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SOME PRINCIPLES OF NORMAL COORDINATE ANALYSIS OF TRANSITION METAL COMPLEXES

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CONTENTS

A. INTRODUCTION

The coordination chemistry of transition elements has become very attractive in the last decade. Several new fields such as, for example, the theoretical interpretation of complex formation, catalysis with coordination compounds, bioinorganic chemistry and the study of dissymmetry have become important [1—3]. Also, more sophisticated studies of the electronic structure and chemical bonding have become possible, thanks to the development of new physical methods, such as magnetic circular dichroism (mcd) spectroscopy. One technique, which has been used for a long time, mainly to get

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information about the metal—ligand bond strength, is vibrational spectroscopy. It is well known that a serious interpretation of the strength of chemical bonds using vibrational spectroscopy can only be provided by normal coordinate analysis. This, in essence, means the calculation of the force constants from the vibrational frequencies. Since the number of independent force constants is in general larger than the number of vibrational frequencies (of a single molecule without considering isotopic substitution), it is problematical to calculate a unique set of physically reasonable force constants. As a consequence of this fact, values of metal—ligand stretching force constants differing sometimes by more than a factor of three have been published in the past.

Since metal and other isotopes are now available commercially, isotopic substitution techniques can be employed to obtain better information about the force constants. In addition, new theoretical formalisms related to the use of heavy and very heavy atom isotopic substitution techniques for the calculation of force constants, have been developed (see the following Sects.) and hence it appears worthwhile to write a critical review on the normal coordinate analysis of transition metal complexes.

B. MOLECULAR VIBRATIONS OF FREE AND COMPLEXED LIGANDS

(i) Introduction

In many coordination compounds it is easy to recognize fundamental frequencies which may be associated with the ligand vibrations. Their magnitudes are often comparable with those in the corresponding free molecules or ions. On the other hand, some frequencies of ligand vibrations may be found to be substantially different in various complexes and different from those of the free ligands. These kinds of frequency shifts have attracted many investigators, and much experimental evidence has been accumulated [4—6]. Many mechanisms have been proposed in order to explain the frequency shifts. The method of normal coordinate analysis seems to be the best approach to the studies of these phenomena.

In some work there were attempts to reproduce the frequencies of ligand vibrations by a normal coordinate analysis of the ligand isolated from the rest of the complex, then different force constants from those of the corresponding free molecule had to be assumed as an inevitable consequence of the frequency shifts. Such results should not be interpreted in general as proof for the necessary existence of substantially different force fields in the free and complexed ligands. Those conclusions may be misleading because the treatment completely neglects the coupling between ligands and the rest of the complex, i.e. the framework. It is likewise erroneous to assume that such frequency shifts arise entirely due to kinematic coupling, since the influence of force constant changes might in general be large.

Cyvin [7—9] has proposed a model procedure which could be employed in

the normal coordinate analysis of transition metal complexes (also in the case of complexes exhibiting a high degree of kinematic coupling; see the results [24] for the complex $Ni(PF_3)_4$). In this approach, part of the coupling between the ligand and framework vibrations is referred to as the kinematic coupling [7—9]. The description of the method is as follows (citation of Cyvin [9]):

"(1) Construct the coordinates of molecular vibrations so that they can be classified as (a) ligand vibrations, (b) ligand—framework coupling and (c) framework vibrations. (2) Transfer the force constants for ligand vibrations from a force field of a free ligand. (3) Estimate the rest of the principal force constants. (4) Assume that all interaction force constants vanish when they pertain to pairs of coordinates belonging to different groups of the above classification.

In this approach the F matrix is block-diagonal with no mixing between coordinates classified under different groups. Non-vanishing interaction terms in the G matrix occur, however, and give rise to the effect of kinematic coupling. Point (2) may be modified by changing the force constants from those of the free molecule to a hypothetical free ligand. Then one may still refer to the effect as a kinematic coupling, as long as the condition (4) is maintained "

(ii) Coordination compounds with diatomic ligands

The main ideas of kinematic coupling were explained by Gans [7] by means of a treatment of extremely simple molecular models. This idea inspired Cyvin [10,11] to a systematic treatment of a few simple linear models, among which is perhaps the most simple model for a complex: linear M···A—B, where A—B is considered as the ligand.

The M···A—B model of symmetry $C_{\infty v}$ has two vibrational modes along the molecular axis. Assume the force constant for the A—B stretching, say f_1, to be the same as in the free A—B molecule. Then

$$\lambda_1^0 = f_1(\mu_A + \mu_B) \tag{1}$$

gives the frequency of the free A—B molecule. Here the usual symbols are applied: $\lambda = 4\pi^2 c^2 \omega^2$, and μ_X is the inverse mass of atom X. In addition, assume f_2 to be the force constant of the M···A stretching, and neglect the interaction force constant. The normal coordinate analysis is easily performed for this model, which represents a two-dimensional secular equation problem for the linear vibrations. The F matrix is diagonal, but a non-vanishing off-diagonal term in the G matrix (viz. $-\mu_A$) is inevitable. This term gives rise to the kinematic coupling. The normal coordinate analysis yields the following result for the ligand frequency.

$$\lambda_1 = \lambda_1^0 + \Delta\lambda \tag{2}$$

where $\Delta\lambda > 0$ and thus represents a positive frequency shift. The explicit formula for $\Delta\lambda$ reads

$$\Delta\lambda = [\tfrac{1}{4}(\lambda_1^0 + \lambda_2^0)^2 + f_1 f_2 \mu_A^2 - \lambda_1^0 \lambda_2^0]^{1/2} - \tfrac{1}{2}(\lambda_1^0 - \lambda_2^0) \tag{3}$$

where

$$\lambda_2^0 = f_2(\mu_M + \mu_A) \tag{4}$$

Cyvin [10,11] has pointed out that the metal—ligand stretching frequency within this simple approximation may be represented in terms of the same frequency shift, i.e.

$$\lambda_2 = \lambda_2^0 - \Delta\lambda \tag{5}$$

A frequency-level diagram for this model is given in Fig. 1(a).

A corresponding treatment was performed for the linear symmetrical B—A···M···A—B model [10]. A schematical representation of the result is shown in Fig. 1(b). In this case it is convenient to introduce a preliminary splitting of λ_2^0 into

$$\lambda_2' = \lambda_2^0 + f_2\mu_M, \qquad \lambda_2'' = \lambda_2^0 - f_2\mu_M \tag{6}$$

Then the symmetrical (s) and antisymmetrical (a) ligand frequencies are shifted according to

$$\lambda_1^s = \lambda_1^0 + \Delta\lambda^s, \qquad \lambda_1^a = \lambda_1^0 + \Delta\lambda^a \tag{7}$$

where $\Delta\lambda^s$ and $\Delta\lambda^a$ are both obtained by eqn. (3) on substituting λ_2^0 by λ_2'' and λ_2', respectively. Moreover, the locations of the lower stretching frequencies are fixed by the same frequency shifts, which must be reckoned from the preliminary shifted values (6) rather than λ_2^0 itself.

$$\lambda_2^s = \lambda_2'' - \Delta\lambda^s, \qquad \lambda_2^a = \lambda_2' - \Delta\lambda^a \tag{8}$$

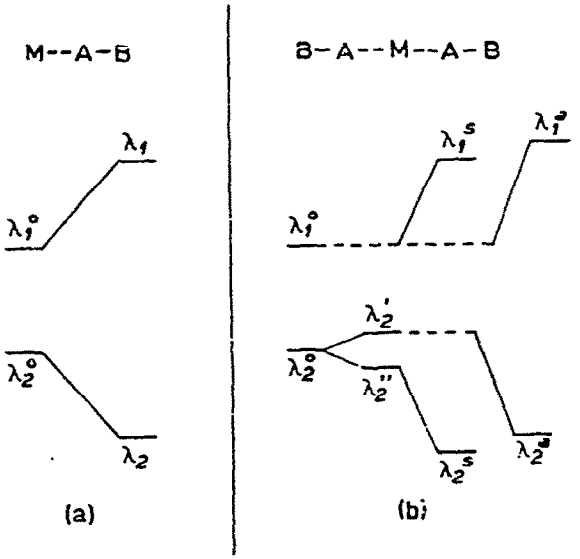

Fig. 1. Schematic representation of vibrational frequencies and frequency shifts (in terms of λ values) in linear coordination compounds of the types (a) MAB and (b) $M(AB)_2$.

This model is especially interesting because of its principal application to transition metal cyano complexes. Cyvin [11] has quoted the available experimental frequencies for $[Cu(CN)_2]^-$ [12], $[Ag(CN)_2]^-$ [12—14], $[Au(CN)_2]^-$ [12,14,15] and $Hg(CN)_2$ [14,16,17]. In general these data are not sufficiently complete or accurate to allow a conclusive decision about the validity of the simple approximation for the normal coordinate analysis described above. Nevertheless some encouraging results may be quoted for $Hg(CN)_2$ [10,11], for which the available experimental data are the most extensive. The simple force field was found to be applicable when properly choosing the f_1 and f_2 force constant values [10,11]: $f_1 = 17.53$ mdyn Å^{-1} and $f_2 = 2.6$ mdyn·Å^{-1}.

The calculated frequency shifts in terms of $\Delta\lambda$ values (cf. eqns. (7) and (8)) are shown in Table 1 along with the data based on the experimental frequencies [17]. It should be pointed out that these frequency shifts, which are due to kinematic coupling, are very small in this case. Furthermore, the λ_1^0 value does not agree with the frequency of the free CN^- ion (2080 cm^{-1}) [4,12]. Accordingly the force constant for this ion is significantly smaller than the present f_1 value. It is an example where the frequency shift due to complexation is nearly influenced by the force constant change only.

The vibrational modes with frequencies ν_1 (ν_1^s) and ν_3 (ν_1^a) of the above example represent an illustration of in-phase and out-of-phase ligand vibrations. On the other hand the model is too simple to furnish an illustration of ligand—framework coupling. Examples of such modes are found in the bent symmetrical $M(AB)_2$ model [9] and in many higher-coordinated complexes. A particularly great number of examples are found among cyano complexes and carbonyls. For instance, highly symmetrical four-coordinated complexes of this kind are known, some possessing the tetrahedral (T_d) structure and others the square-planar (D_{4h}) structure.

It may be instructive to work out the classification of vibrational modes for the two models mentioned above. In both cases the four diatomic ligands give rise to four ligand vibrations in the complex, one in-phase (totally symmetric) and the other out-of-phase of different kinds. They are found to be distributed according to

$$\Gamma(\text{lig}; T_d) = A_1 + F_2 \qquad (9)$$

TABLE 1

Frequency shifts in terms of $\Delta\lambda$ values (mdyn Å^{-1} amu^{-1}) for $Hg(CN)_2$

Experimental [a]	Calculated [b]
(From ν_1) 0.120 (From ν_2) 0.115 }	0.121 ($\Delta\lambda^s$)
(From ν_3) 0.123 (From ν_4) 0.127 }	0.122 ($\Delta\lambda^a$)

[a] Solid state frequencies from ref. 17. [b] Taken from Cyvin's work (refs. 10 and 11).

and

$$\Gamma(\text{lig}; D_{4h}) = A_{1g} + B_{1g} + E_u \quad (10)$$

in the tetrahedral and planar model, respectively. In the latter case we have adopted Cyvin's [18] conventions concerning the orientation of cartesian axes. The ligand—framework coupling may be described as a linear bending. There are eight modes of this type in each of the models

$$\Gamma(\text{cpl}; T_d) = E + F_1 + F_2 \quad (11)$$

$$\Gamma(\text{cpl}; D_{4h}) = A_{2g} + B_{2g} + E_g + A_{2u} + B_{2u} + E_u \quad (12)$$

Finally we have the framework vibrations, which may be identified with the nine vibrational modes in each of the XY_4 (T_d) and XY_4 (D_{4h}) models [18]

$$\Gamma(\text{fr}; T_d) = A_1 + E + 2F_2 \quad (13)$$

$$\Gamma(\text{fr}; D_{4h}) = A_{1g} + B_{1g} + B_{2g} + A_{2u} + B_{2u} + 2E_u \quad (14)$$

(iii) Coordination compounds with trigonal ligands

(a) Tetrahedral symmetry

Introduction. Many coordination compounds with trigonal ligands are known. Transition metal ammines are among those which in particular have been studied extensively. A typical tetrahedral ammine is $[Zn(NH_3)_4]^{2+}$ [19—22]. Another coordination compound belonging to the same structure is $Ni(PF_3)_4$, for which complete normal coordinate analyses have recently been reported [23,24]. The most recent normal coordinate analysis of $[Zn(NH_3)_4]^{2+}$ due to Cyvin et al. [25] is reviewed below.

Symmetry coordinate correlations. A group-theoretical problem is encountered when constructing the symmetry coordinates for a tetrahedral coordination compound with trigonal ligands. It concerns the correlations between the local C_{3v} symmetry coordinates for the isolated ligands and the overall T_d symmetry coordinates for the whole compound. Cyvin et al. [26,27] have solved this problem and derived a set of useful equations to be used in the construction of coordinates for molecular models of the type considered. Successful applications to the $Ni(PF_3)_4$ model are reported in detail [27,28]. It seems worthwhile to collect here all these equations which together form a consistent set of symmetry-adapted coordinates.

