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Preliminary communication

SiH AND GeH STRETCHING FREQUENCY VARIATIONS IN ROTATIONAL CONFORMERS OF $>MHCH_2X$ COMPOUNDS

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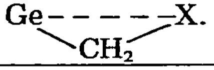
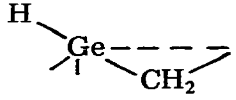
Summary

IR spectra of the species $GeHD_2CH_2F$ and $GeHD_2CH_2Cl$ are reported which show two bands each, assigned to the solitary GeH bond either *gauche* or *trans* to the halogen atom, the splittings being 17 cm^{-1} (F) and 25 5 cm^{-1} (Cl), respectively. Similar pairs of bands are identified as due to $GeHD_2CH_2Br$, $SiHD_2CH_2Cl$ and $SiHD_2CH_2Br$ in earlier spectra

This conformational effect of halogen on ν(SiH) or ν(GeH) accounts for the doublets seen earlier in the spectra of R_2MHCH_2Cl and $R_2MHCHCl_2$ compounds by Egorochkin et al and alternatively attributed by them to "free", and "intramolecularly bonded" germanium of the type  $\overset{\text{Ge}-----\text{X}}{\searrow CH_2 \nearrow}$.

Introduction. In several recent papers, Egorochkin et al. [1,2] have reported doublets in the GeH stretching region of the IR spectra of organogermanes containing the groupings $>GeHCH_2Cl$ and $>GeHCHCl_2$ These doublets they suppose to derive from germanium atoms which are either "free", or "intramolecularly-bonded" as represented by  $\overset{H\searrow}{\underset{\swarrow\ |}{>}}\text{Ge}----\text{Cl}$ $(\searrow CH_2 \nearrow)$ Similar conclusions were drawn for some R_2SiHCH_2Cl compounds [3].

A more plausible explanation for these doublets is that they derive from the rotational conformers that must be present The effects of rotational conformation on CH bond strengths have been demonstrated in many molecules by the partial deuteration method which yields "isolated" CH stretching frequencies, ν^{is}(CH) [4]. In particular the β effects of halogen have been studied extensively in alkyl halides [5] and chloralkanes [6]. For example, ν^{is}(CH) values for bonds respectively *gauche* and *trans* to Cl in EtCl are 2972 4 and 2945.0 cm^{-1} [5].

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We have now reinvestigated the gas phase IR spectra of the molecules GeH_3CH_2F, GeD_3CH_2F, GeH_3CH_2Cl and GeD_3CH_2Cl and found ν(GeH) doublets due to $GeHD_2$ impurity species in the GeD_3 compounds. Similar doublets due to MHD_2 impurity species can likewise be identified in earlier work on SiD_3CH_2Cl, SiD_2CH_2Br [7] and GeD_3CH_2Br [8]. These are all molecules for which selective microwave studies [9—11], and the earlier vibrational spectra elsewhere than in the ν(MH) region [7,8], leave no doubt that only one structure for the MH_3CH_2X species is present in the gas phase.

Experimental. IR spectra were recorded on a Nicolet 7199 'FTIR spectrometer with a resolution of 0 25 cm^{-1} and a frequency accuracy of 0.01 cm^{-1} $GeCl_3CH_2Cl$ was prepared and reduced by $LiAlH_4$ or $LiAlD_4$ as in [7] The corresponding fluorides were prepared by treating CH_2BrF with germyl sodium-h_3 or -d_3 as in [11].

Results. The IR spectra are shown in Fig. 1, the corresponding frequencies in Table 1.

