INFRARED AND RAMAN SPECTRA
OF GASEOUS OXALIC ACID

by

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of the University of Surrey

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March, 1973

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ACKNOWLEDGEMENTS

I would like to thank my supervisor, Dr. B. C. Stace, for giving me every assistance during the project and also for providing the necessary background knowledge that has enabled me to undertake this project.

A scholarship from the Colombo Plan is gratefully acknowledged.

SUMMARY

The vibrational spectrum of gaseous oxalic acid was studied. Oxalic acid is a planar molecule with C_{2h} symmetry and 18 fundamentals. Two structures based on electron diffraction studies have previously been proposed:

I

II

8 infrared bands of gaseous oxalic acid were observed in the frequency range $4000 - 350 \text{ cm}^{-1}$. 5 were assigned to inplane fundamental modes, 2 were assigned to out of plane fundamental modes, and only 1 was assigned to combination mode.

5 Raman bands of gaseous oxalic acid were observed and all were assigned to inplane fundamental modes.

Previously 6 infrared bands have been observed but no previous Raman study of the vapour has been published.

A Urey-Bradley force field (refined by trial and error) was used to calculate frequencies, potential energy distributions and normal modes of vibration for both structures. The spectroscopic assignments and vibrational analysis are equally consistent with

the two proposed structures and therefore support a centrosymmetric structure.

The contours of the infrared bands do not help in assigning the fundamentals because the inplane bands are A-B hybrids. In addition the moments of inertia of both structures are too close to be able to decide between the two structures.

The infrared spectra were recorded with a 60 cm path gas cell and a Perkin-Elmer 457 spectrometer. Temperatures between 70°C and 125°C were used.

The Raman spectra were recorded with a Spex 1401 spectrometer and approximately 2 watts at 5145Å⁰ from a Spectra-Physics 164 laser. Temperatures between 140°C and 185°C were used.

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INTRODUCTION

Oxalic acid exists in three solid forms, α , β , and the dihydrate. The structures have been studied using X-rays and Neutron diffraction methods.

Many vibrational studies of carboxylic acids have been carried out and complete assignment of the vibrational modes of formic and acetic acids have been made. Several papers have been published on the infrared and Raman spectra of oxalic acid in both solution and the solid phase. None of them give complete spectra and their assignment. This may be due to the following reasons:-

- (1) There is no complete work on the infrared and Raman spectra of the free molecule.
- (2) In the condensed phases the vibrational spectrum is not only affected by intramolecular forces but also by intermolecular forces.
- (3) In solution the spectrum is influenced by the solvent effect.
- (4) All forms of solid oxalic acid are hydrogen bonded into polymers. Thus, their spectra are strongly influenced by the hydrogen bonds.

It is clear from the above that the vibrational modes of oxalic acid in condensed phases are quite complicated. Differences in their structures result in the differences in their vibrational spectra. This was clearly shown in the spectra of Bellamy and Pace in 1963 (62).

In order to be able to complete the work of assignment and interpretation a knowledge of the vibrational modes of the free molecules is required. With this in mind infrared and Raman spectra of gaseous oxalic acid were studied and the results are presented in this thesis.

Before this work started a paper on the infrared spectrum of gaseous oxalic acid was published by Pava and Stafford (98). Three bands were observed and were assigned to gaseous oxalic acid. The second paper appeared during the course of this work. This paper was published by Bardet, Fleury and Tabacik (109) on the infrared absorption bands of gaseous oxalic acid and the Raman bands of oxalic acid in solution and in the solid phase. They recorded more infrared gaseous oxalic acid bands. Unfortunately this paper was badly written and assignments of some gaseous oxalic acid bands are wrong and some are very doubtful as pointed out in section 12.2.

No Raman spectrum of gaseous oxalic acid has previously been reported.

Two papers were published on the structure of gaseous oxalic acid using the electron diffraction method. The first paper was published by Shibata and Kimura (104) before this work started. The second paper appeared during the course of this work. This latter paper was published by Nahlovska, Nahlovsky and Strand (78). Both papers interpreted their results on the basis of a planar trans conformation. Two possible models due to the positions of H atoms were suggested by the latter paper (see section 13.3).

The force field calculations were made using both models for the reason that some evidence may be obtained to distinguish between them. In fact this problem had not been expected before this work started.

An initial set of force constants for gaseous oxalic acid was taken from the values for gaseous acetic acid published by Nakamoto and Kishida (39).

A Urey-Bradley force field was used for the inplane frequencies.

Vibrational frequencies, potential energy distributions and normal modes were computed for both structures and also for the deuterated forms.

CHAPTER 1

MOTION IN CARTESIAN CO-ORDINATES

1.1 Quantum mechanical description on the basis of the harmonic oscillator model

According to the Born-Oppenheimer approximation the total wave function Ψ for a molecule may be taken as an approximation to be

$$\Psi = \psi_E \psi_v \psi_R \psi_T \quad \text{..... 1.1}$$

where ψ_E , ψ_v , ψ_R , ψ_T are the electronic, vibrational, rotational and translational wave functions respectively.

Here we are concerned only with the vibrational wave function ψ_v . The wave equation in normal co-ordinates will then have the form

$$-\frac{h^2}{8\pi^2} \sum_{k=1}^{3N-6} \frac{\partial^2 \psi_v}{\partial Q_k^2} + \frac{1}{2} \sum_{k=1}^{3N-6} \lambda_k Q_k^2 \psi_v = W_v \psi_v \quad \text{..... 1.2}$$

where W_v is the vibrational energy. The wave equation in this form is separable into $3N-6$ equations, one for each normal co-ordinate. So

$$W_v = W(1) + W(2) + \dots + W(3N-6) \quad \text{..... 1.3}$$

and

$$\psi_v = \psi(Q_1) \cdot \psi(Q_2) \cdot \dots \cdot \psi(Q_{3N-6}) \quad \dots\dots\dots 1.4$$

Then it will be seen that the wave equation is satisfied if the function $\psi(Q_k)$ and the energy W_k satisfy equations of the type

$$-\frac{h^2}{8\pi^2} \frac{d^2 \psi(Q_k)}{d Q_k^2} + \frac{1}{2} \lambda_k Q_k^2 \psi(Q_k) = W_k \psi(Q_k) \quad \dots\dots\dots 1.5$$

Each of these equations is a differential equation in one variable, Q_k . In fact this equation is the well-known wave equation for the linear harmonic oscillator, expressed in terms of the normal co-ordinate Q_k . The solution ψ_v of the vibrational problem is therefore expressible, as a product of harmonic oscillator functions $\psi(Q_k)$ while the total vibrational energy W_v is the sum of the energies of $3N-6$ harmonic oscillators.

The solutions of the harmonic oscillator equation are called Hermite orthogonal functions and are of the form

$$\psi_{v_k}(Q_k) = N_{v_k} e^{-\frac{1}{2} r_k Q_k^2} H_{v_k} \left(\frac{r_k}{\alpha_k} Q_k \right) \quad \dots\dots\dots 1.6$$

in which N_{v_k} is the normalising factor

$$N_{v_k} = \left[\left(\frac{r_k}{\pi} \right)^{\frac{1}{2}} \frac{1}{2^{v_k} (v_k!)} \right]^{\frac{1}{2}} \quad \dots\dots\dots 1.7$$

r_k is the quantity $4\pi^2\nu_k/h$ and $H_{\nu_k}(r_k^{\frac{1}{2}} Q_k)$ is the Hermite polynomial of degree ν_k in Q_k .

The energy levels of a linear harmonic oscillator are given by the expression

$$W_v = (v + \frac{1}{2}) h\nu \quad \dots\dots 1.8$$

where v is the vibrational quantum number. Consequently, the vibrational energy of a molecule with several harmonic frequencies ν_k is of the form

$$W = (v_1 + \frac{1}{2})h\nu_1 + (v_2 + \frac{1}{2})h\nu_2 + \dots\dots + (v_{3N-6} + \frac{1}{2})h\nu_{(3N-6)} \quad \dots\dots 1.9$$

That is, every normal co-ordinate Q_k has associated with it a quantum number ν_k and a normal frequency ν_k .

1.2 Normal modes of vibration

If we assume that the particles behave as harmonic oscillators, each atom is oscillating about its equilibrium position with a simple harmonic motion according to the equation

$$q_i = A_i \cos(\lambda^{\frac{1}{2}}t + \epsilon) \quad \dots\dots 1.10$$

The frequency $\lambda^{\frac{1}{2}}/2\pi$ and the phase ϵ of motion of each ^{atoms}~~co-ordinate~~ is the same, but the amplitudes A_i may be, and usually are,

different for each co-ordinate q_i . On account of the equality in phase and frequency, each atom reaches its position of maximum displacement at the same time and each atom passes through its equilibrium position at the same time. A mode of vibration having all these characteristics is called a normal mode of vibration, and its frequency is known as a normal, or fundamental, frequency of the molecule.

The number of degrees of freedom possessed by the molecule is the number of the co-ordinates required to specify completely the position of the nuclei. Each nucleus requires 3 co-ordinates to define its position and so a molecule of N atoms has $3N$ degrees of freedom. Three are accounted for by the translational motion of the centre of mass and another three are accounted for by the rotational motion about the centre of mass. So the remaining $(3N-6)$ are associated with the internal vibrational motion of the atoms in the non-linear molecule. Each vibrational degree of freedom corresponds to a normal mode of vibration of the molecule.

1.3 Motion in cartesian displacement co-ordinates

There is no general theory or technique for dealing with an anharmonic force field in molecules, and thus, in order to be able to solve the vibrational problem (i.e. calculating vibrational frequencies) it is necessary to assume that the vibration of molecules is harmonic (5).

Consider N nuclei at their equilibrium positions with cartesian axes attached. The displacements of all nuclei are

defined by $3N$ displacement co-ordinates, $\Delta x_1, \Delta y_1, \Delta z_1, \Delta x_2, \Delta y_2, \Delta z_2, \dots, \Delta x_N, \Delta y_N, \Delta z_N$. For simplicity we used q'_i as cartesian displacement co-ordinates so that q'_i runs from 1 to $3N$.

The kinetic energy of the molecule in cartesian displacement co-ordinates is

$$2T = \sum_i m_i \dot{q}'_i{}^2 \quad \dots\dots 1.11$$

The potential field in which the nuclei move is a function of the displacement co-ordinates.

$$V = V(q'_1, q'_2, q'_3, \dots, q'_{3N}) \quad \dots\dots 1.12$$

The potential function V may always be expanded in a Taylor series in the q'_i about the equilibrium positions of the nuclei. Using the subscript zero to denote the equilibrium position gives

$$V = V_0 + \sum_{i=1}^{3N} \left(\frac{\partial V}{\partial q'_i} \right)_0 q'_i + \frac{1}{2} \sum_{i,j=1}^{3N} \left(\frac{\partial^2 V}{\partial q'_i \partial q'_j} \right)_0 q'_i q'_j + \dots \quad \dots\dots 1.13$$

If higher terms in this expression are ignored for small displacements this corresponds to an harmonic potential function. The potential energy is measured relative to the value when the atoms are in their equilibrium positions, hence $V_0 = 0$. The equilibrium positions correspond to a stable minimum in the potential

energy surface, hence all first derivatives are zero, that is,

$$\left(\frac{\delta V}{\delta q'_i} \right)_0 = 0.$$

The resulting potential function is

$$2V = \sum_{i,j=1}^{3N} \left(\frac{\delta^2 V}{\delta q'_i \delta q'_j} \right)_0 q'_i q'_j \quad \dots\dots 1.14$$

By Taylor's Theorem

$$\begin{aligned} \left(\frac{\delta^2 V}{\delta q'_i \delta q'_j} \right)_0 &= \text{constant} \\ \therefore 2V &= \sum_{i,j=1}^{3N} b'_{ij} q'_i q'_j \quad \dots\dots 1.15 \end{aligned}$$

where $b'_{ij} = b'_{ji}$.

1.4 Motion in mass weighted cartesian displacement co-ordinates

$$\text{If we define } q_i = \sqrt{m_i} q'_i \quad \dots\dots 1.16$$

$$\text{The kinetic energy expression becomes } 2T = \sum \dot{q}_i^2 \quad \dots\dots 1.17$$

The potential energy expression becomes

$$2V = \sum_{i,j=1}^{3N} b_{ij} q_i q_{ij} \quad \dots\dots 1.18$$

where $b_{ij} = b'_{ij}/\sqrt{m_i m_j}$ and $b_{ij} = b_{ji}$

The Lagrangian equation of motion is

$$\frac{d}{dt} \left(\frac{\delta L}{\delta \dot{q}_i} \right) - \frac{\delta L}{\delta q_i} = 0 \quad \dots\dots 1.19$$

where $L = T - V$.

On substituting 1.17 and 1.18 in 1.19, the equation gives a set of $3N$ linear second order homogeneous differential equations

$$\ddot{q}_i + \sum_j^{3N} b_{ij} \dot{q}_j = 0 \quad \text{..... 1.20}$$

The solution of this form of differential equation may be written as

$$q_i = A_i \cos(\lambda^{\frac{1}{2}} t + \epsilon) \quad \text{..... 1.21}$$

where A_i is the amplitude, $\lambda^{\frac{1}{2}}/2\pi$ is the frequency, and ϵ is the phase angle.

The $3N$ values of λ may be evaluated by differentiation and substituting back into 1.20. This gives

$$\sum_j^{3N} b_{ij} A_j - \lambda A_i = 0 \quad \text{..... 1.22}$$

which can be rearranged into

$$\sum_{j \neq i}^{3N} b_{ij} A_j + (b_{ii} - \lambda) A_i = 0 \quad \text{..... 1.23}$$

Homogeneous simultaneous equations have solutions other than the trivial one $A_1 = A_2 = A_3 = \dots = 0$ if the determinant of the coefficients is zero. Hence

$$\begin{vmatrix} b_{11}^{-\lambda} & b_{12} & \dots & b_{1,3N} \\ b_{21} & b_{22}^{-\lambda} & \dots & b_{2,3N} \\ \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots \\ b_{3N,1} & \dots & \dots & b_{3N,3N}^{-\lambda} \end{vmatrix} = 0 \quad \dots\dots 1.24$$

which may be written as

$$|b_{ij} - \lambda \delta_{ij}| = 0 \quad \dots\dots 1.25$$

Equation 1.24 has $3N$ roots which are the values of λ which cause the determinant to vanish. For a non-linear molecule six roots will be zero and for a linear molecule 5 roots will be zero. These zero roots represent translational and rotational motions of the molecule which have zero frequency of vibration.

1.5 Determination of the form of the normal modes

Let one of the roots be λ_k . Substitution in 1.24 gives $3N$ linear homogeneous equations and therefore can only be solved to give the ratio between the amplitudes A_{ik} . These amplitudes do not define unique values, which is consistent with the fact that we are dealing with harmonic motion and the frequency is independent of the amplitude.

For convenience a set of normalised amplitudes are used. These can be calculated such that they are in the same ratio as

the A_{ik} . If the constant of proportionality is K_k then

$$A_{ik} = K_k l_{ik} \quad \text{..... 1.26}$$

and the normalisation condition is that

$$\sum l_{ik}^2 = 1 \quad \text{..... 1.27}$$

so that there is a column vector l_{ik} corresponding to the λ_k .

The column vectors for all λ can be written to form a matrix L of dimension $3N$ in which

$$X = LQ \quad \text{..... 1.28}$$

where X = matrix representing cartesian displacement co-ordinates

Q = matrix representing normal co-ordinates

and

$$L = \begin{array}{c} \begin{array}{ccc} \lambda_1 & \lambda_2 & \lambda_{3N} \end{array} \\ \begin{array}{ccc} l_{11} & l_{12} \cdot \cdot \cdot \cdot \cdot \cdot \cdot & l_{1,3N} \\ l_{21} & l_{22} \cdot \cdot \cdot \cdot \cdot \cdot \cdot & l_{2,3N} \\ l_{31} & l_{32} \cdot \cdot \cdot \cdot \cdot \cdot \cdot & l_{3,3N} \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot \\ l_{3N,1} & l_{3N,2} & l_{3N,3N} \end{array} \end{array} \quad \text{..... 1.29}$$

One can construct vectors, attached to each atom, to show the relative magnitude and direction of the displacements from the values ϵ_{ik} . That is from $\epsilon_{1k}, \epsilon_{2k}, \epsilon_{3k}$ for atom 1, $\epsilon_{4k}, \epsilon_{5k}, \epsilon_{6k}$ for atom 2, , and $\epsilon_{3N-2,k}, \epsilon_{3N-1,k}, \epsilon_{3N,k}$ for atom N for the kth vibration corresponding to λ_k . Such diagrams represent normal modes of vibration.

CHAPTER 2

MOTION IN INTERNAL CO-ORDINATES

2.1 Kinetic energy in terms of internal co-ordinates

The cartesian displacement co-ordinates can be transformed into internal co-ordinates R by the equation

$$R = Bq' \quad \text{..... 2.1}$$

$$\text{or } R = Dq \quad \text{..... 2.2}$$

where R = matrix representing internal co-ordinates
 q' = matrix representing cartesian displacement co-ordinates
 q = matrix representing mass-weighted cartesian displacement co-ordinates
 B and D are matrices of transformations from cartesian co-ordinates to internal co-ordinates in which

$$D = Bm^{-\frac{1}{2}} \quad \text{..... 2.3}$$

m = diagonal matrix of masses

In terms of mass-weighted cartesian displacement co-ordinates, the kinetic energy is given by

$$2T = \dot{q}^t q \quad \text{..... 2.4}$$

If p_j is the momentum conjugate to q_j

$$p_j = \frac{\delta T}{\delta \dot{q}_j} = \dot{q}_j \quad \text{..... 2.5}$$

Thus, the kinetic energy can be simply written in terms of the momenta as

$$2T = p^t p \quad \text{..... 2.6}$$

Suppose that T is now considered as a function of the velocities in the internal co-ordinates. Using the rules for partial differentiation (1)

$$p_j = \frac{\delta T}{\delta \dot{q}_j} = \sum_n \frac{\delta T}{\delta \dot{R}_n} \cdot \frac{\delta \dot{R}_n}{\delta \dot{q}_j} \quad \text{..... 2.7}$$

$$\text{Since } \frac{\delta T}{\delta \dot{R}_n} = P_n \text{ and } \frac{\delta \dot{R}_n}{\delta \dot{q}_j} = D_{nj}$$

then equation 2.7 becomes in matrix form

$$p = D^t P \quad \text{..... 2.8}$$

and

$$p^t = P^t D \quad \text{..... 2.9}$$

Substituting 2.8 and 2.9 in 2.6, the equation becomes

$$2T = P^t (D D^t) P \quad \text{..... 2.10}$$

$$= P^t G P \quad \text{..... 2.11}$$

If $|G| \neq 0$, G^{-1} exists and by Hamilton's equations

$$\dot{R}_n = \frac{\delta T}{\delta P_n} \quad \dots\dots 2.12$$

then

$$\dot{R} = GP \quad \dots\dots 2.13$$

which can be solved for P

$$P = G^{-1} \dot{R} \quad \dots\dots 2.14$$

Thus, the kinetic energy in terms of the internal co-ordinates is

$$2T = \dot{R}^t G^{-1} \dot{R} \quad \dots\dots 2.15$$

2.2 Potential energy in terms of internal co-ordinates

The potential energy of a vibrating molecule can be expanded as a power series in the internal co-ordinate system by Taylor's theorem

$$V = V_o + \sum_{i=1}^n \left(\frac{\delta V}{\delta R_i} \right)_o R_i + \frac{1}{2} \sum_{i,j}^n \left(\frac{\delta^2 V}{\delta R_i \delta R_j} \right)_o R_i R_j + \text{higher terms} \quad \dots\dots 2.16$$

where n is the number of internal co-ordinates and the subscript o denotes the equilibrium position.

Assuming an harmonic potential function the higher terms in 2.16 can be ignored. $V_0 = 0$ when the potential energy is measured relative to the value when the atoms are in their equilibrium position. At equilibrium the potential energy must be minimum, hence

$$\left(\frac{\delta V}{\delta R_i} \right)_0 = 0 \quad \text{for } i = 1, 2, \dots, n$$

The resulting potential function for the harmonic oscillator model is

$$V = \frac{1}{2} \sum_{i,j=1}^n \left(\frac{\delta^2 V}{\delta R_i \delta R_j} \right)_0 R_i R_j \quad \dots\dots 2.17$$

By Taylor's theorem

$$\left(\frac{\delta^2 V}{\delta R_i \delta R_j} \right)_0 = f_{ij} = f_{ji} \quad \dots\dots 2.18$$

where the f 's are the force constants in internal co-ordinates.

The potential energy can be expressed as

$$2V = \sum_{i,j=1}^n f_{ij} R_i R_j \quad \dots\dots 2.19$$

In matrix form equation 2.19 becomes

$$2V = R^T F R \quad \dots\dots 2.20$$

where F is the matrix representing the force constants f_{ij} .

2.3 The secular equation in terms of internal co-ordinates

Both the kinetic energy and the potential energy can be expressed in the same internal co-ordinates as

$$2T = \dot{R}^t G^{-1} \dot{R} \quad \text{..... 2.21}$$

$$2V = R^t F R \quad \text{..... 2.22}$$

From Lagrange's equation of motion

$$\frac{d}{dt} (\delta T / \delta \dot{R}_i) + \delta V / \delta R_i = 0 \quad \text{..... 2.23}$$

Substituting 2.21 and 2.22 in 2.23 the equation becomes

$$\sum_{j=1}^n ((G^{-1}_{ij}) \ddot{R}_j + f_{ij} R_j) = 0 \quad \text{..... 2.24}$$

where n is the number of internal co-ordinates.

Equation 2.24 forms n homogeneous second order differential equations for which the solutions are

$$R_i = A_i \cos(\lambda^{1/2} t + \epsilon) \quad \text{..... 2.25}$$

where A_i is the amplitude, $\lambda^{1/2}/2\pi$ is the frequency, and ϵ is phase angle.

Substituting 2.25 into 2.24 the vibrational problem leads to a secular equation

$$\begin{vmatrix} F_{11} - (G^{-1})_{11}\lambda & F_{12} - (G^{-1})_{12}\lambda & \dots & F_{1n} - (G^{-1})_{1n}\lambda \\ F_{21} - (G^{-1})_{21}\lambda & F_{22} - (G^{-1})_{22}\lambda & \dots & F_{2n} - (G^{-1})_{2n}\lambda \\ \dots & \dots & \dots & \dots \\ F_{n1} - (G^{-1})_{n1}\lambda & F_{n2} - (G^{-1})_{n2}\lambda & \dots & F_{nn} - (G^{-1})_{nn}\lambda \end{vmatrix} = 0 \quad \dots\dots 2.26$$

Here $\lambda = 4\pi^2\nu^2$.

Symbolically equation 2.26 can be written as

$$|F - G^{-1}\lambda| = 0 \quad \dots\dots 2.27$$

Another form of the secular equation can be obtained by multiplying 2.27 by the determinant of G, that is, by $|G|$, using the rules for the multiplication of determinants. The secular equation becomes

$$|GF - E\lambda| = 0 \quad \dots\dots 2.28$$

where E is the unit matrix (3 page 63 - 65).

Because both F and G are symmetrical, rows and columns in 2.28 can be interchanged to yield another form which can be written as

$$|FG - E\lambda| = 0 \quad \dots\dots 2.29$$

CHAPTER 3

MOTION IN SYMMETRY CO-ORDINATES

3.1 Symmetry co-ordinates

Symmetry co-ordinates may be described as follows:-

- (1) They are related to the internal co-ordinates by the transformation

$$S = UR \quad \text{..... 3.1}$$

where S = matrix representing symmetry co-ordinates

R = matrix representing internal co-ordinates

U = matrix of transformation.

In other words, they are linear combinations of internal co-ordinates.

- (2) They must themselves form representations for the class of vibrations for which they are to be used. This means that the co-ordinates must have the same symmetry and anti-symmetry properties as the vibrational modes themselves (1).
- (3) They must form a complete orthogonal set that is

$$\sum_k S_{jk} S_{ik} = 0 \quad \text{..... 3.2}$$

i and j refer to different symmetry co-ordinates (4).

- (4) The number of symmetry co-ordinates will equal the number of fundamental vibrations. If it exceeds the number of vibrations then this implies a redundancy, that is, certain

combinations of these internal co-ordinates will be equivalent to no vibrational motion at all and therefore correspond to a zero frequency (1).

- (5) With these co-ordinates the vibrational problem for each symmetry class can be solved independently (3).

Under symmetry co-ordinates both kinetic and potential energies have the form

$$2T = \dot{\mathbf{S}}^t \underline{\mathbf{G}}^{-1} \dot{\mathbf{S}} \quad \text{..... 3.3}$$

$$2V = \mathbf{S}^t \underline{\mathbf{F}} \mathbf{S} \quad \text{..... 3.4}$$

Substituting 3.1 into 3.3 and 3.4 we have

$$2T = \dot{\mathbf{R}}^t \mathbf{U}^t \underline{\mathbf{G}}^{-1} \mathbf{U} \dot{\mathbf{R}} \quad \text{..... 3.5}$$

$$2V = \mathbf{R}^t \mathbf{U}^t \underline{\mathbf{F}} \mathbf{U} \mathbf{R} \quad \text{..... 3.6}$$

On comparing 3.5 and 3.6 with 2.21 and 2.22 we have

$$\underline{\mathbf{G}} = \mathbf{U} \mathbf{G} \mathbf{U}^t \quad \text{..... 3.7}$$

$$\underline{\mathbf{F}} = \mathbf{U} \mathbf{F} \mathbf{U}^t \quad \text{..... 3.8}$$

If S_j and S_k belong to different symmetry types there will be at least one symmetry operation with respect to which S_j and S_k behave differently, that is, there will be at least one symmetry operation for which $S_j S_k$ changes sign. Since the potential energy must be invariant with respect to all symmetry operations, it follows that g_{jk} and f_{jk} are zero whenever S_j and S_k belong to different species (2). Therefore the secular equation

$$|\underline{G} \underline{F} - E\lambda| = 0 \quad \text{..... 3.9}$$

assumes the block form as indicated in Fig. 1 where all elements outside the shaded area are zero, since they correspond to S_j and S_k of different species. Each shaded square corresponds to one species. The determinant can now be written as a product of factors corresponding to each species. Each of these factors put equal to zero gives the normal frequencies of these species.

Fig. 1

Form of secular determinant set up
in terms of symmetry co-ordinates

3.2 Construction of symmetry co-ordinates

Symmetry co-ordinates may be written as

$$S_j = \sum_k U_{jk} r_k \quad \text{..... 3.10}$$

where S_j is the j th symmetry co-ordinate, r_k is the k th internal co-ordinate, and U_{jk} is the suitable coefficient for r_k . In matrix notation equation 3.10 becomes

$$S = UR \quad \text{..... 3.11}$$

The symmetry co-ordinates selected are not necessarily unique but they must have definite properties. Since they are not unique, a perfectly general method for obtaining them cannot be given (4). A simple rule for construction of trial symmetry co-ordinates was described by Wilson, Decius and Cross (3 pp 117 - 121) using the expression

$$S^A = N \sum_{\hat{R}} \chi_{\hat{R}}^A \hat{R} S_1 \quad \text{..... 3.12}$$

where S^A is the symmetry co-ordinate of the vibration species A (Ag, etc.), $\chi_{\hat{R}}^A$ is the character corresponding to $\hat{R}$ of the vibration of species A, $\hat{R}$ is the operator in the point group, S_1 is the generating co-ordinate, and N is the normalising factor. The generating co-ordinate S_1 may be a single internal co-ordinate or linear combination of internal co-ordinates.

The trial symmetry co-ordinates must be normal, orthogonal, and they must transform properly (4). The condition for normality is

$$\sum_k U_{jk} U_{jk} = 1 \quad \text{..... 3.13}$$

where U_{jk} is a coefficient in the j th symmetry co-ordinate and the summation is carried over the k internal co-ordinates. The condition therefore requires the sum of the squares of the coefficients in each symmetry co-ordinate to be one.

The condition for orthogonality is

$$\sum_k U_{jk} U_{lk} = 0 \quad \text{..... 3.14}$$

where l and j refer to different symmetry co-ordinates. That is, the sum of the products of the coefficients in the corresponding internal co-ordinates (same internal co-ordinates) of two different symmetry co-ordinates is equal to zero and this must be true for every pair of symmetry co-ordinates.

CHAPTER 4

MOTION IN NORMAL CO-ORDINATES

The normal co-ordinates Q_k can be expressed in terms of the mass-weighted cartesian displacement co-ordinates q_i by the linear equation

$$Q_k = \sum_{i=1}^{3N} l_{ki} q_i \quad \text{..... 4.1}$$

in which the coefficients l_{ki} have been chosen so that in terms of the new co-ordinates the kinetic and potential energies have the forms

$$2T = \sum_k \dot{Q}_k^2 \quad \text{..... 4.2}$$

$$2V = \sum_k \lambda Q_k^2 \quad \text{..... 4.3}$$

In other words, the potential energy in terms of the normal co-ordinates involves no cross products but only squares of Q 's.

In matrix notation equations 4.2 and 4.3 become

$$2T = \dot{Q}^t \dot{Q}$$

$$2V = Q^t \Lambda Q$$

where Λ is the diagonal matrix of the λ values.

The transformation between the mass-weighted cartesian co-ordinates and the normal co-ordinates is an orthogonal trans-

formation. This can be proved as follows:-

$$\begin{aligned} 2T &= \dot{Q}^t \dot{Q} \\ &= \dot{q}^t \ell^t \ell \dot{q} \\ &= \dot{q}^t \dot{q} \quad \text{only if } \ell^t = \ell^{-1} \end{aligned}$$

That is, ℓ is an orthogonal matrix.

The diagrams which represent normal modes of motion can also be used to represent normal co-ordinates if the vectors are drawn so as to represent displacements, not only in ordinary units, but in the mass-adjusted scale of co-ordinates q_i . Then the component of a vector along the direction of co-ordinates q_i is proportional to ℓ_{ik} . That is, the diagram represents not only the relative amplitudes of the atoms during the normal mode of motion, but also the coefficients in the transformation.

4.2 Determination of normal co-ordinates

For a vibrating molecule there will be only one normal co-ordinate Q_k associated with one mode of vibration ν_k . The normal co-ordinate is related to the internal co-ordinates by

$$R = LQ \quad \dots\dots 4.4$$

where R = matrix of internal co-ordinates
 L = matrix of transformation
 Q = matrix of normal co-ordinates

L is chosen so that

$$2T = \dot{Q}^t \dot{Q} \quad \dots\dots 4.5$$

$$2V = Q^t \Lambda Q \quad \dots\dots 4.6$$

where Λ is the diagonal matrix of the latent roots.

Substituting 4.4 in 4.5 and 4.6 we have

$$2T = R^t (L^{-1})^t L^{-1} \dot{R} \quad \dots\dots 4.7$$

$$2V = R^t (L^{-1})^t \Lambda L^{-1} R \quad \dots\dots 4.8$$

Comparing 4.7 and 4.8 with 2.21 and 2.22 we have

$$G = L L^t \quad \dots\dots 4.9$$

$$\text{and } \Lambda = L^t F L \quad \dots\dots 4.10$$

Application of Newton's equations of motion in the Lagrange form and substitution of a trial periodic solution of the form

$$R_i = A_i \cos(\lambda^{\frac{1}{2}} t + \epsilon) \quad \dots\dots 4.11$$

where A_i is the amplitude, $\lambda^{\frac{1}{2}}/2\pi$ is the frequency, and ϵ is phase angle, leads to the equations

in which symmetry co-ordinates and normal co-ordinates are related by the equation

$$S = LQ \quad \text{..... 4.16}$$

thus $S^t = Q^t L^t$ 4.17

Substituting 4.16 and 4.17 into 4.15 we have

$$2V = Q^t L^t F LQ \quad \text{..... 4.18}$$

In normal co-ordinates the potential energy may be expressed as

$$2V = Q^t \Lambda Q \quad \text{..... 4.19}$$

On comparing 4.18 with 4.19 we have

$$\Lambda = L^t F L \quad \text{..... 4.20}$$

For one normal vibrational frequency λ_k the relation from 4.20 may be written as

$$\lambda_k = \sum_{i,j} f_{ij} l_{ik} l_{jk} \quad \text{..... 4.21}$$

in which the potential energy is

$$V(\lambda_k) = 1/2 Q_k^2 \sum_{i,j} f_{ij} \ell_{ik} \ell_{jk} \quad \text{..... 4.22}$$

where $f_{ij} \ell_{ik} \ell_{jk}$ is the potential energy distribution in each symmetry co-ordinate. The term is generally large when $i = j$, which is quite useful for band assignments. For example, if this term is exceedingly large for S_i , this normal vibration can be assigned to the group vibration represented by S_i . If both $f_{ii} \ell_{ik}^2$ and $f_{jj} \ell_{jk}^2$ are relatively large compared with those of other symmetry co-ordinates, the normal vibration is assigned to a coupled vibration between those represented by symmetry co-ordinates S_i and S_j .

CHAPTER 5

G-MATRIX

5.1 Construction of the G matrix

Generally the G matrix in internal co-ordinates can be constructed by the following steps:-

- (a) Evaluate the matrix B which determines the contribution of each cartesian displacement co-ordinate q_i , to the internal co-ordinates ΔR_t (ΔR is from now on being used in place of R for the internal displacement co-ordinate).
- (b) Evaluate the D matrix from

$$D = B\mu^{\frac{1}{2}} \quad \text{..... 5.1}$$

where $\mu^{\frac{1}{2}}$ = diagonal matrix of square roots of reciprocal masses.

- (c) The G matrix in terms of internal co-ordinates can be evaluated from

$$G = DD^t \quad \text{..... 5.2}$$

5.2 Evaluation of the B matrix

The B matrix elements are evaluated using Wilson's S vector technique (2, 3) where the unit vectors e_{ij} are assumed along bonds connecting atoms i and j. Thus, for any bond between atom i and j

$$e_{ij} = -e_{ji} \quad \text{..... 5.3}$$

These bond vectors can easily be expressed in terms of cartesian displacement vectors on each atom. The movement of each atom is described by a vector S_{t_i} , related to the bond vector e_{ij} .

1. Bond stretching co-ordinates (ΔR)

Fig. 2

Let ΔR be the increase in the distance between atoms 1 and

2. Clearly

$$S_{t_1} = e_{21} = -e_{12} \quad \dots\dots 5.4$$

$$S_{t_2} = e_{12} \quad \dots\dots 5.5$$

If these are expressed in cartesian displacement vectors, the coefficient of S_{t_i} will be the B matrix elements associated with the co-ordinate ΔR .

2. Valence angle bending co-ordinates

Fig. 3

Consider the bond system shown in Fig. 3 and defined by atoms 1, 2 and 3. e_{21} and e_{23} are unit vectors directed along

the bonds 2-1 and 2-3 respectively.

The S_{t_i} vectors are given as follows:-

$$S_{t_1} = \frac{\cos \phi \, e_{21} - e_{23}}{r_{12} \sin \phi} \quad \dots\dots 5.6$$

$$S_{t_3} = \frac{\cos \phi \, e_{23} - e_{21}}{r_{23} \sin \phi} \quad \dots\dots 5.7$$

$$\text{and } S_{t_2} = -S_{t_1} - S_{t_3} \quad \dots\dots 5.8$$

The coefficients of S_{t_i} in terms of cartesian displacement vectors are the B matrix elements corresponding to the particular angle bending co-ordinate concerned.

3. Angle between a bond and a plane defined by two bonds

Fig. 4

This type of the co-ordinate is the angle formed by a bond 4,1 and the plane of the three atoms 2,3 and 4, all four atoms being in one plane. For this situation the magnitudes of the vectors are

$$S_{t_1} = \frac{1}{r_{41}} \quad \text{"end atom"} \quad \dots\dots 5.9$$

$$S_{t_2} = \frac{\sin \phi_2}{r_{42} \sin \phi_1} \quad \text{"anchor atom" 5.10}$$

$$S_{t_3} = \frac{\sin \phi_3}{r_{43} \sin \phi_1} \quad \text{"anchor atom" 5.11}$$

$$S_{t_4} = -S_{t_1} - S_{t_2} - S_{t_3} \quad \text{"apex atom" 5.12}$$

4. Torsion

Fig. 5

The torsion angle $\Delta \gamma$ is defined as the change from the equilibrium configuration in the angle between the planes defined by the nuclei 1, 2 and 3 and 2, 3 and 4. The S_{t_i} vectors may be written as

$$S_{t_1} = \frac{1}{r_{12} \sin \phi_2} \cdot \frac{e_{21} \times e_{23}}{\sin \phi_2} \quad \text{..... 5.13}$$

$$S_{t_4} = \frac{1}{r_{34} \sin \phi_3} \cdot \frac{e_{34} \times e_{32}}{\sin \phi_3} \quad \text{..... 5.14}$$

$$S_{t_2} = -\frac{r_{23} - r_{12} \cos \phi_2}{r_{23} r_{12} \sin \phi_2} \cdot \frac{e_{21} \times e_{23}}{\sin \phi_2} - \frac{\cos \phi_3}{r_{23} \sin \phi_3} \cdot \frac{e_{34} \times e_{32}}{\sin \phi_3} \quad \text{..... 5.15}$$

$$S_{t_3} = - \frac{r_{23} - r_{34} \cos \phi_3}{r_{23} r_{34} \sin \phi_3} \cdot \frac{e_{34} \times e_{32}}{\sin \phi_3} - \frac{\cos \phi_2}{r_{23} \sin \phi_2} \cdot \frac{e_{21} \times e_{23}}{\sin \phi_2} \dots 5.16$$

NOTE

1. The sum of the S_{t_i} vectors is zero.
2. All S vector expressions are taken from Steele (2) and Wilson, Decius and Cross (3). There is a sign error in the expression for S_{t_2} in (3 p.61). The sign before the second term should be + and not -.

CHAPTER 6
FORCE FIELDS

6.1 Force constants

The vibration frequencies and the form of $(3N-6)$ normal vibrations of an N atomic molecule depends upon

- (1) the atomic masses;
- (2) geometrical distribution of the vibrating nuclei;
- (3) the force field which tends to restore the molecule to its internal equilibrium configuration during any distortion.

The atomic masses and their geometrical distribution must be known before any force constant calculation can be attempted. The force field arises from the fact that the equilibrium positions of the nuclei correspond to a minimum in the electronic energy of the molecule. Displacement of the nuclei causes a slight increase in the electronic energy.

However, in so far as one is concerned with the normal state of the molecule, one of the best representations of its condition is provided by the force field for the molecule; that is, a representation of the forces that arise when the atoms are displaced from their equilibrium positions. This becomes a determination of the various 'force constants' for the bonds in the molecule and for the angular location of the atoms. The force constant calculations have also been used as supporting evidence for molecular geometry.

One should not attempt to define more force constants than there are frequencies available. This often means that all the terms in the general quadratic expression cannot be evaluated and the problem must be approximated by writing at least some force constants equal to zero (5).

Practically, as an approximation, a first set of force constants for a molecule may be obtained from other molecules under the restrictions that

- (1) They are of similar types (e.g. bond stretch + bond stretch, angle bending + angle bending, etc.).
- (2) They are acting between the same nuclei.
- (3) They were calculated using the same type of force field.

In many cases they may also be obtained by extrapolation of the sets of force constants of similar molecules, e.g. a set of halogenated molecules.

6.2 Force fields

Although the general valence force field is supposed to be the best force field to apply to the molecule because it consists of all possible interactions between atoms in a molecule, the number of force constants required is more than the number of frequencies available. This makes it difficult to apply to polyatomic molecules.

As in the oxalic acid molecule, for example, there are altogether 63 force constants (using 1st model - see section 16.1, 16.2) in the potential field of the inplane vibrations and only

13 inplane fundamental frequencies. Thus, it is impossible to work out all the force constants. It is also very difficult to apply the modified valence force field because there are too many force constants to eliminate, e.g. there are 50 force constants of the inplane vibrations of oxalic acid to eliminate in order to make the calculation possible.

Two force fields that are often applied to polyatomic molecules are the valence force field and the Urey-Bradley force field.

In the valence force field it is assumed that

- (a) there is a strong restoring force in the line of every valence bond if the distance of the two atoms bound by this bond is changed;
- (b) there is also a restoring force opposing a change of the angle between two valence bonds.

The potential energy in the valence force field is a purely quadratic function of the changes of the valence bonds and valence angles and there is no cross term in the potential energy. In many cases this force field failed to give a close fit of calculated to observed frequencies for polyatomic molecules.

One of the most well known force fields for polyatomic molecules is the Urey-Bradley force field. In this force field the potential energy is expressed in terms of force constants and geometry. It is supposed to be better than the valence force field for the following reasons:-

- (1) In Urey-Bradley force fields a large number of force constants is reduced systematically and the potential

energy not only includes the pure quadratic terms, but also some cross terms.

- (2) For many cases the Urey-Bradley force field gives a better fit of the calculated to the observed frequencies.

For most polyatomic molecules the force constants have been calculated using the Urey-Bradley force field. Thus, transference and extrapolation of force constants among molecules can be made easier using this force field.

For the reasons mentioned above, the Urey-Bradley force field was selected to apply to the oxalic acid molecule.

6.3 Urey-Bradley force field

In the Urey-Bradley force field the potential energy change due to a change in bond length (Δr_i) and bond angle ($\Delta \alpha_i$) can be expressed as:

$$\begin{aligned}
 V = & \sum \left[K'_i r_{i0} (\Delta r_i) + \frac{1}{2} K_i (\Delta r_i)^2 \right] \\
 & + \sum \left[H'_i r_{i0}^2 (\Delta \alpha_i) + \frac{1}{2} H_i r_{i0}^2 (\Delta \alpha_i)^2 \right] \\
 & + \sum \left[F'_i q_{i0} (\Delta q_i) + \frac{1}{2} F_i (\Delta q_i)^2 \right]
 \end{aligned}
 \quad \text{..... 6.1}$$

where Δr_i = change in bond length

$\Delta \alpha_i$ = change in bond angle

Δq_i = change in distance between non bonded atoms

K = stretching force constant

H = bending force constant

F = repulsive force constant

r_{i0} , $r_{i\alpha}$ and q_{i0} are the equilibrium values of distances which are inserted in order to make all the force constants, K'_i , H'_i , F'_i , K_i , H_i and F_i dimensionally similar.

Here Δq in the above expression needs to be eliminated.

The following expressions for the Δq 's are in (1), (13), (25).

There are two types of Δq_{ij} :

(i) That where atoms i and j are bonded to a common atom

k. Δq can be eliminated as follows:-

$$\text{From } q_{ij}^2 = r_i^2 + r_j^2 - 2r_i r_j \cos \alpha_{ij} \quad \text{..... 6.2}$$

$$\begin{aligned} (q_{ij} + \Delta q_{ij})^2 &= (r_i + \Delta r_i)^2 + (r_j + \Delta r_j)^2 - 2(r_i + \Delta r_i)(r_j + \Delta r_j) \cos(\alpha_{ij} + \Delta \alpha_{ij}) \\ &= (r_i + \Delta r_i)^2 + (r_j + \Delta r_j)^2 - 2(r_i + \Delta r_i)(r_j + \Delta r_j) \\ &\quad (\cos \alpha_{ij} \cos \Delta \alpha_{ij} - \sin \alpha_{ij} \sin \Delta \alpha_{ij}) \quad \text{..... 6.3} \end{aligned}$$

in which for a small angle change

$$\cos(\Delta \alpha_{ij}) = 1 - \Delta \alpha_{ij}^2 / 2$$

$$\sin(\Delta \alpha_{ij}) = \Delta \alpha_{ij}$$

$$\begin{aligned} \text{Then } (q_{ij} + \Delta q_{ij})^2 &= (r_i + \Delta r_i)^2 + (r_j + \Delta r_j)^2 - 2(r_i + \Delta r_i)(r_j + \Delta r_j) \\ &\quad \{ \cos \alpha_{ij} (1 - \Delta \alpha_{ij}^2 / 2) - \sin \alpha_{ij} \cdot \Delta \alpha_{ij} \} \quad \text{..... 6.4} \end{aligned}$$

Subtracting 6.2 from 6.4 and then neglecting terms of higher than second order in small quantities we have

$$\begin{aligned} q_{ij}\Delta q_{ij} = & \Delta r_i(r_i - r_j \cos \alpha_{ij}) + \Delta r_j(r_j - r_i \cos \alpha_{ij}) + r_i r_j \sin \alpha_{ij} \cdot \Delta \alpha_{ij} \\ & + (\Delta r_i)^2/2 + \Delta r_j^2/2 - \Delta r_i \Delta r_j \cos \alpha_{ij} + (r_i \Delta r_j + r_j \Delta r_i) \Delta \alpha_{ij} \sin \alpha_{ij} \\ & - (\Delta q_{ij})^2/2 + (r_i r_j (\Delta \alpha_{ij})^2/2) \cos \alpha_{ij} \end{aligned} \quad \dots\dots 6.5$$

On squaring 6.5, retaining terms only to the second order as before and substituting the resulting expression for $(\Delta q_{ij})^2$ back into 6.4 we get

$$\begin{aligned} \Delta q_{ij} = & S_{ij}(\Delta r_i) + S_{ji}(\Delta r_j) + (t_{ij} t_{ji} r_i r_j)^{1/2} \cdot \Delta \alpha_{ij} + \frac{1}{2q_{ij}} (t_{ij}^2 (\Delta r_i)^2 \\ & + t_{ji}^2 (\Delta r_j)^2 - S_{ij} S_{ji} r_i r_j (\Delta \alpha_{ij})^2 - 2t_{ij} t_{ji} \Delta r_i \Delta r_j + 2t_{ij} S_{ji} r_j \Delta r_i \cdot \\ & \Delta \alpha_{ij} + 2t_{ji} S_{ij} r_i \Delta r_j \cdot \Delta \alpha_{ij}) \end{aligned} \quad \dots\dots 6.6$$

where $S_{ij} = (r_i - r_j \cos \alpha_{ij})/q_{ij}$

and $t_{ij} = r_j \sin \alpha_{ij}/q_{ij}$

By substituting Δq , the potential energy is then expressed in an independent set of co-ordinates. However, this substitution has the effect of introducing the F'_{ij} into the coefficients of the quadratic terms. The coefficients of F_{ij} and F'_{ij} are shown in Table 1 below:

Table 1

The coefficients of F_{ij} and F'_{ij} when atoms i and j
are bonded to a common atom k

f vector	F_{ij}	F'_{ij}
$(\Delta r_i)^2$	S_{ij}^2	t_{ij}^2
$(\Delta r_j)^2$	S_{ji}^2	t_{ji}^2
$(r_i \Delta \alpha_{ij})^2$	$t_{ij} t_{ji} (r_j/r_i)$	$-S_{ij} S_{ji} (r_j/r_i)$
$\Delta r_i \Delta r_j$	$S_{ij} S_{ji}$	$-t_{ij} t_{ji}$
$\Delta r_i (r_i \Delta \alpha_{ij})$	$S_{ij} \sqrt{t_{ij} t_{ji}} (r_j/r_i)^{1/2}$	$t_{ij} S_{ji} (r_j/r_i)$
$\Delta r_j (r_i \Delta \alpha_{ij})$	$S_{ji} \sqrt{t_{ij} t_{ji}} (r_j/r_i)^{1/2}$	$t_{ij} S_{ij}$

(ii) That where atoms i and j are bonded respectively to two other atoms k and l which are in turn connected by a bond kl. The coefficients of F_{ij} and F'_{ij} may be obtained in a similar way and are shown in Table 2.

Table 2

The coefficients of F_{ij} and F'_{ij} when atoms i and j are
bonded to two other atoms k and l which are in turn
connected by a bond kl

f vector	F_{ij}	F'_{ij}
$(\Delta r_i)^2$	v_{ij}^2	$(1 - v_{ij}^2)$
$(\Delta r_j)^2$	v_{ji}^2	$(1 - v_{ji}^2)$
$(\Delta R_{kl})^2$	a_{ij}^2	b_{ij}^2

f vector	F_{ij}	F'_{ij}
$(\Delta r_i \Delta r_j)$	$v_{ij} v_{ji}$	$\cos(\alpha_{i\ell} + \alpha_{jk}) - v_{ij} v_{ji}$
$\Delta r_i \Delta R_{k\ell}$	$-a_{ij} v_{ij}$	$a_{ij} v_{ij} - \cos \alpha_{i\ell}$
$\Delta r_j \Delta R_{k\ell}$	$-a_{ij} v_{ji}$	$a_{ij} v_{ji} - \cos \alpha_{jk}$
$(r_i \Delta \alpha_{i\ell})^2$	u_{ij}^2	$(v_{ij} q_{ij}/r_i) + (1 - u_{ij}^2)$
$(r_j \Delta \alpha_{jk})^2$	u_{ji}^2	$(v_{ji} q_{ij}/r_j) + (1 - u_{ji}^2)$
$r_i \Delta \alpha_{ij} r_j \Delta \alpha_{jk}$	$u_{ij} u_{ji}$	$-\left[\cos(\alpha_{jk} + \alpha_{i\ell}) + u_{ij} u_{ji}\right]$
$r_i \Delta \alpha_{i\ell} \Delta r_i$	$-u_{ij} v_{ij}$	$u_{ij} (q_{ij} + r_i v_{ij})/r_i$
$r_i \Delta \alpha_{i\ell} \Delta r_j$	$-u_{ij} v_{ji}$	$v_{ji} u_{ij} - \sin(\alpha_{jk} + \alpha_{i\ell})$
$r_i \Delta \alpha_{i\ell} \Delta R_{k\ell}$	$u_{ij} a_{ij}$	$\sin \alpha_{i\ell} - a_{ij} u_{ij}$
$r_j \Delta \alpha_{jk} \Delta r_i$	$-u_{ji} v_{ij}$	$v_{ij} u_{ji} - \sin(\alpha_{jk} + \alpha_{i\ell})$
$r_j \Delta \alpha_{jk} \Delta r_j$	$-u_{ji} v_{ji}$	$u_{ji} (q_{ij} + r_j v_{ji})/r_j$
$r_j \Delta \alpha_{jk} \Delta R_{k\ell}$	$u_{ji} a_{ij}$	$\sin \alpha_{jk} - a_{ij} u_{ji}$

in which $a_{ij} = (R_{k\ell} - r_i \cos \alpha_{i\ell} - r_j \cos \alpha_{jk})/q_{ij}$

$$b_{ij} = (r_i \sin \alpha_{i\ell} - r_j \sin \alpha_{jk})/q_{ij}$$

$$u_{ij} = a_{ij} \sin \alpha_{i\ell} + b_{ij} \cos \alpha_{i\ell}$$

$$u_{ji} = a_{ij} \sin \alpha_{jk} - b_{ij} \cos \alpha_{jk}$$

$$v_{ij} = a_{ij} \cos \alpha_{i\ell} - b_{ij} \sin \alpha_{i\ell}$$

$$v_{ji} = a_{ij} \cos \alpha_{jk} + b_{ij} \sin \alpha_{jk}$$

CHAPTER 7

FORCE CONSTANTS CALCULATIONS

7.1 Method of trial and error

The main part of the calculation in vibrational problems is to find a good set of force constants in a specific force field which will give calculated frequencies fitting well to the observed values. Thus, the observed values and their assignments must be obtained before a calculation is performed. The method of trial and error may be applied by first guessing a set of force constants and then calculating the frequencies. If both observed and calculated values do not agree well, that set of force constants is modified. The process is repeated until a satisfactory set of force constants is found.