Figure 2 shows the tetrahedral $X(YZ_2)_4$ model with the numbering of the atoms chosen for the sake of definition. The four ligands are designated A, B, C and D. We must account for local symmetry coordinates of a_1, a_2 and e (species designations in small letters for the C_{3v} symmetry group) in order to cover all possibilities. The Figure tends to define the conventions adopted for a mutual orientation of such coordinates.

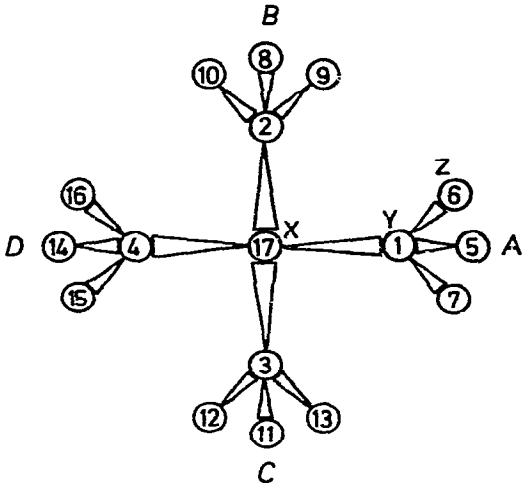

Fig. 2. Numbering of atoms in the tetrahedral $X(YZ_3)_4$ model. Stretching vibrations for ligand A: $r_1^A(1—5)$, $r_2^A(1—6)$, $r_3^A(1—7)$. Correspondingly $r_1^B(2—8)$, ···, $r_3^D(4—16)$. Torsions for ligand A: $\tau_1^A(5—1—17—4)$, $\tau_2^A(6—1—17—3)$, $\tau_3^A(7—1—17—2)$. Correspondingly $\tau_1^B(8—2—17—3)$, ···, $\tau_3^D(16—4—17—3)$.

The local symmetry a_1 coordinates may be represented by

$$S_r^X(a_1) = 3^{-1/2}(r_1^X + r_2^X + r_3^X) \tag{15}$$

where X = A, B, C or D. They transform just like the central (X—Y) bond stretching and give rise to four T_d symmetry coordinates when properly combined: $4a_1(A_1 + F_2)$; species designations in capital letters for the T_d symmetry group. The a_2 coordinates are represented by

$$S_\tau^X(a_2) = 3^{-1/2}(\tau_1^X + \tau_2^X + \tau_3^X) \tag{16}$$

and give rise to four T_d symmetry coordinates correlated according to: $4a_2$-$(A_2 + F_1)$. Finally we must consider a degenerate pair of e coordinates. It may be taken as

$$S_{ra}^X(e) = 6^{-1/2}(2r_1^X - r_2^X - r_3^X), \qquad S_{rb}^X(e) = 2^{-1/2}(r_2^X - r_3^X) \tag{17}$$

or

$$S_{\tau a}^X(e) = 2^{-1/2}(-\tau_2^X + \tau_3^X), \qquad S_{\tau b}^X(e) = 6^{-1/2}(2\tau_1^X - \tau_2^X - \tau_3^X) \tag{18}$$

These two sets are oriented consistently. Each of them gives rise to eight T_d symmetry coordinates: $4e(E + F_1 + F_2)$. Below we give the complete set of expressions which combines the local C_{3v} symmetry coordinates for the four ligands into overall T_d symmetry coordinates for the whole compound.

$$S(A_1) = \tfrac{1}{2}[S^A(a_1) + S^B(a_1) + S^C(a_1) + S^D(a_1)]$$
$$S(A_2) = \tfrac{1}{2}[S^A(a_2) + S^B(a_2) + S^C(a_2) + S^D(a_2)]$$
$$S_a(E) = \tfrac{1}{2}[S_a^A(e) + S_a^B(e) + S_a^C(e) + S_a^D(e)]$$
$$S_b(E) = \tfrac{1}{2}[S_b^A(e) + S_b^B(e) + S_b^C(e) + S_b^D(c)]$$
$$S'_a(F_1) = 2^{-1/2}[S^B(a_2) - S^C(a_2)]$$
$$S'_b(F_1) = 2^{-1/2}[-S^A(a_2) + S^D(a_2)]$$
$$S'_c(F_1) = \tfrac{1}{2}[S^A(a_2) - S^B(a_2) - S^C(a_2) + S^D(a_2)]$$
$$S''_a(F_1) = \tfrac{1}{4}[6^{1/2}S_a^A(e) - 2^{1/2}S_b^B(e) + 2^{1/2}S_b^C(e) - 6^{1/2}S_a^D(e)] \quad (19)$$
$$S''_b(F_1) = \tfrac{1}{4}[2^{1/2}S_b^A(e) - 6^{1/2}S_a^B(e) + 6^{1/2}S_a^C(e) - 2^{1/2}S_b^D(e)]$$
$$S''_c(F_1) = \tfrac{1}{2}[S_b^A(e) - S_b^B(e) - S_b^C(e) + S_b^D(e)]$$
$$S'_a(F_2) = 2^{-1/2}[S^A(a_1) - S^D(a_1)]$$
$$S'_b(F_2) = 2^{-1/2}[S^B(a_1) - S^C(a_1)]$$
$$S'_c(F_2) = \tfrac{1}{2}[S^A(a_1) - S^B(a_1) - S^C(a_1) + S^D(a_1)]$$
$$S''_a(F_2) = 24^{-1/2}[3^{1/2}S_a^A(e) + 3S_b^B(e) - 3S_b^C(e) - 3^{1/2}S_a^D(e)]$$
$$S''_b(F_2) = 24^{-1/2}[3S_b^A(e) + 3^{1/2}S_a^B(e) - 3^{1/2}S_a^C(e) - 3S_b^D(e)]$$
$$S''_c(F_2) = \tfrac{1}{2}[-S_a^A(e) + S_a^B(e) + S_a^C(e) - S_a^D(e)]$$

The tetramminezinc(II) ion. The symmetry coordinates of $[Zn(NH_3)_4]^{2+}$ may be classified into (a) ligand vibrations, (b) ligand—framework coupling and (c) framework vibrations (see above). They are distributed among the symmetry species of the T_d group in the following way [28]

$$\Gamma(a) = 2A_1 + 2E + 2F_1 + 4F_2 \quad (20)$$

for the ligand vibrations, which consist of the NH stretching ($A_1 + E + F_1 + 2F_2$) and NH_3 deformation (HNH bending; $A_1 + E + F_1 + 2F_2$) modes.

$$\Gamma(b) = A_2 + E + 2F_1 + F_2 \quad (21)$$

for the ligand—framework coupling consisting of NH_3 rocking ($E + F_1 + F_2$) and NH_3 torsion ($A_2 + F_1$).

$$\Gamma(c) = A_1 + E + 2F_2 \quad (22)$$

for the ZnN_4 framework vibrations.

An approximate force field was produced on the basis of the ligand—framework correlated coordinates. Figure 3 shows a mapping of the diagonal blocks. It is implied that all interaction terms outside the full-drawn diagonal blocks were neglected. Table 2 shows the calculated and observed [21,22] frequencies. The inactive A_2 frequency is omitted. In the column "Approx. 1" the

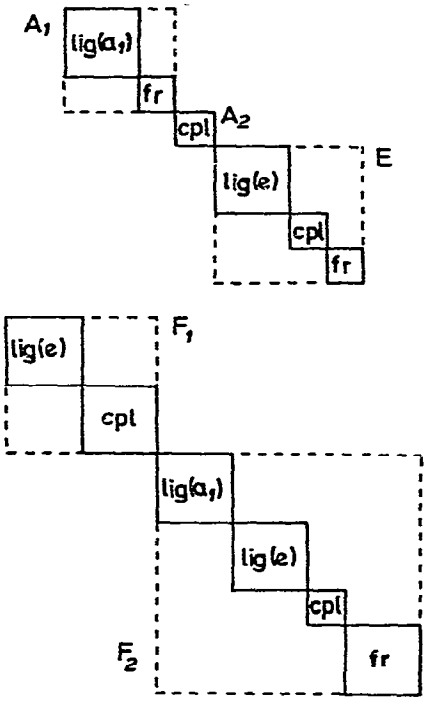

Fig. 3. Mapping of the approximate F matrix for $[Zn(NH_3)_4]^{2+}$. It is based on the classification of the symmetry coordinates into those of ligand vibrations ("lig"), ligand—framework coupling ("cpl") and framework vibrations ("fr").

ligand force constant blocks ($a_1 + e$) are only slight modifications of those from gaseous NH_3; cf. Table 3. The NH_3 gas frequencies ("Free ligands") are included in Table 2 in order to show the pure effect of kinematic coupling. It is seen to give positive frequency shifts from free to coordinated ligands, but the differences are relatively small (<25 cm^{-1}, except for a larger shift for one inactive F_1 frequency). These predictions are not confirmed by the experimental data. This is what could be expected because other effects are likely to be larger than the presumably small kinematic coupling in this case. Hence a large change in the force constants for the ligand vibrations seems to be inevitable. In "Approx. 2" (cf. Table 2) the ligand-vibration force constant blocks are changed in order to fit the observed frequencies better, but the block-diagonal structure of the force-constant matrix (Fig. 3) is maintained. In the original work [25] another round of refinements of the force constants is reported, and the final force field was used to calculate the frequencies of the two isotopic compounds $[^{68}Zn(NH_3)_4]^{2+}$ and $[^{64}Zn(ND_3)_4]^{2+}$. The general agreement with observed values was found to be satisfactory. The work [25] cited should be consulted for details concerning the developed force constants of ligand—framework coupling and the framework vibrations.

TABLE 2

Calculated and observed frequencies (cm^{-1}) for $[Zn(NH_3)_4]^{2+}$ along with the gas frequencies of NH_3 [a]

Free ligands	$[Zn(NH_3)_4]^{2+}$		
	Approx. 1 [b]	Approx. 2 [b]	Obs.
3337 A_1	3338	3223	3233
950	974	1226	1253
—	421	429	432
3444 E	3445	3273	3275
1627	1634	1603	1596
—	585	681	685
—	148	156	156
3444 F_1	3445	3273	—
1627	1719	1686	—
—	626	626	—
—	318	317	—
3444 F_2	3445	3273	3275
3337	3337	3223	3150
1627	1634	1602	1596
950	967	1222	1239
—	590	681	685
—	404	420	412
—	152	156	156

[a] Ref. 25. The calculated values of the frequencies correspond to the force field adjusted to fit the frequencies of $[^{64}Zn(NH_3)_4]^{2+}$ and the H/D isotope shifts in $[Zn(NH_3)_4]^{2+}$. [b] See the text.

(b) Non-tetrahedral symmetry

In the molecular model of $[Zn(NH_3)_4]^{2+}$ treated above the trigonal symmetry of the ligands are preserved in the overall tetrahedral structure. In other cases of ammine complexes this condition cannot be fulfilled for any orientation of the ammine groups in a rigid structure. Also for ammine complexes of this category complete normal coordinate analyses have been performed.

Among four-coordinated ammines with a planar square framework $[Cu(NH_3)_4]^{2+}$ is a typical representative. A normal coordinate analysis on the basis of the C_{4v} model (with supplementary computation for C_{4v}) has been reported [29].

The D_{3d} model for a six-coordinated ammine complex with the octahedral framework has recently been studied [30]. The model was used in a normal coordinate analysis for $[Ni(NH_3)_6]^{2+}$.

For all the models mentioned above the symmetry coordinates were analysed in terms of the vibrational modes for the ligands and the framework in

TABLE 3

Force constants (mdyn $Å^{-1}$) for the free NH_3 ligand and the ligand vibrations in ammine ions

Species	a_1		e		Ref.
Free NH_3	6.48	0.42 0.48	6.45	−0.16 0.59	25
$[Zn(NH_3)_4]^{2+}$	6.05	0.39 0.75	5.82	−0.14 0.56	25
$[Cu(NH_3)_4]^{2+}$	5.84	0.38 0.82	5.88	−0.15 0.59	29
$[Ni(NH_3)_6]^{2+}$	5.92	0.38 0.70	6.08	−0.14 0.55	30

a similar way as described for the $[Zn(NH_3)_4]^{2+}$ model. The necessary group-theoretical correlations and detailed specifications of the complete sets of symmetry coordinates are found in the cited references [29,30]. The reader is referred in particular to the transformations corresponding to eqns. (19). These equations for the $[Cu(NH_3)_4]^{2+}$ and $[Ni(NH_3)_6]^{2+}$ models [29,30] with necessary definitions of symbols and conventions were too voluminous to be included here.

