (A′, A″) |
| 931, 920 | B | vs | 914sh | vs | $SiH_3$ sym. def. |
| | | | 896b | vs | |
| | | | 884 | s | |
| 868 | | vw | 870 | w | |
| | | | 844 | vw | |
| | | | 814 | w | |
| 804 | C | s | 797 | s | $CH_2$ rock. |
| 802 | C | s | | | |
| 795sh | | m | | | |

TABLE 4. (continued)

| Vapor | | | Solid | | Assignments |
|---|---|---|---|---|---|
| $cm^{-1}$ | Type | Int. | $cm^{-1}$ | Int. | |
| | | | 777 | w | |
| | | | 764 | w | |
| 746, 733 | B | m | 738 | m | C–Si str. |
| 693, 681 | B | m | 674 | m | C–Br str. |
| | | | 635 | vw | |
| | | | 587 | vw | |
| 564 | | vw | 557 | w | |
| | | | 518 | m | |
| 510, 504, 497 | AB | s | 499 | s | $SiH_3$ rock. (A′, A″) |
| | | | 481 | w | |
| | | | 399 | vw | |

TABLE 5. INFRARED SPECTRA OF BROMOMETHYLSILANE-$d_3$

| Vapor | | | Solid | | Assignments |
|---|---|---|---|---|---|
| $cm^{-1}$ | Type | Int. | $cm^{-1}$ | Int. | |
| 3115b | | vw | | | |
| 3114b | | vw | | | |
| 3006 | C | w | 3006 | w | $CH_2$ antisym. str. |
| | | | 2999sh | vw | |
| 2966, 2961, 2954 | A | m | 2959sh | w | |
| | | | 2954 | mw | $CH_2$ sym. str. |
| 2867b | | vw | | | |
| 2852 | | vw | | | |
| 2777, 2766 | B | vw | | | |
| 2528, 2516 | B | vw | | | 1393+1133=2526 |
| 2263b | | vw | 2253 | vvw | 1133×2=2266 |
| 2203 | C | vw | | | |
| 2169, 2157 | B | vw | 2173b | vvw | $BrCH_2SiH_3$ |
| 2138 | | vw | | | 1393+749=2142 |
| 1876b | | vw | | | |
| 1809b | | vw | | | 1133+678=1811 |
| 1710b | | w | | | |
| 1603 | C | vs | 1591sh | vs | $SiD_3$ asym. str. (A″) |
| 1596, 1585 | B | vs | 1587 | vs | $SiD_3$ asym. str. (A′) |
| 1570, 1565, 1558 | A | vs | 1560, 1588 | s | $SiD_3$ sym. str. |
| | | | 1539sh | vw | |
| 1501b | | w | | | |
| | | | 1486sh | vvw | 1059+428=1487 |
| 1401sh | | w | | | |
| 1399, 1393, 1388 | A | m | 1380 | ms | $CH_2$ sci. |
| 1360 | | vw | | | 749+612=1361 |
| 1352 | | vw | | | 678×2=1356 |
| 1289 | | vw | 1289b | vvw | 678+612=1290 |

TABLE 5. (continued)

| Vapor | | | Solid | | Assignments |
|---|---|---|---|---|---|
| $cm^{-1}$ | Type | Int. | $cm^{-1}$ | Int. | |
| 1280 | | vw | | | |
| | | | 1243 | vvw | |
| 1196sh | | vw | | | |
| 1181sh | | vw | | | |
| 1170sh | | vw | | | 749+426=1175 |
| 1139, 1128 | B | m | 1132, 1129 | m | $CH_2$ wag. |
| | | | 1104 | vvw | |
| | | | 1074 | vvw | 647+428=1075 |
| 1056 | C | w | 1059 | mw | $CH_2$ twist. |
| | | | 1054 | vw | |
| 986, 974 | B | vvw | | | |
| 910, 898 | B | vvw | | | |
| 844 | C | vw | 846 | vw | 412+426=838 |
| 840sh | | mw | | | |
| 834 | | w | 830 | vw | |
| 819, 810 | B | mw | 821 | vw | |
| 772sh | | m | 776sh | vvw | |
| 753 | C | vs | 747 | vs | $CH_2$ rock. |
| 745 | B | vs | 740 | vs | C–Si str. |
| | | | 721sh | w | |
| 686, 678 | C | vs | 677 | vs | $SiD_3$ asym. def. (A″) |
| 666, 657 | B | vs | 660 | vs | $SiD_3$ asym. def. (A′) |
| | | | 654, 647 | vs | $SiD_3$ sym. def. |
| 618, 607 | B | mw | 604 | mw | C–Br str. |
| 567sh | | vw | | | |
| 559b | | vw | | | |
| 530 | | vw | 539 | vw | |
| | | | 526sh | vvw | |
| | | | 482 | vw | |
| | | | 456 | vvw | |
| 432, 420 | B | s | 428 | s | $SiD_3$ rock. (A′) |
| 412sh | | m | 417 | m | $SiD_3$ rock. (A″) |
| | | | 353 | vw | |

