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The development of a least squares model for the determination of compliance constants from various combinations of vibration frequency, mean square amplitudes of vibration and centrifugal distortion data is discussed. The resultant model is applied to frequency and mean square amplitude data for NO_2 and N_2O_4 and to frequency and centrifugal distortion data for SO_2. For NO_2 and SO_2 it was possible to use various combinations of data and weight matrices so that some statements could be made regarding the utility of the model.

A recently developed theory concerning the anharmonicity effect due to the presence of the low frequency torsion made in X_2Y_4 type molecules was applied to N_2O_4 giving results which point to a plausible explanation for some of the unusual bands observed for this type molecule.

APPLICATION OF THE LEAST SQUARES CRITERION TO THE DETERMINATION OF MOLECULAR COMPLIANCE CONSTANTS

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INTRODUCTION

The potential energy of a polyatomic molecule is most conveniently expressed using an harmonic oscillator model resulting in a quadratic potential function containing either force constants or compliance constants. When these constants are known it is possible to use them to accurately predict various physical and chemical properties of the molecules involved. The determination of these potential constants from observed data is subject to many general limitations. Anharmonicity together with Fermi resonance and an inability in most cases to accurately determine the band centers all combine to make it difficult or impossible to find a set of frequencies which are completely consistent with a quadratic potential function. For these reasons the least squares approach using high speed computers was introduced by Mann, et al (12,43-51) and has been used mainly by Overend and collaborators (16,1289-1295 and later papers) and Schactschneider (19, 1-90) to determine a best fit set of force constants from frequency data.

Frequency data from one isotopic form of a molecule is insufficient (except in the simplest polyatomic molecules)

to determine the complete potential function in the quadratic approximation, thus frequency data from various isotopically substituted molecules is combined in the calculation. Often however the isotopic shifts are small and difficult to resolve (except for the D for H substitution) and since the constants are determined by the shifts some error is introduced. Sometimes for the above and other reasons it is impossible to get the complete set of isotopic frequency data and one cannot determine all of the constants. To overcome this deficiency it is possible to use various other observables to replace or supplement frequency data. Mean square amplitudes of vibration from gas phase electron diffraction experiments, centrifugal distortion constants from microwave and infrared experiments and Coriolis coupling constants from infrared experiments all are related to the potential constants.

In this thesis a least squares model is developed using frequency data, mean amplitude data and centrifual distortion data to determine compliance constants. The model developed is general and can be applied to any molecule for which there is sufficient data. Coriolis coupling constants were not included here since they are generally applicable only to molecules having degenerate

modes and because they are not as sensitive to changes in the constants as the other data types.

I. MOLECULAR COMPLIANCE CONSTANTS

Compliance constants have only recently been seriously considered for the expression of the molecular potential function. The advantages of their use was first discussed by Decius (6,241-248). Previous to this time the G,F method introduced by Wilson (22,1047-1052) was most generally used.

The G,F method is developed from the basic defining equations for the kinetic and potential energies (23,309-310).

Kinetic energy: $2T = \dot{S}^t G^{-1} \dot{S}$ (I,1)

Potential energy: $2V = S^t F S$ (I,2)

where S is the vector of internal coordinate displacements; $\dot{S}$, the vector of their derivatives with respect to time; G^{-1}, a matrix whose elements are a function of the geometry of the molecule and the masses of the component atoms; and F, the "force constant" matrix. The kinetic and potential energies in terms of normal coordinates are

Kinetic energy: $2T = \dot{Q}^t E \dot{Q}$ (I,3)

Potential energy: $2V = Q^t \Lambda Q$ (I,4)

If L is the transformation from normal coordinates to internal displacement coordinating $S = LQ$, equations (I,1) and (I,3) may be combined to give

$$2T = \dot{S}^t G^{-1} \dot{S} = \dot{Q}^t L^t G^{-1} L \dot{Q} = \dot{Q}^t E \dot{Q} \qquad (I,5)$$

so that

$$L^t G^{-1} L = E \qquad (I,6)$$

and equations (I,2) and (I,4) may be combined to give

$$2V = S^t F S = Q^t L^t F L Q = Q^t \Lambda Q \qquad (I,7)$$

so that $L^t F L = \Lambda$ (I,8)

