Volume 21
Number 1
January 1982

Inorganic Chemistry

Contribution from the Chemical Laboratories,
University of Kent, Canterbury, Kent CT2 7NH, England

Splitting of Degenerate Vibrational Modes due to Symmetry Perturbations in Tetrahedral M_4 and Octahedral M_6 Clusters

J. A. CREIGHTON

Received February 9, 1981

The splitting of the degenerate vibrations of tetrahedral M_4 and octahedral M_6 clusters due to asymmetry in the distribution of force constants or atomic masses in the clusters is systematically investigated. It is shown that force field or mass perturbations which retain a C_3 symmetry axis do not split some of the triply degenerate vibrations to first-order terms in the force constant or mass differences, and these modes are therefore rather insensitive to the asymmetry for relatively small perturbations. Similarly there is no first-order splitting of the doubly degenerate vibration of M_4 due to a perturbation purely of the masses to any lower symmetry. These results account for the very small splitting of the $t_2(T_d)$ cluster mode observed for $Rh_4(CO)_{12}$ (C_{3v}), and other metal cluster compounds are noted for which the splittings of degenerate cluster vibrations due to asymmetry are also expected to be small.

Introduction

Vibrational spectroscopy has generally been regarded as a sensitive technique for investigating molecular symmetry, and the splitting of degenerate vibrations of highly symmetric molecules as a result of the introduction of asymmetry into the force field or the atomic mass distribution has been much used for detecting this asymmetry. The sensitivity usually shown by degenerate vibrations to a descent in symmetry is due to the first-order dependence of the splitting of these vibrations on the force constant or mass differences which constitute the asymmetry, and approximate first-order relationships have been derived for the splitting of the degenerate vibrations of some simple molecules as a result of force constant perturbations.[1]

It has recently been reported,[2] however, that in a simple valence force field (SVFF) approximation, the t_2 vibration of a tetrahedral M_4 cluster is not split to a first-order approximation by a force constant perturbation of C_{3v} symmetry, although such a perturbation formally splits the t_2 vibration into an a_1 and e component. In this particular case, therefore, vibrational spectroscopy is a rather insensitive method of detecting the asymmetry in the force field. Thus, for example, the M_4 cluster in $Rh_4(CO)_{12}$ has C_{3v} symmetry due to the presence of bridging carbonyl ligands along the edges of one of the faces of the tetrahedral cluster, but the t_2 cluster vibration was found[2] to show no detectable splitting in solution at 2-cm^{-1} resolution, although there is evidence from studies on related molecules[3] that there is a considerable difference between the stretching force constants for carbonyl-bridged and unbridged M–M bonds.

The vibrational spectra of metal cluster compounds in the ν(M–M) region have been relatively little explored but are of potential importance as a source of information on the structures of the parent clusters and on the strength of bonding within the cluster inferred from the M–M force constants. It is important for the interpretation of the spectra in this region, and for the evaluation of vibrational spectroscopy as a structural technique in this field, that their sensitivity to cluster asymmetry is understood. This paper therefore systematically investigates the effect of force constant or mass perturbations on the degenerate vibrations of tetrahedral M_4 and octahedral M_6 clusters with the use of a SVFF approximation in order to determine which types of asymmetry result in first-order splittings and which in only second-order splittings of these vibrations.

General Theory

The vibration frequencies of an asymmetrically bonded molecule such as $Rh_4(CO)_{12}$ may be considered to be derived from those of a related structure of higher symmetry as a result of a perturbation of the symmetry of the intramolecular force field. The frequencies $(\nu_i)_0$ of the unperturbed molecule, and those ν_i of the perturbed structure, are related to the atomic masses and force constants by[4]

$$\Lambda_0 = \mathbf{L}_0^{-1}\mathbf{G}_0\mathbf{F}_0\mathbf{L}_0 \qquad \Lambda = \mathbf{L}^{-1}\mathbf{G}_0\mathbf{F}\mathbf{L}$$

where Λ_0 and Λ are diagonal matrices with elements $(\lambda_i)_0 = 4\pi(\nu_i)_0^2$ and $\lambda_i = 4\pi\nu_i^2$, respectively. The symmetrized matrices **L**, **G**, and **F** have the usual significance,[4] and the zero subscripts refer to the unperturbed structure. These equations show that changing the force constant matrix **F** has a direct first-order effect on the vibration frequencies but that there is also a secondary effect due to additional mixing of vibrations in the lower symmetry which changes the **L** matrix. Writing