TABLE 6. INFRARED SPECTRA OF CHLOROMETHYLGERMANE-$d_0$

| Vapor | | | Solid | | Assignments |
|---|---|---|---|---|---|
| $cm^{-1}$ | Type | Int. | $cm^{-1}$ | Int. | |
| 3001sh | | w | 2987 | w | $CH_2$ antisym. str. |
| 2988sh | | m | | | |
| 2963, 2951 | B | m | 2955 | w | $CH_2$ sym. str. |
| 2868 | | mw | | | |
| 2812 | | vw | | | 1408×2=2816 |
| 2798 | | vw | | | |
| 2589, 2578 | B | vw | | | 1177+1408=2585 |
| 2217b | | w | | | |
| 2115 | C | vs | 2098 | vs | $GeH_3$ asym. str. (A′, A″) |

TABLE 6. (continued)

| Vapor | | | Solid | | Assignments |
|---|---|---|---|---|---|
| $cm^{-1}$ | Type | Int. | $cm^{-1}$ | Int. | |
| 2092, 2080 | B | vs | 2091 | vs | $GeH_3$ sym. str. |
| 1909 | | vw | | | 1116+787=1903 |
| 1764, 1752 | B | vvw | | | 879×2=1758 |
| 1578, 1565 | B | vvw | | | 826+743=1569 |
| 1464b | | vvw | | | 826+641=1467 |
| 1416, 1408, 1404 | AB | w | 1396 | m | $CH_2$ sci. |
| 1391, 1379 | B | vw | 1382 | w | 743+641=1384 |
| | | | 1371b | w | 879+494=1373 |
| 1359, 1353, 1347 | | vw | 1350 | w | |
| 1281 | | vw | | | 787+492=1279, 641×2=1282 |
| 1264, 1254, 1244 | | vw | | | |
| 1184, 1177, 1172 | AB | w | 1174 | m | $CH_2$ wag. |
| | | | 1154 | w | decomposed compound? |
| 1142, 1134 | B | w | 1141 | vw | 641+492=1133 |
| 1116sh | | w | 1116 | m | $CH_2$ twist. |
| 1077, 1075 | B | vvw | 1091 | vw | |
| | | | 1079b | vw | |
| | | | 1043 | vw | |
| 994, 983 | B | vw | 1003b | vw | 492×2=984 |
| | | | 934 | vw | |
| 888, 879, 875sh | C, AB | s | 879 | s | $GeH_3$ asym. def. (A″) |
| | | | 868 | s | $GeH_3$ asym. def. (A′) |
| 834, 826, 822 | A | vs | 836sh | w | |
| | | | 827 | s | $GeH_3$ sym. def. |
| 798b | | s | 808 | s | |
| 787 | C | s | 778 | s | $CH_2$ rock. |
| 749, 737 | B | m | 723 | m | C–Cl str. |
| | | | 705sh | vw | |
| | | | 670 | vw | |
| 648, 635 | B | m | 644 | s | C–Ge str. |
| 615 | | m | 619 | w | |
| 601, 591 | B | w | 599 | w | |
| | | | 555 | w | |
| 496, 488 | B | s | 494 | s | $GeH_3$ rock. (A′, A″) |
| 432 | | vw | 444b | vw | |

Table 7. Infrared spectra of chloromethylgermane-$d_3$

| Vapor | | | Solid | | Assignments |
|---|---|---|---|---|---|
| $cm^{-1}$ | Type | Int. | $cm^{-1}$ | Int. | |
| 3004sh | C | w | 3008 | vw | $CH_2$ antisym. str. |
| 2989sh | | w | 2971b | vw | |
| 2968, 2957 | B | m | 2954 | m | $CH_2$ sym. str. |
| | | | 2920b | vw | |
| 2868 | | w | 2859b | vw | |
| 2804b | | vw | | | |
| 2589, 2578 | B | vw | 2561 | vw | 1408+1178=2586 |
| 2115 | C | | | | |
| 2092, 2080 | B | w | 2096 | w | $ClCH_2GeH_3$ |
| 1606 | | vw | | | |
| 1523 | C | vs | 1513 | vs | $GeD_3$ asym. str. (A″) |
| 1510b | | vs | | | |
| 1504 | A | | | | $GeD_3$ asym. str. (A′) |
| 1498, 1493 | B | vs | 1498 | vs | $GeD_3$ sym. str. |
| 1414, 1408, 1402 | AB | w | 1394 | m | $CH_2$ sci. |
| | | | 1382 | vw | 754+633=1387 |
| | | | 1370 | vw | 754+613=1367 |
| 1358, 1353, 1347 | | vw | 1349 | vw | 743+607=1350, 759+591=1350 |
| 1185, 1178, 1173 | AB | m | 1175 | m | $CH_2$ wag. |
| 1142 | | m | 1154 | vw | decomposed compound? |
| 1134b | | w | | | 759+379=1138, 743+393=1136 |
| 1112sh | | w | 1115 | w | $CH_2$ twist. |
| 1084b | | vw | 1080 | vw | |
| | | | 1043 | vw | |
| | | | 983 | vw | 583+397=980 |
| | | | 845 | vw | |
| | | | 796 | w | 397×2=794 |
| | | | 783 | w | 397+383=780 |
| | | | 778 | w | 383×2=766 |
| 759 | C | s | 754 | s | $CH_2$ rock. |
| 749, 737 | B | s | 725 | s | C–Cl str. |
| | | | 704 | w | |
| 638sh | | s | | | C–Ge str. |
| 624 | C | s | 633 | s | $GeD_3$ asym. def. (A″) |
| 607sh | | s | 613 | s | $GeD_3$ asym. def. (A′) |
| | | | 603 | s | |
| 596, 586 | B | vs | 583, 574 | vs | $GeD_3$ sym. def. |
| | | | 498 | w | |
| | | | 492 | vw | |
| | | | 443 | w | |
| | | | 428 | w | |
| 399, 388 | B | s | 397 | s | $GeD_3$ rock. (A′) |
| 379sh | | m | 383 | m | $GeD_3$ rock. (A″) |