The combination of (I,6) and (I,8) leads to the equation

$$GFL = L\Lambda \qquad (I,9)$$

which leads to the secular equation

$$GF - E\lambda_k = 0 \qquad (I,10)$$

In place of equation (I,2) the equation

$$2V = \mathfrak{F}^t C \mathfrak{F} \quad \text{may be written.} \qquad (I,11)$$

Where $\mathfrak{F}$ is the generalized force vector,

$$\mathfrak{F} = -\left(\frac{\partial V}{\partial S}\right) = -FS \qquad (I,12)$$

and $C = F^{-1}$ the "compliance constant" matrix. (I,13)

Equation (I,6) may be rewritten as

$$M^t G M = E \qquad (I,14)$$

where $M = (L^{-1})^t$ (I,15)

and (I,8) as

$$M^t C M = \underline{\Phi} \qquad (I,16)$$

or as $$L \underline{\Phi} L^t = C \qquad (I,16')$$

where $$\underline{\Phi} = \Lambda^{-1} \qquad (I,17)$$

From (I,14)

$$M^t = M^{-1} K$$

where

$$K = G^{-1} \qquad (I,18)$$

so (I,16) may be written as

$$M^{-1} K C M = \underline{\Phi}$$

and multiplying both sides by M gives

$$K C M = M \underline{\Phi} \qquad (I,19)$$

which leads to the secular equation

$$|KC - E\emptyset_k| = 0 \qquad (I,20)$$

At this point it should be explained that nothing is to be lost by considering the compliance constant matrix rather than the force constant potential function. In the

following it will be shown rather that the use of compliance constants might be more natural from the point of view of its determination.

The most generally applicable advantage of the compliance matrix is in the uniqueness of its elements. In the treatment of molecular vibrations, redundant coordinates sometimes arise which are employed in order to use the general method (23,102-145) for factoring the secular determinant. In the force constant language their employ leads to ambiguity in the definition of the elements of F. Such an ambiguity does not arise in the compliance constant treatment of the same problem.

It can be assumed with no loss of generality that one is dealing with a single symmetry species and its associated factor of the secular determinant. If $\hat{S}$ is the vector of symmetry displacement coordinates including the redundancies and $\hat{\underline{S}}$ is the corresponding vector without the redundancies and A is a rectangular matrix defining the transformation

$$\hat{S} = A\,\hat{\underline{S}}$$

Then for force constants

$$2V = \hat{S}^t F \hat{S} = \hat{\underline{S}}^t A^t F A \hat{\underline{S}} = \hat{\underline{S}}^t \mathbb{F}\, \hat{\underline{S}} \qquad (I,21)$$

where F is the force constant matrix corresponding to the $\hat{S}$ coordinates and $\mathbb{F}$ the force constant matrix corresponding to the $\hat{\underline{S}}$ coordinates.

For compliance constants

$$\hat{\underline{f}} = -\left(\frac{\partial V}{\partial \underline{S}}\right), \quad \hat{\underline{f}}' = -\left(\frac{\partial V}{\partial \hat{\underline{S}}}\right)$$

$$\hat{\underline{f}}' = -\left(\frac{\partial V}{\partial \hat{\underline{S}}}\right) = -\left(\frac{\partial \underline{S}}{\partial \hat{\underline{S}}}\right)\left(\frac{\partial V}{\partial \underline{S}}\right) = A^t \underline{f}$$

Then

$$2V = \hat{\underline{f}}^t \mathbb{C}\, \hat{\underline{f}} = \underline{f}^t A\, \mathbb{C}\, A^t \underline{f} = \underline{f}^t C\, \underline{f} \qquad (I,22)$$

where C is the compliance matrix corresponding to $\underline{f}$ and $\mathbb{C}$ the compliance matrix corresponding to $\hat{\underline{f}}$.

