Asian Journal of Chemistry Vol. 5, No. 3 (1993), 507–512

On the Determination of Force Field Using Centrifugal Distortion Constants by Parametric Method: Application to Systems of 3 × 3 Order

S. MOHAN* and N. SUNDARAGANESAN

Raman School of Physics
Pondicherry University, JIPMER Campus
Pondicherry-605 006, India

The centrifugal distortion constants are used as additional parameters in fixing the unique force field of XYZ_2 planar type (C_{2v}), molecules which consists of a third order vibrational species A_1 and a second order vibrational species B. It may be emphasised here that this method is applied for a problem of third order for the first time.

INTRODUCTION

The determination of an unequivocal set of force constants using the vibrational frequencies alone is not possible due to the more number of force constants than the available frequencies. Hence to overcome this difficulty different approaches have been adopted by the earlier workers. The number of unknowns in the secular equations may be restricted by use of physically meaningful force fields, *viz.*, central force field[1], simple valence force field[2], orbital valence force field[3], Urey-Bradley force field[4], modified Urey-Bradley force field[5], hybrid bond force field[6] and general quadratic valence force field[7].

Besides using proper force fields, certain approximation methods such as progressive rigidity method[8–10], L-matrix approximation method[11], potential energy distribution method[12] have also been used for the calculation of force constants in polyatomic molecules using a general valence force field. Another method used in fixing the force field is the parametric method. In this method additional parameters such as isotopic shifts[13], centrifugal distortion constants[14] and vibrational mean amplitudes[15] have been used to fix the molecular force field. All the above methods have been applied only for 2 × 2 vibrational problems so far. Ramaswamy *et al.*[16] have extended the parametric approach to the third order vibrational problem using the isotopic frequencies as additional data to fix the force field for XYZ bent type molecule. This method can be applied only to molecules which exist in three different isotopic forms (for example, $^{16}O^{14}NF$, $^{16}O^{15}NF$, $^{18}O^{15}NF$).

In the present investigation, a new parametric method has been formulated using centrifugal distortion constants as additional parameters for 3×3 vibrational problems and the same is applied to planar XYZ_2 (C_{2v}) type molecules.

Theoretical considerations

Wilson[17], Wilson and Howard[18] and Nielson[19] have developed the theory of centrifugal distortion in the study of the rotational spectra of asymmetric rotor molecules. The distortion constants are given as

$$Z_{\alpha\beta v\delta} = -(2I^e_{\alpha\alpha}I^e_{\beta\beta}I^e_{vv}I^e_{\delta\delta})^{-1}\sum_{ij} J^i_{\alpha\beta,\delta}J^j_{v\delta,\delta}N_{ij} \quad (1)$$

where I^e_{xx}, I^e_{yy} and I^e_{zz} are the principal moments of inertia and $J^i_{\alpha\beta,\delta}$ are the partial derivatives at equilibrium of the instantaneous inertia tensor components with respect to symmetry coordinates and N_{ij} are compliance matrix elements. Cyvin[20–22] has formulated the matrix form of the theory for centrifugal distortion.

Let $t_{\alpha\beta v\delta}$ be defined as

$$t_{\alpha\beta v\delta} = -2I^e_{\alpha\alpha}I^e_{\beta\beta}I^e_{vv}I^e_{\delta\delta} \quad (2)$$

$$= \sum_{ij} J^i_{\alpha\beta,\delta}J^j_{v\delta,\delta}N_{ij} \quad (3)$$

Equation (3) may be written as

$$t = J'_S N J_S \quad (4)$$

Substituting

$$J_{\alpha\beta,\delta} = G^{-1}T_{\alpha\beta,\delta} \quad (5)$$

$$t = T'_S(G'^{-1})NG^{-1}T_S \quad (6)$$

The elements of the T_S matrix can be calculated from molecular geometry and G^{-1} is the kinetic energy matrix of Wilson[23]; t may be written in L-matrix notation as

