CHAPTER II

GENERAL THEORY

MOLECULAR VIBRATIONS IN SMALL FINITE MOLECULES

The present section deals with molecular dynamics of finite molecules. For a molecule having \( N \) atoms the vibrational degree of freedom are \((3N - 5)\) or \((3N - 6)\) depending on whether the molecule is linear or non-linear.

The six non-genuine degrees of freedom of a non linear molecule correspond to the free translations and rotations of the molecule. However, for a linear molecule the rotation about the line joining the nuclei of different atoms is not distinguishable as free rotation. Therefore a linear molecule has only 2 possible free rotations. Corresponding to \((3N-6)\) or \((3N-5)\) degrees of freedom there are as many fundamental normal modes of vibration. All other modes are linear combination of these vibrations. The Wilson's GF matrix method is being extensively used for the normal mode calculation.

This method makes the use of internal coordinates (viz. the changes in bond lengths, bond angles, out of plane bonds and torsional motions). The internal coordinates are easiest and simplest and can best visualise the physical nature of
molecular vibrations. They also permit the transferability
of force constants from a group in one molecule to the corres-
ponding group in another molecule in the similar environment.
The smaller amplitude and harmonic nature of molecular
vibrations provide a linear transformation between various
displacement coordinates. The internal coordinate $R$ is
related to the cartesian coordinate in matrix notation as
follows
$$ R = B X $$
(2.1)
where $B$ is a transformation matrix and depends upon the geometry
of the molecule. The kinetic energy of vibrations in terms
of internal coordinates is given by
$$ 2T = \dot{R}' G^{-1} \ddot{R} $$
(2.2)
where $\dot{R}'$ is transpose of $\dot{R}$. The inverse kinetic energy
matrix ($G$ matrix) is a convenient way of introducing the
kinetic energy term into the molecular vibrational problem.
In order to avoid most of the errors incurred when setting
up a transformation algebraically, the numerical $G$ matrix is
evaluated by a digital computer. The $G$ matrix can be
expressed in matrix notation as
$$ G = BM^{-1} B' $$
(2.3)
where $M^{-1}$ is the diagonal matrix of reciprocal atomic masses.
The potential energy in matrix notation can be written as
$$ 2V = R'F \cdot R $$
(2.4)
where $F$ is the potential energy matrix and its elements are the linear function of the force constants $f_k$. In practice it is computed through the basis matrix ($Z$ matrix) where

$$F_{ij} = \sum_k Z_{ijk} f_k \ldots \quad (2.5)$$

and $f_k$'s are the force constants (3). Since the potential energy is expressed in terms of $\Delta r_i$, $\Delta \alpha_{ij}$ and $\Delta q_{ij}$ which are not independent coordinates, the equilibrium condition that $\delta V = 0$ does not necessarily imply that $\delta V/\delta r = 0$. If the redundant coordinates $\Delta q_{ij}$ are removed by a substitution such as

$$\Delta q_{ij} = s_{ij} \Delta r_i + s_{ji} \Delta r_j + \frac{1}{2} q_{ij} \left\{ t_{ij}^2 (\Delta r_i)^2 + t_{ji}^2 (\Delta r_j)^2 \ldots \right\}$$

then potential energy is expressed in an independent set of coordinates and the partial derivatives $\delta V/\delta r_i$ and $\delta V/\delta \alpha_{ij}$ may be equated to zero and the linear terms get removed from $V$. However, the substitution of equation (2.6) has the effect of introducing additional terms into the coefficients of quadratic terms and we determine the linear force constants...
along with the quadratic ones. For each $q_{ij}$ an equation is set up like eq. (2.6) and the $Z$ matrix is formed from the coefficients of these substitution relationship. In the present calculations, $Z$ matrix is evaluated by a digital computer, using cartesian coordinates and force constant definition as input data. The problem of molecular vibrations reduces to the solution of following secular equation

$$|G.F - I\lambda| = 0 \quad \ldots \quad (2.7)$$

where $I$ is the identity matrix of the order of $G \times F$ matrices. The eigen values $\lambda'$s are related to the vibrational frequencies $\nu'$s through the relation

$$\lambda = 4\pi^2 \nu^2 c^2 \quad \ldots \quad (2.8)$$

$\nu'$s are known as the normal modes of vibration. The normal coordinates $\Omega$ are related to the internal coordinates $R$ in the matrix notation as follows

$$R = L\Omega \quad \ldots \quad (2.9)$$

The column vectors $L$ are given by the relation

$$(GF) L = \lambda L \quad \ldots \quad (2.10)$$

In each normal mode of vibration all the atoms in molecule vibrate in phase with the same frequency $\nu_k$ at a particular instant having different amplitudes of vibration. The extent of vibrational coupling between various internal coordinates
in a given normal mode $Q_K$ is quantitatively described by the elements of the eigen vector $L_K$ belonging to the eigen value $\lambda_K$.

