1973

CHARACTERISATION OF HALOGEN AND PSEUDOHALOGEN DERIVATIVES OF THE METHYLGERMANES.

RAYMOND T. HEMMINGS
University of Windsor

Recommended Citation
HEMMINGS, RAYMOND T., "CHARACTERISATION OF HALOGEN AND PSEUDOHALOGEN DERIVATIVES OF THE METHYLGERMANES." (1973). *Electronic Theses and Dissertations*. 1388.
https://scholar.uwindsor.ca/etd/1388

CHARACTERISATION OF HALOGEN AND PSEUDOHALOGEN DERIVATIVES OF THE METHYLGERMANES

BY

Raymond T. Hemmings

A Dissertation
submitted to the Faculty of Graduate Studies through the Department
of Chemistry in partial fulfillment of the requirements for the Degree
of Doctor of Philosophy at the University of Windsor.

Windsor, Ontario
1973

437358

INDEX

CHAPTER IV THE VIBRATIONAL SPECTRA OF THE MONO- AND DI-HALOGENO-METHYLGERMANES

CHAPTER V THE CHARACTERISATION OF SOME MIXED HALOGENO-(METHYL)GERMANES

CHAPTER VI THE CHARACTERISATION OF PSEUDOHALOGEN DERIVATIVES OF THE METHYLGERMANES

....

List of abbreviations used:

Me, methyl; Et, ethyl; Pr, propyl; Bu, butyl
M, molecular weight
v.p., vapour pressure
n.m.r., nuclear magnetic resonance; i.r., infrared
p.p.m., parts per million
Ps, pseudohalogen or pseudohalide; X, halogen
ν, stretch; δ, deformation; ρ, rock
f[M-X], M-X (stretching) force constant
PED, potential energy distribution

ABSTRACT

Comparative synthetic routes to the series of halogeno-methylgermanium hydrides $MeGeH_2X$, Me_2GeHX, and $MeGeHX_2$ (X = F,Cl,Br,I) are reported. These include reactions of germanic hydrogen in Me_nGeH_{4-n} species with (a) free halogen, (b) hydrogen halides, (c) boron trihalides, and (d) thionyl halides, and interhalogen 'exchange' reactions of $MeGeH_nX_{3-n}$ species with (a) hydrogen halides and (b) lead(II) fluoride. Their vibrational spectra and those of the specifically deuteriated analogues $MeGeD_2X$, CD_3GeH_2X, $MeGeDX_2$ are presented in detail. The assignments are discussed in terms of isotopic frequency shifts, Raman polarisation data, and gaseous infrared band contours, and supported by an independent normal coordinate analysis.

The relative effects of substituents on the α- and β-proton chemical shifts in the ^1H n.m.r. spectra of the methylgermanes are considered by comparison with related carbon and silicon species. The calculated "carbon-germanium bond shift" is discussed and a modified form of the usual additivity relationship for vicinal interproton coupling is proposed.

The vibrational spectra of the trihalogeno(methyl)germanes $MeGeI_3$ and $MeGeF_3$ are reported. Several features in the solid-phase Raman spectrum of the latter are suggestive of association and point to the need for a direct structural investigation.

A ^1H n.m.r. spectroscopic study of the reactions of $MeGeH_nX_{3-n}$ (n = 1,2,3; X = Cl,Br,I) is described in which 'mixed' halide species MeGeHXY and $MeGeX_2Y$ are formed. The redistribution equilibria of

$MeGeHX_2/MeGeHY_2$ species are followed; systems involving exchange of Cl and I show the most significant deviation from random distribution.

Exchange reactions with (a) silver(I) pseudohalides, AgPs (Ps = CN, NCO, NCS), (b) azido(trimethyl)silane, Me_3SiN_3, and (c) sodium azide lead to the formation of pseudohalogen derivatives, $MeGeH_2Ps$, Me_2GeHPs, $MeGe(Ps)_3$, from the corresponding halides. Unstable dipseudohalides, $MeGeH(Ps)_2$, are observed in the ^1H n.m.r. and mass spectra but are not isolated. The Raman spectrum of cyanogermane, GeH_3CN, is reported and the vibrational spectra of cyano(trimethyl)germane, Me_3GeCN, discussed in detail. Several spectral features in these and the new species are suggestive of structural isomerism.

PREFACE

The field of organogermanium chemistry is one that has seen a considerable upsurge of interest since the discovery of the first organogermane, tetraethylgermane, by Winkler (1887).[1] A review by Johnson[2] (1951) contained about 230 organogermanium compounds which had increased to some 500 at the time of Rijkens first review[3] (1960). By 1963 the excellent reviews of Quane and Bottei[4] and Rijkens again[5] included reference to over 1000 known organogermanes, while Dub's tabulations of Group IV compounds[6] (1967) included over 1500 references to compounds of germanium. Standard texts which have influenced the current research include those by Stone,[7] Ebsworth,[8] Glockling,[9] and Amberger and Wiberg,[10] with further excellent review material by Glockling and Hooton,[11] and Hooton.[12] More recently Mackay and Watt[13] reviewed the chemistry of chain compounds of Si, Ge, Sn and Pb; Van Dyke[14] discussed the inorganic derivatives of germane and digermane; Drake and Riddle[15] covered the chemistry of Group V and VI derivatives of silicon and germanium hydrides.

The literature more than indicates the growing interest in organogermane chemistry, and it is with some surprise that one discovers the available physical data on organogermanium hydrides (with at least one Ge-H bond) is still comparatively sparse, this being particularly true of the halide derivatives. The properties undoubtedly depend on the size and number of organic groups; much of the earlier work as far as it exists is therefore concerned with the more amenable per- or polyalkylgermanes of comparatively low volatility and high thermal stability e.g., $RGeH_3$, R_2GeH_2, R_3GeH ($R = C_2H_5, C_3H_7, C_4H_9, C_5H_{11}, C_6H_{13}$).[16-21]

Despite the ease of preparation[22] surprisingly little is known of the 'inorganic' chemistry of the simplest organogermanes, the methylgermanes $MeGeH_3$, Me_2GeH_2, Me_3GeH. The hydrides themselves have been the subject of microwave,[23] pyrolysis,[24] and vibrational[25] studies, whilst the fully substituted halides, ie. Me_nGeX_{4-n} (X = Cl,Br,I) also have well established synthetic routes[26] and lend themselves ideally to vibrational analysis.*

The present work was carried out to synthesise and characterise spectroscopically the halogen and pseudohalogen derivatives of methyl- and dimethyl-germane, ie. $MeGeH_2X$, Me_2GeHX, $MeGeHX_2$ and $MeGeX_3$ (X = F,Cl,Br,I,CN,N_3,NCO,NCS). As a series of compounds they are particularly well suited to a systematic study. The presence of the proton in the molecule presents both an invaluable n.m.r. nucleus and an ideal centre for isotopic substitution by ^2H (deuterium), this giving rise to large infrared (and Raman) frequency shifts which are an obvious aid to the interpretation of vibrational spectra. It was of interest to determine whether trends in the spectroscopic properties of these species could be related to changes in electronic distribution or bonding in the molecules.

---

* See Chapter III.

CHAPTER ONE

THE SYNTHESIS OF HALOGEN DERIVATIVES OF THE METHYLGERMANES

I.1 INTRODUCTION

This chapter is concerned primarily with the syntheses of some new derivatives of germane containing both germanium-halogen bonds and germanium-carbon(methyl) bonds. Germanium-halogen bonds are particularly labile and play an important role in essentially every branch of organogermanium chemistry; therefore before any one class of organogermanes can be investigated (in this study, the methylgermanes) it is essential to have well established synthetic routes available for the halide derivatives. For the most part routes to the fully substituted species are well defined[26] and so emphasis here will be given to the hydridic species which have received much less attention. It is worth noting that fully substituted alkylgermanes are in general stable to a wide range of chemicals but that the hydridic species, e.g. the germyl halides, GeH_3X, are thermally unstable with respect to disproportionation and polymerisation. In an investigation of this type we might therefore expect the methylgermyl halides to have an increased stability as a result of the methyl substituents. It is likely that the Ge-H bond may be the controlling factor in the choice of syntheses.

The synthesis of a halogeno-organogermane can be approached in essentially three ways: by the introduction of organo groups into germanium halides or hydrides (synthesis of Ge-C bonds); by the direct halogenation of an alkylated germane (synthesis of Ge-X bonds); or by the interconversion of organogermanium derivatives (these include reactions where halogen, hydrogen or oxygen etc., exchange with halogen). A consideration of the suitability of these approaches with respect to the present work is now presented.

(a) The introduction of organo groups into germanium halides or hydrides: The earlier methods involved the reaction of an alkyl halide with either metallic germanium[27] (usually as an alloy) or a germanium(II) halide.[26]

$$\text{Ge} + n\text{RX} \longrightarrow \text{R}_n\text{GeX}_{4-n} \qquad [1]$$

$$\text{GeX}_2 + \text{RX} \longrightarrow \text{RGeX}_3 \qquad [2]$$

Other methods have largely involved the use of alkali metal coupling (Wurtz) reactions[28] or organo-metal reagents reacting with and replacing a halogen attached to germanium with an organic grouping. Among the more successful of these have been Grignard reactions,[29] and syntheses involving alkylaluminium,[30] organolithium,[29] zinc dialkyl,[31] and organomercury[32] reagents. Schmidt and Ruidisch have compared these methods for fully substituted germanes.[33] Mackay et al have successfully used the Grignard reaction to synthesise alkylpolygermanes[34] by an in situ reaction with the highly unstable iodopolygermanes,

$$\geqq\text{Ge-I} + \text{MeMgI} \longrightarrow \geqq\text{Ge-Me} + \text{MgI}_2 \qquad [3]$$

Other reactions where the germanium-carbon bond is formed include diazo addition reactions,[35] the addition of a germanium hydride to olefinic or acetylenic systems,[36]

$$\geqq\text{Ge-H} + \text{CH}_2\text{=CH}_2 \longrightarrow \geqq\text{Ge-C}_2\text{H}_5 \qquad [4]$$

and the reaction of a germanium anion with an organic halide (e.g. germyl potassium with methyl iodide),[22]

$$\geqq\text{Ge}^-\text{K}^+ + \text{R-X} \longrightarrow \geqq\text{Ge-R} + \text{KX} \qquad [5]$$

As yet these reactions have not been successfully applied to the direct synthesis of organogermanium halides but they are of considerable importance in establishing the germanium-carbon skeleton which may then be halogenated. However, reactions are known where a germanium hydride condenses with an organic halide, e.g.

$$HGeCl_3 + Br\text{-}CH_2CH{=}CH_2 \longrightarrow HBr + Cl_3GeCH_2{=}CH_2 \ 50\% \qquad [6]$$

but this reaction generally has not been found to be applicable to alkyl and aryl halides and only occurs with allylic halides.[37]

It becomes clear, however, that for the synthesis of hydridic species this type of approach involves the use of relatively unstable germyl halides GeH_3X or GeH_2X_2, in somewhat extreme reaction conditions. Reactions of this type, whilst of some considerable theoretical interest, were not considered to be suited to the synthetic problem and as such were not pursued.

(b) Direct halogenation of an alkylated germane: Reactions which fall into this category are those where either a germanium-hydrogen or germanium-carbon bond is replaced by a germanium-halogen bond. These are conveniently discussed together because the reactions are very similar, the difference being one of reactivity.

Tetraalkyl germanes have been cleaved by Br_2[38] and I_2[39] although catalysts such as aluminium trihalides are generally required. The

$$\geqq Ge\text{-}CH_3 + X_2 \xrightarrow{AlX_3} \geqq Ge\text{-}X + CH_3\text{-}X \qquad [7]$$

products are alkyl halides and alkylgermanium halides. Germanium hydrides on the other hand react vigorously with free halogen (Cl_2,Br_2,I_2) in the absence of catalyst, usually to replace hydrogen by halogen and to liberate hydrogen halide. These reactions have been studied for

$$\geqq Ge\text{-}H + X_2 \longrightarrow \geqq Ge\text{-}X + HX \qquad [8]$$

germane[40,34,41-44] digermane,[45,46] trigermane,[47] and R_nGeH_{4-n} species[21,48] ($R{=}C_4H_9$). Hydrogen halides, by comparison, are much milder ~~and only~~ HF has been used to cleave tetraalkyl germanes;[49] HCl, HBr and HI are efficient halogenating agents for germanium hydrides in the presence of a catalyst, typically aluminium trihalides. Reactions reported include those with germane[41,45,50,51] and R_nGeH_{4-n}[52,53] where the products are usually the germanium halide and hydrogen,

$$\geqq Ge{-}H + HX \xrightarrow{AlX_3} \geqq Ge{-}X + H_2 \quad (X = Cl, Br) \qquad [9]$$

Earlier workers[16-18] found that many organic halogen compounds (e.g. R-X, CX_3COOH, RCClO, $ROCH_2Cl$) were efficient halogenating agents for the bulkier alkylgermanes, reflux conditions usually being employed. Thus the reaction of germanium hydride with an alkyl halide (usually a bromide or iodide) gives,

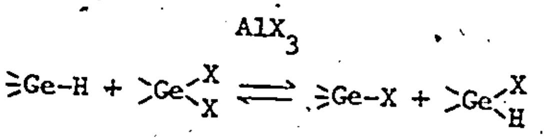
$$\geqq Ge{-}H + RX \longrightarrow \geqq Ge{-}X + RH \qquad [10]$$

Reactivity and yield were found to be in the order I>Br>Cl and $RGeH_3 > R_2GeH_2 > R_3GeH$. The only analogous reaction for unsubstituted germane was that reported by Griffiths and Beach[54] in which low yields of GeH_3I were obtained from the reactions of CF_3I with germane in a sealed tube.

A wide range of inorganic (metal and non-metal) halides are reduced by germanium hydrides with the formation of the corresponding germanium halide. Anderson[16,21] showed that mercuric halides HgX_2 (X=Cl,Br,I), $PdCl_2$, $TiCl_4$, $KAuCl_4$, K_2PtCl_6, $VOCl_3$, CrO_2Cl_2, and $CdCl_2$ all reacted with peralkylgermanes to evolve hydrogen with the metal passing into a lower state of oxidation. Satgé and co-workers[18-20] have demonstrated the similar usefulness of $AlCl_3$, CCl_4, $GeCl_4$ and SO_2Cl_2 for the bulkier alkylgermanes at reflux temperatures. More recently Mackay, MacDiarmid, and co-workers[45] have used heated silver halides, AgX (X=Br,Cl), for the direct halogenation of mono- and digermane; Anderson and Drake[55] have reported high yields of monochlorogermane from the reaction of germane with thionyl chloride and other studies indicated that boron trihalides, BX_3 (X=Br,Cl) could be used to effect direct halogenation of germane[56] and digermane.[57] In addition, Ebsworth and co-workers[58] reported useful reactions for monogermyl species using tin tetrahalides. However, there are at present no direct methods of converting parent germanes to fluorogermanes although Van Dyke[59] has used PF_5 to fluorinate $C_2H_5GeH_3$.

Other reactions in this general category are the catalysed redistribution reactions of germanium alkyls with germanium halides[60,61] and of alkylgermanium hydrides with alkylgermanium halides,[17,18] where Ge-C and Ge-H bonds are replaced by Ge-halogen bonds.

$$GeR_4 + GeX_4 \rightleftharpoons GeR_nX_{4-n} \qquad [11]$$



$$\geq Ge{-}H + {>}Ge{<}^{X}_{X} \xrightleftharpoons{AlX_3} \geq Ge{-}X + {>}Ge{<}^{X}_{H} \qquad [12]$$

These types of reactions, however, are expected to have little importance in view of the difficulty in separating the mixture of compounds which inevitably results from the equilibria [11] and [12].

(c) <u>The interconversion of organogermanium derivatives</u>: Most of the known inorganic derivatives of the germanes have been prepared by the appropriate reactions of halogenogermane intermediates. Interconversion of halides (and pseudohalides) bound to germanium has been achieved by reactions with salts of antimony,[62] lead,[45,63,64] mercury,[65,66] and silver[45,67,65] (often called Swarts reactions). This type of reaction has provided the most convenient route to germanium fluorides; thus silver (I)- or lead(II)- fluoride exchanged with bromogermane to give fluorogermane,[63,67] although in the corresponding reaction of iododigermane with AgF the identification of Ge_2H_5F was only tentative.[45] In these reactions the exchanging halogen on germanium is usually iodide or bromide (rarely chloride) and the halogen on the heavy-metal is usually fluoride or chloride. Convenient exchanges also occur with hydrogen halides,[65,68] and silyl compounds[69] and these are useful for converting 'hard' halogens bound to germanium to 'softer' halogens.

$$\geqq\text{Ge–X} + \text{M–Y} \longrightarrow \geqq\text{Ge–Y} + \text{MX} \qquad [13]$$

$$\underset{(\text{or } \geqq\text{Si–X})}{\geqq\text{Ge–Y} + \text{H–X}} \longrightarrow \geqq\text{Ge–X} + \underset{(\geqq\text{Si–Y})}{\text{HY}} \qquad [14]$$

(Where X = 'electropositive' halogen; Y = 'electronegative' halogen; M = Sb,Pb,Hg,Ag)

The yields from these reactions are high although the changes in bond energy are usually very low; for this reason they are considered as entropy-controlled reactions. The equilibrium constant for the chlorogermane–hydrogen iodide reaction (2600 at 30°)[69] is sufficiently high that iodogermane was formed quantitatively,

$$\text{GeH}_3\text{Cl} + \text{HI} \longrightarrow \text{GeH}_3\text{I} + \text{HCl} \qquad [15]$$

Similarly HBr reacted with GeH_3Cl[69] and R_nGeCl_{4-n}[68] quantitatively to replace chlorine by bromine.

In view of the ease in obtaining the hydrogen halides the exchange reaction with a silicon moiety[69] does not present a sensible synthetic prospect for halide derivatives. These reactions are of some considerable importance in the syntheses of pseudohalides and are discussed in Chapter VI. Similarly exchange reactions with boron trihalides are discussed in Chapter V.

The conversion of germoxane linkages, i.e. Ge–O–Ge, to germanium-halogen bonds has been achieved by free halogen,[21] hydrogen halide,[19] and boron trifluoride.[53] Griffiths and Onyszchuk[53] obtained good yields of fluoro(trimethyl)germane, Me_3GeF, by the cleavage of hexamethyldigermoxane, $(Me_3Ge)_2O$ with BF_3. However, attempts by the same workers to synthesise the corresponding hydridic germoxane, $(MeGeH_2)_2O$, or mixed ether, $MeGeH_2OMe$ by interaction of $MeGeH_2Br$ with $AgCO_3$ or NaOMe, respectively, gave complex disproportionation products. Ge–O species containing Ge–H bonds are notably unstable and $(GeH_3)_2O$ has only been prepared by indirect methods;[66,70] Massol and Satgé, however, have reported $(RGeH_2)_2O$ and $(R_2GeH)_2O$ species, (R = ethyl,n-butyl) which apparently have some stability,[19] although the isolation of the fluorides by HF cleavage was unsatisfactory.[71] In view of these difficulties germoxane cleavage reactions were not pursued.

The partial reduction of fully substituted alkylgermanium halides of the type R_nGeX_{4-n} is also at first sight an attractive prospect. However, the $NaBH_4$, $LiAlH_4$ or LiH reductions have all given the fully hydrogenated product;[72] there was evidence to suggest that in the reduction of germanium tetrachloride by $LiAlH_4$ the formation of polygermane was preceded by the formation of GeH_2Cl_2 which decomposed into $GeCl_2$ and hydrogen.[50] As indicated above, germanium hydrides themselves are reducing agents so the redistribution reaction of Et_3GeH with Et_2GeX_2 to give Et_2GeHX (X = Cl,Br)[17,18] may be regarded as a partial reduction reaction.

Before the commencement of this study, the literature contained only two reports relating specifically to hydridic halogeno(methyl)-germanes: Amberger and Boeters(1961)[52] reported that the aluminium trichloride catalysed gas phase reaction of hydrogen chloride with methyl- and dimethylgermane gave high yields of the chloro(methyl)-germanes, $MeGeH_2Cl$, $MeGeHCl_2$, and $MeGeCl_3$ and chloro(dimethyl)germanes, Me_2GeHCl and Me_2GeCl_2. Griffiths and Onyszchuk,[53] however, only isolated the dichloride, $MeGeHCl_2$, from a similar reaction at 100°, although they recovered the monobromide, $MeGeH_2Br$, in 53% yield from the analagous reaction with hydrogen bromide.

The particular use of these halides was indicated[73] by the facile exchange reaction of silyl phosphine, SiH_3PH_2, with chloro(methyl)germane to give the mixed hydride phosphino(methyl)germane, $MeGeH_2PH_2$, in high yield; the analogous reaction with dichloro(methyl)germane, $MeGeHCl_2$, gave the mixed chloro-phosphine, $MeGeH(Cl)PH_2$. More recently bromo-(methyl)germane, $MeGeH_2Br$, was used in a reaction with lithium tetra-arsinoaluminate to give the mixed hydride, $MeGeH_2AsH_2$, in high yield.[74]

During the course of this research a parallel study of $MeGeH_2X$ and the carbon functional species, $CH_2(X)GeH_3$, (X = Cl,Br,I) appeared;[75,76] this was concerned primarily with the extent of [p→d] π-bonding between germanium and the halogens and apparently contained no consideration of the fluoro- or polyhalogeno- species which appear in this work. At the same time $MeGeH_2F$ and Me_2GeHF were reported in a preliminary communication concerning the relative stabilities of some organofluorogermanes.[71]

In this chapter emphasis is on the initial work with methylgermane from which synthetic routes were devised which were considered to be the most suitable for later use on di- and trimethylgermane and in the large scale preparation of samples of the highest purity for subsequent vibrational and ^1H n.m.r. analysis and vapour pressure studies.

I.2 EXPERIMENTAL*

For convenience, the synthesis and characterisation of chlorides, bromides, iodides, and fluorides are dealt with separately. In many of the reactions described below small quantities of fully substituted

---

* A description of the vacuum line, the associated apparatus (e.g. reaction vessels, storage vessels, vapour pressure apparatus and low temperature baths) and experimental techniques may be found in Appendix 1. The preparation and purification of compounds considered as starting materials are given in Appendix 2.

germanes e.g. $MeGeCl_3$, Me_2GeCl_2, Me_3GeCl, were obtained. As these are now available commercially or have well defined synthetic routes it was considered unnecessary to devise conditions for their preparation from the parent hydride; where they appear they must be considered as by-products. Unless otherwise stated the initial identification of the new compounds came from ^1H n.m.r., i.r., and mass spectra with additional characterisation from molecular weights and vapour pressure determinations. The ^1H n.m.r. and vibrational spectra of the pure compounds appear in Chapters II, III and IV.

I.2.1 Preparation of chloro(methyl)-, chloro(dimethyl)-, and dichloro-(methyl)-, germanes.

(a) Reaction of methylgermane with hydrogen chloride: In preliminary experiments conditions similar to those used by Amberger and Boeters[52], were used. Various reaction temperatures, proportion of reactants and reaction times for methylgermane were then investigated. The 1:1 aluminium trichloride catalysed gas phase reaction between $MeGeH_3$ and HCl at room temperature yielded a mixture containing $MeGeH_2Cl$ (ca.50%), $MeGeHCl_2$ (ca.45%) and $MeGeCl_3$ (ca.5%), the overall yield of the reaction varying between 60% and 80%.

In one experiment, $MeGeH_3$ (2.0 mmol) and HCl (1.5 mmol) were condensed into a reaction vessel (150 ml, type 'D') containing $AlCl_3$ (ca.2g) sublimed on the inside wall, and allowed to react at -45°. After one hour the mixture was cooled to -196° and hydrogen (ca.1.7 mmol) pumped off. Fractionation of the products gave small amounts of $MeGeHCl_2$ [ca.0.2 mmol; Found: M,158; calc. for $MeGeHCl_2$,159.54] in a trap at -63°, $MeGeH_2Cl$ [ca.1.2 mmol; Found: M,126; calc. for $MeGeH_2Cl$,125.15] held in a trap at -95°, and unreacted $MeGeH_3$ (ca.0.5 mmol) condensing in a -196° following trap. Enhanced yields of $MeGeHCl_2$ and $MeGeCl_3$

were obtained by higher HCl; hydride ratios and by room temperature reactions. Thus apparently no $MeGeH_2Cl$ was formed with a 3:1 ratio and $MeGeHCl_2$ (35%) and $MeGeCl_3$ (60%) were recovered. However, careful analysis of the products from these reactions provided strong evidence for cleavage of the C–Ge bond occurring to the extent of ca.15% since Me_2GeHCl and Me_2GeCl_2 were identified in the ^1H n.m.r., vibrational and mass spectra. In a control experiment $MeGeH_2Cl$ (ca.1.0 mmol) was distilled at −196° into a 10 ml vessel (type'C') containing $AlCl_3$ (ca.0.5g) sublimed round the walls. After ca. 3 hours the ^1H n.m.r. spectrum of the total products after bleeding of a trace of non-condensable gas, indicated the presence of $MeGeH_2Cl$, Me_2GeHCl, $MeGeHCl_2$ and Me_2GeCl_2 in the approximate ratio 4:2:1:1. The a priori assignments being confirmed by additional peaks in the mass spectra at m/e135-142 ($H_nC_2GeCl^+$) and m/e171-181 ($H_nC_2GeCl_2^+$).

(b) Reaction of mono-, di-, and tri-methylgermane with boron trichloride: Preliminary experiments with $MeGeH_3$ indicated that poor conversions to chloro-species (less than 10%) were obtained in gas-phase reactions and liquid-phase reactions run in sealed tubes or small reaction vessels. The incomplete reactions were clarified by the appearance of bands in the i.r. spectra assignable to BH_nCl_{3-n} species[77] in addition to those attributable to $MeGeH_3$, B_2H_6, and chlorinated products. The ^1H n.m.r. spectra of reaction mixtures of this sort gave broad resonances having no apparent H-H' coupling but with similar chemical shifts to the pure chloro-species, $MeGeH_2Cl$ and $MeGeHCl_2$. Lowering the temperature of the n.m.r. probe to −100° was ineffective in slowing the exchange process so that interproton coupling could be observed. A similar phenomenon was observed when pure $MeGeH_2Cl$ was sealed with B_2H_6

(1:1); in this case decomposition was rapid at room temperature with the reaction tube showing considerable deposits of yellow material ($MeGeH_3$ and GeH_4 were later identified in the i.r.[25] of the volatile products when the tube was reopened). $MeGeHCl_2$ and $MeGeCl_3$ were apparently unaffected when sealed with B_2H_6.

Optimum yields were obtained with the reactants in the condensed phase at ca.-78° in large reaction vessels (e.g. 250-500 ml,type'D'). In this way the reduction of BCl_3 to B_2H_6 was usually complete in 1 hour and no evidence was obtained for the partially reduced species, BH_nCl_{3-n}. The reaction could be conveniently monitored by measuring the B_2H_6 evolved which was separated from the starting materials and chlorinated products by fractionation at -130°.

In a typical experiment, $MeGeH_3$ (1.02 mmol) and BCl_3 (0.30 mmol) were maintained at -78° for 1 hour. The mixture was allowed to warm to room temperature (ca.10 min) to complete the reaction when fractionation of the volatile products gave $MeGeH_2Cl$ [0.68 mmol; Found: M,125; calc. for $MeGeH_2Cl$,125.15] in a trap at -95°, small amounts of $MeGeHCl_2$ (0.13 mmol) in one at -45° and B_2H_6 (ca.0.15 mmol -identified by its i.r. spectrum[78]) in a -196° following trap. Traces of oily liquid remained in the reaction vessel giving a ^1H n.m.r. singlet resonance at 1.58δ, indicating the presence of $MeGeCl_3$.[79] A further series of reactions was carried out with increasing amounts of BCl_3. With a ratio of $MeGeH_3$:BCl_3 of 1:1 the distribution of chloro(methyl)germanes was $MeGeH_2Cl$ (ca.15%), $MeGeHCl_2$ (ca.40%) and $MeGeCl_3$ (ca.45%). In most reactions the yields based on $MeGeH_3$ consumed were between 70% and 95% and no evidence for any disproportionation by-products was obtained. Optimum yeilds of $MeGeH_2Cl$ were obtained with a ratio of $MeGeH_3$:BCl_3

of 4:1 when unreacted $MeGeH_3$ was obtained along with B_2H_6 in the -196° following trap. Separation of these components was effected by distillation onto a large excess of $(C_2H_5)_3N$: when the B_2H_6 formed a solid adduct leaving $MeGeH_3$ which could be separated from excess amine by fractionation at -78°.

Me_2GeH_2 (ca.3.0 mmol) and BCl_3 (0.76 mmol) were allowed to react as above. After 1 hour the mixture was brought to room temperature to complete the reaction and fractionated through traps at -23°, -78°, and -196°. The -23° trap contained a trace of Me_2GeCl_2, (identified in the ^1H n.m.r.[80] and i.r.[37] spectra) and Me_2GeHCl (ca.2.1 mmol) was recovered from the -78° trap [Found: M,138.8; calc. for Me_2GeHCl,139.11]. The -196° trap was shown to contain a mixture of B_2H_6 (ca.0.35 mmol) and Me_2GeH_2 (ca.0.8 mmol) which could be separated by refractionation at -126° when the latter was involatile.

In the same way Me_3GeH (ca.2.0 mmol) and BCl_3 (0.6 mmol) reacted to give Me_3GeCl (1.9 mmol) condensing at -45° (identified by its ^1H n.m.r.[81] and i.r.[82] spectra); traces of Me_3GeH were obtained in a -95° trap and B_2H_6 (ca.0.3 mmol) condensed in a -196° following trap.

(c) Reaction of methylgermane with thionyl chloride: $MeGeH_3$ (ca.2.5 mmol) and $SOCl_2$ (ca.2.2 mmol) were condensed at -196° into a thick-walled tube (ca.5 mm o.d.,80 mm long) having a tapered end, and allowed to warm to room temperature. After 16 hours the ^1H n.m.r. spectrum showed only traces of residual $MeGeH_3$ with additional broad resonances at approximately 5.3δ and 0.8δ. The tube was frozen at -196° and broken open on the vacuum line in the conventional manner and the products fractionated. Traces of yellow material which was soluble in CS_2 (and therefore probably sulphur) remained in the reaction tube. A mixture of $MeGeH_2Cl$ and SO_2 (ca.3.0 mmol), identified spectroscopically, were obtained in a trap at -95°. (These were eventually separated by repeated distillation at -83° when SO_2 passed into a -196° following trap, $MeGeH_2Cl$ (ca.2.0 mmol) condensing out with no indication from its ^1H n.m.r. and i.r. spectra of any further impurity.) A -196° following trap contained a mixture of unreacted $MeGeH_3$, HCl and traces of SO_2. No evidence was obtained for the formation of any poly-chlorinated products.

I.2.2 Preparation of bromo(methyl)-, bromo(dimethyl)-, and dibromo(methyl)-, germanes.

(a) Reaction of methylgermane with hydrogen bromide: In a typical reaction $MeGeH_3$ (2.95 mmol) and HBr (2.96 mmol) were allowed to react over a sublimed $AlBr_3$ catalyst (ca.2g) in a reaction vessel (350 ml, type'D') at -45°. After 1 hour non-condensable gas was removed through a series of liquid nitrogen traps. Repeated passage of the condensable products through a trap at -95° gave a mixture of unreacted $MeGeH_3$ and HBr (ca.1.1 mmol) in a -196° following trap. The bromo-products condensing at -95° were then redistilled through traps held at -23°, -45° and -196°. Bromo(methyl)germane, $MeGeH_2Br$ [ca.1.0 mmol; Found; M, 167; calc. for $MeGeH_2Br$,169.60] was obtained in the -196° trap, with dibromo(methyl)germane, $MeGeHBr_2$ (ca.0.8 mmol) in one at -45° and traces of tribromo(methyl)germane, $MeGeBr_3$, identified from the ^1H n.m.r.[80] of the contents of the -23° trap. Other experiments with varying reactant ratios gave the expected redistribution of products with enhanced yields of poly-bromides being obtained with larger amounts of HBr. Again, as with the chlorides, ^1H n.m.r. and mass spectral evidence indicated some C-Ge bond cleavage which was more prevalent in room temperature reactions. Thus additional peaks in the mass spectra at m/e

176–186 ($H_nC_2GeBr^+$) and m/e258–266 ($H_nC_2GeBr_2^+$) confirmed the *a priori* assignment of the n.m.r. spectra.

(b) *Reaction of methylgermane with boron tribromide*:* As with the analagous reactions with BCl_3 this series provided excellent synthetic routes to both mono- and di-bromo(methyl)germane. Enhanced yields of the desired product could be obtained by varying the amount of BBr_3 used. In one experiment $MeGeH_3$ (*ca*.1.5 mmol) and BBr_3 (*ca*.0.35 mmol) were condensed into a reaction vessel (150 ml type'D') held at −196°. The mixture was allowed to warm to −78° (*ca*.30 min) and then to −63° (ca. 30 min) and finally to room temperature (10 min) to complete the reaction. Fractionation of the volatile products through traps at −45°, −95° and −196° produced good separation. A small amount of $MeGeHBr_2$ (*ca*.0.2 mmol) condensed at −45° with pure $MeGeH_2Br$ [*ca*.1.2 mmol; Found: M,169; calc. for $MeGeH_2Br$,169.60] being obtained in the −95° trap. The −196° following trap contained B_2H_6 (*ca*.0.2 mmol −identified by its i.r.[78] spectrum) with only a trace of unreacted $MeGeH_3$. With a $MeGeH_3$:BBr_3 ratio of 3:2 the product distribution was $MeGeH_2Br$(30%), $MeGeHBr_2$(60%) and $MeGeBr_3$(10%) with a corresponding increase in the amount of B_2H_6 formed.

(c) *Reaction of methylgermane with bromine*: In a typical reaction Br_2 (total 0.7 mmol) was added to $MeGeH_3$ (*ca*.1.1 mmol) at −196° in four successive amounts. Between each addition the reaction vessel (500 ml, type'D') was allowed to warm to room temperature until the Br_2 colour disappeared. The mixture was then cooled to −196° and a trace of non-condensable gas pumped off. The ^1H n.m.r. spectrum of the total sample was then recorded and indicated the presence of $MeGeH_3$, $MeGeH_2Br$,

---

* see Appendix 2 for the reaction of GeH_4 with BBr_3

$MeGeHBr_2$, and $MeGeBr_3$ in the approximate ratio 8:10:3:1. After fractionation $MeGeH_3$ (ca.0.42 mmol) and $MeGeH_2Br$ [ca.0.50 mmol; Found:M,169, calc. for $MeGeH_2Br$,169.60] were obtained pure, $MeGeHBr_2$ and $MeGeBr_3$ being hard to separate by trap to trap distillation.

(d) Reaction of methylgermane with thionyl bromide: Typically $MeGeH_3$ (ca.1.2 mmol) and $SOBr_2$ (ca.1.0 mmol) were condensed into a 150 ml reaction vessel held at -196° and allowed to warm to room temperature. The initially bright orange colour quickly disappeared, the reaction being quenched with a -78° bath when effervescence became too violent. After ca.30 min a yellow deposit of sulphur was evident and fractionation of the volatile products gave $MeGeH_2Br$ (0.95 mmol) in a trap at -78° and a mixture of $MeGeH_3$, SO_2 and HBr (all identified in the i.r. spectrum) in a -196° following trap.

(e) Reaction of chloro-methylgermanes with hydrogen bromide: This provided the most convenient route to the bromides if sufficient quantities of the corresponding chlorides were available. Typically, $MeGeH_2Cl$ (0.75 mmol) and excess HBr (ca.2 mmol) were condensed into a reaction vessel (100 ml,type'F') held at -196°. On warming to room temperature signs of effervescence appeared, the reaction being quenched if it became too violent. After 30 min, reaction was complete and pure $MeGeH_2Br$ (ca.0.75 mmol) was isolated by repeated fractionation and condensation at -95°, HCl and the excess HBr being obtained in a -196° following trap. In the same way quantitative yields of $MeGeHBr_2$, $MeGeBr_3$ and Me_2GeHBr were obtained by treating the appropriate chloride, $MeGeHCl_2$, $MeGeCl_3$, or Me_2GeHCl, with excess hydrogen bromide.

I.2.3 Preparation of iodo(methyl)-, iodo(dimethyl)-, and diiodo(methyl)-, germanes.

(a) Reaction of methylgermane with hydrogen iodide: Typically, $MeGeH_3$ (1.69 mmol) and HI (1.71 mmol) were allowed to react over a sublimed AlI_3 catalyst in a reaction vessel (150 ml) at room temperature. After 15 minutes hydrogen was removed through a series of liquid nitrogen traps and the products fractionated at −78°. The products condensing at this temperature sealed for ^1H n.m.r. analysis were shown to be a mixture of mono- and diiodo(methyl)germane, $MeGeH_2I$ and $MeGeHI_2$ in the ratio 10:3. Traces of a yellow subliming material remaining in the traps were soluble in CCl_4 and were subsequently shown from the ^1H n.m.r. spectrum[79] to be triiodo(methyl)germane, $MeGeI_3$. A mixture of $MeGeH_3$ and HI (total ca.0.5 mmol) was obtained in the −196° trap. The mixture of mono- and diiodo(methyl)germanes was conveniently separated by fractionation at −23° when pure $MeGeH_2I$ [ca.1.1 mmol; Found:M,213; calc. for $MeGeH_2I$, 216.60] was obtained in a −196° following trap. No evidence for C–Ge bond cleavage was obtained in these experiments.

(b) Reaction of methylgermane with boron triiodide: $MeGeH_3$ (0.75 mmol) was distilled over BI_3 (ca.0.5 mmol) held on a glass sinter in a reaction vessel (25 ml, type 'H') at −196°. The mixture was then maintained at −78° and allowed to warm to room temperature after 30 minutes. Distillation of the products gave as expected B_2H_6 (ca.0.2 mmol) and traces of $MeGeH_3$ volatile at −78° with a mixture of iodides condensing. The ^1H n.m.r. spectrum of this fraction indicated the presence of $MeGeH_2I$, $MeGeHI_2$ and $MeGeI_3$ in the ratio 6:3:1. Further experiments were not attempted due to the difficulty of handling the solid BI_3.

(c) Reaction of mono-, di-, and tri-methylgermane with iodine:* A

---

* See Appendix 2 for reaction of GeH_4 with iodine

slight excess of the germane and resublimed iodine were condensed into a reaction vessel (10 ml, type 'C') which was then maintained at -78°. The reactions were occasionally accelerated by local warming with the fingers but quenched as they became too vigorous. After 15 minutes brown solutions were usually obtained showing no signs of solid I_2 and after 30 minutes reaction was complete as shown by the disappearance of the I_2 colour. Fractionation of the products at -78° permitted unreacted germane and HI to pass into a -196° trap, the iodides being involatile at this temperature. In this way pure $MeGeH_2I$ [Found: M, 215; calc. for $MeGeH_2I$, 216.60] and Me_2GeHI [Found: M, 226; calc. for Me_2GeHI, 230.57] were obtained in yields of 87% and 91% respectively with germane: iodine ratios of ca. 3:2. Higher yields (based on I_2 consumed) were obtained with excess germane but these were uneconomical in view of the price of germanes. Any di-iodo species were conveniently removed by passage through a -23° trap. High yields of $MeGeHI_2$ were hard to achieve by this method. If excess I_2 was used the product was contaminated with large amounts of $MeGeI_3$ which were hard to remove on the vacuum line. In one experiment $MeGeH_3$ (1.6 mmol) and I_2 (ca. 2.3 mmol) were allowed to react as above. After HI and $MeGeH_3$ had been removed at -78° the products were shown to contain $MeGeH_2I$ (0.4 mmol), $MeGeHI_2$ (1.1 mmol) and traces of $MeGeI_3$.

In a control experiment, Me_3GeH (10.2 mmol) was distilled onto iodine (3.3g; ca. 9.4 mmol) in a 20 ml finger attached to the vacuum line. The mixture was allowed to react at -63° (ca. 15 min). With the vessel open to a manifold the reaction was accelerated by local warming with the fingers. At ca. -30° a violent exothermic reaction took over such that >1 atmosphere pressure was generated before quenching was applied. Freezing the mixture at -196° revealed large amounts of non-condensable gas which was bled off through a series of U-traps held at -196°. After repeating this procedure several times a dark brown reaction mixture was obtained with no further increase in pressure. The excess iodine was removed by adding Me_3GeH in small amounts (total ca. 6.7 mmol) and allowing further reaction to occur. Finally Me_3GeI (15.9 mmol) was separated from HI and unreacted Me_3GeH by fractionation and condensation at -45°.

(d) Reaction of chloro- or bromo-methylgermanes with hydrogen iodide: As with the bromides this provided the most convenient synthetic route to the iodides if sufficient quantities of the corresponding chlorides (or, less preferably, bromides) were available. Typically, $MeGeH_2Cl$ (0.95 mmol) and excess HI (ca. 2 mmol) were condensed into a reaction vessel (110 ml) which was then allowed to warm to room temperature. After 15 minutes reaction was complete and pure iodo(methyl)germane, $MeGeH_2I$, [0.95 mmol; Found: M, 218; calc. for $MeGeH_2I$, 216.60] was obtained by repeated fractionation at -78°; HCl and excess HI were obtained in a -196° following trap. By an identical procedure $MeGeH_2Br$ (0.41 mmol) was used to give $MeGeH_2I$ (0.40 mmol). In the same way quantitative yields of Me_2GeHI, $MeGeHI_2$, and $MeGeI_3$ were obtained by treating the corresponding chlorides Me_2GeHCl, $MeGeHCl_2$, or $MeGeCl_3$, respectively, with excess hydrogen iodide. In experiments where excess HI was not used on the di- and tri-halides mixed halogeno-species, e.g. MeGeHClI or MeGeHBrI were identified. The a priori assignment of the extra peaks in the ^1H n.m.r. spectra being confirmed by the mass spectra. These reactions are discussed in Chapter V.

I.2.4 Preparation of fluoro(methyl)-, fluoro(dimethyl)-, difluoro-(methyl)-, and trifluoro(methyl)-, germanes.

(a) Reaction of methylgermane with boron trifluoride: $MeGeH_3$ (1.90 mmol) and BF_3 (2.0 mmol) showed no sign of reaction after 2 hours at -78° or 24 hours at room temperature in a sealed tube. Both were recovered unchanged after passage through a trap at -95° as indicated by the i.r. spectra.[25,78] Similarly Me_3GeH and BF_3 (1:2) did not react after 20 hours in the liquid phase.

(b) Reaction of mono-, iodo-, bromo-, or chloro-methylgermanes with lead(II) fluoride: In a typical experiment $MeGeH_2Br$ (0.95 mmol) was passed through a column (type'E') loosely packed with a mixture of glass wool and PbF_2 (ca.20g) at room temperature. After five double passes spectroscopic analysis of the total products indicated that all the bromide had been consumed. The ^1H n.m.r. spectra of the products volatile at -126° and -78° showed the presence of $MeGeH_3$ (ca.0.03 mmol) and fluoro(methyl)germane, $MeGeH_2F$, [ca.0.85 mmol; Found:M,108.1; calc. for $MeGeH_2F$,108.69]. The first order splitting pattern in the ^1H n.m.r. spectrum of the latter was only observed at low temperatures and high dilution when the 'collapsing' of the ^{19}F coupling owing to exchange processes was avoided. In another experiment $MeGeH_2Cl$ (0.70 mmol) was converted to $MeGeH_2F$ (0.42 mmol) after five double passes, although the amount of disproportionation had apparently increased, with $MeGeH_3$ (ca.0.3 mmol) being obtained in the -196° following trap. When $MeGeH_2I$ was used as a starting material, no $MeGeH_3$ was detected in the two double passes needed for complete reaction. By an identical procedure Me_2GeHI (1.20 mmol) was converted to Me_2GeHF [1.15 mmol; Found:M,121; calc. for Me_2GeHF,122.66] after five double passes with no trace of

Me_2GeH_2, although again disproportionation was evident from liquid samples kept at room temperature for extended periods.

In a control experiment two samples of 'pure' $MeGeH_2F$ were sealed up in the liquid phase, one sample being kept at -78° and the other at room temperature. After one week no change was observed in the ^1H n.m.r. spectrum of the 'cold' sample but the 'hot' sample gave additional resonances of 0.35 and 3.45δ ($MeGeH_3$)^{83} and 0.88 and 6.68δ($MeGeHF_2$), (spectra again being recorded on dilute solutions) the disproportionation occurring to the extent of ca.5% as estimated by integration.

(c) Reaction of dibromo(methyl)germane with lead(II) fluoride: Preliminary experiments indicated that $MeGeHI_2$ was an unsuitable starting material due to its low volatility and that very slow conversion occurred with the analagous chloride, $MeGeHCl_2$. In one experiment $MeGeHBr_2$ (ca.1.2 mmol) was passed through the fluorinating column as above. After five double passes Raman spectroscopic examination revealed considerable amounts of residual bromide necessitating repacking of the column. A further five double passes gave pure difluoro(methyl)germane, $MeGeHF_2$ [ca.0.9 mmol; Found:M,122; calc. for $MeGeHF_2$,126.63] condensing in a -78° trap but passing through one at -45°. Traces of $MeGeH_2F$ (<0.1 mmol) but no $MeGeH_3$ were obtained in a -196° following trap, the products being characterised in the first place by the ^1H n.m.r. spectra of dilute solutions. The -45° trap contained traces of a crystalline material which did not liquify at room temperature but which could be readily sublimed around the vacuum line. A gas phase i.r. spectrum of this material indicated that it was probably $MeGeF_3$ although the small quantity did not allow a full characterisation. Liquid samples of $MeGeHF_2$ showed no apparent decomposition after five days in sealed tubes.

(d) Reaction of tribromo(methyl)germane with lead(II) fluoride: Again preliminary experiments showed a very poor conversion using the chloride $MeGeCl_3$, as starting material, inseparable mixtures of fluorochlorides, $MeGeF_nCl_{3-n}$, being indicated by the ^1H n.m.r. spectra. Similarly, the involatility of $MeGeI_3$ (m.pt ca.45°) precluded its use in the gas phase fluorination. Reactions in solvents (n-butyl ether,benzene) although promising at first (from the immediate formation of yellow lead iodide) gave indication of solvent breakdown and a mixture of inseparable products. Reactions of $MeGeBr_3$ by comparison were much more successful. In one experiment, $MeGeBr_3$, (ca.1.1 mmol) was passed through the fluorinating column fitted with U-traps at both ends (see appendix) the initial runs being aided by the occasional application of high vacuum. After ten double passes ^1H n.m.r. examination of the products dissolved in CCl_4 (ca.5%) revealed a broadened resonance at 1.31δ which could not be resolved satisfactorily even at lower temperatures in dilute solution in CS_2. A further five double passes through a freshly packed column gave a volatile material (ca.0.95 mmol) which did not liquify at room temperature but sublimed readily around the vacuum line. This was shown qualitatively from the Raman spectrum to contain no residual bromide and with a gas phase molecular weight determination [Found:M,146; calc. for $MeGeF_3$,144.6] was assumed to be $MeGeF_3$. Tensiometrically pure samples had a sublimation pressure of ca.16 mm Hg at room temperature and melted sharply between 40–42° in sealed tubes, (38.5 given in reference 26). $MeGeF_3$, like GeF_4[84] gave no signs of attacking glass and was apparently stable at room temperature although traces of SiF_4 were observed in some preparations where, presumably, the PbF_2 contained residual moisture. $MeGeF_3$ had only slight solubility in CCl_4, $CHCl_3$ and CS_2 and fumed in moist air.

I.2.5 Reactions of the hydrides with some metal and non-metal halides.

(a) Reaction of methylgermane with trichloro(methyl)germane: $MeGeH_3$ (0.5 mmol) and $MeGeCl_3$ (ca.1.5 mmol) were sealed in a semi-micro n.m.r. tube at -196° and allowed to warm to room temperature. After ca. 2 days the ^1H n.m.r. spectrum of the contents showed that no reaction had occurred with peaks at 1.61δ ($MeGeCl_3$)[79] and 0.30, 3.42δ ($MeGeH_3$)[83] assignable only to the starting materials. After ca. 30 days additional resonances at 0.8, 5.4δ ($MeGeH_2Cl$) and 1.15, 6.8δ ($MeGeHCl_2$) in the approximate ratio 1:1 confirmed a small degree (<5%) of chlorination had occurred. Control experiments in the gas phase (ca.5 hours) gave no indication of reaction. Other experiments where a small amount of $AlCl_3$ catalyst was introduced into the mixtures gave improved conversion to chlorides, ca. 15% (gas phase) and ca.30% (liquid phase) although the latter reactions gave evidence for disproportionation products with additional peaks at 3.1δ (GeH_4);[63] 5.1δ (GeH_3Cl);[63] 0.78, 5.6δ (Me_2GeHCl) and 1.14δ (Me_2GeCl_2)[80] appearing in the ^1H n.m.r. spectra.

(b) Reaction of the hydrides with methyl iodide: 1 mmol samples of GeH_4, $MeGeH_3$ or Me_3GeH and excess MeI (ca.2 mmol) were sealed together in semi-micro n.m.r. tubes with a trace of T.M.S. for reference. Sequential recording of the ^1H n.m.r. spectra showed essentially no reaction had occurred after 1 hour at room temperature. After 2 months no more than 1% conversion to Me_3GeI, (singlet at 0.98δ)[81] had occurred in the Me_3GeH system. Integration of the ^1H n.m.r. spectra showed that only an estimated 5% conversion had occurred in the $MeGeH_3$ system with the resonances assignable to $MeGeH_2I$ (1.1 and 4.7δ) and CH_4 (0.13δ).[85]

In the germane system the estimated 8% of iodogermane and methane produced, (resonances at 3.5δ[63] and 0.13δ), was accompanied by copious amounts of 'metallic' yellow solids. Further monitoring of the reaction in this case was prevented by explosion of the reaction tube.

(c) Reaction of the hydrides with carbon tetrachloride: After prolonged exposure to CCl_4 in sealed tubes samples of the hydridic halogermanes showed signs of both chlorination and exchange reactions. This had also been observed in the $MeSiH_2Cl/CCl_4$ system.[86] To investigate this further and to see if the reactivity was in the Ge-H bond, 1 mmol samples of GeH_4, $MeGeH_3$ or Me_3GeH were sealed in n.m.r. tubes with excess CCl_4 (ca.3 mmol) and a trace of T.M.S. After 1 hour no change was observed in the ^1H n.m.r. spectra showing the comparative unreactivity of the systems. After 3 months ^1H n.m.r. examination revealed no more than a trace of GeH_3Cl (singlet at 5.1δ)[63] in the GeH_4 system, an estimated 10% conversion to $MeGeH_2Cl$ (resonances at 0.8,5.3δ) in the $MeGeH_3$ system, and over 40% formation of Me_3GeCl (singlet at 0.78δ)[81] in the Me_3GeH system. The formation of the chlorides was accompanied in each case by a proportional amount of $CHCl_3$ (singlet at 7.25δ),[87] thus in the Me_3GeH case the integrated intensities of $\delta\underline{Me}_3GeCl:\delta C\underline{H}Cl_3$ were ca. 9:1. The ^1H n.m.r. spectra of halide samples sealed in contact with CCl_4 for extended periods (ie.>7 days) showed a parallel reactivity in the order I > Br > Cl > F, and Me_3 > Me_2 > Me, with both Ge-H bonds and Ge-X bonds reacting. Thus a sample of Me_2GeHBr had undergone 'complete' reaction after 2 months with resonances only attributable to $CHCl_3$ (7.25δ), Me_2GeBr_2 (1.44δ), $Me_2GeBrCl$ (1.33δ), and Me_2GeCl_2 (1.14δ),[79] being observed in the ^1H n.m.r. Thus it was necessary to record the solution spectra of the halides as soon as possible after sealing; the solvent reaction was also arrested by storing the samples at -78°.

(d) Reaction of the hydrides with $TiCl_4$ and PCl_3: 1 mmol samples of $MeGeH_3$ or GeH_4 and a trace of T.M.S. were sealed with a slight excess of $TiCl_4$ or PCl_3 (ca.1.5 mmol in each case) and left at room temperature. Sequential recording of the ^1H n.m.r. spectra of all four systems revealed very slow reactivity. After 2 months the $TiCl_4$ systems were noticeably violet; integration of the ^1H n.m.r. spectra showed only ca. 4% reaction in the GeH_4 system (GeH_3Cl at 5.1δ).[76] Breaking the tubes open on the vacuum line indicated the formation of non-condensable gas (~0.2 mmol). After 1 month no change was observed in either of the PCl_3- hydride reactions. After 2 months both tubes showed yellow deposits with correspondingly small amounts of chlorinated products evident in the ^1H n.m.r. (<5% in both cases). Traces of HCl were observed in the i.r. spectra of the species volatile at -126° when the tubes were reopened on the vacuum line.

I.2.6 Physical properties: The halides are all stable colourless liquids at room temperatures except for $MeGeI_3$ (pale yellow solid, m.pt.45°) and $MeGeF_3$ (colourless solid,m.pt.42°). The compounds are amenable to storage for short periods in sealed glass tubes, although disproportionation leading to the deposition of polygermanes, e.g. $(MeGeH)_n$, occurs on prolonged standing. The volatility of the compounds makes them ideally suited to vacuum line handling, although prolonged exposure to manometer mercury and hydrocarbon grease is undesirable. The fluorides are particularly sensitive to traces of moisture when they will even attack pyrex glass to liberate SiF_4; the fluorides also have a marked tendency to sublime rather than distil around the vacuum line.

(Table I.1) Physical data for the halides

Compound	Vapour pressure eqn. Log ρ(mm) =	Range (°C)	ΔH_{vap} (cal mole^{-1})	b.pt. (extrap)	m.pt. (°C)	Trouton's constant[e]
$MeGeH_2Cl$	$7.53 - 1560/T$	-40,+21	7131	62	-100	21.3
Me_2GeHCl	$7.33 - 1614/T$	-28,+29	7382	89	-74	20.4
$MeGeHCl_2$[a]	$7.55 - 1800/T$	-10,+30	8250	112	-61	21.4
$MeGeH_2Br$	$6.4 - 1330/T$	-42,+19[b]	6071	102	-83	16.2
Me_2GeHBr	$6.6 - 1500/T$	-20,+23	6864	131	-	17.0
$MeGeHBr_2$	v.p. $\simeq$ 13mm Hg[c]	20°	-	-	-	-
$MeGeH_2I$	$8.3 - 2044/T$	-20,+18[b]	9353	104	-72	24.8
Me_2GeHI	$6.2 - 1509/T$	-8,+34	6905	175	-	15.4
$MeGeHI_2$	v.p. $\simeq$ 3mm Hg[c]	20°	-	-	-	-
$MeGeH_2F$	$6.95 - 1339/T$	-45, -1[b]	6127	56	-46	18.6
Me_2GeHF	$7.98 - 1715/T$	-21,+21	7847	63	-31	23.3
$MeGeHF_2$	v.p. $\simeq$ 52mm Hg[c]	0°	-	-	-	-
$MeGeF_3$	subl. p. $\simeq$ 16mm Hg[c]	23°	-	96.5[d]	+42	-

a. ref.53; b. sample showed signs of decomposition; c. vapour pressure relationship not measured; d. ref.26 (obtained directly at 751mm); e. ΔS vap in cal deg^{-1} mole^{-1}

Physical data for the halides are given in Table I.1. The vapour pressure measurements for the chlorides were obtained in different temperature ranges from those reported.[52] For the monomethyl derivatives, $MeGeH_2X$ (X = F,Br,I) signs of decomposition were apparent after contact with mercury in the vapour pressure apparatus; the dimethyl species, Me_2GeHX (X = F,Cl,Br,I), were apparently unaffected so the data are believed to be more reliable. The boiling points were obtained by extrapolation from plots of log ρ vs. 1/T.

I.3 DISCUSSION

To provide a framework on which to discuss the reactivity of the methyl-substituted germanes it would be useful to know the polarities and electron-distribution in the various bonds as these undoubtedly have a strong influence on the modes of reaction. The interpretation of physical data in terms of electronegativity scales has caused much controversy, particularly for the Group IV elements.[88] Pritchard and Skinner[89] have pointed out that the electronegativity of an element is influenced by its molecular environment in such a variety of ways as to preclude exact measurement. This is a rationale for the disparity of values appearing in the literature. Most scales[88-92] place carbon as the most electronegative of the Group IV elements (e.g. C,2.45; Si,1.95; Ge,2.20; Sn,2.10)[92] whilst the halogens are usually given higher values (e.g. F,3.90; Cl,3.15; Br,2.95; I,2.65).[91] It is unwise to assign any particular electronegativity value to hydrogen but a value close to or slightly greater than that for germanium seems reasonable for H bonded to a Group IV el[illegible]nt.[88-92] If carbon and hydrogen may be assumed negative with respect to germanium then in the system C-Ge-H, germanium should be a centre for nucleophilic attack and Ge-H should be nucleophilic.

This assumption is largely confirmed by an examination of the experimental bond moments,[93,94] e.g. Ge-H, 1.0D; Ge-C, 0.7D; ($Ge-CH_3$, 0.3D); H-C, 0.4D; Ge-Cl, 3.1D; Ge-Br, 3.0D; Ge-I, 2.8D (the positive end of the dipole is to the left). These indicate that Ge-H and Ge-C bonds are weakly polar so that perturbations (e.g. the presence of electronegative groups on germanium) may cause a reversal, indeed every indication is that in $GeHCl_3$ the bond polarity is reversed, ie. $\overset{\delta-}{Ge}-\overset{\delta+}{H}$.

Unlike carbon, silicon and germanium may both be considered to have low lying d-orbitals suitable for π-bonding with ligand orbitals of the correct symmetry.[8] The presence of [p→d] π-bonding in silicon chemistry has been invoked to describe certain structural features, e.g. the planarity of $(SiH_3)_3N$,[95] but its presence is considered even more controversial in germanium chemistry.[8] Another facet of the 'availability' of d-orbitals is the possibility of increased coordination about germanium such that concerted reaction mechanisms and low activation energies are likely.[96,97]

Another useful approach to assist in the understanding of the various syntheses comes from an estimation of enthalpies of reactions from bond energy data[98] (Table I.2). This approach is subject to the criticism that it excludes the entropy term which is necessary in the evaluation of the free energy change in the reaction. For reactions involving covalent gaseous molecules at normal temperatures the entropy term is usually dominated by the enthalpy term, this being particularly true when equal numbers of bonds are involved in both reactants and products. Under these circumstances the estimated enthalpy (Table I.3) may give a good indication of the free energy change for a particular reaction.

(Table 1.2) Selected mean thermochemical bond energies*

Electropositive atom, M	Energy of M–X bond (Kcal mole^{-1}) H	F	Cl	Br	I	Compound
H	104	135	103	87.5	71.5	HX
C	125	116	78	68	51	CX_4
Si	77	139	93.5	74	56	SiX_4
Ge	69	111	82	66	51	GeX_4
B	†	154	106	88	65	BX_3
P	77	117	76	63	44	PX_3
X	104	38	58	46	36	X_2

*Taken in part from ref. 98 and converted to Kcal mole^{-1}; data refer to average energy of one M–X bond; † B–H is 91.5; B–H–B is 105. In addition: C–C, 83 (C_2H_6); Si–Si, 46 (Si_2H_6); Ge–Ge, 38 (Ge_2H_6); Si–C, 72 ($SiMe_4$); Ge–C, 61 ($GeMe_4$).

(Table 1.3) Estimated enthalpies for some reactions involving germanium–hydrogen and germanium–halogen bonds

Reaction	$-\Delta H_{calc.}$ (Kcal mole^{-1})* Cl	Br	I	Rates**
a. GeH + X_2 → GeX + HX	58	38.5	17.5	Fast†
b. 2GeH + X_2 → 2GeX + H_2	72	24	32	Fast
c. GeC + X_2 → GeX + CX	11	27	−3	n.o.
d. CH + X_2 → CX + HX	−2	−15.5	−38.5	n.o.
e. GeH + HX → GeX + H_2	14	13.5	14.5	v.slow
f. 6GeH + $2BX_3$ → 6GeX + B_2H_6	16	10	78	Fast†
g. 3GeH + PX_3 → 3GeX + PH_3	42	33	45	v.slow
h. GeH + CX → GeX + CH	60	33	56	v.slow
i. GeF + HX → GeX + HF	3	2.5	3.5	v.fast¶
j. GeCl + HX → GeX + HCl	–	−0.5	0.5}	
k. GeBr + HX → GeX + HBr	–	–	1.0	

* calculated from bond energy data given in Table I.2; ** *ca.* room temperature; † below −45°; ¶ For $GeH_3Cl + HI = GeH_3I + HCl$, K = 2600 at +30°[80]

For the halide exchange reaction (i-k) ΔH is apparently very small and the equilibrium constant, K, is probably controlled by the entropy term. However, the rates of such interconversions are known to be high. Of interest is that some of the systems (c,e,g,h) have appreciable changes in enthalpy but in fact the reactions are not observed to any extent at room temperature. However, in the presence of a catalyst (c,e) or at reflux temperatures (h) significant rates of reaction have been observed so that these appear to be kinetically controlled reactions which undoubtedly have high activation energies. Furthermore the thermodynamic approach confirms the observed[56] reactivity of germane with BCl_3 ($\Delta H_{calc.} = -16$ Kcal mole^{-1}) and predicts a greater change in enthalpy for the corresponding silane reaction ($\Delta H_{calc.} = -39$ Kcal mole^{-1}); the available experimental evidence for the latter suggested that no reaction occurs in the gas phase at 0°[99] (see section I.3.3); this again may indicate an unusually high energy barrier. Further attention will be given to the question of reactivity in the following discussion of the observed reactions of the methylgermanes.

I.3.1 Reactions with free halogen.

The methylgermanes react with bromine or iodine with the replacement of hydrogen attached to germanium and liberation of the corresponding hydrogen halide, reactions [16].

$$\left.\begin{array}{l} MeGeH_3 + X_2 \longrightarrow MeGeH_2X + HX \quad [16a] \\ MeGeH_2X + X_2 \longrightarrow MeGeHX_2 + HX \quad [16b] \end{array}\right\} (X = Br, I)$$

The reaction with chlorine has not been reported for germane but is undoubtedly very vigorous ($\Delta H_{calc.} = -58$ Kcal mole^{-1}). Even under the mildest conditions it is difficult to achieve monobromination with bromine although no C-Ge bond cleavage is observed as might be expected from the estimated enthalpies (Table I.3). Iodination, by comparison, is more moderate so that halogenation may be controlled so as to replace only one hydrogen in methyl- or dimethyl-germane at lower temperatures.

It has been suggested[10] that in the gas phase the reaction with bromine probably takes place, as in the case of the corresponding silanes,[100] by means of a substantially non-polar four-centre reaction, Fig.I.1. In place of the weakly polarised Ge-H bond ($\overset{\delta+}{\mathrm{Ge}}-\overset{\delta-}{\mathrm{H}}$; electronegativities: Ge,2.02; H,2.20 Pauling units[90]), a substantially more strongly polarised Ge-X bond is formed ($\overset{\delta+}{\mathrm{Ge}}-\overset{\delta-}{\mathrm{X}}$; electronegativities: F,3.90; Cl,3.15; Br,2.95; I,2.65).[91]

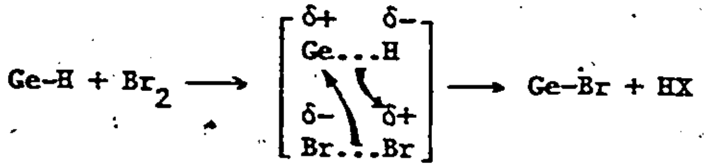


Fig.I.1 Proposed mechanism for the gas phase bromination of germanium hydrides

In the liquid phase, as in the iodine reactions at -63°, the replacement probably takes place, as postulated for the silanes,[101] by a polar reaction mechanism, Fig.I.2. In this case electrophilic attack of the halogen on the hydrogen atom is followed by nucleophilic attack of more halogen on the germanium atom. This type of mechanism is supported by the fact that the reaction of GeH_4 with iodine takes place in the polar GeH_3I substantially faster than in the gas phase.[42,43] In addition the reaction of liquid germane with iodine* under pressure in sealed tubes can also give excellent yields (ca.80%) of GeH_3I com-

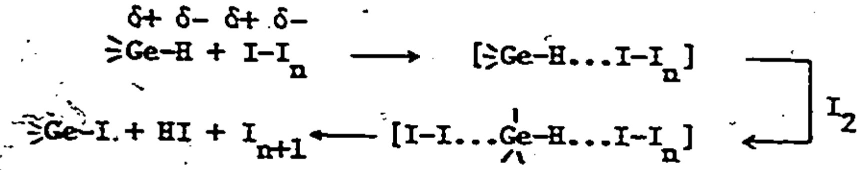


Fig.I.2 Proposed mechanism for the liquid phase iodination of germanium hydrides.
(n = undetermined; n = 3 in the SiH_4 reaction)

---

* See Appendix 2

pared to the comparable gas phase results.

Some deviation from the 'normal' mechanism apparently occurs in the reaction of trimethylgermane, Me_3GeH, with iodine in the condensed phase above -30°. A violent exothermic reaction occurs in which substantial amounts of hydrogen are formed together with the expected Me_3GeI and HI, and the yield based on iodine consumed often exceeds 170% (ca. 95% based on Me_3GeH). In this case the 'normal' reaction may be accompanied by the spontaneous dissociation of hydrogen iodide to hydrogen and more iodine, reactions [17].

$$Me_3GeH + I_2 \longrightarrow Me_3GeI + HI \qquad [17a]$$

$$2HI \rightleftharpoons H_2 + I_2 \qquad [17b]$$

The mechanism is undoubtedly more complex although it may be speculated that an autocatalysis is involved where hydrogen iodide acts as the halogenating agent.

For the reaction of iodine with the methylgermanes it is now clear that more stringent conditions are required as the methyl substitution decreases which may tentatively be attributed to a weakening of the Ge-H bond in the order $GeH_4 > MeGeH_3 > Me_2GeH_2 > Me_3GeH$. This will be discussed further in connection with the vibrational spectra (Chapter IV.5).

I.3.2 Reactions with hydrogen-halide.

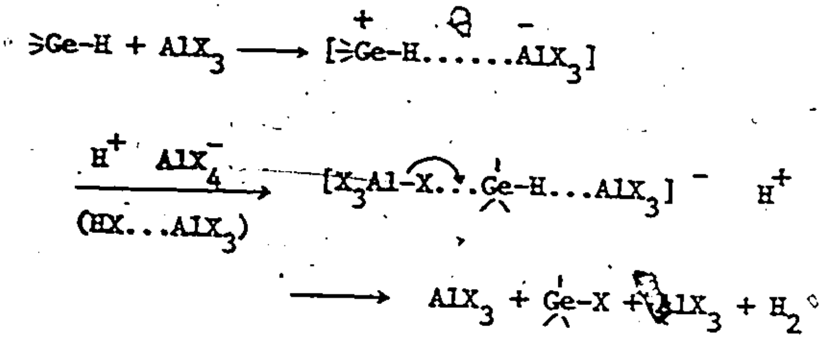
Hydrogen halide-aluminium trihalide catalysed gas phase reactions, which were useful in the preparation of halogeno-monogermanes[50,41,45,51], work efficiently with the methylgermanes, reactions [18], providing

$$\left.\begin{array}{l} MeGeH_3 + HX \\ MeGeH_2X + HX \\ MeGeHX_2 + HX \end{array}\right] \xrightarrow[X\,=\,Cl,Br,I]{AlX_3} \left[\begin{array}{ll} MeGeH_2X + H_2 & [18a] \\ MeGeHX_2 + H_2 & [18b] \\ MeGeX_3 + H_2 & [18c] \end{array}\right.$$

useful routes to the mono- and di-chlorides, -bromides, and -iodides.

