1181. *A Normal Co-ordinate Analysis of the Octahedral Species* cis- *and* trans-$[L_2MX_4]$.

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A normal co-ordinate analysis of the octahedral species *cis-* and *trans-*$[L_2MX_4]$ is carried out by Wilson's method and the *F-* and *G*-matrix elements of the secular equations are tabulated. By disregarding off-diagonal terms in the potential-energy matrix and making reasonable assumptions about force constants, vibrational frequencies for co-ordination compounds of some tetrahalides of Group IV are approximately calculated.

With the increased availability of infrared (and Raman) spectrometers capable of working to about 50 cm.$^{-1}$ (and $\Delta\nu = 50$ cm.$^{-1}$) a combination of these two techniques has become a powerful tool for examining stereochemistry in solution, particularly for the non-transition elements where the lack of partially filled *d*-shells renders many other spectroscopic techniques inapplicable. The use of infrared spectroscopy in the cæsium bromide region to study the *cis–trans* isomerism of adducts of the type L_2MX_4 has outlined the importance of such techniques.[1] We have examined the vibrations of these two isomeric forms using Wilson's *F–G* matrix method.[2]

(1) *cis*-L_2MX_4 (C_{2v}).—Fig. 1 shows our choice of internal co-ordinates to describe the vibrations of such a molecule. The corresponding *f* matrix which is symmetrical about the diagonal is given in Table 1 and defines the relevant force constants. Cartesian co-ordinates being used, the representation of the molecule after the removal of translational and rotational degrees of freedom is

$$\Gamma\text{mol} = 6a_1(\text{IR,R}) + 2a_2(\text{R}) + 3b_1(\text{IR,R}) + 4b_2(\text{IR,R})$$

whereas using internal co-ordinates (Fig. 1) we find

$$\Gamma\text{mol} = 8a_1 + 2a_2 + 3b_1 + 5b_2$$

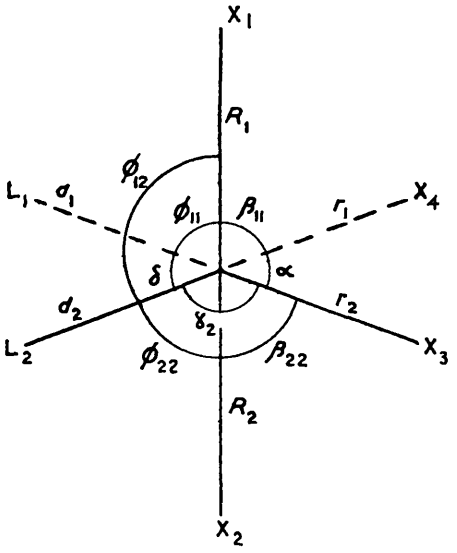

FIG. 1. Internal co-ordinates for *cis*-L_2MX_4.

[1] I. R. Beattie, G, P. McQuillan, L. Rule, and M. Webster, *J.*, 1963, 1514; I. R. Beattie, T. Gilson, M. Webster, and (in part) G. P. McQuillan *J.*, 1964, 238; I. R. Beattie and L. Rule, *J.*, 1965, 2995.
[2] E. B. Wilson, jun., *J. Chem. Phys.*, 1939, **7**, 1047; 1941, **9**, 76.

TABLE 1.

The *f* matrix for *cis*-L_2MX_4.

