

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

IV. Force Constants and Compliant for Boric Acid

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An in-plane harmonic force field for boric acid has been determined from vibrational frequency data for three isotopic varieties. The molecule is assigned to a $X(YZ)_3$ model of C_{3h} symmetry, where it was found inevitable to introduce *complex* symmetry coordinates in species E' . The vibrational secular equation was solved in terms of real matrices also in the case of E' , in which each of the 4×4 complex matrices was represented by a real 8×8 matrix. The valence force-constants (*i.e.* force constants based on valence coordinates; they should not be confused with the valence force field approximation) and compliant are given, and their connection with the symmetrized elements is treated; the out-of-plane constants are included in the theoretical part of the treatment. The relations are particularly interesting when species E' is involved; the complex elements are related to valence force-constants and compliant, which naturally all are real.

It has recently been pointed out¹ that the molecular vibrations of boric acid $-B(OH)_3-$ when assigned to the structure of C_{3h} symmetry, should be treated in complex symmetry coordinates. The necessary extension of the Wilson GF matrix method,² and its application to the $X(YZ)_3$ molecular model in question, has been discussed elsewhere.³ The work has been continued

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simultaneously at NTH (Trondheim, Norway) and OSU (Oregon), but along somewhat different lines. Firstly, a numerical solution for the force constants was found by means of a perturbation method.⁴ Secondly, emphasis was laid on the method of real-matrix representation of complex matrices.³ The present paper includes some further details of this method and its application to the case of boric acid. The results of numerical computations are reported as to a harmonic force field for the in-plane vibrations. Allowance was made for the possibility of complex force constants when based on a complex symmetry-coordinate set.

The secular equation ²

$$\mathbf{GF}L = \mathbf{L}\lambda \quad (1)$$

holds even with the complex matrices. The characteristic values of \mathbf{GF} , *viz.* the frequency parameters $\lambda_k = 4\pi^2c^2\omega_k^2$, are real on account of the Hermitian nature of \mathbf{G} and \mathbf{F} . In compliance-matrix language ⁵ one has

$$\mathbf{NML} = \mathbf{L}\sigma \quad (2)$$

where \mathbf{N} , \mathbf{M} , and σ are the inverse matrices of \mathbf{F} , \mathbf{G} , and λ , respectively. In the present computations the form (2) was chosen rather than (1). The problem was solved by means of the mentioned method of a representation in terms of real matrices,³ which shall be outlined shortly in the next section.

During our previous work on boric acid,^{1,3,4} we were not aware of a recent contribution by Krishnan,^{6,7} who re-investigated the Raman spectrum of crystalline boric acid, and produced an Urey-Bradley force field for the in-plane vibrations. Therein Krishnan ⁷ corrected two of the erroneous \mathbf{G} -matrix elements from Pistorius,⁸ with the results identical to ours.¹ But Krishnan too neglected the interaction terms of the \mathbf{G} matrix, which exist on account of the application of real coordinates.^{1,3}

All computations of force fields of boric acid so far, including the present work, have been based on vibrational frequencies from data on the crystalline phase, which were transferred to a hypothetical gaseous phase. However, the free molecules of gaseous $\text{B}(\text{OH})_3$ do exist, and have been investigated by Margrave and Randall,⁹ who moreover established the spectroscopic evidence of the C_{3h} structure. The gaseous frequencies ⁹ of in-plane vibrations appear to be comparable to those of the crystalline phase. As to the out-of-plane frequencies it seems quite unreasonable to transfer ω_5 (OH torsion) from the crystalline phase to gas because of the absence of hydrogen bonds between neighbour molecules in the latter case. As a matter of fact, Randall ⁹ has suggested $\omega_5 = 303 \text{ cm}^{-1}$ for gaseous $^{11}\text{B}(\text{OH})_3$, while the corresponding crystalline-phase frequency is ¹⁰ 824 cm^{-1} . For this reason the numerical computations of out-of-plane force constants were not included in the present paper; one should await a final assignment of gas-phase frequencies from the significant work of Margrave and Randall.⁹ Also by the same reason the conclusions of the present calculations even for the in-plane vibrations should not be stretched too far.

REAL-MATRIX REPRESENTATION OF COMPLEX MATRICES

A complex matrix

$$\mathbf{A} = \text{Re}(\mathbf{A}) + i \text{Im}(\mathbf{A}) \quad (3)$$

may be represented by a real matrix \mathcal{A} as

$$\mathcal{A} = \begin{bmatrix} \text{Re}(\mathbf{A}) & \text{Im}(\mathbf{A}) \\ -\text{Im}(\mathbf{A}) & \text{Re}(\mathbf{A}) \end{bmatrix} \quad (4)$$

