Mean Amplitudes of Vibration and Shrinkage Effect of Boron Trihalides, Calculated from Urey-Bradley Force Constants

E. MEISINGSETH

Institutt for teoretisk kjemi, Norges tekniske høgskole, Trondheim, Norway

In a preliminary report [1] the Urey-Bradley force constants have been calculated for the boron trihalides. It seems reasonable to use these force constants for calculating the mean amplitudes of vibration and the shrinkage effect of the molecules in question. This kind of calculations, based on Urey-Bradley force constants have not been reported previously in the literature.

The mean amplitudes of vibration for the bonded XY atoms (u_{XY}) and non-bonded YY atoms (u_{YY}) have been calculated. Following the teoretical treatment of Cyvin [2], u_{XY} and u_{YY} may be expressed in terms of the elements of the symmetrized mean-square amplitude matrix (Σ):

$$u_{XY} = (1/3(\Sigma_1 + 2\Sigma_3)]^{\frac{1}{2}}$$

$$u_{YY} = [\Sigma_1 + 1/2(\Sigma_3 + 1/3\Sigma_4) - 3^{\frac{1}{2}}\Sigma_{34}]^{\frac{1}{2}}$$

Table 1. Calculated mean amplitudes of vibration (u)*

Molecule	Interatomic distance	u (Å) $T = 0$	298°K
BF_3	B——F	0.0425 (0.0424)	0.0426 (0.0425)
	F——F	0.0521 (0.0517)	0.0558 (0.0552)
BCl_3	B——Cl	0.0478 (0.0478)	0.0491 (0.0491)
	Cl——Cl	0.0532 (0.0536)	0.0683 (0.0683)
BBr_3	B——Br	0.0483 (0.0479)	0.0516 (0.0506)
	Br——Br	0.0485 (0.0461)	0.0768 (0.0726)
BI_3	B——I	0.0613 (0.0508)	0.0587 (0.0570)
	I——I	0.0494 (0.0449)	0.0948 (0.0848)

* Cyvin's [7] values in parentheses.

Table 2. Calculated shrinkage effect (δ) *.

Molecules	δ (Å). $T = 0$	298°K
BF_3	0.00331 (0.00334)	0.00364 (0.00371)
BCl_3	0.00338 (0.00328)	0.00452 (0.00441)
BBr_3	0.00340 (0.00347)	0.00516 (0.00564)
BI_3	0.00325 (0.00311)	0.00541 (0.00510)

* Meisingseth and Cyvin's [6] values in parentheses.

The shrinkage effect which have been observed for linear-chain molecules by electron-diffraction studies of Bastiansen *et al.*[3-5], may be defined as the difference between the observed and calculated interatomic distance. The shrinkage effect for the molecules here considered may be expressed in terms of the Σ-matrix elements [6]:

$$\delta = 1/6R(3^{-\frac{1}{2}}\Sigma_2 - 1/2\,3^{\frac{1}{2}}\Sigma_3 + 1/2\,3^{\frac{1}{2}}\Sigma_4 + \Sigma_{34})$$

where R is the equilibrium interatomic distance.

The results obtained for the mean amplitudes of vibration are given in Table 1 and are in good agreement with those reported by Cyvin [7], as calculated from general quadratic potential function. In Table 2 the calculated shrinkage effects are presented and are compared to those previously calculated by Meisingseth and Cyvin [6]. Here again a good agreement is observed.

1. Meisingseth, E. *Acta Chem. Scand.* **16** (1962) *In press.*
2. Cyvin, S. J. *Acta Chem. Scand.* **13** (1959) 1809.
3. Almenningen, A. Bastiansen, O., and Munthe-Kaas, T. *Acta Chem. Scand.* **10** (1956) 261.
4. Almenningen, A., Bastiansen, O. and Trætteberg, M. *Acta Chem. Scand.* **13** (1959) 1699.
5. Bastiansen, O. and Trætteberg, M. *Acta Cryst.* **13** (1960) 1108.
6. Meisingseth, E. and Cyvin, S. J. *J. Mol. Spectroscopy. In press.*
7. Cyvin, S. J. *Acta Chem. Scand.* **13** (1959) 334.

Received March 6, 1962.