The tetramminecopper(II) ion. The symmetry coordinates of $[Cu(NH_3)_4]^{2+}$ based on the C_{4h} model are classified into the three types of vibrations in the following way [29].

$$\Gamma(a) = 4A_g + 4B_g + 2E_g + 2A_u + 2B_u + 4E_u \quad (23)$$

for the ligand vibrations,

$$\Gamma(b) = A_g + B_g + 2E_g + 2A_u + 2B_u + E_u \quad (24)$$

for the ligand—framework coupling, and

$$\Gamma(c) = A_g + 2B_g + A_u + B_u + 2E_u \quad (25)$$

for the framework vibrations. Figure 4 shows a mapping of the appropriate symmetry coordinates. The correlations with the symmetry species of the C_{3v} and D_{4h} local symmetries are indicated for the ligand and framework vibrations, respectively.

Table 4 shows the calculated frequencies for $[^{63}Cu(^{14}NH_3)_4]^{2+}$ with an approximate force field on the basis of the ligand—framework correlated coordinates. The approximation corresponds to "Approx. 2" in the report on $[Zn(NH_3)_4]^{2+}$ (cf. Table 2). The ligand force constants of $[Cu(NH_3)_4]^{2+}$ are included in Table 3 and display the same trends of deviation from those of

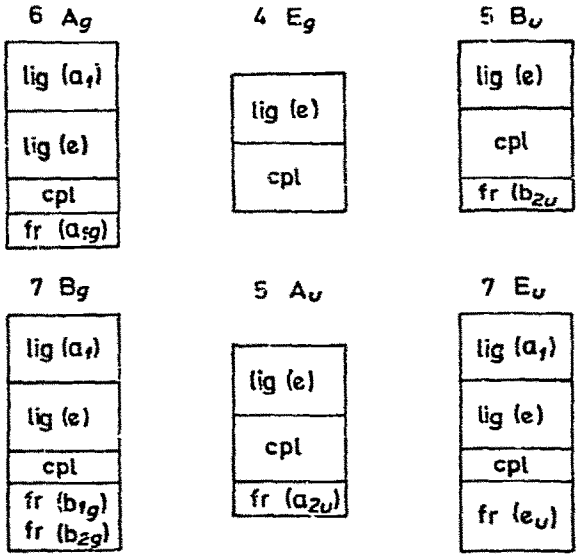

Fig. 4. Mapping of the symmetry coordinates for the $[Cu(NH_3)_4]^{2+}$ model (C_{4h}). Species designations in parentheses pertain to the symmetry groups C_{3v} and D_{4h} for the ligand ("lig") and framework ("fr") vibrations, respectively. "cpl" refers to ligand–framework coupling.

TABLE 4

Calculated and observed frequencies (cm^{-1}) for $[^{63}Cu(^{14}NH_3)_4]^{2+}$ (see ref. 29 and the text)

Species [C_{4h}]	Calc.	Obs. [a]	Species [C_{4h}]	Calc.	Obs. [a]
A_g	3290	3290	A_u	3290	3290
	3169	3169		1665	1654
	1643	1654		741	735
	1282	1282.5		241	226.5
	722	735		178	(200) [c]
	421	420 [b]	B_u	3290	3290
B_g	3291	3290		1669	1654
	3169	3169		737	735
	1645	1654		214	(200) [c]
	1279	1282.5		181	(200) [c]
	732	735	E_u	3290	3290
	376	375 [b]		3169	3169
	300	(300) [c]		1644	1654
E_g	3290	3290		1276	1282.5
	1666	1654		736	735
	730	735		430	426.0
	194	(200) [c]		255	256

[a] The frequencies listed under E_u and the one at 226.5 cm^{-1} belonging to the A_u species were measured in the IR spectrum. Frequencies corresponding to vibrations of the same type and pertaining to ligand and ligand–framework coupling vibrations were assumed to be the same in all the species. For details, see ref. 29. [b] Measured Raman data corresponding to aqueous solution. [c] Estimated values.

gaseous NH_3. The force constants of framework vibrations are comparable to values obtained from computations for a point-mass model (see Sect. D(ii) below). For the complete account of the force field of the whole complex the original work [29] should be consulted. The calculated frequencies for $[^{63}Cu(^{15}NH_3)_4]^{2+}$ and $[^{63}Cu(^{14}ND_3)_4]^{2+}$ are reported [29] in good agreement with experimental data, along with calculations for $[^{63}Cu(^{15}ND_3)_4]^{2+}$.

The hexamminenickel(II) ion. The $[Ni(NH_3)_6]^{2+}$ model was analysed on the basis of the D_{3d} symmetry [30]. Classification of the vibrational modes

$$\Gamma(a) = 4A_{1g} + 2A_{2g} + 6E_g + 2A_{1u} + 4A_{2u} + 6E_u \quad (26)$$

for the ligand vibrations,

$$\Gamma(b) = A_{1g} + 2A_{2g} + 3E_g + 2A_{1u} + A_{2u} + 3E_u \quad (27)$$

for the ligand—framework coupling, and

$$\Gamma(c) = 2A_{1g} + 2E_g + A_{1u} + 2A_{2u} + 3E_u \quad (28)$$

for the framework vibrations. Figure 5 shows a mapping of the symmetry coordinates. Correlation with the symmetry species of the C_{3v} and O_h local symmetries are indicated.

The same approach was used [30] to deduce a force field as in the case of $[Cu(NH_3)_4]^{2+}$ described above. Table 5 shows the calculated and observed frequencies for $[^{58}Ni(NH_3)_6]^{2+}$. Table 3 includes the force constants obtained

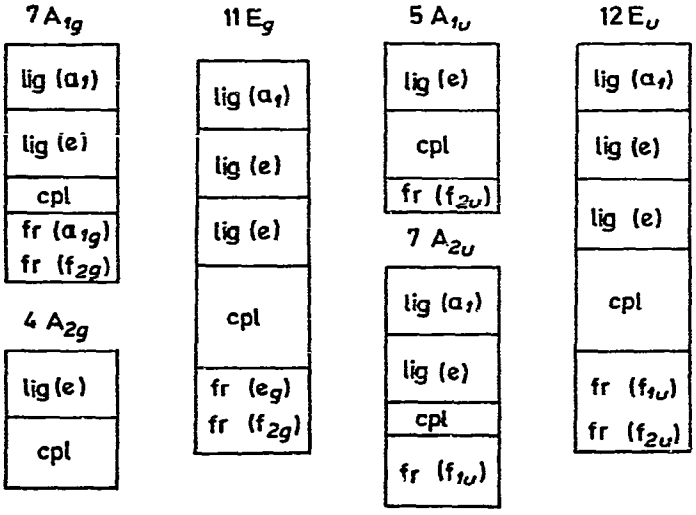

Fig. 5. Mapping of the symmetry coordinates for the $[Ni(NH_3)_6]^{2+}$ model (D_{3d}). Species designations in parentheses pertain to the symmetry groups C_{3v} and O_h for the ligand ("lig") and framework ("fr") vibrations, respectively. "cpl" refers to ligand—framework coupling.

TABLE 5

Calculated and observed frequencies (cm^{-1}) for $[^{58}Ni(NH_3)_6]^{2+}$ (see ref. 30)

Species $[D_{3d}]$	Calc. [a]	Obs. [b]	Species $[D_{3d}]$	Calc. [a]	Obs. [b]
A_{1g}	3345	3345	A_{1u}	3344	3345
	3190	3190		1603	1607
	1577	1607		682	685
	1181	1176		211	(200) [d]
	677	685		157	(160) [d]
	369	370 [c]	A_{2u}	3344	3345
	234	235 [c]		3190	3190
A_{2g}	3344	3345		1576	1607
	1603	1607		1176	1176
	680	685		684	685
	208	(200) [d]		335	335.2
E_g	3345	3345		213	217
	3344	3345	E_u	3345	3345
	3190	3190		3344	3345
	1606	1607		3190	3190
	1576	1607		1606	1607
	1174	1176		1576	1607
	686	685		1176	1176
	672	685		695	685
	265	265 [c]		674	685
	226	235 [c]		335	335.2
	206	(200) [d]		224	217
				196	(200) [d]
				153	(160) [d]

[a] Calculations performed for the ^{14}N isotope. [b] Frequencies corresponding to vibrations of the same type and pertaining to ligand vibrations and ligand—framework coupling were assumed to be equal in all the species. It was further assumed that the two frequencies pertaining to framework vibrations occurring in A_{2u} are the same as the two occurring in E_u. With the exception of the last two frequencies listed under E_u all the others were measured in the IR spectrum. For details, see ref. 30. [c] See footnote b to Table 4. [d] See footnote c to Table 4.

for the ligand vibrations. The cited work [30] should be consulted for further details, including calculated frequencies for a number of isotopic ions of $[Ni(NH_3)_6]^{2+}$.

C. CALCULATION OF "EXACT" FORCE CONSTANTS

Rigorous calculations of force constants in the General Valence Force Field (GVFF) can only be made if additional data (isotopic frequency shifts, Coriolis coupling constants, centrifugal distortion constants and mean ampli-

tudes of vibration, etc.) are known. The general theory underlying the calculation of exact force constants using such additional data has been described elsewhere [31—33]. In the following, the utility of isotopic shifts in fixing the precise values of the force constants will be discussed for coordination compounds.

(i) Calculation of force constants from isotopic shifts

The accuracy of force constant determination using the isotopic shifts depends on (i) the accuracy of the isotopic shift measurements, and (ii) the sensitivity of the force constants to the isotopic shifts [34—36]. However, not all frequencies are independent of each other because of the existence of the well-known product and sum rules [37,38] among the frequencies. The problem of determining the $\frac{1}{2}n(n+1)$ symmetry force constants is further complicated by the fact that the relationships among the force constants and the isotopic shifts (or frequencies of different isotopic molecules) are not linear. Hence, more than $\frac{1}{2}n(n+1)$ independent relations are generally required to define a force field without any assumptions or ambiguities.

In favorable cases, where the number of isotope shift data is sufficient (or more) to determine the GVFF constants, the following procedure is adopted [31—33]. The isotopic frequencies and an initial set of force constants are fed into a computer. The differences $[\nu^2(\text{obs}) - \nu^2(\text{calc})]$ are computed for each isotopic molecule and the force constants are adjusted until the above factor becomes negligible for all frequencies involved. This constitutes the well-known "least-squares procedure", the details of which can be found elsewhere [33,39]. In such a procedure, the Jacobians which define the variation of the force constants with respect to the isotopic shifts $\Delta\lambda_i$ (or more precisely $\Delta\lambda_i/\lambda_i$) are needed. For small frequency shifts, these Jacobians can be easily constructed by using the first order perturbation theory [37,40].

As shown by Wilson et al. [37], the frequency shifts due to the substitution of heavy and very heavy atoms can be computed rather accurately from the relation

$$\Delta = \Delta\Lambda\Lambda^{-1} = L^{-1}\Delta G(L^t)^{-1} \tag{29}$$

where $(\Delta\Lambda)_i$ is the shift in the square of the i'th frequency due to isotopic substitution and $(\Delta G)_{ij}$ elements represent the change in the elements of the inverse kinetic energy matrix. The L-matrix represents the relative amplitudes of vibration and is the eigenvector matrix of GF. In all the following discussions, the matrices corresponding to the parent molecule are denoted without any superscripts whereas those correponding to the isotopically substituted molecule are denoted with +. It should be noted that the matrix product on the right-hand side of eqn. (29) is not strictly diagonal, but is valid within the framework of the first order perturbation theory.

Tsuboi [40] employed eqn. (29) to obtain the Jacobians of the factor $(\Delta\lambda_a/\lambda_a)$ with respect to the force constants. The Jacobians are given by the

relation

$$\frac{\partial(\Delta\lambda_a/\lambda_a)}{\partial K_b} = 2\sum_{1\neq k} \Delta_{k1}(L^t B_b L)_{k1}/(\lambda_k - \lambda_1) \tag{30}$$

where the K_b elements are the independent force constants, leading to the relation

$$F = \Sigma B_b K_b \tag{31}$$

in which the potential energy matrix F is in the same coordinate system as G and Δ is defined by the left-hand side of eqn. (29). In deriving eqn. (30), the validity of the relations

$$\Delta L = -L\Delta p \tag{32}$$

and

$$\Delta(L^{-1}) = \Delta p L^{-1} \tag{33}$$

where Δp is an orthogonal matrix defined by $(\Delta p)_{ab} = (L^t \delta F L)_{ab}/(\lambda_a - \lambda_b)$ and $(\Delta p)_{aa} = 0$ has been assumed. The above relations are reasonably valid when the error in L (i.e. ΔL) due to those associated with Λ and Λ^+ is small [33].

The Jacobians $\partial(\lambda_a^+/\lambda_a)/\partial F_{ij}$ in a form similar to the one given by eqn. (30) can be derived using the first order perturbation theory. Since this derivation has so far not been reported anywhere in literature, we give below the results of such a study.

