First Order Perturbation Theory in the Study of Molecular Vibrations: Isotopic Rules and Properties of the Different Approximations

A. Alix

Laboratoire de Recherches Optiques, Faculté des Sciences de Reims, Cédex (France)

and N. Mohan, A. Müller *, and S. N. Rai

Institute of Chemistry University of Dortmund, 46 Dortmund, West Germany

The first order perturbation expressions for various molecular constants such as isotopic shifts ($\Delta\lambda_i$, $\Delta\lambda_i/\lambda_i$), inverse isotopic shifts ($\Delta\sigma_i$, $\Delta\sigma_i/\sigma_i$), Coriolis coupling constants ($\Delta\zeta_{ij}$) and mean amplitudes of vibration ($\mathbf{\Delta\Sigma}_{ij}$) obtained using different equations and approximations are given in detail.

The mathematical and physical properties of the different approximations are discussed extensively. Incidentally some isotopic rules obtained using the first order perturbation theory are presented.

1. Introduction

The first order perturbation theory has been widely used in the study of molecular vibrations as related to isotopic frequency shifts, change in the normal coordinates due to isotopic substitution, Jacobians related to the force constants and compliances, kinematic perturbation etc...[1−7]. We have recently extended this procedure for the study of centrifugal distortion, Coriolis coupling constants and mean amplitudes of vibration in isotopically substitued molecules [8, 9]. Different isotopic rules have also been formulated by several authors [1, 10−15].

One has to understand here the meaning of "First Order Perturbation" in the sense that one considers all and only all the first order terms in the general expanded development of any equation. This approach is in fact valid only for heavy atom isotopic substitution. Here, we give the equations obtained from the first order perturbation theory for different quantities ($\Delta\lambda_i/\lambda_i$, $\Delta\zeta_{ij}$, $\Delta\Sigma_{ij}$ etc...) with emphasis on the approximations involved in various procedures. Some isotopic rules holding in the framework of this formalism have also been proposed.

2. Procedural Details

A) Isotopic Shift $\Delta\mathbf{\Lambda}$

From the standard secular equations in the **G F**-matrix formalism of Wilson et al. [1] one has for the "unperturbed" molecule

* Reprint requests to Prof. Dr. A. Müller, Institute of Chemistry, University of Dortmund, *D-4600 Dortmund*, August-Schmidt-Straße, Postfach 500.

$$\mathbf{G\,F\,L} = \mathbf{L\Lambda} \qquad (1)$$

and for an isotopically substitued "perturbed" molecule

$$\mathbf{G^* F L^*} = \mathbf{L^* \Lambda^*}. \qquad (2)$$

With the definitions

$$\begin{aligned}\mathbf{G^*} &= \mathbf{G} + \mathbf{\Delta G}, \\ \mathbf{L^*} &= \mathbf{L} + \mathbf{\Delta L}, \\ \text{and } \mathbf{\Lambda^*} &= \mathbf{\Lambda} + \mathbf{\Delta\Lambda}\end{aligned} \qquad (3)$$

one deduces the equation for the isotopic shift $\mathbf{\Delta\Lambda}$ [7]

$$\mathbf{\Delta\Lambda} = \mathbf{L}^{-1}\mathbf{\Delta G}\,(\mathbf{L}^{-1})^+ \mathbf{\Lambda} + [\mathbf{\Lambda}\,(\mathbf{L}^{-1}\,\mathbf{\Delta L}) - (\mathbf{L}^{-1}\,\mathbf{\Delta L})\,\mathbf{\Lambda}]. \qquad (4)$$

The normalization condition

$$\mathbf{L\,L^+} = \mathbf{G} \qquad (5)$$

leads to the following first order equation in $\mathbf{\Delta G}$:

$$\mathbf{\Delta G} = \mathbf{L}\,(\mathbf{\Delta L})^+ + \mathbf{\Delta L\,L^+}. \qquad (6)$$

Substituting Eq. (6) in (4), one has

$$\mathbf{\Delta\Lambda} = (\mathbf{\Delta L})^+ (\mathbf{L}^{-1})^+ \mathbf{\Lambda} + \mathbf{\Lambda}\,(\mathbf{L}^{-1}\,\mathbf{\Delta L}). \qquad (7)$$

Since the experimentally observeds shifts ($\Delta\lambda_i$) are the diagonal elements of the matrix $\mathbf{\Delta\Lambda}$, one has

$$(\mathbf{\Delta\Lambda})_{ii} = [\mathbf{L}^{-1}\,\mathbf{\Delta G}\,(\mathbf{L}^{-1})^+ \mathbf{\Lambda}]_{ii} \qquad (8)$$

$$\begin{aligned}(\mathbf{\Delta\Lambda})_{ij} &= [\mathbf{L}^{-1}\,\mathbf{\Delta G}\,(\mathbf{L}^{-1})^+ \mathbf{\Lambda}]_{ij} \\ &+ [\mathbf{\Lambda}\,(\mathbf{L}^{-1}\,\mathbf{\Delta L}) - (\mathbf{L}^{-1}\,\mathbf{\Delta L})\,\mathbf{\Lambda}]_{ij} = 0.\end{aligned} \qquad (9)$$

