Preparation and Properties of some Silyl- and Germyl-halogenoacetylenes and of Digermylacetylene

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The compounds $\mathrm{H_3SiCCCl}$, $\mathrm{D_3SiCCCl}$, $\mathrm{H_3SiCCBr}$, $\mathrm{H_3GeCCCl}$, $\mathrm{H_3GeCCGeH_3}$, and $\mathrm{H_3SiCCSiH_3}$ have been prepared by reaction of silyl or germyl halides with the lithium and sodium derivatives Li(CCCl), $\mathrm{Li_2C_2}$, and Na(CCBr). They have been characterised by a variety of physical and spectroscopic techniques (i.r., Raman, u.v., and photoelectron spectroscopy). Normal-co-ordinate analysis of the vibrational data shows that most vibrations of these molecules are isolated, but that the two low-frequency stretches and the two skeletal bends are strongly coupled.

THE silyl- and germyl-substituted acetylenes $\mathrm{H_3MCCH}$ (M = Si or Ge), $\mathrm{H_3SiCCSiH_3}$, and $\mathrm{H_3SiCCMe}$ have been prepared and their vibrational spectra reported.[1-4] The photoelectron spectra of silylacetylene and disilylacetylene have also been reported.[5] We have prepared the new compounds $\mathrm{H_3MCCCl}$ (M = Si or Ge), $\mathrm{H_3SiCCBr}$, and $\mathrm{H_3GeCCGeH_3}$ and studied their physical properties and their electronic and vibrational spectra. A new preparation of disilylacetylene is also described, together with a fuller account of some of its spectroscopic properties.

The chloroacetylenes were prepared by the reaction of $\mathrm{SiBrH_3}$, $\mathrm{SiBrD_3}$, or $\mathrm{GeClH_3}$ with chloroethynyl-lithium, Li(CCCl), generated by reaction of 1,2-dichloroethylene with methyl-lithium in diethyl ether. The product of reaction of excess of LiMe with tetrabromoethane, essentially pure $\mathrm{Li_2C_2}$, reacted with $\mathrm{SiBrH_3}$ or $\mathrm{GeClH_3}$ to give disilyl- or digermyl-acetylene. Reaction of 1,2-dibromoethylene with sodium in liquid ammonia gave Na(CCBr) (CAUTION: dangerously sensitive to shock, explosive when dry), which reacted with $\mathrm{SiFH_3}$ to give $\mathrm{H_3SiCCBr}$. The reactions involved are presumed to be

$$\mathrm{2LiMe + CHClCHCl \xrightarrow{OEt_2} LiCl + Li(CCCl) + 2MeH} \quad (1)$$

$$\mathrm{Li(CCCl) + SiBrH_3 \longrightarrow LiBr + H_3SiCCCl} \quad (3)$$

$$\mathrm{4LiMe + CHBr_2CHBr_2 \xrightarrow{OEt_2} 2LiBr + 2MeBr + 2MeH + LiCCLi} \quad (3)$$

$$\mathrm{LiCCLi + 2SiBrH_3 \longrightarrow 2LiBr + H_3SiCCSiH_3} \quad (4)$$

$$\mathrm{2Na + CHBrCHBr \xrightarrow{NH_3} NaBr + Na(CCBr) + H_2} \quad (5)$$

$$\mathrm{Na(CCBr) + SiFH_3 \longrightarrow NaF + H_3SiCCBr} \quad (6)$$

(1)—(6), with analogous reactions for the germyl compounds starting with $\mathrm{GeClH_3}$.

EXPERIMENTAL

Silyl bromide, [^{2}H$_3$]silyl bromide, and germyl chloride were prepared by standard methods and handled in a vacuum system. Lithium and sodium derivatives of acetylenes were prepared *in vacuo* or dry $\mathrm{N_2}$ using commercial starting materials. Reactions between solid and volatile reactants were carried out *in vacuo*, after removing solvent by pumping at room temperature, and volatile products were fractionated on the vacuum line.

