

Third, Fourth and Fifth Order Vibrational Problems by the Method of Isotani

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A new technique has been adopted in this paper in solving the secular equation $|H - \lambda E| = 0$ where $H = GF$, so as to get the force constants for a series of molecules of the type XY_3Z , XY_3ZW and XY_3ZVW belonging to the point group C_{3v} involving third, fourth and fifth order vibrational problems respectively.

INTRODUCTION

Generally force constants are evaluated by solving the secular equation $|GF - \lambda E| = 0$. But the inherent difficulty in solving the secular equation is that there are more unknown elements than the number of equations. For an $n \times n$ problem there are $n(n + 1)/2$ unknown force constants and n known fundamental vibrational frequencies. To get over this difficulty one must supply $n(n - 1)/2$ equations additionally. In some approximation methods¹⁻⁶, constraints are imposed either on the elements of F or on the elements of L -matrix so as to obtain the necessary additional equations. We present here the Isotani's method⁷ which involves evaluation of off-diagonal force constants using expressions for them obtained on the basis of experimental force constants of high symmetry molecules.

An $n \times n$ problem has been solved by first finding the $n(n - 1)/2$ off-diagonal force constants. Using these off-diagonal force constants the remaining n diagonal force constants are determined by using the Newton-Raphson iterative method of solving n non-linear equations in n unknowns. In doing so a new technique is employed exploiting the symmetry in the secular equations.

A new technique of solving secular equations

To solve the n non-linear equations in n unknowns (F_{ij}) obtained from the secular equation $|GF - \lambda E| = 0$ after substituting for all the off-diagonal elements F_{ij} from Isotani's formula, the Newton-Raphson method is used here.

The method involves mainly the calculation of the values of the functions and their derivatives at the corresponding points. Here a new technique is developed

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to obtain these values of functions and derivatives in a unique way using the symmetry in the secular equations.

The functions f_i consist of the difference between the sum of all the principal minors of order i of the matrix H and a similar sum for a diagonal matrix Λ having λ_i on their diagonals. The sum of all the principal minors of various orders can be directly obtained from the characteristic equation of the corresponding matrices.

To determine the derivatives of the function, one has to look at their pattern and decide on the mode of calculation. The derivative of f_i with respect to F_{kk} involves the sum of all principal minors of order i involving H'_{kk} only, where H' is the matrix obtained by replacing the k th column of H -matrix by the k th column of G -matrix. To obtain the derivatives of f_i with respect to F_{kk} the k th column in H -matrix is replaced by the k th column of G -matrix and the sum of the principal minors of order i is determined and from this the sum of the principal minors of order i in a truncated H -matrix (leaving out the k th row and k th column) is subtracted.

In the present investigation a fresh attempt is made to calculate the symmetrized force constants involved in the third, fourth and fifth order problems (A_1 species and E species) in SiH_3X , SiH_3XY and SiH_3XYZ by the new technique introduced here. The valence force constants are then obtained from the symmetrized force constants.

Interaction coordinates

The compliance constants are determined as inverse of force constants and used in the calculation of interaction coordinates. The interaction coordinate $(I)_k$ introduced by Jones *et. al.*⁸ is the displacement of coordinate l resulting from minimising energy after unit displacement of the coordinate k . The interaction coordinates are related to the compliance constants by

$$(I)_k = (n_{lk}/n_{kk})$$

Using these coordinates, it is possible to determine the amount of stretching or contraction of the bonds for a particular change in another bond or angle for minimum energy configuration.

RESULTS AND DISCUSSION

The results of symmetrized force constants F_{ij} determined by Isotani's method and the corresponding F_{ii} and F_{jj} values are reported in Tables 1 and 2 for one particular species of three molecules, one of each type. The F_{ii} values assume consistent values and the mean value taken is thus justified. The final values of F_{ij} satisfying the secular equations obtained as the solution by the new technique are given in these Tables along with the mean values which are used as initial sets.

TABLE 1
SYMMETRIZED FORCE CONSTANTS FOR XY_3Z AND XY_3ZW TYPE MOLECULES
FOR A_1 SPECIES (mdyn/Å)

Molecule	F_{11}	F_{22}	F_{33}	F_{44}	F_{ij}
SiH ₃ F	2.86	5.12	—	—	0.36
	2.86	—	0.25	—	0.88
	—	5.25	0.25	—	-0.23
Mean values	2.86	5.19	0.25	—	—
Final values	2.86	5.34	0.26	—	—
SiH ₃ CN	2.88	1.87	—	—	0.32
	2.88	—	18.51	—	0.15
	2.88	—	—	0.22	0.09
	—	3.16	17.23	—	-0.31
	—	1.88	—	0.22	-0.07
	—	—	18.43	0.22	—
Mean values	2.88	2.30	18.06	0.22	—
Final values	2.88	3.37	16.98	0.23	—