---

[1] Creighton, J. A. *J. Chem. Soc., Dalton Trans.* **1974**, 2289. Brintzinger, H.; Hester, R. E. *Inorg. Chem.* **1966**, *5*, 980. Hester, R. E.; Grossman, W. E. L. *Ibid.* **1966**, *5*, 1308.

[2] Creighton, J. A.; Heaton, B. T. *J. Chem. Soc., Dalton Trans.* **1981**, 1498.

[3] Onaka, S.; Shriver, D. F. *Inorg. Chem.* **1976**, *15*, 915.

[4] Wilson, E. B.; Decius, J. C.; Cross, P. C. "Molecular Vibrations"; McGraw-Hill: New York, 1955; pp 189 and 309.

0020-1669/82/1321-0001$01.25/0

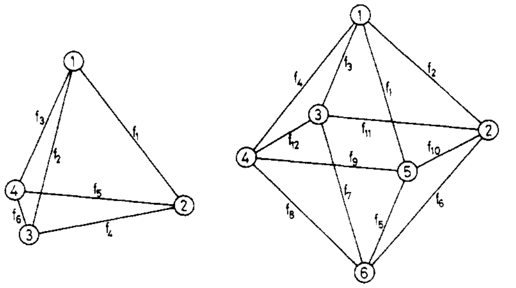

Figure 1. Numbering of atoms and force constants in the M_4 and M_6 clusters.

Table I. Diagonal Blocks of the G and F Matrices for a Tetrahedral M_4 Cluster

	a_1 Block
$g_{11} = \mu_1 + \mu_2 + \mu_3 + \mu_4$	$f_{11} = \Sigma f_i/6\ (i = 1\text{–}6)$
	e Block
$g_{22} = g_{33} = g_{11}/4$	$f_{22} = \Sigma(4f_i + f_j)/12$ $\left.\right\}(i = 1, 6;\ j = 2\text{–}5)$
$g_{23} = f_{23} = 0$	$f_{33} = \Sigma f_j/4$
	t_2 Block
$g_{44} = g_{55} = g_{66} = g_{11}/2$	$f_{44} = (f_1 + f_6)/2$
$g_{45} = (\mu_1 - \mu_2 - \mu_3 + \mu_4)/4$	$f_{55} = (f_2 + f_5)/2$
$g_{46} = (\mu_1 - \mu_2 + \mu_3 - \mu_4)/4$	$f_{66} = (f_3 + f_4)/2$
$g_{56} = (\mu_1 + \mu_2 - \mu_3 - \mu_4)/4$	$f_{45} = f_{46} = f_{56} = 0$

$\mathbf{L} = \mathbf{L}_0\mathbf{C}$, it is clear from the standard relationship[4] $\mathbf{L}_0\tilde{\mathbf{L}}_0 = \mathbf{G}_0 = \mathbf{L}\tilde{\mathbf{L}}$ that $\mathbf{C}$, which describes the additional vibrational mixing in the lower symmetry, is an orthogonal matrix. Thus

$$\Lambda = \tilde{\mathbf{C}}[\mathbf{L}_0^{-1}\mathbf{G}_0\mathbf{F}\mathbf{L}_0]\mathbf{C} \tag{1}$$

As may now be seen by assuming no additional vibrational mixing in the lower symmetry and thus by setting $\mathbf{C}$ equal to a unit matrix, the diagonal elements of the matrix $[\mathbf{L}_0^{-1}\mathbf{G}_0\mathbf{F}\mathbf{L}_0]$ are the quantities λ_i for the perturbed molecule correct to first-order terms in the perturbed force constants. The off-diagonal elements contribute the effect on the λ_i of the additional vibrational mixing in the lower symmetry, but since the elements of $\mathbf{C}$ are themselves functions of the perturbed force constants, these off-diagonal elements only contribute second-order and higher terms in the perturbed force constants to the λ_i.