Preparations.—(*a*) 1-*Chloro*-2-*silylacetylene*. Methyl-lithium (12.0 mmol) in diethyl ether was transferred under nitrogen to a glass ampoule fitted with a greaseless tap. The contents were cooled to 195 K, the ampoule was evacuated to remove nitrogen, and 1,2-dichloroethylene (*cis* or *trans*) (6.0 mmol) condensed in at 77 K on a vacuum line. Reaction commenced on warming the system to room temperature, rapid effervescence showing the formation of methane. After evolution of methane had ceased the gas was pumped away and the ether solvent removed by pumping, first at a low temperature to prevent bumping. Finally, the white solid residue was freed from as much residual ether as possible by pumping at room temperature for at least 1 h. Silyl bromide (6.0 mmol) was then condensed into the vessel and the contents allowed to react at room temperature for 5 min. The volatile products were transferred to a trap at 77 K; fractionation at 177, 153, and 77 K gave the impure *product*, contaminated with a trace amount of diethyl ether (trapped at 177 K) with the major volatile by-products HCCCl (trapped at 153 K) and $\mathrm{SiH_4}$ (trapped at 77 K). Removal of ether from the product was achieved by formation of a complex with $\mathrm{BF_3}$, which does not react with $\mathrm{H_3SiCCCl}$. Excess of gaseous $\mathrm{BF_3}$ was added to the gaseous impure product; fractionation at 238, 153, and 77 K gave $\mathrm{OEt_2{\cdot}BF_3}$ trapped at 238 K, excess of $\mathrm{BF_3}$ at 77 K, and pure $\mathrm{H_3SiCCCl}$ (4.1 mmol, 68% based on $\mathrm{SiBrH_3}$) at 153 K.

Similar reactions using $\mathrm{SiBrD_3}$ or $\mathrm{GeClH_3}$ gave $\mathrm{D_3SiCCCl}$ or $\mathrm{H_3GeCCCl}$ (the latter in rather lower yields, *ca.* 55%). Diethyl ether could be removed from the germyl derivative by trap-to-trap distillation, and treatment with $\mathrm{BF_3}$ was unnecessary. Reactions using $\mathrm{SiFH_3}$ and $\mathrm{SiClH_3}$ produced $\mathrm{H_3SiCCCl}$, but gave no advantages over the use of $\mathrm{SiBrH_3}$.

(*b*) *Disilylacetylene*. Methyl-lithium (20 mmol) and 1,1,2,2-tetrabromoethane (5 mmol) were allowed to react together in diethyl ether at room temperature (1 h). Volatile products and solvent were removed *in vacuo* and the residual solid was pumped for 1 h to remove residual ether. Silyl bromide (10 mmol) was condensed into the

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[1] E. A. V. Ebsworth, S. G. Frankiss, and W. J. Jones, *J. Mol. Spectroscopy*, 1964, **13**, 9.

[2] R. W. Lovejoy and D. R. Baker, *J. Chem. Phys.*, 1967, **46**, 658.

[3] D. W. Robinson and R. B. Reeves, *J. Chem. Phys.*, 1962, **37**, 2625.

[4] R. C. Lord, D. W. Mayo, H. E. Opitz, and J. S. Peake, *Spectrochim. Acta*, 1958, **12**, 147.

[5] W. Ensslin, H. Bock, and G. Becker, *J. Amer. Chem. Soc.*, 1974, **96**, 2757.

evacuated ampoule and allowed to react at room temperature for 5 min. Volatile products were condensed in a trap at 77 K, and fractionated at 153 K. Silane and H_3SiCCH were volatile at this temperature; the trap at 153 K contained a mixture of $H_3SiCCSiH_3$ and ether, from which the latter was removed by prolonged evaporation *in vacuo* at 195 K. This left pure $H_3SiCCSiH_3$ (3.5 mmol, 70%).

A similar reaction using $GeClH_3$ in place of $SiBrH_3$ gave *digermylacetylene* (50% yield), condensing at 209 K *in vacuo*.