Because of the different dimensions of $L$ vectors for stretching and bending coordinates it is preferable to use the potential energy distribution to characterize the form of normal coordinates. The potential energy distribution is the fractional part of potential energy of normal mode of vibration contributed by each force constant. If each $F_{ij}$ $L_{ik}$ $L_{jk}$ term is divided by the total sum of $F_{ij}$ $L_{ik}$ $L_{jk}$ terms for this vibration (which is equal to $\lambda_K$) then

$$(\text{PED})^K_i = \frac{F_{ij} \cdot L_{ik} \cdot L_{jk}}{\lambda_K} \quad \ldots \quad (2.11)$$

when diagonal terms are much greater than the off-diagonal terms then an approximate potential energy distribution in the normal mode $Q_K$ associated with $i^{th}$ internal coordinate can be defined in percentage (4) as

$$(\text{PED})^K_i \% = \frac{F_{ij} L_{ik}^2}{\lambda_K} \times 100 \quad \ldots \quad (2.12)$$

A normal vibration that is accompanied with a change in electric dipole moment is infrared active whereas for a Raman active mode involves change in electrical
polarizability\(^{(5)}\). For a transition between two vibrational levels \(v'\) and \(v''\) the transition probability is proportional to the square of the transition moment \((M)^{v'v''}\) expressed by the space integral

\[
(M)^{v'v''} = \int \psi_{v'}^* \psi_{v''} \bar{\mu} \, dJ \tag{2.13}
\]

\(\bar{\mu}\) is a dipole moment vector with the components \(M_x, M_y, M_z\) and \(\psi_{v'}, \psi_{v''}\) are the eigen functions of two vibrational levels. For a non symmetric molecule all transitions are allowed whereas for a symmetrical molecule only those transition are IR active for which at least one component of the integrand is totally symmetric. Group theoretically, a vibrational transition \(v' \rightarrow v''\) is allowed if at least one component of the dipole moment \(\bar{\mu}\) has the same symmetry species as the product \(\psi_{v'}, \psi_{v''}\). Raman absorption shifts also have analogous selection rules. For a Raman active transition at least one of the six integrands \(\psi_{v'}, \psi_{v''}\) \(\propto \mu_k\) should be totally symmetric \(\mu_k\) can assume any of the \(\alpha_{xx}, \alpha_{yy}, \alpha_{zz}\)

\(\alpha_{yz}, \alpha_{xz}, \alpha_{xy}\) values.

FORCE CONSTANTS EVALUATION:

One of the main problems in the evaluation of a suitable force field is that the number of observed frequencies
is almost always smaller than the number of force constants in the general harmonic force field. (In fact, the observed frequencies are anharmonic). For most of the molecules the data are far short of the number of force constants and hence in order to proceed with the calculations, some approximations are made. We assume that some force constants can be neglected (assuming a model such as Urey-Bradley force field). Even though the problem is very difficult, however, if the approximations in the potential functions are made with some care, the force constants will be still physically significant and capable of meaningful comparison particularly between related molecules that have been analysed to the same degree of approximation. This philosophy has been followed in the work reported in the thesis. In order to obtain the "best fit" with the observed frequencies the following procedure is adopted.

Suppose we are given approximate $F$ matrix $F_o$ and the observed frequencies $\lambda_{obs}$ (related through a constant), we solve the secular matrix equation

$$G F_o L_o = L_o \lambda_o \ldots$$  \hspace{1cm} (2.14)

Let $\Delta \lambda_i = \lambda_i^{obs} - \lambda_{io}$ in the above equation.

It can be shown that in the first order approximation,

$$\overline{\Delta \lambda} = J \Delta F$$
Where $J$ is computed from $L_0$. We wish to compute the corrections to $F_0$ so that the errors $\Delta \lambda$ are minimized.

We use the theory of least squares and calculate.

$$J^t F \Delta \lambda = (J^t PJ)^{-1} J^t \Delta F$$

Where $P'$ is a weighting matrix and $J'$ is transpose of $J$. The solution to this equation is obtained by inverting $(J^t PJ)$ to give

$$\Delta F = (J^t PJ)^{-1} J^t \Delta \lambda$$

If the number of frequencies is greater than the number of $F$ matrix elements, the matrix $J^t PJ$ should be non-singular and we obtain the corrections $\Delta F$ which will minimize the sum of the weighted squares of the residuals.

If the corrections $\Delta F$ are fairly large, the linear relation between force constant and frequency term in the matrix equation (2.14) breaks down. In such a situation, further refinement using higher order terms in the Taylor's series expansion of $\Delta \lambda$ is needed. Such a procedure has been developed by King et al (6) and extensively used by Schachtschneider and Snyder (7).
REFERENCES