*Vibrations of the $CH_2$ Group.* The $CH_2$ stretching vibrations are expected near 3000 $cm^{-1}$. In this region, almost all higher bands were of the *c*-type, while the lower bands were of the *ab*- or *b*-type, indicating that the former bands should be assigned to the $CH_2$ antisymmetric stretching vibration and the latter to this symmetric vibration. These two bands were observed at slightly higher frequencies for molecules with heavier atoms or groups attached to the $CH_2$ group.

The $CH_2$ deformation vibrations are expected in the 700—1500 $cm^{-1}$ region. For these molecules, the $CH_2$ scissors, wagging, twisting, and rocking vibrations were observed as *a*- or *ab*-type bands at about 1400 $cm^{-1}$, as *ab*- or *b*-type bands at 1100—1200 $cm^{-1}$, as *c*-type bands at 1050—1120 $cm^{-1}$, and as *c*-type bands at about 800 $cm^{-1}$. It is noted that the $CH_2$ twisting vibrations for $XCH_2YH_3(-D_3)$ are observed clearly as *c*-type bands, similar to those for $CH_2X_2$(X=Cl, Br),[9] and unlike those for $CH_3CH_2YH_3(-D_3)$[4] and $CH_3CH_2X$,[10] whose $CH_2$ twisting vibrations are not well separated from the $CH_2$ wagging vibrations.

The broad absorptions observed in the gaseous state at 1000—1200 $cm^{-1}$ may be assigned to the vibrations for decomposed compounds, because no corresponding absorptions are observed in the solid state.

*Vibrations of the $YH_3(-D_3)$ (Y=Si, Ge) Group.* For $CH_3YH_3(-D_3)$, $CH_3CH_2YH_3(-D_3)$, and $XCH_2YH_3(-D_3)$, the corresponding vibrations of $YH_3(-D_3)$ group are expected in the same frequency region and give rise to a similar type of bands in the gaseous state. A very strong *c*-type band assigned to the $SiH_3$ asymmetric stretching vibrations of both *A′* and *A″* species and an *ab*-type band assigned to the symmetric stretching vibration were observed at 2197 and 2168 $cm^{-1}$ for $ClCH_2SiH_3$, and at 2197 and 2164 $cm^{-1}$ for $BrCH_2SiH_3$, respectively. The separations between the $SiH_3$ asymmetric and symmetric stretching vibrations for $CH_3YH_3$ and $CH_3CH_2YH_3$ have been reported to be smaller than 6 $cm^{-1}$. On the other hand, a larger separation of about 30 $cm^{-1}$ was observed for $XCH_2YH_3$. However, as no other fundamental vibrations are expected in this region, mixing with the other vibrations cannot be considered. As the $YD_3$ stretching vibrations were observed in the 1500—1600 $cm^{-1}$ region, mixing with a nearby vibration such as the $CH_2$ scissors at about 1400 $cm^{-1}$ was expected. The separations for $CH_3YD_3$ and $CH_3CH_2YD_3$ have been reported to be about 20 $cm^{-1}$. For $XCH_2YD_3$, these separations and also a splitting between *A′* and *A″* species of the $YD_3$ asymmetric stretching vibrations were observed.

