Characteristic Normal Modes of Vibration and Generalized Normal Forces: Basic Properties and Relation to Fundamental Molecular Constants

A. J. P. Alix
Laboratoire de Recherches Optiques Faculté des Sciences, Reims Cédex, France

and E. Rytter
Institutt for uorganisk kjemi, Norges tekniske høgskole, Universitetet i Trondheim, Trondheim-NTH, Norway

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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 successfully 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 (Fij, Cij, ζij, wi, Σij, δμ/δSi, δξ/δSi, δγ/δSi, ...).

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]

\[ S = LQ \quad \text{or} \quad Q = L^{-1}S. \] (1)

A normal coordinate, Qk, is said to be completely characteristic of a symmetry coordinate, Si, if there is only one non-zero element, Lij, in the column k of L [2]:

\[ L_{jk} = 0 \quad \text{for all} \quad j \neq i, \] (2)

equivalent to

\[ (L^{-1})_{ik} = 0 \quad \text{for all} \quad j \neq k. \] (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

\[ f_k^{Q} = - \frac{\partial V}{\partial Q_k} = - \lambda_k Q_k \] (4)

and

\[ f_i = - \frac{\partial V}{\partial S_i} = - \sum_j F_{ij} S_j, \] (5)

Reprint requests to Pr. Alain J. P. Alix, Laboratoire de Recherches Optiques, Faculté des Sciences, B. P. 347, 51062 Reims Cédex, France.
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 $f_k$ of $f_i$ in CCNC and CCNF cases.

1. Characteristic Normal Mode of Vibration (CCNC)

Combination of the fundamental equations [1]

$$LL^{-1} = E$$
$$G^{-1} = \tilde{L}^{-1}L^{-1}$$

with the definition of a CCNC, yields the following values for some of the $L$ and $L^{-1}$ matrix elements:

$$(6)$$

The elements in the $i$'th row of $L$ are undetermined, except for $L_{ik}$. Furthermore, $L_{ik} = 1/(L^{-1})_{ki}$.

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

$$2V = \tilde{Q}\Delta Q = \tilde{S}FS,$$  
$$2T = \tilde{Q}E\tilde{Q} = \tilde{S}G^{-1}\tilde{S},$$

and

$$2E = \tilde{Q}\Delta Q + \tilde{Q}E\tilde{Q} = \tilde{S}FS + \tilde{S}G^{-1}\tilde{S}. $$

The corresponding energy distributions, PED, KED and TED, for the $k$'th vibration are defined by

$$V^{(k)}_{ij}(S) = F_{ij} L_{ik} L_{jk} \lambda_k,$$  
$$T^{(k)}_{ij}(S) = (G^{-1})_{ij} L_{ik} L_{jk} \lambda_k,$$

and

$$E^{(k)}_{ij}(S, \dot{S}) = (F_{ij} \dot{\lambda}_k^{-1} + (G^{-1})_{ij}) L_{ik} L_{jk}/2.$$  

Previously, other symbols have been employed, like $E^{(k)}_{ij}$, $E^{(k)}_{ij,ai}$, 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]

$$V^{(k)}_{ij} = 0 \quad \text{or} \quad T^{(k)}_{ij} = 0 \quad \text{or} \quad E^{(k)}_{ij} = 0$$

for all $j \neq i$.  

(16)

It follows that

$$V^{(k)}_{ii} = T^{(k)}_{ii} = E^{(k)}_{ii} = 1$$

and

$$V^{(k)}_{ij} = T^{(k)}_{ij} = E^{(k)}_{ij} = 0$$

for all $h$ and $j$ except $h = j = i$.  

(17)

(18)

Note that for example $V^{(g)}_{ij} = \delta_{ij}, j = 1, 2, \ldots$, 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 $V^{(g)}_{ii} = T^{(g)}_{ii} = 0$. 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 $\iota$'th column of $L$ [8]. Instead, one 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 $E^{(b)}_{ii}, j = 1, 2, \ldots$, 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.

