Laser-source Raman Spectroscopy and the Raman Spectra of the Methyldiboranes

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THE recently established technique of laser-source Raman spectroscopy has enabled spectra to be obtained from small quantities of material. This can further be adapted for studying unstable compounds that present severe practical difficulties in investigation of i.r. spectra. We have obtained the Raman spectra of several methyldiboranes, which disproportionate very rapidly at room temperature and are only obtained pure in small quantities. Decomposition near room temperature is probably responsible for significant differences between the i.r. spectra of gaseous samples as reported by Lehmann *et al.*[1] and those obtained by means of multiple-interference i.r. spectroscopy.[2] Study of these compounds is of particular interest in determining what changes occur in the BH_2B bridge system of diborane when 1, 2, 3, and 4 terminal hydrogen atoms are successively substituted by methyl groups. Raman spectral data have been reported only for tetramethyldiborane $B_2H_2Me_4$.[3]

The purified samples, prepared by repeated low-temperature fractionation of equilibrated mixtures of pure diborane and trimethylborane BMe_3,[4] were sealed at $-196°$ into Pyrex capillary tubing of 1·5 mm. bore. The amount of material required was *ca.* 0·1 cm.^{3} in the liquid phase at $-70°$. Each tube had a rounded base through which the laser beam could be passed while the tube was held in a specially designed Dewar-cell holder and cooled with acetone and dry ice. The incident light from 4880 Å argon-ion laser excitation was focussed down to a thin beam such as to give a scattering volume in the form of a narrow cylinder of diameter *ca.* 0·1 mm. within the sample. The scattered light was collected through the side of the glass tube by a lens. To enlarge the small signal obtained a spectrometer was arranged such that it collected light from as large a solid angle as practical. Thus a lens of 5 cm. diameter was used at *ca.* 5 cm. from the sample and 40 cm. from the spectrometer. Polarisation data were obtained by rotating the plane of polarisation of the incident beam.

In this way we measured the Raman spectra of liquid mono-, 1,1-di-, tri-, and tetra-methyldiborane at $-70°$, at which temperature no measurable decomposition occurs. The Raman lines (wavenumbers correct to ± 3 cm.$^{-1}$ for sharp peaks), their polarisation states, and peak heights (expressed relative to 100 for the strongest peaks for each compound at about 2900 cm.$^{-1}$, no correction being made for the variation in photomultiplier sensitivity, which falls steadily to about 35% of its original value at 3000 cm.$^{-1}$ from the exciting line) are listed in the Table. To make the preliminary vibrational assignments, given in the Table, we have used the vibrational assignments calculated by Smith and Mills[5] for B_2H_6 and by Woodward *et al.*[6] for BMe_3, which compounds are regarded as end members of the series. The number of observed lines is here considerably increased because of greater molecular complexity and reduced molecular symmetry.

In the BH_2B bridge system, the B–B stretching frequency, which occurs as a strong polarised peak (split due to the natural isotopic constitution of boron) at 788 cm.$^{-1}$ in B_2H_6,[5] shifts progressively to lower frequencies as methyl groups are substituted for terminal hydrogen atoms. At the same time the splitting arising from the presence of ^{10}B is reduced, but is still apparent in the spectra of B_2H_5Me and BH_3BHMe_2 as a shoulder on the high-frequency side. The symmetric in-phase