$$t = T'_S(L_{-1})'\Lambda^{-1}L^{-1}T_S \quad (7)$$

In the parametric method, the L-matrix is written as

$$L = L_0 A \quad (8)$$

where A is an orthogonal matrix

Thus $$t = T'_S(L_0^{-1})'A\Lambda^{-1}A'L_0^{-1}T_s \quad (9)$$

By varying the values of the parameters in the A matrix, it is possible to find all the t values that fit the observed frequencies. Then the F matrix is evaluated using the expression

$$F = (L_0^{-1})'A\Lambda A'L_0^{-1}$$

Application to XYZ_2 type molecules

The vibrational modes of a planar XYZ_2 type molecule belonging to C_{3v} symmetry is classified as = $3A_1 + 2B_1 + B_2$. In the present investigation only the inplane force constants corresponding to A_1 and B_1 species have been determined.

A_1 Species

The orthogonal matrix A used in this work is of the form (Refer appendix)

$$\begin{pmatrix} a_1 & a_3 & a_6 \\ a_2 & a_4 & a_7 \\ 0 & a_5 & a_8 \end{pmatrix}$$

Let the L_0^{-1}, matrix elements be U, V, W, X, Y and Z.

Let the T_S matrix elements be J, M, N, P, Q and S_1 (Refer appendix) and $1/\lambda_1$, $1/\lambda_2$, $1/\lambda_3$ are the elements of Λ^{-1} matrix. Using these matrices in expression (9), the t elements are obtained and they are given below :

$$t_{xxx} = 1/\lambda_1(a_1\alpha_1 + a_2\alpha_2)^2 + 1/\lambda_2(a_3\alpha_1 + a_4\alpha_2 + a_5\alpha_5)^2 + 1/\lambda_3(a_6\alpha_1 + a_7\alpha_2 + a_8\alpha_5)^2 \quad (11)$$

$$t_{yyyy} = 1/\lambda_1(a_1\alpha_1 + a_2\alpha_3)^2 + 1/\lambda_2(a_3\alpha_1 + a_4\alpha_3 + a_5\alpha_6)^2 + 1/\lambda_3(a_6\alpha_1 + a_7\alpha_3 + a_8\alpha_6)^2 \quad (12)$$

$$t_{zzzz} = 1/\lambda_1(a_2\alpha_4)^2 + 1/\lambda_2(a_4\alpha_4 + a_5\alpha_7)^2 + 1/\lambda_3(a_7\alpha_4 + a_8\alpha_7)^2 \quad (13)$$

$$t_{xxyy} = 1/\lambda_1(a_1\alpha_1 + a_2\alpha_2)(a_1\alpha_1 + a_2\alpha_3) + 1/\lambda_2(a_1\alpha_1 + a_4\alpha_2 + a_5\alpha_5)(a_3\alpha_1 + a_4\alpha_3 + a_5\alpha_6) + 1/\lambda_3(a_6\alpha_1 + a_7\alpha_2 + a_8\alpha_5)(a_6\alpha_1 + a_7\alpha_3 + a_8\alpha_6) \quad (14)$$

$$t_{xxzz} = 1/\lambda_1(a_1\alpha_1 + a_2\alpha_2)(a_2\alpha_4) + 1/\lambda_2(a_3\alpha_1 + a_4\alpha_2 + a_5\alpha_5)(a_4\alpha_4 + a_5\alpha_7) + 1/\lambda_3(a_6\alpha_1 + a_7\alpha_2 + a_8\alpha_5)(a_7\alpha_4 + a_8\alpha_7) \quad (15)$$

$$t_{yyzz} = 1/\lambda_1(a_1\alpha_1 + a_2\alpha_3)(a_2\alpha_4) + 1/\lambda_2(a_3\alpha_1 + a_4\alpha_3 + a_5\alpha_6)(a_4\alpha_4 + a_5\alpha_7) + 1/\lambda_3(a_6\alpha_1 + a_7\alpha_3 + a_8\alpha_6)(a_6\alpha_4 + a_8\alpha_7) \quad (16)$$

The constants used in the above equations are described in the Appendix.

The above method has been aplied to COF_2 and NFO_2 molecules. The structural parameters, vibrational frequencies and the observed centrifugal distortion values are taken from references (COF_2 : 24NOF_2 : 25).