By contrast, the Ge-Ge bond in digermane was cleaved by hydrogen chloride-aluminium chloride.[45] With larger amounts of HX and higher reaction temperatures increased yields of the di- and tri-halides [18b, 18c] are accompanied by the formation of disproportionation products and probably catalyst deactivation, as proposed for the analagous reaction with germane.[14] This is not surprising in view of the fact that $AlCl_3$ has been used to catalyse the redistribution of alkyl-germanes and -halides[17,18] where the formation of intermediate aluminium-alkyls has been suggested.[68]

A polar reaction mechanism (Fig.I.3) has been postulated:[10]



$$\geqslant Ge{-}H + AlX_3 \longrightarrow [\overset{+}{\geqslant Ge}{-}H\ldots\ldots\overset{-}{AlX_3}]$$

$$\xrightarrow[(HX\ldots AlX_3)]{H^+\ AlX_4^-} [X_3Al{-}X\ldots Ge{-}H\ldots AlX_3]^- \quad H^+$$

$$\longrightarrow AlX_3 + Ge{-}X + AlX_3 + H_2$$

Fig.I.3 Proposed reaction mechanism for the aluminium trihalide catalysed halogenation of germanes by hydrogen halide.

Confirmation of this may come from kinetic measurements, yet to be obtained, which in turn could determine whether the rate-determining step is the nucleophilic attack of AlX_4^- on germanium or the electrophilic attack of AlX_3 on hydrogen.

I.3.3 Reactions with boron trihalide.

The reactivity of boron trihalides towards Group IV halides is now well established. Boron trichloride is reduced by Si_2H_6,[99] Si_3H_8,[102] CH_3SiH_3,[103] but not SiH_4,[99] and boron tribromide is reduced by both SiH_4 and Si_2H_8.[104] Preliminary studies indicated that germane could be halogenated by boron tri-chloride and -bromide[56] although the yields were low. The corresponding reaction of BCl_3 with digermane[57] gave some Ge_2H_5Cl but there was considerable decomposition to monogermyl species. By contrast there is no cleavage of the C-Ge bond when the methylgermanes react with boron tri-chloride, -bromide, or -iodide which are quantitatively reduced to diborane, reactions [19]. The relative

$$\left.\begin{array}{l}6MeGeH_3 + 2BX_3\\ 3MeGeH_3 + 2BX_3\\ 2MeGeH_3 + 2BX_3\end{array}\right]\xrightarrow{X = Cl,Br,I}\left[\begin{array}{l}MeGeHX_2 + B_2H_6\\ 3MeGeHX_2 + B_2H_6\\ 2MeGeX_3 + B_2H_6\end{array}\right.\qquad\begin{array}{r}[19a]\\ [19b]\\ [19c]\end{array}$$

yields of the halogeno-derivatives can be altered by varying the reactant ratio so that increased amounts of BX_3 give markedly improved yields of di- and tri-halogeno(methyl)germanes (this is idealised in reactions [19]). By comparison boron trifluoride does not fluorinate the methylgermanes; this is not surprising in view of its inertness to other simple or mixed Group IV hydrides.[45,105]

Using the same conditions for the reaction of germane with BBr_3 good yields of monobromogermane are obtained with only traces of dibromogermane; diborane is again recovered almost quantitatively, reaction [20]. In a corresponding reaction of germane with BCl_3 low

$$6GeH_4 + 2BBr_3 \longrightarrow 6GeH_3Br + B_2H_6 \qquad [20]$$

yields of chlorogermane were accompanied by poly-chlorinated species and disproportionation, although further work is needed to clarify the products. It does, however, indicate a reactivity which is apparently not shown by silane.[99]

The reactions undoubtedly involve complex equilibria and this is supported by the identification of partially reduced species, BH_nCl_{3-n}, in some of the incomplete reactions, such as those in the gas phase. It is also worth emphasising that sealed tube reactions gave poor conversions, suggesting that one step at least in the equilibria may be pressure dependent. The first step in the reduction may give rise to dichloroborane, reaction [21]. Further chlorination of the chloro(methyl)germane may then occur with complete reduction of the

$$MeGeH_3 + BCl_3 \rightleftharpoons MeGeH_2Cl + BHCl_2 \qquad [21]$$

dichloroborane to diborane. The situation is certainly not as simple as this since BH_nCl_{3-n} species are known to undergo rapid disproportionation,[77] this being particularly true of monochloroborane, reaction [22]. This is further supported by the experimental observation that

$$3BH_2Cl \rightleftharpoons B_2H_5Cl + BHCl_2 \rightleftharpoons B_2H_6 + BCl_3 \qquad [22]$$

diborane reacts with chloro(methyl)germane to produce some methylgermane, reaction [23].

$$B_2H_6 + MeGeH_2Cl \rightleftharpoons MeGeH_3 + \underset{\text{unstable}}{[B_2H_5Cl]} \qquad [23]$$

In view of these observations, any reaction mechanism would be highly speculative. However the initial step presumably involves either the electrophilic attack of boron on hydrogen or the nucleophilic attack of halogen on germanium. In either case a four centre mechanism (Fig.1.4) could be involved where vacant germanium d-orbitals overlap with filled

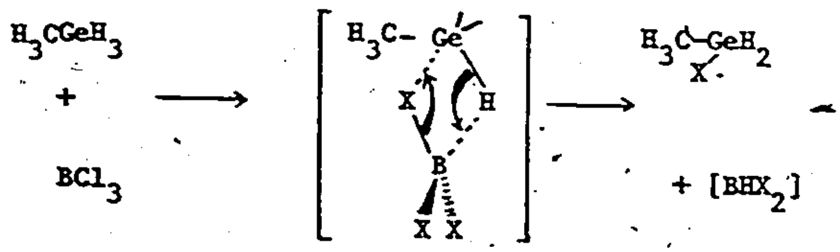


Fig.1.4 Proposed mechanism for the reaction of germanes with boron trihalides.

halogen p-orbitals.

The reactivity of the boron trihalides (ie. the nucleophilicity of the halogen or electrophilicity of the BX_3 moiety) is complicated by the different [p→p]π-interactions between the boron atom and the attached halogens. BCl_3, BBr_3, and BI_3 all have the same apparent reactivity and this is largely supported by the enthalpy calculations ($\Delta H = -16, -10$ and -78 Kcal $mole^{-1}$, respectively). The unreactivity of BF_3 is not surprising in view of the calculated enthalpy change ($\Delta H = +98$ Kcal $mole^{-1}$). It is interesting to note, however, the BF_3 is effective in cleaving siloxane[106] and germoxane[53] linkages.

I.3.4 Reactions with thionyl halide.

The usefulness of thionyl halides is shown by methylgermane reacting with SOX_2 (X = Cl,Br) to give exclusively the monohalides according to reaction [24]:

$$2MeGeH_3 + 2SOX_2 \xrightarrow[\text{liq.}]{(X = Cl,Br)} 2MeGeH_2X + SO_2 + S + 2HX \qquad [24]$$

Preliminary experiments indicate that the corresponding reaction of germane with thionyl bromide may also be useful in the direct synthesis of monobromogermane*, reaction [25]: The volatile products from these

$$2GeH_4 + 2SOBr_2 \longrightarrow 2GeH_3Br + SO_2 + S + 2HX \qquad [25]$$

reactions, ie. germyl halide, sulphur dioxide and hydrogen halides are easily separated by conventional trap to trap techniques; thionyl halides, however, rapidly attack hydrocarbon grease and mercury making their handling in the vacuum line somewhat inconvenient.

The reason for these reactions stopping at the mono-substitution product is not clear; the presence of a halogen attached to germanium is expected to affect the Ge-H bond polarity and reduce the nucleophilic (hydridic) nature of Ge-H. This argument would be reasonable if the nucleophilic attack of Ge-H on sulphur were important and would explain the observed behaviour (case 1,Fig.I.5). However, the halogen attached

---

* High yields of GeH_3Br are obtained by few direct methods[41,45]

to germanium is also nucleophilic and may actually override the weak nucleophilicity of the Ge-H such that it shields the rest of the molecule from further attack (case 2). An exchange reaction between chlorogermane and thionyl bromide may clarify this point.

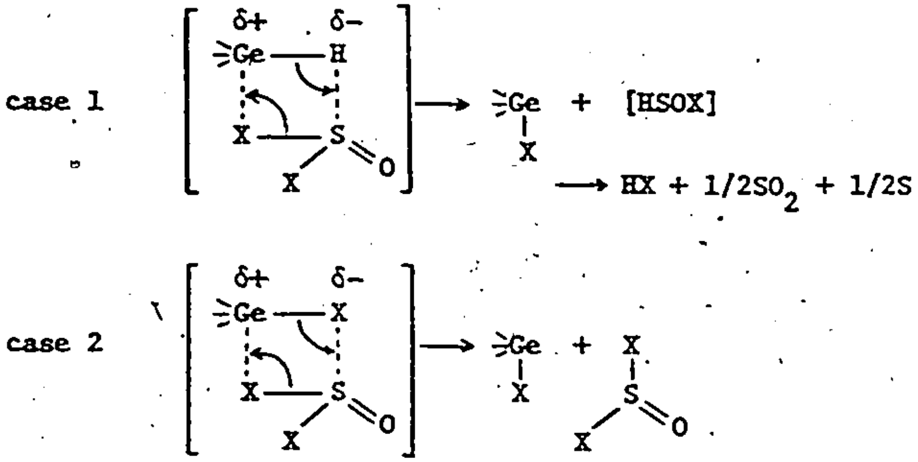


Fig.I.5 Proposed mechanism for the reaction of germanes with thionyl halides.

I.3.5. Reactions with some metal and non-metal halides.

Carbon tetrachloride, titanium tetrachloride, phosporus trichloride, and methyl iodide all have only slight halogenating action on germane and the methylgermanes in sealed tubes. Even for the most reactive system (ie. $Me_3GeH + CCl_4$) no more than 10% conversion to chloride occurs after ca.30 days so that the room temperature reactions are of little synthetic importance. The probable reactions are given for selected systems, reactions [26]:

$$Me_3GeH + CCl_4 \longrightarrow Me_3GeCl + CHCl_3 \qquad [26a]$$

$$MeGeH_3 + TiCl_4 \xrightarrow{?} MeGeH_2Cl + TiCl_3 + TiCl_2 + H_2 \qquad [26b]$$

$$GeH_4 + PCl_3 \xrightarrow{?} GeH_3Cl + (PHCl)_n + HCl \qquad [26c]$$

$$MeGeH_3 + CH_3I \longrightarrow MeGeH_2I + CH_4 \qquad [26d]$$

Chloroform is readily identified in the carbon tetrachloride reactions

[26a] and the lowering of the oxidation state of titanium [26b] is indicated by the characteristic violet colour of Ti(III) and the evolution of hydrogen. The small amounts of chlorinated germane obtained in the PCl_3 reactions [26c] are accompanied by the formation of additional products probably resulting from the decomposition of the initially formed PH_nCl_{3-n} species.[107] For the reactions with methyl iodide [26d] methane is obtained with small amounts of iodinated products, although in the GeH_4 system copious amounts of yellow solids, probably polymeric germanium hydride $(GeH_2)_n$, were also produced. Enthalpy calculations (Table I.2) indicate that reactions [26a], [26c], and [26d] should all proceed so the lack of reactivity may be due to unusually high activation energy barriers.

The reaction between trichloro(methyl)germane and methylgermane [27] was carried out to check the usefulness of the redistribution reactions

$$MeGeCl_3 + MeGeH_3 \longrightarrow MeGeH_2Cl + MeGeHCl_2 \qquad [27]$$

previously reported[17,18] for some higher alkylgermanes. However, the extended liquid-phase reaction times required to observe any significant product formation lead to competing redistribution reactions where dimethylgermanes are also produced, this being particularly pronounced when $AlCl_3$ is introduced as a catalyst. Cleavage of the carbon-germanium bond probably proceeds via the formation of aluminium-alkyls as was suggested earlier in the hydrogen halide-aluminium trihalide reactions.[68]

I.3.6 Halide exchange reactions

The results from this study confirm the usefulness of exchange reactions for the interconversion of halides bound to germanium with lead(II) fluoride or hydrogen halides. Mono- or di-chloro-, bromo-, or iodo-derivatives are converted into the corresponding fluorides by interaction with lead(II) fluoride at room temperature, reactions [28].

$$\text{e.g.}\quad \left.\begin{array}{l} MeGeH_2X \\ MeGeHX_2 \\ Me_2GeHX \end{array}\right] \xrightarrow[X\,=\,Cl,Br,I]{PbF_2} \left[\begin{array}{ll} MeGeH_2F & [28a] \\ MeGeHF_2 & [28b] \\ Me_2GeHF & [28c] \end{array}\right.$$

The best yields are obtained with the iodo-derivatives where presumably the 'soft' iodine, in the Pearson sense,[108] has a greater affinity for the 'soft' lead than does the 'hard' fluorine:

$$\text{viz.}\quad \overset{h\ \ s}{Ge{-}I} + \overset{s\ \ h}{Pb{-}F} \longrightarrow \overset{h\ \ h}{Ge{-}F} + \overset{s\ \ s}{Pb{-}I}$$

(where h = 'hard', s = 'soft')

Estimations of the enthalpies for the conversion of one halogen gives -27,-28, and -32 Kcal mole^{-1} for Ge-Cl, Ge-Br, Ge-I bonds, respectively, indicating again that the entropy term may be important in the free energy change.

It should be noted here that the fluorogermanes are particularly sensitive to traces of moisture and other impurities[71] which probably explains the apparent lack of stability reported[19] for $C_2H_5GeH_2F$. The disproportionation of GeH_3F to GeH_2F_2 and GeH_4 was rapid at room temperature[67] and evidence for similar disproportionations for mono- and difluoro species is obtained in this study, reactions [29].

$$2\ MeGeH_2F \rightleftharpoons MeGeHF_2 + MeGeH_3\ \text{(liq)} \qquad [29a]$$

$$2\ MeGeHF_2 \rightleftharpoons MeGeH_2F + MeGeF_3\ \text{(gas)} \qquad [29b]$$

The vibrational spectra* show a definite increase in the Ge-F stretching frequency from mono- to trifluoride and with the corresponding increase in the Ge-F stretch force-constants[109] suggest stronger Ge-F bonds as the number of such bonds in a molecule increases.

---

* see Chapters III and IV.

Quantitative conversions to bromo- and iodo-derivatives were obtained by treating the chlorides or bromides with the appropriate hydrogen halide according to reactions [30]. In contrast to the 'heavy-metal' salt

e.g.

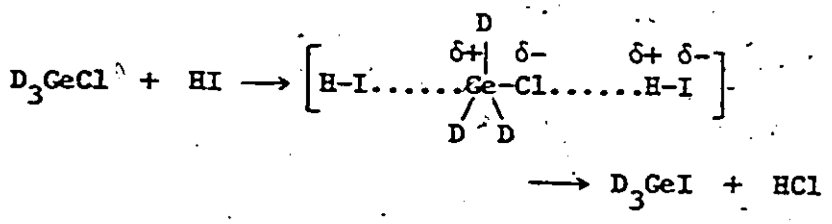
$$\left.\begin{aligned} &MeGeH_2Cl + HX \longrightarrow MeGeH_2X + HCl && [30a]\\ &MeGeHCl_2 + 2HX \longrightarrow MeGeHX_2 + 2HCl && [30b]\\ &MeGeCl_3 + 3HX \longrightarrow MeGeX_3 + 3HCl && [30c] \end{aligned}\right\} X = Br, I$$

conversion this type of conversion may be explained in terms of the greater affinity of the 'soft' iodine (bromine) for the 'soft' germanium over the 'hard' hydrogen. The estimated enthalpy changes in these reactions are very small so that they are considered entropy-controlled

viz $$\overset{s\ \ h}{Ge{-}Cl} + \overset{h\ \ s}{H{-}I} \longrightarrow \overset{s\ \ s}{Ge{-}I} + \overset{h\ \ h}{H{-}Cl}$$

reactions .

Some indication of the mechanism for the reactions is given by the lack of hydrogen-deuterium exchange in the reaction of $[^2H_3]$ chlorogermane with hydrogen iodide, reaction [31]; germanium is therefore unlikely to



$$D_3GeCl + HI \longrightarrow \left[H{-}I\cdots\cdots\overset{\overset{D}{|}\,\delta+\ \ \delta-}{\underset{D\ \ D}{Ge}}{-}Cl\cdots\cdots\overset{\delta+\ \delta-}{H{-}I}\right] \longrightarrow D_3GeI + HCl \qquad [31]$$

have any interaction with the proton of hydrogen iodide in the transition state which would be achieved in the polar mechanism suggested above.

I.4 MASS SPECTRA

The observation of 'parent' peaks in the expected m/e ranges for the chloride, bromide, and iodide species confirms the molecular weight determinations and the a priori assignment of the ^1H n.m.r. spectra (chapter II). However, the data are inconclusive for the fluorides as no fluorine-containing fragments were observed under the experimental conditions at the ionising potential of 70eV; in these systems peaks attributable only to molecular breakdown products (ie. H_nGe^+ and H_nCGe^+) were identified.

(Table I.4) Observed mass spectral parent peaks for the halides

Parent	Cl		Br		I	
fragment*	Obs.m/e	M.W.†	Obs.m/e	M.W.	Obs.m/e	M.W
H_nCGeX	119-127	125.15	166-174	169.60	209-218	216.60
H_nC_2GeX	135-142	139.11	176-186	183.57	227-234	230.57
H_nCGeX_2	156-166	159.54	244-254	248.44	340-346	342.44
$H_nC_2GeX_2$	171-181	173.56	258-266	262.46	354-358	356.47
H_nCGeX_3	190-202	193.98	322-334	327.34	n.o.¶	468.35

* not observed for X = F; † calculated molecular weight;
¶ compound involatile at room temperature

Problems of halogen exchange either in the inlet system or analyser chamber of the mass spectrometer (AEI MS10c2) caused a lack of confidence in the quantitative nature of much of the data. The purity of the samples was established unequivocally by the ^1H n.m.r. spectra allowing the possibility of sample impurity to be rejected. Analysis of the (H_nGe^+) and (H_nCGe^+) fragments in some spectra revealed 'abnormal' splitting patterns which could be rationalised by the presence of $MeGeH_3$, presumably arising from disproportionation. For this reason the intensity data in most cases are thought to have little significance and are not reported. However, it was possible to identify characteristic fragments resulting from molecular breakdown at the ionising potential of 70eV apparently arising from loss of halogen, carbon, or both. These were consistently observed at: m/e 70-77 (H_nGe^+); m/e 83-93 (H_nCGe^+);

(Table 1.5) The mass spectrum of methylgermane, $MeGeH_3$

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
70	32.5	H_nGe^+ (n = 0,1,2,3)	83	5.8	H_nCGe^+ (n = 1,2,3,4,5)
71	12.9		84	10.0	
72	69.1		85	29.2	
73	41.3		86	40.0	
74	100.0		87	72.5	
75	48.3		88	57.5	
76	65.0		89	93.3	
77	26.3		90	62.1	
78	10.4		91	67.1	
79	4.6		92	11.3	
			93	11.9	

(Table 1.6 The mass spectrum of trichloro(methyl)germane, $MeGeCl_3$

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
70	3.9	$(^{70}Ge^+ - ^{76}Ge^+)$	140	1.8	$GeCl_2^+$
72	5.3		142	3.9	
73	1.5		144	5.5	
74	7.4		146	3.3	
76	1.5		155	34.9	$H_nCGeCl_2^+$ (n = 3)
82	0.5	H_nCGe^+ (n = 0,1,2,3)	157	72.8	
83	1.9		158	16.4	
84	1.1		159	100.0	
85	2.1		160	11.2	
86	2.0		161	62.5	
87	3.1		163	16.2	
88	2.3		165	1.5	
89	2.1		175	15.1	$GeCl_3^+$
91	0.4		177	35.7	
105	15.4	$GeCl^+$	178	6.1	
107	24.3		179	52.9	
108	6.1		180	5.5	
109	34.0		181	40.1	
110	2.2		183	15.3	
111	15.8		185	2.6	
113	1.8		190	4.2	$H_nCGeCl_3^+$ (n = 3)
119	0.3	H_nCGeCl^+ (n = 2,3)	192	9.7	
120	0.4		193	1.5	
121	0.7		194	14.3	
122	0.5		195	1.7	
123	1.5		196	10.8	
124	1.5		198	3.9	
125	1.5				
126	0.7				

(Table 1.7) The mass spectrum of monochloro(methyl)germane, $MeGeH_2Cl$

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
70	18.7	H_nGe^+ (n = 0,1,2)	105	13.5	H_nGeCl^+ (n = 0,1,2)
71	12.8		106	6.8	
72	26.5		107	30.1	
73	51.7		108	17.5	
74	42.6		109	47.6	
75	25.4		110	22.3	
76	10.2		111	31.1	
77	9.1		112	6.8	
			113	6.8	
83	3.1	H_nCGe^+ (n = 1,2,3,4,5)	119	1.9	H_nCGeCl^+ (n = 2,3,4,5)
84	8.1		120	2.9	
85	26.0		121	18.4	
86	26.5		122	6.8	
87	77.0		123	31.1	
88	43.5		124	14.6	
89	100.0		125	36.9	
90	48.1		126	5.8	
91	77.2		127	14.6	
92	6.9				
93	18.1				

(Table 1.8) The mass spectrum of monoiodo(methyl)germane, $MeGeH_2I$

m/e	Relative Intensity	Assignment	m/e	Relative Intensity	Assignment
70	15.0	H_nGe^+ (n = 0,1,2)	127	15.9	$^{127}I^+$
71	5.5		128	9.9	$H^{127}I^+$
72	20.1				
73	30.2		197	30.2	H_nGeI^+ (n = 0,1,2)
74	30.0		198	7.9	
75	10.3		199	49.8	
76	7.3		200	22.3	
77	2.6		201	68.5	
			202	16.3	
83	4.0	H_nCGe^+ (n = 1,2,3,4,5)	203	27.3	
84	6.4				
85	20.9		209	1.0	H_nCGeI^+ (n = 0,1,2,3,4,5)
86	20.5		210	3.5	
87	70.7		211	6.5	
88	32.2		212	61.0	
89	94.9		213	11.0	
90	39.2		214	82.0	
91	82.2		215	33.0	
92	6.4		216	100.0	
93	17.3		217	?	
			218	23.0	

m/e 96–108 ($H_nC_2Ge^+$); m/e 105–113 (H_nGeCl^+); m/e 149–159 (H_nGeBr^+); m/e 197–203 (H_nGeI^+); m/e 140–149 ($H_nGeCl_2^+$); m/e 228–334 ($H_nGeBr_2^+$); m/e 324–330 ($H_nGeI_2^+$). For the parent hydride $MeGeH_3$, the trihalide $MeGeCl_3$, and the monohalides $MeGeH_2Cl$, $MeGeH_2I$, the spectra are considered to be unperturbed and are reported in full (Tables I.5–8); the intensities are reported relative to the most abundant fragment as 100%, and the assignments have been generalised into 'monoisotopic' ion-groups.

Extensive discussion must await further studies of appearance potentials and metastables on higher resolution equipment but a few points of speculation arise from the existing data. The polyisotopic nature of germanium leads to complicated spectra but the observed distribution and intensities may be correlated with the known abundances of germanium (Table I.9).

(Table I.9) Mass and abundances of germanium isotopes*

Isotope	mass (^{12}C)	% Abundance
^{70}Ge	69.924277	20.56
^{72}Ge	71.921740	27.42
^{73}Ge	72.923360	7.79
^{74}Ge	73.921150	36.47
^{76}Ge	75.921360	7.76

* ref.9

The absence of hydrocarbon fragment ions indicates that fragmentation leaves the electron deficiency on the germanium-containing fragment, as might be expected from the relative electronegativities of carbon and germanium. Furthermore the analysis of complex polyisotopic fragments gives an indication of the percentage ion current carried by the individual monoisotopic fragment-ions.

In the methylgermane spectrum (Table I.5) detailed analysis shows that the molecular ion $CH_3GeH_3^+$ is not present in any detectable amount. This appears to be a common feature in the mass spectra of organogermanes.[291] Similarly the ion $CH_3SiH_3^+$ has a very low abundance in methylsilane.[292] The range m/e 83-93 contains ions resulting from the stripping of hydrogen from the skeleton, ie. H_nCGe^+ (n = 1,2,3,4,5); the gradual fall off in intensity with decreasing hydrogen content (Table I.10) may indicate a step-wise process. The range m/e 70-79 contains the ions H_nGe^+ (n = 0,1,2,3) resulting from Ge-C bond cleavage. The ion H_3Ge^+ constitutes only 7% of the total ion yield which suggests methyl radical loss is not favourable. The ions H_2Ge^+, HGe^+, and Ge^+ may arise from simultaneous removal of more than one group bonded to germanium, as proposed for the analogous methylsilane.[292]

(Table I.10) Comparison of monoisotopic mass spectra for $MeSiH_3$ and $MeGeH_3$

Ion	Relative abundance*	
	Si†	Ge
M^+	8.03	18.5
MH^+	2.98	7.6
MH_2^+	6.92	14.7
MH_3^+	3.64	6.6
CH^+	0.66	n.o.
CHM^+	3.87	3.2
CH_2M^+	5.68	5.3
CH_3M^+	13.94	11.6
CH_3MH^+	21.53	14.3
$CH_3MH_2^+$	21.53	18.5
$CH_3MH_3^+$	0.20	n.o.

* percentage of total ionisation at 70eV;
† ref.292.

Elimination of CH_4 is supported by the observation of metastable transitions in several related systems.[185,291,292] The relative ion-yields obtained for methylgermane are compared to those of methylsilane in Table I.10. The greater abundance of H_3Ge^+ compared to H_3Si^+ suggests M-C bond cleavage is more favourable for germanium than silicon, which is at least consistent with the accepted bond energies (Si-C,72; Ge-C, 61 Kcal mole^{-1}).[98] Previous workers[292] attributed the high abundance of the CH_3SiH^+ ion to a resonance contribution by the hypothetical structure $CH_2{=}SiH_2$. By comparison the CH_3GeH^+ ion appears to be 'normal', the most abundant ion being $CH_3GeH_2^+$. The 'out-of-step' abundances of the MH_2^+ and M^+ ions in both cases further suggest that CH_4 elimination may be important, ie.,

$$[CH_3MH_3^+] \rightarrow MH_2^+ + CH_4$$
$$CH_3MH^+ \rightarrow M^+ + CH_4$$

The spectrum of trichloro(methyl)germane (Table I.6) is complicated by the two isotopes of chlorine (ie. ^{35}Cl,75.77; ^{37}Cl,24.23%) but contains features which are easily recognised. The molecular ion $CH_3GeCl_3^+$ (6.6%) is observed and in this respect $MeGeCl_3$ is similar to tetrachlorogermane where $GeCl_4^+$ constitutes 16.9% of the ion-yield.[291] The relative abundances of the fragment ions are: $H_nCGeCl_2^+$ (45.5) > $GeCl_3^+$ (24.9) > $GeCl^+$ (14.9) > $H_nCGeCl_3^+$ (6.6) > Ge^+ (2.8), H_nCGe^+ (2.2), $GeCl_2^+$ (2.1) > H_nCGeCl^+(1.0). The high abundance of the $CGeCl_2^+$ ion compared to the $GeCl_3^+$ ion implies that Ge-Cl cleavage is more favourable than Ge-C cleavage. The relative ion-yields $GeCl_3^+$ (24.9) > GeH_3^+ (6.6) further suggest that Ge-C cleavage is more favourable in $MeGeH_3$ than $MeGeCl_3$. By analogy with methylgermane, fragmentations involving elimination of CH_3Cl are also likely which may explain the apparent high yield of $GeCl^+$, ie., $CH_3GeCl_2^+ \rightarrow GeCl^+ + CH_3Cl$

The many routes available for fragmentation of the monohalides, $MeGeH_2Cl$ and $MeGeH_2I$ (Tables 1.7 and 8) give rise to complex monoisotopic spectra. The molecular ions $[CH_3GeH_2Cl^+]$ and $[CH_3GeH_2I^+]$ are not observed and the high yield of H_nCGe^+ ions in both cases (Table I.11) implies that Ge-X bond cleavage is more important than Ge-H and Ge-C bond cleavage. The observation of HI^+ ions is strongly suggestive of HI elimination, this being supported by the ion CH_3GeI^+ accounting for >85% of the ions H_nCGeI^+. We defer further comments until more extensive data are available.

(Table I.11) Monoisotopic contributions in the main fragments for the halides

	H_nGe^+	H_nCGe^+	H_nGeX^+	H_nCGeX^+	H_nX^+
$MeGeH_3$	[47.1]	[52.9]	—	—	—
n = 6	—	—			
5	—	35			
4	—	27			
3	14	22			
2	31	10			
1	16	6			
0	39	—			
$MeGeH_2Cl$	[20.6]	[45.8]	[19.5]	[14.1]	—
n = 5	—	45	—	—	
4	—	17	—	75	
3	—	25	—		
2	<5	9	16	25	
1	40	4	26		
0	55	—	58		
$MeGeH_2I$	[11.5]	[37.4]	[21.0]	[27.7]	[2.4]
n = 5	—	45	—	—	
4	—	17	—	—	
3	—	25	—	85	
2	3	9	20	8	
1	26	4	17	5	
0	71	—	63	2	

[ ] indicates percentage abundance of polyisotopic fragment. The monoisotopic contributions are expressed as percentages of the polyisotopic fragment.

CHAPTER TWO

THE PROTON MAGNETIC RESONANCE SPECTRA OF THE METHYLGERMANES

II.1 INTRODUCTION

The interpretation of nuclear magnetic resonance (n.m.r.) parameters for compounds of the Group IV elements has provoked much discussion and controversy in the literature. Most studies have been concerned with empirical correlations of such parameters as the chemical shift or coupling constant with changes in physical constants produced by substituent effects. The data are undoubtedly of great empirical significance[8] but it is still uncertain how the measurements are related to the electronic distribution within the molecule.

A general theory of nuclear shielding has been given by Ramsey[110] and modifications of this have led to expressions[111,112] dividing the observed screening constant (σ) into terms arising from the shielding due to the immediate surrounding electron cloud (σ_1) and that due to more distant electrons (σ_d). In certain cases correlations have been made between the chemical shift and σ-electron densities in emphasising the importance of inductive and electromeric effects in determining σ_1. This approach is unsound when applied to compounds with protons bonded to a heavier Group IV element than carbon,[63,113] as is illustrated by the lack of understanding of the effect responsible for the low-field shift of protons attached to silicon or germanium compared to those on carbon (viz; $C\underline{H}_4$,0.13δ; $Si\underline{H}_4$,3.20δ; GeH_4,3.15δ). The importance of σ_d in determining the chemical shift is still controversial[114-117] although recent semi-quantitative calculations on the methylsilanes[115] imply that diamagnetic anisotropy and related phenomena are unlikely to account for more than a small part of the observed shifts. This means that at present there is at least one factor in the interpretation of M-H chemical shifts that is not understood so that any evaluation of the way δ(MH) changes with substitution at M must be somewhat speculative.

The data presented here for the methylgermanes are discussed in comparison with earlier studies[114,115,118-121] on the formally analogous ethyl, C_2H_5-, disilanyl, Si_2H_5-, methylsilene, MeSiH<, methylsilyl, $MeSiH_2$-, and digermanyl, Ge_2H_5-, derivatives. The α-proton chemical shifts generally follow trends which reflect the inductive effect of the substituent and in this respect they are similar to the simple methyl, CH_3-, silyl, SiH_3-, or germyl, GeH_3-, derivatives. The β-proton chemical shifts are apparently not primarily controlled by the inductive effect of the substituent and it is usual to invoke second order phenomena such as magnetic anisotropy,[85,117] Van der Waals or dispersion forces,[116] or "bond-shifts"[114,115,118,120] to explain the observed shifts; agreement among even semi-quantitative calculations of the relative importance of these effects is poor.[119,117]

The spin-spin interactions between vicinal protons (ie. J(HH') in $MH_3MH'_2X$) have also been studied extensively and an empirical additivity relationship for ethyl[121] and methylsilyl[115,119] compounds has been proposed. No similar relationship is apparent in the disilanyl series,[118] this being attributed to the larger distance over which the coupling is transmitted.

It was therefore of interest to study the analogous methylgermyl compounds to see how far the n.m.r. parameters followed those of the related carbon and silicon species. The calculated "carbon-germanium bond shift", Δ^{X}_{C-Ge}, is discussed and a modified form of the usual additivity relationship for vicinal interproton coupling is proposed.

II.2 EXPERIMENTAL

The ^1H n.m.r. spectra were recorded on a Jeol C60HL high resolution spectrometer at 60 MHz. Because of their air sensitivity, the halides were sealed with the solvent and reference in pyrex glass capillaries (ca.3 mm o.d.) which were then placed inside standard n.m.r. tubes (5 mm o.d.) and surrounded by CCl_4 to ensure good sample spinning. The spectrometer was calibrated with ethylbenzene in the field-field mode and using the standard sweep width of 10 p.p.m. the chemical shifts are believed to be accurate to ±0.02 p.p.m.; the coupling constant data were generally recorded at a sweep width of 2 p.p.m. when the mean deviation was typically ±0.05 Hz for proton coupling, $|J_{HH}^{vic}|$, and ±0.1 Hz for satellite spectra, $|J_{CH}|$.

Choice of solvent: Previous investigations of the related silanes and germanes utilised cyclohexane both as a solvent and internal standard, it being nonpolar and relatively anisotropic and therefore unlikely to significantly affect the chemical shifts. This was tried initially but interference of its main resonance ($\delta C\underline{H}$ = 1.44 p.p.m.) with the methyl resonances of the samples made it unsatisfactory. Carbon disulphide and benzene were both efficient solvents but on close examination large dilution shifts were apparent, particularly in the latter (ca.±10%). This behaviour indicated considerable solvent-solute interactions[122] so chemical shifts measured in these solvents were thought to be unreliable. Carbon tetrachloride* was selected when the dilution shifts (ie. δ pure compound $-\delta$ infinitely dilute compound) for the monohalides $MeGeH_2X$ (X = Cl,Br,I) were found to be insignificant and within the mean deviation for chemical shift determination. The redetermined shifts for

---

* The reactivity of germanium hydrides towards CCl_4 is discussed in Chapter I.

the parent hydrides GeH_4, Me_nGeH_{4-n} in carbon tetrachloride (ca.5% v/v) were in excellent agreement with literature values (±0.02 p.p.m.) so the data for the halides are thought to be comparable with those of the related silanes and germanes.

The ^1H n.m.r. spectra of the halogeno-methylgermanes were satisfactorily analysed as first order, indicating an increased effective symmetry by rapid rotation about the C-Ge bond; A_2X_3 ($MeGeH_2X$); AX_3 ($MeGeHX_2$); AX_6 (Me_2GeHX). The magnetically active fluorine nucleus (^{19}F, 100% abundant; I = 1/2) produces additional coupling (JHF>JHH') to give spectra of the type A_2X_3P ($MeGeH_2F$), AX_3P_2 ($MeGeHF_2$), and AX_6P (Me_2GeHF). The magnetically active carbon nucleus (^{13}C,1.1% abundant; I = 1/2) gives rise to satellite spectra spaced equally either side of the methyl resonance ($|J_{CH}|$, ca.130 HZ); these were observed only in concentrated solutions. The more abundant isotopes of germanium (^{70}Ge,20.4%; ^{72}Ge,27.4%; ^{74}Ge,36.6%) have no magnetic nuclear moments; coupling with the active ^{73}Ge nucleus (^{73}Ge, 7.8% abundant; I = 9/2) is not observed in the methylgermanes and has been reported only in the highly symmetrical molecules GeH_4[63] and $GeMe_4$;[123] this may be due to the quadrupole induced relaxation of ^{73}Ge.[63]

Typical ^1H n.m.r. spectra are displayed in Fig.II.1 and the observed parameters for $MeGeH_2X$, Me_2GeHX, and $MeGeHX_2$ are collected in Table II.1 with those of the related germanes reported in the literature. The spectra of the hydrido-fluoro species were recorded in dilute solution in CS_2 (ca.1% v/v) at -50° to prevent 'collapsing' of H-H and H-F coupling; these observations are at least consistent with an exchange process and from the disappearance of J(H'F) prior to J(HH') in $MeGeH_2'F$ it is suggested that it is the fluorine atoms which are exchanging.

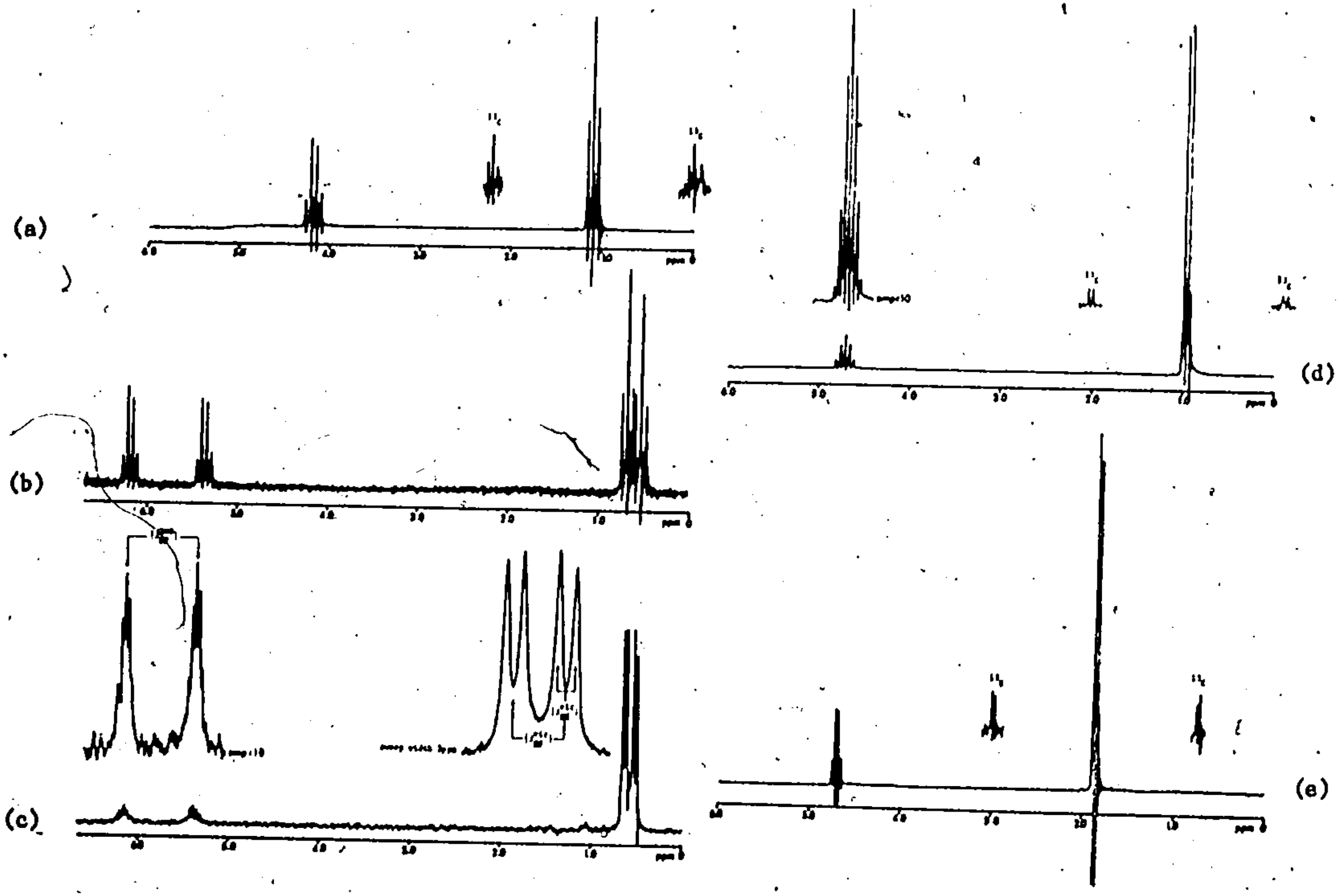


Fig.II.1 The ^{1}H n.m.r. spectra of (a) $MeGeH_2I$; (b) $MeGeH_2F$; (c) Me_2GeHF; (d) Me_2GeHI; (e) $MeGeHI_2$

(Table II.1) The ^{1}H n.m.r. parameters* of the halogenogermanes and -methylgermanes

Compound	(δMe)	(δGeH')	$\lvert J^{vic}_{HH'}\rvert$	$\lvert J^{vic}_{HF}\rvert$	$\lvert J^{gem}_{H'F}\rvert$	$\lvert J_{CH}\rvert$
GeH_4 [a,1]	–	3.15	–	–	–	–
$MeGeH'_3$ [b]	0.35	3.49	4.33	–	–	129.0
$Me_2GeH'_2$ [b]	0.29	3.73	3.95	–	–	128.5
Me_3GeH' [b]	0.21	3.92	3.40	–	–	127.0
Me_4Ge [b]	0.13	–	–	–	–	125.0
GeH'_3F [a]	–	5.68	–	–	42.4	–
GeH'_2F_2 [a]	–	7.01	–	–	43.8	–
$MeGeH'_2F$ [c,m]	0.62	5.77	2.72	7.1	44.1	129.0
$Me_2GeH'F$ [c,m]	0.59	5.79	2.20	7.0	46.8	128.2
Me_3GeF [d]	0.51	–	–	6.8	–	128.8
$MeGeH'F_2$ [m]	0.88	6.68	e	5.7	59.7	e
Me_2GeF_2	0.84	–	–	5.6	–	131.4
$MeGeF_3$	1.31	–	–	e	–	138.0[f]
GeH'_3Cl [a]	–	5.11	–	–	–	–
GeH'_2Cl_2 [a]	–	6.47	–	–	–	–
$MeGeH'_2Cl$	0.73	5.30	2.92	–	–	131.5
$Me_2GeH'Cl$	0.80	5.55	2.70	–	–	129.8
Me_3GeCl [d]	0.78	–	–	–	–	128.3
$MeGeH'Cl_2$	1.14	6.74	1.20	–	–	133.1
Me_2GeCl_2	1.14[g,h]	–	–	–	–	132.4
$MeGeCl_3$	1.58[i,j]	–	–	–	–	136.8
GeH'_3Br [a]	–	4.50	–	–	–	–
GeH'_2Br_2 [a]	–	5.74	–	–	–	–
$MeGeH'_2Br$	0.88	4.88	3.21	–	–	131.6
$Me_2GeH'Br$	0.94	5.25	2.73	–	–	130.1
Me_3GeBr [d]	0.88	–	–	–	–	129.2
$MeGeH'Br_2$	1.44	6.28	1.47	–	–	133.2
$MeGeBr_2$	1.44[h]	–	–	–	–	132.1
$MeGeBr_3$	1.98[j]	–	–	–	–	135.9

Con'd

(Table II.1) Con'd

Compound	(δMe)	(δGeH')	$\lvert J^{vic}_{HH'} \rvert$	$\lvert J^{vic}_{HF} \rvert$	$\lvert J^{gem}_{H'F} \rvert$	$\lvert J_{CH} \rvert$
GeH'_3I[a]	–	3.46	–	–	–	–
GeH'_2I_2[k]	–	3.61	–	–	–	–
$MeGeH'_2I$	1.11	4.12	3.27	–	–	132.3
$Me_2GeH'I$	1.08	4.71	2.91	–	–	130.8
Me_3GeI[d]	0.98	–	–	–	–	129.8
$MeGeH'I_2$	1.87	4.68	2.05	–	–	135.0
Me_2GeI_2	1.91[h]	–	–	–	–	134.3
$MeGeI_3$	2.61[i]	–	–	–	–	138.0[f]

* The spectra were recorded at ambient temperature in carbon tetrachloride solutions (ca.5% v/v). Chemical shifts (δ±0.02 p.p.m.) are in p.p.m. to low field of tetramethylsilane as internal standard. Deviations for coupling constants are J(HH')±0.05 Hz, $J(^{13}CH)$±0.2Hz, J(HF)±0.1Hz. $J(^{13}CH)$ measurements from neat liquid.

a. ref.63; b. ref.83; c. in good agreement with values of C.H. Van Dyke, private communication (1969) and ref.71; d. ref.81; e. not observed; f. recorded at ca.+50°; g. ref.124; h. compare with approximate δ values for Me_2GeX_2 (X = Cl,Br,I) of 1.18, 1.46 and 1.90δ respectively given in ref.125; i. ref.126; j. compare with approximate δ values for $MeGeX_3$ (X = Cl,Br,I) of 1.7, 2.2 and 2.3δ respectively given in ref.79; k. ref.65; l. $J(^{73}GeH)$=87.8Hz; m. recorded in CS_2 soln. (ca.1% v/v) at -50°.

In the $MeGeH_2X$ series (X = Cl,Br,I) the GeH_2 resonance appears as a 1:3:3:1 quartet, intensity two, and the CH_3 resonance is a well defined 1:2:1 triplet, intensity three, at higher field. Additional coupling is observed in $MeGeH_2F$ due to ^{19}F such that both resonances are duplicated. In the $MeGeHX_2$ series (X = Cl,Br,I) the GeH resonance is a 1:3:3:1 quartet, intensity one, while the corresponding CH_3 resonance is a 1:1 doublet, intensity three; in $MeGeHF_2$ both resonances are triplicated (1:2:1) although J(HH') is no longer observed. In the Me_2GeHX series (X = Cl,Br,I) the GeH resonance is a septet (theoretically,1:6:15:20:15:6:1) intensity one and the CH_3 resonance appears as a doublet (1:1), intensity six; in Me_2GeHF both resonances are duplicated. For the fully substituted species $MeGeX_3$, Me_2GeX_2, Me_3GeX the methyl resonance is a singlet at high field.

II.3 RESULTS AND DISCUSSION

(a) The α-proton chemical shift

For the series $MeGeH_2X$, $MeGeHX_2$, and Me_2GeHX (X = F,Cl,Br,I) the GeH resonance shifts to lower field as the halogen changes from iodine to fluorine; a comparison of these data with those reported[63] for the parent germanes, GeH_3X and GeH_2X_2, shows that the effect cannot be described by additive substituent parameters with the possible exception of the bromides; the largest deviations from additivity (Table II.2) are observed with the fluorides (mean deviations: F,0.56; Cl,0.22; Br,0.07; I,0.24 p.p.m). A similar low-field shift in the GeH resonance is observed with increasing methyl substitution; in this case the additivity is good for the monohalides (Table II.2b) but is poorer when extended to the dihalides (mean deviations: H,.04; F,0.12; Cl,0.03; Br,0.11;

I,0.19; CH_3, 0.02 p.p.m.). These results suggest that the more polar or bulkier substituents in polysubstituted methylgermanes give rise to irregular changes in the effective shielding of the germanium proton, which further implies that the α-proton shifts are determined only partly by inductive changes in local diamagnetic shielding. Similar effects have been observed for α-substitution in alkyl-,[127] and methylsilyl-,[115,119] derivatives.

(Table II.2) The effect of α-substitution by (a) halogen and (b) methyl on α-proton chemical shifts in halogen derivatives of germane and methylgermane*

(a) X	$\delta GeH_4 - \delta Ge\underline{H}_3X$	$\delta Ge\underline{H}_3X - \delta Ge\underline{H}_2X_2$	$\delta MeGe\underline{H}_3 - \delta MeGe\underline{H}_2X$	$\delta MeGe\underline{H}_2X - \delta MeGe\underline{H}X_2$	$\delta Me_2GeH_2 - \delta Me_2Ge\underline{H}X$
F	−2.53	−1.33	−2.28	−0.91	−2.06
Cl	−1.96	−1.36	−1.81	−1.44	−1.82
Br	−1.35	−1.24	−1.39	−1.40	−1.52
I	−0.31	−0.15	−0.63	−0.56	−0.98

(b) X	$\delta Ge\underline{H}_3X - \delta MeGe\underline{H}_2X$	$\delta Ge\underline{H}_2X_2 - \delta MeGe\underline{H}X_2$	$\delta MeGe\underline{H}_2X - \delta Me_2Ge\underline{H}X$
H	−0.34	−0.34	−0.24
F	−0.09	+0.33	−0.02
Cl	−0.19	−0.27	−0.25
Br	−0.38	−0.54	−0.37
I	−0.66	−1.07	−0.59
CH_3	−0.24	−0.19	−0.19

* data taken from Table II.1; the negative signs imply a shift down-field on substitution.

For the methyl and ethyl derivatives Spiesecke and Schneider[85] showed that in plots of $\delta(C\underline{H}_3X)$ and $\delta(CH_3C\underline{H}_2X)$ vs. the electronegativity of X (E_x) the points for F,O,N and H lie on a straight line; the points for I,Br,Cl, and F lie on a second line, whose gradient is less, the failure of the two lines to coincide being explained in terms of the differences in the magnetic anisotropies of the carbon-halogen bonds compared to the first row elements where this effect is expected to be minimal.

Ebsworth and Turner,[113] and Van Dyke and MacDiarmid[118] showed that for the analogous silicon compounds the correlation of $\delta(Si\underline{H}_3X)$[113] and $\delta(SiH_3Si\underline{H}_2X)$[118] vs. E_x is different from the carbon compounds; the points for F,O, and N lie on a straight line which does not pass through the point for H whilst a line through the points for I,Br, and Cl does not pass through the point for F and is much steeper than the (F,O,N) line. Though these differences between carbon and silicon derivatives may be partly due to the different effects of anisotropy it has been pointed out that this sort of explanation is unlikely to account for certain observed anomalies (e.g. $\delta Si\underline{H}_3F > \delta Si\underline{H}_2F_2$[113] and $\delta SiH_3 > \delta SiH_2$ in SiH_3SiH_2I[118]). It is generally thought that the chemical shifts of protons bound to silicon are likely to be affected by (p→d) π-bonding and by contraction in the d-orbitals of silicon that the substituent may cause. Many of the observations in the disilanes[118] are also consistent with an extra interaction across the Si-Si bond or across space. This type of behaviour may also be important in the germanes although it is generally considered[8] that germanium participates in (p→d) π-bonding to a lesser extent than silicon.

Ebsworth and Frankiss[115] showed that $\delta(Si\underline{H}XYZ)$ increases linearly with $\delta(C\underline{H}XYZ)$ for several methyl- and silyl- derivatives, with the marked exception of iodo- and polyfluoro- species. This linearity was interpreted as indicating a common cause of the relative changes in δSiH and δCH while the slope, δSi/δC of 0.4 suggested that SiH resonances are less sensitive to changes in the rest of the molecule than are CH resonances. This is also apparent when it is considered that the proton resonances for monosilane (3.20δ) appears to low field of that in methane (0.13δ) while trichlorosilane (6.07δ) gives a resonance substantially to high field of chloroform (7.25δ).

For the germyl, GeH_3, compounds for which extensive data are now available (Table II.3) the GeH resonance shifts to low field with increasing substituent electronegativity (Fig.II.2). The points I,Br,Cl again fall on a straight line, whilst those for F,O, and N form another line in an analogous manner to the corresponding silicon compounds.[113]

(Table II.3) Chemical shift[a] and electronegativity (E_x)[b] data for (a) MH_3X; (b) MH_2XY; (c) $(MH_3)_3X$ and (d) $(MH_3)_2X$ (M = Si,Ge)

(a) X	E_x	δGeH[c]	δSiH[e]
H	2.20	3.15	3.20
C	2.65	3.49	3.55
F	3.90	5.68	4.76
Cl	3.15	5.11	4.59
Br	2.95	4.50	4.17
I	2.65	3.46	3.44

(b) XY	E_x	δGeH[c,d]	δSiH[e,f]
F_2	7.80	7.01	4.71
Cl_2	6.30	6.47	5.40
Br_2	5.90	5.74	5.17
I_2	5.30	3.61	4.03
ClBr	6.10	6.20	5.36
ClI	5.80	5.65	5.21
BrI	5.60	4.91	4.82

(c) X	E_x	δGeH[g]	δSiH[f,h]
N	3.05	4.91	4.43
P	2.15	4.12	3.92
As	2.10	3.98	3.81
Sb	2.05	3.61	3.72

(d) X	E_x	δGeH[i]	δSiH[e,j]
O	3.50	5.28	4.61
S	2.60	4.67	4.35
Se	2.55	4.35	4.12
Te	2.30	3.59	3.71

a. δ values in p.p.m. to low field of T.M.S. (±0.2 p.p.m.); b. ref.91; c. ref.63; d. refs.41,56,65; e. ref.113; f. ref.205; g. ref.257; S. Cradock, E.A.V. Ebsworth, G. Davidson, and L.A. Woodward, J.Chem. Soc.(A),1229(1967); E.A.V. Ebsworth, D.W.H. Rankin, and G.M. Sheldrick, J.Chem.Soc.(A),2828(1968); h. E.A.V. Ebsworth and G.M. Sheldrick, Trans Faraday Soc.,62,3282(1966); i. ref.257a; J.H.Burger and U. Goetze, Inorg.Nucl.Chem.Letters,3,5499(1967).

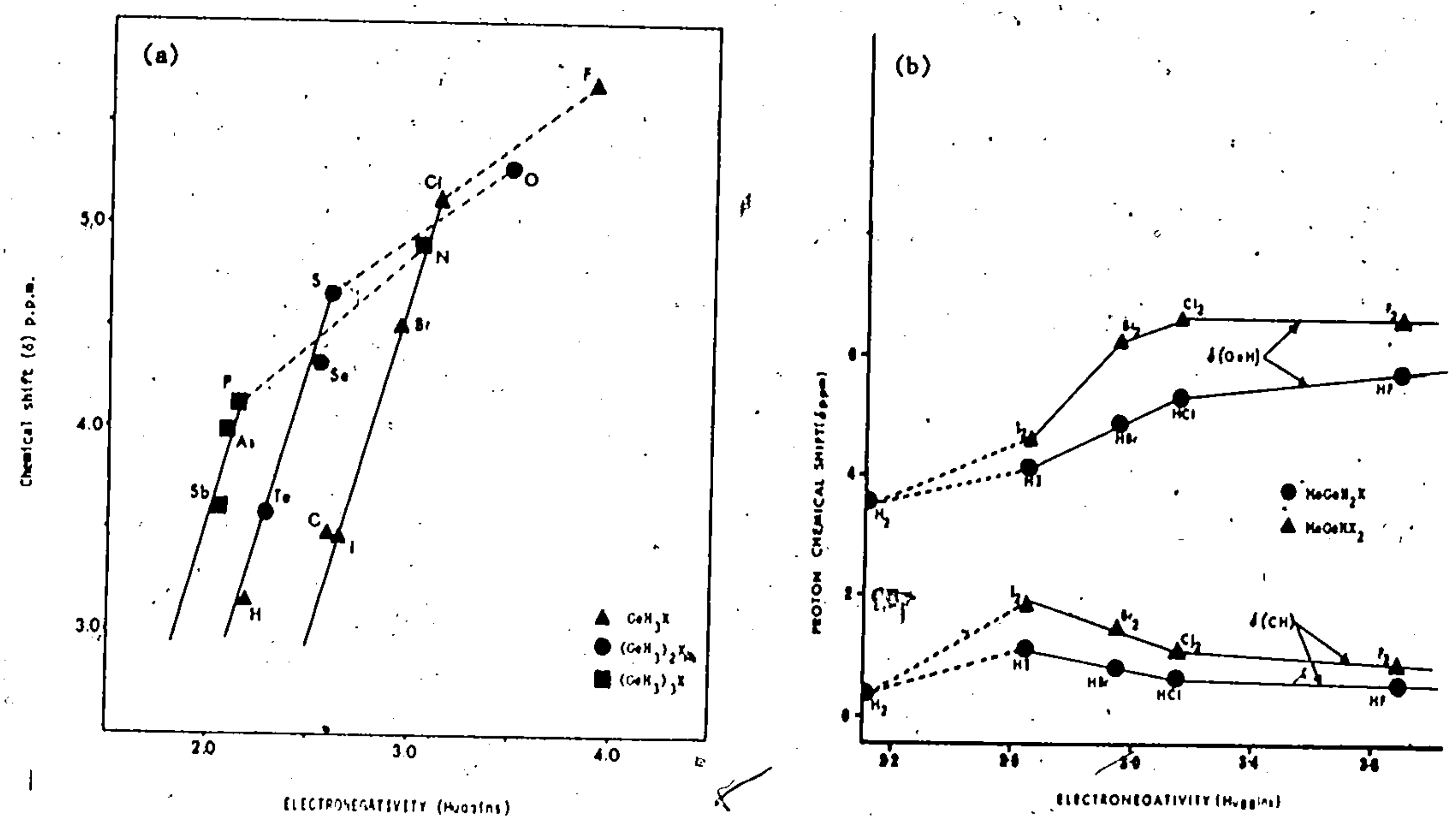


Fig.II.2 The relationship between proton chemical shift and substituent electronegativity (Huggins) in (a) germyl-, (b) methylgermyl- compounds

However, the significance of these relationships is less clear when the data for the silanes and germanes (Fig.II.2a) are extended to include the Group V and VI derivatives. It is immediately obvious that any number of straight-line relationships over a limited number of points may be drawn, e.g. through (Sb,As,P), (T,Se,S), and (Cl,Br,I). An alternative interpretation is that there is a 'regular' change in M-H shielding throughout the Groups, the first-row element of the Group being offset by approximately the same amount. It is tempting to attribute these deviations to the reduced effective electronegativity of the first-row elements by (p→d) π-bonding to silicon or germanium but there is little justification for this in terms of current theory.[8] As a point of speculation it is noted that the 'Group relationships' are nearly parallel, this also being true of the GeH_2XY series, $XY = Cl_2, Br_2, I_2$ (not shown); this implies that the M-H resonance is controlled by factors (as yet unclarified) peculiar to each Group and superimposed on these are the electronegativity and/or anisotropic dependencies.* The similarity of the germyl and silyl compounds in this respect is further emphasised by plots of $\delta(Ge\underline{H}_3X)$ vs. $\delta(Si\underline{H}_3X)$ which are remarkably linear within the quoted error limits for δ values (Fig.II.3) except for fluorine (divergence 0.3 p.p.m.). It appears that relative change in SiH_3- and GeH_3- resonances have a common cause while the slope of 1.4 implies that δGeH is more susceptible than δSiH to substituent effects. For the polysubstituted germanes and silanes this relationship is less certain; plots of $\delta(Ge\underline{H}XYZ)$ vs. $\delta(Si\underline{H}XYZ)$ are only approximately linear, the largest deviations being observed for the more bulky or electronegative substit-

---

* A similar 'Group dependence' is apparent in ^{13}C-H couplings, section II.3c.

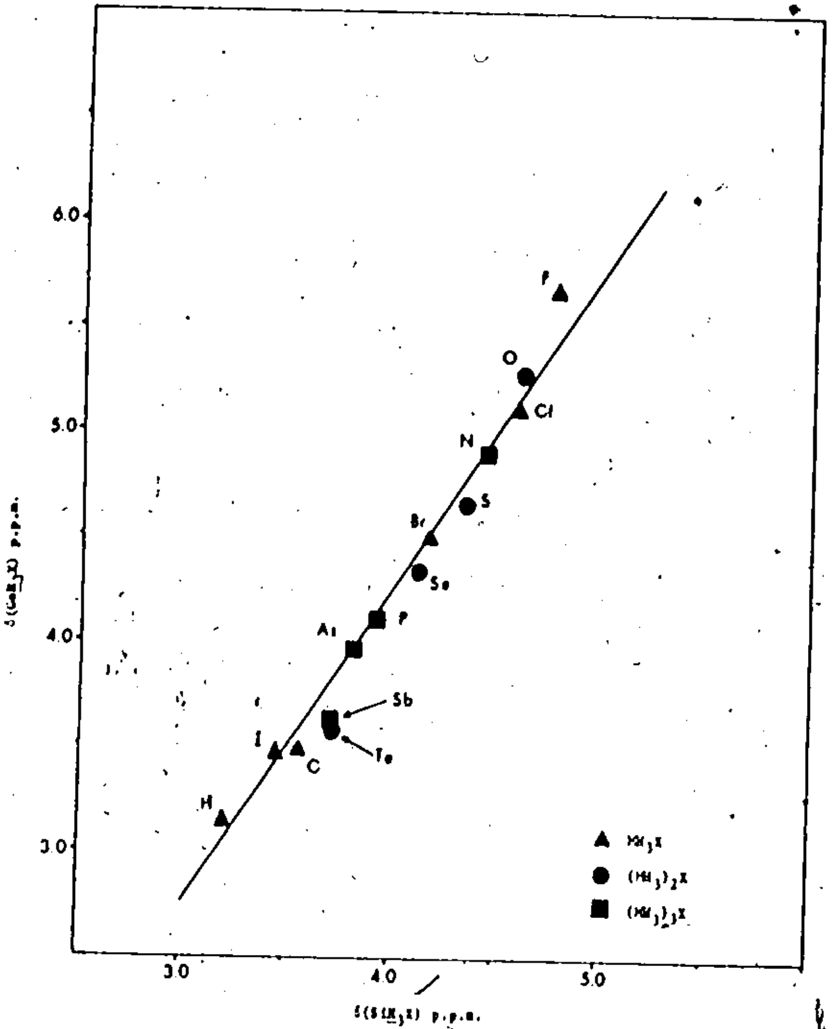


Fig.II.3 Relationship between the proton chemical shifts in silyl- and germyl-compounds

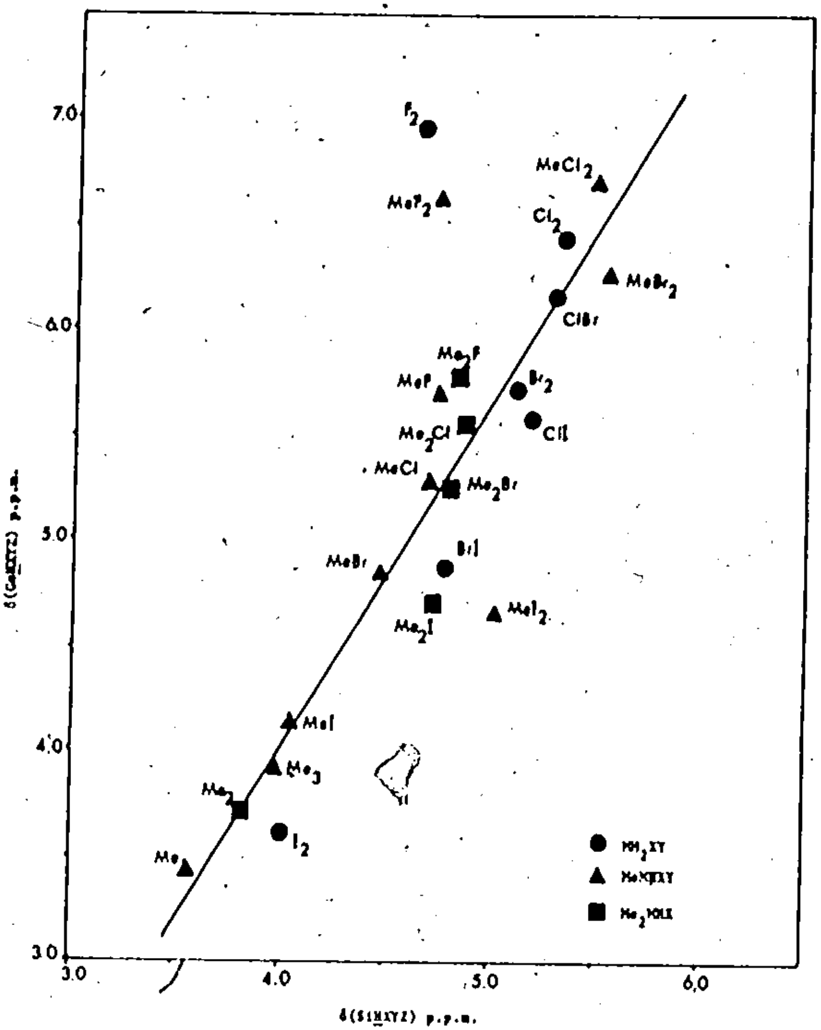


Fig.II.4 Relationship between the α-proton chemical shifts in polysubstituted silanes and germanes uents (Fig. II.4); the order of sensitivity apparently remains the same since the slope, δGe/δSi, is 1.7. However these data indicate that for the substituted methanes, silanes, and germanes, the sensitivity of the M-H resonance to α-substitution decreases in the order CH > GeH > SiH.

Since substituents do not in general have an additive effect on the α-proton chemical shift in substituted alkanes, silanes and germanes. it is unwise to attempt to relate the observed shifts to the individual properties (such as electronegativity) of the substituents. It is perhaps fortuitous that the order of sensitivity does reflect the expected increasing importance of (p→d) π-bonding but in view of uncertainty as to what is responsible for the low field shifts from CH_4 to SiH_4 or GeH_4 this observation may have little significance.

(b) The β-proton chemical shift

For all series $MeGeH_2X$, $MeGeHX_2$, Me_2GeHX, Me_nGeX_{4-n} the CH_3 resonance shifts to lower field as the halogen changes from fluorine to iodine; the downfield shift increases with the number of halogen substituents (ie. $\delta \underline{Me}GeH_2X < \delta \underline{Me}GeHX_2 < \delta \underline{Me}GeX_3$) but decreases with increasing methyl substitution (ie. $\delta \underline{Me}GeH_2X > \delta \underline{Me}_2GeHX > \delta \underline{Me}_3GeX$). In contrast to the α-shifts it is apparent that the β-proton shifts in the methylgermanes are approximately additive properties of the α-substituents (Table II.4); the mean deviations for halogen substituents (F,.04; Cl,.06; Br,.05; I,.02 p.p.m.) are close to the error limits for δ values, this being even more striking for methyl substitution (Table II.4b). These observations suggest that the β-chemical shifts in the methylgermanes can be described in terms of contributions from individual substituents; in this respect the methylgermanes are similar to the methylsilanes.[119] It is clear from plots of $\delta(\underline{Me}GeHXY)$ vs. E_x (Fig. II.2b) that the β-

(Table II.4) The effect of α-substitution by (a) halogen and (b) methyl on the β-proton chemical shifts in the halogeno(methyl)germanes*.

