Spectroscopic Calculations on Sulphur Hexafluoride

II. Mean- Square Perpendicular Amplitudes and Shrinkage Effects

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The Bastiansen-Morino shrinkage effect [1,2] was first observed by electron-diffraction in the study of some linear-chain molecules. In the linear case, and in special nonlinear cases, the shrinkage effect may be computed from the harmonic vibrations analysis [3]. In the present work such calculations have been performed for sulphur hexafluoride.

The mean-square *perpendicular* amplitudes [4,5] for the three different types of distances (identified by the subscripts XY, YY and YXY) are expressed in terms of the Σ-matrix elements as follows.

$$\langle \Delta x_{XY}^2 \rangle = \langle \Delta y_{XY}^2 \rangle = \tfrac{1}{8}\Sigma_{22}(F_{1u}) + \tfrac{1}{16}\Sigma(F_{2s}) + \tfrac{1}{8}\Sigma(F_{2u})$$

$$\langle \Delta x_{YY}^2 \rangle = \tfrac{1}{2}\Sigma(E_g) + \tfrac{1}{2}\Sigma_{11}(F_{1u}) + \tfrac{1}{8}\Sigma_{22}(F_{1u}) - \tfrac{1}{2}\Sigma_{12}(F_{1u}) + \tfrac{1}{8}\Sigma(F_{2u})$$

$$\langle \Delta y_{YY}^2 \rangle = \tfrac{1}{8}\Sigma(F_{2s}) + \tfrac{1}{2}\Sigma(F_{2u})$$

$$\langle \Delta x_{YXY}^2 \rangle = \langle \Delta y_{YXY}^2 \rangle = \tfrac{1}{4}\Sigma(F_{2s})$$

The mean-square perpendicular amplitudes are given numerically in Table 1. (For the Σ-matrix elements, see Table 1 of Ref. [6]).

Table 1. Mean-square perpendicular amplitudes for sulphur hexafluoride (Å² units).

Atom pair	Abs.temp.	$\langle \Delta x^2 \rangle$	$\langle \Delta y^2 \rangle$
SF (Bonded)	0	0.002059	0.002059
	298	0.002487	0.002487
S / FF (F...F)	0	0.002319	0.003357
	298	0.002757	0.004619
FF (F—S—F)	0	0.001694	0.001694
	298	0.001987	0.001987

Table 2. Shrinkage effects for sulphur hexafluoride (Å units).

Atom pair	Shrinkage effect $T = 0$	Shrinkage effect 298 °K
S / FF (F...F)	0.00057	0.00058
FF (F—S—F)	0.00207	0.00252

The two shrinkage effects are given by

$$\delta_{YY} = 2\tfrac{1}{2}K_{XY} - K_{YY} \quad \text{(nonlinear)}$$
$$\delta_{YXY} = 2K_{XY} - K_{YXY} \quad \text{(linear)}$$

where the K-values are defined by $K_{ij} = (\langle \Delta x_{ij}^2 \rangle + \langle \Delta y_{ij}^2 \rangle)/2r_{ij}^e$ [7]. The final expressions in terms of the Σ-matrix elements read

$$\delta_{YY} = (2\tfrac{1}{2}/R)[-\tfrac{1}{8}\Sigma(E_g) - \tfrac{1}{8}\Sigma_{11}(F_{1u}) + \tfrac{3}{32}\Sigma_{22}(F_{1u}) + \tfrac{1}{8}\Sigma_{12}(F_{1u}) + \tfrac{1}{32}\Sigma(F_{2g}) - \tfrac{1}{32}\Sigma(F_{2u})]$$

$$\delta_{YXY} = (1/R)[\tfrac{1}{4}\Sigma_{22}(F_{1u}) + \tfrac{1}{4}\Sigma(F_{2u})]$$

Here R is the equilibrium X—Y distance. Using the value of $R = 1.58$Å [8] for S—F, the shrinkage effects were calculated with the results given in Table 2.

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