Here "Re" and "Im" denote the real and imaginary parts, respectively. The dimension of \mathcal{A} is twice that of \mathbf{A} . The representation is such that the sets of (a) all square nonsingular matrices \mathbf{A} of a given dimension, and (b) the corresponding matrices \mathcal{A} , form isomorphic groups with respect to matrix multiplication. In consequence, the secular equation (2) may be solved in the real-matrix representation according to

$$\mathcal{N} \mathcal{M} \mathcal{L} = \mathcal{L} \sigma \quad (5)$$

where \mathcal{N} , \mathcal{M} , and \mathcal{L} have been formed from the corresponding complex matrices in consistence with eqns. (3), (4), and particularly

$$\sigma = \begin{bmatrix} \sigma & \mathbf{0} \\ \mathbf{0} & \sigma \end{bmatrix} \quad (6)$$

One has

$$\mathcal{N} = \mathcal{M} \sigma \mathcal{L}', \quad \mathcal{M}^{-1} = \mathcal{L} \mathcal{L}' \quad (7)$$

which are the real-matrix representations of the following relations for the corresponding complex matrices.

$$\mathbf{N} = \mathbf{L} \sigma \mathbf{L}', \quad \mathbf{M}^{-1} = \mathbf{L} \mathbf{L}' \quad (8)$$

Notice that the transpose of a matrix \mathcal{A} of the form (4), viz.

$$\mathcal{A}' = \begin{bmatrix} \text{Re}(\mathbf{A})' & -\text{Im}(\mathbf{A})' \\ \text{Im}(\mathbf{A})' & \text{Re}(\mathbf{A}) \end{bmatrix} \quad (9)$$

is the real-matrix representation of the *associate* matrix of \mathbf{A} , i.e.

$$\mathbf{A}^\dagger = \text{Re}(\mathbf{A})' - i \text{Im}(\mathbf{A})' \quad (10)$$

Here it shall also be proved explicitly that \mathcal{A}^{-1} is the representation of \mathbf{A}^{-1} . This fact is seen by performing the matrix multiplication

$$\begin{bmatrix} \text{Re}(\mathbf{A}) & \text{Im}(\mathbf{A}) \\ -\text{Im}(\mathbf{A}) & \text{Re}(\mathbf{A}) \end{bmatrix} \begin{bmatrix} \text{Re}(\mathbf{A}^{-1}) & \text{Im}(\mathbf{A}^{-1}) \\ -\text{Im}(\mathbf{A}^{-1}) & \text{Re}(\mathbf{A}^{-1}) \end{bmatrix} \quad (11)$$

in terms of the submatrices. The first factor in (11) is \mathcal{A} , and it shall be proved that the second factor is \mathcal{A}^{-1} . This is true because of

$$\begin{aligned} \text{Re}(\mathbf{A}) \text{Re}(\mathbf{A}^{-1}) - \text{Im}(\mathbf{A}) \text{Im}(\mathbf{A}^{-1}) &= \mathbf{E} \\ \text{Re}(\mathbf{A}) \text{Im}(\mathbf{A}^{-1}) + \text{Im}(\mathbf{A}) \text{Re}(\mathbf{A}^{-1}) &= \mathbf{0} \end{aligned} \quad (12)$$

The relations (12) follow from

$$\mathbf{A}\mathbf{A}^{-1} = [\operatorname{Re}(\mathbf{A}) + i \operatorname{Im}(\mathbf{A})] [\operatorname{Re}(\mathbf{A}^{-1}) + i \operatorname{Im}(\mathbf{A}^{-1})] = \mathbf{E} \quad (13)$$

If \mathbf{A} is a Hermitian matrix (as is the case with \mathbf{F} , \mathbf{G} , \mathbf{M} , and \mathbf{N}), the corresponding real-matrix representation \mathcal{A} is a symmetric matrix; $\mathcal{A} = \mathcal{A}'$, with skew-symmetric off-diagonal blocks; $\operatorname{Im}(\mathbf{A}) = -\operatorname{Im}(\mathbf{A})'$.

IN-PLANE VALENCE FORCE-CONSTANTS

The planar vibrations of the considered molecular model belong to the species A' and E' . For the symmetry coordinates, see Ref. 3. The degenerate species E' constitutes the most interesting part, since here it is found necessary to introduce the complex symmetry coordinates. It seems worth while treating the connections between the in-plane valence force-constants and symmetrized force-constants in some detail. Table 1 shows the notation and definitions of in-plane valence force-constants, which are the usual *real* quantities.

In species A' the following equations are found, and are of the familiar type.

$$\begin{aligned} F_{11} &= f_a + 2f_{aa}, & F_{22} &= f_r + 2f_{rr}, & F_{33} &= f_\beta + 2f_{\beta\beta}, \\ F_{12} &= f_{ar} + f_{ar}' + f_{ar}'', & F_{13} &= f_{a\beta} + f_{a\beta}' + f_{a\beta}'', & F_{23} &= f_{r\beta} + f_{r\beta}' + f_{r\beta}'' \end{aligned} \quad (14)$$

These equations (14) were first given by Pistorius.⁸

The corresponding equations for species E' contain complex coefficients and read as follows.