(i) First Approximation $\mathbf{\Delta L} = 0$

This is the commonly used approximation found in the earlier works [1, 8, 9]. With this assumption one obtains from Eq. (7) the result

$$\mathbf{\Delta\Lambda} = 0 \qquad (10)$$

which has no physical meaning and hence the earlier authors used Eq. (4) to estimate the isotopic shifts

i. e. $\quad \boldsymbol{\varDelta\varLambda} \, \boldsymbol{\varLambda}^{-1} = \boldsymbol{L}^{-1} \, \boldsymbol{\varDelta G} \, (\boldsymbol{L}^{-1})^{+}$. $\quad$ (11)

With the help of Eq. (11), one can deduce the isotopic sum rule

$$\sum_i (\boldsymbol{\varDelta\varLambda})_i (\boldsymbol{\varLambda}^{-1})_i = \mathrm{Tr}[\boldsymbol{L}^{-1} \, \boldsymbol{\varDelta G} \, (\boldsymbol{L}^{-1})^{+}]$$
$$= \mathrm{Tr}[(\boldsymbol{L}^{-1})^{+} \, \boldsymbol{L}^{-1} \, \boldsymbol{\varDelta G}] \quad (12)$$

or

$$\sum_i \varDelta\lambda_i/\lambda_i = \mathrm{Tr}[\boldsymbol{G}^{-1} \, \boldsymbol{\varDelta G}] \, . \quad (13)$$

From Eq. (13), one may deduce the relation

$$\sum_i \lambda_i^*/\lambda_i = \mathrm{Tr}[\boldsymbol{G}^{-1} \, \boldsymbol{G}^*] \, . \quad (14)$$

In the quadratic $(n = 2)$ cases, this Eq. (14) together with the familiar Teller-Redlich product rule

$$\Pi_i \lambda_i^*/\lambda_i = \det[\boldsymbol{G}^{-1} \, \boldsymbol{G}^*] \quad (15)$$

enables one to determine the individual ratios (λ_1^*/λ_1) and (λ_2^*/λ_2). It is thus seen from Eqs. (14) and (15) that these ratios are the eigenvalues of the matrix product $[\boldsymbol{G}^{-1} \, \boldsymbol{G}^*]$.

(i.i) Second Approximation

$$[\boldsymbol{\varLambda} (\boldsymbol{L}^{-1} \, \boldsymbol{\varDelta L}) - (\boldsymbol{L}^{-1} \, \boldsymbol{\varDelta L}) \boldsymbol{\varLambda}] = 0 \, . \quad (16)$$

This approximation is more general than the previous one, in that $\boldsymbol{\varDelta L}$ is not assumed to be zero; only the diagonal elements of the above equation are considered. This approximation implies that

$$\boldsymbol{\varLambda} (\boldsymbol{L}^{-1} \, \boldsymbol{L}^*) = (\boldsymbol{L}^{-1} \, \boldsymbol{L}^*) \boldsymbol{\varLambda} \, . \quad (17)$$

This Eq. (17) in turn means that the matrices $\boldsymbol{\varLambda}$ and $(\boldsymbol{L}^{-1} \, \boldsymbol{L}^*)$ commute; but $\boldsymbol{\varLambda}$ itself being diagonal, it is clear that $(\boldsymbol{L}^{-1} \, \boldsymbol{L}^*)$ must be diagonal itself.

Let

$$\boldsymbol{L}^{-1} \, \boldsymbol{L}^* = \boldsymbol{d} \quad \text{or} \quad \boldsymbol{L}^* = \boldsymbol{L} \, \boldsymbol{d} \, . \quad (18)$$

Then one deduces from Eq. (4) that

$$\boldsymbol{\varDelta\varLambda} = \boldsymbol{L}^{-1} \, \boldsymbol{\varDelta G} \, (\boldsymbol{L}^{-1})^{+} \boldsymbol{\varLambda}$$
$$= [\boldsymbol{L}^{-1} \, \boldsymbol{G}^* \, (\boldsymbol{L}^{-1})^{+} - \boldsymbol{E}] \boldsymbol{\varLambda} \quad (19)$$

or

$$\boldsymbol{\varDelta\varLambda} \, \boldsymbol{\varLambda}^{-1} = (\boldsymbol{L}^{-1} \, \boldsymbol{L}^*) \, (\boldsymbol{L}^{-1} \, \boldsymbol{L}^*)^{+} - \boldsymbol{E}$$
$$= \boldsymbol{d}^2 - \boldsymbol{E} \, . \quad (20)$$

It follows from Eq. (20) that since $\boldsymbol{d}^2$ and $\boldsymbol{E}$ are diagonal, $\boldsymbol{\varDelta\varLambda} \, \boldsymbol{\varLambda}^{-1}$ is also diagonal.