(*c*) 1-*Bromo*-2-*silylacetylene*. Sodium (230 mg, 10 mmol) was dissolved in liquid ammonia (*ca.* 5 cm^3) and 1,2-dibromoethylene (5 mmol) condensed in. When the blue colour had been discharged (after *ca.* 30 min at 209 K) the H_2 and ammonia were cautiously removed, keeping the solution at 209 K. When all the liquid had evaporated the solid was allowed to warm slowly to room temperature and left under dynamic vacuum for several hours to remove residual ammonia. The dry material was extremely sensitive to shock and stringent precautions were taken against the effects of possible explosions. Silyl fluoride (5 mmol) was allowed to react with the dry solid for 5 min at room temperature, and the volatile products were removed and fractionated at 177 K to remove SiH_4 and $O(SiH_3)_2$. The impure product still contained HCCBr, which was removed by prolonged evaporation from a trap held at 195 K. This left pure $H_3SiCCBr$ (2 mmol, 40%). The use of $SiBrH_3$ in place of $SiFH_3$ gave no $H_3SiCCBr$.

Instruments.—Routine i.r. spectra in connection with preparations and fractionations were obtained using Perkin-Elmer 457 or 577 grating spectrophotometers. Definitive i.r. spectra of pure samples were run on a Perkin-Elmer 225 (200—5 000 cm^{-1}) or a Beckman RIIC IR720 interferometer (20—400 cm^{-1}). Raman spectra were obtained using a Cary 83 with 488-nm argon-ion excitation or a Spex instrument at the University of Glasgow with 514.5-nm argon-ion excitation. Mass spectra were recorded using an A.E.I. MS902, and n.m.r. spectra using Varian Associates HA100 (^1H) and XL100 (^{13}C) instruments. Photoelectron spectra were run on a modified Perkin-Elmer PS16, and u.v. spectra in 100-mm gas cells on a Unicam SP 800 spectrometer.

RESULTS AND DISCUSSION

Physical Properties.—The compounds prepared were characterised by determination of their molecular weights (Dumas bulb), vapour pressures over a range of temperature, and melting points. In addition, exact mass measurements on selected peaks in the mass spectra confirmed the atomic compositions of the most abundant ions in the *m*/*e* range close to the expected molecular ion; in general, these had one hydrogen atom less than the expected molecular ion. Measured masses were within 2 p.p.m. of those expected. The physical data are listed in Table 1. Vapour-pressure data for disilylacetylene have been published previously;[4] our sample gave vapour pressures agreeing very closely with those calculated from the relation given.

Mass Spectra.—Each compound gave a group of peaks (because of Si or Ge isotopes and ready M–H bond cleavage) in the region expected for the molecular ion. Major breakdown paths for the halogenoacetylenes involve loss of halogen, followed by M–C bond cleavage; an alternative path, which involves a metastable ion, leads to extrusion of C_2 leaving $[MXH_n]^+$, which gave rise to the strongest group of peaks at high ionising voltage in the spectrum of $H_3SiCCCl$. Disilyl- and digermyl-acetylenes fragment both by loss of MH_n groups giving $[H_nMCO]^+$ and by extrusion of C_2 giving $[M_2H_n]^+$.

TABLE 1

Physical properties of silyl- and germyl-acetylenes

Compound	*M*	Vapour pressure * *a*/K	 *b*	B.p. (*T*/K)	M.p.
$H_3SiCCCl$	90 ± 3	−1 645	8.263	305	187
$H_3SiCCBr$	135 ± 3	−1 763	8.194	332	234
$H_3GeCCCl$	139 ± 4	−1 761	8.232	329	117
$H_3GeCCGeH_3$	173 ± 5	−1 824	8.078	351	255
$H_3SiCCSiH_3$	90 ± 3	−1 434 †	7.417 †	316 †	214

* From $\log_{10}(p/\text{Torr}) = a(T/\text{K})^{-1} + b$. † From ref 4.

N.M.R. Spectra.—The ^1H n.m.r. spectra of the silyl compounds (in solution in $SiMe_4$ or $CDCl_3$) showed a single main peak in each case, with ^{29}Si satellites. The germyl compounds gave only a single peak. The ^{13}C spectrum of $H_3SiCCBr$ contained two peaks; no ^{29}Si satellites were observed because of the very low spectrum intensity associated with long relaxation times. Chemical shifts and coupling constants are listed in Table 2.

Electronic Spectra.—The photoelectron spectra of the halogenoacetylenes, excited with He(I) (21.22 eV) radiation, contain three bands at binding energies <15 eV, of which two are strong and comparatively narrow while the third is much broader and has a lower peak height, although the relative areas are similar for all three bands. In this region we expect the bands associated with $\pi(CC)$ and halogen np_π levels, as in the halogenoacetylenes HCCX,[6] and the MH bonding levels ($a_1 + e$ in C_{3v}) derived from M np atomic orbitals. Analogy with the spectra of silylacetylene[5] and the halogenoacetylenes[6] suggests that the two strong bands are associated with combinations of acetylene and halogen levels, interacting very strongly, and that the broader band between them (or underlying the second strong band in the spectrum of $H_3SiCCBr$) is due to ionisation from both a_1 and e levels associated with the MH_3 group. The e level may well be involved in

TABLE 2

N.m.r. parameters for silyl- and germyl-acetylenes

Compound	Solvent	$\delta(^1H)$ [a]/ p.p.m.	$\delta(^{13}C)$ [b]/ p.p.m.	$^1J(^{29}SiH)$ [c]/ Hz
$H_3SiCCCl$	$SiMe_4$	3.82	n.o.	217
$H_3SiCCBr$	$CDCl_3$	3.90	6.6, 74.9	220
$H_3SiCCSiH_3$	$SiMe_4$	3.81	n.o.	216
$H_3GeCCCl$	$SiMe_4$	4.00	n.o.	
$H_3GeCCGeH_3$	$CDCl_3$	4.09	n.o.	

[a] ±0.02 p.p.m. [b] ±0.1 p.p.m.; n.o. = not observed. [c] ±1 Hz.

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[6] E. Kloster-Jensen and E. Heilbronner, *Helv. Chim. Acta* 1970, **53**, 331, 1073.

hyperconjugative interactions as in H_3SiCCH, but this effect cannot readily be distinguished in the presence of the strongly interacting halogen-atom levels. The a_1 level probably gives rise to the first maximum of the broad band; it will have both MH and MC σ-bonding character, probably with MH predominating.

At >15 eV each spectrum contains a band of moderate intensity near 17 eV that we may assign to the CX bonding level, and a weaker band near 19 eV that we attribute to the σ-bonding level derived from the M *ns* valence orbital, which will be largely MC bonding. The remaining bonding level (CC σ, corresponding to $1a_1$ in H_3SiCCH where it is found [5] at 20.4 eV)* is expected to be shifted to higher binding energy by the substitution of a halogen atom for hydrogen. A weak broad band at 23.4 eV binding energy in the spectrum of $H_3SiCCCl$ excited by He(II) (40.8 eV) radiation is probably due to this level. No bands are observed that can be associated with halogen *ns* lone-pair levels. The assignments suggested above are set out in Table 3, together with the spectrum of digermylacetylene, with assignments analogous to those for disilylacetylene.[5]

TABLE 3

Photoelectron spectra (vertical ionisation potentials in eV) of silyl- and germyl-acetylenes

H_3Si-CCCl	H_3Si-CCBr	H_3Ge-CCCl	Assignment	H_3Ge-$CCGeH_3$	Assignment
10.22	10.17	10.19	$3e$(CC π–X np)	10.13	$2e_g$(CC π)
12.54	12.52	12.45	$5a_1$(MH,MC)	12.1	$3a_{1g}$(GeH,GeC)
12.7 13.2	13.2	12.75	$2e$(MH)	12.6	$1e_u$ $1e_g$(GeH)
13.92	13.8	13.83	$1e$(X np + CC π)	14.0	$2a_{2u}$(GeH, GeC)
17.2	16.4	17.1	$4a_1$(CX)		
18.7	18.6	18.8	$3a_1$(MC,MH)	18.1	$2a_{1g}$(GeC,GeH)
23.4 *	n.o.	n.o.	$2a_1$(CC σ)	19.23	$1a_{2u}$(GeC, GeH)

* He(II) excitation.

Vibrational fine structure is present on the first bands of the spectra of $H_3SiCCCl$ and $H_3SiCCBr$, and on the second band of $H_3SiCCCl$. In all three cases, as for H_3SiCCH, the vibrational interval is *ca.* 900 cm^{-1}; this may be assigned to the SiH_3 deformation mode, excited because of hyperconjugative interactions, or to the SiC stretching mode. Only in H_3SiCCl is the band due to the SiH bonding levels distinct enough to show the effects of Jahn–Teller distortion in the ion. No clear splittings due to halogen-atom spin–orbit coupling can be seen.

The u.v. spectra of the three MH_3 halogenoacetylenes have been recorded; for the chlorides the only feature attributable to the acetylene is a strong band starting near 43 000 cm^{-1} with intensity increasing to beyond 50 000 cm^{-1}. The compound $H_3SiCCBr$ showed a similar strong band starting near 39 000 cm^{-1}, with a broad maximum at 47 000 cm^{-1}, followed by increasing absorption after a minimum near 49 000 cm^{-1}. These bands are very similar in energy to those observed for HCCCl [7] and HCCBr [8] near 50 000 and 48 000 cm^{-1} respectively; however, there is no sign of the long progression reported for HCCCl on the corresponding band of $H_3SiCCCl$. We attribute the bands to $\pi^* \leftarrow \pi$ transitions, as in the monohalogenoacetylenes.

Vibrational Spectra.—(*a*) *Halogenoacetylenes.* The halogenoacetylenes H_3MCCX are expected to have linear skeletons, with C_{3v} symmetry; there are then five fundamental vibrations of a_1 symmetry and five of e symmetry, all active in both the i.r. and Raman spectra. In the i.r. spectrum of the gas, bands of the two symmetry species can in general be distinguished by means of their band contours, a_1 vibrations giving rise to parallel bands with *PQR* contours and e modes giving perpendicular bands which may or may not show progressions of *Q* sub-branches depending on the value of the coriolis zeta constant. In general one expects values of zeta near zero for vibrations involving the hydrogen atoms, giving *Q*-branch progressions, and values of zeta near unity, giving broad featureless bands for other modes of this symmetry species. In the Raman spectrum of the liquid the two symmetry species can in principle be distinguished using polarisation data; the gas-phase Raman spectrum gives band-contour information inasmuch as bands due to a_1 vibrations should show a very sharp prominent *Q* branch, which may be the only discernible feature, whereas e modes give rise to broader bands in which *O*, *P*, *R*, and *S* branches may give a single or a double maximum. In principle, *Q* sub-branches may form progressions in each branch as in the i.r., but we have not resolved them.

The observed bands are listed in Supplementary Publication No. SUP 22245 (3 pp.),† with suggested assignments. The assignments for $H_3SiCCCl$ are typical, and are now discussed in detail. The 2 000—2 200 cm^{-1} region is expected to contain bands due to three fundamentals, the acetylenic CC stretch, ν_2, and the SiH stretching modes of a_1 and e symmetry, ν_1 and ν_6 respectively; two strong parallel bands are observed in the i.r., with superimposed *Q* sub-branches from the perpendicular band, and there are two strong polarised bands in the Raman spectrum of the liquid. The gas-phase Raman spectrum shows two strong bands, one very sharp as expected for a symmetric vibration, assigned to ν_1, with ν_6 hidden beneath it, and one broader band that has a sequence of ' hot bands ' to lower frequency; we assign this group to ν_2 with hot bands due to excitation of the low-frequency bend. The band due to ν_2 is overlaid by ν_6 in the i.r., but the corresponding band in the i.r. spectrum of $D_3SiCCCl$ shows a broad irregular contour due to a set of overlapping hot bands.

