

## Short Communications

### Mean Amplitudes of Vibration and Bastiansen-Morino Shrinkage Effects in Some Octahedral $XY_6$ Molecules

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Spectroscopic calculations of mean amplitudes of vibration<sup>1</sup> and shrinkage effects<sup>2</sup> are of great interest in modern electron-diffraction studies on gas molecules. The recent communications on sulphur hexafluoride<sup>3</sup> contain some aspects of the theory. The same procedure was used in the present calculations on six octahedral hexafluorides.

Vibrational frequencies of the presently considered molecules have been collected by Pistorius<sup>4</sup>. They were used for a recalculation of force constants, following the same principles as described exhaustively in the mentioned paper<sup>4</sup>. To obtain the shrinkage effects, some estimates of equilibrium distances are needed. In the present work the following values were used.

SF <sub>6</sub> :	S-F = 1.58 Å <sup>5</sup>
SeF <sub>6</sub> :	Se-F = 1.70 Å <sup>5</sup>
TeF <sub>6</sub> :	Te-F = 1.84 Å <sup>5</sup>
MoF <sub>6</sub> :	Mo-F = 1.830 Å <sup>6</sup>
WF <sub>6</sub> :	W-F = 1.89 Å <sup>7</sup>
UF <sub>6</sub> :	U-F = 1.994 Å <sup>6</sup>

The final results for mean amplitudes of vibration (Table 1) and shrinkage effects (Table 2) contain the recalculated values

Table 1. Mean amplitudes of vibration for six octahedral hexafluorides (Å units).

Atom pair (Distance)	SF <sub>6</sub>	SeF <sub>6</sub>	TeF <sub>6</sub>	MoF <sub>6</sub>	WF <sub>6</sub>	UF <sub>6</sub>
XF (Bonded)	0.04103 <sup>a</sup> 0.04190 <sup>b</sup>	0.03881 0.04005	0.03782 0.03916	0.04104 0.04482	0.03723 0.03853	0.04000 0.04236
FF $\left( \begin{array}{c} X \\ / \quad \backslash \\ F \dots F \end{array} \right)$	0.05557 0.06041	0.05795 0.07092	0.06712 0.07793	0.06442 0.07891	0.06898 0.08185	0.08126 0.10512
FF (F-X-F)	0.05100 0.05301	0.05119 0.05319	0.05109 0.05304	0.05140 0.05349	0.05031 0.05209	0.05571 0.05952

<sup>a</sup> Absolute zero.

<sup>b</sup> Absolute temperature of 298°K.

Table 2. Bastiansen-Morino shrinkage effects for six octahedral hexafluorides (Å units).

Molecule	Nonlinear FF $\begin{pmatrix} X \\ F \dots F \end{pmatrix}$	Linear FF (F—X—F)
SF <sub>6</sub>	0.000644 <sup>a</sup> 0.000677 <sup>b</sup>	0.002071 0.002520
SeF <sub>6</sub>	0.000560 0.000721	0.002132 0.005431
TeF <sub>6</sub>	0.000601 0.001056	0.002385 0.003305
MoF <sub>6</sub>	0.001100 0.001843	0.002666 0.004897
WF <sub>6</sub>	0.000591 0.001213	0.002327 0.003412
UF <sub>6</sub>	0.000812 0.000868	0.003122 0.006977

<sup>a,b</sup> See footnote to Table 1.

for sulphur hexafluoride along with the values for the five additional hexafluorides here considered.

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## Coriolis C Matrix and the Mean-Square Amplitude $\Sigma$ Matrix in the Problem of Rotation-Vibration Interaction

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The "Coriolis" C matrix method developed by Meal and Polo<sup>1</sup> will probably become the standard method for studying Coriolis interaction in rotating-vibrating molecules. The method has been applied to specific molecular models by several authors<sup>2</sup>, and has also been considered in general by Mills<sup>3</sup>.

The Coriolis interaction is closely connected with the force constants of a molecule. In fact the Coriolis coefficients ( $\zeta$ -values) may be calculated through the L matrix ( $S = LQ$ ), which is obtainable from the force constants. One has

$$\zeta^{\alpha} = L^{-1} C^{\alpha} \widetilde{L}^{-1} \quad (1)$$

using the conventional symbols<sup>1</sup>. Here the  $C^{\alpha}$  matrix may be defined by

$$C^{\alpha} = B M^{\alpha} \widetilde{B} \quad (2)$$

We prefer to think of the B matrix as associated with the usual cartesian displacements ( $S = BX$ ) rather than the mass-weighted coordinates  $q_i = m_i^{-1/2} x_i$ . Then the  $M^{\alpha}$  matrix must be defined in the following way. It consists of the blocks  $M_1^{\alpha}, M_2^{\alpha}, \dots, M_N^{\alpha}$  ( $N =$  number of atoms) along the main diagonal, which are defined for  $\alpha = x, y, z$  by

$$M_1^x = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \mu_i \\ 0 & -\mu_i & 0 \end{bmatrix}$$

$$M_1^y = \begin{bmatrix} 0 & 0 & -\mu_i \\ 0 & 0 & 0 \\ \mu_i & 0 & 0 \end{bmatrix}$$

$$M_1^z = \begin{bmatrix} 0 & \mu_i & 0 \\ -\mu_i & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$\mu_i$  denotes as usual the inverse mass of the  $i$ -th atom. Our eqn. (2) appears to be a slight modification of eqn. (II-3) from the ingenious work of Meal and Polo<sup>1</sup>. Our equation shows more closely the analogy with the definition of the G matrix, which usually is written in the form