

Unique force field for boron trihalides

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(Received 24 June 1974, revised 5 September 1974)

An attempt has been made to fix the unique force field for the degenerate species of boron trihalides through parametric representation method using isotopic frequencies and observed Coriolis coupling constants. The parameter ϕ was found to be $26^{\circ}16'$, 14° and 9° for BF_3 , BCl_3 and BBr_3 respectively. Other molecular constants like mean amplitudes of vibration, Coriolis coupling constants and rotational distortion constants were also calculated.

1. INTRODUCTION

Evaluation of potential energy matrix (F) making use of a set of observed vibrational frequencies alone has posed a problem since for N values of $\Lambda (= 4\pi^2\nu^2c^2)$ there exist $N(N+1)/2$ solutions for force constants. To isolate the true F matrix, the different kinematic methods (Herranz & Castano 1966, Torkington 1949, Strey 1967, Billes 1966) have been proposed. For the unique determination of the force field additional data like the Coriolis coupling constants (Duncan & Mills 1964a), mean amplitude of vibration (Morino *et al* 1960), rotational distortion constants (Duncan & Mills 1964b) and infrared band intensities (Levin 1970) are generally used. The use of isotopic data in conjunction with Green's function (DeWames *et al* 1964a, 1964b, 1966, Ramaswamy & Rangarajan 1971, Ramaswamy & Shanmugam 1972) and or the parametric methods (Jordanov & Nikolova 1972a, 1972b, 1972c, Ananthakrishnan & Aruldas 1972) have also been widely used.

In the present paper BY_3 ($Y = \text{F, Cl, Br}$) planar type molecules (D_{3h} point group) have been taken for a general study of these methods with a view to fix the unique force field. Force constants for the (1×1) species A_1 and A_2 can be determined directly from the observed frequencies by a first degree secular equation. The parametric representation of Jordanov & Nikolova (1972a, 1972b, 1972c) and Ananthakrishnan & Aruldas (1972) were used to get unambiguous force constants for the degenerate species e . Other molecular parameters like mean vibrational amplitude, Coriolis coupling constants and rotational distortion constants were also calculated for these boron trihalides. The vibrational frequencies, bond lengths and Coriolis coupling constants used in the present

calculations are summarized in table 1 along with the references from which they are taken.

Table 1. Vibrational frequencies (cm^{-1}), bond lengths (\AA) and Coriolis coupling constants for some XY_3 planar type molecules

Molecule	ν_2	ν_3	ν_4	Bond length \AA	Coriolis coupling constant ζ_{41}
$^{10}\text{BF}_3$	888	1481.9	485.46	1.295	-0.81 ± 0.02^b -0.809^c
$^{11}\text{BF}_3$	888	1428.8	483.74		
$^{10}\text{BCl}_3$	471	993.7	243	1.73	
$^{11}\text{BCl}_3$	471	954.2	243		
$^{10}\text{BBr}_3$	282.5	856	155	1.87	
$^{11}\text{BBr}_3$	282.5	819	155		

^a Ladd *et al* (1963); ^b Duncan (1964); ^c Gini *et al* (1970).

2. THEORETICAL CONSIDERATIONS

For an N dimensional problem, $N(N-1)/2$ free parameters are necessary to achieve a unique solution for ϕ . The choice of the parameter ϕ differs in various methods. The F and G matrices are governed by the relation

$$F = \tilde{L}^{-1} \Lambda L^{-1}, \quad (1)$$

and

$$G = L \tilde{L}. \quad (2)$$

A matrix $L_0 = VT^{\dagger}$ was constructed using V , the eigen vector matrix and T , the eigen value matrix of G . This matrix is related to the true L matrix by the relation

$$L = L_0 A, \quad \dots \quad (3)$$

where A is an orthogonal matrix. For $N = 2$, we need a single parameter and hence the matrix A is given by

$$A = \begin{pmatrix} \cos \phi & \sin \phi \\ -\sin \phi & \cos \phi \end{pmatrix} \quad (4)$$

