Characteristic Normal Modes of Vibration and Generalized Normal Forces:

Basic Properties and Relation to Fundamental Molecular Constants

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A survey is given of the simplified formulae for energy distributions, force constants, secular equations, Coriolis coupling constants, isotopic substitutions, compliances, mean amplitudes, bond moment and polarizability parameters, interaction coordinates and restoring forces in the cases where either a completely characteristic normal mode or a generalized normal force can be assumed.

The obtained results may be of use for the following main purposes: (i) computation of quantities which can be employed in the assignment of spectra, band shapes, intensities ... (ii) evaluation of fundamental molecular constants and isotopic shifts which can be approximated with good accuracy.

As illustration, the equations have been applied sucessfully to two-dimensional cases and to Molybdenum-hexacarbonyl.

Introduction

During many years there have been discussions of how characteristic modes should be recognized. A practical basis for this purpose has been searched for; particularly, several kinds of energy distributions have been developed and suggested. In the present paper, we use the basic definition of *completely* characteristic modes linked to the eigenvector matrix, **L**. The resulting formulation is given for *all* principal molecular constants and concepts in vibrational analysis, including energy distributions, force and compliance constants, secular equations, Coriolis coupling constants, isotopic substitutions, mean amplitudes and infrared and Raman intensities.

The main applications of the results are in spectral assignments and in approximate computation of molecular constants (F_{ij}, C_{ij}, ζ_{ij}^{α}, ν_i^*, Σ_{ij}, $\partial\mu/\partial S_i$, $\partial\alpha/\partial S_i$, $\partial\gamma/\partial S_i$, ...).

There are, however, two principal possibilities for the choice of basis for a classification, namely, displacement coordinates and forces. Therefore, both symmetry coordinates and generalized symmetry forces have been treated.

i) The transformation between symmetry and normal coordinates in vibrational analysis is given by [1]

$$\mathbf{S} = \mathbf{L}\,\mathbf{Q} \quad \text{or} \quad \mathbf{Q} = \mathbf{L}^{-1}\mathbf{S}\,. \tag{1}$$

A normal coordinate, $\mathbf{Q}_k$, is said to be *completely characteristic* of a symmetry coordinate, S_i, if there is only one non-zero element, L_{ik}, in the column k of **L** [2]:

$$L_{jk} = 0 \quad \text{for all} \quad j \neq i\,, \tag{2}$$

equivalent to

$$(\mathbf{L}^{-1})_{ji} = 0 \quad \text{for all} \quad j \neq k\,. \tag{3}$$

This definition means that *a single symmetry coordinate* can be used in the description of *a normal mode*.

ii) The generalized normal and symmetry forces, defined by

$$f_k^{Q} = -\,\partial V/\partial Q_k = -\,\lambda_k\,Q_k \tag{4}$$

and

$$f_i = -\,\partial V/\partial S_i = -\sum_j F_{ij}\,S_j\,, \tag{5}$$

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respectively, are not those frequently employed in the literature. The close relation with compliants, however, already has been reported in detail [4—7]. Therefore, we find it important to develop further properties of generalized forces, specially when the normal force is completely characteristic.

The abbreviations CCNC (completely characteristic normal coordinate) and CCNF (completely characteristic normal force) are introduced. Furthermore, it is assumed that Q_k is characteristic of S_i and $f_k{}^Q$ of f_i in CCNC and CCNF cases.

1. Characteristic Normal Mode of Vibration (CCNC)

Combination of the fundamental equations [1]

$$\mathbf{L}\,\mathbf{L}^{-1} = \mathbf{E} \quad \text{and} \quad \mathbf{G}^{-1} = \tilde{\mathbf{L}}^{-1}\,\mathbf{L}^{-1} \tag{6}$$

with the definition of a CCNC, yields the following values for some of the **L** and $\mathbf{L}^{-1}$ matrix elements: (δ is the Kronecker symbol)
k'th column;

$$\mathbf{L}_{jk} = \pm\,(\mathbf{G}^{-1})_{ii}^{-1/2}\,\delta_{ij}\,, \quad j = 1, 2, \ldots, \tag{7}$$

i'th column;

$$(\mathbf{L}^{-1})_{ji} = \pm\,(\mathbf{G}^{-1})_{ii}^{1/2}\,\delta_{jk}\,, \quad j = 1, 2, \ldots, \tag{8}$$

and *k*'th row;

$$(\mathbf{L}^{-1})_{kj} = \pm\,(\mathbf{G}^{-1})_{ii}^{-1/2}\,(\mathbf{G}^{-1})_{ij}\,, \qquad j = 1, 2, \ldots. \tag{9}$$

The elements in the *i*'th row of **L** are undetermined, except for L_{ik}. Furthermore,

$$L_{ik} = 1/(\mathbf{L}^{-1})_{ki}\,.$$

a) Vibrational energy distributions. In the usual **G F**-formalism [1], the potential, kinetic and total energy are expressed as

$$2\,V = \tilde{\mathbf{Q}}\,\mathbf{\Lambda}\,\mathbf{Q} = \tilde{\mathbf{S}}\,\mathbf{F}\,\mathbf{S}\,, \tag{10}$$

$$2\,T = \dot{\tilde{\mathbf{Q}}}\,\mathbf{E}\,\dot{\mathbf{Q}} = \dot{\tilde{\mathbf{S}}}\,\mathbf{G}^{-1}\,\dot{\mathbf{S}}\,, \tag{11}$$

and

$$2\mathbf{E} = \tilde{\mathbf{Q}}\,\mathbf{\Lambda}\,\mathbf{Q} + \dot{\tilde{\mathbf{Q}}}\,\mathbf{E}\,\dot{\mathbf{Q}} = \tilde{\mathbf{S}}\,\mathbf{F}\,\mathbf{S} + \dot{\tilde{\mathbf{S}}}\,\mathbf{G}^{-1}\,\dot{\mathbf{S}}\,. \tag{12}$$

The corresponding energy distributions, PED, KED and TED, for the *k*'th vibration are defined by [8—15]

$$V_{ij}^{(k)}(\mathbf{S}) = F_{ij}\,L_{ik}\,L_{jk}/\lambda_k\,, \tag{13}$$

$$T_{ij}^{(k)}(\dot{\mathbf{S}}) = (G^{-1})_{ij}\,L_{ik}\,L_{jk}\,, \tag{14}$$

and

$$E_{ij}^{(k)}(\mathbf{S}, \dot{\mathbf{S}}) = (F_{ij}\,\lambda_k^{-1} + (\mathbf{G}^{-1})_{ij})\,L_{ik}\,L_{jk}/2\,. \tag{15}$$

Previously, other symbols have been employed, like $E_{ij}^{(k)}$, $E_{(\mathbf{F},\mathbf{G}^{-1})_{ij}}^{(k)}$, etc. The former of these notations is convenient when there is *no doubt* about the coordinates used as basis for the distributions.

