

FORCE CONSTANTS FOR THE BF_3 MOLECULE

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INTRODUCTION

The method of normal co-ordinates (Wilson, 1939 and 1941) has been applied in the following calculations for the molecule BF_3 . Of the two plausible models—Pyramidal and Plane symmetrical—for BF_3 , the latter has been used in the present calculations as it has been confirmed both by electron diffraction experiments and measurements of dipole moments (Herzberg, 1945). In the plane symmetrical model BF_3 has three in-plane and one out-of-plane vibrations. The simple valence force field is inapplicable to account for the out-of-plane vibration unless a separate angle bending constant is introduced. In this paper, the stretching, bending and interaction force constants are calculated with the observed Raman and infra-red frequencies (Herzberg, 1945) of B^{11}F_3 . The correctness of these values is verified by utilising the set of force constants thus obtained to calculate the corresponding frequencies for the isotopic molecule B^{10}F_3 and comparing these with the observed values.

CALCULATIONS

The Plane symmetrical BF_3 molecule belongs to the point group D_{3h} . From the group characters, it is seen that this molecule has one non-degenerate type A_1' vibration, one non-degenerate type A_1'' vibration and two doubly degenerate type E_1' vibrations. Out of the above six modes, one is non-planar type A_1'' vibration, which is not considered in the present paper.

CONSTRUCTION OF THE SYMMETRY CO-ORDINATES

The internal co-ordinates from the structure of the molecule are $\Delta d_1, \Delta d_2, \Delta d_3$, the changes in the three B-F distances and $\Delta \alpha_1, \Delta \alpha_2, \Delta \alpha_3$, the changes in the inter-bond angles. (Fig. 1.) The symmetry co-ordinates for each species are constructed as linear* combinations of equivalent internal co-ordinates in such a manner that they satisfy orthogonality, normalisation and transformation† properties. In this case $\Delta d_1, \Delta d_2$ and Δd_3 form one set of internal co-ordinates, and $\Delta \alpha_1, \Delta \alpha_2$ and $\Delta \alpha_3$ form another set of internal co-ordinates. The set of symmetry co-ordinates thus formed is given below. For the type A_1' vibration,

$$R_1 = 3^{-\frac{1}{2}} (\Delta d_1 + \Delta d_2 + \Delta d_3) \quad \dots \quad \dots \quad \dots \quad (1)$$

$$R_2 = 3^{-\frac{1}{2}} (\Delta \alpha_1 + \Delta \alpha_2 + \Delta \alpha_3) = 0 \quad (\text{Redundant co-ordinate})$$

* Most general expression for the symmetry co-ordinate is $R_j = \sum_k U_{jk} r_k$ where r_k is the k -th internal co-ordinate and U_{jk} is the coefficient of k -th internal co-ordinate in j -th symmetry co-ordinate, the condition for normalisation and orthogonality being $\sum_k (U_{jk})^2 = 1$ and $\sum_k U_{jk} U_{lk} = 0$ respectively.

† Each symmetry co-ordinate should transform according to the characters of the vibration type concerned under all covering operations of the point group of the molecule,

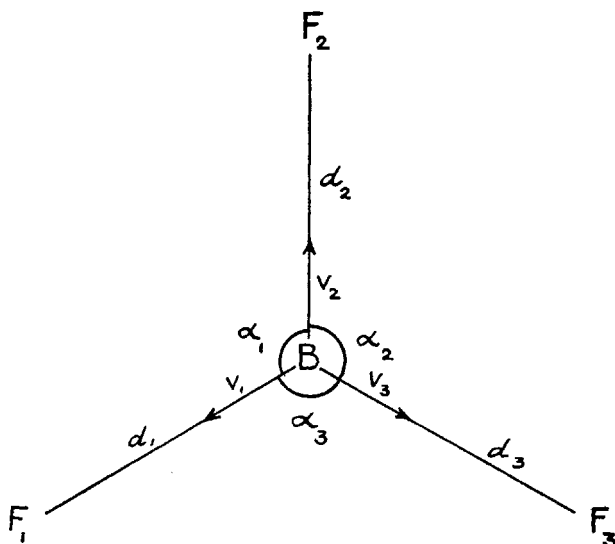


FIG. 1.

F_1 , F_2 , F_3 are the three fluorine atoms.

$B-F_1 = d_1$, $B-F_2 = d_2$, $B-F_3 = d_3$.

