Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

THE VIBRATIONAL SPECTRA OF THE METHYLBROMOGERMANES

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(Received February 16th, 1970)

SUMMARY

The IR and Raman spectra of the methylbromogermanes have been measured. Vibrational assignments are proposed based on characteristic group frequencies, rotational splitting in the IR (in gas phase) and Raman polarisation data.

INTRODUCTION

In a previous study [1a] of the spectra of Me_nGeCl_{4-n} the number of bands observed in the low frequency range was notably less than the number of fundamentals. This was explained on the basis of the piling up of several skeletal fundamentals. A change of the relative mass of the halogen *vs.* the carbon atom could cancel this accidental degeneracy. Furthermore, the use of the laser as a light source in the Raman effect improves the resolution of the spectra. Moreover the rocking vibrations of the methyl group can be easily observed with the intensity gain by the use of laser excitation. For these reasons we decided to investigate the vibrational spectra of Me_nGeBr_{4-n} (see also ref. 1b). Depolarisation measurements together with the IR rotational splitting in the gas phase leads to a safer assignment of these fundamentals.

EXPERIMENTAL

CH_3GeBr_3 (I) and $(CH_3)_2GeBr_2$ (II) were prepared by passing CH_3Br over a mixture of germanium and copper[2]. $(CH_3)_3GeBr$ (III) was obtained by bromination of $(CH_3)_4Ge$[3]. Pure samples were isolated by fractional distillation over a spinning band column.

IR spectra were recorded on a Perkin–Elmer 225 grating instrument using CsI windows for the 600 cm^{-1} to 200 cm^{-1} region for both liquid and gas phase.

The Raman spectra were recorded on a Coderg PH_1 spectrometer. The light source for the Raman excitation being an O.I.P. He/Ne laser with an output of 200 mW for the 6.328 Å line. Depolarisation measurements were made by two successive recordings with the polarisation vector of the incident light turned over 90° by a half wave plate. A slit width of 2 cm^{-1} was used throughout the work. Relative intensities are not indicated as the sensitivity of the photomultiplier with S 20 response characteristics decreases strongly with increasing wavelength.

The frequencies observed in the liquid phase and their assignment to the fundamentals as discussed in the following section are given in Tables 1–3. The IR spectra in the gas phase differs from that in the liquid phase only by a slight displacement of Ge–Br stretching vibrations and the rotational splitting of few bands. The character Tables and the numbering of the fundamentals are the same as in the previous publication on methylgermanium chlorides[1a].

DISCUSSION

The CH stretching and the CH deformation fundamentals each yield two bands in the 2900 cm^{-1} and the 1250–1400 cm^{-1} region, respectively. Polarisation data allows to assign the highest frequency to the antisymmetric, the lowest to the symmetric modes. The antisymmetric stretch shows a doublet structure for (II) and (III) which might be due to a small frequency shift between the different antisymmetric modes. The CH_3 *sym* deformation in (I) shows a shoulder at the low frequency side which could arise from Fermi resonance with the overtone of the Ge–C stretch.

TABLE 1

METHYLTRIBROMOGERMANE, (I)
Vibrational frequencies in cm^{-1}.

IR Liquid	Raman		Assignment
	Liquid	Depol.	
3818 vw			$\nu_7+\nu_9$ (=3822)
3732 vw			$\nu_1+\nu_9$ (=3739)
3004 w	3002	Dp.	ν_7 (E) C–H asym. stretch.
2921 w	2918	0.04	ν_1 (A_1) C–H sym. stretch.
1857 vw			$\nu_2+\nu_3$ (=1855)
1398 m	1401	Dp.	ν_8 (E) CH_3 asym. deform.
1243 vw	1245	0.28	ν_2 (A_1) CH_3 sym. deform.
	1296		
818 vs	822	Dp.	ν_9 (E) CH_3 rocking
612 s	617	0.27	ν_3 (A_1) Ge–C stretch.
355 vw			$\nu_4+\nu_{11}$ (=357)
309 vs	312	Dp.	ν_{10} (E) Ge–Br asym. stretch.
263 s	264	0.03	ν_4 (A_1) Ge–Br sym. stretch.
	162	Dp.	ν_{12} (E) C–Ge–Br_3 bending
	125	0.54	ν_5 (A_1) Ge–Br_3 sym. deform.
	94	Dp.	ν_{11} (E) Ge–Br_3 asym. deform.

The CH_3 rocking in (I) arises as a depolarised band in the Raman spectra at 822 cm^{-1}. In (II) there are four CH_3-rocking modes, ν_5 (A_1), ν_{12} (A_2), ν_{17} (B_1) and ν_{25} (B_2). In the appropriate spectral region the IR spectrum shows three frequencies, the Raman spectrum four. This is in accordance with the nature of the expected fundamentals as the ν_{12} rocking is inactive in the IR. ν_5 is assigned to the polarised band at 851 cm^{-1} in the Raman spectrum. In the IR spectrum in the gas phase the band at 850 cm^{-1} shows a P and R branch respectively at 847 cm^{-1} and 852 cm^{-1} as can be expected from the moments of inertia for the A_1 fundamentals. The PQR

TABLE 2

DIMETHYLDIBROMOGERMANE, (II)
Vibrational frequencies in cm^{-1}.