Equivalent necessary and sufficient conditions for a CCNC, i.e. (2), are [3]

$$V_{jj}^{(k)} = 0 \quad \text{or} \quad T_{jj}^{(k)} = 0 \quad \text{or} \quad E_{jj}^{(k)} = 0 \quad \text{for all} \quad j \neq i\,. \tag{16}$$

It follows that

$$V_{ii}^{(k)} = T_{ii}^{(k)} = E_{ii}^{(k)} = 1 \tag{17}$$

and

$$V_{hj}^{(k)} = T_{hj}^{(k)} = E_{hj}^{(k)} = 0 \quad \text{for all } h \text{ and } j \text{ except } h = j = i\,. \tag{18}$$

Note that for example $V_{ij}^{(k)} = \delta_{ij}$, $j = 1, 2, \ldots$, does not guarantee a CCNC since there may be zeros in the off-diagonal elements of **F**. The simplest sufficient condition, however, is given by $V_{ii}^{(k)} = T_{ii}^{(k)} \neq 0$. In other words, corresponding diagonal terms in PED and KED can only be equal and non-zero if the mode is completely characteristic.

To decide if the normal mode is "rather characteristic" of a symmetry coordinate, it is not enough to examine the displacements of the symmetry coordinates, i.e., the *k*'th column of **L** [8]. One instead should look at the energy distributions [8—15]. It should be mentioned that a simplification occurs when (16) is almost fulfilled for a particular energy distribution. Then it is not necessary to evaluate the interaction terms because these automatically will be small. (The interaction terms may be important when there is more than one significant diagonal element [3].) However, a small diagonal element in PED may correspond to a large element in KED, and *vice versa*. Since the TED combine potential and kinetic energy, it can be concluded, that *the mode is "rather characteristic" if* $E_{jj}^{(k)}$, $j = 1, 2, \ldots$, *are small except for* $j = i$.

b) Force constants. It has been shown [16] that if Q_k is completely characteristic of S_i, the force constant F_{ii} attains *one* of its stationary values, *viz.*

$$F_{ii} = (\mathbf{G}^{-1})_{ii}\,\lambda_k\,. \tag{19}$$

In fact, there is a one to one correspondence between the possible stationary values of the diagonal force constants and the n^2 possibilities for completely characteristic normal co-ordinates.

It is recognized that F_{ii} has its maximal or minimal value when the modes with largest or smallest λ_k, respectively, are completely characteristic of S_i.

Let us now look at the *reverse situation* and assume that (19) is fulfilled without imposing restrictions on $\mathbf{L}$ beforehand. We use the general expression for force constants [16, 17],

$$F_{ij} = (\mathbf{G}^{-1})_{ij}\,\lambda_k + \sum_{l} (\mathbf{L}^{-1})_{li}\,(\mathbf{L}^{-1})_{lj}\,(\lambda_l - \lambda_k) \qquad (20)$$

for any given eigenvalue λ_k. Combination of (19) and (20) for the diagonal elements yields $\sum_{l} (\mathbf{L}^{-1})^2_{li}$ $(\lambda_l - \lambda_k) = 0$, which implies $(\mathbf{L}^{-1})_{li} = 0$ for $l \neq k$ only when λ_k has an extremal value, since the terms $(\lambda_l - \lambda_k)$ then are all positive or negative. Thus it has been demonstrated that the fulfilment of (19) *alone is a sufficient condition for a CCNC when λ_k is the maximal or minimal eigenvalue.*

The off-diagonal elements in the case of a CCNC are obtained by introducing (8) into (20), which becomes

$$F_{ij} = (\mathbf{G}^{-1})_{ij}\,\lambda_k\,, \quad j = 1, 2, \ldots, \qquad (21)$$

i.e. the i'th row and column of $\mathbf{F}$ are determined completely. Again the *reverse situation* may be investigated. (20) and (21) result in a set of linear equations which in matrix notation can be written as $\tilde{\mathbf{L}}^{-1}\,(\mathbf{\Lambda} - \mathbf{\Lambda}_k)\,\mathbf{L}_i^{-1} = 0$, where $\mathbf{\Lambda}_k$ has all diagonal elements equal to λ_k and $\mathbf{L}_i^{-1}$ is the matrix consisting of the i'th column of $\mathbf{L}^{-1}$. Since $\mathbf{L}^{-1}$ is nonsingular, it follows that $(\lambda_l - \lambda_k)(\mathbf{L}^{-1})_{li} = 0$ and $(\mathbf{L}^{-1})_{li} = 0$ for all $l \neq k$, and (21) is a sufficient condition for a completely characteristic vibration.

A remarkable property concerning the signs of the off-diagonal force-constants can be deduced from (21). If the real solution is assumed to be close to the CCNC result, the interaction constants F_{ij} and $(\mathbf{G}^{-1})_{ij}$ have the same sign. This rule may be of interest when a starting $\mathbf{F}^{(0)}$-matrix is chosen in an iterative process.

c) Secular equation. A CCNC represents splitting off from the secular equation of a one-dimensional factor. This decoupling can be seen from

$$\begin{aligned}(\mathbf{G}\,\mathbf{F})_{ji} &= (\mathbf{L}\,\mathbf{\Lambda}\,\mathbf{L}^{-1})_{ji} = \sum_{l} L_{jl}\,\lambda_l\,L^{-1}_{li} \\ &= \delta_{ji}\,\lambda_k\,, \quad j = 1, 2, \ldots, \end{aligned} \qquad (23)$$

where (7) and (8) have been introduced. The n'th order secular determinant $|\mathbf{GF} - \lambda\mathbf{E}|$ then has $(n-1)$ zero elements in column i, giving the common linear factor $((\mathbf{GF})_{ii} - \lambda)$ with $(\mathbf{GF})_{ii} = \lambda_k$. (23) does not imply a CCNC, particularly, $(\mathbf{GF})_{ii} = \lambda_k$ alone does not guarantee that Q_k is characteristic of S_i, cf. a triangular form of $\mathbf{L}$ [18].