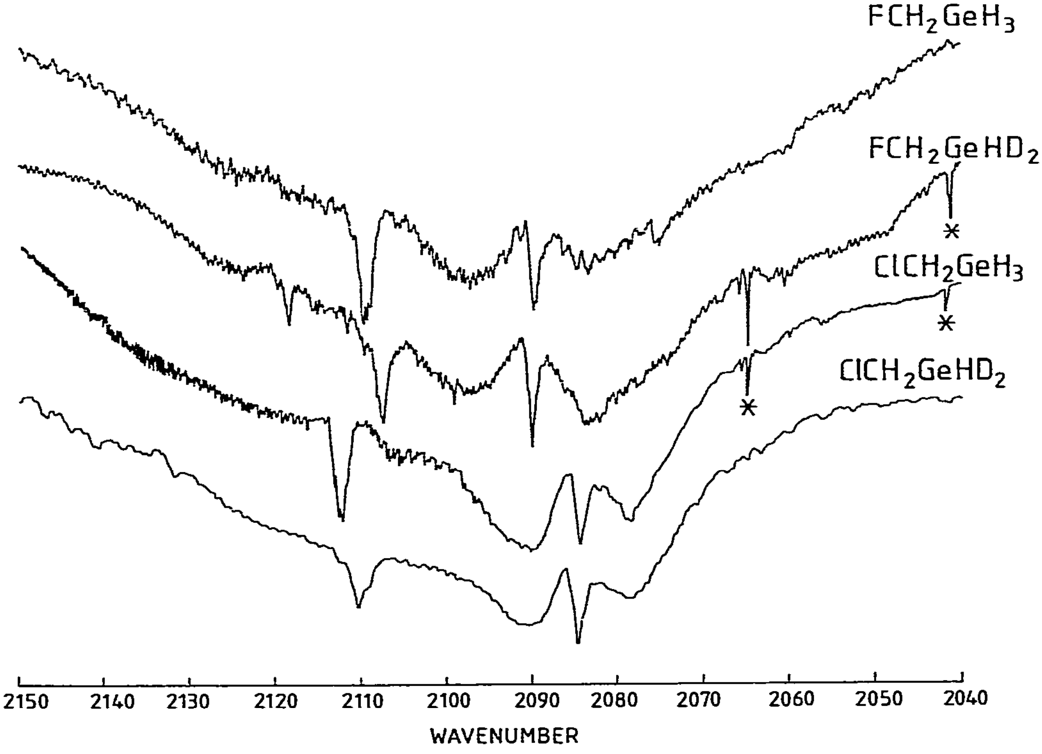

Fig 1. IR spectra in vapour phase of GeH_3CH_2F, GeH_3CH_2Cl and GeH impurities in GeD_3CH_2F and GeD_3CH_2Cl. H_2O lines are identified by ★ A further impurity peak at 2117 cm^{-1} is present in the GeD_3CH_2F spectrum

TABLE 1

GeH AND SiH STRETCHING FREQUENCIES (cm^{-1})
(H^H, H^X signify hydrogens respectively *trans* to H X)

		X = F	Cl	Br
$GeHD_2CH_2X$	$\nu(GeH^H)$	2107 4 C^a	2110 2 C^a	2108 C^b
	$\nu(GeH^X)$	2090.1 A^a	2084.74 A^a	2079,'B'^{b}
	$\Delta\nu(H^H - H^X)$	17 3	25 5	29(2)
GeH_3CH_2X	$\nu_{as}(GeH_2{}^H)$	2109 4,C^a	2112 58 C^a	2112 C^c
	$\nu(GeH^X)$	2089 8 A^a	2084 74 A^a	2080 5 B^c
$SiHD_2CH_2X$	$\nu(SiH^H)$		2193,C^b	2193,C^b
	$\nu(SiH^X)$		2166,B^b	2162 B^b
	$\Delta\nu(H^H - H^X)$		27	31
SiH_3CH_2X	$\nu_{as}(SiH_2{}^H)$		2197,C^c	2197 C^c
	$\nu(SiH^X)$		2168 A/B^c	2164 A/B^c

[a] This work. [b] Deduced from data in [7,8] assuming (A) their MH_3 frequencies are more accurate than their MHD_2 impurity ones, (B) a calibration shift of 2 cm^{-1} as evidenced by a comparison of our and their data for GeH_3CH_2Cl and (C) a 2 cm^{-1} shift from $\nu(MHD_2)$ to $\nu_{as}(MH_2{}^H)$. The resulting uncertainties must be about ± 2 cm^{-1} [c] Data in [7,8]

Assignment. Two bands are seen in each case, a type C one at high frequency, and an A/B one, lower down. The spectra of the GeH impurity species in the GeD_3 compounds are almost identical with those of the pure GeH_3 species, only the higher band being displaced by about 2 cm^{-1} * The impurity species is identified as primarily $GeHD_2$ on two grounds. First extensive experience with $LiAlD_4$ reductions of MCl_3 groups have shown us that the proportion of MH_2D species resulting is of minor importance. Secondly, a simple calculation shows that a third of the molecules of such species (those with two identical MH bonds) will produce a high frequency $\nu_{as}(MH_2)$ band coincident in frequency with the $\nu_{as}(MH_3)$ band. Only a trace of such absorption is visible in Fig. 1 for the fluoride, perhaps more for the chloride**.