f	Δr_1	Δr_2	ΔR_1	ΔR_2	Δd_1	Δd_2	$\Delta\alpha$	$\Delta\delta$	$\Delta\gamma_1$	$\Delta\gamma_2$	$\Delta\beta_{11}$	$\Delta\beta_{12}$	$\Delta\beta_{21}$	$\Delta\beta_{22}$	$\Delta\phi_{11}$	$\Delta\phi_{12}$	$\Delta\phi_{21}$	$\Delta\phi_{22}$
Δr_1	f_r	f_{rr}	f_{rR}	f_{rR}	f_{rd}	f'_{rd}	$f_{r\alpha}$	$f_{r\delta}$	$f_{r\gamma}$	$f'_{r\gamma}$	$f_{r\beta}$	$f'_{r\beta}$	$f_{r\beta}$	$f'_{r\beta}$	$f_{r\phi}$	$f'_{r\phi}$	$f_{r\phi}$	$f'_{r\phi}$
Δr_2		f_r	f_{rR}	f_{rR}	f'_{rd}	f_{rd}	$f_{r\alpha}$	$f_{r\delta}$	$f'_{r\gamma}$	$f_{r\gamma}$	$f_{R\beta}$	$f_{r\beta}$	$f'_{r\beta}$	$f_{r\beta}$	$f'_{r\phi}$	$f_{r\phi}$	$f'_{r\phi}$	$f_{r\phi}$
ΔR_1			f_R	f_{RR}	f_{Rd}	f_{Rd}	$f_{R\alpha}$	$f_{R\delta}$	$f_{R\gamma}$	$f_{R\gamma}$	$f_{R\beta}$	$f_{R\beta}$	$f'_{R\beta}$	$f'_{R\beta}$	$f_{R\phi}$	$f_{R\phi}$	$f'_{R\phi}$	$f'_{R\phi}$
ΔR_2				f_R	f_{Rd}	f_{Rd}	$f_{R\alpha}$	$f_{R\delta}$	$f_{R\gamma}$	$f'_{R\gamma}$	$f'_{R\beta}$	$f'_{R\beta}$	$f_{R\beta}$	$f_{R\beta}$	$f'_{R\phi}$	$f'_{R\phi}$	$f_{R\phi}$	$f_{R\phi}$
Δd_1					f_d	f_{dd}	$f_{d\alpha}$	$f_{d\delta}$	$f_{d\gamma}$	$f'_{d\gamma}$	$f_{d\beta}$	$f'_{d\beta}$	$f_{d\beta}$	$f'_{d\beta}$	$f_{d\phi}$	$f'_{d\phi}$	$f_{d\phi}$	$f'_{d\phi}$
Δd_2						f_d	$f_{d\alpha}$	$f_{d\delta}$	$f'_{d\gamma}$	$f_{d\gamma}$	$f'_{d\beta}$	$f_{d\beta}$	$f'_{d\beta}$	$f_{d\beta}$	$f'_{d\phi}$	$f_{d\phi}$	$f'_{d\phi}$	$f_{d\phi}$
$\Delta\alpha$							f_α	$f_{\alpha\delta}$	$f_{\alpha\gamma}$	$f_{\alpha\gamma}$	$f_{\alpha\beta}$	$f_{\alpha\beta}$	$f_{\alpha\beta}$	$f_{\alpha\beta}$	$f_{\alpha\phi}$	$f_{\alpha\phi}$	$f_{\alpha\phi}$	$f_{\alpha\phi}$
$\Delta\delta$								f_δ	$f_{\delta\gamma}$	$f_{\delta\gamma}$	$f_{\delta\beta}$	$f_{\delta\beta}$	$f_{\delta\beta}$	$f_{\delta\beta}$	$f_{\delta\phi}$	$f_{\delta\phi}$	$f_{\delta\phi}$	$f_{\delta\phi}$
$\Delta\gamma_1$									f_γ	$f_{\gamma\gamma}$	$f_{\gamma\beta}$	$f'_{\gamma\beta}$	$f_{\gamma\beta}$	$f'_{\gamma\beta}$	$f_{\gamma\phi}$	$f'_{\gamma\phi}$	$f_{\gamma\phi}$	$f'_{\gamma\phi}$
$\Delta\gamma_2$										f_γ	$f'_{\gamma\beta}$	$f_{\gamma\beta}$	$f'_{\gamma\beta}$	$f_{\gamma\beta}$	$f'_{\gamma\phi}$	$f_{\gamma\phi}$	$f'_{\gamma\phi}$	$f_{\gamma\phi}$
$\Delta\beta_{11}$											f_β	$f''_{\beta\beta}$	$f'_{\beta\beta}$	$f''_{\beta\beta}$	$f'_{\beta\phi}$	$f'_{\beta\phi}$	$f''_{\beta\phi}$	$f^\circ_{\beta\phi}$
$\Delta\beta_{12}$												f_β	$f''_{\beta\beta}$	$f'_{\beta\beta}$	$f''_{\beta\phi}$	$f^\circ_{\beta\phi}$	$f'_{\beta\phi}$	$f''_{\beta\phi}$
$\Delta\beta_{21}$													f_β	$f'_{\beta\beta}$	$f^\circ_{\beta\phi}$	$f''_{\beta\phi}$	$f'_{\beta\phi}$	$f'_{\beta\phi}$
$\Delta\beta_{22}$														f_β	$f_{\beta\phi}$	$f^\circ_{\beta\phi}$	$f''_{\beta\phi}$	$f^\circ_{\beta\phi}$
$\Delta\phi_{11}$															f_ϕ	$f'_{\phi\phi}$	$f''_{\phi\phi}$	$f'_{\phi\phi}$
$\Delta\phi_{12}$																f_ϕ	$f'_{\phi\phi}$	$f''_{\phi\phi}$
$\Delta\phi_{21}$																	f_ϕ	$f'_{\phi\phi}$
$\Delta\phi_{22}$																		f_ϕ

so that there will be three redundant co-ordinates ($2a_1+b_2$). There are forty independent force constants in the potential-energy function.