It can be shown by the same procedure that $(\mathbf{C}\,\mathbf{G}^{-1})_{ji} = \delta_{ij}/\lambda_k$ and $(\mathbf{\Sigma}\,\mathbf{G}^{-1})_{ji} = \delta_{ji}\Delta_k$ in secular equations involving compliances and mean amplitudes.

d) Coriolis coupling constants. The general formula [19]

$$\zeta^{\alpha}_{k1} = \sum_{ij} (\mathbf{L}^{-1})_{ki}\,(\mathbf{L}^{-1})_{1j}\,\mathbf{C}^{\alpha}_{ij}\,, \quad \alpha = x, y, z\,, \qquad (24)$$

for the Coriolis coupling constants shows that ζ^{α}_{kk} for a CCNC is determined by

$$\begin{aligned}\zeta^{\alpha}_{kk} &= (\mathbf{G}^{-1})^{-1}_{ii}\,(\mathbf{G}^{-1}\,\mathbf{C}^{\alpha}\,\mathbf{G}^{-1})_{ii} \\ &= \overline{\mathbf{C}}^{\alpha}_{ii}/(\mathbf{G}^{-1})_{ii}\,. \end{aligned} \qquad (25)$$

An a priori assignment of completely characteristic normal modes therefore can be used in a preliminary analysis of rotational structure and band shapes. Even a rough approximation of zetas may be very useful for band assignments. Further, we like to point out that (25) fixes the sign of ζ^{α}_{kk} when a suitable system of coordinates has been used for the molecule. The correlation between observed and calculated coupling constants has been demonstrated by Freeman [20, 21] for the bending modes of XY_3 and XY_4 molecules.

e) Isotopic frequency shifts. From the assumption of completely characteristic normal coordinates Q_k and $Q_k{}^*$ of two isotopic molecules, it follows from (21) and the Born-Oppenheimer approximation that

$$\lambda_k/\lambda_k{}^* = (\mathbf{G}^{-1*})_{ii}/(\mathbf{G}^{-1})_{ii} \qquad (26)$$

and

$$\lambda_k/\lambda_k{}^* = (\mathbf{G}^{-1*})_{ij}/(\mathbf{G}^{-1})_{ij} \quad \text{for all} \quad j \neq i\,. \qquad (27)$$

The isotopic relation (27) is rarely fulfilled, but (26) *is found to hold remarkably well for molecules where rather characteristic modes are suspected* (*see the examples*). *This equation, therefore, is valuable for assignments and also may be a basis for force constant calculations.* Combination with the Teller-Redlich product rule [22] $\Pi(\lambda_j/\lambda_j{}^*) = |\mathbf{G}|/|\mathbf{G}^*|$ gives the reduced rule

$$\prod_{l \neq k} (\lambda_l/\lambda_l{}^*) = |\mathbf{G}^{ii}|/|\mathbf{G}^{ii*}|\,. \qquad (28)$$

(26) and (27) imply the conditions

$$(\mathbf{G}^{-1})_{ij}/(\mathbf{G}^{-1})_{ii} = (\mathbf{G}^{-1*})_{ij}/(\mathbf{G}^{-1*})_{ii}\,, \quad j = 1, 2, \ldots, \tag{29}$$

for both Q_k and $Q_k{}^*$ to be fully characteristic. This kinetic situation is rare and is impossible for many geometrical arrangements, for example substitution of one equivalent set of atoms in $XY_2(C_{2v})$, $XY_3(D_{3h})$, $XY_3(C_{3v})$, $XY_4(T_d)$, $XY_4(D_{4h})$ and $XY_6(O_h)$. Of course, this fact does not mean that the CCNC solution is unimportant, since it represents a good approximation for many modes.

f) *Spectral intensities.* The integrated infrared intensities are [23]

$$A_k = \frac{N\pi d_k}{3c^2}\left(\frac{\partial\mu}{\partial Q_k}\right)^2 = \frac{N\pi d_k}{3c^2}\,(\tilde{\mathbf{L}}\,\boldsymbol{\mu}'\,\mathbf{L})_{kk}\,, \tag{30}$$

where N and c are fundamental constants, d_k is the degeneracy and $\boldsymbol{\mu}'$ a matrix of dipole moment derivatives with $\mu'_{ij} = (\partial\mu/\partial S_i)(\partial\mu/\partial S_j)$. The dipole moment derivatives are connected by

$$\left(\frac{\partial\mu}{\partial Q_k}\right) = \sum_j \mathbf{L}_{jk}\left(\frac{\partial\mu}{\partial S_j}\right). \tag{31}$$

A characteristic coordinate gives the particularly simple results

$$\left(\frac{\partial\mu}{\partial Q_k}\right) = \pm\,(\mathbf{G}^{-1})_{ii}^{-1/2}\left(\frac{\partial\mu}{\partial S_i}\right)$$

and

$$A_k = \frac{N\pi d_k}{3c^2}\,\frac{\mu'_{ii}}{(\mathbf{G}^{-1})_{ii}}\,. \tag{32}$$

Very good values for the bond moment parameters $(\partial\mu/\partial S_i)$ are found by using these expressions [24].

Raman intensities follow the same procedure. From the intensity equation [25]

$$I_k = K\left(\frac{\partial\beta}{\partial Q_k}\right)^2 = K\,(\mathbf{L}\,\boldsymbol{\beta}'\,\mathbf{L})_{kk}\,, \tag{33}$$

where K depends on the excitation and fundamental frequencies and β is a linear combination of $\bar{\alpha}$ and γ with $\bar{\alpha}$ being the mean polarizability and γ the anisotropy, it follows for a CCNC that

$$I_k = K\,\beta'_{ii}/(\mathbf{G}^{-1})_{ii}\,. \tag{34}$$

2. Characteristic Generalized Force (CCNF)

If (4) and (5) are written in matrix notation as

$$\mathbf{f}^Q = -\,\boldsymbol{\Lambda}\,\mathbf{Q} \quad \text{and} \quad \mathbf{f} = -\,\mathbf{F}\,\mathbf{S}\,, \qquad \mathbf{S} = -\,\mathbf{C}\,\mathbf{f}\,, \tag{35}$$

it follows from fundamental relations that [6]

$$\mathbf{f} = \tilde{\mathbf{L}}^{-1}\,\mathbf{f}^Q \quad \text{and} \quad \mathbf{f}^Q = \tilde{\mathbf{L}}\,\mathbf{f}\,. \tag{36}$$