(a)	X	$\delta\underline{Me}GeH_3$ $-\delta\underline{Me}GeH_2X$	$\delta\underline{Me}GeH_2X$ $-\delta\underline{Me}GeHX_2$	δMe_2GeH_2 $-\delta\underline{Me}_2GeHX$
	F	−0.27	−0.26	−0.30
	Cl	−0.38	−0.41	−0.51
	Br	−0.53	−0.56	−0.65
	I	−0.76	−0.76	−0.79
	X	$\delta\underline{Me}_2GeHX$ $-\delta\underline{Me}_2GeX_2$	$\delta\underline{Me}GeHX_2$ $-\delta\underline{Me}GeX_3$	$\delta\underline{Me}_3GeH$ $-\delta\underline{Me}_3GeX$
	F	−0.25	−0.43	−0.30
	Cl	−0.34	−0.44	−0.57
	Br	−0.50	−0.54	−0.67
	I	−0.83	−0.74	−0.77
(b)	X	$\delta\underline{Me}GeH_2X$ $-\delta\underline{Me}_2GeHX$	$\delta\underline{Me}GeHX_2$ $-\delta\underline{Me}_2GeX_2$	$\delta\underline{Me}_2GeHX$ $-\delta\underline{Me}_3GeX$
	H	+0.06	+0.06	+0.08
	F	+0.03	+0.04	+0.08
	Cl	−0.07	0.00	+0.02
	Br	+0.06	0.00	+0.06
	I	+0.03	−0.04	+0.10
	CH_3	+0.08	+0.08	+0.08

* data from Table II.1; the positive sign implies a shift upfield on substitution.

shifts are not primarily controlled by the inductive effect of the halogen; the inductive effect of the halogen would be expected to produce a deshielding from iodine to fluorine whereas the reverse is observed experimentally. Similar trends are observed in ethyl,[114] methylsilyl,[115,119] disilanyl,[118] and digermanyl[120] halides so this appears to be a general phenomenon which is not peculiar to the methylgermyl system.

The linearity of plots of δ(<u>Me</u>CXYZ) <u>vs</u>. δ(<u>Me</u>SiXYZ) implied[119] that it is unnecessary to invoke special bonding properties of silicon (e.g. (p→d) π-bonding) to account for the β-proton shifts in the methylsilanes. The corresponding plots of δ(<u>Me</u>GeXYZ) <u>vs</u>. δ(<u>Me</u>SiXYZ) are also approximately linear (slope <u>ca</u>.1.1; average deviation, 0.08 p.p.m.), the largest deviations being observed for the polyfluorides (Fig.II.5). It therefore appears that with the possible exception of the fluorides, similar effects determine the β-proton resonance in the ethanes, methylsilanes, and methylgermanes; the slopes δC/δSi, 1.4,[119] and δGe/δSi, 1.1, imply that the sensitivity of the β-proton shift to α-substitution is in the order C > Ge > Si.

Spiesecke and Schneider[85] suggested that the anomalous low-field shift of the β-protons in ethyl compounds correlated with increasing atomic volume and therefore could arise from magnetic anisotropy associated with the C-X system. This was disputed by Cavanaugh and Daily[114] who pointed out that the linearity of $\delta(C\underline{H}_3X)$ <u>vs</u>. E_x plots was not consistent with halogen anisotropic effects, and from distance and angular dependence calculations proposed that the α- and β-shifts in the ethyl halides were determined principally by inductive withdrawal (by the subtituent) plus a factor acting equally at the α- and β-positions; this factor they termed the "C-C bond shift" which they considered to arise from regular changes in the paramagnetic term (contained in σ_1)

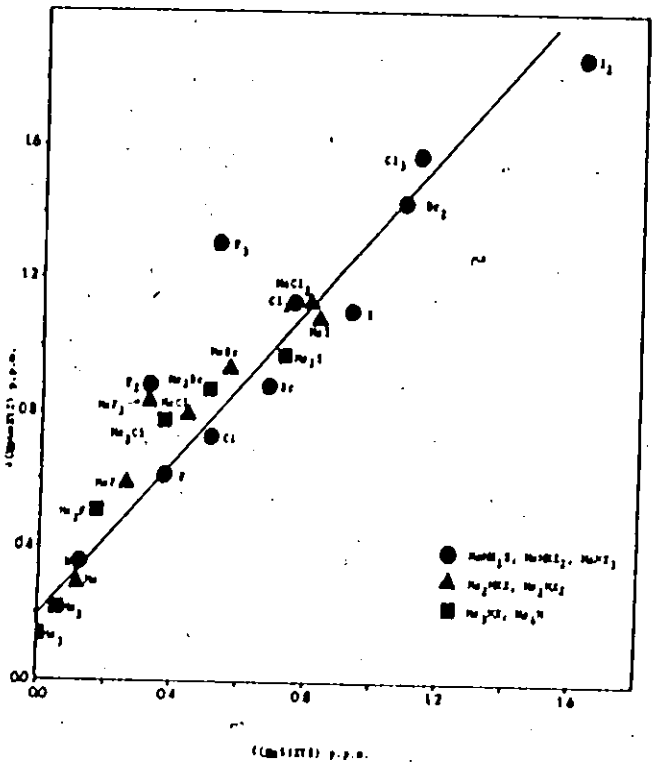


Fig.II.5 Relationship between the β-proton chemical shifts in polysubstituted silanes and germanes

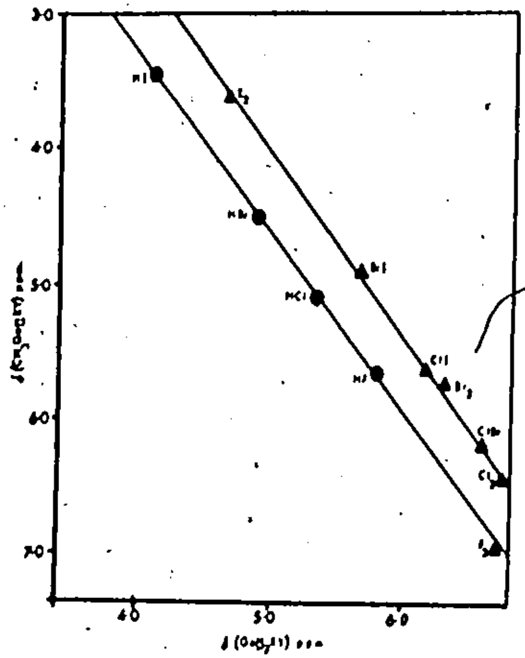


Fig.II.6 'Bond shift' plot

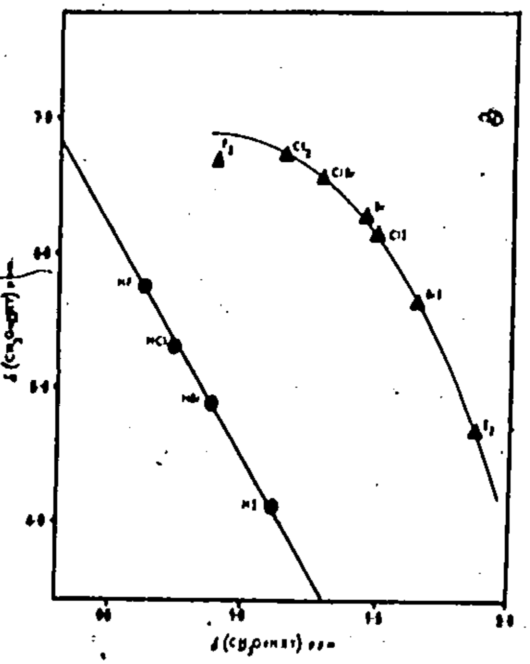


Fig.II.7 'Internal shift' plot

in the Ramsey[110] equation due to changes in the excitation energy denominator when a C-C bond replaces a C-H bond.

Schaefer et al[116] developed these arguments for ^1H and ^{13}C nuclei in aliphatic and aromatic halides and suggested that intramolecular Van der Waals or dispersion forces could contribute to the observed low field shifts. Although the magnitude of this effect is not known it is expected to decrease rapidly ($1/r^6$) with increasing group separation (r). A comparison of the shortest H...I distance in CH_3CH_2I (ca.2.72Å) with SiH_3SiH_2I (ca.68Å) where δMH_β shows a low-field shift suggests that dispersion interactions are at least an order of magnitude too small to account for the observed shifts.[119]

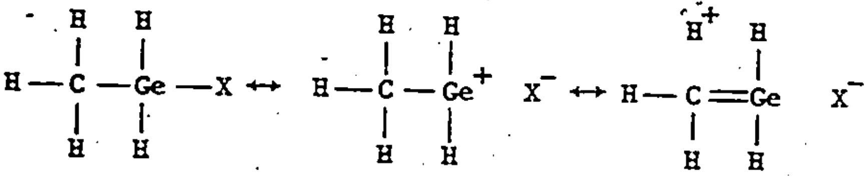
As mentioned previously the observed screening constant (σ) for a proton may be divided into two parts,[111] the shielding due to the immediate electron cloud (σ_1) and that due to more distant electrons (σ_d). The contribution of long range shielding (σ_d) from an α-substituent X, having axial symmetry to the β-proton shift can be related[119] within the limits of the dipolar approximation to the anisotropy of the magnetic susceptibility of X by the equation:[112]

$$\sigma_d = \Delta\chi\ (1-3\cos^2\theta)\ /3R^3 \qquad [1]$$

where $\Delta\chi$ is the difference between longitudinal and transverse magnetic susceptibilities of X, R is the distance between the induced magnetic dipole of the substituent and the β-proton, and θ is the acute angle between the radius vector and the symmetry axis of X.

Calculations of long-range shielding of the β-protons in alkyl[115] and methylsilyl halides[115,119] averaged over the appropriate internal rotations with the dipole placed (arbitrarily) at the centre of X and $\Delta\chi$ taken as 10% of the ionic susceptibility of X^-, predicted high field shifts which are an order of magnitude smaller than the observed low-field shifts. It was therefore stressed that either the dipolar approximation was too approximate (and this seems likely) or the long-range shielding provides only a minor contribution to the β-proton shifts in such compounds.

A decrease in shielding of the β-protons could arise from contributions of resonance structures such as B and C, which are expected to



$\mathrm{H{-}CH_2{-}GeH_2{-}X \leftrightarrow H{-}CH_2{-}GeH_2^{+}\;X^{-} \leftrightarrow H^{+}\;H_2C{=}GeH_2\;X^{-}}$

[A] [B] [C]

to be more important for compounds containing heavier elements; this would be consistent with the observed low-field shift of the β-protons in MeGeXYZ along the series X = F,Cl,Br,I although the magnitude of this effect is not known.

If it is reasonable to assume that dispersion effects and magnetic anisotropy are minimal for the methylgermanes then, by analogy with the ethanes,[114] disilanes,[118] digermanes,[120] and methylsilanes,[115,119] there must be an effect arising from the presence of the C-Ge bond.

(c) The carbon-germanium bond shift

The data in Table II.2 show that when a proton attached to germanium is substituted by a methyl group a decreased shielding of the remaining protons is observed; in terms of the accepted +I nature of the methyl group this is unexpected, an upfield shift would be predicted. The methyl substitution may reduce the formal positive charge of germanium (in $\overset{\delta+}{\mathrm{Ge}}$-$\overset{\delta-}{\mathrm{H}}$), this leading to a weakening of the Ge-H bond (see Chapter IV) and a reduction of the formal negative charge on the proton; since the GeH shift is likely to be controlled by the shielding produced in the vicinity of the proton (σ_1) a reduction in electron density could rationalise the downfield shift. Alternatively it could be argued that carbon, being more electronegative than hydrogen (C,2.65; H,2.20) inductively withdraws electrons from the Ge-H bonds; however although this is consistent with the likely mechanism for halogen substitution it is unlikely to account for the high frequency shift in the GeH stretching frequency and increase in f[GeH] for the latter, both of which indicate <u>stronger</u> Ge-H bonds.

Plots of δ(MeGe$\underline{H}$XY) <u>vs</u>. δ(Ge$\underline{H}$XY) are linear (Fig.II.6) except for the difluoride (divergence 0.4 p.p.m.); this indicates that the C-Ge bond introduces a constant increment for each halogen, the largest shift being apparent for the iodide. In the ethanes,[114] disilanes,[118] digermanes,[120] and methylsilanes,[115,119] this effective replacement of a proton in MH_3X (M = C,Si,Ge) by $M'H_3$ (M' = C,Si,Ge) has been termed the "M-M' bond shift", $\Delta^{X}_{M-M'}$; by analogy the observations in the methylgermanes permit the "carbon-germanium bond shift", Δ^{X}_{C-Ge}, to be calculated:

$$\Delta^{X}_{C-Ge} = \delta(Ge\underline{H}_3X) - \delta(MeGe\underline{H}_2X) \qquad [2a]$$

$$= \delta(M\underline{H}_2XY) - \delta(MeGe\underline{H}XY) \qquad [2b]$$

the data for the methylgermanes are given in Table II.5, and compared with the related carbon and silicon derivatives in Table II.6. For the halides Δ^{X}_{C-M} (M = C,Si,Ge), apparently increases with decreasing electronegativity of the substituent. It is a general conclusion that bond shifts are not the result of anisotropic effects of the attached halogen or of the M-M' bond[114,115,118,119] although the "C-C bond shift" was though to arise from changes in the paramagnetic shielding.[114]

(Table II.5) Carbon-germanium bond shift data* for (a) $MeGeH_2X$ (b) MeGeHXY and (c) Me_2GeHX

(a)	X	$\delta Ge\underline{H}_3X$[a]	$\delta MeGe\underline{H}_2X$	Δ^X_{C-Ge}	$\delta \underline{Me}GeH_2X$	$\delta Me+\Delta^X_{C-Ge}$
	H	3.15	3.49	−0.34	0.35	−0.01(0.69)[c]
	F	5.68	5.77	−0.09	0.62	0.51
	Cl	5.11	5.30	−0.19	0.73	0.54
	Br	4.50	4.88	−0.38	0.88	0.50
	I	3.46	4.12	−0.66	1.11	0.45
	CH_3	3.49	3.73	−0.28	0.29	0.01(0.57)[c]
(b)	XY	$\delta Ge\underline{H}_2XY$[a]	$\delta MeGe\underline{H}XY$	Δ^X_{C-Ge}	$\delta \underline{Me}GeHXY$	$\delta Me+\Delta^X_{C-Ge}$
	F_2	7.01	6.68	+0.32	0.88	1.20
	Cl_2	6.47	6.74	−0.27	1.14	0.87
	ClBr	6.20[b]	6.56	−0.36	1.28	0.92
	Br	5.74	6.28	−0.46	1.44	0.98
	ClI	5.65[b]	6.14	−0.49	1.48	0.99
	BrI	4.91[b]	5.64	−0.73	1.64	0.91
	I_2	3.61	4.68	−1.07	1.87	0.80
(c)	X	$\delta MeGe\underline{H}_2X$	$\delta Me_2Ge\underline{H}X$	Δ^X_{C-Ge}	$\delta \underline{Me}_2GeHX$	$\delta Me+\Delta^X_{C-Ge}$
	H	3.49[a]	3.73	−0.24	0.29	0.05(0.53)[c]
	F	5.77	5.79	−0.02	0.59	0.57
	Cl	5.30	5.55	−0.25	0.80	0.55
	Br	4.88	5.25	−0.37	0.94	0.57
	I	4.12	4.71	−0.59	1.08	0.49
	CH_3	3.73	3.92	−0.19	0.21	0.02(0.40)[c]

* Chemical shifts (δ) are in p.p.m. to low field of T.M.S., $\Delta^X_{C-Ge} = \delta(Ge\underline{H}_3X) - \delta(MeGe\underline{H}_2X)$, data from Table II.1;
a. ref.63; b. ref.56; c. values in parentheses obtained by subtraction.

A detailed discussion of $\Delta^X_{M-M'}$ requires a knowledge of the susceptibility ($\Delta\chi$) of the M-M' bond, and for the alkanes (the simplest system) $\Delta\chi_{C-C}$ is still uncertain. A value of 7×10^{-30} cm^3 $mole^{-1}$ has been deduced from n.m.r. studies of cyclohexane[129] whereas studies of long chain paraffins imply $\Delta\chi_{C-C}$ is small and negative[130] and a m.o. study predicted $\Delta\chi_{C-C}$

should be zero.[131]

It has been noted in the ethanes[114] and methylsilanes[115] that the bond effect apparently works to deshield the α- and β-protons equally because the addition of the bond shift, Δ^{X}_{C-M}, of a particular compound $MeMH_2X$ (M = C,Si) to δMe for that compound gives an approximately constant value within the series; the corresponding data for the methylgermanes are collected in Table II.5. This general feature appears to hold well except for X = H or CH_3 and it is also valid for substitution of a second methyl group; it is noted that if Δ^{X}_{C-Ge} (X = H, CH_3) is subtracted from δMe then good agreement is observed.

(Table II.6) Catenation shifts, Δ^{X}_{M-M} and $\Delta^{X}_{M-M'}$, in MH_3X, M_2H_5X, and $MH_3M'H_2X$ compounds (M = C,Si,Ge; M = Si,Ge; X = F,Cl,Br,I)

X	Δ^{X}_{C-C} [a]	Δ^{X}_{C-Si} [b]	Δ^{X}_{Si-C} [c]	Δ^{X}_{C-Ge}	Δ^{X}_{Si-Si} [d]	Δ^{X}_{Ge-Ge}
F	−0.23	−0.01	–	−0.09	−0.54	–
Cl	−0.51	−0.13	−0.03	−0.19	−0.27	−0.28[e]
Br	−0.81	−0.32	−0.01	−0.38	−0.13	−0.18[e]
I	−1.12	−0.64	+0.02	−0.66	+0.10	+0.01[e]
CH_3	−0.46	−0.27	–	−0.24	−0.12	−0.09
H	−0.75	−0.35	–	−0.34	−0.06	−0.09

a. ref.114; b. ref.115; c. ref.128; d. ref.118; e. ref.120.

These results imply that when the β-proton shift is 'corrected' for the presence of the C-Ge bond a 'constant' shielding and hence electronic environment about the β-protons is predicted. It therefore seems that it is unnececessary to invoke second-order effects. The small residual down-field β-proton shift compared to the parent hydride may reflect the true inductive effect of the substituent. It is perhaps fortuitous that the 'corrected' shifts follow the predicted inductive effect.

In the series of disilane[118] and digermane[120] derivatives Δ^{X}_{M-M} (M = Si,Ge) decreases with decreasing electronegativity of the ligand whilst it was noted that subtraction of Δ^{X}_{M-M} from δMH_3 gives a roughly constant value for the β-shift; there was no explanation for this but it was suggested[118] that there might be an electronic interaction across the Si-Si bond from the SiH_2 group to the SiH_3 group if by analogy with the ethanes and methylsilanes the anisotropic effects of the Si-Si bond or substituent are unimportant.

It has been reported[119] that marked deviations from this rule occur with the dihalogeno(methyl)silanes so the existence of a general phenomenon is questionable.

(d) Internal chemical shift

In the ethyl compounds[132] a correlation was found between the internal chemical shift, i.e. $\delta CH_3 - \delta CH_2$, and substituent electronegativity: the magnitude of the shift decreases as the electronegativity of the attached halogen decreases. It has been calculated[85,132] that the CH_2 resonance will fall at a higher field than the CH_3 resonance only when E_x = <1.71; thus in Et_3Al (E_{Al} = 1.5) δCH_2 is observed at higher field than δCH_3. However, no such simple relationship is apparent in the analogous silicon compounds, SiH_3SiH_2X, and the plot ($\delta SiH_3 - \delta SiH_2$) vs. E_x resembles the $\delta(SiH_3X)$ vs. E_x plots;[113,118] it would appear that the electronegativity values are modified to varying extents by (p→d) π-bonding to silicon.[118]

The methylsilyl- and methylgermyl- halides are not strictly comparable to ethyl- and disilanyl- halides in this respect since there are already two different types of proton in the parent hydrides $MeSiH_3$ and $MeGeH_3$; it is therefore questionable whether similar correlations would have any significance. This is emphasised by plots of $\delta(\text{MeGe}\underline{\text{H}}\text{XY})$ vs. $\delta(\underline{\text{Me}}\text{GeHXY})$; the points for X = F,Cl,Br, and I lie on a straight line (Fig.II.7) which does not pass through the points for the dihalides.

(e) Spin-spin coupling constants

Unlike carbon and silicon, germanium has no magnetic isotope suitable for ready observation of satellite spectra; discussion is therefore confined to vicinal interproton coupling, $|J_{HH}^{vic}|$, and the directly bound ^{13}C-H coupling, $|J_{CH}|$, between the methyl protons and the magnetically active carbon nucleus (^{13}C, 1.1% abundant; I = 1/2). The observed $|J_{HH}^{vic}|$ values for the methylgermanes are given with those of the related compounds (Table II.7).

(Table II.7) Vicinal spin-spin coupling constant data* ($|J_{HH}^{vic}|$)HZ

XY	MeGeHXY		MeSiHXY		GeH_3GeHXY		SiH_3SiHXY	
	Obs.	Calc.[a]	Obs.[b]	Calc.	Obs.[c]	Calc.	Obs.[d]	Calc.
HH	4.33	-	4.68	-	-	-	4.0	-
HF	2.72	2.71	3.27	3.28	-	-	2.7	2.69
HCl	2.92	3.06	3.61	3.64	4.1	4.14	3.0	2.89
HBr	3.21	3.15	3.71	3.74	4.2	4.23	3.0	2.92
HI	3.27	3.27	3.86	3.90	4.4	4.42	3.0	2.99
F_2	n.o.	<u>ca</u>.0	1.22	1.37	-	-	2.8	-
Cl_2	1.20	1.24	2.29	2.32	-	-	2.1	-
Br_2	1.47	1.55	2.52	2.57	-	-	2.3	-
I_2	2.05	2.09	2.94	2.94	-	-	-	-
ClBr	1.27[e]	1.37	-	-	-	-	2.25	-
ClI	1.65[e]	1.63	-	-	-	-	-	-
BrI	1.83[e]	1.95	-	-	-	-	-	-
±(Hz)	0.05		av.0.06		0.06		0.05	

* no significant dependence of $|J_{HH}^{vic}|$ on concentration was observed.

a. calculated from equation no.4-10; b. ref.115,119; c. ref.120;
d. ref.118; and J.E. Drake and N.Goddard, <u>J.Chem.Soc.(A)</u>,2587(1970).
e. see Chapter V.

The absolute values of comparable coupling constants generally decrease in the order ethyl > digermanyl > methylsilyl > methylgermyl > disilanyl. If these have the same sign (assumed positive)[133] and the changes are primarily due to the changing H-H' distance as previously suggested[118] the high values of $|J_{HH}^{vic}|$ for digermanyl compounds are out of place.

For ethyl[121] and methylsilyl[115,119] compounds a coupling additivity relationship has been expressed (equation 3):

$$|J_{HH}^{vic}| = A(I - \kappa\Delta E) \qquad [3]$$

where 'A' is a constant with the value approximately that of J(HH') in the parent hydride (viz. C_2H_6 and $MeSiH_3$); 'κ' is a small arbitrary constant and $\Delta E = E_x - E_h$, ie. the difference in Huggins electronegativity[91] of the substituent X, and hydrogen.

For the mono- and di- substituted methylsilanes this relationship gave $|J_{HH}^{vic}|$ values calculated to ±0.3Hz and ±0.7Hz respectively. It is clear from plots of $|J_{HH}^{vic}|$ *vs.* ΔE that a better description results from treating the mono- and di-substituted derivatives individually (Fig.II.8). Graphical extrapolation of the straight line plots gives the following values for the constants 'A' and 'κ';-

$$|J_{HH}^{vic}| \quad [MeSiH_2X] = 4.11\ (1-0.12\Delta E) \qquad [4]$$

$$|J_{HH}^{vic}| \quad [MeSiHXY] = 3.50\ [1-0.18(\Delta E_x+\Delta E_y)] \qquad [5]$$

$$|J_{HH}^{vic}| \quad [MeGeH_2X] = 3.48\ (1-0.13\Delta E) \qquad [6]$$

$$|J_{HH}^{vic}| \quad [MeGeHXY] = 2.82\ [1-0.30(\Delta E_x+\Delta E_y)] \qquad [7]$$

$$|J_{HH}^{vic}| \quad [Me_2GeHX] = 3.16\ (1-0.18\Delta E) \qquad [8]$$

$$|J_{HH}^{vic}| \quad [GeH_3GeH_2X] = 4.70\ (1-0.13\Delta E) \qquad [9]$$

$$|J_{HH}^{vic}| \quad [SiH_3SiH_2X] = 3.1\ (1-0.08\Delta E) \qquad [10]$$

The average errors of .03, .05, .05, .08, .02, .03, and .05HZ for the values of $|J_{HH}^{vic}|$ obtained from equations 4-10 are close to the error

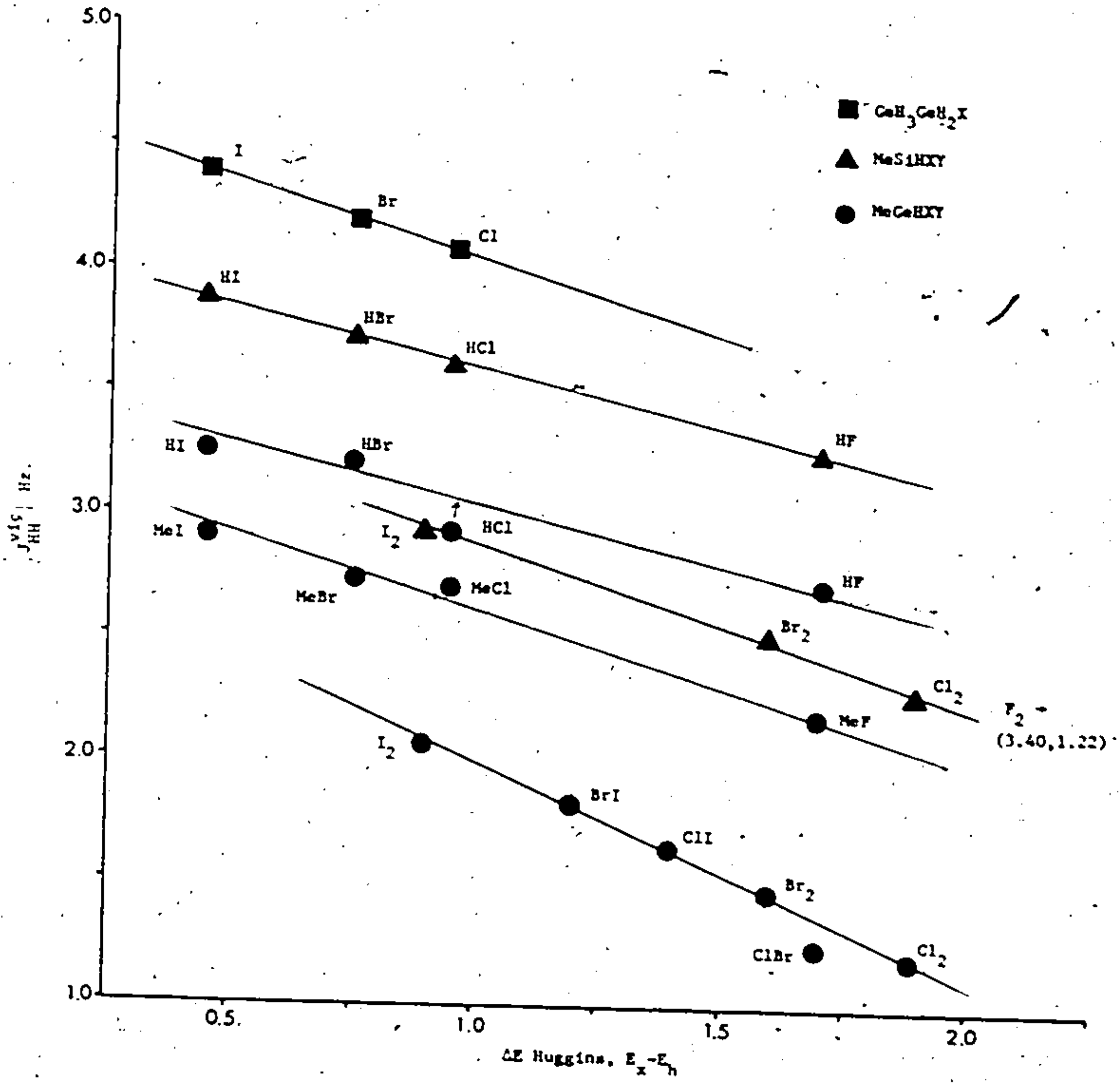


Fig.II.8 The relationship between the vicinal proton coupling constant, $|J_{HH}^{vic}|$, and electronegativity for digermanyl-, methylsilyl, and methylgermyl- halides limits quoted for experimental values (Table II.6). In the disubstituted methylgermanes H-H' coupling for $MeGeH'F_2$ was not observed; from expression [7] $|J_{HH}^{vic}|$ is calculated to be -0.04Hz (±0.08), ie. effectively zero within the quoted error limits.

The magnitude of $|J_{HH}^{vic}|$ decreases markedly with increasing halogen substitution; if the coupling is determined principally by the Fermi contact term then this implies a diversion of s-character from the H-C-Ge-H bonds into Ge-halogen bonds. The same effect is noticed with increasing methyl substitution, though less markedly; thus in the series $MeGeH_3 \rightarrow Me_2GeH_2 \rightarrow Me_3GeH$ $|J_{HH}^{vic}|$ has the value 4.33, 3.95 and 3.40Hz.

Several workers have observed additivity relationships for directly bound ^{13}C-H coupling (e.g. equation 11), and in many cases the magnitude has been attributed to the s-character in the carbon hybrid orbital.[111,134]

$$|J_{CH}|\ [CHXYZ] = |J_{CH}|\ [CH_4] + \Delta_x + \Delta_y + \Delta_z \qquad [11]$$

$$\text{where } \Delta_x = |J_{CH}|\ [CH_3X] - |J_{CH}|\ [CH_4]$$

Similar relationships for ^{29}Si-H[135] and Sn-H[136] couplings do not hold unless interaction terms are introduced[137,138] the theory not being sufficiently precise to allow satisfactory interpretation of the deviations from additivity.[8]

Values for $|J_{CH}|$ for the methylgermanes (Table II.1) lie in the range 127-138Hz which is significantly larger than in the methylsilanes (118-127Hz) but comparable with the date in the methylstannanes[81] and methylplumbanes.[139] This is hard to rationalise in terms of the relative inductive effects of Si,Ge,Sn, and Pb although it appears that the more 'electronegative' group attached to carbon reduces the s-character in the C-H orbitals. It is interesting to note that for methyl derivatives $|J_{CH}|$ is more strongly dependent on the Group of the α-substituent and particularly insensitive to changes in electronegativity within each Group, e.g. CH_3-Group IV (118-133Hz); CH_3-Group V (131-140Hz); CH_3-Group VI (138-148HZ); CH_3-Group VII (149-152Hz). It is therefore unlikely that inductive withdrawal can account for the wide range of $|J_{CH}|$ values in methylsilicon and methylgermanium compounds. With few exceptions it appears that $|J_{CH}|$ increases with increasing halogen substitution (ie. $MeGeH_2X \rightarrow MeGeHX_2 \rightarrow MeGeX_3$), increases with decreasing halogen electronegativity (ie. $MeGeH_2F \rightarrow MeGeH_2I$), and decreases with increasing methyl substitution (ie. $MeGeH_2X \rightarrow MeGeHX \rightarrow Me_3GeX$). However it is not possible to describe these effects by simple additive substituent parameters, particularly when more than one halogen is involved. There is also no simple correlation between $|J_{CH}|$ and $|J^{vic}_{HH}|$ although the former increases as the latter decreases for each series. Similar trends were observed in the methylsilanes.[115,119] The value of $|J^{vic}_{HF}|$ show a slight decrease with both increasing fluorine and methyl substitution so that similar effects which give rise to the $|J^{vic}_{HH}|$ are expected. $|J^{gem}_{HF}|$ has similar values in GeH_3F[63] and $MeGeH_2F$ and Me_2GeHF (42.4, 44.1, and 46.8Hz respectively) a slight increase being apparent with increasing methyl substitution. For the difluorides $|J^{gem}_{HF}|$ is 43.8Hz (GeH_2F_2)[63] and 59.7Hz ($MeGeHF_2$) which shows there is some large effect altering the coupling when a methyl group is present in the molecule.

CHAPTER THREE

THE VIBRATIONAL SPECTRA OF TRIIODO(METHYL)GERMANE AND TRIFLUORO(METHYL)GERMANE

III.1 INTRODUCTION

The vibrational spectra of the organogermanes have been interpreted by several workers. Studies of the hydride species, of the general type R_nGeH_{4-n}, were among the first to appear in the literature and assignments have been made for methyl-,[25] ethyl-,[141] phenyl-,[142] and vinyl-[143] germanes. For the fully substituted species, of the type R_nGeX_{4-n}, interest has been centred on the chlorides and bromides of the methyl-,[82,144-149] phenyl-,[150,151,142] and vinyl-[152] germanes. Reports on the corresponding iodo- and fluoro-species are limited to an article by Cross and Glockling[153] in which five of the twelve normal modes were observed for $MeGeI_3$, the characterisation of the skeletal region being notably absent. It was therefore of some considerable interest to study in detail the vibrational spectra of triiodo- and trifluoro-(methyl)-germane with the intention of confirming the assignments of previous authors, and to characterise the normal modes associated with the $-GeI_3$ and $-GeF_3$ groupings, which in turn would assist in the interpretation of the more complex spectra of the hydridic methylgermane derivatives described in this thesis.

Additional interest in the fluorogermanes came from recent publications[154-156] on the related tin fluorides which provided good evidence for polymeric fluorine-bridged species. Another recent study by Licht and Koehler[157] on R_3GeF compounds (R = Me,Et,n-Pr,n-Bu,Ph) indicated large frequency shifts in the region 700-500 cm^{-1} on passing through solid, liquid, and gaseous phases, which could be interpreted as arising from some form of intermolecular interaction. Germanium(II) fluoride, GeF_2, is a fluorine bridged chain-polymer with parallel chains cross linked by weak fluorine bridges[158] (the germanium coordination in this case is considered as a distorted trigonal bipyramidal arrangement of four fluorine atoms and one non-bonding electron pair). In K_2GeF_6 the germanium coordination is extended to six with an octahedral arrangement of fluorine atoms,[159] and the vibrational frequencies and force constants have been determined.[160] Evidence for five coordinate germanium, ie. GeF_5^-, came from the preparation of Ph_3AsGeF_5,[161] and negative ion mass spectra[162] whilst the sub-fluoride formed by the reduction of GeF_4 with germanium, $(GeF_2)_3GeF_4$ was thought to have no Ge-Ge bonds.[163]

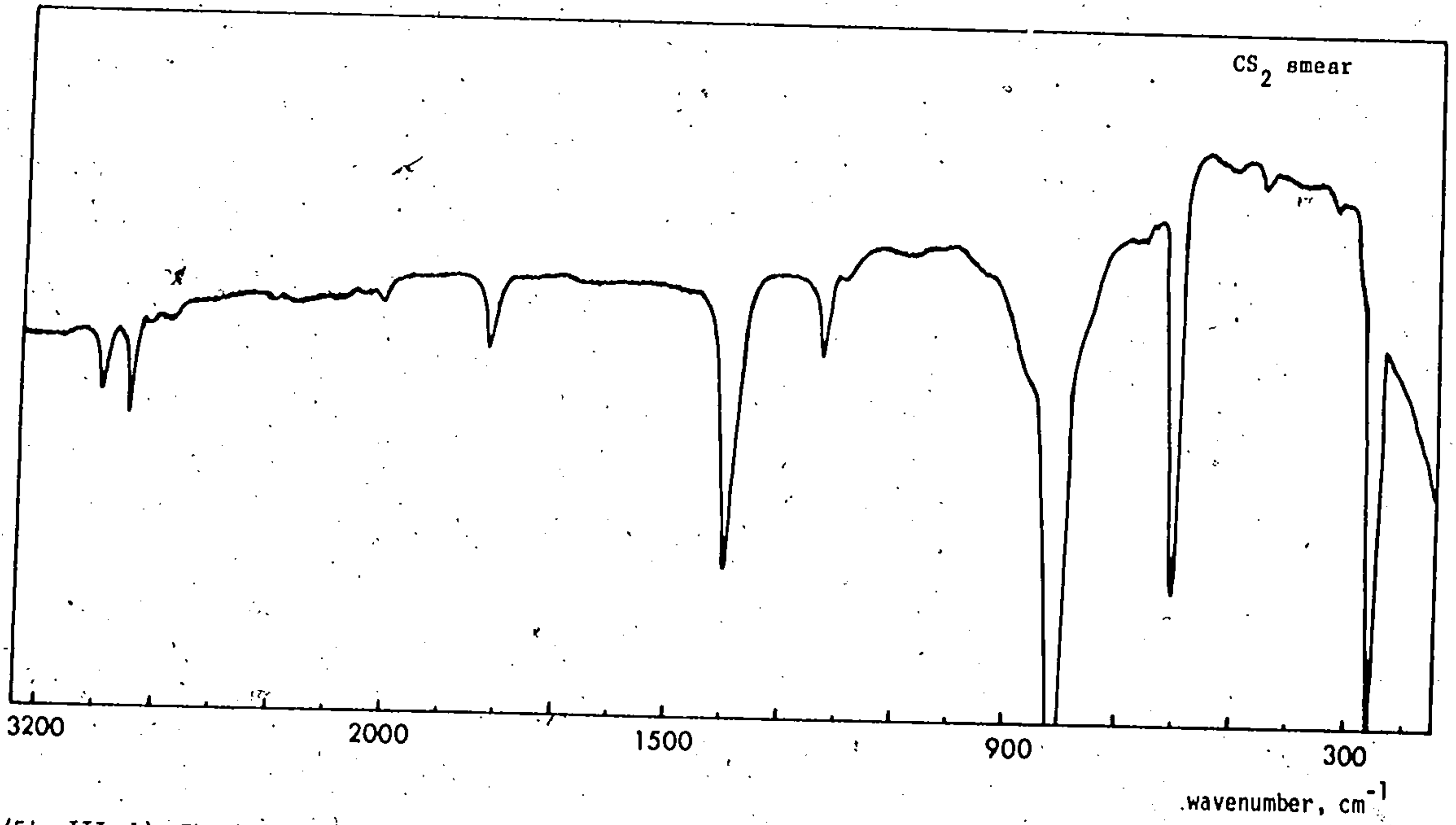
Germanium fluorides therefore show a marked propensity towards co-ordination numbers greater than the 'normal' four with intermolecular association occuring through bridging fluorine atoms. To investigate this further the vibrational spectra of $MeGeF_3$ in solid, liquid, and gaseous phases are examined to show how far the observed fundamentals can be correlated with those predicted by the expected C_{3v} symmetry. The proposed assignments for $MeGeF_3$ and $MeGeI_3$ are facilitated by comparison with parallel studies on the corresponding di- and trimethyl species, Me_2GeX_2[164] and Me_3GeX[165] (X = I and F), and confirmed by a normal coordinate analysis (NCA), described elsewhere.[109,164,166]

Near the completion of this work a vibrational analysis of $MeGeI_3$ and its deuteriated analogue, CD_3GeI_3, was reported,[167] the results of which were in excellent agreement with our studies.

III.2 EXPERIMENTAL

(a) Preparation of triiodo(methyl)germane: Flood et al[26] have reported virtually quantitative yields of $MeGeI_3$ by allowing GeI_2 and methyl iodide to react in a sealed tube at 110°. High yields of $MeGeI_3$ were more conveniently obtained by the reaction of excess hydrogen iodide with trichloro(methyl)germane. Typically, $MeGeCl_3$ (ca.1.1 mmol) and HI (ca.4 mmol) were condensed into a 50 ml reaction vessel at -196° and allowed to warm to room temperature. Reaction was complete after one hour when infrared analysis showed the only volatiles to be hydrogen chloride (ca.3.3 mmol) condensing in a trap at -196° and hydrogen iodide (ca.0.7 mmol) condensing in a trap held at -126°. The pale yellow solid remaining in the reaction vessel was purified by sublimation and subsequently shown from its melting point (45°)^{26} and the absence of proton containing impurities in the ^1H n.m.r. spectrum (singlet at 2.61δ)^{79} to be pure $MeGeI_3$. The infrared spectrum of the region 4000-200 cm^{-1} was recorded with the sample (as a CS_2 smear) held between CsI plates in an air-tight liquid cell. The Raman spectra were recorded with the samples in sealed pyrex glass tubes (ca.3 mm o.d.,5 mm length). The solid-phase Raman spectrum was recorded at room temperature and the liquid-phase spectrum with the sample heated to ca.50° by a controlled hot air source. The experimental infrared and Raman spectra are shown (Figs.III. 1 & 2) with the observed frequencies and assignments listed in Table III.1.

(b) Trifluoro(methyl)germane: $MeGeF_3$ was obtained by the reaction of $MeGeBr_3$ with lead(II) fluoride as previously described (Chapter I.2). Samples for spectral analysis melted sharply between 40-42° in sealed tubes (38.5° given in ref.26) and had a sublimation pressure of ca.16 mm Hg at ambient temperature. The experimental i.r. and Raman spectra obtained for gas, liquid and solid samples are shown, (Fig.III.3 and 4) with the observed frequencies and assignments listed in Table III.2.



(Fig. III. 1) The infrared spectrum of $MeGeI_3$

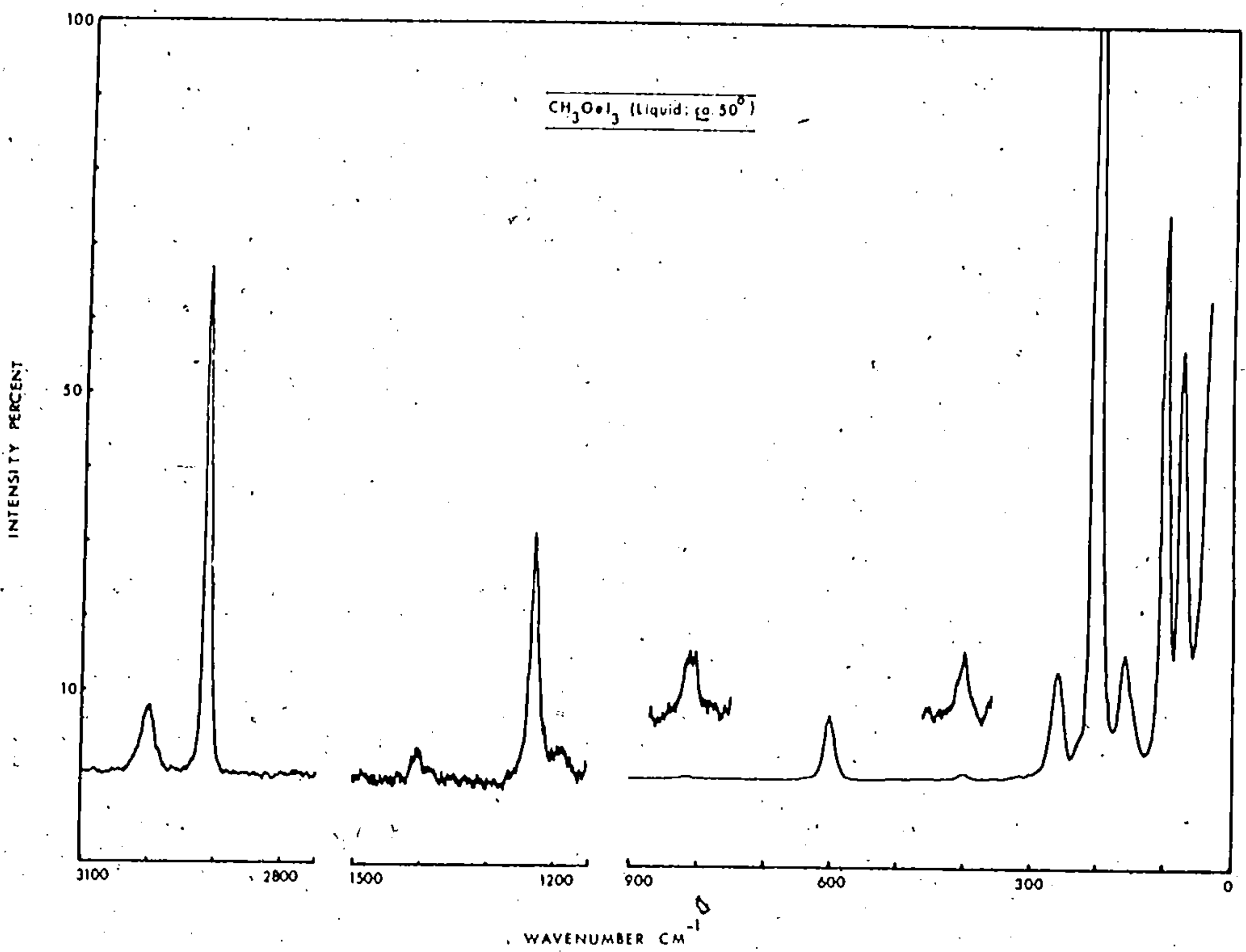


Fig.III.2 The liquid phase Raman spectrum of $MeGeI_3$ recorded at ca. 50°

(Table III.1) The vibrational spectra (cm^{-1}) of triiodo(methyl)germane¶

Infrared	Raman			
(CS_2 smear)†	(liq)*	(solid)†	calc.	Assignment
3140 vw	–	–	–	$\nu_7 + \nu_{11} = 3151$
3002 m	3001 wm,dp	2997 w	3002.0	ν_7
2910 m	2914 ms,p	2908 m	2910.0	ν_1
2845 vw	–	–	–	$\nu_7 - \nu_{11} - 2853$
2440 w	–	–	–	$2\nu_2 = 2456$
2039	–	–	–	$\nu_2 + \nu_9 = 2040$
1831 m	1828 vvw	–	–	$\nu_2 + \nu_3 = 1829$
1394 s	1404 vw,dp	1396 vw	1394.0	ν_8
1228 m	1229 w,p	1230 w	1228.5	ν_2
1195 vw	1192 vw,sh	–	–	$2\nu_3 = 1202$
875 br,sh	–	–	–	$\nu_9 + \nu_{12} = 877$
810 s	805 vw,dp	810 vvw	809.9	ν_9
630 w,sh	–	–	–	$\nu_2 - \nu_3 = 629$
601 s	598 m,p	607 m	600.9	ν_3
450 w	–	–	–	$\nu_{10} + \nu_4 = 451$
–	385 vw,p	–	–	$2\nu_4 = 400$
260 s	–	–	–	$\nu_4 + \nu_{12} = 263$
251 s	258 m,dp	242 m	241.5	ν_{10}
200 s	200 vvs,p	196 vs	191.5	ν_4
	156 m,dp	149 m	148.5	ν_{11}
	98 s,p	91 s	90.2	ν_5
	72 s,dp	62 s	67.3	ν_{12}

¶ In all spectra Tables: m = medium, s = strong, w = weak, v = very, sh = shoulder, br = broad, p = polarised, dp = depolarised;
† recorded at room temperature; * recorded at *ca.* + 50°

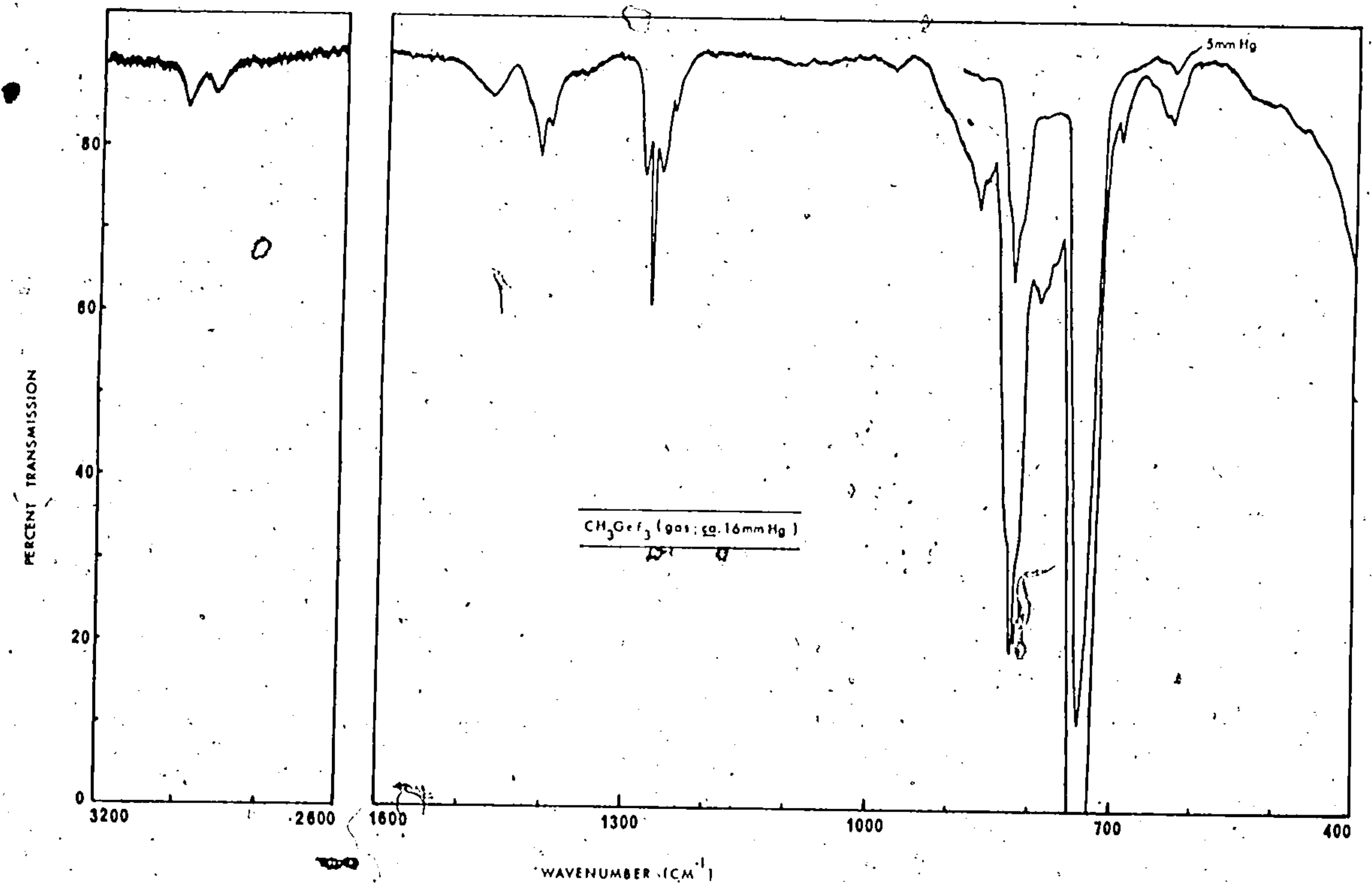


Fig.III.3 The gas phase infrared spectrum of $MeGeF_3$

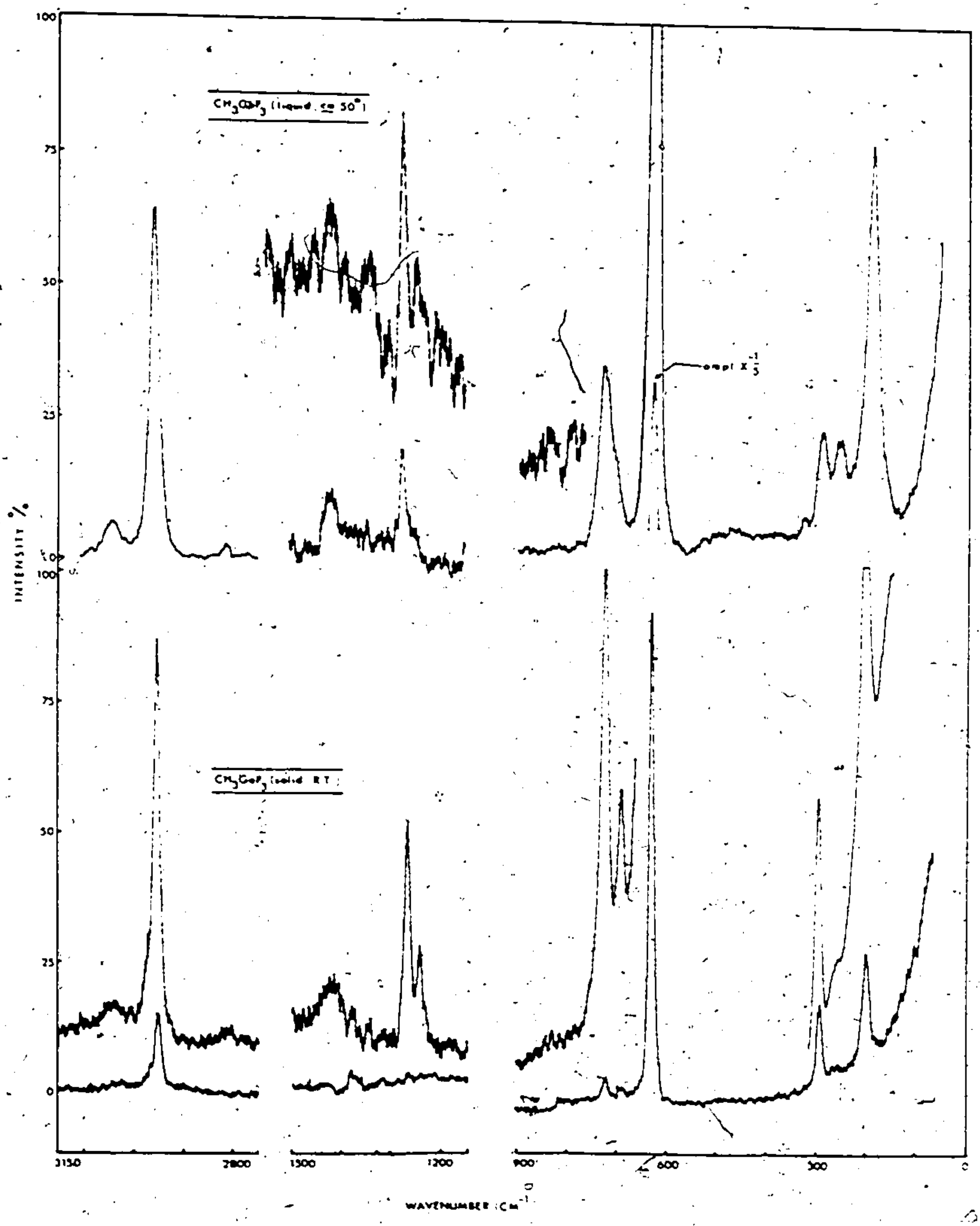


Fig.III.4 The Raman spectra of MeGeF$_3$

(Table III.12) The vibrational spectra (cm^{-1}) of trifluoro(methyl)germane

Infrared (gas)†	(soln.,CCl_4)†	Raman (liquid)*	(solid)†	calc.	Assignment
ca.3040 vvw	ca.3026 vw	3035 wm,dp	3036 vw	3034.3	ν_7
ca.2950 vvw	2946 w	2949 s,p	2952 s	2948.2	ν_1
–	–	2813 w,p	2815 vw		2 x 1410 = 2820
1480 w	–	–	–		2 x 744 = 1488
R 1416 } m P 1407	1416 wm	1410 vw,dp	1417 vvw	1410.8	ν_8
–	–	1349 vvw,p	–		730 + 630 = 1360
R 1288 Q 1277} m P 1267	1269 m	1269 w,p	1270 w	1269.2	ν_2
1252 sh	1251 sh	1243 sh,p	1245 w		2 x 628 = 1256
877 vw	n.o	–	–		744 + 136 = 880
833 s	827 s¶	837 vw,dp	838 vvw	838.5	ν_9
791 vw	n.o.	796 vvw,dp	–		1410 - 630 = 780
744 vs	734 vs¶	740 vw,sh		742.3	ν_{10}
730 wsh	n.o.	730 ms,p	721 m	727.0	ν_4
–	–	–	690 wm		νGeF**
634 m	632 w	630 vs,p	628 vs	626.2	ν_3
		320 wsh;p	n.o.		136 + 194 = 330
		292 m,dp	289 s	290.3	ν_{12}
		254 m,dp	250 wsh	251.1	ν_5
		194 s,dp	196 s	192.6	ν_{11}
		136 wsh,p	138 wsh		ν_6?

---

† Spectra recorded at room temperature; * Spectrum recorded at ca.+ 50°; ¶ obtained from a CS_2 solution; ** see text

III.3 DISCUSSION

The molecules are assumed to have C_{3v} symmetry. The twelve fundamental modes (Table III.3) are divided into 5 non-degenerate a_1-vibrations; 6 doubly degenerate e-vibrations and a single a_2-vibration. The a_1- and e-modes should all be infrared active with the former polarised and the latter depolarised in the Raman effect. The a_2-mode is inactive. The eleven active fundamentals can be divided into five which are largely associated with motions of the CH_3 group and the six which can be considered as $CGeX_3$ skeletal vibrations. The assignments of these two groups of fundamentals (Tables III.1 and 2) are discussed separately below.

(Table III.3) Fundamental vibrations for $MeGeX_3$ species

Mode	Species	Activity	Conventional Description*
ν_1	a_1	IR,R pol	CH_3 stretch (sym)
ν_2			CH_3 def (sym)
ν_3			GeC stretch
ν_4			GeX_3 stretch (sym)
ν_5			GeX_3 def (sym)
ν_6	a_2	inactive	CH_3 torsion
ν_7	e	IR,R dep	CH_3 stretch (asym)
ν_8			CH_3 def (asym)
ν_9			CH_3 rock
ν_{10}			GeX_3 stretch (asym)
ν_{11}			GeX_3 rock
ν_{12}			GeX_3 def (asym)

* C_{3v} symmetry assumed.

Vibrations of the methyl group (ν_1, ν_7, ν_2, ν_8 and ν_9): Depolarised bands in the Raman at 3001 cm^{-1} (iodide) and 3035 cm^{-1} (fluoride) which appear at 3002 and 3040 cm^{-1} respectively in the i.r. are assigned to the asymmetric CH_3 stretching mode ν_7. The symmetric stretching mode,

ν_1, is confidently assigned to Raman polarised bands at 2914 cm^{-1} (iodide) and 2949 cm^{-1} (fluoride). Correspondingly, medium absorptions at 2910 and 2950 cm^{-1} are observed in the infrared spectra. The CH_3 deformation modes occur in the expected regions. Polarised bands at 1229 cm^{-1} (iodide) and 1269 cm^{-1} (fluoride) in the Raman spectra, which appear at 1228 and 1277 cm^{-1} respectively in the i.r., are unambiguously assigned to the symmetric CH_3 deformation mode, ν_2. Similarly, i.r. bands at 1394 cm^{-1} (iodide) and 1415 cm^{-1} (fluoride) with Raman depolarised counterparts at 1404 and 1416 cm^{-1}, respectively, are excellent candidates for the asymmetric CH_3 deformation mode, ν_8. The CH_3 rocking mode, ν_9, is attributable to the strong bands at 810 and 833 cm^{-1} in the i.r. spectra of the iodide and fluoride. The corresponding bands are extremely weak in the Raman effect and are only observed with high levels of laser excitation using the argon ion source. Thus very weak depolarised bands at 806 cm^{-1} (iodide) and 837 cm^{-1} (fluoride) confirm the infrared assignment. No band is observed that can be satisfactorily assigned to the CH_3 torsion, ν_6. A weak feature at 136 cm^{-1} in the Raman spectrum of $MeGeF_3$ may be tentatively assigned as such, although the selection rules prohibit its appearance. This would be supported by the presence of a sum band attributable to $\nu_6 + \nu_{11}$ at ca. 330 cm^{-1}.

In general the vibrations of the methyl group are relatively insensitive to changes in substituent and are found in the same ranges for both $MeGeX_3$ (X = F,Cl,Br or I) and Me_nGeX_{4-n} (n = 1,2,3 ; X = I or F) series. The gradual lowering of frequency for all the CH modes from fluorine to iodine is probably largely related to a mass effect but the NCA[109] indicates a slight decrease in f[C-H].

Vibrations of the skeleton (ν_3, ν_4, ν_5, ν_{10}, ν_{11} and ν_{12}): The 6 skeletal fundamentals are divided into 3 of species a_1, and 3 of species e.

Polarised Raman bands at 598 and 200 cm^{-1} (iodide) and 630 and 730 cm^{-1} (fluoride) are excellent candidates for a_1-fundamentals and are confidently assigned to the GeC stretching mode, ν_3, and the GeX_3 (X = I or F) symmetric stretching mode, ν_4. The asymmetric stretching e-fundamentals are assigned for each molecule on a comparative basis. For $MeGeI_3$ a strong i.r. band at 251 cm^{-1} having a depolarised Raman counterpart at 258 cm^{-1} is a firm choice for the asymmetric GeI_3 stretch, ν_{10}. The corresponding bands were assigned at 264 cm^{-1} in GeI_4[168] and 245 cm^{-1} in Me_2GeI_2.[166] The asymmetric GeF_3 stretch, ν_{10}, is expected to be weak in the Raman effect but strong in the infrared and as such is tentatively assigned to the same band envelope as ν_4 in the Raman spectrum, there being a pronounced shoulder on the higher wavenumber side. It is then reasonable to assign ν_{10} to the very strong band at 744 cm^{-1} in the i.r., on the assumption that the lower wavenumber shoulder is now ν_4. The splitting of the symmetric and asymmetric GeX stretching modes in the GeX_4 series (Table III.4) decreases from iodine (109 cm^{-1}) to fluorine (62 cm^{-1}). In the $MeGeX_3$ series (Table III.5) this splitting is considerably reduced but still decreases from iodine (58 cm^{-1}) to chlorine (31 cm^{-1}).[144,145] The splitting of the GeF stretches in $MeGeF_3$ is therefore expected to be small which would be consistent with our assignments of the bands at 744 cm^{-1} (asym) and 730 cm^{-1} (sym).

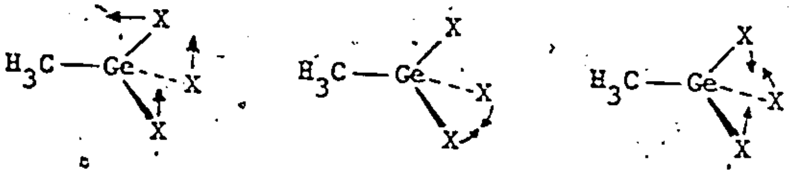
(Table III.4) Fundamental frequencies (cm^{-1}) for GeX_4 species[a]

Mode	GeF_4	$GeCl_4$	$GeBr_4$	GeI_4
GeX_4 str. (sym)	738	396	234	155
GeX_4 def. (sym)	205	134	78	60
GeX_4 str. (asym)	800	453	328	264
GeX_4 def. (asym)	260	172	111	81

a. ref. 168

Some disparity in the original assignments for the skeletal deformations, ν_5 and ν_{12}, and rock, ν_{11}, in $MeGeCl_3$ and $MeGeBr_3$ is apparent. Aronson and Durig[145] have assigned ν_{11} to the lowest band (144 cm^{-1}) in the Raman spectrum of $MeGeCl_3$ on the assumption that ν_5 and ν_{12} were apparently degenerate (179 cm^{-1}). Van de Vondel et al,[144,147] however, have placed the asymmetric deformation, ν_{12}, at lowest wavenumber in both $MeGeBr_3$ (94 cm^{-1}) and $MeGeCl_3$ (141 cm^{-1}); correspondingly the rock, ν_{11}, was assigned as the highest band in $MeGeBr_3$ (162 cm^{-1}) leaving ν_5 attributable only to the intermediate band (125 cm^{-1}). The same workers assumed ν_{11} and ν_5 were degenerate in $MeGeCl_3$ (180 cm^{-1}).

The GeX_3 rock involves a change in the CGeX angle (Fig.III.5) with comparatively little effect on the XGeX angles. It might therefore be expected at about the same frequency as the CGeX angle deformation in the $MeGeH_2X$ series: [Chapter IV.3 : F, 215 cm^{-1}; Cl, 181 cm^{-1}; Br, 164 cm^{-1}; I, 149 cm^{-1}]. The GeX_3 asymmetric deformation involves a motion where the XGeX angle changes and the CGeX angle remains virtually unaffected.



(ν_{12}) (ν_{11}) (ν_5)

Fig.III.5 Approximate motions for the skeletal deformations

This can be compared with the GeX_2 scissors vibration in the $MeGeHX_2$ series [Chapter IV.4 : F, 280 cm^{-1}; Cl, 150 cm^{-1}; Br, 101 cm^{-1}; I, 74 cm^{-1}]. The GeX_3 symmetric deformation is a 'breathing-type' mode where both CGeX and XGeX angles alter and as such is expected to occur at a frequency midway between the rock and asymmetric deformation. It should be remembered that the latter modes depend on the nature of 'X' so that a reversal could occur through the homologous series.

This type of approach confirms the assignments of Van de Kelen et al,[144,147] but would disagree with those of Aronson and Durig.[145] By comparison with the analagous bands in the $MeGeH_2X$ series, the GeX_3 rock, ν_{11}, is assigned to depolarised bands at 156 cm^{-1} (iodide) and 194 cm^{-1} (fluoride) in the Raman spectra. The GeX_3 asymmetric deformation, ν_{12}, is similarly assigned by comparison with $MeGeHX_2$ series to Raman depolarised bands at 72 cm^{-1} (iodide) and 292 cm^{-1} (fluoride). The remaining skeletal mode, ν_5, is therefore assigned to bands at 98 cm^{-1} (iodide) and 254 cm^{-1} (fluoride) in the Raman spectra; the depolarisation factors of these a_1 modes are <u>ca</u>.0.4 and 0.8, respectively. This again is consistent with the mixing of mode expected in the symmetric deformation and is particularly marked in the fluoride. The ordering of skeletal fundamentals is supported by the NCA[164] and the suggested mixing of modes is apparent in the potential energy distributions (PED's) amongst the force constants ie. GeI_3 (sym) def. - 42% f[IGeI]; GeI_3 rock - 32% f[GeI], 71% f[CGeI]; GeI_3 (asym) def. - 12% f[GeI], 90% f[GeI].

The assignments for $MeGeI_3$ are in excellent agreement with those proposed simultaneously by Durig et al.[167] Their studies were further supported by an analysis of the specifically deuteriated analogue, CD_3GeI_3. However on the basis of available experimental evidence their assignment of the CH_3 torsional mode, ν_6, is indeed tenuous. A careful search was made on liquid, solid and solution samples using the argon ion laser excitation but no evidence for the weak 123 cm^{-1} band obtained with the weaker helium neon laser excitation could be found in any spectra. Assuming this was not an experimental artifact, then it is interesting to speculate that a difference band ($\nu_4-\nu_{12}$), ie. 195-67=128, might well be expected in view of the observed intensity of corresponding sum band ($\nu_4+\nu_{12}$), ie. 195+67=262.

Some interesting points arise from a comparison of the skeletal modes (Table III.5) for the now complete series, $MeGeX_3$ (X = F,Cl,Br,I). With the proposed assignments, the skeletal deformations follow predictable patterns which may be considered as being controlled by the mass and electronegativity of the halogen. For the bromide and iodide the GeX_3 symmetric deformation, ν_5, lies between the GeX_3 rock, ν_{11}, and the GeX_3 asymmetric deformation, ν_{12}, due to the much greater effective mass of the halogen compared to the methyl group. For the chloride a change-over point is noticed with ν_5 and ν_{11} apparently degenerate at 180 cm^{-1} and ν_{12} remaining the lowest mode at 141 cm^{-1}. For the fluoride the deformations have exchanged positions and both occur above the rock, although the symmetric mode still lies in the intermediate position.

(Table III.5) Comparison of skeletal frequencies (cm^{-1}) for the $MeGeX_3$ series*

Mode	$MeGeF_3$	$MeGeCl_3$[a]	$MeGeBr_3$[b]	$MeGeI_3$
GeC stretch	630	630(630)	617	598
GeX_3 str. (asym)	744†	424(428)	312	258
GeX_3 str. (sym)	730	398(397)	264	200
GeX_3 rock	194	180(144)	162	156
GeX_3 def. (sym)	254	180(179)	125	98
GeX_3 def. (asym)	292	141(179)	94	72

* Raman (liq) values; † i.r. (gas); a. ref.144; b. ref.147;
( ) indicates values taken from ref.145.

