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Spectroscopic Studies on $X(YZ)_3$ Type Molecules

II. Application of Complex Symmetry Coordinates to Molecular Vibrations of Boric Acid with Symmetry C_{3h}

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Molecular vibrations of the boric acid model, $X(YZ)_3$, of symmetry C_{3h} are treated theoretically. Complex symmetry coordinates have been introduced in the doubly degenerate species E'. An extension of the **GF** matrix theory from Wilson, Decius and Cross to the case of complex matrices is applied. Also reported is a method for solving the secular equation $\mathbf{GFL} = \mathbf{L}\Lambda$ in terms of real numbers, convenient for machine solution. In this method the complex matrices are represented by real matrices twice the usual size.

I. INTRODUCTION

Molecules having equivalent atoms that may be interchanged with one another by only proper or improper rotations about a fixed axis fall into the C_n and S_n point groups. The C_{nh} symmetry groups differ only from C_n groups by the addition of a horizontal reflection plane perpendicular to the rotation axis. These three types of groups, viz. C_n, S_n, and C_{nh}, are the only Abelian groups among the chemically important symmetry groups, and they also share the common characteristic that they are the only groups whose character tables contain complex numbers. Their complex characters arise necessarily from the purely cyclic nature of the C_n and S_n groups and the predominantly cyclic nature of the C_{nh} groups.

It is difficult to find examples of molecules with structures belonging to one of the Abelian groups. Therefore it is natural that almost no work has been done on the molecular vibrations of such molecules. In fact we have found only one paper among the vast number of works based on the Wilson

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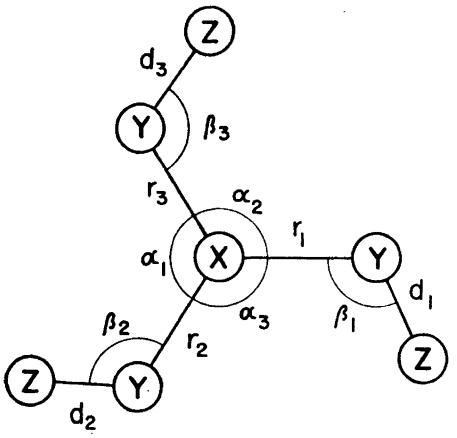

Fig. 1. Planar $X(YZ)_3$ molecular model of symmetry C_{3h}. In-plane valence coordinates are given.

GF matrix method.[1] This paper concerns isolated molecules of boric acid, which have been assigned to a planar molecular model of symmetry C_{3h}, and treated incorrectly by Pistorius.[2] In the present work we point out some of the special features arising from the complex numbers of the character table, and give a mathematically correct normal-coordinate analysis of the boric acid molecular model. Hereby a set of complex coordinates are utilized in the Wilson **GF** matrix method probably for the first time, although the methods are well known from other fields of applied mathematics.

II. MOLECULAR MODEL

The planar $X(YZ)_3$ molecular model of symmetry C_{3h} here considered, is shown in Fig. 1. As valence coordinates we use ($i = 1, 2, 3$) *

d_i for YZ stretchings,
r_i for XY stretchings,
Ra_i for YXY bendings,
$(RD)^{\frac{1}{2}}\ \beta_i$ for XYZ bendings,
$R\gamma_i$ for out-of-plane bendings, and
$(RD)^{\frac{1}{2}}\ \tau_i$ for torsions.

These coordinates differ only in trivial changes of notation from those defined by Pistorius.[2] We use R and D to denote the equilibrium distances of XY and YZ, respectively. The equilibrium XYZ interbond angle will be identified by the symbol B.

* It should be noted that the introduction of three out-of-plane bendings $R\gamma_i$ as done by Pistorius [2] is quite unnecessary. It has only formal meaning because all of the coordinates γ_1, γ_2, and γ_3 are identical! They are given in terms of the out-of-plane cartesian displacements by

$$R\gamma_i = z_4 + z_5 + z_6 - 3z_7$$

Consequently two of the redundant conditions as given by Pistorius [2] are trivial and could easily be avoided. The only unavoidable redundancy is the familiar one which occurs among the α coordinates.

