

Spectroscopic Calculations on Sulphur Hexafluoride

II. Mean-Square Perpendicular Amplitudes and Shrinkage Effects

S. J. CYVIN and E. MEISINGSETH

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

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 analysis³. 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.

$$\begin{aligned} \langle \Delta x_{XY}^2 \rangle &= \langle \Delta y_{XY}^2 \rangle = \frac{1}{8} \Sigma_{22}(F_{1u}) \\ &\quad + \frac{1}{16} \Sigma(F_{2g}) + \frac{1}{8} \Sigma(F_{2u}) \\ \langle \Delta x_{YY}^2 \rangle &= \frac{1}{2} \Sigma(E_g) + \frac{1}{2} \Sigma_{11}(F_{1u}) \\ &\quad + \frac{1}{8} \Sigma_{22}(F_{1u}) - \frac{1}{2} \Sigma_{12}(F_{1u}) + \frac{1}{8} \Sigma(F_{2u}) \\ \langle \Delta y_{YY}^2 \rangle &= \frac{1}{8} \Sigma(F_{2g}) + \frac{1}{2} \Sigma(F_{2u}) \\ \langle \Delta x_{YXY}^2 \rangle &= \langle \Delta y_{YXY}^2 \rangle = \frac{1}{4} \Sigma(F_{2g}) \end{aligned}$$

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 (\AA^2 units).

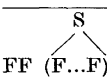
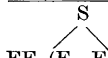
Atom pair	Abs.temp.	$\langle \Delta x^2 \rangle$	$\langle \Delta y^2 \rangle$
SF (Bonded)	0	0.002059	0.002059
	298	0.002487	0.002487
	0	0.002319	0.003357
	298	0.002757	0.004619
FF (F-S-F)	0	0.001694	0.001694
	298	0.001987	0.001987

Table 2. Shrinkage effects for sulphur hexafluoride (\AA units).

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

The two shrinkage effects are given by

$$\begin{aligned} \delta_{YY} &= 2\frac{1}{2}K_{XY} - K_{YY} \quad (\text{nonlinear}) \\ \delta_{YXY} &= 2K_{XY} - K_{YXY} \quad (\text{linear}) \end{aligned}$$

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

$$\begin{aligned} \delta_{YY} &= (2\frac{1}{2}/R) [-\frac{1}{8} \Sigma(E_g) \\ &\quad - \frac{1}{8} \Sigma_{11}(F_{1u}) + \frac{3}{32} \Sigma_{22}(F_{1u}) \\ &\quad + \frac{1}{8} \Sigma_{12}(F_{1u}) \\ &\quad + \frac{1}{32} \Sigma(F_{2g}) - \frac{1}{32} \Sigma(F_{2u})] \\ \delta_{YXY} &= (1/R) [\frac{1}{4} \Sigma_{22}(F_{1u}) + \frac{1}{4} \Sigma(F_{2u})] \end{aligned}$$

Here R is the equilibrium X-Y distance. Using the value of $R = 1.58 \text{\AA}$ ⁸ for S-F, the shrinkage effects were calculated with the results given in Table 2.

- Bastiansen, O. and Trøttestad, M. *Acta Cryst.* **13** (1960) 1108.
- Morino, Y. *Acta Cryst.* **13** (1960) 1107.
- Morino, Y., Cyvin, S. J., Kuchitsu, K. and Iijima, T. *J. Chem. Phys.* **36** (1962) 1109.
- Morino, Y. and Hirota, E. *J. Chem. Phys.* **23** (1955) 737.
- Cyvin, S. J. *Spectrochim. Acta* **17** (1961) 1219.
- Bye, B. H. and Cyvin, S. J. *Acta Chem. Scand.* **17** (1963) 1804.
- Cyvin, S. J. *Tidsskr. Kjemi, Bergvesen, Met.* **22** (1962) 44.
- Gaunt, J. *Trans. Faraday Soc.* **49** (1953) 1122.

Received July 2, 1963.