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MOLECULAR CONSTANTS OF CF_2S AND CF_2Se MOLECULES BY KINETIC CONSTANTS METHOD

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All the general quadratic valence force field potential constants of CF_2S and CF_2Se molecules are freshly evaluated using kinetic constants. From the potential constants obtained, vibrational mean amplitudes, Coriolis coupling constants and centrifugal distortion constants were calculated. The results are briefly discussed. Furthermore, it was shown that the kinetic constants method leads to acceptable sets of molecular constants.

1. *Introduction*

Wilson's group theoretical method of analysis of molecular vibrations has been of great service in the study of molecular forces [1]. The present paper relating to the potential constants of CF_2S and CF_2Se molecules adopts Wilson's techniques coupled with kinetic constants. The kinetic constants of molecules appear to be of basic significance in the study of molecular vibrations. They have been evaluated and utilised advantageously in different cases [2–6] to obtain reasonable and acceptable sets of potential constants in polyatomic molecules in a simple manner. This elegant procedure has been used here to evaluate all the independant potential constants of CF_2S and CF_2Se molecules. Furthermore, the present set of potential constants are utilised to evaluate the vibrational mean amplitudes, Coriolis coupling constants and the centrifugal distortion constants of CF_2S and CF_2Se molecules. The recent vibrational frequencies given by Hass and Willner [7] for these molecules are used in the present investigation. The results are within the expected range. Thus, it appears that the molecular kinetic constants play a major role in molecular architecture and effectively participate in molecular dynamics.

2. *Theoretical considerations*

CF_2S and CF_2Se molecules belong to the symmetry of the point group C_{2v} and hence has six non-degenerate normal modes of vibration belonging to the symmetry class $3A_1+2B_1+B_2$. The symmetry coordinates used in the present investigation are the same

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as those given by Oka and Morino [8]. The most general quadratic potential energy function in terms of internal coordinates has been considered and hence F matrix elements have been obtained. Following Ford and Thomas [9] the redundancy constraints are utilised to reduce the F matrix to the following simple form:

A_1 Species

$$\begin{bmatrix} f_D & \sqrt{2}f_{Dd} & \sqrt{1.5}f_{D\alpha} \\ & f_d+f_{dd} & -\sqrt{3D/d}\,(f'_{d\beta}+f''_{d\beta}) \\ & & (3D/d)\,(f_\beta+f_{\beta\beta}) \end{bmatrix},$$

B_1 Species

$$\begin{bmatrix} f_d-f_{dd} & -\sqrt{D/d}\,(f'_{d\beta}-f''_{d\beta}) \\ & (D/d)\,(f_\beta-f_{\beta\beta}) \end{bmatrix},$$

B_2 Species

$$[(D/d)f_\delta].$$

The notation of force constants as well as the kinetic constants are indicated below.

Nature of the constant	Force constant	Kinetic constant
XY stretching	f_D	k_D
XZ stretching	f_d	k_d
XY/XZ interaction	f_{Dd}	k_{Dd}
XZ/XZ interaction	f_{dd}	k_{dd}
ZXZ bending	f_α	k_α
YXZ bending	f_β	k_β
ZXZ/YXZ interaction	$f_{\alpha\beta}$	$k_{\alpha\beta}$
YXZ/YXZ interaction	$f_{\beta\beta}$	$k_{\beta\beta}$
XY/ZXZ interaction	$f_{D\alpha}$	$k_{D\alpha}$
XY/YXZ interaction	$f_{D\beta}$	$k_{D\beta}$
XZ/ZXZ interaction	$f_{d\alpha}$	$k_{d\alpha}$
XZ_1/YXZ_2 interaction	$f'_{d\beta}$	$k'_{d\beta}$
XZ_1/YXZ_1 interaction	$f''_{d\beta}$	$k''_{d\beta}$
Out of plane bending	f_δ	k_δ

The kinetic constants [2–6] are derived from a knowledge of G matrix elements using Wilson's expression $2T = \tilde{\dot{S}}G^{-1}\dot{S}$.

The method of kinetic constants for evaluating the force constants has been found to give quite similar results in different molecular types as mentioned earlier [2–6]. The determination of symmetry force constants involved in the secular equation from the n_i vibrational frequencies alone has been a mathematically underdetermined problem so far. Therefore, any genuine attempt to evaluate all the symmetry force constants associated with a problem in the order of $n > 1$ should involve the incorporation of at least $n_i(n_i-1)/2$ additional data other than the n_i frequencies.

The procedure of kinetic constants seem to relate the off-diagonal elements to the diagonal elements of the F matrix through the relation:

$$F_{ij}/F_{jj} = K_{ij}/K_{jj} \quad (i < j;\, i, j = 1, 2, 3).$$

Thus, the equations involving A_1 species and B_1 species are solved easily.