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

(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.
(26) and (27) imply the conditions
\[ (G^{-1})_{ij}/(G^{-1})_{ii} = (G^{-1*})_{ij}/(G^{-1*})_{ii}, \]
\[ j = 1, 2, \ldots, \]
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 \( XY_2(C_{2v}) \), \( XY_3(C_{3v}) \), \( XY_4(T_d) \), \( XY_4(D_{4h}) \) 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]
\[ A_k = \frac{N \pi d_k}{3c^2} \left( \frac{\partial \mu}{\partial Q_k} \right)^2 = \frac{N \pi d_k}{3c^2} (\tilde{L} \mu' L)_{kk}, \]
where \( N \) and \( c \) are fundamental constants, \( d_k \) is the degeneracy and \( \mu' \) 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
\[ \left( \frac{\partial \mu}{\partial Q_k} \right) = \sum_j L_{jk} \left( \frac{\partial \mu}{\partial S_j} \right). \]
A characteristic coordinate gives the particularly simple results
\[ \left( \frac{\partial \mu}{\partial Q_k} \right) = \pm (G^{-1})_{ii}^{-1/2} \left( \frac{\partial \mu}{\partial S_i} \right) \]
and
\[ A_k = \frac{N \pi d_k}{3c^2} \frac{\mu'_{ii}}{(G^{-1})_{ii}}. \]
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]
\[ I_k = K \left( \frac{\partial \beta}{\partial Q_k} \right)^2 = K (L \beta' L)_{kk}, \]
where \( K \) depends on the excitation and fundamental frequencies and \( \beta \) is a linear combination of \( \tilde{z} \) and \( \gamma \) with \( \tilde{z} \) being the mean polarizability and \( \gamma \) the anisotropy, it follows for a CCNC that
\[ I_k = K \beta_{ii}/(G^{-1})_{ii}. \]

2. Characteristic Generalized Force (CCNF)

If (4) and (5) are written in matrix notation as
\[ \mathbf{f}^0 = -\mathbf{A} \mathbf{Q} \quad \text{and} \quad \mathbf{f} = -\mathbf{FS}, \]
\[ \mathbf{S} = -\mathbf{CF}, \]
it follows from fundamental relations that [6]
\[ \mathbf{f} = \tilde{\mathbf{L}}^{-1} \mathbf{f}^0 \quad \text{and} \quad \mathbf{f}^0 = \tilde{\mathbf{L}} \mathbf{f}. \]
The generalized normal force \( f_j^0 \) is said to be completely characteristic of a symmetry force \( f_i \) if \( (\tilde{L}^{-1})_{ik} \) is the only non-zero element in the \( k \)'th column of \( \tilde{L}^{-1} \). From (6) we then have
\[ L_{ij} = \pm G_{ii}^{1/2} \delta_{jk}, \quad j = 1, 2, \ldots, \]
\( k \)'th column;\[ L_{jk} = \pm G_{ii}^{-1/2} G_{ij}, \quad j = 1, 2, \ldots, \]
and
\[ (L^{-1})_{kl} = \pm G_{ii}^{-1/2} \delta_{kl}, \quad j = 1, 2, \ldots, \]
with \( (L^{-1})_{kl} = 1/L_{kl} \). 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]
\[ 2V = \mathbf{f}^0 \Lambda^{-1} \mathbf{f}^0 = \tilde{\mathbf{f}} \mathbf{C} \tilde{\mathbf{f}}, \]
\[ 2T = \tilde{\mathbf{f}}^0 \Lambda^{-2} \mathbf{f}^0 = \tilde{\mathbf{f}} (\mathbf{C} \Lambda^{-1} \mathbf{C}) \tilde{\mathbf{f}} \]
\[ = \tilde{\mathbf{f}} (L \Lambda^{-2} \tilde{L}) \tilde{\mathbf{f}}, \]
and
\[ 2E = 2V + 2T. \]
The corresponding energy distributions have been defined as [3, 5]
\[ V_{ij}^{(b)}(\mathbf{f}) = C_{ij} (L^{-1})_{kl} (L^{-1})_{ij} \lambda_k, \]
\[ T_{ij}^{(b)}(\mathbf{f}) = (\mathbf{C} \Lambda^{-1} \mathbf{C})_{ij} (L^{-1})_{ij} (L^{-1})_{kl} \lambda_k^2, \]
and
\[ E_{ij}^{(b)}(\mathbf{f}, \tilde{\mathbf{f}}) = (C_{ij} + (\mathbf{C} \Lambda^{-1} \mathbf{C})_{ij} \lambda_k) \lambda_k^2 / (L^{-1})_{kl} (L^{-1})_{ij} \lambda_k / 2. \]
Equations (16)–(18) are valid for a CCNF when \( V_{ij}^{(b)}(\mathbf{f}) \) is substituted for \( V_{ij}^{(b)}(\mathbf{S}) \), 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
\[ C_{ij} = G_{ii}/\lambda_k \]
occurs for \( L_{ij} = 0, j \neq k \). (42) is sufficient for \( f_j^0 \) to be completely characteristic of \( f_i \) only if \( \lambda_k \) corresponds to the highest or lowest frequency.
Furthermore, the CCNF definition leads to
\[ C_{ij} = G_{ij}/\lambda_k, \quad j = 1, 2, \ldots \]  
(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
\[ C = \mathbf{L} \Lambda^{-1} \mathbf{L} \quad \text{and} \quad \mathbf{G}^{-1} C = \mathbf{L} \Lambda^{-2} \mathbf{L}, \]
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 \( \Sigma = \mathbf{L} \Delta \mathbf{L} [6] \), and the compliances essentially have the same properties, whence
\[ \Sigma_{ij} = G_{ij} \Delta_k, \quad j = 1, 2, \ldots \]  
(44)
for a CCNF, including the same reverse properties and sign information as above.