The $SiH_3$ asymmetric deformation of *A′* and *A″* vibrations were assigned to the strong *c*-type band at 950 $cm^{-1}$ for $ClCH_2SiH_3$ and at 944 $cm^{-1}$ for $BrCH_2SiH_3$. This symmetric vibration was assigned to the very strong *b*-type band at 925 $cm^{-1}$ for both $ClCH_2SiH_3$ and $BrCH_2SiH_3$. For $ClCH_2SiD_3$, the strong bands at 700 (*c*-type) and 676 $cm^{-1}$ were assigned to the $SiD_3$ asymmetric vibrations of the *A″* and the *A′*

10) T. Shimanouchi, Tables of Molecular Vibrational Frequencies, Part I, Bulletin NSRDSNBS 6, p. 40—41, NBS 6, Washington, D. C. (1967) and F. A. Miller and F. E. Kiviat, *Spectrochim. Acta*, **25A**, 1363 (1969).

species respectively. However, this symmetric vibration is considered to mix with the C–Si stretching vibration. Also, for $BrCH_2SiD_3$, the assignments of four bands due to the C–Si, C–Br stretchings, and $SiD_3$ deformations vibrations with the same symmetry may be complicated, since these vibrations are expected in the same frequency region. These vibrations were assigned on the basis of a normal vibration calculation. For $ClCH_2GeH_3$ and $BrCH_2SiH_3$, both the $A'$ and $A''$ vibrations of the $YH_3$ rocking were assigned to the strong *ab*- or *b*-type bands near 500 $cm^{-1}$. However, for $ClCH_2SiH_3$, a weak *c*-type band assigned to the $A''$ vibration of the $SiH_3$ rocking was observed at 509 $cm^{-1}$. This $A'$ vibration was assigned to the strong *ab*-type band at 557 $cm^{-1}$. The $YD_3$ rocking vibrations were observed as strong *b*-type bands ($A'$) at about 400 $cm^{-1}$ and as medium-intensity bands ($A''$) on the lower frequency side of the former bands.

The vibrational assignments for $ClCH_2GeH_3(-D_3)$ were made similarly; they are given in Tables 6 and 7.

The splittings of the $YH_3(-D_3)$ rocking vibrations ($(\nu_{10}—\nu_{17})$ in Tables 8—10) can be compared for related molecules: 87 $cm^{-1}$ (72 $cm^{-1}$) for $CH_3CH_2SiH_3(-D_3)$>48 $cm^{-1}$ (46 $cm^{-1}$) for $ClCH_2SiH_3(-D_3)$> 0 $cm^{-1}$ (14 $cm^{-1}$) for $BrCH_2SiH_3(-D_3)$ and 29 $cm^{-1}$ (35 $cm^{-1}$) for $CH_3CH_2GeH_3(-D_3)$>0 $cm^{-1}$ (14 $cm^{-1}$)

Table 8. Fundamental vibrations of chloromethylsilane[a] ($cm^{-1}$)

| Vibn. No. | Description | $ClCH_2SiH_3$ | | | $ClCH_2SiD_3$ | | |
|---|---|---|---|---|---|---|---|
| A′ 1 | $CH_2$ sym. str. | 2948 | *ab*[b] | 15[c] s[d] | 2951 | *ab* | 15 m |
| 2 | $SiH_3(-D_3)$ asym. str. | 2197[e] | | | 1595 | — | —vs |
| 3 | $SiH_3(-D_3)$ sym. str. | 2168 | *ab* | 15 vs | 1568 | *ab* | 15 vs |
| 4 | $CH_2$ sci. | 1410 | *ab* | 15 m | 1405 | *ab* | 15 m |
| 5 | $CH_2$ wag. | 1182 | *b* | 15 wm | 1175 | *ab* | 15 w |
| 6 | $SiH_3(-D_3)$ asym. def. | 925 | | | 676 | — | — s |
| 7 | $SiH_3(-D_3)$ sym. def. | 925 | *b* | 10 vs | 643 | *a* | 14 s |
| 8 | C–Cl str. | 764 | *b* | 17 m | 696 | *b* | 15 vs |
| 9 | C–Si str. | 719 | *b* | 12 m | 772 | *b* | 14 s |
| 10 | $SiH_3(-D_3)$ rock. | 557 | *ab* | 14 s | 455 | *b* | 14 s |
| 11 | Cl–C–Si bend. | — | | | — | | |
| A″ 12 | $CH_2$ antisym. str. | 2989 | *c* | — s | 2993 | *c* | — s |
| 13 | $SiH_3(-D_3)$ asym. str. | 2197 | *c* | — vs | 1603 | *c* | — vs |
| 14 | $CH_2$ twist. | 1110 | *c* | — m | 1105 | *c* | — w |
| 15 | $SiH_3(-D_3)$ asym. def. | 950 | *c* | — s | 700 | *c* | — vs |
| 16 | $CH_2$ rock. | 815 | *c* | — s | 765 | *c* | — s |
| 17 | $SiH_3(-D_3)$ rock. | 509 | *c* | — mw | 409 | *c* | — m |
| 18 | $SiH_3(-D_3)$ torsion | — | | | — | | |

a) Frequencies for the gaseous state. Frequencies of the *b*-type bands are average values of P–R branches and those of the *a*-, *ab*-, and *c*-type bands are values of Q branch.
b) *a*, *b*, *c*=*a*-type, *b*-type, and *c*-type infrared band contours in the asymmetric top case, respectively.
c) P–R spacing.
d) s, m, w=strong, medium, weak; v=very.
e) Used twice.