Before proceeding further it is instructive to compare the treatment of an X(YZ)$_3$ planar molecule of symmetry D_{3h} having a linear X—Y—Z bond to the case here considered, namely an X(YZ)$_3$ molecule with C_{3h} symmetry because of the angle B ($\neq 180°$) formed by the X—Y—Z atoms. The planar X(YZ)$_3$ molecule of D_{3h} gives rise to vibrations having the representation

$$\Gamma_{vib}(D_{3h}) = 2\,A_1' + A_2' + 2\,A_2'' + 4\,E' + E''$$

A choice of symmetry coordinates which transform according to the requirements of symmetry group D_{3h} is readily made to give an orthogonal **U** matrix (**S** = **UR**). The resulting **G** matrix shows no abnormalities. The symmetry coordinates given by Pistorius [2] are in fact those that, with minor rearrangements and changes of sign, would be suitable coordinates for group D_{3h}.

The planar X(YZ)$_3$ molecule of the symmetry C_{3h} gives rise to vibrations having the representation

$$\Gamma_{vib}(C_{3h}) = 3\,A' + 2\,A'' + 4\,E' + E''$$

An inspection of the character tables of D_{3h} and C_{3h} given in Table 1 shows that A_1' of D_{3h} and A' of C_{3h} transform similarly as do A_1'' of D_{3h} and A'' of C_{3h}. However, the doubly degenerate E representations are quite different since E' of D_{3h} is a two-dimensional representation with real characters while E' of C_{3h} is equivalent to two one-dimensional representations including imaginary numbers for characters. The situation is similar for the E'' representations.

A simple addition of the two one-dimensional representations of E' (C_{3h}) yields real characters which are identical to the characters of corresponding operations in point group D_{3h}. The real coordinates based upon these real characters will yield satisfactory results for the A' and A'' species because

Table 1. Character tables for the symmetry groups D_{3h} and C_{3h}. $\varepsilon = \exp(2\pi i/3)$.

D_{3h}	E	$2C_3$	$3C_2$	σ_h	$2S_3$	$3\sigma_v$
A_1'	1	1	1	1	1	1
A_2'	1	1	−1	1	1	−1
E'	2	−1	0	2	−1	0
A_1''	1	1	1	−1	−1	−1
A_2''	1	1	−1	−1	−1	1
E''	2	−1	0	−2	1	0

C_{3h}	E	C_3	C_3^2	σ_h	S_3	S_3^5
A'	1	1	1	1	1	1
E'	1	ε	ε^*	1	ε	ε^*
	1	ε^*	ε	1	ε^*	ε
A''	1	1	1	−1	−1	−1
E''	1	ε	ε^*	−1	$-\varepsilon$	$-\varepsilon^*$
	1	ε^*	ε	−1	$-\varepsilon^*$	$-\varepsilon$

of their direct correspondence in the groups C_{3h} and D_{3h}. Also by virtue of the fact that the E'' species contains only one degenerate symmetry coordinate in the present case, it appears that the corresponding **F** and **G** matrix elements must be real, and the real coordinates as chosen by Pistorius are satisfactory for E'' as well.

III. NON-DEGENERATE SPECIES AND SPECIES E''

The applied symmetry coordinates belonging to the species A', A'', and E'' are real and identical to those of Pistorius.[2] They are given below in our notation.

$$\begin{aligned}
\text{Species } A': \quad S_1 &= 3^{-\frac{1}{2}}\,(d_1 + d_2 + d_3)\\
S_2 &= 3^{-\frac{1}{2}}\,(r_1 + r_2 + r_3)\\
S_3 &= 3^{-\frac{1}{2}}\,(RD)^{\frac{1}{2}}\,(\beta_1 + \beta_2 + \beta_3)\\
\text{Species } A'': \quad S_4 &= 3^{-\frac{1}{2}}\,R(\gamma_1 + \gamma_2 + \gamma_3)\\
S_5 &= 3^{-\frac{1}{2}}\,(RD)^{\frac{1}{2}}\,(\tau_1 + \tau_2 + \tau_3)\\
\text{Species } E'': \quad S_{10a} &= 6^{-\frac{1}{2}}\,(RD)^{\frac{1}{2}}\,(2\tau_1 - \tau_2 - \tau_3)\\
S_{10b} &= 2^{-\frac{1}{2}}\,(RD)^{\frac{1}{2}}\,(\tau_2 - \tau_3)
\end{aligned}$$