The generalized normal force $f_k{}^Q$ is said to be completely characteristic of a symmetry force f_i if $(\tilde{\mathbf{L}}^{-1})_{ik}$ is the only non-zero element in the k'th column of $\tilde{\mathbf{L}}^{-1}$ [2]. From (6) we then have

i'th row;

$$L_{ij} = \pm\,G_{ii}^{1/2}\,\delta_{jk}\,, \quad j = 1, 2, \ldots, \tag{37}$$

k'th column;

$$L_{jk} = \pm\,G_{ii}^{-1/2}\,G_{ij}\,, \quad j = 1, 2, \ldots, \tag{38}$$

and

$$(\mathbf{L}^{-1})_{kj} = \pm\,G_{ii}^{-1/2}\,\delta_{ij}\,, \quad j = 1, 2, \ldots, \tag{39}$$

with $(\mathbf{L}^{-1})_{ki} = 1/L_{ik}$. From (1) and (39) it is seen that an alternative interpretation of a CCNF is that S_i is non-zero only for the k'th normal mode.

a) *Vibrational energy distributions.* The potential, kinetic and total energies are expressed in terms of generalized forces by the quadratic forms [4, 26]

$$\begin{aligned} 2V &= \tilde{\mathbf{f}}^Q\,\boldsymbol{\Lambda}^{-1}\,\mathbf{f}^Q = \tilde{\mathbf{f}}\,\mathbf{C}\,\mathbf{f}\,, \\ 2T &= \tilde{\dot{\mathbf{f}}}^Q\,\boldsymbol{\Lambda}^{-2}\,\dot{\mathbf{f}}^Q = \tilde{\dot{\mathbf{f}}}\,(\mathbf{C}\,\mathbf{G}^{-1}\,\mathbf{C})\,\dot{\mathbf{f}} \\ &= \tilde{\dot{\mathbf{f}}}\,(\mathbf{L}\,\boldsymbol{\Lambda}^{-2}\,\tilde{\mathbf{L}})\,\dot{\mathbf{f}}\,, \end{aligned} \tag{40}$$

and

$$2E = 2V + 2T\,.$$

The corresponding energy distributions have been defined as [3, 5]

$$V_{ij}^{(k)}(\mathbf{f}) = C_{ij}\,(\mathbf{L}^{-1})_{ki}\,(\mathbf{L}^{-1})_{kj}\,\lambda_k\,,$$

$$T_{ij}^{(k)}(\dot{\mathbf{f}}) = (\mathbf{C}\,\mathbf{G}^{-1}\,\mathbf{C})_{ij}\,(\mathbf{L}^{-1})_{ki}\,(\mathbf{L}^{-1})_{kj}\,\lambda_k{}^2\,,$$

and

$$\begin{aligned} E_{ij}^{(k)}(\mathbf{f}, \dot{\mathbf{f}}) = {} & (C_{ij} + (\mathbf{C}\,\mathbf{G}^{-1}\,\mathbf{C})_{ij}\,\lambda_k) \\ & \cdot (\mathbf{L}^{-1})_{ki}\,(\mathbf{L}^{-1})_{kj}\,\lambda_k/2\,. \end{aligned} \tag{41}$$

Equations (16)—(18) are valid for a CCNF when $V_{jj}^{(k)}(\mathbf{f})$ is substituted for $V_{jj}^{(k)}(\mathbf{S})$, etc., and thus give the necessary and sufficient conditions for a CCNF. The discussion which follows (16)—(18) still remains valid in terms of generalized normal forces and characteristic forces.

b) *Compliances.* A stationary compliant

$$C_{ii} = G_{ii}/\lambda_k \tag{42}$$

occurs for $L_{ij} = 0$, $j \neq k$ [5]. (42) is sufficient for f_k^Q to be completely characteristic of f_i only if λ_k corresponds to the highest or lowest frequency.

Furthermore, the CCNF definition leads to

$$C_{ij} = G_{ij}/\lambda_k\,, \quad j = 1, 2, \ldots . \tag{43}$$

A derivation similar to the one performed for force constants concerning the consequences of these equations gives analogous results. Fulfilment of (43) means that there is a characteristic force, while the limited restriction of (42) gives the same result only for $\lambda_k^{\text{max.}}$ and $\lambda_k^{\text{min.}}$. Information of the signs of the coupling compliances may be inferred from the signs of the G_{ij} elements.

Due to the similarity of the expressions

$$\mathbf{C} = \mathbf{L}\boldsymbol{\Lambda}^{-1}\tilde{\mathbf{L}} \quad \text{and} \quad \mathbf{C}\mathbf{G}^{-1}\mathbf{C} = \mathbf{L}\boldsymbol{\Lambda}^{-2}\tilde{\mathbf{L}}\,,$$

stationary compliances and stationary values of the characteristic matrix in the kinetic energy expressions occur simultaneously.

c) Mean square amplitudes. The mean square amplitudes of the symmetry coordinates $\boldsymbol{\Sigma} = \mathbf{L}\boldsymbol{\Delta}\tilde{\mathbf{L}}$ [6], and the compliances essentially have the same properties, whence

$$\Sigma_{ij} = G_{ij}\,\Delta_k\,, \quad j = 1, 2, \ldots \tag{44}$$

for a CCNF, including the same reverse properties and sign information as above.

