

## 1214. *The Vibrational Spectra of Some Addition Compounds of Trimethylamine*

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From an examination of the vibrational spectra of adducts of the type  $\text{MCl}_4\cdot\text{NMe}_3$  ( $\text{M} = \text{Si, Ge, Sn, or Ti}$ ) it is suggested that the compounds are molecular with  $C_{3v}$  symmetry. Similar studies on  $\text{VX}_3\cdot 2\text{NMe}_3$  ( $\text{X} = \text{Cl or Br}$ ) lead to a monomeric species with a planar  $\text{VX}_3$  unit and probable  $D_{3h}$  symmetry. Calculations of the vibrational frequencies of molecules of the form  $\text{MCl}_4\cdot\text{NMe}_3$  with either  $C_{3v}$  or  $C_{2v}$  symmetry suggest that (for the force constants adopted) coupling of ligand and acceptor modes is not very serious. G-matrices are reported for  $C_{3v}\cdot\text{A}_3\text{BWX}_3\text{Y}$  and for  $C_{2v}\cdot\text{LWX}_2\text{Y}_2$  (using general  $C_{3v}$  or  $C_{2v}$  angles, respectively).

By analogy with phosphorus, arsenic, and antimony, it is reasonable to suppose that five-co-ordinate compounds of silicon, germanium, and tin should be fairly easily accessible. Established cases of five-co-ordination in Group IV include the trigonal-bipyramidal ion <sup>1</sup>  $\text{SnCl}_5^-$  and the 1 : 1 adduct <sup>2</sup>  $\text{Me}_3\text{SnCl}\cdot\text{py}$  (where py = pyridine). Many 1 : 2 adducts of the type  $\text{MX}_4\cdot 2\text{L}$  are known ( $\text{M} = \text{Si, Ge, or Sn}$ ;  $\text{X} = \text{halogen}$ ;  $\text{L} = \text{unidentate ligand}$ ), but trimethylamine is unusual in forming a number of 1 : 1 addition compounds.<sup>3</sup> It is fairly obvious that steric hindrance of the methyl groups in trimethylamine could favour  $C_{3v}$  symmetry for molecular  $\text{MX}_4\cdot\text{NMe}_3$ , although, on the basis of electronegativity, either  $C_{2v}$  or  $C_{3v}$  symmetry appears to be acceptable.<sup>4</sup> The vibrational spectra of such species are of interest primarily for studying their stereochemistry in solution and in the solid state, but also (in the case of molecular species) for defining the effect of co-ordination of one unidentate ligand on the  $\text{MX}_4$  acceptor modes.

<sup>1</sup> R. F. Bryan, *J. Amer. Chem. Soc.*, 1964, **86**, 733.

<sup>2</sup> R. Hulme, *J.*, 1963, 1514.

<sup>3</sup> I. R. Beattie, *Quart. Rev.*, 1963, **17**, 382.

<sup>4</sup> E. L. Meuterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, 1964, **3**, 1298.

Table I summarises the excellent spectra which were obtained for a number of addition compounds of trimethylamine, both solid-state and solution data being given where possible. Our reasons for tabulating these frequencies under ligand and acceptor modes will become clear. Inspection of Table I immediately suggests two ligand frequencies

TABLE I

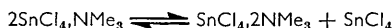
The vibrational spectra of some adducts of trimethylamine ( $\nu$  or  $\Delta\nu$  in  $\text{cm}^{-1}$ ) \*

Compound	State and technique	NMe <sub>3</sub> deform.				Acceptor modes		Unassigned	
		sym.	antisym.	antisym.	antisym.	sym.	sym.		
SiCl <sub>4</sub> .NMe <sub>3</sub>	I.r., solid (cold) † Raman, solid (cold)	537w	410sh	582vs	394s	361s	280w		
TiCl <sub>4</sub> .NMe <sub>3</sub>	I.r. solid	505w	434sh	456s §	370s	344m			
	I.r., soln. benzene †	499w	436sh	457s	396s	345m			
	Raman, soln. benzene †				391br	345s (pol.)	174	151	
GeCl <sub>4</sub> .NMe <sub>3</sub>	I.r., solid (cold) †	517w	435w	413s	353m	302s			
	I.r., soln. benzene- GeCl <sub>4</sub> †		Obscured	415sh	357s	324m			
	Raman, soln. benzene- NMe <sub>3</sub> †	513m (pol.)	Obscured	417sh	362s (pol.)	330m (pol.)	232w (pol.)	203m (depol.)	
SnCl <sub>4</sub> .NMe <sub>3</sub>	I.r., solid	504w	427w	370vs	338s	307s			
	I.r., soln. benzene †	499w	426w	367vs	345s	317s			
	Raman, soln. benzene †			368?	346s (pol.)	318m (pol.?)			
SnCl <sub>4</sub> .2NMe <sub>3</sub>	I.r., solid (mull)	516w	432vw	319vs					
VCl <sub>3</sub> .2NMe <sub>3</sub>	I.r., soln. benzene †	505m	442m	409s	—	—	325w	298w	
VBr <sub>3</sub> .2NMe <sub>3</sub>	I.r., soln. benzene †	508m	439w	345vs	—	—	290w		

\* Range 600—280  $\text{cm}^{-1}$  (except in the case of Raman data). † Benzene, MCl<sub>4</sub>, and free trimethylamine bands not reported [solutions containing free GeCl<sub>4</sub> are obscured in the region of  $\nu_3$  (i.r.) and  $\nu_1$  and  $\nu_3$  (Raman)]. ‡ Spectra showed traces of free tetrachloride. § Apparently split (450 and 462  $\text{cm}^{-1}$ ).