Since we have found some computational errors or misprints in three of the expressions for the **G**-matrix elements given by Pistorius [2] for the out-of plane A'' and E'' species, the **G**-matrix elements as calculated herein are given below. The symbols μ_X, μ_Y, and μ_Z are as usual used to denote the inverse masses of the X, Y, and Z atoms, respectively.

$$(G_{ij} = G_{ji})$$

Species A':

$$G_{11} = \mu_Y + \mu_Z,\ G_{12} = \mu_Y\cos B,\ G_{13} = -\,(D/R)^{\frac{1}{2}}\,\mu_Y\sin B$$
$$G_{22} = \mu_Y,\ G_{23} = -\,(R/D)^{\frac{1}{2}}\,\mu_Y\,\sin B$$
$$G_{33} = [(R/D) + (D/R) - 2\cos B]\,\mu_Y + (R/D)\mu_Z$$

Species A'':

$$G_{44} = 27\,\mu_X + 9\mu_Y$$
$$G_{45} = -\,9(D/R)^{\frac{1}{2}}\,(3^{\frac{1}{2}} + \cot B)\,\mu_X - 3[(D/R)^{\frac{1}{2}}\,(3^{\frac{1}{2}} + \cot B) - (R/D)^{\frac{1}{2}}\,\mathrm{cosec}\,B]\,\mu_Y$$
$$G_{55} = 3(D/R)\,(3^{\frac{1}{2}} + \cot B)^2\,\mu_X + (R/D)\,(\mu_Z/\sin^2 B) + [(R/D) + (D/R) + 2(D/R)\sin B(3^{\frac{1}{2}}\cos B + \sin B) - 2(\cos B + 3^{\frac{1}{2}}\sin B)]\,(\mu_Y/\sin^2 B)$$

Species E'':

$$G_{10\,10} = \{(D/R)\sin^2 B + [(R/D)^{\frac{1}{2}} - (D/R)^{\frac{1}{2}}\cos B]^2\}\,(\mu_Y/\sin^2 B) + (R/D)(\mu_Z/\sin^2 B)$$

IV. SPECIES E' IN TERMS OF COMPLEX COORDINATES

Two degenerate sets of complex symmetry coordinates of species E' have been constructed from the character table (*cf.* Table 1) including its complex number ε and ε^*, viz.

$$\varepsilon = \exp(2\pi i/3),\ \varepsilon^* = \exp(-2\pi i/3)$$

The resulting coordinates follow.

$$S_{6a} = 3^{-\frac{1}{2}}\ (d_1 + \varepsilon d_2 + \varepsilon^* d_3)$$
$$S_{7a} = 3^{-\frac{1}{2}}\ (r_1 + \varepsilon r_2 + \varepsilon^* r_3)$$
$$S_{8a} = 3^{-\frac{1}{2}}\ (R\alpha_1 + \varepsilon\alpha_2 + \varepsilon^*\alpha_3)$$
$$S_{9a} = 3^{-\frac{1}{2}}\ (RD)^{\frac{1}{2}}\ (\beta_1 + \varepsilon\beta_2 + \varepsilon^*\beta_3)$$

$$S_{6b} = 3^{-\frac{1}{2}}\ (d_1 + \varepsilon^* d_2 + \varepsilon d_3)$$
$$S_{7b} = 3^{-\frac{1}{2}}\ (r_1 + \varepsilon^* r_2 + \varepsilon r_3)$$
$$S_{8b} = 3^{-\frac{1}{2}}\ R(\alpha_1 + \varepsilon^*\alpha_2 + \varepsilon\alpha_3)$$
$$S_{9b} = 3^{-\frac{1}{2}}\ (RD)^{\frac{1}{2}}\ (\beta_1 + \varepsilon^*\beta_2 + \varepsilon\beta_3)$$