Within the frame of the Born—Oppenheimer approximation, the potential energy constants (reflective of the electronic properties of the molecule) are invariant under isotopic substitution. Hence, one has the relation

$$(L^{-1})^t \Lambda L^{-1} = (L^{+-1})^t \Lambda^+ (L^+)^{-1} \tag{34}$$

or

$$(L^{-1}L^+)^t \Lambda (L^{-1}L^+) = \Lambda^+ \tag{35}$$

Let

$$(L^{-1}L^+) = A \tag{36}$$

Equation (35) can be simplified in the form

$$A^t \Lambda A = \Lambda^+ \tag{37}$$

Hence,

$$A^t \Lambda A \Lambda^{-1} = \Lambda^+ \Lambda^{-1} \tag{38}$$

Now, let us assume that $(\Lambda^+\Lambda^{-1})$ changes to $(\Lambda^+\Lambda^{-1} + 0)$ due to the errors in the frequencies. Using eqns. (32) and (33), it can easily be shown that, in this

process, A changes to $(E + \delta P)L^{-1}L^{+}\ (E - \delta P^{+})$. From eqn. (38) we have

$$[(E - \delta P^{+})^{t}A^{t} + A^{t}\delta P^{t}]\Lambda[A(E - \delta P^{+}) + \delta PA]\Lambda^{-1} = (\Lambda^{+}\Lambda^{-1} + 0) \tag{39}$$

Retaining only the first powers of the correction terms δP and δP^{+} in the expansion of eqn. (39) we have

$$0 = \delta(\Lambda^{+}\Lambda^{-1}) = [\delta P^{+}A^{t}\Lambda A\Lambda^{-1} - A^{t}\Lambda A\delta P^{+}\Lambda^{-1} + A\cdot\Lambda\delta PA\Lambda^{-1} + A^{t}\delta P^{t}\Lambda A\Lambda^{-1}] \tag{40}$$

or

$$0 = \delta(\Lambda^{+}\Lambda^{-1}) = [\delta P^{+}\Lambda^{+}\Lambda^{-1} - \Lambda^{+}\delta P^{+}\Lambda^{-1} + A^{t}\Lambda\delta PA\Lambda^{-1} + A^{t}\delta P^{t}\Lambda A\Lambda^{-1}] \tag{41}$$

Since $\delta(\Lambda^{+}\Lambda^{-1})$ should be diagonal and since $(\delta P)_{ii} = (\delta P^{+})_{ii} = 0$, we have

$$[\delta(\Lambda^{+}\Lambda^{-1}]_{aa} = [A^{t}(\Lambda\delta P + \delta P^{t}\Lambda)A\Lambda^{-1}]_{aa} \tag{42}$$

Hence,

$$[\delta(\lambda_a^{+}/\lambda_a)] = 2\sum_{\substack{k,1\\k<1}} A_{ka}A_{1a}(\lambda_k - \lambda_1)\delta P_{k1}\lambda_a^{-1} \tag{43}$$

Thus, one obtains from eqn. (43) with the help of eqn. (31) the Jacobians $\partial(\lambda_a^{+}/\lambda_a)/\partial K_b$ in the form

$$\frac{\partial(\lambda_a^{+}/\lambda_a)}{K_b} = 2\sum_{k<1} A_{ka}A_{1a}\lambda_a^{-1}(L^{t}B_bL)_{k1} \tag{44}$$

When all the force constants F_{ij} are independent, we have $B = E$ and $K = F$. Considering $n = 2$ cases, eqn. (30) and eqn. (44) reduce respectively to the form

$$\frac{\partial(\Delta\lambda_a/\lambda_a)}{\partial F_{ii}} = 2\Delta_{ab}L_{ia}L_{ib}/(\lambda_a - \lambda_b)$$

$$\frac{\partial(\Delta\lambda_a/\lambda_a)}{\partial F_{ij}} = 2\Delta_{ab}(L_{ia}L_{jb} + L_{ib}L_{ja})/(\lambda_a - \lambda_b)$$

$$\frac{\partial(\Delta\lambda_a/\lambda_a)}{\partial F_{jj}} = 2\Delta_{ab}L_{ja}L_{jb}/(\lambda_a - \lambda_b) \tag{45}$$

and

$$\frac{\partial(\lambda_a^{+}/\lambda_a)}{\partial F_{ii}} = 2A_{ia}A_{ja}L_{ia}L_{ib}/\lambda_a$$

$$\frac{\partial(\lambda_a^{+}/\lambda_a)}{\partial F_{ij}} = 2A_{ia}A_{ja}(L_{ia}L_{jb} + L_{ib}L_{ja})/\lambda_a$$

$$\frac{\partial(\lambda_a^{+}/\lambda_a)}{\partial F_{jj}} = 2A_{ia}A_{ja}L_{ja}L_{jb}/\lambda_a \tag{46}$$

Equations (45) and (46) show that it is not only the difference $(\lambda_a - \lambda_b)$ but also the absolute value of λ_a which controls the force constants derived from the isotopic shift in λ_a. Since

$$\frac{\partial(\lambda_a^*/\lambda_a)}{\partial F_{nm}} = \frac{\partial(1 + \Delta\lambda_a/\lambda_a)}{\partial F_{nm}} = \frac{\partial(\Delta\lambda_a/\lambda_a)}{\partial F_{nm}} \qquad (n,m = i,j) \tag{47}$$

and

$$\Delta = AA^t - E \tag{48}$$

(see, eqn. (29)), the following relation should be satisfied for complete equivalence of eqns. (45) and (46); i.e.

$$(A_{ia}A_{ja} + A_{ib}A_{jb}) \equiv A_{ia}A_{ja}(\lambda_a - \lambda_b)/\lambda_a \tag{49}$$

or

$$\frac{A_{ib}A_{jb}}{A_{ia}A_{ja}} = -\frac{\lambda_b}{\lambda_a} \tag{50}$$

(ii) Calculation of force constants from Coriolis coupling constants

The Coriolis coupling constants symbolising the interaction of vibration and rotation can be obtained for instance from a contour analysis of vibrational bands in the gas phase. Although the Coriolis coupling constants serve as a useful constraint on the force field, their utility is limited due to the fact that accurate values of these constants cannot be determined experimentally for substances in condensed phases. A detailed theory of the Coriolis coupling constants and its application for the determination of force constants can be found elsewhere [18,31—33,39].

The Coriolis coupling constants ζ^α (α = axis of rotation; α = symmetry axis for degenerate modes) are related to the L-matrix elements through the equation

$$\zeta^\alpha = L^{-1}C^\alpha(L^{-1})^t \tag{51}$$

where C^α like G is dependent on the masses of the atoms and their geometrical configuration only. It may be noted that eqn. (51) is similar to eqn. (29). Hence the derivatives $\partial\zeta^\alpha_{aa}/\partial K_b$ are given by the relation (K_b is the same as defined in eqn. (30))

$$\frac{\partial\zeta^\alpha_{aa}}{\partial K_b} = 2\zeta^\alpha_{ab}(L^tB_bL)_{kl}/(\lambda_k - \lambda_l) \tag{52}$$

For $n = 2$ cases, we have for independent force constants

$$\frac{\partial\zeta^\alpha_{aa}}{\partial F_{ii}} = 2\zeta^\alpha_{ab}L_{ia}L_{ib}/(\lambda_a - \lambda_b) \tag{53a}$$

$$\frac{\partial\zeta^\alpha_{aa}}{\partial F_{ij}} = 2\zeta^\alpha_{ab}(L_{ia}L_{jb} + L_{ib}L_{ja})/(\lambda_a - \lambda_b) \tag{53b}$$

Equations (53) show that the force constants are better controlled by the Coriolis constants corresponding to degenerate modes ("first order" Coriolis coupling constants) when the frequencies are low and lie close together so that $(\lambda_a - \lambda_b)$ is small.

It is worth noting that for XY_n (n = 3, 4, 6) type molecules $|\Delta G|$ is zero for central atom substitution. If we assume that the force constants derived from the Coriolis coupling constants and the isotopic shifts due to heavy and very heavy atom substitution independently (possible for n = 2 cases) agree exactly we have

$$\frac{(\partial \Delta_{aa}/\partial F_{nm})_{bridge}}{\partial \zeta^{\alpha}_{aa}/\partial F_{nm}} = \pm \frac{(\Delta\lambda_a \Delta\lambda_b/\lambda_a\lambda_b)_{bridge}}{\zeta^{\alpha}_{aa}\zeta^{\alpha}_{bb} - |C^{\alpha}||G^{-1}|} \tag{54}$$

Equation (54) offers a direct way of studying the relative effectiveness of the Coriolis coupling constants and small frequency shifts due to bridge atom substitution in controlling the force constants.

In Tables 6—9 are given nearly all known exact force constants of typical transition metal complexes derived using the isotopic shifts and Coriolis coupling constants. The accuracy of the values demonstrate that even in complicated cases (e.g., $Ni(CO)_4$ and $[Zn(CN)_4]^{2-}$) the exact force constants can now be calculated using mainly the isotopic substitution technique. As seen from Table 8, the interaction valence force constant $f_{Ni-C/C-O}$ (=0.55 ± 0.08 mdyn Å^{-1}) is considerably larger than $f_{Zn-C/C-N}$ (=0.01 ± 0.08 mdyn Å^{-1}) (see Table 8 and footnote i to Table 11). This reflects the difference in the polarity of the M—C bonds (M = metal) in the two cases. Such studies constitute an important contribution of exact force constants calculation to the understanding of chemical bonding; but, such interpretations are meaningful only when the exact force constants can be determined, rather precisely.

(iii) Calculation of exact force constants for coordination compounds with low frequency vibrations

In this Sect. we deal with the utility of small shifts (10—2 cm^{-1}) determined with a rather large uncertainty (e.g. ±1.0 cm^{-1}) in fixing the accurate values of the force constants, as revealed by the investigations of Müller et al. [22,41,42]. As shown below, the normal coordinate analysis of certain compounds has some special advantages.

Using the Jacobians [40] obtained in eqn. (45) (n = 2 case), we have

$$\frac{\partial(\Delta\lambda_1/\lambda_1)}{\partial F_{11}} = 2\Delta_{12}L_{11}L_{12}/(\lambda_1 - \lambda_2)$$

$$\frac{\partial(\Delta\lambda_1/\lambda_1)}{\partial F_{12}} = 2\Delta_{12}(L_{11}L_{22} + L_{12}L_{21})/(\lambda_1 - \lambda_2)$$

$$\frac{\partial(\Delta\lambda_1/\lambda_1)}{\partial F_{22}} = 2\Delta_{12}L_{21}L_{22}/(\lambda_1 - \lambda_2) \tag{55}$$

TABLE 6

Exact force constants of some transition metal complexes with T_d and O_h symmetry

	Sources of additional data	Force constants (mdyn Å^{-1}) [a]			Ref.
		F_{33}	F_{34}	F_{44}	
CrO_4^{2-}	$\Delta\nu_3(^{50}Cr/^{53}Cr)$ (Cs_2SO_4-host lattice)	5.23 ± 0.17	0.08 ± 0.12	0.43 ± 0.02	58
MoO_4^{2-}	$\Delta\nu_3(^{92}Mo/^{100}Mo)$	5.14 ± 0.21	−0.22 ± 0.21	0.38 ± 0.03	57
	$\Delta\nu_3(^{92}Mo/^{100}Mo)$ (Cs_2SO_4-host lattice)	5.28 ± 0.12	−0.08 ± 0.13	0.36 ± 0.01	58
MoS_4^{2-}	$\Delta\nu_3(^{92}Mo/^{100}Mo)$	2.84 ± 0.12	−0.01 ± 0.07	0.203 ± 0.011	57
RuO_4	ζ_3, ν_1	6.62 ± 0.09	0.12 ± 0.12	0.378 ± 0.003	45
RuO_4	$\Delta\omega_3(^{16}O/^{18}O, ^{96}Ru/^{102}Ru)$; $\Delta\omega_4(^{16}O/^{18}O)$; ζ_3, ζ_4 ($Ru^{16}O_4$); ζ_3, ζ_4 ($Ru^{18}O_4$); u(RuO), u(O···O)	6.82 ± 0.05	0.07 ± 0.04	0.410 ± 0.015	45

OsO_4	ζ_3, ζ_4, ν_i	7.80 ± 0.05	−0.05 ± 0.10	0.425 ± 0.005	75
	$u(OsO), u(O\cdots O); \upsilon_i$	7.21 ± 0.51	0.67 $^{+0.43}_{-0.60}$	0.55 ± 0.12	76
	$\zeta_3(Os^{16}O_4), \zeta_3(Os^{18}O_4), \Delta\nu_3(^{16}O/^{18}O)$	8.01 ± 0.08	−0.012 ± 0.08	0.454 ± 0.018	77
	$\zeta_3(Os^{16}O_4), \zeta_3(Os^{18}O_4), \Delta\omega_3(^{16}O/^{18}O)$	8.11 ± 0.08	0.10 ± 0.10	0.47 ± 0.01	46
VCl_4	$u(VCl), u(Cl\cdot\cdot Cl), \nu_i$	2.09 ± 0.16	−0.15 ± 0.06	0.12 ± 0.02	78
$TiCl_4$	ζ(Raman), ν_i	3.13	0.34	0.12	79
	$\Delta\nu_3(^{46}Ti/^{50}Ti)$	2.64 ± 0.05	0.04 ± 0.02	0.098 ± 0.003	60
RhF_6	ζ_4, ν_i	4.30 ± 0.10	0.10 ± 0.10	0.29 ± 0.01	80
WF_6	ζ_3, ν_i	4.78 ± 0.10	0.20 ± 0.10	0.28 ± 0.01	80
	ζ_3, ν_i	4.80	0.18	0.27	81
	ζ_3, ω_i	5.08 ± 0.10	0.19 ± 0.02	$0.26_9 \pm 0.01_7$	81
MoF_6	$\Delta\nu_i(^{92}Mo/^{100}Mo)$	4.65	0.25	0.25	82
$[PdCl_6]^{2-}$	$\Delta\nu_3(^{104}Pd/^{110}Pd)$	1.80 ± 0.11	0.20 ± 0.08_5	0.18 ± 0.00_3	42

[a] Corresponds to the (2 × 2) block which is F_2 for (T_d) and F_{1u} for (O_h). The force constants for this block can be fixed only with the help of additional data.