Jordanov & Nikolova (1972a, 1972b, 1972c) fixed the A matrix by using the isotopic frequencies as additional parameter. They expressed the force constant matrices F and F^* of two isotopic species by the relations

$$F = \tilde{L}_0^{-1} A \Lambda \tilde{A} \tilde{L}_0^{-1} \quad \dots (5)$$

and

$$F^* = \tilde{L}_0^{-1*} A^* \Lambda^* \tilde{A}^* \tilde{L}_0^{-1*} \quad \dots (6)$$

The Born-Oppenheimer approximation ($F = F^*$) yields

$$\Lambda^* = \tilde{A} (\tilde{L}_0^{-1} L_0^*) A \Lambda \tilde{A} (\tilde{L}_0^{-1} L_0^*) A^* \quad \dots (7)$$

The asterisk stands for the isotopic molecule. Assuming $A = A^*$, Λ^* was calculated for various values of ϕ ranging from 0 to 180°. A graph was drawn between ϕ and the calculated isotopic frequencies. The intersection of the frequency curves with the experimental values plotted as straight lines parallel to the abscissa were taken as the true value of ϕ to represent the A matrix. Force constants were calculated for the boron trihalides from relation (5) and the results are given in tables 2 and 3.

Table 2. Symmetrized force constants (mdyn/Å) of BF_3 calculated by different methods.

Method	Parameter ϕ	F_{11}	F_{33}	F_{44}	F_{34}
Jordanov & Nikolova	27°15'	8.8459*	6.9240	0.5032	-0.5300
Using :					
$\zeta_{44} : -0.81 \pm 0.02$	25°15'	8.8459	6.5439	0.5194	-0.3938
$\zeta_{44} : -0.809$	25°18'	8.8459	6.5548	0.5190	-0.3976
Most probable value	26°16'	8.8459	6.7642	0.5129	-0.4717
Ginn <i>et al</i> (1970)	—	—	$6.68_3 \pm 0.05$	$0.509_5 \pm 0.002$	$-0.37_7 \pm 0.02$

* This number of significant figures is retained to secure internal consistency in calculations.

Table 3. Valence force constants (mdyn/Å) of BF_3 , BCl_3 and BBr_3 .

Valence force constants	BF_3		BCl_3		BBr_3	
	Present work	DeWames <i>et al</i> (1966)	Present work	DeWames <i>et al</i> (1966)	Present work	DeWames <i>et al</i> (1966)
f_a	7.4580*	7.1478	3.7612	3.7881	3.1291	3.0669
f_{aa}	0.6939	0.8378	0.4096	0.4192	0.2583	0.3445
f'_{aa}	0.1572	0.1064	0.0651	0.0677	0.0749	0.0614
f''_{aa}	-0.3144	-0.2128	-0.1303	-0.1354	-0.1497	-0.1227
f_{aa}	-0.1708	-0.1758	-0.0756	-0.0761	-0.0666	-0.0679
f_a	0.3416	0.3517	0.1512	0.1523	0.1333	0.1358

* As under table 2,

With a proper A matrix, the relations governing ϕ and ζ values are

$$\tan \phi = \frac{-J_{34} \pm [J_{34}^2 - (J_{33} - \zeta_{44})(J_{44} - \zeta_{33})]^{1/2}}{(J_{33} - \zeta_{44})} \quad (8)$$

and

$$\tan \phi = \frac{J_{34} \pm [J_{34}^2 - (J_{33} - \zeta_{33})(J_{44} - \zeta_{33})]^{1/2}}{(J_{44} - \zeta_{33})}, \quad (9)$$

with $J = L_0^{-1} C \tilde{L}_0^{-1}$ where C is the matrix (Meal & Polo 1956) which depends on the mass and geometry of the molecule. For XY_3 planar type molecules, the elements of the C matrix are

$$C_{33} = 3/2\mu_x; \quad C_{34} = \frac{\sqrt{3}}{d} (3/2\mu_x + \mu_y); \quad C_{44} = \frac{9}{2\sqrt{3}d^2} \mu_x.$$

These values are essentially the same as the one reported by Kristiansen & Cyvin (1963). Using the observed ζ value of Duncan (1964) and Ginn *et al* (1970) the solution of ϕ was fixed from relation (8). The force constant matrix F was calculated from relation (5) and the results are given in table 2.