Characteristic normal forces may be expected for a "$\nu\delta\delta$" assignment in 3×3 problems and similar cases [27]. For two-dimensional blocks, this situation is identical to a CCNC for the mode with lowest frequency. Good correspondence between the calculated and experimental mean amplitudes has been obtained in this case, in particular for XY_n type molecules with $m_x > m_y$ [28–31].

d) Secular equation. The $\mathbf{C}\mathbf{G}^{-1}$, $\boldsymbol{\Sigma}\mathbf{G}^{-1}$ and $\mathbf{G}\mathbf{F}$ matrices can be expressed as follows when (37) and (39) are used:

$$\begin{aligned}
(\mathbf{C}\,\mathbf{G}^{-1})_{ij} &= (\mathbf{L}\,\boldsymbol{\Lambda}^{-1}\,\mathbf{L}^{-1})_{ij} \\
&= \sum L_{il}\,\lambda_l^{-1}\,L_{lj}^{-1} = \delta_{ij}/\lambda_k\,, \\
(\boldsymbol{\Sigma}\,\mathbf{G}^{-1})_{ij} &= \delta_{ij}\,\Delta_k \quad \text{and} \\
(\mathbf{G}\,\mathbf{F})_{ij} &= \delta_{ij}\,\lambda_k\,, \quad j = 1, 2, \ldots .
\end{aligned} \tag{45}$$

Thus, the secular determinant $|\mathbf{C}\mathbf{G}^{-1} - \lambda^{-1}\mathbf{E}|$ has the linear factor $((CG^{-1})_{ii} - \lambda^{-1})$ for any characteristic $f_k{}^Q$. Simultaneously, $((GF)_{ii} - \lambda)$ is split off from $|\mathbf{G}\mathbf{F} - \lambda\mathbf{E}|$; the same result which is found for a CCNC. This means that an identical splitting of the secular determinant occurs for characteristic normal forces and modes, but the solutions for the force field are, of course, different.

e) Coriolis coupling. A CCNF transforms (24) for ζ_{kk}^{α} into

$$\zeta_{kk}^{\alpha} = C_{ii}^{\alpha}/G_{ii}\,, \quad \alpha = x, y, z\,, \tag{46}$$

giving values which again may be used in sign determination and preliminary analysis of rotational structure.

f) Isotopic frequency shifts. It is found that a characteristic normal force leads to

$$\begin{aligned}
\lambda_k/\lambda_k{}^* &= G_{ii}/G_{ii}^*\,, \\
\lambda_k/\lambda_k{}^* &= G_{ij}/G_{ij}^* \quad \text{for all} \quad j \neq i\,,
\end{aligned}$$

and

$$\prod_{l \neq k} (\lambda_l/\lambda_l{}^*) = |(\mathbf{G}^{-1*})^{ii}|/|(\mathbf{G}^{-1})^{ii}|\,; \tag{47}$$

equations which may be helpful in bond assignments and evaluation of force fields (except (47 b)).

g) Spectral intensities. (30) and (31) are simplified to

$$\left(\frac{\partial\mu}{\partial Q_k}\right) = \pm\, G_{ii}^{-1/2} \sum_i G_{ij} \left(\frac{\partial\mu}{\partial S_j}\right)$$

and

$$A_k = \frac{N\pi\,d_k}{3\,c^2}\, G_{ii}^{-1}\,(\mathbf{G}\,\boldsymbol{\mu}'\,\mathbf{G})_{ii}\,. \tag{48}$$

An equivalent expression is found for the Raman intensities, (33), namely

$$I_k = K\,G_{ii}^{-1}\,(\mathbf{G}\,\boldsymbol{\beta}'\,\mathbf{G})_{ii}\,. \tag{49}$$

h) Interaction coordinates. An interesting result derived from the concept of characteristic normal forces concerns the so-called "interaction coordinates" [7, 32]. An interaction coordinate, $(S_j)_i$ *is not a coordinate at all*, but the value (displacement) of the coordinate S_j which would minimize the energy of the system if S_i is constrained to a unit positive displacement. These coordinates have been used to evaluate reasonable limits for interaction force constants and as a link to the electronic structure of the molecule. It has been shown that [32]

$$(S_j)_i = C_{ij}/C_{ii}\,, \quad j = 1, 2, \ldots . \tag{50}$$

It follows from (43) that, if any $f_k{}^Q$ is completely characteristic of f_i, then

$$(S_j)_i = G_{ij}/G_{ii}\,, \quad j = 1, 2, \ldots, \tag{51}$$

and the interaction coordinates are determined fully. It is pointed out that the reverse is not general. Fulfilment of (51) for all j does not guarantee a CCNF unless $n = 2$.

i) Generalized symmetry restoring forces. The situation described above as displacement of the coordinate S_i and relaxation of the other coordinates to attain the minimum potential energy is characterized by

$$(\partial V/\partial S_j) = 0 \text{ or } f_j = 0 \text{ for all } j \neq i. \quad (52)$$

The corresponding value of f_i is connected to the generalized symmetry restoring force, F_i, which is defined by [33]

$$(\partial V/\partial S_i)_{V_{\min}} = F_i S_i, \quad \text{or}$$
$$f_i = -F_i S_i, \quad \text{for} \quad f_j = 0 \quad \text{and} \quad j \neq i. \quad (53)$$

Since $(\partial V/\partial S_i) = F_{ii} S_i$ for $S_j = 0$, $j \neq i$, it is seen that F_{ii} represents the force required for stretching of S_i when all other coordinates remain fixed, while F_i tells how hard it is to stretch S_i when the other coordinates are relaxed to give minimum energy.

Introduction of (51) into (35) gives

$$f_i = -\left(\frac{\partial V}{\partial S_i}\right)_{V_{\min}} = -(1/C_{ii})\, S_i, \quad (54)$$

showing that $F_i = 1/C_{ii}$. The situation of a characteristic normal force implies stationary C_{ii} values and thus $F_i = \lambda_k/G_{ii}$. It is noteworthy that the restoring force, in contrast to the force constant, is independent of coordinate definition other than for S_i.

Additional Remarks

a) "A priori assignment"

In the two preceeding sections, we have studied in detail the properties and the consequence of assuming that in the case of a CCNC, S_i fully characterizes the normal coordinate Q_k and respectively in the case of a CCNF, f_i fully characterizes the normal force $f_k{}^Q$.

For the study of real cases, it is not restrictive to use the "a priori" partial assignment stating that the normal mode Q_i of frequency λ_i is required to involve the symmetry coordinate S_i; in other words, we may suppose that $L_{ii} \neq 0$ and simply use all the obtained results by putting $k = i$.

b) Multiplicity of CCNC and/or CCNF

Clearly seen from the conditions stated by (2, 7) (respectively (37, 39)), two or more than one CCNC(CCNF) are not generally simultaneously possible (except if the **G**-matrix is partially or completely diagonal). But if, however, appropriate off-diagonal elements of **G** are small enough, then several normal modes of vibration may simultaneously be rather characteristic (the situation is the same for the normal force, by considering the form of the matrix $\mathbf{G}^{-1}$).