Generally the vibrational frequencies are calculated using the secular equation

$$|\underline{G} \underline{F} - I\lambda| = 0 \quad \text{..... 7.1}$$

If $\underline{G}$ and $\underline{F}$ are expressed in symmetry co-ordinates, the secular determinant may be factorised into several smaller blocks. Each block belongs to a species and each species can be solved separately. In this way the calculation for a molecule of high symmetry can be solved more easily.

In the case of oxalic acid the number of independent force constants required by the Urey-Bradley force field to describe the 13 inplane vibrations is 13. They are ordinarily found by trial

and error methods and may be judged acceptable if they appear to be reasonable in magnitude and if the normal frequencies to which they lead are in good agreement with the observed fundamentals. The inplane vibrational frequencies of oxalic acid can be calculated from the 13×13 matrix which contains two smaller matrices. A 7×7 matrix belongs to the A_g species and a 6×6 matrix belongs to the B_u species. Each of these is too large to be solved by hand. With the aid of the computer it is possible to carry out the calculation without difficulty.

7.2 Method of least squares refinement (24)

Generally the first set of force constants may be obtained by guessing or transferring the force constants from another molecule. The refinement of this approximate set of force constants will be performed by trial and error. The criterion for this is that the percentage discrepancy between calculated and observed frequencies should be as small as possible with the largest discrepancy not greater than 5%.

A further systematic refinement of force constants may be obtained by the least squares method. This method is used to adjust or refine the force constants in accordance with a prescribed and definite mathematical process. This method is very convenient because it can be easily adapted for matrix operation.

It is supposed that a set of d experimental frequencies (ν_0) is available and the problem involves r independent force constants

in which $d \geq r$. Here our purpose is to adjust the force constants until the calculated frequencies are fitted to the observed frequencies; in other words, to get the minimum variance. Ideally for the best fit the variance will become zero, this will not be so because of experimental error and the approximate force field used.

We define the measure of fit or the variance as

$$S^{i-1} = \sum_{n=1}^d W_n (v_n^i - v_n^0)^2 \quad \text{..... 7.2}$$

where $n = 1, 2, \dots, d$

v_n^0 = observed frequencies

v_n^i = calculated frequencies where the index i labels the stage of calculation and may have the value 1, 2, 3, . . .

W_n = weighting factors

The frequencies calculated from the i th set of force constants are indicated by v^i . The differences between the frequencies of the $(i + 1)$ th and i th sets are given by

$$\Delta v_n^i = v_n^{i+1} - v_n^i \quad \text{..... 7.3}$$

A corresponding expression

$$\Delta k_m^i = k_m^{i+1} - k_m^i \quad \text{..... 7.4}$$

applies to the adjustments in the force constants. The new variance becomes

$$S^i = \sum_{n=1}^d W_n (v_n^{i+1} - v_n^0)^2 \quad \dots\dots 7.5$$

Applying 7.3 the equation 7.5 becomes

$$S^i = \sum_{n=1}^d W_n (v_n^i + \Delta v_n^i - v_n^0)^2 \quad \dots\dots 7.6$$

In matrix notation equation 7.6 can be written as

$$S^i = \begin{bmatrix} v^i + \Delta v^i - v^0 \end{bmatrix}^t W \begin{bmatrix} v^i + \Delta v^i - v^0 \end{bmatrix} \quad \dots\dots 7.7$$

where the brackets denote a column or row matrix. W is a diagonal matrix whose elements represent the statistical weights of the observed frequencies.

If W is taken as $1/v$, then the best fit will be on an absolute basis in the frequencies. On the other hand, if W is taken as $1/v^2$, the best fit will be a percentage basis in the frequencies.

A relation between Δv^i and Δk^i is assumed by

$$\Delta v^i = J \Delta k^i \quad \dots\dots 7.8$$

where J, the Jacobian matrix, is defined with elements

$$J_{nm}^i = \frac{\delta v_n^i}{\delta k_m^i} \quad \dots\dots 7.9$$

and dimension $d \times r$.

Substituting 7.8 in 7.7 and collecting the terms, the expression becomes

$$S^i = \begin{bmatrix} v^i - v^0 \end{bmatrix}^t W \begin{bmatrix} v^i - v^0 \end{bmatrix} + 2 \begin{bmatrix} v^i - v^0 \end{bmatrix}^t W J^i \begin{bmatrix} \Delta k^i \end{bmatrix} + \begin{bmatrix} \Delta k^i \end{bmatrix}^t J^{it} W J^i \begin{bmatrix} \Delta k^i \end{bmatrix} \quad \dots\dots 7.10$$

If S^i is minimum

$$\frac{\delta S^i}{\delta \Delta k^i} = 0 = 2 \begin{bmatrix} v^i - v^0 \end{bmatrix}^t W J^i + 2 \begin{bmatrix} \Delta k^i \end{bmatrix}^t J^{it} W J^i \quad \dots\dots 7.11$$

Transposing the terms we have

$$\Delta k^i = (J^{it} W J^i)^{-1} J^{it} W \begin{bmatrix} X^i \end{bmatrix} \quad \dots\dots 7.12$$

where $\begin{bmatrix} X^i \end{bmatrix} = \begin{bmatrix} v^i - v^0 \end{bmatrix}$

Then $\begin{bmatrix} \Delta k^i \end{bmatrix}$ values determined from 7.12 are used to form a new set of force constants.

The vector $\begin{bmatrix} X^i \end{bmatrix}$ is easily constructed from the differences between the experimental frequencies and the calculated frequencies from the i th set of force constants.

The elements of the diagonal matrix W are usually taken to be $1/(v_n^0)^2$ in order to ensure that the frequencies are fitted on a percentage rather than an absolute basis.

7.3 Method of obtaining the Jacobian matrix for the least squares method

There are two methods of determining the Jacobian elements.

1st method

The first method was suggested by Mann, Shimanouchi, Meal and

Fano (24). They calculated the Jacobian matrix by making a successive variation of each force constant in turn, followed by repeated calculation of the frequencies. In this method it is necessary that the force constants of the first set are not very far from the final values. This means that the adjustments are in the nature of refinements rather than gross changes. The Jacobian matrix is constructed in the following way.

Let the first set of force constants be the i th set. The $(i + 1)$ th set of force constants can be obtained by giving a small increment $0.01 \text{ md/\AA}^0$ to one of the r force constants. Both sets are then used to calculate the s fundamental frequencies. Thus, a column of the Jacobian matrix is obtained by

$$[J] = \frac{\Delta v_n^i}{\Delta k} = \frac{v_n^{i+1} - v_n^i}{\Delta k}$$

in which $\Delta k = 0.01 \text{ md/\AA}^0$.

The same increment is then given to each of the other force constants in turn. In this way all the $r \times s$ elements of the Jacobian matrix are obtained.

2nd method

The second method is described in Wilson, Decius and Cross (3), Overend and Scherer (25), Mills (68), and Steele (1).

This method gives the Jacobian elements in terms of the latent vectors L of the secular equation $|GF - I\lambda|L = 0$.

As mentioned before in equation 4.9 and 4.10

$$G = LL^t$$

..... 7.13

$$L^t_{FL} = A \quad \text{..... 7.14}$$

It is assumed that the change in the latent vectors are insignificant for small changes in the calculated frequencies, that is, Δv is quite small. A small correction ΔF is required to reduce the error in the calculated frequencies.

Let the error be given by

$$v_{cal} - v_{obs} = \Delta v$$

If we define

$$H = L^t_{\Delta FL} \quad \text{..... 7.15}$$

the secular determinant for the perturbed problem would have the form

$$\begin{vmatrix} \lambda^0_1 + H_{11} - \lambda & H_{12} & H_{13} & \dots & \dots & \dots \\ H_{21} & \lambda^0_2 + H_{22} - \lambda & H_{23} & \dots & \dots & \dots \\ H_{31} & H_{32} & \lambda^0_3 + H_{33} - \lambda & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots \end{vmatrix} = 0 \quad \text{..... 7.16}$$

The first order approximation to this would give the nth root as

$$\lambda_n = \lambda_n^0 + H_{tt} \quad \text{..... 7.17}$$

Substituting 7.15 into 7.17 we have

$$\lambda_n = \lambda_n^0 + \sum_{t', t''} l_{t'n} l_{t'n} \Delta F_{t' t''}$$

or
$$\Delta \lambda_n = \sum_{t', t''} l_{t'n} l_{t'n} \Delta F_{t' t''} \quad \text{..... 7.18}$$

If we define J as

$$J = \frac{\delta \lambda_n}{\delta F_{t' t''}}$$

we have

$$\frac{\delta \lambda_n}{\delta F_{t' t''}} = 2 l_{t'n} l_{t'n} \quad \text{..... 7.19}$$

and
$$\frac{\delta \lambda_n}{\delta F_{t' t'}} = l_{t'n} l_{t'n} \quad \text{..... 7.20}$$

where t' and t'' denote row and column numbers in F, and $l_{t'n}$ is the entry in the nth row of L_n .

Thus one row of the Jacobian matrix can be obtained by combinations of l_n elements, where l_n is the unperturbed vectors corresponding to the nth root. The complete Jacobian can be

constructed by taking combinations of elements of all $\mathbf{t}$ vectors by using equations 7.19 and 7.20.

7.4 A problem in the least squares method

Although the least squares method provides a convenient mathematical expression for a computer to handle, and also provides a new set of calculated frequencies which are quite close to the observed frequencies, there are still some difficulties that may occur in the calculation.

(a) It was assumed that the relationship between $\Delta\lambda$ and Δk is linear

$$\Delta\lambda = J\Delta k$$

This is not true in most cases and if the initial force constants are bad guesses, a bad fit will be obtained in the calculation.

(b) Singularity of the matrix $(J^t W J)$ is the other major problem. In the least squares method the force constant refinements are performed using the expression

$$\Delta k = (J^t W J)^{-1} J^t W [X]$$

The main part is the term $(J^t W J)$. If this matrix is singular, that is, $|J^t W J| = 0$, the problem is unresolvable. (This means that there is a set or sets of force constants which can be varied without affecting the vector $J^t W [X]$). When the matrix $(J^t W J)$ is nearly singular, errors may occur in taking its inverse, causing corresponding errors in the calculated force constant

correction (Δk). This also implies that the original $J = \Delta\lambda/\Delta k$ is ill conditioned, in other words the initial data do not suffice to fix the force field. The degree of singularity varies with the choice of the initial set of force constants.

It is possible to check how close the matrix is to singularity by looking at the product of its diagonal elements. If the product of its diagonal elements is much greater than the value of its determinant the matrix is close to being singular. If the two values are close together, the matrix is non-singular (123).

7.5 The uncertainties in the calculation

Uncertainties in the calculation may occur for the following reasons:-

- (1) The uncertainty caused by the experimental errors in measuring the frequencies which usually are only a few wave numbers from the true values.
- (2) The force field is only approximate, and so there must be a related uncertainty in the calculated frequencies.
- (3) The use of an harmonic force field to fit observed frequencies which have not been corrected for anharmonicity.
- (4) The uncertainty caused by the assumption of linearity in the relationship between $\Delta\lambda$ and Δk .

CHAPTER 8

INFRARED TRANSITIONS

8.1 Harmonic vibration selection rules

A transition with emission or absorption of radiation can occur between the vibrational states v' and v'' if one or more of the integrals $\int \psi_{v'}^* M_x \psi_{v''} d\tau_v$, $\int \psi_{v'}^* M_y \psi_{v''} d\tau_v$, $\int \psi_{v'}^* M_z \psi_{v''} d\tau_v$, is not zero.

In general the electric moment is not necessarily a linear function of the co-ordinates of the atoms, it can be expanded as a power series in the normal co-ordinates (2), (3).

$$M_x = M_x^0 + \sum_{k=1}^{3N-6} \left(\frac{\delta M_x}{\delta Q_k} \right)_0 Q_k + \text{higher terms} \quad \text{..... 8.1}$$

with similar equations describing M_y and M_z .

For the harmonic oscillator model the higher terms are assumed to be relatively small. Thus, M can be written as

$$M = M^0 + \sum_{k=1}^{3N-6} \left(\frac{\delta M}{\delta Q_k} \right)_0 Q_k \quad \text{..... 8.2}$$

In order that a vibrating mode shall interact with radiation it is necessary that the dipole moment should change during the vibration, i.e. $\frac{\delta M}{\delta Q_k} \neq 0$. This condition will hold if at least one

of the components $\frac{\delta M_x}{\delta Q_k}$, $\frac{\delta M_y}{\delta Q_k}$, or $\frac{\delta M_z}{\delta Q_k}$ along the co-ordinate axes

changes during the vibration. The integral for M_x becomes

$$\int \psi_{v'}^* M_X \psi_{v''} d\tau_v = M_X^0 \int \psi_{v'}^* \psi_{v''} d\tau_v + \sum_{k=1}^{3N-6} \left(\frac{\delta M_X}{\delta Q_k} \right)_0 \int \psi_{v'}^* Q_k \psi_{v''} d\tau_v \dots\dots 8.3$$

The first term vanishes unless $v' = v''$ because of orthogonality of the functions ψ_v . Therefore the permanent electric moment M^0 has no influence on the intensity of the vibrational transitions. The integral in the second term can be split into factors as shown below:-

$$\begin{aligned} \int \psi_{v'}^* Q_k \psi_{v''} d\tau_v &= \int \psi_{v'_1}^* (Q_1) \psi_{v''_1} (Q_1) dQ_1 \cdot \int \psi_{v'_2}^* (Q_2) \psi_{v''_2} (Q_2) dQ_2 \\ &\dots\dots \int \psi_{v'_k}^* (Q_k) Q_k \psi_{v''_k} (Q_k) dQ_k \dots\dots\dots \dots\dots 8.4. \end{aligned}$$

Because of the orthogonality of the functions $\psi_v(Q)$ the integral will vanish unless $v'_1 = v''_1, v'_2 = v''_2, \dots$ etc., with the exception of v'_k and v''_k . For these quantum numbers, it must be true that $v'_k = v''_k + 1$ or $v'_k = v''_k - 1$ if the factor $\int \psi_{v'_k}^* (Q_k) Q_k \psi_{v''_k} (Q_k) dQ_k$ is to be different from zero (3 pp 42 - 43).

So on the basis of an harmonic oscillator model the only vibrational transitions which occur with the emission or absorption or radiation are those in which only one quantum number is changed by one unit only. That is $\sum \Delta v = \pm 1$.

8.2 Anharmonicity

On the basis of the harmonic oscillator model only fundamentals should appear in the absorption or emission spectra. Not

all fundamentals are allowed but only those associated with normal modes of vibration which cause a change in the electric dipole moment of the molecule.

Experimentally, i.e. for some molecules, it is found that not only fundamentals appear, but also overtones and combinations with relatively weaker intensities. It is certain from the evidence that the harmonic oscillator approximation is not perfect, the actual behaviour of the particles is anharmonic.

There are two types of anharmonicity:

(1) Mechanical anharmonicity: This is dealing with the anharmonicity in the potential function. That is, the cubic, quartic and higher terms in the potential energy expression

$$V = \frac{1}{2} \sum_{j,k}^{3N-6} \left(\frac{\delta^2 V}{\delta Q_j \delta Q_k} \right)_0 Q_j Q_k + \text{higher terms} \quad \dots\dots 8.5$$

must be considered. These terms give rise to the occurrence of the overtones and combinations. So there must be a small correction to the frequencies for the anharmonicity. The factor itself could be of much interest in many cases, and correction for it will normally make only small changes of the order of a few per cent in the force constants (5).

(2) Electrical anharmonicity: This type of anharmonicity is concerned with the dipole moment expression.

$$M = M^0 + \sum_k^{3N-6} \left(\frac{\delta M}{\delta Q_k} \right)_0 Q_k + \text{higher terms} \quad \dots\dots 8.6$$

These higher terms also cause overtones and combinations to occur.

Thus, they should not be ignored.

Due to the anharmonic nature of vibration the harmonic selection rule, $\Delta v = \pm 1$, no longer holds, that is

$$\sum \Delta v = \pm 1, \pm 2, \pm 3, \dots \pm n \quad \text{..... 8.7}$$

and such overtones as appear may not be exactly integral multiples of the fundamental frequencies. Transitions which correspond to smaller value of $\sum \Delta v$ are generally more intense.

In order to be able to make a small correction for anharmonicity, it is necessary to have information not only on fundamentals, but also on overtone, combination and difference bands. Unfortunately, there is a great dearth of information on anharmonicity and only for a very limited number of polyatomic molecules can this correction be made.

As for oxalic acid the information is not enough to deal with anharmonicity we will assume that the particles behave as harmonic oscillators and neglect the small amount of correction in the frequencies for anharmonicity.

CHAPTER 9

RAMAN TRANSITIONS

9.1 Raman polarizability tensor

A Raman transition can occur only if the amplitude of the dipole moment induced by the incident radiation changes during the vibration considered.

For an isotropic molecule the magnitude of the induced dipole moment P is given by

$$P = \alpha E \quad \text{..... 9.1}$$

where α is the polarizability and E is the electric vector of the incident radiation of frequency ν .

In general, however, for an anisotropic molecule equation 9.1 must be replaced by the complete expression

$$\begin{aligned} P_x &= \alpha_{xx} E_x + \alpha_{xy} E_y + \alpha_{xz} E_z \\ P_y &= \alpha_{yx} E_x + \alpha_{yy} E_y + \alpha_{yz} E_z \\ P_z &= \alpha_{zx} E_x + \alpha_{zy} E_y + \alpha_{zz} E_z \end{aligned} \quad \text{..... 9.2}$$

in which the quantities α_{FF} , are independent of the components of the electric vector, but are dependent upon the orientation of the molecule relative to the non-rotating axes x, y, z . The quantities α_{FF} , are called the components of a tensor by virtue of their transformation under changes of the co-ordinate system (2), (3).

In general the direction of the induced dipole is not parallel to the direction of the incident electric field vector. It can be shown, however, that a set of axes in the molecule exists such that the relation between P and E when referred to these axes, assumes the simple form

$$\begin{aligned} P_1 &= \alpha_1 E_1 \\ P_2 &= \alpha_2 E_2 \\ P_3 &= \alpha_3 E_3 \end{aligned} \quad \text{..... 9.3}$$

Such axes are called the principal axes of polarizability and the associated α_i , $i = 1, 2, 3$, the principal values of the polarizability. For an isotropic case

$$\alpha_1 = \alpha_2 = \alpha_3 = \alpha$$

9.2 Expansion of the polarizability in the normal co-ordinates

The components of the polarizability have been assumed to be independent of the time. For a molecule executing small vibrations the polarizability may be expanded in terms of the normal co-ordinates

$$\alpha_i = \alpha_i^0 + \sum_k \left(\frac{\delta \alpha_i}{\delta Q_k} \right)_0 Q_k + \text{higher terms} \quad \text{..... 9.4}$$

$$\text{where } Q_k = Q_k^0 \cos(2\pi \nu_k t + \epsilon) \quad \text{..... 9.5}$$

in which Q_k^0 is the amplitude of the kth normal co-ordinate,

ν_k is the associated frequency and ϵ is the phase angle.

On applying equations 9.4 and 9.5 together with the expression for the oscillating electric vector

$$E_i = E_{oi} \cos 2\pi \nu_o t \quad \dots\dots 9.6$$

$$\text{into } P_i = \alpha_i E_i \quad \dots\dots 9.7$$

the corresponding component of the oscillating induced dipole moment P_i would, therefore, be of the form

$$P_i = E_{oi} \left[\alpha_i^0 \cos 2\pi \nu_o t + \sum_k \left(\frac{\delta \alpha_i}{\delta Q_k} \right)_0 Q_k^0 \{ \frac{1}{2} \cos 2\pi (\nu_o + \nu_k) t + \frac{1}{2} \cos 2\pi (\nu_o - \nu_k) t \} + \text{higher terms} \right] \quad \dots\dots 9.8$$

Here ν_o is the incident or the Rayleigh frequency and $\nu_o \pm \nu_k$ is the Raman frequency.

The higher terms in the polarizability expansion leads to overtones and combinations, in a fashion similar to the infrared transitions.

9.3 Degree of depolarization

Fig. 6

Schematic representation of experimental conditions

defining $I_{\perp}$ and $I_{\parallel}$

Here the y axis is taken in the direction of propagation of the incident light, z is the direction of the electric vector E of the incident radiation, and x is the direction of the observation.

The degree of depolarization ρ is defined as the ratio of the intensity of the scattered light polarized perpendicular to the incident electric vector E , called $I_{\perp}$, to that polarized parallel to E , called $I_{\parallel}$.

$$\rho = \frac{I_{\perp}}{I_{\parallel}} \quad \text{..... 9.9}$$

In liquid and gas phases the polarizability can be averaged over all orientations of the system (3 p.46). Thus, when the linear polarized incident light is used and the observations are made in a direction perpendicular to the electric vector E , the degree of depolarization is

$$\rho_L = \frac{3\beta^2}{45\alpha^2 + 4\beta^2} \quad \text{..... 9.10}$$

where α is the spherical part of polarizability and β is the anisotropic part, which are defined by

$$\alpha = \frac{1}{3}(\alpha_1 + \alpha_2 + \alpha_3) \quad \text{..... 9.11}$$

$$\beta^2 = \frac{1}{2}[(\alpha_1 - \alpha_2)^2 + (\alpha_2 - \alpha_3)^2 + (\alpha_3 - \alpha_1)^2] \quad \text{..... 9.12}$$

If $\beta = 0$, $\rho_L = 0$

If $\alpha = 0$, and $\beta \neq 0$, $\rho_L^{\max} = \frac{3}{4}$

Thus, for a linear polarized incident beam when the degree of depolarization is $\frac{3}{4}$, it is called depolarized. If the degree of depolarization is smaller than $\frac{3}{4}$, it is said to be polarized (partly or completely).

Measurements of the degree of depolarization are very useful for the assignment of the Raman bands. This is because only the Raman bands corresponding to totally symmetric vibrations can have a degree of depolarization smaller than $\frac{3}{4}$, that is, can be polarized (2).

9.4 Raman selection rules

A transition in the Raman spectrum can occur between two vibrational states v' and v'' only if at least one of the integrals

$$\begin{aligned} \int \psi_{v'}^* P_x \psi_{v''} d\tau_v \\ \int \psi_{v'}^* P_y \psi_{v''} d\tau_v \\ \int \psi_{v'}^* P_z \psi_{v''} d\tau_v \end{aligned} \quad \dots\dots 9.13$$

is not zero where v'' and v' represent lower and upper vibrational states, $\psi_{v'}^*$ represents the complex conjugate of the vibrational wave function of the lower state. P_x , P_y and P_z are the components of the induced dipole moment along x, y and z axes respectively. Each of the components of the induced dipole moment depends not only on one component of the incident electric vector but on all x, y and z components as shown in equation 9.2.

Every one of the six components of polarizability in general changes when the nuclei are displaced from their equilibrium

positions. For small displacements the polarizability can be expanded as

$$\alpha_{xx} = \alpha_{xx}^0 + \left(\frac{\delta \alpha_{xx}}{\delta Q_i} \right)_0 Q_i + \text{higher terms} \quad \dots\dots 9.14$$

similarly for α_{yy} , α_{zz} , α_{xy} , α_{xz} & α_{yz} . The incident electric vectors may be written as

$$\begin{aligned} E_x &= E_x^0 \cos 2\pi \nu t \\ E_y &= E_y^0 \cos 2\pi \nu t \\ E_z &= E_z^0 \cos 2\pi \nu t \end{aligned} \quad \dots\dots 9.15$$

On applying equations 9.14 and 9.15 to equation 9.2, it becomes

$$\begin{aligned} P_x &= (\alpha_{xx} E_x^0 + \alpha_{xy} E_y^0 + \alpha_{xz} E_z^0) \cos 2\pi \nu t + \sum \left[\left(\frac{\delta \alpha_{xx}}{\delta Q_i} \right)_0 E_x^0 + \right. \\ &\quad \left. \left(\frac{\delta \alpha_{xy}}{\delta Q_i} \right)_0 E_y^0 + \left(\frac{\delta \alpha_{xz}}{\delta Q_i} \right)_0 E_z^0 \right] Q_i^0 \times \frac{1}{2} \left[\cos 2\pi(\nu + \nu_i)t + \right. \\ &\quad \left. \cos 2\pi(\nu - \nu_i)t \right] + \text{higher terms} \quad \dots\dots 9.16 \end{aligned}$$

and similarly for P_y and P_z . That is, the induced dipole moment oscillates with the frequency ν of the incident radiation leading to Rayleigh scattering, and with frequency $\nu \pm \nu_i$, leading to the Raman scattering. Thus, a transition will appear in the Raman

spectrum if and only if at least one of the six components of the

change of polarizability $\left(\frac{\delta \alpha_{xx}}{\delta Q_i} \right)_0$, $\left(\frac{\delta \alpha_{yy}}{\delta Q_i} \right)_0$, $\left(\frac{\delta \alpha_{zz}}{\delta Q_i} \right)_0$, $\left(\frac{\delta \alpha_{xy}}{\delta Q_i} \right)_0$, $\left(\frac{\delta \alpha_{xz}}{\delta Q_i} \right)_0$ and $\left(\frac{\delta \alpha_{yz}}{\delta Q_i} \right)_0$ is different from zero.

As in infrared, if we assume that the molecule behaves as an harmonic oscillator, the selection rule is

$$\Delta V = \pm 1$$

That is, only fundamentals are allowed.

Experimentally it is found that the fundamentals are usually most intense but other transitions such as overtones and combinations also appear. This suggests that the harmonic oscillator approximation is not perfect, the actual behaviour of the molecule is anharmonic.

As in infrared spectra, both mechanical and electrical anharmonicity account for overtone and combination bands. The anharmonic selection rule is

$$\Delta V = \pm 1, \pm 2, \dots$$

CHAPTER 10

ENERGY LEVELS OF ASYMMETRIC TOP MOLECULES

10.1 Rotational energy levels of asymmetric top molecules

According to quantum mechanics, the energy levels of asymmetric top molecules cannot be represented by an explicit formula analogous to that for the symmetric top. There are $J + 1$ sublevels of different energy for a symmetric top molecule for each value of J , namely those with $K = 0, 1, 2 \dots J$, of which all but one ($K = 0$) are doubly degenerate with respect to the directions of rotation. For an asymmetric top molecule this degeneracy is removed, thus, for each value of J there are $2J + 1$ different energy levels. This splitting may be called K -type doubling. Each energy level is distinguished by a subscript T added to J such that T takes the values

$$T = -J, -J + 1, \dots +J \quad \text{..... 10.1}$$

It is assumed that for the lowest level in the group $T = -J$, for the next level $T = -J + 1$, and so on.

The three principal moments of inertia of an asymmetric top are I_A , I_B , and I_C in which $I_A < I_B < I_C$. The rotational constants in which the vibrational influence is taken into account can be expressed as follows:-

$$\begin{aligned} A_v &= A_e - \sum_i \alpha_i^{(A)} \left(v_i + \frac{d_i}{2} \right) \\ B_v &= A_e - \sum_i \alpha_i^{(B)} \left(v_i + \frac{d_i}{2} \right) \\ C_v &= A_e - \sum_i \alpha_i^{(C)} \left(v_i + \frac{d_i}{2} \right) \end{aligned} \quad \text{..... 10.2}$$

The respective α_i are small compared to the rotational constants for the equilibrium position.

$$A_e = \frac{h}{8\pi^2 c I_A^{(e)}}$$

$$B_e = \frac{h}{8\pi^2 c I_B^{(e)}}$$

$$C_e = \frac{h}{8\pi^2 c I_C^{(e)}}$$

There is no direct method of getting the energy levels of the asymmetric top molecule. An approximate illustration of the energy levels of the asymmetric top molecule is given by connecting with smooth curves the two limiting cases of the symmetric top molecule (2). One in which $I_B = I_C$ (prolate) and the other in which $I_B = I_A$ (oblate). By letting I_B decrease gradually from $I_B = I_C$ to $I_B = I_A$ we expect to find a continuous change of the energy levels.

Fig. 7 - Energy levels of the asymmetric top; correlation to those of symmetric tops

The diagram in Fig. 7 taken from Herzberg (2 page 45) shows the approximate energy levels of asymmetric top molecules obtained by joining by smooth curves the levels of a given J on the right, without intersection for low values of J, with the levels of the same J on the left.

In 1929 Wang (102) has shown that the splitting (K-type) increases with increasing J but much less rapidly for the higher K values. Furthermore, the average of the levels of the same K deviates from a horizontal, that is, does not follow exactly $\frac{1}{2}(B + C)J(J + 1)$. The average of all levels with a certain J follows accurately the formula

$$\frac{\sum F(J_T)}{2J + 1} = \frac{1}{3}(A + B + C)J(J + 1) \quad \dots\dots 10.3$$

This relation is very useful in checking the calculated levels and the correct assignment of the observed levels.

Fig. 8 - Rotational energy of a slightly asymmetric top (b about 0.01) as a function of J (after Dieke and Kistiakowsky (127)) - The term $\frac{1}{2}(B + C)J(J + 1)$ is subtracted from the energy, that is, the deviations of the curves from horizontal lines represent the deviations from the levels of the symmetric top. (2 page 49)

10.2 Quantitative formulae for the energy levels

The quantitative formulae of the energy levels of the asymmetric top molecule have been determined by many authors. Among them two have been used in numerical calculations. The first one which is due to Wang (102) is

$$F(J_T) = \frac{1}{2}(B + C)J(J + 1) + \left(A - \frac{1}{2}(B + C) \right) W_T \quad \text{..... 10.4}$$

The second one, due to Ray (120) as corrected by King, Hainer and Cross (121) is

$$F(J_T) = \frac{1}{2}(A + C)J(J + 1) + \frac{1}{2}(A - C)E_T \quad \text{..... 10.5}$$

The $(2J + 1)$ values of W_T or E_T for a given J are the roots of a secular determinant of degree $(2J + 1)$. Fortunately this determinant can be factored into a number of determinants of smaller degree leading to a number of algebraic equations. The values of W_T or E_T have been calculated for at least up to $J = 40$ (14).

For a given J

$$E_T(K) = E_{-T}(-K)$$

So Ray's equation is preferable because it is only needed to calculate the energy levels on one side of the most asymmetric

case ($K = 0$). Those on the other side are then immediately given.

10.3 Symmetry properties of the total wave function

In quantum mechanics, according to the Born-Oppenheimer approximation the total wave function for a molecule can be expressed as a product of functions of various co-ordinates,

$$\Psi = \psi_E \psi_v \psi_R \psi_T \psi_n \quad \dots\dots\dots 10.6$$

where the subscripts E, v, R, T, n represent electronic, vibrational, rotational, translational, and nuclear spin co-ordinates respectively. Since the translational function ψ_T does not involve the internal co-ordinates it is therefore neglected. For most stable molecules the electronic ground state is totally symmetric (7 p.129). Hence, in such a case, the symmetry of the total wave function Ψ may be obtained by finding the symmetry of ψ_v , ψ_R , and ψ_n separately and then taking the direct product of their irreducible components.

Symmetry properties of the vibrational wave function

Since the vibrational eigenfunction is a function of the normal co-ordinates, its behaviour with respect to symmetry operations depends upon the behaviour of the normal co-ordinates with respect to the symmetry operations. Both the normal co-ordinates and the vibrational wavefunctions have symmetry properties corresponding to the various irreducible representations of the symmetry point group for the molecule. Thus, the

symmetry of the wavefunctions can be explained using group theory.

For every molecule the vibrational ground state is totally symmetric and non-degenerate. The fundamental wavefunction belongs to the same symmetry species as the normal co-ordinates. For non-degenerate vibrations symmetry species of the n overtones may be obtained from the direct product of the irreducible representation of the corresponding fundamental taken $(n + 1)$ times. That is, if n is odd the wavefunction is totally symmetric, if n is even its symmetry species will be the same as the fundamental wavefunction. Symmetry of the combination and difference wavefunctions can also be taken from the direct product of the irreducible representations of all the fundamental components in that level.

Symmetry properties of the rotational wave function of asymmetric top molecules

For planar asymmetric top molecules there is no inversion doubling (2). The asymmetric top rotor functions are distinguished by their behaviour with respect to rotation by 180° , C_2^a , C_2^b , C_2^c , about the three principal axes (7).

For a rotation by 180° about the axis of largest moment of inertia (c axis) in a totally symmetric vibrational and electronic ground state the largest level J_{+J} of each set of a given J is +ve, the two next highest are -ve, the two next +ve, and so on.

For a rotation by 180° about the axis of smallest moment of inertia (a axis) in a totally symmetrical vibrational and electronic ground state, the lowest level J_{-J} of each set of a

given J is +ve, the two next higher are -ve, the next two +ve, and so on.

The symmetry of the rotational energy levels with respect to a rotation by 180° about the axis of intermediate moment of inertia (b axis) in a totally symmetrical vibrational and electronic ground state can be easily found from the product of the two signs (one belongs to the rotation about c axis, the other belongs to rotation about a axis) for each energy level.

Thus, the symmetry of the rotational energy levels of an asymmetric top molecule may be distinguished by their behaviour + or - with respect to the three operation, C_2^a , C_2^b , C_2^c . Since one of these operations is equivalent to the other two carried out in succession, it is sufficient to determine the behaviour with respect to two of them; usually C_2^c and C_2^a are chosen. Therefore there are four different types of levels briefly described by ++, +-, -+, and -- where the first sign refers to the behaviour with respect to C_2^c , the second to the behaviour with respect to C_2^a .

Symmetry properties of nuclear spin wave function and statistical weight

In those molecules in which an exchange of identical nuclei can be brought about by a rotation about one of the principal axes, the total eigenfunction must be symmetric (Bose-Einstein statistics) or antisymmetric (Fermi-Dirac statistics) with respect to an exchange of the identical nuclei.

In cases where there is only one pair of identical nuclei to exchange, the number of the symmetric nuclear spin wave functions is $(2I + 1)(I + 1)$, and the number of the antisymmetric nuclear spin wave functions is $(2I + 1)I$. Altogether there is a total of $(2I + 1)^2$ nuclear spin wave functions (18).

In cases of molecules in which there are more than one pair of identical nuclei that are exchanged by a rotation about a two-fold axis, the resultant statistics must be considered. In general, the number of the symmetric nuclear spin wave function can be derived from the expression

$$\frac{1}{2} \left[(2I_x + 1)^2 (2I_y + 1)^2 (2I_z + 1)^2 \dots + (2I_x + 1)(2I_y + 1)(2I_z + 1) \dots \right] \quad \text{..... 10.7}$$

and the number of the antisymmetric nuclear spin wave functions can be derived from

$$\frac{1}{2} \left[(2I_x + 1)^2 (2I_y + 1)^2 (2I_z + 1)^2 \dots - (2I_x + 1)(2I_y + 1)(2I_z + 1) \dots \right] \quad \text{..... 10.8}$$

where $I_x, I_y, I_z \dots$ are the nuclear spin of each pair of identical nuclei that are exchanged by a rotation of 180° . The resultant statistics is Bose statistics if there is an even number of nuclei following Fermi statistics in the group (XYZ . . .), it is Fermi statistics if there is an odd number of nuclei following Fermi statistics (2).

If all exchanged nuclei have zero spin, only those levels occur where the total eigenfunction is symmetric with respect to an exchange of identical nuclei, that is, for a totally symmetric electronic and vibrational state the antisymmetric rotational levels are missing.

For an asymmetric top molecule of point group C_{2h} with more than one pair of identical nuclei that are exchanged by a rotation about the two-fold axis, the above symmetry properties apply when C_2 coincides with one of the three axes. Which levels have the greater statistical weight depends on the resultant statistics.

For gaseous oxalic acid there are four pairs of identical nuclei that are exchanged by a rotation of 180° about the z axis (symmetry axis). All exchanged nuclei have spin zero except that of hydrogen with $\frac{1}{2}$ spin quantum number. Thus, it is assumed that the resultant statistics is Fermi statistics. On applying 10.7 and 10.8 together with the Fermi statistics the ratio of the statistical weight of the symmetric and antisymmetric rotational levels is $\frac{1}{3}$.

10.4 The energy level diagram of the asymmetric top molecule in the C_{2h} point group

The rotational energy levels of the asymmetric top molecule in the C_{2h} point group may be distinguished by A (symmetric) or B (antisymmetric) with respect to a rotation by 180° , that is, by their behaviour + or - with respect to the same rotation (2).

If C_2 coincides with the axis of the largest moment of inertia, the rotational levels ++ and +- are A, and the levels -+ and -- are B respectively.

If C_2 coincides with the axis of the intermediate moment of inertia, the rotational levels ++, and -- are A and the levels +- and -+ are B respectively.

If C_2 coincides with the axis of the smallest moment of inertia, the rotation levels ++ and -+ are A and the levels +- and -- are B respectively. Here the ++, +-, -+ and -- levels have the same meaning as previously.

The rovibronic species may be obtained by

- (1) the multiplication rules, which for point group C_{2h} are

$$A \times A = A$$

$$A \times B = B \times A = B$$

$$B \times B = A$$

- (2) adding the subscript g or u into the rotational sub-group, depending on whether the vibronic state is g or u (7).

Figs. 9 and 10 illustrate the energy levels of the asymmetric top molecule in the C_{2h} point group (i.e. gaseous oxalic acid) when C_2 coincides with the axis of largest moment of inertia. The first signs of the rotational levels (++, +-, -+, --) gives for planar molecules the 'parity', the behaviour with respect to the inversion, for vibrational states that are symmetric with respect to the plane of the molecule (Ag and Bg). For vibrational states that are antisymmetric with respect to this plane (Au, Bu) the parities are reversed. In these diagrams it is assumed that

- (a) the electronic ground state is totally symmetric,
- (b) the resultant statistics is Fermi statistics.

	ψ_R	$\psi_R \psi_V$	ψ_n	ψ
4_{+4} ————— $++$	A	A	B	B
4_{+3} ————— $++$	B	B	A	B
4_{+2} ————— $--$	B	B	A	B
4_{+1} ————— $+-$	A	A	B	B
4_0 ————— $++$	A	A	B	B
4_{-1} ————— $--$	B	B	A	B
4_{-2} ————— $--$	B	B	A	B
4_{-3} ————— $+-$	A	A	B	B
4_{-4} ————— $++$	A	A	B	B
3_{+3} ————— $+-$				
3_{+2} ————— $--$				
3_{+1} ————— $--$	B	B	A	B
3_0 ————— $++$	A	A	B	B
3_{-1} ————— $+-$	A	A	B	B
3_{-2} ————— $--$	B	B	A	B
3_{-3} ————— $+-$	B	B	A	B
2_{+2} ————— $++$	A	A	B	B
2_{+1} ————— $+-$	B	B	A	B
2_0 ————— $--$	B	B	A	B
2_{-1} ————— $+-$	A	A	B	B
2_{-2} ————— $++$	A	A	B	B
1_{+1} ————— $+-$	A	A	B	B
1_0 ————— $--$	B	B	A	B
1_{-1} ————— $--$	B	B	A	B
0_0 ————— $++$	A	A	B	B

A vibrational level

Fig. 9 - the rotational energy levels for Ag and Au vibrational levels of a C_{2h} molecule when C_2 coincides with the axis of largest moment of inertia

	ψ_R	ψ_{RV}	ψ_n	ψ
$4_{+4} = \text{=====} \begin{smallmatrix} + \\ + \end{smallmatrix}$ $4_{+3} = \text{=====} \begin{smallmatrix} - \\ + \end{smallmatrix}$	$\begin{smallmatrix} A \\ B \end{smallmatrix}$	$\begin{smallmatrix} B \\ A \end{smallmatrix}$	$\begin{smallmatrix} A \\ B \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \end{smallmatrix}$
$4_{+2} = \text{=====} \begin{smallmatrix} - \\ - \end{smallmatrix}$ $4_{+1} = \text{=====} \begin{smallmatrix} + \\ - \end{smallmatrix}$	$\begin{smallmatrix} B \\ A \end{smallmatrix}$	$\begin{smallmatrix} A \\ B \end{smallmatrix}$	$\begin{smallmatrix} B \\ A \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \end{smallmatrix}$
$4_0 = \text{=====} \begin{smallmatrix} + \\ + \end{smallmatrix}$	A	B	A	B
$4_{-1} = \text{=====} \begin{smallmatrix} - \\ + \end{smallmatrix}$ $4_{-2} = \text{=====} \begin{smallmatrix} - \\ - \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \end{smallmatrix}$	$\begin{smallmatrix} A \\ A \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \end{smallmatrix}$
$4_{-3} = \text{=====} \begin{smallmatrix} + \\ - \end{smallmatrix}$ $4_{-4} = \text{=====} \begin{smallmatrix} + \\ + \end{smallmatrix}$ $3_{+3} = \text{=====} \begin{smallmatrix} + \\ - \end{smallmatrix}$ $3_{+2} = \text{=====} \begin{smallmatrix} - \\ - \end{smallmatrix}$	$\begin{smallmatrix} A \\ A \\ A \\ B \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \\ B \\ A \end{smallmatrix}$	$\begin{smallmatrix} A \\ A \\ A \\ B \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \\ B \\ B \end{smallmatrix}$
$3_{+1} = \text{=====} \begin{smallmatrix} - \\ + \end{smallmatrix}$ $3_0 = \text{=====} \begin{smallmatrix} + \\ + \end{smallmatrix}$ $3_{-1} = \text{=====} \begin{smallmatrix} + \\ - \end{smallmatrix}$	$\begin{smallmatrix} B \\ A \\ A \end{smallmatrix}$	$\begin{smallmatrix} A \\ B \\ B \end{smallmatrix}$	$\begin{smallmatrix} B \\ A \\ A \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \\ B \end{smallmatrix}$
$3_{-2} = \text{=====} \begin{smallmatrix} - \\ - \end{smallmatrix}$ $3_{-3} = \text{=====} \begin{smallmatrix} - \\ + \end{smallmatrix}$ $2_{+2} = \text{=====} \begin{smallmatrix} + \\ + \end{smallmatrix}$ $2_{+1} = \text{=====} \begin{smallmatrix} - \\ + \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \\ A \\ B \end{smallmatrix}$	$\begin{smallmatrix} A \\ A \\ B \\ A \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \\ A \\ B \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \\ B \\ B \end{smallmatrix}$
$2_0 = \text{=====} \begin{smallmatrix} - \\ - \end{smallmatrix}$	B	A	B	B
$2_{-1} = \text{=====} \begin{smallmatrix} + \\ - \end{smallmatrix}$ $2_{-2} = \text{=====} \begin{smallmatrix} + \\ + \end{smallmatrix}$ $1_{+1} = \text{=====} \begin{smallmatrix} + \\ - \end{smallmatrix}$ $1_0 = \text{=====} \begin{smallmatrix} - \\ - \end{smallmatrix}$ $1_{-1} = \text{=====} \begin{smallmatrix} - \\ + \end{smallmatrix}$ $0_0 = \text{=====} \begin{smallmatrix} + \\ + \end{smallmatrix}$	$\begin{smallmatrix} A \\ A \\ A \\ B \\ B \\ A \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \\ B \\ A \\ A \\ B \end{smallmatrix}$	$\begin{smallmatrix} A \\ A \\ A \\ B \\ B \\ A \end{smallmatrix}$	$\begin{smallmatrix} B \\ B \\ B \\ B \\ B \\ B \end{smallmatrix}$

B vibrational level

Fig. 10 - the rotational energy levels for the Bg and Bu vibrational levels of a C_{2h} molecule when C₂ coincides with the axis of largest moment of inertia

CHAPTER 11

ROTATION-VIBRATION SELECTION RULES FOR

ASYMMETRIC TOP MOLECULES

11.1 Infrared rotation-vibration selection rules of asymmetric top molecules

The infrared rotation-vibration selection rules are assumed to be the same as those for rotation and vibration separately, except that it is now the direction of the change of dipole moment during the vibration that matters for the rotational selection rules (2). Thus, the selection rules are

$$\Delta v = \pm 1, \pm 2, \dots \dots \dots \pm n$$

$$\Delta J = 0, \pm 1; \quad J = 0 \leftarrow \text{---} \rightarrow J = 0$$

Furthermore, the selection rules for asymmetric top molecules are different for the different orientations of the transition moment.

If the transition moment lies in the axis of least moment of inertia (A-type band), only the transitions

$$++ \longleftrightarrow --, \quad +- \longleftrightarrow +-$$

can take place.

If the transition moment lies in the axis of intermediate moment of inertia (B-type band), only the transitions

$$++ \longleftrightarrow --, \quad +- \longleftrightarrow +-$$

can take place.

If the transition moment lies in the axis of largest moment of inertia (C-type band), only the transitions

can take place.

If the transition moments do not lie along any axis of moment of inertia, that is, it has more than one component along the principal axes, that transition will give rise to a hybrid band. Thus, a hybrid band consists of a superposition of two or all three of A-, B-, and C- types. The relative intensity contributions in a hybrid band depend upon the square of the dipole moment components along the inertial axes.

11.2 Theoretical infrared band envelopes of asymmetric rotator molecules

For polyatomic molecules the resolution and the analysis of the rotational structure of the infrared bands appear to be rather limited. The structure of the unresolved bands of asymmetric top molecules has been studied in great detail by many authors.

The first paper was published in 1938 by Badger and Zumwalt (26). They carried out calculations concerning the band envelopes of asymmetric top molecules. Three types of bands, A, B, C, corresponding to the transitions in which the dipole moments lie along the minor, intermediate and major axes respectively, were calculated and drawn for different sets of parameter ρ ($= \frac{1}{3}, \frac{1}{2}, \frac{3}{4}$ and $\frac{5}{4}$) and S ($= \frac{1}{2}, 0, +\frac{1}{2}$) where $\rho = \frac{A - C}{B}$ and $S = \frac{2B - A - C}{A - C}$.

The second paper was published by Varsanyi (112) in 1959 on the band contours of the infrared vapour spectra of some dihalogenobenzene molecules. He had reported an approximate procedure for determining band contours and also applied it with success in analysing contours of bands in the infrared spectra of 1,3 difluorobenzene, o-bromo-fluorobenzene and m-bromo-fluorobenzene.

The third paper was published by Parkin (69) in 1965. A computer program was developed to save the computer time and also allow the computer to accommodate a much larger scale problem. This program calculated the frequencies and intensities of a band for a molecule with any degree of asymmetry in either of the combining states, and integrated these lines into a contour which was printed out from the computer in a direct usable form. The integrated envelope of the band was computed from assumed molecular constants. It was then compared with the observed contour, and then the constants were modified until a sufficiently good fit was obtained.

The fourth paper was published by Seth Paul and Dijkstra (55) on calculations of PR separations for both symmetric top and asymmetric top molecules. A few useful expressions and tables of variable parameters were given. The calculated PR separation of 87 molecules together with their observed values were also given in this paper.

Seth Paul also published 2 more papers in 1968. One of them published by himself (126) was a review paper on calculations

of PR separations for all kinds of molecules. The other paper was published by him and Meyer (125) on the calculation of PR separations of hybrid bands in vapour phase infrared spectra.

The last paper was published in 1968 by Ueda and Shimanouchi (71). The program for the calculation of the band envelopes of asymmetric top molecules that they used was similar to that of Parkin. The A, B and C types envelopes were calculated for 40 typical molecules and were presented in this paper in graphical form. This is currently the most useful set of calculations available.

11.3 Raman rotation-vibration selection rules for the asymmetric top molecules

The Raman rotation-vibration selection rules for asymmetric top molecules have been derived by Placzek and Teller (122). The vibrational selection rules are the same as discussed before. The rotational selection rules are

$$\Delta J = 0, \pm 1, \pm 2 \quad (J' + J'' \geq 2)$$

' and '' indicate the initial and final states. All transitions between various rotational levels of the two vibrational states that obey these rules are possible.

Furthermore, we have additional selection rules which depend on the components of the polarizability that are not zero for the particular vibrational transition. Let x, y, z be the a, b, c axes respectively.

Generally, if the magnitude of at least one of $\left[\alpha_{xx}\right]^{nm}$, $\left[\alpha_{yy}\right]^{nm}$, and $\left[\alpha_{zz}\right]^{nm}$ are not zero, the transitions in which

$$++ \longleftrightarrow ++, +- \longleftrightarrow +-, -+ \longleftrightarrow -+, -- \longleftrightarrow --$$

are allowed.

If the magnitude of $\left[\alpha_{xy}\right]^{nm}$ is not zero, the transitions in which

$$++ \longleftrightarrow +-, -+ \longleftrightarrow --$$

are allowed.

If the magnitude of $\left[\alpha_{xz}\right]^{nm}$ is not zero, the transitions in which

$$++ \longleftrightarrow --, +- \longleftrightarrow -+$$

are allowed.

If the magnitude of $\left[\alpha_{yz}\right]^{nm}$ is not zero, the transitions in which

$$++ \longleftrightarrow -+, +- \longleftrightarrow --$$

are allowed.

For the totally symmetric Raman bands the transitions between the rotational levels of the same symmetry species of the two vibrational states are allowed. Since the rotational constants in the upper and the lower states are very nearly the same and the transitions in which $\Delta J = 0$ is possible, it is obvious that a large number of lines of the Q branch will coincide near the band origin. This sharp strong central maximum will in general be the only feature that is observed.

For non-totally symmetric Raman bands the transitions between the rotational levels of different symmetry species of the two vibrational states are allowed. Therefore, the lines of the Q branch do not, in general, coincide at the origin. Whether the bands form a central maximum or not depends on the asymmetry of the molecule and on the polarizability of the molecule. The three cases in which $[\alpha_{xy}]^{nm} \neq 0$, $[\alpha_{xz}]^{nm} \neq 0$, and $[\alpha_{yz}]^{nm} \neq 0$ are comparable with C-type, B-type, and A-type bands in infrared, except for the additional transitions $\Delta J = \pm 2$. In general the bands with $[\alpha_{xz}]^{nm} \neq 0$ will have a central maximum, the other non-totally symmetric Raman bands will not have such a sharp central maximum of outstanding intensity as to the totally symmetric Raman bands, but will be more or less broad.

