

# MIXING OF NORMAL VIBRATIONS AND ISOTOPIC FREQUENCY RULES FOR $X_3Y_4$ ( $D_{2d}$ Point Group) AND $XY_3Z_2$ ( $D_{3h}$ Point Group) MOLECULAR MODELS

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The method of Green's function analysis and the partitioning technique is used to derive the isotopic frequency rules for the  $X_3Y_4$  (allene) molecular model and the  $XY_3Z_2$  model. The choice of the mixing parameter matrix in the case of a secular equation of the order  $3 \times 3$  is investigated. The symmetrized force constants corresponding to two  $3 \times 3$  secular problems pertaining to the  $a_1$  and  $b_2$  species of allene are reported here. A few aspects of the difficulty of applying Green's function procedure to vibrational problems of order greater than  $2 \times 2$  are outlined from the point of view of the determination of the mixing parameter.

## 1. Introduction

The problems of normal coordinate analysis with elegant and unique solutions were shown to be possible by Green's function and partitioning techniques in the case of highly symmetric and simple molecules [1-4]. The type of molecules investigated by Wolfram *et al.* [1, 2] and Ramaswamy *et al.* [3, 4] belong to the group of highly symmetric molecules with an atom at the centre being common to the group of other atoms. In such cases, the evaluation of the isotopic frequency rules and their mass scaling become quite simple. However, it seems to be of interest to investigate the situations in which (i) there is a central atom common to a particular chromophoric group and (ii) when a particular atom forms the centre of two or three groups of atoms, whether or not the same mass scaling relations hold. In the case of molecules which are highly unsymmetric as in the case of linear  $XYZ$  type molecules, the isotopic rules may be formulated for the cases of  $X$ ,  $Y$  or  $Z$  atom substitutions [4].

Further, there is also the problem of the choice of the mixing parameter matrix, which is quite a task when the system involved is not highly symmetric or when the order of the secular equation is high. However, it would be quite appropriate to think of a method which would be applicable in general for the normal coordinate analysis of any molecular

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system. It is of interest to investigate the applicability of the method to the solution of a higher order equation. The present paper deals with the evaluation of the potential constants of the  $a_1$  and  $b_2$  species of allene. The potential constants for the  $e$  species were not evaluated because the choice of the mixing parameter becomes very difficult. The isotopic frequency rules for the various species are reported. The isotopic frequency rules for the  $XY_3Z_2$  molecular model are also given.

## 2. Normal coordinates

The construction of normal coordinates involves the construction of external symmetry coordinates and the choice of the mixing parameter matrix. The problem which presents itself is the choice of the mixing parameter matrix. Each normal mode of a particular species corresponds to a mixed representation of the different symmetry coordinates of the same species. A true representation of a particular normal coordinate will involve the correct choice of the mixing parameter matrix, which will be reflected in the values obtained for the various molecular constants.

The most general representation of the normal coordinate ( $Q_i$ ) is given by

$$Q_i = \sum_j a_{ij} S_j^E \quad (1)$$

where  $S_j^E$  represents the  $j^{\text{th}}$  external symmetry coordinate and  $a_{ij}$  is the mixing coefficient. The summation is over all the  $3n$  cartesian symmetry coordinates corresponding to the vibrations in the particular irreducible representation. Since the normal coordinates have to be orthonormalized, the relations

$$Q_i^2 = 1 \quad (2)$$

and

$$Q_i, Q_k = 0, \quad i \neq k \quad (3)$$

form the additional conditions in the choice of  $Q^s$ .

In the practical calculations, a suitable choice of the mixing parameter is made, making use of the orthonormalization condition and the nature of the relative mixing of the various methods. When there are two vibrations in a particular species, the relative mixing of the two symmetry coordinates can be represented in terms of a single parameter. This type of problem is encountered in the type  $XY_2$  bent symmetrical  $XY_3$  planar,  $XY_3$  pyramidal,  $XY_4$  tetrahedral *etc.* molecular models (complete reference in Ref. [4]).