3. Examples

a) Two-dimensional cases and isotopic shifts. It often can be assumed that the lowest frequency corresponds to a characteristic normal coordinate in 2×2 cases, when the difference between the primary force constants is large. This assumption leads to a solution of the inverse eigenvalue problem which can be represented by a lower triangular **L**-matrix, an approximation which has been used by many authors and formulated in several apparently different ways [10, 16, 34–45]. However, the mathematical form may vary, and the equivalence of the solutions is not recognized always.

For Q_2 characteristic of S_2, identical $f_1{}^Q$ characteristic of f_1, the CCNC and CCNF expressions treated in the previous sections are reduced to

$$V_{22}^{(2)} = V_{f_i f_i}^{(1)} = T_{22}^{(2)} = 1, \quad \text{etc.},$$
$$V_{11}^{(2)} = V_{12}^{(2)} = V_{f_2 f_2}^{(1)} = V_{f_1 f_2}^{(1)} = 0, \quad \text{etc.}, \quad (55)$$

$$F_{12} = (\mathbf{G}^{-1})_{12}\, \lambda_2, \quad F_{22} = (\mathbf{G}^{-1})_{22}\, \lambda_2, \quad (56)$$

$$\lambda_1/\lambda_1{}^* = G_{11}/G_{11}^*,$$
$$\lambda_2/\lambda_2{}^* = (\mathbf{G}^{-1*})_{22}/(G^{-1})_{22}, \quad (57)$$

$$\lambda_1/\lambda_1{}^* = G_{12}/G_{12}^*,$$
$$\lambda_2/\lambda_2{}^* = (\mathbf{G}^{-1*})_{12}/(\mathbf{G}^{-1})_{12}, \quad (58)$$

$$C_{11} = G_{11}/\lambda_1, \qquad C_{12} = G_{12}/\lambda_1,$$
$$\Sigma_{11} = G_{11}\, \Delta_1, \qquad \Sigma_{12} = G_{12}\, \Delta_1, \quad (59)$$

$$\xi_{11}^{\alpha} = C_{11}^{\alpha}/G_{11} \quad \text{and}$$
$$\xi_{22}^{\alpha} = (\mathbf{G}^{-1})_{22}^{-1}\, (\mathbf{G}^{-1}\, \mathbf{C}^{\alpha}\, \mathbf{G}^{-1})_{22}$$
$$= \overline{\mathbf{C}}_{22}^{\alpha}/(\mathbf{G}^{-1})_{22}. \quad (60)$$

The isotopic relations have been examined for 28 pairs of molecules (Table 1). The results are arranged according to increasing kinematic coupling, [3, 46] $|G_{12}(G_{11}\, G_{22})^{-1/2}|$.

Application of (58) results in shifts in the wrong direction for central atom substitution and otherwise very large deviations from the observe shifts. These data clearly are of minor interest, and they

Table 1. Observed and calculated isotopic shifts (cm^{-1})^{a}.

Molecule	Kinematic coupling	$\Delta\nu_1$(obs)	$\Delta\nu_1$(calc)^{b}	$\Delta\nu_2$(obs)	$\Delta\nu_2$(calc)^{b}	Deviation $\Delta\nu_1$ %	Reference (obs)
PH_3-PD_3(E)	.02–.05	691	690	332	330	0	[47]
H_2S-D_2S(A_1)	.03–.06	774	750	343	354	3	[48]
PH_3-PD_3(A_1)	.04–.08	691	694	285	282	0	[47]
H_2O-D_2O(A_1)	.06–.11	1068.4	1058.3	442.1	447.1	1	[48]
SiH_4-SiD_4(F_2)	.06–.12	639	640	250	250	0	[47]
NH_3-ND_3(A_1)	.07–.12	1011	983	229	255	3	[47]
NH_3-ND_3(E)	.08–.14	925	947	466	464	2	[47]
$Os^{16}O_4$-$Os^{18}O_4$(F_2)	.14–.15	48.7	49.0	16.3	15.8	1	[49]
CH_4-CD_4(F_2)	.14–.24	821	812	331	334	1	[47]
CH_4-CT_4(F_2)	.14–.32	1164	1156	477	482	1	[47]
$^{102}RuO_4$-$^{96}RuO_4$(F_2)	.23–.24	5.2	4.7	2.1	2.2	10	[50, 51]
$^{100}MoO_4^{2-}$-$^{92}MoO_4^{2-}$(F_2)	.23–.24	7.0	6.4	2.6	2.9	9	[51, 52]
$Ru^{16}O_4$-$Ru^{18}O_4$(F_2)	.23–.25	42.2	43.3	15.1	14.8	3	[50]
CD_4-CT_4(F_2)	.24–.32	343	343	146	147	0	[47]
$^{124}SnCl_4$-$^{116}SnCl_4$(F_2)	.35–.36	3.1	3.8	1.3	1.1	23	[51]
$^{100}MoS_4^{2-}$-$^{92}MoS_4^{2-}$(F_2)	.37–.39	6.8	6.1		2.0	10	[52]
$^{15}NO_2$-$^{14}NO_2$(A_1)	.40–.41	13.2	11.3	9.7	11.4	14	[53]
$^{30}SiF_4$-$^{28}SiF_4$(F_2)	.54–.55	17.4	16.4	3.0	3.4	6	[53]
$^{35}ClCN$-$^{37}ClCN$(Σ^+)	.63–.64	0.3	0.0	8.2	8.6	5	[54]
$^{16}OCl_2$-$^{18}OCl_2$(A_1)	.64–.66	25.1	20.9	1.5	4.1	17	[55]
$^{79}BrCN$-$^{81}BrCN$(Σ^+)	.68–.68	0.0	0.0	1.8	1.8	0	[54]
$Si^{35}Cl_4$-$Si^{37}Cl_4$(F_2)	.69–.70	5.7	6.3	5.3	4.8	11	[51]
$^{11}BO_3^{3-}$-$^{10}BO_3^{3-}$(E)	.69–.71	42.9	42.2	3.6	4.0	2	[56]
$^{11}BF_3$-$^{10}BF_3$(E)	.72–.74	51.2	51.3	1.6	2.6	0	[57]
$^{13}CF_4$-$^{12}CF_4$(F_2)	.73–.74	37.6	33.9	2.5	4.8	10	[58]
$^{11}BCl_3$-$^{10}BCl_3$(E)	.83–.84	39.5	38.6		0.9	2	[57]
$^{11}BBr_3$-$^{10}BBr_3$(E)	.92–.92	37.1	36.5		0.3	2	[57]
$^{11}BI_3$-$^{10}BI_3$(E)	.95–.95	32.9	32.4		0.1	2	[59]

[a] Harmonic frequencies are used for the hydrides. Necessary geometrical constants are taken from Isotani [35].