TABLE 2
SYMMETRIZED FORCE CONSTANTS FOR XY_3ZVW TYPE MOLECULE
FOR A_1 , SPECIES (mdyn/Å)

Molecule	F_{11}	F_{22}	F_{33}	F_{44}	F_{55}	F_{ij}
SiH ₃ CCH	2.83	2.32	—	—	—	0.34
	2.82	—	14.96	—	—	-0.06
	2.84	—	—	6.00	—	0.25
	2.83	—	—	—	0.27	0.10
	—	3.68	14.28	—	—	0.33
	—	2.55	—	5.99	—	1.25
	—	2.34	—	—	0.27	-0.09
	—	—	15.55	6.09	—	1.06
	—	—	14.88	—	0.27	-0.25
	—	—	—	5.99	0.28	-0.30
	Mean values	2.83	2.72	14.91	6.01	0.28
Final values	2.83	4.31	14.78	6.02	0.29	—

The general quadratic valence force field has been employed in the investigation of force constants for SiH₃X (X = F, Cl, Br, I). SiH₃CN and SiH₃CCH and their isotopically substituted molecules. The force constants thus calculated are presented in Table 3 for the molecules SiH₃X and their deuterated derivatives and in Table 4 for SiH₃CN and SiH₃CCH and their deuterated derivatives. From these Tables it is found that the Si-H stretching valence force constants (f_r) is

almost the same to a reasonable extent for all the molecules under investigation. For SiH_3Z and SiD_3Z molecules, as the mass of Z atom increases the Si-Z stretching force constant f_R and H-Si-X bending force constant (f_β) progressively decrease for the halogenated derivatives. The H-Si-H bending force constant f_α is nearly same (0.17 mdyn/\AA) for the molecules in Table 1. All the interaction force constants maintain a consistent trend of low values in all the molecules. The C=N stretching force constant in SiH_3CN obtained in the present work (16.98 mdyn/\AA) is found to agree very closely with the value of 16.89 mdyn/\AA as reported by Krishna Pillai and Ramasamy earlier⁹. The C=C stretching force constant in SiH_3CCH (14.78 mdyn/\AA) appears to concur with the values ($14.34, 14.67$ and 14.60 mdyn/\AA) as reported by Gnanasekaran *et. al.*¹⁰, Natarajan and Rajendran¹¹ and Goggin and Woodward¹².

TABLE 3
VALENCE FORCE CONSTANTS OF XY_3Z TYPE MOLECULES (mdyn/\AA)

f value	SiH_3F	SiD_3F	SiH_3Cl	SiD_3Cl	SiH_3Br	SiH_3I	SiD_3I
f_r	2.77	2.82	2.78	2.87	2.78	2.80	2.84
f_R	5.34	5.30	2.97	2.95	2.45	1.86	2.01
f_α	0.19	0.22	0.17	0.20	0.17	0.17	0.17
f_β	0.24	0.25	0.17	0.17	0.17	0.16	0.14
f_{rr}	0.04	0.02	0.04	0.02	0.04	0.03	0.02
f_{rR}	0.21	0.14	0.20	0.11	0.19	0.18	0.12
$f_{r\alpha}$	-0.03	-0.03	-0.04	-0.04	-0.04	-0.04	-0.04
$f'_{r\alpha}$	0.05	0.05	0.05	0.05	0.05	0.05	0.04
$f_{r\beta}$	0.04	0.01	0.04	0.01	0.04	0.04	0.01
$f_{R\alpha}$	-0.09	-0.08	-0.03	-0.06	-0.02	-0.01	-0.02
$f_{\alpha\alpha}$	-0.03	-0.03	-0.04	-0.05	-0.05	-0.05	-0.05
$f_{\alpha\beta}$	-0.10	-0.11	-0.06	-0.09	-0.09	-0.08	-0.07

TABLE 4
VALENCE FORCE CONSTANTS OF XY_3ZV AND XY_3ZVW TYPE MOLECULES (mdyn/\AA)

f_{ij}	SiH_3CN	SiD_3CN	SiH_3CCH	SiD_3CCH	f_{ij}	SiH_3CN	SiD_3CN	SiH_3CCH	SiD_3CCH
f_r	2.84	2.91	2.77	2.85	f_{rR}	0.18	0.13	0.20	0.14
f_R	3.37	3.34	4.41	4.66	$f_{r\alpha}$	0.09	0.21	0.14	0.15
f_D	16.98	17.00	14.78	14.71	$f'_{r\alpha}$	-0.05	-0.03	-0.03	-0.03
f_d	—	—	6.02	6.02	$f_{r\beta}$	0.05	0.03	0.04	0.02
f_α	0.11	0.12	0.18	0.18	$f_{r\phi}$	0.10	0.06	0.14	0.03
f_β	0.30	0.27	0.24	0.24	$f'_{r\phi}$	-0.01	-0.01	-0.02	-0.01
f_ϕ	0.04	0.03	0.04	0.04	$f_{\beta\beta}$	—	—	-0.04	-0.02
f_θ	—	—	0.06	0.06	$f_{\phi\phi}$	—	—	-0.02	-0.02
f_{rr}	0.02	0.03	0.04	0.04					