The observation of the width of Raman lines gives a very significant way of observation of their state of polarization. In the case when a degree of depolarization of $\frac{1}{2}$ is observed for a Raman line it is probable, but not certain, that it corresponds to a non-totally symmetric vibration, the observation

of the line-width would confirm the assignment. On the other hand, if the line is sharp, only the ones for which the degree of depolarization is less than $\frac{1}{2}$ will be a totally symmetric Raman lines (2).

CHAPTER 12

VIBRATIONAL MODES OF OXALIC ACID AND REVIEW

OF PREVIOUS WORK

12.1 Vibrational modes of gaseous oxalic acid

Gaseous oxalic acid is a trans-planar molecule. It contains a centre of symmetry, a mirror plane (σ_h), and a two-fold axis of rotation. Thus, it is classified in C_{2h} point group.

Table 3

C_{2h}	E	C_2	i	σ_h		
Ag	1	1	1	1	R_z	x^2, y^2, z^2, xy
Bg	1	-1	1	-1	R_x, R_y	xz, yz
Au	1	1	-1	-1	T_z	
Bu	1	-1	-1	1	T_x, T_y	

Being an eight atomic molecule, the gaseous oxalic acid has 18 fundamental modes of vibration.

Table 4

C_{2h}	E	$C_2(z)$	i	$\sigma(xy)$
Γ_{total}	24	0	0	8
$\Gamma_{\text{trans.}}$	3	-1	-3	1
Γ_{rot}	3	-1	3	-1
$\Gamma_{\text{vib.}}$	18	2	0	8
$\Gamma_{\text{vib.}} = 7Ag + 2Bg + 3Au + 6Bu$				

Table 4 shows the symmetry species of the modes of vibration of gaseous oxalic acid as obtained by group theory. All atoms are in the xy plane and z is the two-fold axis.

Applying the rule of mutual exclusion it is not expected to see Raman fundamentals in the infrared spectrum, and vice versa. The types of vibration and activity are shown in Table 5.

Table 5

Species	Number	Type	Activity
Ag	7	in plane	Raman
Bg	2	out of plane	Raman
Au	3	out of plane	Infrared
Bu	6	in plane	Infrared

12.2 Review of previous work on gaseous oxalic acid

One paper on gaseous oxalic acid was published before this work started by Pava and Stafford (98). The infrared spectrum was recorded between 4000 cm^{-1} to 400 cm^{-1} . Only 4 gaseous oxalic acid bands were observed at 3485 cm^{-1} , 1820 cm^{-1} , 1325 cm^{-1} , and 1240 cm^{-1} at temperatures between 110° - 140°C . No gaseous oxalic acid bands were observed between 1000 cm^{-1} to 400 cm^{-1} . All observed frequencies agree well with the present work except the band at 1240 cm^{-1} which was observed at 1275 cm^{-1} in my work. A spectrum of deuterated oxalic acid was also recorded at approximately the same temperature and was presented in their paper.

Three bands of deuterated oxalic acid were observed at 2575 cm^{-1} , 1810 cm^{-1} , and 1220 cm^{-1} respectively. Assignment of two bands, O - H stretch and C = O stretch, were made without any calculation. It was reported that spectra of gaseous oxalic acid and deuterated oxalic acid were first observed at approximately 105°C .

According to their work the spectrum of gaseous oxalic acid recorded was subject to interference not only by solid oxalic acid from the condensation process, but also by the high background caused by decomposition products.

Table 6
Infrared absorption frequencies of gaseous oxalic acid
and deuterated oxalic acid observed by
Pava and Stafford

<u>Frequency cm^{-1}</u>		Assignment
Oxalic acid	Deuterated oxalic acid	
3485 sh	2575 sh	O - H (D) stretch
1830 } vs	1820 } vs	C = O stretch
1810 } vs	1800 } vs	
1325 s	1220 vs	
1240 br		

sh = sharp, vs = very strong, s = strong, br = broad

A second paper appeared during the course of this work. This was published by Bardet, Fleury and Tabacik (109). Infra-red bands of gaseous oxalic acid were observed at approximately 112°C . Raman spectra of oxalic acid in aqueous solution and in the crystal phase (α -form) were also reported in the same paper. Assignments of both infrared and Raman bands were made.

Unfortunately, although they observed more gaseous oxalic acid infrared absorption frequencies than previously, this paper was badly written for the following reasons:-

- (1) No spectra were presented in this paper.
- (2) Although the authors mentioned that the calculations were made using the structure given by Shibata and Kimura (104) and the Urey-Bradley force field, they did not give any details of their calculations at all.
- (3) If they had made a calculation at least
 - (a) a set of force constants should be given;
 - (b) a set of calculated frequencies should be given.
- (4) No relative intensities for either infrared or Raman bands were given.
- (5) Some assignments are very doubtful. Firstly, they did not mention the presence of impurity bands. Two bands at 1760 cm^{-1} and 1105 cm^{-1} , which they assigned to gaseous oxalic acid, were found in my work to be formic acid bands. Secondly, they assigned difference bands by ignoring the corresponding combination bands. Two bands at 1364 cm^{-1} and 720 cm^{-1} were assigned to difference bands without the corresponding bands at 2119 cm^{-1} and

1825 cm^{-1} being observed. According to theory (2) it is expected that a combination band is stronger than the difference band by the Boltzman factor

$$\frac{I(\nu_j - \nu_i)}{I(\nu_j + \nu_i)} \approx e^{\frac{-h c \nu_i}{K T}}$$

where ν is expressed in wave numbers.

Table 7

Infrared absorption frequencies of gaseous oxalic acid
observed by Bardet, Fleury, and Tabacik

band position (cm^{-1})	their assignment mode species	Compare with the present work
3484	ν_8 Bu	agree
1820	ν_9 Bu	agree
1760	$\nu_{10} + \nu_7$	disagree (formic acid)
1364	$\nu_2 - \nu_{13}$	disagree (no combination band)
1324	ν_{10} Bu	agree
1280	ν_{11} Bu	agree
1105	$\nu_7 + \nu_{16}$	disagree (formic acid)
949	$\nu_{13} + \nu_{15}$	not observed
913	$\nu_7 + \nu_{17}$	not observed
821	$\nu_7 + \nu_{13}$	disagree (impurity)
720	$\nu_{11} - \nu_{15}$	disagree (no combination band)
668	ν_{16} Au	agree

band position (cm ⁻¹)	their assignment mode species	Compare with the present work
565	ν_{12} Bu	not observed
452	ν_{17} Au	agree
380	ν_{13} Bu	not observed

They have given different symbols for the inplane vibrational modes. Thus, for simplicity, Table 8 is given.

Table 8

Inplane fundamental modes of gaseous oxalic acid

<u>my symbols</u>	<u>their symbols</u>	<u>planar modes of vibration</u>
ν_1	ν_5	Ag symmetric C-C stretch
ν_2	ν_2	Ag symmetric C=O stretch
ν_3	ν_3	Ag symmetric C-O stretch
ν_4	ν_1	Ag symmetric O-H stretch
ν_5	ν_7	Ag symmetric $(-\text{C} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix})$ angle deformation mode*
ν_6	ν_6	Ag symmetric $(-\text{C} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix})$ angle rocking mode*
ν_7	ν_4	Ag symmetric C-O-H angle bending mode
ν_8	ν_9	Bu anti-symmetric C=O stretch
ν_9	ν_{10}	Bu anti-symmetric C-O stretch
ν_{10}	ν_8	Bu anti-symmetric O-H stretch
ν_{11}	ν_{12}	Bu anti-symmetric $(-\text{C} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix})$ angle deformation mode
ν_{12}	ν_{13}	Bu anti-symmetric $(-\text{C} \begin{smallmatrix} \text{O} \\ \diagup \diagdown \end{smallmatrix})$ angle rocking mode
ν_{13}	ν_{11}	Bu anti-symmetric C-O-H angle bending mode

* See section 15.4

A third paper on gaseous oxalic acid also appeared during the course of this work. This paper by Cyvin and Alfheim (79) deals with molecular vibrations and mean amplitudes of oxalic acid monomer. They did not perform any experiment. The calculation was made using one oxalic acid band from Nahlovska, Nahlovsky and Strand (78), the observed data from Murata and Kawai (51) which was the Raman spectrum of oxalic acid solution in methanol, and the observed infrared data of Pava and Stafford (98) mentioned above. The out of plane frequencies were calculated from force constants from formic acid and acetic acid monomers.

Table 9

Inplane calculated frequencies for oxalic acid monomer
from Cyvin and Alfheim (79)

Species	No.	$\nu(\text{cm}^{-1})$	origin	approximate mode
Ag	1	3506	calc.	$\nu(\text{O-H})$
Ag	2	2257	calc.	$\nu(\text{C=O})$
Ag	3	1762	soln. (51)	$\nu(\text{C-C})$
Ag	4	1457	soln. (51)	$\delta(\text{C-O-H})$
Ag	5	852	soln. (51)	$\delta(\text{C-C=O})$
Ag	6	590	soln. (51)	$\nu(\text{C-O})$
Ag	7	432	soln. (51)	$\delta(\text{C-C-O})$
Bu	8	3475	vapour(78)	$\nu(\text{O-H})$
Bu	9	1820	vapour(98)	$\nu(\text{C=O})$
Bu	10	1325	vapour(98)	$\delta(\text{C-O-H})$

Species	No.	$\nu(\text{cm}^{-1})$	origin	approximate mode
Bu	11	1240	vapour(98)	$\nu(\text{C-O})$
Bu	12	656	calc.	$\delta(\text{C-C=O})$
Bu	13	480	calc.	$\delta(\text{C-C-O})$
Bg	1	869	calc.	-
Bg	2	505	calc.	-
Au	1	696	calc.	-
Au	2	471	calc.	-
Au	3	90	calc.	-

Although most of the calculated infrared frequencies (Bu) are fitted well with the observed frequencies, it was found that:-

- (1) Their calculated Raman frequencies do not agree with the observed Raman frequencies of gaseous oxalic acid in my present work, e.g. the observed Raman band at 1185 cm^{-1} .
- (2) Their calculated Raman frequencies and their assignments are completely different from my work.
- (3) The calculated Raman frequency (2237 cm^{-1}) of the symmetric C=O stretch is much higher than one would expect for acid carbonyl vibrations.

12.3 Summary of previous work on solid oxalic acid and solutions

Solid oxalic acid exists in three forms α , β , and dihydrate as shown in Figures 11, 12,13 respectively. The structure of each form has been published in many papers using

both X-rays and neutron diffraction methods (86), (87), (88), (89), (90), (91), (92), (93).

Fig. 11

α -oxalic acid

In α -oxalic acid the carbonyl and hydroxyl groups of a single COOH are each associated with different oxalic acid molecules giving rise to a planar sheet structure.

Fig. 12

β -oxalic acid

In β -oxalic acid the molecules are linked together in long chains by cyclic hydrogen bonds.

Fig. 13

Oxalic acid dihydrate

The structure of the dihydrate is similar to that of the β -form but with two molecules of water symmetrically placed between the carbonyl groups.

So far no complete work on the vibrational spectrum of solid oxalic acid has been made. The following papers have been published on the spectra of oxalic acid in solution and in the solid phase.

(1) Marigan and Bardet (124) published a paper on the Raman spectrum of oxalic acid dihydrate crystal. In this paper 7 bands were observed, one band at 1647 cm^{-1} was assigned to the vibrational mode of H_2O , the other six were assigned to oxalic acid dihydrate bands at 449 cm^{-1} , 575 cm^{-1} , 724 cm^{-1} , 850 cm^{-1} , 1469 cm^{-1} , and 1761 cm^{-1} .

(2) Murata and Kawai (51) published their work on the infrared and Raman spectra of oxalic acid solution in methanol. Four

strong bands at 432 cm^{-1} , 852 cm^{-1} , 1457 cm^{-1} , and 1762 cm^{-1} , and one weak band at 590 cm^{-1} were observed in the Raman spectrum. In the infrared only three bands at 720 cm^{-1} , 1245 cm^{-1} , and 1650 cm^{-1} were observed.

(3) Bellamy and Pace (62) published a long paper on the infrared spectrum of solid oxalic acid. In this paper infrared spectra of α , β , and the dihydrate forms of oxalic acid including a table of bands and some assignments were given.

(4) Lorenzelli and Alemagna (110) published a paper on the far infrared spectrum of oxalic acid dihydrate between 400 cm^{-1} - 70 cm^{-1} .

(5) The work of Bardet, Fleury and Tabacik (109) has been considered in section 12.2. They included some data on solution and solid phase spectra as well as the vapour phase results already discussed.

From the papers above it is obvious that the differences in the solid oxalic acid structures result in differences in their vibrational spectra. Since the structure of gaseous oxalic acid is different from that of the solid and also this work is dealing with the infrared and Raman spectra of gaseous oxalic acid, we will not discuss the vibrational spectra of solid oxalic acid anymore.

CHAPTER 13

PHYSICAL AND CHEMICAL PROPERTIES OF OXALIC ACID

13.1 Physical and chemical properties

The physical and chemical properties of oxalic acid were published in (75). The sublimation of the anhydrous oxalic acid starts at a temperature somewhat below 100°C and proceeds rapidly at 125°C . Partial decomposition takes place before the melting point at $185 - 190^{\circ}\text{C}$, and its decomposition products include formic acid, carbon monoxide, carbon dioxide, and water. Dehydrating agents, such as sulphuric acid, accelerate the thermal decomposition of all forms of the acid. The anhydrous acid is quite soluble in anhydrous ethyl ether, 23.6 gm per 100 gm of solvent, while the corresponding value for the dihydrate is 1.47 gm per 100 gm. Anhydrous oxalic acid may be crystallised from warm nitric or sulphuric acid.

Oxalic acid crystallises from water as the dihydrate but readily loses its water of crystallisation when heated rapidly. Complete removal of water may be accomplished by heating under reduced pressure or by refluxing in a low boiling solvent capable of forming a water azeotrope. Its solubility in water increases with temperature. Approximate solubility values are given by the following formulas: from 0°C to 60°C the solubility is given by

$$S = 3.42 + 0.168t + 0.0048t^2;$$

and from 50°C to 90°C by

$$S = 0.333t + 0.003t^2;$$

where S = gm $(\text{COOH})_2$ per 100 gm solution, t = °C.

Table 10

Physical and chemical properties of oxalic acid

Oxalic acid anhydrous, $(\text{COOH})_2$ (presumably α form)

Melting point	187°C
vapour pressure, range 60°C - 105°C	$\log P_{\text{mm}} = -(4726.95/T) + 12.2229$
specific heat, range -200 - +50°C	$C_p = 0.259 + 0.00076T$
heat of combustion	60.1 kcal/mole
heat of formation at 18°C	195.36 kcal/mole
heat of solution (in water)	-9.58 kJ/mole
heat of sublimation	21.65 kcal/mole
heat of decomposition	197.60 kcal/mole
thermal conductivity at 0°C	9.0×10^{-3} watt/(cm ²) (°C/cm)
ionization constant, K_1	6.5×10^{-2}
K_2	6.0×10^{-5}
coefficient of expansion at 25°C	1.784×10^{-4} ml/(gm) (°C)

Oxalic acid dihydrate $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$

melting point	101.5
density, d_4^{20}	1.653
refractive index, n_D^{20}	1.475
heat of solution (in water)	-35.5 kJ/mole

13.2 Vapour pressure of anhydrous oxalic acid

In 1926 W. Albert Noyes Jr., and Delbert E. Wobbe worked out an approximate equation to calculate the vapour pressure of anhydrous oxalic acid at different temperatures.

Since at temperatures higher than 105°C the oxalic acid decomposes quite rapidly it is obvious that

- (a) direct measurements of the vapour pressure are very difficult to carry out;
- (b) the values obtained would be of doubtful accuracy.

Hence they performed the vapour pressure measurements at temperatures ranging from 60°C to 105°C. The desired values agree well with the calculated values using the expression

$$\log_{10} P = -(4726.95/T) + 12.223$$

P is expressed in millimetres and temperature is expressed in degrees absolute.

It is assumed that this expression can be used for the purpose of extrapolation. A graph which shows the relation between the vapour pressure and the temperature is then obtained.

Table 11

The calculated pressure of anhydrous oxalic acid
at different temperatures

Temperature °C	Calculated pressure in mm
80	0.068
90	0.159
100	0.355
110	0.759
120	1.567
130	3.116

Fig. 14

The vapour pressure of oxalic acid against temperature

13.3 Molecular structure of gaseous oxalic acid

Two papers were published on the structure of gaseous oxalic acid using the electron diffraction method.

The first paper was published before this work started by Shibata and Kimura (104). They interpreted their results on the basis of a planar trans-conformation (Fig. 15) with the following parameters:-

$$\begin{array}{ll} \text{C - C distance} & = 1.54^{\circ}\text{A} \pm 0.06^{\circ}\text{A} \\ \text{C = O distance} & = 1.22^{\circ}\text{A} \pm 0.02^{\circ}\text{A} \\ \text{C - O distance} & = 1.37^{\circ}\text{A} \pm 0.02^{\circ}\text{A} \\ \angle \text{O} = \text{C} - \text{O} & = 125^{\circ} \pm 3^{\circ} \\ \angle \text{O} = \text{C} - \text{C} & = 122^{\circ} \pm 5^{\circ} \end{array}$$

In their calculation they assumed that the scattering effect of hydrogen atoms is negligible.

The second paper appeared during the course of this work and was published by Nahlovska, Nahlovsky and Strand(78). They also interpreted their results on the basis of planar trans-conformation with the following parameters:-

$$\begin{array}{ll} \text{C - C distance} & = 1.548\text{A} \pm 0.004\text{A} \\ \text{C = O distance} & = 1.203\text{A} \pm 0.001\text{A} \\ \text{C - O distance} & = 1.339\text{A} \pm 0.002\text{A} \\ \text{O - H distance} & = 1.056\text{A} \pm 0.014\text{A} \\ \angle \text{O} = \text{C} - \text{O} & = 125^{\circ} \pm 0.2^{\circ} \\ \angle \text{O} = \text{C} - \text{C} & = 123.1^{\circ} \pm 0.9^{\circ} \\ \angle \text{C} - \text{O} - \text{H} & = 104.4^{\circ} \pm 2.3^{\circ} \end{array}$$

Two models of gaseous oxalic acid were suggested in the latter paper. In the first model the O - H bonds pointed away from the neighbouring carbonyl oxygens as shown in Fig. 15.

The second model was obtained by rotating the hydrogen atoms 180° around the C - O bonds as shown in Fig. 16. With the O - H bonds pointing towards the neighbouring carbonyl oxygens, hydrogen bonds are formed. Both models fitted the electron diffraction data quite well.

Fig. 15
First model

Fig. 16
Second model

The authors suggested that the structure of gaseous oxalic acid is more likely to be the second model because of

- (a) the frequency shift of the O - H stretching band from the free O - H stretching band position;
- (b) the O - H bond length is longer than the free O - H bond, which they thought was caused by the weak intramolecular effect of H bond.

Comment

I would like to say that the evidence that they have given is not yet enough to conclude that there are H-bonds in the single molecule because of the following reasons:-

- (a) Usually when there is H-bonding the O - H asymmetric stretching frequency is accompanied by band broadening. According to the spectrum recorded this band is at 3475 cm^{-1} , approximately 280 cm^{-1} from the O - H asymmetric stretch of water (2), and it is quite sharp.
- (b) At room temperature the oxalic acid becomes polymerized. It is more likely that with the first model it will be easier for free molecules to become polymers.
- (c) As both models fitted the electron diffraction data quite well, thus, more information is required before the conclusion is made.

With the above possibilities in mind, the subsequent calculations are made on both models.

CHAPTER 14

PRINCIPAL MOMENTS OF INERTIA AND PRINCIPAL AXES

OF GASEOUS OXALIC ACID

14.1 (a) Principal moments of inertia of the gaseous oxalic acid

First model

Fig. 17

Gaseous oxalic acid 1st model

Let the oxalic acid molecule be in the xy plane in which the origin is at the centre of the C - C bond and the x axis coincides with this bond.

Using molecular parameters given by Nahlovská, Nahlovský and Strand (78) we have

$$C - C = R = 1.548 \text{ \AA}$$

$$C = O = r_1 = r'_1 = 1.208 \text{ \AA}$$

$$C - O = r_2 = r'_2 = 1.339 \text{ \AA}$$

$$O - H = r_3 = r'_3 = 1.056 \text{ \AA}$$

$$\angle \text{C-C-O} = \alpha_1 = \alpha'_1 = 123.1^\circ$$

$$\angle \text{C-C-O} = \alpha_2 = \alpha'_2 = 111.9^\circ$$

$$\angle \text{O-C-O} = \alpha_3 = \alpha'_3 = 125.0^\circ$$

$$\phi = \phi' = 56.9^\circ$$

$$\angle \text{C-O-H} = \beta = \beta' = 104.4^\circ$$

$$\theta = \theta' = 7.5^\circ$$

$$\begin{aligned} I_x &= 2m_O(r_1 \sin \phi)^2 + 2m_O(r_2 \sin(\alpha_3 - \phi))^2 + 2m_H(r_2 \sin(\alpha_3 - \phi) - r_3 \sin \theta)^2 \\ &= 84.60248 \text{ amu. (A)}^2 \end{aligned}$$

$$\begin{aligned} I_y &= 2m_C\left(\frac{R}{2}\right)^2 + 2m_O\left(r_1 \cos \phi + \frac{R}{2}\right)^2 + 2m_O\left(r_2 \cos(\alpha_3 - \phi) + \frac{R}{2}\right)^2 \\ &\quad + 2m_H(r_3 \cos \theta + r_2 \cos(\alpha_3 - \phi) + \frac{R}{2})^2 \\ &= 142.81338 \text{ amu. (A)}^2 \end{aligned}$$

$$\begin{aligned} I_z &= I_x + I_y \\ &= 227.41586 \text{ amu. (A)}^2 \end{aligned}$$

$$\begin{aligned} I_{xy} &= -2m_O(r_1 \sin \phi)(r_1 \cos \phi + \frac{R}{2}) + 2m_O(r_2 \sin(\alpha_3 - \phi))(r_2 \cos(\alpha_3 - \phi) + \frac{R}{2}) \\ &\quad + 2m_H(r_2 \sin(\alpha_3 - \phi) - r_3 \sin \theta)(r_3 \cos \theta + r_2 \cos(\alpha_3 - \phi) + \frac{R}{2}) \\ &= 9.32566 \text{ amu. (A)}^2 \end{aligned}$$

$$I_{xz} = \sum m_i x_i z_i = 0$$

$$I_{yz} = \sum m_i y_i z_i = 0$$

The matrix X is constructed in which

$$X = \begin{vmatrix} I_x & -I_{xy} & -I_{xz} \\ -I_{yx} & I_y & -I_{yz} \\ -I_{zx} & -I_{zy} & I_z \end{vmatrix} \quad \dots\dots 14.1$$

The three roots or the three principal moments of inertia can be determined by solving the determinantal equation of X (18), thus

$$\begin{vmatrix} 84.60248 - I & -9.32566 & 0 \\ -9.32566 & 142.81538 - I & 0 \\ 0 & 0 & 227.41586 - I \end{vmatrix} = 0 \quad \dots\dots 14.2$$

Thus, the three principal moments of inertia are 83.14496 amu.(A)², 144.2709 amu.(A)² and 227.41586 amu.(A)²

(b) Principal axes of the gaseous oxalic acid

First model

Let a, b, c be the three principal axes about which

$$I_a = 83.14496 \text{ amu. (A)}^2$$

$$I_b = 144.2709 \text{ amu. (A)}^2$$

$$I_c = 227.41586 \text{ amu. (A)}^2$$

The matrix C can be diagonalized by an orthogonal matrix S
so that

$$S^{-1}XS = \begin{vmatrix} I_a & 0 & 0 \\ 0 & I_b & 0 \\ 0 & 0 & I_c \end{vmatrix} \quad \text{..... 14.3}$$

As the oxalic acid is a planar molecule the problem is
easier because the z axis coincides with the c axis and, thus,
the matrices X and S can be reduced to second order so that

$$S^{-1}XS = \begin{vmatrix} I_a & 0 \\ 0 & I_b \end{vmatrix} \quad \text{..... 14.4}$$

If $I = 83.14496 \text{ amu. (A)}^2$ and $e_1 = \frac{1}{\sqrt{1}} (i\ell_1 + jm_1)$ then

$$\begin{vmatrix} 84.60248 - 83.14496 & -9.32566 \\ -9.32566 & 142.81533 - 83.14496 \end{vmatrix} = 0 \quad \text{..... 14.5}$$

that is

$$1.45752\ell_1 - 9.32566m_1 = 0 \quad \text{..... 14.6}$$

$$-9.32566\ell_1 + 59.66842m_1 = 0 \quad \text{..... 14.7}$$

$$\therefore e_1 = 0.988i + 0.15442j$$

If $I = 144.2709 \text{ amu. (A)}^2$ and $c_2 = \frac{1}{\sqrt{I}} (ie_2 + jm_2)$ then

$$\begin{vmatrix} 84.60248 - 144.2709 & -9.32566 \\ -9.32566 & 142.81338 - 144.2709 \end{vmatrix} = 0 \quad \text{..... 14.8}$$

that is

$$-59.66842i_2 - 9.32566m_2 = 0 \quad \text{..... 14.9}$$

$$-9.32566i_2 - 1.45752m_2 = 0 \quad \text{..... 14.10}$$

$$\therefore c_2 = -0.15442i + 0.988j$$

The transformation matrix S can be constructed from e_1 and e_2 as shown below

$$\therefore S = \begin{vmatrix} 0.988 & -0.15442 \\ 0.15442 & 0.988 \end{vmatrix} \quad \text{..... 14.11}$$

The transformation matrix here can be written as

$$S = \begin{vmatrix} \cos \theta & -\sin \theta \\ \sin \theta & \cos \theta \end{vmatrix} \quad \text{..... 14.12}$$

On comparing 14.11 and 14.12 we have

$$\theta = 8^\circ 53'$$

That is, the a and b axes are $8^{\circ}53'$ inclined to the x and y axes respectively, as shown in Fig. 17.

14.2 Principal moments of inertia and the principal axes of gaseous oxalic acid

Second model

Fig. 18

Gaseous oxalic acid 2nd model

The molecule is in the xy plane in which the C - C bond coincides with the x axis. Using the molecular parameters given by Nahlovská, Nahlovský and Strand (78) and the same method as before, the results are

$$\begin{aligned} I_a &= 88.37968 \quad \text{amu. (A)}^2 \\ I_b &= 133.15992 \quad \text{amu. (A)}^2 \\ I_c &= 221.5396 \quad \text{amu. (A)}^2 \end{aligned}$$

The c axis coincides with the z axis and the a and b axes are at $7^{\circ}28'30''$ inclined to the x and y axes respectively as shown in Fig. 18.

CHAPTER 15

THE G-MATRIX OF THE INPLANE VIBRATIONS

OF GASEOUS OXALIC ACID 1ST MODEL

G-matrices for both models were constructed using the method described in chapter 5.

15.1 Evaluation of the B-matrix of the inplane vibrations

Fig. 19

In the first model of gaseous oxalic acid there are 15 internal co-ordinates, 7 bond stretching co-ordinates and 8 angle bending co-ordinates, as follows:-

Bond stretching co-ordinates

ΔR = change in C-C distance

$\Delta r_1 = \Delta r'_1$ = change in C=O distance

$\Delta r_2 = \Delta r'_2$ = change in C-O distance

$\Delta r_3 = \Delta r'_3$ = change in O-H distance

Angle bending co-ordinates

$\Delta\alpha = \Delta\alpha' =$ change in C-C-O angle
Angle bending co-ordinates

$\Delta\alpha_1 = \Delta\alpha'_1 =$ change in C-C-O angle

$\Delta\alpha_2 = \Delta\alpha'_2 =$ change in C-C-O angle

$\Delta\beta = \Delta\beta' =$ change in C-O-H angle

For simplicity each atom is labelled by a number as shown in Fig. 19 above. B-matrix elements are evaluated using Wilson's S vector method (see section 5.2) and the results are:

B-matrix elements of the inplane vibration of gaseous oxalic acid

(1st model)

Since $r_1 = r'_1$, $r_2 = r'_2$, $r_3 = r'_3$, $\alpha_1 = \alpha'_1$, $\alpha_2 = \alpha'_2$,

$\alpha_3 = \alpha'_3$, $\beta = \beta'$, $\phi = \phi'$, $\theta = \theta'$

the elements of the B-matrix can be written as:-

$$(\Delta R, \Delta x_1) = -1$$

$$(\Delta R, \Delta x_2) = 1$$

$$(\Delta r_1, \Delta x_2) = -\cos \phi$$

$$(\Delta r'_1, \Delta x_1) = \cos \phi$$

$$(\Delta r_1, \Delta y_2) = \sin \phi$$

$$(\Delta r'_1, \Delta y_1) = -\sin \phi$$

$$(\Delta r_1, \Delta x_3) = \cos \phi$$

$$(\Delta r'_1, \Delta x_6) = -\cos \phi$$

$$(\Delta r_1, \Delta y_3) = -\sin \phi$$

$$(\Delta r'_1, \Delta y_6) = \sin \phi$$

$$(\Delta r_2, \Delta x_2) = -\cos(\alpha_3 - \phi)$$

$$(\Delta r'_2, \Delta x_1) = \cos(\alpha_3 - \phi)$$

$$(\Delta r_2, \Delta y_2) = -\sin(\alpha_3 - \phi)$$

$$(\Delta r'_2, \Delta y_1) = \sin(\alpha_3 - \phi)$$

$$(\Delta r_2, \Delta x_4) = \cos(\alpha_3 - \phi)$$

$$(\Delta r'_2, \Delta x_7) = -\cos(\alpha_3 - \phi)$$

$$(\Delta r_2, \Delta y_4) = \sin(\alpha_3 - \phi)$$

$$(\Delta r'_2, \Delta y_7) = -\sin(\alpha_3 - \phi)$$

$$\begin{aligned}
 (\Delta r_3, \Delta x_4) &= -\cos \theta & (\Delta r'_3, \Delta x_7) &= \cos \theta \\
 (" , \Delta y_4) &= \sin \theta & (" , \Delta y_7) &= -\sin \theta \\
 (" , \Delta x_5) &= \cos \theta & (" , \Delta x_8) &= -\cos \theta \\
 (" , \Delta y_5) &= -\sin \theta & (" , \Delta y_8) &= \sin \theta
 \end{aligned}$$

$$\begin{aligned}
 (r_1 \Delta \alpha_1, \Delta y_1) &= \frac{r_1}{R} & (r_2 \Delta \alpha_2, \Delta y_1) &= \frac{r_2}{R} \\
 (" , \Delta x_2) &= -\{\sin \phi\} & (" , \Delta x_2) &= -\sin(\alpha_3 - \phi) \\
 (" , \Delta y_2) &= -\{\frac{r_1}{R} + \cos \phi\} & (" , \Delta y_2) &= \frac{r_2}{R} + \cos(\alpha_3 - \phi) \\
 (" , \Delta x_3) &= \sin \phi & (" , \Delta x_4) &= \sin(\alpha_3 - \phi) \\
 (" , \Delta y_3) &= \cos \phi & (" , \Delta y_4) &= -\cos(\alpha_3 - \phi)
 \end{aligned}$$

$$\begin{aligned}
 (\sqrt{r_1 r_2} \Delta \alpha_3, \Delta x_2) &= \{r_2 \sin \phi + r_1 \sin(\alpha_3 - \phi)\} / \sqrt{r_1 r_2} \\
 (" , \Delta y_2) &= \{r_2 \cos \phi - r_1 \cos(\alpha_3 - \phi)\} / \sqrt{r_1 r_2} \\
 (" , \Delta x_3) &= -r_2 \sin \phi / \sqrt{r_1 r_2} \\
 (" , \Delta y_3) &= -r_2 \cos \phi / \sqrt{r_1 r_2} \\
 (" , \Delta x_4) &= -r_1 \sin(\alpha_3 - \phi) / \sqrt{r_1 r_2} \\
 (" , \Delta y_4) &= r_1 \cos(\alpha_3 - \phi) / \sqrt{r_1 r_2}
 \end{aligned}$$

$$\begin{aligned}
 (r'_1 \Delta \alpha'_1, \Delta x_1) &= \sin \phi & (r'_2 \Delta \alpha'_2, \Delta x_1) &= \sin(\alpha_3 - \phi) \\
 (" , \Delta y_1) &= \frac{r_1}{R} + \cos \phi & (" , \Delta y_1) &= -\{\frac{r_2}{R} + \cos(\alpha_3 - \phi)\} \\
 (" , \Delta y_2) &= -\frac{r_1}{R} & (" , \Delta y_2) &= \frac{r_2}{R} \\
 (" , \Delta x_6) &= -\sin \phi & (" , \Delta x_7) &= -\sin(\alpha_3 - \phi) \\
 (" , \Delta y_6) &= -\cos \phi & (" , \Delta y_7) &= \cos(\alpha_3 - \phi)
 \end{aligned}$$

$$\begin{aligned}
 (\sqrt{r_1 r_2} \Delta \alpha'_3, \Delta x_1) &= -(r_2 \sin \phi + r_1 \sin(\alpha_3 - \phi)) / \sqrt{r_1 r_2} \\
 (\quad " \quad , \Delta y_1) &= (r_1 \cos(\alpha_3 - \phi) - r_2 \cos \phi) / \sqrt{r_1 r_2} \\
 (\quad " \quad , \Delta x_5) &= r_2 \sin \phi / \sqrt{r_1 r_2} \\
 (\quad " \quad , \Delta y_5) &= r_2 \cos \phi / \sqrt{r_1 r_2} \\
 (\quad " \quad , \Delta x_7) &= r_1 \sin(\alpha_3 - \phi) / \sqrt{r_1 r_2} \\
 (\quad " \quad , \Delta y_7) &= -r_1 \cos(\alpha_3 - \phi) / \sqrt{r_1 r_2}
 \end{aligned}$$

$$\begin{aligned}
 (\sqrt{r_2 r_3} \Delta \beta, \Delta x_2) &= -r_3 \sin(\alpha_3 - \phi) / \sqrt{r_2 r_3} \\
 (\quad " \quad , \Delta y_2) &= r_3 \cos(\alpha_3 - \phi) / \sqrt{r_2 r_3} \\
 (\quad " \quad , \Delta x_4) &= (r_3 \sin(\alpha_3 - \phi) - r_2 \sin \theta) / \sqrt{r_2 r_3} \\
 (\quad " \quad , \Delta y_4) &= -(r_3 \cos(\alpha_3 - \phi) + r_2 \cos \theta) / \sqrt{r_2 r_3} \\
 (\quad " \quad , \Delta x_5) &= r_2 \sin \theta / \sqrt{r_2 r_3} \\
 (\quad " \quad , \Delta y_5) &= r_2 \cos \theta / \sqrt{r_2 r_3}
 \end{aligned}$$

$$\begin{aligned}
 (\sqrt{r_2 r_3} \Delta \beta', \Delta x_1) &= r_3 \sin(\alpha_3 - \phi) / \sqrt{r_2 r_3} \\
 (\quad " \quad , \Delta y_1) &= -r_3 \cos(\alpha_3 - \phi) / \sqrt{r_2 r_3} \\
 (\quad " \quad , \Delta x_7) &= (r_2 \sin \theta - r_3 \sin(\alpha_3 - \phi)) / \sqrt{r_2 r_3} \\
 (\quad " \quad , \Delta y_7) &= (r_2 \cos \theta + r_3 \cos(\alpha_3 - \phi)) / \sqrt{r_2 r_3} \\
 (\quad " \quad , \Delta x_8) &= -r_2 \sin \theta / \sqrt{r_2 r_3} \\
 (\quad " \quad , \Delta y_8) &= -r_2 \cos \theta / \sqrt{r_2 r_3}
 \end{aligned}$$

All the other elements are zero

15.2 D-matrix elements of the inplane vibration of gaseous oxalic acid

(1st model)

$$(\Delta R, \Delta x_1) = -\sqrt{\mu_C}$$

$$(\Delta R, \Delta x_2) = \sqrt{\mu_C}$$

$$(\Delta r_1, \Delta x_2) = -\sqrt{\mu_C} \cos \phi$$

$$(\Delta r_1, \Delta y_2) = \sqrt{\mu_C} \sin \phi$$

$$(\Delta r_1, \Delta x_3) = \sqrt{\mu_O} \cos \phi$$

$$(\Delta r_1, \Delta y_3) = -\sqrt{\mu_O} \sin \phi$$

$$(\Delta r'_1, \Delta x_1) = \sqrt{\mu_C} \cos \phi$$

$$(\Delta r'_1, \Delta y_1) = -\sqrt{\mu_C} \sin \phi$$

$$(\Delta r'_1, \Delta x_6) = -\sqrt{\mu_O} \cos \phi$$

$$(\Delta r'_1, \Delta y_6) = \sqrt{\mu_O} \sin \phi$$

$$(\Delta r_2, \Delta x_2) = -\sqrt{\mu_C} \cos(\alpha_3 - \phi)$$

$$(\Delta r_2, \Delta y_2) = -\sqrt{\mu_C} \sin(\alpha_3 - \phi)$$

$$(\Delta r_2, \Delta x_4) = \sqrt{\mu_O} \cos(\alpha_3 - \phi)$$

$$(\Delta r_2, \Delta y_4) = \sqrt{\mu_O} \sin(\alpha_3 - \phi)$$

$$(\Delta r'_2, \Delta x_1) = \sqrt{\mu_C} \cos(\alpha_3 - \phi)$$

$$(\Delta r'_2, \Delta y_1) = \sqrt{\mu_C} \sin(\alpha_3 - \phi)$$

$$(\Delta r'_2, \Delta x_7) = -\sqrt{\mu_O} \cos(\alpha_3 - \phi)$$

$$(\Delta r'_2, \Delta y_7) = -\sqrt{\mu_O} \sin(\alpha_3 - \phi)$$

$$(\Delta r_3, \Delta x_4) = -\sqrt{\mu_O} \cos \theta$$

$$(\Delta r_3, \Delta y_4) = \sqrt{\mu_O} \sin \theta$$

$$(\Delta r_3, \Delta x_5) = \sqrt{\mu_H} \cos \theta$$

$$(\Delta r_3, \Delta y_5) = -\sqrt{\mu_H} \sin \theta$$

$$(\Delta r'_3, \Delta x_7) = \sqrt{\mu_O} \cos \theta$$

$$(\Delta r'_3, \Delta y_7) = -\sqrt{\mu_O} \sin \theta$$

$$(\Delta r'_3, \Delta x_8) = -\sqrt{\mu_H} \cos \theta$$

$$(\Delta r'_3, \Delta y_8) = \sqrt{\mu_H} \sin \theta$$

$$(r_1 \Delta \alpha_1, \Delta y_1) = \sqrt{\mu_C} (r_1/R)$$

$$(r_1 \Delta \alpha_1, \Delta x_2) = -\sqrt{\mu_C} \sin \phi$$

$$(r_1 \Delta \alpha_1, \Delta y_2) = -\sqrt{\mu_C} \{r_1/R + \cos \phi\}$$

$$(r_1 \Delta \alpha_1, \Delta x_3) = \sqrt{\mu_O} \sin \phi$$

$$(r_1 \Delta \alpha_1, \Delta y_3) = \sqrt{\mu_O} \cos \phi$$

$$(r_2 \Delta \alpha_2, \Delta y_1) = -\sqrt{\mu_C} (r_2/R)$$

$$(r_2 \Delta \alpha_2, \Delta x_2) = -\sqrt{\mu_C} \sin(\alpha_3 - \phi)$$

$$(r_2 \Delta \alpha_2, \Delta y_2) = +\sqrt{\mu_C} \{r_2/R + \cos(\alpha_3 - \phi)\}$$

$$(r_2 \Delta \alpha_2, \Delta x_4) = \sqrt{\mu_O} \sin(\alpha_3 - \phi)$$

$$(r_2 \Delta \alpha_2, \Delta y_4) = -\sqrt{\mu_O} \cos(\alpha_3 - \phi)$$

$$(\sqrt{r_1 r_2} \Delta \alpha_3, \Delta x_2) = \sqrt{\mu_c} \{r_2 \sin \phi + r_1 \sin(\alpha_3 - \phi)\} / \sqrt{r_1 r_2}$$

$$(\quad, \Delta y_2) = \sqrt{\mu_c} \{r_2 \cos \phi - r_1 \cos(\alpha_3 - \phi)\} / \sqrt{r_1 r_2}$$

$$(\quad, \Delta x_3) = -\sqrt{\mu_0} r_2 \sin \phi / \sqrt{r_1 r_2}$$

$$(\quad, \Delta y_3) = -\sqrt{\mu_0} r_2 \cos \phi / \sqrt{r_1 r_2}$$

$$(\quad, \Delta x_4) = -\sqrt{\mu_0} r_1 \sin(\alpha_3 - \phi) / \sqrt{r_1 r_2}$$

$$(\quad, \Delta y_4) = \sqrt{\mu_0} r_1 \cos(\alpha_3 - \phi) / \sqrt{r_1 r_2}$$

$$(r'_1 \Delta \alpha'_1, \Delta x_1) = \sqrt{\mu_c} \sin \phi$$

$$(\quad, \Delta y_1) = \sqrt{\mu_c} \{r_1/R + \cos \phi\}$$

$$(\quad, \Delta y_2) = -\sqrt{\mu_c} (r_1/R)$$

$$(\quad, \Delta x_6) = -\sqrt{\mu_0} \sin \phi$$

$$(\quad, \Delta y_6) = -\sqrt{\mu_0} \cos \phi$$

$$(r'_2 \Delta \alpha'_2, \Delta x_1) = \sqrt{\mu_c} \sin(\alpha_3 - \phi)$$

$$(\quad, \Delta y_1) = -\sqrt{\mu_c} \{r_2/R + \cos(\alpha_3 - \phi)\}$$

$$(\quad, \Delta y_2) = \sqrt{\mu_c} (r_2/R)$$

$$(\quad, \Delta x_7) = -\sqrt{\mu_0} \sin(\alpha_3 - \phi)$$

$$(\quad, \Delta y_7) = \sqrt{\mu_0} \cos(\alpha_3 - \phi)$$

$$(\sqrt{r'_1 r'_2} \Delta \alpha'_3, \Delta x_1) = -\sqrt{\mu_c} \{r_2 \sin \phi + r_1 \sin(\alpha_3 - \phi)\} / \sqrt{r'_1 r'_2}$$

$$(\quad, \Delta y_1) = \sqrt{\mu_c} \{r_1 \cos(\alpha_3 - \phi) - r_2 \cos \phi\} / \sqrt{r'_1 r'_2}$$

$$(\quad, \Delta x_6) = \sqrt{\mu_0} r_2 \sin \phi / \sqrt{r'_1 r'_2}$$

$$(\quad, \Delta y_6) = \sqrt{\mu_0} r_2 \cos \phi / \sqrt{r'_1 r'_2}$$

$$(\quad, \Delta x_7) = \sqrt{\mu_0} r_1 \sin(\alpha_3 - \phi) / \sqrt{r'_1 r'_2}$$

$$(\quad, \Delta y_7) = -\sqrt{\mu_0} r_1 \cos(\alpha_3 - \phi) / \sqrt{r'_1 r'_2}$$

$$(\sqrt{r_2 r_3} \Delta \beta, \Delta x_2) = -\sqrt{\mu_c} r_3 \sin(\alpha_3 - \phi) / \sqrt{r_2 r_3}$$

$$(\quad, \Delta y_2) = \sqrt{\mu_c} r_3 \cos(\alpha_3 - \phi) / \sqrt{r_2 r_3}$$

$$(\quad, \Delta x_4) = \sqrt{\mu_o} \{r_3 \sin(\alpha_3 - \phi) - r_2 \sin \theta\} / \sqrt{r_2 r_3}$$

$$(\quad, \Delta y_4) = -\sqrt{\mu_o} \{r_3 \cos(\alpha_3 - \phi) + r_2 \cos \theta\} / \sqrt{r_2 r_3}$$

$$(\quad, \Delta x_5) = \sqrt{\mu_H} r_2 \sin \theta / \sqrt{r_2 r_3}$$

$$(\quad, \Delta y_5) = \sqrt{\mu_H} r_2 \cos \theta / \sqrt{r_2 r_3}$$

$$(\sqrt{r_2 r_3} \Delta \beta', \Delta x_1) = \sqrt{\mu_c} r_3 \sin(\alpha_3 - \phi) / \sqrt{r_2 r_3}$$

$$(\quad, \Delta y_1) = -\sqrt{\mu_c} r_3 \cos(\alpha_3 - \phi) / \sqrt{r_2 r_3}$$

$$(\quad, \Delta x_7) = \sqrt{\mu_o} \{r_2 \sin \theta - r_3 \sin(\alpha_3 - \phi)\} / \sqrt{r_2 r_3}$$

$$(\quad, \Delta y_7) = \sqrt{\mu_o} \{r_2 \cos \theta + r_3 \cos(\alpha_3 - \phi)\} / \sqrt{r_2 r_3}$$

$$(\quad, \Delta x_8) = -\sqrt{\mu_H} r_2 \sin \theta / \sqrt{r_2 r_3}$$

$$(\quad, \Delta y_8) = -\sqrt{\mu_H} r_2 \cos \theta / \sqrt{r_2 r_3}$$

All the other elements are zero

$$\mu_c = \frac{1}{m_c}$$

$$\mu_o = \frac{1}{m_o}$$

$$\mu_H = \frac{1}{m_H}$$

where m_c , m_o , m_H are the masses of carbon, oxygen and hydrogen atoms respectively.