[b] Calculated by Equation (57).

have been excluded from the table. In contrast, the relation (57) gives remarkably good correspondance with the observed values, also for considerable kinematic couplings. This conclusion is valid even though the experimental uncertainties are 10% or larger for some of the smaller shifts. Therefore, the applicability of (57) for bond assignments apparently is large.

b) Molybdenum hexacarbonyl. This molecule illustrates the quantities which can be calculated from predictions of the form of the **L**-matrix. The "exact" force field has been reported by Jones et al. [60], and the molecular geometry and symmetry coordinates are as described by them. The present calculations are based on harmonic C-O stretching frequencies and CCl_4-solution data for A_{1g}, E_g and F_{1u} symmetries while the F_{2g} and F_{2u} frequencies are for the vapour.

Table 2. The "exact" **L**-matrix of $Mo[^{12}C^{16}O]_6$.

	A_{1g}		E_g	
	ν_1	ν_2	ν_3	ν_4
CO stretch	0.382	0.014	0.382	0.008
MoC stretch	−0.225	0.181	−0.222	0.184
	F_{1u}			
	ν_6	ν_7	ν_8	ν_9
CO stretch	0.382	−0.001	0.000	−0.002
MoC stretch	−0.218	0.095	0.216	0.036
MoCO bend	0.002	−0.431	−0.134	0.072
CMoC bend	−0.000	−0.226	−0.008	0.083
	F_{2g}		F_{2u}	
	ν_{10}	ν_{11}	ν_{12}	ν_{13}
MoCO bend	0.442	0.063	0.444	0.046
CMoC bend	−0.259	0.100	−0.180	0.077

In view of the high C-O frequency compared to the other frequencies, it can be expected that the following **L**-matrix elements are close to zero:

A_{1g}: L_{12}, E_g: L_{34} and
F_{1u}: L_{67}, L_{68} and L_{69}.

The "exact" matrix is given in Table 2, and it is verified that the predictions are reasonable. In other words, there are pure M_0-C stretching modes in A_{1g} and E_g and a normal force completely characteristic of f_{CO} in these species as well as in F_{1u}. A more comprehensive interpretation may be that the force working in the high frequency vibration belonging to the three species is connected entirely to the carbonyl coordinate.

The **L**-approximations give the following force contants, compliances and isotopic shifts ("exact" values in parentheses):

A_{1g}: $F_{11} = 19.38\,(17.84)$, $F_{12} = 1.52\,(0.23)$, $F_{22} = 2.67\,(2.77)$, $C_{11} = 0.0540\,(0.0560)$, $C_{12} = -0.031\,(-0.005)$, $C_{22} = 0.393\,(0.362)$, $\Delta\nu_1\,(^{16-18}\mathrm{O}) = 51.3\,(47.0)$, $\Delta\nu_1\,(^{12-13}\mathrm{C}) = 47.5\,(50.6)$, $\Delta\nu_2\,(^{16-18}\mathrm{O}) = 13.8\,(16.6)$, $\Delta\nu_2\,(^{12-13}\mathrm{C}) = 7.2\,(6.1)$;

E_g: $F_{33} = 17.60\,(16.83)$, $F_{34} = 1.44\,(0.79)$, $F_{44} = 2.52\,(2.55)$, $C_{33} = 0.0596\,(0.0603)$, $C_{34} = -0.034\,(-0.019)$, $C_{44} = 0.416\,(0.398)$, $\Delta\nu_1\,(^{16-18}\mathrm{O}) = 48.8\,(46.6)$, $\Delta\nu_1\,(^{12-13}\mathrm{C}) = 45.2\,(46.8)$, $\Delta\nu_2\,(^{16-18}\mathrm{O}) = 13.3\,(14.5)$, $\Delta\nu_2\,(^{12-13}\mathrm{C}) = 6.8\,(6)$;

F_{1u}: $C_{66} = 0.0603\,(0.0607)$, $C_{67} = -0.034\,(-0.045)$, $C_{68} = 0.000\,(-0.017)$, $C_{69} = 0.000\,(-0.022)$, $\Delta\nu_1\,(^{16-18}\mathrm{O}) = 48.5\,(49.4)$ and $\Delta\nu_1\,(^{12-13}\mathrm{C}) = 45.0\,(45.1)$.

The units are mdyn/Å, Å/mdyn and cm^{-1}, respectively. Best correspondence between exact and approximate values is found for F_{22}, F_{44}, C_{11}, C_{33} and C_{66}. This result is general and may be correlated with the zero value of the sensibilities of F_{22} and C_{11} for characteristic Q_2 and f_1^Q when L_{12} is changed from zero. Derivation with respect to L_{12} for 2-blocks yields

$$\Delta F_{12} = \frac{(\lambda_2 - \lambda_1)}{|G|^{1/2}}\frac{L_{12}}{L_{11}}, \quad \Delta F_{11} = -2\,\Delta F_{12}\frac{L_{21}}{L_{11}}, \quad \Delta F_{22} = 0;$$

$$\Delta C_{12} = \frac{(\lambda_1 - \lambda_2)}{\lambda_1 \lambda_2}|G|^{1/2}\frac{L_{12}}{L_{11}}, \quad \Delta C_{22} = 2\Delta C_{12}\frac{L_{21}}{L_{11}} \quad \text{and} \quad \Delta C_{11} = 0. \tag{61}$$

These equations and the calculated potential constants show that the relative error is largest for the interaction constants. The error, i.e. the deviation of L_{12} from zero, is found to be most serious for large kinematic coupling [34, 35], as in the case of the hexacarbonyls (0.76). Furthermore, it is noteworthy that the best results are obtained for the F_{1u}-block and the worse for A_{1g}, compatible with the size of the **L**-elements in Table 2.