From (I,21)

$$\mathbb{F} = A^t F A \qquad (I,23)$$

Since A cannot be inverted it is impossible to define F in terms of $\mathbb{F}$.

But from (I,22)

$$C = A\, \mathbb{C}\, A' \qquad (I,24)$$

so that the elements of C may be defined in terms of those of $\mathbb{C}$ and although they are not linearly independent they are certainly uniquely defined.

It should here be noted that one obtains different compliance constants depending on what kind of internal coordinates are used for their definition. In particular,

the use of symmetry coordinates simplifies the solution of the secular determinant in exactly the same way as in the G,F case.

If the symmetry coordinates are defined by the orthogonal transformation

$$\hat{S} = US \qquad (I,25)$$

Then

$$\hat{G} = UGU^t \qquad (I,26)$$

and

$$\hat{F} = UFU^t \qquad (I,27)$$

Inverting equations (I,26) and (I,27) gives

$$\hat{K} = UKU^t \qquad (I,28)$$

$$\hat{C} = UCU^t \qquad (I,29)$$

where as before

$$K = G^{-1} \quad \text{and} \quad C = F^{-1}$$

Since $\hat{G}$ and $\hat{F}$ are factored, $\hat{K}$ and $\hat{C}$ are also factored in the same manner.

As the right sides of equations (I,28) and (I,29) have the same form as (I,26) and (I,27) , the techniques described by Wilson, Decius, and Cross (23,102-145) may be applied just by writing C for F and K for G .

Frequency Calculation

The calculation of frequencies from compliance constant data is quite analogous to the calculation from force constant data:

$$\lambda_k = 4\pi^2\nu_k^2 = 4\pi^2c^2\omega_k^2 \quad \text{and since}$$

$$\bar{\Phi} = \Lambda^{-1}, \quad \phi_k = \frac{1}{\lambda_k} = 1/4\ \pi^2c^2\omega_k^2 \qquad (I,30)$$

The only complication to solution of the secular determinant (I,2) is that usually only G is available and not K [1/]. If there are not redundancies, G may simply be inverted; but if redundancies are present, it is necessary to remove them and thus the rows and columns corresponding to them before inversion. As previously discussed, there is no loss of generality.

The secular equation can then be solved and the frequencies calculated from (I,30).

1/ See however (17,1133-1138).

Mean Square Amplitude Calculation

The mean square amplitudes of vibration are also easily calculated after solution of the secular equation. Solution gives the elements of and also the eigenvector matrix M from which the transformation matrix L can be determined.

If R is the vector of the interatomic displacement coordinates the mean square amplitude matrix (14,726-733) is given by $\langle RR' \rangle$. If R is related to the internal coordinates used to define the matrix M (and thus L) by the transformation

$$R = VS \qquad (I,31)$$

we have

$$\langle RR' \rangle = \langle VSS'V' \rangle = V \langle SS' \rangle V' \qquad (I,32)$$

and since $S = LQ$

$$V \langle SS' \rangle V' = VL \langle QQ' \rangle L'V' = VL \Delta L'V' \qquad (I,33)$$

where Δ is a diagonal matrix whose elements are

$$\Delta_i = (h/8 \pi^2 c \omega_i) \coth (hc \omega_i/2kT) \qquad (I,34)$$

Introducing the notation of Cyvin (4,828-834)

$$\langle RR' \rangle = \bar{\bar{\Sigma}}_R \qquad (I,35)$$

$$\langle SS' \rangle = L \Delta L' = \bar{\bar{\Sigma}}_S \qquad (I,36)$$

$$\bar{\Sigma}_R = V \bar{\Sigma}_S V' \qquad (I,37)$$

Thus, in order to obtain mean square amplitudes, it is necessary to evaluate V ; solve the secular equation; transpose and invert the eigenvector matrix; choose a temperature and use equations (I,34), (I,36), and (I,37).

