

Calculated Mean Amplitudes of Vibration in Boron Trihalides

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The mean amplitudes of vibration from spectroscopic data in boron trifluoride, trichloride and tribromide are recalculated. The results are presented together with new calculations for boron triiodide.

Bakken¹ has presented a list of mean amplitude values for a number of four-atomic molecules including boron trifluoride, trichloride and tribromide. Professor Morino during his stay in Trondheim pointed out a discrepancy between Bakken's values and unpublished values obtained by T. Iijima for the non-bonded distances in boron trifluoride and trichloride. In the present work a recalculation of the mean amplitudes of the three mentioned

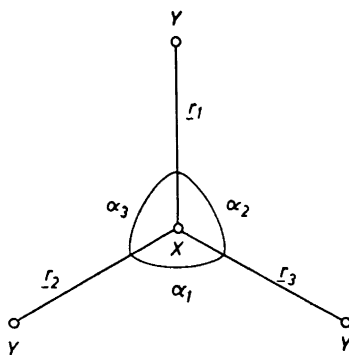


Fig. 1. Internal coordinates for plane symmetrical XY_3 molecules. The symbols denote displacements from the equilibrium distances and angles. Symmetry coordinates:

$$\begin{aligned} \text{Symm. species } A'_1: & \quad S_1 = 3^{-\frac{1}{2}}(r_1 + r_2 + r_3) \\ \text{Symm. species } E': & \quad \begin{cases} S_3 = 6^{-\frac{1}{2}}(2r_1 - r_2 - r_3) \\ S_4 = 6^{-\frac{1}{2}}(2\alpha_1 - \alpha_2 - \alpha_3) \end{cases} \end{aligned}$$

R denotes the equilibrium X-Y distance.

molecules has been performed together with the calculations for boron triiodide. These calculations revealed an error in the numerical calculations of Bakken.

*General treatment*²⁻⁵. The molecular model (XY_3) is that of D_{3h} symmetry in the equilibrium position. Small harmonic vibrations are assumed. It is found that only 3 symmetry coordinates (see Fig. 1) are needed for setting up the energy matrices for the in-plane vibrations. The adopted symbols for the force constants of the symmetrized potential energy matrix are given by

$$K_1 \text{ (symmetry species } A'_1); \left[\begin{matrix} K_2 \Gamma \\ \Phi \end{matrix} \right] \text{ (symmetry species } E').$$

The secular equation yields the following equations for the vibrational frequencies ($\lambda = 4\pi^2\nu^2$),

$$\begin{aligned} \lambda_1 &= K_1\mu_Y \\ \lambda_3 + \lambda_4 &= \frac{1}{2}(K_2 + 3\Phi) (3\mu_X + 2\mu_Y) + 3\frac{1}{2}\Gamma\mu_X \\ \lambda_3\lambda_4 &= 3(K_2\Phi - \Gamma^2) (3\mu_X + \mu_Y) \mu_Y \end{aligned}$$

where μ_X and μ_Y denote the inverse masses of X and Y, respectively. The two types of interatomic distance deviations will be represented by $r_{XY} = r_1$

Table 1. Experimental fundamental frequencies and calculated force constants of boron trihalides.

Fundamentals (gaseous state) in cm^{-1} units ^a				
	¹¹ BF ₃	¹¹ BCl ₃	¹¹ BBr ₃	¹¹ BI ₃
ν_1	888	471	278	190
ν_3	1 453.5	954.2	819.8	704.1
ν_4	480.4	243	148	100
	¹⁰ BF ₃	¹⁰ BCl ₃	¹⁰ BBr ₃	¹⁰ BI ₃
ν_3	1 504.7	993.7	856.1	737.0
Force constants in mdyne/Å units ^b				
	BF ₃	BCl ₃	BBr ₃	BI ₃
K_1	8.8236	4.6324	3.6374	2.6984
K_2	7.4068	3.3424	3.3021	1.7292
Φ	0.50013	0.23082	0.18071	0.15079
Γ	-0.63980	-0.19575	-0.34545	-0.03493

^a The data for BF₃ and BCl₃ are from Ref.⁶; those of BBr₃ and BI₃ from Ref.⁷.

^b The additional solutions arising from the quadratic secular equation yield unreliable force constant values which have been rejected.

Table 2. Mean amplitudes of vibration in boron trihalides.

Mean amplitude (Å)	Abs. temp. °K	Molecule			
		¹¹ BF ₃	¹¹ BCl ₃	¹¹ BBr ₃	¹¹ BI ₃
<i>u</i> _{XY}	0	0.0424	0.0478	0.0479	0.0508
	298	0.0425	0.0491	0.0506	0.0570
<i>u</i> _{YY}	0	0.0517	0.0536	0.0461	0.0449
	298	0.0552	0.0689	0.0726	0.0848

and $r_{YY} = \frac{1}{2} 3^{\frac{1}{2}} (r_2 + r_3) + \frac{1}{2} R\alpha_1$. They are connected with the symmetry coordinates by the following linear combinations.

$$r_{XY} = 3^{-\frac{1}{2}} S_1 + 6^{-\frac{1}{2}} 2S_3$$

$$r_{YY} = S_1 - 2^{-\frac{1}{2}} S_3 + 6^{-\frac{1}{2}} S_4$$

To compute the corresponding mean amplitudes, *viz.* $u_{XY} = \langle r_{XY}^2 \rangle_{Av}^{1/2}$ and $u_{YY} = \langle r_{YY}^2 \rangle_{Av}^{1/2}$, the interatomic distance deviations need be expressed in terms of the normal coordinates. Consequently the transformation between the symmetry coordinates and the normal coordinates is required. (For a detailed theoretical treatment, see especially Refs. 4, 5).

Numerical computations. The applied experimental values of vibrational frequencies are given in Table 1. Calculated force constants which are consistent with these frequency values are also included in the table.

The data from Table 1 have been used for computations of the mean amplitudes of vibration (*u*) for the boron halides of the ¹¹B isotope. The resulting values of *u* at the absolute zero point and the temperature 298 °K are given in Table 2.

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