The mean vibrational amplitudes, Coriolis coupling constants and rotational distortion constants were calculated from the well known relations of Cyvin (1959), Meal & Polo (1956) and Kivelson & Wilson (1952, 1953) and the results are given in table 4.

Table 4. Mean amplitudes of vibration (\AA), Coriolis coupling constants^a and rotational distortion constants (cm^{-1}) of BF_3 , BCl_3 and BBr_3 .

Molecule	Mean amplitudes of vibration $\sigma_{X-Y}(\text{\AA})$	Coriolis coupling constants		Rotational distortion constants $\times 10^{-7} (\text{cm}^{-1})$		
		ζ_{33}	ζ_{44}	D_J	D_K	D_{JK}
BF_3	0.0430*	0.789	-0.789	2.8515	1.9972	-4.8500
	(0.0431) ^a		(-0.809) ^b	$(4 \times 10^{-7})^d$	$(2 \times 10^{-7})^d$	$(5 \times 10^{-7})^d$
BCl_3	0.050	0.881	-0.881	0.2991	0.2192	-0.4900
	(0.050)		(-0.874) ^c			
BBr_3	0.0515	0.940	-0.940	0.0419	0.0298	-0.0677
	(0.0518) ^a		(-0.903) ^c			

^a Cyvin (1969c); ^b Ginn *et al* (1970); ^c Kristiansen & Cyvin (1963); ^d Ginn *et al* (1968).

* As under table 2.

3. DISCUSSION

Ladd *et al* (1963) in their attempt to fix unique force constants for the E species have drawn a graph between F_{33} and a function of β , incorporating the

force constants of $^{10}\text{BF}_3$ and $^{11}\text{BF}_3$ and chose F_{33} corresponding to a minimum value. The remaining force constants F_{34} and F_{44} were calculated from the force constant ellipses drawn between F_{34} and F_{33} and F_{44} . Lindeman & Wilson (1956) fixed the force constants of BF_3 by transferring the potential constants from other related molecules to the one in question. DeWames *et al* (1964a, 1964b, 1966) used the isotopic frequencies as the additional parameter and thereby fixed the force field through Green's function analysis. Duncan (1964) and McKeon (1966) fixed the force field of BF_3 by drawing a graph between F_{34} and F_{33} , F_{44} and ζ_{44} and chose the correct set corresponding to the intersection of the calculated ζ curve with the observed values. Ananthakrishnan & Aruldas (1972) fixed the force constants for BF_3 in the parametric representation using the observed ζ value.

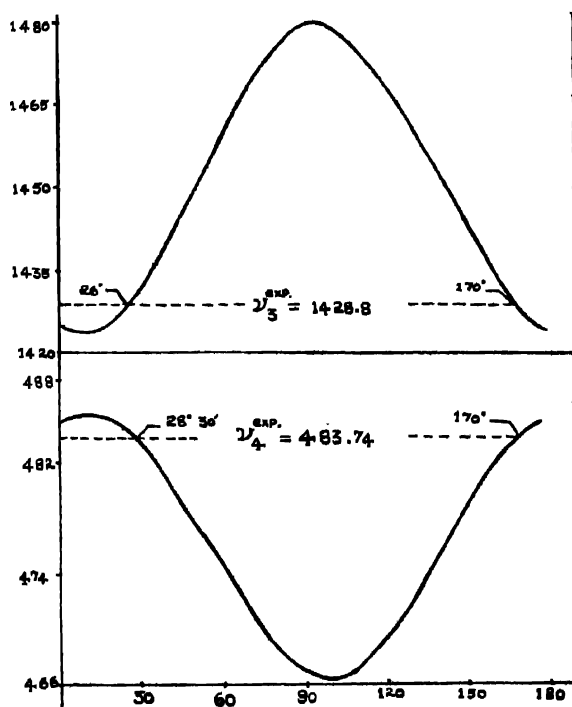


Fig. 1. Plot of frequency ν_3^* of BF_3 versus the angle ϕ for the degenerate species of the isotopic pair $^{10}\text{BF}_3$ and $^{11}\text{BF}_3$.