Our ortho-normal symmetry co-ordinates, using 90° angles, were

a_1 $S_1 = \frac{1}{\sqrt{2}}(\Delta r_1+\Delta r_2)$ $S_2 = \frac{1}{\sqrt{2}}(\Delta R_1+\Delta R_2)$ $S_3 = \frac{1}{\sqrt{2}}(\Delta\alpha-\Delta\delta)$

$S_4 = \frac{1}{2}(\Delta\alpha+\Delta\delta-\Delta\gamma_1-\Delta\gamma_2)$

$S_5 = \frac{1}{2\sqrt{2}}(\Delta\beta_{11}+\Delta\beta_{12}+\Delta\beta_{21}+\Delta\beta_{22}-\Delta\phi_{11}-\Delta\phi_{12}-\Delta\phi_{21}-\Delta\phi_{22})$

$S_6 = \frac{1}{\sqrt{2}}(\Delta d_1+\Delta d_2]$ $S_6{}^* = \frac{1}{2}(\Delta\alpha+\Delta\delta+\Delta\gamma_1+\Delta\gamma_2) \equiv 0$

$S_6{}^{**} = \frac{1}{2\sqrt{2}}(\Delta\beta_{11}+\Delta\beta_{12}+\Delta\beta_{21}+\Delta\beta_{22}+\Delta\phi_{11}+\Delta\phi_{12}+\Delta\phi_{21}+\Delta\phi_{22}) \equiv 0$

a_2 $S_7 = \frac{1}{2}(\Delta\beta_{11}-\Delta\beta_{12}-\Delta\beta_{21}+\Delta\beta_{22})$ $S_8 = \frac{1}{2}(\Delta\phi_{11}-\Delta\phi_{12}-\Delta\phi_{21}+\Delta\phi_{22})$

b_1 $S_9 = \frac{1}{\sqrt{2}}(\Delta R_1-\Delta R_2)$ $S_{10} = \frac{1}{2}(\Delta\beta_{11}+\Delta\beta_{12}-\Delta\beta_{21}-\Delta\beta_{22})$

$S_{11} = \frac{1}{2}(\Delta\phi_{11}+\Delta\phi_{12}-\Delta\phi_{21}-\Delta\phi_{22})$

b_2 $S_{12} = \frac{1}{\sqrt{2}}(\Delta r_1-\Delta r_2)$

$S_{13} = \frac{1}{2\sqrt{2}}(\Delta\beta_{11}-\Delta\beta_{12}+\Delta\beta_{21}-\Delta\beta_{22}+\Delta\phi_{11}-\Delta\phi_{12}+\Delta\phi_{21}-\Delta\phi_{22})$

$S_{14} = \frac{1}{\sqrt{2}}(\Delta\gamma_1-\Delta\gamma_2)$ $S_{15} = \frac{1}{\sqrt{2}}(\Delta d_1-\Delta d_2)$

$S_{15}{}^* = \frac{1}{2\sqrt{2}}(-\Delta\beta_{11}+\Delta\beta_{12}-\Delta\beta_{21}+\Delta\beta_{22}+\Delta\phi_{11}-\Delta\phi_{12}+\Delta\phi_{21}-\Delta\phi_{22}) \equiv 0 \ldots (1)$

* and ** Redundant co-ordinates.

Using the appropriate matrix multiplication between equations (1) and Table 1, the following F-matrix elements result:

a_1 $F_{11} = f_r+f_{rr}$ $F_{12} = 2f_{rR}$ $F_{13} = f_{r\alpha}-f_{r\delta}$

$F_{14} = \frac{1}{\sqrt{2}}(f_{r\alpha}+f_{r\delta}-f_{r\gamma}-f'_{r\gamma})$ $F_{15} = f_{r\beta}+f'_{r\beta}-f_{r\phi}-f'_{r\phi}$; $F_{16} = f_{rd}+f'_{rd}$

$F_{22} = f_R+f_{RR}$ $F_{23} = f_{R\alpha}-f_{R\delta}$ $F_{24} = \frac{1}{\sqrt{2}}(f_{R\alpha}+f_{R\delta}-2f_{R\gamma})$

$F_{25} = f_{R\beta}+f'_{R\beta}-f_{R\phi}-f'_{R\phi}$ $F_{26} = 2f_{Rd}$

$F_{33} = \frac{1}{2}(f_\alpha+f_\delta-2f_{\alpha\delta})$ $F_{34} = \frac{1}{2\sqrt{2}}(f_\alpha-f_\delta-2f_{\alpha\gamma}+2f_{\delta\gamma})$

$F_{35} = f_{\alpha\beta}-f_{\alpha\phi}-f_{\delta\beta}+f_{\delta\phi}$; $F_{36} = f_{d\alpha}-f_{d\delta}$

$$F_{44} = \frac{1}{4}(f_\alpha+2f_\gamma+f_\delta+2f_{\alpha\delta}-4f_{\alpha\gamma}-4f_{\delta\gamma}+2f_{\gamma\gamma})$$

$$F_{45} = \frac{1}{\sqrt{2}}(f_{\alpha\beta}-f_{\alpha\phi}+f_{\delta\beta}-f_{\delta\phi}-f_{\gamma\beta}-f'_{\gamma\beta}+f_{\gamma\phi}+f'_{\gamma\phi})$$

$$F_{46} = \frac{1}{\sqrt{2}}(f_{d\alpha}+f_{d\delta}-f_{d\gamma}-f'_{d\gamma})$$

$$F_{55} = \frac{1}{2}(f_\beta+f_{\beta\beta}+f'_{\beta\beta}+f''_{\beta\beta}-2f_{\beta\phi}-2f'_{\beta\phi}-2f''_{\beta\phi}-2f^\circ_{\beta\phi}+f_\phi+f_{\phi\phi}+f'_{\phi\phi}+f''_{\phi\phi})$$