The vibrations of tetrahedral M_4 and octahedral M_6 clusters are of species $a_1 + e + t_2$ and $a_{1g} + e_g + t_{1u} + t_{2g} + t_{2u}$ of the point groups T_d and O_h, respectively. These clusters thus have the convenient property that there is only one vibration in each symmetry class, and $\mathbf{G}_0$ and $\mathbf{L}_0$ for each symmetry class are therefore constant matrices. If $\mathbf{F}$ for a given symmetry class is also a constant matrix, then $[\mathbf{L}_0^{-1}\mathbf{G}_0\mathbf{F}\mathbf{L}_0]$ for that class is also constant. It is thus seen that the necessary condition for the absence of first-order splitting of a degenerate vibration in these clusters is that $\mathbf{F}$ is a constant matrix for that symmetry class.

It may similarly be shown that the vibration frequencies resulting from a perturbation of the atomic masses are given by

$$\Lambda = \mathbf{C}^{-1}[\mathbf{L}_0^{-1}\mathbf{G}\mathbf{F}_0\mathbf{L}_0]\mathbf{C}$$

where $\mathbf{C}$ is here a nonorthogonal matrix. Since $\mathbf{L}_0$ and $\mathbf{F}_0$ are constant matrices for all the symmetry classes of the M_4 or M_6 clusters, the necessary condition for no first-order splitting of the degenerate vibration in a given symmetry class as a result of a mass perturbation is thus that the $\mathbf{G}$ matrix for that class is a constant matrix.

Tetrahedral M_4 Cluster. With the numbering of atoms and bond stretching force constants f_i as shown in Figure 1, the diagonal blocks of the G and F matrices of a tetrahedral M_4 cluster are as given in Table I. The a_1 and e symmetry coordinates used in determining these matrices were as used previously for the P_4 molecules,[5] whereas for the t_2 species it was more convenient to use $S_4 = (r_{12} - r_{34})/2^{1/2}$, $S_5 = (r_{13} - r_{24})/2^{1/2}$, and $S_6 = (r_{14} - r_{23})/2^{1/2}$. The possible subgroups of T_d generated by perturbing the force constants of a M_4 cluster are C_{3v}, D_{2d}, and lower order groups which are themselves subgroups of D_{2d}. The correlation between the species of the M_4 cluster vibrations in these subgroups with those in T_d, showing the formal splitting of the degenerate vibrations in the lower symmetries, is given in Table II.

Table II. Correlation of the Vibrational Representations for M_4 (T_d) and M_6 (O_h) Clusters with Those of Some Significant Subgroups

M_4

T_d	C_{3v}	D_{2d}
a_1	a_1	a_1
e	e	$a_1 + b_1$
t_2	$a_1 + e$	$b_2 + e$

M_6

O_h	D_{3d}	D_3	C_{3v}	C_3	D_{4h}
a_{1g}	a_{1g}	a_1	a_1	a	a_{1g}
e_g	e_g	e	e	e	$a_{1g} + b_{1g}$
t_{1u}	$a_{2u} + e_u$	$a_2 + e$	$a_1 + e$	a + e	$a_{2u} + e_u$
t_{2g}	$a_{1g} + e_g$	$a_1 + e$	$a_1 + e$	a + e	$b_{2g} + e_g$
t_{2u}	$a_{1u} + e_u$	$a_1 + e$	$a_2 + e$	a + e	$b_{2u} + e_u$

In the case of a C_{3v} perturbation, the retention of a C_3 symmetry element, taken here to pass through atom 1, requires that $f_1 = f_2 = f_3$ and $f_4 = f_5 = f_6$. Thus here by symmetry $\mathbf{F}(t_2)$ remains a constant matrix, and there is therefore no first-order splitting of the t_2 vibration as a result of a C_{3v} force constant perturbation. Since the e vibration is also unsplit in this symmetry, the vibrational spectra of M_4 clusters in which the force fields have C_{3v} symmetry therefore closely resemble the spectra of fully tetrahedral M_4 clusters, as already reported for $Rh_4(CO)_{12}$.[2] For M_4 clusters of D_{2d} or lower symmetry point groups, however, the relationships between the force constants imposed by symmetry do not require that $\mathbf{F}(t_2)$ or $\mathbf{F}(e)$ are constant matrices, and thus for M_4 clusters with force fields of these symmetries, there is a first-order splitting of both the t_2 and e vibrations of the cluster.