At this stage it would seem that there is no advantage to using the compliance constants rather than the force constants. In fact, it seems that the G,F treatment would be more appropriate as the L matrix is obtained directly. It will be shown below that this conclusion is premature and that the compliance language is really more natural when dealing with mean square amplitudes.

If we choose our internal coordinates so that the transformation matrix, V , is the identity matrix, E , we may express (I,30) and (I,31) as

$$\bar{\Sigma}_R = \bar{\Sigma}_S = L \Delta L' \qquad (I,38)$$

If Δ_k is now written in the form

$$\Delta_k = kT\phi_k x_k \coth x_k \qquad (I,39)$$

where

$$x_k = \frac{hc\omega_k}{2kT}$$

and $x_k \coth x_k$ expanded as

$$x_k \coth x_k = 1 + x_k^2/3 + x_k^4/45 + \cdots \qquad (I,40)$$

It is easily seen that

$$\lim_T (\Delta_k/kT) = \phi_k \qquad (I,41)$$

and thus that

$$\lim_{T\to\infty} \frac{1}{kT} S = \lim_{T\to\infty} \frac{1}{kT} (L \Delta L') = L \underline{\Phi} L' \qquad (I,42)$$

From (I,16')

$$C = L \underline{\Phi} L'$$

and thus

$$\lim_{T\to\infty} \frac{1}{kT} \bar{\Sigma}_S = C \qquad (I,43)$$

Centrifugal Distortion Constants

Another observed molecular property is the centrifugal distortion constant which Kivelson and Wilson (11,1229-1236) have expressed as a linear combination of the compliance constants.

The centrifugal distortion constants are the in the Hamiltonian for the semi-rigid rotor,

$$H = \frac{1}{2} \sum_{\alpha} \sigma_{\alpha\alpha} \; P_{\alpha}^{2} + \frac{1}{4} \sum_{\alpha\beta\gamma\delta} \tau_{\alpha\beta\gamma\delta} \; P_{\alpha} \; P_{\beta} \; P_{\gamma} \; P_{\delta} \quad (I,44)$$

The parameters of this equation may be determined if enough data from microwave or infrared analysis is available. Kivelson and Wilson have shown that if the geometry and compliance constants are known, one may calculate the distortion constants using the formulas:

$$t_{\alpha\beta\gamma\delta} = -2(I^{0}_{\alpha\alpha} \; I^{0}_{\beta\beta} \; I^{0}_{\gamma\gamma} \; I^{0}_{\delta\delta}) \; \tau_{\alpha\beta\gamma\delta} \quad (I,45)$$

and

$$t_{\alpha\beta\gamma\delta} = \sum_{i} \; \sum_{j} \left[J^{(i)}_{\alpha\beta} \right] \circ \left[J^{(j)}_{\gamma\delta} \right] {}^{\circ} C_{ij} \quad (I,46)$$

where

α , β , γ , and δ refer to the cartesian coordinates x, y, z ; $I^{0}_{\alpha\alpha}$, $I^{0}_{\beta\beta}$, $I^{0}_{\gamma\gamma}$, $I^{0}_{\delta\delta}$ are the principal

moments of inertia for the equilibrium configuration which must be expressed in the principal axis coordinates[2/] ; and

$$J^{(k)}_{\alpha\beta} = (\partial I / \partial R_k)_{\underline{S}=\underline{0}} \qquad (I,47)$$

where R_k is the coordinate whose displacement is the internal coordinate S_k .

Since $S_k = R_k - R^0_k$

$$(\partial I_{\alpha\beta} / \partial R_k)_{\underline{S}=\underline{0}} = (\partial S_k / \partial R_k)(\partial I_{\alpha\beta} / \partial S_k)_{\underline{S}=\underline{0}}$$

$$= (\partial I_{\alpha\beta} / \partial S_k)_{\underline{S}=\underline{0}} \qquad (I,48)$$

The evaluation of these quantities is discussed in Appendix I.

