

UREY-BRADLEY FORCE FIELD: SF₄ MOLECULE

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ABSTRACT

The force constants of SF₄ molecule have been evaluated using the Urey-Bradley force field and compared with those obtained by F-G matrix method. Using the Urey-Bradley constants, the fundamental vibrational frequencies are calculated and compared with the observed frequencies.

G-MATRIX

The SF₄ molecule belongs to the point group C_{2v} and has 4a₁ + 1a₂ + 2b₁ + 2b₂ vibrations. The internal co-ordinates and the geometry of the system are shown in Fig. 1. The symmetry co-ordinates are given by Venkateswarlu and Krishna Pillai.¹ The elements of the kinetic energy matrix, as obtained here, are given below and in a few cases they are slightly different from those given earlier by Venkateswarlu and Krishna Pillai.

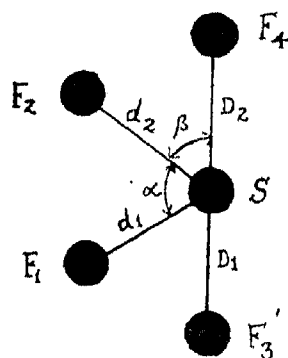


FIG. 1

For the a₁ type:

$$G_{11} = \mu_F + \mu_S (1 + \cos \alpha)$$

$$G_{22} = \mu_F$$

$$G_{33} = \frac{2\mu_F + 2\mu_S (1 - \cos \alpha)}{d^2}$$

$$G_{44} = -\frac{2\mu_F \cos^2 \beta}{d^2 \sin^2 \beta} + \frac{\mu_F [(1 + \cos \alpha) - 2 \cos^2 \beta]}{D^2 \sin^2 \beta} \\ + \frac{2\mu_S}{\sin^2 \beta} \left[(1 + \cos \alpha) \left(\frac{1}{D} - \frac{\cos \beta}{d} \right)^2 \right. \\ \left. + 4 \cos \beta \left(\frac{1}{D} - \frac{\cos \beta}{d} \right) \left(\frac{1}{d} - \frac{\cos \beta}{D} \right) \right]$$

$$G_{12} = 2\mu_S \cos \beta$$

$$G_{13} = \frac{-\sqrt{2}\mu_S \sin \alpha}{d}$$

$$G_{14} = -\sqrt{2}\mu_S \frac{\left[(1 + \cos \alpha) \left(\frac{1}{D} - \frac{\cos \beta}{d} \right) + \left(\frac{1}{d} - \frac{\cos \beta}{D} \right) 2 \cos \beta \right]}{\sin \beta}$$

$$G_{24} = \frac{-2\sqrt{2}\mu_S \cos \beta \left(\frac{1}{D} - \frac{\cos \beta}{d} \right)}{\sin \beta}$$

$$G_{23} = \frac{-2\sqrt{2}\mu_S \cos \beta (1 - \cos \alpha)}{d \sin \alpha}$$

$$G_{34} = \frac{2\mu_F \cos \beta (1 - \cos \alpha)}{d^2 \sin \alpha \sin \beta} + 2\mu_S (1 - \cos \alpha) \\ \times \frac{\left[(1 + \cos \alpha) \left(\frac{1}{D} - \frac{\cos \beta}{d} \right) + \left(\frac{1}{d} - \frac{\cos \beta}{D} \right) 2 \cos \beta \right]}{d \sin \alpha \sin \beta}$$

For the a_2 type:

$$G_{55} = \frac{2\mu_F}{d^2 \sin^2 \beta} + \frac{\mu_F (1 - \cos \alpha)}{D^2 \sin^2 \beta}$$

For the b_1 type:

$$G_{66} = \mu_F + \mu_S (1 - \cos \alpha)$$

$$G_{77} = \frac{-2\mu_F \cos^2 \beta}{d^2 \sin^2 \beta} + \frac{\mu_F (1 - \cos \alpha)}{D^2 \sin^2 \beta} \\ + \frac{2\mu_S (1 - \cos \alpha) \left(\frac{1}{D} - \frac{\cos \beta}{d} \right)^2}{\sin^2 \beta}$$

$$G_{67} = \frac{-\sqrt{2}\mu_S (1 - \cos \alpha) \left(\frac{1}{D} - \frac{\cos \beta}{d} \right)}{\sin \beta}$$

or the b_2 type:

$$G_{88} = \mu_F + 2\mu_S$$

$$G_{99} = \frac{2\mu_F}{d^2 \sin^2 \beta} + \frac{\mu_F [(1 + \cos \alpha) - 2 \cos^2 \beta]}{D^2 \sin^2 \beta}$$

$$+ \frac{4\mu_S \left(\frac{1}{d} - \frac{\cos \beta}{D} \right)^2}{\sin^2 \beta}$$

$$G_{89} = \frac{-2\sqrt{2}\mu_S \left(\frac{1}{d} - \frac{\cos \beta}{D} \right)}{\sin \beta}$$

where μ_F , μ_S are the reciprocal masses of the F and S atoms, d and D are the S-F and S-F' bond lengths and α , β are the F-S-F and F-S-F' angles respectively.