Table 9. Fundamental vibrations of bromomethylsilane[a] ($cm^{-1}$)

| Vibn. No. | Description | $BrCH_2SiH_3$ | | | $BrCH_2SiD_3$ | | |
|---|---|---|---|---|---|---|---|
| A′ 1 | $CH_2$ sym. str. | 2958 | *ab*[b] | 11[c] s[d] | 2961 | *a* | 12 m |
| 2 | $SiH_3(-D_3)$ asym. str. | 2197[e] | | | 1590 | *b* | 11 vs |
| 3 | $SiH_3(-D_3)$ sym. str. | 2164 | *ab* | 13 vs | 1565 | *ab* | 12 vs |
| 4 | $CH_2$ sci. | 1398 | *ab* | 12 m | 1393 | *a* | 11 m |
| 5 | $CH_2$ wag. | 1135 | *b* | 13 m | 1133 | *b* | 11 m |
| 6 | $SiH_3(-D_3)$ asym. def. | 925[e] | | | 661[e] | | |
| 7 | $SiH_3(-D_3)$ sym. def. | 925 | *b* | 11 vs | 661 | *b* | 9 vs |
| 8 | C–Si str. | 739 | *b* | 13 m | 749 | *b* | 8 vs |
| 9 | C–Br str. | 687 | *b* | 12 m | 612 | *b* | 11 m |
| 10 | $SiH_3(-D_3)$ rock. | 504 | *ab* | 13 s | 426 | *b* | 12 s |
| 11 | Br–C–Si bend. | — | | | — | | |
| A″ 12 | $CH_2$ antisym. str. | 3005 | — | — m | 3006 | *c* | — w |
| 13 | $SiH_3(-D_3)$ asym. str. | 2197 | *c* | — vs | 1603 | *c* | — vs |
| 14 | $CH_2$ twist. | 1060 | *c* | — m | 1056 | *c* | — w |
| 15 | $SiH_3(-D_3)$ asym. def. | 944 | *c* | — s | 678 | *c* | — vs |
| 16 | $CH_2$ rock. | 804 | *c* | — s | 753 | *c* | — vs |
| 17 | $SiH_3(-D_3)$ rock. | 504[e] | | | 412 | — | — m |
| 18 | $SiH_3(-D_3)$ trosion | — | | | — | | |

a, b, c, d, e) See a), b), c), d), and e) of Table 8.

Table 10. Fundamental vibrations of chloromethylgermane[a)] ($cm^{-1}$)

| Vibn. No. | Description | $ClCH_2GeH_3$ | | | $ClCH_2GeD_3$ | | |
|---|---|---|---|---|---|---|---|
| A′ 1 | $CH_2$ sym. str. | 2957 | *b*[b)] | 12[c)] m[d)] | 2962 | *b* | 11 m |
| 2 | $GeH_3(-D_3)$ asym. str. | 2115[e)] | | | 1504 | — | — vs |
| 3 | $GeH_3(-D_3)$ sym. str. | 2086 | *b* | 12 vs | 1497 | *ab* | 11 vs |
| 4 | $CH_2$ sci. | 1408 | *ab* | 12 w | 1408 | *ab* | 12 w |
| 5 | $CH_2$ wag. | 1177 | *ab* | 11 w | 1178 | *ab* | 12 m |
| 6 | $GeH_3(-D_3)$ asym. def. | 881 | *ab* | 13 s | 607 | — | — s |
| 7 | $GeH_3(-D_3)$ sym. def. | 826 | *a* | 12 vs | 591 | — | 10 vs |
| 8 | C–Cl str. | 743 | *b* | 12 m | 743 | *b* | 12 m |
| 9 | C–Ge str. | 641 | *b* | 13 m | 638 | — | — s |
| 10 | $GeH_3(-D_3)$ rock. | 492 | *b* | 8 s | 393 | *b* | 11 s |
| 11 | Cl–C–Ge bend. | — | | | — | | |
| A″ 12 | $CH_2$ antisym. str. | 3001 | — | — w | 3004 | *c* | — w |
| 13 | $GeH_3(-D_3)$ asym. str. | 2115 | *c* | — vs | 1523 | *c* | — vs |
| 14 | $CH_2$ twist. | 1116 | — | — w | 1112 | — | — w |
| 15 | $GeH_3(-D_3)$ asym. def. | 879 | *c* | — s | 624 | *c* | — s |
| 16 | $CH_2$ rock. | 787 | *c* | — s | 759 | *c* | — s |
| 17 | $GeH_3(-D_3)$ rock. | 492[e)] | | | 379 | — | — m |
| 18 | $GeH_3(-D_3)$ torsion | — | | | — | | |

a, b, c, d, e) See a), b, c), d), and e) of Table 8.

for $ClCH_2GeH_3(-D_3)$. It is expected that the skeletal bending vibrations go away from the $YH_3(-D_3)$ rocking vibration gradually in this order: C–C–Y<Cl–C–Y< Br–C–Y. The splittings decrease in the same order. Moreover, the ratio $((\nu_{10}-\nu_{17})/\nu_{17}$ in Tables 8—10) for the $YH_3$ rocking vibration is smaller than that for the $YD_3$ rocking vibration. This shows that the splittings increase when the frequencies of the $YH_3(-D_3)$ rocking and the skeletal bending vibrations become closely spaced together. It seems that the $YH_3(-D_3)$ rocking vibration is affected by the skeletal bending vibration.