The interaction coordinates reported in Table 5 reveal certain interesting characteristics relating to molecular vibration. The interaction coordinates directly indicate how a change in a particular coordinate affects another coordinate when all the coordinates are allowed to adjust themselves for minimisation of energy. For example, stretching in r_2 leads to a contraction in bond length r_1 . Similarly stretching in X-Z bond length R is accompanied by contraction in X-Y bond length r_1 . Similarly stretching in X-Z bond length R is accompanied by contraction in X-Y bond length r_1 . Increase of bond angle α_1 appears to bring about an extension of the bond lengths R and r_1 . Increase in angle α_2 brings about a decrease in α_1 .

TABLE 5
INTERACTION COORDINATES OF XY_3Z , XY_3ZW AND XY_3ZVW TYPE
MOLECULES

Molecules	$-(r_1)_{r_2}$	$-(r_1)_R$	$-(r_1)_{\alpha_1}$	$-(R)_{\alpha_1}$	$-(\alpha_1)_{\alpha_2}$	$-(\alpha_1)_{\beta_1}$
SiH ₃ F	0.01	0.09	0.01	0.02	0.25	0.10
SiD ₃ F	0.02	0.06	0.02	0.02	0.31	0.09
SiH ₃ Cl	0.01	0.08	0.01	0.02	0.23	-0.07
SiD ₃ Cl	0.01	0.05	0.01	0.03	0.20	0.06
SiH ₃ Br	0.01	0.07	0.00	0.01	0.22	0.14
SiH ₃ I	0.01	0.06	0.00	0.01	0.20	0.15
SiD ₃ I	0.01	0.02	0.00	0.01	0.15	0.16
SiH ₃ CN	0.03	0.07	0.02	0.01	0.36	-0.20
SiD ₃ CN	0.03	0.05	0.02	0.01	0.34	-0.19
SiH ₃ CCH	0.20	0.08	0.02	0.01	0.30	0.07
SiD ₃ CCH	0.03	0.07	0.02	0.02	0.29	0.10

By taking SiH₃F molecule as an example a few cases are discussed. These cases hold good subject to principle of minimisation of energy.

(1) $(r_1)_{r_2} = -0.01$ i.e., if $\Delta r_2 = x \text{ \AA}$ then $\Delta r_1 = -0.01 \times x \text{ \AA}$. From this we understand that if r_2 is stretched by $x \text{ \AA}$, r_1 contracts by $0.01 \times x \text{ \AA}$.

(2) $(r_1)_{\alpha_1} = 0.01$ i.e., if $r \Delta \alpha_1 = x \text{ \AA}$ -radians, then $\Delta r_1 = 0.01x \text{ \AA}$, which means that if $\Delta \alpha_1 = x$ radians then $\Delta r_1 = (0.01xr) \text{ \AA}$. Therefore X-Y bond stretches by $(0.01xr) \text{ \AA}$ for an increase of x radians in Y_2XY_3 angle.

(3) $(\alpha_1)_{\alpha_2} = -0.25$ i.e., if $r \Delta \alpha_2 = x \text{ \AA}$ -radians, then $r \Delta \alpha_1 = -0.25x \text{ \AA}$ -radians. This means that if α_2 increases by x radians, α_1 decreases by $0.25 \times x$ radians.

(4) $(\alpha_1)_{\beta_1} = 0.10$ i.e., if $\sqrt{rR} \Delta \beta_1 = x \text{ \AA}$ -radians, then $r \Delta \alpha_1 = 0.10x \text{ \AA}$ -radians. This means that if β_1 will increase by x -radians, α_1 will increase by $0.1x \sqrt{R/r}$ radians.

It clearly seen that $(r_1)_{r_2}$ is almost same for the halogens substituted in

SiH_3X type molecules. It is observed that the ratio $(r_1)_R$ decreases when the mass of Z-atom increases (Table 5).

Conclusion

It may be concluded that the new technique adopted to solve the secular equation for a series of similar molecular types involving third, fourth and fifth order vibrational problems yields reasonably good results. The advantage of this new technique is that there is no limitation on its applicability and on its extension to any n th order problem.

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