The allene molecule belongs to the  $D_{2d}$  point group. The internal coordinates for the vibrations of  $a_1$  and  $b_2$  species of allene vibrations are represented in Fig. 1. The vibrations of this molecule are classified according to the irreducible representation

$$\tau = 3a_1 + b_1 + 3b_2 + 4e$$

The  $a_1$  and  $b_2$  species of allene provide the vibrational problem of the order  $3 \times 3$ . In the case of the situation involving a problem of order greater than two, different types of mixing involving (i) a single mixing parameter (ii) two mixing parameters and (iii) three

or more parameters become conceivable (depending upon the order of the problem involved). As simple examples the following three sets of linear combinations may be visualized.

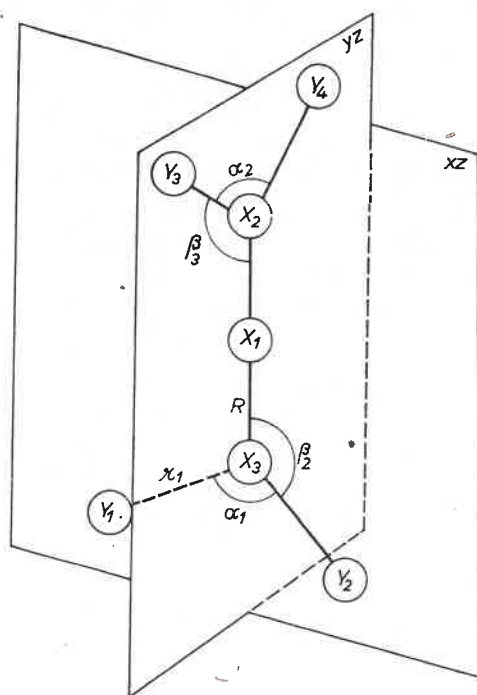


Fig. 1. Internal coordinates for  $a_1$  and  $b_2$  species vibrations of allene ( $X_3Y_4$ ) model

Set (i)

$$\begin{aligned}
 Q_1 &= (a_1 S_1^E + S_2^E - S_3^E) (a_1^2 + 2)^{-1/2} \\
 Q_2 &= (2S_1^E - a_1 S_2^E + a_1 S_3^E) \{2(a_1^2 + 2)\}^{-1/2} \\
 Q_3 &= (S_2^E + S_3^E) 2^{-1/2}
 \end{aligned} \tag{4}$$

Set (ii)

$$\begin{aligned}
 Q_1 &= (aS_1^E + \sqrt{2ab} S_2^E + bS_3^E) (a+b)^{-1} \\
 Q_2 &= (bS_1^E - \sqrt{2ab} S_2^E + aS_3^E) (a+b)^{-1} \\
 Q_3 &= \left( S_1^E + \frac{(b-a)}{\sqrt{2ab}} S_2^E - S_3^E \right) \left( \frac{a+b}{\sqrt{2ab}} \right)^{-1}
 \end{aligned} \tag{5}$$

Set (iii)

$$\begin{aligned}
 Q_1 &= (\sqrt{2a'b'} S_1^E + a' S_2^E + b' S_3^E) (a' + b')^{-1} \\
 Q_2 &= (\sqrt{2a'b'} S_1^E - b' S_2^E - a' S_3^E) (a' + b')^{-1} \\
 Q_3 &= \left( \frac{b' - a'}{\sqrt{2a'b'}} S_1^E + S_2^E - S_3^E \right) \left( \frac{a' + b'}{\sqrt{2a'b'}} \right)^{-1}
 \end{aligned} \tag{6}$$

Set (iv)

$$\begin{aligned}
 Q_1 &= (a_2 S_1^E + S_2^E) (a_2^2 + 1)^{-1/2} \\
 Q_2 &= (S_1^E - a_2 S_2^E) (a_2^2 + 1)^{-1/2} \\
 Q_3 &= S_3^E
 \end{aligned} \tag{7}$$

$Q_1$  — CH symm. stretch;  $Q_2$  — CH symm. deform.;  $Q_3$  — CC symm. stretch.

The above linear combinations represent the arbitrariness in the choice of the mixing parameter. In set (i)  $S_2^E$  and  $S_3^E$  are taken to be mixed in equal proportions in each  $Q$ . In set (iv) the  $\text{CH}_2$  symmetry stretching and bending are mixed relative to each other, while the  $\text{C} = \text{C}$  stretching represented by  $Q_3$  is assumed to be an uncoupled vibration. The sets (ii) and (iii) introduce additional constraints on the sign of  $a$  and  $b$ , viz. both should either be positive or negative.

