

# MEAN AMPLITUDES OF VIBRATION AND CORIOLIS COUPLING CONSTANTS OF SOME $XY_3Z$ TYPE SILICON COMPOUNDS

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## ABSTRACT

A theoretical treatment of the generalised mean-square amplitudes of vibration of some silicon compounds of  $XY_3Z$  type molecules is presented. The numerical values evaluated for the parallel and perpendicular mean-square amplitudes for all the bonded and non-bonded atom pairs are tabulated. The L matrix elements and Coriolis coefficients have also been evaluated for these molecules.

THE vibrational problem of the axially symmetric  $XY_3Z$  type molecules has been the subject of investigation of various authors in the experimental and theoretical fields.<sup>1-10</sup> Recently high resolution infrared spectra<sup>2</sup> have been obtained for a large number of molecules of this type containing the silyl group. This type of molecules has been subjected to normal co-ordinate analysis by several workers applying different types of potential functions. Mean amplitudes of vibration in molecules which may be determined either by spectroscopic methods or by electron diffraction data will enable one to understand the non-rigid model of molecules. Similarly spectroscopic calculations on molecular constants such as force constants and mean amplitudes will be useful in evaluating the rotation-vibration interaction constants known as Coriolis coupling constants in molecules, for, they may be used for a detailed interpretation of vibrational spectra of the molecules. Coriolis coupling constants, rotation distortion constants and mean amplitudes of vibration for a few molecules of the present type have been reported recently.<sup>2, 11</sup> But no attempt has so far been made for the computation of generalised mean-square amplitudes of vibration for this type of molecules. So the aim of the present investigation is to calculate the generalised mean-square amplitudes of vibration, viz., parallel and perpendicular mean-square amplitudes of vibration and mean cross-products and Coriolis coupling constants for some silicon

compounds of  $XY_3Z$  model. No electron diffraction results are available at present for a comparison of the results presented in this investigation. However, these values may be useful in future electron diffraction studies on these molecules. The symmetrized mean-square amplitudes of vibration for these molecules have been reported earlier by the authors. All the molecules chosen in the present investigation possess tetrahedral symmetry.

The molecules belong to the symmetry group  $C_{3v}$  and give rise to 3 non-degenerate  $A_1$  vibrations and 3 doubly degenerate  $E$  type vibrations. The symmetry co-ordinates, molecular parameters and kinetic energy elements are taken from references [6, 7, 10].

(a) *Generalised mean-square amplitude matrices.*—The expressions for the generalised mean-square amplitudes of vibration for the molecules are derived by the method suggested by Morino and Hirota.<sup>12</sup> Substituting the symmetrized mean-square amplitudes  $\Sigma_{ij}$  which have been calculated earlier, the generalised mean-square amplitude values are evaluated. Some general conclusions have been drawn from the results obtained.

(b) *Coriolis coupling constants.*—Application of Jahn's rule<sup>13</sup> shows that the non-vanishing element of the  $\zeta^\alpha$  matrices ( $\alpha = x, y, \text{ or } z$ ) for  $XY_3Z$  molecules result from the  $E \times E$  coupling. The calculation of Coriolis coupling constants requires the transformation relating the  $(3N - 6)$  normal co-ordinates of the molecules to  $3N$  co-ordinates. The normal co-ordinate transformation matrix ( $S = LQ$ ) elements have been computed for the degenerate species for the molecules chosen in the present work and are used for calculating the Coriolis constants. The  $C^\alpha$  elements are obtained by the vector method of Meal and Polo,<sup>14</sup> according to the formula

$$C_{ij}^\alpha = \sum_t \mu_t (S_i^t \times S_j^t) \cdot e_\alpha,$$

where  $\mu_t$  is the reciprocal mass of the atom  $t$ ,  $S_i^t$  and  $S_j^t$  are  $S$  vectors and  $e_\alpha$  is a unit vector in the direction of  $x, y, z$  co-ordinates; the sum being extended over all atoms in the molecule. The non-vanishing  $C^z$  matrices are given as:

$$C^z_{4a, 4b} = \frac{4}{3} \mu_x$$

$$C^z_{4a, 5b} = C^z_{5a, 4b} = -\sqrt{2} \mu_x \left( \frac{1}{3} \sqrt{\frac{R}{r}} + \sqrt{\frac{r}{R}} \right)$$