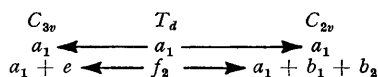
in each infrared spectrum (assigned by us <sup>5</sup> to symmetric and antisymmetric ligand deformations, for vibrations around 500 and 430  $\text{cm}^{-1}$ , respectively). These frequencies are readily located by their unchanging position and their (relatively) low intensity. At first sight, for adducts of the type MCl<sub>4</sub>.NMe<sub>3</sub>, it is possible (from the infrared spectrum) to assign a third ligand frequency around 350  $\text{cm}^{-1}$ . However, the Raman spectral data show conclusively that this vibration is a highly symmetrical acceptor frequency.

In solution in benzene, TiCl<sub>4</sub>.NMe<sub>3</sub> has been reported to be monomeric.<sup>6</sup> Our spectral results, taken in conjunction with the cryoscopic observations, confirm the previous work. Similarly, we find that SnCl<sub>4</sub>.NMe<sub>3</sub> is monomeric in benzene, with some dissociation according to the equilibrium:



The close similarity of solution and solid state data shown in Table I for SnCl<sub>4</sub>.NMe<sub>3</sub> and TiCl<sub>4</sub>.NMe<sub>3</sub> suggests that they are molecular in the solid state. (It may be noted here that a value of 7 D has been quoted <sup>7</sup> for the dipole moment of SnCl<sub>4</sub>.NMe<sub>3</sub>, but no experimental details were given.)

A molecular compound of the type MCl<sub>4</sub>.L is likely to attain approximately trigonal-bipyramidal stereochemistry with L in either an axial or an equatorial position. Lowering the symmetry of tetrahedral MCl<sub>4</sub> to C<sub>3v</sub> or C<sub>2v</sub> results in splitting of the two "stretching" modes of the tetrahedron, as follows:



<sup>5</sup> See also F. Watari, *Z. anorg. Chem.*, 1964, **332**, 322; R. L. Amster and R. C. Taylor, *Spectrochim. Acta*, 1964, **20**, 1487.

<sup>6</sup> G. W. A. Fowles and R. A. Hoodless, *J.*, 1963, 33.

<sup>7</sup> H. A. Brune and W. Zeil, *Z. Phys. Chem. (Frankfurt)*, 1962, **32**, 384.

With the exception of  $a_1$  ( $T_d$ ), all these vibrations are infrared and Raman active. In the case of  $\text{SnCl}_4\cdot\text{NMe}_3$  and  $\text{TiCl}_4\cdot\text{NMe}_3$  it is evident that in the caesium bromide region, after removal of ligand vibrations, there remain only three frequencies assignable as metal-chlorine "stretching modes." With one exception these are active in both the Raman and the infrared. The missing band is in the Raman effect for the strongly coloured  $\text{TiCl}_4\cdot\text{NMe}_3$ . As this band is clearly a high-frequency (antisymmetric) acceptor mode it is expected to be strong in the infrared but weak in the Raman. The absence of this band in the Raman effect is thus not surprising, as only dilute solutions could be examined owing to low solubility in benzene. Summarising, we may note that for the two compounds under discussion there are probably three metal-chlorine "stretching" modes, a high-frequency antisymmetric mode, and two lower-frequency symmetric modes. This clearly strongly suggests the (expected)  $C_{3v}$  symmetry.

The most convincing demonstration of the correctness (or otherwise) of this qualitative rationalisation of the spectra would be to calculate the vibrational spectra of these molecules, including in these calculations  $\text{GeCl}_4\cdot\text{NMe}_3$  and  $\text{SiCl}_4\cdot\text{NMe}_3$ .

Table 2 summarises our results for the metal-halogen stretching frequencies, using reasonable values of force constants (see Appendix) and trigonal-bipyramidal angles. The observed values given in Table 2 are for solution studies. From these calculations

TABLE 2  
Calculated and observed "M-Cl stretching vibrations" for  $\text{MCl}_4\cdot\text{NMe}_3$

M	Symmetry	Frequency ‡ (cm. <sup>-1</sup> )				M	Symmetry	Frequency ‡ (cm. <sup>-1</sup> )			
Si	( $C_{3v}$ ) calc.	625	574	366		Ge	( $C_{3v}$ ) calc.	434	419	329	
	( $C_{2v}$ ) calc.	585	666	535	346		( $C_{2v}$ ) calc.	403	453	419	303
	obs.*	582		361	394 †		obs.		417	320	362 †
Ti	( $C_{3v}$ ) calc.	479		447	331	Sn	( $C_{3v}$ ) calc.	376		363	315
	( $C_{2v}$ ) calc.	448	505	432	310		( $C_{2v}$ ) calc.	360	390	362	299
	obs.		457	396	345 †		obs.		368	318	346 †

