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PARAMETRIC APPROACH TO THE FORCE FIELD STUDIES OF SOME XYZ_3 TYPE MOLECULES

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An attempt has been made to extend the parametric representation technique to 3 × 3 vibrational problems by constructing a simple orthogonal matrix in terms of angle parameters S_θ and C_θ. From the explicit relations connecting them with centrifugal distortion constants and coriolis coupling constants, the force field has been fixed for four XYZ_3 type molecules. The results obtained are satisfactory and provide scope for extension to many other molecules.

Key Words : Force Field; Parametric Representation Technique; 3 × 3 Vibration; Orthogonal Matrix; Centrifugal Distortion Constants; Coriolis Coupling Constants; XYZ_3 Molecule

INTRODUCTION

THE parametric approach is an elegant method in fixing the intermolecular force field. It incorporates various spectroscopic data in the solution of problems associated with intermolecular vibrations. Several investigators have utilised data like isotopic frequencies, mean amplitudes of vibration and centrifugal distortion constants as additional data.[1–3] This is because of the fact that as the order of the problem increases, the vibrational frequencies available are very much less than the number of force constants. The centrifugal distortion constants and the coriolis coupling constants are very powerful and sensitive and hence can be of immense value in solving the vibrational problems of higher order. The above constants have been used by Mohan *et al.*[4,5] in solving 2×2 vibrational problems. The method has also been extended to 3×3 vibrational problems by Ramaswamy *et al.*[6] in which three different angular parameters have been used to form the orthogonal matrix. In the present investigation, a much simpler orthogonal matrix has been formulated to solve the 3×3 vibrational problems of XYZ_3 molecules using both centrifugal distortion constants and coriolis coupling constants.

THEORY

The basic theory for the present calculations is briefly outlined here.

The well-known secular equation of Wilson[7] is given by

$$\mathbf{GFL} = \mathbf{L\Lambda}, \qquad \ldots (1)$$

where **G** is the inverse kinetic energy matrix and **F** is the potential energy matrix, $\mathbf{\Lambda}$ is the diagonal matrix of vibrational eigen values with elements $\lambda_k = 4\pi^2c^2\gamma_k^2$ (γ_k is the wave number of the kth mode) and **L** is the eigen vector satisfying the normalising condition

$$\mathbf{LL'} = \mathbf{G}. \qquad \ldots (2)$$

The **L** matrix can be written as

$$\mathbf{L} = \mathbf{L_0A}, \qquad \ldots (3)$$

where **A** is the orthogonal matrix. The **F** matrix is given by

$$\mathbf{F} = (\mathbf{L}_o^{-1})'\ \mathbf{A\Lambda A'}\ \mathbf{L}_o^{-1}. \qquad \ldots (4)$$

For a 3×3 case, the **A** matrix can be chosen in a simple form as given below

$$\begin{bmatrix} C_\theta & S_\theta & 0 \\ S_\theta & C_\theta & 0 \\ 0 & 0 & 1 \end{bmatrix} \qquad \ldots (5)$$

$\mathbf{L}_o$ matrix elements can be obtained using the relation

$$\mathbf{L}_o\,\mathbf{L}_o' = \mathbf{G}. \qquad \ldots (6)$$

In terms of the **A** matrix, the coriolis coupling constants and the centrifugal distortion constants are given as

$$\zeta^\alpha = \mathbf{A'}\ \mathbf{L}_o^{-1}\ \mathbf{C}^\alpha(\mathbf{L}_o^{-1})'\ \mathbf{A} \qquad \ldots (7)$$

and

$$t = \mathbf{T}_\theta'(\mathbf{L}_o^{-1})'\ \mathbf{A\Lambda}^{-1}\ \mathbf{A'}\ \mathbf{L}_o^{-1}\ \mathbf{T}_\theta. \qquad \ldots (8)$$

C is the matrix as given by Meal and Polo[8] and $\mathbf{T}_\theta$ matrix can be obtained for a given model from the equilibrium position vectors of the atoms.[7]

In the case of XYZ_3 molecules, experimental values of coriolis constants and centrifugal constants are available in plenty. The frequency distribution of XYZ_3 molecules is $\Gamma = 3\,\mathbf{A}_1 + 3\,\mathbf{E}$. The coriolis constants are due to the couplings $A_1 \times E$ and $E \times E$. The experimental values are available for $E \times E$ coupling, hence have been used for the solution of E species. The experimental values of the centrifugal distortion constants D_J and D_{JK} are available, which are advantageously used in solving A_1 species. Since both the constants are sensitive, one can fix the force field to a great degree of accuracy, adopting this procedure.

Thus equation (6) leads to the determination of **A** matrix for **E** species and equation (7) for A_1 species. From the knowledge of 'A', the **L** matrices are obtained and hence the **F** and $\mathbf{\Sigma}$ matrix, where $\mathbf{\Sigma}$ is the mean square amplitude matrix.