15.3 G-matrix elements in internal co-ordinates of the inplane
vibration of gaseous oxalic acid (1st model)

$$\begin{aligned}
 G(1,1) &= 2\mu_C \\
 G(1,2) &= -\mu_C \cos \phi \\
 G(1,3) &= -\mu_C \cos \phi \\
 G(1,4) &= -\mu_C \cos(\alpha_3 - \phi) \\
 G(1,5) &= -\mu_C \cos(\alpha_3 - \phi) \\
 G(1,6) &= 0 \\
 G(1,7) &= 0 \\
 G(1,8) &= -\mu_C \sin \phi \\
 G(1,9) &= -\mu_C \sin(\alpha_3 - \phi) \\
 G(1,10) &= \mu_C \{r_2 \sin \phi + r_1 \sin(\alpha_3 - \phi)\} / \sqrt{r_1 r_2} \\
 G(1,11) &= -\mu_C \sin \phi \\
 G(1,12) &= -\mu_C \sin(\alpha_3 - \phi) \\
 G(1,13) &= \mu_C \{r_2 \sin \phi + r_1 \sin(\alpha_3 - \phi)\} / \sqrt{r_1 r_2} \\
 G(1,14) &= -\mu_C r_3 \sin(\alpha_3 - \phi) / \sqrt{r_2 r_3} \\
 G(1,15) &= -\mu_C r_3 \sin(\alpha_3 - \phi) / \sqrt{r_2 r_3} \\
 \\
 G(2,1) &= -\mu_C \cos \phi \\
 G(2,2) &= \mu_C + \mu_O \\
 G(2,3) &= 0 \\
 G(2,4) &= \mu_C \cos \alpha_3 \\
 G(2,5) &= 0 \\
 G(2,6) &= 0 \\
 G(2,7) &= 0
 \end{aligned}$$

$$\begin{aligned}
 G(2,8) &= -\mu_c \frac{r_1}{R} \sin \phi \\
 G(2,9) &= \mu_c \frac{r_2}{R} \sin \phi + \mu_c \sin \alpha_3 \\
 G(2,10) &= -\mu_c r_1 \sin \alpha_3 / \sqrt{r_1 r_2} \\
 G(2,11) &= -\mu_c \frac{r_1}{R} \sin \phi \\
 G(2,12) &= \mu_c \frac{r_2}{R} \sin \phi \\
 G(2,13) &= 0 \\
 G(2,14) &= \mu_c r_3 \sin \alpha_3 / \sqrt{r_2 r_3} \\
 G(2,15) &= 0
 \end{aligned}$$

$$\begin{aligned}
 G(3,1) &= -\mu_c \cos \phi \\
 G(3,2) &= 0 \\
 G(3,3) &= \mu_c + \mu_0 \\
 G(3,4) &= 0 \\
 G(3,5) &= \mu_c \cos \alpha_3 \\
 G(3,6) &= 0 \\
 G(3,7) &= 0 \\
 G(3,8) &= -\mu_c \frac{r_1}{R} \sin \phi \\
 G(3,9) &= \mu_c \frac{r_2}{R} \sin \phi \\
 G(3,10) &= 0 \\
 G(3,11) &= -\mu_c \frac{r_1}{R} \sin \phi \\
 G(3,12) &= \mu_c \frac{r_2}{R} \sin \phi + \mu_c \sin \alpha_3 \\
 G(3,13) &= -\mu_c r_1 \sin \alpha_3 / \sqrt{r_1 r_2} \\
 G(3,14) &= 0 \\
 G(3,15) &= \mu_c r_3 \sin \alpha_3 / \sqrt{r_2 r_3}
 \end{aligned}$$

$$\begin{aligned}
 G(4,1) &= -\mu_C \cos(\alpha_3 - \phi) \\
 G(4,2) &= \mu_C \cos \alpha_3 \\
 G(4,3) &= 0 \\
 G(4,4) &= \mu_C + \mu_O \\
 G(4,5) &= 0 \\
 G(4,6) &= +\mu_O \cos \beta \\
 G(4,7) &= 0 \\
 G(4,8) &= \mu_C \frac{r_1}{R} \sin(\alpha_3 - \phi) + \mu_C \sin(\alpha_3) \\
 G(4,9) &= -\mu_C \frac{r_2}{R} \sin(\alpha_3 - \phi) \\
 G(4,10) &= -\mu_C r_2 \sin \alpha_3 / \sqrt{r_1 r_2} \\
 G(4,11) &= \mu_C \frac{r_1}{R} \sin(\alpha_3 - \phi) \\
 G(4,12) &= -\mu_C \frac{r_2}{R} \sin(\alpha_3 - \phi) \\
 G(4,13) &= 0 \\
 G(4,14) &= -\mu_O r_2 \sin \beta / \sqrt{r_2 r_3} \\
 G(4,15) &= 0
 \end{aligned}$$

$$\begin{aligned}
 G(5,1) &= -\mu_C \cos(\alpha_3 - \phi) \\
 G(5,2) &= 0 \\
 G(5,3) &= \mu_C \cos \alpha_3 \\
 G(5,4) &= 0 \\
 G(5,5) &= \mu_C + \mu_O \\
 G(5,6) &= 0 \\
 G(5,7) &= \mu_O \cos \beta \\
 G(5,8) &= \mu_C \frac{r_1}{R} \sin(\alpha_3 - \phi) \\
 G(5,9) &= -\mu_C \frac{r_2}{R} \sin(\alpha_3 - \phi) \\
 G(5,10) &= 0 \\
 G(5,11) &= \mu_C \frac{r_1}{R} \sin(\alpha_3 - \phi) + \mu_C \sin \alpha_3
 \end{aligned}$$

$$G(5,12) = -\mu_c \frac{r_2}{R} \sin(\alpha_3 - \phi)$$

$$G(5,13) = -\mu_c r_2 \sin \alpha_3 / \sqrt{r_1 r_2}$$

$$G(5,14) = 0$$

$$G(5,15) = -\mu_o r_2 \sin \beta / \sqrt{r_2 r_3}$$

$$G(6,1) = 0$$

$$G(6,2) = 0$$

$$G(6,3) = 0$$

$$G(6,4) = \mu_o \cos \beta$$

$$G(6,5) = 0$$

$$G(6,6) = \mu_o + \mu_H$$

$$G(6,7) = 0$$

$$G(6,8) = 0$$

$$G(6,9) = -\mu_o \sin \beta$$

$$G(6,10) = \mu_o r_1 \sin \beta / \sqrt{r_1 r_2}$$

$$G(6,11) = 0$$

$$G(6,12) = 0$$

$$G(6,13) = 0$$

$$G(6,14) = -\mu_o r_3 \sin \beta / \sqrt{r_2 r_3}$$

$$G(6,15) = 0$$

$$G(7,1) = 0$$

$$G(7,2) = 0$$

$$G(7,3) = 0$$

$$G(7,4) = 0$$

$$\begin{aligned}
 G(7,5) &= \mu_0 \cos \beta \\
 G(7,6) &= 0 \\
 G(7,7) &= \mu_0 + \mu_H \\
 G(7,8) &= 0 \\
 G(7,9) &= 0 \\
 G(7,10) &= 0 \\
 G(7,11) &= 0 \\
 G(7,12) &= -\mu_0 \sin \beta \\
 G(7,13) &= \mu_0 r_1 \sin \beta / \sqrt{r_1 r_2} \\
 G(7,14) &= 0 \\
 G(7,15) &= -\mu_0 r_3 \sin \beta / \sqrt{r_2 r_3}
 \end{aligned}$$

$$\begin{aligned}
 G(8,1) &= -\mu_c \sin \phi \\
 G(8,2) &= -\mu_c \frac{r_1}{R} \sin \phi \\
 G(8,3) &= -\mu_c \frac{r_1}{R} \sin \phi \\
 G(8,4) &= \mu_c \frac{r_1}{R} \sin(\alpha_3 - \phi) + \mu_c \sin \alpha_3 \\
 G(8,5) &= \mu_c \frac{r_1}{R} \sin(\alpha_3 - \phi) \\
 G(8,6) &= 0 \\
 G(8,7) &= 0 \\
 G(8,8) &= \mu_c \left\{ 2 \frac{r_1^2}{R^2} + 2 \frac{r_1}{R} \cos \phi + 1 \right\} + \mu_0 \\
 G(8,9) &= -2\mu_c (r_1 r_2 / R^2) - \mu_c \frac{r_1}{R} \cos(\alpha_3 - \phi) - \mu_c \frac{r_2}{R} \cos \phi - \mu_c \cos \alpha_3 \\
 G(8,10) &= \{ \mu_c (r_1^2 / R) \cos(\alpha_3 - \phi) + \mu_c r_1 \cos \alpha_3 - \mu_c (r_1 r_2 / R) \cos \phi \\
 &\quad - \mu_c r_2 - \mu_0 r_2 \} / \sqrt{r_1 r_2} \\
 G(8,11) &= 2\mu_c (r_1^2 / R^2) + 2\mu_c (r_1 / R) \cos \phi \\
 G(8,12) &= -2\mu_c (r_1 r_2 / R^2) - \mu_c (r_1 / R) \cos(\alpha_3 - \phi) - \mu_c (r_2 / R) \cos \phi
 \end{aligned}$$

$$\begin{aligned} G(8,13) &= \{\mu_c (r_1^2/R) \cos(\alpha_3 - \phi) - \mu_c (r_1 r_2/R) \cos \phi\} / \sqrt{r_1 r_2} \\ G(8,14) &= \{-\mu_c r_3 \cos \alpha_3 - \mu_c (r_1 r_3/R) \cos(\alpha_3 - \phi)\} / \sqrt{r_2 r_3} \\ G(8,15) &= -\mu_c (r_1 r_3/R) \cos(\alpha_3 - \phi) / \sqrt{r_2 r_3} \end{aligned}$$

$$\begin{aligned} G(9,1) &= -\mu_c \sin(\alpha_3 - \phi) \\ G(9,2) &= \mu_c \frac{r_2}{R} \sin \phi + \mu_c \sin \alpha_3 \\ G(9,3) &= \mu_c (r_2/R) \sin \phi \\ G(9,4) &= -\mu_c (r_2/R) \sin(\alpha_3 - \phi) \\ G(9,5) &= -\mu_c (r_2/R) \sin(\alpha_3 - \phi) \\ G(9,6) &= -\mu_0 \sin \beta \\ G(9,7) &= 0 \\ G(9,8) &= -2\mu_c (r_1 r_2/R^2) - \mu_c (r_1/R) \cos(\alpha_3 - \phi) - \mu_c (r_2/R) \cos \phi \\ &\quad - \mu_c \cos \alpha_3 \\ G(9,9) &= \mu_c \{(2r_2^2/R^2) + (2r_2/R) \cos(\alpha_3 - \phi) + 1\} + \mu_0 \\ G(9,10) &= \{\mu_c (r_2^2/R) \cos \phi + \mu_c r_2 \cos \alpha_3 - \mu_c (r_1 r_2/R) \cos(\alpha_3 - \phi) \\ &\quad - \mu_c r_1 - \mu_0 r_1\} / \sqrt{r_1 r_2} \\ G(9,11) &= -2\mu_c (r_1 r_2/R^2) - \mu_c (r_1/R) \cos(\alpha_3 - \phi) - \mu_c (r_2/R) \cos \phi \\ G(9,12) &= 2\mu_c (r_2^2/R^2) + 2\mu_c (r_2/R) \cos(\alpha_3 - \phi) \\ G(9,13) &= \{\mu_c (r_2^2/R) \cos \phi - \mu_c (r_1 r_2/R) \cos(\alpha_3 - \phi)\} / \sqrt{r_1 r_2} \\ G(9,14) &= \{\mu_c (r_2 r_3/R) \cos(\alpha_3 - \phi) + \mu_c r_3 + \mu_0 r_3 - \mu_0 r_2 \cos \beta\} / \\ &\quad \sqrt{r_2 r_3} \\ G(9,15) &= \mu_c (\sqrt{r_2 r_3}/R) \cos(\alpha_3 - \phi) \end{aligned}$$

$$G(10,1) = \mu_c \{r_2 \sin \phi + r_1 \sin(\alpha_3 - \phi)\} / \sqrt{r_1 r_2}$$

$$G(10,2) = -\mu_c r_1 \sin \alpha_3 / \sqrt{r_1 r_2}$$

$$G(10,3) = 0$$

$$G(10,4) = -\mu_c r_2 \sin \alpha_3 / \sqrt{r_1 r_2}$$

$$G(10,5) = 0$$

$$G(10,6) = \mu_o r_1 \sin \beta / \sqrt{r_1 r_2}$$

$$G(10,7) = 0$$

$$G(10,8) = \{\mu_c (r_1^2/R) \cos(\alpha_3 - \phi) + \mu_c r_1 \cos \alpha_3 - \mu_c (r_1 r_2/R) \cos \phi - \mu_c r_2 - \mu_o r_2\} / \sqrt{r_1 r_2}$$

$$G(10,9) = \{\mu_c (r_2^2/R) \cos \phi + \mu_c r_2 \cos \alpha_3 - \mu_c (r_1 r_2/R) \cos(\alpha_3 - \phi) - \mu_c r_1 - \mu_o r_1\} / \sqrt{r_1 r_2}$$

$$G(10,10) = \mu_c \{r_1/r_2 + (r_2/r_1) - 2 \cos \alpha_3\} + \mu_o \{r_1/r_2 + (r_2/r_1)\}$$

$$G(10,11) = \{\mu_c (r_1^2/R) \cos(\alpha_3 - \phi) - \mu_c (r_1 r_2/R) \cos \phi\} / \sqrt{r_1 r_2}$$

$$G(10,12) = \{\mu_c (r_2^2/R) \cos \phi - \mu_c (r_1 r_2/R) \cos(\alpha_3 - \phi)\} / \sqrt{r_1 r_2}$$

$$G(10,13) = 0$$

$$G(10,14) = \{\mu_c r_3 \cos \alpha_3 - \mu_c (r_1 r_3/r_2) - \mu_o (r_1 r_3/r_2) + \mu_o r_1 \cos \beta\} / \sqrt{r_1 r_3}$$

$$G(10,15) = 0$$

$$G(11,1) = -\mu_c \sin \phi$$

$$G(11,2) = -\mu_c (r_1/R) \sin \phi$$

$$G(11,3) = -\mu_c (r_1/R) \sin \phi$$

$$G(11,4) = \mu_c (r_1/R) \sin(\alpha_3 - \phi)$$

$$G(11,5) = \mu_c (r_1/R) \sin(\alpha_3 - \phi) + \mu_c \sin \alpha_3$$

$$G(11,6) = 0$$

$$G(11,7) = 0$$

$$G(11,8) = 2\mu_c (r_1^2/R^2) + 2\mu_c (r_1/R) \cos \phi$$

$$G(11,9) = -2\mu_c (r_1 r_2/R^2) - \mu_c (r_1/R) \cos(\alpha_3 - \phi) - \mu_c (r_2/R) \cos \phi$$

$$G(11,10) = \{\mu_c (r_1^2/R) \cos(\alpha_3 - \phi) - \mu_c (r_1 r_2/R) \cos \phi\} / \sqrt{r_1 r_2}$$

$$G(11,11) = \mu_c \{2 (r_1^2/R^2) + 2 (r_1/R) \cos \phi + 1\} + \mu_0$$

$$G(11,12) = -2\mu_c (r_1 r_2/R^2) - \mu_c (r_1/R) \cos(\alpha_3 - \phi) - \mu_c (r_2/R) \cos \phi \\ - \mu_c \cos \alpha_3$$

$$G(11,13) = \{\mu_c (r_1^2/R) \cos(\alpha_3 - \phi) + \mu_c r_1 \cos \alpha_3 - \mu_c (r_1 r_2/R) \cos \phi \\ - \mu_c r_2 - \mu_0 r_2\} / \sqrt{r_1 r_2}$$

$$G(11,14) = -\mu_c (r_1 r_3/R) \cos(\alpha_3 - \phi) / \sqrt{r_2 r_3}$$

$$G(11,15) = \{\mu_c (r_1 r_3/R) \cos(\alpha_3 - \phi) - \mu_c r_3 \cos \alpha_3\} / \sqrt{r_2 r_3}$$

$$G(12,1) = -\mu_c \sin(\alpha_3 - \phi)$$

$$G(12,2) = \mu_c (r_2/R) \sin \phi$$

$$G(12,3) = \mu_c (r_2/R) \sin \phi + \mu_c \sin \alpha_3$$

$$G(12,4) = -\mu_c (r_2/R) \sin(\alpha_3 - \phi)$$

$$G(12,5) = -\mu_c (r_2/R) \sin(\alpha_3 - \phi)$$

$$G(12,6) = 0$$

$$G(12,7) = -\mu_0 \sin \beta$$

$$G(12,8) = -2\mu_c (r_1 r_2/R^2) - \mu_c (r_1/R) \cos(\alpha_3 - \phi) - \mu_c (r_2/R) \cos \phi$$

$$G(12,9) = 2\mu_c (r_2^2/R^2) + 2\mu_c (r_2/R) \cos(\alpha_3 - \phi)$$

$$G(12,10) = \{\mu_c (r_2^2/R) \cos \phi - \mu_c (r_1 r_2/R) \cos(\alpha_3 - \phi)\} / \sqrt{r_1 r_2}$$

$$G(12,11) = -2\mu_c (r_1 r_2/R^2) - \mu_c (r_1/R) \cos(\alpha_3 - \phi) - \mu_c (r_2/R) \cos \phi - \mu_c \cos \alpha_3$$

$$G(12,12) = \mu_c \{2 \frac{r_2^2}{R} + 2 \frac{r_2}{R} \cos(\alpha_3 - \phi) + 1\} + \mu_0$$

$$G(12,13) = \{\mu_c r_2^2 \cos \alpha_3 + \mu_c (r_2^2/R) \cos \phi - \mu_c (r_1 r_2/R) \cos(\alpha_3 - \phi) \\ - \mu_c r_1 - \mu_0 r_1\} / \sqrt{r_1 r_2}$$

$$G(12,14) = \mu_c (\sqrt{r_2 r_3}/R) \cos(\alpha_3 - \phi)$$

$$G(12,15) = \{\mu_c (r_2 r_3/R) \cos(\alpha_3 - \phi) + \mu_c r_3 + \mu_0 r_3 - \mu_0 r_2 \cos \beta\} / \sqrt{r_2 r_3}$$

$$\begin{aligned}
 G(13,1) &= \mu_c \{r_2 \sin \phi + r_1 \sin(\alpha_3 - \phi)\} / \sqrt{r_1 r_2} \\
 G(13,2) &= 0 \\
 G(13,3) &= -\mu_c r_1 \sin \alpha_3 / \sqrt{r_1 r_2} \\
 G(13,4) &= 0 \\
 G(13,5) &= -\mu_c r_2 \sin \alpha_3 / \sqrt{r_1 r_2} \\
 G(13,6) &= 0 \\
 G(13,7) &= \mu_o r_1 \sin \beta / \sqrt{r_1 r_2} \\
 G(13,8) &= \{\mu_c (r_1^2/R) \cos(\alpha_3 - \phi) - \mu_c (r_1 r_2/R) \cos \phi\} / \sqrt{r_1 r_2} \\
 G(13,9) &= \{\mu_c (r_2^2/R) \cos \phi - \mu_c (r_1 r_2/R) \cos(\alpha_3 - \phi)\} / \sqrt{r_1 r_2} \\
 G(13,10) &= 0 \\
 G(13,11) &= \{\mu_c (r_1^2/R) \cos(\alpha_3 - \phi) + \mu_c r_1 \cos \alpha_3 - \mu_c (r_1 r_2/R) \cos \phi \\
 &\quad - \mu_c r_2 - \mu_o r_2\} / \sqrt{r_1 r_2} \\
 G(13,12) &= \{\mu_c r_2 \cos \alpha_3 + \mu_c (r_2^2/R) \cos \phi - \mu_c (r_1 r_2/R) \cos(\alpha_3 - \phi) \\
 &\quad - \mu_c r_1 - \mu_o r_1\} / \sqrt{r_1 r_2} \\
 G(13,13) &= \mu_c \{(r_1/r_2) + (r_2/r_1) - 2 \cos \alpha_3\} + \mu_o \{(r_1/r_2) + (r_2/r_1)\} \\
 G(13,14) &= 0 \\
 G(13,15) &= \{\mu_c r_3 \cos \alpha_3 - \mu_c (r_1 r_3/r_2) - \mu_o (r_1 r_3/r_2) + \mu_o r_1 \cos \beta\} \\
 &\quad / \sqrt{r_1 r_3}
 \end{aligned}$$

$$\begin{aligned}
 G(14,1) &= -\mu_c r_3 \sin(\alpha_3 - \phi) / \sqrt{r_2 r_3} \\
 G(14,2) &= \mu_c r_3 \sin \alpha_3 / \sqrt{r_2 r_3} \\
 G(14,3) &= 0 \\
 G(14,4) &= -\mu_o r_2 \sin \beta / \sqrt{r_2 r_3} \\
 G(14,5) &= 0 \\
 G(14,6) &= -\mu_o r_3 \sin \beta / \sqrt{r_2 r_3} \\
 G(14,7) &= 0
 \end{aligned}$$

$$\begin{aligned}
 G(14,8) &= \{-\mu_c r_3 \cos \alpha_3 - \mu_c (r_1 r_3 / R) \cos(\alpha_3 - \phi)\} / \sqrt{r_2 r_3} \\
 G(14,9) &= \{\mu_c (r_2 r_3 / R) \cos(\alpha_3 - \phi) + \mu_c r_3 + \mu_0 r_3 - \mu_0 r_2 \cos \beta\} / \sqrt{r_2 r_3} \\
 G(14,10) &= \{\mu_c r_3 \cos \alpha_3 - \mu_c (r_1 r_3 / r_2) - \mu_0 (r_1 r_3 / r_2) + \mu_0 r_1 \cos \beta\} / \sqrt{r_1 r_3} \\
 G(14,11) &= -\mu_c (r_1 r_3 / R) \cos(\alpha_3 - \phi) / \sqrt{r_2 r_3} \\
 G(14,12) &= \mu_c (\sqrt{r_2 r_3} / R) \cos(\alpha_3 - \phi) \\
 G(14,13) &= 0 \\
 G(14,14) &= \mu_c (r_3 / r_2) + \mu_0 \{(r_2 / r_3) + (r_3 / r_2) - 2 \cos \beta\} + \mu_H (r_2 / r_3) \\
 G(14,15) &= 0
 \end{aligned}$$

$$\begin{aligned}
 G(15,1) &= -\mu_c r_3 \sin(\alpha_3 - \phi) / \sqrt{r_2 r_3} \\
 G(15,2) &= 0 \\
 G(15,3) &= \mu_c r_3 \sin \alpha_3 / \sqrt{r_2 r_3} \\
 G(15,4) &= 0 \\
 G(15,5) &= -\mu_0 r_2 \sin \beta / \sqrt{r_2 r_3} \\
 G(15,6) &= 0 \\
 G(15,7) &= -\mu_0 r_3 \sin \beta / \sqrt{r_2 r_3} \\
 G(15,8) &= -\mu_c (r_1 r_3 / R) \cos(\alpha_3 - \phi) / \sqrt{r_2 r_3} \\
 G(15,9) &= \mu_c (\sqrt{r_2 r_3} / R) \cos(\alpha_3 - \phi) \\
 G(15,10) &= 0 \\
 G(15,11) &= \{-\mu_c (r_1 r_3 / R) \cos(\alpha_3 - \phi) - \mu_c r_3 \cos \alpha_3\} / \sqrt{r_2 r_3} \\
 G(15,12) &= \{\mu_c (r_2 r_3 / R) \cos(\alpha_3 - \phi) + \mu_c r_3 + \mu_0 r_3 - \mu_0 r_2 \cos \beta\} / \sqrt{r_2 r_3} \\
 G(15,13) &= \{\mu_c r_3 \cos \alpha_3 - \mu_c (r_1 r_3 / r_2) - \mu_0 (r_1 r_3 / r_2) + \mu_0 r_1 \cos \beta\} / \sqrt{r_1 r_3} \\
 G(15,14) &= 0 \\
 G(15,15) &= \mu_c (r_3 / r_2) + \mu_0 \{(r_2 / r_3) + (r_3 / r_2) - 2 \cos \beta\} + \mu_H (r_2 / r_3)
 \end{aligned}$$

15.4 Symmetry co-ordinates of the inplane vibration of gaseous oxalic acid 1st model

The transformation table of the internal co-ordinates of oxalic acid 1st model is given below.

Table 12

C_{2h}	E	C_2	i	σ_h
ΔR	ΔR	ΔR	ΔR	ΔR
Δr_1	Δr_1	$\Delta r'_1$	$\Delta r'_1$	Δr_1
$\Delta r'_1$	$\Delta r'_1$	Δr_1	Δr_1	$\Delta r'_1$
Δr_2	Δr_2	$\Delta r'_2$	$\Delta r'_2$	Δr_2
$\Delta r'_2$	$\Delta r'_2$	Δr_2	Δr_2	$\Delta r'_2$
Δr_3	Δr_3	$\Delta r'_3$	$\Delta r'_3$	Δr_3
$\Delta r'_3$	$\Delta r'_3$	Δr_3	Δr_3	$\Delta r'_3$
$\Delta \alpha_1$	$\Delta \alpha_1$	$\Delta \alpha'_1$	$\Delta \alpha'_1$	$\Delta \alpha_1$
$\Delta \alpha_2$	$\Delta \alpha_2$	$\Delta \alpha'_2$	$\Delta \alpha'_2$	$\Delta \alpha_2$
$\Delta \alpha_3$	$\Delta \alpha_3$	$\Delta \alpha'_3$	$\Delta \alpha'_3$	$\Delta \alpha_3$
$\Delta \alpha'_1$	$\Delta \alpha'_1$	$\Delta \alpha_1$	$\Delta \alpha_1$	$\Delta \alpha'_1$
$\Delta \alpha'_2$	$\Delta \alpha'_2$	$\Delta \alpha_2$	$\Delta \alpha_2$	$\Delta \alpha'_2$
$\Delta \alpha'_3$	$\Delta \alpha'_3$	$\Delta \alpha_3$	$\Delta \alpha_3$	$\Delta \alpha'_3$
$\Delta \beta$	$\Delta \beta$	$\Delta \beta'$	$\Delta \beta'$	$\Delta \beta$
$\Delta \beta'$	$\Delta \beta'$	$\Delta \beta$	$\Delta \beta$	$\Delta \beta'$

The generating co-ordinates for oxalic acid may be written as

Ag set $S_1 = \Delta R$

$$S_2 = \Delta r_1 + \Delta r'_1$$

$$S_3 = \Delta r_2 + \Delta r'_2$$

$$S_4 = \Delta r_3 + \Delta r'_3$$

$$S_5 = (\Delta \alpha_3 + \Delta \alpha'_3) - (\Delta \alpha_1 + \Delta \alpha'_1 + \Delta \alpha_2 + \Delta \alpha'_2)$$

$$S_6 = (\Delta \alpha_2 + \Delta \alpha'_2) - (\Delta \alpha_1 + \Delta \alpha'_1)$$

$$S_7 = \Delta \alpha_3 + \Delta \alpha_1 + \Delta \alpha_2 + \Delta \alpha'_3 + \Delta \alpha'_1 + \Delta \alpha'_2$$

$$S_8 = \Delta \beta + \Delta \beta'$$

Bu set $S_9 = \Delta r_1 - \Delta r'_1$

$$S_{10} = \Delta r_2 - \Delta r'_2$$

$$S_{11} = \Delta r_3 - \Delta r'_3$$

$$S_{12} = (\Delta \alpha_3 - \Delta \alpha'_3) - (\Delta \alpha_2 - \Delta \alpha'_2 + \Delta \alpha_1 - \Delta \alpha'_1)$$

$$S_{13} = (\Delta \alpha_2 - \Delta \alpha'_2 - \Delta \alpha_1 + \Delta \alpha'_1)$$

$$S_{14} = (\Delta \alpha_3 + \Delta \alpha_1 + \Delta \alpha_2) - (\Delta \alpha'_3 + \Delta \alpha'_1 + \Delta \alpha'_2)$$

$$S_{15} = \Delta \beta - \Delta \beta'$$

S_7 and S_{14} can be picked as redundant co-ordinates because the sum of all angle changes around a point in a plane would be zero and thus not affect the kinetic or potential energies. So the generating co-ordinates reduce from 15 to 13 which correspond to the 13 inplane vibrations of the gaseous oxalic acid molecule.

Normalized symmetry co-ordinates may be obtained using equation 3.12 with Table 12 and normalized using equation 3.13.

Thus, the normalized symmetry co-ordinates of gaseous oxalic acid 1st model may be written as

Ag set

$$\begin{aligned}
 S_1 &= \Delta R && \text{symmetric C-C stretch} \\
 S_2 &= \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r'_1) && \text{" C=O " } \\
 S_3 &= \frac{1}{\sqrt{2}}(\Delta r_2 + \Delta r'_2) && \text{" C-O " } \\
 S_4 &= \frac{1}{\sqrt{2}}(\Delta r_3 + \Delta r'_3) && \text{" O-H " } \\
 S_5 &= \frac{1}{\sqrt{3}}(\Delta \alpha_3 + \Delta \alpha'_3) - \frac{1}{2\sqrt{3}}(\Delta \alpha_2 + \Delta \alpha'_2 + \Delta \alpha_1 + \Delta \alpha'_1) \\
 &&& \text{symmetric } (-\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}) \text{ angle deformation} \\
 S_6 &= \frac{1}{2}(\Delta \alpha_2 - \Delta \alpha_1 + \Delta \alpha'_2 - \Delta \alpha'_1) \\
 &&& \text{symmetric } (-\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}) \text{ angle rocking} \\
 S_7 &= \frac{1}{\sqrt{2}}(\Delta \beta + \Delta \beta') && \text{symmetric C-O-H angle bending}
 \end{aligned}$$

Bu set

$$\begin{aligned}
 S_8 &= \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r'_1) && \text{anti-symmetric C=O stretch} \\
 S_9 &= \frac{1}{\sqrt{2}}(\Delta r_2 - \Delta r'_2) && \text{" C-O " } \\
 S_{10} &= \frac{1}{\sqrt{2}}(\Delta r_3 - \Delta r'_3) && \text{" O-H " } \\
 S_{11} &= \frac{1}{\sqrt{3}}(\Delta \alpha_3 - \Delta \alpha'_3) - \frac{1}{2\sqrt{3}}(\Delta \alpha_2 - \Delta \alpha'_2 + \Delta \alpha_1 - \Delta \alpha'_1) \\
 &&& \text{anti-symmetric } (-\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}) \text{ angle deformation} \\
 S_{12} &= \frac{1}{2}(\Delta \alpha_2 - \Delta \alpha'_2 - \Delta \alpha_1 + \Delta \alpha'_1) \\
 &&& \text{anti-symmetric } (-\text{C} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}) \text{ angle rocking} \\
 S_{13} &= \frac{1}{\sqrt{2}}(\Delta \beta - \Delta \beta') && \text{anti-symmetric C-O-H angle bending}
 \end{aligned}$$

From the normalized symmetry co-ordinates, the U matrix may be obtained as shown in Table 13.

Table 13

U-matrix for gaseous oxalic acid 1st model

	ΔR	Δr_1	$\Delta r'_1$	Δr_2	$\Delta r'_2$	Δr_3	$\Delta r'_3$	$\Delta \alpha_1$	$\Delta \alpha_2$	$\Delta \alpha_3$	$\Delta \alpha'_1$	$\Delta \alpha'_2$	$\Delta \alpha'_3$	$\Delta \beta / \Delta \beta'$
S_1	1													
S_2		$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$											
S_3				$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$									
S_4						$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$							
S_5								$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	
S_6								$-\frac{1}{2}$	$\frac{1}{2}$		$-\frac{1}{2}$	$\frac{1}{2}$		
S_7														$\frac{1}{\sqrt{2}}$ $\frac{1}{\sqrt{2}}$
S_8		$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$											
S_9				$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$									
S_{10}						$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$							
S_{11}								$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	
S_{12}								$-\frac{1}{2}$	$\frac{1}{2}$		$\frac{1}{2}$	$-\frac{1}{2}$		
S_{13}														$\frac{1}{\sqrt{2}}$ $-\frac{1}{\sqrt{2}}$

15.5 Numerical values of G-matrix in symmetry co-ordinates

G(1,1) = 0.166667
G(1,2) = -0.064359
G(1,3) = -0.043957
G(1,4) = 0
G(1,5) = 0.254615
G(1,6) = -0.00751
G(1,7) = -0.097107
G(1,8) = G(1,9) = G(1,10) = G(1,11) = G(1,12) = G(1,13) = 0

G(2,1) = -0.064359
G(2,2) = 0.145833
G(2,3) = -0.047798
G(2,4) = 0
G(2,5) = -0.085632
G(2,6) = 0.210708
G(2,7) = 0.060621
G(2,8) = G(2,9) = G(2,10) = G(2,11) = G(2,12) = G(2,13) = 0

G(3,1) = -0.043957
G(3,2) = -0.047798
G(3,3) = 0.145835
G(3,4) = -0.015543
G(3,5) = -0.081206
G(3,6) = -0.228183
G(3,7) = -0.068167
G(3,8) = G(3,9) = G(3,10) = G(3,11) = G(3,12) = G(3,13) = 0

G(4,1) = 0
G(4,2) = 0
G(4,3) = -0.015543
G(4,4) = 1.062491
G(4,5) = 0.071662
G(4,6) = -0.042806
G(4,7) = -0.05376
G(4,8) = G(4,9) = G(4,10) = G(4,11) = G(4,12) = G(4,13) = 0

G(5,1) = 0.254615
G(5,2) = -0.085632
G(5,3) = -0.081206
G(5,4) = 0.071662
G(5,5) = 0.579780
G(5,6) = 0.037330
G(5,7) = -0.229755
G(5,8) = G(5,9) = G(5,10) = G(5,11) = G(5,12) = G(5,13) = 0

G(6,1) = -0.00751
G(6,2) = 0.210708
G(6,3) = -0.228183
G(6,4) = -0.042806
G(6,5) = 0.03733
G(6,6) = 0.801268
G(6,7) = 0.138167
G(6,8) = G(6,9) = G(6,10) = G(6,11) = G(6,12) = G(6,13) = 0

G(7,1) = -0.097107
G(7,2) = 0.060621
G(7,3) = -0.068167
G(7,4) = -0.05376
G(7,5) = -0.229755
G(7,6) = 0.138167
G(7,7) = 1.493328
G(7,8) = G(7,9) = G(7,10) = G(7,11) = G(7,12) = G(7,13) = 0

G(8,1) = G(8,2) = G(8,3) = G(8,4) = G(8,5) = G(8,6) = G(8,7) = 0
G(8,8) = 0.145833
G(8,9) = -0.047798
G(8,10) = 0
G(8,11) = -0.080808
G(8,12) = 0.048269
G(8,13) = 0.060621

G(9,1) = G(9,2) = G(9,3) = G(9,4) = G(9,5) = G(9,6) = G(9,7) = 0
G(9,8) = -0.047798
G(9,9) = 0.145835
G(9,10) = -0.015543
G(9,11) = -0.086549
G(9,12) = -0.048269
G(9,13) = -0.068167

$$\begin{aligned} G(10,1) &= G(10,2) = G(10,3) = G(10,4) = G(10,5) = G(10,6) \\ &= G(10,7) = 0 \\ G(10,8) &= 0 \\ G(10,9) &= -0.015543 \\ G(10,10) &= 1.062491 \\ G(10,11) &= 0.071662 \\ G(10,12) &= -0.042806 \\ G(10,13) &= -0.05376 \end{aligned}$$

$$\begin{aligned} G(11,1) &= G(11,2) = G(11,3) = G(11,4) = G(11,5) = G(11,6) \\ &= G(11,7) = 0 \\ G(11,8) &= -0.080808 \\ G(11,9) &= -0.086549 \\ G(11,10) &= 0.071662 \\ G(11,11) &= 0.58227 \\ G(11,12) &= 0.005829 \\ G(11,13) &= -0.227848 \end{aligned}$$

$$\begin{aligned} G(12,1) &= G(12,2) = G(12,3) = G(12,4) = G(12,5) = G(12,6) \\ &= G(12,7) = 0 \\ G(12,8) &= 0.048269 \\ G(12,9) &= -0.048269 \\ G(12,10) &= -0.042806 \\ G(12,11) &= 0.005829 \\ G(12,12) &= 0.098036 \\ G(12,13) &= 0.073938 \end{aligned}$$

$G(13,1) = G(13,2) = G(13,3) = G(13,4) = G(13,5) = G(13,6)$
 $= G(13,7) = 0$
 $G(13,8) = 0.060621$
 $G(13,9) = -0.068167$
 $G(13,10) = -0.05376$
 $G(13,11) = -0.227848$
 $G(13,12) = 0.073938$
 $G(13,13) = 1.493328$

CHAPTER 16

CONSTRUCTION OF THE F-MATRIX OF THE INPLANE VIBRATIONS

OF GASEOUS OXALIC ACID 1ST MODEL

16.1 Urey-Bradley force field of gaseous oxalic acid (1st model)

Fig. 20

The potential energy of gaseous oxalic acid can be expressed as

$$\begin{aligned}
 V = & \frac{1}{2} K_{CC} (\Delta R)^2 + K'_{CC} R (\Delta R) \\
 & + \frac{1}{2} K_{C=O} (\Delta r_1)^2 + K'_{C=O} r_1 (\Delta r_1) \\
 & + \frac{1}{2} K_{C=O} (\Delta r'_1)^2 + K'_{C=O} r'_1 (\Delta r'_1) \\
 & + \frac{1}{2} K_{C-O} (\Delta r_2)^2 + K'_{C-O} r_2 (\Delta r_2) \\
 & + \frac{1}{2} K_{C-O} (\Delta r'_2)^2 + K'_{C-O} r'_2 (\Delta r'_2) \\
 & + \frac{1}{2} K_{O-H} (\Delta r_3)^2 + K'_{O-H} r_3 (\Delta r_3) \\
 & + \frac{1}{2} K_{O-H} (\Delta r'_3)^2 + K'_{O-H} r'_3 (\Delta r'_3) \\
 & + \frac{1}{2} H_{C-C=O} (r_1 \Delta \alpha_1)^2 + H'_{C-C=O} r_1 (r_1 \Delta \alpha_1)
 \end{aligned}$$

$$\begin{aligned}
 & + \frac{1}{2} H_{C-C=O} (r'_1 \Delta \alpha'_1)^2 + H_{C-C=O} r'_1 (r'_1 \Delta \alpha'_1) \\
 & + \frac{1}{2} H_{C-C-O} (r'_2 \Delta \alpha'_2)^2 + H_{C-C-O} r'_2 (r'_2 \Delta \alpha'_2) \\
 & + \frac{1}{2} H_{C-C-O} (r'_2 \Delta \alpha'_2)^2 + H_{C-C-O} r'_2 (r'_2 \Delta \alpha'_2) \\
 & + \frac{1}{2} H_{O-C=O} (\sqrt{r'_1 r'_2} \Delta \alpha'_3)^2 + H_{O-C=O} \sqrt{r'_1 r'_2} (\sqrt{r'_1 r'_2} \Delta \alpha'_3) \\
 & + \frac{1}{2} H_{O-C=O} (\sqrt{r'_1 r'_2} \Delta \alpha'_3)^2 + H_{O-C=O} (\sqrt{r'_1 r'_2} \Delta \alpha'_3) \sqrt{r'_1 r'_2} \\
 & + \frac{1}{2} H_{C-O-H} (\sqrt{r'_2 r'_3} \Delta \beta)^2 + H_{C-O-H} \sqrt{r'_2 r'_3} (\sqrt{r'_2 r'_3} \Delta \beta) \\
 & + \frac{1}{2} H_{C-O-H} (\sqrt{r'_2 r'_3} \Delta \beta')^2 + H_{C-O-H} \sqrt{r'_2 r'_3} (\sqrt{r'_2 r'_3} \Delta \beta') \\
 & + \frac{1}{2} F_{C_1 O_3} (\Delta q_{13})^2 + F_{C_1 O_3} q_{13} (\Delta q_{13}) \\
 & + \frac{1}{2} F_{C_2 O_6} (\Delta q_{26})^2 + F_{C_2 O_6} q_{26} (\Delta q_{26}) \\
 & + \frac{1}{2} F_{C_1 O_4} (\Delta q_{14})^2 + F_{C_1 O_4} q_{14} (\Delta q_{14}) \\
 & + \frac{1}{2} F_{C_2 O_7} (\Delta q_{27})^2 + F_{C_2 O_7} q_{27} (\Delta q_{27}) \\
 & + \frac{1}{2} F_{O_3 O_4} (\Delta q_{34})^2 + F_{O_3 O_4} q_{34} (\Delta q_{34}) \\
 & + \frac{1}{2} F_{O_6 O_7} (\Delta q_{67})^2 + F_{O_6 O_7} q_{67} (\Delta q_{67}) \\
 & + \frac{1}{2} F_{O_4 O_6} (\Delta q_{46})^2 + F_{O_4 O_6} q_{46} (\Delta q_{46}) \\
 & + \frac{1}{2} F_{O_3 O_7} (\Delta q_{37})^2 + F_{O_3 O_7} q_{37} (\Delta q_{37}) \\
 & + \frac{1}{2} F_{C_2 H_5} (\Delta q_{25})^2 + F_{C_2 H_5} q_{25} (\Delta q_{25}) \\
 & + \frac{1}{2} F_{C_1 H_8} (\Delta q_{18})^2 + F_{C_1 H_8} q_{18} (\Delta q_{18})
 \end{aligned}$$

In which we assume that $F_{O_6 H_8}$, $F_{O_3 H_5}$, $F_{C_1 H_5}$, $F_{C_2 H_8}$, $F_{O_6 H_5}$, $F_{O_3 H_8}$ and $F_{H_5 H_8}$ are small compared with each of the force constants above and we neglect them to make the calculation possible.

For simplicity of writing let

$$\begin{array}{lll}
 K_{CC} & = & K_1 \\
 K_{C=O} & = & K_2 \\
 K_{C-O} & = & K_3 \\
 K_{O-H} & = & K_4 \\
 H_{C-C=O} & = & H_1 \\
 H_{C-C-O} & = & H_2 \\
 H_{O-C=O} & = & H_3 \\
 H_{C-O-H} & = & H_4 \\
 F_{C_1O_3} & = & F_{C_2O_6} = F_1 \\
 F_{C_1O_4} & = & F_{C_2O_7} = F_2 \\
 F_{O_5O_4} & = & F_{O_6O_7} = F_3 \\
 F_{O_4O_6} & = & F_{O_3O_7} = F_4 \\
 F_{C_2H_5} & = & F_{C_1H_8} = F_5
 \end{array}$$

So there are 13 force constants in the Urey-Bradley force field of the inplane vibration of the gaseous oxalic acid molecule.

16.2 Evaluation of F-matrix

The first step in the evaluation of the F-matrix is to eliminate all Δq in the potential energy expression. Using Table 1 and 2 in section 6.3 and substituting all the q values in the Urey-Bradley potential energy of gaseous oxalic acid molecule and neglecting all first order terms, the potential expression in

terms of internal co-ordinates of gaseous oxalic acid is

$$\begin{aligned}
 V = & \frac{1}{2}(\Delta R)^2 (K_{CC} + S_{13}^2 F_1 + t_{13}^2 F'_1 + S_{26}^2 F_1 + t_{26}^2 F'_1 + S_{14}^2 F_2 \\
 & + t_{14}^2 F'_2 + S_{27}^2 F_2 + t_{27}^2 F'_2 + a_{64}^2 F_4 + b_{64}^2 F'_4 + a_{37}^2 F_4 + b_{37}^2 F'_4) \\
 & + \frac{1}{2}(\Delta r_1)^2 (K_{C=O} + S_{31}^2 F_1 + t_{31}^2 F'_1 + S_{34}^2 F_3 + t_{34}^2 F'_3 + v_{37}^2 F_4 \\
 & + (1 - v_{37}^2) F'_4) \\
 & + \frac{1}{2}(\Delta r'_1)^2 (K_{C=O} + S_{62}^2 F_1 + t_{62}^2 F'_1 + S_{67}^2 F_3 + t_{67}^2 F'_3 + v_{64}^2 F_4 \\
 & + (1 - v_{64}^2) F'_4) \\
 & + \frac{1}{2}(\Delta r_2)^2 (K_{C-O} + S_{41}^2 F_2 + t_{41}^2 F'_2 + S_{43}^2 F_3 + t_{43}^2 F'_3 + S_{25}^2 F_5 \\
 & + t_{25}^2 F'_5 + v_{46}^2 F_4 + (1 - v_{46}^2) F'_4) \\
 & + \frac{1}{2}(\Delta r'_2)^2 (K_{C-O} + S_{72}^2 F_2 + t_{72}^2 F'_2 + S_{76}^2 F_3 + t_{76}^2 F'_3 + S_{18}^2 F_5 \\
 & + t_{18}^2 F'_5 + v_{73}^2 F_4 + (1 - v_{73}^2) F'_4) \\
 & + \frac{1}{2}(\Delta r_3)^2 (K_{O-H} + S_{52}^2 F_5 + t_{52}^2 F'_5) \\
 & + \frac{1}{2}(\Delta r'_3)^2 (K_{O-H} + S_{81}^2 F_5 + t_{81}^2 F'_5) \\
 & + \frac{1}{2}(r_1 \Delta \alpha_1)^2 (H_{C-C=O} + \frac{R}{r_1} (t_{13} t_{31} F_1 - S_{13} S_{31} F'_1) + u_{37}^2 F_4 + ((v_{37}^2 q_{37}/ \\
 & r_1) + (1 - u_{37}^2) F'_4) \\
 & + \frac{1}{2}(r'_1 \Delta \alpha'_1)^2 (H_{C-C=O} + \frac{R}{r'_1} (t_{26} t_{62} F_1 - S_{26} S_{62} F'_1) + u_{64}^2 F_4 \\
 & + ((v_{64}^2 q_{64}/r'_1) + (1 - u_{64}^2) F'_4) \\
 & + \frac{1}{2}(r_2 \Delta \alpha_2)^2 (H_{C-C-O} + \frac{R}{r_2} (t_{14} t_{41} F_2 - S_{14} S_{41} F'_2) + u_{46}^2 F_4 \\
 & + ((v_{46}^2 q_{46}/r_2) + (1 - u_{46}^2) F'_4)
 \end{aligned}$$

$$+ \frac{1}{2}(r'_2 \Delta \alpha'_2)^2 (H_{C-C-O} + \frac{R}{r'_2} (t_{27} t_{72} F_2 - S_{27} S_{72} F'_2) + U_{73}^2 F_4 \\ + ((v_{73} a_{37}/r'_2) + (1 - U_{73}^2) F'_4)$$

$$+ \frac{1}{2}(\sqrt{r'_1 r'_2} \Delta \alpha_3)^2 (H_{O-C=O} + t_{34} t_{43} F_3 - S_{34} S_{43} F'_3) \\ + \frac{1}{2}(\sqrt{r'_1 r'_2} \Delta \alpha'_3)^2 (H_{O-C=O} + t_{67} t_{76} F_3 - S_{67} S_{76} F'_3) \\ + \frac{1}{2}(\sqrt{r'_2 r'_3} \Delta \beta)^2 (H_{C-O-H} + t_{25} t_{52} F_5 - S_{25} S_{52} F'_5) \\ + \frac{1}{2}(\sqrt{r'_2 r'_3} \Delta \beta')^2 (H_{C-O-H} + t_{18} t_{81} F_5 - S_{18} S_{81} F'_5) \\ + (\Delta R) (\Delta r_1) (S_{13} S_{31} F_1 - t_{13} t_{31} F'_1 - a_{37} v_{37} F_4 + (a_{37} v_{37} - \cos \alpha_1) F'_4) \\ + (\Delta R) (\Delta r'_1) (S_{26} S_{62} F_1 - t_{26} t_{62} F'_1 - a_{64} v_{64} F_4 + (a_{64} v_{64} - \cos \alpha'_1) F'_4) \\ + (\Delta R) (\Delta r_2) (S_{14} S_{41} F_2 - t_{14} t_{41} F'_2 - a_{64} v_{46} F_4 + (a_{64} v_{46} - \cos \alpha_2) F'_4) \\ + (\Delta R) (\Delta r'_2) (S_{27} S_{72} F_2 - t_{27} t_{72} F'_2 - a_{37} v_{73} F_4 + (a_{37} v_{73} - \cos \alpha'_2) F'_4) \\ + \Delta R (r_1 \Delta \alpha_1) (\sqrt{\frac{R}{r_1}} S_{13} \sqrt{t_{13} t_{31}} F_1 + t_{13} S_{31} F'_1 + U_{37} a_{37} F_4 \\ + (\sin \alpha_1 - a_{37} U_{37}) F'_4)$$

$$+ \Delta R (r'_1 \Delta \alpha'_1) (\sqrt{\frac{R}{r'_1}} S_{26} \sqrt{t_{26} t_{62}} F_1 + t_{26} S_{62} F'_1 + U_{64} a_{64} F_4 \\ + (\sin \alpha'_1 - a_{64} U_{64}) F'_4)$$

$$+ (\Delta R) (r_2 \Delta \alpha_2) (\sqrt{\frac{R}{r_2}} S_{14} \sqrt{t_{14} t_{41}} F_2 + t_{14} S_{41} F'_2 + U_{46} a_{64} F_4 \\ + (\sin \alpha_2 - a_{64} U_{46}) F'_4)$$

$$+ (\Delta R) (r'_2 \Delta \alpha'_2) (\sqrt{\frac{R}{r'_2}} S_{27} \sqrt{t_{27} t_{72}} F_2 + t_{27} S_{72} F'_2 + U_{73} a_{37} F_4 \\ + (\sin \alpha'_2 - a_{37} U_{73}) F'_4)$$

$$+ (\Delta r_1) (\Delta r_2) (S_{34} S_{43} F_3 - t_{34} t_{43} F'_3)$$

$$+ (\Delta r_1) (\Delta r'_2) (v_{37} v_{73} F_4 + (\cos(\alpha'_2 + \alpha_1) - v_{37} v_{73}) F'_4)$$

$$\begin{aligned}
 & + (\Delta r_1)(r_1 \Delta \alpha_1) \left(\sqrt{\frac{R}{r_1}} S_{31} \sqrt{t_{13} t_{31}} F_1 + \frac{R}{r_1} t_{31} S_{13} F'_1 - u_{37} v_{37} F_4 \right. \\
 & + \left. \{u_{37}(q_{37} + r_1 v_{37})/r_1\} F'_4 \right) \\
 & + (\Delta r_1)(\sqrt{r_1 r_2} \Delta \alpha_3) (S_{34} \sqrt{t_{34} t_{43}} F_3 + \sqrt{\frac{r_2}{r_1}} t_{34} S_{43} F'_3) \\
 & + (\Delta r_1)(r'_2 \Delta \alpha'_2) (-u_{73} v_{37} F_4 + \{v_{37} u_{73} - \sin(\alpha'_2 + \alpha_1)\} F'_4) \\
 & + (\Delta r'_1)(\Delta r_2)(v_{64} v_{46} F_4 + \{\cos(\alpha_1 + \alpha'_2) - v_{64} v_{46}\} F'_4) \\
 & + (\Delta r'_1)(\Delta r'_2)(S_{67} S_{76} F_3 - t_{67} t_{76} F'_3) \\
 & + (\Delta r'_1)(r_2 \Delta \alpha_2) (-u_{46} v_{64} F_4 + \{v_{64} u_{46} - \sin(\alpha_2 + \alpha'_1)\} F'_4) \\
 & + (\Delta r'_1)(r'_1 \Delta \alpha'_1) \left(\sqrt{\frac{R}{r'_1}} S_{62} \sqrt{t_{26} t_{62}} F_1 + \frac{R}{r'_1} t_{62} S_{26} F'_1 - u_{64} v_{64} F_4 \right. \\
 & + \left. \{u_{64}(q_{64} + r'_1 v_{64})/r'_1\} F'_4 \right) \\
 & + (\Delta r'_1)(\sqrt{r'_1 r'_2} \Delta \alpha'_3) (S_{67} \sqrt{t_{67} t_{76}} F_3 + \sqrt{\frac{r'_2}{r'_1}} t_{67} S_{76} F'_3) \\
 & + (\Delta r_2)(\Delta r_3)(S_{25} S_{52} F_5 - t_{25} t_{52} F'_5) \\
 & + (\Delta r_2)(r_2 \Delta \alpha_2) \left(\sqrt{\frac{R}{r_2}} S_{41} \sqrt{t_{14} t_{41}} F_2 + \frac{R}{r_2} t_{41} S_{14} F'_2 - u_{46} v_{46} F_4 \right. \\
 & + \left. \{u_{46}(q_{64} + r_2 v_{46})/r_2\} F'_4 \right) \\
 & + (\Delta r_2)(\sqrt{r_1 r_2} \Delta \alpha_3) (S_{43} \sqrt{t_{34} t_{43}} F_3 + \sqrt{\frac{r_1}{r_2}} t_{43} S_{34} F'_3) \\
 & + (\Delta r_2)(r'_1 \Delta \alpha'_1) (-u_{64} v_{46} F_4 + \{v_{46} u_{64} - \sin(\alpha_2 + \alpha'_1)\} F'_4) \\
 & + (\Delta r_2)(\sqrt{r_2 r_3} \Delta \alpha_3) (S_{25} \sqrt{t_{25} t_{52}} F_5 + \sqrt{\frac{r_3}{r_2}} t_{25} S_{52} F'_5) \\
 & + (\Delta r'_2)(\Delta r'_3)(S_{18} S_{81} F_5 - t_{18} t_{81} F'_5) \\
 & + (\Delta r'_2)(r_1 \Delta \alpha_1) (-u_{37} v_{73} F_4 + \{v_{73} u_{37} - \sin(\alpha'_2 + \alpha_1)\} F'_4) \\
 & + (\Delta r'_2)(r'_2 \Delta \alpha'_2) \left(\sqrt{\frac{R}{r'_2}} S_{72} \sqrt{t_{27} t_{72}} F_2 + \frac{R}{r'_2} t_{72} S_{27} F'_2 - u_{73} v_{73} F_4 \right. \\
 & + \left. \{u_{73}(q_{37} + r'_2 v_{73})/r'_2\} F'_4 \right) \\
 & + (\Delta r'_2)(\sqrt{r'_1 r'_2} \Delta \alpha'_3) (S_{76} \sqrt{t_{67} t_{76}} F_3 + \sqrt{\frac{r'_1}{r'_2}} t_{76} S_{67} F'_3) \\
 & + (\Delta r'_2)(\sqrt{r'_2 r'_3} \Delta \alpha'_3) (S_{18} \sqrt{t_{18} t_{81}} F_5 + \sqrt{\frac{r'_3}{r'_2}} t_{18} S_{81} F'_5)
 \end{aligned}$$

$$\begin{aligned}
 & + (Ar_3)(\sqrt{r_2 r_3} \Delta \beta) (S_{52} \sqrt{t_{25} t_{52}} F_5 + \sqrt{\frac{r_2}{r_3}} t_{52} S_{25} F'_5) \\
 & + (Ar'_3)(\sqrt{r'_2 r'_3} \Delta \beta') (S_{81} \sqrt{t_{18} t_{81}} F_5 + \sqrt{\frac{r'_2}{r'_3}} t_{81} S_{18} F'_5) \\
 & + (r_1 \Delta \alpha_1)(r'_2 \Delta \alpha'_2) (u_{37} u_{73} F_4 - \{\cos(\alpha'_2 + \alpha_1) + u_{37} u_{73}\} F'_4) \\
 & + (r_2 \Delta \alpha_2)(r'_1 \Delta \alpha'_1) (u_{64} u_{46} F_4 - \{\cos(\alpha_2 + \alpha'_1) + u_{64} u_{46}\} F'_4)
 \end{aligned}$$