F-MATRIX

In the present investigation the Urey-Bradley potential function in the general form was taken and after eliminating the q co-ordinates, the elements of the potential energy matrix were obtained as

$$F(a_1): \begin{bmatrix} K_d + 2S_1^2 F_\alpha & 2(S_0 S_1 F_\beta & 2\rho_0 d (t_1 S_0 F_\alpha' & \sqrt{2\rho_0} \sqrt{Dd} (t_1 S_0 F_\beta' \\ + t_1^2 F_\beta' & - t_0 t_1 F_\beta') & + t_0 S_1 F_\alpha) & + t_0 S_1 F_\beta) \\ + S_1^2 F_\beta & & & \\ & K_D + t_0^2 F_\beta' & 0 & \sqrt{2\rho} \sqrt{dD} (t_0 S_1 F_\beta' \\ & + S_0^2 F_\beta & & + t_1 S_0 F_\beta) \\ & & d^2 (H_\alpha - S_0 S_1 F_\alpha' & 0 \\ & & + t_0 t_1 F_\alpha) & \\ & & & dD (H_\beta - S_0 S_1 F_\beta' \\ & & & + t_0 t_1 F_\beta) \end{bmatrix}$$

$$F(a_2): [dD (H_\beta - S_0 S_1 F_\beta' + t_0 t_1 F_\beta)]$$

$$F(b_1): \begin{bmatrix} K_d + 2t_1^2 F_\alpha' + t_1^2 F_\beta' + S_1^2 F_\beta & \sqrt{2\rho} \sqrt{dD} (t_1 S_0 F_\beta' + t_0 S_1 F_\beta) \\ & dD (H_\beta - S_0 S_1 F_\beta' + t_0 t_1 F_\beta) \end{bmatrix}$$

$$F(b_2): \begin{bmatrix} K_D + t_0^2 F_\beta' + S_1^2 F_\beta & \sqrt{2\rho} \sqrt{dD} (t_0 S_1 F_\beta' + t_1 S_0 F_\beta) \\ & dD (H_\beta - S_0 S_1 F_\beta' + t_0 t_1 F_\beta) \end{bmatrix}$$

where

$$\begin{aligned}
 S_{ij} &= (d_i - d_j \cos \alpha_{ij})/q_{ij} & t_{ij} &= d_j \sin \alpha_{ij}/q_{ij} \\
 S_{ji} &= (d_j - d_i \cos \alpha_{ij})/q_{ij} & t_{ji} &= d_i \sin \alpha_{ij}/q_{ij} \\
 K_D &= \text{S-F' stretching constant;} & H_\alpha &= \text{F-S-F bending constant;} \\
 K_d &= \text{S-F stretching constant;} & H_\beta &= \text{F-S-F' bending constant;} \\
 F_\alpha &= \text{F-F repulsion constant;} & F_\beta &= \text{F-F' repulsion constant.}
 \end{aligned}$$

RESULTS

The S-F distance used in the present investigation is 1.58 Å, as in SF₆.² The observed³ frequencies and those calculated using the Urey-Bradley force constants are given in Table I.

The values of the Urey-Bradley force constants along with the values obtained by the F-G matrix method using the revised G matrix elements are given in Table II.

TABLE I
Vibrational frequencies of SF₄ molecule (cm.⁻¹)

		a ₁				a ₂	b ₁		b ₂	
		σ ₁	σ ₂	σ ₃	σ ₄	σ ₅	σ ₆	σ ₇	σ ₈	σ ₉
Observed	..	889	235	557	715	645	532	867	463	728
Calculated	..	899	233	552	721	645	532	867	463	728

TABLE II
Potential energy constants (10⁵dynes/cm) of SF₄ molecule

Urey-Bradley method	K _D	K _d	H _α	H _β	F _{FF}	F _{F'F}	F' _{FF}	F' _{F'F}		
	2.048	4.813	1.5417	0.7230	1.1240	1.3012	-0.0932	-0.1021		
F-G Matrix method	f _D	f _d	f _{dd}	f _{DD}	f _{Dd}	f _α	f _β	f _{dα}	f _{dβ}	f _{Dβ}
	2.752	5.805	1.195	1.248	1.000	1.084	1.332	0.269	0.416	0.302

In the F-G matrix method the various force constants will have the usual significance. The results of our calculations showed that the S-F stretching constant, corresponding to the fluorine atoms in the equatorial positions of

the base of the pyramidal structure, is nearly two times that of the atoms at the apex of the pyramid.

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