With this interpretation of the impurity bands in GeD_3CH_2F, Cl we can now identify similar bands in GeD_3CH_2Br [8] and SiD_3CH_2Cl, Br [7] as due not to MH_3 species, but to MHD_2 and possibly MH_2D ones The gas phase contours then immediately identify the MH bonds concerned. The type C band derives from the MH_a bonds out of the skeletal plane, the type A one from the single MH_s bond in the plane. We denote these bonds by MH^H and MH^X according as they lie *trans* to H (*gauche* to X) and *trans* to X respectively. Our choices of ν^{is}(MH) for these molecules are then listed in Table 1.

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*The indistinguishability at low resolution of the MH_3 and MHD_2 bands was clearly responsible for the earlier misassignments of the latter to MH_3CH_2X impurity [7,8]

**The same calculation shows that the other MH_2D species (those with 2 different MH bonds) produce frequencies coincident with those of the MHD_2 ones Thus our interpretation of the spectra is quite independent of the proportions of MHD_2 and MH_2D Both yield "isolated" MH stretching frequencies. This curious result is linked with the virtual identity of the MH_3 and MHD_2/MH_2D spectra and stems from the fact that coupling between two GeH bond stretching motions in a GeH_3 or GeH_2 group is negligible as soon as the bonds differ slightly in strength The lower band in the GeH_3 spectrum is about 100% $\nu(GeH^X)$, its description as $\nu_s(GeH_3)$ is wholly inappropriate Coupling between identical GeH bonds amounts to only 2 cm^{-1}.

TABLE 2

SUBSTITUENT EFFECTS OF HALOGEN ON ν^{is}(GeH) AND ν^{is}(CH)

$S^{X} = \nu^{is}(MH)_{MH_3CH_3X} - \nu^{is}(MH)_{MH_3CH_3}$

	S_g^X	S_t^X		S_g^X	S_t^X
GeH_3CH_2F	22.8	5.5	CH_3CH_2F	23.5	7.0
Cl	25.6	0.1	Cl	22.4	−5.0
Br	23(2)	−6(2)	Br	21.5	−13.6
			I	18.6	−22.0

ν^{is}(MH) for reference compounds

GeH_3CH_3	2084.6	CH_3CH_3	2950

Discussion. The *gauche* and *trans* effects of halogen produce ν(GeH) differences of 17.3 (F), 25.5 (Cl) and 29 cm^{-1} (Br) in the GeH_3CH_2X compounds. Similar differences due to conformation must also occur in R_2GeHCH_2X and $R_2GeHCHX_2$ compounds. Since the splittings reported by Egorochkin et al. for the latter, where X = Cl, lie in the range 19—24 cm^{-1}, we conclude that they originate from the two conformations of the GeH bond relative to chlorine, rather than from "free" and "intramolecularly-bonded" germanium The data in their work which concern the effects of temperature and substituents on the relative intensities of the two bands, then bear on the relative stabilities of the two conformers, in which either a GeH or a GeR bond is *trans* to halogen.

Our reassignment of the $MHCH_2X$ and $MHCHX_2$ ν(MH) doublets does not preclude the possibility of intramolecular M---Cl bonding in $M(CH_2)_3Cl$ systems as proposed in [12]. Here the problem is to disentangle the effects of the primary conformational variation in ν(GeH), which arises from $\nu(MH^{H})$ and $\nu(MH^{CH_2})$ and is expected from our work on alkylgermanium compounds to be about 6 cm^{-1} [13], from those of the M---Cl bonding, which appear to be about 3 cm^{-1} [12].

It remains to consider whether the *trans* and *gauche* effects of halogen in GeH_3CH_2X compounds are in any way unusual, as compared for instance, to those in ethyl halides.

Table 2 compares the substituent effects for the two series. The absolute *gauche* effects S_g^X are very similar, the proportional effect on ν(GeH) being 50% greater than that on ν(CH). The trend in S_t^X, F > Cl > Br, is the same in both cases, but rather less pronounced for GeH than for CH. No dramatic conclusions emerge from the comparison.

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