Vibrational mean amplitudes

Utilizing Cyvin's equation (11) $\Sigma = L\Delta L'$, the symmetrized mean square amplitudes and hence the valence mean square amplitude quantities for both the bonded and the non-bonded distances are evaluated at 298. 16 K using the present set of force constants. On the basis of these values, the mean amplitudes of vibration for these molecules are evaluated.

Compliance constants

The compliance constants are also calculated for these cases by the Decius method [10].

Coriolis coupling constants

The Coriolis vibration-rotation constants $\zeta^{\alpha}(\alpha = x, y, z)$ in this type of molecules arise from the couplings:

$$A_1 \times B_2, \quad A_1 \times B_1, \text{ and } B_1 \times B_2.$$

The Coriolis matrix elements $C_{ij}^{\alpha}(\alpha = x, y, z)$ are obtained according to the vector method of Meal and Polo (12). The matrices are related to the C^{α} matrices by a relation having the form: $\zeta = L^{-1}C^{\alpha}(L')^{-1}$, where L is the normal coordinate transformation matrix.

Centrifugal distortion constants

Cyvin et al. [13] have reformulated the theory of centrifugal distortion by introducing certain new elements $T_{\alpha\beta,s}$ instead of partial derivatives of the inertia tensor components $J_{\alpha\beta,s}$ of Kivelson and Wilson [14]. The quantities $T_{\alpha\beta\nu\delta}$ are easily obtained using Cyvin's method. The nonvanishing $T_{\alpha\beta\nu\delta}$ matrix elements in terms of the symmetry coordinates are given below:

$$T_{XX,S_1} = 2D, \qquad T_{YY,S_1} = 2D, \qquad T_{ZZ,S_2} = \sqrt{8}\, ds^2,$$

$$T_{XX,S_2} = \sqrt{8}\, dc^2, \qquad T_{YY,S_2} = \sqrt{8}\, d, \qquad T_{ZZ,S_3} = -\sqrt{24}\, dcs,$$

$$T_{XX,S_3} = \sqrt{24}\, dcs, \qquad T_{ZX,S_4} = \sqrt{8}\, dcs,$$

$$T_{ZX,S_5} = -\sqrt{8}\, ds^2.$$

where $c = \cos(\alpha/2)$ and $s = \sin(\alpha/2)$.

3. *Results and discussion*

The structural parameters and the vibrational frequencies used in the present investigation are given in Table I. Table II gives the kinetic constants evaluated in the present investigation for CF_2S and CF_2Se molecules.

TABLE I

Structural parameters and vibrational frequencies (cm^{-1})

Molecule	$D(A)$	$d(A)$	α	$\nu_1(A_1)$	$\nu_2(A_1)$	$\nu_3(A_1)$	$\nu_4(B_1)$	$\nu_5(B_1)$	$\nu_6(B_2)$	Ref.
CF_2S	1.589	1.315	107°11′	1365.2	789.3	526.2	1200	418	623.2	[7]
CF_2Se	1.73	1.32	107°	1287	705	432	1207	351	575	[7]

TABLE II

Kinetic constants (10^{-23} g)

Molecule	k_D k_d	k_{Dd} k_{dd}	k_α k_β	$-k_{D\alpha}$ $k_{d\alpha}$ $-k'_{d\beta}$	k_δ
CF_2S	3.2409 2.4042	0.7324 0.2317	0.4915 0.4348	0.6593 0.2338 0.6810	0.2221
CF_2Se	5.1067 2.5677	1.1542 0.2604	0.5685 0.4853	1.0399 0.1471 0.5915	0.2186

The algebraic sum of the bond-angle interaction kinetic constants of these molecules vanishes. Again the sum of the bending and the angle-angle interaction kinetic constants also vanishes. These complimentary kinetic constants are found to satisfy the following four kinetic constraints:

$$\sqrt{d/D}\, k_{D\alpha}+2k_{D\beta} = 0, \qquad \sqrt{d/D}\, k_{d\alpha}+k'_{d\beta}+k''_{d\beta} = 0,$$

$$\sqrt{d/D}\, k_\alpha+2k_{\alpha\beta} = 0, \qquad \sqrt{d/D}\, k_\alpha-2(k_\beta+k_{\beta\beta}) = 0.$$

These results are analogous to the results obtained in other molecular types by Thirugnanasambandam and Mohan [2–6]. Table III deals with the evaluated force constants of CF_2S and CF_2Se molecules. As expected, the force constants $f_{D\alpha}$ and $f'_{d\beta}$ as well as the corresponding kinetic constants are negative in these molecules. The high value for the force constants viz, f_D and f_{Dd} are indicative of heavy mixing between normal modes. From Table IV it can be seen that the compliance constants exhibit trends opposite to those of the force constants.