Turning now instead to the effects on the degenerate vibrations of mass perturbations which do not significantly affect the force constants of the M_4 cluster, it can be seen that the possible subgroups of T_d resulting from the substitution of atoms in the cluster by atoms of one other type are C_{3v} and C_{2v}. The symmetry relationships between the reciprocal masses in C_{3v} and C_{2v} respectively $\mu_1 \neq \mu_2 = \mu_3 = \mu_4$ and $\mu_1 = \mu_2 \neq \mu_3 = \mu_4$ do not diagonalize $\mathbf{G}(t_2)$, and to achieve this it is necessary also to make the transformation

$$\mathbf{G}' = \mathbf{T}\mathbf{G}\tilde{\mathbf{T}} \qquad \mathbf{F}' = \mathbf{T}\mathbf{F}\tilde{\mathbf{T}} \tag{2}$$

where $\mathbf{T}$ is an orthogonal matrix:

$$\mathbf{T} = \begin{bmatrix} \cos\theta & \sin\theta\cos\phi & \sin\theta\sin\phi \\ -\sin\theta & \cos\theta\cos\phi & \cos\theta\sin\phi \\ 0 & -\sin\phi & \cos\phi \end{bmatrix}$$

This amounts to redefining the symmetry coordinates and has no effect on $\mathbf{F}_0$ since $\mathbf{F}_0(t_2)$ is a constant matrix. With the above relationships between the reciprocal masses, and with $\phi = 45.0°$ and $\Theta = 54.7356°$ (C_{3v}) or $0.0°$ (C_{2v}), $\mathbf{G}(t_2)$ becomes

$$\begin{array}{llll} C_{3v}: & g_{44} = \mu_1 + \mu_2 & C_{2v}: & g_{44} = \mu_1 + \mu_3 \\ & g_{55} = (\mu_1 + 7\mu_2)/4 & & g_{55} = (3\mu_1 + \mu_3)/2 \\ & g_{66} = (\mu_1 + 7\mu_2)/4 & & g_{66} = (\mu_1 + 3\mu_3)/2 \end{array}$$

$$g_{45} = g_{46} = g_{56} = 0$$

---

(5) Pistorius, C. W. F. T. *J. Chem. Phys.* **1958**, *29*, 1421.

Table III. Diagonal Block of the **G** and **F** Matrices for an Octahedral M_6 Cluster

