MEAN AMPLITUDES OF VIBRATION AND CORIOLIS COUPLING CONSTANTS OF SOME XY₃Z TYPE SILICON COMPOUNDS

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ABSTRACT

A theoretical treatment of the generalised mean-square amplitudes of vibration of some silicon compounds of XY₃Z 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 XY₃Z type molecules has been the subject of investigation of various authors in the experimental and theoretical fields. Recently high resolution infrared spectra 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. 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. Substituting the symmetrized mean-square amplitudes $Z'$ 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 shows that the non-vanishing element of the $C^a$ matrices ($a = x, y, z$) 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 $C^a$ elements are obtained by the vector method of Meal and Polo, according to the formula

$$C_{ij}^a = \sum \mu_t (S_i^t \times S_j^t) \cdot e_a,$$

where $\mu_t$ is the reciprocal mass of the atom $t$, $S_i^t$ and $S_j^t$ are $S$ vectors and $e_a$ 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:

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

$$C^z_{6a, 6b} = C^z_{6a, 6b} = -\sqrt{2} \mu_x \left( \frac{1}{3} \sqrt{\overline{R}} + \sqrt{\overline{r}} \right)$$