One deduces that

$$\boldsymbol{\varDelta}\lambda_i/\lambda_i = d_i^2 - 1 \quad (21)$$

or

$$\lambda_i^*/\lambda_i = d_i^2 \, . \quad (22)$$

This means that the ratios $(\varDelta\lambda_i/\lambda_i)$ and (λ_i^*/λ_i) are the diagonal elements of the matrices

$$[\boldsymbol{L}^{-1} \, \boldsymbol{\varDelta G} \, (\boldsymbol{L}^{-1})^{+}] \quad \text{and} \quad [\boldsymbol{L}^{-1} \, \boldsymbol{G}^* \, (\boldsymbol{L}^{-1})^{+}]$$

respectively. The eigenvalues being invariant under proper orthogonal transformations, it is clear that one can choose any $\boldsymbol{L}$-matrix which satisfies the normalization condition defined by Equation (15). Thus the equations

$$(\varDelta\lambda_i/\lambda_i) = \text{E.V.} \, [\, (\boldsymbol{L}_{(0)})^{-1} \, \boldsymbol{\varDelta G} \, (\boldsymbol{L}_{(0)})^{-1+}],$$
$$(\lambda_i^*/\lambda_i) = \text{E.V.} \, [\, (\boldsymbol{L}_{(0)})^{-1} \, \boldsymbol{G}^* \, (\boldsymbol{L}_{(0)})^{-1+}] \quad (24)$$

also hold, and can be used for pratical calculations.

This special approximation [Eq. (18)] is identical to the solution obtained by Jordanov[16] in his study of the extremal properties of $\boldsymbol{\varDelta\varLambda}_i$ in the general case using the secular Eqs. (1) and (2). It was later shown by Alix et al.[16] that Eq. (18) holds also in the case of the first order perturbation treatment.

A significance of this approximation [Eq. (18)] might be understood using the following arguments: Within the framework of the Born-Oppenheimer approximation, one has

$$(\boldsymbol{L}^{-1})^{+} \boldsymbol{\varLambda} (\boldsymbol{L}^{-1}) = (\boldsymbol{L}^{*-1})^{+} \boldsymbol{\varLambda}^* (\boldsymbol{L}^{*-1}) \quad (25)$$

or

$$\boldsymbol{\varLambda}^* = (\boldsymbol{L}^*)^{+} (\boldsymbol{L}^{-1})^{+} \boldsymbol{\varLambda} \, (\boldsymbol{L}^{-1} \, \boldsymbol{L}^*)$$
$$= (\boldsymbol{\varLambda}^{1/2} \, \boldsymbol{L}^{-1} \, \boldsymbol{L}^*)^{+} \, (\boldsymbol{\varLambda}^{1/2} \, \boldsymbol{L}^{-1} \, \boldsymbol{L}^*) \, . \quad (26)$$

Hence, it follows that

$$\boldsymbol{E} = [\boldsymbol{\varLambda}^{1/2} \, \boldsymbol{L}^{-1} \, \boldsymbol{L}^* \boldsymbol{\varLambda}^{*-1/2}]^{+} (\boldsymbol{\varLambda}^{1/2} \, \boldsymbol{L}^{-1} \, \boldsymbol{L}^* \boldsymbol{\varLambda}^{*-1/2}) \, . \quad (27)$$

From Eq. (27) one deduces that

$$\boldsymbol{\varLambda}^{1/2} (\boldsymbol{L}^{-1} \, \boldsymbol{L}^*) \boldsymbol{\varLambda}^{*-1/2} = \boldsymbol{R} \quad \text{(orthogonal)} \, . \quad (28)$$

If the solutions

$$\boldsymbol{L} = \boldsymbol{L}^{(0)} \quad \text{and} \quad \boldsymbol{L}^* = \boldsymbol{L}^{(0)*}$$

with

$$(\boldsymbol{L}^{(0)})_{ii} > 0; \quad (\boldsymbol{L}^{(0)})_{ij} = 0 \, , \quad \lambda_i > \lambda_j \text{ for } i < j \quad (29)$$

and $\boldsymbol{L}^{(0)*}$ satisfying equation similar to (29), make Eq. (28) valid, one has

$$\boldsymbol{\varLambda}^{*-1/2} \, [\, (\boldsymbol{L}^{(0)})^{-1} \, \boldsymbol{L}^{(0)*}]^{+} \boldsymbol{\varLambda}^{1/2} = \boldsymbol{\varLambda}^{*1/2}$$
$$\cdot [\, (\boldsymbol{L}^{(0)*})^{-1} \, \boldsymbol{L}^{(0)}] \boldsymbol{\varLambda}^{-1/2} \, . \quad (30)$$

$$\underbrace{\qquad\qquad}_{\text{upper triangular}} \qquad \underbrace{\qquad\qquad}_{\text{lower triangular}}$$

Hence, one deduces that the product matrix $[\, (\boldsymbol{L}^{(0)})^{-1} \, \boldsymbol{L}^{(0)*}]$ must be diagonal. In analogy with the results derived in Eq. (20), if one assumes that

$$(\boldsymbol{L}^{(0)})^{-1} \, \boldsymbol{L}^{(0)*} = \boldsymbol{d} = \boldsymbol{\varLambda}^{*1/2} \boldsymbol{\varLambda}^{-1/2} \quad (31)$$

then $\boldsymbol{R}$ is in fact the unit matrix $\boldsymbol{E}$.