TABLE 7

Exact force constants for ZXY_3 type compounds (E species)

Molecule	Force constants [a,b] derived from Coriolis data						Ref. for data
	F_{44}	F_{45}	F_{46}	F_{55}	F_{56}	F_{66}	
$FMnO_3$	6.08 ± 0.03	0.0 [f]	0.0 [f]	0.40 ± 0.00	0.0 [f]	0.26 ± 0.01	83 [c,e]
OVF_3	3.74 ± 0.50	0.14 ± 0.20	−0.50 ± 0.20	0.18 ± 0.05	−0.08 ± 0.05	0.43 ± 0.30	84 [c,e]
	3.34 ± 0.54	−0.02 ± 0.11	−0.69 ± 0.27	0.15 ± 0.01	−0.02 ± 0.05	0.56 ± 0.18	85 [d,e]
$OVCl_3$	2.72 ± 0.06	0.00 ± 0.07	0.10 ± 0.10	0.16 ± 0.15	−0.14 ± 0.07	0.46 ± 0.12	85 [d,e]

[a] All force constants are in units of mdyn $Å^{-1}$. [b] The force constants correspond to the order: ν_{as} (asymmetric stretch), δ_{as} (deformation) and ρ (rocking). [c] The Coriolis coupling constants obtained from IR band contour analysis were used as input data. [d] The Coriolis coupling constants derived from Raman band contour analysis were used to constrain the force field. [e] Since the Coriolis coupling constants in conjunction with the vibrational frequencies alone are insufficient to fix the force field unambiguously, these force constant sets are not very accurate. [f] Constrained at this value.

TABLE 8

Exact force constants [a] for $Ni(CO)_4$ and $[Zn(CN)_4]^{2-}$

Force constant [b]	$Ni(CO)_4$	$[Zn(CN)_4]^{2-}$
$F_{11}(A_1)$ mdyn Å^{-1}	18.22 ± 0.09	17.37 ± 0.09
$F_{12}(A_1)$ mdyn Å^{-1}	0.23 ± 0.07	0.21 ± 0.08
$F_{22}(A_1)$ mdyn Å^{-1}	2.36 ± 0.02	1.81 ± 0.01
$F_{33}(E)$ mdyn Å	0.44 ± 0.12	0.32 ± 0.06
$F_{34}(E)$ mdyn Å	0.1 ± 0.1 [c]	0.20 ± 0.04
$F_{44}(E)$ mdyn Å	0.23 ± 0.04	0.65 ± 0.07
$F_{55}(F_2)$ mdyn Å^{-1}	17.73 ± 0.12	17.2 ± 0.1
$F_{56}(F_2)$ mdyn	0.0 ± 0.2 [c]	0.0 [c]
$F_{57}(F_2)$ mdyn Å^{-1}	0.62 ± 0.13	−0.06 ± 0.10
$F_{58}(F_2)$ mdyn	0.0 ± 0.2 [c]	0.0 [c]
$F_{66}(F_2)$ mdyn Å	0.60 ± 0.11	0.22 ± 0.06
$F_{67}(F_2)$ mdyn	−0.10 ± 0.14	0.0 ± 0.1
$F_{68}(F_2)$ mdyn Å	0.1 ± 0.1 [c]	0.09 ± 0.08
$F_{77}(F_2)$ mdyn Å^{-1}	1.98 ± 0.14	1.32 ± 0.09
$F_{78}(F_2)$ mdyn	0.2 ± 0.1 [c]	0.25 ± 0.18
$F_{88}(F_2)$ mdyn Å	0.21 ± 0.05	0.6 ± 0.1

[a] For details see ref. 86 and the work cited under footnote [i] to Table 11. The isotopic shifts corresponding to $C/^{13}C$ and $^{16}O/^{18}O$ substitutions as well as the Coriolis coupling constants were all used to derive the potential energy constants for $Ni(CO)_4$ in ref. 86 while the $^{64}Zn/^{68}Zn$, $C/^{13}C$ and $N/^{15}N$ shifts in crystalline $K_2Zn(CN)_4$ were used by Jones and Swanson in their factor-group analysis of the potential energy constants. [b] For the definition of the symmetry coordinates and for the correlation between the symmetry and valence force constants, see ref. 86. [c] Constrained at this value.

where

$$\Delta_{12} = (-L_{21}L_{22}\Delta G_{11} + L_{11}L_{22}\Delta G_{12} + L_{12}L_{21}\Delta G_{12} - L_{11}L_{12}\Delta G_{22})/|G| \qquad (56)$$

Similar expressions with a negative sign are valid for $\partial(\Delta\lambda_2/\lambda_2)\partial F_{ij}$. These equations show that the force constants are effectively controlled by the shift (or $\Delta\lambda_i/\lambda_i$) when Δ_{12} is a maximum. A close examination of the expression for Δ_{12} would reveal that for any given sign combination of L_{12} and L_{21} (L_{11} and L_{22} can, without loss of generality, be assumed to have the same sign), two terms inside the bracket in eqn. (56) have a common sign, which is opposite to that of the other two terms. In other words, Δ_{12} is always very small. However, the magnitude of the Jacobian is also controlled by the term $(\lambda_1 - \lambda_2)$. For low frequency vibrations, which are close together, this factor $(\lambda_1 - \lambda_2)$ is very small with the result that the Jacobians assume large values in this case.

In general, transition metal complexes exhibit their metal—ligand stretching vibrations below 400 cm^{-1}. It is found that, in these cases, even small shifts (~3 cm^{-1}) determined with a large uncertainty (±1 cm^{-1}) are useful in fixing the accurate values of the force constants; see for example the force

TABLE 9

Exact force constants in symmetry coordinates [a] for metal hexacarbonyls [b]

Species	Force constant	$Cr(CO)_6$	$Mo(CO)_6$	$W(CO)_6$	Dimension
A_{1g}	F_{11}	18.11 ± 0.16	18.13 ± 0.31	18.10 ± 0.03	mdyn Å^{-1}
	F_{12}	0.38 ± 0.13	0.36 ± 0.25	0.36 ± 0.02	mdyn Å^{-1}
	F_{22}	2.44 ± 0.02	2.61 ± 0.04	3.10 ± 0.01	mdyn Å^{-1}
E_g	F_{33}	16.84 ± 0.07	16.84 ± 0.04	16.78 ± 0.10	mdyn Å^{-1}
	F_{34}	0.63 ± 0.05	0.68 ± 0.04	0.82 ± 0.08	mdyn Å^{-1}
	F_{44}	2.55 ± 0.01	2.42 ± 0.01	2.81 ± 0.01	mdyn Å^{-1}
F_{1g}	F_{55}	0.375 ± 0.001	0.346 ± 0.001	0.385 ± 0.001	mdyn Å
F_{1u}	F_{66}	17.22 ± 0.11	17.39 ± 0.06	17.21 ± 0.04	mdyn Å^{-1}
	F_{67}	0.78 ± 0.13	0.88 ± 0.07	0.91 ± 0.06	mdyn Å^{-1}
	F_{68}	(0 ± 0.2) [c]	(0 ± 0.2) [c]	(0 ± 0.2) [c]	mdyn
	F_{69}	(0 ± 0.5) [c]	(0 ± 0.5) [c]	(0 ± 0.5) [c]	mdyn
	F_{77}	1.64 ± 0.16	1.43 ± 0.12	1.80 ± 0.07	mdyn Å^{-1}
	F_{78}	−0.18 ± 0.09	−0.07 ± 0.08	−0.04 ± 0.06	mdyn
	F_{79}	(−0.3 ± 0.1) [c]	(−0.3 ± 0.1) [c]	(−0.3 ± 0.1) [c]	mdyn
	F_{88}	0.55 ± 0.22	0.48 ± 0.09	0.47 ± 0.07	mdyn Å
	F_{89}	−0.21 ± 0.12	−0.30 ± 0.07	−0.34 ± 0.04	mdyn Å
	F_{99}	0.79 ± 0.46	0.83 ± 0.25	0.93 ± 0.14	mdyn Å
F_{2g}	$F_{10\,10}$	0.39 ± 0.10	0.44 ± 0.02	0.41 ± 0.11	mdyn Å
	$F_{10\,11}$	−0.17 ± 0.02	−0.11 ± 0.01	−0.13 ± 0.05	mdyn Å
	$F_{11\,11}$	0.54 ± 0.16	0.34 ± 0.02	0.39 ± 0.14	mdyn Å
F_{2u}	$F_{12\,12}$	0.59 ± 0.13	0.55 ± 0.10	0.64 ± 0.10	mdyn Å
	$F_{12\,13}$	−0.11 ± 0.12	−0.19 ± 0.09	−0.14 ± 0.10	mdyn Å
	$F_{13\,13}$	0.35 ± 0.12	0.39 ± 0.13	0.33 ± 0.10	mdyn Å

[a] For the definition of the symmetry force constants in terms of the valence force constants, see ref. 36. The force constants correspond to the gas phase frequencies. The values are from ref. 86, in which the observed frequencies, isotopic shifts and the Coriolis coupling constants were used as additional data. [b] All the molecules belong to O_h. [c] Constrained at this value.

constants of $[PdCl_6]^{2-}$ (O_h, ^{104}Pd—^{110}Pd), $[SnCl_6]^{2-}$ (O_h, ^{116}Sn—^{124}Sn), $[Cr(NH_3)_6]^{3+}$ (O_h, ^{50}Cr—^{53}Cr), $[Ni(NH_3)_6]^{2+}$ (O_h, ^{58}Ni—^{62}Ni), $[Cu(NH_3)_4]^{2+}$ (D_{4h}, ^{63}Cu—^{65}Cu), $[Pd(NH_3)_4]^{2+}$ (D_{4h}, ^{104}Pd—^{110}Pd) and $[Zn(NH_3)_4]^{2+}$ (T_d, ^{64}Zn—^{68}Zn) presented in Table 10 (for details, see refs. 22, 41, 42).

An approximate expression for studying the influence of the errors associated with the isotopic frequency shifts (i.e. $\Delta\lambda_i/\lambda_i$) on the force constants in $n = 2$ cases has been reported in literature [43]. The derivation is based on the first order perturbation theory and the assumption that the lower frequency mode is completely characteristic (i.e. $L_{ij} = 0$ for $i < j$ where the higher frequency mode is bond stretching and the lower one is the interbond bending; $\nu\delta$ case).

TABLE 10

Force constants of some transition metal complexes showing their sensitivity to isotopic frequency shifts [a]

	Isotopic substitution	Shift in cm^{-1} ($\Delta\nu_3$) [b]	Force constants (mdyn $Å^{-1}$)		
			F_{33}	F_{34}	F_{44}
$[PdCl_6]^{2-}$	$^{104}Pd/^{110}Pd$	3.5 ± 0.5 [e]	1.80 ± 0.11	$0.20 \pm 0.08_5$	$0.18 \pm 0.00_3$
		(4.0 ± 1.0 [c,d])	1.71 ± 0.22	0.14 ± 0.14	0.18 ± 0.01
$[SnCl_6]^{2-}$	$^{116}Sn/^{124}Sn$	3.2 ± 0.8 [e]	1.55 ± 0.10	0.21 ± 0.09	0.18 ± 0.02
		(4.0 ± 1.0 [c,d])	1.45 ± 0.16	0.13 ± 0.09	0.18 ± 0.01
$[Cr(NH_3)_6]^{3+}$	$^{50}Cr/^{53}Cr$	4.0 ± 1.0 [e]	1.59 ± 0.09	0.26 ± 0.08	0.21 ± 0.02
$[Cu(NH_3)_4]^{2+}$	$^{63}Cu/^{65}Cu$	2.0 ± 1.0 [e]	1.29 ± 0.22	-0.17 ± 0.18	0.25 ± 0.06
$[Pd(NH_3)_4]^{2+}$	$^{104}Pd/^{110}Pd$	3.0 ± 1.0 [e]	1.93 ± 0.14	$-0.17_5 \pm 0.17$	0.34 ± 0.06
$[Ni(NH_3)_6]^{2+}$	$^{58}Ni/^{62}Ni$	2.2 ± 1.0 [e]	0.87 ± 0.04	0.18 ± 0.05	0.15 ± 0.02
$[Zn(NH_3)_4]^{2+}$	$^{64}Zn/^{68}Zn$	2.0 ± 0.6 [e]	$1.38 \pm 0.03_5$	0.19 ± 0.07	0.10 ± 0.02

[a] The skeletal force constants for the ammine complexes a~e derived assuming the validity of the point mass model (see, refs. 22 and 41). The data presented can be found in ref. 42. [b] Corresponds to the stretching frequency in the two dimensional block. [c] The shifts are those calculated using the L-matrix approximation method (see, ref. 67). [d] Assumed error to show the sensitivity. [e] Experimental results (see, refs. 22, 41 and 42).

