ACTA CHEMICA SCANDINAVICA 19 (1965) 1749–1754

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

Part III. Calculation of Force Constants and Fundamental Frequencies of Boric Acid

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The inclusion of imaginary elements in the **G** matrix resulting from the introduction of complex symmetry coordinates for species E' of boric acid produced significant changes in three of the four fundamental frequencies of this species. The changes in frequency calculated by perturbation theory and by the use of real matrices twice the size of the actual matrices containing imaginary elements were in good agreement. However the final **F** matrix giving optimum agreement with the experimental data was only very slightly changed from the matrix obtained by ignoring the imaginary elements. Calculation of valence type force constants showed a strong interaction between the B–O stretching vibrations.

I. INTRODUCTION

In the preceding paper of this series [1] the molecular vibrations of the boric acid model, $X(YZ)_3$, of symmetry C_{3h} were treated theoretically after introducing complex symmetry coordinates in the double degenerate species E' to obtain a **G** matrix which was correctly diagonalized. The complex symmetry coordinates gave a **G** matrix which was properly Hermitian, but since it contained imaginary elements, the numercial solution of the secular equation $\mathbf{GFL} = \mathbf{L}\Lambda$ was more complicated than usual. A method of solving this equation by representing the complex matrices by real matrices of twice the usual size was suggested and is herein employed to calculate new force constants for the boric acid molecule using the corrected **G** matrix elements previously given.[1]

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The fundamental frequencies of boric acid are taken from the published vibrational data of Servoss and Clark [2] and of Bethell and Sheppard [3] for $H_3{}^{11}BO_3$ and are therefore the same as those used by Pistorius [4] in the previous study of boric acid.

Table 1. Force constants of boric acid in units of 10^5 dynes cm^{-1}.

Species A'

F	1	2	3
1	5.896	0.070	−0.005
2		7.800	0.267
3	symmetrial		0.392

Species A''

F	4	5
4	0.134	0.076
5	0.076	0.169

Species E'

F	6	7	8	9
6	5.536	−0.019	−0.005	−0.008
7		4.913	−0.149	−0.065
8			0.650	−0.022
9	symmetrical			0.498

Species E''

$F_{10,10} = 0.012$

Table 2. Fundamental frequencies of boric acid in cm^{-1}.

Description	Designation	Symmetry type	$H_3{}^{11}BO_3$ (experimental)	$H_3{}^{11}BO_3$ (calculated)
O—H stretch	ν_1	A'	3250	3253
B—O stretch	ν_2		1060	1061
BOH bending	ν_3		881	882
BO_3 bending	ν_4	A''	648	649
OH torsion	ν_5		824	825
O—H stretch	ν_6	E'	3150	3153
B—O stretch	ν_7		1428	1429
OBO bending	ν_8		544	544
BOH bending	ν_9		1183	1184
OH torsion	ν_{10}	E''	209	209

II. CALCULATION OF L MATRIX AND F MATRIX NEGLECTING THE IMAGINARY PART OF THE G MATRIX

The first and simplest approach was to check the effect of the corrected real $\mathcal{G}$-matrix elements on the solution of the secular equation $\mathcal{G}\mathbf{FL} = \mathbf{L}\Lambda$ for the characteristic frequencies using the F matrix elements given by Pistorius.[4] The machine solution using a GIER-Algol program series for polyatomic molecules gave frequencies which were in serious disagreement with the calculated frequencies reported by Pistorius and also therefore in disagreement with the experimental ones. A new **F** matrix, as given in Table 1, was calculated which gave agreement with the experimentally observed frequencies as shown in Table 2. The **F** matrix elements as given in Table 1 are believed to be correct for species A', A'', and E'', but not necessarily for species E' since as a first approximation, only the real portion of the **G** matrix was used in the calculations.

III. EFFECT OF THE OFF-DIAGONAL BLOCKS OF THE G MATRIX ON THE CALCULATED FREQUENCIES

A. Perturbation approximation

It was shown in the preceding paper that the elements of the **G** matrix may be written as

$$\mathbf{G}_{iaja} = \mathbf{G}_{ibjb}{}^{*} = \mathcal{G}_{iaja} - i\mathcal{G}_{iajb}$$

