

Vibrational Mean-Square Amplitude Matrices

VI. Planar Symmetrical XY₃ Molecules

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The mean-square amplitude quantities for the planar symmetrical XY₃ molecular model are treated theoretically. The L matrix elements ($S = LQ$), and the symmetrized mean-square amplitude matrix elements at the temperatures $T = 0$ and 298 °K, are given numerically for the four boron trihalides.

The vibrations of planar symmetrical XY₃ molecules have been subjected to several investigations. For publications containing theoretical considerations on this problem, and involving force constant determinations, references are made to ¹⁻⁷. For the computations of mean amplitudes of vibration from spectroscopic data, it is referred to ⁷⁻⁹. To the knowledge of the author, no determinations of mean amplitudes of vibration have so far been performed from electron-diffraction, for any molecule of the structure here considered. In the present paper, the mean-square amplitude quantities of planar symmetrical XY₃ molecules are treated, and numerical values for boron trihalides are reported.

THEORETICAL TREATMENT

For the in-plane vibrations of the considered molecular model there exist four independent harmonic vibrational constants. The following set of constants consists of mean-square amplitude quantities, based on a set of valence force coordinates.

$$\sigma = \langle r_1^2 \rangle = \langle r_2^2 \rangle = \langle r_3^2 \rangle \quad (1)$$

$$\sigma' = \langle r_1 r_2 \rangle = \langle r_2 r_3 \rangle = \langle r_3 r_1 \rangle \quad (2)$$

$$\tau = R^2 \langle \alpha_1^2 \rangle = R^2 \langle \alpha_2^2 \rangle = R^2 \langle \alpha_3^2 \rangle \quad (3)$$

$$\tau' = R^2 \langle \alpha_1 \alpha_2 \rangle = R^2 \langle \alpha_2 \alpha_3 \rangle = R^2 \langle \alpha_3 \alpha_1 \rangle \quad (4)$$

$$\varrho = R \langle r_1 \alpha_1 \rangle = R \langle r_2 \alpha_2 \rangle = R \langle r_3 \alpha_3 \rangle \quad (5)$$

$$\varrho' = R \langle r_1 \alpha_2 \rangle = R \langle r_1 \alpha_3 \rangle = R \langle r_2 \alpha_3 \rangle \\ = R \langle r_2 \alpha_1 \rangle = R \langle r_3 \alpha_1 \rangle = R \langle r_3 \alpha_2 \rangle \quad (6)$$

In these equations, R is the equilibrium X—Y bond length, r representing the deviations of the interatomic X—Y distances, and α the inter-bond angle deviations, from their equilibrium values. The numbering of the coordinates is the same as that used in previous papers ^{7,9}. From the redundant condition $\alpha_1 + \alpha_2 + \alpha_3 = 0$ it is found

$$\tau + 2\tau' = 0, \quad \varrho + 2\varrho' = 0 \quad (7)$$

for the quantities defined by eqns (3)–(6).

The interatomic distance deviations between the non-bonded atom pairs may be taken into account instead of the angle displacements, and designated r_1^* , r_2^* and r_3^* . Then the following mean-square amplitude quantities are to be introduced.

$$\tau^* = \langle (r_1^*)^2 \rangle = \langle (r_2^*)^2 \rangle = \langle (r_3^*)^2 \rangle \quad (8)$$

$$\varrho^* = \langle r_1 r_1^* \rangle = \langle r_2 r_2^* \rangle = \langle r_3 r_3^* \rangle \quad (9)$$

$$\begin{aligned} \varrho'^* &= \langle r_1 r_2^* \rangle = \langle r_1 r_3^* \rangle = \langle r_2 r_3^* \rangle \\ &= \langle r_2 r_1^* \rangle = \langle r_3 r_1^* \rangle = \langle r_3 r_2^* \rangle \end{aligned} \quad (10)$$

These quantities may be expressed in terms of the quantities from eqns. (1)–(6) by the following linear combinations.

$$\tau^* = \frac{3}{2}(\sigma + \sigma') + \frac{1}{6}(\tau - \tau') - 3^{-\frac{1}{2}}(\varrho - \varrho') \quad (11)$$

$$\varrho^* = 3^{\frac{1}{2}} \sigma' + \frac{1}{3}(\varrho - \varrho') \quad (12)$$

$$\varrho'^* = \frac{1}{2} 3^{\frac{1}{2}} (\sigma + \sigma') - \frac{1}{6}(\varrho - \varrho') \quad (13)$$

The vibrational analysis is facilitated by introducing symmetry coordinates. The elements of the symmetrized mean-square amplitude matrix are given by

$$\Sigma_1 = \langle S_1^2 \rangle = \sigma + 2\sigma' \quad (14)$$

$$\Sigma_3 = \langle S_{3a}^2 \rangle = \langle S_{3b}^2 \rangle = \sigma - \sigma' \quad (15)$$

$$\Sigma_4 = \langle S_{4a}^2 \rangle = \langle S_{4b}^2 \rangle = \tau - \tau' \quad (16)$$

$$\Sigma_{34} = \langle S_{3a} S_{4a} \rangle = \langle S_{3b} S_{4b} \rangle = \varrho - \varrho' \quad (17)$$

Table 1. Symmetry coordinates for the planar symmetrical XY₃ molecular model.