Plot of frequency ν_4^* of BF_3 versus the angle ϕ for the degenerate species of the isotopic pair $^{10}\text{BF}_3$ and $^{11}\text{BF}_3$.

In calculating the force constants of BF_3 by Jordanov & Nikolova's (1972c) method, using relation (7) Λ^* and hence ν^* was calculated. Graphs were drawn between ϕ and ν_3^* and ν_4^* and shown in figure 1. It is seen from the graph that

there are two solutions for ϕ corresponding to the intersection of the calculated and observed isotopic frequencies. The mean values are $27^\circ 15'$ and 170° . Using these two values for ϕ , A matrix was constructed and force constants were calculated from relation (5). It was found that the $B-F$ band force constant calculated using $\phi = 170^\circ$ leads to abnormal values for BF stretching force constant.

Duncan (1964) computed ζ_{44} as -0.81 ± 0.02 by comparing the calculated band contour with the observed one. Using this ζ_{44} value the parameter ϕ was calculated from relation (8) and it was found to be $25^\circ 15'$. Subsequently Ginn *et al* (1970) reported a value of -0.809 for ζ_{44} from the ν_4 band analysis. The value of ϕ obtained for $\zeta_{44} = -0.809$ was $25^\circ 18'$. A mean value of $\phi = 26^\circ 16'$ which will reproduce both the isotopic frequencies and the Coriolis coupling constants was chosen to represent the correct parameter ϕ for BF_3 . With this value of $\phi = 26^\circ 16'$, the F matrix elements ($F_{33} = 6.7642$ mdyn/Å; $F_{23} = -0.4717$ mdyn/Å; $F_{44} = 0.5125$ mdyn/Å) obtained are in good agreement with the values ($F_{33} = 6.68$ mdyn/Å; $F_{34} = -0.37$ mdyn/Å; $F_{44} = 0.509$ mdyn/Å) reported by Ginn *et al* (1970).

The mean amplitude of vibration (0.0430 Å) calculated for the $B-F$ bond at $\phi = 26^\circ 16'$ is in agreement with the value (0.043 Å) reported by Cyvin (1969c). The Coriolis coupling constant ζ_{44} (-0.789) is in agreement with the value (-0.809) observed by Ginn *et al* (1970). The rotational distortion constants ($D_K = 1.9972 \times 10^{-7}$ cm $^{-1}$; $D_{JK} = -4.85 \times 10^{-7}$ cm $^{-1}$) are in good agreement with the values ($D_K = 2 \times 10^{-7}$ cm $^{-1}$; $D_{JK} = -5 \times 10^{-7}$ cm $^{-1}$) reported by Ginn *et al* (1968).

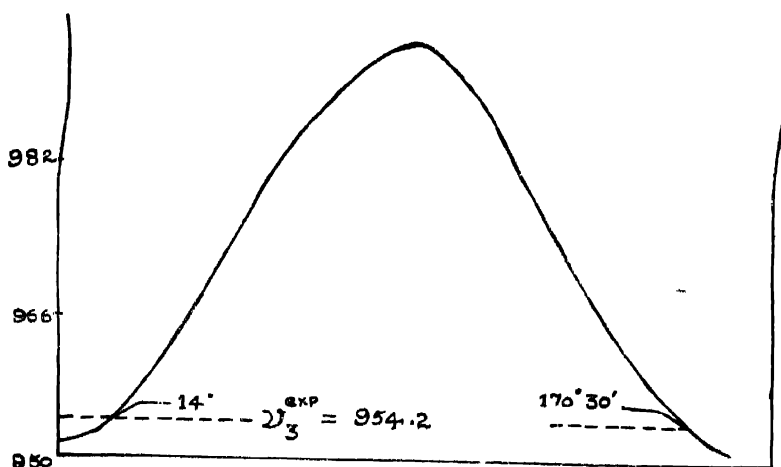


Fig. 2. Plot of frequency ν_3^* of BCl_3 versus the angle ϕ for the degenerate species of the isotopic pair $^{10}BCl_3$ and $^{11}BCl_3$.