The different linear combinations or any number of linear combinations of symmetry coordinates forming the normal coordinates seems to complicate the problem of the exact representation of the true situation. However, the choice can be made exact by calculating the different molecular constants and by testing the reproducibility of the experimental results. This explains clearly the difficulty involved in the choice of the coefficients of the different symmetry modes in the representation of the various normal modes of vibrations. A similar difficulty arises for the case of the  $b_2$  species also and hence similar linear combinations are chosen. These are

Set (i)

$$\begin{aligned}
 Q_5 &= (c_1 S_5^E + d_1 S_7^E) (c_1^2 + d_1^2)^{-1/2} \\
 Q_6 &= S_6^E \\
 Q_7 &= (d_1 S_5^E - c_1 S_7^E) (c_1^2 + d_1^2)^{-1/2}
 \end{aligned} \tag{8}$$

Set (ii)

$$\begin{aligned}
 Q_5 &= (\sqrt{2cd} S_5^E + S_6^E - dS_7^E) (c+d)^{-1} \\
 Q_6 &= \left( \frac{d-c}{\sqrt{2cd}} S_5^E - dS_6^E - cS_7^E \right) \left( \frac{c+d}{\sqrt{2cd}} \right)^{-1} \\
 Q_7 &= (\sqrt{2c'd'} S_5^E - dS_6^E - cS_7^E) (c+d)^{-1}
 \end{aligned} \tag{9}$$

Set (iii)

$$\begin{aligned}
 Q_5 &= (\sqrt{2c'd'} S_5^E + S_6^E + dS_7^E) (c+d)^{-1} \\
 Q_6 &= (\sqrt{2c'd'} S_5^E + dS_6^E - cS_7^E) (c+d)^{-1} \\
 Q_7 &= \left( \frac{d'-c'}{\sqrt{2c'd'}} S_5^E + S_6^E - S_7^E \right) \left( \frac{c'+d'}{\sqrt{2c'd'}} \right)^{-1}
 \end{aligned} \tag{10}$$

$Q_5$  — CH asymmetric stretch;

$Q_6$  — CC asymmetric stretch and

$Q_7$  — CH asymmetric bend.

The  $b_1$  vibration is uniquely represented by  $S_4^E$ .

The choice of the linear combination of the normal vibrations of the  $e$  species becomes still more difficult. However, the following combinations may be possible. The mixing between ( $\nu$  CH) and  $\delta(\text{CH}_2)$  is comparable. Similarly mixing between  $\text{CH}_2$  wagging and twisting vibrations may also be conceived. These are represented as

$$\begin{aligned} Q_{8\alpha} &= (S_{8\alpha}^E + gS_{9\alpha}^E)(1 + g^2)^{-1/2} \\ Q_{9\alpha} &= (gS_{8\alpha}^E - S_{9\alpha}^E)(1 + g^2)^{-1/2} \\ Q_{10\alpha} &= (S_{10\alpha}^E + g'S_{11\alpha}^E)(1 + g'^2)^{-1/2} \\ Q_{11\alpha} &= (g'S_{10\alpha}^E + S_{11\alpha}^E)(1 + g'^2)^{-1/2} \end{aligned} \quad (11)$$

where  $\alpha$  represents  $a$  or  $b$  corresponding to the degenerate species;  $g$  and  $g'$  are the mixing coefficients. The most general linear combinations may also be chosen with the proper orthonormalization conditions. A suitable choice of linear combinations of the symmetry coordinates is made for the normal coordinate representation and the normal coordinate transformation matrix [3, 4] can be formed.

#### $XY_3Z_2$ molecular model

The trigonal bipyramidal molecules of the  $XY_3Z_2$  molecular model correspond to the point group  $D_{3h}$ ; Fig. 2 represents the position of the various atoms in the  $XY_3Z_2$  trigonal bipyramidal model and the choice of the Cartesian axes. The various vibrations of

