SHORT COMMUNICATIONS

MOLECULAR FORCE FIELD—PARAMETRIC APPROACH

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THE force field study of some $XY_3(C_{3v})$ type molecules has been attempted using the parametric representation method. Experimental data such as rotation-vibration coupling constants have been used to evaluate the best fit force field. The symmetrized force constants evaluated for these molecules agree quite well with the values reported in the literature. Further, the centrifugal distortion constants have also been calculated and compared with observed values.

The determination of symmetry force constants from the vibrational frequencies alone is a mathematically undetermined problem. This is so because n_i vibrational frequencies of a given species are not sufficient for estimating the $n_i(n_i + 1)/2$ force constant elements F_{ij} in general. In the parametric approach the additional $n_i(n_i - 1)/2$ data for the determination of force constants are imposed on the parameter matrix which may be expressed in terms of trigonometrical functions of angle parameters. A simple method to evaluate the force field for some pyramidal $XY_3(C_{3v})$ molecules by the method of parametric representation using rotation-vibration coupling constants as additional data are presented here for the first time.

The symmetry coordinates S and the normal coordinates Q in molecules are related through the relation, $S = LQ$ where L is the normal coordinate transformation matrix. The significance of the matrix L is that many molecular properties can be expressed in terms of its elements. The relations like $F = \tilde{L}^{-1}\lambda L^{-1}$, $\Sigma = L\Delta\tilde{L}$ and $\zeta^\alpha = L^{-1}C^\alpha \tilde{L}^{-1}$ are well known. The F, Σ and ζ matrices in the above equations stand for the symmetry force constants[1], the symmetrized mean square amplitudes[2] and the Coriolis coupling coefficients[3] respectively. Therefore, if the elements of matrix L are known, the force constants may be directly computed from the vibrational frequencies of the molecule.

In the parameteric method, the transformation matrix L is written as, $L = L_0 A$ where A is an orthogonal matrix. Thus, $F = \tilde{L}_0^{-1}A\lambda\tilde{A}L_0^{-1}$. The matrix L_0 is a triangular matrix and its elements can be obtained from $L_0\tilde{L}_0 = G$. The orthogonal matrix A consists of only one parameter a. In the 2×2 vibrational problem,

$$A = (1 + a^2)^{-1/2} \begin{bmatrix} 1 & a \\ -a & 1 \end{bmatrix}$$

where $a = -\tan \phi$; ϕ is the angle parameter. The expression for Coriolis coupling constant is also written as,

$$\zeta^\alpha = \tilde{A}L_0^{-1}C^\alpha\tilde{L}_0^{-1}A,$$

where C^α are Coriolis matrix elements[3] which may be evaluated using the geometry of molecule. The matrix A elements are determined with the help of experimentally observable Coriolis coupling values.

According to Jahn's rule[4] for pyramidal XY_3 molecules, the Coriolis coupling constants $\zeta^\alpha(\alpha = X, Y, Z)$ arise from $A_1 \times E$ (second order) and $E \times E$ (first order) couplings. The ζ_{33} and ζ_{44} values corresponding to $E \times E$ coupling and the ζ_{13} value corresponding to $A_1 \times E$ coupling are experimentally available. Taking the available experimental values of ζ^α, the matrix A can be computed. The detailed procedure of determination of the values of A has been described elsewhere[5-7]. Using the values of A, thus determined the symmetrized force constants F are determined. Using the set of potential constants obtained in the present study, the centrifugal distortion constants have been evaluated.

In the present work, NH_3, ND_3 and NT_3 molecules have been chosen to verify the validity of the method described above. The structural parameters, vibrational frequencies and observed Coriolis coupling values are taken from literature[8-13]. The values of a and the best fit F matrix evaluated in this investigation are presented in table 1. The values of F elements obtained by the present method agree quite well with the literature values[14], thus proving the validity of using Coriolis coupling constants to fix the force field. In view of Herzberg's statement[15] viz 'since the isotopic molecules have the same electronic structure, the potential function under the influence of which the nuclei are moving is the same

Table 1 *The a values and symmetrized force constants $(10^2 \ Nm^{-1})$*

Molecule	a values $a(A_1)$	$a(E)$	$F_{11}(A_1)$	$F_{22}(A_1)$	$F_{12}(A_1)$	$F_{33}(E)$	$F_{44}(E)$	$F_{34}(E)$
NH_3	−0.0700	0.0245	7.1147	0.2318	0.2092	6.9779	0.3328	−0.1146
ND_3	−0.1300	−0.0094	7.0709	0.2660	0.2175	7.0559	0.3316	−0.1241
NT_3	−0.0345	0.0007	7.2039	0.2407	0.1968	6.8154	0.3300	−0.1380

Table 2 *Centrifugal distortion constants (MHz)*

Molecule	D_J	$-D_{JK}$	D_K	Ref.
NH_3	24.0210	43.9950	22.4321	PW
	24.2700	43.6500	—	9
	24.3100	45.2700	—	16
ND_3	5.8322	10.8921	4.8212	PW
	5.8500	10.9800	—	9
	5.9100	10.4900	—	17
NT_3	2.5802	4.4092	2.0481	PW
	2.5981	4.4720	—	18

to a very high degree of approximation", it is significant to note that the numerical values of the symmetrized force constants for the three isotopically substituted ammonia molecules are close to each other. Using the set of potential constants, derived here, the centrifugal distortion constants for these cases have been evaluated. In table 2, the evaluated values are compared with the observed values[9,16-18]. The close agreement between the calculated and observed values of centrifugal distortion constants brings out the validity of the method of parametric representation described in this note.

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LECTIN-IMMOBILIZED ALBUMINATED POLYETHER URETHANE UREA: TISSUE COMPATIBILITY

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IT was known[1] that the cell growth is normal on albuminated substrates and was that lectins are