Therefore, if one chooses as solutions $\boldsymbol{L}^{(0)}$ and $\boldsymbol{L}^{(0)*}$ for two isotopes of a molecule, then within the framework of the perturbation theory, the extremal values of the isotopic frequency shifts [if (31) is seen to be valid], are obtained and in particular, minimal values for a special choice of the ordering of the $\boldsymbol{d}_i$ elements.

Another significance of the solution given by Eq. (18) might be understood from the following equations:

$$\boldsymbol{G}^* \boldsymbol{F} \boldsymbol{L}^* = \boldsymbol{L}^* \boldsymbol{\Lambda}^* \qquad (32)$$

or

$$\boldsymbol{G}^* \boldsymbol{F} \boldsymbol{L} \boldsymbol{d} = \boldsymbol{L} \boldsymbol{d} \boldsymbol{\Lambda}^* . \qquad (33)$$

Therefore it follows that both $(\boldsymbol{G}^* \boldsymbol{F})$ and $(\boldsymbol{G} \boldsymbol{F})$ have the same eigenvectors. In other words, one has the relations

$$[\boldsymbol{G}^* \boldsymbol{F}, \boldsymbol{G} \boldsymbol{F}] = 0 \qquad (34)$$

$$[\boldsymbol{G} \boldsymbol{F}, \boldsymbol{\Delta} \boldsymbol{G} \boldsymbol{F}] = 0 . \qquad (35)$$

An additional property of this solution follows from the definition of the potential energy distributions (P.E.D.) [18-20].

i.e. $V_{S_i^*}^{*\lambda_k^*} = (\boldsymbol{L}^*)_{ik} [(\boldsymbol{L}^*)^{-1}]_{ki}$

$$= (\boldsymbol{L})_{ik} \, \boldsymbol{d}_k \, \boldsymbol{d}_k^{-1} \, (\boldsymbol{L})_{ki}^{-1} = V_{S_i}^{\lambda_k} . \qquad (36)$$

Equation (36) implies that the P.E.D. for the different isotopes of a molecule are identical in the first order perturbation treatment.

The signs of the elements of the diagonal matrix $\boldsymbol{d}$ can be deduced by further simplifications of Equation (21). This Eq. (21) can be approximated by another one containing only first order terms of $\boldsymbol{d}_i$

i.e. $\Delta \lambda_i / \lambda_i = d_i^2 - 1 = (d_i + 1)(d_i - 1)$

$$\cong 2 (d_i - 1). \qquad (37)$$

It is thus clear from Eq. (37) that for factor $\Delta \lambda_i / \lambda_i$ would have a larger value with negative elements d_i than when one has positive elements. Physically, for heavy atom substitution the factor $\Delta \lambda_i / \lambda_i$ varies very little and on this basis, one would prefer positive value of the d_i elements. This assumption about the sign of the d_i does not lead to any loss of generality.

B) Inverse Isotopic Shift

The same study as enunciated in sec (A) can be made for the inverse isotopic shift using the relation

$$\boldsymbol{F}^{-1}(\boldsymbol{G}^{-1}) \boldsymbol{L} = \boldsymbol{L}(\boldsymbol{\Lambda}^{-1}) = \boldsymbol{L} \boldsymbol{\sigma} . \qquad (38)$$

Here, below, we summarize the results:

(i) First approximation: $\boldsymbol{\Delta L} = 0$, $\boldsymbol{\Delta \Lambda} \cong$ diagonal

$$\sum_i \Delta \sigma_i / \sigma_i = \text{Tr}[\boldsymbol{G} \boldsymbol{\Delta} (\boldsymbol{G}^{-1})] \qquad (39)$$

or

$$\sum_i \sigma_i^* / \sigma_i = \text{Tr}[\boldsymbol{G} \boldsymbol{G}^{*-1}] . \qquad (40)$$

Using the definition

$$\boldsymbol{\Phi}_i^{-1} = \frac{(\lambda_i^*)^{-1} - (\lambda_i)^{-1}}{(\lambda_i)^{-1}} = \frac{\sigma_i^* - \sigma_i}{\sigma_i} \qquad (41)$$

we get

$$\text{Tr}(\boldsymbol{\Phi})^{-1} = \text{Tr}[\boldsymbol{G} \boldsymbol{\Delta} (\boldsymbol{G}^{-1})] \qquad (42)$$

where

$$\boldsymbol{\Delta} (\boldsymbol{G}^{-1}) = (\boldsymbol{G}^*)^{-1} - \boldsymbol{G}^{-1}.$$

(ii) Second Approximation: $\boldsymbol{L}^* = \boldsymbol{L} \boldsymbol{d}$

$$\sigma_i^* / \sigma_i = 1/d_i^2 \dots . \qquad (43)$$

C) Coriolis Coupling Constants

1. First Approach

The isotope effect on the values of the Coriolis coupling constants can be studied using the relation

$$\boldsymbol{C} = \boldsymbol{L} \boldsymbol{\zeta} \boldsymbol{L}^+ \qquad (44)$$

where $\boldsymbol{C}$ and $\boldsymbol{\zeta}$ are the familiar matrices encountered in the study of rotation vibration interaction [21, 22]. Differentiating Eq. (44), replacing by finite increments and readjusting, one gets the relation

$$\boldsymbol{\Delta \zeta} = \boldsymbol{L}^{-1} \boldsymbol{\Delta C}(\boldsymbol{L}^{-1})^+ - [(\boldsymbol{L}^{-1} \boldsymbol{\Delta L}) \boldsymbol{\zeta} + \boldsymbol{\zeta}$$
$$(\boldsymbol{\Delta L}^+ \boldsymbol{L}^{-1+})] . \qquad (45)$$