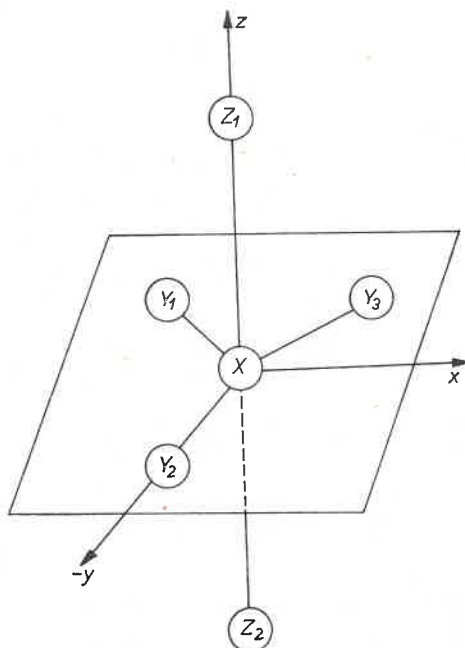


Fig. 2. Choice of Cartesian axes and  $XY_3Z_2$  molecular model

the above model fall under the representation

$$\tau = 2a_1 + 2a_2 + 3e' + e''.$$

The normal coordinates ( $Q$ ) for the  $a_1$  and  $a_2$  species can be written as  
For the  $a_1$  species

$$\begin{aligned} Q_1 &= (S_1^E + pS_2^E)(1+p^2)^{-1/2} \\ Q_2 &= pS_1^E - S_2^E)(1+p^2)^{-1/2} \end{aligned} \quad (12)$$

For the  $a_2$  species

$$\begin{aligned} Q_3 &= (qS_3^E + S_4^E)(1+q^2)^{-1/2} \\ Q_4 &= (S_3^E - qS_4^E)(1+q^2)^{-1/2} \end{aligned} \quad (13)$$

where  $p$  and  $q$  are the parameters representing the mixing. The  $e''$  vibrations will be represented as

$$Q_{8\beta} = S_{8\beta}^E \quad (14)$$

where  $\beta = a$  or  $b$  defining the two vibrations belonging to the doubly degenerate normal mode of the particular frequency. The choice of the linear combination of the external symmetry coordinates in the case of  $e''$  species present the same difficulty as in the case of the  $a_1$  or  $b_2$  species vibrations of allene. It is quite possible to choose a suitable linear combination by making use of the complete vibrational data for the molecule and verifying the reproducibility of all the molecular constants.

### 3. Isotopic frequency rules

The isotopically substituted molecule is treated as a perturbed system and the secular determinantal equation [1]

$$|\varepsilon\omega^2G(\omega^2) + I| = 0 \quad (15)$$

is solved to obtain the isotopic frequency relation. The isotopic frequency product rules are uniquely defined, while the sum rule, the sum of two by two products *etc.* which explains the nature of mixing of the molecular vibration, vary with the different choices of linear combinations.

For allene:

The isotopic product rule obtained for different substitutions for the different species of the vibrations of allene are given as:

For central atom substitution:

For the  $a_1$  species

$$\frac{\omega_1^2 \omega_2^2 \omega_3^2}{\omega_1^2 \omega_2^2 \omega_3^2} = \left( \frac{1}{\varepsilon} + \frac{m_C}{M} \right) / \left( \frac{1}{\varepsilon} + \frac{m_C}{M} + \frac{1}{2} \right) \quad (16)$$

For the  $b_2$  species

$$\frac{\omega_5^{i2}\omega_6^{i2}\omega_7^{i2}}{\omega_5^2\omega_6^2\omega_7^2} = \left(\frac{1}{\varepsilon} + \frac{m_C}{M}\right) / \left(\frac{1}{\varepsilon} + 1\right) \quad (17)$$

and for the  $e$  species

$$\frac{\omega_8^{i2}\omega_9^{i2}\omega_{10}^{i2}\omega_{11}^{i2}}{\omega_8^2\omega_9^2\omega_{10}^2\omega_{11}^2} = \left(\frac{1}{\varepsilon} + \frac{m_C}{M}\right) / \left(\frac{1}{\varepsilon} + 1\right) \quad (18)$$

where  $\varepsilon = \frac{M_C^i - M_C}{M_C}$  in which  $M_C$  and  $M_C^i$  are the masses of the carbon atom and its isotope.

$$M = 3M_C + 4M_H,$$

$M_H$  being the mass of the Hydrogen atom.