$$F_{56} = f_{d\beta}+f'_{d\beta}-f_{d\phi}-f'_{d\phi} \qquad F_{66} = f_d+f_{dd}$$

a_2 $F_{77} = f_\beta-f_{\beta\beta}-f'_{\beta\beta}+f''_{\beta\beta}$ $\qquad F_{78} = f_{\beta\phi}-f'_{\beta\phi}-f''_{\beta\phi}+f^\circ_{\beta\phi}$

$$F_{88} = f_\phi-f_{\phi\phi}-f'_{\phi\phi}+f''_{\phi\phi}$$

b_1 $F_{99} = f_R-f_{RR}$ $\qquad F_{9,10} = \sqrt{2}(f_{R\beta}-f'_{R\beta})$ $\qquad F_{9,11} = \sqrt{2}(f_{R\phi}-f'_{R\phi})$

$$F_{10,10} = f_\beta+f_{\beta\beta}-f'_{\beta\beta}-f''_{\beta\beta} \qquad F_{10,11} = f_{\beta\phi}+f'_{\beta\phi}-f''_{\beta\phi}-f^\circ_{\beta\phi}$$

$$F_{11,11} = f_\phi+f_{\phi\phi}-f'_{\phi\phi}-f''_{\phi\phi}$$

b_2 $F_{12,12} = f_r-f_{rr}$ $\qquad F_{12,13} = f_{r\beta}-f'_{r\beta}+f_{r\phi}-f'_{r\phi}$

$$F_{12,14} = f_{r\gamma}-f'_{r\gamma} \qquad F_{12,15} = f_{rd}-f'_{rd}$$

$$F_{13,13} = \frac{1}{2}(f_\beta-f_{\beta\beta}+f'_{\beta\beta}-f''_{\beta\beta}+f_\phi-f_{\phi\phi}+f'_{\phi\phi}-f''_{\phi\phi}+2f_{\beta\phi}-2f'_{\beta\phi}+2f''_{\beta\phi}-2f^\circ_{\beta\phi})$$

$$F_{13,14} = f_{\gamma\beta}-f'_{\gamma\beta}+f_{\gamma\phi}-f'_{\gamma\phi} \qquad F_{13,15} = f_{d\beta}-f'_{d\beta}+f_{d\phi}-f'_{d\phi}$$

$$F_{14,14} = f_\gamma-f_{\gamma\gamma} \qquad F_{14,15} = f_{d\gamma}-f'_{d\gamma} \qquad F_{15,15} = f_d-f_{dd}$$

Similarly, by using standard techniques, the *G*-matrix elements are found to be ($x_1 = x_2 = x$; $x_3 = x_4 = x'$; μ_x = reciprocal mass of x in atomic weight units, etc.):

a_1 $G_{11} = \mu_x'+\mu_m$ $\qquad G_{12} = 0$ $\qquad G_{13} = -\mu_m(1/r+1/d)$

$$G_{14} = -\frac{\mu_m}{\sqrt{2}}(2/r-2/d) \qquad G_{15} = -2\mu_m/R \qquad G_{16} = -\mu_m$$

$$G_{22} = \mu_x \qquad G_{23} = 0 \qquad G_{24} = 0 \qquad G_{25} = 0 \qquad G_{26} = 0$$

$$G_{33} = \mu_x'/r^2+\mu_L/d^2+\mu_m(1/r+1/d)^2$$

$$G_{34} = \sqrt{2}\mu_x'/r^2-\sqrt{2}\mu_L/d^2+\sqrt{2}(1/r^2-1/d^2)\mu_m$$

$$G_{35} = \frac{\mu_m}{R}(2/r+2/d) \qquad G_{36} = \mu_m(1/r+1/d))$$

$$G_{44} = 2\mu_x'/r^2+2\mu_L/d^2+2\mu_m(1/r-1/d)^2 \qquad G_{45} = \frac{4\mu_m}{R\sqrt{2}}(1/r-1/d)$$

$$G_{46} = \sqrt{2}\mu_m(1/r-1/d)$$

$$G_{55} = 2\mu_x/R^2+4\mu_m/R^2 \qquad G_{56} = 2\mu_m/R \qquad G_{66} = \mu_L+\mu_m$$

a_2 $G_{77} = \mu x/R^2+2\mu_x'/r^2$ $\qquad G_{78} = \mu_x/R^2$ $\qquad G_{88} = \mu_x/R^2+2\mu_L/d^2$

b_1 $G_{99} = \mu_x + 2\mu_m$ $G_{9,10} = -\frac{4}{\sqrt{2}}\mu_m/r$ $G_{9,11} = -4\mu_m/\sqrt{2}d$

$G_{10,10} = \mu_x/R^2 + 2\mu_x'/r^2 + 4\mu_m/r^2$ $G_{10,11} = -\mu_x/R^2 + 4\mu_m/rd$