With these coordinates the **G** matrix diagonalizes properly. The E' blocks contain complex elements and are Hermitian rather than symmetric. The two blocks corresponding to the a and b coordinates are conjugate to each other, and all elements combining an a and b coordinate vanish. The elements are given explicity in the following.

$$(G_{ji} = G_{ij}^*)$$
$$G_{6a\ 6a} = G_{6b\ 6b} = \mu_Y + \mu_Z$$
$$G_{6a\ 7a} = G_{6b\ 7b} = \mu_Y \cos B$$
$$G_{6a\ 8a} = G_{6b\ 8b}^* = 3^{\frac{1}{2}} i\mu_Y \sin B$$
$$G_{6a\ 9a} = G_{9b\ 6b} = -\ (D/R)^{\frac{1}{2}}\ \mu_Y \sin B$$
$$G_{7a\ 7a} = G_{7b\ 7b} = \tfrac{3}{2}\mu_X + \mu_Y$$
$$G_{7a\ 8a} = G_{7b\ 8b} = \tfrac{3}{2} 3^{\frac{1}{2}} \mu_X$$
$$G_{7a\ 9a} = G_{7b\ 9b}^* = -\ (R/D)^{\frac{1}{2}}\ \mu_Y \sin B + \tfrac{3}{2}(D/R)^{\frac{1}{2}} i\mu_X$$
$$G_{8a\ 8a} = G_{8b\ 8b} = \tfrac{9}{2}\mu_X + 3\mu_Y$$
$$G_{8a\ 9a} = G_{8b\ 9b}^* = \tfrac{3}{2} 3^{\frac{1}{2}} (D/R)^{\frac{1}{2}}\ i\mu_X - 3^{\frac{1}{2}}[(R/D)^{\frac{1}{2}} \cos B - (D/R)^{\frac{1}{2}}] i\mu_Y$$
$$G_{9a\ 9a} = G_{9b\ 9b} = \tfrac{3}{2}(D/R)\mu_X + [(R/D) + (D/R) - 2\cos B]\ \mu_Y + (R/D)\mu_Z$$

V. CONNECTION TO A TREATMENT IN REAL COORDINATES

As stated above it is possible to construct a set of real coordinates based upon the real characters obtained by adding the two one-dimensional representations of E'. Pistorius [2] in fact has given such a set, which is connected with our complex coordinates by the unitary transformations

$$S_{ja} = 2^{-\frac{1}{2}}(\mathcal{S}_{ja} + i\mathcal{S}_{jb}),\ S_{jb} = 2^{-\frac{1}{2}}\ (\mathcal{S}_{ja} - i\mathcal{S}_{jb})$$

for $j = 6, 7, 8, 9$. Accordingly the real coordinates ($\mathcal{S}$) for the d-type (YZ stretching) taken as an example, are

$$\mathcal{S}_{6a} = 6^{-\frac{1}{2}}\ (2d_1 - d_2 - d_3),\ \mathcal{S}_{6b} = 2^{-\frac{1}{2}}\ (d_2 - d_3)$$

with the same combinations of r_i, $R\alpha_i$ and $(RD)^{\frac{1}{2}}\ \beta_i$ for the other types. It should be noted that similar sets of eight coordinates could be constructed in many various ways, each following the usual rules. One observes for instance that d_1, d_2, d_3, $(d_2 - d_3)$, *etc.*, all transform in the same way under the symmetry operations. The above set (and similar sets) of real coordinates $\mathcal{S}$ are however mathematically speaking not true symmetry coordinates since they do not form true degenerate sets. This statement becomes evident from the fact