The isotopic rules for the symmetric substitution (allene- $d_0$  to allene- $d_4$ ) are obtained from the above rules by the following procedure. The allene molecule can be considered to be of the form  $YCY$ , where the  $Y$ 's refers to the end methylene groups. In the case of the symmetric substitution, the isotopic rules have to be modified by using the mass scaling factor. This mass scaling factor can be written in terms of the reduced mass of  $CH_2$  and the substituted  $CD_2$  groups. In the isotopic frequency rules  $M_C$  is replaced by

$$M_C \frac{{}^{\mu}CD_2}{{}^{\mu}CH_2}, \quad M_C^i \text{ by } M_C; \quad \text{and } \omega_j^2 \text{ by } \omega_j^2 \frac{{}^{\mu}CH_2}{{}^{\mu}CD_2}.$$

Then,

$$\varepsilon = \frac{{}^{\mu}CH_2 - {}^{\mu}CD_2}{{}^{\mu}CD_2}$$

where

$${}^{\mu}CH_2 = \frac{2M_C M_H}{M_C + 2M_H}$$

and

$${}^{\mu}CD_2 = \frac{2M_C M_D}{M_C + 2M_D}$$

in which  $M_C$ ,  $M_H$  and  $M_D$  refer to the masses of the carbon, hydrogen and deuterium atoms. The isotopic product rules were found to be well reproduced for the allene- $d_0$  and allene- $d_4$  substitution. The vibrational data were taken from the Infrared work of Lord and Venkateswarlu [5], liquid phase Raman work of Lord and Ocampo [6] and the gas phase Raman Spectra of Brødersen and Richardson [7]. The vibrational data used

in the calculations and the isotopic rules for the non-degenerate vibrations ( $a_1$  and  $b_2$  species) of allene are given in Table I.

TABLE I

Vibrational wavenumbers (in  $\text{cm}^{-1}$ ), internuclear separations (in  $\text{\AA}$ ), interbond angles and isotopic product rules for allene (References [5, 6, 7] and [10])

$$r_{\text{CH}} = 1.061 \text{ \AA}; R_{\text{CC}} = 1.309 \text{ \AA}; \widehat{\text{HCH}} = 116^\circ 30'$$

Species	Wave number symbol	Vibrational wavenumbers (in $\text{cm}^{-1}$ )		Isotopic product rule	
		Allene $d_0$	Allene $d_4$	Observed	Calculated
$a_1$	$\omega_1$	3015.0	2195	0.2550	0.2515
	$\omega_2$	1442.6	1228		
	$\omega_3$	1072.6	874		
$b_2$	$\omega_5$	3006.8	2230	0.2899	0.2885
	$\omega_6$	1957.0	1921		
	$\omega_7$	1398.0	1034		

For  $XY_3Z_2$  molecular model

In the case of the symmetric vibration, for the central ( $X$ ) atom substitution, direct mass scaling is sufficient. For  $a_2'$  species for the central atom substitution, the isotopic rules are

$$\frac{\omega_3^{i^2} \omega_4^{i^2}}{\omega_3^2 \omega_4^2} = \left( \frac{1}{\varepsilon} + \frac{M_x}{M} \right) / \left( \frac{1}{\varepsilon} + 1 \right) \quad (19)$$

and

$$\begin{aligned} \omega_3^{i^2} + \omega_4^{i^2} = & \left\{ \left( \frac{1}{\varepsilon} + \frac{M_x}{M} \right) (\omega_3^2 + \omega_4^2) (1 + q^2) + \right. \\ & \left. + \frac{m}{M} (\omega_4^2 + q^2 \omega_3^2) \right\} / \left( \frac{1}{\varepsilon} + 1 \right) (1 + q^2) \end{aligned} \quad (20)$$

where  $m = 2M_z + 3M_Y$ ;  $M = M_x + 3M_Y + 2M_z$ ,  $M_x$ ,  $M_Y$  and  $M_z$  being the masses of  $X$ ,  $Y$  and  $Z$  atoms.  $q$  is the mixing parameter defined in an earlier Section. The isotopic product rules for the  $e$  species are given by

$$\frac{\omega_5^{i^2} \omega_6^{i^2} \omega_7^{i^2}}{\omega_5^2 \omega_6^2 \omega_7^2} = \left( \frac{1}{\varepsilon} + \frac{M_x}{M} \right) / \left( \frac{1}{\varepsilon} + 1 \right) \quad (21)$$

In the isotopic rules defined by equations (19), (20) and (21)  $\varepsilon = M_x^i - M_x / M_x$  where  $i$  refers to the isotope.