The solution of the secular equation for the real portion of the **G** matrix, *i.e.* $\mathcal{G}_{aa}$, was obtained above and since the elements of $\mathcal{G}_{ab}$ are numerically small compared to those of $\mathcal{G}_{aa}$ and furthermore are non-diagonal it seemed appropriate to attempt to calculate the effect of the off-diagonal blocks by second-order perturbation theory. Thus for $\mathbf{H} = \mathbf{GF}$ we need to find a matrix **A** which diagonalizes **H** and then calculate the second order correction to the characteristic wave lengths by the well known perturbation approximation

$$\chi_i^{(2)} = \sum_{k \neq i} \frac{|\widetilde{\mathbf{A}}_i \mathbf{H}' \mathbf{A}_k|^2}{\lambda_i^{(0)} - \lambda_k^{(0)}}$$

However, to apply this method it is necessary that **H** be Hermitian and that

$$\widetilde{\mathbf{A}}_i{}^{*}\mathbf{A}_k = \delta_{ik}$$

The **G** matrix is already Hermitian but **GF** or **H** is not and therefore we must apply a transformation matrix to the symmetry coordinates that transforms **GF** into a Hermitian matrix. Calling this transformation matrix C and denoting the transformed matrices by $\bar{\mathbf{S}}$, $\bar{\mathbf{G}}$, $\bar{\mathbf{F}}$ and $\bar{\mathbf{H}}$ we have that

$$\bar{\mathbf{S}} = \mathbf{CS}$$

$$\bar{\mathbf{G}} = \mathbf{CG}\widetilde{\mathbf{C}}$$

$$\bar{\mathbf{F}} = \widetilde{\mathbf{C}}^{-1}\mathbf{F}\,\mathbf{C}^{-1}$$

The transformed matrix $\bar{\mathbf{H}}$ will then be Hermitian if

$$\bar{\mathbf{F}} = \widetilde{\mathbf{C}}^{-1}\,\mathbf{F}\,\mathbf{C}^{-1} = \mathbf{E}$$

and this relationship is fulfilled by the condition that

$$\mathbf{C} = \mathbf{F}^{\frac{1}{2}}$$

where $\mathbf{F}$ is a diagonal matrix.
Thus we have $\bar{\mathbf{H}}$ given by

$$\bar{\mathbf{H}} = \bar{\mathbf{G}}\,\bar{\mathbf{F}} = \bar{\mathbf{G}} = \mathbf{F}^{\frac{1}{2}}\,\mathbf{G}\,\widetilde{\mathbf{F}}^{\frac{1}{2}}$$

and since

$$\widetilde{\mathbf{A}}\;\bar{\mathbf{G}}\;\mathbf{A} = \Lambda$$

it can readily be shown that

$$\mathbf{G} = (\mathbf{F}^{\frac{1}{2}}\,\mathbf{A}\,\Lambda^{\frac{1}{2}})\;(\Lambda^{\frac{1}{2}}\,\widetilde{\mathbf{A}}\;\widetilde{\mathbf{F}}^{-\frac{1}{2}}) = \mathbf{L}\;\widetilde{\mathbf{L}}$$

or

$$\mathbf{A} = \mathbf{F}^{\frac{1}{2}}\;\mathbf{L}\Lambda^{-\frac{1}{2}}$$

and the perturbation correction becomes

$$\lambda_i^{(2)} = \sum_{k \neq i} \frac{|\widetilde{\mathbf{A}}_i \bar{G}_{ab} \mathbf{A}_k|^2}{\lambda_i^{(0)} - \lambda_k^{(0)}}$$

The transformation matrix $\mathbf{A}$ may thus be calculated from the $\mathbf{L}$ and Λ matrices obtained in part II together with the diagonal portion of the F matrix shown in Table 1. The second order corrections, $\lambda_i^{(2)}$, to the characteristic frequencies calculated by this method are listed in Table 3. However, the terms

$$\pm \frac{|\widetilde{\mathbf{A}}_7\;\bar{\mathbf{G}}'\;\mathbf{A}_9|^2}{\lambda_7^{(0)} - \lambda_9^{(0)}}$$

are strictly speaking too large to give good results by perturbation theory and therefore the corrections to ν_7 and ν_9 given in Table 3 are somewhat in error as a result.

Table 3. Effect of including the imaginary elements in the **G** matrix of species E' on the fundamental frequencies.

Description	Designation	$\Delta\nu$ from perturbation (diagonal **F** matrix)	$\Delta\nu$ from real 8 × 8 matrix (complete **F** matrix)
O—H stretch	ν_6	+ 1.8	+ 1.5
B—O stretch	ν_7	+ 92.1	+ 61.9
OBO bending	ν_8	− 28.3	− 27.7
BOH bending	ν_9	−112.2	− 70.2

B. Real matrices of twice normal size

A more exact method and one which is not limited by either the perturbation approximations or the necessity of using a diagonal **F** matrix was described in the preceding paper [1] — namely a method wherein a complex matrix is represented by a real matrix of twice the normal size. Thus for species E' an 8×8 matrix was employed and the solution of the secular equation gave frequencies which were corrected as shown in Table 3. The agreement with the $\Delta\nu$'s calculated from perturbation theory is very good for ν_6 and ν_8 but not as good for ν_7 and ν_9 for reasons as mentioned above. The corrections to the fundamental frequencies of ν_7, ν_8, and ν_9 were thought to be too large to be ignored and therefore an improved **F** matrix was sought that would yield a better correlation with the experimentally observed frequencies.