$$C_{4a, 6b}^z = C_{6a, 4b}^z = \sqrt{2}\mu_Y + \frac{4\sqrt{2}}{3}\mu_X$$

$$C_{5a, 5b}^z = \frac{3}{2}\mu_Z \frac{r}{R} + \frac{3}{2}\mu_X \left( \frac{1}{3}\sqrt{\frac{R}{r}} + \sqrt{\frac{r}{R}} \right)^2$$

$$C_{5a, 6b}^z = C_{6a, 5b}^z = \mu_Y \sqrt{\frac{R}{r}} + 2\mu_X \left( \frac{1}{3}\sqrt{\frac{R}{r}} + \sqrt{\frac{r}{R}} \right)$$

$$C_{6a, 6b}^z = \frac{8}{3}\mu_X + \frac{\mu_Y}{2}$$

The  $\zeta^a$ -matrix is related to the  $C^z$  matrix by the relation  $\zeta^z = L^{-1}C^zL^{-1}$ ,  $L$  is the normal co-ordinate transformation matrix and has been obtained by the method of characteristic vectors. For symmetric top molecules the zeta sum rule is given by,

$$\sum \zeta_i = \frac{I_A}{2I_B}$$

where  $I_A$  denotes the moment of inertia of the molecule along the Z-axis, and  $I_B$  is the moment of inertia along the X or Y-axis. A suitable set of zeta values conforming to the relations given above has been calculated and their numerical values are reported.

## RESULTS AND DISCUSSION

The generalised mean-square amplitudes of vibration for these molecules are presented in Table I. From the values presented in Table I, we may conclude that the mean-square amplitudes for the  $S_4$ -H bond possess a characteristic value. Substitution of deuterium decreases the mean-square amplitude values. Non-bonded mean-square amplitude values also show a decrease with deuterium substitution. The mean-square parallel amplitude values in the  $S_4$ -X (X = F, Cl, Br or I) bond increase as we pass from lower to higher member of the halogen series. No such clear variations could be seen in the case of mean-square perpendicular amplitudes. It is observed that in all cases bending mean-square amplitudes are larger than the bond-stretch values. Similarly non-bonded mean-square amplitude values also increase as the higher member of halogen group is substituted. It is evident from the results in Table I that all cross-products are zero for the X-Z bond because of molecular symmetry. Similar may be the reason that only  $\langle(\Delta z)(\Delta x)\rangle$  and  $\langle(\Delta x)(\Delta y)\rangle$  are present for the X-Y and Y...Z atom pair.

TABLE I  
Generalised mean-square amplitudes ( $\text{\AA}^2$ ) of  $XY_3Z$  silicon compounds

Molecule	Atom pair	$\langle(\Delta z)^2\rangle$	$\langle(\Delta x)^2\rangle$	$\langle(\Delta y)^2\rangle$	$\langle(\Delta z)\rangle$ $\langle(\Delta x)\rangle$	$\langle(\Delta x)\rangle$ $\langle(\Delta y)\rangle$
SiD <sub>3</sub> H	.. Si-H	0.007830	0.022230	0.022230	..	..
	Si-D	0.005500	0.015835	0.008919	0.005621	..
	D...D	0.009656	0.009160	0.009112	..	0.001221
	H...D	0.032380	0.027617	0.025047	0.024520	..
SiH <sub>3</sub> F	.. Si-F	0.001604	0.000426	0.000426	..	..
	Si-H	0.007752	0.018678	0.014371	0.005015	..
	H...H	0.016340	0.014429	0.037000	..	0.001500
	F...H	0.018180	0.010778	0.015659	0.012807	..
SiH <sub>3</sub> I	... Si-I	0.003686	0.000139	0.000139	..	..
	... Si-H	0.007805	0.023013	0.019817	0.005442	..
	.. H...H	0.016180	0.017500	0.040433	..	-0.001543
	.. I...H	0.019650	0.013344	0.017209	0.010330	..
SiF <sub>3</sub> H	... Si-H	0.007691	0.022025	0.022025	..	..
	Si-F	0.001604	0.003406	0.004215	0.000248	..
	F...F	0.003151	0.003862	0.000739	..	0.000348
	F...H	0.022560	0.020305	0.025718	0.017479	..
SiF <sub>3</sub> D	... Si-D	0.005403	0.016671	0.016671	..	..
	Si-F	0.001595	0.002257	0.003970	0.000808	..
	F...F	0.003609	0.003691	0.000650	..	0.000557
	F...D	0.017510	0.015971	0.019493	0.013505	..
SiCl <sub>3</sub> H	... Si-H	0.007745	0.018804	0.018804	..	..
	Si-Cl	0.002989	0.006536	0.019347	0.001293	..
	... Cl...Cl	0.006141	0.006341	0.000206	..	0.000504
	.. H...Cl	0.022560	0.019574	0.037598	0.004291	..