The isotopic product rules for the simultaneous symmetric substitution of  $Z$  atoms are

$$\frac{\omega_1^{i2}\omega_2^{i2}\omega_3^{i2}\omega_4^{i2}}{\omega_1^2\omega_2^2\omega_3^2\omega_4^2} = \left(\frac{1}{\varepsilon} + \frac{M_z}{M}\right) \left/ \left(\frac{1}{\varepsilon} + 1\right)\right. \quad (22)$$

and

$$\frac{\omega_5^{i2}\omega_6^{i2}\omega_7^{i2}\omega_8^{i2}}{\omega_5^2\omega_6^2\omega_7^2\omega_8^2} = \left(\frac{1}{\varepsilon} + \frac{M_z}{M} + \frac{M_z R^2}{I_x}\right) \left/ \left(\frac{1}{\varepsilon} + 1\right)\right. \quad (23)$$

in which  $R$  is the  $X-Z$  bond distance and  $I_x = 3/2M_y r^2 + 2M_z R^2$ ,  $r$  being the  $X-Y$  bond distance.

The product rules which have been obtained here are essentially similar to the Teller-Redlich product rules [8]. The isotopic product rules cannot be verified to any specific case of  $XY_3Z_2$  type molecule because of the lack of vibrational isotopic data.

#### 4. Potential energy and constants and multiplicity of solutions

The evaluation of the potential energy constants and other molecular constants involves the determination of Wilson's dynamical  $L$  matrix [9] which is defined in terms of the  $B$  matrix and the mixing parameter matrix as [4]

$$L = B\dot{A} \quad (24)$$

in which  $B$  is defined by

$$B = UDS \quad (25)$$

where  $U$  is the transformation from internal to internal symmetry coordinates,  $D$  is the transformation from Cartesian to internal coordinates and  $S$  is the matrix of transformation between external symmetry coordinates and Cartesian coordinates. The matrix  $B$  satisfies the condition that  $B\dot{B} = G$ , in which  $G$  is the Inverse Kinetic Energy matrix [9].

For a particular set of internal symmetry coordinates, it is quite possible to obtain various  $B$  matrices for a particular species for the particular molecular model, because of the different choices of representation for the transformation from (external) Cartesian symmetry coordinates to Cartesian coordinates. This leads to multiple  $B$  matrices. These considerations regarding the construction of the external symmetry coordinates lead to the conclusion that multiple representations for normal coordinates as linear combinations of external symmetry coordinates are possible. Of all the linear combinations of a particular set of Cartesian symmetry coordinates only a particular linear combination will satisfy the dynamics of the molecule, which will be reflected in the reproducibility of the exact set of all the molecular constants.

Choosing various linear combinations of Cartesian symmetry coordinates, the mixing parameters and hence the potential constants can be determined. All the constants obtained for different sets will not be coincident. Model calculations have been performed for specific cases of the  $a_1$  and  $b_2$  species vibrations of the allene molecule by taking dif-

ferent linear combinations, and they are given in Table II. The problem of the choice of linear combination for the  $4 \times 4$  case of  $e$  species becomes still more difficult. The potential constants for  $XY_3Z_2$  types could not be evaluated because of lack of vibrational isotopic data.

TABLE II  
Symmetrized "F" matrix elements for the  $a_1$  and  $b_2$  species vibrations for different sets of representations (linear combinations)<sup>1</sup>

Species	$a_1$ species	$F_{11}$	$F_{22}$	$F_{33}$	$F_{12}$	$F_{13}$	$F_{23}$
	$F'$ elements						
	$b_2$ species	$F_{55}$	$F_{77}$	$F_{66}$	$F_{57}$	$F_{56}$	$F_{67}$
$a_1$	(i)	5.306	0.590	12.347	-0.468	-2.808	0.546
	(ii)	4.789	0.638	10.860	-0.648	-2.011	0.537
	(iii)	5.164	0.422	11.172	-0.615	-2.968	0.949
$b_2$	(i)	4.959	0.698	9.575	-0.555	-1.527	0.510
	(ii)	5.234	1.001	8.622	-0.636	-0.464	1.589
	(iii)	6.168	0.934	8.612	-0.169	-1.781	1.713

<sup>1</sup> (i), (ii) and (iii) refer to the linear combinations given in the Section 2.