*Skeletal Vibrations.* The $XCH_2YH_3(-D_3)$ molecules have four skeletal vibrations: the C–Y stretching, C–X stretching, X–C–Y bending, and $YH_3(-D_3)$ torsional vibrations. The latter two vibrations were expected in the region below 300 $cm^{-1}$, which were not observed in the present study. The C–Y and C–X stretching vibrations have the same symmetry, and their bands are expected to appear in the same spectral region of 600—800 $cm^{-1}$, mixing with each other. Two strong or medium *b*-type bands were observed in this region. These vibrations were assigned on the basis of a comparison of the infrared spectra of $ClCH_2SiH_3(-D_3)$, $BrCH_2SiH_3(-D_3)$, and $ClCH_2GeH_3(-D_3)$ and the normal vibration calculations.

*Overtone and Combination Vibrations.* The assignments of some overtone and combination vibrations are given in Tables 2—7. For all of the $XCH_2YH_3(-D_3)$, the $CH_2$ scissors and $CH_2$ wagging combination vibrations were observed as *b*-type bands near 2500 $cm^{-1}$. The unassigned weak absorptions may be due to the combination or overtone vibrations for the X–C–Y bending and the $YH_3(-D_3)$ torsion, or to the difference vibrations for fundamentals.

## Normal Vibration Calculation

In order to get information about the vibrational assignments and the molecular forms for the rotational isomerism, a set of force constants of the molecules containing silicon or germanium atoms are investigated. The Urey-Bradley force field may be the most effective force field for this purpose.[11] We have attempted to establish the transferability of the set of force constants for similar molecules.

At first, the force constants for $CH_3YH_3$ were transferred from those for $XYH_3$[1] and $(CH_3)_4Si$.[2] The force constants of H(C–Y–H), H(Y–C–H), F(C·Y·H), and F(Y·C·H) were, then, obtained by adjusting the calculated frequencies towards the observed.

Secondly, the force constants for $CH_3YH_3$ and $XCH_2CH_2X$[12] were transferred to those for $XCH_2YH_3$, where the structural parameters were of the same values used in the calculation of the moments of inertia, but assuming tetrahedral angles. Symmetry coordinates are the usual, commonly-used ones.[3,9]

As no X–C–Y bending vibrations were observed in the present study, the force constants of H(X–C–Y) and F(X·C·Y) could not be determined. For them we used the values for $XCH_2CH_2X$.

In the simple Urey-Bradley force field, the $YH_3(-D_3)$ rocking, $CH_2$ rocking, and $CH_2$ twisting frequencies of the *A″* species strongly suggest the necessity of some modification of the force field. Therefore, *trans* coupling, *t*, and *gauche* coupling, *g*, were added, assuming the *gauche* coupling to be $g=-0.5\,t$.[13] When all the transferred force constants of bending and repulsion were used, the mean errors of the calculated and observed frequencies for these molecules could not be made smaller than 2%. The assumption was made that some bending force constants were variable for each molecule and that the repulsion force constants were transferable.

The set of force constants obtained is listed in Table

11) T. Shimanouchi, *Pure Appl. Chem.*, **7**, 131 (1963).
12) Y. Abe and T. Shimanouchi, Symposium on Molecular Structure, Osaka (1966).
13) T. Shimanouchi, *Nippon Kagaku Zasshi*, **86**, 768 (1965).

TABLE 11. FORCE CONSTANTS OF $ClCH_2SiH_3$, $BrCH_2SiH_3$, AND $ClCH_2GeH_3$

| Force const.[a] | Adjusted force constants | | | | | | |
|---|---|---|---|---|---|---|---|
| | $ClCH_2SiH_3$ | $BrCH_2SiH_3$ | $ClCH_2GeH_3$ | $CH_3SiH_3$ | $CH_3GeH_3$ | $XSiH_3$[b] | $XGeH_3$[b] |
| K(C–H) | 4.390 | 4.497 | 4.439 | 4.438 | 4.484 | — | — |
| K(Y–H) | 2.638 | 2.632 | 2.556 | 2.586 | 2.514 | 2.669 | 2.602 |
| H(H–Y–C) | 0.113 | 0.133 | 0.123 | 0.094 | 0.119 | — | — |
| H(H–Y–H) | 0.170 | 0.170 | 0.160 | 0.180 | 0.170 | 0.180 | 0.170 |
| H(H–C–X) | 0.147 | 0.145 | 0.140 | — | — | — | — |
| H(H–C–Y) | 0.104 | 0.085 | 0.130 | 0.123 | 0.120 | — | — |
| $\kappa(YH_3)$ | 0.056 | 0.034 | 0.026 | 0.103 | 0.059 | 0.131 | 0.091 |
| $\kappa(CH_2)$ | 0.027 | 0.026 | 0.011 | −0.006 | −0.002 | — | — |
| $t_1$ | 0.017 | −0.019 | 0.099 | — | — | — | — |
| $t_2$ | 0.082 | 0.097 | 0.076 | 0.062 | 0.092 | — | — |

