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# The Infrared Spectra of the Digermanyl Halides, $Ge_2H_5X$, and Related Species

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*The infrared spectra of $Ge_2H_5X$ ($X = Cl, Br, I$) and of $Ge_2D_5Cl$ have been recorded in the region 4000-250 $cm^{-1}$ and partially assigned. This tentative assignment is supported from the spectra of $Ge_2H_5D$ and $Ge_2D_5H$.*

## Introduction

The preparation and properties of the digermanyl halides, $GeH_3GeH_2X$, ($X = Cl, Br, I$) have been reported recently.[1] These compounds are structurally the simplest derivatives of digermane and are important as key intermediates in any approach to the substitution chemistry of digermane. They are also of interest as analogues of the ethyl halides. The digermanyl halides are too unstable for full study but their infra-red spectra may be measured in the gas phase at pressures which are sufficiently low to avoid rapid decomposition. Band contours are observed in sufficient detail to allow a tentative assignment of the vibrational modes, supported by comparisons within this group of molecules and with related molecules. Such characteristic features and partial assignments of these spectra are reported here. Most attention has been focussed on the chloride, which is the most stable of the halides, and its deuterium analogue, $GeD_3GeD_2Cl$, has also been studied.

These molecules may be discussed in terms of the $C_s$ point group with the symmetry plane passing through the three heavy atoms and one hydrogen of the $GeH_3$ group. There are then eleven a′ fundamentals and seven a″ modes. As the axis of largest moment of inertia is out-of-plane, the a″ modes should show a C-type contour with a central Q branch. Most of the in-plane modes show a doublet PR contour, with a weak Q branch for the lighter halides. Although these molecules are relatively asymmetric tops, calculation of the P-R separation of the a′ modes,[2] assuming normal bond lengths[3] and tetrahedral angles, gives values in reasonable agreement with the average of the observed separations. Table I lists the vibration modes with their approximate description, numbered for $GeH_3GeH_2Br$. (For convenience, this numbering sequence will be used for all the molecules discussed here.) If the vibrations of the $Ge_2H_5$ group are compared with those of the $C_2H_5$ group for which Pentin[4] has reported normal coordinate calculations, it may be concluded that the conventional description of vibrations given in Table I is fairly accurate for GeH modes but with some mixing between rocks and skeletal modes. A simplified 3-particle calculation on the skeleton, using force constants from $GeH_3X$[5] and digermane,[6] gives skeletal stretches in reasonable agreement with those observed and predicts the bending mode, $\nu_{11}$, at 173 $cm^{-1}$ for the chloride and 126 $cm^{-1}$ for the bromide.

**Table I.** Vibrations of the $GeH_3GeH_2X$ Molecule According to the $C_s$ Point Group

| Conventional Description of the Vibration | Symmetry Class a′ | a″ |
|---|---|---|
| $GeH_2$ stretch | $\nu_1$ | $\nu_{12}$ |
| $GeH_3$ stretch (asym.) | $\nu_2$ | $\nu_{13}$ |
| $GeH_3$ stretch (sym.) | $\nu_3$ | |
| $GeH_2$ bend (scissors) | $\nu_4$ | |
| $GeH_3$ deformation (asym.) | $\nu_5$ | $\nu_{14}$ |
| $GeH_3$ deformation (sym.) | $\nu_6$ | |
| $GeH_3$ wag | $\nu_7$ | |
| $GeH_2$ twist | | $\nu_{15}$ |
| $GeH_2$ rock | | $\nu_{16}$ |
| $GeH_3$ rock | $\nu_8$ | $\nu_{17}$ |
| GeX stretch | $\nu_9$ | |
| GeGe stretch | $\nu_{10}$ | |
| GeGeX deformation | $\nu_{11}$ | |
| torsion | | $\nu_{18}$ |
| Band Contour | A, B, A-B | C |

## Experimental Section

$Ge_2H_5X$, $X = Cl, Br, I$ were prepared and characterised as previously described[1] and $Ge_2D_5Cl$ was prepared similarly from $Ge_2D_6$. Reaction of $Ge_2H_5I$ with PbF gave small yields of a compound whose ir spectrum indicated it was $Ge_2H_5F$. We were unable to isolate a pure sample. $Ge_2H_5D$ and $Ge_2D_5H$ were prepared by the action of $LiAlD_4$ or $LiAlH_4$ in monoglyme on the corresponding chloride or iodide. The digermanes were purified by distillation at − 83°C and obtained in better

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[1] K. M. Mackay, P. Robinson, E. J. Spanier and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, *28*, 1377 (1966).