2/ The moment of inertia matrix is then diagonal.

II. THE LEAST SQUARE CRITERION

Section One was concerned with the description of molecular compliance constants and with the derivation of various physically observable properties from the compliance constants.

The object of this project is to take observed physical properties [3] and to determine the compliance constants from them.

The usual technique employed is to express the observables as linear functions of the parameters of interest and to use the least squares criterion to arrive at a statistical estimate.

In general, for N pieces of independent data, y_j ; in terms of the m parameters (13,328-359):

$$y_j = \alpha_j + \beta_1 X_{j1} + \beta_2 X_{j2} + \cdots + \beta_m X_{jm} + e_j \qquad (II,1)$$

$$j=1,N$$

where y_j is the j^{th} observed value of y corresponding to the set of known values $(\alpha_j, X_{j1}, \ldots, X_{jm})$ and the expected value of

$$e_j \ , \ E(e_j) = \underline{0} \quad j=1,N \qquad (II,2)$$

[3] In the present case: vibrational frequencies, mean square amplitudes of vibration and centrifugal distortion constants.

and the covariance

$$E(e_k e_1) = \sigma^2/p_k \quad k = 1 \qquad (II,3)$$
$$= 0 \quad k \neq 1$$

In matrix notation these relations may be expressed as

$$Y = \alpha + X\beta + e \qquad (II,1')$$

$$E(e) = 0 \qquad (II,2')$$

$$Cov(e) = E(ee') = \sigma^2 p^{-1} \qquad (II,3')$$

where p^{-1} is a diagonal matrix whose elements are

$$1/p_k$$

The least square criterion can now be applied. It is desired to find a set of solutions $\hat{\beta}_1, \hat{\beta}_2, \ldots, \hat{\beta}_m$ such that

$\Sigma_1 \left[p_1 e_1^2 \right]$ is a minimum (21,181-210) .

$$\sum_1 p_1 e_1^2 = \sum_1 p_1 (y_1 - \alpha_1 - \beta_1 X_{11} - \beta_2 X_{12} - \ldots - \beta_m X_{1m})^2 \qquad (II,4)$$

To minimize the partial derivatives with respect to the parameters $_k$ are taken out and set equal to zero.

$$\frac{\partial}{\partial \beta_k} \sum p_1 e_1^2 = \sum_1 2 p_1 X_{1k} (y_1 - \alpha_1 - \beta_1 X_{11} -$$

$$\ldots - \beta_m X_{1m}) = 0 \qquad (k=1,m) \qquad (II,5)$$

$$= \sum_1 p_1 x_{1k}(y_1 - \quad_1) - \beta_1 \sum p_1 x_{11} x_{1k} - \beta_2 \sum p_1 x_{12} x_{1k} -$$

$$\cdots - \beta_m \sum p_1 x_{1m} x_{1k} = 0 \qquad (k=1,m) \qquad (II,6)$$

(II,6) may be rewritten as

$$\hat{\beta}_1 \sum p_1 x_{11} x_{1k} + \cdots + \hat{\beta}_m \sum p_1 x_{1m} x_{1k} =$$

$$\sum p_1 x_{1m}(y_1 - \alpha_1) \quad (k=1,m) \qquad (II,7)$$

where the $\hat{\beta}$ are the estimates for the parameters β.

The above equations are summarized in matrix notation as

$$e'Pe = (Y - \alpha - X\beta)' \; P(y - \alpha - X\beta) \qquad (II,4')$$

$$\frac{\partial}{\partial \beta}(e'Pe) = X'P(Y - \alpha) - X'PX\hat{\beta} = 0 \qquad (II,6')$$

$$X'PX\hat{\beta} = X'P(Y - \alpha) \qquad (II,7')$$

Then if $S = X'PX$ and S is of rank m, equation (II,7') has the solution

$$\hat{\beta} = S^{-1}X'P(Y - \alpha) \qquad (II,8)$$

An estimate of the general variance σ^2, $\hat{\sigma}^2$, based on the estimate $\hat{\beta}$ may be written as

$$\hat{\sigma}^2 = \frac{1}{N-m}\left[(Y - \alpha - X\hat{\beta})' \; P(Y - \alpha - X\hat{\beta}) \right] \quad (II,9)$$

$$\text{or } \hat{\sigma}^2 = \frac{1}{N-m}\left[(Y - \alpha)'P(Y - \alpha) - \hat{\beta}'X'P(Y - \alpha) \right] \quad (II,9')$$

Before discussing how these equations may be used to determine compliance constants it is important to describe some of the more important properties of the general estimates.

