UREY—BRADLEY FORCE CONSTANTS, 
MEAN AMPLITUDES OF VIBRATION, 
SHRINKAGE EFFECT AND CORIOLIS CONSTANTS 
IN IF5 AND IOF5

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(Received 26. I. 1967)

Force constants of the molecules IF5 and IOF5 have been calculated using the Urey—Bradley force field. The theory of mean square amplitude matrices is applied to these cases and the parallel and perpendicular mean square amplitudes at 300°K are determined. The perpendicular amplitudes are employed for calculating the BASTIANSEN—MORINO shrinkage effects. The Coriolis constants of these molecules are also evaluated.

Introduction

The molecules IF5 and IOF5 possess C4v symmetry. The numbering of atoms and orientation of the principal axes are given in Figs. 1 and 2. The symmetry coordinates and frequencies used in the present study are the same as those given by BEGUN, FLETCHER and SMITH for IF5 [1] and SMITH and BEGUN for IOF5 [2].

Urey—Bradley force field

The application of the Urey—Bradley force field gives the following F-matrices for the two molecules. The values of the off-diagonal elements will reduce to zero.

For IF5:

\[
F_{11} = K_r + 4(t_0^2 F'_{16} + s_0^2 F_{16}),
\]
\[
F_{22} = K_r + 4s^2 F_{12} + t_1^2 F'_{16} + s_1^2 F_{16},
\]
\[
F_{33} = H_\beta - s_0 s_1 F'_{16} = t_0 t_1 F_{16},
\]
\[
F_{44} = K_r + 4t^2 F'_{12} + t_1^2 F'_{16} + s_1^2 F_{16},
\]
\[
F_{55} = F_{33},
\]
\[
F_{66} = H_x - s^2 F_{12} + t^2 F_{12},
\]
\[
F_{77} = K_r + 2(t^2 F'_{12} + s^2 F_{12}) + t^2 F'_{16} + s_1^2 F_{16},
\]
\[
F_{88} = F_{33},
\]
\[
F_{99} = F_{66},
\]
where $K$ and $H$ represent the stretching and bending constants. $F$ and $F'$ are the repulsion constants between the atoms indicated by subscripts attached to $F$. $F' = -0.1 F$ as assumed by Shimano. $t_0, s_{01}$ etc. are the usual constants employed in the Urey—Bradley field, which depend upon the structural parameters of the molecule.

For IOF$_5$:

\begin{align*}
F_{11} &= K_S + 4(t_{12}^2 F_{17}^2 + s_{12}^2 F_{17}), \\
F'_{22} &= K_R + 4(t_{11}^2 F_{16}^2 + s_{11}^2 F_{16}), \\
F_{33} &= K_r + 4s_{11}^2 F_{12} + t_{10}^2 F_{16} + s_{10}^2 F_{16} + t_{12}^2 F_{17} + s_{12}^2 F_{17}, \\
F_{44} &= \frac{1}{2} [H_\beta - s_{01} s_{10} F_{16} + t_{01} t_{10} F_{16} + H_\gamma - s_{21} s_{12} F_{17} + t_{21} t_{12} F_{17}], \\
F_{55} &= K_r + 4t_{12}^2 F_{16} + t_{10}^2 F_{16} + s_{10}^2 F_{16} + s_{12}^2 F_{17} + s_{12}^2 F_{17}, \\
F_{66} &= F_{44}, \\
F_{77} &= H_\alpha - s_{11}^2 F_{12} + t_{11}^2 F_{12}, \\
F_{88} &= K_r + 2(t_{11}^2 F_{1} + s_{11}^2 F_{2}) + t_{10}^2 F_{16} + s_{10}^2 F_{16} + t_{12}^2 F_{17} + s_{12}^2 F_{17}, \\
F_{99} &= H_\gamma - s_{21} s_{12} F_{17} + t_{21} t_{12} F_{17}, \\
F_{10,10} &= H_\beta - S_{01} S_{10} F_{16} + t_{01} t_{10} F_{16}, \\
F_{11,11} &= F_{77}. \\
\end{align*}

Parallel and perpendicular amplitudes

The mean square amplitudes $\sigma'_s$ for any pair of atoms is obtained by the solution of the secular equation $| \Sigma G^{-1} - E \lambda | = 0^3$ and using the relations between $\Sigma'_s$ and $\sigma'_s$ which, in the present case, are as follows: