Extremal Compliance Constants for Molecular Vibrations

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The occurrence of a stationary or extremal diagonal compliance constant in the general secular equation for molecular vibrations leads to pecularities in the normal coordinates, in the distribution of potential energy among the compliance constants, and in the secular determinant which then possesses a linear factor.

The purpose of this note is to examine the stationary and extremal properties of compliance constants for molecular vibrations. Comparison with the corresponding recently derived properties of force constants [1, 2] would reveal the considerable analogy that exists, but, for brevity, attention is here focussed on the properties of compliance constants.

(I) In terms of the matrix $\boldsymbol{C}$ of compliance constants, defined [3, 4] by $\boldsymbol{C} \equiv \boldsymbol{F}^{-1}$ as the inverse of the matrix of force constants, the vibrational secular equation may be written as the pair of equations $\boldsymbol{C} = \boldsymbol{L}\,\boldsymbol{\Lambda}^{-1}\,\tilde{\boldsymbol{L}}$ and $\mathbf{G} = \boldsymbol{L}\,\tilde{\boldsymbol{L}}$, so that the i-th compliance constant is expressible as $C_{ii} = \sum_{r}^{n} L_{ir}^2\, \Lambda_r^{-1}$, in which the n elements of the i-th row of $\boldsymbol{L}$ are subject to the constraint $G_{ii} = \sum_{r}^{n} L_{ir}^2$. The constrained stationary values of C_{ii} are found, by means similar to those already described [1, 2], to be

$$C_{ii} = G_{ii}\,\Lambda_r^{-1} \, (r = 1, \ldots, n) . \tag{1}$$

A stationary value of C_{ii} occurs if all except any one, say L_{ir}, of the elements in the i-th row of $\boldsymbol{L}$ vanish, i. e., if

$$L_{is} = 0\,(s \neq r), \qquad L_{ir} = \pm G_{ii}^{\frac{1}{2}} . \tag{2}$$

The n stationary values of C_{ii} occur in succession as each one of the n elements in the i-th row of $\boldsymbol{L}$ attains its upper limiting magnitude, which may be proved maximal.

(II) Since the original expression for C_{ii} may be rewritten as

$$C_{ii} = G_{ii}\,\Lambda_r^{-1} + \sum_{s}^{n} (\Lambda_s^{-1} - \Lambda_r^{-1})\; L_{is}^2 ,$$

it follows that the upper and lower bounds to C_{ii} are stationary, so that the greatest and least values of C_{ii} are, respectively, maximal and minimal:

$$C_{ii}^{\max} = G_{ii}\,\Lambda_r^{-1} \text{ if } \quad \Lambda_r < \text{all } \Lambda_s \quad (s \neq r)$$

and

$$C_{ii}^{\min} = G_{ii}\,\Lambda_r^{-1} \quad \text{ if } \quad \Lambda_r > \text{all } \Lambda_s \quad (s \neq r) .$$

The nature of the (n-2) stationary C_{ii} values of intermediate magnitude is not easily determined [1].

(III) If C_{ii} attains its r-th stationary value, $G_{ii}\,\Lambda_r{}^{-1}$, then:

(a) The i-th row and r-th column of $\boldsymbol{L}$ are given, respectively, by Eq. (2) and by $L_{\alpha r} = \pm G_{ii}^{\frac{1}{2}} G_{i\alpha}$ $(\alpha = 1, \ldots, n)$.

(b) The i-th row and column of $\boldsymbol{C}$ are given by $C_{i\alpha} = C_{\alpha i} = G_{i\alpha}\,\Lambda_r{}^{-1}$ $(\alpha = 1, \ldots, n)$.

(c) The secular determinant $|\boldsymbol{C}\,\mathbf{G}^{-1} - \Lambda^{-1}\,\mathbf{E}|$ has the linear factor $[(C\,G^{-1})_{ii} - \Lambda^{-1}]$ because, from Eq. (2), in the i-th row of $\boldsymbol{C}\,\mathbf{G}^{-1} = \boldsymbol{L}\boldsymbol{\Lambda}^{-1}\,\boldsymbol{L}^{-1}$ only the diagonal element is nonzero: $(C\,G^{-1})_{ii} = \Lambda_r{}^{-1}$, $(C\,G^{-1})_{is} = 0\ (s \neq i)$. The secular determinant $|\boldsymbol{C} - \Lambda^{-1}\,\mathbf{G}|$ has the linear factor $[C_{ii} - \Lambda^{-1}\,G_{ii}]$.

(IV) If the *a priori* partial assignment of Λ_i to C_{ii} is made so that $L_{ii} \neq 0$ if $C_{ii} = G_{ii}\,\Lambda_i{}^{-1}$ is stationary, the i-th row and column of $\boldsymbol{L}$ are determined: $L_{ii} = \pm G_{ii}^{\frac{1}{2}}$, $L_{is} = 0 \ (s \neq i)$; $L_{\alpha i} = \pm G_{ii}^{-\frac{1}{2}}\, G_{i\alpha}$ $(\alpha = 1, \ldots, n)$. The normal coordinate Q_i is then the only normal mode containing any of the symmetry coordinate S_i, although Q_i is not wholly determined by S_i alone.

(V) Since the quantities

$$V^{(k)}(F_{\alpha\beta}) = L_{\alpha k}\, L_{\beta k}\, F_{\alpha\beta}\, \Lambda_k^{-1}$$

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[1] D. E. FREEMAN, Chem. Phys. Letters **2**, 615 [1968]; J. Mol. Structure, in press.

[2] G. STREY and K. KLAUSS, Z. Naturforsch. **23 a**, 1717 [1968].

[3] J. C. DECIUS, J. Chem. Phys. **38**, 241 [1963].

[4] D. PAPOUSEK and J. PLIVA, Spectrochim. Acta **21**, 1147 [1965].

define the fractional potential energy (P. E.) contributions associated with the n^2 force constants $F_{\alpha\beta}$ in the k-th mode, it follows for the conditions in (IV) that in any mode except the i-th the P. E. contributions associated with any force constant involving S_i must be zero; whereas, in the i-th mode, the P. E. contributions associated with all the force constants are nonvanishing, and, in particular, $V^{(i)}(F_{ii}) = G_{ii} F_{ii} \Lambda_i^{-1} = C_{ii} F_{ii}$.

(VI) In the representation of generalized forces [4], the normal forces $\mathfrak{f}$ conjugate to the normal coordinates $\mathbf{Q}$ are given by $\mathfrak{f} = -\boldsymbol{\Lambda}\,\mathbf{Q}$. The P. E. of the i-th normal force $\mathfrak{f}_i$ is

$$\tfrac{1}{2}\,\mathfrak{f}_i^2 \Lambda_i^{-1} = \tfrac{1}{2}\,\mathfrak{f}_i^2\,(L^{-1} C \widetilde{L}^{-1})_{ii}$$

$$= \tfrac{1}{2}\,\mathfrak{f}_i^2 \sum_{\alpha,\beta} (L^{-1})_{i\alpha} (L^{-1})_{i\beta}\, C_{\alpha\beta}\,.$$

Hence the quantities

$$V^{(i)}(C_{\alpha\beta}) = (L^{-1})_{i\alpha} (L^{-1})_{i\beta}\, C_{\alpha\beta}\, \Lambda_i$$

define the fractional P. E. contributions associated with the n^2 compliance constants $C_{\alpha\beta}$. Therefore, for the conditions in (IV), all of the P. E. of the i-th generalized force is associated exclusively with the stationary compliance constant $C_{ii} = G_{ii} \Lambda_i^{-1}$, i. e., $V^{(i)}(C_{\alpha\beta}) = 0$ unless $\alpha = \beta = i$, in which case $V^{(i)}(C_{ii}) = 1$.