Increases in [Ge-X] and f[Ge-C] from iodine to fluorine are noted in the calculations[164] so that other factors such as the 'stiffening' of bonds for the more electronegative halogens may well be contributing to the trends in the Ge-X_3 and Ge-C stretching modes.

Thus the i.r. and liquid phase Raman spectra of $MeGeI_3$ and $MeGeF_3$ may be satisfactorily assigned on the basis of C_{3v} symmetry, with no strong evidence for any intermolecular association. The solid phase Raman spectrum of $MeGeF_3$ on the other hand, shows several features which differ quite markedly from the liquid spectrum. Accepting solid state effects may have some bearing on the differences, it is conceivable that the appearance of a sharp extra band in the GeF stretching region at 690 cm^{-1} and the apparent disappearance of the GeF_3 symmetric deformation (see Figs.III.3 and III.4) indicates a degree of assocation, possibly by fluorine bridging (Fig.III.6), as is proposed for $MeSnF_3$.[155]

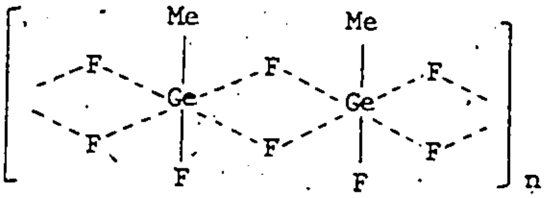


Fig.III.6 Tentative structure for $MeGeF_3$ in the solid state

Extensive discussion on this interesting possibility must await normal coordinate calculations assuming other symmetry groups which in turn will be more meaningful if based on direct structural evidence yet to be obtained. It is worth noting, however, that the ^1H n.m.r. spec[illegible] of dilute solutions of $MeGeF_3$ in CS_2 even at low temperatures gave no indication of the expected H-F (^{19}F, 100% abundant; I = 1/2) coupling which is observed in the hydridic species, ie. $MeGeH_2F$, Me_2GeHF or $MeGeHF_2$, described in Chapter II. Similar anomalous spectra were obtained with SiF_4- and GeF_4- amine complexes[169] which showed only a single ^{19}F resonance, although in this case the lack of coupling was rationalised by a rapid cis-trans isomerisation. This type of behaviour is at least consistent with either an exceptionally rapid equilibrium or some form of intermolecular association. ^{19}F n.m.r. studies in the nematic or solid phases may give some indication of the nature of this interaction.

CHAPTER FOUR

THE VIBRATIONAL SPECTRA OF THE MONO- AND DI-HALOGENO-METHYLGERMANES

IV.I INTRODUCTION

The vibrational analysis of the halogenated methylgermanes, introduced for the fully substituted species, Me_nGeX_{4-n}, in the previous Chapter, is now extended to the hydridic species, $MeGeH_2X$, $MeGeHX_2$, and Me_2GeHX (X = F,Cl,Br,I), from which several new group frequencies are characterised.

The simpler derivatives of germane have received much attention in recent years and these studies provide a frame of reference for the present investigation (Table IV.1). It will be assumed that the spectral regions for the certain vibrational modes are sufficiently characterised as to require no further explanation. These may be summarised as follows: Ge-H stretching, 2150-2050 cm^{-1}; CH_3 stretching, 3000-2900 cm^{-1}; CH_3 bending (2 bands), ca.1400 cm^{-1} and ca.1250 cm^{-1}; Ge–C stretching, ca.600 cm^{-1}; Ge-X stretching, ca.700 cm^{-1} (F), ca.400 cm^{-1} (Cl), ca.

(Table IV.1) Vibrational studies of selected germane derivatives

Germanium hydride	Reference
GeH_4, GeD_4, GeH_3D, $GeHD_3$	170,171
GeH_3X, GeD_3X } (X = F,Cl,Br,I)	172-176
GeH_2X_2, GeD_2X_2	65,69,177-181
$GeHCl_3$, $GeDCl_3$	182
GeH_3GeH_2X (X = Cl,Br,I,Me,Et)	34,183
MH_3GeH_3 (M = C,Si,Ge)	25,184
Me_3MGeH_3 (M = Si,Ge)	185
R_nGeH_{4-n} (R = Me,Et,Ph,CH_2=CH)	25,141-143
$Me_nGe_2H_{6-n}$	186
methylpolygermanes ($Me_{2n+2}Ge_n$)	187

280 cm^{-1} (Br), ca.230 cm^{-1} (I); GeH bending and deformations, 900-400 cm^{-1}; skeletal deformations,$<$300 cm^{-1}.

Prior this study only limited spectroscopic data were available concerning partially-halogenated organogermanes. Satgé and co-workers [19,20,188,189] have reported the Ge-H stretching frequency for species of the type, $R_nGeH_{3-n}X$ ($R = C_2H_5$, $n-C_4H_9$, Ph; X = Cl,Br,I), and Amberger[40] has recorded the i.r. spectra of $MeGeH_2Cl$ and $MeGeHCl_2$ although in both cases no assignment to normal modes was published. During the course of this research the i.r. spectra of $MeGeH_2X$ (X = Cl,Br,I) were reported [75,76] in which the skeletal modes were unidentified and the assignment of the GeH_2 modes differed from the present study in several ways; at the same time Van Dyke et al[71] reported the i.r. absorption frequencies of $MeGeH_2F$ and Me_2GeHF although no assignment of the spectra was undertaken.

In this Chapter the detailed analyses of the infrared and Raman spectra recorded for three series of halogeno-methylgermanes, $MeGeH_3X$, $MeGeHX_2$, and Me_2GeHX (X = F,Cl,Br,I) and their deuteriated analogues, $MeGeD_2X$, CD_3GeH_2X, and $MeGeDX_2$, are presented. The proposed assignments of the normal modes for each molecule are supported again by normal coordinate analysis (NCA), the details of which may be found elsewhere.[164]

IV.2 EXPERIMENTAL

The preparation of the protonated species $MeGeH_2X$, $MeGeHX_2$, and Me_2GeHX (X = F,Cl,Br,I) from $MeGeH_3$ or Me_2GeH_2 was described in Chapter I. Tensiometric samples were estimated to contain less than 2% proton impurity from the ^1H n.m.r. spectra. The specifically deuteriated species $MeGeD_2X$, CD_3GeH_2X, and $MeGeDX_2$ were prepared in an analagous manner by halogenation of $MeGeD_3$ or CD_3GeH_3. The chloro- and bromo- compounds were obtained by the boron trihalide method; the iodo- compounds came from the reactions with elemental iodine; the fluorides were obtained by the exchange reaction of lead(II) fluoride with the corresponding bromide. In all cases the deuterium isotopic content was >95% as estimated from the integration of proton resonances (e.g. $C\underline{H}_3$) against residual proton impurity resonances (e.g. $Ge\underline{H}DX$) in the ^1H n.m.r. spectra.

The i.r. spectra were recorded at room temperature using a gas cell (50 or ~~100 mm~~ path length) fitted with KBr windows; spectra of liquids were recorded with the sample between CsI plates in an air-tight holder. The Raman spectra were recorded for neat liquid samples contained in sealed Pyrex-glass capillaries (ca. 3 mm o.d.) using either helium-neon or argon-ion laser excitation. Strong sharp bands could be estimated to ±1 cm^{-1} in the i.r. and ±4 cm^{-1} in the Raman effect, calibrations being carried out in the usual manner.

All the molecules are assumed to belong to the C_s point group if they have all-tetrahedral angles and are in the staggered configuration (e.g. Fig.IV.1). The 18 fundamentals for both $MeGeH_2X$ and $MeGeHX_2$

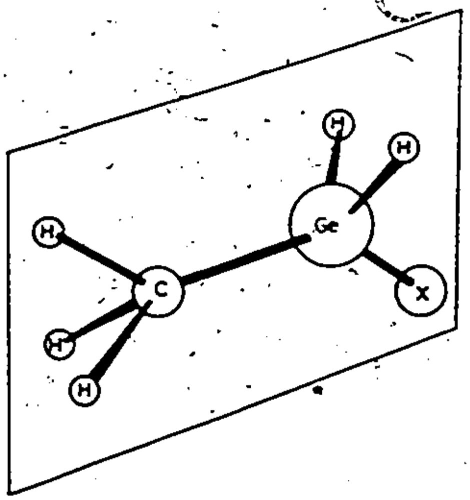


Fig.IV.1 The molecule CH_3GeH_2X in its staggered configuration.

series by the usual group theory considerations are divided into those symmetric, 11a', or antisymmetric, 7a", with respect to the molecular plane or symmetry; similarly in the Me_2GeHX series the 27 fundamentals are divided into 15a' and 12a". All the fundamentals involve a change in the molecular dipole and also, in principle the polarisability, and as such all bands should be both i.r. and Raman active. The a'-vibrations are polarised in the Raman effect whilst a"-vibrations remain depolarised.

The analysis of i.r. gas-phase band contours gives much information to assist the vibrational assignments. For the $MeGeH_2X$ series the 11a'-vibrations produce dipole moment changes parallel to the least and/or intermediate moments of inertia and so are expected to give rise to vapour phase bands of A- and/or B-type contour; the a"-vibrations produce dipole changes parallel to the greatest moment of inertia and so should give C-type contours. By comparison in the $MeGeHX_2$ series the moments of inertia are altered such that the a'-vibrations produce dipole moment changes essentially parallel to either the axis of intermediate or greatest moment of inertia and so are expected to give B- or C-type band contours; the a"-vibrations may also be expected to give A-type contours. With the difluoride, $MeGeHF_2$, the moment of least inertia alters so that while its analogues are 'pseudo-oblate' tops it is closer to being a prolate top; as a consequence a"-vibrations might be expected to be B-type rather than A-type although as the two moments of inertia are very close not too much reliance can be placed on band contours in this instance. By the same generalisations the a'-vibrations in the Me_2GeHX series (X = Cl,Br,I) are expected to give A- and C-type gas phase contours (B- or C-type for X = F) whilst the a"-vibrations should produce B-type contours (A-type for X = F).

Initial investigations with the $MeGeH_2X$ series suggested some overlap of the fundamentals below 900 cm^{-1}; the GeH_2 bend (scissors) was apparently contained in a complex band envelope extending from 800-900 cm^{-1} while the GeH_2 twist and wag could not be assigned to discreet bands other than a single feature at ca.720 cm^{-1}. Deuteriation at germanium produced the expected low frequency shift in all GeH modes and allowed the positive identification of the twist, wag, and rock but the bend was now apparently contained in the same envelope as the GeC stretch. Deuteriation at carbon was effective in establishing the position of the GeH_2 bend at ca.800 cm^{-1} at the same time clarifying the overlapping methyl rocking modes and allowing positive identification of 17 of the 18 fundamentals. Deuteriation only at germanium provided adequate confirmation of the CGeH deformations in the $MeGeHX_2$ series facilitating the unambiguous assignment of 17 of the 18 normal modes. In the Me_2GeHX series the problem of overlapping fundamentals was not apparent, so that the a priori assignment of the vibrational spectra was possible. The assignments were confirmed in all instances by the calculated frequencies obtained in the NCA.[164]

IV.3 MONOHALOGENO(METHYL)GERMANES, $MeGeH_2X$ (X = F,Cl,Br,I)

The conventional descriptions of the 18 fundamental vibrations are given in Table IV.2 with their symmetry species and expected i.r. band contours. The experimental gas phase i.r. and Raman spectra of the three isotopic species, $MeGeH_2Cl$, $MeGeD_2Cl$, and CD_3GeH_2Cl are displayed (Figs.IV.2 and IV.3) to provide representative examples. The observed frequencies and assignment to fundamentals are listed in Tables IV.3-6

Vibrations of the methyl group (ν_1, ν_{12}, ν_2, ν_4, ν_{14}, ν_5, ν_9, ν_{15}, ν_{18}): Depolarised bands in the Raman spectra in the 3000 cm^{-1} region which appear as weak bands in the i.r. are assigned to the

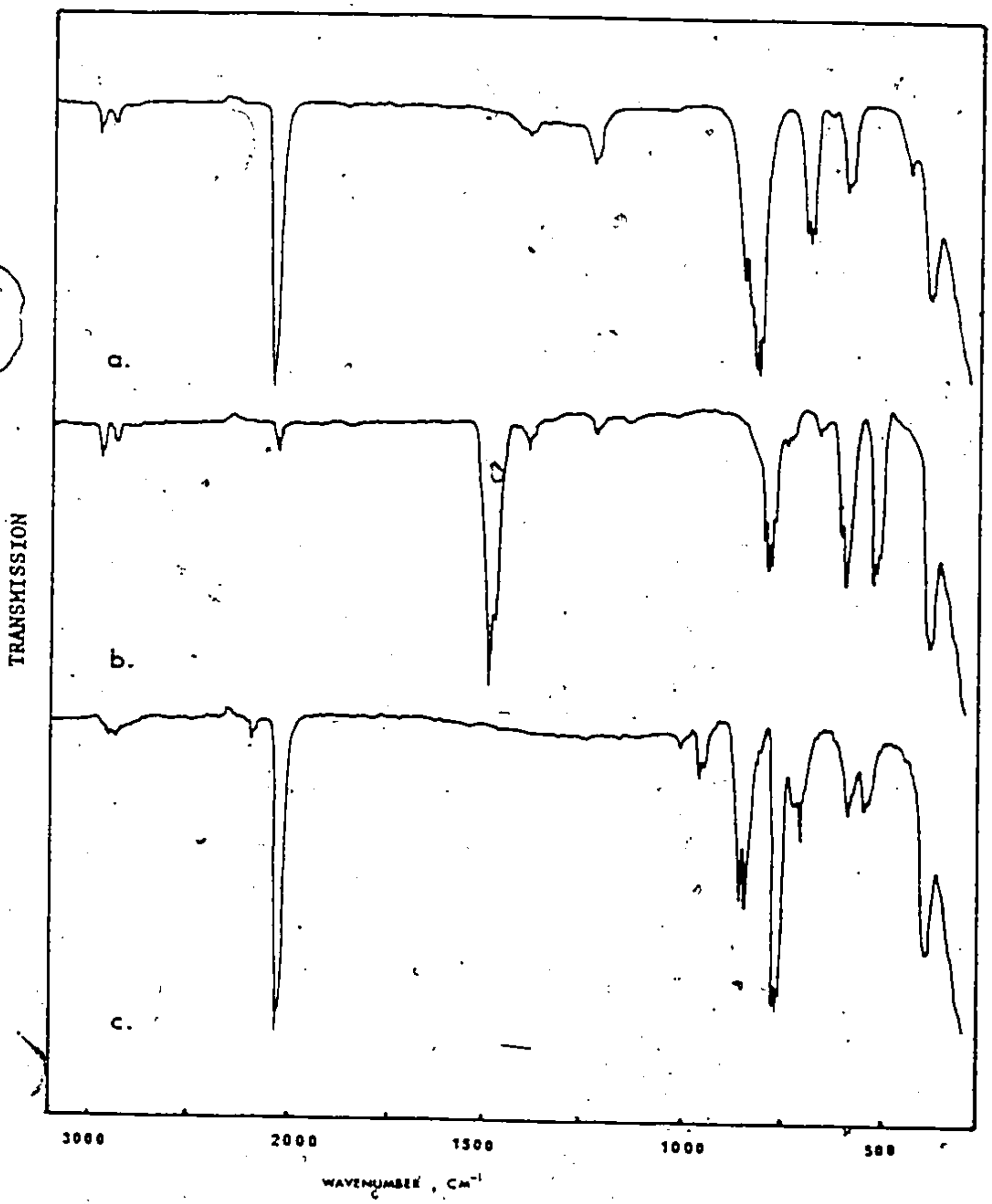


Fig.IV.2 Gas phase infrared spectra of the monochloro(methyl)germanes: (a) $MeGeH_2Cl$; (b) $MeGeD_2Cl$; (c) CD_3GeH_2Cl

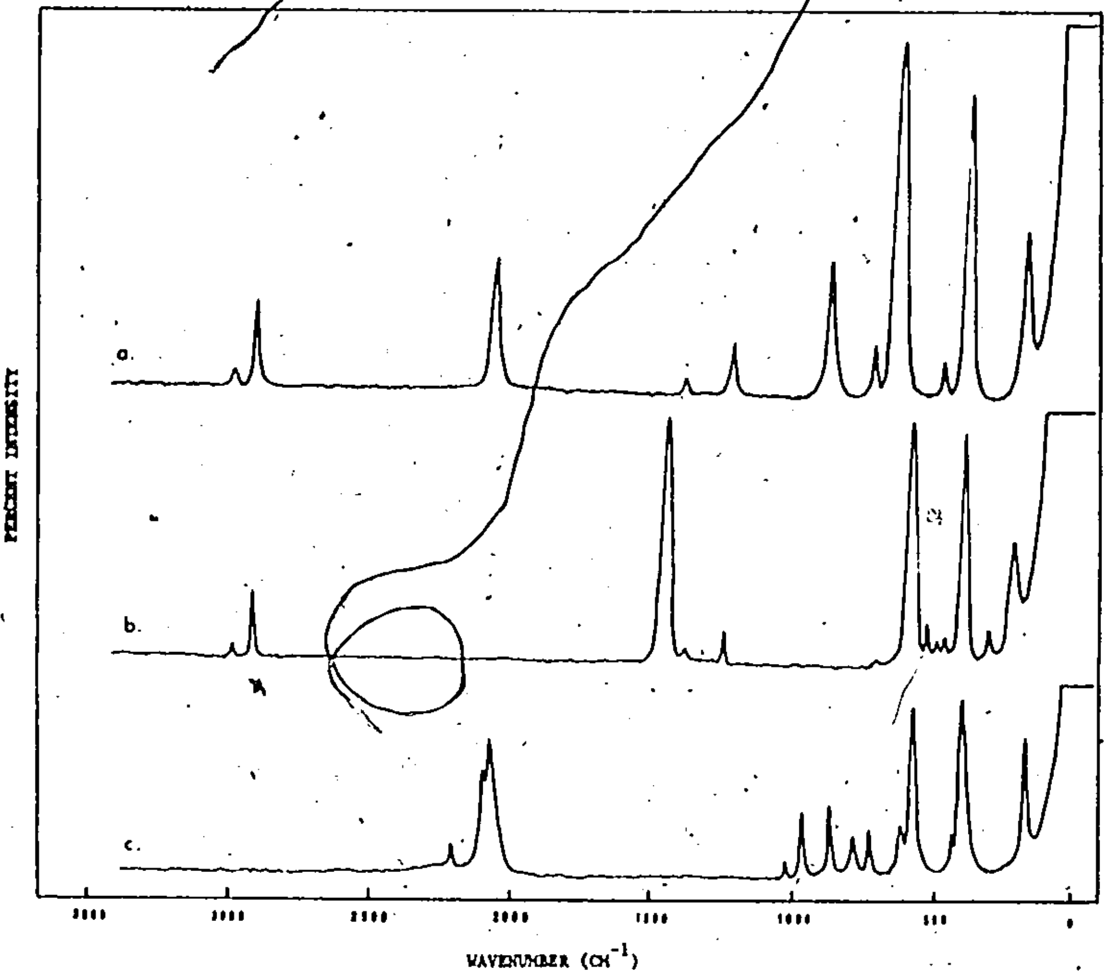


Fig.IV.3 Liquid phase Raman spectra of the monochloro(methyl)germanes:

(a) $MeGeH_2Cl$; (b) $MeGeD_2Cl$; (c) CD_3GeH_2Cl

Table IV.2 Vibrations to be expected of the molecules of type CH_3GeH_2X with their symmetry type and expected i.r. band contours

Vibration*	A'	A''
Band contour	A–B	C
CH_3 stretch (a)	ν_1	ν_{12}
CH_3 stretch (s)	ν_2	
GeH_2 stretch	ν_3	ν_{13}
CH_3 def (a)	ν_4	ν_{14}
CH_3 def (s)	ν_5	
GeH_2 bend	ν_6	
GeH_2 wag	ν_7	
GeX stretch	ν_8	
CH_3 rock	ν_9	ν_{15}
GeC stretch	ν_{10}	
GeH_2 twist		ν_{16}
GeH_2 rock		ν_{17}
CGeX def	ν_{11}	
CH_3 torsion		ν_{18}

All bands i.r. and Raman active.

* C_s symmetry assumed.

asymmetric CH_3 stretches, ν_1 and ν_{12}. As expected, and as is confirmed by the calculations these bands are nearly accidentally degenerate. However, in the i.r. spectra of the lighter halogen derivatives they are sufficiently separated for the C-type structure of ν_{12} to be apparent (Fig.IV.4a). The symmetric CH_3 stretching mode, ν_2, is assigned to a weak i.r. absorption, at ca.2935 cm^{-1} which has a strongly polarised Raman counterpart in the same region. As would be expected these modes shift considerably to lower wavenumber in the deuteriated species, CD_3GeH_2X (X = Cl,Br); the asymmetric CD_3 stretch appears at ca.2250 cm^{-1} and the symmetric at 2133 cm^{-1} although the latter overlaps with the GeH_2 stretching modes in the i.r. spectra. The CH_3 deformation modes occur in the expected regions; the two asymmetric CH_3 deformations, ν_4 and ν_{14}, give rise to one band envelope in the 1400 cm^{-1} region in the i.r. (Fig.IV.4b) with a corresponding depolarised Raman band supporting the assignment. On deuteriation, the corresponding band appears at ca.

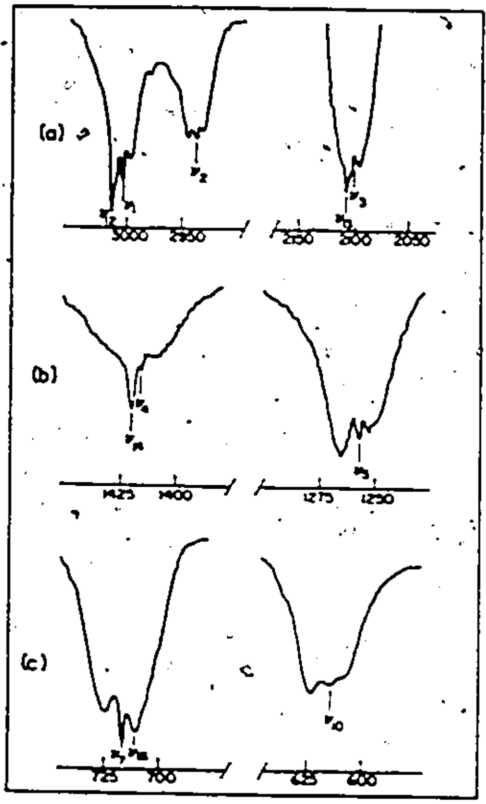


Fig. IV.4 Gaseous i.r. band contours of CH_3GeH_2Br.

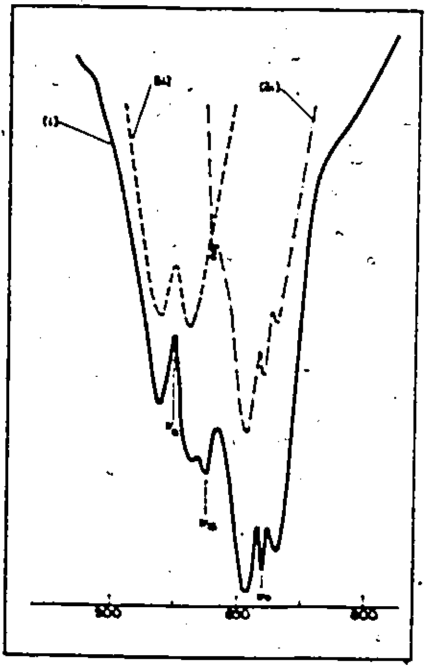


Fig. IV.5 The 850 cm^{-1} region of the gaseous i.r. spectrum of CH_3GeH_2Br (i) including the remaining band contours found in CD_3GeH_2Br (ii) and CH_3GeD_2Br (iii).

(a) MeGeH$_2$F

Infrared (gas)	Raman (liquid)	Calculated	Assignment
3012 3004 w	3000 dp w	3008.1 3008.2	ν_1 ν_{12}
2936 m	2930 p m	2936.0	ν_2
2142 s	2130 dp m	2141.8	ν_{13}
2104 s	2100 p s	2104.0	ν_3
1420 m	1416 dp w	1430.9 1429.8	ν_4 ν_{14}
1279 1266 1254 s	1260 p m	1275.8	ν_5
915 885 m	880 p m	903.7	ν_6
858 s	860 dp m	867.9	ν_{15}
854 850 846 s	840 p m	853.0	ν_8
731 721 710 sh m	740 p w	734.7	ν_7
705 s		729.9	ν_{16}
700 sh 690 s	700 w	683.8	ν_9
633 w	618 p s	621.7	ν_{10}
478 vw	479 dp w	484.1	ν_{17}
	215 p w	213.6	ν_{11}

(b) MeGeD$_2$F

Infrared (gas)	Raman (liquid)	Calculated	Assignment
3016 s 3005 sh	3005 dp w	3010.7 3010.6	ν_{12} ν_1
2940 s	2924 p m	2939.9	ν_2
2820 w			
2105 vw			GeH Impurity
1542 s		1544.9	ν_{13}
1515 s	1509 p s	1515.1	ν_3
1423 w		1434.7 1435.7	ν_4 ν_{14}
1275 1262 1255 m	1262 p m	1271.9	ν_5
825 m		832.4	ν_{15}
809 m		816.7	ν_8
699 692 683 s		689.3	ν_9
640 sh 625 m	619 p s 598 p m	644.1 613.8	ν_{10} ν_6
578 565 555 m	565 dp w	565.8	ν_7
		569.4	ν_{16}
	379 dp w	378.0	ν_{17}
	219 p m	219.8	ν_{11}

Table IV.3 The vibrational spectra of the monofluoro(methyl)germanes (cm^{-1})

(a) $MeGeH_2Cl$

Infrared (gas)		Raman (liquid)	Calculated	Assignment
3013 w			3006.3	ν_{12}
3010 sh 3003 2996 } w		2996 dp w	3006.2	ν_1
2943 2936 2930 } w		2923 p m	2925.7	ν_2
2833 vw				
2109 s	*C*		2106.9	ν_{13}
2100 2097 } s	*B*	2093 p s	2101.1	ν_3
			1431.7	ν_4
1421 w		1420 dp w		
			1433.9	ν_{14}
1257 w		1250 p m	1257.2	ν_5
868 860 } m	*B*	863 p m	864.0	ν_6
843 sh			849.3	ν_{15}
834 826 820 } s			833.4	ν_7
724 717 711 } s		716 p m	714.7	ν_8
			720.3	ν_{16}
624 616 608 } m		618 p s	616.6	ν_{10}
463 w		458 dp m	460.5	ν_{17}
421 415 408 } s	*A*	383 p s	414.4	ν_9
		181 p s	170.4	ν_{11}

(b) $MeGeD_2Cl$

Infrared (gas)		Raman (liquid)	Calculated	Assignment
3016 w			3006.6	ν_{12}
		3010 dp w		
3004 w			3006.5	ν_1
2930 w		2920 p m	2927.9	ν_2
2110 vw		2106 p vw		GeH Impurity
1522 s	*C*		1521.0	ν_{13}
		1507 p s		
1518 1506 } s	*B*		1513.1	ν_3
			1436.6	ν_4
1425 vw		1420 dp w		
			1437.0	ν_{14}
1264 vw		1253 p m	1273.0	ν_5
831 s	*C*		830.3	ν_{15}
820 810 803 } s			817.3	ν_6
633 } s			623.6	ν_{16}
		619 p s		
624 } s			620.2	ν_7
584 574 565 } s		563 p m	580.0	ν_8
			457.3	ν_{10}
415 s		379 p s	413.0	ν_9
		360 sh	357.2	ν_{17}
		178 p m	170.7	ν_{11}

(c) CD_3GeH_2Cl

Infrared (gas)		Raman (liquid)	Calculated	Assignment
2240 w			2238.1	ν_{12}
		2252 dp m		
2236 sh			2237.8	ν_1
2135 sh		2133 p s	2133.0	ν_2
			2104.9	ν_{13}
2098 2090 } s		2103 p s		
			2093.0	ν_3
1040 vw		1040 dp w	1049.6	ν_{14}
			1048.1	ν_4
995 m		992 p m	993.0	ν_5
882 866 } s	*B*	878 p m	880.7	ν_6
796 786 780 } s	*A*	790 dp m	789.2	ν_7
730 m	*C*	736 dp m	733.4	ν_{15}
610 m		615 dp m	614.2	ν_{16}
			612.6	ν_8
568 m		567 s	567.6	ν_{10}
		434 dp w	435.9	ν_{17}
410 s		383 p s	410.0	ν_9
		186 p s	186.0	ν_{11}

Table IV.4 The vibrational spectra (cm^{-1}) of the monochloro(methyl)germanes

(a) $MeGeH_2Br$

Infrared (gas)		Raman (liquid)	Calculated	Assignment
3018 w			3007.4	ν_{10}
		3005 dp w		
3009 3002 2996 w			3007.2	ν_1
2936 w		2925 p m	2934.6	ν_2
2106 s			2103.9	ν_{11}
2102 2096 s	B	2091 p s	2099.0	ν_3
			1443.3	ν_{12}
1430 w		1420 dp w	1441.3	ν_4
1262 1250 w		1247 p m	1256.8	ν_5
883 868 sh	B	866 p m	882.6	ν_6
864 m	C		870.4	ν_{13}
847 840 835 s			847.4	ν_7
709 705 701 s		704 m	707.3	ν_8
			723.9	ν_{14}
620 610 m	B	610 p s	616.3	ν_9
484 w		480 dp w	440.2	ν_{15}
		276 p s	274.4	ν_9
		162 p m	163.1	ν_{11}

(b) $MeGeD_2Br$

Infrared (gas)		Raman (liquid)	Calculated	Assignment
			3001.1	ν_1
3001 w		2995 dp w		
			3001.2	ν_{10}
2930 w		2930 p m	2920.9	ν_2
2103 vw		2095 vw		GeH impurity
1575 vw				
1520 s	C		1519.9	ν_{11}
1514 sh 1507 s	B	1518 p s	1510.0	ν_3
1433 w		1420 dp vw	1436.4	ν_4
			1435.6	ν_{12}
1261 1253 w 1247		1248 p m	1262.2	ν_5
833 m	C		839.8	ν_{13}
818 810 806 s			817.0	ν_6
633 sh s		618 p s	620.7	ν_{14}
622		592 p m	620.2	ν_7
			541.6	ν_8
539 s		535 p m		
531 sh			540.0	ν_{15}
490 w		490 dp w		
		350 dp w	345.3	ν_{11}
		277 p s	277.1	ν_9
		158 p m	158.7	ν_{11}

(c) CD_3GeH_2Br

Infrared (gas)		Raman (liquid)	Calculated	Assignment
2240 w			2237.7	ν_{10}
		2240 dp w		
2225 sh			2237.6	ν_1
2100 s		2140 p s	2140.2	ν_2
		2105 m	2104.9	ν_{11}
2090 sh				
		2090 m	2090.1	ν_3
			1042.7	ν_{12}
1035 w		1030 dp m		
			1040.3	ν_4
978 968 m		975 p m	999.1	ν_5
874 863 s	B	860 p m	874.0	ν_6
780 774 768 s		780 p w	779.6	ν_7
739 s		738 dp m	733.3	ν_{13}
			692.0	ν_{14}
688 s		680 dp s	690.6	ν_8
660 s		660 p s	660.6	ν_{14}
415 w			429.4	ν_{15}
		282 p s	281.7	ν_9
		140 p s	141.6	ν_{11}

Table IV.5 The vibrational spectra (cm^{-1}) of the monobromo(methyl)germanes

(a) $MeGeH_2I$

Infrared (gas)		Raman (liquid)	Calculated	Assignment
3018 vw		3013	3002.2	ν_{12}
3010 3002 vw 2994		3000 w	3002.1	ν_1
2929 vw		2917 p m	2929.0	ν_2
2104 s	C	2110 dp s	2103.9	ν_{13}
2098 s		2082 p	2098.1	ν_3
1422 vw			1430.4	ν_4
		1415 dp w		
1416			1431.1	ν_{14}
1260 1249 vw		1245 p m	1263.6	ν_5
882 866 m	B	865 p m	872.8	ν_6
853 m	C	850 w*	860.3	ν_{15}
845 840 s 835		830 w	847.2	ν_8
702 694 m 685		690 dp m	698.2	ν_7
			706.7	ν_{16}
614 607 m	B	604 p s	612.8	ν_{10}
442 vw		445 dp w	430.9	ν_{17}
		226 p s	225.8	ν_9
		149 p s	148.4	ν_{11}

(b) $MeGeD_2I$

Infrared (gas)		Raman (liquid)	Calculated	Assignment
			2999.3	ν_{12}
2999 w		2995 dp w		
			2999.2	ν_1
2932 w		2917 p m	2931.8	ν_2
2095		2090 p vw		GeH Impurity
1516 s	C	1513 dp m	1515.5	ν_{13}
1509 1500 s	B	1498 p s	1504.6	ν_3
			1432.5	ν_4
1421 w		1415 dp w		
			1433.8	ν_{14}
1255 w		1245 p m	1264.6	ν_5
831 m	C	830 dp w	837.6	ν_{15}
816 810 s 805		810 p w	816.9	ν_8
630 618 s		608 p s	625.4	ν_{10}
		585 p s	617.3	ν_6
520 s			525.7	ν_7
		510 m		
513 sh			526.1	ν_{16}
		336 dp w	331.9	ν_{17}
		228 p s	229.2	ν_9
		160 p s	160.4	ν_{11}

Table IV.6 The vibrational spectra (cm^{-1}) of the monoiodo(methyl)germanes

1040 cm^{-1}. The symmetric CH_3 deformation mode, ν_5, is readily assigned to a band in the 1250 cm^{-1} region which shifts to ca.990 cm^{-1} on deuteriation. It is clearly polarised in the Raman effect and an A-type contour is evident, particularly in the i.r. spectrum of $MeGeH_2Br$ (Fig.IV.4b). The unambiguous assignment of the CH_3 rocking modes, ν_{15}, and ν_9, comes from the spectra of the isotopic species $MeGeD_2X$ in which no overlap with GeH_2 modes can occur. The asymmetric rock, ν_{15}, is confidently assigned to the higher wavenumber feature at ca.870 cm^{-1} which appears as a clear C-type band in all the i.r. spectra and is depolarised in the Raman effect. The symmetric CH_3 rock, ν_9, is observed at lower wavenumber as an A-type band (Fig.IV.5) and where the data are clear is Raman polarised. No band is observed in any spectra that can be satisfactorily assigned to the CH_3 torsion, ν_{18}.

In general the frequencies of the methyl fundamentals are insensitive to changes in the halogen substituent and are therefore probably well decoupled from the skeletal vibrations. Only a slight lowering of frequency from fluorine to iodine is observed but at the same time it is interesting to note that deuteriation at the germanium atom causes the CH_3 stretches to shift to higher wavenumber for any one halogen.

Vibrations of the GeH_2 group (ν_3, ν_{13}, ν_6, ν_7, ν_{16}, ν_{17}): The Ge-H stretches appear in the expected region of the spectra. The a'-symmetric GeH_2 stretch, ν_3, is assigned to the low wavenumber feature at ca.2100 cm^{-1} in all spectra being polarised in the Raman effect and showing a clear B-type contour in some i.r. gas spectra. The corresponding a"-asymmetric mode, ν_{13}, appears as a weak depolarised band in the Raman which shows a C-type contour in the i.r. (Fig.IV.4a). Similar features are noted for the GeD_2 stretching modes in the deuteriated species, $MeGeD_2X$, which are seen in the 1500 cm^{-1} region. Some difficulty was incurred in assigning the GeH_2 bending mode, ν_6 (scissors). In the $MeGeH_2X$ series, ν_6 apparently overlaps with the CH_3 rocking mode (Fig.IV.5) and on deuteriation at germanium with the GeC stretching region. However in the isotopic species, CD_3GeH_2X (X = Cl,Br), a clear B-type band is observed at ca.875 cm^{-1} which is confidently assigned to ν_6, this being supported by the NCA.[164] By comparison the GeH_2 bend was tentatively assigned at 934 cm^{-1} in the GeH_3GeH_2X (X = Cl,Br,I) species[183] and the SiH_2 bend in $MeSiH_2X$ (X = F,Cl,Br,I) species at ca.955 cm^{-1}.[190]

For the corresponding series of monohalogeno(methyl)silanes $MeSiH_2X$, the SiH_2 wagging mode, ν_7, was assigned close to the bending mode (scissors) with the twisting mode at lower wavenumber.[190] By analogy this would place the wagging mode in the $MeGeH_2X$ series at ca.820 cm^{-1} which would be under the methyl rocking modes and the twisting mode at ca.700 cm^{-1} which should have a C-type contour. However, in the isotopic species, CD_3GeH_2X (X = Cl,Br), no band is seen in the 820 cm^{-1} region and the band at ca.700 cm^{-1} is readily interpreted as resulting from the overlapping of A- and C-type bands (Fig.IV.4c). Thus both the GeH_2 wagging mode, ν_7, which should be A-type and the GeH_2 twisting mode, ν_{16}, are assigned to this feature. These two modes were also assumed to be accidentally degenerate in Me_2GeH_2.[25] The band contour alters considerably in the $MeGeD_2X$ species as would be expected if there was a slight relative change in the positions of the two modes on deuteriation. The calculations indicate that both bands are considerably mixed showing large dependence on both f[CGeH] and f[HGeX].[164]

The GeH_2 rock was not assigned in the GeH_3GeH_2X series[183] and the SiH_2 rock has been assigned at ca.500 cm^{-1} in the $MeSiH_2X$ series.[190] The corresponding band, ν_{17}, in the $MeGeH_2X$ series appears as a weak feature in the i.r. spectra at ca.460 cm^{-1} which is weak and depolarised in the Raman effect. Deuteriation at germanium causes it to shift to ca.350 cm^{-1} although in both isotopic species the position is markedly affected by the nature of the attached halogen. Calculations again indicate a large dependence on f[HGeX].[164]

Vibrations of the CGeX skeleton (ν_{10}, ν_{8}, ν_{11}): The GeC stretching mode, ν_{10}, is unambiguously assigned to a sharp Raman polarised band at ca.615 cm^{-1} in all spectra; the corresponding i.r. band shows A- or B-type structure (Fig.IV.4c). The analagous band was assigned at 602 cm^{-1} in $MeGeH_3$[25] and at 601 cm^{-1} in $MeGeI_3$ (see Chapter III). The GeX stretching modes, ν_{8}, appear in the expected region of the spectrum as strongly polarised bands in the Raman effect. The corresponding i.r. absorptions for the bromide and iodide lie outside the KBr range but a definite A-type contour is discernible for the chloride at ca.400 cm^{-1} whilst the fluoride has more of a B-type contour at ca.695 cm^{-1}. The CGeX angle deformation, ν_{11}, is attributed to the lowest wavenumber mode in all the Raman spectra in the 215-150 cm^{-1} region. As further confirmation of its designation as an a'-vibration it is clearly polarised.

The CH_3 stretches and deformations, and the GeH_2 stretches lie in well defined regions of the spectra and the NCA indicates they are all essentially pure modes. The same is true of the CGeX deformation, the GeC stretch, and the GeX stretch although for $MeGeH_2F$ considerable mixing with f[CGeH], f[HGeF], and f[GeC] is apparent in the GeF stretch. The GeH_2 deformations, ν_{6}, ν_{7}, ν_{16} and ν_{17}, are all mixed modes and as expected they show large dependencies on f[CGeH], f[HGeH], and f[HGeX].[164]

For the related methylsilanes[190] the frequencies of the bending and wagging modes varied almost linearly with the electronegativity of the halogen, although no such relationship held for the twisting and rocking frequencies. The corresponding frequencies for Me_2GeH_2 and the $MeGeH_2X$, and GeH_2X_2 series are collected in Table IV.7. No simple linear relationships are apparent for the germanium compounds although the decrease in wavenumber does at least reflect the changing electronegativity of the halogen. The near degeneracy of the wag and twist in the $MeGeH_2X$ series is strikingly different from the GeH_2X_2 series where they are well defined and widely separated. Considering the narrow ranges for all the modes and their mixed nature any further comments would be too highly speculative.

(Table IV.7) Correlation of GeH_2 deformation frequencies (cm^{-1})

	scissors	Wag	Twist	Rock
$MeGeH_2F$	900	721	705	472
$MeGeH_2Cl$	875	717	717	463
$MeGeH_2Br$	875	705	705	456
$MeGeH_2I$	873	694	694	442
Me_2GeH_2 [a]	890	662	662	430
GeH_2F_2 [b]	860	813	n.o.	596
GeH_2Cl_2 [b]	854	779	648†	524
GeH_2Br_2 [b]	848	757	640†	492
GeH_2I_2 [b*]	821	706	628†	451

a. ref.25; b. ref.177-181

gas i.r. values except* mull or † Raman

IV.4 DIHALOGENO(METHYL)GERMANES, $MeGeHX_2$ (X = F,Cl,Br,I):

The conventional descriptions of the 18 fundamentals appear in Table IV.8 with their classification into symmetry species. The experimental i.r. and Raman spectra of the isotopic species, $MeGeHCl_2$ and $MeGeDCl_2$, are displayed (Figs.IV.6 and 7) with the observed frequencies and assignments for all molecules listed in Tables IV.9-12. As for the

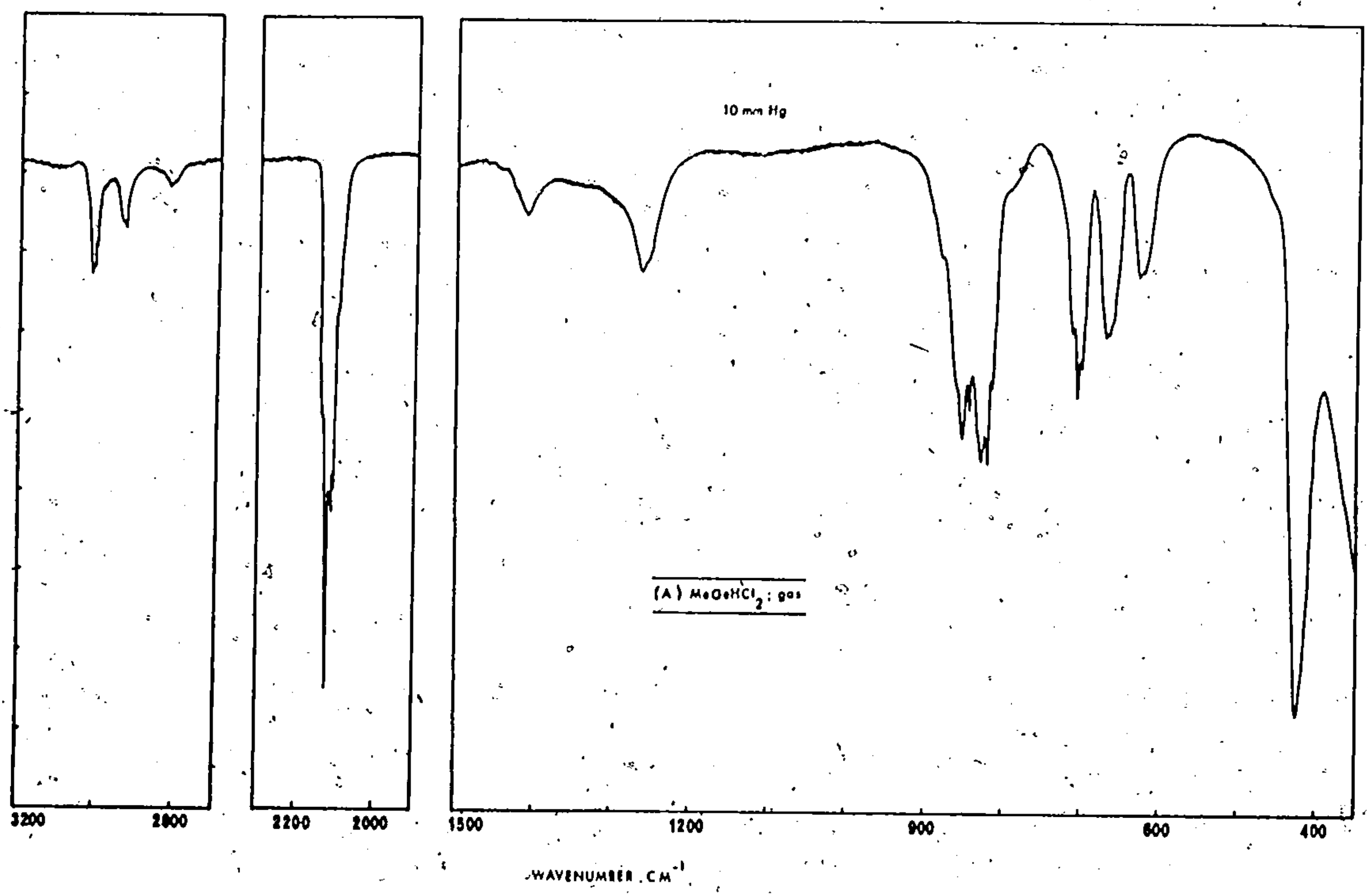


Fig.IV.6a The gas phase infrared spectrum of MeGeHCl$_2$

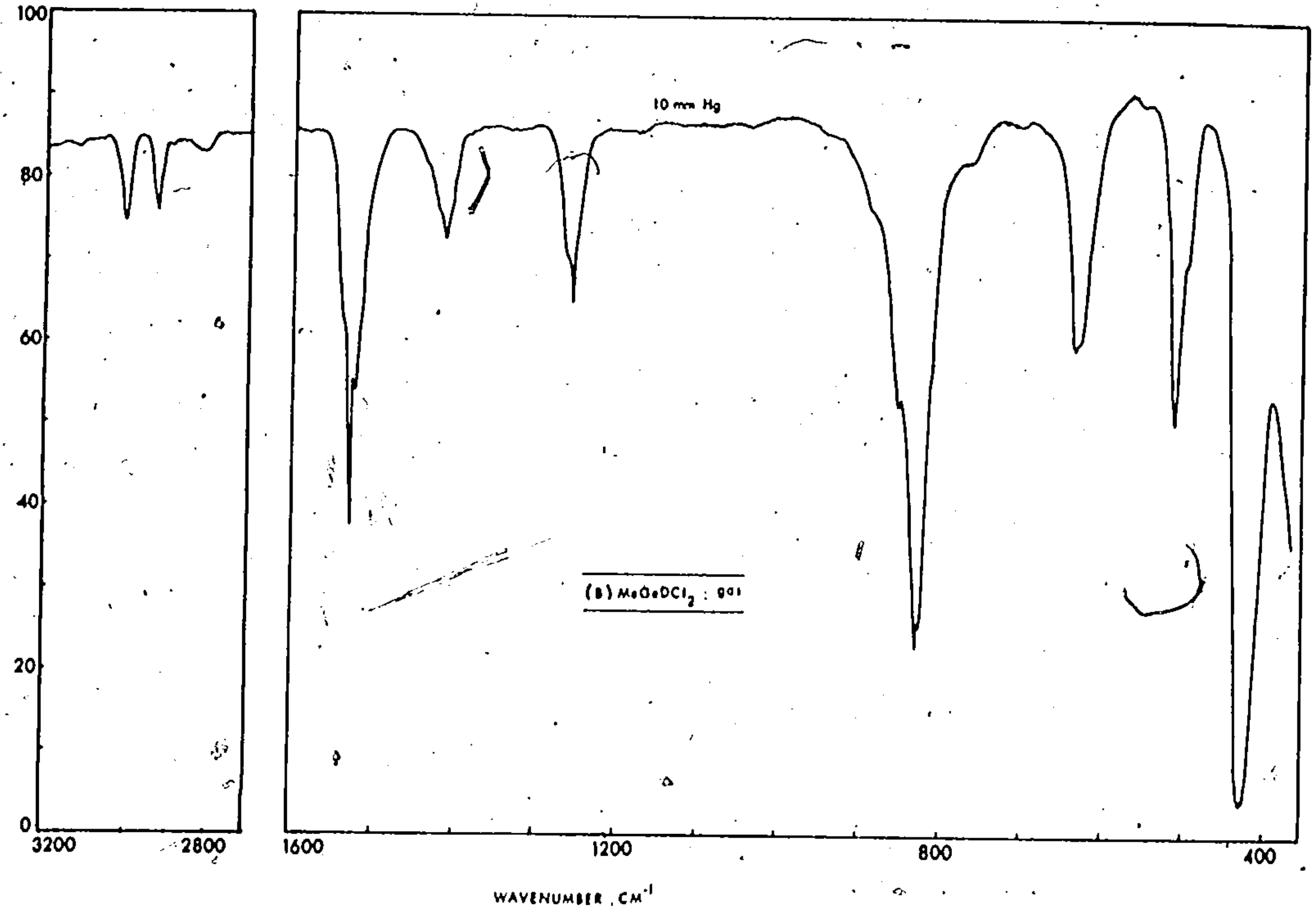


Fig.IV.6b The gas phase infrared spectrum of $MeGeDCl_2$

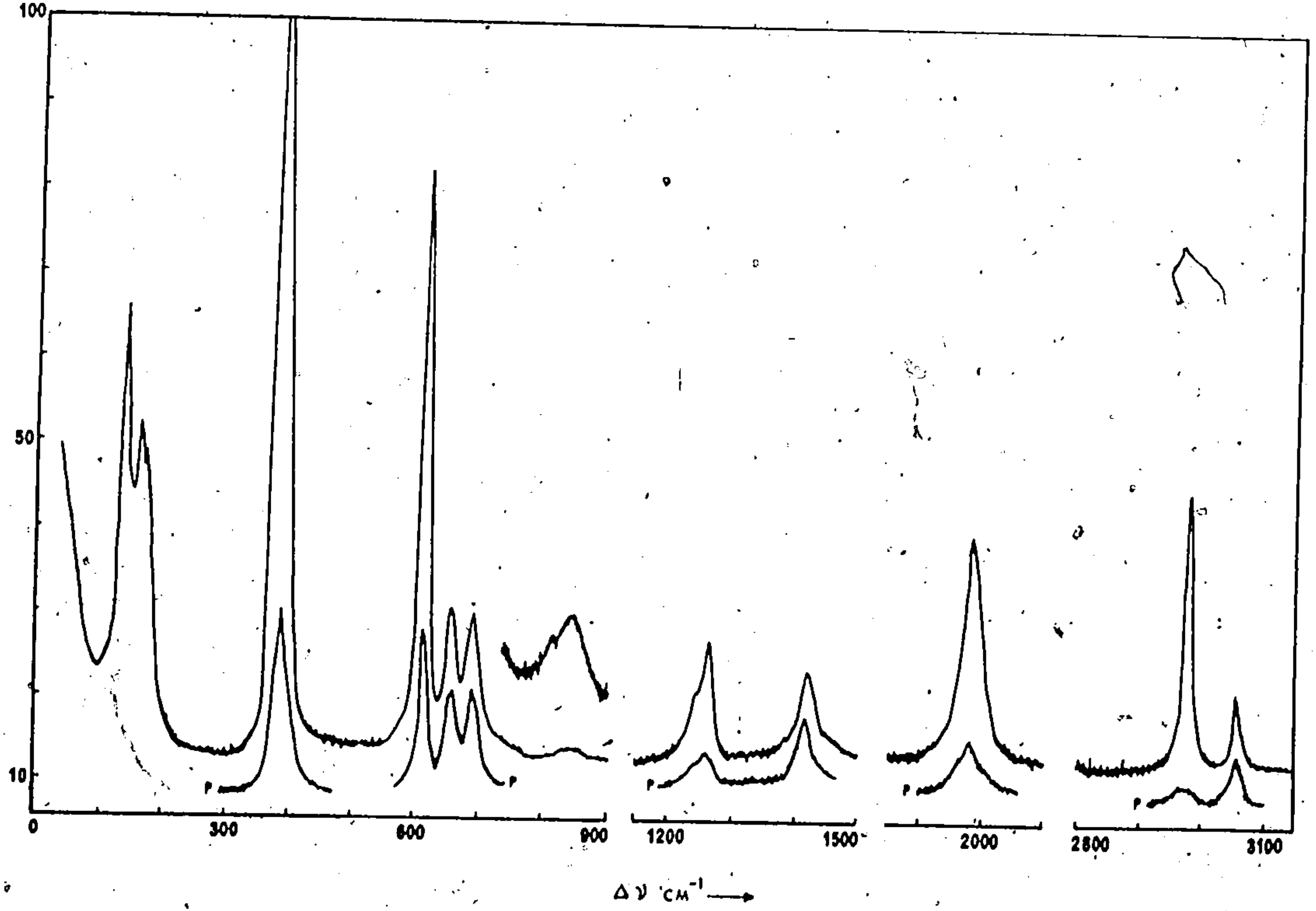


Fig.IV.7a The liquid phase Raman spectrum of $MeGeHCl_2$ (Ar-laser)

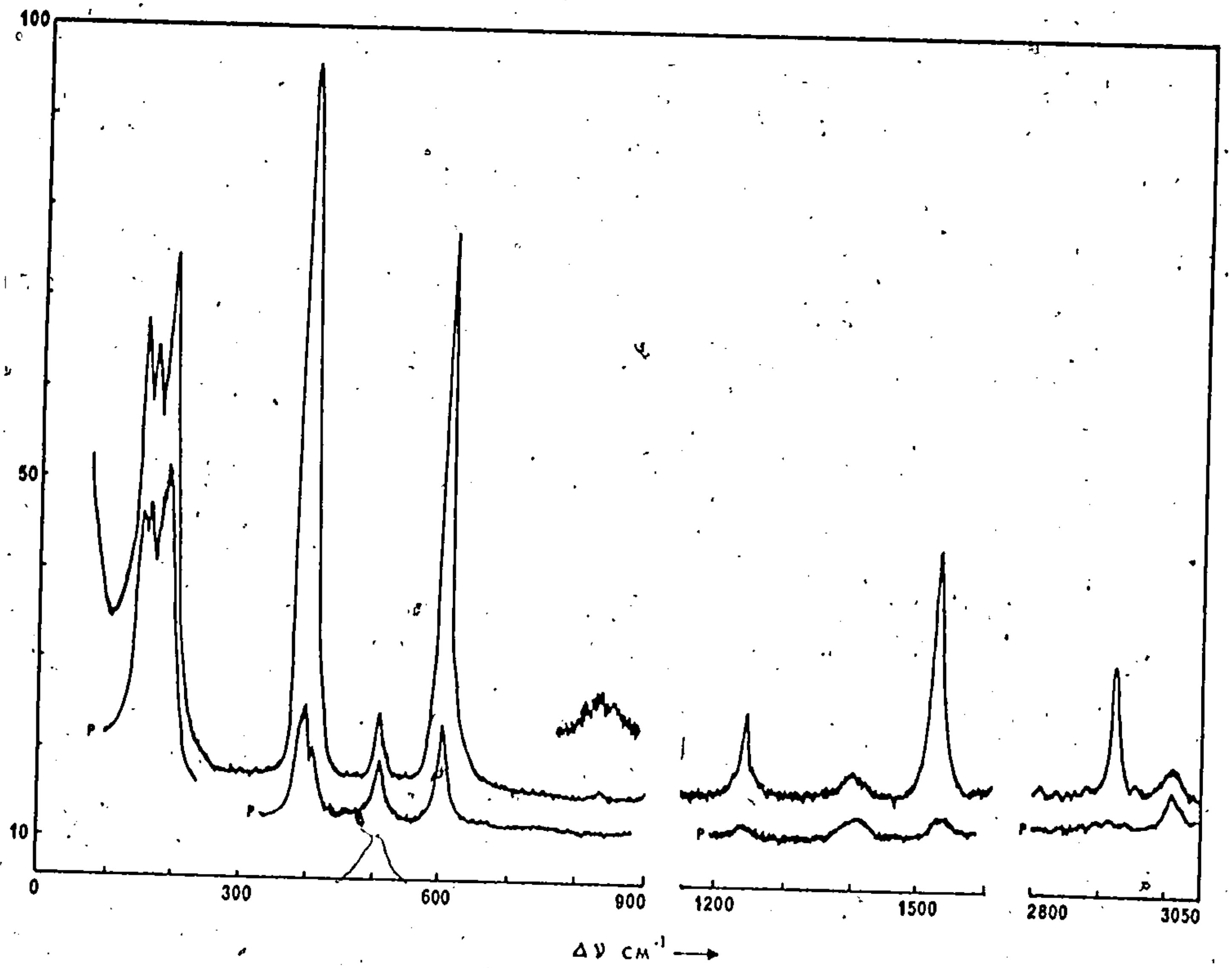


Fig.IV.7b The liquid phase Raman spectrum of $MeGeDCl_2$ (Ar-laser)

(Table IV.8) Description of fundamental frequencies for molecules of the type CH_3GeHX_2

Vibration†	a'	a"
CH_3 stretch (a)	ν_1	ν_{12}
CH_3 stretch (s)	ν_2	
GeH stretch	ν_3	
CH_3 def (a)	ν_4	ν_{13}
CH_3 def (s)	ν_5	
CH_3 rock	ν_6	ν_{14}
CGeH def	ν_7	ν_{15}
GeC stretch	ν_8	
GeX_2 stretch	ν_9	ν_{16}
GeX_2 wag	ν_{10}	
GeX_2 def (sc.)	ν_{11}	
GeX_2 twist		ν_{17}
CH_3 torsion		ν_{18}

All bands i.r. and Raman active

† Cs symmetry assumed

monohalogeno-series the assignments are conveniently discussed in terms of fundamentals involving the methyl group, GeH group, and heavy-atom skeleton.

Vibrations of the methyl group (ν_1, ν_{12}, ν_2, ν_4, ν_{13}, ν_5, ν_6, ν_{14}, ν_{18}): The CH_3 stretching modes, ν_1, ν_2, and ν_{12}, give rise to two bands in the 2900–3000 cm^{-1} region. The two asymmetric stretches, ν_1 and ν_{12}, are not resolved in any spectra and are assigned to the same band envelope in both the i.r. and Raman effects at ca.3000 cm^{-1}; the symmetric stretch, ν_2, is clearly polarised in the Raman spectra and appears at ca.2920 cm^{-1}. Two general trends are apparent in these modes; in all cases there is a slight shift to higher wavenumber on deuteriation and a lowering in wavenumber as the halogen changes from fluorine to

Table IV.9

a: Vibrational spectra (cm^{-1}) of MeGeHF$_2$

I.r. (gas)	Raman (liq.)	Calculated	Assignment
3020vw	3000w	3019·1	ν_1
		3019·1	ν_{10}
2945vw	2930m,P	2942·9	ν_2
2159sh 2150s 2142sh } C	2120s,P	2150·0	ν_3
1425vw	1428w	1427·1	ν_4
		1425·7	ν_{11}
1280 1272w 1264 } C	1254m,P	1272·1	ν_5
855sh	n.o.	854·6	ν_6
846sh 840m 836sh } A	n.o.	839·6	ν_{12}
733sh	n.o.	738·4	ν_{13}
725m	n.o.	729·5	ν_7
700s	n.o.	698·1	ν_{14}
690s	n.o.	640·0	ν_8
634s	630s,P	631·0	ν_9
n.o.	280m,P	279·9	ν_{15}
n.o.	218m	216·9	ν_{17}
		214·3 ~	ν_{16}

b: Vibrational spectra (cm^{-1}) of MeGeDF$_2$

I.r. (gas)	Raman (liq.)	Calculated	Assignment
3022vw	3012vw	3021·3	ν_1
		3021·2	ν_{10}
2948vw	2932m,P	2947·5	ν_2
2147vw			GeH impurity
1535s	1530s,P	1535·0	ν_3
1422w	n.o.	1422·9	ν_4
		1421·7	ν_{11}
1262m	1248m,P	1261·9	ν_5
850s	n.o.	849·5	ν_6
830s	n.o.	829·2	ν_{12}
710s	n.o.	715·3	ν_7
		713·0	ν_{13}
630m	630s,P	627·8	ν_8
520s	522w,dP	519·9	ν_{14}
490sh	498m,P	489·9	ν_9
n.o.	285w,P	286·3	ν_{15}
n.o.	229m	229·6	ν_{17}
		220·0	ν_{16}

Table IV.10

a: Vibrational spectra (cm^{-1}) of MeGeHCl$_2$

I.r. (gas)	Raman (liq.)	Calculated	Assignment
3010w	3008w	3010·2	ν_1
		3010·0	ν_{10}
2930w	2932s,P	2930·0	ν_2
2125s	2130s,P	2125·0	ν_3
1412w	1407w	1412·9	ν_4
		1410·9	ν_{11}
1261m	1250m,P	1262·2	ν_5
855sh 846s 837sh } C	852vw	845·2	ν_6
829s 822s 815s } A	825vw	831·6	ν_{12}
714s 707s 701s } A	700m,dP	707·1	ν_{13}
671m 667m 663m }	640m	647·5	ν_7
629m 622m } B	625s,P	623·4	ν_8
422s	400s,dP	400·0	ν_{14}
	392P	392·0	ν_9
n.o.	179m	179·0	ν_{17}
n.o.	172m	168·9	ν_{16}
n.o.	150s,P	150·0	ν_{15}

b: Vibrational spectra (cm^{-1}) of MeGeDCl$_2$

I.r. (gas)	Raman (liq.)	Calculated	Assignment
3015w	3010w	3013·9	ν_1
		3013·8	ν_{10}
2940w	2920m,P	2938·5	ν_2
2120w			GeH impurity
1531s	1530m,P	1531·0	ν_3
1420w	1420vw	1423·5	ν_4
		1421·4	ν_{11}
1262m	1245w,P	1262·0	ν_5
846sh	n.o.	845·7	ν_6
822s	n.o.	821·9	ν_{12}
625m	600s,P	628·0	ν_7
515s	510w,dP	514·2	ν_{13}
495sh	500w	497·3	ν_8
420s	400s,dP	398·6	ν_{14}
	395P	393·0	ν_9
n.o.	180m	181·3	ν_{17}
n.o.	175m	172·6	ν_{16}
n.o.	150m,P	151·0	ν_{15}

Tables IV.9 & 10 The vibrational spectra of the difluoro- and dichloro-(methyl)germanes

Table IV.11

a; Vibrational spectra (cm^{-1}) of MeGeHBr$_2$

I.r. (gas)	Raman (liq.)	Calculated	Assignment
3009w	3008w	3009.0 3009.0	ν_1 ν_{10}
2936w	2917m,P	2935.1	ν_2
2114s 2107s } B	2112m,P	2110	ν_3
1418w	1405w	1418.1 1412.8	ν_4 ν_{11}
1258w	1248m,P	1258.0	ν_5
848sh 839s 832sh } C	n.o.	839.2	ν_6
823 820 817 } A	n.o.	820.9	ν_{12}
704sh 694s 687s } A	676m,dP	698.6	ν_{13}
653m	646m,P	652.5	ν_7
621m 616m } B	615s,P	618.4	ν_8
n.o.	290m,dP	290.8	ν_{14}
n.o.	270s,P	268.8	ν_9
n.o.	166s	166.0	ν_{15}
n.o.	163s,P	162.2	ν_{10}
n.o.	101s	101.1	ν_{11}

b; Vibrational spectra (cm^{-1}) of MeGeDBr$_2$

(Liq. film)	Raman (liq.)	Calculated	Assignment
2994w	2994w,dP	2994.0 2994.0	ν_1 ν_{10}
2916w	2916s,P	2914.0	ν_2
2100vw	2100vw,P		GeH impurity
1517m	1517s,P	1517.0	ν_3
1400m	1400w	1403.9 1401.5	ν_4 ν_{11}
1243m	1242m,P	1243.0	ν_5
840s	n.o.	849.6	ν_6
822s	n.o.	822.0	ν_{12}
610m	630s,P	610.0	ν_8
486s	485m	486.8	ν_{13}
482sh	485m	483.3	ν_7
290s	290m,sh,dP	285.4	ν_{14}
278sh	280s,P	273.5	ν_9
n.o.	172s	171.6	ν_{15}
n.o.	165s	160.0	ν_{10}
n.o.	100s,P	104.6	ν_{11}

Table IV.12

a; Vibrational spectra (cm^{-1}) of MeGeHI$_2$

I.r. (liq.)	Raman (liq.)	Calculated	Assignment
2990vw	2990w	2990.0 2990.0	ν_1 ν_{10}
2915w	2912m,P	2914.9	ν_2
2060s	2062s,P	2060.0	ν_3
1645vw			$\nu_6 + \nu_8 = 1646$
1620vw			$2\nu_{11} = 1624$
1400m	1400w	1400.1 1396.0	ν_4 ν_{11}
1238m	1238m,P	1244.2	ν_5
850s	852vw,P	848.4	ν_6
812s	815vw,dP	810.4	ν_{12}
656s	654m	655.8	ν_{13}
634s	628m	637.8	ν_7
607s	603s,P	602.6	ν_8
248s	248m,dP	246.9	ν_{14}
222s	222s,P	220.1	ν_9
n.o.	149m	147.3	ν_{15}
n.o.	140m	128.9	ν_{10}
n.o.	74s,P	75.8	ν_{11}

b; Vibrational spectra (cm^{-1}) of MeGeDI$_2$

(Liq. film)	Raman (liq.)	Calculated	Assignment
3140vw			$\nu_1 + \nu_{15} = 3147$
2997w	2990w,dP	2996.3 2996.2	ν_1 ν_{10}
2912m	2907m,P	2910.8	ν_2
2760vw			$\nu_2 - \nu_{15} = 2762$
2460vw			$2\nu_5 = 2470$
2080w			GeH impurity
1498s	1505s,P	1498.0	ν_3
1400s	1420w	1404.3 1401.3	ν_4 ν_{11}
1235s	1250m,P	1234.6	ν_5
848s	n.o.	847.9	ν_6
816s	n.o.	815.2	ν_{12}
607s	599s,P	610.9	ν_8
469s	475m	470.3 468.7	ν_{13} ν_7
233s	250m,dP	239.6	ν_{14}
221s	216s,P	212.4	ν_9
n.o.	158m	158.2	ν_{15}
n.o.	150m	146.8	ν_{10}
n.o.	72s,P	77.3	ν_{11}

Tables IV.11 & 12 The vibrational spectra of the dibromo- and diiodo-(methyl)germanes iodine, as is observed in the $MeGeH_2X$ series. The CH_3 deformations, ν_4, ν_{13}, and ν_5, all occur in typical positions; the asymmetric modes ν_4 and ν_{13} are unresolved in a depolarised Raman band in the 1400 cm^{-1} region and the symmetric mode, ν_5, is unambiguously assigned to a polarised band at ca.1250 cm^{-1}. The CH_3 rocking modes, ν_6 and ν_{14}, exhibit only weak features in the Raman effect and were not clearly observed with the levels of laser excitation available from the earlier He-Ne source, other than for $MeGeHI_2$. With the Ar-laser the lower wavenumber feature is clearly depolarised (Fig.IV.7) and so is assigned to ν_{14}. This is supported by the gas-phase i.r. spectra of $MeGeHCl_2$ (Fig.IV.6) in which the lower wavenumber band shows the A-type structure expected for an a"-vibration whilst the higher wavenumber feature has a hybrid contour. No band assignable to the CH_3 torsion, ν_{18}, was observed in any spectra.