IR Liquid	Raman		Assignment
	Liquid	Depol.	
3760 vw			$\nu_1+\nu_{25}$ (=3769)
3690 vw			$\nu_2+\nu_{25}$ (=3684)
2998 w	2994	Dp.	ν_1, ν_{10}, ν_{15}, ν_{21} C–H asym. stretch.
2913 w	2912	0.05	ν_2, ν_{22} C–H sym. stretch.
2780 vw			$2\nu_3$ (=2800)
2460 vw			$2\nu_4$ (=2488)
1870 vw			$\nu_4+\nu_{26}$ (=1877)
1828 vw			$\nu_4+\nu_6$ (=1832)
1400 m	1403	Dp.	ν_3, ν_{11}, ν_{16}, ν_{23} CH_3 asym. deform.
1244 m	1244	0.24	ν_4, ν_{24} sym. deform.
850 vs	851	Pol.	ν_5 (A_1) CH_3 rocking
823 vs	826	Dp.	ν_{17} (B_1) CH_3 rocking
	785	Dp.	ν_{12} (A_2) CH_3 rocking
771 m	772	Dp.	ν_{25} (B_2) CH_3 rocking
633 s	635	Dp.	ν_{26} (B_2) Ge–C asym. stretch.
588 s	589	0.12	ν_6 (A_1) Ge–C sym. stretch.
392 vw			$\nu_{18}+\nu_9$ (=387)
290 vs	291	Dp.	ν_{18} (B_1) Ge–Br asym. stretch.
272 vs	267	0.05	ν_7 (A_1) Ge–Br sym. stretch.
	179	0.79	ν_8 (A_1) Ge–C_2 deform.
	161	Dp.	ν_{19} (B_1) Ge–C_2 wagging
	149	Dp.	ν_{27} (B_2) Ge–C_2 rocking
	97	0.79	ν_9 (A_1) Ge–Br_2 deform.

splitting observed in the IR band at 823 cm^{-1} allows one to assign this band to ν_{17}, as the B_1 species should result into a type *A* band[4a]. A corresponding depolarised Raman band was found at 826 cm^{-1}. The remaining IR band at 771 cm^{-1} is ascribed to ν_{25}. The Raman spectrum shows a band at 772 cm^{-1} and a shoulder at 785 cm^{-1}; both are depolarised. The former corresponds to ν_{25} and we attribute the second to ν_{12}. Nevertheless the possibility remains that in the 770–790 cm^{-1} region combination tones arise from the Ge–C asymmetric stretch and the Ge–C rocking or Ge–C wagging modes as mentioned earlier[1]. However, the low intensities expected for these combination bands in the Raman effect favour the first assumption.

In product (III) two CH_3 rocking bands are observed in the Raman as well as in the IR spectra; the Raman band at 834 cm^{-1} is polarised and can be assigned to ν_5. In accordance with the frequency calculations made by Durig *et al.*[4b] this band can also be assigned to ν_{19} whereas the depolarised band at 768 cm^{-1} is to be ascribed to ν_{20}.

The Ge–C and Ge–Br stretching fundamentals can easily be assigned by comparison with the results for the Me_nGeCl_{4-n} series and for $GeBr_4$[5].

The Raman spectrum of (I) shows two bands at 94 cm^{-1} and 125 cm^{-1} respectively. The latter is polarised and should be attributed to the symmetric Ge–Br_3 deformation, whereas the former should be assigned to the antisymmetric deforma-

TABLE 3

TRIMETHYLBROMOGERMANE, (III)
Vibrational frequencies in cm^{-1}.

IR Liquid	Raman		Assignment
	Liquid	Depol.	
3820 vw			$\nu_1+\nu_5$ (=3814)
3740 vw			$\nu_1+\nu_{20}$ (=3740)
3660 vw			$\nu_2+\nu_{20}$ (=3670)
2980 m	2983	Dp.	ν_1, ν_{13}, ν_{14} C–H asym. stretch.
2910 m	2909	0.06	ν_2, ν_{15} C–H sym. stretch.
2793 vw			$2\nu_3$ (=2810)
2457 vw			$2\nu_5$ (=2486)
1858 vw			$\nu_4+\nu_{21}$ (=1859)
1812 vw			$\nu_4+\nu_6$ (=1815)
1405 m	1410	Dp.	ν_3, ν_{16}, ν_{17} CH_3 asym. deform.
1243 s	1254	0.34	ν_4, ν_{18} CH_3 sym. deform.
834 vs	834	Pol.	ν_5, ν_{19} (E) CH_3 rocking
760 m	768	Dp.	ν_{20} (E) CH_3 rocking
616 vs	620	Dp.	ν_{21} (E) Ge–C asym. stretch.
572 s	574	0.04	ν_6 (A_1) Ge–C sym. stretch.
265 vs	263	0.10	ν_7 (A_1) Ge–Br sym. stretch.
	192	0.78	ν_8 (A_1), ν_{22} (E) Ge–C_3 deform.
	152	Dp.	ν_{23} (E) Br–Ge–C_3 bending

tion. Both values are in good agreement with the data for $GeBr_4$. The remaining band at 162 cm^{-1} should be the C–Ge–Br_3 bending (ν_{12}). In (III) only two bands are observed in this region. In this case the Ge–C_3 symmetric and antisymmetric deformation fundamentals overlap each other at 192 cm^{-1}. The band at 152 cm^{-1} is assigned to the C_3–Ge–Br bending mode.

In (II) the bands at 97 cm^{-1} and 179 cm^{-1} can be attributed respectively to the $GeBr_2$ and GeC_2 deformation. Both the bands are weakly polarised. The remaining two bands at 161 cm^{-1} and 149 cm^{-1} are assigned to the GeC_2 wagging and GeC_2 rocking respectively as the rocking mode usually occurs at a lower frequency[6,7].

The twisting mode ν_{13} cannot be attributed to a band. Probably this low intensity band is obscured by one of the earlier mentioned bands.

No indication for the CH_3 torsion frequency could be obtained for these samples.

Batuev[8] and Mironov[9] have published the Raman spectra of the above samples without indicating any depolarisation data. These authors, however, did not make an assignment. Moreover their results differ in several points from ours.

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