(VII) In the model of progressive rigidity [5], in which L is chosen to be lower triangular when the sequence $\Lambda_1 > \Lambda_2 > \ldots > \Lambda_n$ of frequencies is assigned to the sequence $S_1, S_2, \ldots, S_n$ of symmetry coordinates, the condition for the minimal value of C_{11}, $C_{11} = G_{11} \Lambda_1^{-1}$, is automatically satisfied. Indeed, each of the diagonal compliance constants C_{ii} determined in this model is minimal in the partial system in which Λ_i is the highest frequency.

(VIII) In general the r-th stationary values of force and compliance constants are connected by the relation

$$\Lambda_r = F_{ii} (G^{-1})_{ii}^{-1} = C_{ii}^{-1} G_{ii}\,,$$

i. e., $F_{ii} C_{ii} = (G^{-1})_{ii} G_{ii}$, so that if $\mathbf{G}$ is almost diagonal, the stationary values of F_{ii} and C_{ii} are almost inverses. Only for the second degree secular equation is it also true that, for $\Lambda_1 > \Lambda_2$, the minimal values of C_{11} and F_{22} are merely different representations of the same unique solution which coincides with the model of progressive rigidity.

(IX) If a constant characteristic group frequency Λ_0 is assigned in two different but related molecules, the transferability of the relevant compliance constant can be understood if its value is stationary; for, in the relation $\Lambda_0 = G_{ii}/C_{ii} = G'_{ii}/C'_{ii}$, the diagonal $\mathbf{G}$ elements are necessarily identical for a given symmetry coordinate. Stationary compliance constants of analogous coordinates in isotopic molecules are not generally identical; however, the "isotope rule" $G_{ii}/\Lambda_i = g_{ii}/\lambda_i$ is often approximately obeyed, in which case the stationary compliance constants are nearly equal.

(X) In Fadini's initial approximation to a molecular force field [6], the diagonal force constants are taken as $F_{ii} = G_{ii}^{-1} \Lambda_i$ and all off-diagonal $\boldsymbol{F}$ and $\mathbf{G}$ elements are ignored. Although the ignoration of the off-diagonal $\mathbf{G}$ elements, which are *a priori* known generally to be non-zero, is an objectionable aspect of this approximation, the following interpretation is of some interest: Fadini's approximation corresponds to setting each diagonal compliance constant equal to a stationary value, $C_{ii} = G_{ii} \Lambda_i^{-1}$, and to ignoring all off-diagonal compliance constants; the condition for all C_{ii} to be simultaneously stationary is, of course, that $\boldsymbol{L}$, and hence $\boldsymbol{G}$, be diagonal.

(XI) Since the mean-square amplitude matrix [7] $\sum\,(= \boldsymbol{L}\,\boldsymbol{\delta}\,\widetilde{\boldsymbol{L}})$ occurs in secular equations formally identical to those in which $\boldsymbol{C}(= \boldsymbol{L}\,\boldsymbol{\Lambda}^{-1}\,\widetilde{\boldsymbol{L}})$ occurs, it follows that Σ_{ii} and C_{ii} simultaneously possess stationary properties that are identical, except for differences in the definitions of the frequency parameters $\boldsymbol{\delta}$ and $\boldsymbol{\Lambda}^{-1}$.

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[5] D. E. Freeman, J. Mol. Spectry. **27**, 27 [1968]. — G. Strey, Z. Naturforsch. **24 a**, 729 [1969].

[6] A. Fadini, Z. Naturforsch. **21 a**, 426 [1966]. — H. J. Becher and R. Mattes, Spectrochim. Acta **23 A**, 2449 [1967]. — H. J. Becher and K. Ballein, Z. Phys. Chem. Frankfurt **54**, 302 [1967].

[7] S. J. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Elsevier Publishing Company, Amsterdam 1968.