(i) First Approximation

Using the approximation $\boldsymbol{\Delta L} = 0$ in Eq. (45), one gets a simplified equation of the form

$$\boldsymbol{\Delta \zeta} = \boldsymbol{L}^{-1} \boldsymbol{\Delta C}(\boldsymbol{L}^{-1})^+ . \qquad (46)$$

Hence,

$$\sum_i \boldsymbol{\Delta \zeta}_i = \text{Tr} [\boldsymbol{G}^{-1} \boldsymbol{\Delta C}] . \qquad (47)$$

This relation can be compared with the one derived from the exact isotopic rule [21, 22]

i.e. $\sum_i \boldsymbol{\zeta}_i = \text{Tr} [\boldsymbol{G}^{-1} \boldsymbol{C}] \qquad (48)$

which leads to the equation

$$\sum_i \boldsymbol{\zeta}_i^* - \sum_i \boldsymbol{\zeta}_i = \sum_i \boldsymbol{\Delta \zeta}_i = \text{Tr} [(\boldsymbol{G}^*)^{-1} \boldsymbol{C}^* - \boldsymbol{G}^{-1} \boldsymbol{C}]$$
$$\qquad (49)$$

or

$$\sum_i \boldsymbol{\Delta \zeta}_i = \text{Tr} [\boldsymbol{G}^{-1} \boldsymbol{\Delta C} + \boldsymbol{\Delta} (\boldsymbol{G}^{-1}) \boldsymbol{C}^*] \qquad (50)$$

where $\boldsymbol{\Delta} (\boldsymbol{G}^{-1})$ is the same matrix as defined above in Equation (42). It is thus seen from Eqs. (47)

and (50) that the two relations are identical if the matrices $\mathbf{G}$ and $\mathbf{G}^*$ are the same.

(ii) Second Approximation

Use of the second approximation defined by Eq. (18) in Eq. (45) leads to the result

$$\varDelta \zeta = [\mathbf{L}^{-1} \varDelta \mathbf{C} (\mathbf{L}^{-1})^+] - [\mathbf{d}^2 \zeta + \zeta \mathbf{d}^2 + 2 \zeta]. \tag{51}$$

2. Second Approach

As suggested in our earlier paper [8] the equation

$$\mathbf{L}^+ \mathbf{F} \mathbf{K} = \varLambda (\mathbf{E} - \zeta) \mathbf{L}^+ \tag{52}$$

where

$$\mathbf{K} = \mathbf{G} - \mathbf{C}$$

can be used to study the mass effect on the ζ constants in isotopically substitued molecules.

Following the procedure outlined in the earlier sections and after some simplifications and rearrangements, one obtains with the first order perturbation theory, the equation

$$\begin{aligned} \varLambda^{-1} \varDelta \varLambda = &[\mathbf{L}^{-1} \varDelta \mathbf{K} (\mathbf{L}^{-1})^+ + \varDelta \zeta] [\mathbf{E} - \zeta]^{-1} \\ &+ \varLambda^{-1} [\varDelta \mathbf{L}^+ (\mathbf{L}^{-1})^+ \{\varLambda (\mathbf{E} - \zeta)\} \\ &- \{\varLambda (\mathbf{E} - \zeta)\} (\varDelta \mathbf{L}^+ (\mathbf{L}^{-1})^+]. \end{aligned} \tag{53}$$

(i) First Approximation

Use of the assumption $\varDelta \mathbf{L} = 0$ leads to the result

$$\varLambda^{-1} \varDelta \varLambda = [\mathbf{L}^{-1} \varDelta \mathbf{K} (\mathbf{L}^{-1})^+ + \varDelta \zeta] [\mathbf{E} - \zeta]^{-1}. \tag{54}$$

(ii) Second Approximation

The second approximation as outlined in Eq. (18) yields the following equation for $\varDelta \mathbf{K} = 0$ (for $n = 2$ cases; symmetric and spherical top molecules for rotation about the figure axis, see our earlier work [8]:

$$\begin{aligned} \varLambda^{-1} \varDelta \varLambda &= \varDelta \zeta (\mathbf{E} - \zeta)^{-1} + \varLambda^{-1} (\varLambda \zeta \mathbf{d} - \mathbf{d} \zeta \varLambda) \\ &= \varDelta \varLambda \varLambda^{-1} = \mathbf{d}^2 - \mathbf{E}. \end{aligned} \tag{55}$$

Hence, we obtain

$$\begin{aligned} \varDelta \zeta = (\mathbf{d}^2 - \mathbf{E}) (\mathbf{E} - \zeta) - (\zeta \mathbf{d} \\ - \varLambda^{-1} \mathbf{d} \zeta \varLambda) (\mathbf{E} - \zeta). \end{aligned} \tag{56}$$