$G_{11,11} = 2\mu_L/d^2 + 4\mu_m/d^2 + \mu_x/R^2$

b_2 $G_{12,12} = \mu_x' + \mu_m$ $G_{12,13} = -2\mu_m/R$

$G_{12,14} = -\mu_m(1/r + 1/d)$ $G_{12,15} = \mu_m$

$G_{13,13} = 2\mu_x/R^2 + 4\mu_m/R^2$ $G_{13,14} = \frac{2\mu_m}{R}(1/r + 1/d)$ $G_{13,15} = -2\mu_m/R$

$G_{14,14} = \mu_x'/r^2 + \mu_L/d^2 + \mu_m(1/r + 1/d)^2$ $G_{14,15} = -\mu_m(1/r + 1/d)$

$G_{15,15} = \mu_L + \mu_m$

(2) *trans*-$L_2MX_4(D_{4h})$.—Fig. 2 shows our choice of interval co-ordinates for this molecule, while the corresponding f matrix is given in Table 2. The representation of the molecule after removal of translational and rotational degrees of freedom for Cartesian co-ordinates is

$$\Gamma_{\text{mol}} = 2a_{1g}(\text{R}) + 2a_{2u}(\text{IR}) + b_{1g}(\text{R}) + b_{2g}(\text{R}) + b_{2u}(\text{inactive}) + e_g(\text{R}) + 3e_u(\text{IR}),$$

whereas using internal co-ordinates (Fig. 2) we find

$$\Gamma_{\text{mol}} = 4a_{1g} + 2b_{1g} + 2a_{2u} + b_{2g} + b_{2u} + e_g + 3e_u$$

resulting again in three redundant co-ordinates ($2a_{1g} + b_{1g}$). In this case because of the higher symmetry there are fewer force constants necessary, only sixteen.

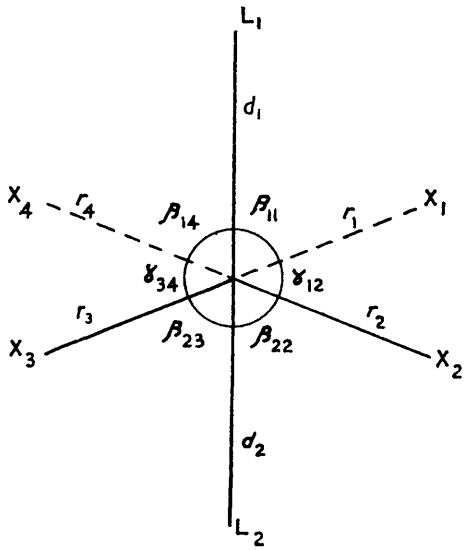

FIG. 2. Internal co-ordinates for *trans*-L_2MX_4.

Proceeding with a similar analysis, our orthonormal symmetry co-ordinates are:

a_{1g} $S_1 = \frac{1}{2}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$ $S_2 = \frac{1}{\sqrt{2}}(\Delta d_1 + \Delta d_2)$

$S_2^* = (\Delta\gamma_{12} + \Delta\gamma_{23} + \Delta\gamma_{34} + \Delta\gamma_{14}) \equiv 0$

$S_2^{**} = \frac{1}{2}(\Delta\beta_{11} + \Delta\beta_{12} + \Delta\beta_{13} + \Delta\beta_{14} + \Delta\beta_{21} + \Delta\beta_{22} + \Delta\beta_{23} + \Delta\beta_{24}) \equiv 0$

TABLE 2.

The f matrix for *trans*-L_2MX_4.