Results and Discussion

In Table I, the fundamental frequencies and interatomic distances of the XYZ_3 molecules are given. Table II presents the experimental values of ζ and the $\mathbf{S}_\theta$ and

C_θ parameters obtained for E species. Table III gives the experimental values of D_j, D_{jk} and the S_θ and C_θ values for the A_1 species. Table IV deals with the force constants evaluated in the present investigation. The values for C–F, C–H, C–Cl and Ge–Br agree well with the earlier values.[9,10] It is interesting to find that the C–H and C–D bond force constants are not affected by isotopic substitution, as pointed out by Herzberg.[11] This is brought out by the values obtained in the present investigation. In addition, the interaction force constants assumed the same sign as obtained in earlier works. This is in support of the uniqueness in fixing the force field by parameter approach. The mean square and mean amplitudes of vibration are presented in Table V. The values obtained for the mean amplitudes of C–Cl and C–H distances may be compared with the experimental electron diffraction results 0.06 ± 0·004 and 0.089 ± 0.01. A reported by Bartell and Brockway.[12]

TABLE I

Interatomic distances and the vibrational frequencies of the molecules [cm^{-1}]

No.	Molecule	D [Å] X–Y distance	d [Å] X–Z distance	ν_1 (A_1)	ν_2 (A_1)	ν_3 (A_1)	ν_4 (E)	ν_5 (E)	ν_6 (E)	Reference
1	CFH_3	1.382	1.095	1059	3031	1490	3132	1206	1498	13,9
2	CFD_3	1.382	1.095	1002	2173	1153	2329	926	1087	13,9
3	$CClD_3$	1.778	1.086	708	2212	1045	2354	779	1076	13,14
4	$GeBrH_3$	2.298	1.440	305	2116	833	2127	578	871	15,10

TABLE II

Experimental values of ζ *and the* S_θ *and* C_θ *values for the solution of E species*

No.	Molecule	ζ_4	ζ_5	$-\zeta_6$	Ref.	S_θ	C_θ
1	CFH_3	0.089	0.284	0.280	9	0.20	0.9798
2	CFD_3	0.182	0.240	0.293	9	0.05	0.9988
3	$CClD_3$	0.175	0.185	0.320	16	0.09	0.9959
4	$GeBrH_3$	—0.038	0.197	0.145	17	0.02	0.9998

TABLE III

Experimental values of D_j *and* D_{jk} *aad the* S_3 *and* C_θ *values for the solution of* A_1 *species*

No.	Molecule	D_j	D_{jk}	Ref.	S_θ	C_θ
1	CFH_3	0.0604	0.4392	9	0.12	0.9928
2	CFD_3	0.0342	0.2217	9	0.15	0.9885
3	$CClD_3$	0.0108	0.1027	18	0.20	0.9798
4	$GeBrH_3$	0.0006	0.0130	19	0.01	0.9999

TABLE IV

Force constants [10^5N/*m*] *of* XYZ_3 *molecules*

No.	Molecule	f_D / f_d	f_{Dd} / f_{dd}	f_α / f_θ	$-f_{\alpha\alpha}$ / $-f_{D\alpha}$	$-f_{d\alpha}'$ / $f_{d\alpha}''$	$-f_{\alpha\theta}'$ / $-f_{d\theta}'$
1	CFH_3	6.1399	0.1297	0.1028	0.0221	0.0269	0.0421
		5.3002	0.0173	0.1490	0.1535	0.0174	0.1475
2	CFD_3	5.8035	0.2971	0.1023	0.0186	0.0416	0.0343
		5.5932	0.1833	0.1313	0.1687	0.0293	0.0648
3	$CClD_3$	4.4387	0.0242	0.0914	0.0253	0.0439	0.0291
		5.4758	0.0268	0.0897	0.1520	0.0261	0.0769
4	$GeBrH_3$	2.5294	0.3639	0.0375	0.0112	0.0320	0.0182
		2.6437	0.0043	0.0326	0.0379	0.0012	—0.0051

TABLE V

Mean square amplitudes [$10^{-5}A^2$] *and Mean amplitudes* [A°] *of vibration*

No.	Molecule	σ_D(X–Y) / σ_d(X–Z)	σ_p(Y..Z) / σ_Q(Z..Z)	l_D(X–Y) / l_d(X–Z)	l_p(Y..Z) / l_Q(Z..Z)
1	CFH_3	2.1700	8.6297	0.0466	0.0929
		6.1056	15.5648	0.0781 (0.089 ± 0.010)*	0.1248
2	CFD_3	2.2956	7·0477	0.0479	0.0839
		4.2996	10.6325	0.0656	0.1031
3	$CClD_3$	2.7663	8.9327	0.0526 (0.060 ± 0.004) *	0.0945
		4.2838	11.6953	0.0655	0.1081
4	$GeBrH_3$	2.3104	18.5646	0.0481	0.1363
		8.0315	24.7482	0.0896	0.1574

*Experimental value.[12]

CONCLUSION

A simple 3 × 3 orthogonal matrix has been used in the present investigation to solve the vibrational problem of a few XYZ_3 molecules using coriolis and centrifugal distortion constants. The results point out that the force field can be accurately fixed by the parameter approach.

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