It is certainly desired that the expected value of all possible estimates $\hat{\beta}$ should be β. (S is assumed of rank m).

$$E(\hat{\beta}) = E\left[(S^{-1}X'P(Y - \alpha)\right]$$

$$= S^{-1}X'PE\left[Y - \alpha\right]$$

$$= S^{-1}X'PE\left[X\beta + e\right]$$

$$= S^{-1}X'PX\beta + E(e)$$

$$= S^{-1}X'PX\beta = S^{-1}S\beta$$

$$E(\hat{\beta}) = \beta \quad (II,10)$$

The variance estimate $\hat{\sigma}^2$ is defined by (II,9)

$$E(\hat{\sigma}^2) = E\left[\frac{1}{N-m}\left[(Y - \alpha - X\hat{\beta})'P(Y - \alpha - X\hat{\beta})\right]\right]$$

$$= \frac{1}{N-m}\left[N\sigma^2 + E\left[\beta'S\beta - \hat{\beta}'S\hat{\beta}\right]\right]$$

$$= \frac{1}{N-m} \left[N\sigma^2 - E \left[e'PXS^{-1}X'Pe \right] \right]$$

$$= \frac{1}{N-m} \left[N\sigma^2 - m\sigma^2 \right]$$

$$E(\hat{\sigma}^2) = \sigma^2 \qquad \text{(II,11)}$$

The covariance of $\hat{\beta}$, $\text{Cov}(\hat{\beta})$, is defined as

$$\text{Cov}(\hat{\beta}) = E\left[(\hat{\beta} - \beta)(\hat{\beta} - \beta)' \right]$$

$$= S^{-1}X'PE(ee')PXS^{-1}$$

$$= \sigma^2 (S^{-1}X'PP^{-1}PXS^{-1})$$

$$= \sigma^2 (S^{-1}X'PXS^{-1})$$

$$= \sigma^2 S^{-1} \qquad \text{(II,12)}$$

If we estimate $\text{Cov}(\hat{\beta})$ by

$$\hat{\text{Cov}}(\hat{\beta}) = S^{-1}\hat{\sigma}^2$$

it is seen from (II,11) that

$$E\left[\hat{\text{Cov}}(\hat{\beta})\right] = S^{-1}E(\hat{\sigma}^2) = \sigma^2 S^{-1}$$

and thus

$$E\left[\hat{\text{Cov}}(\hat{\beta})\right] = \text{Cov}(\hat{\beta}) \qquad \text{(II,13)}$$

Application of Least Squares to Curve Fitting

It is assumed that a function $f_j(x_1, x_2, \ldots, x_m)$ can be represented by a truncated Taylor series of the form

$$f_j(x_1, x_2, \ldots, x_m) = f_j^o (x_1^o, x_2^o, \ldots, x_m^o) + \sum_{i=1}^{m} \left(\partial f_j / \partial x_i \right)_{\underline{x}^o} \Delta x_i \qquad (II,13)$$

and that there are N such functions to each of which corresponds an observed value, f_j^{obs}. If $e_j = f_j^{obs} - f_j$, (II,13) may be written as

$$f_j^{obs} = f_j^o + \Sigma \left(\partial f_j / \partial x_i \right)^o \Delta x_i + e_j \qquad (II,14)$$