TABLE I (Contd.)

Molecule	Atom pair	$\langle(\Delta z)^2\rangle$	$\langle(\Delta x)^2\rangle$	$\langle(\Delta y)^2\rangle$	$\langle\langle z \rangle\rangle$ $\langle\langle \Delta x \rangle\rangle$	$\langle\langle \Delta x \rangle\rangle$ $\langle\langle \Delta y \rangle\rangle$
SiBr <sub>3</sub> H	Si-H	0.007745	0.032102	0.032102	..	..
	Si-Br	0.003375	0.003394	0.008705	0.000779	..
	Br...Br	0.015540	0.006600	0.000054	..	0.000302
	H...Br	0.023780	0.020032	0.027783	0.019218	..
SiBr <sub>3</sub> Cl	Si-Cl	0.002965	0.009457	0.009457	..	..
	Si-Br	0.003393	0.010273	0.005685	0.006499	..
	Br...Br	0.006310	0.006054	0.003932	..	0.000252
	Cl...Br	0.014160	0.011250	0.013433	0.010952	..
SiI <sub>3</sub> Cl	Si-Cl	0.002927	0.011872	0.011872	..	..
	Si-I	0.003680	0.009303	0.008174	0.002287	..
	I...I	0.007698	0.008133	0.003040	..	0.000817
	Cl...I	0.013930	0.015634	0.017276	0.014024	..
SiCl <sub>3</sub> Br	Si-Br	0.003357	0.006045	0.006045	..	..
	Si-Cl	0.003030	0.009123	0.016660	0.004516	..
	Cl...Cl	0.006004	0.006689	0.012356	..	0.002507
	Br...Cl	0.011190	0.007036	0.006847	0.005725	..
SiCl <sub>3</sub> I	Si-I	0.003697	0.001195	0.001195	..	..
	Si-Cl	0.003040	0.007613	0.003797	0.001286	..
	Cl...Cl	0.006035	0.004467	0.006856	..	0.000191
	I...Cl	0.011990	0.004097	0.000895	0.006594	..

The Coriolis coupling constants for these molecules are reported in Table II. The values given satisfy quite well the sum rule. From these

values the large value of  $\zeta_{4,6}^z$  and its regular variation with the substituted atom indicates that the Coriolis interaction between the  $\nu_4$  and  $\nu_6$  vibrations be the strongest of all.

TABLE II  
*Coriolis coupling constants in  $XY_3Z$  silicon compounds*

$\zeta$ values	$\zeta_{4,4}^z$	$\zeta_{5,5}^z$	$\zeta_{6,6}^z$	$\zeta_{4,5}^z$	$\zeta_{4,6}^z$	$\zeta_{5,6}^z$
Molecule						
SiD <sub>3</sub> H	.. 0.01709	0.83730	-0.23435	-0.21283	0.88470	-0.04840
SiH <sub>3</sub> F	... 0.04162	0.12874	-0.08930	-0.05202	0.92626	-0.36240
SiH <sub>3</sub> I	.. 0.04107	0.04974	-0.07246	-0.04307	0.92424	-0.37445
SiF <sub>3</sub> H	... 0.46000	0.98052	-0.56116	-0.02514	0.79970	-0.04380
SiF <sub>3</sub> D	.. 0.47390	0.95542	-0.58829	0.06830	0.73961	-0.23180
SiCl <sub>3</sub> H	... 0.61883	0.99557	-0.68210	-0.00822	0.71480	-0.02280
SiBr <sub>3</sub> H	.. 0.78487	0.99838	-0.81945	-0.00077	0.56970	-0.02390
SiBr <sub>3</sub> Cl	.. 0.86996	0.64500	-0.83011	-0.18180	0.40460	0.32848
SiI <sub>3</sub> Cl	.. 0.92160	0.64540	-0.88425	-0.13900	0.31420	0.30070
SiCl <sub>3</sub> Br	.. 0.71984	0.37050	-0.74738	-0.29990	0.57040	0.18520
SiCl <sub>3</sub> I	... 0.71014	0.37660	-0.71378	-0.32940	0.56480	0.25050

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