CHEMISTRY 273

MODES OF NUCLEAR MOTION WITH ZERO FREQUENCY OF "VIBRATION"

(SEE WILSON, DECIUS, AND CROSS, PP. 22-25)

Consider the 3N nuclear coordinates in the mass weighted Cartesian system:

$$q_{x\alpha} = \sqrt{m_\alpha \Delta x_\alpha} \quad \text{for atom } \alpha\text{, etc.}$$

A new set of 3N coordinates can be defined in terms of an orthogonal transformation among the q's. In the new set of coordinates the first three variables represent the X_{cm}, Y_{cm}, Z_{cm} coordinates of center-of-mass and the three coordinates $\Re_x$, $\Re_y$, $\Re_z$ represent rotations of a coordinate system fixed with respect to the atoms of the molecule.

W–D–C give the transformations

$$\mathcal{W}_1 = X_{cm} = N_1 \sum_{\alpha=1}^{N} m_\alpha^{1/2} q_{x\alpha} \qquad \mathcal{W}_4 = \Re_x = N_4 \sum_{\alpha=1}^{N} m_\alpha^{1/2} (b_\alpha q_{z\alpha} - c_\alpha q_{y\alpha})$$

$$\mathcal{W}_2 = Y_{cm} = N_2 \sum_{\alpha=1}^{N} m_\alpha^{1/2} q_{y\alpha} \qquad \mathcal{W}_5 = \Re_y = N_5 \sum_{\alpha=1}^{N} m_\alpha^{1/2} (c_\alpha q_{x\alpha} - a_\alpha q_{z\alpha})$$

$$\mathcal{W}_3 = Z_{cm} = N_3 \sum_{\alpha=1}^{N} m_\alpha^{1/2} q_{z\alpha} \qquad \mathcal{W}_6 = \Re_z = N_6 \sum_{\alpha=1}^{N} m_\alpha^{1/2} (a_\alpha q_{y\alpha} - b_\alpha q_{x\alpha})$$

where $(a_\alpha, b_\alpha, c_\alpha)$ are the x, y, z coordinates of the equilibrium position of atom α relative to the center-of-mass, and the N's are the normalizing coefficients which insure that the transformation $(q_1, q_2, \ldots, q_{3N}) \to (\mathcal{W}_1, \mathcal{W}_2, \ldots, \mathcal{W}_{3N})$ is orthonormal. The proof that the coordinates $\mathcal{W}_1 \ldots \mathcal{W}_6$ are orthogonal can be carried out explicitly. Since one can find 3N – 6 linearly independent coordinates orthogonal to $\mathcal{W}_1 \ldots \mathcal{W}_6$, and orthogonal to one another, the exact form of $\mathcal{W}_7 \to \mathcal{W}_{3N}$ is not germane.

To show that $\mathcal{W}_1 \ldots \mathcal{W}_6$ are normal coordinates with zero force constants we must show:

(1) $\mathcal{W}_1, \mathcal{W}_2, \mathcal{W}_3$ represent translations in the x, y, z directions;

(2) $\mathcal{W}_4$, $\mathcal{W}_5$, $\mathcal{W}_6$ represent rotations about the x, y, z axes fixed in a molecular reference;

(3) that $F_{11} = F_{22} = F_{33} = F_{44} = F_{55} = F_{66} = 0$ and all off diagonal elements $F_{1j} = F_{2j} = F_{3j} = F_{4j} = F_{5j} = F_{6j} = 0$ and $F_{j1} = F_{j2} = F_{j3} = F_{j4} = F_{j5} = F_{j6} = 0$, i.e., the force constant matrix contains an "isolated" 6×6 block for $\mathcal{W}_1 \ldots \mathcal{W}_6$.

(1) and (2) are verified by showing that the transformation $x_\alpha \rightarrow x_\alpha + \tau$ for all α (atoms) (i.e., x translation of molecule by τ) changes $\mathcal{W}_1 \rightarrow \mathcal{W}_1 + N_1 \tau \sum_\alpha m_\alpha$ while leaving all other $\mathcal{W}$'s unchanged and similarly for $\mathcal{W}_2$ and $\mathcal{W}_3$. For rotations, one must show that rotations about the x, y and z axes affect only $\mathcal{W}_4$, $\mathcal{W}_5$, and $\mathcal{W}_6$, respectively. This is done utilizing the fact that $\mathcal{W}_i = \sum_j \ell_{ij} q$ and that the ℓ_{ij} form a unitary matrix.

[Note for example that $\ell_{11} = N_1 m_\alpha^{1/2}$].

You should be able to do these proofs for yourselves, but in case not see W.D.C., p. 23-24.

To prove 3, one notes that the potential energy

$$U = \frac{1}{2}\sum_{ij} u_{ij} q_i q_j = \frac{1}{2}\sum_{ij} F_{ij} \mathcal{W}_i \mathcal{W}_j$$

where F_{ij} are the force constants in the $\mathcal{W}$ coordinate system: $F_{ij} = \frac{\partial^2 U}{\partial \mathcal{W}_i \partial \mathcal{W}_j}$. By assumption translations and rotations do not change U. Thus $\frac{\partial U}{\partial \mathcal{W}_1} = \frac{\partial U}{\partial \mathcal{W}_2} = \cdots \frac{\partial U}{\partial \mathcal{W}_6} = 0$ and all $F_{ij} = 0$ if i or j = 1 through 6.

The matrix of F's in the $\mathcal{W}$ coordinate system is

$$\left(\begin{array}{cccccc|ccc}
0 & & & & & & & & \\
 & 0 & & & & & & & \\
 & & 0 & & & & & 0 & \\
 & & & 0 & & & & & \\
 & & & & 0 & & & & \\
 & & & & & 0 & & & \\
\hline
 & & & & & & F_{77} & & F_{7,3N} \\
 & & & 0 & & & \vdots & & \\
 & & & & & & F_{3N,7} & \ldots & F_{3N,3N}
\end{array}\right)$$

with the first 6×6 block diagonalized with 6 zero eigenvalues.

Subsequent diagonalization of the (3N-6) X (3N-6) block provides the transformation of the $\mathcal{W}$'s to the normal coordinate $\mathcal{Q}$'s