Assuming that $\varDelta \varLambda$ is diagonal, one deduces the $\varDelta \zeta_{ii}$ values from Eq. (56),

$$\begin{aligned} \varDelta \zeta_{ii} = (\varDelta \lambda_i / \lambda_i) (1 - \zeta_{ii}) - \sum_{\substack{k, 1 \\ k = 1 \neq i}} \zeta_{ik} (\mathbf{L}^{*+} \mathbf{L}^{-1})_{lk} \\ \cdot [(\mathbf{E} - \zeta)^{-1}]_{li}. \end{aligned} \tag{57}$$

Now we have from Eq. (57), the relations

$$\varDelta \zeta_{ii} = (d_i^2 - 1) (1 - \zeta_{ii}) - \sum_{k \neq i} \zeta_{ik} d_k [(\mathbf{E} - \zeta)^{-1}]_{ki} \tag{58}$$

and for the simple $i = 1$ cases, Eq. (58) reduces in part to the form

$$\varDelta \zeta_{11} = (d_1^2 - 1) (1 - \zeta_{11}) - \zeta_{12} d_2 [(\mathbf{E} - \zeta)^{-1}]_{21} \tag{59}$$

which is nearly the expression given in Eq. (13) of Reference [8].

D) Mean Amplitude of Vibration

1. First Approach

From the equation (see Ref. [22]),

$$\mathbf{L} \delta \mathbf{L}^+ = \mathbf{\Sigma} \tag{60}$$

one obtains using the first order perturbation theory, an equation for studying the mass effect on mean amplitudes of the form

$$\mathbf{L} \delta \varDelta \mathbf{L}^+ + \mathbf{L} \varDelta \delta \mathbf{L}^+ + \varDelta \mathbf{L} \delta \mathbf{L}^+ = \varDelta \mathbf{\Sigma}. \tag{61}$$

(i) First Approximation

The simplified form of Eq. (61) under the assumption that $\varDelta \mathbf{L} = 0$ reads

$$\varDelta \mathbf{\Sigma} = \mathbf{L} \varDelta \delta \mathbf{L}^+. \tag{62}$$

Since the $\varDelta \mathbf{\Sigma}_{ii}$ quantities defined in Eq. (62) depend only on the squares of the $\mathbf{L}$-matrix elements ($\mathbf{L}_{ij}^2$), it is evident that the signs of $\varDelta \mathbf{\Sigma}_{ii}$ are defined purely by the signs of the $\varDelta \delta_j$ elements; for substitution of an atom by a heavier one, $\varDelta \delta_i$ elements are positive and hence Eq. (62) leads to the result that in this case $\varDelta \mathbf{\Sigma}_{ii}$ are positive. It should however be noted that this conclusion is not physically justifiable i. e. in a real situation $\varDelta \mathbf{\Sigma}_{ii}$ (say i corresponds to bond stretching vibration) decreases with increasing mass of the atoms constituting the molecule.

Using Eqs. (62) and (60), the equation

$$\begin{aligned} \varDelta \mathbf{\Sigma} \mathbf{\Sigma}^{-1} &= \mathbf{L} \varDelta \delta \mathbf{L}^+ (\mathbf{L} \delta \mathbf{L}^*)^{-1} \\ &= \mathbf{L} \varDelta \delta \delta^{-1} \mathbf{L}^{-1} \end{aligned} \tag{63}$$

can be deduced. It is clear that the values of the elements of the diagonal matrix ($\varDelta \delta \delta^{-1}$) are the eigenvalues of the unsymmetrical matrix ($\varDelta \mathbf{\Sigma} \mathbf{\Sigma}^{-1}$) and the eigenvector matrix of ($\varDelta \mathbf{\Sigma} \mathbf{\Sigma}^{-1}$) is the $\mathbf{L}$-matrix for the unperturbed molecule.

(ii) Second Approximation

A second approximation of Eq. (61) would be

$$\mathbf{L} \delta \varDelta \mathbf{L}^+ + \varDelta \mathbf{L} \delta \mathbf{L}^+ = 0. \tag{64}$$

After some manipulations of this Eq. (64), one would obtain

$$L \, \delta \, L^{*+} + L^* \, \delta \, L^+ = 2 \, \Sigma \, . \quad (65)$$

Hence,

$$\Sigma_{ii} = (L \, \delta \, L^{*+})_{ii} \, . \quad (66)$$

2. Second Approach

As outlined in our earlier paper [9] the isotope effect on mean amplitudes of vibration can be studied with the help of the equation

$$\Sigma \, F \, L = L \, \Lambda \, \delta \, . \quad (67)$$

The first order perturbation theory in this case leads to the result [9]

$$\Sigma \, F \, \Delta L + \Delta \Sigma \, F \, L = \Delta L \Lambda \, \delta + L \Lambda \, \Delta \delta + L \, \Delta \Lambda \, \delta \, . \quad (68)$$

From Eq. (68) we get

$$\Delta \Sigma = L \, \Delta \delta \, L^+ + L \, \Delta \Lambda \, \delta \, \Lambda^{-1} \, L^+ \\ - \Sigma \, F \, \Delta L \, L^{-1} \, F^{-1} + \Delta L \, L^{-1} \, \Sigma \, . \quad (69)$$