Characteristic normal forces may be expected for a "\( \delta \delta \delta \)" assignment in \( 3 \times 3 \) 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 \( X Y_n \) type molecules with \( m_x > m_y \) [28—31].

d) Secular equation. The \( \mathbf{G}^{-1}, \Sigma \mathbf{G}^{-1} \) and \( \mathbf{G} \mathbf{F} \) matrices can be expressed as follows when (37) and (39) are used:
\[
\begin{align*}
(C \mathbf{G}^{-1})_{ij} &= (\mathbf{L} \Lambda^{-1} \mathbf{L}^{-1})_{ij} \\
&= \sum L_{ii} \lambda_i^{-1} L_{ij}^{-1} = \delta_{ij} / \lambda_k, \\
(S \mathbf{G}^{-1})_{ij} &= \delta_{ij} \Delta_k \quad \text{and} \\
(G \mathbf{F})_{ij} &= \delta_{ij} \lambda_k, \quad j = 1, 2, \ldots
\end{align*}
\]
(45)
Thus, the secular determinant \( |C \mathbf{G}^{-1} - \lambda^{-1} \mathbf{E}| \) has the linear factor \( (C \mathbf{G}^{-1})_{ii} - \lambda \) for any characteristic \( f_k \). Simultaneously, \( (G \mathbf{F})_{ii} - \lambda \) is split off from \( |G \mathbf{F} - \lambda \mathbf{E}| \); 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 \( \zeta_{kk} \) into
\[ \zeta_{kk} = C_{ii} / G_{ii}, \quad x = x, y, z, \]  
(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
\[ \lambda_k/\lambda_k^* = G_{ii}/G_{ii}^*, \]  
\[ \lambda_k/\lambda_k^* = G_{ij}/G_{ij}^* \quad \text{for all} \quad j \neq i, \]
and
\[ \prod_{i < k} (\lambda_i/\lambda_i^*) = \| (G^{-1})^t \| / \| (G^{-1})^t \| ; \]  
(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
\[
\left( \frac{\partial \mu}{\partial Q_k} \right) = \pm G_{ii}^{-1/2} \sum_i G_{ij} \left( \frac{\partial \mu}{\partial S_f} \right)
\]
and
\[ A_k = \frac{N \pi d_k}{3 c^2} G_{ii}^{-1} (G \mathbf{f} \mathbf{G})_{ii}. \]  
(48)
An equivalent expression is found for the Raman intensities, (33), namely
\[ I_k = K G_{ii}^{-1} (G \mathbf{G} \mathbf{G})_{ii}. \]  
(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]
\[ (S_j)_i = C_{ij} / C_{ii}, \quad j = 1, 2, \ldots \]  
(50)
It follows from (43) that, if any \( f_k \) is completely characteristic of \( f_i \), then
\[ (S_j)_i = G_{ij} / G_{ii}, \quad j = 1, 2, \ldots, \]  
(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

