

635. *The Vibrational Spectrum and Structure of Trimethylgallium.*

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The infrared and Raman spectra of trimethylgallium in the gaseous and liquid phases, respectively, have been recorded and analysed. The results are consistent with a simple planar GaC_3 skeleton; no evidence of appreciable association in either phase has been found.

WHEREAS the states of association of the simpler boron and aluminium trialkyls are now well established, only sparse data have so far been collected for the analogous derivatives of gallium. On the basis of earlier results, Lewis and Rundle¹ concluded that trimethylgallium may exhibit a slight tendency to dimerise at low temperatures; vapour-density measurements² correspond to a simple monomeric species, and if association does take place in the liquid it must involve relatively weak bonding since the compound has a virtually "normal" boiling point and Trouton constant.³ These observations do not, however, rule out the possibility of appreciable association of trimethylgallium in the condensed phases. It is thus significant that the molecular weight of triethylgallium in benzene and in cyclohexane indicates that the molecules are largely dimeric;⁴ trivinylgallium is also reported⁵ to be dimeric in cyclohexane.

¹ Lewis and Rundle, *J. Chem. Phys.*, 1953, **21**, 986.

² Kraus and Toonder, *Proc. Nat. Acad. Sci. U.S.A.*, 1933, **19**, 292.

³ Long and Sackman, *Trans. Faraday Soc.*, 1958, **54**, 1797.

⁴ Dennis and Patnode, *J. Amer. Chem. Soc.*, 1932, **54**, 182; Strohmeier, Humpfner, Miltenberger, and Seifert, *Z. Elektrochem.*, 1959, **63**, 537.

⁵ Oliver and Stevens, *J. Inorg. Nuclear Chem.*, 1962, **24**, 953.

We have extended some preliminary observations⁶ on the infrared spectrum of gaseous trimethylgallium (over the range 400–4000 cm^{-1}), and have recorded the Raman spectrum of the pure liquid; no evidence for association in either phase has been encountered. Indeed, the results are entirely consistent with a simple monomeric species with trigonal, planar symmetry. The observed frequencies, relative intensities, and states of polarisation of the infrared and Raman bands are given in Table 1. Since the completion of this work, we have learnt from Dr. L. A. Woodward of an independent investigation of the

TABLE I.
Vibrational frequencies of trimethylgallium.

Infrared (gas) ν (in cm^{-1})	Raman (liquid) * $\Delta\nu$ (in cm^{-1})	Assignment (D_{3h} symmetry assumed)
3046m, sh	—	$2 \times \text{ca. } 1430 + 162.5 (E')$
2999s	—	C–H asym. stretch (e' or a_2'')
—	2961s, br, dp	C–H asym. stretch (e'')
2914s, br	—	C–H sym. stretch (e')
—	2903vs, p	C–H sym. stretch (a_1')
2865m, sh	—	$2 \times \text{ca. } 1430 (E')$
1786vw	—	$1198 + 577 (E')$
1730vw	—	$1205 + 521.5 (E')$
—	1428vw	CH_3 asym. deform. (e' or e'')
1356vw	—	$1198 + 162.5 (E')$
—	(?) 1328vw	$727 + 612 (E')$
1211 } s	—	CH_3 sym. deform. (e')
1205 } s	—	
1198 } s	—	
—	1198s, p	CH_3 sym. deform. (a_1')
—	1186w, sh	$570 + 612 (A_1'' + A_2'' + E'')$
—	1139w, sh	$2 \times 570 (A_1' + A_2' + E')$
—	1038vw	$2 \times 521.5 (A_1')$
769s	769w, probably dp	CH_3 rock (e')
727ms	—	CH_3 rock (a_2'')
—	612w, sh	CH_3 rock (e'')
587 } vs	570s, dp	Ga–C asym. stretch (e')
577 } vs	—	
571 } vs	—	
—	521.5vs, p	Ga–C sym. stretch (a_1')
—	465w	$\text{ca. } 300 + 162.5 (E'')$
—	162.5s, dp	GaC_3 in-plane deform. (e')

* p = polarised; dp = depolarised.

vibrational spectrum of trimethylgallium; the results, which he has kindly shown us prior to publication,⁷ agree well with ours.