\* Solid state only; other "obs." data are for solution studies. † Most intense Raman band. Correlation of the observed and calculated  $a_1$  frequencies is difficult, as the signs of  $S_4$  and  $S_5$  ( $C_{3v}$ ) in the calculated normal co-ordinates vary with the choice of angle ( $b_2$ ). Further difficulty arises due to the proposed weak axial metal-chlorine bond. ‡ Calculated frequencies for  $\text{MCl}_3\text{Cl}'$  ( $C_{3v}$ ) follow the order:  $\text{MCl}_3$  antisym. str. ( $e$ ),  $\text{MCl}'$  str. ( $a_1$ ),  $\text{MCl}_3$  sym. str. ( $a_1$ ); for  $\text{MCl}_2\text{Cl}_2'$  follow the order  $\text{MCl}_2$  and  $\text{MCl}_2'$  antisym. str. ( $b$ ),  $\text{MCl}_2$  and  $\text{MCl}_2'$  sym. str. ( $a_1$ ).

it is apparent that  $C_{3v}$  symmetry is acceptable for the germanium, tin, and titanium compounds. The full results for the model  $\text{Me}_3\text{NMX}_3\text{Y}$  ( $C_{3v}$  symmetry) (not quoted here for brevity) also fully validate our approximation of division into ligand and acceptor modes, even where these are quite close and of the same symmetry. In the case of the M-Cl' vibration of  $\text{SiCl}_4\cdot\text{NMe}_3$ , the difference between the observed and calculated values is disturbing, although we notice a similar trend in the case of the germanium compound. Bearing in mind the crude consideration of a trigonal-bipyramid as based on  $sp^2$  plus  $pd$  hybridisation, it is possible that the Si-Cl link in the (linear) N-Si-Cl grouping has an appreciably lower force constant than that of the "equatorial" Si-Cl in the  $\text{Si-Cl}_3$  group. We also note that we are unable to think of a chemically reasonable formulation which gives a preferable result to that obtained for  $C_{3v}$  stereochemistry.\*

There remain now three weak bands which have not been assigned. A polarised band at 232 cm.<sup>-1</sup> in the Raman spectrum of  $\text{GeCl}_4\cdot\text{NMe}_3$  could be the ubiquitous Ge-N stretch, although we have reservations about this. Similarly, a weak band at 280 cm.<sup>-1</sup> in the infrared spectrum of  $\text{SiCl}_4\cdot\text{NMe}_3$  is likely to be a ligand frequency but could be the silicon-nitrogen vibration.

In the case of the compounds  $\text{VX}_3\cdot 2\text{NMe}_3$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) the spectra in the solid state

\* If the adduct were  $[\text{Me}_3\text{NSiCl}_3]^+\text{Cl}^-$  the "silicon-chlorine stretching modes" would be expected to occur at appreciably higher frequencies than those reported here.

and in solution were virtually identical. The molecular weight data<sup>8</sup> taken in combination with the spectral data show that these compounds are monomeric. The interpretation of the spectra requires very little comment; a planar  $VX_3$  grouping with probable  $D_{3h}$  symmetry is readily apparent. It should be noted that in a previous investigation<sup>8</sup> the band at  $439\text{ cm}^{-1}$  in  $VBr_3 \cdot 2NMe_3$  was not observed. We note (a) that this compound would be unique in a wide variety of trimethylamine adducts if it did not show a band near  $430\text{ cm}^{-1}$ , and (b) that this band is of much lower intensity than the  $508\text{ cm}^{-1}$  band and occurs near the cut-off point of the (potassium bromide) prism used in the previous work.

#### EXPERIMENTAL

$SiCl_4 \cdot NMe_3$ .—The spectrum of this well-characterised<sup>9</sup> compound was taken in a low-temperature cell by allowing an approximately equimolar mixture of trimethylamine and silicon tetrachloride vapours to condense on to a caesium bromide plate in contact with a copper block cooled by liquid air. This compound is stable only at low temperatures.

$GeCl_4 \cdot NMe_3$ .—The spectrum of this compound was taken as described above for  $SiCl_4 \cdot NMe_3$ . However, the enhanced stability of this adduct over its silicon analogue allowed solution studies. Quite good solution spectra were obtained by allowing the adduct to dissolve in benzene containing either excess germanium tetrachloride (i.r.) or excess trimethylamine (Raman); the Raman cell was thermostatted at  $30^\circ$  to allow the necessary reproducibility for polarisation measurements. Polythene plates were used in the infrared cell to avoid the possibility of halogen exchange.

$SnCl_4 \cdot NMe_3$ .—A mixture of 1 : 1 and 2 : 1 adducts has been reported to form from the gas-phase reaction of trimethylamine with tin tetrachloride.<sup>9</sup> The pure crystalline 1 : 1 adduct can be obtained by vacuum-recrystallisation of the product from the direct reaction, using tin tetrachloride as the solvent. The product consisted of colourless, well-formed thin plates. Spectra were taken in Nujol mulls and also by sublimation on to a cooled plate. The molecular weight was determined cryoscopically in benzene (obs. 321, 328; calc. 320). It is interesting that recrystallisation of the adduct from benzene yielded a benzene solvate having an infrared spectrum different from that of the unsolvated complex. Removal of the benzene in a vacuum system caused collapse of the crystals of solvate, but the remaining adduct had a spectrum identical with that of the free adduct prepared as described above. [Analysis of the crystalline material obtained from the tetrachloride recrystallisation was carried out by hydrolysis and potentiometric determination of chloride (Found: Cl, 44.2. Calc. for  $C_3H_9Cl_4NSn$ : Cl, 44.4%).]