Vibrations of the GeH group (ν_3, ν_7, ν_{15}): The GeH stretching mode, ν_3, is assigned to the polarised band observed in the 2100 cm^{-1} region of the Raman spectra; the corresponding gaseous i.r. bands are strong and show mixed contours varying between C-type for $MeGeHF_2$ and $MeGeDCl_2$, and B-type in $MeGeHBr_2$. On deuteriation the expected shift to the 1500 cm^{-1} region occurs although the band contours are less well defined. The CGeH deformation modes, ν_7 and ν_{15}, arise from the in-plane and out-of-plane motions of the hydrogen with respect to the plane of symmetry (Fig.IV.8). The a'-mode, ν_7, involves deformation of both the CGeH

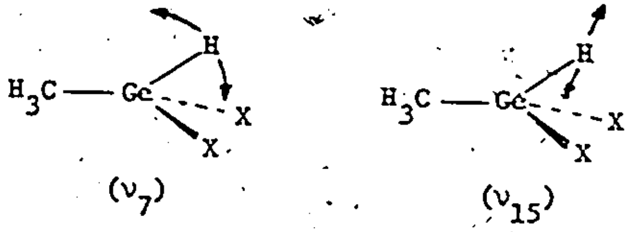


Fig.IV.8 Approximate motions for the CGeH deformations and HGeX bond angles, whilst the a"-mode, ν_{15}, alters only the HGeX angle; the fewer interactions of the a"-mode suggest its assignment to the higher wavenumber feature, thus the depolarised Raman band at ca. 700 cm^{-1} which shifts to ca.510 cm^{-1} on deuteriation is attributed to ν_{15}. The a'-mode is assigned at ca.640 cm^{-1} although it is apparently depolarised in the Raman effect, undoubtedly due to mixing with other modes. This band is observed at ca.500 cm^{-1} in the isotopic species, $MeGeDX_2$, so that the separation of the deformations noticeably decreases with deuteriation. The same occurs when the mass of the attached halogens increases, so that in $MeGeDI_2$ the two bands are accidentally degenerate. The PED's confirm the strong dependence on f[HGeX] for both modes with an additional marked dependence on f[CGeH2]for the in-plane mode, ν_7; for $MeGeHF_2$ additional mixing with GeF stretching modes is also apparent[164] as might be expected from their appearance in the same spectral region.

Vibrations of the $CGeX_2$ skeleton (ν_8, ν_9, ν_{16}, ν_{10}, ν_{11}, ν_{17},): The GeC stretching mode, ν_8, is confidently assigned to a sharp polarised band at ca.600 cm^{-1} in all the Raman spectra. For $MeGeHBr_2$ where the Ge-C dipole is fairly well aligned with the intermediate axis of inertia the B-type contour is clear in its i.r. spectrum. In the difluoride where the Ge-C bond is aligned with the axis of least moment the band has more of an A-type contour as is expected. The GeX_2 stretching modes, ν_9 and ν_{16}, appear as polarised and depolarised bands respectively in the Raman effect for all the halides except the difluoride. The corresponding i.r. bands for $MeGeHBr_2$ and $MeGeHI_2$ lie outside the KBr range but for $MeGeHCl_2$ ν_9 and ν_{16} apparently lie in the same band envelope at ca.420 cm^{-1}; in the i.r. of gaseous $MeGeHF_2$ a distinct shoulder appears on the high wavenumber side of a medium band envelope at ca.725 cm^{-1} which is assigned to the GeF_2 stretches although the corresponding Raman bands were not observed with the helium-neon laser.

The skeletal deformation modes, ν_{11}, ν_{10}, and ν_{17}, arise from motions approximately described as GeX_2 scissoring, wagging, and twisting respectively (Fig.IV.9). Little change in the CGeH angle is expected for ν_{11} (sc) and this is assigned, by comparison with the GeH_2X_2[177-181]

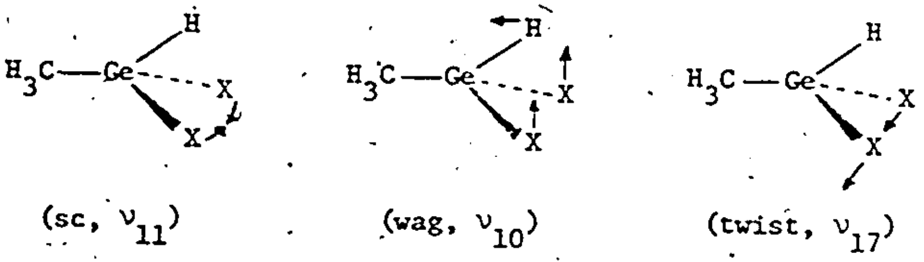


Fig.IV.9 Approximate motions for the skeletal deformations

and Me_2GeX_2[146,147] series, to a polarised Raman band at lowest wavenumber in all spectra except the difluoride; in this case it is assigned as the highest of the skeletal deformations at ca.280 cm^{-1} by analogy with the asymmetric GeF_3 deformation in $MeGeF_3$ (Chapter III). In ν_{10}, the GeX_2 angle remains nearly constant with varying change in the HGeX and CGeH angles although in the twist, ν_{17}, these also remain nearly constant. The separation between ν_{10} and ν_{17} is very small, apparently decreasing as the halogen becomes more electronegative; the a'-species, ν_{10}, is assignable to the lower wavenumber feature since it is polarised to some extent in most spectra, and the a"-species, ν_{17}, is assigned to the depolarised shoulder at higher wavenumber, this being confirmed by the NCA. In $MeGeHF_2$ both modes are apparently contained in an unresolved envelope at 215 cm^{-1}. It is interesting to note that as the size of the halogen increases, there is an increasing dependence on f[HGeX] for the twist but for the wag the dependence on the particular force constants is remarkably similar for all 8 molecules.[164]

(Table IV.13) Comparison of skeletal frequencies (cm^{-1}) for the $MeGeHX_2$ series*

Mode	$MeGeHF_2$	$MeGeHCl_2$	$MeGeHBr_2$	$MeGeHI_2$
GeC stretch	630	625	615	603
GeX_2 str.(mean)	799[8]	396[8]	280[20]	235[26]
GeX_2 twist	215	179	166	149
GeX_2 wag	215	172	163	140
GeX_2 bend(sc)	280 (270†,259)	150 (163,146)	101 (105,97)	74 (96¶,73)

* Raman (liq) values; † calculated; ¶ Raman solid; ( ) indicates frequency of corresponding mode in GeH_2X_2[177-181] and Me_2GeX_2[146,147] respectively; [ ] indicates separation of asym. and sym. modes.

The skeletal frequencies all show a clear shift to low wavenumber with decreasing halogen electronegativity but with a corresponding increase in the separation of the GeX_2 stretches, ν_9 and ν_{16} (Table IV.13). At the same time, deuteriation at germanium apparently has the effect of slightly increasing the wavenumber of the skeletal deformations. As might be expected the GeX_2 scissors mode for the $MeGeHX_2$ series is midway between the analogous modes in the GeH_2X_2 and Me_2GeX_2 series. The ordering of the GeX_2 scissors, wag, and twist is similar to that proposed for the GeX_3 skeletal deformations (see Table III.5); the GeX_2 wag compares to the GeX_3 symmetric deformation in being a mixed mode intermediate to the purer mode involving GeX_2 scissoring (GeX_3 asymmetric deformation) and GeX_2 twisting (GeX_3 rock). The analogy extends to a reversal of the scissors and twist in the fluoride (a reversal of the GeX_3 asymmetric deformation and rock was apparent in $MeGeF_3$).

IV.5 MONOHALOGENO(DIMETHYL)GERMANES, Me_2GeHX (X = F,Cl,Br,I):

The conventional descriptions of the 27 normal modes are given in Table IV.14 with their classification into symmetry species and the expected band contours. Representative experimental spectra are displayed for the bromo-species, Me_2GeHBr (Figs. IV.10 and IV.11) with the observed frequencies and assignment to fundamentals listed for all molecules in Tables IV.15 and 16.

(Table IV.14) Fundamental vibrations for $(CH_3)_2GeHX$ species†

Conventional Description * Band Contour¶	a' A–C	a" B
CH_3 stretch (a)	ν_1, ν_2	ν_{16}, ν_{17}
CH_3 stretch (s)	ν_3	ν_{18}
Ge–H stretch	ν_4	
Ge–X stretch	ν_5	
GeC_2 stretch	ν_6	ν_{19}
CH_3 def (a)	ν_7, ν_8	ν_{20}, ν_{21}
CH_3 def (s)	ν_9	ν_{22}
CH_3 rock	ν_{10}, ν_{11}	ν_{23}, ν_{24}
GeHX def	ν_{12} (bend)	ν_{25} (twist)
GeC_2 def	ν_{13}	
CGeX def	ν_{14}	ν_{26}
CH_3 torsion	ν_{15}	ν_{27}

† All bands i.r. and Raman active; *(a) and (s) refer to the local Cs symmetry of a CH_3 group; ¶ For the fluoride a' are (B–C) and a" are A.

Vibrations of the methyl groups: The extra methyl group increases considerably the complexity of the methyl fundamentals and the almost total lack of band contours does not permit the individual modes to be assigned unambiguously. The asymmetric CH_3 stretching modes, ν_1, ν_2,

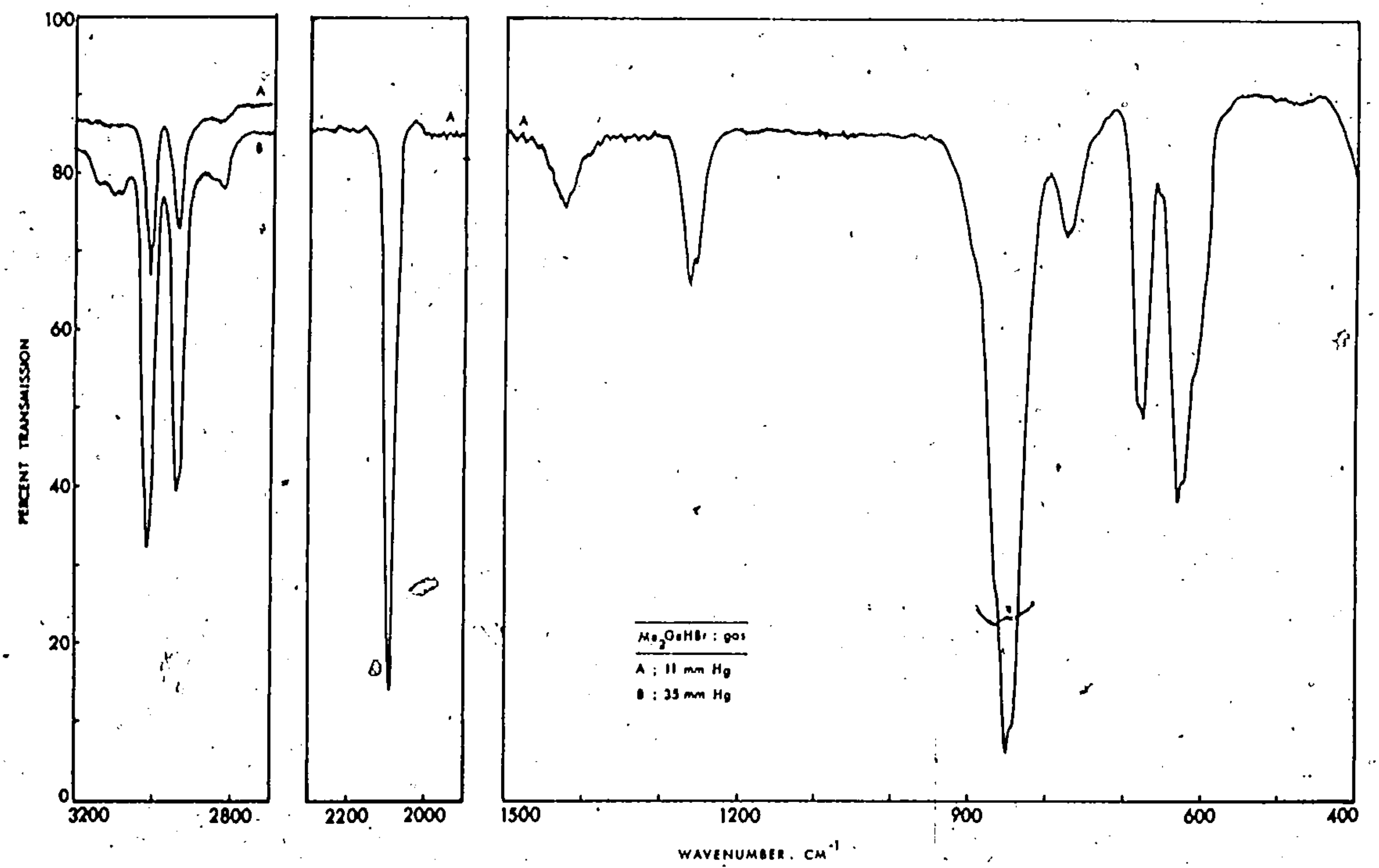


Fig.IV.10 The gas phase infrared spectrum of Me_2GeHBr

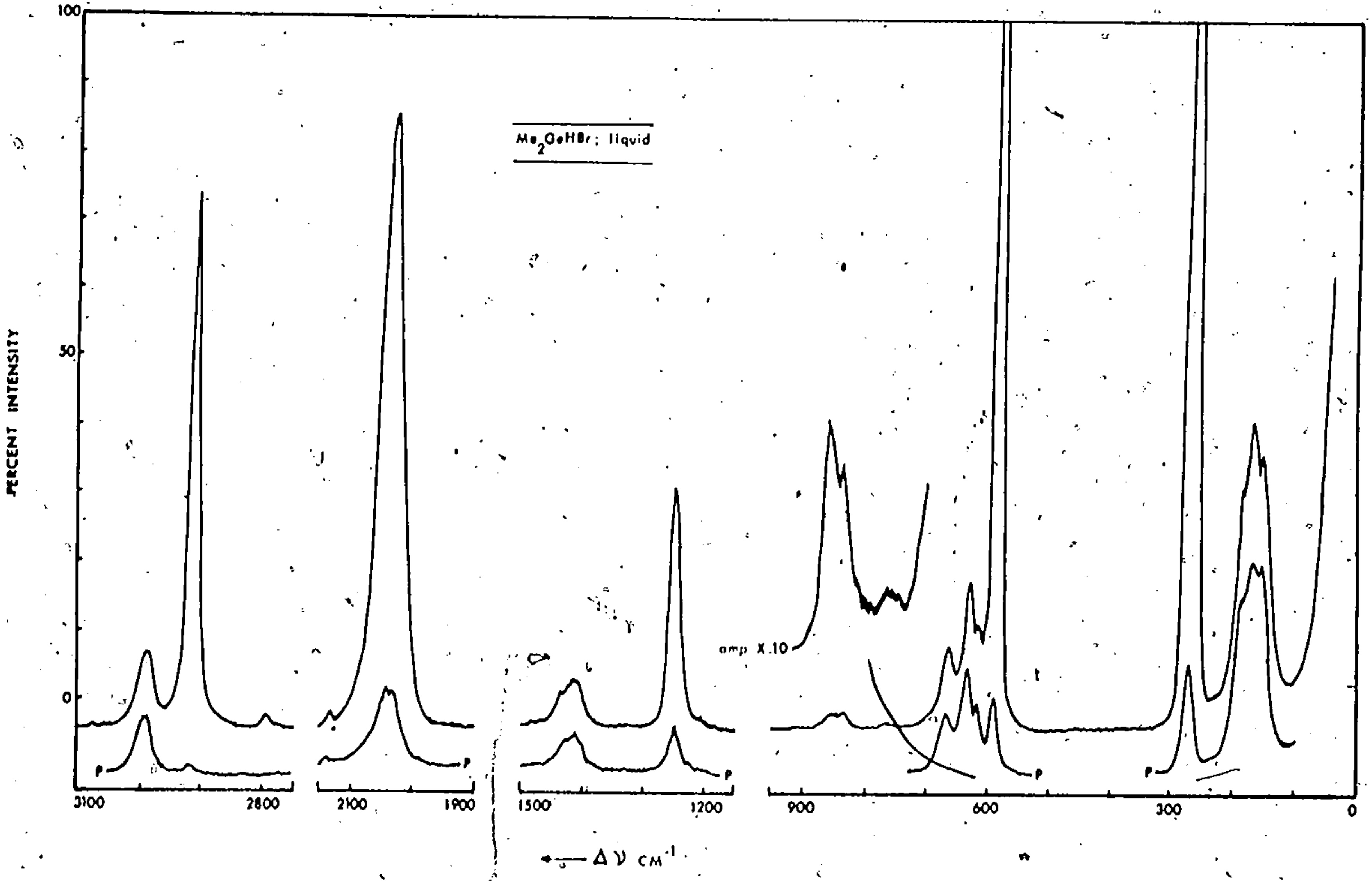


Fig.IV.11 The liquid phase Raman spectrum of Me$_2$GeHBr

(Table IV.15) The vibrational spectra (cm^{-1}) of fluoro- and chloro(dimethyl)germane*

Me_2GeHF			Me_2GeHCl			
i.r.(gas)	Raman(liq)	Calc.	i.r.(gas)	Raman(liq)	Calc.	Assignment
3770 w	–					2930 + 845 = 3775
3198 vs	–					3004 + 190 = 3194
3076 w	–		3118 w 3080 w	– –		2922 + 190 = 3112
3004 } m 2993	3001 m,dp	3001.4 3001.3} 3001.2 3000.7	3004 } m 2971	3001 w,dp	3001.3 3001.2} 3001.2 3000.7	$\nu_1, \nu_2, \nu_{16}, \nu_{17}$
2930 vs	2924 s,p	2925.8} 2925.6	2929 m	2922 s,p	2921.8} 2921.7	ν_3, ν_{18}
2825 w	2812 w,p		2812 w	2804 vw,p		3004 − 190 = 2814
2678 vw	–					1424 + 1256 = 2680
2490 vw	–		2485 vw	–		2 x 1256 = 2512
2250 vw	–		2256 vw	–		841 + 1423 = 2264
2097 A 2085} vs 2075	2086 s,p	2086.0	C 2083 vs	2089 s,p	2089.0	ν_4
1885 sh	–		1890 vw	–		1256 + 622 = 1878
1860 vw	–					1252 + 598 = 1850
1505 vw	–		1600 vw	–		
1424 m	1423 vs,dp	1424.3 1423.8} 1419.9 1419.3	1423 vs } 1417 sh	1416 w,dp	1418.2 1417.7} 1414.0 1413.3	$\nu_7, \nu_8, \nu_{20}, \nu_{21}$
1324 vw	–					622 + 707 = 1329
1265 A 1256} m 1248	1252 m,p	1251.2 1250.9	1259 }m 1251	1251 m,p	1252.1} 1251.4	ν_9, ν_{22}
1082 vw	–		1077 vw	–		1251 − 190 = 1066
1040 sh	–					1251 − 222 = 1034
			890 sh	–		
	858 sh,dp	854.5	862 sh	862 w,dp	848.2	ν_{23}
845 s,br	845 w,dp	847.7	850 841} vs 835	830 w,dp	842.3	ν_{10}
762 } m 757	n.o	763.3} 756.1	770 m	758 vw,dp	760.1} 755.7	ν_{24}, ν_{11}
719 A 707} m 697	715 m,dp	712.7	688 m	690 m,dp	690.0	ν_{25} (+ν_5 fluoride)
674} sh 665 m	645 ms,dp	637.3	660 w	641 m,dp	641.3	ν_{12}
633} sh 622 s	n.o.	621.6	B 628} 618 s	620 sh,dp	619.9	ν_{19}
610 sh	600 vs,p	595.3	600 sh	599 vs,p	598.6	ν_6
		676.1	406 s	382 vs,p	382.0	ν_5
	190 s,p	191.0		190 sh,dp	189.1	ν_{13}
	222 s,p	221.1} 218.7		182 vs,p	179.2} 176.7	ν_{26}, ν_{14}

---

* In Tables IV.15,16 the Raman data were obtained with the Ar-laser.

(Table IV,16) The vibrational spectra (cm^{-1}) of bromo- and iodo(dimethyl)germane

Me$_2$GeHBr			Me$_2$GeHI			
i.r.(gas)	Raman(liq)	Calc.	i.r.(gas)	Raman(liq)	Calc.	Assignment
3780 vw	-					2921 + 862 = 3783
3125 vw	-		3122 w	-		
3089 vw	-		3088 w	-		
3002 m	2998 vw,dp	2998.3 2998.2} 2998.1 2997.7	3003 sh 2992 m	2998 2987 } w,dp	2992.5 2992.5} 2992.2 2991.7	ν_1, ν_2, ν_{16}, ν_{17}
2928 m	2921 s,p	2920.8} 2920.7	2926 m	2916 s,p	2915.7} 2915.6	ν_3, ν_{18}
2806 vw	2805 w,p		2810 vw	2801 vw,p		
C 2083 s	2083 s,p	2083.0	C 2077 s	2076 s,p	2076.0	ν_4
1890 sh	-					
1847 vw	-		1842 w	-		1252 + 598 = 1850
1422 m	1414 w,dp	1416.7 1416.3} 1412.5 1411.9	1418 m	1409 w,dp	1410.2 1409.7} 1405.9 1405.2	ν_7, ν_8, ν_{20}, ν_{21}
1257 } m 1248	1251 m,p	1251.0} 1248.1	1256 } m 1248	1247 m,p	1249.8} 1246.4	ν_9, ν_{22}
960 vw	-					1251 - 279 = 972
890 sh	-		890 sh	-		
861 sh	862 w,dp	854.3	867 sh	856 w,dp	841.8	ν_{23}
849 842} vw 836	840 w,p	849.0	843 839} vw 835	824 w,p	836.3	ν_{10}
768 m	770 vw,p	772.9} 768.1	763 m	756 vw,dp	756.0} 755.5	ν_{24}, ν_{11}
	675 m,dp	674.7		653 m,dp	654.2	ν_{25}
649 s,br			654 s,br			{
	641 m,dp	640.9		637 m,dp	636.9	ν_{12}
B 625 617} s	623 m,dp	622.9	615 s	618 m,dp	615.5	ν_{19}
598 sh	596 vs,p	596.6	591 s	589 vs,p	589.9	ν_6
	279 vs,p	279.0		231 vs,p	230.5	ν_5
	187 sh,dp	187.1		187 m,dp	187.3	ν_{13}
	170 ms,dp	169.3		161 ms,dp	160.5	ν_{26}
	154 ms,dp	155.0		142 sh,dp	143.5	ν_{14}

ν_{16} and ν_{17}, are assigned to the same band envelope in the 3000 cm^{-1} region which is depolarised in the Raman effect. Some splitting of this band is apparent particularly in the i.r. spectra but the Raman polarisation data do not allow the component a'- and a"-modes to be distinguished. The symmetric CH_3 stretching modes, ν_3 and ν_8, are confidently assigned to a single band in the 2925 cm^{-1} region which is intense and strongly polarised in the Raman. The CH_3 asymmetric deformations, ν_7, ν_8, ν_{20} and ν_{21}, are all apparently contained in a single unresolved band envelope in the 1420 cm^{-1} region which is depolarised in the Raman spectra and therefore gives no information regarding the a'-species, ν_7 and ν_8. The symmetric CH_3 deformations ν_9 and ν_{22}, appear as expected in the 1250 cm^{-1} region. In the Raman effect the weak band is strongly polarised as might be expected for the a'-species, ν_9, while in the i.r. spectra the corresponding band appears as B-type (A-type for the fluoride) as expected for the a"-mode, ν_{22}. Four methyl rocks are expected, two of a'-species, ν_{10} and ν_{11}, and two of a"-species, ν_{23}, ν_{24}. Coupling between these modes gives rise to bands in both 830 and 760 cm^{-1} regions and these are only assigned with confidence by means of the NCA results. The bands have no definite gaseous contours in their i.r. spectra and are of very low intensity with no clear degrees of polarisation in the Raman effect. No assignment of the CH_3 torsions, ν_{15} and ν_{27}, is possible from the available spectra.

Vibrations of the GeH group (ν_4, ν_{12}, ν_{25}): The GeH stretching mode, ν_4, appears low at ca.2080 cm^{-1} in this series, its designation as an a'-species being confirmed by the observation of a strongly polarised Raman band. The i.r. band contours are apparently C-type for the chloro-, bromo-, and iodo-species but of more mixed character in Me_2GeHF

By comparison with the $MeGeHX_2$ series the deformations involving the GeH group, ν_{25} and ν_{12}, are considered as HGeX rather than CGeH deformations. Neither band is obviously polarised in the Raman effect so it is not possible to unanbiguously assign the a'- and a"-species by inspection. The separation of the two modes decreases with increasing mass of halogen so that in the gas phase i.r. of Me_2GeHI only a single band appears at 654 cm^{-1} whilst in Me_2GeHCl two clearly resolved bands appear at 688 and 660 cm^{-1}. In the fluoride the situation is further complicated by ν_{25} overlapping with the GeF stretch although ν_{12} appears as a clear B-type band at 669 cm^{-1} in agreement with the expected contour for this a'-species. ν_{12} involves the in-plane whilst ν_{25} the out-of-plane bending motion of the HGeX moiety (Fig.IV.12). The latter involves less interaction with the CH_3 groups and so is expected at higher wavenumber. NCA calculations support the mixed nature of the modes.[164]

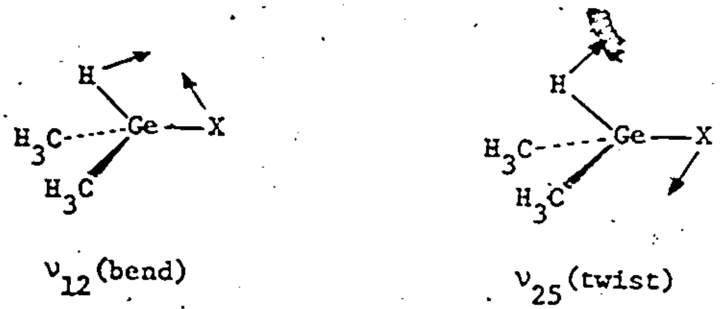


Fig.IV.12 Approximate motions for the HGeX deformations

Vibrations of the C_2GeX skeleton (ν_6, ν_{19}, ν_5, ν_{13}, ν_{14}, ν_{26}): The GeC_2 stretching modes, ν_6 and ν_{19}, are unambiguously assigned to two distinct band envelopes in the 630-590 cm^{-1} region. The symmetric mode, ν_6, is intense in the Raman effect and strongly polarised but appears as a low frequency shoulder in the i.r. spectra of the lighter halogens; only in Me_2GeHI is it clearly resolved at 591 cm^{-1}. The asymmetric GeC_2 stretching mode, ν_{19}, by comparison is only weak in the

Raman and appears as a high-frequency clearly-depolarised shoulder on ν_6. It is not observed in Me_2GeHF. In the i.r. spectra ν_{19} is now the intense mode and has a distinct B-type contour in Me_2GeHCl and Me_2GeHBr confirming the earlier predictions, although the expected A-type contour is not fully resolved for Me_2GeHF. The GeX stretching mode, ν_5, is confidently assigned to a Raman polarised band in the typical position with the corresponding i.r. absorption only being observed for the chloride and fluoride in the KBr range. The GeC_2 deformation ν_{13}, is assigned by comparison with the Me_2GeX_2 series in which the corresponding mode appears consistently in the 180 cm^{-1} region.[146,147,164,165] It is remarkably unaffected by the nature of the halogen and appears distinctly polarised at 190 cm^{-1} (F,Cl) or 187 cm^{-1} (Br,I). The CGeX deformations, ν_{14} and ν_{26}, are assigned to the remaining features in the low wavenumber region of the Raman spectra. In the lighter chloro- and fluoro-species an unresolved but polarised envelope at 182 and 222 cm^{-1} respectively is attributed to both modes. This accidental degeneracy of skeletal modes has been observed in $MeGeCl_3$[145] and Me_2GeCl_2.[146] However in Me_2GeHBr and Me_2GeHI the envelope is clearly resolved into two depolarised components. The out-of-plane motion of the halogen in the a"-mode, ν_{26}, is not expected to couple with the other skeletal modes and calculations show that it is essentially pure with a strong dependence on the f[CGeX]. The in-plane mode, ν_{14} is expected to interact strongly with the methyl groups, this being confirmed by the PED's which indicate it to be a very mixed mode with dependence on f[CGeX], f[CGeH], and f[HGeX].[164] It is therefore no surprise that it does not give rise to the expected polarised band. In view of the interactions the a"-mode, ν_{26} is assigned to the higher wavenumber feature at 170(Br) and 161(I) cm^{-1} and the a'-mode, ν_{14}, is attributed to lines at 154 cm^{-1} (Br) and 142 cm^{-1}(I). This is confirmed by the NCA.[164]

IV.6 DISCUSSION

The vibrational spectra of the three series, $MeGeH_2X$, $MeGeHX_2$, and Me_2GeHX, are satisfactorily assigned on the basis of the C_s point group in each case. Some deviation from the expected band contours is observed in the Me_2GeHX series but this is only apparent in modes which are undoubtedly very mixed. No evidence is found in any spectra for the methyl-torsional modes; these are expected to be extremely weak in the Raman effect and by comparison with related systems[25,145,191] where they have been observed they are expected in the 200-100 cm^{-1} region. Far infrared spectroscopy with solid-phase species may assist in identifying these modes in the halogeno-methylgermanes which in turn may give an estimation of the barrier to rotation of the C-Ge bond.

The results from this work now permit the a priori assignment of the vibrational spectra of other systems containing $MeGeH_2$-, Me_2GeH-, or MeGeH< groupings. The present assignments also confirm the established group frequencies expected for both methyl and halogen moieties bound to germanium and several distinct trends are now apparent throughout the various homogolous series (Tables IV.17-19). These trends may have some bearing on the electron distributions in the molecules although as with force constant data any deductions must necessarily be of an intuitive rather than theoretical nature.[8] Subsequent discussion is limited to those modes which are shown by the NCA to exhibit strong dependence on their respective force constants so that they may be considered unaffected by coupling.

(Table IV.17) Comparison of GeH[a] stretching frequencies (cm^{-1})

	F	Cl	Br	I
GeH_3X^a	2128	2126	2138	2118
$GeH_2X_2^b$	2164	2142	2130	2100*
$MeGeH_2X^c$	2123	2105	2102	2101
$MeGeHX_2$	2150	2125	2111	2080†
Me_2GeHX	2085	2083	2083	2077

values are for i.r. gas phase except * i.r. mull, † i.r. liquid; a. ref.172, av. of $A_1 + 2E_1$; b. ref.180, av. of $A_1 + B_1$; C. av. of a' + a"

The Ge-H stretching frequency is expected to reflect the inductive nature of the substituents on germanium. An increase in the frequency can be regarded as arising from either enhanced 's' character in the Ge-H bonding σ-orbitals or an increase in the Ge-H bond polarity, ie. Ge more positive in $\overset{\delta+}{Ge}$-$\overset{\delta-}{H}$. Increasing halogen substitution, ie. $GeH_3X \rightarrow GeH_2X_2$ or $MeGeH_2X \rightarrow MeGeHX_2$, increasing halogen electronegativity, ie. I → Br → Cl → F, and decreasing methyl substitution, ie. $Me_2GeHX \rightarrow MeGeH_2X \rightarrow GeH_3X$, produce this effect (Table IV.17).

For the chlorosilanes the increase in the Si-H stretching frequency, in the series $SiH_3Cl < SiH_2Cl_2 < SiHCl_3$, has been attributed to enhanced 's' character in the Si-H bond due to preferred binding of the halogen moieties to the silicon p-orbitals.[192,193] The similar increase in the C-H stretching frequency in the series $CHCl_3 > CH_2Cl_2 > CH_4$ may be caused by similar effects although in both cases the increased M-H polarity would also explain the observed trend. Overlap integrals[194] confirm that for carbon the C-H bond strength decreases with decreasing 's' character in the order sp > sp^2 > sp^3 although the extrapolation of this to small changes in σ-orbitals for sp^3 hybrids about silicon or germanium must be handled with caution.

For increasing halogen electronegativity the trends are consistent with either polarity or 's' character approaches. The C-H force constants and stretching frequencies for the CH_3X series, however, show a decrease from iodide to fluoride which has been attributed to poor overlap of carbon and halogen orbitals.[195] Also in the SiH_3X series no apparent trend is observed in the average Si-H stretching frequencies[192,196] although the SiH_2X_2 series[180,197] produces the expected trend with halogen electronegativity. For all the halogenogermane series (Table IV.17) the increasing Ge-H stretching frequencies and force constants follow increasing halogen electronegativities which appear to be additive except for $GeH_3I \rightarrow GeH_2I_2$. In this case the difference may arise from the steric influence of the two iodines or solid state effects. It therefore seems likely that germanium-halogen overlap is good and that the absence of any trend with silicon could indicate a transition point from the poor overlap of carbon.

The replacement of hydrogen attached to germanium by a methyl group causes both the Ge-H absorption frequency and force constant to decrease, this being most marked in the Me_nGeH_{4-n} (n = 0-3) series,[171,25] ie: GeH_4, 2106 cm^{-1}; $MeGeH_3$, 2084 cm^{-1}; Me_2GeH_2, 2071 cm^{-1}; Me_3GeH, 2049 cm^{-1}. This would be consistent with the accepted +I nature of the methyl group reducing the Ge-H bond polarity or alternatively diverting 's' character from Ge-H into Ge-C σ-orbitals. A considerable reduction in the sensitivity to halogen substitution is also apparent particularly in the Me_2GeHX series, which may be explained by the buffering effect of the Ge-C σ-bonds.

The NCA shows a parallel increase in the GeH force constant in all cases which may be interpreted in terms of increasing Ge-H bond strength,[8] however, in many instances this is a dangerous assumption and the validity of force constant calculation still awaits a more sound theoretical basis.

Earlier workers[198] attempted to correlate ν(Si-H) to the sum of the electronegativities of the substituents on silicon. This was later developed using the more general application of Taft inductive factors (σ*) to give empirical equations of the sort,

$$\nu(\text{Si-H})\text{cm}^{-1} = 2106 + 17.5\sigma^* \qquad \text{[ref.199]}$$
$$\nu(\text{Ge-H})\text{cm}^{-1} = 2008 + 16.5\sigma^* \qquad \text{[ref.188,189,200]}$$

Correlations of this type, whilst of some empirical application rely solely on the values chosen for the σ* coefficients for the various substituents; these are commonly obtained from kinetic measurements in quite different systems so it is no surprise that the empirical equation derived from one series, e.g. $MeGeH_2X$, does not transfer satisfactorily to other series, e.g. GeH_3X or $MeGeHX_2$. Indeed it is increasingly evident that spectral data may provide a better method of refining the Taft σ* coefficients than chemical kinetic data themselves.

The GeX stretching frequencies for the halogeno-germanes and -methylgermanes are collected in Table IV.18. There is a clear drop in frequency in any series as the halogen changes from fluorine through to iodine. A small increase in the frequency is apparent as the number of halogens attached to germanium increases. It is tempting to attribute these effects to changes in strength of the germanium-halogen bond but the changes are small and comparisons of force constants indicate no obvious trend. In the fluoro(methyl)germanes (Chapter I.3) the marked propensity for disproportionation to poly-fluoro species suggested a 'downhill' process associated with the formation of stronger bonds.

(Table IV.18) Comparison of GeX stretching frequencies (cm^{-1})

	F	Cl	Br	I
GeH_3X[a]	672	390	285	242
GeH_2X_2[b]	720*	404	285	220†
$MeGeH_2X$	700	383	274	226
$MeGeHX_2$	729(8)*	396(8)	280(20)	235(26)
Me_2GeHX	715	382	279	231
$MeGeX_3$	732(14?)	418(31)[c]	296(48)[d]	239(58)
Me_2GeX_2	676(12)[e]¶	393(14)[f]	279(24)[d]	231(22)[e]
Me_3GeX	659[g]	375[h]	263[d]	224[i]

Values are for Raman liquid phase except * i.r. gas † Raman solid ¶ i.r. sol$^{\underline{n}}$; For the polyhalides the av. or weighted av. GeX frequency is given; ( ) indicates the separation between sym. and asym. modes; a. ref.57; b. ref.180,181; c. ref.145; d. ref.147; e. ref.164; f. ref.146; g. ref.165,157; h. ref.82; i. ref.165,166.

Furthermore, in the Me_nSnCl_{4-n} series both f[SnCl] and f[SnC] have been reported[201] to increase with increased chlorine substitution;* the heats of hydrolysis of the chlorosilanes, Me_nSiCl_{4-n}, were similarly found to correspond to an Si-Cl bond strengthening of 2 Kcal mole^{-1} per Si-Cl bond;[203] and the non random redistribution equilibria of fluoro-silanes[204] favoured the formation of poly-fluoro species, further implying an enhanced Si-F bond strength. In many instances it is impossible to distinguish the effect of increasing halogen substitution from decreasing methyl substitution which is also expected to produce an apparent bond strengthening.

The Ge-C stretching frequency (Table IV.19) reflects changing

---

* Recent calculations using a MVFF indicate that similarly f[GeF] increases in series $Me_3GeF < Me_2GeF_2 < MeGeF_3$, ref.202.

halogen and methyl substitution in much the same way as the Ge-H and Ge-X frequencies. As the halogen changes from fluorine to iodine a decrease in frequency is observed and with the corresponding decrease in

(Table IV.19) Comparison of GeC stretching frequencies (cm^{-1})

	F	Cl	Br	I
$MeGeH_2X$	622	616	615	610
$MeGeHX_2$	634	625	618	607*
Me_2GeHX	619(18)	611(23)	609(23)	603(24)
$MeGeX_3$	634	629[a]	612*[b]	598*
Me_2GeX_2	620(52)[c]	613(42)[d]	610(45)*[b]	606(44)*[c]
Me_3GeX	600(46)[e]	605(43)[f]	601(44)*[b]	601(47)[e]

Values are for i.r. gas phase except * i.r. liquid;
a. ref.145; b. ref.147; c. ref.164; d. ref.146;
e. ref.165,157; f. ref.82; For the polymethyl-species the weighted average GeC frequency is given;
( ) indicates the separation of sym. and asym. modes.

f[GeC][164] implies a slight weakening of the Ge-C bond. The substitution of hydrogen in $MeGeH_2X$ for a second methyl group to give Me_2GeHX results in a lowering of the Ge-C frequency as is observed in the Me_nGeH_{4-n} series,[25] ie. $MeGeH_3$, 602 cm^{-1}; Me_2GeH_2, 597 cm^{-1}; Me_3GeH, 596 cm^{-1}. This is again reflected in the force constants.[164] However on the substitution of hydrogen in $MeGeH_2X$ for a second halogen to give $MeGeHX_2$ whilst producing the expected increase in Ge-C frequency apparently gives rise to a lower Ge-C force constant which emphasises the caution needed in handling this sort of spectroscopic data. In the series Me_nGeX_{4-n} (n = 1,2,3) increasing methyl substitution accompanies decreasing halogen substitution so it would be unwise to decide on an a priori basis which effect is dominant.

CHAPTER FIVE

THE CHARACTERISATION OF SOME MIXED HALOGENO(METHYL)GERMANES

V.1 INTRODUCTION

In Chapter I many examples of reactions involving exchange and substitution reactions of germanium-hydrogen and germanium-halogen bonds were presented, the syntheses being determined largely by favourable free energy changes. Under certain conditions many of these reactions, particularly those involving polyhalides, did not go to completion and several features in the ^1H n.m.r. and vibrational spectra of the products suggested that additional species containing different halogen substituents bonded to germanium were present.

The exchanges of halogens and/or other substituents (e.g. OCH_3, SCH_3, OPh, NMe_3, NCO, NCS) in fully substituted methyl-silanes, and -germanes have been well documented by Moedritzer and Van Wazer.[207-210] Their findings indicated that exchange of labile substituents at silicon or germanium is rapid (of the order of mins.) and that for most systems equilibria are usually achieved between 1 and 100 hr. The greatest deviations from random distribution of components were observed in systems with substituents of widely differing electronegativities (e.g. for scrambling at dimethylgermanium[207] the Cl_2/I_2 system favoured Me_2GeI_2 and Me_2GeClI, while the Cl_2/Br_2 and Br_2/I_2 exchanges were apparently random).

Fritz and Kummer[206] detected 'mixed' dihalogenosilanes amongst the products of the reactions between the monophenylhalogenosilane and the hydride of a different halogen, ie.,

$$PhSiH_2X + HY \longrightarrow C_6H_6 + SiH_2XY \qquad [1]$$

Species of this kind were further studied by Ebsworth et al[205] who identified mixed halogenosilanes in the ^1H n.m.r. spectra of redistribution reactions of two different dihalogenosilanes and from reactions of hydrogen halides with dihalogenosilanes, ie.,

$$\left.\begin{array}{ll} SiH_2X_2 + SiH_2Y_2 \rightleftharpoons 2SiH_2XY & [2] \\ SiH_2X_2 + HY \rightleftharpoons SiH_2XY + HX & [3] \end{array}\right\} X = Cl,Br,I$$

The equilibria in the latter reactions were found to be essentially random, and in this respect they closely resembled the dimethylsilicon scrambling reactions reported earlier.[207] No evidence for the participation of silanic hydrogen was apparently obtained[205] although studies with methylsilane/chloro-methylsilane systems indicated that Si-H bonds are also labile to redistribution in the presence of a catalyst (e.g. $R_4N^+X^-$).[209] The Raman spectrum of SiH_2Cl_2/SiH_2I_2 mixtures showed additional features consistent with the separate entity SiH_2ClI.[205]

Prior to this study the analogous hydridic-germanium species had received little attention: Cradock and Ebsworth[69] identified the mixed dihalogenogermane, GeH_2BrI, in the reaction of GeH_2Br_2 with GeH_2I_2, with no indication of the participation of germanic hydrogen; and recently Barker and Drake[56] have observed GeH_2ClBr and GeH_2ClI in similar equilibrium mixtures and in exchange reactions with boron trihalides and hydrogen halides.

In this chapter several exchange reactions between a halogeno(methyl)germane and (a) another halogeno(methyl)germane, (b) a hydrogen halide, and (c) a boron trihalide are discussed. It was of particular interest to see whether discreet mixed halides, e.g. MeGeHXY, could be isolated or whether such species existed only in equilibrium mixtures of the 'parent' halides, $MeGeHX_2$ and $MeGeHY_2$. Some evidence for the participation of germanic hydrogen in the equilibria is obtained from reactions where traces of boron compounds are presumed to be present.

V.2 EXPERIMENTAL

The halogeno(methyl)germanes were prepared from methylgermane as described in Chapter I and were estimated to contain no more than 1% proton containing impurities from the ^{1}H n.m.r. spectra. The boron trihalides, BCl_3 and BBr_3, and the hydrogen halides, HCl, HBr, and HI were obtained as described in Appendix 2. The mixed species were identified in the ^{1}H n.m.r. spectra of product mixtures described in sections (a)-(d), the a priori assignments being confirmed by the observation of 'parent' peaks in the mass spectra (section V.2.e). All attempts to isolate the components of the mixtures by distillative separation were unsuccessful.

(a) Exchange reactions between two dihalogeno(methyl)germanes: Various proportions of the dihalides $MeGeHCl_2$, $MeGeHBr_2$, and $MeGeHI_2$, (Table V.1) were distilled into semi-micro n.m.r. tubes at -196°. The tubes were sealed after the addition of CS_2 (ca.2 mmol) and a trace of T.M.S. and the contents allowed to react at room temperature. Sequential recording of the ^{1}H n.m.r. spectra showed that in most cases significant formation of the 'mixed' products had occurred within 15 min. with equilibria usually being reached after 1-2 hr. The ^{1}H n.m.r. data given in Tables V.1 and 2 were obtained when no further change was observed in the intensities of the proton resonances. The intensity data are reported for the GeH resonances of the component species as these were more widely separated than the CH_3 resonances. A typical ^{1}H n.m.r. spectrum given by an equilibrium mixture of $MeGeHCl_2$ and $MeGeHBr_2$ is shown in Fig.V.1.

In the $MeGeHCl_2$/$MeGeHBr_2$ system (1:1) after extended periods at room temperature (>10 hr.) additional resonances at (0.73,5.30),

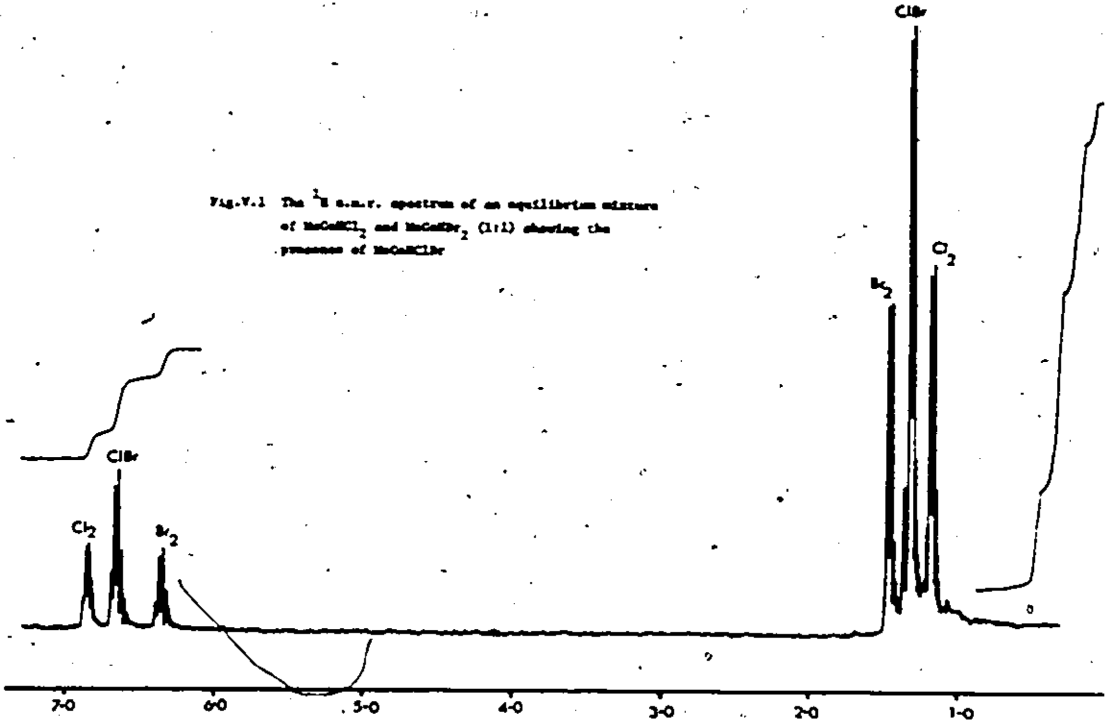


Fig.V.1 The ^{1}H n.m.r. spectrum of an equilibrium mixture of MeGeHCl$_2$ and MeGeHBr$_2$ (1:1) showing the presence of MeGeHClBr

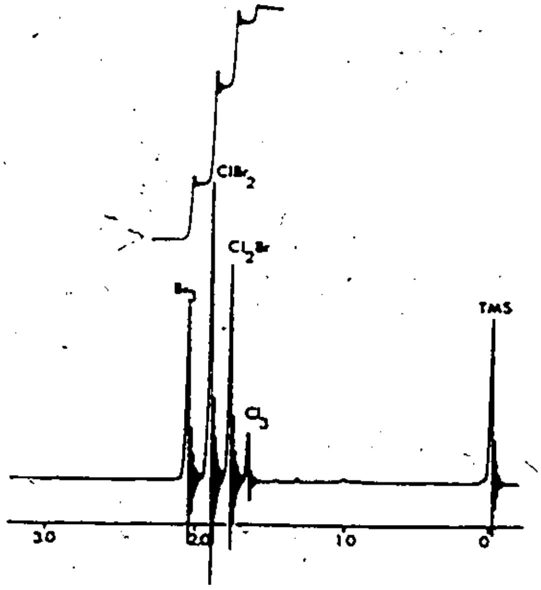


Fig.V.2 The ^{1}H n.m.r. spectrum of an equilibrium mixture of MeGeCl$_3$ and MeGeBr$_3$ (*ca*.1:2) showing the presence of MeGeCl$_2$Br and MeGeClBr$_2$

(0.88,4.88), 1.58, 1.67, 1.79, and 1.98 p.p.m. appeared; these were assigned to $MeGeH_2Cl$, $MeGeH_2Br$, $MeGeCl_3$, $MeGeCl_2Br$, $MeGeClBr_2$ and $MeGeBr_3$, respectively, accounting for some 30% of the product mixture. Similar disproportionations were not observed in the Cl_2/I_2 or Br_2/I_2 systems. In a control experiment no reaction was observed between $MeGeH_2Cl$ and $MeGeH_2Br$ (<u>ca</u>.1:1) when they were sealed together in CS_2.

(Table V.1) Equilibrium data for the exchange reactions of dihalogeno(methyl)germanes

	X	Y	$MeGeHX_2$ mmol	$MeGeHY_2$ mmol	Equilibrium Ratio* X_2	XY	Y_2	$K_{25°}$†
a.	Cl	Br	0.26	0.24	6.8	11.0	5.3	0.30
b.	Cl	Br	0.49	0.22	10.7	6.4	1.2	0.31
c.	Cl	Br	0.33	0.53	0.9	6.1	12.9	0.29
d.	Cl	I	0.30	0.39	11.3	13.9	11.8	0.68
e.	Cl	I	0.58	0.34	11.9	3.9	0.6	0.44
f.	Br	I	0.22	0.26	4.7	11.6	10.1	0.35
					Random distribution			0.25

* Obtained from integrated intensities of ^1H n.m.r. resonances; † $K = [X_2][Y_2]/[XY]^2$.

(b) <u>Reactions of dihalogeno(methyl)germanes with hydrogen halides:</u>

Typically, $MeGeHCl_2$ (0.51 mmol) and HI (<u>ca</u>.0.9 mmol) were condensed into an n.m.r. tube and held at -78°. After 1 hr. volatile products at that temperature (ie. H_2,HCl,HI) were removed and the tube was sealed after the addition of CS_2 (<u>ca</u>.2 mmol) and a trace of T.M.S. The ^1H n.m.r. spectrum recorded after 2 hr. gave resonances readily attributable to $MeGeHCl_2$ and $MeGeHI_2$ and unfamiliar resonances intermediate to these at 1.48 and 6.14 p.p.m. which were assigned to MeGeHClI in the ratio 1:18:5. Singlet resonances at 1.17, 2.17, and 2.61 p.p.m. were assigned to $MeGeCl_2I$, $MeGeClI_2$, and $MeGeI_3$ and accounted for some 3% of the product mixture.

In a similar experiment $MeGeHBr_2$ (0.60 mmol) and HI (0.59 mmol) were allowed to react. After removal of hydrogen halides and non-condensable gas at -78° solvent and a trace of T.M.S. were added and the tube sealed. After 2 hr. the ^1H n.m.r. spectrum showed the presence of $MeGeHBr_2$ and $MeGeHI_2$ and additional signals intermediate to these at 1.64 and 5.64 p.p.m. attributable to MeGeHBrI in the ratio 2:2:3. A further series of resonances at 1.98, 2.10, 2.35, and 2.61 p.p.m. were assigned to $MeGeBr_3$, $MeGeBr_2I$, $MeGeBrI_2$, and $MeGeI_3$ and accounted for some 20% of the product mixture.

No reaction was observed in the analogous reactions of (i) HCl with $MeGeHBr_2$ or $MeGeHI_2$ or (ii) HBr with $MeGeHI_2$, the starting materials being recovered essentially unchanged.

(c) Reaction of mono- and di-halogeno(methyl)germanes with boron trihalides: Typically $MeGeH_2Cl$ (0.50 mmol) and BBr_3 (0.18 mmol) were condensed into a reaction vessel (10 ml, type 'C') and held at -78°. After 1 hr. distillation through a trap at -95° removed the volatile boron species (e.g. B_2H_6) and the ^1H n.m.r. spectrum of the remaining mixture indicated the presence of $MeGeH_2Br$, $MeGeHBr_2$, $MeGeH_2Cl$, $MeGeHCl_2$, and MeGeHClBr in the ratio ca. 13:1:7:1:4.

In an analogous reaction $MeGeHBr_2$ (0.60 mmol) and BCl_3 (0.21 mmol) were allowed to react at -78°. After ca. 2 hr. the products volatile at -95° were removed under vacuum and the remaining halide mixture sealed with CS_2 solvent and T.M.S. The ^1H n.m.r. spectrum indicated the presence of $MeGeH_2Br$, $MeGeHBr_2$, $MeGeH_2Cl$, $MeGeHCl_2$ and MeGeHClBr in the ratio ca. 13:1:7:1:4.

(Table V.2) The ^1H n.m.r. parameters of some mixed halogeno(methyl)germanes*

Compound	δ(Me)	δ(GeH')	$\|J^{vic}_{HH'}\|$
$MeGeH'Cl_2$†	1.14	6.74	1.20
MeGeH'ClBr	1.28	6.56	1.27
$MeGeH'Br_2$†	1.44	6.28	1.47
$MeGeCl_3$†	1.58	–	–
$MeGeCl_2Br$	1.67(1.80)	–	–
$MeGeClBr_2$	1.79(1.94)	–	–
$MeGeBr_3$†	1.98	–	–
MeGeH'ClI	1.48	6.14	1.65
MeGeH'BrI	1.64	5.64	1.83
$MeGeH'I_2$†	1.87	4.68	2.05
$MeGeCl_2I$	1.77(1.98)	–	–
$MeGeClI_2$	2.17(2.37)	–	–
$MeGeBr_2I$	2.10(2.32)	–	–
$MeGeBrI_2$	2.35(2.57)	–	–
$MeGeI_3$†	2.61	–	–

* The spectra were recorded at room temperature in CS_2 solution (ca.20% v/v). Chemical shifts (δ) are in p.p.m. (±0.04 p.p.m.) to low field of tetramethylsilane as internal reference. Coupling constants $|J^{vic}_{HH'}|$ are in Hz (±0.05 Hz);

† see chapter II, data included for comparison;

( ) indicates values given in ref.208 for neat liquids

$MeGeHCl_2$ (0.18 mmol) and BBr_3 (0.06 mmol) were reacted as above. The ^1H n.m.r. spectrum of the products showed resonances due to $MeGeHCl_2$, $MeGeHBr_2$, and MeGeHClBr in the ratio ca. 6:1:3. In the corresponding reaction of $MeGeHBr_2$ (0.30 mmol) with BCl_3 (0.11 mmol) the ^1H n.m.r. spectrum indicated that less reaction had occurred; the major products were $MeGeHBr_2$ and MeGeHClBr in the ratio ca. 2:1 with only a trace of

$MeGeHCl_2$. I.r. analysis of the products volatile at -78° in both reactions confirmed that no more than a trace of B_2H_6 was formed.

(d) <u>Exchange reactions of trihalogeno(methyl)germanes</u>: These reactions were carried out to confirm the identification of the 'mixed' trihalides observed in the ^1H n.m.r. spectra of many of the systems described above. Details of more extensive experiments where equilibrium constants have been obtained may be found in the literature.[208] Approximately equimolar quantities of pairs of the trihalides $MeGeCl_3$, $MeGeBr_3$, or $MeGeI_3$ (<u>ca</u>.0.5 mmol of each) were sealed in semi-micro n.m.r. tubes with CS_2 and a trace of T.M.S. Sequential recording of the ^1H n.m.r. spectra showed that significant formation of the 'mixed' species had occurred after 10 min at room temperature. The chemical shift data (Table V.2) were generally obtained after 24 hr. when the mixtures had reached equilibrium. The ^1H n.m.r. spectrum of a typical equilibrium mixture of $MeGeCl_3$ with $MeGeBr_3$ is shown in Fig.V.2.

Mixed trihalides were ~~also~~ conveniently obtained by (i) the reaction of HBr with $MeGeCl_3$ or (ii) the reaction of HI with $MeGeCl_3$ or $MeGeBr_3$ when a deficit of the hydrogen halide was employed. The germanium halide (<u>ca</u>.2 mmol) and the hydrogen halide (<u>ca</u>.3-5 mmol) were distilled into a reaction vessel (150 ml, type 'I') held at -196° on the vacuum line. The mixture was allowed to attain room temperature and left to react (1 hr.); the products volatile at -78° were then removed and the remaining ~~mixture~~ distilled into the side arm held at -196° (heating being necessary for the polyiodides). CS_2 and a trace of T.M.S. were then added and the side arm sealed off at the constriction. The semi-micro tube thus obtained was allowed to equilibrate at room temperature. The product distributions obtained for these systems as indicated by the

^1H n.m.r. spectra were very similar to those observed for the redistribution of two trihalides. The chemical shifts were noticeably sensitive to the composition of the mixture (e.g. δMeGeI$_3$ had values ranging from 2.5 to 2.8 p.p.m.). The n.m.r. data for the 'mixed' trihalides (Table V.2) are given only for equimolar equilibrium mixtures of starting materials.

(e) Mass Spectra: From the mass spectra of the product mixtures described in sections V.2.a-d 'parent' peaks (unipositive ions) for the mixed species were consistently observed at m/e 209 ($MeGeHClBr^+$), m/e 256 ($MeGeHClI^+$), m/e 299 ($MeGeHBrI^+$), m/e 245 ($MeGeCl_2Br^+$), m/e 288 ($MeGeClBr_2^+$), m/e 292 ($MeGeCl_2I^+$), m/e 378 ($MeGeBr_2I^+$), and m/e 382 ($MeGeClI_2^+$).

V.3 DISCUSSION

The exchange reaction between two dihalogeno(methyl)germanes leads to the formation of an equilibrium mixture containing mixed species where two different halogens are bonded to germanium:

$$\text{e.g.} \qquad MeGeHCl_2 + MeGeHBr_2 \rightleftharpoons 2MeGeHClBr \qquad [4]$$

The equilibrium constant, K, for the various systems may be calculated from the integrated intensities of the component species in the ^1H n.m.r. spectra of the mixtures according to the equation:

$$K_{25^\circ} = \frac{[MeGeHX_2][MeGeHY_2]}{[MeGeHXY]^2} \qquad [5]$$

Values for K_{25° are given in Table V.1 for various proportions of dihalides. Using the approach of Moedritzer and Van Wazer[207–210] we note that the only significant deviation from a random distribution of components is observed in the $MeGeHCl_2$/$MeGeHI_2$ system whilst the $MeGeHCl_2$/

$MeGeHBr_2$ and $MeGeHBr_2/MeGeHI_2$ exchanges are essentially random with allowance for experimental error. Similar results were obtained for scrambling of halogens in SiH_2XY and Me_2GeXY systems,[205,207] and are compared with the MeGeHXY systems in Table V.3.

(Table V.3) Equilibrium constants for the exchange of substituents in dihalogeno -silanes, -dimethylgermanes, and -methylgermanes

X	Y	K at 39°[a] SiH_2XY	K at 35°[b] Me_2GeXY	K at 25° MeGeHXY
Cl	Br	0.33	0.302	0.30[c]
Cl	I	0.15	0.674	0.56[d]
Br	I	0.44	0.344	0.35
Random value		0.25	0.25	0.25

a. ref.205; b. ref.207; c. average of .30,.31,.29; d. average of .68,.44.

It is not clear whether the deviations given in Table V.3 are significant. For exchange at germanium the 'high' values for K obtained for the Cl_2/I_2 system suggest the preferential formation of Ge-I bonds compared to Ge-Cl bonds, whereas the 'low' value for the corresponding exchange at silicon implies Si-Cl bonds are preferred to Si-I bonds. These observations at least reflect the Pearson concept[108] of polarisability and preferred bonding and give further insight into the synthetic halogen-exchange reactions, discussed in Chapter I.

In the related methylsilanes/chloro(methyl)silanes traces of tetra-alkylammonium salt catalysed the redistribution of silanic hydrogens with halogens.[209] There is some indication from the limited experimental data for the participation of germanic hydrogen in the $MeGeHCl_2/MeGeHBr_2$ system. The observation of mono- and tri-halogeno species may be rationalised by a disproportionation, e.g.,

$$2MeGeHClBr \rightleftharpoons MeGeH_2Cl + MeGeClBr_2 \qquad [6]$$

The 'mixed' trihalide is in further equilibrium with three other possible species, ie.,

$$2MeGeClBr_2 \rightleftharpoons MeGeBr_3 + MeGeCl_2Br \qquad [7]$$

$$2MeGeCl_2Br \rightleftharpoons MeGeCl_3 + MeGeClBr_2 \qquad [8]$$

In view of the fact that additional species of this sort were not observed in the Cl_2/I_2 and Br_2/I_2 exchanges it is unlikely that germanic hydrogen contributes significantly to the major equilibria (equation 4). Traces of boron compounds ~~have been~~ shown[202] to catalyse the disproportionation of several halogeno(methyl)silanes and it has also been noted (chapter I) that B_2H_6 reduces $MeGeH_2Cl$ to $MeGeH_3$ so the anomalous result in this case may arise from a catalysis due to impurities.

Dihalogeno(methyl)germanes exchange with a deficit of hydrogen halide to produce 'mixed' species in addition to the normal exchange product, e.g.,

$$2MeGeHCl_2 + 3HI \rightarrow MeGeHClI + MeGeHI_2 + 3HCl \qquad [9]$$

Surprisingly trihalogeno- species are also formed in these reactions; the absence of monohalogeno- species and the production of hydrogen confirms this is substitution rather than disproportionation, e.g.,

$$MeGeHBr_2 + HI \longrightarrow MeGeBr_2I + H_2 \qquad [10]$$

This reactivity of hydrogen iodide is usually observed in the presence of Lewis acid catalysts such as AlI_3.

The reactivity of boron trihalides towards the methylgermanes was discussed in Chapter I. As expected the tribromide reacts more extensively with mono- and di-chloro(methyl)germane than ~~does boron~~ trichloride with mono- and di-bromo(methyl)germane, since germanium favours being bonded to the heavier halogen. The major reaction of $MeGeH_2Cl$ with BBr_3

and ca. 50% of the reaction of $MeGeH_2Br$ with BCl_3 is substitution to give MeGeHClBr:

$$MeGeH_2Cl + BBr_3 \rightarrow MeGeHClBr + [BHBr_2] \qquad [11]$$

$$MeGeH_2Br + BCl_3 \rightarrow MeGeHClBr + [BHCl_2] \qquad [12]$$

No trihalogeno(methyl)germanes were observed under the experimental conditions used for these reactions. The comparative unreactivity of the germanic hydrogen in the dihalides is further shown by the reactions of $MeGeHCl_2$ and $MeGeHBr_2$ with BBr_3 and BCl_3 where simple exchange is the only observable process to again form MeGeHClBr which then equilibrates:

$$MeGeHCl_2 + BBr_3 \rightleftharpoons MeGeHClBr + BClBr_2 \qquad [13]$$

$$MeGeHBr_2 + BCl_3 \rightleftharpoons MeGeHClBr + BCl_2Br \qquad [14]$$

The mechanism for the exchange of halogens at germanium undoubtedly involves the participation of vacant low-lying orbitals which permit increased coordination about Ge as suggested ~~in~~ Chapter I. The ease with which exchange occurs is likely to be controlled by several factors e.g. the stabilisation of the transition state by the substituents, the temperature, and the 'bridging' ability of the substituent. In this context chlorine (and fluorine)* are expected to be the better 'bridging' groups, although this may only be important in determining the kinetics of the process. In principle redistributions involving exchange of substituents on a given central atom are 'thermoneutral' and ΔH° should equal zero.[207] The non-randomness of equilibria involving I and Cl indicate that this assumption is not valid. It is not clear whether the effect can be rationalised by bond energy differences between the same atoms when in different chemical environments; differences in heats

* ^1H n.m.r. evidence (chapter II) indicates a rapid exchange of fluorine atoms at room temperature; increased coordination in germanium fluorides is well documented (chapter III).

of solution of the initial and 'mixed' species and differences in association of the species in solution may also contribute significantly to the apparent deviation. An estimate of $\Delta H°$ for these processes may be obtained by observing the equilibria as a function of temperature but this was not investigated.

^{1}H n.m.r. spectra: The parameters for the 'mixed' halides (Table V.1) follow the well defined trends observed for the parent species described in Chapter II. The sequential shifts in both the CH_3- and GeH-proton resonances with changing halogen electronegativity permit the a priori assignment of the signals for the 'mixed' halides. The observation of separate signals for the components of the equilibria confirms that the exchange process is slow on the n.m.r. time scale.

Vibrational spectra: the 'instantaneous' nature of both infrared and Raman spectroscopy allows a further confirmation of discrete species. The liquid Raman spectrum of the approximately 1:1 mixture of $MeGeHCl_2$ with $MeGeHBr_2$ shows , besides the frequencies due to the starting compounds, lines which may be attributed to the 'mixed' species MeGeHClBr; the observed frequencies are given in Table V.4 with suggested assignments. In 'MeGeHClBr' the C_s plane of symmetry is lost and the molecule is potentially optically active. The GeClBr deformation (sc) is confidently assigned to an additional feature at 132 cm^{-1} intermediate to analogous modes in $MeGeHCl_2$ (150 cm^{-1}) and $MeGeHBr_2$ (105 cm^{-1}). The GeCl and GeBr stretching regions show a definite splitting under high resolution but it is not possible to attempt an individual assignment. The GeH stretching region shows overlapping features at 2130, 2125, and 2120 cm^{-1} which may be assigned unambiguously to the three components of the mixture. The modes associated with the methyl group show no features which distinguish the 'mixed' species from the parent hydrides. The presence of two lines in the GeC stretching region at 623 cm^{-1} and 598 cm^{-1} is unexpected; the GeC stretch appears at 625 cm^{-1} in $MeGeHCl_2$ and 615 cm^{-1} in $MeGeHBr_2$ so the extra line at 598 cm^{-1} may be reasonably attributed to MeGeHClBr although such a lowering in frequency is unusual.

Table .4 The Raman spectrum of 'MeGeHClBr'*

Raman (liq)		Tentative Assignment
ca.2130 ms,p		GeH str. (Cl_2)
ca.2125 ms,p		GeH str. (ClBr)
ca.2120 ms,p		GeH str. (Br_2)
623 ms,p		GeC str. (Cl_2,Br_2)
598 w		GeC str. (ClBr)?
406 m	some depolarised components	GeCl str.
399 m		
395 m		
390 m		
297 s		GeBr str.
284 s		
273 s		
183 m		$GeCl_2$ defs. (twist,wag)
170 m		GeClBr defs.
ca.165 br,sh		$GeBr_2$ defs. (twist,wag)
ca.150 wm		$GeCl_2$ def. (sc)
132 m		GeClBr def. (sc)
105 m		$GeBr_2$ def. (sc)

* a 1:1 equilibrium mixture of $MeGeHCl_2$ and $MeGeHBr_2$

CHAPTER SIX

THE CHARACTERISATION OF PSEUDOHALOGEN DERIVATIVES OF THE METHYLGERMANES*

---

* Presented in part at the 55th meeting of the Chem. Inst. of Canada Inorg. Div. Quebec City, Quebec (1972).

VI.I. INTRODUCTION AND REVIEW

In this chapter the characterisation of derivatives of the methylgermanes is extended to species in which germanium is bonded to a pseudohalide grouping*, ie. $MeGeH_2PS$, Me_2GeHPs, $MeGe(Ps)_3$, where 'Ps' represents: azide ($-N_3$), cyanide (-CN), isocyanate (-NCO), and isothiocyanate (-NCS).

Reviews by Thayer and West[212] and Lappert and Pyszora[213] emphasise the considerable interest shown in the pseudohalide derivatives of Group IV elements. Much controversy has arisen in establishing which atom in the asymmetric pseudohalides is σ-bonded to the central metal atom, there being the possibility of structural isomerism (Table VI.1). Earlier evidence based on chemical reactivity and infrared spectroscopy[214-216] suggested that silicon and germanium cyanides exhibited both iso- and normal- bonding; more recent direct structural evidence from microwave spectroscopy (SiH_3-,[217] GeH_3-[218]) and X-ray crystallography (Me_3Ge-[219]) indicated a predominance of the normal-cyanide; while a variable temper-

(Table VI.1) Pseudohalide groups

Name	'Normal' form	'Iso' form
Cyanide	-CN	-NC
Cyanate	-OCN	-NCO
Thiocyanate	-SCN	-NCS
Selenocyante	-SeCN	-NCSe
Fulminate	-CNO	-(ONC)
Azide	-NNN	-

---

* The term pseudohalogen or pseudohalide (Ps) was first suggested by Birckenbach and Kellerman to describe polyatomic groups resembling halogens or halides in their chemical properties; ref.211.

ature ^1H n.m.r. study of Me_3SiCN gave the mole fraction of isocyanide in the liquid as only 0.0015 at 25°, the data being consistent with rapid exchange of CN groups between Me_3SiCN and Me_3SiNC.[220] By comparison it is reasonably well established that silicon and germanium cyanates and thiocyanates exist in the <u>iso</u>- form; the most convincing evidence coming from microwave spectroscopy (SiH_3-,[221,222] GeH_3-[223]), electron diffraction (Me_3Si-,[224] GeH_3-[225]) and ^{14}N n.m.r. spectroscopy (Me_3Si-,[226] GeH_3-[227]). The azides, being centrosymmetric exhibit no such structural isomerism.

The geometry of the molecular skeleton in the pseudohalides has also received attention particularly as a means of assessing the relative importance of (p→d) π-bonding between the central metal atom and atoms such as nitrogen which have lone pairs of electrons. Ebsworth[8] in an excellent review has summarised the evidence relating to (p→d) π-bonding in Group IV elements; it is generally considered that (p→d) π-bonding is important from nitrogen, oxygen and (probably) fluorine to silicon*, less important from N or O to germanium, and less important still from N or O to tin. A comparison of the available structural data for the pseudohalides of H, C, Si, and Ge illustrates this point (Table VI.2). On the assumption that the cyanates and thiocyanates are nitrogen bonded some striking differences are apparent; the heavy atom skeletons of SiH_3NCO and SiH_3NCS are linear, whereas the H, C, and Ge compounds have significantly bent skeletons.

---

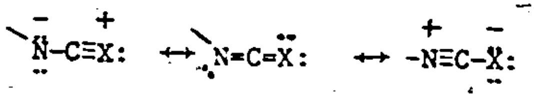
* Evidence from photo-electron spectroscopy[228] for the occurrence of (p→d) π-bonding in chloro-germane, and -silane is strong. The fortuitous interference of the fluorine lone-pair energy levels and the bonding levels precluded similar conclusions for the fluoro-compounds.

(Table VI.2) Structural geometry for triatomic pseudohalides*

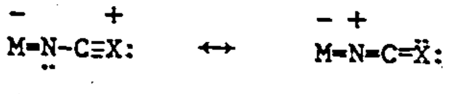
R	Azide ∠R-N-N		Isocyanate ∠R-N-C		Isothiocyanate ∠R-N-C	
H	114°8'±30'	(V)	128° ±30'	(M)	134°59'±10'	(M)
CH_3-	120°±5°	(E)	125°±5°	(E)	142°	(M)
SiH_3-	<180°[a]	(M,V)	180°[b]	(M)	180°[b]	(M)
Me_3Si-	<180°[c]	(M)	150°±3°[d]	(E)	154°±2°[d]	(E)
GeH_3-	119°[e]	(E,V)	141°20'[f]	(E,M,V)	156°±9°	(V)
Me_3Ge-	<180° ?		<180° ?		<180° ?	

* data from ref.228 except where noted; ( ) indicates the experimental method; V, vibrational spectroscopy; M, microwave spectroscopy; E, electron diffraction; a. ref.221,230; b. ref,222; c. ref.231; d. ref.224; e. ref.225,232; f. ref.225,222,233,227; g. ref.234.

The bent skeletal arrangement is expected by an analysis of the resonance structures, ie.,


[A] [B] [C]

The N-C-X portion of the molecule is expected to be linear in A, B, and C; however, the angles at the N atom, ie. M-N-C(X), are 109°, 120° and 180° respectively. If all three forms were to contribute equally, ∠M-N-C(X) should be the average of A,B, and C, viz. 136°. The experimental values for the H,C, and Ge compounds deviate a little from the average value and can be accounted for by postulating nonequivalent contributions of forms A,B, and C to the overall structure. If delocalisation of electrons from nitrogen is permitted then two more resonance forms can be written that take into account (p→d) π-bonding, ie.,


[D] [E]

In D and E the bond angles, ∠M-N-C(X), are 120° and 180° which would give a larger average value to A, B, C, D, and E and therefore implies that if the π-interaction is important then a bond angle greater than 136° is to be expected. Experimentally this is the case with silicon although the Ge-N-C angle in GeH_3NCO[225] of 141° implies some importance to resonance forms D and E. The weaker π-interactions of germanium may be connected with the fact that the 4d-orbitals have radial nodes, whereas the 3d-orbitals of silicon do not.[8] This again is open to question when it is considered that the configuration of nitrogen in both Si_3N_4 and Ge_3N_4 is nearly planar[235] and that trigermylamine, $(GeH_3)_3N$, has a planar structure,[236] both of which imply strong interaction between nitrogen and germanium. The nonlinear heavy atom skeletons in Me_3SiNCO and Me_3SiNCS are also unexpected in comparison with their silyl-analogues. The difference in structure could be interpreted in terms of electron release from the methyl groups to the degenerate pair of d-orbitals that would be of π-symmetry relative to the Si-N bond, thus weakening any π-interactions between the pseudohalogen group and silicon. However it has been pointed out[237] that the data from the electron diffraction technique may be of molecules not in the vibrational ground state and that the bent structures may arise from 'shrinkage' due to the excitation of a low-frequency skeletal bending mode*.

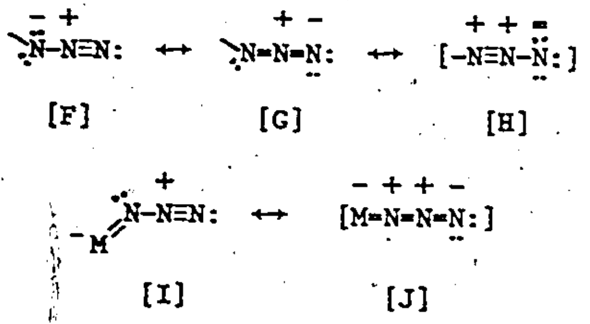
An alternative interpretation of the observed geometries comes from a consideration of the inductive effect of CH_3, SiH_3, and GeH_3 groups. Thus the low electronegativity of silicon relative to carbon could result in an increased contribution of structure 'C' for silicon compounds, hence predicting that ∠Si-N-C(X) be greater than ∠C-N-C(X); this would

---

* This may explain the determined ∠SiNC in SiH_3NCS of 159° by electron diffraction, ref.238.

account for the observed trend in bond angles without invoking (p→d) π-bonding in the silicon compounds. However, silicon and germanium should have about the same inductive effect (most scales give Si and Ge a similar electronegativity) so that the nonlinearity of GeH_3NCO and GeH_3-NCS cannot be explained by this approach; it is therefore likely that the differences are not attributable solely to inductive effects and that electronic efforts such as (p→d) π-bonding may be more important.

The azides of H, C, Si, and Ge all have bent skeletons, which for silicon is unexpected in comparison with the isoelectronic cyanates; furthermore the available data (Table VI.2) indicate that ∠M-N-N is remarkably small for H, C, and Ge (114°-129°), although precise information for Si is not available*. Some explanation comes again from a consideration of the resonance structures:



[F] [G] [H]

[I] [J]

For covalent azides without π-bonding to the central atom forms F and G are important, whereas for azides with π-bonding forms F, G, and I are important; H and J are unlikely due to the adjacent like formal charges. It then follows that the skeletal angle is expected to be between 109° (F) and 120° (G,I) whether π-bonding is present or not, and this is observed experimentally. It also follows that extensive π-bonding may be present even in nonlinear structures so that silicon cyanates and

---

* microwave spectroscopy indicates that SiH_3N_3[221] and Me_3SiN_3[231] have ∠Si-N-N less than 180°.

thiocyanates existing in normal-form are expected to be nonlinear even if there is appreciable π-bonding in the silicon-pseudohalogen linkage.[237] It is worth emphasising also that the inter-atom bond lengths used as a criterion for additional interactions are also suspect. When examining the various canonical forms for the triatomic pseudohalides it becomes apparent that in many cases a change in hybridisation at nitrogen has occurred. Thus although short M-N bond distances are consistent with π-interaction they do not require it since a difference in orbital overlap from one canonical form to another would also produce the observed effect.

In a series of papers[239-241] Anderson described the preparation of alkylgermanium- cyanides, isocyanates, and isothiocyanates of the type R_nGePs_{4-n} (R = C_2H_5, n-C_3H_7, i-C_3H_7, n-C_4H_9; n = 0-4) and n-Bu_2GeHPs (Ps = CN,NCS). Di- and tri-alkylgermanium thiocyanates were obtained in high yield (ca.80%) by the action of thiocyanic acid on the corresponding digermoxane or hydroxide, whereas in the analagous reaction with hydrogen cyanide only the tri-alkylgermoxanes showed a similar reactivity; cyanic acid apparently did not cleave the Ge-O linkage:

$$(R_3Ge)_2O + 2HNCS \longrightarrow 2\ R_3GeNCS + H_2O \qquad [1]$$

$$(R_3Ge)_2O + 2HCN \longrightarrow 2\ R_3GeCN + H_2O \qquad [2]$$

Potassium salts in aqueous solution were also effective in exchange reactions; Allred and Rochow[242] reported satisfactory yields of $Me_2Ge(NCS)_2$ from the reaction of the corresponding chloride with potassium thiosulphate whilst Anderson[239] used triethylgermanium sulphonate with potassium cyanide:

$$Me_2GeCl_2 + 2KNCS \xrightarrow{H_2O} Me_2Ge(NCS)_2 + 2KCl \qquad [3]$$

$$Et_3GeSO_3R + KCN \longrightarrow Et_3GeCN + KSO_3R \qquad [4]$$

The most widely used method for preparing pure pseudohalides involves the use of heavy metal salts such as those of lead(II), mercury(II), and silver(I), this being the standard synthetic route for germanium isocyanates. The hydrides and halides both show a reactivity although the latter are often more convenient and hence more widely used; with stoichiometric quantities one or two hydrogens in Bu_2GeH_2 could be replaced under reflux conditions (ca.90 min):[239,243]

$$2n\text{-}Bu_2GeH_2 + Hg(CN)_2 \xrightarrow{74\%} 2n\text{-}Bu_2GeHCN + Hg + 2H_2 \qquad [5]$$

$$n\text{-}Bu_2GeH_2 + 2AgNCO \longrightarrow n\text{-}Bu_2Ge(NCO)_2 + 2Ag + H_2 \qquad [6]$$

$$2n\text{-}Bu_2GeH_2 + Hg(NCS)_2 \longrightarrow 2n\text{-}Bu_2GeHNCS + Hg + 2H_2 \qquad [7]$$

Most reactions involving germanium halides and heavy metal salts follow the silver salt conversion series proposed by Anderson in his earlier work with organogermanium halides, pseudohalides and esters;[239] thus for R_3Ge species any derivative in the series,

$$I \rightarrow S \rightarrow Br \rightarrow CN \rightarrow NCS,\ Cl \rightarrow NCO \rightarrow O,\ OCOR \rightarrow F$$

may be converted to one to the right by interaction with the silver salt of the required derivative. Anomalies to this series are known[244] so that the bromides and iodides are most commonly used to prepare pseudohalides. Seyferth and Kahlen[214] used silver(I) cyanide to prepare cyano(trimethyl)germane from the iodide; the Me_3GeCN was found to react readily with sulphur at ca. 180° to form the thiocyanate:

$$Me_3GeI + AgCN \longrightarrow Me_3GeCN + AgI \qquad [8]$$

$$Me_3GeCN + S \longrightarrow Me_3GeNCS \qquad [9]$$

The same workers also found that Me_3GeCN formed a stable adduct with boron trifluoride etherate, and reacted with iron pentacarbonyl to form a thermally stable complex with the loss of carbon monoxide:

$$Me_3GeCN + BF_3.O(Et)_2 \longrightarrow Me_3GeCN.BF_3 + Et_2O \qquad [10]$$

$$Me_3GeCN + Fe(CO)_5 \longrightarrow Me_3GeNC.Fe(CO)_4 + CO \qquad [11]$$

This chemical reactivity and infrared evidence based on the observation of an extra band in the C≡N stretching region were thought to indicate the presence of both iso- and normal- forms of the cyanide. However, recent studies on the analogous silicon compound, Me_3SiCN (which exhibits similar reactivity[215] and spectral effects) indicate that at room temperature a mole fraction of no more than 0.0015 of the isocyanide is present,[220] suggesting that the equilibrium $Me_3SiCN \rightleftharpoons Me_3SiNC$ lies far to the left. It then follows that even if the cyanide moiety were nitrogen bonded as suggested[214] in the iron complex, $Me_3GeNC.Fe(CO)_4$, the reactivity could still be explained by the presence of the labile equilibrium $Me_3GeCN \rightleftharpoons Me_3GeNC$ being continuously displaced to the right. This emphasises the inadequacy of chemical reactivity as a criterion for molecular structure.

Schlemper and Britton[219] have determined the crystal structure of Me_3GeCN and from isotropic temperature factors decided that the carbon bonded normal-form was present although it was felt that a small fraction of the isocyanide could be present in solid solution in the cyanide. A linear Ge-C-N group was also indicated confirming the expected C_{3v} symmetry whilst the evaluation of crystal packing further suggested an incipient interaction between Ge and N although the GeN distance, 3.57Å was that expected for a normal Van de Waals interaction.

The work on alkylgermanium pseudohalides was extended to aryl derivatives by Srivastava and Tandon;[245] using silver(I), and lead(II) salts they prepared species of the type Ar_3GePs (Ar = C_6H_5, $C_6H_4CH_3$; Ps = CN,NCO,NCS) from the corresponding bromide, and discussed the i.r. spectra on the basis of the normal- form for the cyanides and the iso-form for the cyanates and thiocyanates.

Srivastava, Griffiths and Onyszchuk[244] used the silver salt conversion series to prepare germyl-, cyanide, isocyanate and isothiocyanate from bromogermane while Cradock and Ebsworth,[69,205] have reported high yields of the same species from the exchange reaction of fluorogermane with the appropriate silyl-pseudohalide:

$$GeH_3Br + AgPS \longrightarrow GeH_3Ps + AgBr \qquad [12]$$

$$GeH_3F + SiH_3Ps \longrightarrow GeH_3Ps + SiH_3F \quad (Ps = CN, NCO, NCS) \qquad [13]$$

Tetracyanogermane was obtained from Me_3SiCN and tetrachlorogermane by heating in xylene and removing the chlorosilane as it was formed.[215] The $Ge(CN)_4$ was isolated as a buff powder which was thought to be polymeric from its insolubility in organic solvents; no vibrational studies have been made to confirm this. By comparison tetra-, isocyanato, and isothiocyanato-germane are liquids conveniently obtained[246,247], by refluxing germanium tetrabromide (or chloride) with the appropriate silver salt in an inert solvent:

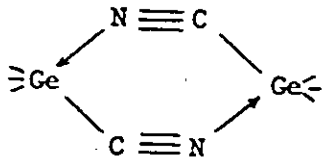
$$4Me_3SiCN + GeCl_4 \xrightarrow{\text{xylene}} 4Me_3SiCl + [Ge(CN)_4] \qquad [14]$$

$$GeBr_4 + 4AgNCO \xrightarrow{\text{benzene}} Ge(NCO)_4 + 4AgBr \qquad [15]$$

The gas phase infrared spectra of GeH_3CN and its isotopically labelled analogues were found to be consistent with the <u>normal</u>- form of cyanide.[248] The Ge-C-N linkage was assumed linear thus permitting the evaluation of the molecule in terms of C_{3v} symmetry which was largely born out by the observed parallel and perpendicular bands. No second band was reported in the C≡N stretching region in the deuteride, GeD_3CN. It was further reasoned that the presence of isocyanide in Me_3GeCN could arise from enhancement of the resonance contributions of the type,

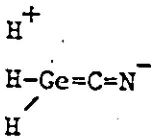
$$\overset{+}{\geqslant Ge} \qquad \overset{-}{\underset{\cdot\cdot}{N}{=}C:}$$

due to alkylation of the germyl cation. The structural isomerism was thought to involve an intermediate of the type,



which requires expansion of the covalent coordination of germanium to five, through participation of its empty d-orbitals. The barrier to rapid isomerism in the case of the alkylated germyl cyanide was then attributed to the absence of empty low-energy orbitals.

Microwave studies[218] of GeH_3CN indicated it to be a classic symmetric top and the dipole moment, 3.99±0.05D, is that of a highly polar molecule; no transitions attributable to germyl isocyanide were detected. The $C\equiv N$ bond length, 1.155±0.001Å, is normal for a covalent cyanide whilst the Ge-C distance, 1.919±0.001Å, is considerably shorter than the same distance in saturated molecules: GeH_3CH_3, 1.945Å; $Ge(CH_3)_4$, 1.98Å. This may point to the importance of canonical structures of the sort,



which implies interaction of the π-cloud in the $C\equiv N$ bond with vacant germanium d-orbitals although strictly no correlation is expected between a bond formed with an sp carbon in $-C\equiv N$ and an sp_3 carbon in $-CH_3$.

The vibrational spectra of GeH_3NCO[233,227] and GeH_3NCS[234] are consistent with the iso-formalism where the pseudohalides are bonded to germanium by the nitrogen atom. The presence of an extra band in the NCO stretching region in the former case was attributed to the presence of small amounts of GeH_3OCN;[233] this was later questioned when ^1H and ^{14}N n.m.r. studies[227] failed to detect a second species which would have been apparent at concentrations as low as 1%, the extra band was then attributed to an overtone in Fermi resonance with the fundamental by comparison with alkyl-thiocyanates and isocyanates.[249] It should be noted however, that the n.m.r. evidence refers to the liquid phase and not the gas phase where the controversy arises. Spectroscopic studies for the analagous trimethyl-species Me_3GeNCO and Me_3GeNCS[250] were limited to reports of the infrared stretching and deformation frequencies of the pseudohalide group and the Ge-N stretching frequency; no consideration of structural isomerism being apparent.

Vibrational studies for $Si(NCO)_4$ indicated a linear Si-N-C-O arrangement and the assignments were consistent with a tetrahedral model; however for $Ge(NCO)_4$ it was concluded that the molecule deviates to some unknown degree from being tetrahedral.[246] The criteria for the <u>iso</u>-form came from the sharp definition of physical properties, a ^{13}C n.m.r. which showed only one type of carbon, and the presence of intense bands between 1200 and 200 cm^{-1}, consistent with the observations in organic isocyanates.

By comparison with the cyanides, cyanates, and thiocyanates, germanium azides were characterised much later (1964). Ruidisch and Schmidt[251] obtained good yields of Me_3GeN_3 and $Me_2Ge(N_3)_2$ by the reactions of sodium azide with the corresponding chloride, while Thayer and West[231] used hydrazoic acid in situ in the reaction of the bromide with an aqueous acidic sodium azide solution:

$$Me_3GeCl + NaN_3 \xrightarrow{Et_2O} Me_3GeN_3 + NaCl \quad (60\%) \qquad [16]$$

$$Me_3GeBr + HN_3 \xrightarrow{H_2O} Me_3GeN_3 + H^+ + Br^- \quad (48\%) \qquad [17]$$

The partial infrared spectra and ultraviolet spectra were recorded for Me_3MN_3 species (M = Si,Ge,Sn,Pb); the results of the latter were thought to indicate dative π-bonding from nitrogen to silicon and germanium. These studies have been extended to arylgermanium azides by several workers.[252]

Cradock and Ebsworth[232] prepared the analogous hydride, GeH_3N_3, by the exchange reaction of fluorogermane with azido(trimethyl)silane:

$$Me_3SiN_3 + GeH_3F \longrightarrow Me_3SiF + GeH_3N_3 \quad (90\%) \qquad [18]$$

The vibrational spectra of GeH_3N_3 were interpreted by assuming a non-linear GeNNN skeleton,[232] which has been confirmed independently by electron diffraction experiments (∠Ge-N-N, 119°).[225]

The present study was carried out to establish synthetic routes to the hydrido-methylgermanium pseudohalides with the intention of verifying the vibrational assignments and group frequencies of previous authors; it was also of interest to see if any spectral feature could be interpreted as arising from <u>iso</u>- or <u>normal</u>- bonding by the pseudohalide moiety and in this respect emphasis will be on the cyanides, these being the most controversial. Initial studies with $MeGeH_2CN$ suggested that some reassessment of the assignment of the skeletal modes for GeH_3CN was necessary; for added confirmation the Raman spectrum of GeH_3CN and the infrared and Raman spectra of Me_3GeCN in solid, liquid, and gaseous phases were recorded and are presented for comparison with the new species (section VI.6). The ^1H n.m.r. spectra of GeH_3CN in CS_2 solution is reported (section VI.5) and provides tentative evidence for the presence of small amounts of isocyanide. It is also interesting to note that dipseudohalogenogermanes, GeH_2Ps_2 have not been isolated and attempts to synthesise digermanyl derivatives, Ge_2H_5Ps, gave only decomposition products.[46] In another study attempts to synthesise dicyanosilane, $SiH_2(CN)_2$, by reaction of SiH_2Cl_2 with AgCN resulted in mixed chloro-cyano species[205] so it was of further interest to investigate $MeGeH(Ps)_2$ species which are expected to have a greater stability than the germyl- or digermanyl- analogues.

VI.2 EXPERIMENTAL

The reactions described in the following sections largely follow standard procedures found in the literature: the mono-cyanides, -isocyanates, and -isothiocyanates were obtained by the passage of gaseous $MeGeH_2X$ or Me_2GeHX (X usually being bromide or iodide) through a column (50-100 ml, type 'E') loosely packed with a mixture of the appropriate silver(I) pseudohalide and glass wool at room temperature; the mono-azides were prepared in high yield by the exchange reaction of azido(trimethyl)silane, Me_3SiN_3, with the appropriate fluorogermane, $MeGeH_2F$ or Me_2GeHF; the tri-pseudohalides were obtained by refluxing $MeGeBr_3$ with the appropriate silver salt (for Ps = CN,NCO,NCS), or $MeGeCl_3$ with sodium azide (for Ps = N_3) in an inert solvent. Attempts to synthesise di-pseudohalides by the interaction of gaseous $MeGeHBr_2$ with the silver salts resulted in extensive decomposition and only tentative identification of $MeGeH(Ps)_2$ species. The mode of decomposition in these reactions is not clear, although the experimental details permit some speculation.

Details of the syntheses are given in sections VI.2.1–4; the new compounds were characterised by their ^1H n.m.r. (section VI.5) and vibrational spectra (section VI.6) with additional confirmation coming from molecular weight determinations, mass spectral parent peaks and hydrogen bromide cleavage reactions, (section VI.3. 1 and 2).

VI.2.1 Preparation of azido(methyl)-, azido(dimethyl)-, triazido(methyl)- and tetraazido-, germanes.

(a) Reactions of trichloro(methyl)- and tetrachloro-germane with sodium azide: Typically $MeGeCl_3$ (10.5 mmol) and Et_2O (ca.20 ml) were distilled under vacuum into a 100 ml round bottomed-flask, fitted with a reflux condenser, containing an excess of dry NaN_3 (ca.4.5 g). The stirred mixture was maintained under reflux (ca.100h). Unwanted solid residue, containing NaN_3 and NaCl, was removed by vacuum filtration to give a clear ether solution which was carefully evaporated to dryness under high vacuum. Fractionation of the last portions of ether to be evaporated gave small amounts of a white subliming solid in a trap at -23° which was subsequently shown to contain mixed azido-chloro species (section b). Triazido(methyl)germane, $MeGe(N_3)_3$ (1.9 g; 85% yield) was isolated as a white powdery solid (found; M, 218; calc. for $MeGe(N_3)_3$, 213.72; m.pt 44-45°). Sensitivity to percussion was not observed.

In another experiment $GeCl_4$ (2.1 g; ca.10 mmol) and excess NaN_3 (ca.5 g) were refluxed in dry T.H.F. (ca.20 ml) for 100 h. After vacuum filtration, evaporation of the solvent was facilitated by the addition of small amounts of Et_2O, and tetraazidogermane, $Ge(N_3)_4$ [ca.1.9 g; ca. 50% yield] remained in the filtration vessel (found: M.255; calc. for $Ge(N_3)_4$, 240). Samples were apparently not sensitive to percussion but explosion occurred when they were exposed to comparatively low powers in the Raman laser beam, so the spectroscopic data are not complete. Unreacted $GeCl_4$ was not identified conclusively in the large volume of solvent but small amounts of white material which sublimed with the last fractions of solvent, were shown qualitatively from the i.r. spectra (CCl_4 soln) to contain bands attributable to both azido- and chloro-moieties. These were tentatively assumed to be partially chlorinated species of the type $GeCl_n(N_3)_{4-n}$. No apparent reaction occurred when $MeGeH_2Cl$ (1.2 mmol) was passed through a column packed with NaN_3 (*ca.*10 g) and glass wool.

(b) *Exchange reactions with azido(trimethyl)silane:* In a typical experiment Me_3SiN_3 (1.60 mmol) and $MeGeH_2F$ (1.70 mmol) were condensed into a 10 ml reaction vessel (type 'C') at -196°. The mixture was warmed to room temperature and allowed to react (5 min). Repeated fractionation through a trap at -78° gave Me_3SiF (*ca.*1.55 mmol; identified by its ^1H n.m.r.[119] and i.r.[253] spectra) and a small amount of unreacted $MeGeH_2F$ (*ca.*0.1 mmol) in a -196° following trap. Distillation of the products in the -78° trap gave pure azido(methyl)germane, $MeGeH_2N_3$ [*ca.*1.54 mmol; found: M, 132; calc. for $MeGeH_2N_3$, 131.68; v.p. *ca.*13 mm.Hg at 20°; parent peaks at m/e 129-135 ($H_nCGeN_3^+$)] in a trap at -45° and a trace of unreacted Me_3SiN_3 in a trap at -196°.

By the same procedure Me_2GeHF (1.11 mmol) and Me_3SiN_3 (0.94 mmol) reacted to give azido(dimethyl)germane, Me_2GeHN_3 [*ca.*0.9 mmol; v.p. *ca.*13 mm Hg at 10°; parent peaks at m/e 142-149 ($H_nC_2GeN_3^+$)] condensing in the -45° trap; excess Me_2GeHF (*ca.*0.2 mmol), Me_3SiF (*ca.*0.9 mmol) and only a trace (<5%) of Me_3SiN_3 were obtained in the -196° trap. The corresponding reaction of Me_3SiN_3 with $MeGeH_2Cl$ gave less than 10% conversion to azide after 30 min at room temperature.

In another experiment $MeGeCl_3$ (*ca.*0.5 mmol) and Me_3SiN_3 (*ca.*1.5 mmol) were sealed together at -196° in a semi-micro n.m.r. tube (type 'G') and allowed to warm to room temperature. After 10 min the ^1H n.m.r. spectrum showed resonances at 0.23 and 1.61δ in the expected ratio 9:1 assignable to Me_3SiN_3[254] and $MeGeCl_3$,[126] respectively. After *ca.*5 days resonances attributable to Me_3SiCl[119] (0.38δ) and $MeGe(N_3)_3$ (1.07δ) had appeared along with resonances at 1.20 and 1.39δ . The latter resonances also appeared in the n.m.r. spectrum given by the volatile material from the reaction of $MeGeCl_3$ with NaN_3 (see section a) and in the n.m.r. spectrum given by equilibrium mixtures of $MeGeCl_3$ and $MeGe(N_3)_3$ and were consistent with the formation of the azido-chloro species $MeGe(N_3)_2Cl$ and $MeGeN_3Cl_2$. Similarly, azido-bromo species $MeGe(N_3)_2Br$ (1.26δ) and $MeGeN_3Br_2$(1.60δ) were observed in the n.m.r. spectrum of equilibrium mixtures of $MeGeBr_3$ and $MeGe(N_3)_3$. Integration of the resonances in both equilibria indicated the distribution of products was not random and that the mixed-species $MeGe(N_3)_nX_{3-n}$ (X = Cl,Br) were preferred.

VI.2.2 Preparation of cyano(methyl)-, cyano(dimethyl)-, and tricyano(methyl)-, germanes.

(a) Reaction of monohalogeno-methylgermanes with silver(I) cyanide: In a typical reaction chloro- or bromo-(methyl)germane (ca.1.5 mmol) was passed through a column of glass wool and AgCN (ca.25 g). After two double passes the silver salt had turned from white to brown and spectroscopic examination of the volatile products confirmed almost all the starting material was consumed. Fractionation gave pure cyano(methyl)germane, $MeGeH_2CN$ [1.35 mmol; found: M,117; calc. for $MeGeH_2CN$, 115.67; v.p. 24 mm Hg at 20°; parent peaks at m/e 111-119 (H_nCGeCN^+)], passing through a trap at -45° but retained in one at -63°. In the chloro-system traces of unreacted $MeGeH_2Cl$ were obtained in a -196° following trap. By the same procedure Me_2GeHI (0.85 mmol) was converted to cyano(dimethyl)germane, Me_2GeHCN [ca.0.8 mmol; v.p. ca.13 mm Hg at 23°; parent peaks at m/e 126-133 ($H_nC_2GeCN^+$)] which condensed in a -45° trap.

(b) Reaction of dibromo(methyl)germane with silver(I) cyanide: $MeGeHBr_2$ (ca.2.1 mmol) was used in a reaction analagous to (a). An exothermic reaction occurred in which the AgCN turned dark brown; after four double passes volatile material (ca.1.2 mmol) was recovered after bleeding off non-condensable gas (ca.0.9 mmol). Distillation of the products gave a mixture of $MeGeH_3$ and HCN (ca.0.2 mmol; identified spectroscopically) in a trap at -196°, traces of $MeGeH_2CN$ (ca.0.3 mmol) in a trap at -45°, and a white involatile residue. The contents of the -45° trap sealed at -196° for n.m.r. analysis rapidly turned white; resonances at 0.67 and 4.35δ were assigned to $MeGeH_2CN$ and weaker resonances at 0.98 and 5.30δ were tentatively assigned to $MeGeH(CN)_2$. This assignment of the latter was supported by the presence of fragments in the mass spectra at m/e 122-129, ($H_nGe(CN)_2^+$), m/e 137-144 ($H_nCGe(CN)_2^+$). Broad features at 3.95, 3.8δ grew with time as the earlier resonances diminished and were possibly due to polymeric material of the type $(HGeCN)_n$. Similar results were obtained when the $MeGeHBr_2$ was streamed over AgCN with nitrogen as a diluent.

(c) Reaction of tribromo(methyl)germane with silver(I) cyanide: By the procedure outlined in section VI.2.1a $MeGeBr_3$ (ca.5 mmol), excess AgCN (ca.5 g) and dry T.H.F. (ca.15 ml) were refluxed (ca.60 hr). The reaction mixture turned from white to black and filtration followed by removal of solvent in a high vacuum led to the isolation of tricyano(methyl)germane, $MeGe(CN)_3$ [found: M,170; calc. for $MeGe(CN)_3$, 165.66]. The white powdery solid liquified in moist air slowly evolving HCN, dissolved in benzene and T.H.F. but was only sparingly soluble in Et_2O and CCl_4.

VI.2.3 Preparation of isocyanato(methyl)-, isocyanato(dimethyl)-, and triisocyanato(methyl)-, germanes.

(a) Reaction of monohalogeno-methylgermanes with silver(I) cyanate:

In a typical experiment $MeGeH_2Br$ (*ca*.2.0 mmol) was passed over AgNCO (*ca*.25 g) held in a column with glass wool. An exothermic reaction ensued in which the contents turned black, and after four double passes the ^1H n.m.r. confirmed all the starting material had been consumed and isocyanato(methyl)germane, $MeGeH_2NCO$ [1.95 mmol; found: M,131; calc. for $MeGeH_2NCO$, 131.66; v.p. *ca*.17 mm Hg at 20°; parent peaks at m/e 128-132 ($H_nCGeNCO^+$)], was obtained after fractionation in a trap at -45°. By the same procedure using $MeGeH_2Cl$ less than 20% conversion to the required isocyanate was obtained after ten double passes, the reaction being accompanied by the formation of non-condensable gas, $MeGeH_3$, and unidentified involatile white material. In a reaction using Me_2GeHI (1.20 mmol) complete conversion to isocyanato(dimethyl)germane, $Me_2GeHNCO$ [*ca*.1.1 mmol; v.p. *ca*.14 mm Hg at 20°; parent peaks at m/e 142-148 ($H_nC_2GeNCO^+$)] was obtained after two double passes condensing in a -45° trap.

The mono-isocyanates showed no signs of decomposition after 2 weeks in sealed tubes but on exposure to mercury vapour or AgNCO disproportionation was rapid; redistribution was evident from the appearance of additional proton resonances of a fraction held at -78° at 0.94, 6.17δ and 0.87δ which were tentatively assigned to $MeGeH(NCO)_2$ and $Me_2Ge(NCO)_2$; traces of $MeGeH_3$ and HNCO were identified in a -196° following trap.

(b) *Reaction of dibromo(methyl)germane with silver(I) cyanate*: In one experiment $MeGeHBr_2$ (1.5 mmol) was streamed over the silver salt in the usual manner. Non-condensable gas (*ca*.0.5 mmol) was bled away through traps at -196° after 6 passes, the AgNCO being noticeably black and warm. The volatile material rapidly turned white at room temperature; fractionation gave HNCO (*ca.*0.1 mmol; identified spectroscopically) in a trap at −196° $MeGeH_2NCO$ (*ca.*0.2 mmol) and an intractable white residue in a trap at −45°, and an oily material in a trap at −23°. The contents of the −23° trap, sealed for ^1H n.m.r. analysis, rapidly turned white and showed resonances assignable to $MeGeH_2NCO$ (0.75, 5.20δ); $MeGeH(NCO)_2$, (0.94,6.17δ); $Me_2Ge(NCO)_2$, (0.87δ); $MeGeH_3$, (0.29, 3.45δ); additional resonances at 3.3δ and 4.15δ were not identified. The presence of the dipseudohalide species was supported by the appearance of weak fragments at m/e 154-159 ($H_nGe(NCO)_2^+$) and m/e 166-171 ($H_nCGe(NCO)_2^+$) in the mass spectra.

(c) *Reaction of tribromo(methyl)germane with silver(I) cyanate:* $MeGeBr_3$ (*ca.*7.5 mmol), excess AgNCO (*ca.*8 g), and benzene (*ca.*15 ml) were stirred under reflux (*ca.*72 h). The reaction mixture turned from brown to black and vacuum filtration followed by evaporation of solvent led to the isolation of triisocyanato(methyl)germane, $MeGe(NCO)_3$ [*ca.*1.36 g, 5.2 mmol; found: m,212; calc. for $MeGe(NCO)_3$, 213.66; m pt. 48-51°]. The white material was soluble in benzene, T.H.F., and $CHCl_3$ but sparingly soluble in Et_2O and CCl_4. No bromo-isocyanato species were detected in any reactions.

VI.2.4 *Preparation of isothiocyanato(methyl)-, isothiocyanato(dimethyl)-, and triisothiocyanato(methyl)-, germane.*

(a) *Reaction of monohalogeno-methylgermanes with silver(I) thiocyanate:* In one experiment $MeGeH_2Br$ (*ca.*2.1 mmol) was streamed over AgNCS (*ca.*25 g) in the usual manner. An exothermic reaction occurred in which the silver salt turned dark brown; isothiocyanato(methyl)germane, $MeGeH_2NCS$ [2.05 mmol; found: M, 146; calc. for $MeGeH_2NCS$, 147.73; parent peaks at m/e 143-148 ($H_nCGeNCS^+$)] was recovered after fractionation and condensation at -45°. In an analagous reaction Me_2GeHI (ca.0.91 mmol) was converted almost quantitatively to isothiocyanato(dmethyl)germane, $Me_2GeHNCS$[0.85 mmol; v.p. ca.5 mm Hg at 20°; parent peaks at m/e 159-163 ($H_nC_2GeNCS^+$)].

Sealed samples of the mono-isothiocyanates showed no signs of decomposition after ten weeks at room temperature; prolonged exposure to mercury vapour or AgNCS resulted in the deposition of yellow residue and features assignable to disproportionation products appeared in the n.m.r. spectra: $Me_2Ge(NCS)_2$, 1.04δ; $MeGeH(NCS)_2$, 1.12,5.80δ; $MeGeH_3$, 0.29, 3.45δ; $MeGe(NCS)_3$, 1.33δ (weak). No apparent conversion to the expected thiocyanate was observed when $MeGeH_2Cl$ was substituted for $MeGeH_2Br$.

(b) <u>Reaction of dibromo(methyl)germane with silver(I) thiocyanate</u>: In a typical experiment $MeGeHBr_2$ (1.8 mmol) was streamed over AgNCS (ca.20 g); an exothermic reaction band passed down the column as the AgNCS turned black. Non-condensable gas (ca.0.7 mmol) was bled away with the collecting bulb held at -196° . The volatile material contained some unreacted $MeGeHBr_2$, and traces of $MeGeH_3$ and $MeGeH_2NCS$ (total ca. 0.3 mmol; identified in the ^1H n.m.r. spectrum) in a trap at -45° and an oily liquid mixed with a yellow sublimable solid in a trap at -23°. The n.m.r. spectrum of this trap showed features assignable to $MeGeH(NCS)_2$ (1.12, 5.80δ); $Me_2Ge(NCS)_2$ (1.33δ); $MeGe(NCS)_3$ (1.33δ); with additional resonances at 3.3, 3.5 and 4.4δ tentatively assigned to polymeric species of the type $(MeGeNCS)_n$ or $(HGeNCS)_n$. The yellow material was insoluble in CS_2 indicating that it contained no free sulphur whilst an i.r. spectrum (CS_2 smear) suggested that it was probably polymeric thiocyanic acid.

(c) Reaction of tribromo(methyl)germane with silver(I) thiocyanate: $MeGeBr_3$ (ca.10.5 mmol), excess AgNCS (ca.7.5 g) and Et_2O (ca.15 ml) were stirred under reflux (ca.70 h). The reaction mixture darkened considerably and vacuum filtration followed by evaporation of solvent led to the isolation of triisothiocyanato(methyl)germane, $MeGe(NCS)_3$ [2.2 g, 8.5 mmol; found: M,210; calc. for $MeGe(NCS)_3$, 213.66; m.pt. 50-53°]. The white material was soluble in Et_2O, benzene, and $CHCl_3$, sparingly soluble in CCl_4 and yellowed on exposure to moist air. No bromo-isothiocyanato species were obtained in the preparative reactions although these were readily identified in equilibrium mixtures of $MeGeBr_3$ with $MeGe(NCS)_3$: $MeGe(NCS)_2Br$, 1.61δ; $MeGe(NCS)Br_2$, 1.83δ.

VI.3 PHYSICAL PROPERTIES

The mono-pseudohalides, $MeGeH_2Ps$ and Me_2GeHPs, ($Ps = N_3$,CN,NCO,NCS) are colourless liquids which show considerable solubility in hydrocarbon tap-grease. They are strikingly less volatile than the analogous halide species, e.g. $MeGeH_2Cl$ or Me_2GeHCl, even though the molecular weights are similar; this may point to some intermolecular association in the liquid phase although it was not possible to substantiate this by vapour pressure measurements. The compounds generally undergo rapid disproportionation in the presence of manometer mercury or the parent silver salt, probably leading to the formation of polygermanes, $(MeGeH)_n$, hydroacids (HPs), parent hydrides ($MeGeH_3$) and species of the type $Me_xGeH_yPs_z$ ($x + y + z = 4$). For this reason attempts to obtain reliable vapour pressure data with the standard apparatus were unsuccessful and the data given in sections VI.2.1-4 can only be regarded as approximate for the low-volatility species.

The di-pseudohalides, $MeGeH(Ps)_2$, were not isolated but may be sublimable solids; it is not certain whether the instability arises from a thermal decomposition at room temperature or catalytic decomposition in the presence of the silver salts or traces of unknown impurities (e.g. hydrogen pseudohalides, HPs). The tri-pseudohalides, MeGe(Ps)$_3$, are low melting point, white involatile solids which seem quite thermally stable although liquefication in moist air (probably liberating the hydroacid) is observed.

VI.3.1 Mass spectra: The problem of sample decomposition extended to the inlet system of the mass spectrometer where an inevitable exposure to mercury occurred. Analysis of the fragments m/e 70-79 (H_nGe^+) and m/e 83-93 (H_nCGe^+) indicated the presence of significant amounts of methylgermane (see chapter I). It is unlikely that this resulted from ion-molecule reactions in the ionisation chamber so that the relative intensities of the peaks are not considered meaningful nor the fragment distribution of the region m/e 70-93 (ie. $^{70}Ge^+ \rightarrow H_5C^{76}Ge^+$). However the observation of parent peaks for the mono-pseudohalides in the expected m/e ranges (Table VI.3) provides confirmatory evidence for the proposed species, this being particularly important for the unstable

(Table VI.3) Observed mass spectral parent peaks for the mono-pseudohalides

Fragment	Range,m/e	Mol.Wt (calc)
$H_nCGeN_3^+$	129-135	131.68
$H_nC_2GeN_3^+$	142-149	145.69
H_nCGeCN^+	111-119	115.67
$H_nC_2GeCN^+$	126-133	129.68
$H_nCGeNCO^+$	128-132	131.66
$H_nC_2GeNCO^+$	142-148	145.67
$H_nCGeNCS^+$	143-148	147.73
$H_nC_2GeNCS^+$	159-163	161.74

di-pseudohalide species (the observed parent peaks for $MeGeH(Ps)_2$ are given in sections VI.2.1-4). In addition to the parent peaks, fragments attributable to 'normal' breakdown products could be identified, although these were inconsistent and are tentative therefore: $MeGeH_2CN$, m/e 96-102 (H_nGeCN^+); $MeGeH_2NCO$, m/e 112-118 (H_nGeNCO^+), 42 (NCO^+), 28 (CO^+); $MeGeH_2NCS$, m/e 143-147 (H_nGeNCS^+), 76 (CS_2^+), 59 ($HNCS^+$), 44 (CS^+), 32 (S^+). For $MeGeH_2N_3$ the isotopic fragmentation patterns of the (H_nGe^+) and (H_nCGe^+) regions were considered unperturbed by the presence of $MeGeH_3$ so the intensities can be meaningful: m/e 28 [I = 1.6] (N_2^+); m/e 70-77 [I = 46] (H_nGe^+); m/e 83-93 [I = 100] (H_nCGe^+); m/e 101-105 [I = 8] ($H_nGeN_2^+$); m/e 114-118 [I = 31] ($H_nGeN_3^+$); m/e 129-135 [I = 18] ($H_nCGeN_3^+$).

VI.3.2 Hydrogen Bromide cleavage reactions: In view of the unsatisfactory mass spectral data further quantitative confirmation was sought by cleavage of known amounts of the mono- and tri-pseudohalides with gaseous HBr (30 min, room temperature, vessel 'F'). The bromides, $MeGeH_2Br$, Me_2GeHBr, and $MeGeBr_3$, resulting from these reactions were identified quantitatively and qualitatively from ^1H n.m.r. and i.r. spectra. The data obtained are collected in Table VI.4. In most cases the recovery of near-quantitative amounts of the bromides confirms that the methylgermanium moieties, $MeGeH_2-$, Me_2GeH-, or $MeGe\equiv$, are present in stoichiometric amounts in monomeric pseudohalide species. The hydrogen pseudohalide species HPs, also resulting from the cleavage showed a marked tendency to polymerise under the experimental conditions so that they were identified only on a qualitative basis.

(Table VI.4) Hydrogen bromide cleavage data

MPs	mmol MPs	mmol HBr	mmol MBr	Other Products
$MeGeH_2N_3$[a]	–	–	–	
Me_2GeHN_3[a]	–	–	–	
$MeGeH_2CN$	1.20	2.0	1.05	HCN[b], white solid
Me_2GeHCN	0.95	2.0	0.85	
$MeGeH_2NCO$	0.85	1.5	0.80	HNCO, white solid
$Me_2GeHNCO$	0.72	2.0	0.69	
$MeGeH_2NCS$	1.20	2.0	1.13	HNCS, pale yellow solid
$Me_2GeHNCS$	1.02	1.8	0.95	
$MeGe(N)_3$[a]	–	–	–	
$MeGe(CN)_3$	0.7	3.5	0.53	HCN[b], white solid
$MeGe(NCO)_3$	1.0	4.0	0.85	white solid
$MeGe(NCS)_3$	0.8	3.0	0.66	yellow solid
$Ge(N_3)_4$[a]	–	–	–	

a. not carried out due to explosive nature of HN_3;

b. identified spectroscopically.

VI.4 DISCUSSION

In keeping with the silver salt conversion series proposed by Anderson[239] bromo- and iodo-methylgermanes are converted to the pseudohalogeno-methylgermanes by interaction with the appropriate silver(I) pseudohalide, reactions [19].

e.g.

$$MeGeH_2Br + AgCN \longrightarrow MeGeH_2CN + AgBr \quad [19a]$$

$$Me_2GeHI + AgNCO \longrightarrow Me_2GeHNCO + AgI \quad [19b]$$

$$MeGeBr_3 + 3AgNCS \longrightarrow MeGe(NCS)_3 + 3AgBr \quad [19c]$$

However, in an analogous reaction it has been noted that chlorogermane is effectively converted to cyanogermane but not to isocyanato- or isothiocyanato-germane,[244] suggesting some deviation from Anderson's conversion series[239] for germanium hydrides. By comparison chloro(methyl)germane is found to give high yields of cyano(methyl)germane [19a], to form an equilibrium mixture with isocyanato(methyl)germane [19b], and does not appear to react with silver(I) thiocyanate [19c]. This implies a repositioning of chloride in the methylgermane series,

$$I \rightarrow Br \rightarrow NCS \rightarrow NCO, \quad Cl \rightarrow CN \rightarrow (N_3) \rightarrow F$$

Experiments to establish the position of azide were not carried out but in view of the fact that azido-alkylgermanes may be obtained from chloroalkylgermanes[251] (albeit in alkali metal salt conversion) and azidogermane is obtained by the exchange of the fluoride with azido(trimethyl)silane,[232] it seems reasonable to place azide between chloride and fluoride.

Repeated attempts to synthesise pure samples of the di-pseudohalides, $MeGeH(Ps)_2$, by passage of gaseous dibromo(methyl)germane over silver salts were unsuccessful despite meticulous drying of the silver salts and dilution with nitrogen. The formation of $MeGeH(Ps)_2$ (Ps = CN,NCO,NCS), is accompanied by the evolution of hydrogen and the formation of intractable material with the corresponding acid. The intractable material was not characterised but is likely to be polymeric germanium hydride or condensed pseudohalide species as suggested by reactions [20]. Cyanic acid was found to catalyse the polymerisation of SiH_3NCO[216] so presumably

$$MeGeHBr_2 + 2AgPs \longrightarrow [MeGeH(Ps)_2] + 2AgBr \qquad [20a]$$

$$n[MeGeH(Ps)_2] \longrightarrow [MeGePs]_n + nHPs \qquad [20b]$$

$$2MeGeH(Ps)_2 \longrightarrow MeGe(Ps)_3 + MeGeH_2Ps \qquad [20c]$$

$$2MeGeH_2Ps \longrightarrow MeGeH_3 + [MeGeH(Ps)_2] \qquad [20d]$$

the presence of hydroacids catalyses further decomposition as well as disproportionation to mono-, and tri- pseudohalogeno species, reactions [20c,d]. No evidence for any Ge-Ge bonds was obtained in the vibrational or mass spectra although this may have arisen from a lack of solubility of the polymeric material in the solvents used. The ^1H n.m.r. spectra given by the reaction products are consistent with the formation of $MeGeH(Ps)_2$ species but at the same time show many additional resonances arising from the continuing decomposition of the di-pseudohalides; these are tentatively attributed to the polymeric and/or condensed species suggested above. It would be interesting to investigate the formation of the di-pseudohalides by an exchange reaction of $MeGeHF_2$ with silicon pseudohalides,[232] where it might be possible to use milder conditions and so avoid the problem of decomposition.

Despite the relative ease of these silver salt reactions, an alternative route was sought for the azido- derivatives because of the instability of silver azide. Monofluorogermane reacted with azido-(methyl)silane to form GeH_3N_3 in high yield;[232] the corresponding reaction of monofluoro-methylgermanes gives virtually quantitative yields of the azido-methylgermanes, reactions [21]. By comparison the equilibrium in the corresponding reaction with chloro(methyl)germane lies far to the left at room temperature making this an unsuitable starting

$$\mathrm{MeGeH_2F + Me_3SiN_3 \rightleftharpoons MeGeH_2N_3 + Me_3SiF} \qquad [21a]$$

$$\mathrm{Me_2GeHF + Me_3SiN_3 \rightleftharpoons Me_2GeHN_3 + Me_3SiF} \qquad [21b]$$

material, but at the same time supporting the position of azide in the conversion series. Similarly, the reaction between trichloro(methyl)-germane and Me_3SiN_3 gives an equilibrium mixture containing mixed species, as was found for the reaction of the azido-silane with dichloro-(dimethyl)silane.[255] These results are at least consistent with the generally accepted concept that exchange in a silyl-germyl system favours the formation of the hard (in the Pearson sense,[108] or less polarisable) moiety bound to silicon. The reaction of $MeGeF_3$ with Me_3SiN_3 was not attempted because it was not possible to prepare the required quantities of fluoride (see chapter I).

Using the method described by Ruidisch and Schmidt[251] triazido(methyl)- and tetraazido-germane are obtained by refluxing the corresponding chloride, $MeGeCl_3$ or $GeCl_4$, with sodium azide in an inert solvent, reactions [22]. Tetraazidosilane was reported to be extremely shock sensitive[256] but no similar instability is apparent for the germanium azides. [$MeGe(N_3)_3$ was even stable for long periods above its melting point but a sample of $Ge(N_3)_4$ did explode when exposed to comparatively low powers in the Raman laser beam].

$$\mathrm{MeGeCl_3 + 3NaN_3 \xrightarrow{ether} MeGe(N_3)_3 + 3NaCl} \qquad [22a]$$

$$\mathrm{GeCl_4 + 4NaN_3 \xrightarrow{THF} Ge(N_3)_4 + 4NaCl} \qquad [22b]$$

In the synthesis of the corresponding tin compound[256] a complex salt, $Sn(N_3)_4.2NaN_3$ was reported; no evidence for similar complex formation by tetraazidogermane is obtained although the cryoscopic molecular weight determination has a high uncertainty due to the low solubility of

$Ge(N_3)_4$. These observations may reflect the familiar difficulty encountered in forcing germanium to increase its coordination to six.

As has been indicated earlier, exchange at silicon or germanium is characteristic of the halogeno-derivatives (chapter I). Exchange with hydrogen halide provided a convenient synthetic route to iodo- and bromo-(methyl)germanes because the formation of the heavier halogen bound to germanium was favoured. The use of a similar route to the pseudohalides would require the reaction of fluorogermanes with hydrogen pseudohalides which was not considered a sensible synthetic prospect. Similarly, the reactions of digermoxanes with hydrogen pseudohalides or of halides with aqueous potassium pseudohalides (section VI.1) were not attempted although they may be of some theoretical interest. However, this type of reaction provides a convenient characterisation of the pseudohalides since parent bromo-methylgermanes are reclaimed by reaction with hydrogen bromide, reactions [23]. The reactions are not suitable for the azides

$$HBr + MeGeH_2Ps \longrightarrow MeGeH_2Br + HPs \qquad [23a]$$

$$3HBr + MeGe(Ps)_3 \longrightarrow MeGeBr_3 + 3HPs \qquad [23b]$$

due to the hazardous nature of the by-product hydrazoic acid.

VI.5 ^1H N.M.R. SPECTRA

The ^1H n.m.r. parameters of the new pseudohalogen derivatives are collected in Table VI.5 along with those of the previously reported germyl-, and trimethylgermyl- species. The spectra are all first order and as such give the same set of mutiplets as the analagous halogeno-species (chapter II). Significant dilution shifts (up to 5%) were observed particularly in the $MeGeH_2Ps$ and Me_2GeHPs series so in accordance with other workers the n.m.r. parameters are reported for the sample in dilute solution (ca.5% in CCl_4) using an internal reference

(Table VI.5) The ^1H n.m.r. parameters* of the pseudohalide derivatives of germane and the methylgermanes

Compound	δ(Me)	δ(GeH')	$\lvert J^{vic}_{HH'}\rvert$	$\lvert J_{CH}\rvert$
GeH'_3N_3[a]	–	5.08	–	–
$MeGeH'_2N_3$	0.69	5.23	3.08	–
$Me_2GeH'N_3$	0.84	5.43	2.70	130.5
Me_3GeN_3[b]	0.54	–	–	132.8
$Me_2Ge(N_3)_2$[b]	0.87	–	–	133.2
$MeGe(N_3)_3$	1.07	–	–	–
GeH'_3CN	–	4.33	–	–
$MeGeH'_2CN$	0.67	4.35	3.80	–
$Me_2GeH'CN$	0.64	4.52	3.36	132.0
Me_3GeCN	0.56	–	–	130.2
$MeGeH'(CN)_2$	0.98	5.30	n.o.	–
$MeGe(CN)_3$	1.09	–	–	–
GeH'_3NCO[c]	–	5.05	–	–
$MeGeH'_2NCO$	0.75	5.20	3.22	–
$Me_2GeH'NCO$	0.62	5.31	2.78	128.3
Me_3GeNCO	0.48	–	–	128.3
$MeGeH'(NCO)_2$	0.94	6.17	1.35	–
$Me_2Ge(NCO)_2$	0.87	–	–	–
$MeGe(NCO)_3$	1.14	–	–	–
GeH'_3NCS[c]	–	5.18	–	–
$MeGeH'_2NCS$	0.75	5.45	3.08	–
$Me_2GeHNCS$	0.71	5.45	2.70	129.8
Me_3GeNCS	0.65	–	–	128.2
$MeGeH'(NCS)_2$	1.12	5.80	1.50	–
$Me_2Ge(NCS)_2$	1.04	–	–	–
$MeGe(NCS)_3$	1.33	–	–	–

* The spectra were recorded at ambient temperature in CCl_4 solution (ca.5%). Chemical shifts (δ± 0.02 p.p.m.) are in p.p.m. to low field of tetramethylsilane as internal standard. J in Hz, ±0.05Hz (HH'), ±0.5Hz (^{13}CH)

a. ref.232 (20% cyclohexane); b. ref.251 (5% CCl_4);

c. ref. 227 (15% cyclohexane).

of tetramethylsilane. The spectra of the neat liquids also show considerable broadening of the resonances which could arise from some degree of intermolecular exchange or association, or from quadrupole relaxation from ^{14}N.

The chemical shifts of the GeH'_2 resonances in $MeGeH'_2NCS$ and $MeGeH'_2NCO$ are close to that of $MeGeH'_2N_3$ strongly suggesting that all three are germanium-nitrogen bonded. The same is true for the GeH' resonance in $Me_2GeH'NCO$, $Me_2GeH'NCS$, and $Me_2GeH'N_3$ and a comparison with the parameters in the germyl species [GeH_3N_3, 5.1δ;[232] GeH_3NCS, 5.18δ;[227] GeH_3NCO, 5.05δ;[227] $(GeH_3)_3N$, 4.9δ;[257] $(GeH_3)_2O$, 5.3δ; $(GeH_3)_2S$, 4.7δ[257a]] further supports this conclusion, particularly as there has been strong n.m.r. evidence that GeH_3-NCO, and -NCS are truly nitrogen bonded.[227] For the cyanides GeH_3CN, $MeGeH_2CN$, and Me_2GeHCN the Ge-H resonance occurs to high field of the other pseudohalides at *ca.*4.3δ which is near the resonance in the germanium-carbon bonded alkylgermanes,[83] viz: $(CH_3)_2GeH_2$, 3.73δ; $(CH_3)_3GeH$; 3.92δ. Whilst this suggests that the cyanides are carbon bonded it is also consistent with a rapid equilibrium between Ge-CN and Ge-NC species in which the Ge-H resonance is observed intermediate to the two extremes. The value of the vicinal coupling constants J(HH') for $MeGeH'_2CN$ (3.80Hz) and $Me_2GeH'CN$ (3.36Hz) are the highest found for derivatives of this type and compare to 3.95 and 3.40 Hz for Me_2GeH_2 and Me_3GeH respectively.[83] The Ge-N bonded species on the other hand show J(HH') values similar to Ge-Cl species (ie. *ca.*3.0, 2.7Hz) implying a similar effective electronegativity and electron distribution in the H-C-Ge-H bonds.

Ebsworth and Frankiss[257b] observed similar effects in comparing silylacetylene, cyanide, isocyanate, and isothiocyanate and concluded that

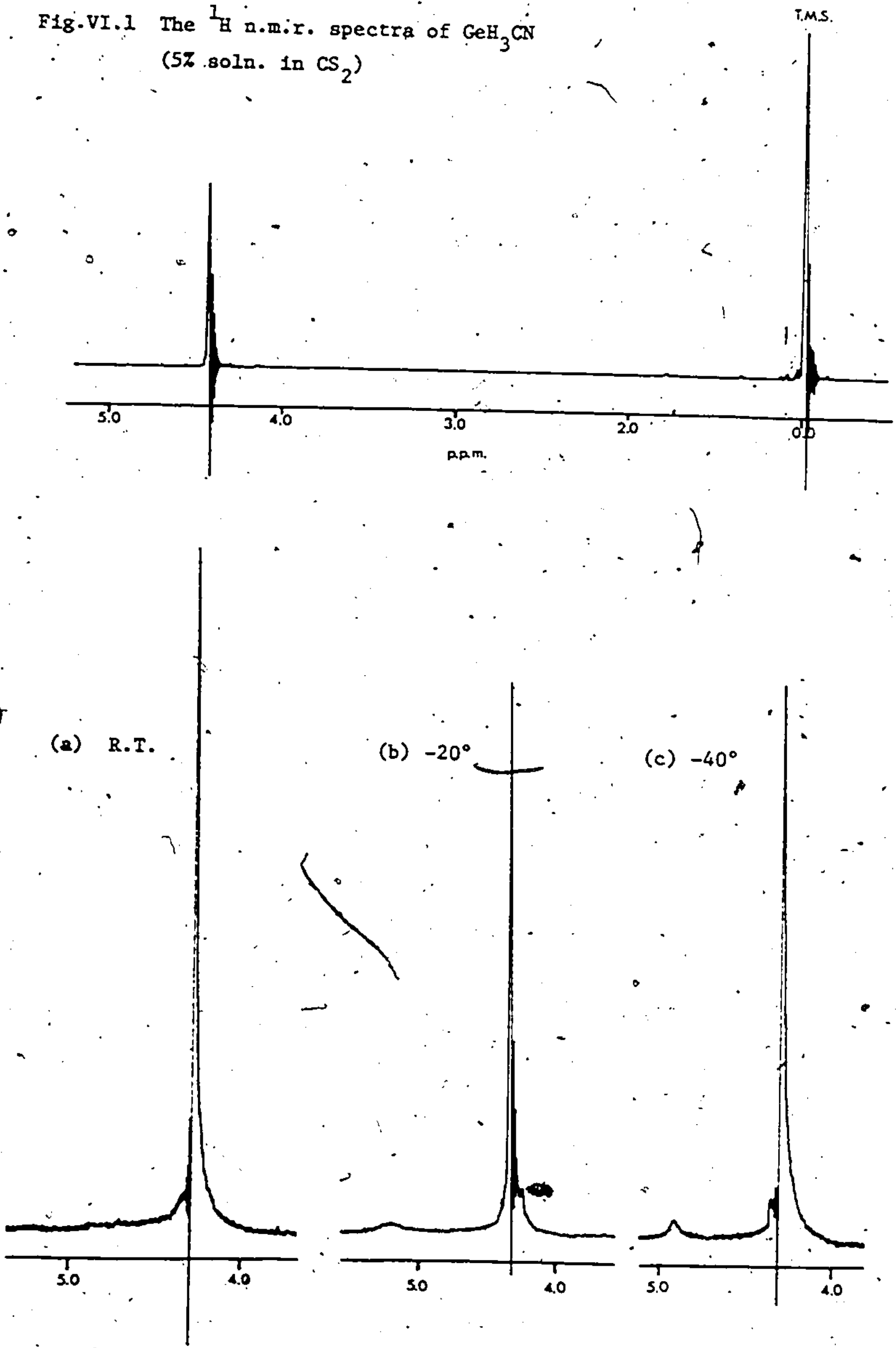
SiH_3CN is largely, if not wholly, carbon bonded. This type of argument is reinforced by the observation that the proton resonance in methyl cyanide[85] is close to the CH_3-proton resonance in methylacetylene,[258] but more than 1 p.p.m. to high field of the proton resonance in methyl-, isocyanide, isocyanate, isothiocyanate. Evidence from microwave spectroscopy also indicated the carbon bonding in silylcyanide.[217]

To examine this further the ^1H n.m.r. spectra of GeH_3CN (ca.5% solution in CS_2) were recorded at low temperature, (Fig.VI.1). A sharp singlet was observed at 4.33δ at room temperature (a); at -20° the singlet broadened and a very weak resonance was appearing at ca.5.0δ (b); at ca.-40° the weaker resonance had grown slightly (c) but at lower temperatures both resonances disappeared presumably due to a lack of solubility. The additional weak resonance at ca. 5.0δ is in the typical H_3Ge-N region (Table VI.5) so its appearance is at least consistent with the presence of the Ge-NC species. This preliminary result is what would be expected for a rapid room temperature isomerisation in the $H_3GeCN \rightleftharpoons H_3GeNC$ system in which the equilibrium lies far to the left. A more intensive study involving a solvent which would permit greater solubility of the GeH_3CN at low temperatures is needed before a realistic estimate of the mole fraction of GeH_3NC can be made.

Spin coupling has been observed between the ^{14}N atom and the α- and β-alkyl protons[259] in the spectra of all alkyl isocyanides so far studied. This was not observed in the silyl- analogues[257b] and is not observed for the germyl-species in this study. Investigations of the resonances for ^{14}N and/or ^{13}C nuclei at low temperatures may provide more definite evidence for the isomerisation.

The variations in the n.m.r. parameters of the pseudohalides with

Fig.VI.1 The ^1H n.m.r. spectra of GeH_3CN (5% soln. in CS_2)

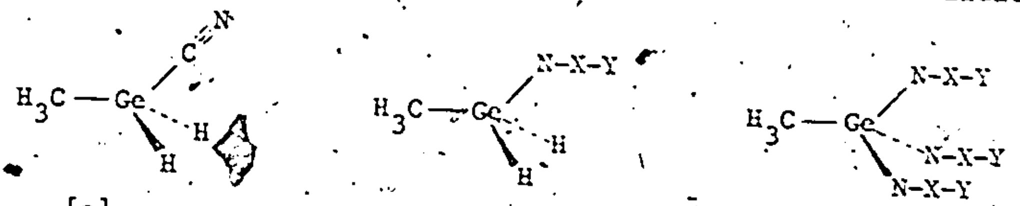


increasing methyl or pseudohalogen substitution at germanium are similar to the analogous halides and require little comment. It is noted that the chemical shifts and coupling constants for the Ge-N bonded species, ie. the azides, isocyanates, and isothiocyanates, are close and show similar trends to those of the corresponding chlorides (chapter II), whilst the cyanides resemble more closely the corresponding iodides. In view of the unknown balance of effects which determine the chemical shifts, (for the germanium protons) it is not clear how far one may compare the inductive effects of the halides and pseudohalides. Based on the observed GeH shifts the order of inductive withdrawal is I < CN < Br < NCS, N_3 < Cl < NCS < F, which is at least consistent with the accepted electronegativity values for the halogens, carbon, and nitrogen.[88-92] In this context it is interesting to note that where the polarisability (or hardness) of the pseudohalides seems to be important, as in the exchange reactions, the order of reactivity, I → Br → NCS → NCO, Cl → CN → F, is such that the cyanide group behaves more like fluoride than bromide. This similarity extends to the intensity of the Raman bands associated with GeF and GeCN moieties (section VI.6) which also depend on polarisability.

VI. 6 VIBRATIONAL SPECTRA

The assignments for the three series of pseudohalides, $MeGeH_2Ps$, Me_2GeHPs, and $MeGe(Ps)_3$ (Ps = N_3, CN, NCO, NCS), are conveniently discussed by comparison with the analogous halides described in chapters III and IV. The replacement of halogen by the polyatomic pseudohalogens introduces additional fundamentals which have distinct group frequencies and it is these modes which best characterise the new species.

Recent electron diffraction studies[225] confirmed the earlier predictions from vibrational spectroscopy[233,232] that the heavy atom skeletons of GeH_3NCO and GeH_3N_3 are nonlinear (section VI.1). Microwave spectroscopy[218] indicated that GeH_3CN is a symmetric top with a linear Ge-C-N linkage. Direct structural data for GeH_3NCS are not available but evidence from vibrational spectroscopy[234] suggested that the Ge-N-C linkage is nonlinear. It is unlikely that the geometries change significantly in the methyl substituted species so the preceding data will be assumed for subsequent discussion. If the pseudohalide group (represented by N-X-Y for N-C-O, N-C-S, N-N-N) is linear and lies in the molecular plane then at best the hydrides possess C_s symmetry (Fig.VI.2 a and b); as a result the methylgermyl moieties, $MeGeH_2$- and Me_2GeH- are expected to give rise to similar sets of a' and a" fundamentals as the analagous halides. The tri-pseudohalides are harder to evaluate on



[a] [b] [c]

Fig.VI.2 Idealised geometries for the pseudohalides

a comparative basis but may at best have pseudo-C_{3v} symmetry as the trihalides (Fig.VI.2c); it is, however, unlikely that all three triatomic groups would adopt the most symmetric arrangement and these species are expected to produce spectral features which characterise this. In addition there is the possibility of intermolecular association via pseudohalide bridging although the molecular weight data indicate this is likely to be minimal.