[2] S. L. Gerhard and D. M. Dennison, *Phys Rev.*, *43*, 197 (1933); T. D. Goldfarb, *J. Chem. Phys.*, *39*, 2860 (1963).

[3] Tables of Interatomic Distances, L. E. Sutton (Editor), Chemical Society Special Publications 11 and 18 (London).

[4] S. E. Rudakova and Yu. A. Pentin, *Optics and Spectroscopy*, *18* 339 (1965); idem with T. F. Tulyakova, *ibid*, *20*, 253 (1966).

[5] D. E. Freeman, K. H. Rhee and M. K. Wilson, *J. Chem. Phys.* *39*, 2908 (1963).

[6] J. E. Griffiths and G. E. Walrafen, *J. Chem. Phys.*, *40*, 321 (1964)

than 80% yield. The deuterium content was estimated to be better than 95% of theoretical for $Ge_2H_5D$ but about 92% for $Ge_2D_5H$.

Spectra were run on gas samples at between 5 and 10 mm pressure in a 10 cm cell fitted with KBr or CsI windows on a Perkin-Elmer 521 Spectrometer. Band positions reported were measured on spectra run at ×5 scale expansion and calibrated with CO, $CO_2$, $NH_3$ and atmospheric water vapour. Positions of sharp bands are accurate to $\pm$ 2.5 $cm^{-1}$. The iodide was too unstable to be run under scale expansion conditions and the frequencies in this spectrum are accurate only to $\pm$ 5 $cm^{-1}$. A similar accuracy applies for the bands of the impure sample of $Ge_2H_5F$. Under these conditions, bands due to digermane (the most prominent decomposition product) could just be detected in the spectrum after 10 minutes for the iodide, about 45 minutes for the bromide, and after 3 hours for the chloride.

The Raman spectrum of $Ge_2H_5Cl$ was run in a 0.2 ml cell on a Cary Model 81 spectrometer. Decomposition occurred within 15 minutes.

## Results and Discussion

The spectrum of the chloride is typical and is shown in the Figure 1. Frequencies and tentative assignments are listed in Table II.

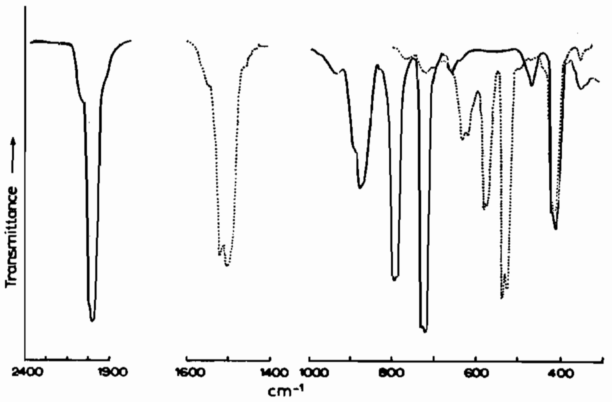

Figure 1. Spectrum of Digermanyl Chloride (———) and Digermanyl Chloride —$d_5$ (— — —) at 8 mm pressure in 10 cm cell.

**Table II.** The infrared gas phase spectra of the digermanyl halides

| $GeH_3GeH_2Cl$ | $GeD_3GeD_2Cl$ | $GeH_3GeH_2Br$ | $GeH_3GeH_2I$ | Assignment |
|---|---|---|---|---|
| 2147 sh, w Q? | | 2144 sh, w Q? | | $\nu_{12}$ |
| 2106 Q | 1519 Q | 2106 Q | | $\nu_{13}$ |
| 2087 vs | 1508 | 2087 | 2100 sh | |
| 2076 | 1500 vs | 2082 vs | 2080 vs | $\nu_1$, $\nu_2$, $\nu_3$ |
| | 1495 | 2075 | | |
| | 1490 | | | |
| 934 sh, br, w | | 934 br, w | 932 br, w | a′,$\nu_4$ |
| 890 sh, m | 631 m | 885 sh, m | | |
| 879 m Q | 616 m | 877 m Q | 872 m Q | a″, $\nu_{14}$ |
| 873 sh R | 604 sh | 870 sh R | | |
| 869 sh Q m | | m | 857 sh, m | a′, $\nu_5$ |
| 863 sh P | | 861 sh P | | |
| 796 R | 575 R | 791 R | 787 R | |
| 792 Q s | 570 Q s | s | s | a′, $\nu_6$ |
| 787 P | 566 P | 784 P | 780 P | |
| 728 R | 528 R | 708 R | 683 R | |
| 721 Q vs | 522 Q vs | vs | vs | a′, $\nu_7$ |
| 716 P | 518 P | 701 P | 678 P | |
| 651 w | | | | $\nu_{15}$? |
| 463 d, w | | 470 vw | 467 vw | a′, $\nu_8$ |
| 348 w | | 346 vw | 335 vw | a″, $\nu_{17}$ |
| 415 | 414 | 305 | | |
| m | m | m | | a′, $\nu_9$ |
| 408 | 407 | 299 | | |