$SnBr_4 \cdot NMe_3$ .—This compound was obtained by heating tin tetrabromide and its reaction product with trimethylamine to  $100^\circ$  *in vacuo*. The product was then sublimed at  $100^\circ$  *in vacuo* (Found: Br, 64.1.  $C_3H_9Br_4NSn$  requires Br, 64.3%). We are not yet able to report the spectrum of this compound as it requires an extended spectral range.

$TiCl_4 \cdot NMe_3$ .—Prepared, as previously described,<sup>6</sup> in an all-glass vacuum system, spectra being obtained *in vacuo* in benzene solution (Raman and infrared), and for the solid by allowing the solution to evaporate on the plates of the cell.

$VX_3 \cdot 2NMe_3$ .—These compounds are well described in the literature.<sup>8</sup> The chloride adduct was obtained by direct reaction of vanadium tetrachloride with trimethylamine.<sup>8</sup> Cryoscopic observation confirmed the previous report that the compound is monomeric in benzene (obs. 280, 310; calc. 276). The bromide adduct was made from vanadium tribromide and trimethylamine.<sup>8</sup> Solid-state spectra were taken as Nujol mulls.

*Spectra*.—Infrared spectra were taken on a Perkin-Elmer 221 instrument equipped with rock salt, grating, and caesium bromide optics, and Raman spectra on a Cary 81 Raman spectrophotometer except for the spectrum of  $TiCl_4 \cdot NMe_3$ , which was taken using a helium source.<sup>10</sup>

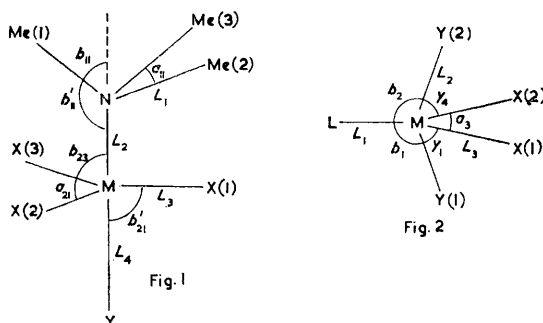
#### APPENDIX

For a molecule of the type  $Me_3NMX_3Y$  the most likely formulation is in terms of  $C_{3v}$  (staggered) configuration so that the methyl groups lie in the  $XM_X$  angle. In this analysis the methyl groups are treated as point masses, and the (inactive) torsional mode is neglected. The normal modes in cartesian co-ordinates split up (after removal of translation and rotation)

<sup>8</sup> G. W. A. Fowles and C. M. Pleass, *Chem. and Ind.*, 1955, 1742.

<sup>9</sup> J. E. Fergusson, D. K. Grant, R. H. Hickford, and C. J. Wilkins, *J.*, 1959, 99.

<sup>10</sup> L. A. Woodward, personal communication.



as  $\Gamma_{\text{mol}} = 6A_1 + A_2 + 7E$ . It should be noted that this analysis involving general angles follows fairly easily from our previous analysis on  $(C_{3v})$   $WXY_3$ . The details of this analysis using Wilson's vector method have already been described.<sup>11</sup>

*Symmetry co-ordinates:*

$$\begin{aligned} a_1 \quad S_1 &= \Delta MN; \quad S_2 = (1/\sqrt{3})[\Delta NMe(1) + \Delta NMe(2) + \Delta NMe(3)]; \\ S_3 &= -[1/\sqrt{3}(1 + n_1^2)][\Delta b_{11}' + \Delta b_{12}' + \Delta b_{13}' - n_1(\Delta a_{11} + \Delta a_{12} + \Delta a_{13})]; \\ S_4 &= \Delta MY; \quad S_5 = (1/\sqrt{3})[\Delta MX(1) + \Delta MX(2) + \Delta MX(3)]; \\ S_6 &= [1/\sqrt{3}(2 + n_2^2)][\Delta b_{21} + \Delta b_{22} + \Delta b_{23} - \Delta b_{21}' - \Delta b_{22}' - \Delta b_{23}' + n_2(\Delta a_{21} + \Delta a_{22} \\ &\quad + \Delta a_{23})]; \end{aligned}$$

where  $n_1 = \sqrt{3} \cos b_1 / \cos(a_1/2)$ ;  $n_2 = \sqrt{3} \cos b_2 / \cos(a_2/2)$ ;

$$\begin{aligned} e \quad S_{7a} &= (1/\sqrt{6})[2\Delta NMe(1) - \Delta NMe(2) - \Delta NMe(3)]; \quad S_{8a} = (1/\sqrt{6})(2\Delta a_{11} - \Delta a_{12} - \Delta a_{13}); \\ S_{9a} &= (1/\sqrt{6})(2\Delta b_{11}' - \Delta b_{12}' - \Delta b_{13}'); \quad S_{10a} = (1/\sqrt{6})[2\Delta MX(1) - \Delta MX(2) - \Delta MX(3)]; \\ S_{11a} &= (1/\sqrt{6})(2\Delta a_{21} - \Delta a_{22} - \Delta a_{23}); \quad S_{12a} = (1/\sqrt{6})(2\Delta b_{21}' - \Delta b_{22}' - \Delta b_{23}'); \\ S_{13a} &= -(1/\sqrt{6})(2\Delta b_{21} - \Delta b_{22} - \Delta b_{23}). \end{aligned}$$