a_{1g} Block	$g_{11} = 2\Sigma\mu_i/3\ (i = 1\text{–}6)$	$f_{11} = \Sigma f_i/12\ (i = 1\text{–}12)$
e_g Block	$\left.\begin{array}{l} g_{22} = \Sigma(4\mu_i + \mu_j)/12 \\ g_{33} = \Sigma\mu_j/4 \end{array}\right\}(i = 1, 6; j = 2\text{–}5)$ $g_{23} = \Sigma(\mu_i - \mu_j)/4(3^{1/2})\ (i = 2, 4; j = 3, 5)$	$\left.\begin{array}{l} f_{22} = \Sigma(f_i + 4f_j)/24 \\ f_{33} = \Sigma f_i/8 \end{array}\right\}(i = 1\text{–}8; j = 9\text{–}12)$ $f_{23} = \Sigma(f_i - f_j)/8(3^{1/2})\ (i = 1, 3, 5, 7; j = 2, 4, 6, 8)$
t_{1u} Block	$\left.\begin{array}{l} g_{44} \\ g_{55} \\ g_{66} \end{array}\right\} = \Sigma(4\mu_i + \mu_j)/4 \left\{\begin{array}{l} (i = 1, 6; j = 2\text{–}5) \\ (i = 2, 4; j = 1, 3, 5, 6) \\ (i = 3, 5; j = 1, 2, 4, 6) \end{array}\right.$ $g_{45} = g_{46} = g_{56} = 0$	$\left.\begin{array}{l} f_{44} \\ f_{55} \\ f_{66} \end{array}\right\} = \Sigma f_i/8 \left\{\begin{array}{l} (i = 1\text{–}8) \\ (i = 2, 4, 6, 8\text{–}12) \\ (i = 1, 3, 5, 7, 9\text{–}12) \end{array}\right.$ $\left.\begin{array}{l} f_{45} \\ f_{46} \\ f_{56} \end{array}\right\} = \Sigma(f_i - f_j)/8 \left\{\begin{array}{l} (i = 2, 8; j = 4, 6) \\ (i = 1, 7; j = 3, 5) \\ (i = 10, 12; j = 9, 11) \end{array}\right.$
t_{2g} Block	$\left.\begin{array}{l} g_{77} \\ g_{88} \\ g_{99} \end{array}\right\} = \Sigma\mu_i/2 \left\{\begin{array}{l} (i = 2\text{–}5) \\ (i = 1, 3, 5, 6) \\ (i = 1, 2, 4, 6) \end{array}\right.$ $g_{78} = g_{79} = g_{89} = 0$	$\left.\begin{array}{l} f_{77} \\ f_{88} \\ f_{99} \end{array}\right\} = \Sigma f_i/4 \left\{\begin{array}{l} (i = 9\text{–}12) \\ (i = 1, 3, 5, 7) \\ (i = 2, 4, 6, 8) \end{array}\right.$ $f_{78} = f_{79} = f_{89} = 0$
t_{2u} Block	$g_{10\,10} = g_{77}/2$ $g_{11\,11} = g_{88}/2$ $g_{12\,12} = g_{99}/2$ $g_{10\,11} = g_{10\,12} = g_{11\,12} = 0$	$f_{10\,10} = f_{44}$ $f_{11\,11} = f_{55}$ $f_{12\,12} = f_{66}$ $f_{10\,11} = -f_{45}$ $f_{10\,12} = f_{46}$ $f_{11\,12} = f_{56}$

Thus $\mathbf{G}(t_2)$ does not remain a constant matrix as a result of either of these mass perturbations. There is therefore in both cases a first-order splitting of the t_2 vibration, and this conclusion may be seen to hold also for mass perturbations of lower symmetries in which there are substitutions involving several kinds of atoms, since for these lower symmetries there are fewer relationships between the reciprocal atomic masses. It may, however, be seen from Table I that $\mathbf{G}(e)$ remains a constant matrix following any change in atomic masses. Thus the e vibration is unsplit to first order by any such change.

Octahedral M_6 Cluster. The diagonal blocks of the **G** and **F** matrices for a M_6 cluster, using the published choice of symmetry coordinates,[6] is given in Table III. It is convenient to divide the subgroups of O_h, generated by force constant or mass perturbations in the M_6 cluster, into those subgroups (D_{3d}, D_3, C_{3v}, C_3) which retain a C_3 axis and D_{4h} and its subgroups (C_{4v}, D_{2d}, D_{2h}, C_{2v}, C_2, C_s) in which all the C_3 axes are lost. Force constant perturbations which retain a C_3 axis (taken here to be perpendicular to the face containing atoms 1, 2, and 5) retain the symmetry relationships between the force constants: $f_1 = f_2 = f_{10}$; $f_7 = f_8 = f_{12}$; $f_3 = f_6 = f_9$; $f_4 = f_5 = f_{11}$. These relationships diagonalize $\mathbf{F}(t_{2g})$, but it is necessary in addition to effect the transformation of (2) with $\theta = 54.7356°$ and $\phi = 45.0°$ in order to diagonalize $\mathbf{F}(t_{1u})$ and $\mathbf{F}(t_{2u})$. This yields **F** matrices with the nonzero elements

$$\begin{aligned} t_{1u}\colon\ & f_{44} = (f_1 + f_7)/2 \\ & f_{55} = f_{66} = (f_1 + 3f_3 + 3f_4 + f_7)/8 \\ t_{2g}\colon\ & f_{77} = f_{88} = f_{99} = (f_1 + f_3 + f_4 + f_7)/4 \qquad (3) \\ t_{2u}\colon\ & f_{10\,10} = (f_3 + f_4)/2 \\ & f_{11\,11} = f_{12\,12} = (3f_1 + f_3 + f_4 + 3f_7)/8 \end{aligned}$$