The F elements corresponding to $n = 2$ cases are given by the relations (ν_1 and ν_2 are the frequencies)

$$F_{11} = (L_{22}^2\lambda_1 + L_{21}^2\lambda_2)/|G| \tag{57a}$$

$$F_{22} = (L_{12}^2\lambda_1 + L_{11}^2\lambda_2)/|G| \tag{57b}$$

$$F_{12} = -(L_{12}L_{22}\lambda_1 + L_{11}L_{21}\lambda_2)/|G| \tag{57c}$$

Considering eqn. (57a) let F_{11} become $(F_{11} + \delta F_{11})$ as L_{22}^2 and L_{21}^2 become $(L_{22}^2 + K_1)$ and $(L_{21}^2 + K_2)$, respectively. These changes can be represented by the relation

$$F_{11} + \delta F_{11} = (L_{22}^2\lambda_1 + L_{21}^2\lambda_2)/|G| + (K_1\lambda_1 + K_2\lambda_2)/|G| \tag{58}$$

The normalisation condition leads to the result

$$(L_{22}^2 + K_1) + (L_{21}^2 + K_2) = L_{22}^2 + L_{21}^2 = G_{22} \tag{59}$$

or

$$K_1 = -K_2 \tag{60}$$

Substitution of eqn. (60) in (58) leads to the result

$$\delta F_{11} = K_1(\lambda_1 - \lambda_2)/|G| \tag{61}$$

The application of the first order perturbation theory yields [31,37,44]

$$\Delta\lambda_1/\lambda_1 = (L_{22}^2\Delta G_{11} - 2L_{12}L_{22}\Delta G_{12} + L_{12}^2\Delta G_{22})/|G| \tag{62}$$

For molecules exhibiting very small mass coupling (i.e. $m_X >> m_Y$ for XY_n type molecules) the setting of $L_{12} = 0$ in eqn. (62) does not lead to serious errors in $\Delta\lambda_1/\lambda_1$. Hence eqn. (62) can be approximated as [44]

$$\Delta\lambda_1/\lambda_1 \simeq L_{22}^2\Delta G_{11}/|G| \tag{63}$$

Thus the error associated with L_{22}^2 (i.e. K_1) is given approximately by the relation

$$\delta(\Delta\lambda_1/\lambda_1) \simeq K_1\Delta G_{11}/|G| \tag{64}$$

Substitution of this result in eqn. (61) gives

$$\delta F_{11}/\delta(\Delta\lambda_1/\lambda_1) \simeq (\lambda_1 - \lambda_2)/\Delta G_{11} \tag{65}$$

Equation (65) shows that the stretching force constant F_{11} (in $n = 2$ cases) is best controlled by the isotopic shift (i.e. $\Delta\lambda_1/\lambda_1$) when the two frequencies ν_1 and ν_2 are both small and lie close together (so that $(\lambda_1 - \lambda_2)$ is small) and when the substitution causes a large change in G_{11}. Equations (46) on the other hand directly show that the accuracy of F_{11} determined using the shift in ν_1 (i.e. λ_1^*/λ_1) increases with decreasing value of the stretching frequency ν_1 (i.e. λ_1). What eqn. (65) seems to suggest is that in some cases even if the difference $(\lambda_1 - \lambda_2)$ is very small (or when λ_1 is small), the accuracy in F_{11} may not be very good when the isotopic substitution leads to very small

change in G_{11} (e.g., complexes involving elements of the third row of transition metals, in general).

(iv) Limitations of the isotopic substitution technique

Though the isotopic shifts could in principle be used to determine the force constants for any molecule, the accuracy of the constants thus determined depends on their sensitivity to the isotopic shifts, and hence it is necessary to distinguish three types of situation.

H/D substitution. Very large frequency shifts are associated with H/D or other light atom substitution (e.g. $^{6}Li—^{7}Li$). The calculation of force constants using large isotopic shifts encounters the following difficulties. Since the difference between the harmonic (ω_i) and the observed (ν_i) frequencies is large for higher frequencies, the force fields determined by using ω and ν separately are widely divergent. Even in cases where the harmonic frequencies have been estimated (mostly empirically), it is generally found difficult to estimate the corresponding uncertainties so that no "true error limits" could be given for the values of the harmonic force constants. Secondly, it is found that for light atom substitution (e.g. H—D), the force constants (especially F_{11} in $n = 2$ cases) are very sensitive to $\Delta\omega$ (i.e. $\omega_{\text{isotopic}} - \omega_{\text{normal}}$) and hence the shifts become virtually useless in fixing the precise values of the force constants [35,37].

Heavy atom substitution. Small frequency shifts are associated with heavy atom substitution (e.g. $^{10}B—^{11}B$, $^{14}N—^{15}N$, $^{16}O—^{18}O$, $^{35}Cl—^{37}Cl$, etc.). Heavy atom substitution technique has been successfully used in recent years for the evaluation of force constants for compounds like RuO_4 ($^{16}O—^{18}O$) [45], OsO_4 ($^{16}O—^{18}O$) [46], XeO_4 ($^{16}O—^{18}O$) [47], $SiCl_4$ ($^{35}Cl—^{37}Cl$) [48], SF_6 ($^{32}S—^{34}S$) [49], CH_3F, CH_3Cl, CH_3Br and CH_3I ($^{12}C—^{13}C$ shifts along with other data) [50], $CHCl_3$ ($^{12}C—^{13}C$ shifts together with other additional data) [51], $SiHF_3$ ($^{29}Si—^{30}Si$ splitting with other pieces of data) [52], ONF, ONCl and ONBr ($^{16}O—^{17}O$, $^{16}O—^{18}O$, $^{14}N—^{15}N$ splittings with other data) [53—55] and CH_2O ($^{12}C—^{13}C$ shifts with other data) [56].

Very heavy atom substitution. The substitution of very heavy atoms (metals such as Ti, Ge, Ru, Sn etc.) causes only small shifts in the vibrational frequencies. Using first order perturbation theory it was shown that small frequency shifts (associated with heavy and very heavy atom substitution) measured accurately (± 0.2 cm^{-1} accuracy) lead to reliable values of the force constants.

This technique has recently been applied with success for the evaluation of force constants for a number of metal inorganic compounds such as $[MoO_4]^{2-}$ ($^{92}Mo—^{100}Mo$) [57,58], $[MoS_4]^{2-}$ ($^{92}Mo—^{100}Mo$) [57], $[CrO_4]^{2-}$ ($^{50}Cr—^{53}Cr$) [58], RuO_4 ($^{96}Ru—^{102}Ru$) [45], $SnCl_4$ ($^{116}Sn—^{124}Sn$) [59], $GeCl_4$ ($^{70}Ge—^{76}Ge$) [60], $TiCl_4$ ($^{46}Ti—^{50}Ti$) [60], etc.

Even in applying the isotopic substitution technique (isotopic frequency shifts with large uncertainties) to coordination compounds exhibiting low frequency fundamentals, it is important to assess the limitations of this approach.

For applying the central atom isotopic substitution technique to complexes of transition elements as an example, the following stable isotopes (differing maximum in mass) could be used theoretically for the first and second row elements

Differing 4 amu in mass: Ti(46—50), Cr(50—54) and Fe(54—58).
Differing 6 amu in mass: Ni(58—64), Zn(64—68) and Zr(90—96).
Differing 8 amu in mass: Mo(92—100), Ru(96—104) and Pd(102—110).
Differing 10 amu in mass: Cd(106—116).

Not only the mass difference due to isotopic substitution, but also the absolute mass of the element concerned, determines the sensitivity of the force constants to the isotopic shift. Considering the same mass differences for the two extreme cases Ti and Cd, we have $\Delta\mu(^{46}Ti/^{50}Ti) = 17.39 \cdot 10^{-4}$ (amu)$^{-1}$ and $\Delta\mu(^{112}Cd/^{116}Cd) = 3.08 \cdot 10^{-4}$ (amu)$^{-1}$. Even for the substitution ($^{106}Cd/^{116}Cd$), $\Delta\mu = 6.62 \cdot 10^{-4}$ (amu)$^{-1}$ which is considerably less than that for $^{46}Ti/^{50}Ti$.

In the case of Cu and Ag the mass difference of the available isotopes is two, whereas for V, it is one. For Cu($^{63}Cu/^{65}Cu$) and V($^{50}V/^{51}V$), the mass change involved might be sufficiently large ($\Delta\mu(^{63}Cu/^{65}Cu) = 4.88 \cdot 10^{-4}$ (amu)$^{-1}$; $\Delta\mu(^{50}V/^{51}V) = 3.92 \cdot 10^{-4}$ (amu)$^{-1}$) for the determination of a reasonably accurate set of force constants, but this may not be the case for Ag($^{107}Ag/^{109}Ag$) [$\Delta\mu = 1.715 \cdot 10^{-4}$ (amu)$^{-1}$]. But for Sc, Mn, Co (all I row), Y, Nb, Rh (all II row), only one stable isotope exists. The mass change involved is in most cases large enough for the determination of the force constants for complexes of the first and second row transition elements.

In contrast to this the absolute mass of the elements in the third row of transition metals is in general large. For Hf(174—180) and W(180—186) the maximum mass difference involved in the substitution is 6 whereas for Os(184—192), Pt(190—198) and Hg(196—204) the corresponding mass difference is 8. The largest value of $\Delta\mu$ in this case is associated with Os ($\Delta\mu = 2.265 \cdot 10^{-4}$ (amu)$^{-1}$) while the smallest value of $\Delta\mu$ is associated with W ($\Delta\mu = 1.80 \cdot 10^{-4}$ (amu)$^{-1}$). From the published results [13,16], it appears that also for complexes associated with the above elements of the third row, the isotopic substitution technique might be applied with success to fix the force constants within reasonable error limits, in some cases. For La(138—139), Ta(180—181), Re(185—187) and Ir(191—193), the mass change is too small to be significant. For Au(197) there is only one stable isotope.

It is worth pointing out here that when one considers complexes of T_d and O_h point groups, the values of ΔG_{33} (F_2 or F_{1u}) for $XY_6/^{\prime}XY_6$ substitution is 3/2 times that for $XY_4/^{\prime}XY_4$ substitution.

For making any quantitative prediction whether the central atom isotopic substitution technique in the above cases is useful in fixing the force con-

stants within reasonable error limits, a rough knowledge of the frequencies involved is necessary; see, eqn. (65). In addition to the theoretical limitations listed above, one should also recognize the experimental shortcomings.

To obtain the experimental data with an accuracy of $\sim\pm 0.2\ cm^{-1}$ in the isotopic frequency shifts, the samples have to be isotopically pure. Only for a few compounds (e.g. RuO_4) [45,61] the resolution of individual isotopic peaks might be possible when measurements are made with the substance in natural abundance. Thus, for example 50 stable isotopic species exist for $SnCl_4$ while the number of stable isotopic species is restricted to twenty five in the case of $TiCl_4$. Although the isotopic substitution technique appears to be very promising, it should also be noted that in some cases, the stable isotopes are not commercially available with sufficient purity.

Another source hindering the accurate measurement of isotopic shifts is the appearance of hot band progressions in the gas phase spectra (e.g. RuO_4) [45,61]. In such cases it is preferable to make measurements using the matrix isolation technique. This has actually been carried out frequently in recent years.

With respect to the accuracy of measurements, it should be mentioned that the bands of many compounds (as solids or in solution) are in general rather broad so that the isotopic shifts thus measured might carry large uncertainties (larger than $\pm 0.5\ cm^{-1}$). Useful methods in such cases might be the matrix isolation technique [59,60] (for volatile substances) and the "host lattice method" [62,63] (for ions). If species doped in host lattices are used for a measurement, it is important to choose relatively less polarizing host lattices. This would ensure that the frequencies and the corresponding isotopic shifts are in the neighbourhood of those for the free ion.

D. "PSEUDO-EXACT" FORCE CONSTANTS

A combination of experimental data (isotopic frequency shifts, Coriolis coupling constants, etc.) and plausible assumptions leads to the determination of the so-called "pseudo-exact" force constants (see Müller et al. for definition [42,64]). In this process, usually, as many assumptions as are needed to solve a problem using the available experimental data, are made. In principle, the order of the secular equation is reduced to any desired extent so that the force constants involved in the reduced block can be calculated without any approximation. This implies that the vibrations involved in the factored-out block do not have much influence on those involved in the remaining block (95% or more pure).