The resulting G-matrix elements follow:

$$\begin{aligned} a_1 \quad G_{11} &= \mu_M + \mu_N; \quad G_{12} = -\sqrt{3}\mu_N \cos b_1; \quad G_{13} = \sqrt{3(1 + n_1^2)}(\mu_N/L_1) \sin b_1; \\ G_{14} &= -\mu_M; \quad G_{15} = \sqrt{3}\mu_M \cos b_2; \quad G_{16} = -\sqrt{3(2 + n_2^2)}(\mu_M/L_3) \sin b_2; \\ G_{22} &= \mu_{Me} + 3\mu_N \cos^2 b_1; \quad G_{23} = -3\sqrt{(1 + n_1^2)}(\mu_N/L_1) \cos b_1 \sin b_1; \\ G_{24} &= G_{25} = G_{26} = 0; \quad G_{33} = (1 + n_1^2)[(\mu_{Me}/L_1^2) + (3\mu_N/L_1^2) \sin^2 b_1]; \\ G_{34} &= G_{35} = G_{36} = 0; \quad G_{44} = \mu_Y + \mu_M; \quad G_{45} = -\sqrt{3}\mu_M \cos b_2; \\ G_{46} &= \sqrt{3(2 + n_2^2)}(\mu_M/L_3) \sin b_2; \quad G_{55} = \mu_X + 3\mu_M \cos^2 b_2; \\ G_{56} &= -3\sqrt{(2 + n_2^2)}(\mu_M/L_3) \cos b_2 \sin b_2; \\ G_{66} &= (2 + n_2^2)[(\mu_X/L_3^2) + (3\mu_M/L_3^2) \sin^2 b_2]. \\ e \quad G_{77} &= \mu_{Me} + (3/2)\mu_N \sin^2 b_1; \quad G_{78} = 3m_1(\mu_N/2L_1) \sin b_1; \\ G_{79} &= -(3/2)[(\mu_N/L_2) + (\mu_N/L_1) \cos b_1] \sin b_1; \\ G_{7,10} &= G_{7,11} = G_{7,12} = 0; \quad G_{7,13} = (3\mu_N/2L_2) \sin b_1; \\ G_{88} &= (\mu_{Me}/L_1^2)(3/p_1^2 + n_1^2/4) + (3\mu_N/2L_1^2)m_1^2; \\ G_{89} &= (\mu_{Me}/2L_1^2)n_1 - (3\mu_N/2L_1L_2)m_1 - (3\mu_N/2L_1^2)m_1 \cos b_1; \\ G_{8,10} &= G_{8,11} = G_{8,12} = 0; \quad G_{8,13} = (3\mu_N/2L_1L_2)m_1; \\ G_{99} &= (\mu_{Me}/L_1^2) + (3\mu_M/2L_2^2) + (3\mu_N/2)[(1/L_2) + (\cos b_1)/L_1]^2; \\ G_{9,10} &= -(3\mu_M/2L_2) \sin b_2; \quad G_{9,11} = -(3\mu_M/2L_2L_3)m_2; \\ G_{9,12} &= (3\mu_M/2L_2L_4) + (3\mu_M/2L_2L_3) \cos b_2; \\ G_{9,13} &= (3\mu_M/2L_2)[(\cos b_2)/L_3 - (1/L_2)] - (3\mu_N/2L_2)[(\cos b_1)/L_1 + (1/L_2)]; \\ G_{10,10} &= \mu_X + (3\mu_M/2) \sin^2 b_2; \quad G_{10,11} = (3\mu_M/2L_3)m_2 \sin b_2; \\ G_{10,12} &= -(3\mu_M/2)[(1/L_4) + (\cos b_2)/L_3] \sin b_2; \\ G_{10,13} &= (3\mu_M/2)[(1/L_4) - (\cos b_2)/L_3] \sin b_2; \\ G_{11,11} &= (\mu_X/L_3^2)[(3/p_2^2) + (n_2^2/4)] + (3\mu_M/2L_3^2)m_2^2; \\ G_{11,12} &= (\mu_X/2L_3^2)n_2 - (3\mu_M/2L_3)[(1/L_4) + (\cos b_2)/L_3]m_2; \\ G_{11,13} &= (\mu_X/2L_3^2)n_2 + (3\mu_M/2L_3)[(1/L_4) - (\cos b_2)/L_3]m_2; \\ G_{12,12} &= (\mu_X/L_3^2) + (3\mu_Y/2L_4^2) + (3\mu_M/2)[(1/L_4) + (\cos b_2)/L_3]^2; \end{aligned}$$

<sup>11</sup> T. R. Gilson, Thesis, London, 1964.

$$G_{12,13} = \mu_X/L_3^2 + (3\mu_M/2)[(1/L_4) + (\cos b_2)/L_3][(\cos b_2)/L_3 - (1/L_2)];$$

$$G_{13,13} = (\mu_X/L_3^2) + (3\mu_M/2)[(\cos b_2)/L_3 - (1/L_2)]^2 + (3\mu_N/2L_2^2);$$

where  $m_{1,2} = \sin(b_{1,2}) \tan(a_{1,2}/2)$ ;  $p_{1,2} = 2 \cos(a_{1,2}/2)$ .