$$\begin{aligned} F_{6a6a} &= F_{6b6b} = f_a - f_{aa} \\ F_{6a7a} &= F_{6b6b}^* = f_{ar} + \varepsilon f_{ar}' + \varepsilon^* f_{ar}'' \\ F_{6a8a} &= F_{6b8b}^* = f_{a\alpha} + \varepsilon^* f_{a\alpha}' + \varepsilon f_{a\alpha}'' \\ F_{6a9a} &= F_{6b9b}^* = f_{a\beta} + \varepsilon f_{a\beta}' + \varepsilon^* f_{a\beta}'' \\ F_{7a7a} &= F_{7b7b} = f_r - f_{rr} \\ F_{7a8a} &= F_{7b8b} = f_{r\alpha} - f_{r\alpha}' \\ F_{7a9a} &= F_{7b9b}^* = f_{r\beta} + \varepsilon^* f_{r\beta}' + \varepsilon f_{r\beta}'' \\ F_{8a8a} &= F_{8b8b} = f_\alpha - f_{\alpha\alpha} \\ F_{8a9a} &= F_{8b9b}^* = f_{\alpha\beta} + \varepsilon f_{\alpha\beta}' + \varepsilon^* f_{\alpha\beta}'' \\ F_{9a9a} &= F_{9b9b} = f_\beta - f_{\beta\beta} \end{aligned} \quad (15)$$

Here

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

Eqns. (15) have been derived from the matrix relation

$$\mathbf{F} = \mathbf{U}\mathbf{f}\mathbf{U}^\dagger \quad (16)$$

where \mathbf{U} is the unitary matrix of the transformation $\mathbf{S} = \mathbf{U}\mathbf{R}$.

Another unitary matrix, \mathbf{u} , has been introduced in order to treat the E' species of boric acid in terms of real coordinates \mathcal{S} ; cf. Ref. 3.

$$\mathbf{S} = \mathbf{u} \mathcal{S}, \quad \mathcal{S} = \mathbf{u}^\dagger \mathbf{S} \quad (17)$$

This matrix is given explicitly below (dots represent zeros).

$$\begin{array}{c}
 \mathcal{S}_{6a} \\
 \mathcal{S}_{7a} \\
 \mathcal{S}_{8a} \\
 \mathcal{S}_{9a} \\
 \mathcal{S}_{6b} \\
 \mathcal{S}_{7b} \\
 \mathcal{S}_{8b} \\
 \mathcal{S}_{9b}
 \end{array}
 \begin{bmatrix}
 \mathcal{S}_{6a} & \mathcal{S}_{7a} & \mathcal{S}_{8a} & \mathcal{S}_{9a} & \mathcal{S}_{6b} & \mathcal{S}_{7b} & \mathcal{S}_{8b} & \mathcal{S}_{9b} \\
 2^{-\frac{1}{2}} & \cdot & \cdot & \cdot & 2^{-\frac{1}{2}}i & \cdot & \cdot & \cdot \\
 \cdot & 2^{-\frac{1}{2}} & \cdot & \cdot & \cdot & 2^{-\frac{1}{2}}i & \cdot & \cdot \\
 \cdot & \cdot & 2^{-\frac{1}{2}} & \cdot & \cdot & \cdot & 2^{-\frac{1}{2}}i & \cdot \\
 \cdot & \cdot & \cdot & 2^{-\frac{1}{2}} & \cdot & \cdot & \cdot & 2^{-\frac{1}{2}}i \\
 2^{-\frac{1}{2}} & \cdot & \cdot & \cdot & -2^{-\frac{1}{2}}i & \cdot & \cdot & \cdot \\
 \cdot & 2^{-\frac{1}{2}} & \cdot & \cdot & \cdot & -2^{-\frac{1}{2}}i & \cdot & \cdot \\
 \cdot & \cdot & 2^{-\frac{1}{2}} & \cdot & \cdot & \cdot & -2^{-\frac{1}{2}}i & \cdot \\
 \cdot & \cdot & \cdot & 2^{-\frac{1}{2}} & \cdot & \cdot & \cdot & -2^{-\frac{1}{2}}i
 \end{bmatrix}$$

If the real force-constant matrix based on the coordinates \mathcal{S} is denoted by \mathcal{F} , one has similarly to eqn. (16)

$$\mathcal{F} = \mathbf{u}^t \mathbf{F} \mathbf{u} \quad (18)$$

This leads to the following explicit relations connecting the force constants from \mathcal{F} and \mathbf{F} ; $i, j = 6, 7, 8, 9$.

$$\begin{aligned}
 \mathcal{F}_{iaja} = \mathcal{F}_{ibjb} &= \frac{1}{2}(\mathcal{F}_{iaja} + \mathcal{F}_{ibjb}) = \frac{1}{2}(\mathcal{F}_{iaja} + \mathcal{F}_{iaja}^*) \\
 &= \text{Re}(\mathcal{F}_{iaja}) = \text{Re}(\mathcal{F}_{ibjb}), \\
 \mathcal{F}_{iajb} = -\mathcal{F}_{ibja} &= \frac{i}{2}(\mathcal{F}_{iaja} - \mathcal{F}_{ibjb}) = -\text{Im}(\mathcal{F}_{iaja}) = \text{Im}(\mathcal{F}_{ibjb})
 \end{aligned} \quad (19)$$

Especially for $i = j$:

$$\mathcal{F}_{iaia} = \mathcal{F}_{ibib} = \text{Re}(\mathcal{F}_{iaia}) = \text{Re}(\mathcal{F}_{ibib}), \quad \mathcal{F}_{iaib} = \mathcal{F}_{ibia} = 0 \quad (20)$$

As a whole, it is seen that the 8×8 \mathcal{F} matrix is the real-matrix representation — in the sense of eqns. (3), (4) — of the 4×4 block from \mathbf{F} which corresponds to the b -coordinates of species E' . When this block is designated \mathbf{F}_b , it should be noticed that

$$\mathbf{F}_a = \mathbf{F}_b^* \quad (21)$$

where \mathbf{F}_a is the corresponding block for the a -coordinates.

Now the force constants from \mathcal{F} may be expressed in terms of the valence force-constants. One finds

$$\begin{aligned}
 \mathcal{F}_{6a7a} = f_a - f_{ad}, \quad \mathcal{F}_{7a7a} = f_r - f_{rr}, \quad \mathcal{F}_{8a8a} = f_\alpha - f_{\alpha\alpha}, \quad \mathcal{F}_{9a9a} = f_\beta - f_{\beta\beta}, \\
 \mathcal{F}_{6a7a} = f_{dr} - \frac{1}{2}(f_{dr}' + f_{dr}''), \quad \mathcal{F}_{6a8a} = f_{d\alpha} - \frac{1}{2}(f_{d\alpha}' + f_{d\alpha}''), \\
 \mathcal{F}_{6a9a} = f_{d\beta} - \frac{1}{2}(f_{d\beta}' + f_{d\beta}''), \\
 \mathcal{F}_{7a8a} = f_{r\alpha} - f_{r\alpha}', \quad \mathcal{F}_{7a9a} = f_{r\beta} - \frac{1}{2}(f_{r\beta}' + f_{r\beta}''), \\
 \mathcal{F}_{8a9a} = f_{\alpha\beta} - \frac{1}{2}(f_{\alpha\beta}' + f_{\alpha\beta}'')
 \end{aligned} \quad (22)$$

These equations (22) have also been given by Pistorius,⁸ but he has erroneously omitted further nonvanishing interaction terms. Presently one has found

$$\begin{aligned}
 \mathcal{F}_{6a7b} = -\frac{1}{2}3^{\frac{1}{2}}(f_{dr}' - f_{dr}''), \quad \mathcal{F}_{6a8b} = \frac{1}{2}3^{\frac{1}{2}}(f_{d\alpha}' - f_{d\alpha}''), \quad \mathcal{F}_{6a9b} = -\frac{1}{2}3^{\frac{1}{2}}(f_{d\beta}' - f_{d\beta}''), \\
 \mathcal{F}_{7a8b} = 0, \quad \mathcal{F}_{7a9b} = \frac{1}{2}3^{\frac{1}{2}}(f_{r\beta}' - f_{r\beta}''), \\
 \mathcal{F}_{8a9b} = -\frac{1}{2}3^{\frac{1}{2}}(f_{\alpha\beta}' - f_{\alpha\beta}'')
 \end{aligned} \quad (23)$$

Here eqns. (14), (22), (23) contain a complete set of 21 independent force constants, which are expressed in terms of the 25 in-plane valence force-constants. The excess number of 4 constants is precisely as expected on account of the redundancy in the α bendings. The vanishing of \mathcal{F}_{7ab} (see eqn. 23) is easily understood by the fact that the appropriate coordinate pair (δ_{7a} , δ_{8b}) only involves the XY_3 atoms, which have the D_{3h} symmetry.

The next step is to express the valence force-constants in terms of the symmetrized force constants. Because of the above mentioned redundancy some indeterminate linear combinations will remain. The obtained result is as follows for the d coordinates and dr interactions.

$$\begin{aligned} f_d &= \frac{1}{3}(F_{11} + 2F_{6a6a}) = \frac{1}{3}(F_{11} + \frac{1}{3}\mathcal{F}_{6a6a}), \\ f_{dd} &= \frac{1}{3}(F_{11} - F_{6a6a}) = \frac{1}{3}(F_{11} - \mathcal{F}_{6a6a}), \\ f_{dr} &= \frac{1}{3}(F_{12} + F_{6a7a} + F_{6a7a}^*) = \frac{1}{3}[F_{12} + 2\text{Re}(F_{6a7a})] = \frac{1}{3}(F_{12} + 2\mathcal{F}_{6a7a}), \\ f_{dr}' &= \frac{1}{3}(F_{12} + \varepsilon^*F_{6a7a} + \varepsilon F_{6a7a}^*) = \frac{1}{3}[F_{12} - \text{Re}(F_{6a7a}) - 3^{\frac{1}{2}}\text{Im}(F_{6a7a})] \\ &= \frac{1}{3}(F_{12} - \mathcal{F}_{6a7a} - 3^{\frac{1}{2}}\mathcal{F}_{6a7b}), \\ f_{dr}'' &= \frac{1}{3}(F_{12} + \varepsilon F_{6a7a} + \varepsilon^*F_{6a7a}^*) = \frac{1}{3}[F_{12} - \text{Re}(F_{6a7a}) - 3^{\frac{1}{2}}\text{Im}(F_{6a7a})] \\ &= \frac{1}{3}(F_{12} - \mathcal{F}_{6a7a} + 3^{\frac{1}{2}}\mathcal{F}_{6a7b}) \end{aligned} \quad (24)$$