(i) An impure sample of $Ge_2H_5F$ contained bands at 2100 sh, 2080 vs (νGeH), 880 sh, 877 m ($\nu_{14}$), 871 sh and 861 sh ($\nu_5$), 804 and 795 m ($\nu_6$), 761, 754 and 748 vs ($\nu_7$), 670 and 662 ms (νGeF), 460 vw ($\nu_8$). (ii) Raman spectrum of $Ge_2H_5Cl$ up to $\Delta\nu$ = 500 $cm^{-1}$, shows bands at 394 (9) sharp ($\nu_9$), 311 (3) br ($\nu_{17}$?), and 264 (10) sharp ($\nu_{10}$). (iii) PR separations in $Ge_2H_5X$: X=Cl, Br, I; calculated[2] 9.5, 7.2, 6.3; observed 9.7, 7.2, 6 (average of $\nu_5$, $\nu_6$, $\nu_7$, $\nu_9$ except for iodide $\nu_6$, $\nu_7$).

*Stretching Modes.* The five GeH stretches form a complex band envelope between 2070 and 2150 $cm^{-1}$ and it is impossible to distinguish each mode. A sharp maximum at 2106 $cm^{-1}$ in the spectra of the chloride and bromide is probably the Q branch of one of the a″ modes. If the sharp, weak 2147 $cm^{-1}$ absorption is also a fundamental, we may speculate that this is the $GeH_2$ antisymmetric mode $\nu_{12}$ (compare νGeH at 2130 $cm^{-1}$ in $GeH_3Cl$[5]) and then the 2106 $cm^{-1}$ band is $\nu_{13}$.

The GeF, GeCl and GeBr stretches, $\nu_9$, occur at 666, 412 and 302 $cm^{-1}$ respectively, somewhat below the frequencies in the germyl halides.[5] The GeI stretch is expected about 240 $cm^{-1}$, below our experimental limit. No band assignable as ν(GeGe) could be seen in the gas phase infrared spectra although the 300-250 $cm^{-1}$ region was carefully examined.[7] However, we

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(7) Ge-Ge stretches were not observed in gas phase i.r. spectra of $Ge_3H_8$ or $Ge_4H_{10}$ though Raman shifts occur near 280 $cm^{-1}$ for each of these compounds (Mackay and Sutton, unpublished observations).

were able to record part of the Raman spectrum of $Ge_2H_5Cl$, as the neat liquid, before the sample decomposed and observed strong sharp Raman shifts at 264 $cm^{-1}$ and 394 $cm^{-1}$. The latter is $\nu_9$ shifted by the change of phase, (compare $\nu GeCl$ at 370 $cm^{-1}$ in solid $GeH_3Cl$ and at 422 $cm^{-1}$ in the gas phase[5]). Thus the band at 264 $cm^{-1}$ in the Raman is probably $\nu_{10}$, the Ge-Ge stretch, in good agreement with the frequency of 268 $cm^{-1}$ observed for digermanes.[6]

*Deformation and Rocking Modes.* The three $GeH_3$ deformations and the bend and wag of the $GeH_2$ group occur in the 700-950 $cm^{-1}$ region. Two very strong type A bands occur in this region which are the most distinctive features of the spectra. One of these varies markedly with halogen substituent, from 721 $cm^{-1}$ in $GeH_3GeH_2Cl$ to 681 $cm^{-1}$ in the iodide spectrum, and is therefore assigned as a $GeH_2$ mode. The other is much less affected by the halogen and lies in the range 793-783 $cm^{-1}$. These bands are assigned, respectively, as $\nu_7$ and $\nu_6$. By extrapolation of the frequency ranges, the strong frequencies at 798 $cm^{-1}$ ($\nu_6$) and 754 $cm^{-1}$ ($\nu_7$) in the impure sample of $Ge_2H_5F$ are similarly assigned. Corresponding bands at 570 $cm^{-1}$ ($\nu_6$) and 522 $cm^{-1}$ ($\nu_7$) are found in the $Ge_2D_5Cl$ spectrum.