The value for $t_{\alpha\beta\nu\delta}$ is obtained from the experimental value of $Z_{\alpha\beta\nu\delta}$. Since the experimental values are available for t_{xxxx}, t_{zzzz}, t_{xxzz} it is sufficient to map these values with a. A horizontal line is drawn on the axis ($t_{\alpha\beta\nu\delta}$ axis) corresponding to the experimental value of $t_{\alpha\beta\nu\delta}$. The intersection point of the line with the curves mentioned earlier gives the value of a. Hence we obtain the three values for "a", each corresponding to t_{xxxx}, t_{zzzz} and t_{xxzz}. The best suitable value is the one which is closer to zero. This is because A matrix is always nearly equal to unity.

For both the molecules under consideration the best "a" value corresponds to t_{xxxx}. The A matrix composed of "a" value is used in expression (10) to get the F elements of A_1 type species.

B_1 Species

The orthogonal matrix A used for this species is of the form

$$A = 1/\theta\begin{pmatrix} 1 & C \\ -C & 1 \end{pmatrix} : \theta = (1 + C^2)^{1/2}$$

Let the L_0^{-1}matrix elements be ε, χ, ψ and T_S matrix elements be ϕ, ξ.

Using these matries in expression (9), the t elements is obtained as given below:

$$t_{xzxz} = 1/\theta^2\{1/\lambda_4(\varepsilon\phi + C\alpha\phi + \psi\xi)^2 + 1/\lambda_5[-C\phi + (\alpha\phi + \psi\xi)]^2\} \quad (17)$$

Different values are given to C in equation (17) and the value for t_{xzxz} is evaluated. The value for t_{xzxz} is obtained from the experimental value of t_{xzxz}. A graph is drawn with C versus t_{xzxz}. A horizontal line is drawn corresponding to the experimental value of t_{xzxz} and the point of intersection of the line with the curve mentioned earlier is the required value of C. This value of C is used to get the orthogonal matrix which in turn is used in the expression (10) to get the F matrix.

The experimentally observed values of the $\tau_{\alpha\beta\nu\delta}$ elements and the "a" values obtained in the present investigation are given in Table 1. Table 2 deals with the evaluated force constants in the present investigation, along with the values reported in the literature. It may be observed from the table that the F matrix elements obtained in the present investigation agree quite well with the literature values.

TABLE 1
VALUES OF $\tau_{\alpha\beta\nu\delta}$ ELEMENTS AND 'a' PARAMETERS

Molecule	Element and its value (MHZ)		a	Element and its value (MHZ)		C
COF_2	$-\tau_{xxxx}$	0.0654*	0.0428	$-\tau_{xzxz}$	0.0352*	0.225
NFO_2	$-\tau_{xxxx}$	0.0398**	–0.26	$-\tau_{xzxz}$	0.0489**	0.0577

*Ref. 24; **Ref. 25

TABLE 2
F_{ij} ELEMENTS (10^5 dynes/cm)

F_{ij}	COF_2		NFO_2	
	PW	EW	PW	EW
F_{11} (A_1)	15.5167	16.0834	4.7342	4.6209
F_{22} (A_1)	8.3058	7.6487	13.4602	11.9204
F_{33} (A_1)	1.1360	0.7929	1.2578	0.6054
F_{12} (A_1)	1.0800	1.9236	–0.3766	0.9695
F_{13} (A_1)	–0.3317	–0.6112	–1.0313	–0.6563
F_{23} (A_1)	1.9391	0.6035	2.9522	0.3333
F_{44} (B_1)	5.2128	6.9604	10.3270	11.2606
F_{55} (B_1)	0.7203	0.6319	0.8467	0.8244
F_{45} (B_1)	0.4188	0.8984	0.2971	0.7664

PW: Present Work
EW: Earlier Work, Ref. 26, 27.

CONCLUSION

A new parametric method with centrifugal distortion constants as additional parameter is developed for a 3 × 3 vibrational problem for the first time in the present work.

