Normal co-ordinate analysis

The molecule \( \text{P}_2\text{I}_4 \) has twelve normal model of vibration given by \( 4A_2 + 3A_3 + 2B_2 + 3B_3 \). The geometry of the molecule and the co-ordinate axes are shown in the figure. A set of the orthonormal symmetry co-ordinates which transform according to the characters of the irreducible representations of the point group \( C_{2h} \) are used. They are given in Table I. The inverse kinetic energy matrix \( G \) is obt-

\[ G = B M^{-1} B', \]

where \( M \) is the diagonal matrix of reciprocal masses and \( B \) is the transformation matrix connecting the symmetry coordinates and the cartesian displacement coordinates in the relation \( S = BX \). A more general potential function based on G.V.F.F. is considered and a reasonable set of potential constants is determined by solution of the secular equation \( |GF - E I| = 0 \).

\[ GF - E I = 0. \]

Generalised mean square amplitudes of vibration

The symmetrised mean square amplitude matrix \( \Sigma \) is calculated from the relation 2

\[ \Sigma = L\Lambda L'. \]

where $L$'s are characteristic vectors and $A$ is a diagonal matrix consisting of the mean square values of the normal co-ordinates given by \(^3\)

$$A_i = \frac{\hbar}{8\pi^2 v_i} \coth \frac{\hbar v_i}{2kT}.$$  

The generalised mean square amplitudes \(^4\) $(\langle Ax \rangle^2)$, $(\langle Ay \rangle^2)$, and the mean cross products $(\langle Ax \rangle \langle Ay \rangle)$, $(\langle Ax \rangle \langle Az \rangle)$, and $(\langle Ay \rangle \langle Az \rangle)$ are calculated using the $\Sigma$ matrix from the relation

$$X = AS \quad \text{where} \quad A = M^{-1}B'G^{-1}.$$

**Coriolis coupling coefficients**

In $P_2I_4$ molecule the active couplings are $A_g \times B_g$ and $A_u \times B_u$, both belonging to $\zeta^x$ and $\zeta^y$. The Coriolis coupling coefficients are calculated from the relation given by MEAL and POLO \(^5\):

$$\zeta = L^{-1}C(L')^{-1}$$

where $C$ matrix is obtained from the geometry and atomic masses.

**Results and discussion**

The molecular parameters used in the calculation are taken from the X-ray diffraction data given by LEUNG and WASER \(^6\) ($D = 2.21\, \text{Å}$, $d = 2.47\, \text{Å}$, $\alpha = 102^\circ 18'$, $\beta = 93^\circ 55'$). The fundamental vibration frequencies given by FRANKISS et al. are used in the normal co-ordinate analysis. The values of the main force constants along with significant interactions are given in Table II. All the values are fairly low. The value of $f_{ij}$ obtained in $A_g$ and $B_u$ species were 0.161 and 0.064 m dyne/Å respectively. The average value is given here. The $P - P$ stretching force constants obtained here (0.702 m dyne/Å) is less than half that obtained for $P_4$ molecule (1.68) by BHAGAVANTAM and VENKATARAMADU \(^7\). The reason for this is mainly due to the large difference in frequencies. The symmetrical stretching frequency in $P_4$ is 606 cm\(^{-1}\) while the $P - P$ stretching frequency in $P_2I_4$ is 303 cm\(^{-1}\). FRANKISS et al. \(^1\) state that 303 and 316 cm\(^{-1}\) are equally probable for $P - P$ stretching. However the calculated frequency of 302 cm\(^{-1}\) is in better agreement with the former. The value of $f_{ij}$ (1.237 md/Å) confirms that the $P - I$ bond is weaker than $P - Br$ bond, ($f_{ij} = 1.63$ md/Å in PBr\(_3\)) and $P - Cl$ bond ($f_{ij} = 2.12$ md/Å in PCl\(_3\)) \(^8\). All interactions other than those given in Table II are neglected as their influence on the frequencies will be very small.

Table III gives the values of the generalised mean square amplitudes and mean cross products for bonded as well as non bonded atom pairs. Inspection of Table III shows that the mean square amplitudes are not very large even though the vibrational frequencies \(^1\) encountered are very low. This is apparently due to the presence of the heavy atom iodine. The mean square amplitudes for the non-bonded atom pair $I_1 \ldots I_4$ have the largest values. This may be due to the predominance of the bending

<table>
<thead>
<tr>
<th>Bond</th>
<th>$f_{ij}$</th>
<th>$f_{ij}$</th>
<th>$f_{ij}$</th>
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<tr>
<td>$P-P$</td>
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<td>0.013210</td>
<td>0.006403</td>
<td>0.002315</td>
<td>0.004073</td>
<td>0.00117</td>
<td>0</td>
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<tr>
<td>$I_1 \ldots I_4$</td>
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<td>0.015733</td>
<td>0.025222</td>
<td>0.013701</td>
<td>0.001471</td>
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<tr>
<td>$P-I$</td>
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<td>0.011771</td>
<td>0.030248</td>
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<td>0.002060</td>
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<tr>
<td>$I_1 \ldots I_1$</td>
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<td>0.000079</td>
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<td>0.000189</td>
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</tr>
</tbody>
</table>

Table II. General valence force constants for $P_2I_4$ (in m dynes/Å).

Table III. Generalised mean square amplitudes of vibration at 300 °K [Å²].

\(^3\) F. BLACK, Z. Physik 74, 295 [1932].
\(^4\) Y. MORINO and E. HIROTA, J. chem. Physics 23, 737 [1955].
\(^6\) Y. C. LEUNG and J. WASER, J. physic. Chem. 60, 539 [1956].
\(^7\) S. BHAGAVANTAM and T. VENKATARAMADU, Proc. Indian Acad. Sci. 8 A, 119 [1938].
vibrations which result from the very low bending force constants.

The values of the Coriolis coupling coefficients are given in Table IV. The results indicate that there is significant coupling between the asymmetric stretching vibration $v_5$ and the $\Pi_2$ wagging mode $v_{11}$ for rotation about the $Y$ axis. The torsional mode $v_{11}$ is not strongly coupled to any vibration except to the $\Pi_2$ scissoring mode $v_{12}$ for rotation about $X$ axis. Another observation is that all couplings between the different bending modes are comparatively weak.

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<table>
<thead>
<tr>
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<th>$A_g \times B_g$</th>
<th>$A_u \times B_u$</th>
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<tr>
<td>$v_8$ $v_9$</td>
<td>$\zeta^x$</td>
<td>$\zeta^y$</td>
</tr>
<tr>
<td>$v_8$ $v_9$</td>
<td>$\zeta^x$</td>
<td>$\zeta^y$</td>
</tr>
<tr>
<td>$v_1$ $v_2$</td>
<td>$-0.150$ $-0.765$</td>
<td>$-0.245$ $-0.050$</td>
</tr>
<tr>
<td>$v_3$ $v_4$</td>
<td>$-0.363$ $0.379$</td>
<td>$0.753$ $0.084$</td>
</tr>
<tr>
<td>$v_5$ $v_6$</td>
<td>$-0.611$ $0.117$</td>
<td>$0.935$ $-0.322$</td>
</tr>
</tbody>
</table>

Table IV. Coriolis coupling coefficients.