An approximate description of the fundamentals arising from the Ge-C-N and Ge-N-X-Y moieties is given in Fig. VI.3 and some representative literature values for the frequencies in germanium pseudohalides are collected in Table VI.6. The fundamental frequencies seem particularly sensitive to phase changes. The stretching frequencies have been

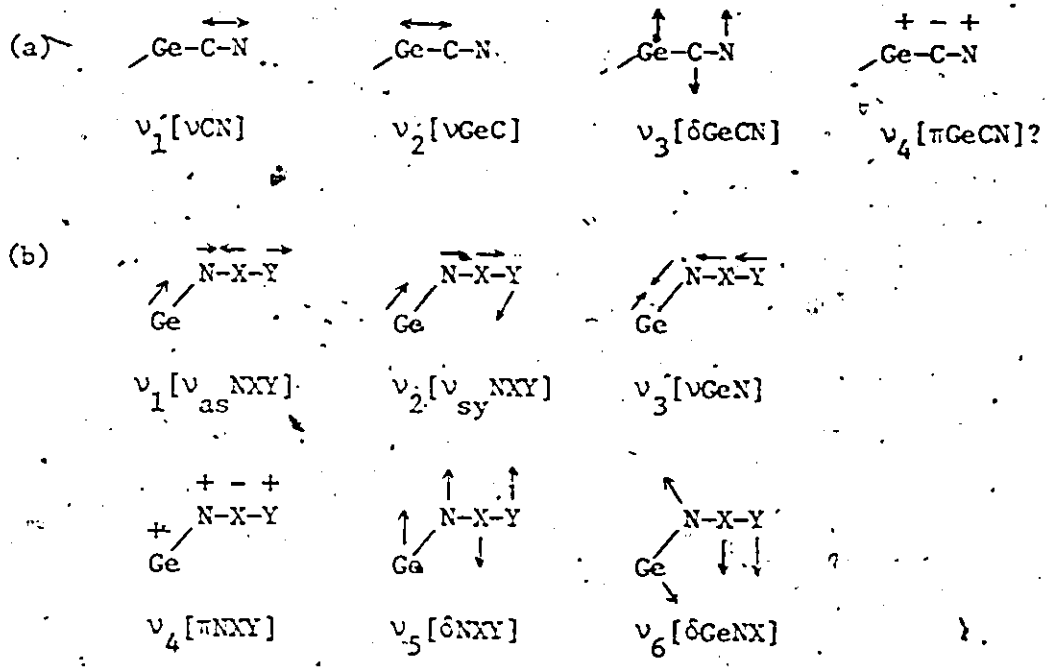


Fig.VI.3 Fundamental vibrations for (a) diatomic and (b) triatomic pseudohalides.[63]

the most studied and are therefore the best characterised. The pseudo-symmetric stretch, ν_2, in organic isocyanates and isothiocyanates occurs at

(Table VI.6) Germanium-pseudohalide fundamental frequencies (cm^{-1})

	cyanide[a]	azide[c]	isocyanate[e]	isothiocyanate[g]
ν_1	2205	2102	2265	2052
ν_2	512	1290	1419	962
ν_3	262[b]	456	493	358
ν_4	?	675	<u>ca</u>.650?	460?
ν_5	–	<u>ca</u>.580?[d]	<u>ca</u>.650?	–
ν_6	–	167[d]	115?[f]	174(147)

a. ref.248(i.r.,gas); b. this work (R,liq); c. ref 250 (i.r.,liq); d. ref.232 (R,liq); e. ref.227(i.r.-gas); f. ref.233 (i.r.,liq); g. ref.234(R.liq).

ca.1400 cm^{-1} and ca.1000 cm^{-1} respectively, at considerably higher frequency than in the normal-bonded species and this provides good evidence for the iso- structure in the germanium and silicon compounds. The cyanide deformations, ν_3 and ν_4, are degenerate in C_{3v} symmetry but may be split into in-plane and out-of-plane components in lower symmetries although this has not been reported. Similarly the triatomic deformations, ν_4 and ν_5, are degenerate if the M-N-X-Y skeleton is linear but again are expected to give rise to in-plane and out-of-plane components if the skeleton is bent. The group frequencies for these modes are ill-defined although they appear to occur in the 450-675 cm^{-1} region (Table VI.6). The low frequency bend, ν_6, is even less certain; it is conceivable that in low symmetries it too would be split and two bands were assigned as such in GeH_3NCS at 147 and 174 cm^{-1} although only one NCS deformation was recognised.[234] It has been attributed to single bands at 248 cm^{-1} in CH_3N_3[260] and 280 cm^{-1} in Me_3SiN_3[250] and rather arbitrarily to bands at 167 cm^{-1} (GeH_3N_3),[232] and 115 cm^{-1} (GeH_3NCO),[233] but these seem low in view of the observation of the lowest fundamental in $Ge(NCO)_4$ at 214 cm^{-1}.[246] the nonlinearity of the triatomic pseudohalides may also show up as a splitting in bands such as the skeletal deformation, ie., δ C-Ge-N(XY). With caution it may be possible to make certain structural implications from the observation of splittings or extra bands in the low frequency region; this aspect will be emphasised in the following sections although in view of the unknown geometries the assignments must be regarded as tentative.

The spectra were obtained as described for the halides and in all cases the sample purity was estimated to be >98% from the ^1H n.m.r. spectra recorded before and after the observations. The i.r. spectra of gaseous samples show few band contours so distinction between individual modes in complex envelopes is not possible; these features are discussed in general terms, e.g. CH_3 stretch, CH_3 def, GeH_2 stretch. In the hydrides the problem of the overlap of GeH_2 bending and CH_3 rocking modes is again apparent but by comparison with the halides (chapter IV.3) an unambiguous assignment is possible.

VI.6.1 <u>The Raman spectrum of cyanogermane</u>: Gaseous samples of GeH_3CN gave i.r. spectra in good agreement with those previously reported;[248] traces of HCN apparent in some spectra (bands at 700 and 3500 cm^{-1}) were removed by distillation through a trap at -45° which retained the GeH_3CN. The ^1H n.m.r. spectrum showed a single sharp resonance at 4.33δ (section VI.5), while the melting point (45-46°)[261] and the vapour pressures (6mm Hg at 0°; <u>ca</u>.20 mm Hg at 20°)[261] indicated a high sample purity. Attempts to obtain the Raman spectrum of pure liquid GeH_3CN were unsuccessful as extensive decomposition occurs at the melting temperature; the same occurred when solid samples were used at room temperature. The spectrum was finally obtained (Fig.VI.4) with GeH_3CN dissolved in carbon disulphide (<u>ca</u>.20-50%) which has a comparatively 'clean' Raman spectrum; the observed frequencies are given in Table VI.7 with the data reported by Goldfarb for comparison. The Raman polarisation data clearly support the assignment of the GeH_3 modes in the i.r. spectra. The GeH_3 a_1-stretching, ν_1, appears as a strong polarised Raman band at 2134 cm^{-1} whilst the e-component, ν_5, is assigned to the shoulder at high frequency (<u>ca</u>.2145 cm^{-1}). The e-type GeH_3 deformation, ν_6, gives rise to [illegible] depolarised band at 868 cm^{-1} which is significantly lower than the 894 cm^{-1} reported for the same band in gaseous GeH_3CN; the a_1 deformation, ν_3, is overlapped by a CS_2 mode but in the polarisation spectrum

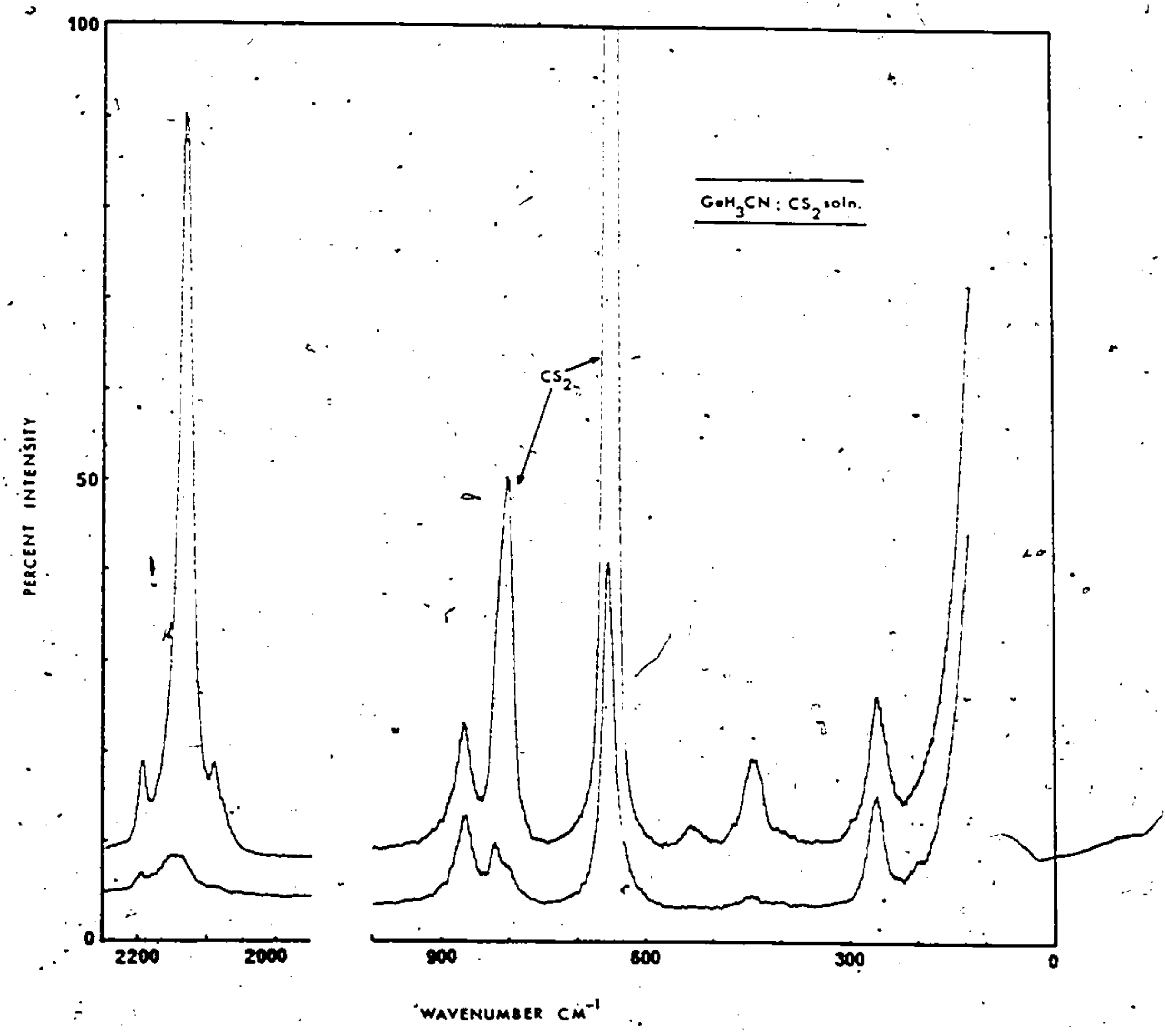


Fig.VI.4 The Raman spectrum of cyanogermane, ca. 50% solution in CS_2

(Fig.VI.4) it is unambiguously assigned to a band at 824 cm^{-1}. The e-type GeH$_3$ rock ν_7, is expected to be weak in the Raman effect[57] and undoubtedly lies under the strong CS$_2$ mode at *ca.*630 cm^{-1}.

(Table VI.7) The vibrational spectra (cm^{-1}) of GeH$_3$CN

Infrared[a] (gas)	Raman(soln)	Assignment[b]
2205	2198 wm,p	ν_2, CN stretch (a_1)
2147.7	*ca.*2145 sh,dp	ν_5, GeH$_3$ stretch (e)
2139.	2134 vs,p	ν_1, GeH$_3$ stretch (a_1)
-	2093 w,p	NC stretch ?
893.7	868 m,dp	ν_6, GeH$_3$ def (e)
839.8 832.3 826.3	824 m,p	ν_3, GeH$_3$ def (a_1)
626	n.o.[d]	ν_7, GeH$_3$ rock (e)
512	510 w,p	ν_4, GeC stretch (a_1)
443[c]	418 m,p	ν_4, GeN stretch (a_1)?
n.o.	262 m,dp	ν_8, GeCN def (e)

a. ref.248; b. C_{3v} point group assumed; c. assigned as an overtone, $2\nu_8$, in ref.248, see text; d. CS$_2$ has a strong band at 630 cm^{-1}.

The CN stretch, ν_2, is assigned to a polarised line at 2198 cm^{-1} in good agreement with the gaseous frequency. A comparable feature at 2093 cm^{-1} is not readily assigned to any gaseous fundamental. It could represent a GeH impurity and the starting material GeH$_3$I has a Raman line at 2099 cm^{-1};[57] however, this is rejected since GeH$_3$I has a much stronger line at *ca.*220 cm^{-1} and this is not observed. The 2093 cm^{-1} is therefore tentatively assigned to the NC stretching of the isomeric isocyanide species, GeH$_3$NC. A similar band was not reported[248] for gaseous GeD$_3$CN but this would easily escape detection at the low vapour pressure at which the spectrum was recorded. It is also noted that isomerisation may only be important in the condensed phase so it would be interesting to examine the i.r. spectra of GeH_3CN or GeD_3CN in solution where there should be no intensity problem.

The second piece of conflicting evidence comes from an examination of the 400-500 cm^{-1} region where the skeletal stretching mode, ν_4, is expected. In gaseous GeH_3CN, ν_4 was assigned to a band at 512 cm^{-1}, whilst an equally prominent absorption at 443 cm^{-1} was assigned to an overtone of the GeCN deformation, ie., $2\nu_8$. Two comparable features are observed in the Raman effect but the assignment of the latter to an overtone is not plausible in view of the observed low frequency spectrum where one depolarised band is observed at 262 cm^{-1} (Fig.VI.4), attributable only to the e-type GeCN deformation, ν_8. The gaseous band at 443 cm^{-1} (418 cm^{-1}, Raman) therefore seems to be a fundamental, and in view of the appearance of a second band in the CN stretching region it could be the isomeric Ge-N(C) stretching mode; this compares with the observed Ge-N stretch in the germanium-nitrogen bonded species, GeH_3N_3 (466 cm^{-1}),[232] GeH_3NCO (459 cm^{-1}),[233] GeH_3NCS (358 cm^{-1}),[234] and $(GeH_3)_3N$ (367 cm^{-1}).[257] This assignment might be questioned in view of the microwave evidence[218] for gaseous GeH_3CN in which no isocyanide transitions were detected. The anomaly may arise from a very high i.r. absorption coefficient for this mode in the isocyanide, present in amounts less than 5% and hence indetectable by the microwave method. The structure of liquid GeH_3CN is not certain and the Raman observations may be consistent with an isomerisation. The apparent low intensity of the 510 cm^{-1} Raman line (Fig.VI.4) may be rationalised by the low polarisability of the Ge-CN linkage in much the same way as Ge-F linkages give very weak Raman lines; the 418 cm^{-1} band may appear of greater intensity than the 510 cm^{-1} band due only to an enhanced polarisability there being no simple relationship between the intensity of Raman bands and the molar concentration. In this respect the ^{1}H n.m.r. evidence (section VI.5) indicates a high (but unknown) percentage of cyanide present in the normal form. The foregoing can only be taken as tentative evidence for the existence of the isomeric forms because a no less reasonable interpretation of these data would be to assign the Ge–C(N) stretching mode, ν_4, to the 443 cm^{-1} band and attribute the 512 cm^{-1} gaseous band (510 cm^{-1}, Raman) to the overtone of the skeletal deformation (2 x 262 = 524 cm^{-1}); indeed the polarised nature of the 418 and 510 cm^{-1} bands fit equally well the a_1–character of ν_4 as well as the A_1+E–character of $2\nu_8$. With this alternative assignment application of the Teller–Redlich isotope rule to the gaseous frequencies[248] for GeH_3CN and GeD_3CN gives the following values:

Parallel Bands: $$\frac{(424)(600)(1536)(2206)}{(443)(832)(2139)(2205)} = 0.496$$

Product rule value. = 0.509

Perpendicular Bands: $$\frac{(249)(491)(627)(1546)}{(256)(626)(894)(2148)} = 0.376$$

Product rule value = 0.368

The agreement between observed and calculated values is more than satisfactory so that such a reassignment cannot be ruled out. It would be of further interest to study the crystal structure of GeH_3CN in the solid phase.

VI.6.2 Cyano(trimethyl)germane: the conventional descriptions of the 26 fundamental vibrations are given in Table VI.8. The experimental i.r. and Raman spectra of Me_3GeCN are displayed (Figs.VI.5a-d) with the observed frequencies and assignment to fundamentals listed in Table VI.9. By comparison with the normal coordinate analysis data reported for

(Table VI.8) Fundamental vibrations of Me_3GeCN

vibration*	Species a_1	 a_2	 e
CH_3 str. (asym)	ν_1	ν_{10}	ν_{14}, ν_{15}
CH_3 str. (sym)	ν_2		ν_{16}
CN stretch	ν_3		
CH_3 def. (asym)	ν_4	ν_{11}	ν_{17}, ν_{18}
CH_3 def. (sym)	ν_5		ν_{19}
CH_3 rock	ν_6	ν_{12}	ν_{20}, ν_{21}
GeC_3 str. (asym)	ν_7		
GeC_3 str. (sym)			ν_{22}
Ge-C(N) stretch	ν_8		
GeCN bend			ν_{23}
GeC_3 def. (asym)			ν_{24}
GeC_3 def. (sym)	ν_9		
GeC_3 rock			ν_{25}
$GeCH_3$ torsion		ν_{13}	ν_{26}
Activity	i.r.,R(p)	inactive	i.r.,R(dp)

* 'asym' and 'sym' refer to the local C_{3v} symmetry of a CH_3 group; the numbering follows that given for Me_3SiCN (ref.220).

Me_3GeCl[82] and Me_3GeI[166] the normal modes associated with the stretching, deforming, and rocking of the methyl groups are assigned to the expected regions, ie., ca.3000,2930 cm^{-1}; ca.1420,1260 cm^{-1}; and ca. 844,780 cm^{-1}, respectively. The symmetric and asymmetric modes are identified clearly by the Raman polarisation data although it is not possible to distinguish between the component a_1 and e modes which give

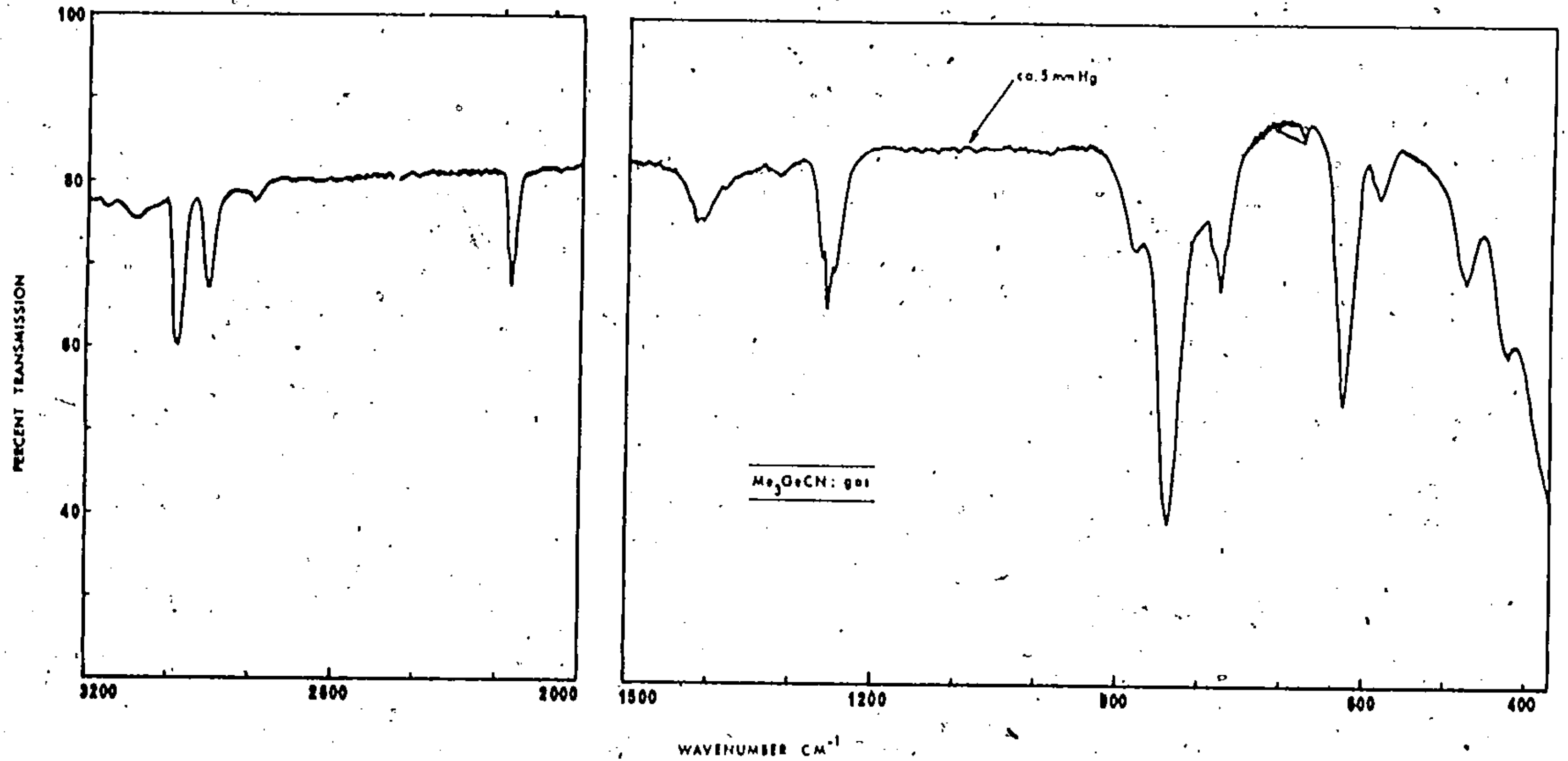


Fig.VI.5a The gas phase infrared spectrum of Me_3GeCN

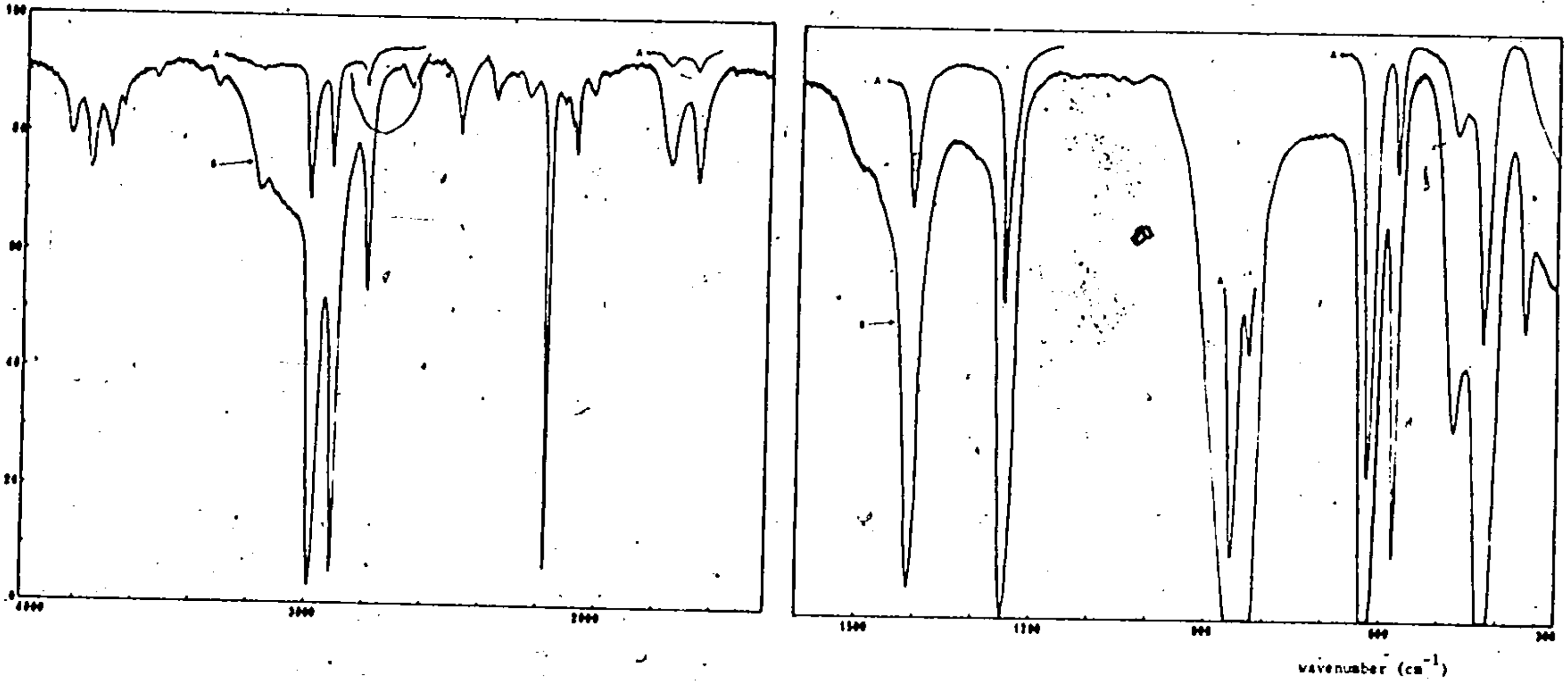


Fig.VI.5b The solution phase infrared spectrum of Me_3GeCN: trace A, 1% in CCl_4; trace B, 15% in CCl_4

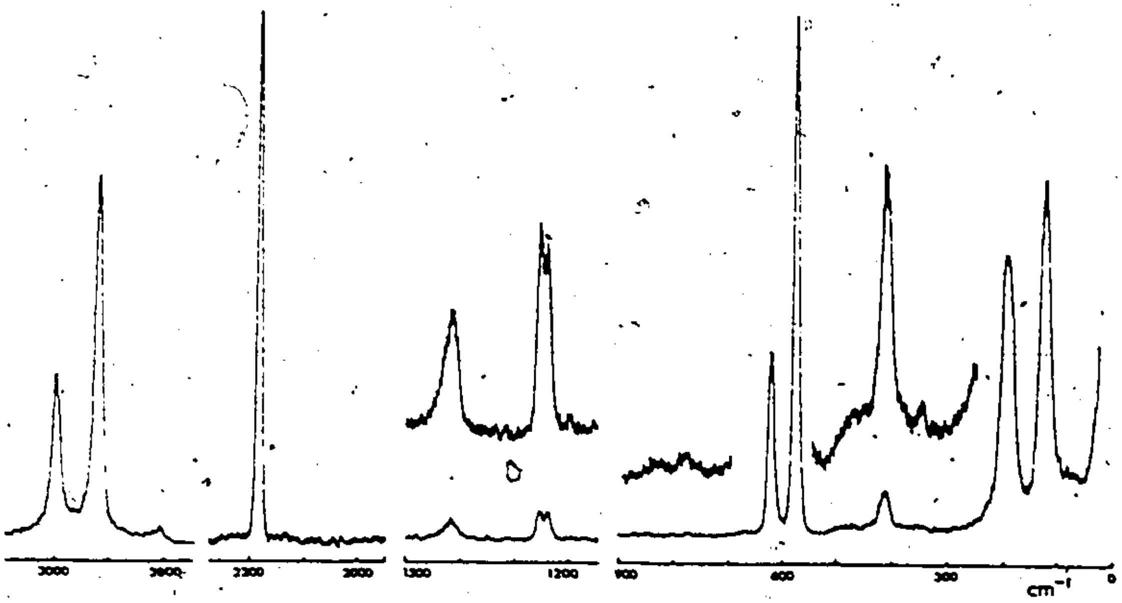


Fig.VI.5c The solid phase Raman spectrum of Me_3GeCN

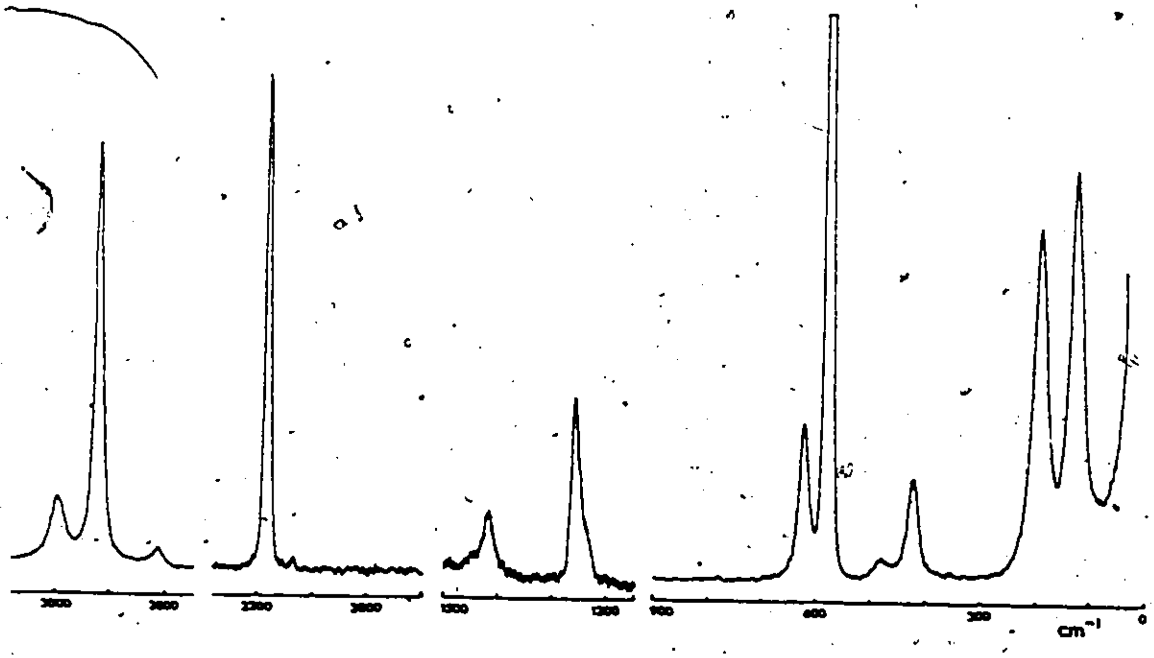


Fig.VI.5d The liquid phase Raman spectrum of Me_3GeCN, recorded at <u>ca</u>.50°

(Table VI.9) The vibrational spectra (cm^{-1}) of cyano(trimethyl)germane

Infrared		Raman		Assignment
(gas)	(CCl$_4$ soln.)	(liquid)*	(solid)	
	3839 vvw			2996 + 844 = 3840
	3768 vw			2925 + 844 = 3769
	3694 vvw			2925 + 780 = 3705
	3654 vvw			2996 + 625 = 3621
	3544 vvw			2925 + 625 = 3550
	3339 vvw			2996 + 355 = 3351
	3178 sh			2996 + 193 = 3189
3002 m				
2997 m	} 2996 ms	3000 m,dp	3001 ms	ν_1, ν_{10}, ν_{14}, ν_{15}
2934 m				
2927 m	} 2925 ms	2922 vs,p	2923 s	ν_2, ν_{16}
2824 vw	2811 w	2925 w,p	2809 w	2187 + 625 = 2812
	2663 vvw			1419 + 1255 = 2674
	2488 vw			2 x 1243 = 2486
	2369 vvw			2996 − 625 = 2371
2196 m	2187 ms	2185 ms,p	2182 m	ν_3
	2138 vvw			2925 − 780 = 2145
	2098 sh			844 + 1255 = 2099
	2086 vw			2925 − 844 = 2081
	2031 vvw			1255 + 780 = 2035
	1880 vw			1255 + 625 = 1880
	1832 vw			1255 + 581 = 1836
1425 wm				
1415 wm	} 1419 ms	1421 w,dp	1418 wm	ν_4, ν_{11}, ν_{17}, ν_{18}
1267 sh		1262 wm,p	1253 wm	
1260 m	} 1255 s	}	}	ν_5, ν_{19}
1252 sh		1254 sh,p	1243 wm	
844 s	844 vvs	839 vvw	835 vvw	ν_6, ν_{20}
–	816 s	–	–	
780 m	n.o.†	785 vvw	784 vvw	ν_{12}, ν_{21}
674 w				479 + 193 = 672
625 s	625 vs	625 m,dp	626 ms	ν_7
582 wm	581 m	582 vs,p	580 vs	ν_{22}
479 m	482 m	476 w,p	ca.480 sh	ν_8 (Ge–CN)**
421 sh	429 s	424 m,p	416 wm	ν_8 (Ge–NC)**
	355 w	349 vw,p	351 vw	ν_{25} + ν_{23}?
		193 s,dp	195 s	ν_9, ν_{24}
		129 s,dp	127 s	ν_{25}

† CCl$_4$ region; * recorded at ca.50°; ** see text.

rise to the band envelopes. The asymmetric GeC_3 stretching mode, ν_7, is assigned to the i.r. band at 625 cm^{-1} having a depolarised Raman counterpart at 625 cm^{-1}. Similarly the symmetric GeC_3 stretch, ν_{22}, gives rise to a strongly polarised line at 582 cm^{-1}. No features assignable to the $GeCH_3$ torsions ν_{13} and ν_{26} were apparent in the spectra.

In the i.r. spectrum of gaseous Me_3GeCN (Fig.VI.5a) only one line is observed in the CN stretching region at 2196 cm^{-1} and this is assigned to ν_3. The low vapour pressure precluded high pressure observations but these should be possible with a heated cell. Similarly in both the solid and liquid phase Raman spectra only one line is observed at 2182 and 2185 cm^{-1}, respectively; in the latter the line is strongly polarised confirming its designation as an a_1 species. However, in the i.r. solution phase (CCl_4) spectrum many absorptions are observed in this region (Fig.VI.5b). The presence of a second line at <u>ca</u>.2100 cm^{-1} has been taken as evidence for the presence of the isocyanide, Me_3GeNC,[214] which was largely based on known absorption frequencies of organic isocyanides. A similar weak band is observed in this study at 2098 cm^{-1}. A variable temperature i.r. cell was not available to examine the temperature dependence of this band but it should be noted that it and many of the other bands observed in the 2100 cm^{-1} region are readily assignable to combination bands (Table VI.9).

The 400-500 cm^{-1} region shows similar features to germyl cyanide and again it seems likely that the skeletal stretching mode, ν_8 , is assignable to two features. A medium band at 479 cm^{-1} in the i.r. with a weak but polarised counterpart at 476 cm^{-1} in the Raman is tentatively assigned to the Ge-C(N) stretch, ν_8. In the gas phase the band at <u>ca.</u> 421 cm^{-1} is in the KBr cut-off region but appears much stronger at

429 cm^{-1} in solution; the corresponding liquid Raman band at 424 cm^{-1} is polarised. In view of the observed low frequency Raman spectrum this band does not appear to be a combination or overtone and is therefore assigned to the isomeric Ge-N(C) stretch, ν_8, by analogy with GeH_3CN.

The GeC_3 deformations, ν_9 and ν_{24}, were not resolved in any spectra and are tentatively assigned to an asymmetric envelope at ca.193 cm^{-1} in the Raman effect, the polarisation data giving no indication of the a_1- and e-components. The GeC_3 rock, ν_{25}, is assigned to the remaining Raman band at 129 cm^{-1} which is depolarised; the principle motion involved in this mode is the deformation of the C-Ge-C(N) angle and it is noted that the frequency is much lower than the corresponding mode in Me_3GeCl (166 cm^{-1}),[82] but comparable to that in Me_3SiCN (138 cm^{-1}).[220] No feature assignable to the GeCN bend, ν_{23}, is observed in any spectra; the corresponding mode in the analogous Me_3SiCN[220] was attributed to a weak feature at 374 cm^{-1}, this suggesting that some reassessment of the band at 469 cm^{-1} in SiH_3CN[262] (assigned as 2.δSiCN) may be necessary. The observation of δGeCN at 262 cm^{-1} in GeH_3CN implies that ν_{23} is unlikely to be contained in the 190 cm^{-1} envelope but such a lowering of frequency is not uncommon in mixed modes.

VI.6.3 Cyano(methyl)-, cyano(dimethyl)-, and tricyano(methyl)- germane: The observed frequencies for $MeGeH_2CN$, Me_2GeHCN, and $MeGe(CN)_3$ are given in Table VI.10, with the proposed assignment of fundamentals. The spectra of the hydrides closely resemble those of the analogous halides so little comment seems necessary. The CN stretching mode is readily assignable to a band in the 2200 cm^{-1} region but without deuteriation it is not possible to establish the presence of a second band which would be overlapped by the GeH stretches. Again the 400-500 cm^{-1} regions

(Table VI.10) The vibrational spectra (cm^{-1}) of the cyanides

$MeGeH_2CN$		Me_2GeHCN		$MeGe(CN)_3$	
i.r.(gas)	Raman(liq)	i.r.(gas)	Raman(liq)	i.r.(CCl_4)	Assignment
3018 m	3008 w,dp	3006 2999 } m	3002 m,dp	3028 m	CH_3 stretch (asym)
2938 m	2930 m,p	2931 m	2928 vs,p	2862 m	CH_3 stretch (sym)
2860 w	–	–	2818 w,p		2 x 1430 = 2860
2202 m	2190 m,p	2203 2197 } m 2290	2189 s,p	2060 m,br*	CN stretch (a')
2122 2118 } vs	2120 s,p	2102 2092 } s 2085	2108 s,p		GeH_2,GeH stretch
1430 m	1429 w	1427 m	1422 w,dp	1409 m	CH_3 def (asym)
1260 m	1255 m,p	1263 1255 } m	1256 m,p	1264 ms	CH_3 def (sym)
888 879 } m	878 s,p				GeH_2 bend (sc)
870 s		ca.865 sh	864 w,dp		CH_3 rock (a")
857 849 } vs 840	830 sh	856 849 } s 843		863 m* 815 m*	CH_3 rock (a')
		785 776 } m	780 vw,dp		CH_3 rock (a'+a")
740 ms 730 ms } 726 sh	735 ms,p				GeH_2 def(twist,wag)
		713 708 } s 703	716 m,dp		GeH def (bend)
		ca.670 w	646 m,dp		GeH def (twist)
		624 s	622 m,dp		GeC stretch (a")
620 ms	618 vs,p	ca.599 sh	599 vs,p	625 m	GeC stretch (a')
500 m	495 sh,p	482 m	479 w,p	510 m	GeC(N) stretch
470 m	475 m,dp				GeH_2 rock (a")
430 m	428 s,p	ca.425 sh	427 m,p	400 m,br	GeH(C) stretch?
	330 w,dp		318 m,dp		overtone?
	257 m,dp		250 vw		GeCN def*
			192 m,dp		GeC_2 def
			151 sh		CGeC(N) def (a")
	135 s,dp		133 s,dp		CGeC(N) def (a')

* see text

for $MeGeH_2CN$ and Me_2GeHCN closely resembles those in GeH_3CN and Me_3GeCN so the same comments are applicable. A strong depolarised band at 135 cm^{-1} in the Raman spectrum of $MeGeH_2CN$ is confidently assigned to the CGeC(N) deformation by comparison with Me_3GeCN; the analogous bands in Me_2GeHCN appear at 151 and 133 cm^{-1} which again is much lower than the halide series. By comparison with the Me_2GeHX series the GeC_2 deformation is assigned to a band at 192 cm^{-1}. In the hydrides Raman lines at 257 cm^{-1} ($MeGeH_2CN$) and 250 cm^{-1} (Me_2GeHCN) may be assigned to the GeCN deformation by comparison with GeH_3CN; it is notable that in Me_2GeHCN this band is very weak which at least indicates some trend in the series $GeH_3CN \rightarrow MeGeH_2CN \rightarrow Me_2GeHCN \rightarrow Me_3GeCN$ which may arise from mixing.

The i.r. spectrum of $MeGe(CN)_3$ is not compatible with the expected C_{3v} symmetry. No sharp line is observed at ca.2200 cm^{-1} although a broad feature at 2060 cm^{-1} may arise from cyanide stretching; this suggests involvement of the Ge-CN moiety in some form of association despite the molecular weight evidence in benzene. Two sharp bands are observed in the CH_3 rocking region at 815 and 863 cm^{-1} whereas the analogous halides exhibit only one such mode; this at least indicates a lowering of symmetry as might arise in associated species. Once again a medium band at 510 cm^{-1} may arise from Ge-C(N) stretching and a broad band at ca.400 cm^{-1} from the isomeric Ge-N(C) stretching by comparison with the other cyanides.

VI.6.4 Azido(methyl)-, azido(dimethyl)-, triazido(methyl)- and tetraazido-germane: The observed frequencies for $MeGeH_2N_3$, Me_2GeHN_3, and $MeGe(N_3)_3$ are given in Table VI.11, with the proposed assignments. As for the cyanides the modes arising from the $MeGeH_2$-,

Me_2GeH-, and $MeGe\lessgtr$ moieties may be recognised by comparison with the analogous halides.

The azide stretching modes for the hydrides are readily assignable to intense i.r. absorptions in the 2130 and 1285 cm^{-1} regions; in the i.r. the former overlaps considerably the GeH_2 stretches in $MeGeH_2N_3$ but appears as a shoulder to high frequency in the Raman effect. It is noticeable that both pseudo-asymmetric and pseudo-symmetric modes are significantly polarised. In the i.r. spectrum of $MeGe(N_3)_3$ the pseudo-asymmetric mode is apparently split into two components at 2146 and 2121 cm^{-1} which suggests some asymmetry in the three azide groups.

Two azide deformations are expected (Fig.VI.3); and i.r. band at 670 cm^{-1} in $MeGeH_2N_3$ having a weak but polarised counterpart at 665 cm^{-1} is tentatively assigned to the N_3 in-plane deformation (ν_4) by comparison with CH_3N_3 (660 cm^{-1})[260] and Me_3GeN_3 (675 cm^{-1}).[250] No distinct features assignable to the N_3 out-of-plane deformation (ν_5) are observed in the hydrides but in $MeGe(N_3)_3$ a depolarised Raman band at 580 cm^{-1} may be assigned as such (CH_3N_3, 560 cm^{-1}).[260] In the hydrides the GeN stretching mode (ν_3) gives rise to a strong i.r. absorption at ca.480 cm^{-1} whilst the corresponding polarised Raman band appears much lower at ca.460 cm^{-1}, this being in good agreement with the observations in GeH_3N_3 [232] and Me_3GeN_3.[250] In $MeGe(N_3)_3$ two GeN stretches are expected but only one i.r. band at 494 cm^{-1} is observed so that both modes are assigned to this feature (a similar near-degeneracy of the GeF stretches in $MeGeF_3$ is observed, chapter III); in the raman spectrum (CCl_4 solution) again only one polarised line at 482 cm^{-1} confirms the i.r. assignment but in solid $MeGe(N_3)_3$ two Raman lines at 485 and 472 cm^{-1} are resolved which may represent the asymmetric and symmetric GeN stretches.

(Table VI.11) The vibrational spectra (cm^{-1}) of the azides

$MeGeH_2N_3$		Me_2GeHN_3		$MeGe(N_3)_3$		
i.r.(gas)	Raman(liq)	i.r.(gas)	Raman(liq)	i.r.(CCl_4)	Raman(CCl_4)	Assignment
3380 m	–	3381 m	–	3368 m	–	2119 + 1283 = 3402
3008 m	3004 w,dp	2997 m	2996 m,dp	2965 m	2960 w,dp	CH_3 stretch (asym)
2932 m	2929 m,p	2929 m	2923 vs,p	2930 sh	2936 w,p	CH_3 stretch (sym)
–	2813 w,p	2805 w	2803 w,p	2820 w	–	2 x 1405 = 2810
–		2552 m	–	2526 m	–	2 x 1283 = 2566
		2201 vw	2190 sh,p			1419 + 766 = 2185
2135 vs[b]	2115 sh,p	2119 vs	2106 s,p	2146 vvs[g] 2121 vvs[g]	2120 vp	NNN stretch (asym)[a]
2080 sh	2094 vs,p	2071 s	2073 s,p			GeH_2,GeH stretch
1405 m	1409 w	1419 wm	1416 w,dp	1405 sh	1420 sh,dp	CH_3 def (asym)
1385 m	–	1385 wm	1360 wbr	1370 ms	–	2 x 688 = 1376
1286 s	1295 m,p	1283 s	1291 s,p	1275 vvs	1285 w,p	NNN stretch (sym)[a]
1255 sh	1255 m,p	1260 1254 } m	1252 s,p		1250 w[d]	CH_3 def (sym)
		1162 vw	1165 vw,p			668 + 482 = 1150
		1071 vw	1075 vw,p			1257 − 191 = 1066
		1004 vw	–		945 w	766 + 227 = 993
881 870 } m	876 m,p					GeH_2 bend (sc)
867 sh	–	860 sh	–			CH_3 rock (a")
846 838 } s 830	841 sh,dp	842 837 } s	850 wm,dp	865 s[g] 830 s[g]	836 m[d] 810 w[d]	CH_3 rock (a')
		766 m	750 vw			CH_3 rock (a',a")
733 ms	737 m,p					GeH_2 def(twist,wag)
–		713 704 } m	709 m,dp			GeH def (bend)
		–	640 m,p			GeH def (twist)
670 m	665 w,p	674 668 } m 663	674 m,p	688 vs	690 w,p	NNN def (a')
		622 vs	618 sh			GeC stretch (a")
621 ms	617 vs,p	596 sh	596 vs,p	640 m	635 m,p	GeC stretch (a')
				578 m	580 w,dp	NNN def (a")
484 s[c]	460 sp[c]	482 s	457 s,p	494 vs	482 s,p[f,g]	GeN stretch
	298 w			328 m[e]	320 w[d]	185 + 110 = 295
					260 m[d]	GeN_3 def
	215 m,p		227 s,p			CGeN def (a')
	185 sh[g]					GeNN def?
			191 s,dp			GeC_2 def
					190 s[d]	GeN_3 def
	110 sh				[130]	torsion?

---

a. strictly pseudo-symmetric, and -antisymmetric; b. νGeH_2 asym. occurs in this region c. ρGeH_2 is expected in this region; d. solid; e. mull; f. 2 bands at ca. 485, 472 cm^{-1} are observed in the solid; g. see text.

The skeletal deformation region of $MeGeH_2N_3$ is expected to contain the CGeN deformation (a'), the GeNN deformation and the CH_3 torsion. A polarised line at 215 cm^{-1} is an obvious choice for the CGeN bend whilst a shoulder at ca.185 cm^{-1} may arise from a non degeneracy introduced by the asymmetry of the azide group as suggested earlier. Alternatively it could be attributed to the GeNN deformation (ν_6) which compares with the assignment at 167 cm^{-1} in GeH_3N_3.[232] A weak feature at 110 cm^{-1} may arise from the CH_3 torsion although this mode is not observed in the halides. In Me_2GeHN_3 the CGeN deformation is split into a' and a" components and a GeC_2 deformation is also expected. The latter mode appears consistently at ca.190 cm^{-1} in the Me_2GeHX series (chapter IV) and is therefore assigned confidently to a depolarised Raman line at 191 cm^{-1}. The a' C_2GeN deformation is assigned to a strong polarised line at 227 cm^{-1}; the corresponding a" C_2GeN deformation is not resolved and by analogy with Me_2GeHF and Me_2GeHCl it may be contained in the 227 cm^{-1} band envelope. At least three low frequency deformations are expected for $MeGe(N_3)_3$ by analogy with the trihalides. In $MeGeCl_3$[145] only two features were observed in the low frequency region due to the accidental degeneracy of fundamentals (see chapter III); a similar situation is apparent in the triazide with only two lines being observed in the Raman spectrum of the solid at 190 and 260 cm^{-1} but without polarisation data it is not possible to attempt an individual assignment.

The spectra of $Ge(N_3)_4$ are not easily assigned on a comparative basis and from the number of observed lines (Table VI.12) a considerable deviation from the possible tetrahedral arrangement of azide groups about germanium is indicated. The lack of solubility of the tetraazide in all but very polar solvents and the high melting point (>100°) are more consistent with a polymeric material although a cryoscopic molecular weight determination suggests monomeric species.

(Table VI.12) Observed frequencies (cm^{-1}) for tetraazidogermane*

Infrared (soln)	Raman (solid)	Tentative Assignment
2130 vs	2160 w	N_3 stretch (asym), in phase
2097 m	2103 w	N_3 stretch (asym), out of phase
1298 m,sh		N_3 stretch (sym), in phase
1268 s	1259 m	N_3 stretch (sym), out of phase
695 m	700 m	N_3 def
598 w	592 w	N_3 def
400 s,br	445 vs	GeN_4 stretch
	417 vs	GeN_4 stretch
	300 w	GeNN def
	269 w	GeN_4 def
	212 w	GeN_4 def

* Bands assignable to fundamentals are listed. The i.r. spectra contain many bands in the 2300-3300 cm^{-1} region which may arise from combinations involving the 2130 cm^{-1} fundamental.

VI.6.5 Isocyanato(methyl)-, isocyanato(dimethyl)-, and triisocyanato(methyl)-germane.

The observed frequencies and assignments for $MeGeH_2NCO$, $Me_2GeHNCO$ and $MeGe(NCO)_3$ are given in Table VI.13. The characteristic NCO pseudo-asymmetric, and -symmetric stretching modes (ν_1 and ν_2) are assigned to intense bands in the i.r. spectra at ca.2270 and 1410 cm^{-1}, the latter providing strong evidence for the iso-structure by comparison with CH_3NCO,[263] SiH_3NCO,[264] and GeH_3NCO[233] (ν_{sy}NCO = 1412, 1450, and 1420 cm^{-1} respectively). Weak bands in the 2370 cm^{-1} region in GeH_3NCO have been attributed to small amounts of GeH_3OCN[233] and similar

(Table VI.13) The vibrational spectra (cm^{-1}) of the isocyanates

$MeGeH_2NCO$		$Me_2GeHNCO$		$MeGe(NCO)_3$	
i.r.(gas)	Raman(liq)	i.r.(gas)	Raman(liq)	i.r.(CCl_4)	Assignment
3660 w,br	–	3640 w	–	3390,3625 w	2268 + 1410 = 3678
		3520 vw	–		2276 + 1259 = 3535
3007 m	3004 w,dp	3000 m	2997 m,dp	3024 s	CH_3 stretch (asym)
2934 m	2932 m,p	2930 w	2925 vs,p	2970 m	CH_3 stretch (sym)
		2800 vw	2802 w,p		2997 – 192 = 2805
2740 w	–	2698 w	2700 vw		2085 + 687 = 2712
2420 vw	–			2440 w	2268 + torsion?
2358 m	2350 w,sh	2342 ms[e]	–	2400 m	3000 – 670 = 2330[d]
2268 vvs	n.o.	2276 vvs	n.o.	2240 vs	NCO stretch (asym)
		2196 sh			1414 + 770 = 2184
2098 s	2109 s,p	2085 s	2090 s,p		GeH_2,GeH stretch
1748 w,br	–	1650 w,br	–	1525,1478 w	combinations
1410 m[b]	1409 s,p[b]	1414 w	1404 vs,p[b]	1412 s[b]	NCO stretch (sym)
		1398 w[a]			CH_3 def (asym)
1265 m	1260 m,p	1263 1255} m	1253 m,p	1265 s	CH_3 def (sym)
				1229,1212	combinations?
888 874} m	879 m,dp				GeH_2 bend (sc)
ca.872 sh		860 sh[a]	864 w,dp		CH_3 rock (a")
854 845} s 840	832 w,p	847 s,br	840 w,br	895 m,br[d] 809 s[d]	CH_3 rock (a')
		770 m			CH_3 rock (a',a")
745 ms	746 m,dp				GeH_2def(twist,wag)
		710 ms	716 m,dp		GeH def (bend)
		–	642 m,dp		GeH def (twist)
680 m,br	682 m,dp	670 m[a]		678 s	NCO def (a")
		627 ms	624 sh,dp		GeC stretch (a")
626 s	625 vs,p	602 s	599 vs,p	634 m	GeC stretch (a')
481 s[c]	460 ms,p	477 s[f]	445 m,p	496 ms,br	GeN stretch
420 sh	420 sh,dp				218 + 184 = 402
	286 w,p	280 w[a]	284 w,p		2 x torsion?
	218 m,dp	218 sh[a]	217 m,dp		CGeN def
			192 m,dp		GeC_2 def
	184 m,p[d]				GeNC def?

a. liquid film; b. masking CH_3 def (asym); c. ρGeH_2 is expected in this region; d. see text e. two bands are observed in the liq. at ca.2370,2340 cm^{-1}; f. appears at 448 cm^{-1} in liquid.

features* are observed in the i.r. spectra of all three derivatives; these are not readily assignable to fundamental or combination bands unless a large anharmonicity is allowed (Table VI.13). Independent n.m.r. evidence for GeH_3NCO[227] was interpreted in favour of the iso-species, there being a single ^{14}N resonance with a similar chemical shift to the alkyl-isocyanates (R-OCN 100 p.p.m. to low field of R-NCO); it is questionable, however, whether this excludes the existence of the labile equilibrium, $GeH_3OCN \rightleftharpoons GeH_3NCO$ lying far to the right. In this respect more conclusive evidence may be obtained from a low temperature study.

A depolarised band in the 680 cm^{-1} region is tentatively assigned to the out-of-plane NCO deformation (ν_4). The corresponding in-plane mode (ν_5) is either inactive or overlapped by other fundamentals; a band at 606 cm^{-1} in Me_3GeNCO[250] assigned to 'δNCO' may represent this mode. In the hydrides the GeN stretch (ν_3) appears as expected at ca.480 cm^{-1} in the i.r.; the corresponding Raman line at ca.460 cm^{-1} is polarised, consistent with the observations in Me_3GeNCO (454 cm^{-1}) and GeH_3NCO (493 cm^{-1}). A depolarised line at 218 cm^{-1} in $MeGeH_2NCO$ is a firm choice for the CGeN deformation by analogy with the azides; the corresponding a' and a"- C_2GeN deformations in $Me_2GeHNCO$ are not resolved and by comparison with Me_2GeHF and Me_2GeHCl (chapter IV) are assigned to a depolarised envelope at 217 cm^{-1}. Griffiths[233] assigned a band at 115 cm^{-1} to a GeH_3NCO skeletal fundamental although other workers[227] found no evidence for this mode; no bands are observed in the 110-120 cm^{-1} region in this study** but a polarised line at 184 cm^{-1} in $MeGeH_2$-NCO may arise from GeNC bending (ν_6) by comparison with the assignment of δGeNN at 167 cm^{-1} in GeH_3N_3.[232] The corresponding mode in $Me_2GeHNCO$

* These are also apparent in the gas phase i.r. spectrum of Me_3GeNCO.[267]

** No Raman lines are observed in this region for Me_3GeNCO[267]

may then be contained in the strong envelope at 192 cm^{-1} assigned to the GeC_2 deformation, although the evidence is inconclusive.

The i.r. spectrum of $MeGe(NCO)_3$ is readily assigned except for the presence of two bands in the methyl rocking region at 809 and 895 cm^{-1} (Table VI.13); a departure from the possible C_{3v} symmetry would be consistent with this observation as suggested for the isoel[illegible] $MeGe(N_3)_3$. The similarity extends to the near degeneracy [illegible] GeN stretching modes assignable to a broad asymmetric envelope at 496 cm^{-1}.

VI.6.6 Isothiocyanato(methyl)-, isothiocyanato(dimethyl)-, and triisothiocyanato(methyl)-germane.

The observed frequencies for $MeGeH_2NCS$, $Me_2GeHNCS$, and $MeGe(NCS)_3$ are given in Table VI.14. The pseudo-asymmetric NCS stretch (ν_1) has been assigned at 2075 cm^{-1} in Me_3GeNCS[250] and by analogy it would be expected to overlap the GeH stretching region in the hydrides. Two bands at 2090 and 2071 cm^{-1} are resolved in the i.r. of $MeGeH_2NCS$ and by comparison with the halides the latter is assigned to the NCS mode; the corresponding Raman bands are at noticeably higher frequency (2120 and 2061 cm^{-1}) which is unusual for a gas to liquid phase change. The variance of this mode is again noted by its appearance at 1980 cm^{-1} in $MeGe(NCS)_3$. The pseudo-symmetric NCS stretch (ν_2) is well established in the 900-1100 cm^{-1} region in organic isothiocyanates[265] and as such is distinguishable from the same mode (ca. 700 cm^{-1}) in the sulphur-bonded species; this provides good evidence for the iso-bonding in the germanium species in which ν_2 is observed at 892 cm^{-1} (Me_3GeNCS),[250] and 962 cm^{-1} (GeH_3NCS).[234] In $MeGeH_2NCS$ and $Me_2GeHNCS$ ν_2 is only assigned with confidence to polarised Raman bands at 968 and 967 cm^{-1}, the corresponding i.r. absorptions being extremely weak; it is also

(Table VI.14) The vibrational spectra (cm^{-1}) of the isothiocyanates

$MeGeH_2NCS$		$Me_2GeHNCS$		$MeGe(NCS)_3$	
i.r.(gas)	Raman(liq)	i.r.(liq)	Raman(liq)	i.r.(CCl)$_4$	Assignment
3002 w	3000 w,dp	2996 m	2995 m,dp	2975 m	CH_3 stretch (asym)
2930 w	2926 m,p	2924 m	2922 vs,p	2940 m	CH_3 stretch (sym)
		2816 w	2818 w,p		2 x 1414 = 2828
		2555 vw	–	2542 w	2074 + 488 = 2562
		2422 m	–	2410 w	2074 + 358 = 2432
		2370 m	–		2996 – 625 = 2371
		2340 w	–		2924 – 600 = 2324
2098 2090} s 2085	2120 s,p	2074 vvs^a	2105 s,p		GeH_2,GeH stretch
2041 s	2061 m,br		2062 s,p	1980 vvs	NCS stretch (asym)^c
1985 sh,br					2 x 968 = 1936
1420 w	1421 w,dp	1415 m	1414 wm,dp	1410 m	CH_3 def (asym)
1380 vw	1375 vw,dp				?
1260 w	1256 m,p	1255 m	1252 m,p	1269 ms	CH_3 def (sym)
		1071 w		1105,1924 w	1255 – 190 = 1065
n.o.	968 m,p	969 vw	967 m,p	993,948 m^b	NCS stretch (sym)^c
	917 w,p^b		910 m,p^b	892 m,br^b	?
882 868} m	866 m,p				
860 m		ca.860 sh	856 sh,dp		GeH_2 bend (sc)
					CH_3 rock (a")
844 838} s 832	832 m,dp	839 s	846 m,p	831 s	CH_3 rock (a')
714 ms	737 m,dp	778 m	ca.780 vw,p		CH_3 rock (a',a")
		706 s	710 m,p		GeH_2 def(twist,wag)
			645 m,p		GeH def (bend)
645 sh	660 w,br	669 w	–		GeH def (twist)
				651 s	472 + 182 = 654
		625 s	626 m,dp		GeC stretch (a")
620 m	618 vs,p	600 s	599 vs,p	625 ms	GeC stretch (a')
		571 w			358 + 210 = 568
		550 m			358 + 190 = 548
–	472 m,dp	488 m	480 w,p		NCS def
458 w	450 w,dp				GeH_2 rock
		419 w	–		2 x 210 = 420
	352 ms,p	358 s	352 ms,p	413 vs,br	GeN stretch
	290 w	283 m	–		2 x torsion?
		260 w			488 – 232 = 256
		251 w			600 – 358 = 242
		ca.232 sh	228 sh,dp		CGeN def (a")
	205 m,p	ca.210 sh	212 s,p		CGeN def(a')
			~190 s,dp		GeC_2 def
	182 s,p^b				GeNC def?

a. envelope contains NCS and GeH stretches; b. see text; c. strictly pseudo-symmetric, -antisymmetric.

noted that equally prominent polarised lines at 917 and 910 cm^{-1} which are not readily assignable to combination or overtones may arise from a splitting of the ν_2 fundamental.* In the i.r. of MeGe(NCS)$_3$ two weak bands at 948 and 993 cm^{-1} assignable to ν_2 provide further evidence for asymmetry whilst the increase in frequency with increasing NCS substitution is similar to the methylsilanes.[266] Only one NCS deformation has been reported for Me_3GeNCS (476 cm^{-1})[250] and GeH_3NCS (467 cm^{-1})[234] although two are expected (Fig.VI.3). In $MeGeH_2NCS$ a Raman line at 472 cm^{-1} is depolarised whilst in $Me_2GeHNCS$ a line at 480 cm^{-1} is polarised so it is impossible to attempt a specific assignment for the in-plane or out-of-plane components, ν_4 and ν_5.

The GeN stretch (ν_3) lies outside the KBr region but in the Raman a polarised line at 352 cm^{-1} in both hydrides is confidently assigned as such by comparison with GeH_3NCS (358 cm^{-1})[234] and Me_3GeNCS (354 cm^{-1}).[267] By analogy with $MeGeH_2N_3$ and $MeGeH_2NCO$ the CGeN deformation is assigned to a polarised band at 205 cm^{-1} in $MeGeH_2NCS$ whilst a second polarised band at 182 cm^{-1} may arise from the GeNC deformation (ν_6); the latter mode may well confirm the 174(147) cm^{-1} lines reported in GeH_3NCS.[234] In $Me_2GeHNCS$ every indication is that the C_2GeN deformations are resolved into in-plane and out-of-plane components, this being consistent with the appearance of polarised and depolarised Raman bands at 212 and 228 cm^{-1}, respectively; this behaviour is similar to Me_2GeHBr and Me_2GeHI where both C_2GeX deformations are resolved (chapter IV). The remaining depolarised line in $Me_2GeHNCS$ at 190 cm^{-1} is a firm choice for the C_2Ge deformation although by analogy with Me_2GeHN_3 and $Me_2GeHNCO$ it may also contain the GeNC deformation.

---

* Polarised lines at 969 and 906 cm^{-1} are observed[267] in the Raman spectrum of liquid Me_3GeNCS.

The i.r. spectrum of $MeGe(NCS)_3$ appears to be more consistent with C_{3v} symmetry than the analogous triazide or triisocyanate; a single band at 831 cm^{-1} assignable to the CH_3 rocking mode suggests that the molecule has an axis of symmetry similar to the trihalides (chapter III). A broad i.r. absorption at 413 cm^{-1} may arise from asymmetric and symmetric GeN stretching by comparison with $MeGe(N_3)_3$ and $MeGe(NCO)_3$.

APPENDIX 1

EXPERIMENTAL TECHNIQUES:

The techniques described in this thesis derive from those developed by Stock and co-workers[268] in their classic work on silicon and boron hydrides. Manipulations of these and the related germanium hydrides require moisture- and oxygen-free conditions and this, combined with the disagreeable nature of the compounds,[269] makes the vacuum method highly desirable. Little is known of the toxicity[270] of the Group IV hydrides, particuarly those of germanium, so it is wise to handle such compounds with all due respect.

Vacuum line techniques have become standardised and are well documented.[268,271-274] The vacuum method has many advantages. Reactions may be carried out inside a 'closed' system with little chance of contamination, thus enabling small-scale quantitative work to be performed as a matter of routine. The volatile nature of the hydrides permits a wide range of rapid and non-destructive characterisation procedures. They are particularly well suited to study by ^{1}H n.m.r., infrared, and Raman spectroscopy, whilst the more recent applications of electron diffraction[225] and photo-electron spectroscopy[228] have led to a better understanding of molecular structure.

A.1.1 The vacuum line

Unless otherwise stated all manipulation of the germanium hydrides were carried out on a conventional but highly adaptable Pyrex-glass vacuum line (Fig.A.1). This featured four manifolds (ca.150 ml) inter-

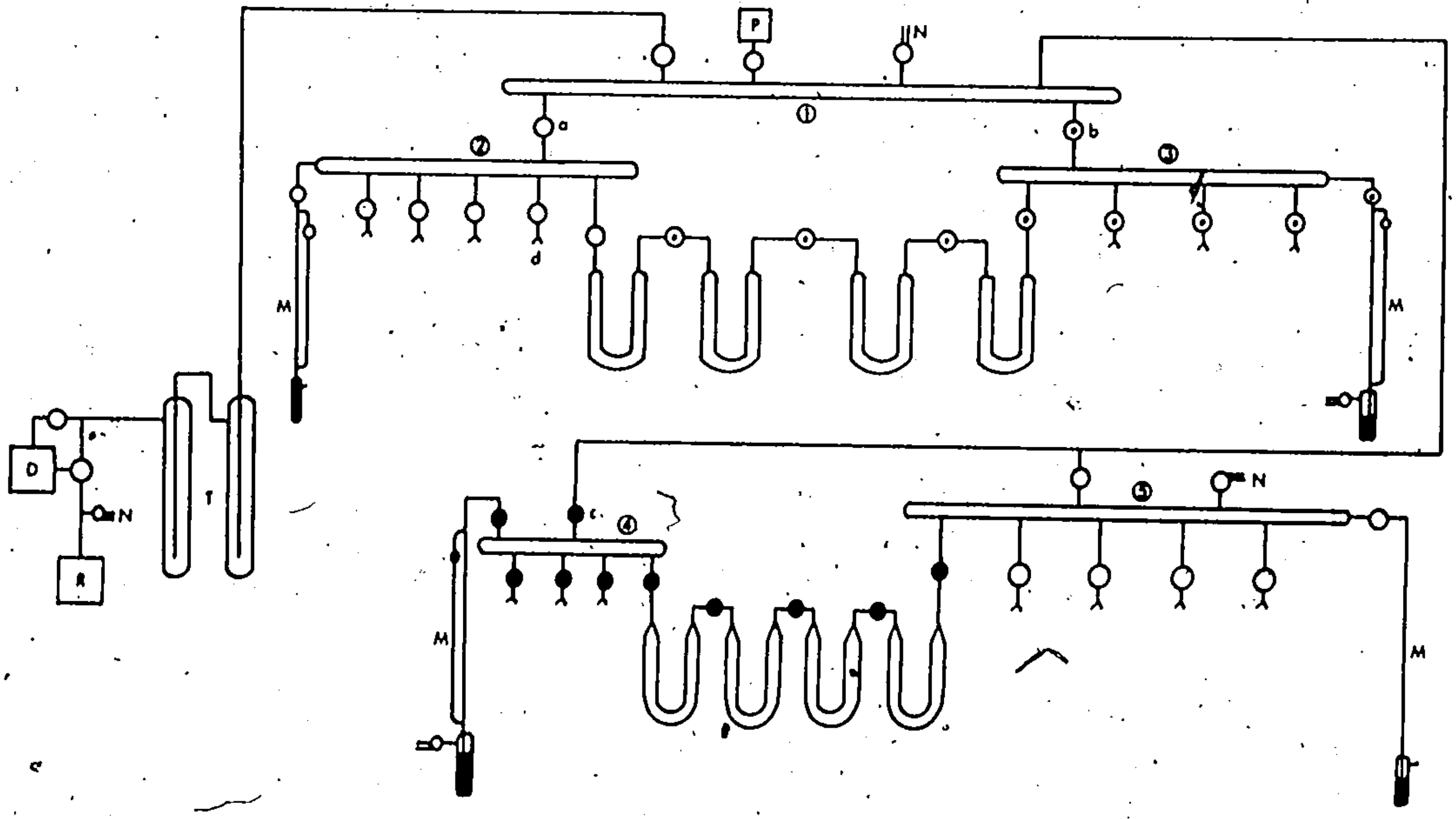


Fig.A.1 The preparative vacuum system:

M	mercury manometer	a	greased 4 mm tap
N	dry nitrogen inlet	b	greaseless diaphragm tap
P	Pirani gauge	c	greaseless teflon/viton tap
R	Rotary vacuum pump	d	FS19 ball joint
T	liquid nitrogen traps		

connected by a central manifold which in turn was connected to the pumping system comprising of rotary pump (R), mercury diffusion pump (D),[273] and two liquid nitrogen 'backing' traps (L). Pressures between 1 Torr and 760 Torr were monitored (±0.5 mm Hg) by mercury manometers (M) whilst a Pirani vacuum gauge (P) recorded pressures below 1 Torr. A pressure of 5×10^{-3} Torr was achieved under most circumstances, this being more than adequate for the compounds under study. Adjacent manifolds were also connected by a series of U-traps fitted with greaseless stopcocks (b or c). Entry points to the manifolds (d) were of the S19 'ball and socket' variety via high-vacuum 4 mm greased (a) or greaseless stopcocks (b, diaphragm; c. teflon/viton O-ring). The greaseless sections (3,4) were generally employed for the synthetic work whilst the greased sections (2,5) were used for more routine procedures (e.g. the transfer of gases from cylinders to glass storage vessels, the large scale preparation of starting materials, or the vacuum drying of heavy-metal salts).