APPENDIX

$a_1 = \frac{1}{\theta}$; $a_2 = \frac{-a}{\theta}$; $a_3 = \frac{\sqrt{3}}{2}\frac{a}{\theta}$;

$a_4 = \frac{\sqrt{3}}{2}\frac{1}{\theta}$; $a_5 = \frac{1}{2}$; $a_6 = \frac{1}{2}\frac{a}{\theta}$;

$a_7 = \frac{1}{2\theta}$; $a_8 = \frac{-\sqrt{3}}{2}$; $\theta = (1 + a^2)^{1/2}$;

$J = 2D$; $N = \sqrt{8}d$; $M = \sqrt{8}dC^2$;

$P = \sqrt{8}dS^2$; $Q = \sqrt{24}dCS$; $S = -\sqrt{24}dCS$;

$\alpha_1 = UJ$; $\alpha_2 = VJ + WM$; $\alpha_3 = VJ + WN$;

$\alpha_4 = WP$; $\alpha_5 = XJ + YM + ZQ$; $\alpha_6 = XJ + YN$;

$\alpha_7 = YP + ZS$; $\phi = \sqrt{8}dCS$; $\xi = \sqrt{8}dCS^2$

REFERENCES

1. D.M. Dennison, *Astrophys. Jl.* **62**, 84 (1925).
2. N. Bjerrum, *Verh. Dtsch. Phys. Ges.*, **16**, 737 (1914).
3. G.F. Heath and J.W. Linnett, *Trans. Far. Soc.*, **44**, 556, 561, 873, 878, 884 (1948); **45**, 264 (1949).
4. H.C. Urey and B.C.A. Bradley, *Phys. Rev.*, **38**, 1969 (1931).
5. T. Shimanouchi, *J. Chem. Phys.*, **26**, 594 (1957).
6. I.M. Mills, *Spectrochim. Acta.*, **19**, 1585 (1963).
7. P. Thirugnanasambandam and S. Mohan, *J.Chem. Phys.*, **61**, 470 (1974).
8. P. Torkington, *J. Chem. Phys.*, **17**, 357 (1949).
9. A. Muller, *Z. Phys. Chem. (Leipzig)*, **238**, 116 (1968).
10. C.J. Peacock and A. Muller, *Molecular Physics*, **14**, 393 (1968).
11. J. Herranz and F. Castano, *Spectrochim. Acta*, **22**, 1965 (1966).
12. H.J. Becher and K. Ballein, *Z. Phys. Chem. (NF)*, **54**, 302 (1967).
13. S. Mohan and S. Rajaraman, *Indian J. Pure & Appl. Phys.*, **20**, 230 (1982).
14. S. Mohan, S. Gunasekaran and K.G. Ravikumar, *Indian J. Pure & Appl. Phys.*, **21**, 121 (1983).
15. S. Mohan, S. Durai and S.P. Dwarakanathan, *Acta Phys. Pol.*, **69A**, 319 (1986).
16. K. Ramaswamy and S. Karunanidhi, *Pramana*, **6**, 579 (1977).
17. E.B. Wilson (Jr.) and J.B. Howard, *J. Chem. Phys.*, **4**, 526 (1936); **5**, 6, (1937).
18. E.B. Wilson and J.B. Howard, *J. Chem. Phys.*, **4**, 260 (1936).
19. N.H. Nielson, *Rev. Mod. Phys.*, **23**, 90 (1951).
20. S.J. Cyvin and G. Hagen, *Chem. Phys. Letters*, **1**, 645 (1968).
21. S.J. Cyvin, et al., *Z. Naturforsch*, **239**, 1649 (1968).
22. B.N. Cyvin, I. Elvebredd and S.J. Cyvin, *Z. Naturforsch*, **24a**, 139 (1969).
23. E.B. Wilson (Jr.), J.C. Decius and P.C. Cross, Molecular Vibrations, McGraw-Hill, New York (1955).
24. A.M. Mirri, *Spectrochim. Acta*, **25A**, 1832 (1969).
25. A.M. Mirri, G. Cazzoli and L. Ferretti, *J. Chem. Phys.*, **49**, 2775 (1968).
26. N. Karunanidhi, Ph.D. Thesis, Madras University, 1976.
27. P. Thirugnanasambandam and N. Karunanidhi, *Indian J. Phys.*, **49**, 658 (1975).

(*Received*: 5 October 1991; *Accepted*: 15 September 1992) AJC–476