For the type E_1' vibration

$$R_{2a} = 6^{-\frac{1}{2}} (2\Delta d_1 - \Delta d_2 - \Delta d_3)$$

$$R_{2b} = 2^{-\frac{1}{2}} (\Delta d_2 - \Delta d_3)$$

$$R_{3a} = 6^{-\frac{1}{2}} (2\Delta\alpha_1 - \Delta\alpha_2 - \Delta\alpha_3)$$

$$R_{3b} = 2^{-\frac{1}{2}} (\Delta\alpha_2 - \Delta\alpha_3)$$

where the suffix a and b denote the degenerate vibrations. Since there are only five vibrational degrees of freedom, only five internal co-ordinates are necessary to define them. But from the structure of the molecule there are six internal co-ordinates. Instead of ignoring one of the internal co-ordinates, one symmetry co-ordinate is constructed in such a manner that it is identically zero. This is justified as this co-ordinate contributes nothing either to P.E. or to K.E. In this case $R_2 = 3^{-\frac{1}{2}} (\Delta\alpha_1 + \Delta\alpha_2 + \Delta\alpha_3)$ is considered to be the redundant co-ordinate, for the sum of the changes of all the angles in a plane around a point is zero.

TRANSFORMATION MATRICES

The transformation matrices which transform the internal co-ordinates of each type of vibrations are then determined. Transformation matrix U for the type A_1' vibration is

$$\begin{array}{c} A_1' \\ R_1 \end{array} \left| \begin{array}{cccccc} \Delta d_1 & \Delta d_2 & \Delta d_3 & \Delta\alpha_1 & \Delta\alpha_2 & \Delta\alpha_3 \\ (3^{-\frac{1}{2}} & 3^{-\frac{1}{2}} & 3^{-\frac{1}{2}} & 0 & 0 & 0) \end{array} \right. \dots \dots (2)$$

For the type E_1' vibration it is written in two ways. Considering the coefficients of the internal co-ordinates in R_{2a} and R_{3a} the U matrix is

$$\begin{pmatrix} 2 \times 6^{-\frac{1}{2}} & -6^{-\frac{1}{2}} & -6^{-\frac{1}{2}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 2 \times 6^{-\frac{1}{2}} & -6^{-\frac{1}{2}} & -6^{-\frac{1}{2}} \end{pmatrix} \dots \dots (3)$$

and considering the symmetry co-ordinates R_{2b} and R_{3b} , the U matrix is

$$\begin{pmatrix} 0 & 2^{-\frac{1}{2}} & -2^{-\frac{1}{2}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 2^{-\frac{1}{2}} & -2^{-\frac{1}{2}} \end{pmatrix} \dots \dots \quad (4)$$

The following table explains the transformations of the internal co-ordinates under all the covering operations of the group D_{3h} .

E	σ_k	(C_3^-, S_3^-)	(C_3^+, S_3^+)	(C_2^1, σ_v^1)	(C_2^2, σ_v^2)	(C_2^3, σ_v^3)
$\Delta d_1 \rightarrow \Delta d_1$	Δd_1	Δd_2	Δd_3	Δd_1	Δd_3	Δd_2
$\Delta d_2 \rightarrow \Delta d_2$	Δd_2	Δd_3	Δd_1	Δd_3	Δd_2	Δd_1
$\Delta d_3 \rightarrow \Delta d_3$	Δd_3	Δd_1	Δd_2	Δd_2	Δd_1	Δd_3
$\Delta \alpha_1 \rightarrow \Delta \alpha_1$	$\Delta \alpha_1$	$\Delta \alpha_2$	$\Delta \alpha_3$	$\Delta \alpha_1$	$\Delta \alpha_3$	$\Delta \alpha_2$
$\Delta \alpha_2 \rightarrow \Delta \alpha_2$	$\Delta \alpha_2$	$\Delta \alpha_3$	$\Delta \alpha_1$	$\Delta \alpha_3$	$\Delta \alpha_2$	$\Delta \alpha_1$
$\Delta \alpha_3 \rightarrow \Delta \alpha_3$	$\Delta \alpha_3$	$\Delta \alpha_1$	$\Delta \alpha_2$	$\Delta \alpha_2$	$\Delta \alpha_1$	$\Delta \alpha_3$

With the help of the transformation table and the coefficients of the internal co-ordinates, the transformation property of the symmetry co-ordinate is verified.