The three remaining modes in this region, $\nu_4$, $\nu_5$ and $\nu_{14}$, are probably to be found in the complex contour between 860 and 935 $cm^{-1}$. In the $Ge_2H_5Cl$ spectrum, the a″ $GeH_3$ mode, $\nu_{14}$, is tentatively assigned to the sharp Q branch at 879 $cm^{-1}$. Then the second $GeH_3$ asymmetric deformation $\nu_5$, which is expected to be close to $\nu_{14}$, could be the three shoulders centred at 869 $cm^{-1}$ (PQR structure). This leaves the higher frequency shoulder about 930 $cm^{-1}$ which may be tentatively assigned as $\nu_4$, the $GeH_2$ mode. Assignments consistent with the above may be made for the bromide and iodide. The corresponding region in the $Ge_2D_5Cl$ spectrum occurs around 620 $cm^{-1}$ and was not clearly resolved. Assignments of these overlapping modes are necessarily more tentative than those of $\nu_6$ and $\nu_7$.

The rocking frequencies, $\nu_8$, $\nu_{15}$, $\nu_{16}$, and $\nu_{17}$, are less easily assigned. Three weak bands remain in the digermanyl chloride spectrum of which two, those near 460 $cm^{-1}$ (doublet) and 350 $cm^{-1}$, are found in similar positions for the other halides. These could be assigned as the $GeH_3$ modes, $\nu_8$ and $\nu_{17}$. The remaining weak band at 651 $cm^{-1}$, which is not seen in the $Ge_2H_5Br$ or $Ge_2H_5I$ spectra, may be one of the $GeH_2$ modes, $\nu_{15}$ or $\nu_{16}$, more probably the twist. The torsion, $\nu_{18}$, would be below 250 $cm^{-1}$.

Further analogues of the halides are the isotopically substituted digermanes, $GeH_3GeH_2D$ and $GeD_3GeD_2H$, whose frequencies are given and partially assigned in Table III. These spectra are similar to those of the halides but there is probably more mixing of deformation modes. As expected from the moments of inertia, Q branches of the type A bands are prominent for the deutero-hydrides, being nearly equal in intensity to the P and R branches.

Finally, it is interesting to compare frequencies in related molecules. The $GeH_2$ wag, $\nu_7$, is the most characteristic frequency in these species and is analogous to the symmetrical deformation mode in $GeH_3X$, $SiH_3X$ and $CH_3X$ species which was reviewed by Jolly.[8] In Table IV, this band is compared with its analogues in the ethyl,[9] disilanyl,[10] germyl[5] and germylene[11] halides. These frequencies change with change in substituent in a similar pattern for all these compound types. The values of $\nu_7$, as do the corresponding frequencies of the silyl and disilanyl halides, show the usual, approximately linear, relationship with the electronegativity of X, and a linear relationship with the volume of X.[10]

**Table III.** Infrared gas phase spectra of deuterodigermanes

| $Ge_2H_5D$ | | $Ge_2D_5H$ | | Tentative Assignment |
|---|---|---|---|---|
| 2112 sh<br>2085<br>2073 | vs | 2087<br>2076 | m | GeH stretches |
| 1506<br>1494 | m | 1510 sh<br>1497<br>1487 | vs | GeD stretches |
| 871 b, m | | 789 w<br>741-696 m<br>(complex) | | $\nu_4$, $\nu_5$<br>and<br>$\nu_{14}$ |
| 815 R<br>808 Q<br>803 P | ms | 599 R<br>593 Q<br>587 P | m | $\nu_6$ |
| 720 R<br>715 Q<br>708 P | vs | 567 R<br>562 Q<br>554 P | vs | $\nu_7$ |
| 610 R<br>600 P | m | | | $\nu_{11}$? |
| 520 R<br>509 P | w | 443 b, w | | $\nu_8$? |
| 367 b, m-w | | | | $\nu_{17}$ |

**Table IV.** Comparison of $\nu_7$ in digermanyl halides with corresponding vibrations in related molecules

| | F | Cl | Br | I | |
|---|---|---|---|---|---|
| $CH_3CH_2X$ | 1365 | 1287 | 1248 | 1208 | $CH_2$ wag (a′) |
| $SiH_3SiH_2X$ | 841 | 807 | 790 | 757 | $SiH_2$ wag (a′) |
| $GeH_3GeH_2X$ | 754 | 721 | 704 | 681 | $GeH_2$ wag (a′) |
| $GeH_3X$ | 859 | 848 | 832 | 806 | $GeH_3$ sym. def. ($a_1$) |
| $GeH_2X_2$ | 814 | 779 | 754 | 708 | $GeH_2$ wag ($b_2$) |

Mixing of a′ $MH_3$ and $MH_2$ deformation frequencies undoubtendly occurs in the $M_2H_5$ groups and is most marked for the ethyl halides. The choice of frequency for the $CH_2$ wag is therefore somewhat arbitrary.

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