Elimination of F from (69) using the familiar relation

$$F = (L^{-1})^+ \, \Lambda \, L^{-1} \quad (70)$$

and some simplifications lead to the equation

$$\Delta \Sigma = L (\Delta \delta + \Delta \Lambda \, \Lambda^{-1} \delta) L^+ + \Delta L \, \delta \, L^+ \\ - L \, \delta \, \Lambda \, L^{-1} \, \Delta L \Lambda^{-1} \, L^+ \, . \quad (71)$$

(i) First Approximation

The assumption that $\Delta L = 0$, enables one to simplify Eq. (71) in the form

$$\Delta \Sigma = L (\Delta \delta + \Delta \Lambda \, \Lambda^{-1} \delta) L^+ \, . \quad (72)$$

The parameter $\Delta \Sigma \, \Sigma^{-1}$ can again be expressed in the form

$$\Delta \Sigma \, \Sigma^{-1} = L (\Delta \delta \, \delta^{-1} + \Delta \Lambda \, \Lambda^{-1}) L^{-1} \, . \quad (73)$$

It is thus clear from Eq. (73) that if one considers the approximation $\Delta \Lambda$ diagonal, L is also the eigenvector matrix of the generally unsymmetrical $\Delta \Sigma \, \Sigma^{-1}$ matrix. The only difference in Eqs. (63) and (73) is that the eigenvalues are different.

(ii) Second Approximation

This approximation is to put the sum of the terms involving ΔL equal to zero in Eq. (69) that is

$$\Delta L \, L^{-1} \, \Sigma - \Sigma \, F \, \Delta L \, L^{-1} \, F^{-1} = 0 \, . \quad (74)$$

So, substituing the relations

$$\Sigma \, F = L \, \delta \, \Lambda \, L^{-1} \quad \text{and} \quad \Delta L = L^* - L$$

we get

$$(\delta \, \Lambda) \, (L^{-1} \, L^*) = (L^{-1} \, L^*) \, (\delta \, \Lambda) \, . \quad (75)$$

Equation (75) indicates that the matrices in brackets commute, and hence $(L^{-1} \, L^*)$ should be diagonal. The same result was shown to hold good for isotopic frequency shifts [see Equation (18)]. Hence, the discussion following Eq. (18) [see II.A (ii)] is valid in this case also.

3. Discussion and Conclusion

The present work includes an extensive discussion of the application of the first order perturbation theory for studying the mass effect on different molecular constants. Special emphasis is put on the mathematical and physical properties of various approximations. The success of the first order perturbation theory in studying the mass effect on molecular constants has already been demonstrated [1-9]. Because of the widespread application of this approach and since no complete discussion both from the mathematical and the physical point of view has so far been reported, we feel that our present study would be of use to the reader in understanding the significance of the various approximations along with their limitations. This work is also intended to be an ellaboration of our earlier works [8, 9] where only a limited set of approximate relations derived using the first approximation of the first order perturbation theory was considered; further the emphasis in our previous papers [8, 9] was more on the physical aspects of the numerical results, rather than on the mathematical properties of the solution.

Since, Eqs. (14) and (14) together constitute a new set of isotopic rules [the trace being derived from perturbation theory i. e. Eq. (14) and the product i. e. Eq. (15) being exact] we tried to estimate the utility of this approach in fixing the isotopic frequency shifts. The numerical values obtained in this way for a number of molecules (those cited in Ref. [8]) are found to be in poor agreement with the experimental data. Hence we conclude that it is better to use the relation $[\Delta \Lambda \, \Lambda^{-1}]_{ii} = [L^{-1} \, \Delta G (L^{-1})^+]_{ii}$ for estimating the frequency shifts as suggested by Wilson et al. [1]. However, the isotopic rule for Coriolis coupling constants derived from perturbation theory [see Eq. (47)] is in reasonably good agreement with the experimental

values. As the validity of any approximation (e. g. $\boldsymbol{\Delta L} = 0$) can be tested only numerically, one should be careful in using these approximations in general.

Finally we like to point out that the second approximation involving "$\boldsymbol{L}^{-1} \boldsymbol{L}^* = \text{diagonal}$" is more general than the usual one $\boldsymbol{\Delta L} = 0$. Further, this choice corresponds to a model of General Valence Force Field defined on the assumption that the $\boldsymbol{\Delta \Lambda}_{ii}$ calculated are extremal (and in particular minimal [16]).