F MATRIX ASSOCIATED WITH THE POTENTIAL ENERGY OF THE MOLECULE

The general * quadratic potential energy in terms of valence type co-ordinates is assumed and is given by

$$\left. \begin{aligned} 2V = f_d (\Delta d_1^2 + \Delta d_2^2 + \Delta d_3^2) + d^2 f_x (\Delta \alpha_1^2 + \Delta \alpha_2^2 + \Delta \alpha_3^2) \\ 2f_{dd} (\Delta d_1 \Delta d_2 + \Delta d_1 \Delta d_3 + \Delta d_2 \Delta d_3) \\ 2df_{\alpha d} (\Delta \alpha_1 + \Delta \alpha_3) \Delta d_1 + (\Delta \alpha_1 + \Delta \alpha_2) \Delta d_2 + (\Delta \alpha_2 + \Delta \alpha_3) \Delta d_3 \\ 2d^2 f_{\alpha x} (\Delta \alpha_1 \Delta \alpha_2 + \Delta \alpha_2 \Delta \alpha_3 + \Delta \alpha_1 \Delta \alpha_3) \end{aligned} \right\} \dots \quad (5)$$

where f_d is the force constant associated with bond stretching, f_x that associated with bending and f_{dd} , $f_{\alpha d}$ and $f_{\alpha \alpha}$ are the constants representing the interactions between stretching and stretching, bending and stretching and bending and bending respectively and 'd' is the equilibrium length of B-F bond. In this P.E. function there are thus five force constants to be determined only by three frequencies. Hence the stretching force constant f_d is calculated from Badger's (Badger, 1935) rule. The remaining four are determined by the three frequencies, f_x and $f_{\alpha \alpha}$ having been obtained only as a difference ($f_x - f_{\alpha \alpha}$).

* In case of valence force field, P.E. is given by $2V = \sum f_{ik} r_i r_k$ (Whittaker) where $f_{ik} = f_{ki}$; i is the force constant associated with i and k which extend over all internal co-ordinates. In terms of the symmetry co-ordinates $2V = \sum F_{jl} R_j R_l$, the relation between f and F being $F = U f U'$.

The f matrix associated with the potential energy function is

$$\begin{bmatrix} f_d & f_{dd} & f_{dd} & df_{\alpha d} & 0 & df_{\alpha d} \\ f_{\alpha d} & f_d & f_{dd} & df_{\alpha d} & df_{\alpha d} & 0 \\ f_{dd} & f_{dd} & f_d & 0 & df_{\alpha d} & df_{\alpha d} \\ df_{\alpha d} & df_{\alpha d} & 0 & d^2f_{\alpha\alpha} & d^2f_{\alpha\alpha} & d^2f_{\alpha\alpha} \\ 0 & df_{\alpha d} & df_{\alpha d} & d^2f_{\alpha\alpha} & d^2f_{\alpha\alpha} & d^2f_{\alpha\alpha} \\ df_{\alpha d} & 0 & df_{\alpha d} & d^2f_{\alpha\alpha} & d^2f_{\alpha\alpha} & d^2f_{\alpha\alpha} \end{bmatrix} \dots \quad (6)$$

The matrix F for type A_1' vibration consists of only one element and that is given by

$$F_{11} = f_d + 2f_{dd} \quad \dots \quad \dots \quad \dots \quad \dots \quad (7)$$

and that of E_1' consists of four elements

$$\begin{bmatrix} F_{22} & F_{23} \\ F_{32} & F_{33} \end{bmatrix} = \begin{bmatrix} (f_d - f_{dd}) & \frac{d}{2}f_{\alpha d} \\ \frac{d}{2}f_{\alpha d} & d^2(f_{\alpha} - f_{\alpha\alpha}) \end{bmatrix}$$

The elements will be the same whether the expression (3) and its transpose or (4) and its transpose matrices are used. In these calculations the latter matrices are used as they involve more vanishing elements and thus lessen the labour.