f	Δr_1	Δr_2	Δr_3	Δr_4	Δd_1	Δd_2	$\Delta\beta_{11}$	$\Delta\beta_{12}$	$\Delta\beta_{13}$	$\Delta\beta_{14}$	$\Delta\beta_{21}$	$\Delta\beta_{22}$	$\Delta\beta_{23}$	$\Delta\beta_{24}$	$\Delta\gamma_{12}$	$\Delta\gamma_{23}$	$\Delta\gamma_{34}$	$\Delta\gamma_{14}$
Δr_1	f_r	f_{rr}	f'_{rr}	f_{rr}	$f_{r\alpha}$	$f_{r\alpha}$	$f_{r\beta}$	$f'_{r\beta}$	$f''_{r\beta}$	$f'_{r\beta}$	$f_{r\beta}$	$f'_{r\beta}$	$f''_{r\beta}$	$f'_{r\beta}$	$f_{r\gamma}$	$f'_{r\gamma}$	$f'_{r\gamma}$	$f_{r\gamma}$
Δr_2		f_r	f_{rr}	f'_{rr}	$f_{r\alpha}$	$f_{r\alpha}$	$f''_{r\beta}$	$f_{r\beta}$	$f'_{r\beta}$	$f''_{r\beta}$	$f'_{r\beta}$	$f''_{r\beta}$	$f'_{r\beta}$	$f''_{r\beta}$	$f_{r\gamma}$	$f_{r\gamma}$	$f'_{r\gamma}$	$f'_{r\gamma}$
Δr_3			f_r	f_{rr}	$f_{r\alpha}$	$f_{r\alpha}$	$f'''_{r\beta}$	$f'_{r\beta}$	$f_{r\beta}$	$f'''_{r\beta}$	$f''_{r\beta}$	$f'''_{r\beta}$	$f_{r\beta}$	$f'_{r\beta}$	$f'_{r\gamma}$	$f_{r\gamma}$	$f_{r\gamma}$	$f_{r\gamma}$
Δr_4				f_r	$f_{r\alpha}$	$f_{r\alpha}$	$f'_{r\beta}$	$f''_{r\beta}$	$f'_{r\beta}$	$f_{r\beta}$	$f'_{r\beta}$	$f''_{r\beta}$	$f'_{r\beta}$	$f_{r\beta}$	$f'_{r\gamma}$	$f'_{r\gamma}$	$f_{r\gamma}$	$f_{r\gamma}$
Δd_1					f_α	$f_{\alpha\alpha}$	$f_{\alpha\beta}$	$f_{\alpha\beta}$	$f_{\alpha\beta}$	$f'_{\alpha\beta}$	$f'_{\alpha\beta}$	$f'_{\alpha\beta}$	$f'_{\alpha\beta}$	$f'^{\alpha\beta}$	$f_{\alpha\gamma}$	$f_{\alpha\gamma}$	$f_{\alpha\gamma}$	$f_{\alpha\gamma}$
Δd_2						f_α	$f'_{\alpha\beta}$	$f'_{\alpha\beta}$	$f'_{\alpha\beta}$	$f_{\alpha\beta}$	$f_{\alpha\beta}$	$f_{\alpha\beta}$	$f_{\alpha\beta}$	$f^{\circ}{}_{\beta\beta}$	$f_{\beta\gamma}$	$f'_{\beta\gamma}$	$f'_{\beta\gamma}$	$f_{\beta\gamma}$
$\Delta\beta_{11}$							f_β	$f_{\beta\beta}$	$f'_{\beta\beta}$	$f_{\beta\beta}$	$f''_{\beta\beta}$	$f''_{\beta\beta}$	$f^{\circ}{}_{\beta\beta}$	$ft_{\beta\beta}$	$f_{\beta\gamma}$	$f'_{\beta\gamma}$	$f'_{\beta\gamma}$	$f'_{\beta\gamma}$
$\Delta\beta_{12}$								f_β	$f_{\beta\beta}$	$f'_{\beta\beta}$	$f^{\circ}{}_{\beta\beta}$	$f''_{\beta\beta}$	$f^{\circ}{}_{\beta\beta}$	$f^{\circ}{}_{\beta\beta}$	$f'_{\beta\gamma}$	$f_{\beta\gamma}$	$f_{\beta\gamma}$	$f'_{\beta\gamma}$
$\Delta\beta_{13}$									f_β	$f_{\beta\beta}$	$ft_{\beta\beta}$	$f^{\circ}{}_{\beta\beta}$	$f''_{\beta\beta}$	$f^{\circ}{}_{\beta\beta}$	$f'_{\beta\gamma}$	$f_{\beta\gamma}$	$f_{\beta\gamma}$	$f'_{\beta\gamma}$
$\Delta\beta_{14}$										f_β	$f^{\circ}{}_{\beta\beta}$	$ft_{\beta\beta}$	$f^{\circ}{}_{\beta\beta}$	$f''_{\beta\beta}$	$f^{\circ}{}_{\beta\gamma}$	$f'_{\beta\gamma}$	$f_{\beta\gamma}$	$f_{\beta\gamma}$
$\Delta\beta_{21}$											f_β	$f^{\circ}{}_{\beta\beta}$	$f'_{\beta\beta}$	$f_{\beta\beta}$	$f_{\beta\gamma}$	$f'_{\beta\gamma}$	$f'_{\beta\gamma}$	$f_{\beta\gamma}$
$\Delta\beta_{22}$												f_β	$f'_{\beta\beta}$	$f'_{\beta\beta}$	$f_{\beta\gamma}$	$f_{\beta\gamma}$	$f_{\beta\gamma}$	$f_{\beta\gamma}$
$\Delta\beta_{23}$													f_β	$f_{\beta\beta}$	$f'_{\beta\gamma}$	$f_{\beta\gamma}$	$f_{\beta\gamma}$	$f_{\beta\gamma}$
$\Delta\beta_{24}$														f_β	$f'_{\beta\gamma}$	$f'_{\beta\gamma}$	$f_{\beta\gamma}$	$f_{\beta\gamma}$
$\Delta\gamma_{12}$															f_γ	$f_{\gamma\gamma}$	$f'_{\gamma\gamma}$	$f_{\gamma\gamma}$
$\Delta\gamma_{23}$																f_γ	$f_{\gamma\gamma}$	$f_{\gamma\gamma}$
$\Delta\gamma_{34}$																	f_γ	$f_{\gamma\gamma}$
$\Delta\gamma_{14}$																		f_γ

a_{2u} $S_3 = \frac{1}{\sqrt{2}}(\Delta d_1 - \Delta d_2)$

$S_4 = \frac{1}{2\sqrt{2}}(\Delta\beta_{11} + \Delta\beta_{12} + \Delta\beta_{13} + \Delta\beta_{14} - \Delta\beta_{21} - \Delta\beta_{22} - \Delta\beta_{23} - \Delta\beta_{24})$