Between 900 and 1 000 cm^{-1}, where we expect and find a parallel and a perpendicular band due to SiH_3

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* Throughout this paper: 1 eV $\approx 1.60 \times 10^{-19}$ J; 1 Torr = (101 325/760) Pa.

† For details see Notices to Authors No. 7 in *J.C.S. Dalton*, 1977, Index issue.

[7] R. Thompson and P. A. Warsop, *Trans. Faraday Soc.*, 1969, **65**, 2806.

[8] R. Thompson and P. A. Warsop, *Trans. Faraday. Soc.*, 1970, **66**, 1871.

deformations, there is in addition a band at 917 cm^{-1}, which has a parallel contour in the i.r., a prominent *Q* branch in the gas-phase Raman, and is polarised in the liquid-phase Raman spectrum. This is clearly a fundamental of a_1 symmetry, ν_4, and must be a skeletal stretch; the other a_1 fundamental, another skeletal stretch, must be assigned to the moderately strong polarised band in the Raman spectrum of the liquid at 448 cm^{-1}, which corresponds to a strong i.r. band of indeterminate contour at 436 cm^{-1} and a strong band in the gas-phase Raman spectrum at 434 cm^{-1}. Like the i.r. band, the gas-phase Raman band has a broad contour, probably because of hot bands.

The three remaining fundamentals, all of *e* symmetry, comprise the silyl rock, ν_8, and two skeletal bends. The rock is clearly seen in the i.r. as a strong band with a progression of *Q* sub-branches near 690 cm^{-1}, but gives no discernible band in the gas-phase Raman spectrum and only a very weak band in the Raman spectrum of the liquid. The higher-frequency bend, ν_9, gives a strong Raman band, depolarised in the liquid phase, and showing two maxima (due to prominent *O* and *S* branches) in the gas phase. The corresponding i.r. band is weak. The lowest-frequency fundamental, ν_{10}, is moderately strong both in the i.r. and in the Raman spectrum; again the gas-phase Raman band has prominent *O* and *S* branches.

A weak band in both the i.r. and Raman spectra near 230 cm^{-1} (gas phase) may be due to $2\nu_{10}$ or to $\nu_9 - \nu_{10}$. Two weak *Q* branches in the gas-phase Raman spectrum in the region of ν_8 must be assigned to the a_1 components of $2\nu_9$ and $\nu_5 + 2\nu_{10}$; $2\nu_9$ appears as a polarised band in the Raman spectrum of the liquid. Many other overtone and combination bands are observed in the spectra, particularly in the i.r.; the assignments are summarised in SUP 22245. A list of the fundamentals for all the halogenoacetylene derivatives we have studied is given in Table 4. The band positions listed for perpendicular bands that show fine structure are derived from detailed analyses that we shall report separately.

TABLE 4

Fundamental vibration band (cm^{-1}) for H_3MCCX

Mode [b]	H_3Si-CCCl	D_3Si-CCCl	H_3Si-CCBr	H_3Ge-CCCl	Description of mode [a]
ν_1 a_1	2 193.1	1 574.8	2 192.8	2 116	ν(MH)
ν_2	2 164.3	2 166.7	2 148.2	2 172	ν(CC)
ν_3	938.9	691.2	932.4	833	$\delta(MH_3)$
ν_4	917.1	922.5	832.2	888	Skeletal str.
ν_5	436	420	360.7	348	Skeletal str.
ν_6 e	2 192.4	1 602.3	2 192.2	2 117.5	ν(NH)
ν_7	946.6	674.3	946.0	884.1	$\delta(MH_3)$
ν_8	682.4	535	681.7	624.3	$\rho(MH_3)$
ν_9	351	344	325.5	339 [c]	Skeletal bend
ν_{10}	119	116	114	116	Skeletal bend

[a] See text for a discussion of mixing of modes. [b] Numbering is appropriate for $H_3SiCCCl$. [c] Liquid-phase Raman spectrum.