Letting $f_j^{obs} = y_j$, $f_j^o = \alpha_j$, $(\partial f_j / \partial x_i)^o = X_{ji}$, and $\Delta x_i = \beta_i$ and referring to equation (II,1) it is seen that given initial values, $x_1^o, x_2^o, \ldots, x_m^o$ and $p_1, p_2, \ldots, p_n$, equation (II,8) may be used to determine corrections, Δx_i, to the x_1^o, x_2^o, ..., x_m^o. If the Δx_i are used to determine new initial values, new x_i^o = old x_i^o $+\Delta x_i$, and (II,8) used again, new corrections, Δx_i, are

obtained. This iteration may be continued until the Δx_i's satisfy some preset convergence criterion and the $x_1, x_2, \ldots, x_m$, there obtained can be said to be the "best fit" parameters for the given data. Since the $x_1^o, x_2^o, \ldots, x_m^o$ obtained after each iteration are considered as constants in the next iteration, the covariance of the "best fit" parameters,

$$\hat{C}ov(\hat{x}) = \hat{C}ov\,(\hat{x}^o + \Delta\hat{x}) = \hat{C}ov(\Delta\hat{x}),$$

where the $\Delta\hat{x}$ and $\hat{x}$ are the vectors of Δx_i's and x_i's resulting from the last iteration, and $\hat{x}^o$, the vector of x_i^o's resulting from the next to last iteration.

In order to use the above technique to determine "best fit" compliance constants the following quantities must be obtained:

$$\hat{x}^o,\ \hat{f}^o,\quad (\partial f_j/\partial x_i)^o,$$

and P. These will be discussed below.

The $\hat{x}^o$ Vector

The x_i^o's here correspond to the compliance constants, C_{ij}, which are elements of the compliance matrix C. In order to simplify the notation and to take advantage of the fact that some of the C_{ij} are equal due to symmetry, a transformation Z (12,43-51) is defined such that

$$C_{ij} = \sum_k Z_{ijk} \, c_k \qquad (II,15)$$

where the c_k are the independent compliance constants of which each C_{ij} is a linear combination. Since $C_{ij} = C_{ji}$, $Z_{ijk} = Z_{jik}$ and only the Z_{ijk} need be specified.

In order to determine a starting $\hat{x}^o$ vector, in the case of compliance constants a c^o vector, usually either values are taken from similar molecules; previously determined force constants are inverted; or a simplified potential is assumed and the simplified secular determinant solved to give estimates of the diagonal and most important off-diagonal constants and the rest are initially set at zero.

The $\hat{f}^0$ Vector

Given the transformation Z and a set of initial values C^0, the f_j^0 of interest, i.e., the ϕ_j^0's, $\langle r_i^2 \rangle^0$, and $t_{\alpha\beta\gamma\delta}^0$'s may be calculated respectively by solving the secular determinant (I,20) to find the ϕ_j^0 and the L^0 matrix, using the ϕ_j's and L in conjunction with (I,34), (I,36) and (I,37) to find the $\langle r_i^2 \rangle^0$ and using equation (I,46) to find the $t_{\alpha\beta\gamma\delta}^0$'s. These quantities must of course be re-evaluated after each iteration.

The $(\partial f_j / \partial x_i)^o$ Matrix

$(\partial \phi_j / \partial C_i)$

Starting with the equation

$$m^t C m = \underline{\Phi} \qquad \text{(I,16)}$$

and from (I,14)

$$m m^t = K , \qquad \text{(II,16)}$$

the perturbation equations

$$\Delta \underline{\Phi} = (\Delta m^t) C^o m^o + m^{ot} (\Delta C) m^o + m^t C^o (\Delta m) \qquad \text{(II,17)}$$

and

$$(\Delta m) m^{ot} + m^o (\Delta m^t) = 0 \qquad \text{(II,18)}$$

can be written.