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

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

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

Since \( (\partial V/\partial S_i) = F_i S_i \) for \( S_j = 0, j \neq i \), it is seen that \( F_i \) 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

\[
f_i = - (\partial V/\partial S_i)_{\text{min}} = - (1/C_{ii}) S_i , \tag{54}
\]

showing that \( F_i = 1/C_{ii} \). The situation of a characteristic normal force implies stationary \( C_{ii} \) values and thus \( F_i = \lambda_i / G_{ii} \). 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 preceding 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 \( f_k^\theta \).

For the study of real cases, it is not restrictive to use the "a priori" partial assignment stating that the normal mode \( Q_k \) of frequency \( \lambda_k \) is required to involve the symmetry coordinate \( S_i \); in other words, we may suppose that \( L_{ii} = 0 \) 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 \( G^{-1} \)).

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 \( 2 \times 2 \) 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 \( j \theta \) characteristic of \( f_1 \), the CCNC and CCNF expressions treated in the previous sections are reduced to

\[
\begin{align*}
V_{11}^{(2)} &= V_{11}^{(1)} = T_{11}^{(2)} = 1 , \quad \text{etc.}, \\
V_{12}^{(2)} &= V_{12}^{(1)} = V_{12}^{(1)} = 0 , \quad \text{etc.}, \\
F_{12} &= (G^{-1})_{12} \lambda_2 , \quad F_{22} = (G^{-1})_{22} \lambda_2 , \tag{56}
\end{align*}
\]

\[
\begin{align*}
\lambda_1/\lambda_1^* &= G_{11}/G_{11}^* , \\
\lambda_2/\lambda_2^* &= (G^{-1})_{22}/(G^{-1})_{22} , \tag{57}
\end{align*}
\]

\[
\begin{align*}
\lambda_1/\lambda_1^* &= G_{12}/G_{12}^* , \\
\lambda_2/\lambda_2^* &= (G^{-1})_{12}/(G^{-1})_{12} , \tag{58}
\end{align*}
\]

\[
\begin{align*}
C_{11} &= G_{11}/\lambda_1 , \quad C_{12} = G_{12}/\lambda_1 , \\
\Sigma_{11} &= G_{11}/\lambda_1 , \quad \Sigma_{12} = G_{12}/\lambda_1 , \tag{59}
\end{align*}
\]

\[
\begin{align*}
\xi_{11}^x &= C_{11}^x /G_{11} \quad \text{and} \\
\xi_{22}^x &= (G^{-1})_{22}^{1/2} (G^{-1} C^x G^{-1})_{22} \\
&= \xi_{22}^x /G_{22} \tag{60}
\end{align*}
\]