IV. THE COMPLETE L MATRIX OF SPECIES E'

Calculation of the **L** matrix when the imaginary part of **G** is included can be carried out in the following way:

The k'th column in **L** is found from the equations

$$(\mathbf{H} - \lambda_k \mathbf{E})\, \mathbf{L}_k = 0 \tag{1}$$

Splitting the matrices **H** and $\mathbf{L}_k$ in a real and imaginary part

$$\mathbf{H} - \lambda_k \mathbf{E} = \mathbf{A}^{(k)} + i\mathbf{B}, \quad \mathbf{L}_k = \mathbf{L}_k^{(r)} + i\mathbf{L}_k^{(i)}$$

and equating the real and imaginary part of (1) to zero, gives

$$\begin{aligned} \mathbf{A}^{(k)}\mathbf{L}_k^{(r)} - \mathbf{B}\,\mathbf{L}_k^{(i)} &= 0 \\ \mathbf{B}\,\mathbf{L}_k^{(r)} + \mathbf{A}^{(k)}\,\mathbf{L}_k^{(i)} &= 0 \end{aligned} \tag{2}$$

We assume that $\mathbf{A}^{(k)} \neq \mathbf{B}$ and that neither $\mathbf{A}^{(k)}$ nor **B** are null-matrices (matrices containing zero-elements only). Eqn. (2) can be solved in two ways:

I: $\mathbf{L}_k^{(i)} = \mathbf{A}^{(k)-1}\,\mathbf{B}\,\mathbf{L}_k^{(r)}$

$$(\mathbf{A}^{(k)} + \mathbf{B}\,\mathbf{A}^{(k)-1}\,\mathbf{B})\,\mathbf{L}_k^{(r)} = 0$$

II. $\mathbf{L}_k^{(i)} = \mathbf{B}^{-1}\,\mathbf{A}^{(k)}\,\mathbf{L}_k^{(r)}$

$$(\mathbf{B} + \mathbf{A}^{(k)}\,\mathbf{B}^{-1}\,\mathbf{A}^{(k)})\,\mathbf{L}_k^{(r)} = 0$$

Which of the two alternatives that should be used depends on the singularity of $\mathbf{A}^{(k)}$ and **B**.

In this case the changes in the λ's when **B** is included are relatively small. $|\mathbf{A}^{(k)}|$ is therefore almost zero and the second alternative (II) was used. In the calculations the previously calculated **F** matrix was used. It was also assumed that the imaginary part of **L** would be small. The real part of **L** was therefore set equal to the **L** matrix obtained in part II, and the imaginary part $\mathbf{L}^{(i)}$ could then be calculated from the equations $\mathbf{L}_k^{(i)} = \mathbf{B}^{-1}\,\mathbf{A}^{(k)}\mathbf{L}_k^{(r)}$. The normalization of **L** was then carried out in 8×8 representation of species E'.

The calculation of new **L** and **F** matrices which gave better agreement with experimental frequencies produced results which were essentially un-

changed from the original calculations (part II) which ignored the contribution of the imaginary elements of the **G**-matrix.

Specifically the **F** matrix was the same (within 0.001 units) as that given in Table 1 for species E' with the exception of F_{77} which change only slightly to a value of 4.909.

V. CALCULATION OF VALENCE-TYPE FORCE CONSTANTS

Expressing the **F** matrix elements in terms of valence-type force constants as done by Pistorius [4] for boric acid one may calculate the simpler valence type force constants using only diagonal elements of the **F** matrix. These calculations yield values which differ only slightly from those reported by Pistorius with the exception of the B—O stretching values where instead were obtained

$$f_r = 5.87$$
$$f_{rr} = 0.96$$

The latter value of 0.96×10^5 dynes cm^{-1} for f_{rr} is considerably different from the value of 0.02×10^5 reported by Pistorius.[4] Furthermore it seems chemically more reasonable that there should exist a strong interaction between the B—O stretching vibrations in the boric acid molecule where each oxygen is bonded to the central boron atom.

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Received June 11, 1965.