Observed Raman frequencies of four methyldiboranes

a Monomethyl-diborane ν/cm.$^{-1}$	SP	RI	*b* 1,1-Dimethyl-diborane ν/cm.$^{-1}$	SP	RI	*c* Trimethyl-diborane ν/cm.$^{-1}$	SP	RI	*d* Tetramethyl-diborane ν/cm.$^{-1}$	SP	RI	Tentative assignment
									280		20	
						296	p	7				
			317	dp	8							
									368		17	
						386	p	8				
									508	p	68	B–B stretch
			513	p	5	513	p	5				
						531	p	2				
						572	p	25	571	p	5	B–B stretch in (*c*)
576	p	25										
614	p	36	619	p	85							B–B stretch in (*b*)
644	p?	11 sh*										
						685?		1				
697	p	32										B–B stretch
						743	p	2	743	dp	8	
						801	p	2*				BC_2 stretch sym.†
802		10										B_2H_6 imp?
						829	p	2*				
			838	p?	7				840	p	23	BC_2 stretch sym.†
						865	p	3				
									874	p	8	
895		8										B–H out-of-plane bend†
						935	p	2				Me in-plane rock?†
						991	p	2				B–C (single) stretch
995	p?	11b										B–C stretch
									1011	dp	5	Me rock
1043	dp	15	1056	dp	9	1049	dp?	5				Me (out-of-plane?) rock†
									1084	dp	7*	Me out-of-plane rock plus BC_2 stretch asym.
									1108	dp	7*	
			1133	dp?	3	1116	dp	vw				BC_2 stretch asym.†
1164	dp?	8	1164	dp	3	1143	dp	vw				BH_2 def. in (*a*) and (*b*) plus B–H in-plane bend in (*a*)†
			1318	p	1	1318		vw	1321	p	4	Me def. sym.
						1421	p?	sh*	1423	p?	14*	Me def. asym.
1430	dp?	13b	1434	dp?	9b	1438	dp?	6	1441	dp?	22*	Me def. asym.
			1533	p	3							B–H_μ asym. (in-phase)?
			1591	dp?	2							
			1675		vw							
						1971	p	1				B–H_μ sym. (in-phase) plus Fermi-resonance lines of combinations and/or overtones
2048	p	16	2091	p	14*	2024	p	4b*	1976	p	16	
2102	p	62	2120	p	14*	2057	p	4*	2047	p	8	
2140	p	24 sh*	2152	p	20*	2122	p	9	2128	p	17	
2502	p	86*	2499	p	53							BH_2 stretch sym.
2519	p	86*				2503	p	11				B–H stretch
2573	dp?	15b	2576	dp	8							BH_2 stretch asym.
2829	p	15	2831	p	11	2829	p	7	2830	p	19	overtone of Me def. asym.
2905	p	100	2909	p	100	2908	p	100	2906	p	100	Me stretch sym.
2947	dp?	29 sh*	2947	dp	20 sh*	2941	dp	14 sh*	2941	dp	29 sh*	Me stretch asym.
			2970	dp	18 sh*	2963	dp	12 bsh*	2985	dp	19 sh*	Me stretch asym.

SP = state of polarisation, RI = relative intensity, p = polarised, dp = depolarised, sh = shoulder, b = broad, vw = very weak, imp. = impurity, def. = deformation, sym. = symmetric, asym. = asymmetric, ? = this datum or assignment uncertain, H_μ = bridge hydrogen atom.

* Intensity probably enhanced by overlap with other lines.

† Assignment based on that of Lehmann *et al.*[1] for corresponding i.r. band.

B–H_μ stretching vibration is totally symmetric in each compound and should give rise to a polarised peak corresponding to one of the peaks between 1970 and 2150 cm.$^{-1}$ in the various spectra. The other B–H_μ stretching vibrations in these complex groups are assigned to overtones and combinations, the intensities of which may be explained by Fermi resonance with the fundamental. Except for the asymmetric in-phase vibrations of the mono-, di-, and tri-methyl compounds, which are known to occur around 1660 cm.$^{-1}$, the remaining bridge vibrations are either Raman inactive or give rise to depolarised lines. These are not observed, presumably because they are too weak, except that in the case of the dimethyl compound the weak line at 1533 cm.$^{-1}$ may correspond to that observed at 1546 cm.$^{-1}$ in the i.r. spectrum,[1] in which it is assigned to the asymmetric in-phase B–H_{μ} stretch.

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