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

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$^{-1}$)\textsuperscript{a}.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Kinematic coupling</th>
<th>$\Delta r_1$ (obs)</th>
<th>$\Delta r_1$ (calc)$^b$</th>
<th>$\Delta r_2$ (obs)</th>
<th>$\Delta r_2$ (calc)$^b$</th>
<th>Deviation $\Delta r_1$ %</th>
<th>Reference (obs)</th>
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<tbody>
<tr>
<td>PH$_3$-PD$_4$(E)</td>
<td>.02 - .05</td>
<td>691</td>
<td>690</td>
<td>332</td>
<td>330</td>
<td>0</td>
<td>[47]</td>
</tr>
<tr>
<td>H$_2$S-D$_2$S(A$_1$)</td>
<td>.03 - .06</td>
<td>774</td>
<td>750</td>
<td>343</td>
<td>354</td>
<td>3</td>
<td>[48]</td>
</tr>
<tr>
<td>PH$_3$-PD$_4$(A$_1$)</td>
<td>.04 - .08</td>
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<td>694</td>
<td>285</td>
<td>282</td>
<td>0</td>
<td>[47]</td>
</tr>
<tr>
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<td>.06 - .11</td>
<td>1068.4</td>
<td>1058.3</td>
<td>442.1</td>
<td>447.1</td>
<td>1</td>
<td>[48]</td>
</tr>
<tr>
<td>SiH$_4$SiD$_4$(F$_2$)</td>
<td>.06 - .12</td>
<td>639</td>
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<td>250</td>
<td>250</td>
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<td>[47]</td>
</tr>
<tr>
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<td>.07 - .12</td>
<td>1011</td>
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<td>3</td>
<td>[47]</td>
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<tr>
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<td>482</td>
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<tr>
<td>$^{152}$RuO$_4$-BaRuO$_4$(F$_2$)</td>
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<td>2.2</td>
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<td>146</td>
<td>147</td>
<td>0</td>
<td>[47]</td>
</tr>
<tr>
<td>$^{12}$SnCl$_4$-$^{16}$SnCl$_4$(F$_2$)</td>
<td>.35 - .36</td>
<td>3.1</td>
<td>3.8</td>
<td>1.3</td>
<td>1.1</td>
<td>23</td>
<td>[51]</td>
</tr>
<tr>
<td>$^{15}$MoO$_4$-BaMoO$_4$- (F$_2$)</td>
<td>.37 - .39</td>
<td>6.8</td>
<td>6.1</td>
<td>6.1</td>
<td>2.0</td>
<td>10</td>
<td>[52]</td>
</tr>
<tr>
<td>$^{15}$NO$_2$-BaNO$_2$(A$_1$)</td>
<td>.40 - .41</td>
<td>13.2</td>
<td>11.3</td>
<td>9.7</td>
<td>11.4</td>
<td>14</td>
<td>[53]</td>
</tr>
<tr>
<td>$^{30}$SiF$_4$-$^{28}$SiF$_4$(F$_2$)</td>
<td>.54 - .55</td>
<td>17.4</td>
<td>16.4</td>
<td>3.0</td>
<td>3.4</td>
<td>6</td>
<td>[53]</td>
</tr>
<tr>
<td>$^{33}$CICN-$^{37}$CICN ($\Sigma^+$)</td>
<td>.63 - .64</td>
<td>0.3</td>
<td>0.0</td>
<td>8.2</td>
<td>8.6</td>
<td>5</td>
<td>[54]</td>
</tr>
<tr>
<td>$^{16}$OCl$_2$-$^{18}$OCl$_2$(A$_1$)</td>
<td>.64 - .66</td>
<td>25.1</td>
<td>20.9</td>
<td>1.5</td>
<td>4.1</td>
<td>17</td>
<td>[55]</td>
</tr>
<tr>
<td>$^{79}$BrCN-$^{81}$BrCN ($\Sigma^+$)</td>
<td>.68 - .68</td>
<td>0.0</td>
<td>0.0</td>
<td>1.8</td>
<td>1.8</td>
<td>5</td>
<td>[54]</td>
</tr>
<tr>
<td>$^{35}$Cl$_4$-$^{37}$Cl$_4$(F$_2$)</td>
<td>.69 - .70</td>
<td>5.7</td>
<td>6.3</td>
<td>5.3</td>
<td>4.8</td>
<td>11</td>
<td>[51]</td>
</tr>
<tr>
<td>$^{11}$BO$_3$-BaBO$_3$- (E)</td>
<td>.69 - .71</td>
<td>42.9</td>
<td>42.2</td>
<td>3.6</td>
<td>4.0</td>
<td>2</td>
<td>[56]</td>
</tr>
<tr>
<td>$^{11}$BF$_3$-BaBF$_3$(E)</td>
<td>.72 - .74</td>
<td>51.2</td>
<td>51.3</td>
<td>1.6</td>
<td>2.6</td>
<td>0</td>
<td>[57]</td>
</tr>
<tr>
<td>$^{13}$CF$_4$-BaCF$_4$(F$_2$)</td>
<td>.73 - .74</td>
<td>37.6</td>
<td>33.9</td>
<td>2.5</td>
<td>4.8</td>
<td>10</td>
<td>[58]</td>
</tr>
<tr>
<td>$^{11}$BCl$_3$-BaBCl$_3$(E)</td>
<td>.83 - .84</td>
<td>39.5</td>
<td>38.6</td>
<td>0.9</td>
<td>2</td>
<td>2</td>
<td>[57]</td>
</tr>
<tr>
<td>$^{11}$BB$_3$-BaBB$_3$(E)</td>
<td>.92 - .92</td>
<td>37.1</td>
<td>36.5</td>
<td>0.3</td>
<td>2</td>
<td>2</td>
<td>[57]</td>
</tr>
<tr>
<td>$^{11}$BBr$_3$-BaBBr$_3$(E)</td>
<td>.95 - .95</td>
<td>32.9</td>
<td>32.4</td>
<td>0.1</td>
<td>2</td>
<td>2</td>
<td>[59]</td>
</tr>
</tbody>
</table>