G MATRIX ASSOCIATED WITH THE KINETIC ENERGY OF THE MOLECULE

The elements of the kinetic energy matrix for the non-degenerate type A_1' vibration are obtained from the equation (9) and for degenerate type E_1' vibrations the equation (10) is used. It has been shown by Wilson that the K.E. can be expressed as a dot * product of two vectors and finally written in the form of a matrix. As there are three equivalent fluorine atoms it is enough if the vectors are obtained for any one of the atoms. The following is the set of the s_{kt} vectors used. (Cleveland, 1948.) Boron atom

$$\left. \begin{aligned} s_{d_1B} &= -V_1 & s_{\alpha_1B} &= \sqrt{3}(V_1 + V_2)/d \\ s_{d_2B} &= -V_2 & s_{\alpha_2B} &= \sqrt{3}\epsilon(V_2 + V_3) \\ s_{d_3B} &= -V_3 & s_{\alpha_3B} &= \sqrt{3}\epsilon(V_1 + V_3) \end{aligned} \right\} \dots \quad (8)$$

* $G_{ji} = \sum_p \mu_p g_p S_j^t \cdot S_i^t$ where $S_j^t = \sum_k U_{jk} s_{kt}$ and $\dots \dots \dots$ (9)

$$G_{ji} = 1/x \sum_p \mu_p g_p (S_{ia}^t \cdot S_{ja}^t + S_{ib}^t \cdot S_{jb}^t + \dots) \dots \dots \dots (10)$$

where μ_p is reciprocal mass of the atom in p -th set of equivalent atoms g_p the number of equivalent atoms in p -th set and x is the degree of degeneracy. (Wilson.)

Fluorine atom

$$s_{A_1F_1} = V_1$$

$$\alpha_{1F_1} = \epsilon (-V_1/2 + V_3) \sqrt{3}/2, \quad \text{where } \epsilon = 1/d, \text{ } d \text{ is the B-F bond length.}$$

$$s_{\alpha_3F_1} = \epsilon (-V_1/2 - V_3) \sqrt{3}/2$$

The rest are zero.

V_1 , V_2 and V_3 are the unit vectors directed along the bonds (shown in Fig. 1). In these calculations, $\alpha_1 = \alpha_2 = \alpha_3 = 120^\circ$ as obtained from the electron diffraction experiments. (Pauling, 1939 and 1941.)

From these s_{ki} vectors and the coefficients of the internal co-ordinates of the symmetry co-ordinates, the following S_j^i vectors can be easily obtained.

$$\left. \begin{aligned} S_1^B &= -(V_1 + V_2 + V_3) 3^{-1/2} & S_1^{F_1} &= V_1/\sqrt{3} \\ S_{2a}^B &= 1/\sqrt{6} (-2V_1 + V_2 + V_3) & S_{2a}^{F_1} &= 2V_1/\sqrt{6} \\ S_{2b}^B &= 1/\sqrt{2} (V_3 - V_2) & S_{3a}^{F_1} &= 2\epsilon/\sqrt{18} \left(V_3 - 2V_2 - \frac{V_1}{2} \right) \\ S_{3a}^B &= \epsilon/\sqrt{2} (V_1 + V_2 - 2V_3) & S_{3b}^{F_1} &= 2\epsilon/\sqrt{6} (V_1/2 + V_3) \\ S_{3b}^B &= \sqrt{3}/\sqrt{2} (V_2 - V_1) \end{aligned} \right\} \dots \quad (11)$$

The only element of G matrix for type A_1' vibration is

$$G_{11} = \mu_F \dots \dots \dots \dots \dots \dots (12)$$

The four elements of G matrix for type E_1' vibrations are

$$\begin{bmatrix} G_{22} & G_{23} \\ G_{32} & G_{33} \end{bmatrix} = \begin{bmatrix} (3/2 \mu_B + \mu_F) & \frac{-3\sqrt{3}}{4} \mu_B \\ \frac{-3\sqrt{3}}{4} \mu_B & \left(9\mu_B + \frac{7}{2} \mu_F \right) \end{bmatrix}$$

where μ_F and μ_B are reciprocal masses of the Fluorine and Boron atoms respectively.