The assignment of fundamentals to their symmetry species is only the first step in analysing the vibrational motions of a molecule. We have attempted to suggest plausible assignments in terms of group frequencies, but it is clear that some modes (in particular the two low-frequency skeletal stretches and the two skeletal bends) can only be described as combinations of local modes. We have attempted to assess the degree to which these and other modes are coupled (mixed) by using normal-co-ordinate analysis (n.c.a.). Unfortunately, as is well known, the vibrational motion of a single isotopic species is very much underdetermined by the frequencies of its normal vibrations, of which there are only 10 (five for each symmetry species) in these molecules, compared with the 30 force constants required to define even a quadratic force field. Data on isotopic molecules, which may be presumed to have the same force field but different mechanical properties (expressed as a *G* matrix), can help to reduce the degree of indeterminacy, but it is still not possible to calculate a force field that is unequivocally correct. (It may be noted that assigning a zero value to any off-diagonal element in the force-constant matrix *F* is just as arbitrary as assigning any other value, and can hardly be regarded as reducing the essential indeterminacy of the problem.)

With these limitations in mind we have carried through the analysis for the isotopic molecules $H_3SiCCCl$ and $D_3SiCCCl$, obtaining a force field that reproduces the observed frequencies for the light molecule exactly, and the shifts observed for all the modes, except those involving SiH or SiD stretching and deformation where the effects of anharmonicity are large, to within 0.4 cm^{-1}. The only non-zero off-diagonal terms in the *F* matrices required are (a_1) between the silyl deformation and both low-frequency skeletal stretches, and between the SiC and CC stretches, and (*e*) between the two skeletal bends and between the SiCC bend and the silyl rock. This appears to represent the minimum degree of complexity of the force field required to reproduce the observed frequencies. Force fields with similar off-diagonal elements were found to reproduce the frequencies for the single isotopic species studied in the cases of $H_3SiCCBr$ and $H_3GeCCCl$.

Inspection of the 'potential-energy-distribution' matrices that result from the n.c.a. confirm that, as might be expected, the acetylenic stretch and the silyl-group vibrations are well represented by single normal modes, as suggested above, except that in $H_3SiCCBr$ the silyl deformation is rather severely mixed with the SiC stretch. The extensive mixing of the two low-frequency bends and of the two low-frequency stretches is confirmed. It must be emphasised that the confirmation of our intuitive assignments is not surprising in view of the pattern of *F*-matrix elements we have selected.

(*b*) *Digermyl- and disilyl-acetylenes*. Digermylacetylene, like its silyl analogue, is expected to have essentially free internal rotation, so its vibrations can be classified in terms of the centrosymmetric D_{3d} model. There are then $4 \times a_{1g}$, $3 \times a_{2u}$, $4 \times e_g$, and $4 \times e_u$ genuine vibrations, excluding the internal rotation, of which a_{1g} and e_g are active only in the Raman spectrum and a_{2u} and e_u are active only in the i.r. Lord *et al.*[4] recorded gas-phase i.r. and liquid-phase Raman spectra for $H_3SiCCSiH_3$; we have also recorded gas-phase Raman data in order to assess the effects of phase on the vibration frequencies. The results are set out in Table 5; our i.r. data agree well with those of Lord *et al.*, but there are definite shifts in the Raman data in the liquid and gaseous phases. This is of some importance when we consider $H_3GeCCGeH_3$, since its low vapour pressure made it impossible to obtain gas-phase Raman spectra.

Liquid-phase Raman spectra with polarisations and gas-phase i.r. spectra for digermylacetylene are listed in Table 6. The polarisation measurements are puzzling, since there appeared to be no clear-cut distinction between *a* and *e* modes; we can only suggest that this is due to the relatively high population of vibrationally excited molecules associated with the low-frequency bend, which results in the observed bands being largely composed of hot bands rather than the fundamentals themselves. The fundamentals are listed with those of disilylacetylene in Table 6. The assignments are based on the use of i.r. band contours to help distinguish *a* and *e* modes, and analogy with disilylacetylene and with other germyl compounds. As for the halogenoacetylenes discussed above, the 'group-frequency' descriptions are subject to some uncertainty due to the effects of mixing of vibrations, although the higher symmetry results in fewer possible couplings, many being forbidden by symmetry.