[1] E. B. Wilson, J. C. Decius, and P. C. Cross, Molecular Vibrations, McGraw-Hill, New York 1955.
[2] I. M. Mills, J. Mol. Spectrosc. **5**, 334 [1960]; Erratum: ibid. **17**, 164 [1965].
[3] M. Tsuboi, J. Mol. Spectrosc. **19**, 4 [1966]; T. Shimanouchi, I. Nakagawa, J. Hirashi, and M. Ishi, J. Mol. Spectrosc. **19**, 78 [1966].
[4] T. Miyazawa, J. Mol. Spectrosc. **13**, 321 [1964]; T. Miyazawa and J. Overend, Bull. Chem. Soc. Japan **39**, 1410 [1966].
[5] G. Strey, J. Mol. Spectrosc. **17**, 265 [1965]; ibid. **19**, 229 [1966].
[6] Ch. V. S. Ramachandra Rao, J. Mol. Spectrosc. **41**, 105 [1972].
[7] B. Jordanov and B. Nikolova, J. Mol. Struct. **13**, 21 [1972].
[8] A. Müller, K. H. Schmidt, and N. Mohan, J. Chem. Phys. **57**, 1752 [1972].
[9] A. Müller and N. Mohan, J. Chem. Phys. **58**, 2994 [1973]; A. Müller, N. Mohan, and A. Alix, J. Chem. Phys., to be published.
[10] L. Mayants, Theoriya: Taschet Kolebaniy Molekul (Theory and Computation of Molecular Vibrations), Akad. Nauk. S.S.S.R. 1960.
[11] S. Brodersen and A. Langseth, J. Mol. Spectrosc. **3**, 114 [1959]; S. Brodersen and T. Johannesen, ibid. **23**, 293 [1967].
[12] L. M. Sverdlov, Opt. Spectrosc. **8**, 17 [1960].
[13] J. Heicklen, J. Chem. Phys. **36**, 721 [1962]/ J. Heicklen, J. Phys. Chem. **70**, 989 [1966].
[14] G. Strey, L. Cederbaum, and K. Engelke, J. Chem. Phys. **54**, 4402 [1971].
[15] R. E. Dewames and T. Wolfram, J. Chem. Phys. **40**, 853 [1964].
[16] B. Jordanov and B. Nikolova, J. Mol. Struct. **15**, 7 [1973]; A. Alix, B. Jordanov, and B. Nikolova, to be published; Yu. N. Panchenko, R. A. Munoz, N. F. Stepnov, and G. S. Koptev, J. Mol. Struct. **12**, 289 [1972].
[17] A. Müller, Z. Physik. Chem. **238**, 116 [1968]; C. J. Peacock and A. Müller, J. Mol. Spectrosc. **26**, 454 [1968]; C. J. Peacock, U. Heidborn, and A. Müller, J. Mol. Spectrosc. **30**, 345 [1969].
[18] A. Alix, These 3⁰ cycle, Reims 1970; A. Alix and L. Bernard, Z. Naturforsch. **27 a**, 593 [1972].
[19] J. M. Freeman and T. Henschall, J. Mol. Spectrosc. **25**, 101 [1968]; G. Keresztury and G. Jalsousky, J. Mol. Struct. **10**, 304 [1971].
[20] P. Pulay and F. Török, Acta Chim. Hung. **47**, 273 [1966]; A. Alix and L. Bernard, C. R. Acad. Sci. Paris **268 B**, 1307 [1969]; **269 B**, 812 [1969]; **270 B**, 66, 151 [1970].
[21] J. H. Meal and S. R. Polo, J. Chem. Phys. **24**, 1119 [1956].
[22] S. J. Cyvin, Molecular Vibrations and Mean Square Amplitudes, Universitets-forlaget, Oslo and Elsevier, Amsterdam 1968.

* Note in proofs:

Some equations were changed, they must read now:

(51) $$\Delta \zeta = [\boldsymbol{L}^{-1} \boldsymbol{\Delta C} (\boldsymbol{L}^{-1})^+] - [\boldsymbol{d}\zeta + \zeta \boldsymbol{d} - 2\,\zeta] \,.$$

(53) $$\boldsymbol{\Delta}^{-1} \boldsymbol{\Delta \Lambda} [\boldsymbol{E} - \zeta]^{-1} = [\boldsymbol{L}^{-1} \boldsymbol{\Delta K} (\boldsymbol{L}^{-1})^+ + \boldsymbol{\Delta}\zeta] + \ldots$$

(55) $$\boldsymbol{\Delta}^{-1} \boldsymbol{\Delta \Lambda} = [\boldsymbol{\Delta}\zeta + (\zeta \boldsymbol{d} - \boldsymbol{d}\zeta)] (\boldsymbol{E} - \zeta) = \ldots$$

(56) $$\boldsymbol{\Delta}\zeta = (\boldsymbol{\Delta \Lambda} \boldsymbol{\Lambda}^{-1}) (\boldsymbol{E} - \zeta) - (\zeta \boldsymbol{d} - \boldsymbol{d}\zeta)$$
$$= (\boldsymbol{d}^2 - \boldsymbol{E}) (\boldsymbol{E} - \zeta) + (\boldsymbol{d}\zeta - \zeta \boldsymbol{d}) \,.$$

(57) $$\boldsymbol{\Delta}\zeta_{ij} = (\Delta \lambda_i/\lambda_i) (\delta_{ij} - \zeta_{ij}) + \zeta_{ij} (\boldsymbol{d}_i - \boldsymbol{d}_j) \,.$$

(58) $$\boldsymbol{\Delta}\zeta_{ij} = (\Delta \lambda_i/\lambda_i) (1 - \zeta_{ii}) = (\boldsymbol{d}_i^2 - 1)(1 - \zeta_{ii})$$

(59) $$\boldsymbol{\Delta}\zeta_{11} = (\boldsymbol{d}_1^2 - 1 (1 - \zeta_{11}) = (\Delta \lambda_1/\lambda_1)(1 - \zeta_{11})$$