The numerical values in this expression are

$$q_{13} = q_{26} = 2.428573 \text{ A}^\circ$$

$$q_{14} = q_{27} = 2.394888 \text{ A}^\circ$$

$$q_{25} = q_{18} = 1.900354 \text{ A}^\circ$$

$$q_{34} = q_{67} = 2.260029 \text{ A}^\circ$$

$$q_{64} = q_{37} = 2.716907 \text{ A}^\circ$$

$$S_{15} = S_{26} = 0.909048$$

$$S_{31} = S_{62} = 0.845502$$

$$t_{15} = t_{26} = 0.416692$$

$$t_{31} = t_{62} = 0.533972$$

$$S_{14} = S_{27} = 0.854918$$

$$S_{41} = S_{72} = 0.80020$$

$$t_{14} = t_{27} = 0.518762$$

$$t_{41} = t_{72} = 0.599734$$

$$S_{34} = S_{67} = 0.874336$$

$$S_{45} = S_{76} = 0.899052$$

$$t_{34} = t_{67} = 0.485322$$

$$t_{45} = t_{76} = 0.437841$$

$$S_{25} = S_{18} = 0.842799$$

$$S_{52} = S_{81} = 0.730914$$

$$t_{25} = t_{18} = 0.538226$$

$$t_{52} = t_{81} = 0.682467$$

$$a_{64} = a_{57} = 0.996399$$

$$b_{64} = b_{57} = -0.084807$$

$$u_{64} = u_{57} = 0.881016$$

$$u_{46} = u_{73} = 0.892867$$

$$v_{64} = v_{57} = -0.473089$$

$$v_{46} = v_{73} = -0.450334$$

The potential energy of gaseous oxalic acid (1st model) is given by substituting these values into the general expression and thus, only 13 force constants are left as follows:-

$$\begin{aligned} V = & \frac{1}{2}(\Delta r)^2(K_{CC} + 1.61801 F_1 + 1.407947 F_2 + 1.984183 F_4) \\ & + \frac{1}{2}(\Delta r_1)^2(K_{C=O} + 0.686361 F_1 + 0.74091 F_3 + 0.146195 F_4) \\ & + \frac{1}{2}(\Delta r'_1)^2(K_{C=O} + 0.686361 F_1 + 0.74091 F_3 + 0.146195 F_4) \\ & + \frac{1}{2}(\Delta r_2)^2(K_{C-O} + 0.604352 F_2 + 0.789124 F_3 + 0.681341 F_5 \\ & \quad + 0.123081 F_4) \\ & + \frac{1}{2}(\Delta r'_2)^2(K_{C-O} + 0.604352 F_2 + 0.789124 F_3 + 0.681341 F_5 \\ & \quad + 0.123081 F_4) \\ & + \frac{1}{2}(\Delta r_3)^2(K_{O-H} + 0.487659 F_5) \\ & + \frac{1}{2}(\Delta r'_3)^2(K_{O-H} + 0.487659 F_5) \\ & + \frac{1}{2}(r_1 \Delta \alpha_1)^2(H_1 + 0.38362 F_1 + 0.860210 F_4) \end{aligned}$$

$$\begin{aligned}
 & + \frac{1}{2}(r'_1 \Delta \alpha'_1)^2 (H_1 + 0.38362 F_1 + 0.860210 F_4) \\
 & + \frac{1}{2}(r_2 \Delta \alpha_2)^2 (H_2 + 0.438769 F_2 + 0.868308 F_4) \\
 & + \frac{1}{2}(r'_2 \Delta \alpha'_2)^2 (H_2 + 0.438769 F_2 + 0.868308 F_4) \\
 & + \frac{1}{2}(\sqrt{r_1 r_2} \Delta \alpha_3)^2 (H_3 + 0.291101 F_3) \\
 & + \frac{1}{2}(\sqrt{r'_1 r'_2} \Delta \alpha'_3)^2 (H_3 + 0.291101 F_3) \\
 & + \frac{1}{2}(\sqrt{r_2 r_3} \Delta \beta)^2 (H_4 + 0.428923 F_5) \\
 & + \frac{1}{2}(\sqrt{r'_2 r'_3} \Delta \beta')^2 (H_4 + 0.428923 F_5) \\
 & + (\Delta r)(\Delta r_1)(0.790852 F_1 + 0.463914 F_4) \\
 & + (\Delta r)(\Delta r'_1)(0.790852 F_1 + 0.463914 F_4) \\
 & + (\Delta r)(\Delta r_2)(0.715217 F_2 + 0.456285 F_4) \\
 & + (\Delta r)(\Delta r'_2)(0.715217 F_2 + 0.456285 F_4) \\
 & + (\Delta r)(r_1 \Delta \alpha_1)(0.450175 F_1 + 0.881856 F_4) \\
 & + (\Delta r)(r'_1 \Delta \alpha'_1)(0.450175 F_1 + 0.881856 F_4) \\
 & + (\Delta r)(r_2 \Delta \alpha_2)(0.471212 F_2 + 0.885833 F_4) \\
 & + (\Delta r)(r'_2 \Delta \alpha'_2)(0.471212 F_2 + 0.885833 F_4) \\
 & + (\Delta r_1)(\Delta r_2)(0.807323 F_3) \\
 & + (\Delta r_1)(\Delta r'_2)(0.291711 F_4) \\
 & + (\Delta r_1)(r_1 \Delta \alpha_1)(0.389272 F_1 + 0.260330 F_4) \\
 & + (\Delta r_1)(\sqrt{r_1 r_2} \Delta \alpha_3)(0.357105 F_3) \\
 & + (\Delta r_1)(r'_2 \Delta \alpha'_2)(0.382731 F_4) \\
 & + (\Delta r'_1)(\Delta r_2)(0.291711 F_4) \\
 & + (\Delta r'_1)(\Delta r'_2)(0.807323 F_3) \\
 & + (\Delta r'_1)(r_2 \Delta \alpha_2)(0.382731 F_4) \\
 & + (\Delta r'_1)(r'_1 \Delta \alpha'_1)(0.389272 F_1 + 0.260330 F_4) \\
 & + (\Delta r'_1)(\sqrt{r'_1 r'_2} \Delta \alpha'_3)(0.357105 F_3) \\
 & + (\Delta r_2)(\Delta r_3)(0.652746 F_5)
 \end{aligned}$$

$$\begin{aligned}
 &+ (\Delta r_2) (r_2 \Delta \alpha_2) (0.420632 F_2 + 0.261129 F_4) \\
 &+ (\Delta r_2) (\sqrt{r_1 r_2} \Delta \alpha_3) (0.378075 F_3) \\
 &+ (\Delta r_2) (r'_1 \Delta \alpha'_1) (0.354512 F_4) \\
 &+ (\Delta r_2) (\sqrt{r_2 r_3} \Delta \beta) (0.475860 F_5) \\
 &+ (\Delta r'_2) (\Delta r'_3) (0.652746 F_5) \\
 &+ (\Delta r'_2) (r_1 \Delta \alpha_1) (0.354512 F_4) \\
 &+ (\Delta r'_2) (r'_2 \Delta \alpha'_2) (0.420632 F_2 + 0.261129 F_4) \\
 &+ (\Delta r'_2) (\sqrt{r'_1 r'_2} \Delta \alpha'_3) (0.378075 F_3) \\
 &+ (\Delta r'_2) (\sqrt{r'_2 r'_3} \Delta \beta') (0.475860 F_5) \\
 &+ (\Delta r_3) (\sqrt{r_2 r_3} \Delta \beta) (0.378217 F_5) \\
 &+ (\Delta r'_3) (\sqrt{r'_2 r'_3} \Delta \beta') (0.378217 F_5) \\
 &+ (r_1 \Delta \alpha_1) (r'_2 \Delta \alpha'_2) (0.807935 F_4) \\
 &+ (r_2 \Delta \alpha_2) (r'_1 \Delta \alpha'_1) (0.807935 F_4)
 \end{aligned}$$

16.3 F-matrix in internal co-ordinates of gaseous oxalic acid (1st model)

$$\begin{aligned}
 F(1,1) &= K_1 + 1.61801 F_1 + 1.407947 F_2 + 1.984183 F_4 \\
 F(1,2) &= 0.790852 F_1 + 0.463914 F_4 \\
 F(1,3) &= 0.790852 F_1 + 0.463914 F_4 \\
 F(1,4) &= 0.715217 F_2 + 0.456285 F_4 \\
 F(1,5) &= 0.715217 F_2 + 0.456285 F_4 \\
 F(1,8) &= 0.450175 F_1 + 0.881856 F_4 \\
 F(1,9) &= 0.471212 F_2 + 0.885833 F_4 \\
 F(1,11) &= 0.450175 F_1 + 0.881856 F_4 \\
 F(1,12) &= 0.471212 F_2 + 0.885833 F_4 \\
 F(1,6) &= F(1,7) = F(1,10) = F(1,13) = F(1,14) = F(1,15) = 0
 \end{aligned}$$

$$\begin{aligned}F(2,1) &= 0.790852 F_1 + 0.463914 F_4 \\F(2,2) &= K_2 + 0.686561 F_1 + 0.74091 F_3 + 0.146195 F_4 \\F(2,4) &= 0.807323 F_3 \\F(2,5) &= 0.291711 F_4 \\F(2,8) &= 0.389272 F_1 + 0.260330 F_4 \\F(2,10) &= 0.357105 F_3 \\F(2,12) &= 0.332731 F_4 \\F(2,3) &= F(2,6) = F(2,7) = F(2,9) = F(2,11) = F(2,13) = F(2,14) \\&= F(2,15) = 0\end{aligned}$$

$$\begin{aligned}F(3,1) &= 0.790352 F_1 + 0.463914 F_4 \\F(3,3) &= K_2 + 0.686361 F_1 + 0.74091 F_3 + 0.146195 F_4 \\F(3,4) &= 0.291711 F_4 \\F(3,5) &= 0.807323 F_3 \\F(3,9) &= 0.382731 F_4 \\F(3,11) &= 0.389272 F_1 + 0.260330 F_4 \\F(3,13) &= 0.357105 F_3 \\F(3,2) &= F(3,6) = F(3,7) = F(3,8) = F(3,10) = F(3,12) = F(3,14) \\&= F(3,15) = 0\end{aligned}$$

$$\begin{aligned}F(4,1) &= 0.715217 F_2 + 0.456285 F_4 \\F(4,2) &= 0.807323 F_3 \\F(4,3) &= 0.291711 F_4 \\F(4,4) &= K_3 + 0.604352 F_2 + 0.789124 F_3 + 0.123081 F_4 + 0.681341 F_5 \\F(4,6) &= 0.652746 F_5 \\F(4,9) &= 0.420632 F_2 + 0.261129 F_4\end{aligned}$$

$$F(4,10) = 0.378075 F_3$$

$$F(4,11) = 0.354512 F_4$$

$$F(4,14) = 0.475860 F_5$$

$$F(4,5) = F(4,7) = F(4,8) = F(4,12) = F(4,13) = F(4,15) = 0$$

$$F(5,1) = 0.715217 F_2 + 0.456285 F_4$$

$$F(5,2) = 0.291711 F_4$$

$$F(5,3) = 0.807323 F_3$$

$$F(5,5) = K_3 + 0.604352 F_2 + 0.789124 F_3 + 0.123081 F_4 + 0.681341 F_5$$

$$F(5,7) = 0.652746 F_5$$

$$F(5,8) = 0.354512 F_4$$

$$F(5,12) = 0.420632 F_2 + 0.261129 F_4$$

$$F(5,13) = 0.378075 F_3$$

$$F(5,15) = 0.475860 F_5$$

$$F(5,4) = F(5,6) = F(5,9) = F(5,10) = F(5,11) = F(5,14) = 0$$

$$F(6,4) = 0.652746 F_5$$

$$F(6,6) = K_4 + 0.487659 F_5$$

$$F(6,14) = 0.378217 F_5$$

$$F(6,1) = F(6,2) = F(6,3) = F(6,5) = F(6,7) = F(6,8) = F(6,9)$$

$$= F(6,10) = F(6,11) = F(6,12) = F(6,13) = F(6,15) = 0$$

$$F(7,5) = 0.652746 F_5$$

$$F(7,7) = K_4 + 0.487659 F_5$$

$$F(7,15) = 0.378217 F_5$$

$$F(7,1) = F(7,2) = F(7,3) = F(7,4) = F(7,6) = F(7,8) = F(7,9)$$

$$= F(7,10) = F(7,11) = F(7,12) = F(7,13) = F(7,14) = 0$$

$$\begin{aligned}
 F(8,1) &= 0.450175 F_1 + 0.881856 F_4 \\
 F(8,2) &= 0.389272 F_1 + 0.260330 F_4 \\
 F(8,5) &= 0.354512 F_4 \\
 F(8,8) &= H_1 + 0.38362 F_1 + 0.86021 F_4 \\
 F(8,12) &= 0.807935 F_4 \\
 F(8,3) &= F(8,4) = F(8,6) = F(8,7) = F(8,9) = F(8,10) = F(8,11) \\
 &= F(8,13) = F(8,14) = F(8,15) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(9,1) &= 0.471212 F_2 + 0.885833 F_4 \\
 F(9,3) &= 0.382751 F_4 \\
 F(9,4) &= 0.420632 F_2 + 0.261129 F_4 \\
 F(9,9) &= H_2 + 0.438769 F_2 + 0.868308 F_4 \\
 F(9,11) &= 0.807935 F_4 \\
 F(9,2) &= F(9,5) = F(9,6) = F(9,7) = F(9,8) = F(9,10) = F(9,12) \\
 &= F(9,13) = F(9,14) = F(9,15) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(10,2) &= 0.357105 F_5 \\
 F(10,4) &= 0.378075 F_5 \\
 F(10,10) &= H_3 + 0.291101 F_5 \\
 F(10,1) &= F(10,3) = F(10,5) = F(10,6) = F(10,7) = F(10,8) \\
 &= F(10,9) = F(10,11) = F(10,12) = F(10,13) = F(10,14) \\
 &= F(10,15) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(11,1) &= 0.450175 F_1 + 0.881856 F_4 \\
 F(11,3) &= 0.389272 F_1 + 0.260330 F_4 \\
 F(11,4) &= 0.354512 F_4
 \end{aligned}$$

$$F(11,9) = 0.807935 F_4$$

$$F(11,11) = H_1 + 0.38362 F_1 + 0.860210 F_4$$

$$F(11,2) = F(11,5) = F(11,6) = F(11,7) = F(11,8) = F(11,10) \\ = F(11,12) = F(11,13) = F(11,14) = F(11,15) = 0$$

$$F(12,1) = 0.471212 F_2 + 0.885835 F_4$$

$$F(12,2) = 0.382731 F_4$$

$$F(12,5) = 0.420632 F_2 + 0.261129 F_4$$

$$F(12,8) = 0.807935 F_4$$

$$F(12,12) = H_2 + 0.438769 F_2 + 0.868308 F_4$$

$$F(12,3) = F(12,4) = F(12,6) = F(12,7) = F(12,9) = F(12,10) \\ = F(12,11) = F(12,13) = F(12,14) = F(12,15) = 0$$

$$F(13,3) = 0.357105 F_3$$

$$F(13,5) = 0.378075 F_3$$

$$F(13,13) = H_3 + 0.291101 F_3$$

$$F(13,1) = F(13,2) = F(13,4) = F(13,6) = F(13,7) = F(13,8) = F(13,9) \\ = F(13,10) = F(13,11) = F(13,12) = F(13,14) = F(13,15) = 0$$

$$F(14,4) = 0.475860 F_5$$

$$F(14,6) = 0.378217 F_5$$

$$F(14,14) = H_4 + 0.428923 F_5$$

$$F(14,1) = F(14,2) = F(14,3) = F(14,5) = F(14,7) = F(14,8) = F(14,9) \\ = F(14,10) = F(14,11) = F(14,12) = F(14,13) = F(14,15) = 0$$

$$\begin{aligned}
 F(15,5) &= 0.475860 F_5 \\
 F(15,7) &= 0.378217 F_5 \\
 F(15,15) &= H_4 + 0.428923 F_5 \\
 F(15,1) &= F(15,2) = F(15,3) = F(15,4) = F(15,6) = F(15,8) \\
 &= F(15,9) = F(15,10) = F(15,11) = F(15,12) = F(15,13) \\
 &= F(15,14) = 0
 \end{aligned}$$

16.4 F-matrix of gaseous oxalic acid (1st model) in symmetry co-ordinates

$$\begin{aligned}
 F(1,1) &= K_1 + 1.61801 F_1 + 1.407947 F_2 + 1.984183 F_4 \\
 F(1,2) &= 1.118434 F_1 + 0.656073 F_4 \\
 F(1,3) &= 1.011470 F_2 + 0.645284 F_4 \\
 F(1,4) &= 0 \\
 F(1,5) &= -0.259909 F_1 - 0.272054 F_2 - 1.020576 F_4 \\
 F(1,6) &= -0.450175 F_1 + 0.471212 F_2 + 0.003977 F_4 \\
 F(1,7) &= 0 \\
 F(1,8) &= F(1,9) = F(1,10) = F(1,11) = F(1,12) = F(1,13) = 0 \\
 \\
 F(2,1) &= 1.118434 F_1 + 0.656073 F_4 \\
 F(2,2) &= K_2 + 0.686361 F_1 + 0.74091 F_3 + 0.146195 F_5 \\
 F(2,3) &= 0.807323 F_3 + 0.291711 F_4 \\
 F(2,4) &= 0 \\
 F(2,5) &= -0.15892 F_1 + 0.291575 F_3 - 0.262529 F_4 \\
 F(2,6) &= -0.275257 F_1 + 0.08655 F_4 \\
 F(2,7) &= 0 \\
 F(2,8) &= F(2,9) = F(2,10) = F(2,11) = F(2,12) = F(2,13) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(3,1) &= 1.01147 F_2 + 0.645284 F_4 \\
 F(3,2) &= 0.807323 F_3 + 0.291711 F_4 \\
 F(3,3) &= K_3 + 0.604352 F_2 + 0.789124 F_3 + 0.123081 F_4 + 0.681341 F_5 \\
 F(3,4) &= 0.652746 F_5 \\
 F(3,5) &= -0.171722 F_2 + 0.308697 F_3 - 0.251334 F_4 \\
 F(3,6) &= 0.297432 F_2 - 0.066032 F_4 \\
 F(3,7) &= 0.47586 F_5 \\
 F(3,8) &= F(3,9) = F(3,10) = F(3,11) = F(3,12) = F(3,13) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(4,1) &= 0 \\
 F(4,2) &= 0 \\
 F(4,3) &= 0.652746 F_5 \\
 F(4,4) &= K_4 + 0.487659 F_5 \\
 F(4,5) &= 0 \\
 F(4,6) &= 0 \\
 F(4,7) &= 0.378217 F_5 \\
 F(4,8) &= F(4,9) = F(4,10) = F(4,11) = F(4,12) = F(4,13) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(5,1) &= -0.259909 F_1 - 0.272054 F_2 - 1.020576 F_4 \\
 F(5,2) &= -0.15892 F_1 + 0.291575 F_3 - 0.262529 F_4 \\
 F(5,3) &= -0.171722 F_2 + 0.308697 F_3 - 0.251334 F_4 \\
 F(5,4) &= 0 \\
 F(5,5) &= (H_1)/6 + (H_2)/6 + \frac{2}{3}H_3 + 0.063937 F_1 + 0.073128 F_2 + 0.194067 F_3 \\
 &\quad + 0.557398 F_4 \\
 F(5,6) &= \frac{H_1}{2\sqrt{3}} - \frac{H_2}{2\sqrt{3}} + 0.110742 F_1 - 0.126662 F_2 - 0.002338 F_4 \\
 F(5,7) &= 0 \\
 F(5,8) &= F(5,9) = F(5,10) = F(5,11) = F(5,12) = F(5,13) = 0
 \end{aligned}$$

$$F(6,1) = -0.450175 F_1 + 0.471212 F_2 + 0.003977 F_4$$

$$F(6,2) = -0.275257 F_1 + 0.08655 F_4$$

$$F(6,3) = 0.297432 F_2 - 0.066032 F_4$$

$$F(6,4) = 0$$

$$F(6,5) = \frac{H_1}{273} - \frac{H_2}{273} + 0.110742 F_1 - 0.126662 F_2 - 0.002338 F_4$$

$$F(6,6) = \frac{H_1}{2} + \frac{H_2}{2} + 0.19181 F_1 + 0.219385 F_2 + 0.056324 F_4$$

$$F(6,7) = 0$$

$$F(6,8) = F(6,9) = F(6,10) = F(6,11) = F(6,12) = F(6,13) = 0$$

$$F(7,1) = 0$$

$$F(7,2) = 0$$

$$F(7,3) = 0.47586 F_5$$

$$F(7,4) = 0.378217 F_5$$

$$F(7,5) = 0$$

$$F(7,6) = 0$$

$$F(7,7) = H_4 + 0.428923 F_5$$

$$F(7,8) = F(7,9) = F(7,10) = F(7,11) = F(7,12) = F(7,13) = 0$$

$$F(8,1) = F(8,2) = F(8,3) = F(8,4) = F(8,5) = F(8,6) = F(8,7) = 0$$

$$F(8,8) = K_2 + 0.686361 F_1 + 0.74091 F_3 + 0.146195 F_4$$

$$F(8,9) = 0.807323 F_3 - 0.291711 F_4$$

$$F(8,10) = 0$$

$$F(8,11) = -0.15892 F_1 + 0.291575 F_3 + 0.04997 F_4$$

$$F(8,12) = -0.275257 F_1 - 0.454713 F_4$$

$$F(8,13) = 0$$

$$F(9,1) = F(9,2) = F(9,3) = F(9,4) = F(9,5) = F(9,6) = F(9,7) = 0$$

$$F(9,8) = 0.807323 F_3 - 0.291711 F_4$$

$$F(9,9) = K_3 + 0.604352 F_2 + 0.789124 F_3 + 0.12381 F_4 + 0.681341 F_5$$

$$F(9,10) = 0.652746 F_5$$

$$F(9,11) = -0.171722 F_2 + 0.308697 F_3 + 0.038123 F_4$$

$$F(9,12) = 0.297432 F_2 + 0.435324 F_4$$

$$F(9,13) = 0.475860 F_5$$

$$F(10,1) = F(10,2) = F(10,3) = F(10,4) = F(10,5) = F(10,6) = F(10,7)$$

$$= 0$$

$$F(10,8) = 0$$

$$F(10,9) = 0.652746 F_5$$

$$F(10,10) = K_4 + 0.487659 F_5$$

$$F(10,11) = 0$$

$$F(10,12) = 0$$

$$F(10,13) = 0.378217 F_5$$

$$F(11,1) = F(11,2) = F(11,3) = F(11,4) = F(11,5) = F(11,6) = F(11,7)$$

$$= 0$$

$$F(11,8) = -0.15892 F_1 + 0.291575 F_3 + 0.04997 F_4$$

$$F(11,9) = -0.171722 F_2 + 0.308697 F_3 + 0.038123 F_4$$

$$F(11,10) = 0$$

$$F(11,11) = \frac{H_1}{6} + \frac{H_2}{6} + \frac{2}{3}H_3 + 0.063937 F_1 + 0.073128 F_2 + 0.194067 F_3$$

$$+ 0.018775 F_4$$

$$F(11,12) = \frac{H_1}{2\sqrt{3}} - \frac{H_1}{2\sqrt{3}} + 0.110742 F_1 - 0.126662 F_2 - 0.002338 F_4$$

$$F(11,13) = 0$$

$$\begin{aligned} F(12,1) &= F(12,2) = F(12,3) = F(12,4) = F(12,5) = F(12,6) \\ &= F(12,7) = 0 \end{aligned}$$

$$F(12,8) = -0.275257 F_1 - 0.454713 F_4$$

$$F(12,9) = 0.297432 F_2 + 0.435324 F_4$$

$$F(12,10) = 0$$

$$F(12,11) = \frac{H_1}{2\sqrt{3}} - \frac{H_2}{2\sqrt{3}} + 0.110742 F_1 - 0.126662 F_2 - 0.002338 F_4$$

$$F(12,12) = \frac{H_1}{2} + \frac{H_2}{2} + 0.19181 F_1 + 0.219385 F_2 + 1.672194 F_4$$

$$F(12,13) = 0$$

$$\begin{aligned} F(13,1) &= F(13,2) = F(13,3) = F(13,4) = F(13,5) = F(13,6) = F(13,7) \\ &= 0 \end{aligned}$$

$$F(13,8) = 0$$

$$F(13,9) = 0.475860 F_5$$

$$F(13,10) = 0.378217 F_5$$

$$F(13,11) = 0$$

$$F(13,12) = 0$$

$$F(13,13) = H_4 + 0.428923 F_5$$

CHAPTER 17

G-MATRIX OF THE INPLANE VIBRATIONS

OF GASEOUS OXALIC ACID 2ND MODEL

17.1 Evaluation of the B-matrix of the inplane vibration of gaseous oxalic acid 2nd model

Fig. 21

In order to simplify the problem each atom of gaseous oxalic acid is labelled by a number as in Fig. 21. For gaseous oxalic acid 2nd model there are altogether 21 internal co-ordinates, 9 are bond stretching co-ordinates and 12 are angle bending co-ordinates, as follows:-

Bond stretching co-ordinates

ΔR = change in C - C distance
 $\Delta r_1 = \Delta r'_1$ = change in C = O distance
 $\Delta r_2 = \Delta r'_2$ = change in C - O distance
 $\Delta r_3 = \Delta r'_3$ = change in O - H distance
 $\Delta r_4 = \Delta r'_4$ = change in O ... H distance

Angle bending co-ordinates

$\Delta \alpha_1 = \Delta \alpha'_1$ = change in C - C = O angle
 $\Delta \alpha_2 = \Delta \alpha'_2$ = change in C - C - O angle
 $\Delta \alpha_3 = \Delta \alpha'_3$ = change in O = C - O angle
 $\Delta \beta = \Delta \beta'$ = change in C - O - H angle
 $\Delta \delta = \Delta \delta'$ = change in O - H ... O angle
 $\Delta \gamma = \Delta \gamma'$ = change in C = O ... H angle

The B-matrix elements are evaluated using Wilson's vector method
 (see section 5.2) and the results are

B-matrix of the inplane vibration of gaseous oxalic acid 2nd model

$$(\Delta R, \Delta x_1) = -1$$

$$(\Delta R, \Delta x_2) = 1$$

$$(\Delta r_1, \Delta x_2) = -\cos \phi \quad (\Delta r_2, \Delta x_2) = -\cos(\alpha_3 - \phi)$$

$$(\Delta r_1, \Delta y_2) = \sin \phi \quad (\Delta r_2, \Delta y_2) = -\sin(\alpha_3 - \phi)$$

$$(\Delta r_3, \Delta x_3) = \cos \phi \quad (\Delta r_4, \Delta x_4) = \cos(\alpha_3 - \phi)$$

$$(\Delta r_3, \Delta y_3) = -\sin \phi \quad (\Delta r_4, \Delta y_4) = \sin(\alpha_3 - \phi)$$

$$\begin{aligned}(\Delta r_3, \Delta x_4) &= \cos \theta & (\Delta r_4, \Delta x_5) &= \cos \psi \\ (" , \Delta y_4) &= -\sin \theta & (" , \Delta y_5) &= \sin \psi \\ (" , \Delta x_5) &= -\cos \theta & (" , \Delta x_6) &= -\cos \psi \\ (" , \Delta y_5) &= \sin \theta & (" , \Delta y_6) &= -\sin \psi\end{aligned}$$

$$\begin{aligned}(\Delta r'_1, \Delta x_1) &= \cos \phi & (\Delta r'_2, \Delta x_1) &= \cos(\alpha_3 - \phi) \\ (" , \Delta y_1) &= -\sin \phi & (" , \Delta y_1) &= \sin(\alpha_3 - \phi) \\ (" , \Delta x_6) &= -\cos \phi & (" , \Delta x_7) &= -\cos(\alpha_3 - \phi) \\ (" , \Delta y_6) &= \sin \phi & (" , \Delta y_7) &= -\sin(\alpha_3 - \phi)\end{aligned}$$

$$\begin{aligned}(\Delta r'_3, \Delta x_7) &= -\cos \theta' & (\Delta r'_4, \Delta x_3) &= \cos \psi \\ (" , \Delta y_7) &= \sin \theta' & (" , \Delta y_3) &= \sin \psi \\ (" , \Delta x_8) &= \cos \theta' & (" , \Delta x_8) &= -\cos \psi \\ (" , \Delta y_8) &= -\sin \theta' & (" , \Delta y_8) &= -\sin \psi\end{aligned}$$

$$\begin{aligned}r_1(\Delta \alpha_1, \Delta x_1) &= 0 & r_2(\Delta \alpha_2, \Delta x_1) &= 0 \\ r_1(" , \Delta y_1) &= r_1/R & r_2(" , \Delta y_1) &= -r_2/R \\ r_1(" , \Delta x_2) &= -\sin \phi & r_2(" , \Delta x_2) &= -\sin(\alpha_3 - \phi) \\ r_1(" , \Delta y_2) &= -\cos \phi - (r_1/R) & r_2(" , \Delta y_2) &= (r_2/R) + \cos(\alpha_3 - \phi) \\ r_1(" , \Delta x_3) &= \sin \phi & r_2(" , \Delta x_4) &= \sin(\alpha_3 - \phi) \\ r_1(" , \Delta y_3) &= \cos \phi & r_2(" , \Delta y_4) &= -\cos(\alpha_3 - \phi)\end{aligned}$$

$$\begin{aligned}\sqrt{r_1 r_2}(\Delta \alpha_3, \Delta x_2) &= \{r_2 \sin \phi + r_1 \sin(\alpha_3 - \phi)\} / \sqrt{r_1 r_2} \\ \sqrt{r_1 r_2}(" , \Delta y_2) &= \{r_2 \cos \phi + r_1 \cos(\alpha_3 - \phi)\} / \sqrt{r_1 r_2} \\ \sqrt{r_1 r_2}(" , \Delta x_3) &= -r_2 \sin \phi / \sqrt{r_1 r_2} \\ \sqrt{r_1 r_2}(" , \Delta y_3) &= -r_2 \cos \phi / \sqrt{r_1 r_2} \\ \sqrt{r_1 r_2}(" , \Delta x_4) &= -r_1 \sin(\alpha_3 - \phi) / \sqrt{r_1 r_2} \\ \sqrt{r_1 r_2}(" , \Delta y_4) &= r_1 \cos(\alpha_3 - \phi) / \sqrt{r_1 r_2}\end{aligned}$$

$$r'_1(\Delta\alpha'_1, \Delta x_1) = \sin \phi'$$

$$r'_1(\quad , \Delta y_1) = (r'/R) + \cos \phi'$$

$$r'_1(\quad , \Delta x_2) = 0$$

$$r'_1(\quad , \Delta y_2) = -r'_1/R$$

$$r'_1(\quad , \Delta x_6) = -\sin \phi'$$

$$r'_1(\quad , \Delta y_6) = -\cos \phi'$$

$$r'_2(\Delta\alpha'_2, \Delta x_1) = \sin(\alpha'_3 - \phi')$$

$$r'_2(\quad , \Delta y_1) = -\cos(\alpha'_3 - \phi') - (r'_2/R)$$

$$r'_2(\quad , \Delta x_2) = 0$$

$$r'_2(\quad , \Delta y_2) = r'_2/R$$

$$r'_2(\quad , \Delta x_7) = -\sin(\alpha'_3 - \phi')$$

$$r'_2(\quad , \Delta y_7) = \cos(\alpha'_3 - \phi')$$

$$\sqrt{r'_1 r'_2}(\Delta\alpha'_3, \Delta x_1) = -(r'_2 \sin \phi' + r'_1 \sin(\alpha'_3 - \phi'))/\sqrt{r'_1 r'_2}$$

$$\sqrt{r'_1 r'_2}(\quad , \Delta y_1) = (r'_1 \cos(\alpha'_3 - \phi') - r'_2 \cos \phi')/\sqrt{r'_1 r'_2}$$

$$\sqrt{r'_1 r'_2}(\quad , \Delta x_6) = r'_2 \sin \phi'/\sqrt{r'_1 r'_2}$$

$$\sqrt{r'_1 r'_2}(\quad , \Delta y_6) = r'_2 \cos \phi'/\sqrt{r'_1 r'_2}$$

$$\sqrt{r'_1 r'_2}(\quad , \Delta x_7) = r'_1 \sin(\alpha'_3 - \phi')/\sqrt{r'_1 r'_2}$$

$$\sqrt{r'_1 r'_2}(\quad , \Delta y_7) = -r'_1 \cos(\alpha'_3 - \phi')/\sqrt{r'_1 r'_2}$$

$$\sqrt{r_2 r_3}(\Delta\beta, \Delta x_2) = r_3 \sin(\beta - \theta)/\sqrt{r_2 r_3}$$

$$\quad (\quad , \Delta y_2) = -r_3 \cos(\beta - \theta)/\sqrt{r_2 r_3}$$

$$\quad (\quad , \Delta x_4) = -(r_2 \sin \theta + r_3 \sin(\beta - \theta))/\sqrt{r_2 r_3}$$

$$\quad (\quad , \Delta y_4) = (r_3 \cos(\beta - \theta) - r_2 \cos \theta)/\sqrt{r_2 r_3}$$

$$\quad (\quad , \Delta x_5) = r_2 \sin \theta/\sqrt{r_2 r_3}$$

$$\quad (\quad , \Delta y_5) = r_2 \cos \theta/\sqrt{r_2 r_3}$$

$$\sqrt{r_3 r_4} (\Delta \delta, \Delta x_4) = r_4 \sin \theta / \sqrt{r_3 r_4}$$

$$" (", \Delta y_4) = r_4 \cos \theta / \sqrt{r_3 r_4}$$

$$" (", \Delta x_5) = \{r_3 \sin \psi - r_4 \sin \theta\} / \sqrt{r_3 r_4}$$

$$" (", \Delta y_5) = -\{r_3 \cos \psi + r_4 \cos \theta\} / \sqrt{r_3 r_4}$$

$$" (", \Delta x_6) = -r_3 \sin \psi / \sqrt{r_3 r_4}$$

$$" (", \Delta y_6) = r_3 \cos \psi / \sqrt{r_3 r_4}$$

$$\sqrt{r'_1 r'_4} (\Delta \gamma, \Delta x_1) = -r'_4 \sin(\gamma - \psi) / \sqrt{r'_1 r'_4}$$

$$" (", \Delta y_1) = -r'_4 \cos(\gamma - \psi) / \sqrt{r'_1 r'_4}$$

$$" (", \Delta x_5) = -r'_1 \sin \psi / \sqrt{r'_1 r'_4}$$

$$" (", \Delta y_5) = r'_1 \cos \psi / \sqrt{r'_1 r'_4}$$

$$" (", \Delta x_6) = \{r'_4 \sin(\gamma - \psi) + r'_1 \sin \psi\} / \sqrt{r'_1 r'_4}$$

$$" (", \Delta y_6) = \{r'_4 \cos(\gamma - \psi) + r'_1 \cos \psi\} / \sqrt{r'_1 r'_4}$$

$$\sqrt{r'_2 r'_3} (\Delta \beta', \Delta x_1) = -r'_3 \sin(\beta' - \theta') / \sqrt{r'_2 r'_3}$$

$$" (", \Delta y_1) = r'_3 \cos(\beta' - \theta') / \sqrt{r'_2 r'_3}$$

$$" (", \Delta x_7) = \{r'_3 \sin(\beta' - \theta') + r'_2 \sin \theta'\} / \sqrt{r'_2 r'_3}$$

$$" (", \Delta y_7) = \{r'_2 \cos \theta' - r'_3 \cos(\beta' - \theta')\} / \sqrt{r'_2 r'_3}$$

$$" (", \Delta x_8) = -r'_2 \sin \theta' / \sqrt{r'_2 r'_3}$$

$$" (", \Delta y_8) = -r'_2 \cos \theta' / \sqrt{r'_2 r'_3}$$

$$\sqrt{r'_3 r'_4} (\Delta \delta', \Delta x_3) = r'_3 \sin \psi' / \sqrt{r'_3 r'_4}$$

$$" (", \Delta y_3) = -r'_3 \cos \psi' / \sqrt{r'_3 r'_4}$$

$$" (", \Delta x_7) = -r'_4 \sin \theta' / \sqrt{r'_3 r'_4}$$

$$" (", \Delta y_7) = -r'_4 \cos \theta' / \sqrt{r'_3 r'_4}$$

$$" (", \Delta x_8) = \{r'_4 \sin \theta' - r'_3 \sin \psi'\} / \sqrt{r'_3 r'_4}$$

$$" (", \Delta y_8) = \{r'_4 \cos \theta' + r'_3 \cos \psi'\} / \sqrt{r'_3 r'_4}$$

$$\begin{aligned}
 \sqrt{r_1 r'_4} (\Delta y'_1, \Delta x_2) &= r'_4 \sin(\gamma' - \psi') / \sqrt{r_1 r'_4} \\
 " (" , \Delta y_2) &= r'_4 \cos(\gamma' - \psi') / \sqrt{r_1 r'_4} \\
 " (" , \Delta x_3) &= -(r_1 \sin \psi' + r'_4 \sin(\gamma' - \psi')) / \sqrt{r_1 r'_4} \\
 " (" , \Delta y_3) &= (r_1 \cos \psi' - r'_4 \cos(\gamma' - \psi')) / \sqrt{r_1 r'_4} \\
 * (" , \Delta x_8) &= +r_1 \sin \psi' / \sqrt{r_1 r'_4} \\
 " (" , \Delta y_8) &= -r_1 \cos \psi' / \sqrt{r_1 r'_4}
 \end{aligned}$$

All other elements are zero.

17.2 D-matrix of the inplane vibration of gaseous oxalic acid 2nd model

$$(\Delta R, \Delta x_1) = -\sqrt{\mu_C}$$

$$(\Delta R, \Delta x_2) = \sqrt{\mu_C}$$

$$(\Delta r_1, \Delta x_2) = -\sqrt{\mu_C} \cos \phi$$

$$(" , \Delta y_2) = \sqrt{\mu_C} \sin \phi$$

$$(" , \Delta x_3) = \sqrt{\mu_O} \cos \phi$$

$$(" , \Delta y_3) = -\sqrt{\mu_O} \sin \phi$$

$$(\Delta r_2, \Delta x_2) = -\sqrt{\mu_C} \cos(\alpha_3 - \phi)$$

$$(" , \Delta y_2) = -\sqrt{\mu_C} \sin(\alpha_3 - \phi)$$

$$(" , \Delta x_4) = \sqrt{\mu_O} \cos(\alpha_3 - \phi)$$

$$(" , \Delta y_4) = \sqrt{\mu_O} \sin(\alpha_3 - \phi)$$

$$(\Delta r_3, \Delta x_4) = \sqrt{\mu_O} \cos \theta$$

$$(" , \Delta y_4) = -\sqrt{\mu_O} \sin \theta$$

$$(" , \Delta x_5) = \sqrt{\mu_H} \cos \theta$$

$$(" , \Delta y_5) = \sqrt{\mu_H} \sin \theta$$

$$(\Delta r_4, \Delta x_5) = \sqrt{\mu_H} \cos \psi$$

$$(" , \Delta y_5) = \sqrt{\mu_H} \sin \psi$$

$$(" , \Delta x_6) = -\sqrt{\mu_O} \cos \psi$$

$$(" , \Delta y_6) = -\sqrt{\mu_O} \sin \psi$$

$$(\Delta r'_1, \Delta x_1) = \sqrt{\mu_C} \cos \phi$$

$$(" , \Delta y_1) = -\sqrt{\mu_C} \sin \phi$$

$$(" , \Delta x_6) = -\sqrt{\mu_O} \cos \phi$$

$$(" , \Delta y_6) = \sqrt{\mu_O} \sin \phi$$

$$(\Delta r'_2, \Delta x_1) = \sqrt{\mu_C} \cos(\alpha_3 - \phi)$$

$$(" , \Delta y_1) = \sqrt{\mu_C} \sin(\alpha_3 - \phi)$$

$$(" , \Delta x_7) = -\sqrt{\mu_O} \cos(\alpha_3 - \phi)$$

$$(" , \Delta y_7) = -\sqrt{\mu_O} \sin(\alpha_3 - \phi)$$

$$\begin{aligned}
 (\Delta r'_3, \Delta x_7) &= -\sqrt{\mu_0} \cos \theta' & (\Delta r'_4, \Delta x_3) &= \sqrt{\mu_0} \cos \psi \\
 (" , \Delta y_7) &= \sqrt{\mu_0} \sin \theta' & (" , \Delta y_3) &= \sqrt{\mu_0} \sin \psi \\
 (" , \Delta x_8) &= \sqrt{\mu_H} \cos \theta' & (" , \Delta x_8) &= -\sqrt{\mu_H} \cos \psi \\
 (" , \Delta y_8) &= -\sqrt{\mu_H} \sin \theta' & (" , \Delta y_8) &= -\sqrt{\mu_H} \sin \psi
 \end{aligned}$$

$$\begin{aligned}
 r_1(\Delta \alpha_1, \Delta x_1) &= 0 & r_2(\Delta \alpha_2, \Delta x_1) &= 0 \\
 " (" , \Delta y_1) &= \sqrt{\mu_c}(r_1/R) & " (" , \Delta y_1) &= -\sqrt{\mu_c}(r_2/R) \\
 " (" , \Delta x_2) &= -\sqrt{\mu_c} \sin \phi & " (" , \Delta x_2) &= -\sqrt{\mu_c} \sin(\alpha_3 - \phi) \\
 " (" , \Delta y_2) &= -\sqrt{\mu_c}(\cos \phi + r_1/R) & " (" , \Delta y_2) &= \sqrt{\mu_c}(r_2/R + \cos(\alpha_3 - \phi)) \\
 " (" , \Delta x_3) &= \sqrt{\mu_0} \sin \phi & " (" , \Delta x_4) &= \sqrt{\mu_0} \sin(\alpha_3 - \phi) \\
 " (" , \Delta y_3) &= \sqrt{\mu_0} \cos \phi & " (" , \Delta y_4) &= -\sqrt{\mu_0} \cos(\alpha_3 - \phi)
 \end{aligned}$$

$$\begin{aligned}
 \sqrt{r_1 r_2}(\Delta \alpha_3, \Delta x_2) &= \sqrt{\mu_c}\{r_2 \sin \phi + r_1 \sin(\alpha_3 - \phi)\}/\sqrt{r_1 r_2} \\
 " (" , \Delta y_2) &= \sqrt{\mu_c}\{r_2 \cos \phi - r_1 \cos(\alpha_3 - \phi)\}/\sqrt{r_1 r_2} \\
 " (" , \Delta x_3) &= -\sqrt{\mu_0} r_2 \sin \phi / \sqrt{r_1 r_2} \\
 " (" , \Delta y_3) &= -\sqrt{\mu_0} r_2 \cos \phi / \sqrt{r_1 r_2} \\
 " (" , \Delta x_4) &= -\sqrt{\mu_0} r_1 \sin(\alpha_3 - \phi) / \sqrt{r_1 r_2} \\
 " (" , \Delta y_4) &= \sqrt{\mu_0} r_1 \cos(\alpha_3 - \phi) / \sqrt{r_1 r_2}
 \end{aligned}$$

$$\begin{aligned}
 r'_1(\Delta \alpha'_1, \Delta x_1) &= \sqrt{\mu_c} \sin \phi' \\
 r'_1(" , \Delta y_1) &= \sqrt{\mu_c} \{(r'_1/R) + \cos \phi'\} \\
 r'_1(" , \Delta x_2) &= 0 \\
 r'_1(" , \Delta y_2) &= -\sqrt{\mu_c} (r'_1/R) \\
 r'_1(" , \Delta x_6) &= -\sqrt{\mu_0} \sin \phi' \\
 r'_1(" , \Delta y_6) &= -\sqrt{\mu_0} \cos \phi'
 \end{aligned}$$

$$r'_2(\Delta\alpha'_2, \Delta x_1) = \sqrt{\mu_c} \sin(\alpha'_3 - \phi')$$

$$" (" , \Delta y_1) = -\sqrt{\mu_c} \{(r'_2/R) + \cos(\alpha'_3 - \phi')\}$$

$$" (" , \Delta x_2) = 0$$

$$" (" , \Delta y_2) = \sqrt{\mu_c} (r'_2/R)$$

$$" (" , \Delta x_7) = -\sqrt{\mu_0} \sin(\alpha'_3 - \phi')$$

$$" (" , \Delta y_7) = \sqrt{\mu_0} \cos(\alpha'_3 - \phi')$$

$$\sqrt{r'_1 r'_2}(\Delta\alpha'_3, \Delta x_1) = -\sqrt{\mu_c} \{r'_2 \sin\phi' + r'_1 \sin(\alpha'_3 - \phi')\} / \sqrt{r'_1 r'_2}$$

$$" (" , \Delta y_1) = \sqrt{\mu_c} \{r'_1 \cos(\alpha'_3 - \phi') - r'_2 \cos\phi'\} / \sqrt{r'_1 r'_2}$$

$$" (" , \Delta x_6) = \sqrt{\mu_0} r'_2 \sin\phi' / \sqrt{r'_1 r'_2}$$

$$" (" , \Delta y_6) = \sqrt{\mu_0} r'_2 \cos\phi' / \sqrt{r'_1 r'_2}$$

$$" (" , \Delta x_7) = \sqrt{\mu_0} r'_1 \sin(\alpha'_3 - \phi') / \sqrt{r'_1 r'_2}$$

$$" (" , \Delta y_7) = -\sqrt{\mu_0} r'_1 \cos(\alpha'_3 - \phi') / \sqrt{r'_1 r'_2}$$

$$\sqrt{r_2 r_3}(\Delta\beta, \Delta x_2) = \sqrt{\mu_c} r_3 \sin(\beta - \theta) / \sqrt{r_2 r_3}$$

$$" (" , \Delta y_2) = -\sqrt{\mu_c} r_3 \cos(\beta - \theta) / \sqrt{r_2 r_3}$$

$$" (" , \Delta x_4) = -\sqrt{\mu_0} \{r_2 \sin\theta + r_3 \sin(\beta - \theta)\} / \sqrt{r_2 r_3}$$

$$" (" , \Delta y_4) = \sqrt{\mu_0} \{r_3 \cos(\beta - \theta) - r_2 \cos\theta\} / \sqrt{r_2 r_3}$$

$$" (" , \Delta x_5) = \sqrt{\mu_H} r_2 \sin\theta / \sqrt{r_2 r_3}$$

$$" (" , \Delta y_5) = \sqrt{\mu_H} r_2 \cos\theta / \sqrt{r_2 r_3}$$

$$\sqrt{r_3 r_4}(\Delta\delta, \Delta x_4) = \sqrt{\mu_0} r_4 \sin\phi / \sqrt{r_3 r_4}$$

$$" (" , \Delta y_4) = \sqrt{\mu_0} r_4 \cos\phi / \sqrt{r_3 r_4}$$

$$" (" , \Delta x_5) = \sqrt{\mu_H} \{r_3 \sin\psi - r_4 \sin\theta\} / \sqrt{r_3 r_4}$$

$$" (" , \Delta y_5) = -\sqrt{\mu_H} \{r_3 \cos\psi + r_4 \cos\theta\} / \sqrt{r_3 r_4}$$

$$" (" , \Delta x_6) = -\sqrt{\mu_0} r_3 \sin\phi / \sqrt{r_3 r_4}$$

$$" (" , \Delta y_6) = \sqrt{\mu_0} r_3 \cos\phi / \sqrt{r_3 r_4}$$

$$\sqrt{r'_1 r'_4} (\Delta \gamma, \Delta x_1) = -\sqrt{\mu_c} r_4 \sin(\gamma - \psi) / \sqrt{r'_1 r'_4}$$

$$" (", \Delta y_1) = -\sqrt{\mu_c} r_4 \cos(\gamma - \psi) / \sqrt{r'_1 r'_4}$$

$$" (", \Delta x_5) = -\sqrt{\mu_H} r'_1 \sin \psi / \sqrt{r'_1 r'_4}$$

$$" (", \Delta y_5) = \sqrt{\mu_H} r'_1 \cos \psi / \sqrt{r'_1 r'_4}$$

$$" (", \Delta x_6) = \sqrt{\mu_0} \{r_4 \sin(\gamma - \psi) + r'_1 \sin \psi\} / \sqrt{r'_1 r'_4}$$

$$" (", \Delta y_6) = \sqrt{\mu_0} \{r_4 \cos(\gamma - \psi) + r'_1 \cos \psi\} / \sqrt{r'_1 r'_4}$$

$$\sqrt{r'_2 r'_3} (\Delta \beta', \Delta x_1) = -\sqrt{\mu_c} r'_3 \sin(\beta' - \theta') / \sqrt{r'_2 r'_3}$$

$$" (", \Delta y_1) = \sqrt{\mu_c} r'_3 \cos(\beta' - \theta') / \sqrt{r'_2 r'_3}$$

$$" (", \Delta x_7) = \sqrt{\mu_0} \{r'_3 \sin(\beta' - \theta') + r'_2 \sin \theta'\} / \sqrt{r'_2 r'_3}$$

$$" (", \Delta y_7) = \sqrt{\mu_0} \{r'_2 \cos \theta' - r'_3 \cos(\beta' - \theta')\} / \sqrt{r'_2 r'_3}$$

$$" (", \Delta x_8) = -\sqrt{\mu_H} r'_2 \sin \theta' / \sqrt{r'_2 r'_3}$$

$$" (", \Delta y_8) = -\sqrt{\mu_H} r'_2 \cos \theta' / \sqrt{r'_2 r'_3}$$

$$\sqrt{r'_3 r'_4} (\Delta \delta', \Delta x_3) = \sqrt{\mu_0} r'_3 \sin \psi' / \sqrt{r'_3 r'_4}$$

$$" (", \Delta y_3) = -\sqrt{\mu_0} r'_3 \cos \psi' / \sqrt{r'_3 r'_4}$$

$$" (", \Delta x_7) = -\sqrt{\mu_0} r'_4 \sin \theta' / \sqrt{r'_3 r'_4}$$

$$" (", \Delta y_7) = -\sqrt{\mu_0} r'_4 \cos \theta' / \sqrt{r'_3 r'_4}$$

$$" (", \Delta x_8) = \sqrt{\mu_H} \{r'_4 \sin \theta' - r'_3 \sin \psi'\} / \sqrt{r'_3 r'_4}$$

$$" (", \Delta y_8) = \sqrt{\mu_H} \{r'_4 \cos \theta' + r'_3 \cos \psi'\} / \sqrt{r'_3 r'_4}$$

$$\sqrt{r'_1 r'_4} (\Delta \gamma', \Delta x_2) = \sqrt{\mu_c} r'_4 \sin(\gamma' - \psi') / \sqrt{r'_1 r'_4}$$

$$" (", \Delta y_2) = \sqrt{\mu_c} r'_4 \cos(\gamma' - \psi') / \sqrt{r'_1 r'_4}$$

$$" (", \Delta x_3) = -\sqrt{\mu_0} \{r'_1 \sin \psi' + r'_4 \sin(\gamma' - \psi')\} / \sqrt{r'_1 r'_4}$$

$$" (", \Delta y_3) = \sqrt{\mu_0} \{r'_1 \cos \psi' - r'_4 \cos(\gamma' - \psi')\} / \sqrt{r'_1 r'_4}$$

$$" (", \Delta x_8) = +\sqrt{\mu_H} r'_1 \sin \psi' / \sqrt{r'_1 r'_4}$$

$$" (", \Delta y_8) = -\sqrt{\mu_H} r'_1 \cos \psi' / \sqrt{r'_1 r'_4}$$

All other elements are zero

$$\mu_C = \frac{1}{m_C}$$

$$\mu_O = \frac{1}{m_O}$$

$$\mu_H = \frac{1}{m_H}$$

where m_H , m_C and m_O are the masses of hydrogen, carbon and oxygen atoms respectively.