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

\textsuperscript{b} Calculated by Equation (57).

have been excluded from the table. In contrast, the relation (57) gives remarkably good correspondence 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.

\textit{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[12C]:

<table>
<thead>
<tr>
<th></th>
<th>$\Lambda_{1g}$</th>
<th>$\Lambda_{2g}$</th>
<th>$\Lambda_{3g}$</th>
<th>$\Lambda_{4g}$</th>
<th>$E_{1g}$</th>
<th>$E_{2g}$</th>
<th>$E_{3g}$</th>
<th>$E_{4g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_1$</td>
<td>0.382</td>
<td>0.014</td>
<td>-0.225</td>
<td>-0.222</td>
<td>0.06</td>
<td>0.181</td>
<td>-0.222</td>
<td>0.184</td>
</tr>
<tr>
<td>$r_2$</td>
<td>-0.218</td>
<td>0.095</td>
<td>0.216</td>
<td>0.036</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_3$</td>
<td>0.002</td>
<td>-0.431</td>
<td>-0.134</td>
<td>0.072</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_4$</td>
<td>-0.00</td>
<td>-0.226</td>
<td>-0.008</td>
<td>0.083</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\Lambda_{1u}$

<table>
<thead>
<tr>
<th></th>
<th>$F_{1u}$</th>
<th>$F_{2u}$</th>
<th>$F_{2u}$</th>
<th>$F_{2u}$</th>
<th>$F_{2u}$</th>
<th>$F_{2u}$</th>
<th>$F_{2u}$</th>
<th>$F_{2u}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_1$</td>
<td>0.382</td>
<td>-0.001</td>
<td>0.000</td>
<td>-0.002</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_2$</td>
<td>-0.218</td>
<td>0.095</td>
<td>0.216</td>
<td>0.036</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_3$</td>
<td>0.002</td>
<td>-0.431</td>
<td>-0.134</td>
<td>0.072</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$r_4$</td>
<td>-0.00</td>
<td>-0.226</td>
<td>-0.008</td>
<td>0.083</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
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 Mo-C stretching modes. Other frequencies, it can be expected 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 constants, compliances and isotopic shifts ("exact" values in parentheses):