Using relation (7), Λ^* and hence ν^* was calculated for BCl_3 . Since there is no change in the bending frequency due to isotopic substitution the graph was drawn between ϕ and ν_3^* alone and is shown in figure 2. It is seen from the figure that there are two solutions for ϕ corresponding to the observed value of the isotopic frequency. The two solutions are 14° and $170^\circ 30'$. The value of $\phi = 14^\circ$ has been taken as the true solution for this molecule. As seen from table 3 the valence force constants calculated for $\phi = 14^\circ$ are in good agreement with the reported work of DeWames *et al* (1966). The bonded mean amplitude vibration (0.050 \AA) calculated for BCl_3 compares well with the value (0.050 \AA) reported by Cyvin (1969c) and the electron diffraction value of ($0.045 \pm 0.003 \text{ \AA}$) Hedberg (1966). The Coriolis coupling constant calculated for the degenerate species E ($\zeta_{44} = -0.881$) is in good agreement with the value ($\zeta_{44} = -0.874$) given by Kristiansen & Cyvin (1963).

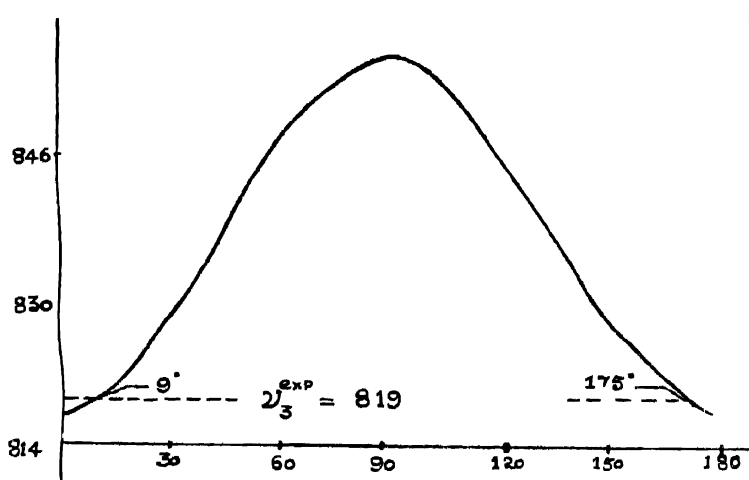


Fig. 3. Plot of frequency ν_3^1 of BBr_3 versus the angle ϕ for the degenerate species of the r_3 and ^{10}BRr .

For $\text{BBr}_3\Lambda^*$ and hence ν^* was calculated from relation (7). A graph was drawn between ϕ and ν_3^* and it is shown in figure 3. It was found that the isotopic frequencies were reproduced at $\phi = 9^\circ$ and 175° . The value of $\phi = 9^\circ$ represents the true state of affair for this molecule and the force constants were calculated at $\phi = 9^\circ$ from relation (5) and the results are given in table 3. As seen from table 3 the valence force constants are in general agreement with the work of DeWames *et al* (1966). The calculated mean amplitude of vibration (0.0515 \AA) and the Coriolis coupling constant ($\zeta_{44} = -0.940$) are in agreement with the values (0.0518 \AA) and ($\zeta_{44} = -0.903$) reported by Cyvin (1969c) and Kristiansen & Cyvin (1963), respectively.

ACKNOWLEDGMENT

One of the authors (L.J.) is thankful to the Council of Scientific and Industrial Research, Government of India, New Delhi for the award of a Junior Research Fellowship.

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