The valence mean square amplitudes and the mean amplitudes for both the bonded and the non-bonded distances at 298.16 K are given in Tables V and VI respectively. The

TABLE III

Potential constants (10^5 dynes/cm)

Molecule	f_D f_d	f_{Dd} $-f_{dd}$	f_α f_β	$-f_{D\alpha}$ $f_{d\alpha}$ $-f'_{d\beta}$	f_δ
CF_2S	11.6206 5.8064	1.5626 0.1824	0.4821 0.3063	0.6477 0.2294 0.3744	0.3061
CF_2Se	13.3433 5.4218	2.0140 0.4869	0.3764 0.2366	0.6886 0.1115 0.2565	0.2565

TABLE IV

Compliance constants (A/mdyne)

Molecule	c_D c_d	$-c_{Dd}$ c_{dd}	c_α c_β	$c_{D\alpha}$ $-c_{d\alpha}$ $c'_{d\alpha}$	c_δ
CF_2S	0.1058 0.1998	0.0366 0.0105	1.0904 1.1651	0.1179 0.1723 0.1808	2.2374
CF_2Se	0.0989 0.2157	0.0444 0.0289	1.0751 1.3853	0.1359 0.0963 0.1346	2.2702

TABLE V

Valence mean square amplitudes (10^{-3} A^2) at 298.16 K

Molecule	σ_D σ_d	$-\sigma_{Dd}$ σ_{dd}	σ_α σ_β	$\sigma_{D\alpha}$ $-\sigma_{d\alpha}$ $\sigma'_{d\beta}$	σ_δ	$(Y \overset{\sigma_p}{\cdots} Z)$ $(Z \overset{\sigma_q}{\cdots} Z)$
CF_2S	1.4331 2.5121	0.7032 0.2427	8.0043 10.9532	1.7156 1.3239 2.2109	22.3397	2.8193 3.9613
CF_2Se	1.2651 2.4134	0.6987 0.1605	10.4525 12.5436	1.7815 1.2490 2.1781	25.1497	2.8279 4.8115

vibrational mean amplitudes evaluated in the present investigation are in the expected range. The present values of the mean amplitudes relating to the bonded as well as the non-bonded distances of the planar XY_2Z molecules compare favourably with the calculated values of the earlier authors wherever such data are available.

TABLE VI

Mean amplitudes (A) at 298.16 K

Molecule	C — S or C — Se	C—F	F...S or F...Se	F...F	Ref.
CF_2S	0.0379	0.0501	0.0531	0.0629	Present work
CF_2Se	0.0356	0.0491	0.0532	0.0694	Present work
CF_2S	—	0.0486	—	0.058	[15]
	0.0381	0.0486	0.059	—	[15]
CF_2O	—	0.0454	—	0.054	[15]
Cd_2S	0.0380	—	—	—	[15]
	0.03728	—	—	—	[16]

TABLE VII

Coriolis coupling constants

Molecule	$-\zeta^x_{16}$	ζ^x_{26}	$-\zeta^x_{36}$	$-\zeta^y_{14}$ ζ^y_{15}	ζ^y_{24} $-\zeta^y_{25}$	$-\zeta^y_{34}$ $-\zeta^y_{35}$	$-\zeta^z_{46}$	ζ^z_{56}
CF_2S	0.8150	0.3869	0.3551	0.7208 0.5084	0.1214 0.3403	0.6824 0.7910	0.9134	0.4075
CF_2Se	0.8230	0.4241	0.3779	0.6515 0.5215	0.1941 0.3803	0.7334 0.7639	0.9444	0.3288

TABLE VIII

Centrifugal distortion constants (MHz)

Molecule	$-\tau_{xxxx}$	$-\tau_{yyyy}$	τ_{xxyy}	$-\tau_{xyxy}$
CF_2S	0.0604	0.0066	0.0071	0.0198
CF_2Se	0.0684	0.0072	0.0062	0.0187

The Coriolis coupling constants of these molecules are presented in Table VII. The zeta values may be seen to obey the following sum rules [17, 18]:

$$(\zeta^x_{16})^2+(\zeta^x_{26})^2+(\zeta^x_{36})^2 = 1,$$

$$(\zeta^y_{14})^2+(\zeta^y_{24})^2+(\zeta^y_{34})^2 = 1,$$

$$(\zeta^y_{15})^2+(\zeta^y_{25})^2+(\zeta^y_{35})^2 = 1,$$

$$(\zeta^z_{46})^2+(\zeta^z_{56})^2 = 1.$$

Furthermore, the high values of the Coriolis coupling constants indicate the strong interaction between A_1XB_2, A_1XB_1 and B_1XB_2 species.

The centrifugal distortion constants of CF_2S and CF_2Se molecules are given in Table VIII and are within the expected range.

4. Conclusion

All the molecular contants have been newly evaluated for CF_2S and CF_2Se molecules by the kinetic constants method. There are, to the author's knowledge, no experimental data available for these molecules for the comparison of the values of Coriolis coupling constants and the centrifugal distortion constants of the present study. It may be seen that a systematic set of molecular constants relating to these molecules are available in the present investigation.

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