Similarly for the other constants:

$$\begin{aligned} f_{d\alpha} - f_{d\alpha}' &= \mathcal{F}_{6a8a} - 3^{-\frac{1}{2}}\mathcal{F}_{6a8a}, \quad f_{d\alpha} - f_{d\alpha}'' = \mathcal{F}_{6a8a} + 3^{-\frac{1}{2}}\mathcal{F}_{6a8b}, \\ f_{a\beta} &= \frac{1}{3}(F_{13} + 2\mathcal{F}_{6a9a}), \quad f_{a\beta}' = \frac{1}{3}(F_{13} - \mathcal{F}_{6a9a} - 3^{\frac{1}{2}}\mathcal{F}_{6a9b}), \\ f_{a\beta}'' &= \frac{1}{3}(F_{13} - \mathcal{F}_{6a9a} + 3^{\frac{1}{2}}\mathcal{F}_{6a9b}), \\ f_r &= \frac{1}{3}(F_{22} + 2\mathcal{F}_{7a7a}), \quad f_{rr} = \frac{1}{3}(F_{22} - \mathcal{F}_{7a7a}), \\ f_{r\alpha} - f_{r\alpha}' &= \mathcal{F}_{7a8a}, \\ f_{r\beta} &= \frac{1}{3}(F_{23} + 2\mathcal{F}_{7a9a}), \quad f_{r\beta}' = \frac{1}{3}(F_{23} - \mathcal{F}_{7a9a} + 3^{\frac{1}{2}}\mathcal{F}_{7a9b}), \\ f_{r\beta}'' &= \frac{1}{3}(F_{23} - \mathcal{F}_{7a9a} - 3^{\frac{1}{2}}\mathcal{F}_{7a9b}), \\ f_{\alpha} - f_{\alpha\alpha} &= \mathcal{F}_{8a8a}, \\ f_{\alpha\beta} - f_{\alpha\beta}' &= \mathcal{F}_{8a9a} + 3^{-\frac{1}{2}}\mathcal{F}_{8a9b}, \quad f_{\alpha\beta} - f_{\alpha\beta}'' = \mathcal{F}_{8a9a} - 3^{-\frac{1}{2}}\mathcal{F}_{8a9b}, \\ f_{\beta} &= \frac{1}{3}(F_{33} + 2\mathcal{F}_{9a9a}), \quad f_{\beta\beta} = \frac{1}{3}(F_{33} - \mathcal{F}_{9a9a}) \end{aligned} \quad (25)$$

IN-PLANE VALENCE COMPLIANCE-CONSTANTS

The compliance-constant⁵ matrix \mathbf{N} is defined by $\mathbf{N} = \mathbf{F}^{-1}$. Relations analogous to eqns. (16) and (18) hold for the valence compliance-constants (\mathbf{n}) and the real-matrix representation (\mathcal{N});

$$\mathbf{N} = \mathbf{U}\mathbf{n}\mathbf{U}^\dagger, \quad \mathcal{N} = \mathbf{u}^\dagger\mathbf{N}\mathbf{u} \quad (26)$$

Hence all the equations (14)–(25) are valid when the force constants are substituted by the corresponding compliants. But, as a consequence of an important general property of invariance of the compliants,⁵ one may evaluate explicitly also the elements which involve a redundant coordinate. Here one has found the following equations in addition to those analogous to eqns. (24), (25).

$$\begin{aligned} n_{d\alpha} &= \frac{2}{3}\mathcal{N}_{6a8a}, \quad n_{d\alpha}' = \frac{1}{3}(-\mathcal{N}_{6a8a} + 3^{\frac{1}{2}}\mathcal{N}_{6a8b}), \quad n_{d\alpha}'' = \frac{1}{3}(-\mathcal{N}_{6a8a} - 3^{\frac{1}{2}}\mathcal{N}_{6a8b}), \\ n_{r\alpha} &= \frac{2}{3}\mathcal{N}_{7a8a}, \quad n_{r\alpha}' = -\frac{1}{3}\mathcal{N}_{7a8a}, \\ n_{\alpha} &= \frac{2}{3}\mathcal{N}_{8a8a}, \quad n_{\alpha\alpha} = -\frac{1}{3}\mathcal{N}_{8a8a}, \\ n_{\alpha\beta} &= \frac{2}{3}\mathcal{N}_{8a9a}, \quad n_{\alpha\beta}' = \frac{1}{3}(-\mathcal{N}_{8a9a} - 3^{\frac{1}{2}}\mathcal{N}_{8a9b}), \quad n_{\alpha\beta}'' = \frac{1}{3}(-\mathcal{N}_{8a9a} + 3^{\frac{1}{2}}\mathcal{N}_{8a9b}) \end{aligned} \quad (27)$$

