

## Normal co-ordinate analysis of $\text{CH}_2\text{F}_2$ and $\text{CD}_2\text{F}_2$ —kinetic constants and optimisation technique

P SIVAKUMAR, C SUBRAMANIAN, B KRISHNA RAO and  
P RAMASAMY

Department of Physics, A.C. College of Technology, Madras 600 025, India

MS received 11 August 1970; revised 26 April 1980

**Abstract.** Kinetic constant method has been extended in combination with optimisation technique to evaluate molecular constants of  $\text{CH}_2\text{F}_2$  and  $\text{CD}_2\text{F}_2$ . The calculated Coriolis coupling and centrifugal distortion constants agree with the experimental values.

**Keywords.** Molecular constants; kinetic constants; methylene fluoride.

### 1. Introduction

In the study of molecular vibrations, the Wilson's FG matrix method in conjunction with kinetic constants has so far been applied to several vibrational problems of order  $n = 2$  and  $n = 3$  (Thirugnanasambandam and Srinivasan 1969; Thirugnanasambandam and Mohan 1974, 1975). The purpose of the present paper is to extend the method of kinetic constants to vibrational problems of order  $n = 4$  with a known method to solve the nonlinear equations obtained using digital computer. The force fields of  $\text{CH}_2\text{F}_2$  and  $\text{CD}_2\text{F}_2$  are obtained. The other molecular constants, viz, mean amplitudes of vibration, Coriolis coupling constants and centrifugal distortion constants have also been computed using these force fields.

### 2. Theoretical considerations

The molecules  $\text{CH}_2\text{F}_2$  and  $\text{CD}_2\text{F}_2$  belong to  $C_{2v}$  point group and have their vibrations distributed as  $4A_1 + A_2 + 2B_1 + 2B_2$ . The symmetry coordinates used in the present calculations are those given by Shimanouchi and Suzuki (1962).

Since there is only one vibration in the  $A_2$  species the matrix element  $F_{55}$  is given by the relation  $F_{55}G_{55} = \lambda_5$ . There are two vibrations in  $B_1$  and  $B_2$  species respectively. The  $F$  matrix elements have been obtained using the additional equations

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

for the  $B_1$  and  $B_2$  species respectively. Here  $K$  elements are the kinetic constants.

In the case of  $A_1$  species since there are four vibrations, the secular equation  $|FG - \lambda I| = 0$  yields four non-linear equations with ten unknowns. These equations are simplified using the relation (1) connecting force constants and the kinetic constants.

By this process, the number of unknown force constants are reduced from ten to four. Now we have four nonlinear equations with four unknowns. Here 24 solutions are possible. To choose a reasonable set from them the optimisation technique of Fletcher and Powell (1963) is used.

The structural parameters and the vibrational frequencies are used from Hiroto *et al* (1970) and Suzuki and Shimonouchi (1973).

The valence force constants obtained are reported in table 1. Utilising the force constants in Cyvin's secular equation (Cyvin 1968), the mean square ampli-

Table 1. Force constants and mean amplitudes

Force constants (m dyne/Å)			Mean amplitudes of vibration (Å) at 298.16° K		
Description	CH <sub>2</sub> F <sub>2</sub>	CD <sub>2</sub> F <sub>2</sub>	Description	CH <sub>2</sub> F <sub>2</sub>	CD <sub>2</sub> F <sub>2</sub>
$f_D$	4.8827	4.9943	1 (X - Y)	0.0780	0.0666
$f_a$	6.4577	6.0544	1 (X - Z)	0.0450	0.0467
$f_{DD}$	0.028	-0.1108	1 (Y ... Y)	0.1232	0.1267
$f_{aa}$	1.4341	1.3063	1 (Z ... Z)	0.0562	0.0566
$f_{Da}$	0.0654	0.1159	1 (Z ... Y)	0.0998	0.0846

Table 2. Coriolis constants

	CH <sub>2</sub> F <sub>2</sub>		CD <sub>2</sub> F <sub>2</sub>		
	a	b	a	b	c
$ \zeta_{55}^a $	0.1344	0.06	0.3396	0.41	..
$ \zeta_{55}^a $	0.5613	0.61	0.4959	0.52	..
$ \zeta_{57}^a $	0.3820	0.38	0.4495	0.41	0.465
$ \zeta_{58}^a $	0.8067	..	0.7611	..	0.7876
$ \zeta_{57}^a $	0.0653	0.06	0.0129	0.08	..
$ \zeta_{59}^a $	0.5357	..	0.4897	..	0.556
$ \zeta_{57}^a $	0.7399	0.72	0.6996	0.70	0.691
$ \zeta_{58}^a $	0.0733	0.07	0.1129	0.11	..
$ \zeta_{59}^a $	0.0137	0.02	0.0244	0.03	..
$ \zeta_{78}^a $	0.4059	0.47	0.4736	0.64	..
$ \zeta_{79}^a $	0.5002	0.47	0.4683	0.17	..

a. Present work; b. Suzuki and Shimanouchi (1973); c. Hirota and Sahara (1975).

tude matrix elements are obtained. The generalised mean square amplitudes were calculated following Morino and Hirota (1955). The values of mean amplitudes of vibration are tabulated in table 1.