| | Force constants transferred from $XYH_3$, $CH_3YH_3$, and $XCH_2CH_2X$[c] | | | | | | |
|---|---|---|---|---|---|---|---|
| Force const.[a] | $ClCH_2SiH_3$ | $BrCH_2SiH_3$ | $ClCH_2GeH_3$ | Force const. | $ClCH_2SiH_3$ | $BrCH_2SiH_3$ | $ClCH_2GeH_3$ |
| K(C–Y) | 1.991 | 1.991 | 1.950 | F(H·Y·C) | 0.149 | 0.149 | 0.077 |
| K(C–X) | 1.697 | 1.346 | 1.697 | F(H·Y·H) | 0.041 | 0.041 | 0.010 |
| H(H–C–H) | 0.349 | 0.349 | 0.349 | F(H·C·X) | 0.558 | 0.421 | 0.558 |
| F(H·C·H) | 0.200 | 0.200 | 0.200 | F(H·C·Y) | 0.271 | 0.271 | 0.240 |
| H(Y–C–X) | 0.087 | 0.102 | 0.087 | Y | 0.080 | 0.080 | 0.080 |
| F(Y·C·X) | 0.747 | 0.644 | 0.747 | | | | |

a) The units are mdyn/Å for stretching, K, bending, H, and repulsion, F, and mdyn·Å for intramolecular tension, $\kappa$, internal rotation, Y, *trans* coupling, $t$ ($t_1$=(YH$_3$, X–C–Y), $t_2$=(YH$_3$, CH$_2$)), and *gauche* coupling, $g$. F′ is taken as −0.1F. The value of Y is assumed from the barrier height 2.55 kcal/mol. The $g$ is assumed as $-0.5\,t$. b) Ref. 1. c) Ref. 12.

11, together with those for $XYH_3$ and $CH_3YH_3$. As the table shows, it was necessary to vary not only the force constants between $XCH_2$ and $YH_3$ groups, H(C–Y–H) and H(Y–C–H), but also the force constants, H(X–C–H) and H(H–Y–H), for each molecule. The latter is a slightly smaller value than those for similar molecules of dihalogenoethane (H(H–C–Cl)=0.175 and H(H–C–Br)=0.160 mdyn/Å), methylsilane, and methylgermane.

The observed and calculated frequencies are given

TABLE 12. OBSERVED AND CALCULATED FREQUENCIES OF CHLOROMETHYLSILANE ($cm^{-1}$)

| Vibn. No. | $ClCH_2SiH_3$ | | | $ClCH_2SiD_3$ | | |
|---|---|---|---|---|---|---|
| | Obs. | Calcd. | Dif.[a] | Obs. | Calcd. | Dif. |
| $A'$ 1 | 2948 | 2974 | 0.9 | 2951 | 2974 | 0.8 |
| 2 | 2197 | 2198 | 0.0 | 1595 | 1598 | −0.4 |
| 3 | 2168 | 2195 | 1.2 | 1568 | 1562 | −0.4 |
| 4 | 1410 | 1420 | 0.7 | 1405 | 1420 | 1.1 |
| 5 | 1182 | 1172 | −0.8 | 1175 | 1169 | −0.5 |
| 6 | 925 | 927 | 0.2 | 676 | 663 | −2.0 |
| 7 | 925 | 916 | −1.0 | 643 | 646 | 0.5 |
| 8 | 764 | 745 | −2.4 | 696 | 710 | 1.9 |
| 9 | 719 | 718 | −0.1 | 772 | 746 | −3.4 |
| 10 | 557 | 560 | 0.6 | 455 | 453 | −0.4 |
| 11 | — | 293 | — | — | 271 | — |
| $A''$ 12 | 2989 | 2967 | −0.8 | 2993 | 2966 | −0.9 |
| 13 | 2197 | 2200 | 0.1 | 1603 | 1592 | −0.7 |
| 14 | 1110 | 1109 | −0.1 | 1105 | 1106 | 0.1 |
| 15 | 950 | 979 | 3.1 | 700 | 679 | −3.0 |
| 16 | 815 | 795 | −2.4 | 765 | 786 | 2.7 |
| 17 | 509 | 516 | 1.3 | 409 | 406 | −0.9 |
| 18 | — | 164 | — | — | 123 | — |
| Mean error 1.10 | | | | | | |

a) (Calcd−Obsd)/Obsd×100 (%).