The secular equation for type A_1' vibration is given by

$$\lambda = F_{11} G_{11} \dots \dots \dots \dots \dots \dots (13)$$

where $\lambda = 4\pi^2\nu_1^2 c^2$, ν_1 being the frequency in cm.^{-1} of type A_1' vibration. For the doubly degenerate vibrations the secular equation is

$$\lambda^2 - \lambda (F_{22}G_{22} + 2F_{23}G_{23} + F_{33}G_{33}) + |F| \cdot |G| = 0 \dots \dots (14)$$

The force constants are calculated by solving the two secular equations (13) and (14) making use of the following data:—

$$\left. \begin{aligned} \nu_1 &= 888 \text{ cm.}^{-1} \text{ type } A_1' \text{ vibration} \\ \nu_2 &= 1445.9 \text{ cm.}^{-1} \\ \nu_3 &= 480.4 \text{ cm.}^{-1} \end{aligned} \right\} \text{ type } E_1' \text{ vibrations} \dots \dots (15)$$

$$\mu_B^{11} = 5.469 \times 10^{22} \text{ gm.}^{-1}$$

$$\mu_F = 3.169 \times 10^{22} \text{ gm.}^{-1}$$

$$\text{B-F bond length} = 1.302 \text{ \AA}$$

$$f_d = 7.099 \times 10^5 \text{ dynes/cm. (Badger's rule).}$$

At this stage the numerical values should be substituted.

$$\text{From (13)} \quad f_d + 2f_{da} = 8.833 \times 10^5 \text{ dynes/cm.}$$

$$\text{Hence} \quad f_{da} = 0.867 \times 10^5 \text{ dynes/cm.}$$

Substituting the two values for λ as obtained from the two frequencies 480.4 and 1445.9 in the equation (14) simultaneously, we obtain

$$30.156 (f_\alpha - f_{\alpha\alpha}) - 7.104 f_{\alpha d} = 11.57 \times 10^5 \quad \dots \quad (16)$$

$$-73.08 f_{\alpha d}^2 + 1821.5 \times 10^5 (f_\alpha - f_{\alpha\alpha}) = 608 \times 10^{10} \quad \dots \quad (17)$$

From (16) and (17) it is seen that

$$73.08 f_{\alpha d}^2 - 429.1 f_{\alpha d} - 90.8 = 0 \quad \dots \quad (18)$$

Equation (18) leads to two sets of values which are given in the following table:—

	I Set	II Set
f_d	7.099×10^5 dynes/cm. (Badger's rule)	
f_{da}	0.867×10^5 dynes/cm.	
$f_{\alpha d}$	-0.2052 ,,	6.077
$f_\alpha - f_{\alpha\alpha}$	0.3352 ,,	1.814

CALCULATIONS OF THE FREQUENCIES OF B^{10}F_3

The force constants of the first set are used in calculating the corresponding vibrational frequencies of the isotopic molecule B^{10}F_3 . The same formulae hold good for the isotopic molecule but with different numerical values for the elements of the K.E. matrix since the value of μ_B^{10} is different from that of μ_B^{11} . Further, the element of the K.E. matrix for type A_1' vibration is equal to μ_F and is thus seen to be dependent only on the mass of the Fluorine atom. Hence the corresponding frequency of the totally symmetric vibration of the isotopic molecule B^{10}F_3 is expected to be the same as that of B^{11}F_3 . In these calculations $\mu_{B^{10}} = 6.010 \times 10^{22} \text{ gm.}^{-1}$

The calculated and the observed frequencies are shown below:—

Calculated	Observed
888 cm.^{-1}	888 cm.^{-1}
1499 ,,	1497 ,,
497 ,,	482 ,,

The agreement is found satisfactory.

VERIFICATION OF THE PRODUCT RULE

Finally the product rule formulated by Redlich and Teller is verified. The rule states that the product of the frequencies of a certain molecule divided by the similar product for the same molecule with isotopic atoms is independent of the P.E. function and depends only on the masses and geometric situation of the case. Wilson expressed this in terms of the K.E. matrix elements and shows that

$$\frac{\Pi_{\lambda} \lambda}{\Pi_{\lambda} \lambda'} = \frac{|G|}{|G'|}$$

Where $\Pi_{\lambda} \lambda$ is the product of all λ 's of the same symmetry class as G .

The primes refer to isotopic molecule. (Glockler, 1943.)

For the type E'_1 vibration

$$\frac{\Pi_{\lambda} \lambda'}{\Pi_{\lambda} \lambda} = \frac{1497^2 \times 482^2}{1445.9^2 \times 480.4^2} = 1.08$$

$$\frac{|G'|}{|G|} = 1.12$$

ABSTRACT

Wilson's F-G matrix method has been applied to determine the force constants for the plane symmetrical molecule BF_3 . The set of the force constants thus obtained are used to determine the vibrational frequencies of the isotopic molecule B^{10}F_3 .

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