Table 1. Notation and definitions of in-plane valence force-constants; $\varrho = (RD)^{\frac{1}{2}}$.

| | d_1 | r_1 | $R\alpha_1$ | $\varrho\beta_1$ |
|------------------|-----------------|----------------|---------------------|---------------------|
| d_1 | f_d | f_{dr} | $f_{d\alpha}$ | $f_{d\beta}$ |
| d_2 | f_{dd} | f_{dr}' | $f_{d\alpha}''$ | $f_{d\beta}'$ |
| d_3 | f_{dd} | f_{dr}'' | $f_{d\alpha}'$ | $f_{d\beta}''$ |
| r_1 | f_{dr} | f_r | $f_{r\alpha}$ | $f_{r\beta}$ |
| r_2 | f_{dr}'' | f_{rr} | $f_{r\alpha}'$ | $f_{r\beta}''$ |
| r_3 | f_{dr}' | f_{rr} | $f_{r\alpha}'$ | $f_{r\beta}'$ |
| $R\alpha_1$ | $f_{d\alpha}$ | $f_{r\alpha}$ | f_{α} | $f_{\alpha\beta}$ |
| $R\alpha_2$ | $f_{d\alpha}'$ | $f_{r\alpha}'$ | $f_{\alpha\alpha}$ | $f_{\alpha\beta}'$ |
| $R\alpha_3$ | $f_{d\alpha}''$ | $f_{r\alpha}'$ | $f_{\alpha\alpha}$ | $f_{\alpha\beta}''$ |
| $\varrho\beta_1$ | $f_{d\beta}$ | $f_{r\beta}$ | $f_{\alpha\beta}$ | f_{β} |
| $\varrho\beta_2$ | $f_{d\beta}''$ | $f_{r\beta}'$ | $f_{\alpha\beta}''$ | $f_{\beta\beta}$ |
| $\varrho\beta_3$ | $f_{d\beta}'$ | $f_{r\beta}''$ | $f_{\alpha\beta}'$ | $f_{\beta\beta}$ |

OUT-OF-PLANE VALENCE FORCE-CONSTANTS AND COMPLIANCE-CONSTANTS

The out-of-plane vibrations for the molecule model in question belong to the species A'' and E'' . For the applied symmetry coordinates, see Ref. 3. The situation here is very simple. As a matter of fact the subscript on γ is rather trivial, because all the three γ 's are defined as exactly identical.³ Hence the redundants among the γ coordinates introduced by Pistorius⁸ can easily be avoided, and it is possible to evaluate all the 4 independent valence force-constants which are specified in Table 2. Their simple connection with the symmetrized force constants is given below.

$$f_{\gamma} = 3F_{44}, \quad f_{\gamma\tau} = F_{45} \quad (28)$$

$$f_{\tau} = \frac{1}{3}(F_{55} + 2F_{10\ 10}), \quad f_{\tau\tau} = \frac{1}{3}(F_{55} - F_{10\ 10}) \quad (29)$$

Eqns. (29) hold also when the force constants are substituted by the corresponding compliance constants. Great care must be taken, however, for the elements which involve the coordinate γ ($= \gamma_i$ for $i = 1, 2, 3$). Since

Table 2. Notation and definitions of out-of-plane valence force-constants; $q = (RD)^\ddagger$.

| | | |
|-----------------|------------------|------------------|
| | $R\gamma_1$ | $\varrho\tau_1$ |
| $R\gamma_1$ | f_γ | $f_{\gamma\tau}$ |
| $R\gamma_2$ | f_γ | $f_{\gamma\tau}$ |
| $R\gamma_3$ | f_γ | $f_{\gamma\tau}$ |
| $\varrho\tau_1$ | $f_{\gamma\tau}$ | f_τ |
| $\varrho\tau_2$ | $f_{\gamma\tau}$ | $f_{\tau\tau}$ |
| $\varrho\tau_3$ | $f_{\gamma\tau}$ | $f_{\tau\tau}$ |

the U matrix is unitary only if $3^{\frac{1}{2}}R\gamma$ is regarded as a coordinate rather than $R\gamma$, it follows that the forms of eqns. (28) are *not* immediately applicable to the compliants. Instead one has found:

$$n_\gamma = \frac{1}{3}N_{44}, \quad n_{\gamma\tau} = \frac{1}{3}N_{45} \quad (30)$$

NUMERICAL COMPUTATIONS

The present numerical computations are based on the observed vibrational frequencies for three isotopic species of boric acid, as quoted by Pistorius.⁸ The molecular parameters are those of Zachariassen¹¹ obtained by an X-ray diffraction study of crystalline boric acid; O—H = 0.88 Å, B—O = 1.362 Å, $\angle BOH = 114^\circ$. Compliance constants were computed by a least-squares fitting procedure based on the secular equation (2), where the real-matrix representation form (5) was used for species E' .