(i) High—low frequency separation method

The theory of the high—low frequency separation (HLFS) method developed by Crawford and Edsall [65] and Wilson [66] is well described in the book of Wilson et al. [37]. Hence, only a brief outline is given below.

The separation of the high frequency vibration in a secular determinant of order n is accomplished by dropping the corresponding rows and columns in G^{-1} and F, and then by solving the reduced secular determinant. This leads to modified expressions for the G matrix elements of the reduced block (G^0) given by

$$G^0_{tt'} = G_{tt'} - \sum_{ss'} G_{ts} X_{ss'} G_{s't'} \tag{66}$$

where s covers the symmetry coordinates S_s to be held rigid while $X_{ss'}$ elements satisfy the relation

$$\sum_{s'} X_{ss'} G_{s's''} = \delta_{ss''} \tag{67}$$

where $\delta_{ss''}$ is Kronecker's delta.

The factoring of the low frequency vibrations on the other hand is achieved simply by dropping the corresponding rows and columns in G and F, and then by solving the reduced secular determinant to obtain the corresponding force constants. Hence, no change in the G matrix elements corresponding to the reduced block is necessary in this case.

The similarity between this and other approximation methods (L-matrix method [67], PED method [68], etc.) in calculating force constants was pointed out by Müller et al. [69] who stressed the special suitability of this method in reducing the order of secular determinants from three to two. The pseudo-extract force constants of the reduced 2 × 2 block after factoring out either the highest or the lowest frequency vibration can be calculated without approximation by using experimental data (isotopic shifts or Coriolis coupling constants). Müller et al. [22,41,70] have applied this method to a number of molecules which contain 3 or 4 vibrations in a single symmetry species. The numerical results for $Ni(CO)_4$, ReO_3Cl, $[Zn(CN)_4]^{2-}$ and $[Zn(NH_3)_4]^{2+}$ (see Tables 11, 12) demonstrate the usefulness of the approach.

The truncation of the problem by dropping the Coriolis coupling constants corresponding to high frequencies can be achieved [71] in a manner similar to the one given above in connection with the isotopic shifts.

Thus, considering symmetric tops [e.g. $XY_3Z(C_{3v})$], when the atoms not lying on the symmetry axis are heavy (i.e. not hydrogen or other light atoms), one can use the equation

$$(C^\alpha_{ij})^0 = C^\alpha_{ij} - \sum_{ss'} C^\alpha_{is} X_{ss'} C^\alpha_{s'j} \tag{68}$$

to truncate the $(C^\alpha)^0$ matrix. But for symmetric tops containing light atoms which do not lie on the symmetry axis, the separation of the Coriolis coupling constant corresponding to high frequency vibrations (HFS) is achieved by simply dropping the corresponding rows and columns from the $(C^\alpha)^0$ matrix. This procedure can be followed in an analogous manner for the separation of Coriolis coupling constants pertaining to low frequency vibrations (LFS). Very useful results for the force constants have been obtained using this pro-

TABLE 11

Pseudo-exact force constants for some transition metal complexes derived using the high–low frequency separation (HLFS) method [a,b]

Complex	Isotopic substitution	Shift in frequency (cm^{-1})	Pseudo-exact force constants for the reduced block [c,d]		
			F_{11}	F_{12}	F_{22}
ReO_3Cl	$^{35}Cl/^{37}Cl$	9.0 ± 1.0	1.03 ± 0.07	0.04 ± 0.25	3.14 ± 0.17
$Ni(CO)_4$	$C/^{13}C$	5.7 ± 1.0	0.52 ± 0.01	−0.13 ± 0.02	1.85 ± 0.00$_6$
			(0.60 ± 0.11) [e]	(−0.10 ± 0.14) [e]	(1.98 ± 0.14) [e]
$[Zn(CN)_4]^{2-}$	$^{64}Zn/^{68}Zn$	2.1 ± 0.6	0.31 ± 0.02 [f]	−0.01 ± 0.02 [f]	1.06 ± 0.07$_5$ [f]
		2.1 ± 0.6	0.29 ± 0.01 [g]	−0.13 ± 0.01 [g]	1.25 ± 0.03 [g]
			(0.26 ± 0.02) [h]	(−0.10 ± 0.05) [h]	(1.28 ± 0.03) [h]
			(0.25 ± 0.20) [i]	(−0.1 ± 0.2) [i]	(1.27 ± 0.20) [i]

[a] The species involved is A_1 for ReO_3Cl and F_2 for the others. [b] The original secular determinants of order 3, 4 and 4 for ReO_3Cl, $Ni(CO)_4$ and $[Zn(CN)_4]^{2-}$, respectively were reduced using the HLFS method. ν_s (ReO-symmetric stretch) was factored out in the case of ReO_3Cl, while the highest and the lowest frequencies ν_{as} (CO or CN-asymmetric stretch) and δ_{as} (CNiC or CZnC-asymmetric bend) were factored out in the case of $Ni(CO)_4$ and $[Zn(CN)_4]^{2-}$ using the HLFS model (see text and refs. 22 and 41 for details). [c] The force constants correspond to the following order of frequencies: ReO_3Cl δ_s (symmetric bend), ν_s (ReCl-symmetric stretch); $Ni(CO)_4$ δ_{as} (NiCO-bend), ν_{as} (NiC-stretch); $[Zn(CN)_4]^{2-}$ δ_{as} (ZnCN-bend), ν_{as} (ZnC-stretch). [d] F_{11} in units of mdyn Å, F_{12} in units of mdyn and F_{22} in units of mdyn $Å^{-1}$. References to the experimental data and the values reported here can be found in ref. 42. For the meaning of the error limits, see footnote j to Table 12. [e] Exact force field data; see ref. 86. [f] There are two solutions for the force field in this case and this is the alternate solution reported in ref. 22. [g] This is the correct solution as seen by comparison with the exact force field data. [h] From the complete force field data obtained by K.H. Schmidt (private communication) using the $^{64}Zn/^{68}Zn$, $^{12}C/^{13}C$ and $^{14}N/^{15}N$ isotopic shifts. The calculations were carried out for the isolated $[Zn(CN)_4]^{2-}$ ion. [i] From the complete force field data reported recently by L.H. Jones and B.I. Swanson, J. Chem. Phys., 63 (1975) 5401. The authors used a lattice force field model in conjunction with the $^{64}Zn/^{68}Zn$, $^{12}C/^{13}C$ and $^{14}N/^{15}N$ isotopic shifts in $K_2Zn(CN)_4$ to fix the force constants.

TABLE 12

Comparison of force constants derived from point mass model and the complete frequency data for the complex

Complex	Skeletal force constants [j] (mdyn Å^{-1})			Ref.
	F_{33}	F_{34}	F_{44}	
$[Zn(NH_3)_4]^{2+}$	1.38 (±0.03) [a,b]	0.18 (±0.06) [a,b]	0.10 (±0.02) [a,b]	22
	1.37 (±0.02) [a,c]	0.16 (±0.03) [a,c]	0.09 (±0.01) [a,c]	22
	1.41 (±0.01) [a,d]	0.27 (±0.08) [a,d]	0.13 (±0.02) [a,d]	87
	1.38 (±0.04) [e,b]	0.19 (±0.07) [e,b]	0.10 (±0.02) [e,b]	p
	1.41 (±0.02) [e,d]	0.27 (±0.08) [e,d]	0.12 (±0.03) [e,d]	p
	1.42 [i]	0.19 [i]	0.11 [i]	25
$[Cu(NH_3)_4]^{2+}$	1.28 (±0.23) [a,g]	−0.17 (±0.18) [a,g]	0.25 (±0.05) [a,g]	41
	1.05 (±0.09) [a,c]	0.01 (±0.04) [a,c]	0.27 (±0.03) [a,c]	41
	1.14 (±0.23) [a,h]	−0.04 (±0.10) [a,d]	0.25 (±0.07) [a,d]	29
	1.09_7 [i]	-0.02_0 [i]	0.30_4 [i]	29

[a] Obtained using the point mass model (PMM) approach. [b] The $^{64}Zn/^{68}Zn$ isotopic shift in $\nu_3(F_2)$ ($\nu_{as}[Zn\text{-}(NH_3)]$) was used as additional data. [c] The NH_3/ND_3 isotopic shift in $\nu_3(F_2)$ was used to constrain the force field. [d] The $NH_3/^{15}NH_3$ isotopic shift in $\nu_3(F_2)$ was employed to fix the force constants. [e] Based on the model of high-low frequency separation (HLFS) wherein all frequencies (and hence the corresponding symmetry coordinates) other than $\nu_{as}[Zn\text{-}(NH_3)]$ and $\delta_{as}[Zn\text{-}(NH_3)]$ (both belonging to F_2) were factored out from a secular equation of order seven. [g] The $^{63}Cu/^{65}Cu$ shift in $\nu_6(E_u)$ ($\nu_{as}[Cu\text{-}(NH_3)]$) was used as the basis in calculating the force constants. [h] The $^{14}NH_3/^{15}NH_3$ shift in $\nu_6(E_u)$ was used as input data. [i] Final force constants pertaining to the whole complex (see the appropriate references for details). [j] The error limits in the values of the force constants correspond only to the experimental uncertainties (frequencies and isotopic shifts). They do not include the uncertainties arising due to the use of the model itself. [p] Present results (see footnote e).

cedure for many $XY_3Z(C_{3v})$ type molecules [71].

An important criterion for studying the validity of the procedure (HLFS method using isotopic shifts or Coriolis coupling constants) is the validity of the Teller—Redlich product rule [37] for the reduced species (in the case of isotopic shifts) or that of the ζ-sum rule [18] for the reduced species (Coriolis coupling constants). In other words the relations

$$\frac{\lambda_a^+\lambda_b^+\cdots\lambda_n^+}{\lambda_a\lambda_b\cdots\lambda_n} = \frac{|G^+|}{|G|} \tag{69a}$$

$$\mathrm{Tr}(G^{-1}C^\alpha) = \Sigma\zeta_{aa} \tag{69b}$$

for the truncated problem should be satisfied as closely as possible for the validity of the HLFS approach (as in the case of ReO_3Cl, $Ni(CO)_4$ and $[Zn(CN)_4]^{2-}$). Some numerical results based on this approach are presented in Table 11. A comparison of these results with the exact force field data, wherever available (see Table 11) indicates the validity of this approach.

(ii) The point mass model

The model is suited for molecules and ions containing hydrogen. In XH_nZ_m type molecules, the XH_m group can, under certain circumstances, be assumed to be a point mass with an aggregate mass of (M_X+nM_H). This assumption is valid only when the coupling of the XZ_m group vibrations and those of the XH_n group is negligible. The force constants of different tetrammine and hexammine complexes have been obtained by assuming the NH_3 group as a point mass and by using the metal isotope shifts as constraints on the force field [41]. This method cannot be applied e.g. for molecules of the type $E(CH_3)_n$ (E = light element belonging to the main group) as in these cases, strong vibrational coupling between $\zeta(CH_3)$ and ν(E—C) is possible. Equation (69) can be used in this case too, to check the validity of the model. The point mass model has been used in the past for the determination of force constants using the isotopic shifts, Coriolis coupling constants and the centrifugal distortion constants [22,41,71,72]. In the normal coordinate analyses for the whole ammine complexes [25,29,30] reported above (Sect. B(iii)) the force constant values from point mass model computations were applied as an initial approximation for the framework force constants. Tables 10 and 12 contain the values of the force constants computed using the point mass model for some ammine complexes. The excellent compatibility of the results obtained using the HLFS method and the point mass model separately (see Table 12) and the very good agreement with the data based on a complete normal coordinate analysis for the whole complex using the isotopic data appears to confirm the validity of the point mass model approach. This model has in fact been used to present the correlation between the first physically reasonable M—N (M = metal) stretching force constants and bond orders for transition metal—ammine complexes [88].

One important point related to the "pseudo-exact" force constants presented in Tables 10—12 should be underlined. In the case of complexes characterized by low frequency vibrations, relatively precise values of the force constants could be estimated, even though, the measured isotopic shifts carry large uncertainties. Thus, in the case of $[Ni(NH_3)_6]^{2+}$ and $[Zn(CN)_4]^{2-}$ for example, the force constants could be fixed with reasonable accuracy, even though the measured shifts carry uncertainties of 50% (see Tables 10—12). Although the error limits given are not the true ones (due to assumptions in the model), they, in view of the good agreement with the exact force constants, demonstrate the usefulness of the model.

E. THE SUM RULE FOR THE ISOTOPIC SHIFTS CORRESPONDING TO EACH INDIVIDUAL FREQUENCY

All isotopic frequency shifts may not serve to obtain useful information on the force constants, since these shifts are related to each other through the well known sum and product rules [37,38,73,74]. These exact sum and

product rules connect a group (with one or more element) of frequencies of different isotopically substituted molecules. As such, they serve as a check on a group of frequencies. Apart from these exact rules, a new sum rule based on the first order perturbation theory could be derived [43]. The utility of this new sum rule of Müller (valid for the substitution of heavy and very heavy atoms) is enhanced by the fact that it is valid for each individual frequency and hence the isotopic shifts associated with each individual frequency could be controlled with the help of this relation.

