UREY-BRADLEY FORCE FIELD: SF_4 MOLECULE

BY DR. K. VENKATESWARLU, F.A.SC. AND MISS R. THANALAKSHMI

(Department of Physics, Annamalai University, Annamalainagar, South India)

Received February 19, 1963

ABSTRACT

The force constants of SF_4 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 SF_4 molecule belongs to the point group C_{2v} and has $4a_1 + 1a_2 + 2b_1 + 2b_2$ 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.

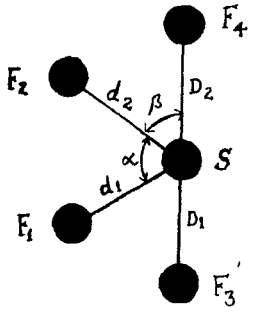

FIG. 1

For the a_1 type:

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

$$G_{22} = \mu_F$$

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

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

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

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

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

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

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

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

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

$$F(a_1): \begin{bmatrix} K_d + 2S_1{}^2F_\alpha + t_1{}^2F_\beta' + S_1{}^2F_\beta & 2(S_0S_1F_\beta - t_0t_1F_\beta') & 2\rho_0 d(t_1S_0F_\alpha' + t_0S_1F_\alpha) & \sqrt{2}\rho_0\sqrt{D}d(t_1S_0F_\beta' + t_0S_1F_\beta) \\ & K_D + t_0{}^2F_\beta' + S_0{}^2F_\beta & 0 & \sqrt{2}\rho\sqrt{d}D(t_0S_1F_\beta' + t_1S_0F_\beta) \\ & & d^2(H_\alpha - S_0S_1F_\alpha' + t_0t_1F_\alpha) & 0 \\ & & & dD(H_\beta - S_0S_1F_\beta' + t_0t_1F_\beta) \end{bmatrix}$$

$$F(a_2): [dD(H_\beta - S_0S_1F_\beta' + t_0t_1F_\beta)]$$

$$F(b_1): \begin{bmatrix} K_d + 2t_1{}^2F_\alpha' + t_1{}^2F_\beta' + S_1{}^2F_\beta & \sqrt{2}\rho\sqrt{d}D(t_1S_0F_\beta' + t_0S_1F_\beta) \\ & dD(H_\beta - S_0S_1F_\beta' + t_0t_1F_\beta) \end{bmatrix}$$

$$F(b_2): \begin{bmatrix} K_D + t_0{}^2F_\beta' + S_1{}^2F_\beta & \sqrt{2}\rho\sqrt{d}D(t_0S_1F_\beta' + t_1S_0F_\beta) \\ & dD(H_\beta - S_0S_1F_\beta' + t_0t_1F_\beta) \end{bmatrix}$$

where

$S_{ij} = (d_i - d_j \cos \alpha_{ij})/q_{ij}$ $\quad t_{ij} = d_j \sin \alpha_{ij}/q_{ij}$

$S_{ji} = (d_j - d_i \cos \alpha_{ij})/q_{ij}$ $\quad t_{ji} = d_i \sin \alpha_{ij}/q_{ij}$

K_D = S-F′ stretching constant; $\quad H_\alpha$ = F-S-F bending constant;

K_d = S-F stretching constant; $\quad H_\beta$ = F-S-F′ bending constant;

F_α = F-F repulsion constant; $\quad F_\beta$ = F-F′ repulsion constant.

RESULTS

The S-F distance used in the present investigation is 1·58 Å, as in SF_6[2]. The observed[3] fequencies 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 SF_4 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 ($10^5 dynes/cm$) of SF_4 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	$f_{d\alpha}$	$f_{d\beta}$	$f_{D\beta}$
	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 flourine atoms in the equitorial positions of

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

ACKNOWLEDGEMENT

One of the authors (R.T.) is thankful to the Council of Scientific and Industrial Research, Government of India, for the award of a Junior Research Fellowship.

REFERENCES

1. Venkateswarlu, K. and Krishna Pillai, M. G. — *Optics and Spectroscopy*, 1961, **11**, 26.
2. Brockway, L. O. and Pauling, L. — *Proc. Natl. Acad. Sci.*, 1933, **19**, 68.
3. Dodd, R. E., Woodward, L. A. and Roberts, H. L. — *Trans. Farad. Soc.*, 1956, **52**, 1052.