The corresponding F-matrix elements for SVFF are:

$$a_1 \quad F_{11} = k_{MN}; \quad F_{22} = k_{NM_0}; \quad F_{33} = (k_{b_1} + n_1^2 k_{a_1})/(1 + n_1^2);$$

$$F_{44} = k_{MY}; \quad F_{55} = k_{MX}; \quad F_{66} = (k_{b_2} + k_{b_2'} + n_2^2 k_{a_2})/(2 + n_2^2).$$

$$e \quad F_{77} = k_{NM_6}; \quad F_{88} = k_{a_1}; \quad F_{99} = k_{b_1'}; \quad F_{10,10} = k_{MX};$$

$$F_{11,11} = k_{a_2}; \quad F_{12,12} = k_{b_2'}; \quad F_{13,13} = k_{b_2}.$$

The case of  $LMX_2Y_2$  ( $C_{2v}$ ) has been considered previously by Zeil and Dietrich<sup>12</sup> but using only angles of 120 and 90°. We shall comment later on some discrepancies between their analysis and ours. Further, we shall report elsewhere the effect of changes in the valence angles on the contributions of the various force constants to the potential energy for certain normal modes of vibration.

In addition to the co-ordinates shown in Figure 2, the following are defined:  $a_1 = \angle LMX_1$ ;  $a_2 = \angle LMX_2$ ;  $b_3 = \angle Y_1MY_2$ ;  $y_2 = \angle Y_1MX_2$ ;  $y_3 = \angle Y_2MX_1$ .

It may initially appear that  $b_3$  is unnecessary, but opening  $a_3$  to 180° will immediately show the need for this internal co-ordinate. At the same time it will be appreciated that this enables us to take advantage of the full symmetry of the problem. Thus we find that  $\Gamma_{mol} = 5A_1 + A_2 + 3B_1 + 3B_2$ . Clearly the matrices for  $B_1$  and  $B_2$  (which differ only by the choice of  $x$  and  $y$ , the  $C_2$  axis being chosen for  $z$ ) will be formally identical apart from a difference in nomenclature of the internal co-ordinates, masses, and force constants. As there are fifteen internal co-ordinates and only twelve normal modes we are left with three redundancy conditions. Two of these ( $\Delta a_1 + \Delta a_2 + \Delta a_3 \equiv 0$  and  $\Delta b_1 + \Delta b_2 + \Delta b_3 \equiv 0$ ) are obvious. The third condition is more complex, involving a relationship between three different kinds of angles,  $a(=a_3)$ ,  $b(=b_3)$ , and  $y(=y_n; n=1-4)$ . The well known trigonometric formula for this situation is

$$\cos y = \cos(a/2) \cos(b/2).$$

Thus,

$$(\partial y / \partial a)_b = [\cos(b/2) \sin(a/2)]/2 \sin y = n_1$$

$$(\partial y / \partial b)_a = [\cos(a/2) \sin(b/2)]/2 \sin y = n_2.$$

Thus, the third redundancy condition becomes

$$\Delta y_1 + \Delta y_2 + \Delta y_3 + \Delta y_4 \equiv 4n_1 \Delta a_3 + 4n_2 \Delta b_3.$$

We may now write out the symmetry co-ordinates:

$$a_1 \quad S_1 = \Delta ML; \quad S_2 = (1/\sqrt{2})[\Delta MY(1) + \Delta MY(2)]; \quad S_3 = (1/\sqrt{2})[\Delta MX(1) + \Delta MX(2)];$$

$$S_4 = [1/\sqrt{(3/2 + 4n_2^2)}][\Delta b_3 - \Delta b_1/2 - \Delta b_2/2 + n_2(\Delta y_1 + \Delta y_2 + \Delta y_3 + \Delta y_4)];$$

$$S_5 = [1/\sqrt{(3/2 + 4n_1^2)}][\Delta a_3 - \Delta a_1/2 - \Delta a_2/2 + n_1(\Delta y_1 + \Delta y_2 + \Delta y_3 + \Delta y_4)].$$

$$a_2 \quad S_6 = (1/2)(\Delta y_1 + \Delta y_4 - \Delta y_2 - \Delta y_3).$$

$$b_1 \quad S_7 = (1/\sqrt{2})[\Delta MX(1) - \Delta MX(2)]; \quad S_8 = (1/\sqrt{2})(\Delta a_1 - \Delta a_2);$$

$$S_9 = (1/2)(\Delta y_1 + \Delta y_3 - \Delta y_2 - \Delta y_4).$$

The resulting G-matrix elements† follow:

$$a_1 \quad G_{11} = \mu_L + \mu_M; \quad G_{12} = -\sqrt{2}\mu_M \cos(b/2); \quad G_{13} = -\sqrt{2}\mu_M \cos(a/2);$$