### 5. Discussion

The symmetrized force constant elements for  $a_1$  and  $b_2$  species of allene evaluated in the present investigation are found to show internal consistency for the different choices of mixing parameters. The constants from the various sets provide a range of values. The range of values for  $F_{11}$  (CH stretch-symm.) obtained as 4.789 m dynes/Å to 5.306 m dynes/Å and for  $F_{55}$  (CH asymm. stretch) obtained as 4.959 m dynes/Å to 6.168 m dynes/Å are quite consistent with the value of 5.122 m dynes/Å (for both species reported by Fletcher and Thompson [10] in their HOFF studies on  $CH_2X$  type molecules. The symmetrized  $F$  elements for CC stretching and CH bending modes obtained here are comparable with the force field studies by Shuler and Fletcher [11], Fletcher and Thompson [10], Venkateswarlu and Krishnapillai [12] and Cyvin [13]. However, an exact comparison is not possible because the methods adopted by the earlier workers were either of the non-iterative type involving high approximations or of the iterative type taking into account some constraints.

Whereas Cyvin [13] considers "the approximate separation of  $CX$  stretching frequencies", Fletcher and Thompson [10] in their application of HOFF to allene treated the terminal  $CH_2$  groups as independent since they are separated by the central carbon atom and assumed  $F_{11} = F_{55}$ ,  $F_{22} = F_{77}$ ,  $F_{12} = F_{57}$ ,  $F_{23} = F_{67}$ . Fletcher and Thompson also assumed zero interaction between the CH stretching and CC stretching modes. Though this type of negligible interaction or zero interaction has been the conception of earlier workers for  $F(\nu CH, \nu CC)$ , the vibrational analysis of ethylene [14] showed a large

negative value for the  $F(\nu\text{CH}, \nu\text{CC})$  of the  $a_{1g}$  species. The range of values obtained for  $F(\nu\text{CH}, \nu\text{CC})$  in the present investigation as  $-2.011$  m dynes/Å to  $-2.968$  m dynes/Å for  $a_1$  species is quite consistent with the value of  $-2.384$  m dynes/Å reported for ethylene [14]. For the  $b_2$  species a negative value is also obtained for the interaction  $F(\nu\text{CH}, \nu\text{CC})$ .

With regard to the exact set of force constant elements, it is found that the sets (ii) and (iii) for the  $a_1$  species and the sets (i) and (iii) for the  $b_2$  species are closer to the correct representation of the vibrations of allene. The constants in the set (ii) of  $a_1$  species and (i) of  $b_2$  species show internal consistency. The set of constants (iii) of  $a_1$  species and (i) of  $b_2$  species are also found to be consistent except for a slight discrepancy. It is quite appropriate to have the set of constants (ii) of  $a_1$  species and (i) of  $b_2$  species or (iii) of  $a_1$  species and (i) of  $b_2$  species.

The above results lead to some of the following observations regarding the applicability of Green's function procedure to the problem of molecular dynamics in the vibrational analysis using isotopic data. The choice of the linear combinations of the external symmetry coordinates for the normal coordinate representation depends upon the relative mixing of the different symmetry modes. Various linear combinations of Cartesian coordinates are possible in the definition of symmetry coordinates and, hence, different choices of mixing. For a problem of  $n^{\text{th}}$  order,  $n^2$  coefficients will represent the mixing of the different vibrations. There are  $n(n-1)/2$  relations for representing the orthogonality of the modes and  $n$  equations as the normalization conditions, which finally reduce the number of parameters to be determined to  $n(n+1)/2$ .

The isotopic product rules for the vibrational frequencies are essentially identical with the Teller-Redlich product rule [8]. The type of mass scaling depends upon the particular molecular system and the configuration of the atoms in the molecule as such. It should be such as to verify the experimentally observed isotopic product rule exactly. It is also found that multiple solutions become possible because of the multiplicity of representations of symmetry coordinates and, hence, the normal modes.

In general, the above considerations result in the conclusion that the problem of vibrational analysis becomes quite a task for large molecules involving higher order systems because of the multiplicity of solutions. However, the most general linear combinations can be assumed, and the coefficients of mixing can be obtained for the various normal modes. The study of Green's function analysis of molecules involving one common centre (central atom), two centres *etc.*, is being investigated presently, taking the most general linear combinations. Results will be published in due course.

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