Table 3. Calculated and observed * frequencies (in cm^{-1}) for isotopic boric acid molecules.

| Species and No. | $^{11}\text{B}(\text{OH})_3$ | | $^{10}\text{B}(\text{OH})_3$ | | $^{11}\text{B}(\text{OD})_3$ | | |
|--------------------|------------------------------|------|------------------------------|------|------------------------------|------|-----|
| | calc. | obs. | calc. | obs. | calc. | obs. | |
| A' | 1 | 3250 | 3250 | 3250 | 2370 | — | |
| | 2 | 1060 | 1060 | 1060 | 1016 | — | |
| | 3 | 881 | 881 | 881 | 664 | — | |
| E' | 6 | 3171 | 3150 | 3171 | 2317 | 2390 | |
| | 7 | 1432 | 1428 | 1487 | 1419 | 1424 | |
| | 8 | 546 | 544 | 547 | 545 | 499 | 504 |
| | 9 | 1187 | 1183 | 1188 | 1195 | 919 | 921 |

* Quoted by Pistorius.⁸

Species A'. The totally symmetric frequencies are in the present case not affected by an isotopic substitution of the central atom. Hence only three independent experimental frequencies are available (*cf.* Table 3) for calculation of a set of six force constants in species *A'*. It was not succeeded to produce a valence force field approximation consistent with all the three observed frequencies. The attempts suggested the existence of a significant interaction compliance constant N_{23} of about -0.025 Å/mdyne. This value is comparable with the similar constant $\mathcal{N}_{7a9a} = -0.017$ Å/mdyne (species *E'*; see below). Also $N_{13} = -0.001$ Å/mdyne was assumed, and has been obtained from the preliminary study of valence force fields.

Species E'. The complete sets of frequencies for three isotopic molecules (see Table 3) provided very useful information for the calculation of compliance constants. Preliminary studies indicated the interaction between α and β type bending coordinates to be the most important one. Hence \mathcal{N}_{8a9a} and \mathcal{N}_{8a9b} , along with the four principal compliants were subjected to an iteration procedure, while nine independent interaction constants were kept fixed. Three of these were assumed equal to zero, and the remaining six equal to non-zero magnitudes obtained from the preliminary calculations.

Table 4. Compliance matrix elements (in Å/mdyne) for boric acid.

| <i>A'</i> | S_1 | S_2 | S_3 | |
|--------------------|--------------------|--------------------|--------------------|--------------------|
| S_1 | 0.170 | 0.000 | -0.001 | |
| S_2 | | 0.106 | -0.025 | |
| S_3 | | | 3.157 | |
| <i>E'</i> | \mathcal{S}_{8a} | \mathcal{S}_{7a} | \mathcal{S}_{8a} | \mathcal{S}_{9a} |
| \mathcal{S}_{8a} | 0.179 | 0.001 | 0.003 | 0.002 |
| \mathcal{S}_{7a} | | 0.188 | 0.066 | -0.017 |
| \mathcal{S}_{8a} | | | 1.406 | -0.586 |
| \mathcal{S}_{9a} | | | | 3.372 |
| | \mathcal{S}_{8b} | \mathcal{S}_{7b} | \mathcal{S}_{8b} | \mathcal{S}_{9b} |
| \mathcal{S}_{8a} | 0 | 0.001 | 0.000 | 0.000 |
| \mathcal{S}_{7a} | -0.001 | 0 | 0 | 0.000 |
| \mathcal{S}_{8a} | -0.000 | 0 | 0 | -1.201 |
| \mathcal{S}_{9a} | -0.000 | -0.000 | 1.201 | 0 |

Table 3 shows the observed and calculated frequencies. In Table 4 the final compliance constants are given. For species *E'* the table corresponds to the four upper rows of the \mathcal{N} matrix, which contain the whole set of fifteen independent elements. The obtained valence force-constants and compliants are found in Table 5.