The Coriolis matrix elements  $C_{ij}^{\alpha}$  ( $\alpha = x, y, z$ ) were obtained following Meal and Polo (1956), and the zeta matrix elements were evaluated using the relation  $\zeta_{ij}^{\alpha} = (L^{-1}) C^{\alpha} (L^{-1})^T$ . The results are presented in table 2 along with the calculated values of Suzuki and Shimanouchi (1973) and Hirota and Sahara (1975).

The quantities  $\tau_{\alpha\beta\gamma\delta}$  have been obtained using the approach of Kivelson and Wilson (1952, 1953). The results are reported in table 3 along with the observed values.

### 3. Computations

Computer program in Fortran IV to evaluate the force fields of  $XY_2Z_2$  type molecules using the method of kinetic constants has been developed. To solve the non-linear equations IBM subroutine based on Fletcher-Powell method was used. Numerical computations were carried out at the Indian Institute of Technology Computer Centre, Madras.

### 4. Conclusions

The ratio of the valence force constants reported  $f(X-D)/f(X-H)$  has the characteristic value of 1.02 which has been observed by Shimanouchi and Suzuki (1962) and Suzuki and Shimanouchi (1973) in the case of substituted methanes. For  $CD_2F_2$  no structural data are available from experiments. Hence the angles are assumed to be tetrahedral. This may be the reason for the slight variation

Table 3.  $\tau$ -matrix elements (MHz)

	$CH_2F_2$				$CD_2F_2$		
	a	b	c	d	a	e	
$\tau_{XXXX}$	-0.0540	-0.0606	-0.06095	-0.06224	-0.01766	-0.0479	-0.05425
$\tau_{YYYY}$	-0.0228	-0.0265	-0.02672	-0.02785	-0.0252	-0.0196	-0.02198
$\tau_{ZZZZ}$	-2.9183	-2.3049	-2.3156	-2.2898	-2.9881	-1.0386	-0.85408
$\tau_{XXYY}$	-0.0332	..	..	..	-0.0202	-0.0280	..
$\tau_{YYZZ}$	-0.0832	..	..	..	0.0677	0.0314	..
$\tau_{ZZXX}$	0.2358	..	..	..	0.1132	0.1206	..
$\tau_{XXYY}$	-0.0003	..	..	..	-0.0001	-0.0006	..
$\tau_{YYZZ}$	-0.0075	..	..	..	-0.0072	-0.0128	..
$\tau_{ZZXX}$	-0.0577	..	..	..	-0.0322	-0.0395	..

a. Present work; b. Hirota *et al* (1970); c. Koutcher and Larkin (1976); d. Venkateswarlu and Joseph (1971); e. Hirota and Sahara (1975).

observed in the values of  $f_D$  for C-H and C-D bonds (table 1). The mean amplitude of vibration 1 ( $X - Y$ ) has the characteristic value 0.0780 in  $\text{CH}_2\text{F}_3$  and 0.066 in  $\text{CD}_2\text{F}_2$ .

Calculated Coriolis constants compare with the calculated values of Suzuki and Shimanouchi (1973) and Hirota and Sahara (1975).

The calculated values of  $\tau$  elements in the present work compared with the experimental values of Hirota *et al* (1970) and Hirota and Sahara (1975) and Koucher and Larkin (1976) show good agreement.

The satisfactory results obtained by combining the method of kinetic constants with optimisation technique are quite encouraging.

## References

- Cyvin S J 1968 *Molecular vibrations and mean amplitudes* (Amsterdam : Elsevier)  
Fletcher R and Powell M J D 1963 *Computer J.* **6** 163  
Hirota E and Sahara M 1975 *J. Mol. Spectrosc.* **56** 21  
Hirota E, Tanaka T, Sakakibara K, Ohashi Y and Morino Y 1970 *J. Mol. Spectrosc.* **34** 222  
Kivelson D and Wilson E B Jr 1952 *J. Chem. Phys.* **20** 1575  
Kivelson D and Wilson E B Jr 1953 *J. Chem. Phys.* **21** 1229  
Koutcher J A and Larkin R H 1976 *J. Mol. Spectrosc.* **60** 373  
Meal J H and Polo S R 1956 *J. Chem. Phys.* **24** 1119, 1126  
Morino Y and Hirota E 1955 *J. Chem. Phys.* **23** 737  
Shimanouchi T and Suzuki I 1962 *J. Mol. Spectrosc.* **8** 222  
Suzuki I and Shimanouchi T 1973 *J. Mol. Spectrosc.* **46** 130  
Thirugnanasambandam P and Mohan S 1974 *J. Chem. Phys.* **61** 470  
Thirugnanasambandam P and Mohan S 1975 *Bull. Soc. Chim. Belg.* **84** 987  
Thirugnanasambandam P and Srinivasan G J 1969 *J. Chem. Phys.* **50** 2467  
Venkateswarlu K and Joseph P J 1971 *Indian J. Pure Appl. Phys.* **9** 480