

Spectroscopic Calculations on Sulphur Hexafluoride

I. Mean-Square Amplitude Matrix and Mean Amplitudes of Vibration

B. H. BYE and S. J. CYVIN

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

Vibrations of octahedral XY_6 type molecules or ions (O_h symmetry) have been studied theoretically by several workers¹⁻⁵. In the present work the mean amplitudes of vibration for sulphur hexafluoride are communicated.

The L matrix (normal coordinate transformation matrix; $S = LQ$) was determined by the standard method of characteristic vectors applied to the GF matrix⁶. The form of the G matrix is given by Pistorius³ and other authors, and need not be repeated here. In the present work the same symmetry coordinates as those specified in the mentioned paper of Pistorius³ were utilized. Numerical force constants were also taken from Pistorius³.

The mean amplitudes of vibration (u)⁷ were calculated by the Σ -matrix method, using $\Sigma = L \tilde{A} L^s$. Σ is the mean-square amplitude matrix. There are three different u -values, viz. u_{XY} for the bonded atom pairs, u_{YY} for the short nonbonded YY atoms, and u_{YXY} for the YY pair of atoms on opposite sides of the central atom.

Table 1. Vibrational constants for sulphur hexafluoride.

Species	Force constants (mdyne/Å)	Mean-square amplitude quantities (Å ²)	
		$T = 0$	298 °K
A_{1g}	6.723	0.001145	0.001201
E_g	4.641	0.001378	0.001507
F_{1u} (11)	5.332	0.002060	0.002107
(22)	1.031	0.008065	0.008670
(12)	-0.914	0.002072	0.002079
F_{2g}	0.768	0.006775	0.007949
F_{2u}	0.699	0.005021	0.007250

Table 2. Mean amplitudes of vibration for sulphur hexafluoride.

Atom pair (Distance)	Mean amplitude of vibration (Å)	
	$T = 0$	298 °K
SF (Bonded)	0.04099	0.04190
$\begin{array}{c} \text{S} \\ \diagup \quad \diagdown \\ \text{FF} (\text{F} \cdots \text{F}) \end{array}$	0.05557	0.06041
FF (F-S-F)	0.05100	0.05301

The squared u -values, i.e. the mean-square amplitudes of vibration (or mean-square *parallel* amplitudes) are expressed linearly in terms of the Σ -matrix elements as follows.

$$\begin{aligned}
 u_{XY}^2 &= \frac{1}{3} \Sigma (A_{1g}) + \frac{1}{3} \Sigma (E_g) + \frac{1}{2} \Sigma_{11}(F_{1u}) \\
 u_{YY}^2 &= \frac{1}{3} \Sigma (A_{1g}) + \frac{1}{3} \Sigma (E_g) \\
 &+ \frac{1}{2} \Sigma_{11}(F_{1u}) + \frac{1}{3} \Sigma_{22}(F_{1u}) - \frac{1}{2} \Sigma_{12}(F_{1u}) \\
 &+ \frac{1}{3} \Sigma (F_{2g}) + \frac{1}{3} \Sigma (F_{2u}) \\
 u_{YXY}^2 &= \frac{2}{3} \Sigma (A_{1g}) + \frac{2}{3} \Sigma (E_g)
 \end{aligned}$$

Here A_{1g} , E_g , etc. refer to the various symmetry species.

For the obtained values of the Σ -matrix elements, see Table 1, where also the force constants of the symmetrized F matrix are included. The final results of mean amplitudes of vibration are given in Table 2. These results are believed to be of great interest in modern electron-diffraction studies⁸.

1. Heath, D. F. and Linnett, J. W. *Trans. Faraday Soc.* **45** (1949) 264.
2. Venkateswarlu, K. and Sundaram, S. *Z. physik. Chem (Frankfurt)* **9** (1956) 174.
3. Pistorius, C. W. F. T. *J. Chem. Phys.* **29** (1958) 1328.
4. Claassen, H. H. *J. Chem. Phys.* **30** (1959) 968.
5. Block, H. *Trans. Faraday Soc.* **55** (1959) 867.
6. Wilson, E. B., Jr., Decius, J. C. and Cross, P. C. *Molecular Vibrations*, McGraw Hill, New York 1955.
7. Cyvin, S. J. *Kgl. Norske Videnskab. Selskabs Skrifter* No. 2 (1959).
8. Cyvin, S. J. *Spectrochim. Acta* **15** (1959).
9. Kimura, M. Nagoya University, Japan. *Private communication*.

Received July 2, 1963.