\[
\begin{align*}
A_{1g} &: F_{11} = 19.38 \ (17.84), \quad F_{12} = 1.52 \ (0.23), \quad C_{11} = 0.0540 \ (0.0560), \\
    &A_{1g} = -0.034 \ (-0.005), \quad C_{22} = 0.393 \ (0.362), \quad \Delta v_{1}^{(16-18O)} = 51.3 \ (47.0), \\
    &A v_{1}^{(12-13C)} = 47.5 \ (50.6), \quad A^{v_{2}}^{(16-18O)} = 13.8 \ (16.6), \quad A v_{2}^{(12-13C)} = 7.2 \ (6.1); \\
E_g &: F_{33} = 17.60 \ (16.83), \quad F_{34} = 1.44 \ (0.79), \quad F_{44} = 2.52 \ (2.55), \quad C_{33} = 0.0596 \ (0.0603), \\
    &C_{34} = -0.034 \ (-0.019), \quad C_{44} = 0.416 \ (0.308), \quad \Delta v_{1}^{(16-18O)} = 48.8 \ (46.6), \\
    &A v_{1}^{(12-13C)} = 45.2 \ (46.8), \quad A^{v_{2}}^{(16-18O)} = 13.3 \ (14.5), \quad A v_{2}^{(12-13C)} = 6.8 \ (6); \\
F_{1u} &: C_{66} = 0.0603 \ (0.0607), \quad C_{67} = -0.034 \ (-0.045), \quad C_{68} = 0.000 \ (-0.017), \\
    &C_{69} = 0.000 \ (-0.022), \quad A v_{1}^{(16-18O)} = 45.5 \ (49.4) \text{ and } \Delta v_{1}^{(12-13C)} = 45.0 \ (45.1).
\end{align*}
\]

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 the sensibilities of \( G \), \( \Delta v_{1} \) and \( \Delta v_{2} \) for characteristic \( F_{12} \) to the zero value of the sensibilities of \( G \), \( \Delta v_{1} \) and \( \Delta v_{2} \) is changed from zero, is found to be most serious for \( A_{1g} \) 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.

Conclusion

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

Table 3. Energy distributions of some Mo$^{[4]}$O$_{6}$ modes (in $\%$).

<table>
<thead>
<tr>
<th></th>
<th>$V$</th>
<th>$T$</th>
<th>$E$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$r_1(A_{1g})$ 2414 cm$^{-1}$</td>
<td>96</td>
<td>233</td>
<td>165</td>
</tr>
<tr>
<td>$r_2(A_{1g})$ 402 cm$^{-1}$</td>
<td>4</td>
<td>95</td>
<td>4</td>
</tr>
<tr>
<td>$r_6(F_{1u})$ 2027 cm$^{-1}$</td>
<td>103</td>
<td>154</td>
<td></td>
</tr>
<tr>
<td>$r_7(F_{1u})$ 593 cm$^{-1}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$r_{10}(F_{2g})$ 478 cm$^{-1}$</td>
<td>63</td>
<td>413</td>
<td>238</td>
</tr>
<tr>
<td>$r_{11}(F_{2g})$ 79 cm$^{-1}$</td>
<td>-19</td>
<td>92</td>
<td>19 55</td>
</tr>
</tbody>
</table>

without having to solve the secular equation $GFL = LA$, in order to determine the eigenvector matrix $L$.

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 $C$ 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 $G$ and $C^\alpha$ matrices share the same property but not $G^{-1}$, $F$, and $C^\alpha$.

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 $C$ and CCNF rather than only upon $F$ and CCNC".

It can be seen from numerous numerical results that the $L^{-1}$ 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 $L$-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.

Acknowledgements

A. J. P. A. wish to thank Dr. L. H. Jones (Los Alamos) for having sent to us detailed material on hexacarbonyls.
A. J. P. Alix et al. • Characteristic Normal Modes and Forces