b_{1g} $S_5 = \frac{1}{2}(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$

$S_5{}^* = \frac{1}{2\sqrt{2}}(-\Delta\beta_{11} + \Delta\beta_{12} - \Delta\beta_{13} + \Delta\beta_{14} - \Delta\beta_{21} + \Delta\beta_{22} - \Delta\beta_{23} + \Delta\beta_{24}) \equiv 0$

b_{2g} $S_6 = \frac{1}{2}(\Delta\gamma_{12} - \Delta\gamma_{23} + \Delta\gamma_{34} - \Delta\gamma_{14})$

b_{2u} $S_7 = \frac{1}{2\sqrt{2}}(\Delta\beta_{11} - \Delta\beta_{12} + \Delta\beta_{13} - \Delta\beta_{14} - \Delta\beta_{21} + \Delta\beta_{22} - \Delta\beta_{23} + \Delta\beta_{24})$

e_g $S_{8a} = \frac{1}{2}(\Delta\beta_{12} - \Delta\beta_{14} - \Delta\beta_{22} + \Delta\beta_{24})$

$S_{8b} = \frac{1}{2}(\Delta\beta_{11} - \Delta\beta_{13} - \Delta\beta_{21} + \Delta\beta_{23})$

* and ** Redundant co-ordinates.

e_u $S_{9a} = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_3)$ $S_{9b} = \frac{1}{\sqrt{2}}(\Delta r_2 - \Delta r_4)$

$S_{10a} = \frac{1}{2}(\Delta\beta_{11} - \Delta\beta_{13} + \Delta\beta_{21} - \Delta\beta_{23})$ $S_{10b} = \frac{1}{2}(\Delta\beta_{12} - \Delta\beta_{14} + \Delta\beta_{22} - \Delta\beta_{24})$

$S_{11a} = \frac{1}{2}(\Delta\gamma_{12} + \Delta\gamma_{14} - \Delta\gamma_{23} - \Delta\gamma_{34})$ $S_{11b} = \frac{1}{2}(\Delta\gamma_{12} - \Delta\gamma_{14} + \Delta\gamma_{23} - \Delta\gamma_{34})$

F-matrix elements:

a_{1g} $F_{11} = f_r + 2f_{rr} + f'_{rr}$ $F_{12} = 2\sqrt{2}f_{rd}$ $F_{22} = f_d + f_{dd}$

a_{2u} $F_{33} = f_d - f_{dd}$ $F_{34} = 2f_{d\beta} - 2f'_{d\beta}$ $F_{44} = f_\beta + 2f_{\beta\beta} + f'_{\beta\beta} - f''_{\beta\beta} - 2f^\circ_{\beta\beta} - f^\dagger_{\beta\beta}$

b_{1g} $F_{55} = f_r - 2f_{rr} + f'_{rr}$

b_{2g} $F_{66} = f_\gamma - 2f_{\gamma\gamma} + f'_{\gamma\gamma}$

b_{2u} $F_{77} = f_\beta - 2f_{\beta\beta} + f'_{\beta\beta} - f''_{\beta\beta} + 2f^\circ_{\beta\beta} - f^\dagger_{\beta\beta}$

e_g $F_{88} = f_\beta - f'_{\beta\beta} - f''_{\beta\beta} + f^\dagger_{\beta\beta}$

e_u $F_{99} = f_r - f'_{rr}$ $F_{9,10} = \sqrt{2}(f_{r\beta} - f''_{r\beta})$ $F_{9,11} = \sqrt{2}(f_{r\gamma} - f'_{r\gamma})$

$F_{10,10} = f_\beta - f'_{\beta\beta} + f''_{\beta\beta} - f^\dagger_{\beta\beta}$ $F_{10,11} = 2(f_{\beta\gamma} - f'_{\beta\gamma})$ $F_{11,11} = f_\gamma - f'_{\gamma\gamma}$

G-matrix elements ($x_1 = x_2 = x_3 = x_4 = x$, etc.);

a_{1g} $G_{11} = \mu_x$ $G_{12} = 0$ $G_{22} = \mu_L$

a_{2u} $G_{33} = \mu_L + 2\mu_m$ $G_{34} = -4\mu_m/r$ $G_{44} = 2\mu_x/r^{2+} + 8\mu_m/r^2$

b_{1g} $G_{55} = \mu_x$

b_{2g} $G_{66} = 4\mu_x/r^2$

b_{2u} $G_{77} = 2\mu_x/r^2$

e_g $G_{88} = 2\mu_x/r^2+2\mu_L/d^2$

e_u $G_{99} = \mu_x+2\mu_m$ $G_{9,10} = -4\mu_m/\sqrt{2}d$ $G_{9,11} = -4\mu_m/\sqrt{2}r$

$G_{10,10} = 2\mu_L/d^2+4\mu_m/d^2$ $G_{10,11} = 4\mu_m/rd$ $G_{11,11} = 2\mu_x/r^2+4\mu_m/r^2$

Calculations.—Vibrational frequencies for representative adducts were calculated by use of the relationship $|FG-E\lambda| = 0$. To maintain the same units throughout, force constants in the F matrix were multiplied by (length) or (length)^2 for terms of the form $f_{r\phi}$ or $f_{\phi\phi}$, respectively. Due to the lack of knowledge of force constants for molecules of this type we put all the off-diagonal terms in the potential-energy matrix equal to zero and put bending force constants (in dynes/cm.) equal to one tenth of the stretching force constants of adjacent bonds (where these have different force constants the arithmetic mean of the two stretching constants was used). For the *cis*-adduct f_{M-X} was also put equal to $f_{M-X'}$. The mass of the ligand was equated arbitrarily to 40 atomic weight units.