that the corresponding **G** matrix does not block out properly, but contains nonvanishing elements for binary terms of the type $\mathcal{S}_{ia}\mathcal{S}_{jb}$. The resulting off-diagonal blocks have erroneously been omitted by Pistorius.[2] The part of the **G** matrix associated with the $\mathcal{S}$ coordinates specified above, shall here be referred to as $\mathcal{G}$. The elements of its diagonal blocks should be identical to those given by Pistorius,[2] but again some computational errors or misprints were found in that paper. The elements in question appear as the real parts of the **G**-matrix elements based on the complex coordinates introduced in Section IV. In fact one has

$$G_{ia\,ja} = G_{ib\,jb}{}^{*} = \mathcal{G}_{ia\,ja} - i\mathcal{G}_{ia\,jb}$$

A mapping of the real $\mathcal{G}$ matrix may be useful. Table 2 shows the zero elements obtained in the particular case here studied. It also shows some general properties: (a) Over-all symmetry; $\mathcal{G}_{ia\,ja} = \mathcal{G}_{ja\,ia}$, $\mathcal{G}_{ib\,jb} = \mathcal{G}_{jb\,ib}$, $\mathcal{G}_{ia\,jb} = \mathcal{G}_{jb\,ia}$, (b) Skew-symmetry of off-diagonal blocks; $\mathcal{G}_{ia\,jb} = -\mathcal{G}_{ja\,ib}$, (c) identity of diagonal blocks; $\mathcal{G}_{ia\,ja} = \mathcal{G}_{ib\,jb}$.

VI. WILSON'S METHOD IN TERMS OF COMPLEX COORDINATES

The familiar **GF** matrix method of Wilson [1] is straightforwardly extended to the general case of complex coordinates.* We use of course the usual real valence coordinates (**R**), but the **U** matrix of

$$\mathbf{S} = \mathbf{UR}$$

is now a unitary matrix rather than orthogonal. The **G** matrix is defined by

$$\mathbf{G} = \mathbf{BM}^{-1}\,\mathbf{B}^{\dagger}$$

where † denotes the associate matrix, and becomes the transpose in the real case. Here **B** is defined by

$$\mathbf{S} = \mathbf{BX}$$

Table 2. Mapping of the $\mathcal{G}$ matrix.[a]

	6*a*	7*a*	8*a*	9*a*	6*b*	7*b*	8*b*	9*b*
6*a*	*A*	*E*	0	*H*	0	0	*L*	0
7*a*	*E*	*B*	*F*	*G*	0	0	0	*M*
8*a*	0	*F*	*C*	0	−*L*	0	0	*K*
9*a*	*H*	*G*	0	*D*	0	−*M*	−*K*	0
6*b*	0	0	−*L*	0	*A*	*E*	0	*H*
7*b*	0	0	0	−*M*	*E*	*B*	*F*	*G*
8*b*	*L*	0	0	−K	0	*F*	*C*	0
9*b*	0	*M*	*K*	0	H	*G*	0	*D*

[a] The equations in Appendix VII and VIII of Ref. 2 are formulated in terms of the general complex matrices.

* Arithmetic expressions for the elements are found from Section IV with the aid of the relations in Section V.

where **X** represents the cartesian displacements as a real column matrix. **M** is a diagonal matrix containing the atomic masses. The kinetic (T) and potential (V) energies are given by the Hermitian forms

$$2T = \dot{\mathbf{S}}^{\dagger}\, \mathbf{G}^{-1}\, \dot{\mathbf{S}} \text{ and } 2V = \mathbf{S}^{\dagger}\, \mathbf{F}\, \mathbf{S}$$

respectively, and are consequently real. The secular equation

$$\mathbf{G}\, \mathbf{F}\, \mathbf{L} = \mathbf{L}\, \Lambda$$

is still valid even with the complex matrices. The characteristic values of **GF**, *viz.* the frequency parameters $\lambda_k = 4\pi^2\, c^2\, \omega_k^2$, are of course real. The normal-coordinate transformation matrix, **L**, satisfies the relations

$$\mathbf{S} = \mathbf{L}\, \mathbf{Q},\ \mathbf{L}\, \mathbf{L}^{\dagger} = \mathbf{G},\ \mathbf{L}\, \Lambda^{-1}\, \mathbf{L}^{\dagger} = \mathbf{F}^{-1}$$