The general simplicity of the spectra strongly supports a monomeric model with high symmetry for the trimethylgallium molecule in the liquid and gaseous phases; a structure analogous to the trimethylaluminium dimer would require appreciably more complicated spectra with, in particular, at least three polarised Raman lines in the low-frequency region ($<700 \text{ cm}^{-1}$).⁸ Particularly cogent evidence in favour of a simple planar GaC_3 skeleton is provided by the activities and states of polarisation of the bands associated with the skeletal vibrations. The selection rules for a planar GaC_3 unit (D_{3h} symmetry) permit three Raman lines (one polarised) and three infrared bands due to fundamentals; the polarised Raman line (arising from the symmetric Ga–C stretching mode) should have no counterpart in the infrared spectrum. The strong Raman and infrared bands observed at frequencies below 700 cm^{-1} comply exactly with these rules, and the fundamentals of the GaC_3 skeleton, given in Table 2, show a striking resemblance to those of a simple planar molecule such as BF_3 .⁹ The frequencies of two of the infrared-active modes lie outside the range investigated in the present work; one of these corresponds to the

⁶ Coates and Mukherjee, *J.*, 1964, 1295.

⁷ Hall, Woodward, and Ebsworth, *Spectrochim. Acta*, in the press.

⁸ Hoffmann, *Z. Elektrochem.*, 1960, **64**, 616; Gray, *Canad. J. Chem.*, 1963, **41**, 1511.

⁹ Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, New York, 1945, p. 298.

TABLE 2.

Fundamental frequencies of the GaC₃ skeleton.

Mode	Raman (liquid) (in cm. ⁻¹)	Infrared (gas) (in cm. ⁻¹) *
Ga-C sym. stretch (<i>a</i> ₁ ')	521·5p	
Out-of-plane deformation (<i>a</i> ₂ '')		(<i>ca.</i> 300)
Ga-C asym. stretch (<i>e</i> ')	570dp	577
In-plane deformation (<i>e</i> ')	162·5dp	(162·5)

* Frequencies in parentheses were not directly observed.

depolarised Raman line at 162·5 cm.⁻¹, and a value of *ca.* 300 cm.⁻¹ is tentatively suggested for the *a*₂'' mode, on the basis of a weak Raman band at 465 cm.⁻¹ assigned to the combination *ca.* 300 + 162·5 cm.⁻¹ (the frequencies of the analogous modes in trimethylborane^{10,11} and trimethylaluminium⁸ are *ca.* 340 and 310—370 cm.⁻¹, respectively).

The symmetry of the molecule as a whole depends on whether the CH₃ groups rotate freely about the Ga-C bonds; for trimethylborane,¹⁰ entropy calculations show that there is free internal rotation which leads to an effective molecular point-group of *D*_{3h}. In the absence of suitable thermodynamic data, we have assumed a similar symmetry for trimethylgallium, and have thus been able to account satisfactorily for the observed vibrational spectra. The activities in the Raman effect and in infrared absorption are shown in Table 3, which lists the fundamental frequencies and approximate descriptions of the vibrational modes involved. Vibrational assignments have been based on the *D*_{3h} selection rules and on analogies with the spectra of related methyl compounds (*e.g.*, trimethylborane^{10,11} and dimethylzinc¹²). The remaining weak bands in the spectra can be ascribed to suitable overtones or combinations of the fundamentals; in all cases, the symmetry species are consistent with the observed activities on the basis of the *D*_{3h} selection rules (see Table 1).

TABLE 3.

Fundamental assignments for trimethylgallium (effective point-group *D*_{3h}).

Species		Raman $\Delta\nu$ (in cm. ⁻¹)	Infrared * ν (in cm. ⁻¹)	Type of mode
<i>a</i> ₁ '	ν_1	2903		C-H sym. stretch
	ν_2	1198	Inactive	CH ₃ sym. deform.
	ν_3	521·5		Ga-C sym. stretch
<i>a</i> ₂ '	ν_4			C-H asym. stretch
	ν_5	Inactive	Inactive	CH ₃ asym. deform.
	ν_6			CH ₃ rock
<i>a</i> ₂ ''	ν_7		2999	C-H asym. stretch
	ν_8	Inactive	(<i>ca.</i> 1430)	CH ₃ asym. deform.
	ν_9		727	CH ₃ rock
	ν_{10}		(<i>ca.</i> 300)	GaC ₃ deform. (out-of-plane)
<i>e</i> '	ν_{11}	—	2999	C-H asym. stretch
	ν_{12}	—	2914	C-H sym. stretch
	ν_{13}	1428	(<i>ca.</i> 1430)	CH ₃ asym. deform.
	ν_{14}	1198	1205	CH ₃ sym. deform.
	ν_{15}	769	769	CH ₃ rock
	ν_{16}	570	577	Ga-C asym. stretch
	ν_{17}	162·5	—	GaC ₃ deform. (in-plane)
<i>e</i> ''	ν_{18}	2961		C-H asym. stretch
	ν_{19}	1428	Inactive	CH ₃ asym. deform.
	ν_{20}	612		CH ₃ rock

* Values in parentheses correspond to fundamentals not actually observed.