17.3 G-matrix in internal co-ordinates of the inplane vibration of gaseous oxalic acid 2nd model

The G-matrix of the gaseous oxalic acid molecule is here expressed in internal co-ordinates in which

$$r_1 = r'_1, r_2 = r'_2, r_3 = r'_3, r_4 = r'_4$$

$$\alpha_1 = \alpha'_1, \alpha_2 = \alpha'_2, \alpha_3 = \alpha'_3, \beta = \beta'$$

$$\gamma = \gamma', \delta = \delta', \phi = \phi', \theta = \theta'$$

$$\psi = \psi'$$

$$G_{1,1} = 2\mu_C$$

$$G_{1,3} = -\mu_C \cos \phi$$

$$G_{1,5} = -\mu_C \cos(\alpha_3 - \phi)$$

$$G_{1,7} = 0$$

$$G_{1,9} = 0$$

$$G_{1,11} = -\mu_C \sin(\alpha_3 - \phi)$$

$$G_{1,13} = -\mu_C \sin \phi$$

$$G_{1,2} = -\mu_C \cos \phi$$

$$G_{1,4} = -\mu_C \cos(\alpha_3 - \phi)$$

$$G_{1,6} = 0$$

$$G_{1,8} = 0$$

$$G_{1,10} = -\mu_C \sin \phi$$

$$G_{1,12} = (\mu_C r_2 \sin \phi + \mu_C r_1 \sin(\alpha_3 - \phi)) / \sqrt{r_1 r_2}$$

$$G_{1,14} = -\mu_C \sin(\alpha_3 - \phi)$$

$$\begin{aligned} G_{1,15} &= (\mu_c r_2 \sin \phi + \mu_c r_1 \sin(\alpha_3 - \phi)) / \sqrt{r_1 r_2} & G_{1,16} &= \mu_c r_3 \sin(\alpha_3 - \phi) / \sqrt{r_2 r_3} \\ G_{1,17} &= 0 & G_{1,18} &= \mu_c r_4 \sin \phi / \sqrt{r_1 r_4} \\ G_{1,19} &= \mu_c r_3 \sin(\alpha_3 - \phi) / \sqrt{r_2 r_3} & G_{1,20} &= 0 \\ G_{1,21} &= \mu_c r_4 \sin \phi / \sqrt{r_1 r_4} \end{aligned}$$

$$\begin{aligned} G_{2,1} &= -\mu_c \cos \phi & G_{2,2} &= \mu_c + \mu_0 \\ G_{2,3} &= 0 & G_{2,4} &= \mu_c \cos \alpha_3 \\ G_{2,5} &= 0 & G_{2,6} &= 0 \\ G_{2,7} &= 0 & G_{2,8} &= 0 \\ G_{2,9} &= \mu_0 \cos \gamma & G_{2,10} &= -\mu_c \frac{r_1}{R} \sin \phi \\ G_{2,11} &= \mu_c \sin \alpha_3 + \mu_c \frac{r_2}{R} \sin \phi & G_{2,12} &= -\mu_c r_1 \sin \alpha_3 / \sqrt{r_1 r_2} \\ G_{2,13} &= -\mu_c \frac{r_1}{R} \sin \phi & G_{2,14} &= \mu_c \frac{r_2}{R} \sin \phi \\ G_{2,15} &= 0 & G_{2,16} &= -\mu_c r_3 \sin \alpha_3 / \sqrt{r_2 r_3} \\ G_{2,17} &= 0 & G_{2,18} &= 0 \\ G_{2,19} &= 0 & G_{2,20} &= \mu_0 r_3 \sin \gamma / \sqrt{r_3 r_4} \\ G_{2,21} &= -\mu_0 r_1 \sin \gamma / \sqrt{r_1 r_4} \end{aligned}$$

$$\begin{aligned} G_{3,1} &= -\mu_c \cos \phi & G_{3,2} &= 0 \\ G_{3,3} &= \mu_c + \mu_0 & G_{3,4} &= 0 \\ G_{3,5} &= \mu_c \cos \alpha_3 & G_{3,6} &= 0 \\ G_{3,7} &= 0 & G_{3,8} &= \mu_0 \cos \gamma \\ G_{3,9} &= 0 & G_{3,10} &= -\mu_c \frac{r_1}{R} \sin \phi \\ G_{3,11} &= \mu_c \frac{r_2}{R} \sin \phi & G_{3,12} &= 0 \\ G_{3,13} &= -\mu_c \frac{r_1}{R} \sin \phi & G_{3,14} &= \mu_c \sin \alpha_3 + \mu_c \frac{r_2}{R} \sin \phi \\ G_{3,15} &= -\mu_c r_1 \sin \alpha_3 / \sqrt{r_1 r_2} & G_{3,16} &= 0 \\ G_{3,17} &= \mu_0 r_3 \sin \gamma / \sqrt{r_3 r_4} & G_{3,18} &= -\mu_0 r_1 \sin \gamma / \sqrt{r_1 r_4} \end{aligned}$$

$$G_{3,19} = -\mu_c r_3 \sin \alpha_3 / \sqrt{r_2 r_3}$$

$$G_{3,21} = 0$$

$$G_{3,20} = 0$$

$$G_{4,1} = -\mu_c \cos(\alpha_3 - \phi)$$

$$G_{4,3} = 0$$

$$G_{4,5} = 0$$

$$G_{4,7} = 0$$

$$G_{4,9} = 0$$

$$G_{4,11} = -\mu_c \frac{r_2}{R} \sin(\alpha_3 - \phi)$$

$$G_{4,13} = -\mu_c \frac{r_1}{R} \sin(\alpha_3 - \phi)$$

$$G_{4,15} = 0$$

$$G_{4,17} = \mu_o r_4 \sin \beta / \sqrt{r_3 r_4}$$

$$G_{4,19} = 0$$

$$G_{4,21} = -\mu_c r_4 \sin \alpha_3 / \sqrt{r_1 r_4}$$

$$G_{4,2} = \mu_c \cos \alpha_3$$

$$G_{4,4} = \mu_c + \mu_o$$

$$G_{4,6} = \mu_o \cos \beta$$

$$G_{4,8} = 0$$

$$G_{4,10} = \mu_c \sin \alpha_3 + \mu_c \frac{r_1}{R} \sin(\alpha_3 - \phi)$$

$$G_{4,12} = -\mu_c r_2 \sin \alpha_3 / \sqrt{r_1 r_2}$$

$$G_{4,14} = -\mu_c \frac{r_2}{R} \sin(\alpha_3 - \phi)$$

$$G_{4,16} = -\mu_o r_2 \sin \beta / \sqrt{r_2 r_3}$$

$$G_{4,18} = 0$$

$$G_{4,20} = 0$$

$$G_{5,1} = -\mu_c \cos(\alpha_3 - \phi)$$

$$G_{5,3} = \mu_c \cos \alpha_3$$

$$G_{5,5} = \mu_c + \mu_o$$

$$G_{5,7} = \mu_o \cos \beta$$

$$G_{5,9} = 0$$

$$G_{5,11} = -\mu_c \frac{r_2}{R} \sin(\alpha_3 - \phi)$$

$$G_{5,13} = \mu_c \sin \alpha_3 + \mu_c \frac{r_1}{R} \sin(\alpha_3 - \phi)$$

$$G_{5,15} = -\mu_c r_2 \sin \alpha_3 / \sqrt{r_1 r_2}$$

$$G_{5,17} = 0$$

$$G_{5,19} = -\mu_o r_2 \sin \beta / \sqrt{r_2 r_3}$$

$$G_{5,21} = 0$$

$$G_{5,2} = 0$$

$$G_{5,4} = 0$$

$$G_{5,6} = 0$$

$$G_{5,8} = 0$$

$$G_{5,10} = \mu_c \frac{r_1}{R} \sin(\alpha_3 - \phi)$$

$$G_{5,12} = 0$$

$$G_{5,14} = -\mu_c \frac{r_2}{R} \sin(\alpha_3 - \phi)$$

$$G_{5,16} = 0$$

$$G_{5,18} = -\mu_c r_4 \sin \alpha_3 / \sqrt{r_1 r_4}$$

$$G_{5,20} = \mu_o r_4 \sin \beta / \sqrt{r_3 r_4}$$

$$\begin{aligned}
 G_{6,1} &= 0 \\
 G_{6,3} &= 0 \\
 G_{6,5} &= 0 \\
 G_{6,7} &= 0 \\
 G_{6,9} &= 0 \\
 G_{6,11} &= \mu_0 \sin \beta \\
 G_{6,13} &= 0 \\
 G_{6,15} &= 0 \\
 G_{6,17} &= -\mu_H r_3 \sin(\theta + \psi) / \sqrt{r_3 r_4} \\
 G_{6,19} &= 0 \\
 G_{6,21} &= 0
 \end{aligned}$$

$$\begin{aligned}
 G_{7,1} &= 0 \\
 G_{7,3} &= 0 \\
 G_{7,5} &= \mu_0 \cos \beta \\
 G_{7,7} &= \mu_0 + \mu_H \\
 G_{7,9} &= -\mu_H \cos(\theta + \psi) \\
 G_{7,11} &= 0 \\
 G_{7,13} &= 0 \\
 G_{7,15} &= -\mu_0 r_1 \sin \beta / \sqrt{r_1 r_2} \\
 G_{7,17} &= 0 \\
 G_{7,19} &= -\mu_0 r_3 \sin \beta / \sqrt{r_2 r_3} \\
 G_{7,21} &= \mu_H r_1 \sin(\theta + \psi) / \sqrt{r_1 r_4}
 \end{aligned}$$

$$\begin{aligned}
 G_{6,2} &= 0 \\
 G_{6,4} &= \mu_0 \cos \beta \\
 G_{6,6} &= \mu_0 + \mu_H \\
 G_{6,8} &= -\mu_H \cos(\theta + \psi) \\
 G_{6,10} &= 0 \\
 G_{6,12} &= -\mu_0 r_1 \sin \beta / \sqrt{r_1 r_2} \\
 G_{6,14} &= 0 \\
 G_{6,16} &= -\mu_0 r_3 \sin \beta / \sqrt{r_2 r_3} \\
 G_{6,18} &= \mu_H r_1 \sin(\theta + \psi) / \sqrt{r_1 r_4} \\
 G_{6,20} &= 0
 \end{aligned}$$

$$\begin{aligned}
 G_{7,2} &= 0 \\
 G_{7,4} &= 0 \\
 G_{7,6} &= 0 \\
 G_{7,8} &= 0 \\
 G_{7,10} &= 0 \\
 G_{7,12} &= 0 \\
 G_{7,14} &= \mu_0 \sin \beta \\
 G_{7,16} &= 0 \\
 G_{7,18} &= 0 \\
 G_{7,20} &= -\mu_H r_3 \sin(\theta + \psi) / \sqrt{r_3 r_4}
 \end{aligned}$$

$$G_{8,1} = 0$$

$$G_{8,3} = \mu_0 \cos \gamma$$

$$G_{8,5} = 0$$

$$G_{8,7} = 0$$

$$G_{8,9} = 0$$

$$G_{8,11} = 0$$

$$G_{8,13} = \mu_0 \sin \gamma$$

$$G_{8,15} = -\mu_0 r_2 \sin \gamma / \sqrt{r_1 r_2}$$

$$G_{8,17} = -\mu_H r_4 \sin(\theta + \psi) / \sqrt{r_3 r_4}$$

$$G_{8,19} = 0$$

$$G_{8,21} = 0$$

$$G_{8,2} = 0$$

$$G_{8,4} = 0$$

$$G_{8,6} = -\mu_H \cos(\theta + \psi)$$

$$G_{8,8} = \mu_0 + \mu_H$$

$$G_{8,10} = 0$$

$$G_{8,12} = 0$$

$$G_{8,14} = 0$$

$$G_{8,16} = \mu_H r_2 \sin(\theta + \psi) / \sqrt{r_2 r_3}$$

$$G_{8,18} = -\mu_0 r_4 \sin \gamma / \sqrt{r_1 r_4}$$

$$G_{8,20} = 0$$

$$G_{9,1} = 0$$

$$G_{9,3} = 0$$

$$G_{9,5} = 0$$

$$G_{9,7} = -\mu_H \cos(\theta + \psi)$$

$$G_{9,9} = \mu_0 + \mu_H$$

$$G_{9,11} = 0$$

$$G_{9,13} = 0$$

$$G_{9,15} = 0$$

$$G_{9,17} = 0$$

$$G_{9,19} = \mu_H r_2 \sin(\theta + \psi) / \sqrt{r_2 r_3}$$

$$G_{9,21} = -\mu_0 r_4 \sin \gamma / \sqrt{r_1 r_4}$$

$$G_{9,2} = \mu_0 \cos \gamma$$

$$G_{9,4} = 0$$

$$G_{9,6} = 0$$

$$G_{9,8} = 0$$

$$G_{9,10} = \mu_0 \sin \gamma$$

$$G_{9,12} = -\mu_0 r_2 \sin \gamma / \sqrt{r_1 r_2}$$

$$G_{9,14} = 0$$

$$G_{9,16} = 0$$

$$G_{9,18} = 0$$

$$G_{9,20} = -\mu_H r_4 \sin(\theta + \psi) / \sqrt{r_3 r_4}$$

$$G_{10,1} = -\mu_c \sin \phi$$

$$G_{10,3} = -\mu_c \frac{r_1}{R} \sin \phi$$

$$G_{10,5} = -\mu_c \frac{r_2}{R} \sin(\alpha_3 - \phi)$$

$$G_{10,7} = 0$$

$$G_{10,9} = \mu_o \sin \gamma$$

$$G_{10,11} = -2\mu_c (r_1 r_2 / R^2) - \mu_c (r_2 / R) \cos \phi \\ - \mu_c (r_1 / R) \cos(\alpha_3 - \phi) - \mu_c \cos \alpha_3$$

$$G_{10,13} = 2\mu_c (r_1^2 / R^2) + 2\mu_c (r_1 / R) \cos \phi$$

$$G_{10,14} = 2\mu_c (r_1 r_2 / R^2) - \mu_c (r_1 / R) \cos(\alpha_3 - \phi) \\ - \mu_c (r_2 / R) \cos \phi$$

$$G_{10,16} = \{ \mu_c r_3 \cos \alpha_3 + \mu_c (r_1 r_3 / R) \cos(\alpha_3 - \phi) \} \\ / \sqrt{r_2 r_3}$$

$$G_{10,18} = -\mu_c (\sqrt{r_1 r_4} / R) \cos \phi$$

$$G_{10,20} = -\mu_o r_3 \cos \beta / \sqrt{r_3 r_4}$$

$$G_{11,1} = -\mu_c \sin(\alpha_3 - \phi)$$

$$G_{11,3} = \mu_c (r_2 / R) \sin \phi$$

$$G_{11,5} = -\mu_c (r_2 / R) \sin(\alpha_3 - \phi)$$

$$G_{11,7} = 0$$

$$G_{11,9} = 0$$

$$G_{11,11} = \mu_c ((2r_2^2 / R^2) + (2r_2 / R) \cos(\alpha_3 - \phi) + 1) \\ + \mu_o$$

$$G_{11,13} = -2\mu_c (r_1 r_2 / R^2) - \mu_c (r_1 / R) \cos(\alpha_3 - \phi) \\ - \mu_c (r_2 / R) \cos \phi$$

$$G_{10,2} = -\mu_c \frac{r_1}{R} \sin \phi$$

$$G_{10,4} = \mu_c \sin \alpha_3 + \mu_c \frac{r_1}{R} \sin(\alpha_3 - \phi)$$

$$G_{10,6} = 0$$

$$G_{10,8} = 0$$

$$G_{10,10} = \mu_c ((2r_1^2 / R^2) + (2r_1 / R) \cos \phi + 1) + \mu_o$$

$$G_{10,12} = \{ \mu_c r_1 \cos \alpha_3 - \mu_c (r_1 r_2 / R) \cos \phi \\ + \mu_c (r_1^2 / R) \cos(\alpha_3 - \phi) - \mu_c r_2 - \mu_o r_2 \} \\ / \sqrt{r_1 r_2}$$

$$G_{10,15} = \{ \mu_c (r_1^2 / R) \cos(\alpha_3 - \phi) - \mu_c (r_1 r_2 / R) \\ \cos \phi \} / \sqrt{r_1 r_2}$$

$$G_{10,17} = 0$$

$$G_{10,19} = \mu_c (r_1 r_3 / R) \cos(\alpha_3 - \phi) / \sqrt{r_2 r_3}$$

$$G_{10,21} = \{ \mu_o r_1 \cos \gamma - \mu_o r_4 - \mu_c r_4 - \mu_c (r_1 r_4 / R) \\ \cos \phi \} / \sqrt{r_1 r_4}$$

$$G_{11,2} = \mu_c \sin \alpha_3 + \mu_c (r_2 / R) \sin \phi$$

$$G_{11,4} = -\mu_c (r_2 / R) \sin(\alpha_3 - \phi)$$

$$G_{11,6} = \mu_o \sin \beta$$

$$G_{11,8} = 0$$

$$G_{11,10} = -2\mu_c (r_1 r_2 / R^2) - \mu_c (r_2 / R) \cos \phi \\ - \mu_c (r_1 / R) \cos(\alpha_3 - \phi) - \mu_c \cos \alpha_3$$

$$G_{11,12} = \{ \mu_c (r_2^2 / R) \cos \phi - \mu_c (r_1 r_2 / R) \\ \cos(\alpha_3 - \phi) + \mu_c r_2 \cos \alpha_3 - \mu_c r_1 \\ - \mu_o r_1 \} / \sqrt{r_1 r_2}$$

$G_{11,14} = 2\mu_c(r_2^2/R^2) + 2\mu_c(r_2/R)\cos(\alpha_3 - \phi)$	$G_{11,15} = \{\mu_c(r_2^2/R)\cos\phi - \mu_c(r_1r_2/R)\cos(\alpha_3 - \phi)\}/\sqrt{r_1r_2}$
$G_{11,16} = \{\mu_0r_2\cos\beta - \mu_0r_3 - \mu_c r_3 - \mu_c(r_2r_3/R)\cos(\alpha_3 - \phi)\}/\sqrt{r_2r_3}$	$G_{11,17} = -\mu_0r_4\cos\beta/\sqrt{r_3r_4}$
$G_{11,18} = \mu_c(r_2r_4/R)\cos\phi/\sqrt{r_1r_4}$	$G_{11,19} = -\mu_c(\sqrt{r_2r_3}/R)\cos(\alpha_3 - \phi)$
$G_{11,20} = 0$	$G_{11,21} = \{\mu_c r_4\cos\alpha_3 + \mu_c(r_2r_4/R)\cos\phi\}/\sqrt{r_1r_4}$
$G_{12,1} = \{\mu_c r_2\sin\phi + \mu_c r_1\sin(\alpha_3 - \phi)\}/\sqrt{r_1r_2}$	$G_{12,2} = -\mu_c r_1\sin\alpha_3/\sqrt{r_1r_2}$
$G_{12,3} = 0$	$G_{12,4} = -\mu_c r_2\sin\alpha_3/\sqrt{r_1r_2}$
$G_{12,5} = 0$	$G_{12,6} = -\mu_0 r_1\sin\beta/\sqrt{r_1r_2}$
$G_{12,7} = 0$	$G_{12,8} = 0$
$G_{12,9} = -\mu_0 r_2\sin\gamma/\sqrt{r_1r_2}$	$G_{12,10} = \{\mu_c r_1\cos\alpha_3 - \mu_c(r_1r_2/R)\cos\phi + \mu_c(r_1^2/R)\cos(\alpha_3 - \phi) - \mu_c r_2 - \mu_0 r_2\}/\sqrt{r_1r_2}$
$G_{12,11} = \{\mu_c r_2\cos\alpha_3 - \mu_c(r_1r_2/R)\cos(\alpha_3 - \phi) + \mu_c(r_2^2/R)\cos\phi - \mu_c r_1 - \mu_0 r_1\}/\sqrt{r_1r_2}$	$G_{12,12} = \mu_c(r_1/r_2 + r_2/r_1 - 2\cos\alpha_3) + \mu_0((r_1/r_2) + (r_2/r_1))$
$G_{12,13} = \{\mu_c(r_1^2/R)\cos(\alpha_3 - \phi) - \mu_c(r_1r_2/R)\cos\phi\}/\sqrt{r_1r_2}$	$G_{12,14} = \{\mu_c(r_2^2/R)\cos\phi - \mu_c(r_1r_2/R)\cos(\alpha_3 - \phi)\}/\sqrt{r_1r_2}$
$G_{12,15} = 0$	$G_{12,17} = \mu_0\sqrt{r_1r_4}\cos\beta/\sqrt{r_2r_3}$
$G_{12,16} = \{\mu_c(r_1r_3/r_2) - \mu_c r_3\cos\alpha_3 + \mu_0(r_1r_3/r_2) - \mu_0 r_1\cos\beta\}/\sqrt{r_1r_3}$	$G_{12,18} = 0$
$G_{12,19} = 0$	$G_{12,20} = \mu_0\sqrt{r_2r_3}\cos\gamma/\sqrt{r_1r_4}$
$G_{12,21} = \{\mu_c(r_2r_4/r_1) - \mu_c r_4\cos\alpha_3 + \mu_0(r_2r_4/r_1) - \mu_0 r_2\cos\gamma\}/\sqrt{r_2r_4}$	

$$G_{13,1} = -\mu_c \sin \phi$$

$$G_{13,3} = -\mu_c (r_1/R) \sin \phi$$

$$G_{13,5} = \mu_c \sin \alpha_3 + \mu_c (r_1/R) \sin(\alpha_3 - \phi)$$

$$G_{13,7} = 0$$

$$G_{13,9} = 0$$

$$G_{13,11} = -2\mu_c (r_1 r_2 / R^2) - \mu_c (r_1/R) \cos(\alpha_3 - \phi) - \mu_c (r_2/R) \cos \phi$$

$$G_{13,13} = \mu_c (2r_1^2 / R^2 + 2(r_1/R) \cos \phi + 1) + \mu_0$$

$$G_{13,15} = \{ \mu_c r_1 \cos \alpha_3 - \mu_c (r_1 r_2 / R) \cos \phi - \mu_c r_2 - \mu_0 r_2 + \mu_c (r_1^2 / R) \cos(\alpha_3 - \phi) \} / \sqrt{r_1 r_2}$$

$$G_{13,17} = -\mu_0 r_3 \cos \gamma / \sqrt{r_3 r_4}$$

$$G_{13,19} = \{ \mu_c (r_1 r_3 / R) \cos(\alpha_3 - \phi) + \mu_c r_3 \cos \alpha_3 \} / \sqrt{r_2 r_3}$$

$$G_{13,21} = -\mu_c (\sqrt{r_1 r_4} / R) \cos \phi$$

$$G_{14,1} = -\mu_c \sin(\alpha_3 - \phi)$$

$$G_{14,3} = \mu_c \sin \alpha_3 + \mu_c (r_2/R) \sin \phi$$

$$G_{14,5} = -\mu_c (r_2/R) \sin(\alpha_3 - \phi)$$

$$G_{14,7} = \mu_0 \sin \beta$$

$$G_{14,9} = 0$$

$$G_{14,11} = 2\mu_c (r_2^2 / R^2) + 2\mu_c (r_2/R) \cos(\alpha_3 - \phi)$$

$$G_{14,12} = \{ \mu_c (r_2^2 / R) \cos \phi - \mu_c (r_1 r_2 / R) \cos(\alpha_3 - \phi) \} / \sqrt{r_1 r_2}$$

$$G_{14,14} = \mu_c (2r_2^2 / R^2 + 2(r_2/R) \cos(\alpha_3 - \phi) + 1) + \mu_0$$

$$G_{14,16} = -\mu_c (\sqrt{r_2 r_3} / R) \cos(\alpha_3 - \phi)$$

$$G_{14,17} = 0$$

$$G_{13,2} = -\mu_c (r_1/R) \sin \phi$$

$$G_{13,4} = \mu_c (r_1/R) \sin(\alpha_3 - \phi)$$

$$G_{13,6} = 0$$

$$G_{13,8} = \mu_0 \sin \gamma$$

$$G_{13,10} = 2\mu_c (r_1^2 / R^2) + 2\mu_c (r_1/R) \cos \phi$$

$$G_{13,12} = \{ \mu_c (r_1^2 / R) \cos(\alpha_3 - \phi) - \mu_c (r_1 r_2 / R) \cos \phi \} / \sqrt{r_1 r_2}$$

$$G_{13,14} = -2\mu_c (r_1 r_2 / R^2) - \mu_c (r_1/R) \cos(\alpha_3 - \phi) - \mu_c (r_2/R) \cos \phi - \mu_c \cos \alpha_3$$

$$G_{13,16} = \mu_c (r_1 r_3 / R) \cos(\alpha_3 - \phi) / \sqrt{r_2 r_3}$$

$$G_{13,18} = \{ -\mu_c (r_1 r_4 / R) \cos \phi - \mu_c r_4 - \mu_0 r_4 + \mu_0 r_1 \cos \gamma \} / \sqrt{r_1 r_4}$$

$$G_{13,20} = 0$$

$$G_{14,2} = \mu_c (r_2/R) \sin \phi$$

$$G_{14,4} = -\mu_c (r_2/R) \sin(\alpha_3 - \phi)$$

$$G_{14,6} = 0$$

$$G_{14,8} = 0$$

$$G_{14,10} = 2\mu_c (r_1 r_2 / R^2) - \mu_c (r_1/R) \cos(\alpha_3 - \phi) - \mu_c (r_2/R) \cos \phi$$

$$G_{14,13} = -2\mu_c (r_1 r_2 / R^2) - \mu_c (r_1/R) \cos(\alpha_3 - \phi) - \mu_c (r_2/R) \cos \phi - \mu_c \cos \alpha_3$$

$$G_{14,15} = \{ \mu_c (r_2^2 / R) \cos \phi - \mu_c (r_1 r_2 / R) \cos(\alpha_3 - \phi) + \mu_c r_2 \cos \alpha_3 - \mu_c r_1 - \mu_0 r_1 \} / \sqrt{r_1 r_2}$$

$$G_{14,18} = \{\mu_c(r_2 r_4/R) \cos \phi + \mu_c r_4 \cos \alpha_3\} / \sqrt{r_1 r_4}$$

$$G_{14,19} = \{-\mu_c(r_2 r_3/R) \cos(\alpha_3 - \phi) - \mu_c r_3 - \mu_o r_3 + \mu_o r_2 \cos \beta\} / \sqrt{r_2 r_3}$$

$$G_{14,20} = -\mu_o r_4 \cos \beta / \sqrt{r_3 r_4}$$

$$G_{14,21} = \mu_c(r_2 r_4/R) \cos \phi / \sqrt{r_1 r_4}$$

$$G_{15,1} = \{\mu_c r_2 \sin \phi + \mu_c r_1 \sin(\alpha_3 - \phi)\} / \sqrt{r_1 r_2}$$

$$G_{15,2} = 0$$

$$G_{15,3} = -\mu_c r_1 \sin \alpha_3 / \sqrt{r_1 r_2}$$

$$G_{15,4} = 0$$

$$G_{15,5} = -\mu_c r_2 \sin \alpha_3 / \sqrt{r_1 r_2}$$

$$G_{15,6} = 0$$

$$G_{15,7} = -\mu_o r_1 \sin \beta / \sqrt{r_1 r_2}$$

$$G_{15,8} = -\mu_o r_2 \sin \gamma / \sqrt{r_1 r_2}$$

$$G_{15,9} = 0$$

$$G_{15,10} = \{\mu_c(r_1^2/R) \cos(\alpha_3 - \phi) - \mu_c(r_1 r_2/R) \cos \phi\} / \sqrt{r_1 r_2}$$

$$G_{15,11} = \{\mu_c(r_2^2/R) \cos \phi - \mu_c(r_1 r_2/R) \cos(\alpha_3 - \phi)\} / \sqrt{r_1 r_2}$$

$$G_{15,12} = 0$$

$$G_{15,13} = \{\mu_c r_1 \cos \alpha_3 + \mu_c(r_1^2/R) \cos(\alpha_3 - \phi) - \mu_c(r_1 r_2/R) \cos \phi - \mu_c r_2 - \mu_o r_2\} / \sqrt{r_1 r_2}$$

$$G_{15,14} = \{\mu_c(r_2^2/R) \cos \phi - \mu_c(r_1 r_2/R) \cos(\alpha_3 - \phi) + \mu_c r_2 \cos \alpha_3 - \mu_c r_1 - \mu_o r_1\} / \sqrt{r_1 r_2}$$

$$G_{15,15} = \mu_c(r_1/r_2 + r_2/r_1 - 2 \cos \alpha_3) + \mu_o(r_1/r_2 + r_2/r_1)$$

$$G_{15,16} = 0$$

$$G_{15,17} = \mu_o \sqrt{r_2 r_3} \cos \gamma / \sqrt{r_1 r_4}$$

$$G_{15,18} = \{\mu_c(r_2 r_4/r_1) - \mu_c r_4 \cos \alpha_3 + \mu_o(r_2 r_4/r_1) - \mu_o r_2 \cos \alpha_3\} / \sqrt{r_2 r_4}$$

$$G_{15,19} = \{\mu_c(r_1 r_3/r_2) - \mu_c r_3 \cos \alpha_3 + \mu_o(r_1 r_3/r_2) - \mu_o r_1 \cos \beta\} / \sqrt{r_1 r_3}$$

$$G_{15,20} = \mu_o \sqrt{r_1 r_4} \cos \beta / \sqrt{r_2 r_3}$$

$$G_{15,21} = 0$$

$$G_{16,1} = \mu_c r_3 \sin(\alpha_3 - \phi) / \sqrt{r_2 r_3}$$

$$G_{16,2} = -\mu_c r_3 \sin \alpha_3 / \sqrt{r_2 r_3}$$

$$G_{16,3} = 0$$

$$G_{16,4} = -\mu_o r_2 \sin \beta / \sqrt{r_2 r_3}$$

$$G_{16,5} = 0$$

$$G_{16,6} = -\mu_o r_3 \sin \beta / \sqrt{r_2 r_3}$$

$$G_{16,7} = 0$$

$$G_{16,8} = \mu_H r_2 \sin(\theta + \psi) / \sqrt{r_2 r_3}$$

$$G_{16,9} = 0$$

$$G_{16,10} = \{\mu_c r_3 \cos \alpha_3 + \mu_c(r_1 r_3/R) \cos(\alpha_3 - \phi)\} / \sqrt{r_2 r_3}$$

$$G_{16,11} = \{\mu_0 r_2 \cos \beta - \mu_0 r_3 - \mu_c r_3 - \mu_c (r_2 r_3 / R) \cos(\alpha_3 - \phi)\} / \sqrt{r_2 r_3}$$

$$G_{16,12} = \{\mu_c (r_1 r_3 / r_2) - \mu_c r_3 \cos \alpha_3 + \mu_0 (r_1 r_3 / r_2) - \mu_0 r_1 \cos \beta\} / \sqrt{r_1 r_3}$$

$$G_{16,13} = \mu_c (r_1 r_3 / R) \cos(\alpha_3 - \phi) / \sqrt{r_2 r_3}$$

$$G_{16,14} = -\mu_c \sqrt{r_2 r_3} / R \cos(\alpha_3 - \phi)$$

$$G_{16,15} = 0$$

$$G_{16,16} = \mu_c (r_3 / r_2) + \mu_H (r_2 / r_3) + \mu_0 (r_2 / r_3) + (r_3 / r_2) - 2 \cos \beta$$

$$G_{16,17} = \{-\mu_0 (r_2 r_4 / r_3) + \mu_0 r_4 \cos \beta - \mu_H (r_2 r_4 / r_3) - \mu_H r_2 \cos(\theta + \psi)\} / \sqrt{r_2 r_4}$$

$$G_{16,18} = \mu_H \sqrt{r_1 r_2} \cos(\theta + \psi) / \sqrt{r_3 r_4}$$

$$G_{16,19} = 0$$

$$G_{16,20} = 0$$

$$G_{16,21} = -\mu_c \sqrt{r_3 r_4} \cos \alpha_3 / \sqrt{r_1 r_2}$$

$$G_{17,1} = 0$$

$$G_{17,3} = \mu_0 r_3 \sin \gamma / \sqrt{r_3 r_4}$$

$$G_{17,5} = 0$$

$$G_{17,7} = 0$$

$$G_{17,9} = 0$$

$$G_{17,11} = -\mu_0 r_4 \cos \beta / \sqrt{r_3 r_4}$$

$$G_{17,13} = -\mu_0 r_3 \cos \gamma / \sqrt{r_3 r_4}$$

$$G_{17,15} = \mu_0 \sqrt{r_2 r_3} \cos \gamma / \sqrt{r_1 r_4}$$

$$G_{17,16} = \{-\mu_0 (r_2 r_4 / r_3) + \mu_0 r_4 \cos \beta - \mu_H (r_2 r_4 / r_3) - \mu_H r_2 \cos(\theta + \psi)\} / \sqrt{r_2 r_4}$$

$$G_{17,17} = \mu_0 (r_3 / r_4) + (r_4 / r_3) + \mu_H (r_3 / r_4) + (r_4 / r_3) + 2 \cos(\theta + \psi)$$

$$G_{17,18} = \{-\mu_H (r_1 r_3 / r_4) - \mu_H r_1 \cos(\theta + \psi) - \mu_0 (r_1 r_3 / r_4) + \mu_0 r_3 \cos \gamma\} / \sqrt{r_1 r_3}$$

$$G_{17,19} = 0$$

$$G_{17,21} = 0$$

$$G_{17,2} = 0$$

$$G_{17,4} = \mu_0 r_4 \sin \beta / \sqrt{r_3 r_4}$$

$$G_{17,6} = -\mu_H r_3 \sin(\theta + \psi) / \sqrt{r_3 r_4}$$

$$G_{17,8} = -\mu_H r_4 \sin(\theta + \psi) / \sqrt{r_3 r_4}$$

$$G_{17,10} = 0$$

$$G_{17,12} = \mu_0 \sqrt{r_1 r_4} \cos \beta / \sqrt{r_2 r_3}$$

$$G_{17,14} = 0$$

$$G_{17,20} = 0$$

$$G_{18,1} = \mu_c r_4 \sin \phi / \sqrt{r_1 r_4}$$

$$G_{18,3} = -\mu_0 r_1 \sin \gamma / \sqrt{r_1 r_4}$$

$$G_{18,5} = -\mu_c r_4 \sin \alpha_3 / \sqrt{r_1 r_4}$$

$$G_{18,2} = 0$$

$$G_{18,4} = 0$$

$$G_{18,6} = \mu_H r_1 \sin(\theta + \psi) / \sqrt{r_1 r_4}$$

$G_{18,7} = 0$	$G_{18,8} = -\mu_0 r_4 \sin \gamma / \sqrt{r_1 r_4}$
$G_{18,9} = 0$	$G_{18,10} = -\mu_c (\sqrt{r_1 r_4} / R) \cos \phi$
$G_{18,11} = \mu_c (r_2 r_4 / R) \cos \phi / \sqrt{r_1 r_4}$	$G_{18,12} = 0$
$G_{18,13} = \{-\mu_c (r_1 r_4 / R) \cos \psi - \mu_c r_4 - \mu_0 r_4 + \mu_0 r_1 \cos \gamma\} / \sqrt{r_1 r_4}$	
$G_{18,14} = \{\mu_c (r_2 r_4 / R) \cos \phi + \mu_c r_4 \cos \alpha_3\} / \sqrt{r_1 r_4}$	
$G_{18,15} = \{\mu_c (r_2 r_4 / r_1) - \mu_c r_4 \cos \alpha_3 - \mu_0 r_2 \cos \alpha_3 + \mu_0 (r_2 r_4 / r_1)\} / \sqrt{r_2 r_4}$	
$G_{18,16} = \mu_H \sqrt{r_1 r_2} \cos(\theta + \psi) / \sqrt{r_3 r_4}$	
$G_{18,17} = \{-\mu_H (r_1 r_3 / r_4) - \mu_H r_1 \cos(\theta + \psi) - \mu_0 (r_1 r_3 / r_4) + \mu_0 r_3 \cos \gamma\} / \sqrt{r_1 r_3}$	
$G_{18,18} = \mu_c (r_4 / r_1) + \mu_H (r_1 / r_4) + \mu_0 (r_1 / r_4) + (r_4 / r_1) - 2 \cos \gamma$	
$G_{18,19} = -\mu_c \sqrt{r_3 r_4} \cos \alpha_3 / \sqrt{r_1 r_2}$	$G_{18,20} = 0$
$G_{18,21} = 0$	
$G_{19,1} = \mu_c r_3 \sin(\alpha_3 - \phi) / \sqrt{r_2 r_3}$	$G_{19,2} = 0$
$G_{19,3} = -\mu_c r_3 \sin \alpha_3 / \sqrt{r_2 r_3}$	$G_{19,4} = 0$
$G_{19,5} = -\mu_0 r_2 \sin \beta / \sqrt{r_2 r_3}$	$G_{19,6} = 0$
$G_{19,7} = -\mu_0 r_3 \sin \beta / \sqrt{r_2 r_3}$	$G_{19,8} = 0$
$G_{19,9} = \mu_H r_2 \sin(\theta + \psi) / \sqrt{r_2 r_3}$	$G_{19,10} = \mu_c (r_1 r_3 / R) \cos(\alpha_3 - \phi) / \sqrt{r_2 r_3}$
$G_{19,11} = -\mu_c (\sqrt{r_2 r_3} / R) \cos(\alpha_3 - \phi)$	$G_{19,12} = 0$
$G_{19,13} = \{\mu_c (r_1 r_3 / R) \cos(\alpha_3 - \phi) + \mu_c r_3 \cos \alpha_3\} / \sqrt{r_2 r_3}$	
$G_{19,14} = \{-\mu_c (r_2 r_3 / R) \cos(\alpha_3 - \phi) - \mu_c r_3 - \mu_0 r_3 + \mu_0 r_2 \cos \beta\} / \sqrt{r_2 r_3}$	
$G_{19,15} = \{\mu_c (r_1 r_3 / r_2) - \mu_c r_3 \cos \alpha_3 + \mu_0 (r_1 r_3 / r_2) - \mu_0 r_1 \cos \beta\} / \sqrt{r_1 r_3}$	
$G_{19,16} = 0$	$G_{19,17} = 0$
$G_{19,18} = -\mu_c \sqrt{r_3 r_4} \cos \alpha_3 / \sqrt{r_1 r_2}$	
$G_{19,19} = \mu_c (r_3 / r_2) + \mu_H (r_2 / r_3) + \mu_0 (r_2 / r_3) + (r_3 / r_2) - 2 \cos \beta$	
$G_{19,20} = \{-\mu_0 (r_2 r_4 / r_3) + \mu_0 r_4 \cos \beta - \mu_H (r_2 r_4 / r_3) - \mu_H r_2 \cos(\theta + \psi)\} / \sqrt{r_2 r_4}$	
$G_{19,21} = \mu_H \sqrt{r_1 r_2} \cos(\theta + \psi) / \sqrt{r_3 r_4}$	

$G_{20,1} = 0$	$G_{20,2} = \mu_0 r_3 \sin \gamma / \sqrt{r_3 r_4}$
$G_{20,3} = 0$	$G_{20,4} = 0$
$G_{20,5} = \mu_0 r_4 \sin \beta / \sqrt{r_3 r_4}$	$G_{20,6} = 0$
$G_{20,7} = -\mu_H r_3 \sin(\theta + \psi) / \sqrt{r_3 r_4}$	$G_{20,8} = 0$
$G_{20,9} = -\mu_H r_4 \sin(\theta + \psi) / \sqrt{r_3 r_4}$	$G_{20,10} = -\mu_0 r_3 \cos \beta / \sqrt{r_3 r_4}$
$G_{20,11} = 0$	$G_{20,12} = \mu_0 \sqrt{r_2 r_3} \cos \gamma / \sqrt{r_1 r_4}$
$G_{20,13} = 0$	$G_{20,14} = -\mu_0 r_4 \cos \beta / \sqrt{r_3 r_4}$
$G_{20,15} = \mu_0 \sqrt{r_1 r_4} \cos \beta / \sqrt{r_2 r_3}$	$G_{20,16} = 0$
$G_{20,17} = 0$	$G_{20,18} = 0$
$G_{20,19} = \{-\mu_0 (r_2 r_4 / r_3) + \mu_0 r_4 \cos \beta - \mu_H (r_2 r_4 / r_3) - \mu_H r_2 \cos(\theta + \psi)\} / \sqrt{r_2 r_4}$	
$G_{20,20} = \mu_0 (r_3 / r_4 + r_4 / r_3) + \mu_H (r_3 / r_4 + r_4 / r_3 + 2 \cos(\theta + \psi))$	
$G_{20,21} = \{-\mu_0 (r_1 r_3 / r_4) + \mu_0 r_3 \cos \gamma - \mu_H (r_1 r_3 / r_4) - \mu_H r_1 \cos(\theta + \psi)\} / \sqrt{r_1 r_3}$	
$G_{21,1} = \mu_C r_4 \sin \phi / \sqrt{r_1 r_4}$	$G_{21,2} = -\mu_0 r_1 \sin \gamma / \sqrt{r_1 r_4}$
$G_{21,3} = 0$	$G_{21,4} = -\mu_C r_4 \sin \alpha_3 / \sqrt{r_1 r_4}$
$G_{21,5} = 0$	$G_{21,6} = 0$
$G_{21,7} = \mu_H r_1 \sin(\theta + \psi) / \sqrt{r_1 r_4}$	$G_{21,8} = 0$
$G_{21,9} = -\mu_0 r_4 \sin \gamma / \sqrt{r_1 r_4}$	
$G_{21,10} = \{\mu_0 r_1 \cos \gamma - \mu_0 r_4 - \mu_C r_4 - \mu_C (r_1 r_4 / R) \cos \phi\} / \sqrt{r_1 r_4}$	
$G_{21,11} = \{\mu_C r_4 \cos \alpha_3 + \mu_C (r_2 r_4 / R) \cos \phi\} / \sqrt{r_1 r_4}$	
$G_{21,12} = \{\mu_C (r_2 r_4 / r_1) - \mu_C r_4 \cos \alpha_3 + \mu_0 (r_2 r_4 / r_1) - \mu_0 r_2 \cos \gamma\} / \sqrt{r_2 r_4}$	
$G_{21,13} = -\mu_C (\sqrt{r_1 r_4} / R) \cos \phi$	$G_{21,14} = \mu_C (r_2 r_4 / R) \cos \phi / \sqrt{r_1 r_4}$
$G_{21,15} = 0$	$G_{21,16} = -\mu_C \sqrt{r_3 r_4} \cos \alpha_3 / \sqrt{r_1 r_2}$
$G_{21,17} = 0$	$G_{21,18} = 0$
$G_{21,19} = \mu_H \sqrt{r_1 r_2} \cos(\theta + \psi) / \sqrt{r_3 r_4}$	
$G_{21,20} = \{-\mu_0 (r_1 r_3 / r_4) + \mu_0 r_3 \cos \gamma - \mu_H (r_1 r_3 / r_4) - \mu_H r_1 \cos(\theta + \psi)\} / \sqrt{r_1 r_3}$	
$G_{21,21} = \mu_C (r_4 / r_1) + \mu_H (r_1 / r_4) + \mu_0 (r_1 / r_4 + r_4 / r_1 - 2 \cos \gamma)$	

17.4 Symmetry co-ordinates of the inplane vibration of gaseous oxalic acid 2nd model

The transformation table of the internal co-ordinates of gaseous oxalic acid 2nd model is given below.

Table 14

C_{2h}	E	C_2	i	σ_h
ΔR	ΔR	ΔR	ΔR	ΔR
Δr_1	Δr_1	$\Delta r'_1$	$\Delta r'_1$	Δr_1
$\Delta r'_1$	$\Delta r'_1$	Δr_1	Δr_1	$\Delta r'_1$
Δr_2	Δr_2	$\Delta r'_2$	$\Delta r'_2$	Δr_2
$\Delta r'_2$	$\Delta r'_2$	Δr_2	Δr_2	$\Delta r'_2$
Δr_3	Δr_3	$\Delta r'_3$	$\Delta r'_3$	Δr_3
$\Delta r'_3$	$\Delta r'_3$	Δr_3	Δr_3	$\Delta r'_3$
Δr_4	Δr_4	$\Delta r'_4$	$\Delta r'_4$	Δr_4
$\Delta r'_4$	$\Delta r'_4$	Δr_4	Δr_4	$\Delta r'_4$
$\Delta \alpha_1$	$\Delta \alpha_1$	$\Delta \alpha'_1$	$\Delta \alpha'_1$	$\Delta \alpha_1$
$\Delta \alpha_2$	$\Delta \alpha_2$	$\Delta \alpha'_2$	$\Delta \alpha'_2$	$\Delta \alpha_2$
$\Delta \alpha_3$	$\Delta \alpha_3$	$\Delta \alpha'_3$	$\Delta \alpha'_3$	$\Delta \alpha_3$
$\Delta \alpha'_1$	$\Delta \alpha'_1$	$\Delta \alpha_1$	$\Delta \alpha_1$	$\Delta \alpha'_1$
$\Delta \alpha'_2$	$\Delta \alpha'_2$	$\Delta \alpha_2$	$\Delta \alpha_2$	$\Delta \alpha'_2$
$\Delta \alpha'_3$	$\Delta \alpha'_3$	$\Delta \alpha_3$	$\Delta \alpha_3$	$\Delta \alpha'_3$
$\Delta \beta$	$\Delta \beta$	$\Delta \beta'$	$\Delta \beta'$	$\Delta \beta$
$\Delta \delta$	$\Delta \delta$	$\Delta \delta'$	$\Delta \delta'$	$\Delta \delta$
$\Delta \gamma$	$\Delta \gamma$	$\Delta \gamma'$	$\Delta \gamma'$	$\Delta \gamma$
$\Delta \beta'$	$\Delta \beta'$	$\Delta \beta$	$\Delta \beta$	$\Delta \beta'$
$\Delta \delta'$	$\Delta \delta'$	$\Delta \delta$	$\Delta \delta$	$\Delta \delta'$
$\Delta \gamma'$	$\Delta \gamma'$	$\Delta \gamma$	$\Delta \gamma$	$\Delta \gamma'$

The same process as in 15.4 applies and the resultant normalised symmetry co-ordinates for gaseous oxalic acid 2nd model are

Ag set

$$\begin{aligned}
 S_1 &= \Delta R && \text{symmetric C-C stretch} \\
 S_2 &= \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r'_1) && \text{symmetric C=O stretch} \\
 S_3 &= \frac{1}{\sqrt{2}}(\Delta r_2 + \Delta r'_2) && \text{symmetric C-O stretch} \\
 S_4 &= \frac{1}{\sqrt{2}}(\Delta r_3 + \Delta r'_3) && \text{symmetric O-H stretch} \\
 S_5 &= \frac{1}{\sqrt{2}}(\Delta r_4 + \Delta r'_4) && \text{symmetric O ... H stretch} \\
 S_6 &= \frac{1}{\sqrt{3}}(\Delta \alpha_3 + \Delta \alpha'_3) - \frac{1}{2\sqrt{3}}(\Delta \alpha_1 + \Delta \alpha_2 + \Delta \alpha'_1 + \Delta \alpha'_2) && \text{symmetric } (-C \leq \overset{O}{O}) \text{ angle deformation} \\
 S_7 &= \frac{1}{2\sqrt{3}}(\Delta \beta + \Delta \gamma + \Delta \beta' + \Delta \gamma') - \frac{1}{\sqrt{3}}(\Delta \delta + \Delta \delta') && \text{symmetric (O-H...O) angle bending}
 \end{aligned}$$

Bu set

$$\begin{aligned}
 S_8 &= \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r'_1) && \text{anti-symmetric C=O stretch} \\
 S_9 &= \frac{1}{\sqrt{2}}(\Delta r_2 - \Delta r'_2) && \text{anti-symmetric C-O stretch} \\
 S_{10} &= \frac{1}{\sqrt{2}}(\Delta r_3 - \Delta r'_3) && \text{anti-symmetric O-H stretch} \\
 S_{11} &= \frac{1}{\sqrt{2}}(\Delta r_4 - \Delta r'_4) && \text{anti-symmetric O...H stretch} \\
 S_{12} &= \frac{1}{\sqrt{3}}(\Delta \alpha_3 - \Delta \alpha'_3) - \frac{1}{2\sqrt{3}}(\Delta \alpha_1 + \Delta \alpha_2 - \Delta \alpha'_1 - \Delta \alpha'_2) && \text{anti-symmetric } (-C \leq \overset{O}{O}) \text{ angle deformation} \\
 S_{13} &= \frac{1}{2\sqrt{3}}(\Delta \beta + \Delta \gamma - \Delta \beta' - \Delta \gamma') - \frac{1}{\sqrt{3}}(\Delta \delta - \Delta \delta') && \text{anti-symmetric (O-H...O) angle bending}
 \end{aligned}$$

From the normalized symmetry co-ordinates the U-matrix in Table 15 is obtained.