VII. COMPUTATIONAL METHOD WITH REAL MATRICES

In the normal-coordinate analysis of the species E' for boric acid one may use a method of representing a complex matrix by a real matrix twice its size. The method may be adapted to ordinary computing programs scheduled for real cases. It is based on the following theorem:

The set of matrices of the form

$$\begin{bmatrix} a & b \\ -b & a \end{bmatrix},$$

where a and b are arbitrary real numbers, except $a = b = 0$, form a group with respect to matrix multiplication, which is isomorphic with the group of the complex numbers

$$a + i\, b$$

with respect to ordinary multiplication.

The theorem holds also for complex matrices

$$\mathbf{A} + i\mathbf{B},$$

which may be represented by the real matrices

$$\begin{bmatrix} \mathbf{A} & \mathbf{B} \\ -\mathbf{B} & \mathbf{A} \end{bmatrix}.$$

Accordingly we introduce the matrices

$$\mathcal{G} = \begin{bmatrix} \mathbf{G}_R & \mathbf{G}_I \\ -\mathbf{G}_I & \mathbf{G}_R \end{bmatrix}, \quad \mathcal{F} = \begin{bmatrix} \mathbf{F}_R & \mathbf{F}_I \\ -\mathbf{F}_I & \mathbf{F}_R \end{bmatrix}, \quad \mathcal{L} = \begin{bmatrix} \mathbf{L}_R & \mathbf{L}_I \\ -\mathbf{L}_I & \mathbf{L}_R \end{bmatrix}$$

in order to represent the corresponding complex matrices, *viz.*

$$\mathbf{G} = \mathbf{G}_R + i\mathbf{G}_I, \quad \mathbf{F} = \mathbf{F}_R + i\mathbf{F}_I, \quad \mathbf{L} = \mathbf{L}_R + i\mathbf{L}_I$$

Because of the Hermitian nature of **G** and **F**, the submatrices $\mathbf{G}_R$ and $\mathbf{F}_R$ are symmetric, while $\mathbf{G}_I$ and $\mathbf{F}_I$ are skew-symmetric. With these new matrices of twice the usual size, one has

$$\mathcal{L}\mathcal{L}' = \mathcal{G}, \qquad \mathcal{L}\,\mathrm{diag}\,(\Lambda^{-1}, \Lambda^{-1})\,\mathcal{L}' = \mathcal{F}^{-1}$$
$$\mathcal{G}\mathcal{F}\mathcal{L} = \mathcal{L}\,\mathrm{diag}\,(\Lambda, \Lambda)$$

These relations conform with the ordinary real case, only with the anomaly that each characteristic value (λ_k) occurs twice. $\mathcal{L}^{\sim\prime}$ denotes the transpose of $\mathcal{L}^{\sim}$, and

$$\mathrm{diag}\,(\Lambda, \Lambda) = \begin{bmatrix} \Lambda & \mathbf{0} \\ \mathbf{0} & \Lambda \end{bmatrix}$$

Let $\mathbf{G}_b$ denote the 4×4 matrix corresponding to the complex b-coordinates of species E' as defined in Section IV. Then the $\mathcal{G}$ matrix as defined here is found to be identical with the matrix of Sextion V designated by the same symbol. With this matrix it would be possible to solve the problem for the corresponding matrix of $\mathbf{L}_b$, provided a suitable set of force constants were known. Then the matrices associated to the a-coordinates would immediately be obtainable according to the relations

$$\mathbf{G}_a = \mathbf{G}_b^* \quad \mathbf{F}_a = \mathbf{F}_b^*, \quad \mathbf{L}_a = \mathbf{L}_b^*$$

REFERENCES

1. Wilson, E. B., Jr., Decius, J. C. and Cross, P. C. *Molecular Vibrations*, McGraw-Hill Book Co., New York 1955.
2. Pistorius, C. W. F. T. *J. Chem. Phys.* **31** (1959) 1454.

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