Let us designate the shift in λ_k corresponding to any one individual frequency, due to the symmetric substitution of atom set 1 as $\Delta\lambda_k^1$, of atom set 2 as $\Delta\lambda_k^2$ and so on and designate the shift in λ_k due to the symmetric substitution of all n types of atoms as $\Delta\lambda_k^{nn}$ (the parent and the substituted atom set involved in $\Delta\lambda_k^{nn}$ being the same as those corresponding to $\Delta\lambda_k^1$, $\Delta\lambda_k^2$, ··· etc.). Since, in this case the L_{ik} coefficients and λ_k are the same for all substitutions, it follows from eqn. (29) that

$$\frac{\Delta\lambda_k^1}{\lambda_k} + \frac{\Delta\lambda_k^2}{\lambda_k} + \cdots + \frac{\Delta\lambda_k^n}{\lambda_k} = \frac{\Delta\lambda_k^{nn}}{\lambda_k} \tag{70}$$

or simply

$$\sum_{p=1}^{n} \Delta\lambda_k^p = \Delta\lambda_k^{nn} \tag{71}$$

Even for symmetric substitutions not involving all sets of atoms constituting the molecule (partial isotopic substitution, e.g., $A_pB_qC_r/A_p^*B_qC_r$, $A_pB_qC_r/A_pB_q^*C_r$ and $A_pB_qC_r/A_p^*B_q^*C_r$), it follows from eqn. (29) that

$$\sum_{p=1}^{m} \Delta\lambda_k^p = \Delta\lambda_k^{mm} \qquad (\text{with } m \leqslant n) \tag{72}$$

The above equation is valid for the isotopic shifts associated with each individual frequency and is naturally approximate. It holds only for heavy and very heavy atom substitution (for which the L-matrix elements change very little due to isotopic substitution). Nevertheless, eqns. (71) and (72) should be useful as a check on the experimental values. Some numerical results confirming the validity of the above rule are presented in Tables 13 and 14.

When the term $(\Delta\nu/\nu)$ is very small, so that only the first power of $\Delta\nu$ is retained in the expansion of eqns. (71) and (72) one obtains the simplified relations

$$\sum_{p=1}^{n} \Delta\nu_k^p = \Delta\nu_k^{nn} \tag{73}$$

$$\sum_{p=1}^{m} \Delta\nu_k^p = \Delta\nu_k^{mm} \quad (m \leqslant n) \tag{74}$$

TABLE 13

Isotopic sum rule for individual frequencies

	Frequency	$\Delta\nu^1$ (in cm^{-1})	$\Delta\nu^2$ (in cm^{-1})	$\Delta\nu^{22}$ (in cm^{-1})		Ref.
				Calc. [a]	Meas.	
		$^{16}O^{14}NF/^{16}O^{15}NF$	$^{16}O^{14}NF/^{18}O^{14}NF$	$^{16}O^{14}NF/^{18}O^{15}NF$		
ONF	ν_1 = [ν(NO)]	32.9 [c]	49.7 [c]	83.5 [c]	83.4 [c]	53
	ν_2 = [δ(ONF)]	17.6 [c]	8.3 [c]	26.1 [c]	26.0 [c]	
	ν_3 = [ν(NF)]	2.5 [c]	8.8 [c]	11.1 [c]	10.7 [c]	
		$^{16}O^{14}N^{35}Cl/^{16}O^{15}N^{35}Cl$	$^{16}O^{14}N^{35}Cl/^{18}O^{14}N^{35}Cl$	$^{16}O^{14}N^{35}Cl/^{18}O^{15}N^{35}Cl$		
ONCl	ν_1 = [ν(NO)]	32.0 [c]	49.5 [c]	82.4 [c]	82.2 [c]	54
	ν_2 = [δ(ONCl)]	14.4 [c]	7.7 [c]	22.3 [c]	22.5 [c]	
	ν_3 = [ν(NCl)]	2.1 [c]	7.1 [c]	9.2 [c]	9.1 [c]	
		$^{16}O^{14}N^{80}Br/^{16}O^{15}N^{80}Br$	$^{16}O^{14}N^{80}Br/^{18}O^{14}N^{80}Br$	$^{16}O^{14}N^{80}Br/^{18}O^{15}N^{80}Br$		
ONBr	ν_1 = [ν(NO)]	31.9 [c]	49.3 [c]	82.1 [c]	82.4 [c]	55
		$^{14}N^{32}S^{35}Cl/^{14}N^{34}S^{35}Cl$	$^{14}N^{32}S^{35}Cl/^{15}N^{32}S^{35}Cl$	$^{14}N^{32}S^{35}Cl/^{15}N^{34}S^{35}Cl$		
NSCl	ν_1 = [ν(SN)]	11.8	30.7	42.8	43.0	89
	ν_2 = [ν(SCl)]	1.2 [b]	3.2_5 [c]	4.4_5 [d]	4.4_5 [d]	
	ν_3 = [δ(NSCl)]	4.8 [b]	2.4 [c]	7.2 [d]	7.1 [d]	

TABLE 13 (continued)

	Frequency	$\Delta\nu^1$ (in cm^{-1})	$\Delta\nu^2$ (in cm^{-1})	$\Delta\nu^{22}$ (in cm^{-1})		Ref.
				Calc. [a]	Meas.	
		$^{14}N^{32}SBr/^{14}N^{34}SBr$	$^{14}N^{32}SBr/^{15}N^{32}SBr$	$^{14}N^{32}SBr/^{15}N^{34}SBr$		
NSBr	$\nu_1 = [\nu(SN)]$	11.9	30.2	42.4	42.4	89
		$^{12}C^{16}OF_2/^{13}C^{16}OF_2$	$^{12}C^{16}OF_2/^{12}C^{18}OF_2$	$^{12}C^{16}OF_2/^{13}C^{18}OF_2$		
COF_2	$\nu_1 = [\nu(CO)]$	49.4 (50.0) [e]	35.8 (36.3) [e]	86.2 (87.3) [e]	86.4 (87.4) [e]	90
	$\nu_2 = [\nu_s(CF)]$	3.1 (3.2) [e]	15.4 (15.6) [e]	18.5 (18.8) [e]	17.6? (17.8?) [e]	
	$\nu_3 = [\delta_s(CF_2)]$	1.6 (1.8) [e]	5.0 (5.0) [e]	6.6 (6.8) [e]	6.6 (6.8) [e]	
	$\nu_6 = [0]$ [f]	24.2 (24.4) [e]	3.8 (3.9) [e]	28.1 (28.4) [e]	28.1 (28.4) [e]	
		$^{116}Sn^{35}Cl_4/^{116}Sn^{37}Cl_4$	$^{116}Sn^{35}Cl_4/^{124}Sn^{35}Cl_4$	$^{116}Sn^{35}Cl_4/^{124}Sn^{37}Cl_4$		
$SnCl_4$	$\nu_3 = [\nu_{as}(SnCl)]$	8.0	3.6	11.7	11.7	59
		$H^{12}C^{35}Cl_3/H^{13}C^{35}Cl_3$	$H^{12}C^{35}Cl_3/H^{12}C^{37}Cl_3$	$H^{12}C^{35}Cl_3/H^{13}C^{37}Cl_3$		
$HCCl_3$	$\nu_2 = [\nu(CCl)]$	17.5	4.7	22.3	22.5	51

[a] $\Delta\nu^{22} = [(\nu + \nu^1)\Delta\nu^1 + (\nu + \nu^2)\Delta\nu^2]/[(\nu + \nu^3)]$ where ν corresponds to the parent molecule, ν^1 and ν^2 to those involving monosubstitutions (i.e., where only one atom of the parent molecule is isotopically substituted) and ν^3 to that involving multisubstitution. For small shifts, this reduces to eqn. (73) (follows from eqn. (71)). [b] The isotopic shift corresponding to the substitution $^{14}N^{32}S^{35}Cl/^{15}N^{32}S^{35}Cl$. [c] This corresponds to the substitution $^{14}N^{32}S^{35}Cl/^{14}N^{32}S^{37}Cl$. [d] Frequency shift pertaining to the isotopic substitution $^{14}N^{32}S^{35}Cl/^{15}N^{32}S^{37}Cl$. [e] This corresponds to the harmonic frequencies. [f] This corresponds to out-of-plane bending vibration.

TABLE 14

Comparison of observed and calculated frequency shifts in the $[Ni(MoS_4)_2]^{2-}$ ion [a] (cm^{-1})

		Observed				Calculated from the force field				
		ν	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	ν	$\Delta\nu_1$	$\Delta\nu_2$	$\Delta\nu_3$	Vibrational mode
B_{2u}	ν_1	455.5	0.5	6.0	6.0	447.4	0.0	5.2	5.2 (5.2)	ν(Mo—S)
	ν_2	323.8	4.7	0.3	5.0	323.4	4.9	0.0	4.9 (4.9)	ν(Ni—S)
	ν_3	181.0	0.7	2.3	2.9	181.1	0.5	2.4	2.9 (2.9)	ρw(Mo=S)
	ν_4	50.0	0.5	0	0.5	50.0	0.6	0	0.6 (0.6)	δ(SNiS')
B_{3u}	ν_5	494.0	0.0	6.0	6.0	484.6	0.0	3.8	3.8 (3.8)	ν(Mo=S)
	ν_6	442.5	0.4	1.4	1.7	440.0	0.8	0.9	1.7 (1.7)	ν(Mo—S)
	ν_7	331.5	4.7	0	4.7	342.8	4.8	0.2	5.0 (5.0)	ν(Ni—S)
	ν_8	222.5	0.3	2.5	2.5	222.6	0.0	1.9	1.9 (1.9)	δ(Mo=S)
	ν_9	179.5	1.2	2.0	3.3	180.4	2.4	1.2	3.6 (3.6)	δ(SNiS)

[a] $\Delta\nu_1 = \nu(^{58}Ni^{92}Mo) - \nu(^{62}Ni^{92}Mo)$; $\Delta\nu_2 = \nu(^{58}Ni^{92}Mo) - \nu(^{58}Ni^{100}Mo)$; $\Delta\nu_3 = \nu(^{58}Ni^{92}Mo) - \nu(^{62}Ni^{100}Mo)$; ν, stretching; δ, bending; ρw, wagging. [b] The values in parentheses are those derived from the approximate form of the new sum-rule (i.e. $\Delta\nu_1 + \Delta\nu_2$) which agrees exactly with those of $\Delta\nu_3$ computed independently using the force field in ref. 91.

F. CONCLUSION

For most of the transition metal complexes, there are a fairly large number of vibrations in any one species (or irreducible representation) as a consequence of which, it may not be possible to determine experimentally as many isotopic frequency shifts as are required for the calculation of all the force constants of a general valence force field (GVFF). Several authors, therefore have published results of normal coordinate analysis on the basis of the Urey—Bradley force field (simple or modified). But in this approach, many important force constants such as the stretching force constant K are influenced very much by the number of interaction terms included. On the other hand, it is well known that K is much smaller than f_r of the GVFF and hence no strict interpretation of the bond strength on the basis of K can be given. Due to this reason, we did not consider the UBFF or any other model force field in our review. We could show that for not too complicated cases (i.e. complexes), the isotopic shifts can be used in many cases (heavy and very heavy atom substitution) to calculate a physically reasonable set of force constants, even if some approximations are involved. Experience has shown that force constant calculations can be regarded as serious only if additional data such as the isotopic frequency shifts, Coriolis coupling constants etc. have been utilised in the calculations. It should however be mentioned that UBFF calculations can often be used for the assignment of frequencies.

With regard to the accuracy of the exact force constants, it is generally found that the isotopic shifts arising due to the substitution of heavy and very heavy atoms in transition metal complexes, can be used as effective constraints on the force field. The accuracies of the force constants derived from the small isotopic shifts (e.g. central atom substitution) and the Coriolis coupling constants independently (possible in $n = 2$ cases) can be comparable with each other. In order to get accurate isotopic shifts, combination of pure isotope and matrix isolation techniques is recommended. The measurement of vapour phase spectra at low temperatures could be useful in minimising the overlapping due to hot bands.

It should be emphasized that for many transition metal complexes, for which the frequencies are low and lie close together, even a crude estimate ($\sim 4 \pm 1$ cm^{-1}) of the isotopic shift could be employed to get reliable values of the metal—ligand stretching force constant. The experimental values of small isotopic shifts pertaining to the substitution of different sets of atoms in a molecule, could be controlled using the simple isotopic sum rule mentioned in the text.

The excellent compatibility of the results for the force constants derived using the HLFS and the PMM approach independently for $[Zn(NH_3)_4]^{2+}$ suggests that both these procedures serve as very good approximations in the case of transition metal—ammine complexes. It is the hope that our review would help the reader in understanding in which cases and under which conditions, reliable values of the exact and pseudo-exact force constants could be obtained using the available experimental data. This, in turn, is expected to lead to reliable interpretation of bond properties.

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