DISCUSSION

The calculated frequencies from the presently derived force field show very good agreement with the observed values (Table 3); the deviations are all below 1 %, except for ω_6 of $^{11}\text{B}(\text{OD})_3$, where it is 3 %. The magnitudes

Table 5. In-plane valence force-constants (f in mdyne/Å) and compliance constants (n in Å/mdyne) for boric acid.

| | $x = d$ | $x = r$ | $x = \alpha$ | $x = \beta$ | | |
|------------|---------|-----------------------|-----------------------|----------------------|----------------------|---------------------------|
| f_x | 5.697 | 6.788 | | 0.426 | | |
| f_{dx} | 0.097 | -0.016 | | -0.006 | | |
| f_{dx}' | | 0.027 | $f_{d\alpha} + 0.025$ | 0.008 | | |
| f_{dx}'' | | -0.011 | $f_{d\alpha} + 0.016$ | 0.001 | $f_{\beta\beta}$ | -0.054 |
| | $x = r$ | $x = \alpha$ | $x = \beta$ | $x = \alpha$ | $x = \beta$ | |
| f_{rx} | 1.321 | | 0.007 | $f_{\alpha\alpha}$ | $f_{\alpha} - 1.170$ | |
| f_{rx}' | | $f_{r\alpha} + 0.393$ | -0.051 | $f_{\alpha\alpha}'$ | | $f_{\alpha\beta} - 0.442$ |
| f_{rx}'' | | | 0.118 | $f_{\alpha\alpha}''$ | | $f_{\alpha\beta} + 0.040$ |
| | $x = d$ | $x = r$ | $x = \alpha$ | $x = \beta$ | | |
| n_x | 0.176 | 0.160 | 0.937 | 3.300 | | |
| n_{dx} | -0.003 | 0.001 | 0.002 | 0.001 | | |
| n_{dx}' | | -0.001 | -0.001 | -0.001 | | |
| n_{dx}'' | | 0.000 | -0.001 | -0.001 | $n_{\beta\beta}$ | -0.072 |
| | $x = r$ | $x = \alpha$ | $x = \beta$ | $x = \alpha$ | $x = \beta$ | |
| n_{rx} | -0.027 | 0.044 | -0.020 | $n_{\alpha\alpha}$ | -0.469 | -0.390 |
| n_{rx}' | | -0.022 | -0.002 | $n_{\alpha\alpha}'$ | | 0.889 |
| n_{rx}'' | | | -0.002 | $n_{\alpha\alpha}''$ | | -0.498 |

of interaction force constants and compliants seem in general to be reasonably small as compared to the principal values. One noticeable exception is the interaction between the α and β -type bendings. The corresponding symmetrized force constant and compliant of species E' amount in the present results to

$$F_{8a9a} = (0.201 - 0.417 i) \text{ mdyne/\AA}$$

and

$$N_{8a9a} = (-0.586 + 1.201 i) \text{ \AA/mdyne,}$$

respectively. Besides the comparatively large magnitudes it is seen that the imaginary parts are by no means negligible.

In Table 6 some valence force-constants and compliants for B—O stretching and in-plane OBO bending in $\text{B}(\text{OH})_3$ are compared with the corresponding

constants in the BF₃ molecule¹² and BO₃³⁻ ion.¹³ The force fields are seen to possess the expected similarities as to the orders of magnitude of the constants. But it seems not justified to make a detailed discussion of their differences because of the approximate nature of the present calculations. Some particular reasons are specified below.

Table 6. Comparison of valence force-constants (f in mdyne/Å) and compliants (n in Å/mdyne) for related compounds.

| | BF ₃ ^a | BO ₃ ³⁻ ^b | B(OH) ₃ |
|-------------------------------|------------------------------|--|-------------------------|
| f_r | 7.29 | 6.3 | 6.8 (5.87) ^c |
| f_{rr} | 0.77 | 0.99 | 1.32 (0.96) |
| n_r | 0.143 | 0.18 | 0.16 |
| n_{rr} | -0.015 | -0.03 | -0.03 |
| $f_\alpha - f_{\alpha\alpha}$ | 0.515 | 0.69 | 1.17 |
| n_α | 1.33 | 1.1 | 0.94 |
| $n_{\alpha\alpha}$ | -0.666 | -0.54 | -0.47 |

^a From Ref. 12.

^b From Ref. 13.

^c Values in parentheses from Ref. 4 (Part III of this series).

1. Usual reservations must be taken because of the underdeterminate nature of the problem due to an insufficient number of observed frequencies for isotopic molecules.

2. Great limits of error must in general be expected in results from isotopic frequencies alone,^{12,14} even if a sufficient number of data were available.

3. The frequencies observed in crystalline boric acid were transferred without modification to a hypothetical free molecule of B(OH)₃; see also the introductory part referring to Margrave and Randall.⁹ It should also be mentioned that the frequency data used here⁸ refer to measurements at room temperature.^{10,15} The results from a low-temperature investigation of Hornig and Plumb¹⁶ have not been taken into account in the present computations.

There is finally one more comment to be made in connection with Table 6. Strictly speaking it is inappropriate to compare the value of $f_\alpha - f_{\alpha\alpha} = 1.17$ mdyne/Å in B(OH)₃ with the values of the other compounds listed. The value will depend on the more or less arbitrary choice of coordinates for displacements involving the H atoms. This inconvenience is not present when regarding the compliance constants n_α and $n_{\alpha\alpha}$. It is here referred to the invariance properties of compliance constants,⁵ which they share with G-matrix elements, but not the ordinary force constants. The approximate constancy of n_α and $n_{\alpha\alpha}$ in the compounds here considered (Table 6) may be taken as a successful application of the theory of compliance constants.

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