Table 15

Transformation matrix of gaseous oxalic acid 2nd model

	ΔR	Δr_1	$\Delta r'_1$	Δr_2	$\Delta r'_2$	Δr_3	$\Delta r'_3$	Δr_4	$\Delta r'_4$	$\Delta \alpha_1$	$\Delta \alpha_2$	$\Delta \alpha_3$	$\Delta \alpha'_1$	$\Delta \alpha'_2$	$\Delta \alpha'_3$	$\Delta \beta$	$\Delta \delta$	$\Delta \gamma$	$\Delta \beta'$	$\Delta \delta'$	$\Delta \gamma'$
S_1	1																				
S_2	$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$																			
S_3			$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$																	
S_4					$\frac{1}{\sqrt{2}}$	$\frac{1}{\sqrt{2}}$															
S_5						$\frac{1}{\sqrt{2}}$		$\frac{1}{\sqrt{2}}$													
S_6										$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$\frac{1}{\sqrt{3}}$						
S_7																$\frac{1}{2\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$
S_8		$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$		$-\frac{1}{\sqrt{2}}$																
S_9				$\frac{1}{\sqrt{2}}$																	
S_{10}					$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$															
S_{11}							$\frac{1}{\sqrt{2}}$	$-\frac{1}{\sqrt{2}}$													
S_{12}										$-\frac{1}{2\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$						
S_{13}																$\frac{1}{2\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{1}{2\sqrt{3}}$	$-\frac{1}{\sqrt{3}}$	$\frac{1}{\sqrt{3}}$	$-\frac{1}{2\sqrt{3}}$

17.5 Numerical values of G-matrix of gaseous oxalic acid 2nd model in
symmetry co-ordinates

$$\begin{aligned}G(1,1) &= 0.166667 & G(1,2) &= -0.064359 \\G(1,3) &= -0.043957 & G(1,4) &= 0 \\G(1,5) &= 0 & G(1,6) &= 0.254615 \\G(1,7) &= 0.091953 \\G(1,8) &= G(1,9) = G(1,10) = G(1,11) = G(1,12) = G(1,13) = 0\end{aligned}$$

$$\begin{aligned}G(2,1) &= -0.064359 & G(2,2) &= 0.145833 \\G(2,3) &= -0.047798 & G(2,4) &= 0 \\G(2,5) &= 0.009076 & G(2,6) &= -0.085632 \\G(2,7) &= -0.080574 \\G(2,8) &= G(2,9) = G(2,10) = G(2,11) = G(2,12) = G(2,13) = 0\end{aligned}$$

$$\begin{aligned}G(3,1) &= -0.043957 & G(3,2) &= -0.047798 \\G(3,3) &= 0.145833 & G(3,4) &= -0.015543 \\G(3,5) &= 0 & G(3,6) &= -0.081206 \\G(3,7) &= -0.13261 \\G(3,8) &= G(3,9) = G(3,10) = G(3,11) = G(3,12) = G(3,13) = 0\end{aligned}$$

$$\begin{aligned}G(4,1) &= 0 & G(4,2) &= 0 \\G(4,3) &= -0.015543 & G(4,4) &= 1.062499 \\G(4,5) &= -0.484054 & G(4,6) &= -0.071662 \\G(4,7) &= 0.768012 \\G(4,8) &= G(4,9) = G(4,10) = G(4,11) = G(4,12) = G(4,13) = 0\end{aligned}$$

$$\begin{aligned}G(5,1) &= 0 & G(5,2) &= 0.009076 \\G(5,3) &= 0 & G(5,4) &= -0.484054 \\G(5,5) &= 1.062513 & G(5,6) &= -0.078403 \\G(5,7) &= 1.361267 \\G(5,8) &= G(5,9) = G(5,10) = G(5,11) = G(5,12) = G(5,13) = 0\end{aligned}$$

$$\begin{aligned}G(6,1) &= 0.254615 & G(6,2) &= -0.085632 \\G(6,3) &= -0.081206 & G(6,4) &= -0.071662 \\G(6,5) &= -0.078403 & G(6,6) &= 0.579780 \\G(6,7) &= 0.230543 \\G(6,8) &= G(6,9) = G(6,10) = G(6,11) = G(6,12) = G(6,13) = 0\end{aligned}$$

$$\begin{aligned}G(7,1) &= 0.091953 & G(7,2) &= -0.080574 \\G(7,3) &= -0.132610 & G(7,4) &= 0.768012 \\G(7,5) &= 1.361267 & G(7,6) &= 0.230543 \\G(7,7) &= 5.042583 \\G(7,8) &= G(7,9) = G(7,10) = G(7,11) = G(7,12) = G(7,13) = 0\end{aligned}$$

$$\begin{aligned}G(8,1) &= G(8,2) = G(8,3) = G(8,4) = G(8,5) = G(8,6) = G(8,7) = 0 \\G(8,8) &= 0.145833 & G(8,9) &= -0.047798 \\G(8,10) &= 0 & G(8,11) &= -0.009076 \\G(8,12) &= -0.080808 & G(8,13) &= 0.051076\end{aligned}$$

$$\begin{aligned}G(9,1) &= G(9,2) = G(9,3) = G(9,4) = G(9,5) = G(9,6) = G(9,7) = 0 \\G(9,8) &= -0.047798 & G(9,9) &= 0.145835 \\G(9,10) &= -0.015543 & G(9,11) &= 0 \\G(9,12) &= -0.086549 & G(9,13) &= -0.060272\end{aligned}$$

$$G(10,1) = G(10,2) = G(10,3) = G(10,4) = G(10,5) = G(10,6) = G(10,7) = 0$$

$$G(10,8) = 0 \qquad G(10,9) = -0.015543$$

$$G(10,10) = 1.062499 \qquad G(10,11) = -0.484054$$

$$G(10,12) = -0.071662 \qquad G(10,13) = 0.768012$$

$$G(11,1) = G(11,2) = G(11,3) = G(11,4) = G(11,5) = G(11,6) = G(11,7) = 0$$

$$G(11,8) = -0.039076 \qquad G(11,9) = 0$$

$$G(11,10) = -0.484054 \qquad G(11,11) = 1.062513$$

$$G(11,12) = 0.078403 \qquad G(11,13) = 1.361267$$

$$G(12,1) = G(12,2) = G(12,3) = G(12,4) = G(12,5) = G(12,6) = G(12,7) = 0$$

$$G(12,8) = -0.080808 \qquad G(12,9) = -0.086549$$

$$G(12,10) = -0.071662 \qquad G(12,11) = 0.078403$$

$$G(12,12) = 0.582270 \qquad G(12,13) = -0.003687$$

$$G(13,1) = G(13,2) = G(13,3) = G(13,4) = G(13,5) = G(13,6) = G(13,7) = 0$$

$$G(13,8) = 0.031076 \qquad G(13,9) = -0.060272$$

$$G(13,10) = 0.768012 \qquad G(13,11) = 1.361267$$

$$G(13,12) = -0.003687 \qquad G(13,13) = 5.005856$$

CHAPTER 18

CONSTRUCTION OF THE F-MATRIX OF THE INPLANE VIBRATIONS

OF GASEOUS OXALIC ACID 2ND MODEL

18.1 Urey-Bradley force field of gaseous oxalic acid 2nd model

The U.B.F.F. for the inplane vibrations of gaseous oxalic acid 2nd model was constructed using K as the stretching force constant, H as the bending force constant, and F the repulsive force constant between non-bonded atoms.

Fig. 22

The potential energy of the oxalic acid can be expressed as

$$\begin{aligned}
 V = & \frac{1}{2} K_{CC} (\Delta R)^2 + K'_{CC} R(\Delta R) \\
 & + \frac{1}{2} K_{C=O} (\Delta r_1)^2 + K'_{C=O} r_1 (\Delta r_1) \\
 & + \frac{1}{2} K_{C=O} (\Delta r'_1)^2 + K'_{C=O} r'_1 (\Delta r'_1) \\
 & + \frac{1}{2} K_{C-O} (\Delta r_2)^2 + K'_{C-O} r_2 (\Delta r_2) \\
 & + \frac{1}{2} K_{C-O} (\Delta r'_2)^2 + K'_{C-O} r'_2 (\Delta r'_2) \\
 & + \frac{1}{2} K_{O-H} (\Delta r_3)^2 + K'_{O-H} r_3 (\Delta r_3)
 \end{aligned}$$

$$\begin{aligned}
 & + \frac{1}{2} K_{O-H} (\Delta r'_3)^2 + K'_{O-H} r'_3 (\Delta r'_3) \\
 & + \frac{1}{2} K_{O..H} (\Delta r_4)^2 + K'_{O..H} r_4 (\Delta r_4) \\
 & + \frac{1}{2} K_{O..H} (\Delta r'_4)^2 + K'_{O..H} r'_4 (\Delta r'_4) \\
 & + \frac{1}{2} H_{C-C=O} r_1^2 (\Delta \alpha_1)^2 + H'_{C-C=O} r_1^2 (\Delta \alpha_1) \\
 & + \frac{1}{2} H_{C-C=O} r'_1{}^2 (\Delta \alpha'_1)^2 + H'_{C-C=O} r'_1{}^2 (\Delta \alpha'_1) \\
 & + \frac{1}{2} H_{C-C=O} r_2^2 (\Delta \alpha_2)^2 + H'_{C-C=O} r_2^2 (\Delta \alpha_2) \\
 & + \frac{1}{2} H_{C-C=O} r'_2{}^2 (\Delta \alpha'_2)^2 + H'_{C-C=O} r'_2{}^2 (\Delta \alpha'_2) \\
 & + \frac{1}{2} H_{O-C-O} r_1 r_2 (\Delta \alpha_3)^2 + H'_{O-C-O} r_1 r_2 (\Delta \alpha_3) \\
 & + \frac{1}{2} H_{O-C-O} r'_1 r'_2 (\Delta \alpha'_3)^2 + H'_{O-C-O} r'_1 r'_2 (\Delta \alpha'_3) \\
 & + \frac{1}{2} H_{C-O-H} r_2 r_3 (\Delta \beta)^2 + H'_{C-O-H} r_2 r_3 (\Delta \beta) \\
 & + \frac{1}{2} H_{C-O-H} r'_2 r'_3 (\Delta \beta')^2 + H'_{C-O-H} r'_2 r'_3 (\Delta \beta') \\
 & + \frac{1}{2} H_{O-H..O} r_3 r_4 (\Delta \delta)^2 + H'_{O-H..O} r_3 r_4 (\Delta \delta) \\
 & + \frac{1}{2} H_{O-H..O} r'_3 r'_4 (\Delta \delta')^2 + H'_{O-H..O} r'_3 r'_4 (\Delta \delta') \\
 & + \frac{1}{2} H_{H..O=C} r'_1 r_4 (\Delta \gamma)^2 + H'_{H..O=C} r'_1 r_4 (\Delta \gamma) \\
 & + \frac{1}{2} H_{H..O=C} r_1 r'_4 (\Delta \gamma')^2 + H'_{H..O=C} r_1 r'_4 (\Delta \gamma') \\
 & + \frac{1}{2} F_{1,5} (\Delta q_{1,5})^2 + F'_{1,5} q_{1,5} (\Delta q_{1,5}) \\
 & + \frac{1}{2} F_{2,6} (\Delta q_{2,6})^2 + F'_{2,6} q_{2,6} (\Delta q_{2,6}) \\
 & + \frac{1}{2} F_{1,4} (\Delta q_{1,4})^2 + F'_{1,4} q_{1,4} (\Delta q_{1,4}) \\
 & + \frac{1}{2} F_{2,7} (\Delta q_{2,7})^2 + F'_{2,7} q_{2,7} (\Delta q_{2,7}) \\
 & + \frac{1}{2} F_{4,6} (\Delta q_{4,6})^2 + F'_{4,6} q_{4,6} (\Delta q_{4,6}) \\
 & + \frac{1}{2} F_{3,7} (\Delta q_{3,7})^2 + F'_{3,7} q_{3,7} (\Delta q_{3,7}) \\
 & + \frac{1}{2} F_{3,4} (\Delta q_{3,4})^2 + F'_{3,4} q_{3,4} (\Delta q_{3,4}) \\
 & + \frac{1}{2} F_{6,7} (\Delta q_{6,7})^2 + F'_{6,7} q_{6,7} (\Delta q_{6,7}) \\
 & + \frac{1}{2} F_{1,5} (\Delta q_{1,5})^2 + F'_{1,5} q_{1,5} (\Delta q_{1,5}) \\
 & + \frac{1}{2} F_{2,8} (\Delta q_{2,8})^2 + F'_{2,8} q_{2,8} (\Delta q_{2,8}) \\
 & + \frac{1}{2} F_{2,5} (\Delta q_{2,5})^2 + F'_{2,5} q_{2,5} (\Delta q_{2,5}) \\
 & + \frac{1}{2} F_{1,8} (\Delta q_{1,8})^2 + F'_{1,8} q_{1,8} (\Delta q_{1,8})
 \end{aligned}$$

in which we assume that $F_{4,6}$, $F_{3,7}$, $F_{3,4}$, $F_{6,7}$, $F_{1,5}$, $F_{2,8}$, $F_{2,5}$ and $F_{1,8}$ are small compared with any force constant above and we neglect them to make the calculation possible.

Let

$$F_{1,3} = F_{2,6} = F_1$$

$$F_{1,4} = F_{2,7} = F_2$$

From the assumption above there will be only 13 force constants in the potential energy expression of the inplane vibration of the oxalic acid molecule.

18.2 Evaluation of the F-matrix

Elimination of q was made using Table I in section 6.3 and substituting all the q values in the potential energy expression. The Urey-Bradley potential energy of the oxalic acid molecule in terms of internal co-ordinates becomes

$$\begin{aligned} V = & \frac{1}{2}(\Delta R)^2(K_{CC} + S_{13}^2 F_1 + t_{13}^2 F'_1 + S_{26}^2 F_1 + t_{26}^2 F'_1 + S_{14}^2 F_2 \\ & + t_{14}^2 F'_2 + S_{27}^2 F_2 + t_{27}^2 F'_2) \\ & + \frac{1}{2}(\Delta r_1)^2(K_{C=O} + S_{31}^2 F_1 + t_{31}^2 F'_1) \\ & + \frac{1}{2}(\Delta r'_1)^2(K_{C=O} + S_{62}^2 F_1 + t_{62}^2 F'_1) \\ & + \frac{1}{2}(\Delta r_2)^2(K_{C-O} + S_{41}^2 F_2 + t_{41}^2 F'_2) \\ & + \frac{1}{2}(\Delta r'_2)^2(K_{C-O} + S_{72}^2 F_2 + t_{72}^2 F'_2) \\ & + \frac{1}{2}(\Delta r_3)^2 K_{O-H} \\ & + \frac{1}{2}(\Delta r'_3)^2 K_{O-H} \\ & + \frac{1}{2}(\Delta r_4)^2 K_{O..H} \\ & + \frac{1}{2}(\Delta r'_4)^2 K_{O..H} \\ & + \frac{1}{2}(r_1 \Delta \alpha_1)^2(H_{C-C=O} + (R/r_1)t_{13}t_{31}F_1 - (R/r_1)S_{13}S_{31}F'_1) \\ & + \frac{1}{2}(r'_1 \Delta \alpha'_1)^2(H_{C-C=O} + (R/r'_1)t_{26}t_{62}F_1 - (R/r'_1)S_{26}S_{62}F'_1) \end{aligned}$$

$$\begin{aligned}
& + \frac{1}{2} (r_2 \Delta \alpha_2)^2 (H_{C-C-O} + (R/r_2) t_{14} t_{41} F_2 - (R/r_2) S_{14} S_{41} F'_2) \\
& + \frac{1}{2} (r'_2 \Delta \alpha'_2)^2 (H_{C-C-O} + (R/r'_2) t_{27} t_{72} F_2 - (R/r'_2) S_{27} S_{72} F'_2) \\
& + \frac{1}{2} r_1 r_2 (\Delta \alpha_3)^2 H_{O-C=O} \\
& + \frac{1}{2} r'_1 r'_2 (\Delta \alpha'_3)^2 H_{O-C=O} \\
& + \frac{1}{2} r_2 r_3 (\Delta \beta)^2 H_{C-O-H} \\
& + \frac{1}{2} r'_2 r'_3 (\Delta \beta')^2 H_{C-O-H} \\
& + \frac{1}{2} r_3 r_4 (\Delta \delta)^2 H_{O-H..O} \\
& + \frac{1}{2} r'_3 r'_4 (\Delta \delta')^2 H_{O-H..O} \\
& + \frac{1}{2} r'_1 r_4 (\Delta \gamma)^2 H_{H..O=C} \\
& + \frac{1}{2} r_1 r'_4 (\Delta \gamma')^2 H_{H..O=C} \\
& + (\Delta R) (\Delta r_1) (S_{13} S_{31} F_1 - t_{13} t_{31} F'_1) \\
& + (\Delta R) (\Delta r'_1) (S_{26} S_{62} F_1 - t_{26} t_{62} F'_1) \\
& + (\Delta R) (\Delta r_2) (S_{14} S_{41} F_2 - t_{14} t_{41} F'_2) \\
& + (\Delta R) (\Delta r'_2) (S_{27} S_{72} F_2 - t_{27} t_{72} F'_2) \\
& + (\Delta R) (r_1 \Delta \alpha_1) (\sqrt{R/r_1}) S_{13} \sqrt{t_{13} t_{31}} F_1 + t_{13} S_{31} F'_1) \\
& + (\Delta R) (r'_1 \Delta \alpha'_1) (\sqrt{R/r'_1}) S_{26} \sqrt{t_{26} t_{62}} F_1 + t_{26} S_{62} F'_1) \\
& + (\Delta R) (r_2 \Delta \alpha_2) (\sqrt{R/r_2}) S_{14} \sqrt{t_{14} t_{41}} F_2 + t_{14} S_{41} F'_2) \\
& + (\Delta R) (r'_2 \Delta \alpha'_2) (\sqrt{R/r'_2}) S_{27} \sqrt{t_{27} t_{72}} F_2 + t_{27} S_{72} F'_2) \\
& + (\Delta r_1) (r_1 \Delta \alpha_1) (\sqrt{R/r_1}) S_{31} \sqrt{t_{13} t_{31}} F_1 + (R/r_1) t_{31} S_{13} F'_1) \\
& + (\Delta r'_1) (r'_1 \Delta \alpha'_1) (\sqrt{R/r'_1}) S_{62} \sqrt{t_{26} t_{62}} F_1 + (R/r'_1) t_{62} S_{26} F'_1) \\
& + (\Delta r_2) (r_2 \Delta \alpha_2) (\sqrt{R/r_2}) S_{41} \sqrt{t_{14} t_{41}} F_2 + (R/r_2) t_{41} S_{14} F'_2) \\
& + (\Delta r'_2) (r'_2 \Delta \alpha'_2) (\sqrt{R/r'_2}) S_{72} \sqrt{t_{27} t_{72}} F_2 + (R/r'_2) t_{72} S_{27} F'_2)
\end{aligned}$$

in which

$$S_{13} = S_{26} = 0.909048$$

$$t_{13} = t_{26} = 0.416692$$

$$S_{31} = S_{62} = 0.845502$$

$$t_{31} = t_{62} = 0.533972$$

$$S_{14} = S_{27} = 0.854918$$

$$t_{14} = t_{27} = 0.518762$$

$$S_{41} = S_{72} = 0.80020$$

$$t_{41} = t_{72} = 0.599734$$

18.3 F-matrix in internal co-ordinates of the gaseous oxalic acid

2nd model

$$F(1,1) = K_1 + 1.61801 F_1 + 1.407947 F_2$$

$$F(1,2) = 0.790852 F_1$$

$$F(1,3) = 0.790852 F_1$$

$$F(1,4) = 0.715217 F_2$$

$$F(1,5) = 0.715217 F_2$$

$$F(1,10) = 0.450175 F_1$$

$$F(1,11) = 0.471212 F_2$$

$$F(1,13) = 0.450175 F_1$$

$$F(1,14) = 0.471212 F_2$$

$$F(1,6) = F(1,7) = F(1,8) = F(1,9) = F(1,12) = F(1,15) = F(1,16)$$

$$= F(1,17) = F(1,18) = F(1,19) = F(1,20) = F(1,21) = 0$$

$$F(2,1) = 0.790852 F_1$$

$$F(2,2) = K_2 + 0.686361 F_1$$

$$F(2,10) = 0.389272 F_1$$

$$F(2,3) = F(2,4) = F(2,5) = F(2,6)$$

$$= F(2,7) = F(2,8) = F(2,9) = F(2,11) = F(2,12) = F(2,13) = F(2,14)$$

$$= F(2,15) = F(2,16) = F(2,17) = F(2,18) = F(2,19) = F(2,20) = F(2,21)$$

$$= 0$$

$$F(3,1) = 0.790852 F_1$$

$$F(3,3) = K_2 + 0.686361 F_1$$

$$F(3,13) = 0.389272 F_1$$

$$F(3,2) = F(3,4) = F(3,5) = F(3,6)$$

$$= F(3,7) = F(3,8) = F(3,9) = F(3,10) = F(3,11) = F(3,12) = F(3,14)$$

$$= F(3,15) = F(3,16) = F(3,17) = F(3,18) = F(3,19) = F(3,20) = F(3,21)$$

$$= 0$$

$$\begin{aligned}
 F(4,1) &= 0.715217 F_2 & F(4,4) &= K_3 + 0.604352 F_2 \\
 F(4,11) &= 0.420632 F_2 & F(4,2) &= F(4,3) = F(4,5) = F(4,6) \\
 &= F(4,7) = F(4,8) = F(4,9) = F(4,10) = F(4,12) = F(4,13) = F(4,14) \\
 &= F(4,15) = F(4,16) = F(4,17) = F(4,18) = F(4,19) = F(4,20) \\
 &= F(4,21) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(5,1) &= 0.715217 F_2 & F(5,5) &= K_3 + 0.604352 F_2 \\
 F(5,14) &= 0.420632 F_2 & F(5,2) &= F(5,3) = F(5,4) = F(5,6) \\
 &= F(5,7) = F(5,8) = F(5,9) = F(5,10) = F(5,11) = F(5,12) = F(5,13) \\
 &= F(5,15) = F(5,16) = F(5,17) = F(5,18) = F(5,19) = F(5,20) = F(5,21) \\
 &= 0
 \end{aligned}$$

$$\begin{aligned}
 F(6,6) &= K_4 & F(6,1) &= F(6,2) = F(6,3) = F(6,4) \\
 &= F(6,5) = F(6,7) = F(6,8) = F(6,9) = F(6,10) = F(6,11) = F(6,12) \\
 &= F(6,13) = F(6,14) = F(6,15) = F(6,16) = F(6,17) = F(6,18) \\
 &= F(6,19) = F(6,20) = F(6,21) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(7,7) &= K_4 & F(7,1) &= F(7,2) = F(7,3) = F(7,4) \\
 &= F(7,5) = F(7,6) = F(7,8) = F(7,9) = F(7,10) = F(7,11) = F(7,12) \\
 &= F(7,13) = F(7,14) = F(7,15) = F(7,16) = F(7,17) = F(7,18) \\
 &= F(7,19) = F(7,20) = F(7,21) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(8,8) &= K_5 & F(8,1) &= F(8,2) = F(8,3) = F(8,4) \\
 &= F(8,5) = F(8,6) = F(8,7) = F(8,9) = F(8,10) = F(8,11) = F(8,12) \\
 &= F(8,13) = F(8,14) = F(8,15) = F(8,16) = F(8,17) = F(8,18) = F(8,19) \\
 &= F(8,20) = F(8,21) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(9,9) &= K_5 & F(9,1) &= F(9,2) = F(9,3) = F(9,4) \\
 &= F(9,5) = F(9,5) = F(9,6) = F(9,7) = F(9,8) = F(9,10) = F(9,11) \\
 &= F(9,12) = F(9,13) = F(9,14) = F(9,15) = F(9,16) = F(9,17) \\
 &= F(9,18) = F(9,19) = F(9,20) = F(9,21) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(10,1) &= 0.450175 F_1 & F(10,2) &= 0.389272 F_1 \\
 F(10,10) &= H_1 + 0.383620 F_1 & F(10,3) &= F(10,4) = F(10,5) \\
 &= F(10,6) = F(10,7) = F(10,8) = F(10,9) = F(10,11) = F(10,12) \\
 &= F(10,13) = F(10,14) = F(10,15) = F(10,16) = F(10,17) = F(10,18) \\
 &= F(10,19) = F(10,20) = F(10,21) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(11,1) &= 0.471212 F_2 & F(11,4) &= 0.420632 F_2 \\
 F(11,11) &= H_2 + 0.438769 F_2 & F(11,2) &= F(11,3) = F(11,5) \\
 &= F(11,6) = F(11,7) = F(11,8) = F(11,9) = F(11,10) = F(11,12) \\
 &= F(11,13) = F(11,14) = F(11,15) = F(11,16) = F(11,17) = F(11,18) \\
 &= F(11,19) = F(11,20) = F(11,21) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(12,12) &= H_3 & F(12,1) &= F(12,2) = F(12,3) = F(12,4) \\
 &= F(12,5) = F(12,6) = F(12,7) = F(12,8) = F(12,9) = F(12,10) = F(12,11) \\
 &= F(12,13) = F(12,14) = F(12,15) = F(12,16) = F(12,17) = F(12,18) \\
 &= F(12,19) = F(12,20) = F(12,21) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(13,1) &= 0.450175 F_1 & F(13,3) &= 0.389272 F_1 \\
 F(13,13) &= H_1 + 0.383620 F_1 & F(13,2) &= F(13,4) = F(13,5) = F(13,6) \\
 &= F(13,7) = F(13,8) = F(13,9) = F(13,10) = F(13,11) = F(13,12) \\
 &= F(13,14) = F(13,15) = F(13,16) = F(13,17) = F(13,18) = F(13,19) \\
 &= F(13,20) = F(13,21) = 0
 \end{aligned}$$

$$\begin{aligned} F(14,1) &= 0.471212 F_2 & F(14,5) &= 0.420532 F_2 \\ F(14,14) &= H_2 + 0.438769 F_2 & F(14,2) &= F(14,3) = F(14,4) \\ &= F(14,6) = F(14,7) = F(14,8) = F(14,9) = F(14,10) = F(14,11) \\ &= F(14,12) = F(14,13) = F(14,15) = F(14,16) = F(14,17) = F(14,18) \\ &= F(14,19) = F(14,20) = F(14,21) = 0 \end{aligned}$$

$$\begin{aligned} F(15,15) &= H_3 & F(15,1) &= F(15,2) = F(15,3) \\ &= F(15,4) = F(15,5) = F(15,6) = F(15,7) = F(15,8) = F(15,9) \\ &= F(15,10) = F(15,11) = F(15,12) = F(15,13) = F(15,14) = F(15,16) \\ &= F(15,17) = F(15,18) = F(15,19) = F(15,20) = F(15,21) = 0 \end{aligned}$$

$$\begin{aligned} F(16,16) &= H_4 & F(16,1) &= F(16,2) = F(16,3) \\ &= F(16,4) = F(16,5) = F(16,6) = F(16,7) = F(16,8) = F(16,9) \\ &= F(16,10) = F(16,11) = F(16,12) = F(16,13) = F(16,14) = F(16,15) \\ &= F(16,17) = F(16,18) = F(16,19) = F(16,20) = F(16,21) = 0 \end{aligned}$$

$$\begin{aligned} F(17,17) &= H_5 & F(17,1) &= F(17,2) = F(17,3) \\ &= F(17,4) = F(17,5) = F(17,6) = F(17,7) = F(17,8) = F(17,9) \\ &= F(17,10) = F(17,11) = F(17,12) = F(17,13) = F(17,14) = F(17,15) \\ &= F(17,16) = F(17,18) = F(17,19) = F(17,20) = F(17,21) = 0 \end{aligned}$$

$$\begin{aligned} F(18,18) &= H_6 & F(18,1) &= F(18,2) = F(18,3) = F(18,4) \\ &= F(18,5) = F(18,6) = F(18,7) = F(18,8) = F(18,9) = F(18,10) = F(18,11) \\ &= F(18,12) = F(18,13) = F(18,14) = F(18,15) = F(18,16) = F(18,17) \\ &= F(18,19) = F(18,20) = F(18,21) = 0 \end{aligned}$$

$$\begin{aligned}
 F(19,19) &= H_4 & F(19,1) &= F(19,2) = F(19,3) \\
 &= F(19,4) = F(19,5) = F(19,6) = F(19,7) = F(19,8) = F(19,9) \\
 &= F(19,10) = F(19,11) = F(19,12) = F(19,13) = F(19,14) = F(19,15) \\
 &= F(19,16) = F(19,17) = F(19,18) = F(19,20) = F(19,21) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(20,20) &= H_5 & F(20,1) &= F(20,2) = F(20,3) \\
 &= F(20,4) = F(20,5) = F(20,6) = F(20,7) = F(20,8) = F(20,9) \\
 &= F(20,10) = F(20,11) = F(20,12) = F(20,13) = F(20,14) = F(20,15) \\
 &= F(20,16) = F(20,17) = F(20,18) = F(20,19) = F(20,21) = 0
 \end{aligned}$$

$$\begin{aligned}
 F(21,21) &= H_6 & F(21,1) &= F(21,2) = F(21,3) \\
 &= F(21,4) = F(21,5) = F(21,6) = F(21,7) = F(21,8) = F(21,9) \\
 &= F(21,10) = F(21,11) = F(21,12) = F(21,13) = F(21,14) = F(21,15) \\
 &= F(21,16) = F(21,17) = F(21,18) = F(21,19) = F(21,20) = 0
 \end{aligned}$$

in which $K_1 = K_{CC}$

$$K_3 = K_{C-O}$$

$$K_5 = K_{O...H}$$

$$H_2 = H_{C-C-O}$$

$$H_4 = H_{C-O-H}$$

$$H_6 = H_{H...O=C}$$

$$F_2 = F_{C_1O_4} = F_{C_2O_7}$$

$$K_2 = K_{C=O}$$

$$K_4 = K_{O-H}$$

$$H_1 = H_{C-C=O}$$

$$H_3 = H_{O-C=O}$$

$$H_5 = H_{O-H...O}$$

$$F_1 = F_{C_1O_3} = F_{C_2O_6}$$

18.4 F-matrix in symmetry co-ordinates of gaseous oxalic acid

(2nd model)

$$\begin{aligned}
 & \text{FM}(1,1) = K_1 + 1.61801 F_1 + 1.407947 F_2 \\
 & \text{FM}(1,2) = 1.118423 F_1 \qquad \text{FM}(1,3) = 1.01147 F_2 \\
 & \text{FM}(1,6) = -0.259909 F_1 - 0.272054 F_2 \\
 & \text{FM}(1,4) = \text{FM}(1,5) = \text{FM}(1,7) = \text{FM}(1,8) = \text{FM}(1,9) = \text{FM}(1,10) \\
 & = \text{FM}(1,11) = \text{FM}(1,12) = \text{FM}(1,13) = 0 \\
 \\
 & \text{FM}(2,1) = 1.118434 F_1 \qquad \text{FM}(2,2) = K_2 + 0.686361 F_1 \\
 & \text{FM}(2,6) = -0.15892 F_1 \qquad \text{FM}(2,3) = \text{FM}(2,4) = \text{FM}(2,5) \\
 & = \text{FM}(2,7) = \text{FM}(2,8) = \text{FM}(2,9) = \text{FM}(2,10) = \text{FM}(2,11) = \text{FM}(2,12) \\
 & = \text{FM}(2,13) = 0 \\
 \\
 & \text{FM}(3,1) = 1.01147 F_2 \qquad \text{FM}(3,3) = K_3 + 0.604352 F_2 \\
 & \text{FM}(3,6) = -0.171722 F_2 \qquad \text{FM}(3,2) = \text{FM}(3,4) = \text{FM}(3,5) \\
 & = \text{FM}(3,7) = \text{FM}(3,8) = \text{FM}(3,9) = \text{FM}(3,10) = \text{FM}(3,11) = \text{FM}(3,12) \\
 & = \text{FM}(3,13) = 0 \\
 \\
 & \text{FM}(4,4) = K_4 \qquad \text{FM}(4,1) = \text{FM}(4,2) = \text{FM}(4,3) \\
 & = \text{FM}(4,5) = \text{FM}(4,6) = \text{FM}(4,7) = \text{FM}(4,8) = \text{FM}(4,9) = \text{FM}(4,10) \\
 & = \text{FM}(4,11) = \text{FM}(4,12) = \text{FM}(4,13) = 0 \\
 \\
 & \text{FM}(5,5) = K_5 \qquad \text{FM}(5,1) = \text{FM}(5,2) = \text{FM}(5,3) \\
 & = \text{FM}(5,4) = \text{FM}(5,6) = \text{FM}(5,7) = \text{FM}(5,8) = \text{FM}(5,9) = \text{FM}(5,10) \\
 & = \text{FM}(5,11) = \text{FM}(5,12) = \text{FM}(5,13) = 0
 \end{aligned}$$

$$FM(6,1) = -0.259909 F_1 - 0.272054 F_2$$

$$FM(6,2) = -0.15892 F_1 \quad FM(6,3) = -0.171722 F_2$$

$$FM(6,6) = H_1/6 + H_2/6 + 2H_3/3 + 0.063937 F_1 + 0.073128 F_2$$

$$FM(6,4) = FM(6,5) = FM(6,7) = FM(6,8) = FM(6,9) = FM(6,10)$$

$$= FM(6,11) = FM(6,12) = FM(6,13) = 0$$

$$FM(7,7) = H_4/6 + 2H_5/3 + \frac{1}{6}H_6$$

$$FM(7,1) = FM(7,2) = FM(7,3) = FM(7,4) = FM(7,5) = FM(7,6)$$

$$= FM(7,8) = FM(7,9) = FM(7,10) = FM(7,11) = FM(7,12) = FM(7,13)$$

$$= 0$$

$$FM(8,8) = K_2 + 0.686361 F_1 \quad FM(8,12) = -0.15892 F_1$$

$$FM(8,1) = FM(8,2) = FM(8,3) = FM(8,4) = FM(8,5) = FM(8,6)$$

$$= FM(8,7) = FM(8,9) = FM(8,10) = FM(8,11) = FM(8,13) = 0$$

$$FM(9,9) = K_3 + 0.604352 F_2 \quad FM(9,12) = -0.171722 F_2$$

$$FM(9,1) = FM(9,2) = FM(9,3) = FM(9,4) = FM(9,5) = FM(9,6)$$

$$= FM(9,7) = FM(9,8) = FM(9,10) = FM(9,11) = FM(9,13) = 0$$

$$FM(10,10) = K_4$$

$$FM(10,1) = FM(10,2) = FM(10,3) = FM(10,4) = FM(10,5) = FM(10,6)$$

$$= FM(10,7) = FM(10,8) = FM(10,9) = FM(10,11) = FM(10,12) = FM(10,13)$$

$$= 0$$

$$FM(11,11) = K_5$$

$$FM(11,1) = FM(11,2) = FM(11,3) = FM(11,4) = FM(11,5) = FM(11,6)$$

$$= FM(11,7) = FM(11,8) = FM(11,9) = FM(11,10) = FM(11,12) = FM(11,13)$$

$$= 0$$

$$FM(12,8) = -0.15892 F_1 \quad FM(12,9) = -0.171722 F_2$$

$$FM(12,12) = H_1/6 + H_2/6 + \frac{2}{3}H_3 + 0.063937 F_1 + 0.073128 F_2$$

$$FM(12,1) = FM(12,2) = FM(12,3) = FM(12,4) = FM(12,5) = FM(12,6)$$

$$= FM(12,7) = FM(12,10) = FM(12,11) = FM(12,13) = 0$$

$$FM(13,13) = H_4/6 + \frac{2}{3}H_5 + \frac{1}{6}H_6$$

$$FM(13,1) = FM(13,2) = FM(13,3) = FM(13,4) = FM(13,5)$$

$$= FM(13,6) = FM(13,7) = FM(13,8) = FM(13,9) = FM(13,10)$$

$$= FM(13,11) = FM(13,12) = 0$$

CHAPTER 19

THE INFRARED EXPERIMENT

19.1 The infrared instrument

The infrared spectrum was recorded with a Perkin Elmer 457 infrared spectrometer.

As shown on Fig. 23, the radiation emitted by the source is split into the sample and the reference beams by the plane mirror M_1 and toroidal mirrors M_2 and M_3 . The toroidal mirror M_2 focuses the sample beam on to the 100% comb, and M_3 focuses the reference beam onto the servo-controlled optical wedge. To ensure that the optical system is uniformly filled, the source image produced by the toroids is double size, i.e. 6 mm wide. The 100% comb is used to adjust the intensity of the sample beam so that pen indicates 100% transmittance when no sample is present. When the 100% comb is moved into or out of the sample beam, the servo-motor moves the optical wedge in the reference beam to equalize the beam intensities, its movement being followed by the pen. The sample and the reference beams are combined by the rotating sector mirror to follow a common optical path. This combined beam is then focused on the monochromator entrance slit by toroidal mirror M_7 . The beam is dispersed by the grating into its spectral components. Rotation of the grating results in the dispersed spectrum being scanned across the monochromator slit. The mechanical width of the monochromator slit determines the width of the wavenumber band emerging from the monochromator. Thus, decreasing the slit width decreases both band width and the

Fig. 23

Diagram of the optical system

intensity of the emerging radiation (i.e. decreases signal to noise ratio). The slit width is adjusted by the slit control on the front panel. After leaving the monochromator the radiation passes through one of a set of optical filters, the correct filter being automatically selected for the spectral region being scanned. This filter absorbs unwanted radiation diffracted from the grating at the same angle as the component of the desired wave number. Finally the transmitted radiation is focused onto a thermocouple detector. The alternating signal on the detector is amplified and fed to a servo-motor which moves the reference beam attenuator to equalize the intensity of the sample and reference beams. The alternating signal is thereby reduced to zero, producing a state of equilibrium.

At the characteristic absorption frequencies of the sample, the intensity of the sample beam changes and an alternating signal called the ERROR signal is then generated by the detector, the amplitude of this signal being proportional to the error between the true transmittance and the indicated transmittance. The error signal is amplified by the 11 Hz amplifier, rectified by the synchronous rectifier, smoothed and modulated to give a 50 Hz signal the phase of which is dependent on which beam is the more intense. After further amplification by the main amplifier this signal is used to drive the servo-motor in a direction depending on the phase of the 50 Hz signal so that the reference beam attenuator is moved to equalize the intensity of the sample and reference beams, thus reducing the error signal to zero. Since the recorder pen is mechanically linked to the attenuator, the pen will be displaced by an amount proportional to the change in sample transmittance.

Fig. 24

The block diagram of the Perkin-Elmer model 457 infrared spectrometer

19.2 Developing the heated cell and the additional optical system

The heated cell is made of stainless steel of cylindrical shape 30 cm in length, 5 cm in diameter, and the wall 0.9 cm thick, with two viton 'O' rings fitted on both ends. Two KBr windows are held over 'O' rings by means of the screw-on caps. The electrical heating element of the cell body is provided with a power supply which can be varied by means of a variac. The cell body is covered by the thermal shield. There are also a high vacuum valve, a silicone rubber septum and a small thermocouple junction hole provided on the cell body.

The X-section of the infrared cell is shown in Fig. 25.

In the beginning, two pieces of cylindrical copper pipe with heating wires were fitted to both windows to prevent excessive cooling of the windows and condensation of the sample (see Fig. 27).

An additional optical system is required because the length of the sample compartment of the Perkin-Elmer 457 infrared spectrometer is shorter than the length of the heated cell. As shown in Fig. 27, the plane mirror A reflects the sample beam through the cell and the concave mirror B at the back of the cell focuses the radiation backwards hitting the plane mirror C which will reflect the radiation through the 100% comb.

An advantage of this optical system is that the sample path length is twice the length of the cell. However, several disadvantages arise as follows:-

Fig. 25

X-section of the infrared heated cell

- (1) The air-path lengths of the sample beam and the reference beam are different. Thus, the spectrum of CO_2 and H_2O in air are added to the sample spectrum.
- (2) There will be some energy loss at the surfaces of the A, B, and C mirrors, since their reflectivity is not 100%.
- (3) There will be considerable reflection losses at the windows as each window is traversed twice.
- (4) There will be some energy loss caused by the size of the cell. The following calculation shows the approximate percentage of energy loss at the position of the second window, since the effective area of the second window is smaller than the area of the beam.

Fig. 26

The effective area of the beam at the sample compartment

From Fig. 27 object distance = u cm
image distance $v = u + 9.3 + 7.7$ cm
focal length of the
concave mirror = 20 cm
 $\therefore u = 33.2$ cm

Let the 2nd KBr window be at 4.2 cm from the concave mirror

$\therefore$ the width of the image at the 2nd window = 2.8 cm
the height of the image at the 2nd window = 9.0 cm
the beam area of the image at the 2nd window = 25.2 cm^2

From Fig. 28a the area of the beam passing through the second

window = 13.26 cm^2
 $\therefore$ the energy loss = 47.2%

Similarly, if the second window is at 7.2 cm from the concave mirror, the area of the beam at the second window is 20 cm^2 and the area of the beam passing through the second window (from Fig. 28b) is 11.92 cm^2 . Thus the energy loss is 40.4%.

The calculation above shows that the closer the heated cell is to the plane mirrors A and C, the smaller the energy loss.

In order to increase the transmittance of the beam and also reduce the condensation problem, the second KBr window was replaced by a concave mirror. The radius of curvature of 33.7 cm was chosen for maximum transmittance and the mirror was specially made. The concave mirror is held over a viton rubber 'O' ring by means of a screw-on cap to which an electric heater was fixed (see Fig. 29).

The final heated cell is shown in Fig. 29. A new vacuum outlet was made with an electric heater attached to it in order to prevent condensation of the oxalic acid taking place in the outlet.

Fig. 27

Optical diagram of the sample beam with original cell

area that light passes
through the second window

$$= \left(\frac{\pi r^2}{360} \times 67.5 \times 2 \right) + (4.2 \times 1.4)$$

$$= 13.26 \text{ cm}^2$$

area that light passes
through at the second
window

$$= \left(\frac{\pi r^2}{360} \times 60 \times 2 \right) + (4.3 \times 1.25)$$

$$= 11.92 \text{ cm}^2$$

Fig. 28a

Fig. 28b

Fig. 29

X-section of the final heated cell. 30 cm path length

19.3 Infrared experiment

At the beginning of the work the experiment was performed by placing some anhydrous oxalic acid in the heated cell and evacuating to eliminate the air spectrum. After pumping for a while the vacuum valve was sealed and the cell was slowly heated up. The spectrum recorded shows that

- (a) the oxalic acid started to sublime at 65°C and slowly condensed on both KBr windows. The condensation process is faster at higher temperatures. This happened because the windows temperature is lower than the cell body temperature;
- (b) at temperatures above 65°C the amount of the decomposition products increased with increase in temperature. These waste products produced quite a high background spectrum.

Thus, handling the sample in this way the spectrum can only be recorded up to 65°C . At temperatures higher than this the condensation of the oxalic acid on both KBr windows and the decomposition products make the gaseous oxalic acid bands undetectable. It is obvious that both problems need to be eliminated.

In order to eliminate the condensation problem, two cylindrical copper pipes fitted with electrical heating wires were attached on both ends of the heated cell to keep the KBr window temperature higher than the cell body. It is reasonable that the KBr windows should be warmed before heating up the cell body.

The experiment was performed again by evacuating the cell containing solid anhydrous oxalic acid and slowly warming the cell up to 100°C. In this experiment the KBr windows were kept at 5°C higher than the cell body. It was found that

- (a) the background spectrum caused by decomposition products is very high and thus some of the gaseous oxalic acid bands are undetectable;
- (b) the spectrum also shows that there is a thin film of solid oxalic acid on both KBr windows. This suggested that the cell temperature is not really lower than the windows. In fact the cell temperature was measured on the cell body and it is possible that the temperature inside the cell is higher than the outside.

Spectrum recorded above suggested that

- (i) elimination of decomposition products is necessary;
- (ii) temperature difference between the cell body and the windows should be higher than 5°C.

Elimination of the decomposition products was accomplished by connecting the heated cell to the vacuum pump and letting the pump operate continuously. In this way it was found that two advantages follow: firstly, the lighter molecules such as H_2O , CO_2 , CO and formic acid which are decomposition products will be pumped out much more quickly than oxalic acid molecules and this eliminates interference by them; secondly, the cell can be heated up to as high a temperature as one wants without an explosion taking place.

In order to increase the transmittance of the beam and also reduce the condensation problem, one KBr window was replaced by a concave mirror of radius of curvature 33.7 cm as shown in Fig. 29 below.

The concave mirror is held over a viton rubber 'O' ring by means of screw-on cap with an electric heater attached.

With this set-up the experiment was performed again. The anhydrous oxalic acid was heated up to about 125°C while the concave mirror and the KBr window were heated up to approximately 10°C higher than the cell body. Several spectra of gaseous oxalic acid were recorded - see figures 34 - 47. Although gaseous oxalic acid bands can be interpreted, it was found that at high temperatures the spectrum was interfered by solid oxalic acid.

The final experiments were performed recently with the same set-up as above. The results are shown in figures 48 - 51. This time the anhydrous oxalic acid was purified by sublimation at approximately 145°C before placing in the heated cell. From the spectra recorded the following results were obtained:-

- (1) Some gaseous oxalic acid bands begin to appear at approximately 70°C .
- (2) No interference by solid oxalic acid or decomposition products except that of potassium oxalate.
- (3) The rate of increase of potassium oxalate increased with temperatures.
- (4) Oxalic acid bands are easily identified.

The purification of the oxalic acid before heating in the infrared cell seems to decrease the rate of decomposition.

19.4 Infrared results and the assignment

Spectrum of cold cell

Figures 30 and 31 show spectra of the cold cell (without KBr windows). Several atmospheric bands were observed as shown in Table 16 below.

Table 16

Band position (cm^{-1})	Assignment (Herzberg 2)
3500 - 4000	ν_3 rotational-vibration H_2O
3720	$\nu_1 + \nu_3$ CO_2
3605	$2\nu_2 + \nu_3$ CO_2
2340	ν_3 CO_2
1300 - 2000	ν_2 rotational-vibration H_2O
667	ν_2 CO_2
500 - 250	pure rotation H_2O

This problem can be eliminated by evacuating the cell.

Figures 32 and 33 show spectra of cold cell (with mirror at one end) after evacuating. It is seen that air bands are not detected.

Spectrum of gaseous oxalic acid

Figures 34 to 51 show spectra of gaseous oxalic acid which were recorded under conditions in Table 17 below.

Table 17

Fig. No.	Temperature °C			Notes
	Mirror	Window	Cell	
34 & 35	126	115	93	At the end of the run it was found that the vacuum valve was blocked by solid oxalic acid.
36 & 37	101	98	92	
38 & 39	108.5	105	101	
40 & 41	125	118.5	115	
42 & 43	-	-	-	was taken during the cooling process.
44 & 45	-	-	-	show spectrum of cold cell left over night (after the above experiment).
46 & 47	-	-	-	show spectrum of cold cell (related to 44 & 45) after gaseous impurities were pumped out.
48 & 49	123	120	115	The oxalic acid was purified before the experiment was performed.
50 & 51	-	-	-	Spectrum of potassium oxalate (related to Figs. 48 & 49).
52 & 53	-	-	-	$\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ + Nujol

Anhydrous oxalic acid was placed in the heated cell which was pumped continuously. With the optical system shown in Figs. 27 and 29 the transmittance of the sample beam after passing through the sample cell was 30%. An attenuator was used in the reference

beam so that the pen moved to about 80% transmittance at 4000 cm^{-1} .

Figures 34 and 35 showed one of the best spectra of gaseous oxalic acid including impurities. It was found at the end of this run that the vacuum valve was blocked by solid oxalic acid. This happened because the vacuum valve was cooler than the rest of the cell. It is noticed that in these spectra the formic acid bands are quite strong.

In order to prevent condensation taking place a new vacuum valve was made with an electric heater attached to it. Spectra in Figures 36 - 47 were taken in the same experiment at different temperatures. Figures 36 - 41 showed spectra of gaseous oxalic acid at approximately 92°C , 101°C , and 115°C respectively. Figures 42 and 43 were taken during the cooling process to observe the behaviour of all bands. It was noticed that the intensities of gaseous oxalic acid bands increased rapidly as the temperature increased and also rapidly decreased during the cooling process.

Figures 44 and 45 were taken after the cell was left over night with vacuum valve closed. The spectrum of the cold cell left over night showed no sign of gaseous oxalic acid bands and only that of impurities and a thin film of solid oxalic acid. Figures 46 and 47 show spectra of a thin film of solid oxalic acid on the KBr window. It was taken after the impurities in the cold cell were pumped away.

Figures 48 and 49 showed spectra of the final experiment in which the oxalic acid was purified before placing into the heated cell. Figures 50 and 51 showed the spectra of potassium oxalate

forming during the experiment. These spectra were taken after the cell was cooled down and the gaseous impurities had been pumped away.

From the spectra mentioned above, 27 bands were observed, 8 were assigned to gaseous oxalic acid, the others were assigned to impurities as shown in Table 18 below. The spectrum number in the table shows the best example of the band. Many bands appear in many spectra.

Table 18

Band position (cm^{-1})	Spectrum Number	Intensities	Assigned to
3720	34		CO_2
3560	34	w	gaseous oxalic acid
3475	34	v.s.	gaseous oxalic acid
2960	34		formic acid
2340	34		CO_2
1812 { 1820	34	v.s.	gaseous oxalic acid
{ 1805			
1760 { 1770	34		formic acid
{ 1750			
1730	46		solid oxalic acid (β -form)
1720	50		potassium hydrogen oxalate
1620	50		potassium hydrogen oxalate
1400	51		potassium hydrogen oxalate

Band position (cm^{-1})	Spectrum Number	Intensities	Assigned to
1325	39	v.s.	gaseous oxalic acid
1275 { 1285 1277 1265	39	v.s.	gaseous oxalic acid
1240	51		potassium hydrogen oxalate
1265*	45		unknown impurity
1225	47		solid oxalic acid (β -form)
1215	51		potassium hydrogen oxalate
1100 { 1115 1103 1085	35		formic acid
1030*	43		unknown impurity
815*	43		unknown impurity
720	51		potassium hydrogen oxalate
700	47		solid oxalic acid (β -form)
667	45		CO_2
660	41	s	gaseous oxalic acid
620	41	w	possibly gaseous oxalic acid
495	51		potassium hydrogen oxalate
460	41	w	gaseous oxalic acid

v.s. = very strong, s = strong, w = weak

* They are definitely impurity bands because they exist in the spectra of the cold cell left after the experiment.

NOTE: The supporting references or spectra for impurity bands are in (62), (128) and (129).

For comparison, the spectrum of potassium hydrogen oxalate monohydrate, $\text{KHC}_2\text{O}_4 \cdot \text{H}_2\text{O}$, in nujol mull is given in figures 52 and 53.

Fig. 33

Fig. 35

Fig. 40

Fig. 45

Fig. 46

Fig. 4-8

Fig. 49

Fig. 51

Fig. 52.

The assignment of the gaseous oxalic acid bands

The assignment of gaseous oxalic acid bands was made on the basis that:

- (1) Gaseous oxalic acid bands are expected to be observed at temperatures above 60°C with their intensities varying with temperatures.
- (2) Impurity bands are still observed in the spectrum of the cooled cell but not gaseous oxalic acid bands.
- (3) It is assumed that fundamentals are stronger than overtones and combinations.
- (4) In the infrared, intensities of the out of plane vibrational bands are usually stronger than the inplane vibrations (119).
- (5) For gaseous oxalic acid it is not expected to see any out of plane fundamentals above 1100 cm^{-1} (109), (4).
- (6) Because of Fermi resonance, two close bands of the same species interact with each other. Thus, if two bands coincide or overlap they should belong to different species.
- (7) Gaseous oxalic acid band shapes are different from impurities because of the different moments of inertia.