A curious feature of the infrared spectrum is the apparent absence (with vapour pressures up to 39 mm.) of a band in the region 1400—1450 cm.⁻¹, corresponding to the

¹⁰ Woodward, Hall, Dixon, and Sheppard, *Spectrochim. Acta*, 1959, **15**, 249.¹¹ Stewart, *J. Res. Nat. Bur. Stand.*, 1956, **56**, 337; Lehmann, Wilson, and Shapiro, *J. Chem. Phys.*, 1958, **28**, 777.¹² Gutowsky, *J. Chem. Phys.*, 1949, **17**, 128.

asymmetric CH_3 deformation modes; the same type of motion also gives rise to only very weak scattering in the Raman effect. Normally, these vibrations would be expected to cause strong infrared absorption. It is perhaps significant, however, that trimethylaluminium⁸ and dimethylberyllium¹³ show little or no absorption in this region, whereas the symmetric CH_3 deformation gives relatively intense bands in all cases. No explanation of this phenomenon in terms of *simple* molecular properties is apparent.

At least three of the observed infrared bands show signs of unresolved rotational fine-structure giving rise to *P*-, *Q*-, and *R*-branches. The approximate P-R separations for the various bands are: 13–14 cm^{-1} (1205 cm^{-1}); 14 cm^{-1} (769 cm^{-1}); 17 cm^{-1} (727 cm^{-1}); and 16 cm^{-1} (577 cm^{-1}). Combining an estimated¹⁴ Ga-C bond length of *ca.* 2.00 Å with the assumed methyl-group dimensions C-H = 1.09 Å and $\angle\text{HCH} = 109^\circ 28'$, we obtain the following values for the principal moments of inertia of the molecule as a whole (assumed to have a planar GaC_3 skeleton): $I_A = I_B = 162 \times 10^{-40}$ gm. cm^2 and $I_C = 323 \times 10^{-40}$ gm. cm^2 . Hence the expected P-R separations of the perpendicular (*e'*) and parallel (*a₂'*) bands have been derived by Gerhard and Dennison's method;¹⁵ the values are *ca.* 16 and *ca.* 25 cm^{-1} , respectively. Satisfactory agreement with the observed separations is evident in the case of the three perpendicular bands; the value for the 727 cm^{-1} band (which should be a parallel band) is smaller than expected, but this may not be significant since the three branches are far from clearly resolved. A difference in band-shape should also be observed, the parallel bands being distinguished by prominent *Q*-branches and the perpendicular bands by *P*-, *Q*-, and *R*-branches of roughly equal intensity; on this basis, the 1205 cm^{-1} band is clearly of the perpendicular type, but lack of definition renders impossible any definite decision about the shapes of the other bands. Nevertheless, it is striking that the observed P-R separations are little smaller than those for the corresponding bands of trimethylborane;¹¹ this provides additional evidence for a simple, planar GaMe_3 molecule in which the gallium atom lies on all three principal axes of rotation (giving, as a result, relatively small moments of inertia for the molecule).

EXPERIMENTAL

Trimethylgallium was prepared from gallium and dimethylmercury,¹⁶ and was purified by fractional distillation. Infrared spectra of the gaseous material were recorded over the range 400–4000 cm^{-1} with a Grubb-Parsons GS2A prism-grating spectrometer. The Raman spectrum of the liquid (sample volume *ca.* 6 ml.) was reproduced photoelectrically by means of a Hilger E612 spectrometer coupled to a pen-recorder; the light-source was a spiral Torontarc arrangement of the type described by Janz, Mikawa, and James.¹⁷ The exciting line was the mercury 4358 Å line, a filter (saturated aqueous potassium nitrite solution) being used to reduce the intensity of the primary lines of shorter wavelength. Qualitative determinations of the states of polarisation of the Raman lines were made by the method of polarised incident light,¹⁸ successive records being taken with suitably oriented polaroid cylinders surrounding the sample tube. The observed frequencies were calibrated from the positions of appropriate strong bands in the spectra of pure carbon tetrachloride, benzene, chloroform, and acetonitrile, and are correct to within ± 2 cm^{-1} for lines that are not very weak or diffuse.

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¹³ Goubeau and Walter, *Z. anorg. Chem.*, 1963, **322**, 58; Bell and Coates, unpublished work.

¹⁴ "Tables of Interatomic Distances and Configurations in Molecules and Ions," Chem. Soc. Special Publ., No. 11, 1958, M29.

¹⁵ Gerhard and Dennison, *Phys. Rev.*, 1933, **43**, 197.

¹⁶ Coates, *J.*, 1951, 2003.

¹⁷ Janz, Mikawa, and James, *Appl. Spectroscopy*, 1961, **15**, 47.

¹⁸ Rank and Kagarise, *J. Opt. Soc. Amer.*, 1950, **40**, 89.