Since $f_1 \neq f_4$ and/or $f_3 \neq f_7$ for perturbations of the force constants of D_{3d}, D_3, C_{3v}, or C_3 symmetries, only $\mathbf{F}(t_{2g})$ remains a constant matrix, and first-order splittings are therefore observed in the t_{1u} and t_{2u} vibrations but not in the t_{2g} cage mode as a result of these perturbations.

A D_{4h} force-field perturbation retains the symmetry relations $f_1 = f_2 = f_3 = f_4 = f_5 = f_6 = f_7 = f_8$ and $f_9 = f_{10} = f_{11} = f_{12}$, where the C_4 axis is here taken to pass through atoms 1 and 6. These relationships diagonalize $\mathbf{F}(t_{1u})$ and $\mathbf{F}(t_{2u})$ to yield the following nonzero elements:

$$\begin{aligned} e_g\colon\ & f_{22} = (f_1 + 2f_9)/3 \\ & f_{33} = f_1 \\ t_{1u},t_{2u}\colon\ & f_{44} = f_{10\,10} = f_1 \\ & f_{55} = f_{66} = f_{11\,11} = f_{12\,12} = (f_1 + f_9)/2 \\ t_{2g}\colon\ & f_{77} = f_9 \\ & f_{88} = f_{99} = f_1 \end{aligned}$$

Since $f_1 \neq f_9$ for this perturbation, none of these matrices is constant, nor can the **F** matrices be constant for any of the subgroups of D_{4h}, for which there are fewer symmetry relationships between the force constants. It is thus clear that all of the degenerate fundamentals of an M_6 cluster are split in first order as a result of force constant perturbations of symmetry D_{4h} or any of its subgroups.

Finally the effect of mass perturbations on the vibrations of an M_6 cluster are examined. The possible subgroups of O_h generated by the substitution of atoms in the cluster by atoms of one other kind are C_{3v} and D_{4h} and its subgroups C_{4v}, D_{2d}, and C_{2v}. The relationships $\mu_1 = \mu_2 = \mu_5 \neq \mu_3 = \mu_4 = \mu_6$ between the masses in a facially trisubstituted cluster (C_{3v}) transform each 3 × 3 block of **G** (Table III) into a constant matrix, with diagonal elements $g_{ii}(t_{2g}) = 2g_{ii}(t_{2u}) = 2g_{ii}(t_{1u})/3 = \mu_1 + \mu_3$. For the other patterns of substitution, it is readily seen from Table III that the degenerate blocks of **G** are in no cases constant matrices. Thus, for example, for trans disubstitution (D_{4h}) for which $\mu_1 = \mu_6 \neq \mu_2 = \mu_3 = \mu_4 = \mu_5$, the nonzero elements of **G** are

$$\begin{array}{llll} e_g\colon & g_{22} = (2\mu_1 + \mu_2)/3 & t_{1u}\colon & g_{44} = 2\mu_1 + \mu_2 \\ & g_{33} = \mu_2 & & g_{55} = g_{66} = (\mu_1 + 5\mu_2)/2 \\ t_{2g}\colon & g_{77} = 2\mu_2 & t_{2u}\colon & g_{10\,10} = \mu_2 \\ & g_{88} = g_{99} = \mu_1 + \mu_2 & & g_{11\,11} = g_{12\,12} = (\mu_1 + \mu_2)/2 \end{array}$$

For *facial* trisubstitution of an M_6 cluster therefore which does not significantly affect the force constants, the change in the masses does not split any of the degenerate vibrations in first order, whereas for all other patterns of substitution there is a first-order splitting of all of the degenerate vibrations due to the asymmetrical distribution of masses.

---

(6) Oxton, I. A. *Inorg. Chem.* **1980**, *19*, 2825.