As shown in Table 18, the bands at 3560 cm^{-1} , 3475 cm^{-1} , 1812 cm^{-1} , 1325 cm^{-1} , 1275 cm^{-1} , 660 cm^{-1} , 620 cm^{-1} , and 460 cm^{-1} were assigned to gaseous oxalic acid. The band at 620 cm^{-1} is doubtful because it is weak and overlapped with the 660 cm^{-1} band.

Assignment of gaseous oxalic acid bands is shown in Table 19 below.

Table 19

Gaseous oxalic acid bands and their assignments

Band position (cm ⁻¹)	Assignment			
	1st model		2nd model	
3560	$\nu_2 + \nu_8$	Bu	$\nu_2 + \nu_8$	Bu
3475	ν_{10}	Bu	ν_{10}	Bu
1812	ν_8	Bu	ν_8	Bu
1325	ν_9	Bu	ν_{13}	Bu
1275	ν_{13}	Bu	ν_9	Bu
660	ν_{11}	Bu	out of plane	Au
620	out of plane	Au?	??	Bu
460	out of plane	Au	ν_{12}	Bu

Only two bands at 3560 cm⁻¹ and 3475 cm⁻¹ were observed in the O-H asymmetric stretching frequency region. The band at 3475 cm⁻¹ is much stronger and thus it was assigned to fundamental ν_{10} , asymmetric O-H stretch, Bu species. The band at 3560 cm⁻¹ was then assigned to combination band, $\nu_2 + \nu_8$, Bu species. ($\nu_2 = 1800$ cm⁻¹, see section 20.4).

The strong band at 1812 cm⁻¹ has two band heads at 1820 cm⁻¹ and 1805 cm⁻¹ respectively. This band was assigned to the inplane fundamental ν_8 , asymmetric C=O stretch, Bu species, because it is the only band in the carbonyl stretching frequency range.

Two strong bands at 1325 cm⁻¹ and 1275 cm⁻¹ were assigned to the interaction of the inplane C-O asymmetric stretch ν_9 and the

inplane C-O-H angle bending mode $\nu_{13}(4)$. The best fit to the calculations is obtained by reversing the assignment for the two models.

Assignments for three bands at 660 cm^{-1} , 620 cm^{-1} , and 460 cm^{-1} were made to fit the calculated frequencies. Thus, their assignments were different for both models. The band at 660 cm^{-1} was assigned to inplane fundamental ν_{11} , $\text{-C}\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$ angle deformation and the other two were assigned to out of plane fundamentals for the first model. For the second model the band at 460 cm^{-1} was assigned to inplane fundamentals ν_{12} , $(\text{O}\dots\text{H-O})$ angle deformation. The band at 660 cm^{-1} was assigned to the out of plane fundamental and the band at 620 cm^{-1} could be assigned to combination band, but see however chapter 22.

19.5 The expected and observed band envelopes of gaseous oxalic acid

As mentioned previously in section 11.2, the theoretical band envelopes and the PR separations for asymmetric top molecules have been studied by many authors (26), (55), (69), (71), (112), (125), (126).

Among them the paper which was published by Ueda and Shimanzuchi seems to be the most useful set. Thus the expected band contours for gaseous oxalic acid were taken from this paper.

The molecular parameters of gaseous oxalic acid are given in Table 20 below.

Table 20

Molecular parameters for gaseous oxalic acid

	First model	Second model
Molecular model
Principal moments of inertia (gm.cm ² x 10 ⁴⁰)	$I_A = 138.02$ $I_B = 239.49$ $I_C = 377.51$	$I_A = 146.71$ $I_B = 221.05$ $I_C = 367.76$
Ueda and Shimanouchi parameters	$x = 2C/B = 1.269$ $y = 1 - (C/A) - (C/B)$ $= 0$	$x = 1.202$ $y = 0$

Using Ueda and Shimanouchi parameters it is expected that the gaseous oxalic acid will have band contours similar to that given in figure 54 for A, B and C type bands.

Fig. 54

The expected band contours for gaseous oxalic acid

(a is the halfwidth of the slit)

These contours were taken from figure No. 3 and No. 4 in the Ueda and Shimanouchi paper in which the corresponding parameters are given below.

<u>No.</u>	x	y	A	B	C
3	1.2	0.0	2.419	1.613	0.968
4	1.3	0.0	2.648	1.426	0.927

Both sets of parameters above give similar band envelopes. That is, the B type envelope has no central Q branch. The A and C type envelopes have strong and sharp Q branch.

At the beginning it was expected that having studied the band contours, the gaseous oxalic acid bands could be assigned to A, B and C type bands. Thus, the out of plane vibrations, which are C type bands, could be picked out.

Unfortunately, this is not to be because

- (1) Both A and C type envelopes are similar and it is difficult to detect the difference between them.
- (2) Most observed band contours of gaseous oxalic acid are not similar to the expected band contours mentioned above. This is because most observed band envelopes are mostly of hybrid bands.

From the spectra recorded the observed band contours do not help to determine C type bands nor to distinguish between the two models. Moreover, the vectors diagrams obtained from the computer, chapter 22, do not allow the type of hybrid to be determined. Thus there is no reason to get the spectra recorded at higher resolution.

CHAPTER 20

RAMAN EXPERIMENT

20.1 Laser Raman instrument

Fig. 55

Sample optics for Spex Raman spectrometer

The Raman instrument used was the Spex 1401 double monochromator with either

- (1) Spectra-Physics He - Ne laser model 125
- (2) Spectra-Physics Ar⁺ laser model 164

As shown in Fig. 55 the laser beam is reflected upwards by a dielectric mirror in a light tight tube beneath the sample

chamber. The interference filter is taken into the beam to reduce interference from non-lasing lines in the discharge (plasma lines). An iris diaphragm reduces interference from the plasma lines and finally a microscope objective lens focuses the beam to a diffraction-limited spot in the sample. Mirror M_1 serves to increase the excitation energy by returning the laser beam through the sample and the collection lens focuses the scattered light on to the spectrometer entrance slit. The light tight tube (tunnel) bridges the illuminator and the spectrometer entrance slit. It contains the polarizing analyser and a crystal quartz polarizing scrambler wedge to effectively depolarize the Raman radiation and avoid measurement errors arising from the polarization effects of the gratings.

Fig. 56 shows the doublemonochromator, that is, one monochromator followed by and coupled to a second. The centres of the entrance slit and exit slit lie in the optical plane of the system at the foci of the concave mirror M_1 and M_6 respectively. Light coming through the entrance slit is collimated by mirror M_1 and reflected onto the grating G_1 . The dispersed light strikes mirror M_2 and is focused onto mirror M_3 which reflects the beam through the slit S_2 and it hits mirror M_4 . The reflected light from M_4 will be collimated by concave mirror M_5 and reflected onto the grating G_2 . The dispersed light strikes the concave mirror M_6 , which brings the spectrum to a focus at the exit slit.

Fig. 56

A double monochromator has the advantage that dispersion at the final slit is twice as much as at the intermediate. One more advantage is that in the second part of the double monochromator the radiation is dispersed, so that the unwanted exciting radiation is rejected.

The photomultiplier used in the Raman experiment is a FW-130 tube. It was claimed that the red sensitivity of the FW-130 is far better than that of an ordinary S-20 photomultiplier. Another significant advantage in signal detection of the FW-130 photomultiplier is derived from its 3.5 mm effective cathode diameter as compared with ordinary tubes having 20 - 50 mm diameter cathode. The rms noise of a cathode surface is proportional to its diameter.

It was also claimed that the dark current of the red sensitivity of FW-130 photomultipliers drops by a factor of approximately 100 when the tube is cooled to -20°C . The cooler used is a thermoelectric chamber with tap water at a flow rate of 10 gph serves as a heat exchanger.

20.2 Raman oven

A Raman oven was designed to use with the Spex 1401 double-monochromator. Its body is made of aluminium of cylindrical shape with dimensions shown in the figures below.

Fig. 57

X-section of Raman oven along the whole length

Fig. 58

Side view X-section of the oven at sample position

Two electrothermal heating wires HC 102 (V200/250 - 120W) were used to heat the oven. These heating wires were insulated with glass fibre. The wattage of these wires can be varied by means of a variac. Both ends of the oven were insulated using Syndanio, the body was insulated using Pyruma fire cement. The length of the oven was 10 cm and its inner diameter was 1.25 cm. On the oven body there were holes for the laser beam to pass through, holes for the scattered beam to pass through and a blind hole for a thermocouple junction.

Fig. 60 shows the curve of the equilibrium temperature against the voltage supply of this Raman oven.

Fig. 59

The Raman oven used

Fig. 60

Temperature curve of the Raman heating cell

Light tight box

A light tight box was designed for the sample compartment to provide air cooling and the sample tube can be put in sideways. There is also a small hole cut at the back of the box closed by a screwed plug which can be opened to observe the laser beam passing through the tube.

The cold air can get into the box by passing through the light tight tube under the sample compartment. The hot air will blow out through the baffled chimney at the top. The baffled chimney was designed so that it is light tight and can be screwed out when any observation of the laser beam that passes through the sample is required.

Fig. 61

Back view of the light tight box

Fig. 62

Side view of the light tight box

The light tight box was made of brass and was painted matt black.

The inside of the aluminium tube of the oven was black anodised in order to reduce the amount of scattered exciting light which is reflected inside and some of which would enter the monochromator.

The first oven made was not anodised and showed a higher background than the anodised one when an empty sample cell was used.

20.5 Raman experiment

At first the Spectra-Physics He - Ne laser model 125 was used. Before any experiment was performed the instrument performance was checked and found that

- (a) the He - Ne laser power had gone down to 58 mw (used to provide 74mw);
- (b) the efficiency of the detector had gone down nearly 10 times. This was detected by comparing the spectrum of CCl_4 in a capillary tube with similar conditions;
- (c) at high sensitivity the detector is very sensitive to the stray light which comes from light leakage at the edges of the double monochromator box. This problem was eliminated by covering the whole monochromator with black polyethylene.

The instrument was lined up by using a CCl_4 vapour tube.

At the beginning a sample tube was prepared using a pyrex ampoule of 1.2 cm diameter. This tube, containing anhydrous oxalic acid, was heated up slowly and evacuated at the same time. The temperature was kept at 120°C for a while then the tube was sealed off and used as sample tube.

The experiment was performed by heating the sample up and recording the spectra at different temperatures from 60°C to 130°C with high sensitivity. So far the spectra showed no band of gaseous oxalic acid at all.

The experiment was finally performed by heating the cell up to 145°C . This time the tube exploded and caused damage to the collection lens. This suggested that at 145°C the decomposition products increased so fast and resulted in increasing of the total pressure inside the tube.

Fig. 63

X-section of Raman heated cell and the sample tube

Handling the sample in this way there are several disadvantages:

- (i) The decomposition products cause the increase of background level at high sensitivity.
- (ii) At high temperature the total pressure increases fast and can cause an explosion.
- (iii) Because the gaseous oxalic acid bands are very weak, it is necessary to heat the tube to more than 145°C , giving the above mentioned disadvantages.

The sample tube was modified by using a long pyrex glass tube, sealed at one end and the other end connected to the vacuum

pump. This tube contained anhydrous oxalic acid at the closed end as shown in Fig. 64. The tube was heated up and evacuated continuously. Although we heated up to 160°C , the recorded spectra showed no bands of gaseous oxalic acid.

Fig. 64

X-section of the heated cell and the modified
sample tube

The experiment was performed again by heating the tube up to 160°C . This time the sample tube was evacuated before heating and then the vacuum tap was closed. In this way some decomposition products, which emerged from the hot end, condensed on the cooler end and resulted in reducing the pressure in the sample tube. Again the spectra recorded still showed no bands of gaseous oxalic acid.

From the above experiments it is obvious that the gaseous oxalic acid bands are very difficult to detect under these circumstances. This suggested that for further experiments the following

items are required:

- (i) A much more powerful laser.
- (ii) A better photomultiplier detector if possible.
- (iii) It may be necessary to heat the sample over 160°C in order to increase the gaseous oxalic acid vapour pressure.

The experiment was performed again with a Spectra-Physics 164 Argon ion laser. The power of the $4880\overset{\text{O}}{\text{\AA}}$ line is 1.7 watts and the power of the $5145\overset{\text{O}}{\text{\AA}}$ line is 2.2 watts. With this powerful argon laser it has the advantage that the instrument can be peaked up using an I_2 vapour tube as the resonance fluorescence lines of I_2 vapour are very strong. Before starting the experiment several trials were made and it was found that

- (i) with the filter the transmittance of the beam at the sample position is 26% and without filter the laser beam at the sample position is 68% of the total intensity. This suggested that it is much better to take the spectrum without the filter as we need maximum laser intensity for weak bands;
- (ii) by placing a concave mirror on the top of the heating cell to reflect the transmitted beam back through the sample it was found that the intensity of the band increased nearly twice;
- (iii) although the $4880\overset{\text{O}}{\text{\AA}}$ line has some advantages over the $5145\overset{\text{O}}{\text{\AA}}$ line (as the intensity of the band varies with the fourth power of the frequencies), it gives more non-lasing lines. These non-lasing lines may

coincide with the gaseous oxalic acid bands and make them undetectable. With 5145 Å line no non-lasing lines could be detected between the region of 150 cm^{-1} to 2000 cm^{-1} . So it was much more convenient to use the 5145 Å line without the filter.

This time anhydrous oxalic acid was filled in a silica tube of similar shape as shown in Fig. 64. The tube was evacuated and sealed. The sample was heated up to a maximum temperature of 180°C . Several spectra of gaseous oxalic acid were recorded at different equilibrium temperatures. This time several bands of gaseous oxalic acid were observed (see 20.4).

At temperatures above 185°C the rate of decomposition is much faster and the intensities of these bands decreased.

20.4 Raman results and the assignment

Fig. 65

The instrument was lined up using an I_2 vapour tube. A silica tube of 1.2 cm diameter containing anhydrous oxalic acid was placed in the heated cell and evacuated. The vacuum valve was closed before heating the cell up. Fig. 65 shows the heated cell was connected to a manometer and a pump during the experiment.

Spectra of gaseous oxalic acid were taken under the following settings:

laser power = 2 watts
detector H.T. = 2 kilovolts
entrance slit = 0.5 millimeter
middle slit = 0.5 millimeter
exit slit = 0.5 millimeter

plus conditions given in Table 21. The vapour pressure of oxalic acid is given in section 20.2.

Figures 66 to 77 show spectra of gaseous oxalic acid taken at different temperatures. It was noticed that the bands at 267 cm^{-1} , 610 cm^{-1} and a broad band between 300 cm^{-1} to 500 cm^{-1} were recorded even in the spectrum of the cold empty cell. These bands were assigned to the scattering caused by the silica tube.

Figures 66 and 67 show spectra recorded from 200 cm^{-1} to 2300 cm^{-1} in which anhydrous oxalic acid was heated up to approximately 126°C . At this temperature no bands of gaseous oxalic acid were observed except that of N_2 , O_2 , CO_2 , and the silica tube.

Table 21
Temperature and scanning details for Raman spectra

Fig.	Sample	Temperature °C	Freq. range (cm^{-1})	Count per second (cps)	Time constant	Scan speed ($\text{cm}^{-1}/\text{min}$)	Chart speed (in/min)
66	Anhydrous oxalic acid	122 - 130	200 - 1300	1K	2	50	0.5
67	"	122 - 130	1300 - 2350	1K	2	50	0.5
68	"	152 - 156	200 - 1200	1K	2	50	0.5
69	"	152 - 156	1200 - 2350	1K	2	50	0.5
70	"	172 - 183	100 - 1200	1K	2	50	0.5
71	"	172 - 183	900 - 1600	1K	2	50	0.5
72	"	172 - 183	1600 - 2300	1K	2	50	0.5
73	"	152	350 - 550	1K	2	25	0.5
74	"	152	750 - 850	1K	2	25	0.5
75	"	152	1750 - 1850	1K	2	25	0.5
76	"	168	2900 - 3350	500	4	25	0.5
77	"	168	3350 - 3700	500	4	25	0.5

Fig.	Sample	Temperature °C	Freq. range (cm^{-1})	Count per second (cps)	Time constant	Scan speed ($\text{cm}^{-1}/\text{min}$)	Chart speed (in/min)
78	formic acid	127	500 - 1150	2K	0.4	250	2.5
79	"	127	1150 - 1850	2K	0.4	250	2.5
80	"	120	2350 - 3700	2K	0.4	250	2.5
81	H ₂ O	110	2800 - 3760	1K	2	50	0.5

Figures 68 and 69 show spectra of gaseous oxalic acid recorded from 200 cm^{-1} to 2300 cm^{-1} at approximately 154°C . Figures 70 to 72 are the best spectra of gaseous oxalic acid recorded so far from 200 cm^{-1} to 2300 cm^{-1} at approximately 177.5°C .

Spectra were recorded up to 3700 cm^{-1} . At high frequency three non lasing lines, two formic acid bands and an H_2O band were observed but none for gaseous oxalic acid as shown in Fig. 76, (77).

Apart from the scattering caused by the silica tube 18 bands were observed. Their assignment is given in Table 22.

For the purpose of correct assignment the spectra of formic acid, CO_2 and H_2O were taken at temperatures between 110°C - 130°C . A table of CO_2 bands with their assignment is given in Herzberg (2 p.274). The supporting references are (13), (130).

Figures 78, 79, 80 show spectra of formic acid between 500 cm^{-1} to 3700 cm^{-1} at approximately 120°C . The spectrum of water was recorded from 200 cm^{-1} to 3700 cm^{-1} at approximately 110°C . Apart from several bands due to pure rotation at low frequency range there is only one vibrational band of water observed in the Raman spectrum at 3655 cm^{-1} as shown in Fig. 81.

It was noted that CO_2 , CO , O_2 , N_2 bands are very sharp and easy to identify. As CO_2 and CO are decomposition products, their spectra can be used for purposes of frequency measurement.

Table 22

Observed Raman bands and their assignment

Band position	Spectrum number	Assignment
267	66	silica tube
300 - 500	66	silica tube
405	70	gaseous oxalic acid
610	66	silica tube
800 } 812 825 }	70	gaseous oxalic acid
1195	70	gaseous oxalic acid
1267	71	$(3\nu_2 - \nu_2)$ CO ₂
1286	71	$2\nu_2$ CO ₂
1388	71	ν_1 CO ₂
1409	71	$(\nu_1 + \nu_2 - \nu_2)$ CO ₂
1423	71	gaseous oxalic acid
1550	67	O ₂
1800	72	gaseous oxalic acid
2143	69	CO
2330	67	N ₂
2954	76	formic acid
3086	76	non lasing line
3237	76	non lasing line
3422	77	non lasing line
3573	77	formic acid
3655	77	ν_1 H ₂ O

Fig. 66

Fig. 67

Fig. 68

Fig. 69

Fig. 70

Fig. 72

2300

2200

2100

2000

1900

1800

1700

1600

cm^{-1}

Fig. 73a (I_{II})

Fig. 73b (I_I)

Fig. 74a (I_{II})

Fig. 74b (I_I)

Fig. 75a (I_i)

Fig. 75b (I_i)

Fig. 76

Fig. 77

Fig. 78

Fig. 79

Fig. 80

Fig. 81

Assignment of the gaseous oxalic acid bands in the Raman spectrum was easily made because

- (1) Oxalic acid band shapes are very distinctive from those of CO_2 , CO , O_2 , N_2 , and H_2O .
- (2) Between 200 cm^{-1} to 1900 cm^{-1} no formic acid bands and non lasing lines were observed in the spectra of gaseous oxalic acid.
- (3) Gaseous oxalic acid bands at 405 cm^{-1} , 812 cm^{-1} and 1800 cm^{-1} are strong enough for depolarization measurements. As shown in figures 73, 74, 75 these bands are completely polarized. Thus, they were assigned to Ag inplane fundamentals, symmetric ($\text{—C}\begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$) inplane angle bending, symmetric C-C stretch, and symmetric C=O stretch respectively.

Although the band at 1195 cm^{-1} is weak and thus a depolarization measurement cannot be made, it was assigned to inplane fundamental Ag, C-O-H symmetric angle bending, ν_7 , because no out of plane fundamentals of gaseous oxalic acid are expected at this frequency.

The band at 1423 cm^{-1} is very weak and the existence is doubtful because the peak height is not much above the noise level. As shown in fig. 71, this band sits at the base of 1410 cm^{-1} line of CO_2 . It was assigned to the fundamental inplane symmetric C-O stretch, ν_3 , of gaseous oxalic acid for the following reasons:-

- (1) According to my calculations there is a calculated Ag fundamental at approximately this position.
- (2) It could probably be that this band corresponds to the 1450 cm^{-1} band which was reported in the spectrum of solution and solid oxalic acid (51), (124).

- (3) It is reasonable to expect a C-O symmetric stretching band to occur at this frequency.

20.5 Comparison between infrared and Raman experiments

Infrared and Raman experiments of the gaseous oxalic acid face different problems as follows:-

- (1) In Raman there is no interference caused by solid oxalic acid whereas in infrared a condensation of solid oxalic acid on the KBr windows is one of the main problems.
- (2) In infrared the heated cell was pumped continuously to eliminate interference caused by decomposition products.

In Raman it was found that:

- (a) No gaseous oxalic acid bands were observed if the cell was pumped continuously.
- (b) No obvious interference was caused by the decomposition products. Main products such as CO_2 , CO , and H_2O gave sharp and strong bands which are useful for frequency measurements.
- (3) Raman bands begin to appear at about 140°C whereas infrared absorption bands begin to appear at approximately 65°C .
- (4) Raman band shapes are very distinctive from the others and thus they are easily identified.
- (5) Raman bands are much more difficult to detect than the infrared absorption bands and thus the Raman experiment needs
 - (a) a very accurate lining up;
 - (b) a powerful laser;
 - (c) a higher temperature heated cell.

CHAPTER 21

FAR-INFRARED EXPERIMENT

It was intended to carry out infrared absorption measurements in the far-infrared using an R.I.I.C. Fourier Transform Spectrometer 520. An R.I.I.C. 1 m gas cell was modified as shown in Fig. 82. The polythene windows were replaced by TPX (poly 4 methyl pentene 1) which can be used up to 140°C or higher. The cell was wound with electric heating tape in such a way that the window temperature was about 5 - 10°C higher than the middle of the cell. This was checked before the cell was fitted to the interferometer. Two 1" thick pieces of Syndanio were used to insulate the cell from the interferometer housing and the detector unit. These pieces of Syndanio were grooved to take the Viton O-rings and drilled to take the bolts. They were vacuum impregnated (commercially) with Midland Silicone M.S. 2728 in order to make them vacuum tight. The piece between the cell and the interferometer was satisfactory but the piece between the cell and the detector was not. The detector compartment which was in connection with this piece could not be pumped down to a low enough pressure.

The attempt to obtain the far infrared spectrum was abandoned as there was not time to obtain more Syndanio and carry out the machining and impregnation.

Fig. 82
X-section of the far infrared heated cell

CHAPTER 22

CALCULATION AND THE ASSIGNMENT OF THE OBSERVED BANDS

OF GASEOUS OXALIC ACID FREQUENCIES

22.1 The inplane force constants and the calculated frequencies of gaseous oxalic acid

Calculations for the gaseous oxalic acid molecule were made using the following data:-

- (1) Molecular parameters given by Nahlovská, Nahlovský and Strand (78) were used. Due to the possibility of different positions of H atoms in this molecule, the calculations were made using both models suggested by them (see section 13.3).
- (2) In this present work the force constants for the inplane vibrations of gaseous oxalic acid were taken from the values for formic acid and acetic acid monomers reported by Nakamoto and Kishida (39). Both sets of force constants were used to calculate the inplane vibrational frequencies for gaseous oxalic acid. The set of force constants taken from acetic acid monomer gave a better fit, thus, this set of force constants was selected as an initial set of force constants for gaseous oxalic acid.

Several force constant refinements were made. It was found that the least squares method could not be applied because of singularity of the $(J^t W J)$ matrix. With the aid of the computer the refinements can be made successfully by trial and error in which small changes of force constants can be judged from the

Jacobian matrix and the discrepancy between the observed and calculated frequencies.

At the beginning measurements of the variance of the calculated and observed values were made using only 8 observed frequencies, 4 were observed in the infrared at 3475 cm^{-1} , 1812 cm^{-1} , 1325 cm^{-1} , and 1275 cm^{-1} , the others were observed in the Raman at 1800 cm^{-1} , 1195 cm^{-1} , 812 cm^{-1} , 405 cm^{-1} . For the following reasons only 8 were used in the beginning:-

- (a) These bands certainly exist.
- (b) They belong to oxalic acid.
- (c) They are all inplane fundamentals.

It was found that the observed bands at 1423 cm^{-1} and 660 cm^{-1} are fitted well with the calculated frequencies for gaseous oxalic acid first model. The bands at 1423 cm^{-1} and 460 cm^{-1} are fitted well with the calculated values for the second model. Thus, these bands were also included in measurements of the variance. That is, for both models the variance is measured from 10 observed fundamentals.

22.2 Calculation using first model

G and F matrices for gaseous oxalic acid first model have been constructed in Chapter 15 and Chapter 16 respectively. With the aid of the computer the calculations were performed and the results are shown in tables below.

Table 23 shows 4 sets of force constants, A, B, C, D, used to calculate the corresponding sets of calculated frequencies shown in Table 24.

Table 23

Sets of force constants

Type of force constants	Set A (md/A°)	Set B (md/A°)	Set C (md/A°)	Set D (md/A°)
K_{C-C}	3.2	3.2	2.5	2.3
$K_{C=O}$	10.9	10.9	10.5	10.3
K_{C-O}	6.0	6.0	6.0	6.0
K_{O-H}	6.5	6.5	6.5	6.5
$H_{C-C=O}$	0.7	0.7	0.7	0.7
H_{C-C-O}	0.2	0.2	0.2	0.2
$H_{O-C=O}$	0.4	0.4	0.45	0.44
H_{C-O-H}	0.5	0.4	0.42	0.42
$F_{C_1O_3} = F_{C_2O_6}$	1.2	1.2	1.2	1.2
$F_{C_1O_4} = F_{C_2O_7}$	0.7	0.7	0.7	0.7
$F_{O_3O_4} = F_{O_6O_7}$	0.7	0.7	0.7	0.7
$F_{O_4O_6} = F_{O_3O_7}$	0.2	0.02	0.02	0.02
$F_{C_2H_5} = F_{C_1H_8}$	0.55	0.55	0.55	0.55

Table 24

Sets of calculated frequencies

Observed frequencies (cm^{-1})		Calculated frequencies (cm^{-1})			
		Set A	Set B	Set C	Set D
<u>Ag species</u>					
ν_1	812	868.2	860.3	840.0	831.6
ν_2	1800	1897.6	1889.6	1862.1	1849.3
ν_3	1423	1519.9	1503.9	1468.1	1453.6
ν_4	-	3490.4	3490.2	3490.3	3490.3
ν_5	405	435.6	404.0	409.3	407.0
ν_6	-	630.9	627.0	626.4	625.8
ν_7	1195	1293.7	1220.6	1231.4	1229.0
<u>Bu species</u>					
ν_8	1812	1806.1	1799.0	1774.3	1761.0
ν_9	1325	1369.2	1324.6	1335.5	1334.4
ν_{10}	3475	3490.2	3490.1	3490.1	3490.1
ν_{11}	660	652.2	647.4	658.9	656.4
ν_{12}	-	356.3	305.2	306.1	305.9
ν_{13}	1275	1262.6	1218.2	1229.7	1228.6

$S \times 10^{-2}$ = 2.63 1.21 0.62 0.44

Measurements of best fit are shown under Table 24. The variance S is defined as the sum of the squares of the percentage discrepancies between the calculated and the observed frequencies. That is

$$S = \sum \left\{ \frac{v_{\text{cal.}} - v_{\text{obs.}}}{v_{\text{obs.}}} \times 100 \right\}^2$$

Having a smaller variance set D becomes a better set than the others. Thus, this set was used for the band assignment and was also used to calculate the potential energy distribution and the modes of vibration.

The above refinements were made by the trial and error method in which small changes of force constants were adjusted with the help of the Jacobian matrix shown in Table 25. This matrix was constructed using the method described by Menn, Shimanouchi, Meal and Fano (24) (see section 7.3).

Table 25

Jacobian Matrix

	ΔK_1	ΔK_2	ΔK_3	ΔK_4	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔF_1	ΔF_2	ΔF_3	ΔF_4	ΔF_5
Δv_1	0.0294	0.0040	0.0127	0.0001	0.0010	0.0335	0.0457	0.0368	0.0666	0.0438	0.0656	0.0273	0.0429
Δv_2	0.0186	0.1306	0.0485	0	0.1873	0.3210	0.0181	0.0868	0.0346	0.0491	-0.0005	0.0454	0.0277
Δv_3	0.1131	0.0041	0.0621	0.0006	0.2168	0.0004	0.2362	0.2186	0.0447	0.0227	0.0327	0.0009	0.2290
Δv_4	0	0	0.0001	1.0611	0.0001	0.0036	0.0024	0.0002	0	0.0026	0.0004	0.0032	0.4933
Δv_5	0.0011	0	0	0	0.0002	0.0641	0.0725	0.0005	0.0023	0.0437	0.0199	0.0885	0
Δv_6	0.0007	0.0006	0.0053	0	0.107	0.0503	0.0108	0	0.0615	0.023	0.0087	0.0153	0.0033
Δv_7	0.0037	0.0066	0.0171	0.0007	0.0064	0.0029	0.0007	1.1504	0.0008	-0.0008	0.0315	-0.0002	0.3577
Δv_8	0	0.1382	0.0378	0	0.0005	0.031	0.0234	0.0919	0.0884	0.0076	0.0042	0.0253	0.0088
Δv_9	0	0.0012	0.0701	0.0008	0.0572	0.6291	0.1681	0.4374	0.0290	0.0931	0.0275	-0.0093	0.3683
Δv_{10}	0	0	0.0002	1.0613	0.0001	0.0031	0.0026	0.0002	0	0.002	0.0004	0.0034	0.4911
Δv_{11}	0	0.0007	0.0031	0.0001	0.0649	0.0292	0.1806	0.0091	0.0203	0.0067	0.0836	0.0156	0.0103
Δv_{12}	0	0	0	0	0.0198	0.0504	0.0069	0.0002	0.0074	0.0218	0.0020	0.1112	0.0003
Δv_{13}	0	0.0058	0.0347	0.0005	0.0070	0	0.0067	0.9546	0.0116	0.0207	0.0407	-0.0046	0.2521

22.3 Assignment of the observed infrared and Raman bands, potential energy distribution and normal modes

Assignment of the observed infrared and Raman bands of gaseous oxalic acid to fit the calculated frequencies for the first model is shown in Table 26.

Table 26

Observed frequencies (cm ⁻¹)		Assignment	Calculated frequencies (cm ⁻¹)	$\Delta\nu = \nu_{\text{calc.}} - \nu_{\text{obs.}}$
Infrared	Raman			
3560		$\nu_2 + \nu_8$ Bu	-	
3475		ν_{10} Bu	3490.1	15.1
1812		ν_8 Bu	1761.0	-51.0
1325		ν_9 Bu	1334.4	9.4
1275		ν_{13} Bu	1228.6	-46.4
660		ν_{11} Bu	656.4	- 3.6
620		Au	-	
460		Au	-	
	1800	ν_2 Ag	1849.3	49.3
	1423	ν_3 Ag	1453.6	30.6
	1195	ν_7 Ag	1229.0	34.0
	812	ν_1 Ag	831.6	19.6
	405	ν_5 Ag	407	2.0

Potential energy distribution

The potential energy distribution of different vibrations was calculated using the method of Morino and Kuchitsu (30) and the results are in Table 27.

Table 27

Potential energy distribution of planar vibrations of gaseous oxalic acid

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}	ν_{13}
C-C sym. str.	47.7	2.7	35.9	0.0	9.6	3.7	4.5						
C=O "	9.1	59.7	5.0	0.0	0.2	4.2	11.2						
C-O "	19.1	16.9	24.5	0.0	0.5	19.8	16.7						
O-H "	0.2	0.0	0.3	99.9	0.1	0.0	0.4						
$\begin{array}{c} \text{O} \\ \parallel \\ (-\text{C}-\text{O}) \end{array}$ sym. deformation	17.4	0.5	15.9	0.0	67.0	4.7	0.6						
$\begin{array}{c} \text{O} \\ \parallel \\ (-\text{C}-\text{O}) \end{array}$ " rocking	1.5	17.9	3.9	0.0	22.3	67.5	0.8						
$\angle \text{C-O-H}$ " bending	5.1	2.2	14.4	0.0	0.3	0.0	66.9						
C=O anti. sym. str.								79.8	0.8	0.0	4.1	0.1	9.0
C-O "								14.7	46.2	0.0	10.7	0.0	30.8
O-H "								0.0	0.6	99.9	0.2	0.0	0.3
$\begin{array}{c} \text{O} \\ \parallel \\ (-\text{C}-\text{O}) \end{array}$ anti sym. deformation								1.2	17.7	0.0	81.2	10.4	1.6
$\begin{array}{c} \text{O} \\ \parallel \\ (-\text{C}-\text{O}) \end{array}$ " " rocking								0.9	0.2	0.0	1.2	89.2	0.3
$\angle \text{C-O-H}$ " " bending								3.4	34.5	0.0	2.6	0.2	57.9

Modes of vibration

The $\mathbf{u}$ vectors in mass adjusted displacement co-ordinates were calculated and the 13 inplane modes of vibration were plotted by the computer as shown in the following figures.

22.4 Calculation using 2nd model

All calculations were repeated using G and F matrices for gaseous oxalic acid 2nd model which have been constructed in Chapters 17 and 18 respectively.

The Jacobian matrix is given in Table 30. Table 28 shows 4 sets of force constants A, B, C, D, used to calculate the corresponding sets of the calculated frequencies in Table 29.

Table 28
Sets of Force Constants

Type of force constant	Force constants (md/A ⁰)			
	Set A	Set B	Set C	Set D
K _{CC}	3.2	3.2	3.2	2.8
K _{C=O}	10.5	10.5	10.5	10.9
K _{C-O}	6.5	6.5	6.5	6.5
K _{O-H}	6.5	6.5	6.5	6.5
K _{O...H}	0.45	0.45	0.45	0.45
H _{C-C=O}	0.45	0.15	0.45	0.45
H _{C-C-O}	0.3	0.3	0.3	0.3
H _{O-C=O}	0.05	0.2	0.1	0.1
H _{C-O-H}	0.85	0.85	0.85	0.85
H _{O-H...O}	0.02	0.02	0.02	0.02
H _{H...O=C}	0.01	0.01	0.01	0.01
F _{C₁O₃} = F _{C₂O₆}	1.2	1.2	1.2	1.2
F _{C₁O₄} = F _{C₂O₇}	0.8	0.8	0.8	0.8

Table 29
Sets of calculated frequencies

Observed frequencies (cm^{-1})		Calculated frequencies (cm^{-1})			
		Set A	Set B	Set C	Set D
<u>Ag species</u>					
ν_1	812	830.6	832.9	832.1	820.95
ν_2	1800	1788.7	1789.6	1789.3	1810.90
ν_3	1423	1420.8	1426.5	1424.6	1409.56
ν_4	-	3471.8	3471.9	3471.9	3471.85
ν_5	-	8.2	8.5	8.4	8.37
ν_6	405	401.3	420.7	414.4	414.56
ν_7	1195	1256.0	1259.8	1258.6	1246.20
<u>Bu species</u>					
ν_8	1812	1786.8	1787.2	1787.0	1812.48
ν_9	1275	1230.7	1236.8	1234.7	1236.99
ν_{10}	3475	3471.8	3471.9	3471.9	3471.85
ν_{11}	-	302.0	302.1	302.0	302.03
ν_{12}	460	432.0	465.0	454.4	454.91
ν_{13}	1325	1323.1	1324.2	1323.8	1324.37

$S \times 10^{-2}$ 0.84 0.63 0.54 0.37

Measurements of fit show that force constants in Set D are better than the others. Thus, this set is used to calculate the potential energy distribution and the modes of vibration.

Table 30

Jacobian Matrix

ΔK_1	ΔK_2	ΔK_3	ΔK_4	ΔK_5	ΔH_1	ΔH_2	ΔH_3	ΔH_4	ΔH_5	ΔH_6	ΔF_1	ΔF_2
Δv_1	0.0299	0.0052	0.0167	0	0.0223	0.0073	0.0295	0	0.0001	0	0.0591	0.0717
Δv_2	0.0227	0.1364	0.0426	0	0.0001	0.0063	0.0253	0.0045	0.0174	0.0043	0.016	0.0935
Δv_3	0.0688	0.0028	0.0647	0.0003	0.2543	0.0308	0.1237	0.3593	1.4968	0.3593	0.0426	-0.0093
Δv_4	0	0	0.0003	1.062	0.2162	0.0006	0.0024	0.0996	0.4002	0.0996	0.0003	0
Δv_5	0	0	0	0	0.0001	0	0.0001	0	0.0001	0	0	0
Δv_6	0.0001	0.0002	0.0005	0.0001	0.0569	0.0319	0.1272	0.0150	0.0586	0.0150	0.0091	0.0096
Δv_7	0.0452	0.0012	0.0210	0	0.5126	0.0196	0.0783	0.3622	1.3886	0.3622	0.0307	0
Δv_8	0	0.1341	0.0491	0.0001	0.0003	0.0029	0.0114	0.0048	0.0197	0.0021	0.1083	0.0210
Δv_9	0	0.0091	0.0860	0	0.0606	0.0292	0.1169	0.0591	0.2080	0.0591	0.0301	0.1069
Δv_{10}	0	0	0.0004	1.0621	0.2168	0.0009	0.0034	0.0992	0.3983	0.0992	0.0004	0.0001
Δv_{11}	0	0	0	0.0002	0.0769	0.0002	0.0007	0.0183	0.0718	0.0183	0	0
Δv_{12}	0	0.0007	0.0015	0.0001	0.0009	0.0590	0.2354	0.0004	0.0014	0.0004	0.0183	0.0190
Δv_{13}	0	0.0021	0.0090	0.0001	0.7080	0.0051	0.0204	0.6525	0.6381	0.6525	0.0059	0.0134

22.5 Assignment of the observed infrared and Raman bands ,

Potential energy distribution and normal modes

Assignment of the observed infrared and Raman bands to fit the calculated frequencies for gaseous oxalic acid 2nd model is given in Table 31.

Table 31

Observed frequencies (cm^{-1})		Assignment		Calculated frequencies (cm^{-1})	$\Delta\nu = \nu_{\text{calc.}} - \nu_{\text{obs.}}$
Infrared	Raman	Mode	Species		
3560		$\nu_2 + \nu_8$	Bu	-	-
3475		ν_{10}	Bu	3471.9	3.1
1812		ν_8	Bu	1812.5	0.5
1325		ν_{13}	Bu	1324.4	-0.6
1275		ν_9	Bu	1237.0	-38.0
660			Au		
620**		combination band Bu			
460		ν_{12}	Bu	454.9	-5.1
	1800	ν_2	Ag	1810.9	10.9
	1423	ν_3	Ag	1409.6	-13.4
	1195	ν_7	Ag	1246.2	51.2
	812	ν_1	Ag	821.0	9.0
	405	ν_6	Ag	414.6	9.6

** The band at 620 cm^{-1} overlaps the band at 660 cm^{-1} which was assigned to the out of plane fundamental, Au species. If the

620 cm^{-1} band was of species Au it would interact with the 660 cm^{-1} Au fundamental. As this has not occurred it was assigned to the Bu species. This band can not be fitted to the calculated values for the inplane fundamentals, and thus it was assigned to combination band. There are two possibilities:

- (a) It could be ($\nu_6 + \nu_{11}$) in which the sum of both calculated values is 716.6 (cm^{-1}). As the value for the anharmonicity shift is too high, the other possibility is preferable.
- (b) It could be the combination of two of the out of plane fundamentals with different species
(Au x Bg = Bu).

The attempt to fit this band as a difference band was also tried but no suitable pair of fundamentals are known.

Potential energy distribution

The potential energy distribution for the planar vibrations for gaseous oxalic acid 2nd model was calculated and the results are in Table 32.

Table 32

Potential energy distribution of planar vibrations of gaseous oxalic acid 2nd model

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}	ν_{13}
C-C sym. str.	52.7	6.1	25.7	0.0	0.0	0.1	27.9						
C=O "	13.0	78.5	2.5	0.0	0.0	1.9	2.0						
C-O "	27.2	14.6	30.7	0.0	0.0	3.2	17.6						
O-H "	0.1	0.0	0.1	97.3	1.7	0.8	0.0						
O..H "	2.3	0.0	9.6	1.4	36.1	24.1	20.2						
(-C $\equiv$ O) sym. deformation	4.7	0.6	3.9	0.0	42.9	56.7	4.1						
$\angle$ O-H..O " bending	0.0	0.2	25.5	1.3	19.2	13.3	28.2						
C=O anti sym. str.								82.5	10.7	0.0	0.0	5.9	2.3
C-O "								16.9	70.4	0.0	0.1	8.8	7.6
O-H "								0.0	0.0	97.3	2.6	0.1	0.1
O..H "								0.0	4.1	1.4	64.4	0.2	30.4
(-C $\equiv$ O) anti sym. deformation								0.3	6.6	0.0	0.5	84.8	1.1
$\angle$ O-H..O " " bending								0.2	8.2	1.3	32.4	0.2	58.5

Modes of vibration

The 2 vectors in mass adjusted displacement co-ordinates for gaseous oxalic acid 2nd model were calculated and 13 inplane modes of vibration were plotted by the computer as in the following figures.

NORMAL MODE 3

NORMAL MODE ψ_3

22.6 The expected frequencies of deuterated oxalic acid monomer

If we assume that the geometry of the deuterated oxalic acid monomer is the same as that for gaseous oxalic acid, the expected frequencies of the deuterated oxalic acid monomer may be obtained by solving the secular equation using the same G and F matrices except here the mass of the hydrogen is replaced by that of deuterium.

Using 1st model

Tables 33 and 34 show the expected frequencies and the potential energy distribution of deuterated oxalic acid monomer. They were calculated using gaseous oxalic acid force constants for 1st model.

Table 33

The calculated frequencies of deuterated oxalic acid monomer
using 1st model

<u>Calculated frequencies</u>			<u>Calculated shift</u>
Oxalic acid	deuterated oxalic acid		H → D
ν_1	831.6	750.2	81.4
ν_2	1849.3	1847.5	1.8
ν_3	1453.6	1423.5	30.1
ν_4	3490.3	2537.4	952.9
ν_5	407.0	396.4	10.6
ν_6	625.8	621.7	4.1
ν_7	1229.0	1017.9	211.1
ν_8	1761.0	1758.1	2.9
ν_9	1334.4	1297.2	37.2
ν_{10}	3490.1	2537.1	953.0
ν_{11}	656.4	614.5	41.9
ν_{12}	305.6	295.7	9.9
ν_{13}	1228.6	983.7	244.9

Table 34

Potential energy distribution of planar vibrations of deuterated oxalic acid monomer (1st model)

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}	ν_{13}
C-C sym. str.	42.4	2.6	39.8	0.0	3.4	1.7	4.7						
C=O "	4.3	60.1	8.6	0.0	0.2	3.7	11.9						
C-O "	7.0	17.3	29.0	0.0	0.4	21.8	18.7						
O-H "	0.3	0.0	0.1	99.6	0.2	0.0	0.2						
$\begin{smallmatrix} \text{O} \\ \diagup \text{C} \diagdown \text{O} \end{smallmatrix}$ sym. deformation	3.3	0.4	16.5	0.2	67.6	5.8	4.9						
$\begin{smallmatrix} \text{O} \\ \diagup \text{C} \diagdown \text{O} \end{smallmatrix}$ " rocking	2.4	18.1	4.0	0.1	22.2	66.1	0.7						
$\angle$ C-O-H " bending	35.4	1.5	2.1	0.0	1.0	0.9	58.9						
C=O anti sym. str.								80.9	6.2	0.0	2.9	0.1	4.6
C-O "								15.1	73.7	0.1	8.6	0.1	5.8
O-H "								0.0	0.0	99.6	0.3	0.1	0.3
$\begin{smallmatrix} \text{O} \\ \diagup \text{C} \diagdown \text{O} \end{smallmatrix}$ anti sym. deformation								1.1	19.1	0.2	70.5	12.1	3.2
$\begin{smallmatrix} \text{O} \\ \diagup \text{C} \diagdown \text{O} \end{smallmatrix}$ " " rocking								0.9	0.4	0.1	3.0	86.8	0.2
$\angle$ C-O-H " " bending								2.0	0.6	0.0	14.7	0.8	80.9

Using 2nd model

The expected frequencies and the potential energy distribution for deuterated oxalic acid were calculated using the constants from gaseous oxalic acid 2nd model. The results are in Tables 35 and 36.

Table 35

Calculated frequencies of deuterated oxalic acid monomer

<u>2nd model</u>		
<u>Calculated frequencies (cm^{-1})</u>		<u>Calculated shift (cm^{-1})</u>
oxalic acid	deuterated oxalic acid	H $\rightarrow$ D
ν_1 820.9	804.5	16.4
ν_2 1810.9	1810.4	0.5
ν_3 1409.6	1358.7	50.9
ν_4 3471.9	2523.7	948.2
ν_5 8.4	8.3	0.1
ν_6 414.6	409.7	4.9
ν_7 1246.2	937.3	308.9
ν_8 1812.5	1811.6	0.9
ν_9 1237.0	1250.2	-13.2
ν_{10} 3471.9	2523.8	948.1
ν_{11} 302.0	298.9	3.1
ν_{12} 454.9	451.4	3.5
ν_{13} 1324.4	938.7	385.7

Table 36

Potential energy distribution of planar vibrations of deuterated oxalic acid monomer (2nd model)

	ν_1	ν_2	ν_3	ν_4	ν_5	ν_6	ν_7	ν_8	ν_9	ν_{10}	ν_{11}	ν_{12}	ν_{13}
C-C sym. str.	40.5	6.1	42.4	0.0	0.0	0.1	19.0						
C=O "	12.7	78.6	4.1	0.0	0.0	1.9	0.4						
C-O "	27.9	14.7	42.6	0.2	0.0	3.3	0.4						
O-H "	0.1	0.0	0.2	97.4	1.7	0.5	0.0						
O..H "	10.6	0.0	0.3	1.2	56.3	23.8	25.6						
($\text{-C}\begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$) sym. deformation	3.2	0.5	6.5	0.1	42.8	56.6	2.3						
$\angle$ O-H..O " bending	5.2	0.1	4.0	1.1	19.2	13.8	52.4						
C=O anti sym. str.								82.7	13.0	0.0	0.0	5.9	0.0
C-O "								16.8	77.8	0.2	0.1	8.7	1.2
O-H "								0.1	0.0	97.3	2.2	0.2	0.0
O..H "								0.0	0.4	1.2	65.7	0.3	52.3
($\text{-C}\begin{smallmatrix} \text{O} \\ \parallel \\ \text{O} \end{smallmatrix}$) anti sym. deformation								0.3	8.0	0.1	0.8	84.4	0.0
$\angle$ O-H..O " " bending								0.1	0.8	1.1	31.2	0.4	66.4

22.7 The out of plane frequencies

The expected out of plane frequencies consist of 3 infrared and 2 Raman active modes. As only 1 or 2 infrared bands could possibly be assigned to out of plane vibrations, and as no out of plane Raman bands were observed, it was considered to be pointless at this stage to make any calculation for the fundamentals.

CHAPTER 23

CONCLUSIONS AND SUGGESTIONS FOR FUTURE WORK

Oxalic acid is an asymmetric top molecule of C_{2h} point group. It has 18 modes of vibration, 13 inplane and 5 out of plane fundamentals as follows:

$$\Gamma = 7A_g + 6B_u + 2B_g + 3A_u$$

7 A_g and 6 B_u are inplane vibrational modes, the others are out of plane.

13 bands of gaseous oxalic acid were observed, 8 in the infrared and 5 in the Raman. 10 were assigned to inplane fundamentals, 2 were assigned to out of plane fundamentals, and only one was assigned to a combination mode.

As a highly asymmetric top molecule of point group C_{2h} the infrared bands are expected to have A, B, C and hybrid type envelopes. In the spectra recorded only 2 bands showed a separation of P and R branches.

The theoretical band envelopes were studied for the reason that the band assignment could possibly be made and the out of plane vibrations could be picked out. The attempt to make the band assignment by comparing the observed band contours of gaseous oxalic acid to that of theoretical band contours given by Ueda and Shimanouchi (71) was made and it was found that

- (a) The theoretical band contours for A and C type bands are usually similar, and thus it is impossible to identify the out of plane modes.

- (b) Most of the gaseous oxalic band shapes are not similar to the expected band contours. This is because most observed band envelopes are hybrid bands.

Thus it is not possible to pick out the out of plane vibrations. Nor is it possible to distinguish between the two models from the observed band contours obtained in this work because the moments of inertia are so similar.

Infrared and Raman experiments face different problems. In the infrared the main problems are the condensation of the sample on the KBr windows and the interference caused by decomposition products. Both problems give a high background, and thus, some gaseous oxalic acid bands may be undetected.

Reduction of both problems is achieved by keeping the window temperatures slightly higher than the cell body and by evacuating the cell continuously.

In the Raman no condensation problem arises and the decomposition products do not interfere so much with the gaseous oxalic acid bands. The gaseous oxalic acid Raman bands are very distinctive from the others. Most of the Raman bands are strong enough for depolarization measurements. Thus, the assignment of the Raman bands was made easier than those in the infrared.

However, as the Raman bands are much more difficult to detect than the infrared, the Raman experiment needs

- (a) very accurate lining up;
- (b) a higher temperature heated cell;
- (c) powerful laser and detector.

The calculations were made using both models of gaseous oxalic acid which were suggested by Nahlovska, Nahlovsky and Strand (78). They published their work on electron diffraction of gaseous oxalic acid during the course of this work.

It was hoped that some useful information might be obtained, and thus the position of the H atoms in this molecule could be distinguished.

Unfortunately, from the results obtained it is difficult to distinguish between the two models for the following reasons:-

- (1) The asymmetric O-H stretching band is shifted to lower frequency without band broadening.
- (2) The out of plane fundamentals can not be picked out.
- (3) Not all the fundamentals were observed.
- (4) The observed values can be fitted quite well to the calculated values for both models.

In order to be able to complete the work the following future work on

- (a) Infrared and Raman spectra of deuterated oxalic acid monomer;
- (b) Far infrared for gaseous oxalic acid;
- (c) Higher resolution infrared spectra and hybrid profile calculations

is required.

Further improvement for the infrared experiment can be made by increasing the pathlength by using a folded path multiple traversal gas cell and heating to a lower temperature to reduce decomposition.

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