The energy distributions with respect to the symmetry coordinates are given in Table 3 for some $M_0[^{12}C^{16}O]_6$ modes. There are analogous distributions in E_g and A_{1g} and in F_{2u} and F_{2g}. The importance of the kinetic energy is seen by comparing the results for ν_1 and ν_2. Both modes are highly characteristic in terms of PED, in spite of the very large difference in nature of the motions. The first mode may be regarded as a C-O stretch which more or less automatically gives rise to a considerable shortening of M_0-C due to the low metal-ligand force constant. However, shortening of M_0-C implies movement of the carbon atom which in turn leads to a considerable contribution to the kinetic energy. On the other hand, ν_2 may be described as a pure metalligand motion with the ligands moving as rigid units. The fundamental difference between ν_1 and ν_2 is illustrated by the total energy distributions, but is completely masked by the PED.

At last it is pointed out that a special case characterized by $E_{10,11} = 0$ and $V_{10,11} = -T_{10,11}$ occurs for ν_{11}. This situation corresponds to $F_{12} = -(G^{-1})_{12}\lambda_2$, or the negative of the solution for a CCNC.

Conclusion

Simplified formulae have been presented for the calculation of molecular constants when normal

Table 3. Energy distributions of some $Mo[^{12}C^{16}O]_6$ modes (in %).

	V	T	E
$\nu_1(A_{1g})$ 2141 cm^{-1}	$\left\|\begin{matrix} 96 & \\ -1 & 5 \end{matrix}\right.$	$\begin{vmatrix} 233 & \\ -137 & 142 \end{vmatrix}$	$\begin{vmatrix} 165 & \\ -69 & 74 \end{vmatrix}$
$\nu_2(A_{1g})$ 402 cm^{-1}	$\left\|\begin{matrix} 4 & \\ 1 & 95 \end{matrix}\right.$	$\begin{vmatrix} 0 & \\ 4 & 91 \end{vmatrix}$	$\begin{vmatrix} 2 & \\ 2 & 93 \end{vmatrix}$
	V		E
$\nu_6(F_{1u})$ 2027 cm^{-1}	$\begin{vmatrix} 103 & & & \\ -3 & 3 & & \\ 0 & 0 & 0 & \\ 0 & 0 & 0 & 0 \end{vmatrix}$		$\begin{vmatrix} 154 & & & \\ -54 & 54 & & \\ 0 & 0 & 0 & \\ 0 & 0 & 0 & 0 \end{vmatrix}$
	V		E
$\nu_7(F_{1u})$ 593 cm^{-1}	$\left\|\begin{matrix} 0 & & & \\ 0 & 6 & & \\ 0 & -2 & 50 & \\ 0 & 4 & 11 & 20 \end{matrix}\right.$		$\left\|\begin{matrix} 0 & & & \\ 0 & 13 & & \\ 0 & 10 & 174 & \\ 0 & -16 & -125 & 175 \end{matrix}\right.$
	V	T	E
$\nu_{10}(F_{2g})$ 478 cm^{-1}	$\begin{vmatrix} 63 & \\ 10 & 17 \end{vmatrix}$	$\begin{vmatrix} 413 & \\ -340 & 369 \end{vmatrix}$	$\begin{vmatrix} 238 & \\ -165 & 192 \end{vmatrix}$
$\nu_{11}(F_{2g})$ 79 cm^{-1}	$\begin{vmatrix} 46 & \\ -19 & 92 \end{vmatrix}$	$\begin{vmatrix} 8 & \\ 19 & 55 \end{vmatrix}$	$\begin{vmatrix} 27 & \\ 0 & 74 \end{vmatrix}$

vibrations can be assumed characteristic of an internal coordinate or force. Practical rules for identifying such vibrations are:

i) If the lowest frequency is fairly well separated, the mode is characteristic of an internal chemical type of coordinate.

ii) If the highest frequency is fairly well separated, the vibration is characterized by a *force* that corresponds to an internal coordinate.

The rules are not claimed to be universal. Moreover, characteristic modes may occur that are not compatible with these principles. It could also be objected that the internal coordinates are not specified, but this fact seldom causes any problems if conventional valence coordinates are chosen.

The calculations are performed for the following main purposes:

i) computation of quantities which can be employed in the assignment of spectra, including frequencies, isotopic shifts, band shapes and intensities.

ii) Evaluation of fundamental molecular properties like force fields (compliances), bond moments and polarizability derivatives (electrooptical parameters), Coriolis coupling constants and mean amplitudes.

A fundamental result of that work is that all obtained equations are directly of use:

i) without having to solve the secular equation $\mathbf{GFL} = \mathbf{L\Lambda}$, in order to determine the eigenvector matrix $\mathbf{L}$.

ii) even in the cases where only partial experimental data are available (i.e., isotopic shifts, intensities, coriolis coupling constants etc.).

Most details have been given for a CCNC since this situation to a larger degree has been recognized in the literature. However, as the above rules and the examples show, it is emphasized that the CCNF is as important. Characteristic forces even may be more significant since they generally are related to stretching frequencies.

Finally, we like to point out the close connection between complete characteristic normal forces and compliants (see (42), (43), (50), (51), (54)). The compliance matrix $\mathbf{C}$ is known to possess the fundamental property of invariance (6), i.e., its elements C_{ij} depend only on the choice of the coordinates S_i and S_j and in particular, a diagonal compliant C_{ii} depends only on the coordinate S_i. The $\mathbf{G}$ and $\mathbf{C}^{\alpha}$ matrices share the same property *but not* $\mathbf{G}^{-1}$, $\mathbf{F}$, and $\bar{\mathbf{C}}^{\alpha}$.

It follows from the above arguments that we may say like Decius [4]: "*spectroscopists have almost nothing to lose and something to gain by concentrating their attention upon* $\mathbf{C}$ *and CCNF rather than only upon* $\mathbf{F}$ *and CCNC*".

It can be seen from numerous numerical results that the $\mathbf{L}^{-1}$ matrix presents more frequently a row containing a single large element, which is the condition for a CCNF (especially in cases where stretching coordinates are involved), than the $\mathbf{L}$-matrix a column containing only one large element, which is required for a CCNC (and occurs especially when bending coordinates are involved).

It seems to us that this fact was obscured by the results of bidimensional problems where CCNC (for $k = i$) and CCNF (for $k = j$) occur simultaneously ($i, j = 1, 2$), especially when S_1 and S_2 are respectively related to stretch and bend internal coordinates.

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