Species	No.	Coordinate
A ₁ '	1	$3^{-\frac{1}{2}}(r_1 + r_2 + r_3)$
E'a	3a	$6^{-\frac{1}{2}}(2r_1 - r_2 - r_3)$
	4a	$6^{-\frac{1}{2}}R(2\alpha_1 - \alpha_2 - \alpha_3)$
E'b	3b	$2^{-\frac{1}{2}}(r_2 - r_3)$
	4b	$2^{-\frac{1}{2}}R(\alpha_2 - \alpha_3)$

The symmetry coordinates (S) are formed as normalized linear combinations of the valence force coordinates, and specified in Table 1. For the mean-square amplitude quantities of eqns. (14)–(17) one has the relations

$$\Delta_1 = \Sigma_1 \mu_Y^{-1} \quad (18)$$

$$\Delta_3 + \Delta_4 = \left[\frac{1}{2}(\Sigma_3 + \frac{1}{3}\Sigma_4)(3\mu_X + 2\mu_Y) - 3^{\frac{1}{2}} \Sigma_{34}\mu_X \right] (3\mu_X + \mu_Y)^{-1} \mu_Y^{-1} \quad (19)$$

$$\Delta_3 \Delta_4 = \frac{1}{3}(\Sigma_3 \Sigma_4 - \Sigma_{34}^2)(3\mu_X + \mu_Y)^{-1} \mu_Y^{-1} \quad (20)$$

Here μ_X and μ_Y denote the inverse masses of the X and Y atoms, respectively, and the values of Δ are connected with the vibrational normal frequencies (ν) through

$$\Delta_k = (h/8\pi^2\nu_k) \coth(h\nu_k/2kT) \quad (21)$$

where h is Planck's constant, k Boltzmann's constant, and T the absolute temperature. Another set of relations, involving the force constants, is given below.

$$\epsilon_1 = K_1 \Sigma_1 \quad (22)$$

$$\epsilon_3 + \epsilon_4 = K_2 \Sigma_3 + \Phi \Sigma_4 + 2\Gamma \Sigma_{34} \quad (23)$$

$$\epsilon_3 \epsilon_4 = (K_2 \Phi - \Gamma^2)(\Sigma_3 \Sigma_4 - \Sigma_{34}^2) \quad (24)$$

The force constants, *viz.* K_1 , K_2 , Φ and Γ , are based on the chosen symmetry coordinates (Table 1), and given in terms of usual valence force coordinates in Ref.⁹ The values of ϵ are given by

$$\epsilon_k = \frac{1}{2} h\nu_k \coth(h\nu_k/2kT) \quad (25)$$

If the coefficients of the transformation connecting the symmetry coordinates (S) with the normal coordinates (Q), *viz.*

$$S_i = \sum_k L_{ik} Q_k \quad (26)$$

are known, the symmetrized mean-square amplitude matrix elements are simply obtained by the following expressions.

$$\Sigma_1 = L_{11}^2 \Delta_1 \quad (27)$$

$$\Sigma_3 = L_{33}^2 \Delta_3 + L_{34}^2 \Delta_4 \quad (28)$$

$$\Sigma_4 = L_{43}^2 \Delta_3 + L_{44}^2 \Delta_4 \quad (29)$$

$$\Sigma_{34} = L_{33} L_{43} \Delta_3 + L_{34} L_{44} \Delta_4 \quad (30)$$

The most important ones of the mean-square amplitude quantities here concerned, are the two designated σ and τ^* , and defined by eqns. (1) and (8), respectively. They are given in terms of the symmetrized mean-square amplitude matrix elements by the expressions

$$\sigma = \frac{1}{3}(\Sigma_1 + 2\Sigma_3) \quad (31)$$

$$\tau^* = \Sigma_1 + \frac{1}{2}(\Sigma_3 + \frac{1}{3}\Sigma_4) - 3^{-\frac{1}{2}}\Sigma_{34} \quad (32)$$

Table 2. Transformation coefficients $L_{i,k}$ in (atomic weight units) $^{-\frac{1}{2}}$ for boron trihalides.