$$G_{14} = 2\sqrt{(3/2 + 4n_2^2)}(\mu_M/L_2) \sin(b/2); \quad G_{15} = 2(\sqrt{3/2 + 4n_1^2})(\mu_M/L_3) \sin(a/2);$$

$$G_{22} = \mu_Y + 2\mu_M \cos^2(b/2); \quad G_{23} = 2\mu_M \cos(b/2) \cos(a/2);$$

$$G_{24} = [-2\sqrt{(3 + 8n_2^2)}](\mu_M/L_2) \sin(b/2) \cos(b/2);$$

$$G_{25} = [-2\sqrt{(3 + 8n_1^2)}](\mu_M/L_3) \sin(a/2) \cos(b/2); \quad G_{33} = \mu_X + 2\mu_M \cos^2(a/2);$$

$$G_{34} = [-2\sqrt{(3 + 8n_2^2)}](\mu_M/L_2) \sin(b/2) \cos(a/2);$$

$$G_{35} = [-2\sqrt{(3 + 8n_1^2)}](\mu_M/L_3) \sin(a/2) \cos(a/2);$$

$$G_{44} = (3 + 8n_2^2)[(\mu_Y/L_2^2) + (2\mu_M/L_2^2) \sin^2(b/2)];$$

$$G_{45} = [2\sqrt{(3 + 8n_2^2)}(3 + 8n_1^2)](\mu_M/L_2L_3) \sin(a/2) \sin(b/2);$$

\* In order to avoid too great a complexity,  $S_4$  and  $S_5$  have been left formally non-orthogonal. This will lead to a term  $F_{45}$  even in SVFF. It may be noted that this situation does not arise for trigonal-bipyramidal angles ( $n_1 = 0$ ).

† Throughout the following analysis  $b_2$  type formulæ may be derived from  $b_1$  by the appropriate exchange of symbols.

<sup>12</sup> W. Zeil and C. Dietrich, *Z. phys. Chem. (Frankfurt)*, 1963, **38**, 36.



$$\begin{aligned}
G_{55} &= (3 + 8n_1^2)[\mu_X/L_3^2 + (2\mu_M/L_3^2) \sin^2(a/2)]. \\
a_2 \ G_{66} &= 2p_x^2\mu_X/L_3^2 + 2p_y^2\mu_Y/L_2^2, \text{ where } p_x = \sin(b/2)/\sin y, \ p_y = \sin(a/2)/\sin y. \\
b_1 \ G_{77} &= \mu_X + 2\mu_M \sin^2(a/2); \\
G_{78} &= (-2\mu_M/L_1) \sin(a/2) - (2\mu_M/L_3) \cos(a/2) \sin(a/2); \\
G_{79} &= (-2\sqrt{2}\mu_M/L_2)p_y \sin(a/2) + (4\sqrt{2}\mu_M/L_3)n_1 \cos(a/2) \sin(a/2); \\
G_{88} &= 2\mu_L/L_1^2 + \mu_X/L_3^2 + (2\mu_M)[1/L_1 + \cos(a/2)/L_3]^2; \\
G_{89} &= (-2\sqrt{2}\mu_X/L_3^2)n_1 + (2\sqrt{2}\mu_M)[(1/L_1 + \cos(a/2)/L_3)(p_y/L_2 - 2n_1 \cos(a/2)/L_3)]; \\
G_{99} &= (8\mu_X/L_3^2)n_1^2 + (2\mu_Y/L_2^2)p_y^2 + (4\mu_M)(p_y/L_2 - 2n_1 \cos(a/2)/L_3)^2.
\end{aligned}$$

The corresponding F-matrix elements for SVFF:

$$\begin{aligned}
a_1 \ F_{11} &= k_{ML}; \ F_{22} = k_{MY}; \ F_{33} = k_{MX}; \ F_{44} = (k_{b_3} + k_{b_1}/2 + 4n_2^2k_y)/(3/2 + 4n_2^2); \\
F_{55} &= (k_{a_3} + k_{a_1}/2 + 4n_1^2k_y)/(3/2 + 4n_1^2); \ F_{45} = 2n_1n_2k_y/\sqrt{(3/2 + 4n_2^2)(3/2 + 4n_1^2)}. \\
a_2 \ F_{66} &= k_y. \\
b_1 \ F_{77} &= k_{MX}; \ F_{88} = k_{a_1}; \ F_{99} = k_y.
\end{aligned}$$