Table IV. Symmetries of Force-Field and Mass Perturbations in M_4 and M_6 Clusters Which Cause Only Second-Order and Higher Splittings of Degenerate Cluster Vibrations

	vib	perturbation of force field	perturbation of masses
M_4 (T_d)	υ_3(e)		C_{2v}
	υ_3(t$_2$)	C_{3v}	
M_6 (O_h)	υ_3(t$_{1u}$)		C_{3v}
	υ_4(t$_{2g}$)	D_{3d}, D_3, C_{3v}, C_3	C_{3v}
	υ_5(t$_{2u}$)		C_{3v}

Results and Discussion

These results are summarized in Table IV, which shows the symmetries of the force fields or mass distributions in M_4 or M_6 clusters which, though they split one or more degenerate vibrations of the clusters to second-order and higher approximations, by symmetry do not do so in first order. It is of note that there is no first-order splitting of the t_{2g} vibration of a M_6 cluster as a result of a C_{3v} perturbation of either the force constants or the masses. Thus for a bimetallic cluster of the type *fac*-M_3M_3', for which both the masses and the force field are perturbated to C_{3v} symmetry, it may be expected that the splitting of the $t_{2g}(O_h)$ mode into a_1 and e components will be relatively small. It may be shown that this is also true of the splitting of the $t_{2g}(O_h)$ vibration of an octahedral mononuclear metal complex *fac*-MX_3Y_3 into a_1 and e components.

So that the quantitative significance of these results could be demonstrated, expressions for the splittings correct to second order have been derived for force-field perturbations of C_{3v} symmetry in a M_4 cluster and of D_{3d} symmetry in a M_6 cluster. To do this it is necessary to derive the full **F** matrix, including the off-diagonal blocks which become nonzero in the lower symmetry. Eigenvalues of $\mathbf{G}_0\mathbf{F}$ correct to second-order terms were then obtained by series expansion. The splittings, relative to the frequencies of the unperturbed clusters, were thus shown to be

M_6 ($O_h \rightarrow D_{3d}$):

$$\frac{\nu_3(a_{2u}) - \nu_3(e_u)}{\nu_3(t_{1u})} = 3\left(\frac{f_1 - f_4}{8f_0}\right) - 3\left(\frac{f_1 - f_4}{8f_0}\right)^2$$

$$\frac{\nu_4(a_{1g}) - \nu_4(e_g)}{\nu_4(t_{2g})} = -24\left(\frac{f_1 - f_4}{8f_0}\right)^2 \qquad (4)$$

$$\frac{\nu_5(a_{1u}) - \nu_5(e_u)}{\nu_5(t_{2u})} = -3\left(\frac{f_1 - f_4}{8f_0}\right) + 9\left(\frac{f_1 - f_4}{8f_0}\right)^2$$

M_4 ($T_d \rightarrow C_{3v}$):

$$\frac{\nu_3(a_1) - \nu_3(e)}{\nu_3(t_2)} = -24\left(\frac{f_1 - f_4}{8f_0}\right)^2$$

For an M_6 cluster in which the bonding has D_{3d} symmetry and in which there is a 10% difference between the force constants f_1 and f_4, the fractional splittings of $\upsilon_3(t_{1u})$ and $\upsilon_2(t_{2u})$ correct to second-order terms are thus shown to be 3.7%. For $\upsilon_4(t_{2g})$, however, the fractional splitting is only 0.37%. This is also seen to be the magnitude of the splitting of $\upsilon_3(t_2)$ of an M_4 cluster as a result of a 10% difference between the force constants f_1 and f_4, and it has already been confirmed experimentally that this splitting in $Rh_4(CO)_{12}$ is indeed very small (<2 cm^{-1}; 1.3%).[2]