$^{11}\text{BF}_3$	Q_1	Q_3	Q_4
S_1	0.2294
S_3	...	0.4346	0.001331
S_4	...	0.5413	0.5230
$^{11}\text{BCl}_3$	Q_1	Q_3	Q_4
S_1	0.1679
S_3	...	0.4051	-0.01749
S_4	...	0.5981	0.3681
$^{11}\text{BBr}_3$	Q_1	Q_3	Q_4
S_1	0.1119
S_3	...	0.3856	0.006125
S_4	...	0.6074	0.2779
$^{11}\text{BI}_3$	Q_1	Q_3	Q_4
S_1	0.08876
S_3	...	0.3789	-0.02293
S_4	...	0.6333	0.1765

These quantities represent the mean-square amplitudes of vibration for the bonded and non-bonded interatomic distances, respectively, and would also be obtainable from electron-diffraction. See, *e.g.* Refs.¹⁰⁻¹⁵

NUMERICAL COMPUTATIONS

In the numerical computations reported in the following, the three vibrational frequencies for $^{11}\text{BY}_3$ ($\text{Y} = \text{F}, \text{Cl}, \text{Br}, \text{I}$) together with r_3 for $^{10}\text{BY}_3$ were used to determine the vibrational constants. The experimental data for BF_3 and BCl_3 have been taken from Ref.⁴, those for BBr_3 and BI_3 from Ref.⁵, and are quoted in a previous paper⁷. This paper⁷ also contains the calculated force constants.

The coefficients $L_{i,k}$ defined by eqn. (26), for the trihalides of the ^{11}B isotope, are given numerically in Table 2. The resulting mean-square amplitude quantities Σ_1 , Σ_3 , Σ_4 and Σ_{34} at the absolute zero point and the temperature 298 °K, are given in Table 3.

Table 3. Mean-square amplitude quantities in Å² units for boron trihalides.

Molecule	Symbol	Mean-square amplitude $T = 0$	quantity 298°K
¹¹ BF ₃	Σ_1	0.000999	0.001027
	Σ_3	0.002191	0.002195
	Σ_4	0.013000	0.015103
	Σ_{34}	0.002753	0.002763
¹¹ BCl ₃	Σ_1	0.001010	0.001242
	Σ_3	0.002921	0.002999
	Σ_4	0.015723	0.024279
	Σ_{34}	0.003835	0.003521
¹¹ BBr ₃	Σ_1	0.000759	0.001297
	Σ_3	0.003063	0.003190
	Σ_4	0.016386	0.033563
	Σ_{34}	0.005011	0.005572
¹¹ BI ₃	Σ_1	0.000699	0.001631
	Σ_3	0.003527	0.004051
	Σ_4	0.014858	0.032465
	Σ_{34}	0.005064	0.003261

The mean amplitudes of vibration are in the present notation given by

$$u_{xy} = \sigma \frac{1}{2}, \quad u_{xy} = (\tau^*) \frac{1}{2} \quad (33)$$

and are obtainable according to eqns. (31) and (32). Their numerical values for the molecules here considered, have been given in Table 2 of Ref.⁷

REFERENCES

1. Heath, D. F. and Linnett, J. W. *Trans. Faraday Soc.* **44** (1948) 873.
2. Heslop, W. R. and Linnett, J. W. *Trans. Faraday Soc.* **49** (1953) 1262.
3. Venkateswarlu, K. and Sundaram, S. *J. Chem. Phys.* **23** (1955) 2368.
4. Lindeman, L. P. and Wilson, M. K. *J. Chem. Phys.* **24** (1956) 242.
5. Wentink, T. Jr. and Tiensuu, V. H. *J. Chem. Phys.* **28** (1958) 826.
6. Pistorius, C. W. F. T. *J. Chem. Phys.* **29** (1958) 1174.
7. Cyvin, S. J. *Acta Chem. Scand.* **13** (1959) 334.
8. Bakken, J. *Acta Chem. Scand.* **12** (1958) 594.
9. Cyvin, S. J. *Spectrochim. Acta* **15** (1959) 341.
10. Debye, P. *J. Chem. Phys.* **9** (1941) 55.
11. Karle, I. L. and Karle, J. *J. Chem. Phys.* **17** (1949) 1052.
12. Bartell, L. S., Brockway, L. O. and Schwendeman, R. H. *J. Chem. Phys.* **23** (1955) 1854.
13. Morino, Y. and Hirota, E. *J. Chem. Phys.* **23** (1955) 737.
14. Bastiansen, O. and Cyvin, S. J. *Nature* **180** (1957) 980.
15. Cyvin, S. J. *Kgl. Norske Videnskab. Selskabs Skrifter. In press.*

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