TABLE 13. OBSERVED AND CALCULATED FREQUENCIES OF BROMOMETHYLSILANE ($cm^{-1}$)

| Vibn. No. | $BrCH_2SiH_3$ | | | $BrCH_2SiD_3$ | | |
|---|---|---|---|---|---|---|
| | Obs. | Calcd. | Dif.[a] | Obs. | Calcd. | Dif. |
| $A'$ 1 | 2958 | 2985 | 0.9 | 2961 | 2985 | 0.8 |
| 2 | 2197 | 2195 | −0.1 | 1590 | 1587 | −0.2 |
| 3 | 2164 | 2192 | 1.3 | 1565 | 1560 | −0.3 |
| 4 | 1398 | 1408 | 0.7 | 1393 | 1408 | 1.0 |
| 5 | 1135 | 1129 | −0.6 | 1133 | 1123 | −0.9 |
| 6 | 925 | 930 | 0.5 | 661 | 667 | 0.9 |
| 7 | 925 | 919 | −0.6 | 661 | 651 | −1.6 |
| 8 | 739 | 717 | −2.9 | 749 | 740 | −1.2 |
| 9 | 687 | 688 | 0.2 | 612 | 613 | 0.2 |
| 10 | 504 | 507 | 0.6 | 426 | 426 | 0.0 |
| 11 | — | 248 | — | — | 234 | — |
| $A''$ 12 | 3005 | 2980 | −0.8 | 3006 | 2980 | −0.9 |
| 13 | 2197 | 2198 | 0.0 | 1603 | 1590 | −0.8 |
| 14 | 1060 | 1061 | 0.1 | 1056 | 1054 | −0.2 |
| 15 | 944 | 965 | 2.3 | 678 | 666 | −1.8 |
| 16 | 804 | 790 | −1.8 | 753 | 771 | 2.3 |
| 17 | 504 | 509 | 0.9 | 412 | 409 | −0.7 |
| 18 | — | 162 | — | — | 122 | — |
| Mean error 0.88 | | | | | | |

a) (Calcd−Obsd)/Obsd×100 (%).

Table 14. Observed and calculated frequencies of chloromethylgermane ($cm^{-1}$)

| Vibn. No. | | $ClCH_2GeH_3$ | | | $ClCH_2GeD_3$ | | |
|---|---|---|---|---|---|---|---|
| | | Obs. | Calcd. | Dif.[a] | Obs. | Calcd. | Dif. |
| $A'$ | 1 | 2957 | 2985 | 0.9 | 2962 | 2985 | 0.8 |
| | 2 | 2115 | 2113 | −0.1 | 1504 | 1508 | 0.3 |
| | 3 | 2086 | 2107 | 1.0 | 1497 | 1494 | −0.2 |
| | 4 | 1408 | 1413 | 0.4 | 1408 | 1413 | 0.4 |
| | 5 | 1177 | 1174 | −0.3 | 1178 | 1172 | −0.5 |
| | 6 | 881 | 871 | −1.2 | 607 | 602 | −0.8 |
| | 7 | 826 | 815 | −1.3 | 591 | 584 | −1.2 |
| | 8 | 743 | 737 | −0.8 | 743 | 725 | −2.4 |
| | 9 | 641 | 645 | 0.7 | 638 | 640 | 0.3 |
| | 10 | 492 | 492 | −0.1 | 393 | 400 | 1.8 |
| | 11 | — | 236 | — | — | 219 | — |
| $A''$ | 12 | 3001 | 2978 | −0.8 | 3004 | 2978 | −0.9 |
| | 13 | 2115 | 2113 | −0.1 | 1523 | 1508 | −1.0 |
| | 14 | 1116 | 1114 | −0.1 | 1112 | 1112 | 0.0 |
| | 15 | 879 | 900 | 2.3 | 624 | 622 | −0.4 |
| | 16 | 787 | 771 | −2.1 | 759 | 774 | 2.0 |
| | 17 | 492 | 496 | 0.9 | 379 | 376 | −0.7 |
| | 18 | — | 161 | — | — | 124 | — |
| Mean error | | 0.90 | | | | | |

a) (Calcd−Obsd)/Obsd×100 (%).

in Tables 12—14. The distribution of the potential energy (PED) among the modes shows that the concept of characteristic group frequencies can be applied to all the halogenomethylsilanes and to halogenomethylgermane except for some modes. It may also be seen that the $CH_2$ rocking, $YH_3$ rocking, and $YH_3$ asymmetric deformation modes of the $A''$ species, and the C–X stretching and $YH_3$ rocking modes of the $A'$ species, show a considerable amount of mixing for $XCH_2YH_3(-D_3)$ (PED, 5—30%). Especially in $ClCH_2GeH_3(-D_3)$, the Ge–C–Cl bending and $GeH_3(-D_3)$ rocking modes show a mixing of about 20% (PED). It seems that the *trans* coupling, $t_1$, largely contributed to this, because this value for $ClCH_2GeH_3$ is significantly larger than that for $XCH_2SiH_3$.

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