A.1.2 Separation of volatile products

Efficient separation of components in gaseous mixtures was achieved by trap-to-trap distillations provided the boiling points of the species differed by at least 15-20°.[273] Slush baths (Table A.1) were used to control trap temperatures but the efficiency of separation varied considerably with quantity and relative composition of the distillate rate of distillation, condensation surface, and system vacuum. The trap temperatures quoted in the text are therefore only one of the factors determining the course of a particular separation.

A.1.3 Storage and reaction vessels

These were constructed of Pyrex-glass, the design being determined by such factors as the volatility, thermal stability, and quantity of the compounds in question (Fig.A.2). The simple hydrides and those that were stable gases at room temperature (e.g. HCl, HBr, GeH_4, $MeGeH_3$) were stored in vessels 'A'(100-3000 ml capacity) fitted with either greased or greaseless stopcocks (4-6 mm) and an MS19 ball-joint for attachment to the vacuum line. Low volatility compounds which attacked or dissolved in grease (e.g. boron halides, Me_nGeX_{4-n}) or were generally unstable at room temperature (e.g. GeH_3X) were stored in the liquid/solid phase in vessels 'B' (10-100 ml capacity) fitted with greaseless stopcocks (teflon-viton) either at room temperature, -78°, or -196°. Break-seal ampoules were employed for the storage of small quantities of the hydrides, these usually being held at -78°. Dry solvents (e.g. C_6H_6, Et_2O, $n-Bu_2O$) were stored under vacuum[274] in contact with drying agents,e.g. $LiAlH_4$/CaH , in vessels(500 ml, type 'F') with teflon stopcocks.

(Table A.1) Low temperature slush bath data*

Material	Slush temp,°C	Material	Slush temp,°C
ice-water†	0	toluene	-95
ice/salt-water†	0 to -15	carbon disulphide	-112
diethyl carbonate	-15	1-bromobutane	-112
carbon tetrachloride	-23	iso-amyl alcohol	-117
ethylene dichloride	-36	methyl cyclohexane	-126
chlorobenzene	-45	n-pentane	-132
diacetone alcohol	-55	iso-pentane	-161
'dry ice'-acetone†	-78	liquid nitrogen	-196
ethyl acetate	-84		

* The indicated slush temperatures (±5°) achieved by cooling the materials listed (except thosemarked †) with liquid nitrogen.

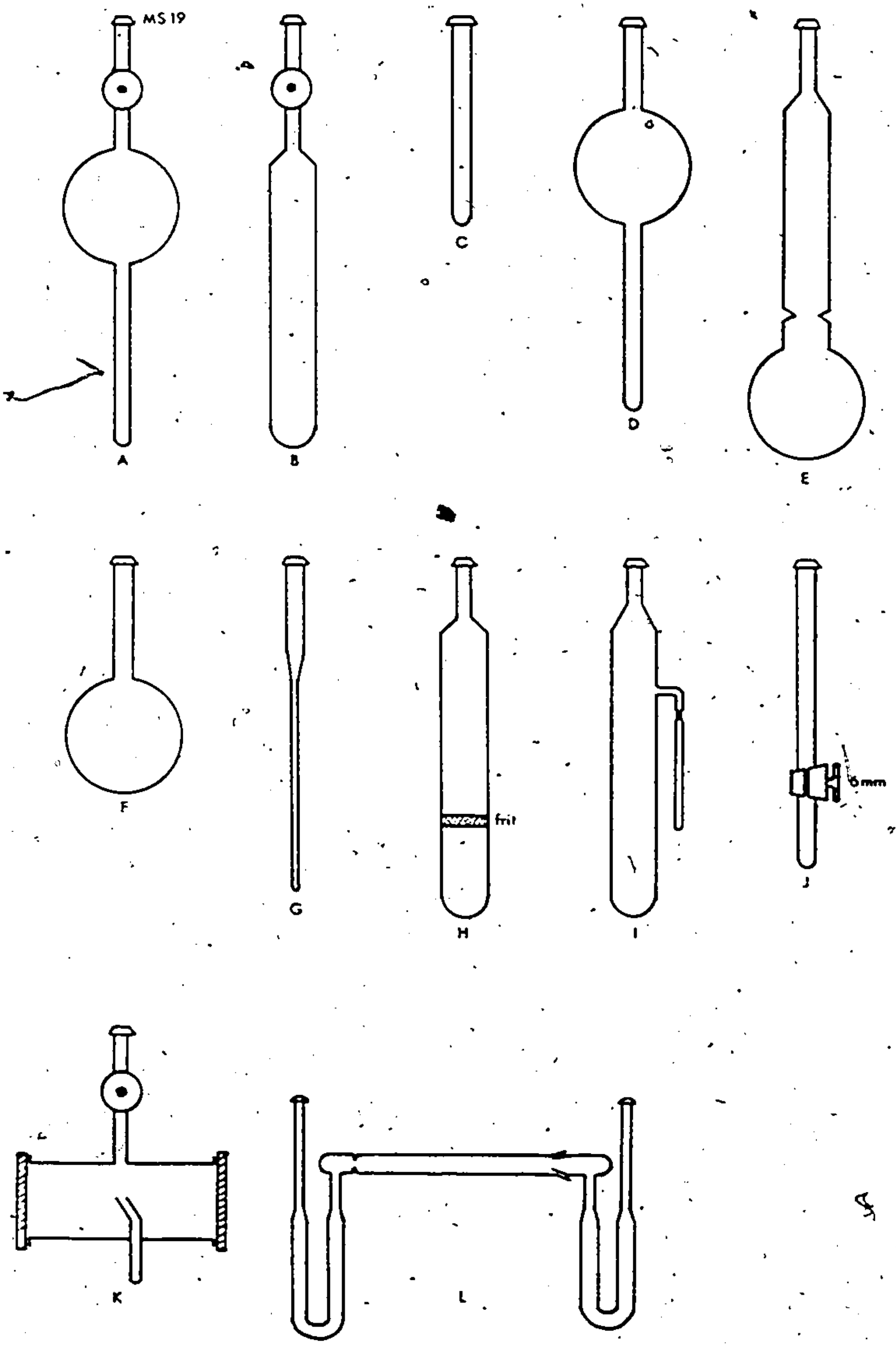


Fig.A.2 Storage and reaction vessels

Reaction vessel design was dictated by both the quantity of reactants and the phase in which reaction occurred. For general gas phase reactions (e.g. HX/AlX_3 reactions) a vessel 'D' (150-1000 ml) was used. For reactions at low pressure or in the condensed phase a vessel 'C' (5-100 ml) was employed; for surface area dependent reactions such as those where a gas reacts with an involatile liquid (e.g. HX/Me_nGeY_{4-n} exchange reactions) vessel 'F' was used. When the products were solid but sublimable (e.g. $MeGeI_3$) a similar vessel 'I' having a constricted side arm which could be sealed as a break-seal ampoule was used. Reactions in which a gas was distilled over a solid (e.g. iodogermane over silver(I) cyanide in the preparation of cyanogermane) were carried out in vessel 'E' (50-200 ml) or for the more involatile reactants (e.g. $MeGeBr_3$) vessel 'L'; in the latter passage of the reactant through the solid was assisted by occasional pumping through the U-traps held at -196°. For sealed tube reactions (e.g. the equilibration of $MeGeHCl_2$ with $MeGeHBr_2$) standard n.m.r. tubes (5 mm o.d.) attached to an MS19 joint or capillaries (1-4 mm o.d.) drawn from the MS19 joint (G) were utilised; both were filled and sealed off on the line. Recovery of samples in semi-micro tubes or ampoules was achieved by reopening them under vacuum in the device "J"[268], operated by turning the tap and thus snapping the tube. The Schlenk tube technique[274] was used wherever solids were handled in the absence of air or moisture (e.g. the resublimation of iodine or the isolation of the tri-pseudohalides); with slight adaptations vacuum filtrations and recrystallisations were carried out by standard method.[273,274]

A.1.4 Instrumentation and physical methods

(a) Infrared spectroscopy: A gas cell of 50 or 100 mm path length, fitted with KBr plates (4000–350 cm^{-1}) was used; a small finger permitted low volatility liquids to be distilled directly into the cell. In general gas pressures ranging from 1 to 200 mm Hg were employed. Solids or involatile liquids were recorded as smears or mulls between CsI plates (4000–200 cm^{-1}) in an air-tight holder; spectra of solutions were obtained using a solution cell (KBr) with an adjustable path-length reference cell. Beckman I.R.12 (4000–200 cm^{-1}) and I.R.10 (4000–400 cm^{-1}) spectrometers were used calibrated in the normal manner. The data so obtained are expected to be accurate to ±1 cm^{-1}.

(b) Raman spectroscopy: Solid and liquid samples were sealed in Pyrex-glass capillaries (*ca*.2 mm o.d., *ca*.50 mm long); spectra of solutions were obtained using a cell (5 mm o.d.) fitted with an optical flat and air-tight cap. A Spectra Physics/Beckman 700 laser-Raman spectrometer with either a helium-neon or argon-ion laser source was used. Sharp features were usually reproducible to ±2 cm^{-1} and accurate to *ca*. ±4 cm^{-1} after calibration.

(c) Nuclear magnetic resonance spectroscopy (^1H n.m.r.): Samples were sealed in Pyrex-glass capillaries (*ca*.2 mm o.d.) which were placed inside standard n.m.r. tubes with CCl_4 to ensure good sample homogeneity. Jeolco C-60HL and C-60 spectrometers fitted with standard variable temperature probes and electronic integrator units were used for ^1H analysis.

(d) Mass spectroscopy: Routine analysis of gaseous samples in the range m/e 10–400 was achieved with an AEI MS10c2 instrument operating at an ionising potential of 70–75 eV. Many features of the inlet system were unsuited to the compounds under study such that inter-halogen exchange and disproportionation reactions occurred before the sample entered the spectrometer.

(e) Molecular weights were determined (i) by weighing a known amount of gas in a small vessel (10 ml) fitted with a greaseless tap, or (ii) cryoscopically by measuring the freezing point depression of a solvent (usually benzene) when a measured amount of the unknown was dissolved in it.[271-274]

(f) Melting points were determined using Stock's plunger technique.[268]

(g) Vapour pressures were measured using vapour pressure thermometers constructed as described by Stock,[268] (SO_2, 4° to -53°; NH_3 -28° to -77°; CO_2, -76° to -110°; C_2H_4 -99° to -159°) and a capillary difference-manometer. The compound under investigation was distilled into a small finger and allowed to expand against the mercury column; the finger was immersed in various slush baths, the exact temperature being determined by the v.p. thermometer.

(h) Boiling points were obtained by extrapolation of $\log\rho$ vs $1/T$ plots. (ρ = vapour pressure, T = temperature).[274]

A.1.5 Quantitative analysis of germanium compounds.

Several analytical methods have been described for determining germanium in its compounds. The inorganic derivatives may be analysed by precipitation of the sulphide, GeS_2, in strong acid solution although some reduction to the insoluble monosulphide occurs. Greater accuracy may be obtained by igniting the sulphides in an open crucible to the white dioxide. Ignition of the tannin complex precipitated from dilute sulphuric acid to GeO_2 has also been used.[275] Acid complexes such as mannitol-[276] or pyrocatechol-[277] ge[illegible]nic acid have enabled germanium to be determined volumetrically by titration with strong base. Alternatively analysis may be carried out photometrically by complex formation.[278]

Organogermanes present several problems due to the difficulty of destroying the organic groups. Arylgermanes are easily decomposed by fuming HNO_3 or H_2SO_4, and ignition over 800° ensures quantitative production of GeO_2. Alkylgermanes, however, are not so amenable due to their high volatility and resistance to oxidation, alkylgermanium oxides having appreciable volatility. This has necessitated the use of sodium perchlorate and steel bombs. It is worth noting also that organogermanes require higher combustion temperatures than organic compounds for carbon-hydrogen analysis.

The expectation of quantitatively acceptable results for the analysis of germanium in the methylgermanes is therefore low and hardly likely to better the more sophisticated criteria of purity. For this reason no analyses results appear in this thesis, although hydrogen bromide cleavage reactions are used with some success in characterising pseudohalide derivatives.

APPENDIX 2

THE PREPARATION AND PURIFICATION OF STARTING MATERIALS

The compounds listed below were either commercially available or had known preparative routes. They are considered 'starting materials' as our interest was not primarily associated with their preparation. Where more than one source was used the order is that of experimental preference. Their purity was checked by infrared/Raman spectroscopy (i.r./R), ^{1}H n.m.r. spectroscopy (n.m.r.), and occasionally by vapour pressure measurements (v.p.), molecular weight determinations (m.w.), and mass spectroscopy (m.s.). Commercial suppliers are referenced alphabetically. (R.T. = room temperature)

ALUMINIUM TRIHALIDES, $AlBr_3$, $AlCl_3$, AlI_3: commercial[a,b,c]; stored at R.T. under N_2; resublimed and dried under vacuum.

AZIDO(TRIMETHYL)SILANE, Me_3SiN_3: prepared[231] by the reaction of Me_3SiCl with NaN_3 in diethyl ether.[d] The pure Me_3SiN_3 was separated from the solvent by fractionation and condensation at −63°. Stored in break-seal ampoules at R.T.; i.r.,[231] n.m.r.[254]

BORON TRIBROMIDE, BBr_3: commercial;[c] degassed at −78° prior to use and stored at R.T. (vessel 'B'); i.r.,[279] v.p.[280]

BORON TRICHLORIDE, BCl_3: commercial;[e] degassed at −112° prior to use. Stored at R.T. in vessel 'B'; i.r.,[279] v.p.[281]

BORON TRIFLUORIDE, BF_3: commercial;[e] middle fractions volatile at −126° were used, stored at R.T. (vessel 'A'); i.r.[78]

BORON TRIIODIDE, BI_3: commercial;[c] stored at R.T. under N_2 and degassed at 0° prior to use.

BROMINE, Br_2: commercial;[a] stored at R.T. and degassed at -78°.

BROMOGERMANE, GeH_3Br: prepared.[282] Typically GeH_4 (3.9 mmol) and BBr_3 (1.1 mmol) were condensed at -196° into a reaction vessel (ca.250 ml, type 'D'); the mixture was allowed to react at -78° (1-2 hr.) and the volatile products distilled through traps at -45°, -95°, and -196°. An unidentified yellow solid remained in the reaction vessel. The contents of the -95° trap were again passed through traps at -63°, -95°, and -196° when the -95° fraction was pure GeH_3Br (2.9 mmol, purity confirmed by i.r.,[172] v.p.,[50] n.m.r.,[63] and m.pt.[50]). Unreacted GeH_4 and B_2H_6 were obtained in the -196° traps and could be separated by distillation onto a large excess of Et_3N, when the volatile products at -78° were pure GeH_4. Stored at -78° in semi-micro ampoules.

BROMO(TRIMETHYL)GERMANE, Me_3GeBr: commercial;[c] degassed at -78° and stored at R.T. (vessel 'B'); i.r.,[147] n.m.r.[81]

[$^2H_3$] CHLOROGERMANE, GeD_3Cl: kindly donated by Dr. G.K. Barker who had prepared[58] it from GeD_4 and $SnCl_4$;[c] i.r.,[172] R.[57]

CHLORO(TRIMETHYL)GERMANE, Me_3GeCl: commercial;[c] degassed at -78° and stored at R.T. (vessel 'B'); i.r.,[82] n.m.r.[81]

CHLORO(TRIMETHYL)SILANE, Me_3SiCl: commercial;[c] distilled through traps at -45°, -78°, and -196°. The pure Me_3SiCl obtained in the -78° trap was stored at R.T. (vessel 'B'); i.r.,[283] n.m.r.[119]

CYANOGERMANE, GeH_3CN: prepared;[244,261] GeH_3I or GeH_3Br (1-2 mmol) was streamed through a column 'E' loosely packed with silver(I) cyanide (ca. 20g) and glass wool or helicles until i.r. analysis showed no halogermane[172] remained. Distillation through a series of traps at -23°, -63°, and -196° gave pure GeH_3CN condensing at -63°. It was stored at -196° in sealed glass ampoules; i.r.,[248] n.m.r., v.p., m.pt.[261]

CYANO(TRIMETHYL)GERMANE, Me_3GeCN: prepared by a slight modification to to that reported.[214] Typically, Me_3GeBr or Me_3GeI (ca. 5 mmol) and excess silver(I) cyanide (ca.8g) were refluxed under N_2 in dry diethyl ether[d] (ca.10 ml). After 24 hr. the mixture was cooled to -196° and the reaction vessel evacuated. Pure Me_3GeCN (typically 4.5-4.8 mmol) was separated from the solvent by vacuum fractionation and condensation at -45° (Et_2O being volatile at this temp.). Stored at R.T. in semi-micro ampoules; i.r., R, n.m.r., m.pt.[214]

DIBROMO(DIMETHYL)GERMANE, Me_2GeBr_2: prepared by the reaction of Me_2GeCl_2 with excess HBr in vessel 'F' (1-5 mmol scale); stored at R.T. (vessel 'B'); i.r./R,[147] n.m.r.[125]

DICHLORO(DIMETHYL)GERMANE, Me_2GeCl_2: commercial;[c] degassed at -78° and stored at R.T. (vessel 'B'); i.r./R,[124] n.m.r.[124]

DIIODO(DIMETHYL)GERMANE, Me_2GeI_2: prepared by the reaction of (i) Me_2GeCl_2 with excess HI or (ii) Me_2GeH_2 with I_2. Stored in the dark at R.T. (vessel 'B'); i.r./R,[166] n.m.r.[125]

DIMETHYLGERMANE, Me_2GeH_2: prepared[22] by the reduction of Me_2GeCl_2 with $LiAlH_4$ in n-Bu_2O.[f] Small amounts of $LiAlH_4$ were slowly added from a tipping-tube to a cooled solution of Me_2GeCl_2 (ca.10 mmol) in dry n-Bu_2O (ca. 10-15 ml) contained in a 100 ml. 2-necked flask fitted with a dry-ice reflux condenser. Crude Me_2GeH_2 was pumped from the reaction vessel as it was formed and passed through traps at -78° (2), -126°, and -196°; the contents of the -126° trap were refractionated through traps at -78° and -95° when pure Me_2GeH_2 was obtained in a -196° following trap. A 95% yield based on Me_2GeCl_2 was typical. Stored at R.T. (vessel 'A'); i.r./R,[25] n.m.r.,[83] v.p.[22]

GERMANE, GeH_4: commercial;[e] purified by passage through traps at -126°

and degassed at -196°. Stored at R.T. (vessel 'A'); i.r.,[170] n.m.r.,[63] v.p.,[284] m.w., m.s.[294]

[$^2H_4$]GERMANE, GeD_4: prepared.[57] 50% [$^2H_3$]phosphoric acid, D_3PO_4, was prepared by distilling D_2O[g] onto dry P_2O_5[a] contained in a 50 ml. thick-walled tube under vacuum; the tube was sealed and held at 100° in a steam bath for several days. The D_3PO_4 (ca.40 ml) was placed in a 250 ml. flask fitted with a tipping tube containing Mg_2Ge alloy and connected to the vacuum line. On mixing alloy hydrolysis was rapid with the vessel emersed in warm water (50°) and vigorous stirring. The volatile products were condensed in a series of traps held at -196°. GeD_4 was separated from the higher germanes (Ge_2D_6,Ge_3D_8 etc.,) by passage through a trap at -126°. Yields varied between 10-40% based on Ge. Stored in greaseless vessel 'B' at -196°; i.r.,[171] v.p.[286]

HYDROGEN BROMIDE, HBr: commercial;[e] degassed at -196° and stored at R.T. (vessel 'A'); i.r.,[287] v.p.[281]

HYDROGEN CHLORIDE, HCl: commercial;[e] degassed at -196° and stored at R.T. (vessel 'A'); i.r.,[287] v.p.[281]

HYDROGEN IODIDE, HI: commercial[a,c], hydriodic acid was 'pumped on' through a series of -196° traps; the crude HI was purified by repeated distillation through traps at -78°. Stored at -78° (vessel 'B'); i.r.,[287] v.p.[281]

IODINE, I_2: commercial;[a] resublimed before use and degassed at -78°.

IODOGERMANE, GeH_3I: prepared.[288] I_2 (ca.0.25 g, ca.1 mmol) was sublimed by the Schlenk-tube technique[274] into a thick-walled tube (5 mm. o.d., 150 mm long) having a constriction and tapered-joint for attachment to the vacuum line. GeH_4 (ca.2-25 mmol) was distilled into the tube held at -196°. The tube was sealed at the constriction and placed in a bath at −78° which was then allowed to warm slowly to R.T. over ca. 1 hr. after which time dark brown/yellow solutions were usually obtained. Reaction was allowed to proceed at R.T. for a further 30 min. or until no trace of iodine remained. (N.B. HIGH INTERNAL PRESSURE >40 ATMOS!). The tube was cooled to −196° and re-opened on the vacuum line in the device 'J' (no more than a trace of non-condensable should be evident). Pure GeH_3I (typically 0.7-0.9 mmol) was separated from poly-iodinated products by passage through a trap at −23° into one at −78°, allowing excess GeH_4 and HI to pass into a −196° following trap. Stored at −78° (vessel 'B'); i.r.,[172] R,[57] n.m.r.,[63] v.p.[65]

IODO(TRIMETHYL)GERMANE, Me_3GeI: prepared by (i) the reaction of Me_3GeH with I_2 (see text) or (ii) the reaction of Me_3GeCl with excess HI. Stored in the dark at R.T. (vessel 'B'); i.r./R,[166] n.m.r.[81]

LEAD(II) FLUORIDE, PbF_2: commercial;[h] dried at 50° in a high vacuum for several days before use.

MAGNESIUM GERMANIDE, Mg_2Ge: prepared.[57] Magnesium[a] (2g) and germanium[c] (3g) powders were finely mixed and placed in a stainless steel boat. This was in turn placed inside a stainless steel tube (ca. 50 mm o.d.) passing through a tube furnace. Hydrogen gas was passed through the tube continuously and the furnace temperature slowly raised to ca. 750°, and held at that temperature overnight. The 'alloy' thus prepared formed as a dark-grey 'cake' which could be ground as a brittle solid; it was usually used immediately but could be stored under N_2.

METHYLGERMANE, $MeGeH_3$: prepared[22] by (i) the reduction of $MeGeCl_3$ with $LiAlH_4$ in n-Bu_2O in yields >90% (based on $MeGeCl_3$) as described for the preparation of Me_2GeH_2 or (ii) the reaction of germyl potassium,

$GeH_3^-K^+$, with MeI in dimethoxyethane[j] in yields in excess of 80% (based on GeH_4). The volatile products from (i) or (ii) were fractionated through traps at -126°, -160°, and -196°. The pure $MeGeH_3$ collecting in the -160° trap was stored at R.T. (vessel 'A'); i.r./R,[25] n.m.r.,[83] v.p.,[22] m.s., m.w.

METHYL[$^2H_3$]GERMANE, $MeGeD_3$: prepared. KOD was first obtained from the reaction of D_2O[g] with potassium[a] metal in a N_2 atmosphere. [$^2H_3$]germyl potassium, $GeD_3^-K^+$, was prepared from the KOD (ca.5g) and GeD_4 (ca. 5 mmol) in dimethyoxyethane (ca.30 ml) and then reacted in situ with MeI (ca.7 mmol). No H-D exchange with the solvent was observed and $MeGeD_3$ with a ^2H-isotopic purity of >95 atom percent was typical (yield based on GeD_4 was ca. 60%). Stored at -196° (vessel 'B'); i.r.,[25] n.m.r.

[$^2H_3$]METHYLGERMANE, CD_3GeH_3: prepared by the method (ii) described for $MeGeH_3$ using CD_3I[k] (99.75) in place of MeI. No H-D exchange was observed and CD_3GeH_3 with a ^2H-isotopic purity of >98 atom percent was typical. Stored at -196° (vessel 'B'); i.r.,[25] n.m.r.

METHYL IODIDE, MeI: commercial.[b] Stored at R.T. (vessel 'B'); n.m.r.,[85] v.p.[281]

PHOSPHORUS TRICHLORIDE, PCl_3: commercial;[d] degassed at -112° and stored at R.T. (vessel 'B'); i.r., v.p.[281]

SILVER(I) PSEUDOHALIDES, AgCN,[c] AgNCO,[l] AgNCS,[l]: commercial; dried in a high vacuum at 50° in the dark for several days prior to use. Stored in the dark under N_2.

SODIUM AZIDE, NaN_3: commercial,[b] dried and stored as above.

<u>SOLVENTS</u>: commercial^{m,n,o} 'spectral-grade' solvents for vibrational and/or ^{1}H-n.m.r. spectroscopy (e.g. CS_2, C_6H_6, CCl_4, $CHCl_3$) were vacuum distilled and stored in vessels 'B'; purity checked by i.r., v.p.[281] Other solvents (e.g. Et_2O,^{d} n-Bu_2O,^{f} T.H.F.,^{b} C_6H_6^{j}) were stored at R.T. over drying agents (e.g. $LiAlH_4$^{a}, CaH^a) and vacuum distilled before use; b.pt.

<u>TETRACHLOROGERMANE, $GeCl_4$</u>: commercial.^{c} Degassed at -78° and stored at R.T. (vessel 'B'); i.r./R,[168] v.p.[281]

<u>TETRAMETHYLSILANE (T.M.S.), Me_4Si</u>: commercial.^{o} Stored at R.T. (vessel 'B'); n.m.r.,[83] v.p.[281]

<u>THIONYL HALIDES, $SOBr_2$, $SOCl_2$</u>: commercial^{b,c} samples were transferred to vacuum vessels in the dry box; the crude halides were degassed at -78° (to remove HCl/HBr and SO_2) and distilled through traps at -23°, -78°, and -196° on the vacuum line; middle fractions obtained from the -78° trap were retained when the i.r. spectra[289] showed no spurious bands. Stored at R.T. (vessel 'B'); v.p.[281]

<u>TITANIUM TETRACHLORIDE, $TiCl_4$</u>: commercial^a product degassed at -45° and stored at R.T. (vessel 'B'); i.r., m.pt.[281]

<u>TRIBROMO(METHYL)GERMANE, $MeGeBr_3$</u>: prepared by the reaction of $MeGeCl_3$ with excess HBr in vessel 'F' at R.T. Stored at R.T. (vessel 'B'); i.r./R,[147] n.m.r.[79]

<u>TRICHLORO(METHYL)GERMANE, $MeGeCl_3$</u>: commercial,^{c} degassed at -78°. Stored at R.T. (vessel 'B'); i.r./R,[144] n.m.r.,[126] m.s.

<u>TRIFLUORO(METHYL)GERMANE, $MeGeF_3$</u>: prepared, see text.

<u>TRIIODO(METHYL)GERMANE, $MeGeI_3$</u>: prepared by the reaction of $MeGeCl_3$ with excess HI in vessel 'F' at R.T.; purified by vacuum-sublimination and stored in break-seal ampoules, i.r./R, n.m.r.,[79] m.pt.[26]

TRIMETHYLGERMANE, Me_3GeH: prepared[22] by the reduction of Me_3GeCl, Me_3GeBr, or Me_3GeI with $LiAlH_4$ in n-Bu_2O by a similar procedure to that described for Me_2GeH_2. The crude product was distilled through traps at -78°, -112°, and -196° when pure Me_3GeH was obtained in the -112° trap. Stored at R.T. (vessel 'B'); i.r./R,[25] n.m.r.,[83] v.p.[22]

Commercial suppliers

a. The British Drug Houses Ltd., Poole, Dorset, Eng.
b. Fisher Scientific Co., Fair Lawn, N.J.
c. Alfa Inorganics Inc., Beverly, Mass.
d. Mallinkrodt, St. Louis, Miss.
e. Matheson Gas Products, East Rutherford, N.J.
f. Aldrich Chemical Co., Milwaukee, Wisc.
g. Merck Sharp and Dohme (Canada) Ltd., Quebec.
h. Allied Chemical, Morristown, N.J.
i. Liquid Carbonic Corp. Ltd.,
j. Matheson Coleman and Bell, Norwood, Ohio.
k. Stohler Isotope Chemicals, Montreal.
l. Eastman Organic Chemicals, Rochester 3, N.Y.
m. J.T. Baker Chemical Co., Phillipsburg, N.J.
n. Anachemia Chemicals Ltd., Montreal
o. NMR Specialties Inc., New Kensington, Pa.

REFERENCES

1. C. Winkler, J. Prakt. Chem. [2], 36, 204 (1887).
2. O.H. Johnson, Chem. Rev., 48, 259 (1951).
3. F. Rijkens, "Organogermanium Compounds", Inst. for Org. Chem. T.N.O., Utrecht, The Netherlands (1960).
4. D. Quane and R.S. Bottei, Chem. Rev., 63, 403 (1963).
5. F. Rijkens and G.J.M. Van der Kerk, "Investigations in the Field of Organogermanium Chemistry", Inst. for Org. Chem. T.N.O., Utrecht, The Netherlands (1964).
6. M. Dub, ed., "Organometallic Compounds", Vol.II, Springer-Verlag, New York, N.Y. (1967).
7. F.G.A. Stone, "Hydrogen Compounds of the Group IV Elements", Prentice-Hall, Englewood Cliffs, N.J. (1962).
8. E.A.V. Ebsworth, "Volatile Silicon Compounds", Pergamon Press (1963); "Organometallic Compounds of the Group IV Elements", A.G. MacDiarmid, ed., Vol.1, part I, Dekker, Inc., New York, N.Y. (1968).
9. F. Glockling, "The Chemistry of Germanium", Academic Press, London (1969).
10. E. Amberger and E. Wiberg, "Hydrides of the Elements of Main Groups I-IV", Elsevier, New York, N.Y. (1971).
11. F. Glockling and K.A. Hooton, "Organometallic Compounds of the Group IV Elements", A.G. MacDiarmid, ed., Vol.1, part II, Dekker Inc., New York, N.Y. (1968).
12. K.A. Hooton, Preparative Inorganic Reactions, 4, 851 (1968).
13. K.M. Mackay and R. Watt, Organomet. Chem. Rev. (A), 4, 137 (1969).
14. C.H. Van Dyke, Preparative Inorganic Reactions, 6, 157 (1971).
15. J.E. Drake and C. Riddle, Quart. Rev., 24, 263 (1970).
16. H.H. Anderson, J. Am. Chem. Soc., 79, 326 (1957).
17. M. Lesbre and J. Satgé, Compt. Rend., 252, 1976 (1961).
18. J. Satgé, Ann. Chim. (Paris), 6, 519 (1961).
19. M. Massol and J. Satgé, Bull. Soc. Chim. France, 2737 (1966).
20. J. Satgé and P.R. Riere, ibid., 1773 (1966).
21. H.H. Anderson, J. Am. Chem. Soc., 82, 3016 (1960).
22. D.S. Rustad, T. Birchall, and W.L. Jolly, Inorg. Synth., 11, 128 (1968); J.E. Griffiths, Inorg. Chem., 2, 375 (1963).
23. A.I. Barchukov and Y.N. Petrov, Opt. i. Spektroskopiya, 4, 799 (1958); V.W. Laurie, J. Chem. Phys., 30, 1210 (1959).

24. J.J. Kohanek, P. Estacio, and M.A. Ring, Inorg. Chem., 8, 2516 (1969).

25. J.E. Griffiths, J. Chem. Phys., 38, 2879 (1963); D.F. Van de Vondel and G.P. Van der Kelen, Bull. Soc. Chim. Belges, 74, 467 (1965).

26. A.P. Belij, A.I. Gorbunov, S. Golubtsov, and N.S. Feldshtein, J. Organometal. Chem., 17 485 (1969), and references therein; V.A. Ponomarenko and G. Ya Vzenkova, Izv. Akad. Nauk SSSR, 1020 (1957); E.A. Flood, K.L. Godfrey, and L.S. Foster, Inorg. Synth., 3, 64 (1960); M. Wieber, C.D. Frohning, and M. Schmidt, J. Organomet. Chem., 6, 427 (1966).

27. A.D. Petrov, V.F. Mironov, and I.E. Golgy, Izv. Akad. Nauk SSSR, 1169 (1956).

28. C. Eaborn and K.C. Pande, J. Chem. Soc., 3200 (1960); H. Gilman and C.W. Gerow, J. Am. Chem. Soc., 79, 342 (1957).

29. R. Fuchs, L.O. Moore, D. Miles and H. Gilman, J. Org. Chem., 21, 1113 (1956).

30. L.I. Zakharkin and O.Yu Okhlobystin, Zh. Obshch. Khim., 31, 3417 (1961).

31. J.H. Lengle and V.H. Dibeler, J. Am. Chem. Soc., 74, 2683 (1952).

32. F.E. Brinckman and F.G.A. Stone, J. Inorg. Nucl. Chem., 11, 24 (1959).

33. M. Schmidt and I. Ruidisch, Z. Anorg. allgem. Chem., 311, 331 (1961).

34. K.M. Mackay, R.D. George, P. Robinson, and R.Watt, J. Chem. Soc., 1920 (1968); Inorg. Synth., in press (1973).

35. D. Seyferth and E.G. Rochow, J. Am. Chem. Soc., 77, 907 (1955).

36. M. Massol, Ph.D. Thesis, Univ. of Toulouse (1967); Ref.4, p. 406; K.M. Mackay and R. Watt, J. Organomet. Chem., 14, 123 (1968); Ref.9 p.p. 91-93.

37. V.F. Mironov, N.G. Dzhurinskaya, and A.D. Petrov, Izv. Akad. Nauk SSSR, 1920 (1960).

38. V.F. Mironov and A.L. Kravchenko, Izv. Akad. Nauk SSSR, 988 (1965).

39. M. Lesbre and P. Mazerolles, Compt. Rend., 246, 1708 (1958).

40. E. Amberger, Ph.D. Thesis, University of München (1961).

41. T.N. Srivastava, J.E. Griffiths, and M. Onyszchuk, Can. J. Chem., 40, 739 (1962); 579 (1962).

42. C.H. Van Dyke and J.T. Wang, Unpublished results.

43. S. Sujishi and W. Ando, Unpublished results.

44. S. Sujishi, Int. Congr. Pure Appl. Chem. München (1959), Abstract A225; Symp. hydrides groups 4,5,6, Berkeley, Calif. [illegible]963).

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

46. K.M. Mackay and P.J. Roebuck, J. Chem. Soc., 1195 (1964).

47. K.M. Mackay and P. Robinson, *J. Chem. Soc.*, 5121 (1965).

48. O.H. Johnson and D.M. Harris, *J. Am. Chem. Soc.*, *72*, 5564 (1950).

49. B.V. Gladshstein, V.V. Rode, and L.Z. Soborovskii, *Zh. Obshch. Khim.*, *29*, 2120 (1959).

50. L.M. Dennis and P.R. Judy, *J. Am. Chem. Soc.*, *51*, 2321 (1929).

51. B.C. Lord and C.M. Steese, *J. Chem. Phys.*, *22*, 542 (1954).

52. E. Amberger and H. Boeters, *Angew. Chem.*, *73*, 114 (1961).

53. J.E. Griffiths and M. Onyszchuk, *Can. J. Chem.*, *39*, 339 (1961).

54. J.E. Griffiths and A.L. Beach, *Can. J. Chem.*, *44*, 1743 (1966).

55. J.W. Anderson and J.E. Drake, *Synth. Inorg. and Metalorg. Chem.*, *1*, 155 (1971).

56. G.K. Barker and J.E. Drake, *Inorg. Nucl. Chem. Letters*, *7*, 39 (1971).

57. C.G. Riddle, Ph.D. Thesis, Southampton University (1969).

58. J.E. Bentham, S. Cradock, and E.A.V. Ebsworth, *Inorg. Nucl. Chem. Letters*, *7*, 1077 (1971).

59. J.E. Bulkowski and C.H. Van Dyke, Unpublished results.

60. P. Mazerolles, *Bull. Soc. Chim. France*, 1911 (1961).

61. F. Rijkens, E. Bulten, W. Drenth, and G.J.M. Van der Kerk, *Recl. Trav. Chim. Pays-Bas. Belge*, *85*, 1223 (1966).

62. H.H. Anderson, *J. Am. Chem. Soc.*, *75*, 814 (1953); V.A. Ponomarenko and G.Ya Vzenkova, *Izv. Akad. Nauk SSSR*, 1020 (1957).

63. E.A.V. Ebsworth, S.G. Frankiss, and A.G. Robiette, *J. Mol. Spectrosc.*, *12*, 299 (1964).

64. D.W.H. Rankin, *J. Chem. Soc. (A)*, 1926 (1969).

65. S. Cradock and E.A.V. Ebsworth, *J. Chem. Soc. (A)*, 12 (1967).

66. T.D. Goldfarb and S. Sujishi, *J. Am. Chem. Soc.*, *86*, 1679 (1964).

67. T.N. Srivastava and M. Onyszchuk, *Proc. Chem. Soc.*, 205 (1961).

68. V.F. Mironov, N.G. Dhurinskaya, and A.D. Petrov, *Izv. Akad. Nauk SSSR*, 1956 (1961).

69. S. Cradock and E.A.V. Ebsworth, *J. Chem. Soc (A)*, 1226 (1967).

70. S. Cradock and E.A.V. Ebsworth, *J. Chem. Soc. (A)*, 1423 (1968).

71. C.H. Van Dyke, J.E. Bulkowski, and N. Viswanathan, *Inorg. Nucl. Chem. Letters*, *7*, 1057 (1971).

72. Ref.10, p.p. 65 et. seq.

73. J.E. Drake, N. Goddard, and C. Riddle, *J. Chem. Soc. (A)*, 2704 (1969).

74. J.W. Anderson and J.E. Drake, *J. Chem. Soc. (A)*, 3131 (1970).

75. J.M. Bellama and C.J. McCormick, *Inorg. Nucl. Chem. Letters*, *7*, 533 (1971).

76. C.J. McCormick, Ph.D. Thesis, University of Maryland (1970).

77. H.W. Myers and R.F. Putnam, *Inorg. Chem.*, *2*, 655 (1963); C.D. Bass, L. Lynds, T. Wolfram, and R.E. DeWames, *Inorg. Chem.*, *3*,1063 (1964).

78. R.C. Lord and E. Nielsen, *J. Chem. Phys.* *19*, 1 (1951); C.R. Bailey, J.B. Hale, and J.W. Thompson, *Proc. Roy. Soc.*, *A161*, 107 (1937).

79. K. Moedritzer and J.R. Van Wazer, *Rev. Chim. Minérale*, *6*, 293 (1969).

80. A.N. Egorochkin, M.L. Khidekel, V.A. Ponomarenko, G.Ya Zueva, and G.A. Razuvaev, *Izv. Akad. Nauk. SSSR*, 347 (1964).

81. H. Schmidbaur and I. Ruidisch, *Inorg. Chem.*, *3*, 599 (1964).

82. J.R. Durig, K.K. Lau, J.B. Turner, and J. Bragin, *J. Mol. Spectrosc.*, *31*, 419 (1969).

83. H. Schmidbaur, *Chem. Ber.*, *97*, 1639 (1964).

84. C.J. Hoffman and H.S. Gutowsky, *Inorg. Synth.*, *4*, 147 (1953).

85. H. Spiesecke and W.G. Schneider, *J. Chem. Phys.*, *35*, 722 (1961).

86. J.M. Bellama, Ph.D. Thesis, University of Pennsylvania (1966).

87. G.V.D Tiers, *J. Phys. Chem.*, *64*, 373 (1960).

88. A.L. Allred and E.G. Rochow, *J. Inorg. Nucl. Chem.*, *5*, 269 (1958); R.S. Drago, *J. Inorg. Nucl. Chem.*, *15*, 237 (1960); and references therein.

89. H.O. Pritchard and H.A. Skinner, *Chem. Rev.*, *55*, 745 (1954).

90. L. Pauling, "Nature of the Chemical Band", 3rd. edn. Oxford University Press (1960).

91. M.L. Huggins, *J. Am. Chem. Soc.*, *75*, 4123 (1953).

92. "Best fit" values given in D.A. Johnson, "Some Thermodynamic Aspects of Inorganic Chemistry", Cambridge University Press (1969).

93. G.N. Kartsev, Ya.K. Syrkin, A.L. Kravchenko, and V.F. Mironov, *J. Struct.Chem. USSR*, 5, 452 (1964).

94. S.O. Wandiga, A.A. Maryott, and J.M. Bellama, Unpublished results.

95. K. Hedberg, *J. Am. Chem. Soc.*, *77*, 6491 (1955); E.A.V. Ebsworth, D.W.H. Rankin, and G.M. Sheldrick, *ibid.*, 2828 (1969).

96. L.H. Sommer, "Stereochemistry, Mechanism and Silicon", McGraw-Hill, New York, N.Y. (1965); C. Eaborn, "Organosilicon Chemistry", Butterworth, London (1960).

97. J.A. Kerr, D.H. Slater, and J.C. Young, *J. Chem. Soc. (A)*, 104 (1966).

98. W.L. Jolly, "The Synthesis and Characterisation of Inorganic Compounds", Prentice-Hall,Inc., Englewood Cliffs, N.J. (1970); W.E. Dassent, "Inorganic Energetics", Penguin Books Ltd., Middx, England (1970).

99. C.H. Van Dyke and A.G. MacDiarmid, *J. Inorg. Nucl. Chem.*, *25*, 1503 (1963).

100. Ref.10, p.p. 514.

101. D.R. Deans and E. Eaborn, J. Chem. Soc., 3169 (1954).

102. J.E. Drake and N. Goddard, Inorg. Nucl. Chem. Letters, 41, 385 (1968).

103. A.J. Vanderwielen and M.A. Ring, ibid., 8, 421 (1972).

104. J.E. Drake and J. Simpson, ibid., 2, 219 (1966).

105. G.K. Barker and N. Goddard, Private communication (1970).

106. H.J. Emeleus and M. Onyszchuk, J. Chem. Soc., 604 (1958).

107. J.W. Anderson, Private communication (1972).

108. R.G. Pearson, J. Am. Chem. Soc., 85, 3533 (1963).

109. J.W. Anderson, G.K. Barker, A.J.F. Clark, J.E. Drake, and R.T. Hemmings, Spectrochim. Acta, to be published (1973).

110. N.F. Ramsey, Phys. Rev., 78, 699 (1950); 86, 243 (1952).

111. P.T. Narisimham and M.T. Rogers, J. Chem. Phys., 31, 1302 (1959).

112. H.M. McConnell, J. Chem. Phys., 27, 226 (1957).

113. E.A.V. Ebsworth and J.J. Turner, J. Phys. Chem., 67, 805 (1963).

114. J.R. Cavanaugh and B.P. Dailey, J. Chem. Phys., 34, 1099 (1961).

115. E.A.V. Ebsworth and S.G. Frankiss, Trans. Faraday Soc., 59, 1518 (1963).

116. T. Schaefer, W.F. Reynolds, and T. Yonemoto, Can. J. Chem., 41, 2969 (1963).

117. K.M. Mackay and R. Watt, J. Organomet. Chem., 6, 336 (1966); 12, 49 (1963).

118. C.H. Van Dyke and A.G. MacDiarmid, Inorg. Chem., 3, 1071 (1964).

119. E.A.V. Ebsworth and S.G. Frankiss, Trans. Faraday Soc., 63, 1574 (1967).

120. E.J. Spanier and A.G. MacDiarmid, J. Inorg. Nucl. Chem., 31, 2976 (1969).

121. C.N. Banwell and N. Sheppard, Disc. Faraday Soc., 34, 115 (1962).

122. A.A. Bothner-By and R.E. Glick, J. Chem. Phys., 26, 1651 (1957).

123. A. Tzalmona, Molec. Phys., 7, 497 (1963).

124. See Reference 80.

125. K. Moedritzer, J. Organomet. Chem., 6, 282 (1966).

126. A.N. Egorochkin, A.I. Burov, V.F. Mironov, T.K. Gar, and N. Vyazankin, Dokl. Akad. Nauk SSSR, 180, 861 (1968).

127. A.A. Bothner-By, Disc. Faraday Soc., 34, 69 (1962).

128. J.M. Bellama and A.G. MacDiarmid, J. Organomet. Chem., 18, 275 (1969).

129. S. Moritz and N. Sheppard, Mol. Phys., 5, 361 (1962).

130. F. Lonsdale, Proc. Roy. Soc., 171, 541 (1939).

131. J.A. Pople, J. Chem. Phys., 37, 53 (1962).

132. B.P. Dailey and J.N. Shoolery, J. Am. Chem. Soc., 77, 3977 (1956).

133. C. Schumann and H. Dreeskamp, J. Mag. Resonance, 3, 204 (1970).

134. E.R. Malinowski, J. Am. Chem. Soc., 83, 4479 (1961).

135. C. Juan and H.S. Gutowsky, J. Chem. Phys., 37, 2198 (1962).

136. G.P. Van der Kelen and Z. Eckhaut, J. Mol. Spectrosc., 10, 141 (1963).

137. A.W. Douglas, J. Chem. Phys., 40, 2413 (1964).

138. T. Vladimiroff and E. Malinowski, ibid., 42, 440 (1965); J. Am. Chem. Soc., 86, 3575 (1964).

139. H.P. Fritz and K.E. Schwarzhaus, J. Organomet. Chem., 1, 297 (1963).

140. N. Muller and D.E. Pritchard, J. Chem. Phys., 31, 768, 1471 (1959).

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

142. J.R. Durig, C.W. Sink, and J.B. Turner, J. Chem. Phys., 49, 3422 (1968); J.R. Durig, J.B. Turner, B.M. Gibson, and C.W. Sink, J. Mol. Struct., 4, 79 (1969).

143. J.R. Durig and J.B. Turner, Spectrochim. Acta, 27A, 1623 (1971).

144. D.F. Van de Vondel and G.P. Van der Kelen, Bull. Soc. Chim. Belges, 74, 453 (1965).

145. J.R. Aronson and J.R. Durig, Spectrochim. Acta, 20, 219 (1964).

146. J.E. Griffiths, Spectrochim. Acta, 20, 1335 (1964).

147. D.F. Van de Vondel, G.P. Van der Kelen, and G. Van Hooydonk, J. Organomet. Chem., 23, 431 (1970).

148. M.I. Batuev, V.A. Ponomerenko, A.D. Matveeva, and G. Vzenhovo, Izv. Akad. Nauk SSSR, 2120 (1959).

149. V.F. Mironov and A.L. Kravchenko, Izv. Akad. Nauk SSSR, 988 (1965).

150. J.R. Durig, B.M. Gibson, and C.W. Sink, J. Mol. Spectrosc., 2, 1 (1968).

151. J.R. Durig, C.W. Sink, and S.F. Bush, J. Chem. Phys., 45, 66 (1966).

152. J.R. Durig and J.B. Turner, Spectrochim. Acta, 27A, 395 (1971).

153. B.J. Cross and F. Glockling, J. Organomet. Chem., 3, 146 (1965).

154. M. Goldstein and W.D. Unsworth, J.Chem.Soc. (A), 2121 (1971).

155. L.E. Levchuk, J.R. Sams, and F. Aubke, Inorg. Chem, 11, 43 (1972).

156. Von K. Licht, H. Geissler, P. Koehler, K. Hottmann, H. Schnorr, and H. Kriegsman, Z. Anorg. allgem. Chem., 385, 271 (1971).

157. Von K. Licht and P. Koehler, Z. Anorg. allgem. Chem., 383, 174 (1971).

158. J. Trotter, M. Akhtar, and N. Bartlett, J. Chem. Soc. (A), 30 (1966).

159. J.L. Hoard and W.B. Vincent, J. Am. Chem. Soc., 64, 1233 (1942).

160. G.M. Begun and A.C. Rutenberg, Inorg. Chem., 6, 2212 (1967).

161. H.C. Clark and K.B. Dixon, Chem.Commun., 717 (1967).

162. S. Cradock, P.W. Harland, and J.C.J. Thynne, Inorg. Nucl. Chem. Letters, 6, 425 (1970).

163. G.P. Adams, J.L. Margrave, and P.W. Wilson, J. Inorg. Nucl. Chem., 33, 1301 (1971).

164. G.K. Barker, Ph.D. Thesis, University of Windsor (1973).

165. J.W. Anderson, Ph.D. Thesis, University of Windsor (1971).

166. J.W. Anderson, G.K. Barker, J.E. Drake, and R.T. Hemmings, Can. J. Chem., 49, 3931 (1971).

167. J.R. Durig, C.F. Jumper, and J.N. Willis,Jr., J. Mol. Spectrosc., 37, 260 (1971).

168. J. Kucirek and D. Papousek, Coll. Czech. Chem. Commun., 25, 31 (1960).

169. A.D. Adley, D.F.R. Gilson, and M. Onyszchuk, Chem. Commun., 813 (1968).

170. J.W. Straley, C.H. Tindal, and H.H. Nielsen, Phys. Rev., 62, 161 (1942).

171. [illegible].W. Levin, J. Chem. Phys., 42, 1244 (1965); D.C. McKean and A.A. Chalmers, Spectrochim. Acta, 23A, 777 (1967); L.P. Lindeman and M.K. Wilson, J. Chem. Phys., 22, 1723 (1954).

172. D.E. Freeman, K.H. Rhee, and M.K. Wilson, J. Chem. Phys., 39, 2908 (1963); 43, 333 (1965).

173. J.E. Griffiths, T.N. Srivastava, and M. Onyszchuk, Can. J. Chem., 40, 579 (1962).

174. J.E. Griffiths, Can. J. Chem., 45, 2639 (1967).

175. J.E. Griffiths and K.B. McAfee,Jr., Proc. Chem. Soc., 456 (1961).

176. R.C. Lord,Jr., and C.M. Steese, J. Chem. Phys., 22, 542 (1954).

177. T.N. Srivastava, J.E. Griffiths, and M. Onyszchuk, Can. J. Chem., 41, 2101 (1963).

178. E.A.V. Ebsworth and A.G. Robiette, Spectrochim. Acta, 20, 1639 (1964).

179. A.L. Beach and J.E. Griffiths, Can. J. Chem., 44, 743 (1966).

180. J.E. Drake, C. Riddle, and D.E. Rogers, J. Chem. Soc. (A), 910 (1969).

181. J.E. Drake and C. Riddle, J. Chem. Soc. (A), 2114 (1969).

182. L.P. Lindeman and M.K. Wilson, Spectrochim. Acta, 9, 47 (1957).

183. K.M. Mackay, P. Robinson, and R.D. George, Inorg. Chim. Acta, 1, 236 (1967).

184. J.A. Lannon, G.S. Weiss, and E.R. Nixon, Spectrochim. Acta, 26A, 221 (1970); J.E. Griffiths and G.E. Walrafen, J. Chem. Phys., 40, 321 (1964); V.A. Crawford, K.H. Rhee, and M.K. Wilson, ibid., 37, 2377 (1962).

185. R.D. George, K.M. Mackay, and S.R. Stobart, J. Chem. Soc. (A), 3250 (1970).

186. R.D. George and K.M. Mackay, J. Chem. Soc. (A), 2122 (1969).

187. M.P. Brown, E. Cartmell, and G.W.A. Fowles, J. Chem. Soc., 506 (1960); F. Glockling, J.R.C. Light, J. Walker, and K.M. Mackay, J. Chem. Soc. (A), 432 (1970); R.J. Cross and F. Glockling, J. Organomet. Chem., 3, 146 (1965); K. Ulbricht and V. Chvalovsky, ibid., 12, 105 (1968).

188. R. Mathis, J. Satgé, and F. Mathis, Spectrochim. Acta, 18, 1463 (1962).

189. R. Mathis, M. Constant. J. Satgé, and F. Mathis, ibid., 20, 515 (1964).

190. E.A.V. Ebsworth, M. Onyszchuk and N. Sheppard, J. Chem. Soc., 1453 (1958).

191. J.R. Durig, S.M. Craven, and J. Bragin, J. Chem. Phys., 52, 2046 (1970).

192. R.P. Hollandsworth and M.A. Ring, Inorg. Chem., 7, 1635 (1968).

193. H.A. Bent, Chem. Rev., 61, 275 (1961).

194. A. Maccoll, Trans. Faraday Soc., 46, 369 (1950).

195. S.C. Wait, R.A. Rader, and T.J. Durnick, J. Mol. Spectrosc., 29, 494 (1969).

196. G.J. Janz and Y. Mikawa, Bull. Chem. Soc. Japan, 34, 1495 (1961).

197. S. Cradock, E.A.V. Ebsworth, and A.G. Robiette, Trans. Faraday Soc., 60, 1502 (1964).

198. A.L. Smith and N.C. Angelotti, Spectrochim. Acta, 412 (1959); V.A. Ponomarenko and Yu P. Egorov, Izv. Akad. Nauk SSSR, 1133 (1960).

199. H.W. Thompson, Spectrochim. Acta, 16, 238 (1960).

200. V.A. Ponomarenko, G.Ya. Zueva, and N.S. Andreev, Izv. Akad. Nauk SSSR, 1758 (1961).

201. P. Taimsalu and J.L. Wood, Spectrochim. Acta, 20, 1043 (1964).

202. A.J.F.Clark, Private communication (1972).

203. M.A. Ring, H.E. O'Neil, A.H. Kadhim, and F. Jappe, J. Organomet. Chem., 5, 124 (1966).

204. D.R. Weyerberg, A.E. Bey, H.F. Stewart, and W.H. Atwell, J. Organomet. Chem., 6, 586 (1966).

205. E.A.V. Ebsworth, A.G. Lee, and G.M. Sheldrick, J. Chem. Soc. (A), 2294 (1968).

206. G. Fritz and D. Kummer, Z. Anorg. Chem., 310, 327 (1963).

207. K. Moedritzer and J.R. Van Wazer, J. Inorg. Nucl. Chem., 28, 957 (1966); 29, 1571 (1967); 29, 1851 (1967).

208. K. Moedritzer and J.R. Van Wazer, Inorg. Chem., 5, 547 (1966); 7, 1638 (1968) J. Chem. Soc. (A), 1124 (1969).

209. K. Moedritzer and J.R. Van Wazer, J. Organomet. Chem., 12, 69 (1968); D.R. Weyenberg, A.E. Bey, and P.J. Ellison, ibid., 3, 489 (1965); 6, 583 (1966).

210. K. Moedritzer, L.C.D. Groenweghe, and J.B. Van Wazer, J. Phys. Chem., 72, 4380 (1968).

211. L. Birckenbach and K. Kellerman, Chem. Ber., 58, 876 (1925).

212. J.S. Thayer and R. West, Adv. Organomet. Chem., 5, 169 (1966).

213. M.F. Lappert and H. Pyszora, Adv. Inorg. Radiochem, 9, 133 (1966).

214. D. Seyferth and N. Kahlen, J. Org. Chem., 25, 809 (1960); J. Am. Chem. Soc., 82, 1080 (1960).

215. T.A. Bither, W.N. Knoth, R.V. Lindsey, and W.H. Sharkley, J. Am. Chem. Soc., 80, 4151 (1958).

216. A.G. MacDiarmid, J. Inorg. Nucl. Chem., 2, 88 (1956).

217. J. Sheridan and A.C. Turner, Proc. Chem. Soc., 21 (1960); N. Muller and R.C. Bracken, J. Chem. Phys., 32, 1577 (1960).

218. R. Varma and K.S. Bukton, J. Chem. Phys., 46, 1565 (1967).

219. E.O. Schlemper and D. Britton, Inorg. Chem., 5, 511 (1966).

220. M.R. Booth and S.G. Frankiss, Spectrochim. Acta, 26A, 859 (1970).

221. E.A.V. Ebsworth, D.R. Jenkins, M.J. Mays, and T.M. Sugden, Proc. Chem. Soc., 21 (1963).

222. D.R. Jenkins, R. Kewley and T.M. Sugden, Proc. Chem. Soc., 220 (1960); Trans. Faraday Soc., 58, 1284 (1962); M.C.L. Gerry, J.C. Thompson, and T.M. Sugden, Nature, 211, 846 (1966).

223. K.R. Ramaprasad, R. Varma, and R. Nielsen, J. Am. Chem. Soc., 90, 6248 (1968).

224. K. Kimura, K. Katada, and S.H. Bauer, J. Am. Chem. Soc., 88, 416 (1966).

225. J.D. Murdoch and D.W.H. Rankin , Chem. Commun., 748 (1972).

226. K.F. Chew, W. Derbyshire, N. Logan, A.H. Norbury, and A.I.P. Sinha, Chem. Commun., 1708 (1970).

227. K.M. Mackay and S.R. Stobart, Spectrochim. Acta, 26A, 373 (1970).

228. S. Cradock, E.A.V. Ebsworth, and J.D. Murdoch, J.C.S. Faraday, 68,(I) 86 (1972); S. Cradock and R.A. Whiteford, Trans. Faraday Soc., 67, 3425 (1971); D.C. Frost, F.G. Herring, A. Katrib, R.A.N. McLean, J.E. Drake, and N.P.C. Westwood, Chem. Phys. Letters, 10, 347 (1971); Can. J. Chem., 49, 4033 (1971); S. Cradock and E.A.V. Ebsworth, Chem. Commun., 57 (1971).

229. A.F. Wells, "Structural Inorganic Chemistry", 3rd. ed., Oxford, London and New York 1962 p.733.

230. E.A.V. Ebsworth and M.J. Mays, J. Chem. Soc., 3450 (1964).

231. J.S. Thayer and R. West, Inorg. Chem, 3, 889 (1964).

232. S. Cradock and E.A.V. Ebsworth, J. Chem. Soc. (A), 1420 (1968).

233. J.E. Griffiths and A.L. Beach, Chem. Commun., 437 (1961); J.E. Griffiths, J. Chem. Phys., 48, 278 (1968).

234. G. Davidson, L.A. Woodward, K.M. Mackay, and P. Robinson, Spectrochim. Acta, 23A, 2383 (1967).

235. D. Hardie and K.H. Jack, Nature, 180, 332 (1957); S.N. Ruddleson and P. Popper, Acta Cryst., 11, 465 (1958).

236. C. Glidewell, D.W.H. Rankin, and A.G. Robiette, J. Chem. Soc. (A) 2935 (1970).

237. C.H. Van Dyke, "Organometallic Compounds of the Group IV Elements", A.G. MacDiarmid, ed., Vol.2, part I, Dekker, Inc., New York, N.Y. (1972).

238. G.M. Sheldrick, Abstr. Chem. Soc./R.I.C. Meeting, Paper 76, Edinburgh, Scotland (1970).

239. H.H. Anderson, J. Am. Chem. Soc., 71, 1799 (1949); 72, 2089 (1950); 73, 5439 (1951); 73, 5800 (1951); 75, 814 (1953); 78, 1692 (1956); 83, 547 (1961).

240. H.H. Anderson, Inorg. Chem., 3, 910 (1964).

241. H.H. Anderson, J. Org. Chem., 20, 536 (1955).

242. E.G. Rochow and A.L. Allred, J. Am. Chem. Soc., 77, 4489 (1958).

243. W. Menzer, Angew. Chem., 70, 656 (1958).

244. T.N. Srivastava, J.E. Griffiths and M. Onyszchuk, Can J. Chem., 40, 739 (1962).

245. T.N. Srivastava and S.K. Tandon, J. Inorg. Nucl. Chem., 30, 1399 (1968); M.C. Henry and W.E. Davidson, Can. J. Chem., 41, 1276 (1963).

246. F.A. Miller and G.L. Carlson, Spectrochim. Acta, 17, 977 (1961).

247. G.S. Forbes and H.H. Anderson, J. Am. Chem. Soc., 65, 2271 (1943); A.W. Laubengayer and L. Reggel, J. Am. Chem. Soc., 65, 1783 (1943); B.S. Green, D.B. Sowerby, and K.Y. Wihksne, Chem. Ind. (London), 1306 (1960).

248. T.D. Goldfarb, J. Chem. Phys., 37, 642 (1962); T.D. Goldfarb and B.P. Zafonte, ibid., 41, 3653 (1964).

249. N.S. Ham, and J.B. Willis, Spectrochim. Acta, 16, 279 (1960); R.M. Badger, J. Chem. Phys., 5, 178 (1937).

250. J.S. Thayer and D.P. Strommer, J. Organomet. Chem., 5, 383 (1966).

251. I. Ruidisch and M. Schmidt, ibid., 1, 493 (1964).

252. W.T. Reichle, Inorg. Chem., 3, 402 (1964); J.S. Thayer and R. West, Inorg. Chem., 3, 406 (1964); E.O. Schlemper and D. Britton, Inorg. Chem., 5, 507 (1966); K. Ruhlmann, A.Reiche, and M. Becker, Chem. Ber., 98, 1814 (1965).

253. H. Kriegsman, Z. Anorg. allgem. Chem., 294, 113 (1958).

254. N. Wiberg and K.H. Schmid, Chem. Ber., 100, 748 (1967).

255. W. Sundermeyer, Chem. Ber., 96, 1293 (1963).

256. V.E. Wiberg and M. Michaud, Z. Naturforsch., 96, 500 (1954).

257. D.W.H. Rankin, Chem. Commun., 194 (1969).

257a S. Cradock, E.A.V. Ebsworth, and D.W.H. Rankin, J. Chem. Soc. (A), 1628 (1969).

257b E.A.V. Ebsworth and S.G. Frankiss, J. Chem. Soc., 661 (1963).

258. J.N. Shoolery, C.E. Johnson, and L. Anderson, J. Mol. Spectrosc., 5, 110 (1960).

259. Kuntz, von Schleyer, and Allerhand, J. Chem. Phys., 35, 1535 (1961).

260. F.A. Miller and D. Bassi, Spectrochim. Acta, 19, 565 (1963).

261. S. Sujishi and J.N. Keith, Abstr. 134th Meeting A.C.S, Inorg. Chem. Div., 1958, p. 44N; S. Sujishi, Final Report, Contract, DA-11-022-ORD-1264, Project TB-2-0001 (817), Control 00R-137-53 (1957).

262. H.R. Linton and E.R. Nixon, Spectrochim. Acta, 10, 299 (1958).

263. E.H. Eyster and R.H. Gillette, J. Chem. Phys., 8, 369 (1940).

264. E.A.V Ebsworth and M.J. Mays, J. Chem. Soc., 4844 (1962).

265. R.P. Hirschmann, R.N. Kniseley, and V.A. Fassel, Spectrochim. Acta, 21, 2125 (1965); 23A, 109 (1967).

266. D.B. Sowerby, J. Inorg. Nucl. Chem., 22, 205 (1961).

267. M. Rouffer, Private communication (1973).

268. A. Stock, "Hydrides of Boron and Silicon", Cornell University Press, Ithaca, N.Y. (1953).

269. K.M. Mackay, "Hydrogen Compounds of the Metallic Elements", Spon (1966).

270. R.H. Dreisbach, "Handbook of Poisoning", Lange Medical Publications (1966).

271. R.T. Sanderson, "Vacuum Manipulations of Volatile Compounds", Wiley, New York, N.Y. (1948).

272. A. Farkas and H.W. Melville, "Experimental Methods in Gas Reactions", MacMillan (1939).

273. W.L. Jolly, "Synthetic Inorganic Chemistry", Prentice-Hall (1960); "The Synthesis and Characterisation of Inorganic Compounds", Prentice-Hall, Englewood Cliffs, N.J. (1970).

274. D.F. Shriver, "The Manipulation of Air Sensitive Compounds", McGraw-Hill, New York, N.Y. (1969).

275. H. Holness, Analyt. Chim. Acta, 2, 254 (1948).

276. D.C. Bradley, L.J. Kay, and W. Wardlaw, J. Chem. Soc., 4916 (1956).

277. E. Wanderlich and E. Gohring, Z. Analyt. Chem., 169, 346 (1959).

278. N.F. Kazarinova and N.L. Vasilera, Zh. Analit, Khim., 13, 765 (1958).

279. T. Wentink and V.H. Tiensu, J. Chem. Phys., 28, 826 (1958).

280. A. Stock and E. Kuss, Ber. Dtsch. Chem. Ges., 47, 3113 (1914).

281. "Handbook of Chemistry and Physics", R.C. West, ed., The Chemical Rubber Co., Cleveland, Ohio (1969).

282. J.W. Anderson, G.K. Barker, J.E. Drake, and R.T. Hemmings, Can. J. Chem., 50, 1607 (1972).

283. A.L. Smith, Spectrochim. Acta, 19, 849 (1963).

284. A.E. Finholt, A.C. Bond,Jr., K.E. Wilzbach, and H.J. Schlesinger, J. Am. Chem. Soc., 69, 2692 (1947).

285. F.E. Saalfeld and H.J. Svec, Inorg. Chem., 2, 46 (1963).

286. A.D. Norman, J. Webster, and W.L. Jolly, Inorg. Synth., 11, 176 (1969).

287. R.H. Pierson, A.N. Fletcher, and E.S.C. Gantz, Anal. Chem., 28, 1218 (1956)

288. J.W. Anderson, G.K. Barker, J.E. Drake, and R.T. Hemmings, Synth. Inorg. and Metalorg. Chem., accepted (1973).

289. D.E. Martz and R.T. Lagemann, J. Chem. Phys., 22, 1193 (1954).

290. L.F. Fieser and M. Fieser, "Reagents for Organic Synthesis", p.1158, Wiley Inc., (1967).

291. F. Glockling and J.R.C. Light, J. Chem. Soc. (A), 717 (1968); D.B. Chambers, F. Glockling, and J.R.C. Light, Quart. Rev., 22, 317 (1968).

292. G.P. Van der Kelen, O. Volders, H. Van Onckelen, and Z. Eeckhaut, Z. Anorg. allgem. Chem., 338, 106 (1965).

VITA AUCTORIS

Date of birth: April 8th, 1948; Westminster, London, England

son of William T. and Marjorie W. Hemmings

Education: Edmonton County Grammar School, Middlesex, England (1959-1966).

Southampton University, England; graduated with Honours Bachelor of Science Degree in Chemistry, June, 1969.

University of Windsor, Ontario, Canada (1969-1973).

Publications:

"Halogeno derivatives of methylgermane", J.Chem. Soc. (A), 3359 (1970).

"Mixed halogeno derivatives of methylgermane", J. Chem. Soc. (A), 600 (1971).

"The vibrational spectra of silane and germane derivatives. Part IV. The infrared and Raman spectra of the iodo(methyl)germanes", Can. J. Chem., 49, 2931 (1971).

"The vibrational spectra of silane and germane derivatives. Part V. The infrared and Raman spectra of the dihalogeno(methyl)germanes", J. Chem. Soc. (A), 3291 (1971).

"The vibrational spectra of silane and germane derivatives. Part VI. The infrared and Raman spectra of the monohalogeno(methyl)germanes", Spectrochim. Acta, 28A, 1113, (1972).

"A convenient synthesis of monobromogermane", Can. J. Chem., 50, 1607 (1972).

"Preparation and characterisation of pseudohalogeno(methyl)germanes and related compounds", Can. J. Chem., 51, 302 (1973).

"Iodogermane and Iodogermane-d_3", Synth. Inorg. and Metalorg. Chem., in press (1973).

"Characterisation of monohalogen and pseudohalogen derivatives of dimethylgermane", Can. J. Chem., to be submitted (1973).

"The vibrational spectra of germane and silane derivatives, Part VII. The infrared and Raman spectra of the fluoro(methyl)germanes, Spectrochim. Acta, to be submitted (1973).