Discussion.—The results shown in Table 3 indicate that for a *cis*-adduct three high-frequency bands are to be expected, the next nearest band lying considerably below this group

TABLE 3.

The four highest frequencies in *cis*-L_2MX_4.

M–L force constant (10^5 dynes/cm.)	Adduct	Frequencies (calc.) ($cm.^{-1}$)			
0	L_2SiF_4	970 b_1	818 b_2	815 a_1	600 a_1
0·5	L_2SiF_4	971 b_1	832 b_2	830 a_1	600 a_1
1·5	L_2SiF_4	975 b_1	864 b_2	862 a_1	600 a_1
0	L_2SiCl_4	529 b_1	425 b_2	425 a_1	258 a_1
0·5	L_2SiCl_4	534 b_1	461 b_2	462 a_1	258 a_1
1·5	L_2SiCl_4	544 b_1	547 b_2	547 a_1	258 a_1
0	L_2SiBr_4	422 b_1	327 b_2	330 a_1	145 a_1
0·5	L_2SiBr_4	430 b_1	384 b_2	385 a_1	145 a_1*
1·5	L_2SiBr_4	446 b_1	498 b_2	498 a_1	201 a_1

Si–F = 1·62, Si–Cl = Ge–Cl = Sn–Cl = 2·13, Si–Br = 2·28, M–L = 2·0 Å $f_{Si-F} = 4{\cdot}0$, $f_{Si-Cl} = 1{\cdot}4$, $f_{Si-Br} = 1{\cdot}0$, $f_{Ge-Cl} = f_{Sn-Cl} = 1{\cdot}4 \times 10^5$ dynes/cm.

* Occurs twice.

(all the bands mentioned here are infrared- and Raman-active). Although in the most general case all the a_1 vibrations interact with one another, the neglect of off-diagonal terms in the F matrix gives rise to one frequency (the symmetric Si–X stretch) which is independent of the force constants except f_R. This explains the accidental degeneracy observed in Table 3 (see footnote) and which would be removed in a more general treatment. In the case of the *trans*-adducts, Table 4 shows that if the metal–ligand force constant is low compared with the metal–halogen, there will be one main band in the same region as the set of three absorptions mentioned for the *cis*-adducts. However, where the metal–ligand force constant is high, the e_u and a_{2u} vibrations (both IR active) will occur in similar regions of the spectrum. Thus, in a crystalline compound, crystal-field resolution of the e_u vibration to a doublet, plus the presence of an a_{2u} vibration, could lead to a spectrum similar to that of a *cis*-adduct. The calculations show that the e_u vibration (approximately M–X antisymmetric stretch) is relatively insensitive to the value of f_{M-L} and also (as further calculations show) to the value of the bending force constants chosen. Calculations were also performed on L_2GeCl_4 and L_2SnCl_4 using the same M–Cl distance and M–Cl force constants as in L_2SiCl_4, in order to examine the effect of increasing the mass of the central atom. It is difficult to go further in

TABLE 4.

The two highest frequencies in *trans*-L_2MX_4.

M–L force constant (10^5 dynes/cm.)	Adduct	Frequencies (calc.) ($cm.^{-1}$)	
1·5	L_2SiF_4	975 e_u	642 a_{2u}
0·5	L_2SiCl_4	532 e_u	347 a_{2u}
1·0	L_2SiCl_4	538 e_u	459 a_{2u}
1·5	L_2SiCl_4	544 e_u	547 a_{2u}
1·5	L_2SiBr_4	446 e_u	537 a_{2u}
0·5	L_2GeCl_4	381 e_u	258 a_{1g}, b_{1g}
1·0	L_2GeCl_4	384 e_u	321 a_{2u}
1·5	L_2GeCl_4	386 e_u	388 a_{2u}
0·5	L_2SnCl_4	336 e_u	258 a_{1g}, b_{1g}
1·0	L_2SnCl_4	337 e_u	279 a_{2u}
1·5	L_2SnCl_4	338 e_u	337 a_{2u}

Bond lengths and force constants used in the calculations are shown in Table 3.

this discussion in the absence of extensive infrared and Raman spectral investigations on selected compounds. The inadequate experimental work so far carried out on such adducts suggests that the M–L force constant is low and that identification of *cis*- and *trans*-isomers *via* infrared and Raman spectroscopic examination will become routine in favourable cases, particularly where solution spectra can be obtained.

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