TABLE 5

Fundamental vibration frequencies for H_3MCCMH_3 (M = Si or Ge)

Mode		$H_3SiCCSiH_3$		$H_3GeCCGeH_3$ [a]	Description of
		This work	Ref. 4	(This work)	vibration
ν_1	Raman a_{1g}	2 198	2 187 [b]	2 105 [b]	$\nu(MH)$
ν_2		2 140	2 132 [b]	2 127 [b]	$\nu(CC)$
ν_3		946	930 [b]	844 [b]	$\delta(MH_3)$
ν_4		411	420 [b]	339 [b]	$\nu(MC)$
ν_5	I.r. a_{2u}	2 189.0	2 170	2 113.1	$\nu(MH)$
ν_6		913.4	912	842.3	$\delta(MH_3)$
ν_7		809.3	807	688.6	$\nu(MC)$
ν_8	Raman e_g	2 194	2 187 [b]	2 105 [b]	$\nu(MH)$
ν_9		947	946 [b]	876 [b]	$\delta(MH_3)$
ν_{10}		680 [c]	607 [b]	624 [b]	$\rho(MH_3)$
ν_{11}		293	297 [b]	278 [b]	$\delta(MCC)$
ν_{12}	I.r. e_u	2 192.1	2 190	2 113.6	$\nu(MH)$
ν_{13}		943.8	946	883.2	$\delta(MH_3)$
ν_{14}		681.8	682	623.4	$\rho(MH_3)$
ν_{15}		102		91	$\delta(MCC)$

[a] Numbering in a_{1g} is appropriate for $H_3SiCCSiH_3$. [b] Liquid phase; all the other values are for the gas phase. [c] From combinations.

TABLE 6

Vibrational bands of $H_3GeCCGeH_3$

Infrared (gas phase)				Raman (liquid phase)		
$\tilde{\nu}/cm^{-1}$	Strength	Contour	Assignment	$\tilde{\nu}/cm^{-1}$	Strength	Polarisation (%)
4 246	vw	br	$\nu_2 + \nu_5$			
4 163	vw	⊥	$\nu_8 + \nu_{12}$			
4 158	vw	∥				
3 015	w	br	$\nu_9 + \nu_{22}$			
2 986	w	br	$\nu_5 + \nu_8$			
2 966	w	br	$\nu_2 + \nu_6$			
2 957	w	br	$\nu_3 + \nu_5$			
2 954	w	⊥	$\nu_6 + \nu_8$			
			ν_2	2 217	w	70
2 116.5	vs	⊥	ν_{12}			
2 113.6	vs	∥	ν_5			
			ν_1, ν_8	2 105	vs	90
1 841	vw	br				
1 760	vw	⊥	$\nu_9 + \nu_{13}$			
1 752	vw	∥				
1 510	vw		$\nu_{10} + \nu_{13}$			
1 480	vw	br	$\nu_9 + \nu_{14}$			
1 430	vw		$\nu_6 + \nu_{10}$			
1 310	vw					
1 255.5	vw	⊥	$\nu_{10} + \nu_{14}$			
1 245.2	vw	∥				
1 135	vw	∥	$\nu_6 + \nu_{11}$			
886.2	vs	⊥	ν_{13}			
			ν_9	876	vs	60
			ν_3	844	vs	80
842.3	vs	∥	ν_6			
756.2	w	∥	?			
688.6	vs		ν_7			
			ν_{10}	624	vw	70
623.9	vs	⊥	ν_{14}			
			$^2\nu_{11}$	596	vw	80
426	vw	br	$\nu_4 + \nu_{15}$			
356	w		$\nu_{11} + \nu_{15}$			
			ν_4	339	vw	
			ν_{11}	278	vs	60
91	m		ν_{15}			

The perpendicular (e_u) i.r. bands show rotational fine structure due to overall and internal rotation; we shall report the results of an analysis of these bands, and those of disilylacetylene, separately.

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