Further examples of compounds in which asymmetry in the cluster force field may be expected to cause only second-order splitting of one of the ν(M–M) fundamentals are found among M_6 clusters in which there are bridging CO or H ligands along only some of the edges of the cluster. Thus in $[(CH_3)_4N]_2[Ni_6(CO)_{12}]$ and $Cs_2[Co_6(CO)_{15}]\cdot 3H_2O$, in which the cluster anion symmetries approximate to D_{3d} and C_{3v}, respectively,[7,8] the CO edge-bridged M–M bonds are substantially shorter than the other bonds and may be expected[3] to have significantly greater stretching force constants than the other bonds. The cluster symmetry is also close to D_{3d} in $Ru_6(CO)_{18}H_2$, in which there are two face-bridging H ligands lying on a C_3 axis, and in the anion of $K_4[Co_6(CO)_{14}]\cdot 6H_2O$, but in these compounds the M–M distances in the faces perpendicular to the C_3 axis are significantly greater than for the other M–M bonds.[9,10] With the exception of $[(CH_3)_4N]_2[Ni_6(CO)_{12}]$, the vibrational spectra of these compounds in the ν(M–M) region do not appear to have yet been investigated, but in each case the effect of the difference in the M–M force constants in splitting the $\upsilon_4(t_{2g})$ cluster mode is expected to be much less than the splitting of the $\upsilon_3(t_{1u})$ and $\upsilon_5(t_{2u})$ modes on account of the retention of the C_3 symmetry axis. The incomplete published vibrational data[11] on $[(CH_3)_4N]_2[Ni_6(CO)_{12}]$ is not sufficient to establish the presence or absence of splitting of any of the fundamentals of this M_6 cluster on account of the D_{3d} symmetry.

The most commonly encountered mass perturbations of the appropriate magnitude for second-order effects to be relatively small are likely to be those resulting from the effect of ligand substitution on the effective masses of the cluster metal atoms. Thus preliminary work[12] on the Raman spectrum of $Rh_4(CO)_{10}(P(OPh)_3)_2$, in which there are phosphite ligands on two of the basal rhodium atoms, has shown that there is a splitting of ca. 15 cm^{-1} in $\upsilon_3(t_2)$. This sensitivity of υ_3 to the effective mass of the cluster metal atoms is in accord with the data of Table IV. On the other hand, mass perturbations due to the substitution of metal atoms in clusters in many cases involves rather large mass changes and in general also substantially affects the cluster force fields and thus, in general, is likely to result in relatively large first- or second-order splittings.

Finally, where there is a first-order splitting of a degenerate vibration as a result of a relatively small force-field or mass perturbation, the order of frequencies of the components may be ascertained by examination of the **G** or **F** matrix elements. It may be seen from (1) that, since $\mathbf{L}_0$ and $\mathbf{G}_0$ are constant matrices for a given symmetry class, the frequencies of the components into which the degenerate vibration is split as a result of a force-field perturbation are to a first-order approximation proportional to the square roots of the elements of **F**. Similarly, for a mass perturbation, the frequencies are proportional to the square roots of the elements of **G** to a first-order approximation. Where **F** or **G** are not diagonal, it is necessary that thay be diagonalized by use of (2). It may thus, for example, be seen from the elements in (3) for $[Ni_6(CO)_{12}]^{2-}$ (D_{3d}), with the assumption that the force constants of the shorter[7] M–M bonds of the $Ni_3(CO)_3(\mu\text{-}CO)_3$ symmetrical triangular faces are greater than those of the other M–M bonds ($f_1 = f_7 > f_3 = f_4$), that $f_{44} > f_{55} = f_{66}$ and thus $\upsilon_3(a_{2u}) > \upsilon_3(e_u)$, as may be confirmed by examination of (4).

---

(7) Calabrese, J. C.; Dahl, L. F.; Cavalieri, A.; Chini, P.; Longoni, G.; Martinengo, S. *J. Am. Chem. Soc.* **1974**, *96*, 2616.

(8) Albano, V.; Chini, P.; Scatturin, V. *J. Organomet. Chem.* **1968**, *15*, 423.

(9) Churchill, M. R.; Wormald, J.; Knight, J.; Mays, M. J. *J. Chem. Soc. D* **1970**, 458.

(10) Albano, V. G.; Bellon, P. L.; Chini, P.; Scatturin, V. *J. Organomet. Chem.* **1969**, *16*, 461.

(11) See: Shriver, D. F.; Cooper, C. B. *Adv. Infrared Raman Spectros.* **1980**, *6*, 127.

(12) Heaton, B. T.; Willis, D. E.; Creighton, J. A., to be submitted for publication.