Putting  $n_1 = 0$ ,  $n_2 = 1/4$ ,  $p = 1$ , and  $p_y = \sqrt{3}/2$  should lead to matrices identical with those derived by Zeil and Dietrich.<sup>12</sup> In all cases, except for  $G_{34}$  ( $a_1$ ),  $G_{79}$  ( $b_1$ ), and  $G_{11,11}$  ( $b_2$ ), this is true. For the case of  $G_{11,11}$  the negative sign given by the previous authors is wrong, as it could only occur in a diagonal term for a negative mass. We have checked the other two cases, where the differences are again minor, but can see no error in our own working. It is, however, interesting to note that on p. 45 of ref. 12 the equations given below the diagrams are not strictly meaningful, as this is not an orthogonal transformation. [The set of equations  $Q_n = \sum_i A_{ni}S_i$  strictly gives the coefficients  $A_{ni}$  of the transformation (of any arbitrary vibration of the molecule expressed in terms) of the  $S_i$  into (an expression in terms of) the normal co-ordinates  $Q_n$ . The summations of ref. 12 are better written  $\sum_i A_{ni}\vec{S}_i$ , indicating that the given summations of the *vectors*  $\vec{S}_i$  give the *vectors*  $\vec{Q}_n$ . The two expressions are only equivalent when the transformation is orthogonal, which is not the case here. If the coefficients  $A_{ni}$  are correctly normalised it is, however, correct to write  $S_i = \sum_n A_{ni}Q_n$ . Correspondingly, if  $A_{ni}^{-1}$  represents a coefficient of the matrix inverse to  $A_{ni}$ , then we may write  $Q_n = \sum_i A_{ni}^{-1}S_i$ , but  $\vec{S}_i = \sum_n A_{ni}^{-1}\vec{Q}_n$  (see Wilson, ref. 13)].

Table 3 summarises the force constants used in the above calculations, together with the

TABLE 3

Force constants \* and interatomic distances † for  $\text{Me}_3\text{NMX}_3\text{Y}$  ( $C_{3v}$ ) and  $\text{LMX}_2\text{Y}_2$  ( $C_{2v}$ )

(I) $\text{Me}_3\text{NMX}_3\text{Y}$ (X = Y = Cl)					(II) $\text{LMX}_2\text{Y}_2$ (L = $\text{Me}_3\text{N}$ , X = Y = Cl)				
	Si	Ge	Ti	Sn		Si	Ge	Ti	Sn
$d_{MN}(L_2)$	2.01	2.09	2.20	2.31	$(L_1)$	2.01	2.09	2.20	2.31
$d_{MX}(L_3)$	2.01	2.09	2.20	2.31	$(L_3)$	2.01	2.09	2.20	2.31
$d_{MY}(L_4)$	2.01	2.09	2.20	2.31	$(L_2)$	2.01	2.09	2.20	2.31
$k_{MN}$	0.8	0.8	0.8	0.8	$k_{ML}$	0.8	0.8	0.8	0.8
$k_{MX}$	2.51	2.12	2.09	1.97	$k_{MX}$	2.51	2.12	2.09	1.97
$k_{MY}$	2.51	2.12	2.09	1.97	$k_{MY}$	2.51	2.12	2.09	1.97
$k_{a_3}$	0.489	0.674	0.503	0.523	$k_{a_1}$	0.367	0.481	0.377	0.392
$k'_{b_3}$	0.489	0.674	0.503	0.523	$k_{a_3}$	0.489	0.674	0.503	0.523
$k_{b_2}$	0.367	0.481	0.377	0.392	$k_{b_1}$	0.367	0.481	0.377	0.392
					$k_{b_2}$	0.122	0.168	0.126	0.131
$k'_{\text{MXX}} \ddagger$	0.150	0.156	0.124	0.080	$k'_{\text{MXX}} \ddagger$	0.150	0.156	0.124	0.080
$k'_{\text{MXY}} \ddagger$	0.150	0.156	0.124	0.080	$k'_{\text{MY}} \ddagger$	0.038	0.039	0.031	0.020
$k_{\text{NMe}} \ddagger$	3.0	1.08	1.23	1.23	$k'_{\text{MXY}} \ddagger$	0.300	0.312	0.248	0.160
$d_{\text{NMe}} \ddagger$	1.47								

\* In md.  $\text{\AA}^{-1}$  (stretching) or md.  $\text{\AA} \text{ rad}^{-2}$  (deformational). † In  $\text{\AA}$  units. ‡ These constants lead to the following modifications to the F-matrices: ( $C_{3v}$ )  $F_{45} = \sqrt{3}k'_{\text{MXY}}$ ;  $F_{55} = k_{\text{MX}} + 2k'_{\text{MXX}}$ ;  $F_{10,10} = k_{\text{MX}} - k'_{\text{MXX}}$ ; ( $C_{2v}$ )  $F_{22} = k_{\text{MY}} + k'_{\text{MY}}$ ;  $F_{33} = k_{\text{MX}} + k'_{\text{MXX}}$ ;  $F_{23} = 2k'_{\text{MXY}}$ ;  $F_{77} = k_{\text{MX}} - k'_{\text{MXX}}$ ;  $F_{10,10} = k_{\text{MY}} - k'_{\text{MY}}$ .

<sup>13</sup> E. B. Wilson, jun., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, 1955.

relevant interatomic distances. The calculations described here were carried out with either tetrahedral,  $120^\circ$  and  $90^\circ$  angles ( $C_{3v}$ ), or with  $120^\circ$  and  $90^\circ$  angles ( $C_{2v}$ ). The force constants were estimated for the tetrahalide residues by taking an arbitrary 0.8 of the values obtaining in the parent tetrahalides for stretching constants, and using the deformational constants unchanged (except where a large angle indicated a reduced value). Since particular interest centred round the metal-halogen stretching modes in this investigation, a stretch-stretch interaction constant was introduced for these bonds.

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