From (II,18)

$$\Delta m^t = -m^{-1} (\Delta m) m^t \qquad \text{(II,19)}$$

From (II,17)

$$\Delta \phi_j = \left[(\Delta m^t) C^o m^o \right]_{jj} + \left[m^{ot} (\Delta C) m^o \right]_{jj} + \left[m^{ot} C^o (\Delta m) \right]_{jj} \qquad \text{(II,20)}$$

Substituting (II,19) into the first term on the right hand side of (II,20) results in

$$\Delta \phi_j = - \left[m^{o-1} (\Delta m) m^{ot} C^o m^o \right]_{jj} + \left[m^{ot} (\Delta C) m^o \right]_{jj}$$

$$+ \left[m^{ot} C^o m^o m^{o-1} (\Delta m) \right]_{jj}$$

$$= - \left[m^{o-1} (\Delta m) \Phi^o \right]_{jj} + \left[m^{ot} (\Delta C) m^o \right]_{jj}$$

$$+ \left[\Phi^o m^{o-1} (\Delta m) \right]_{jj}$$

$$= \left[m^{ot} (\Delta C) m^o \right]_{jj}$$

$$= \sum_k \sum_l m^o_{kj} m^o_{lj} \Delta C_{kl} \qquad \text{(II,21)}$$

Since $C_{kl} = \sum_i Z_{kli} \subset_i$

$$\Delta C_{kl} = \sum_i Z_{kli} \Delta \subset_i \qquad \text{(II,22)}$$

and (II,21) may be written as

$$\Delta \phi_j = \sum_k \sum_l m^o_{kj} m^o_{lj} Z_{kli} \Delta \subset_i \qquad \text{(II,23)}$$

If (II,23) is assumed to be a truncated Taylor series

$$\partial \phi_j / \partial C_i = \sum_k \sum_l m^o_{kj} m^o_{lj} Z_{kli} \qquad (II,24)$$

or as $Z_{kli} = Z_{lki}$

$$\partial \phi_j / \partial C_i = 2 \sum_k \sum_{l>k} m^o_{kj} m^o_{lj} Z_{klj}$$

$$+ \sum_k m^o_{ki} m^o_{ki} Z_{kkj} \qquad (II,24')$$

$\partial \langle r_j^2 \rangle / \partial C_i$

From equation (I,37), $\bar{\bar{\Sigma}}_R = V \bar{\bar{\Sigma}}_S V'$,

for a diagonal element

$$\left[\bar{\bar{\Sigma}}_R\right]_{jj} = \langle r_j^2 \rangle = \sum_k \sum_l V_{jk} \left[\bar{\bar{\Sigma}}_S\right]_{kl} V_{jl}$$

Then the partial derivative

$$\partial \langle r_j^2 \rangle / \partial C_i = \sum_k \sum_l V_{jk} \partial \left[\bar{\bar{\Sigma}}_S\right]_{kl} / \partial C_i V_{jl}$$

where from equation (I,36)

$$\left[\bar{\bar{\Sigma}}_S\right]_{kl} = \sum_m L_{km} \Delta_m L_{lm}$$

$$\begin{aligned} \partial \left[\bar{\bar{\Sigma}}_S\right]_{kl} / \partial C_i = \sum_m \Big[& \partial L_{km} / \partial C_i \, \Delta_m L_{lm} \\ & + L_{km} \, \partial \Delta_m / \partial C_i L_{lm} \\ & + L_{km} \Delta_m (\partial L_{lm} / \partial C_i) \Big] \end{aligned} \quad (II,38)$$

The partial derivative of Δ_m,

$(\partial \Delta_m / \partial C_i)$ is evaluated by the formula

$$(\partial \Delta_m / \partial \phi_m)(\partial \phi_m / \partial C_i) = (\partial \Delta_m / \partial C_i) \quad (II,39)$$

Using the constants consistent with the choice of distances in Angstroms, masses in a.m.u. and compliance constants in Å/millidyne (II,39) gives

$$\partial \Delta_m / \partial C_i = 0.00647 \left[\phi_m^{-\frac{1}{2}} \coth (A_T \phi_m^{-\frac{1}{2}}) + A_T \phi_m^{-1} \operatorname{cosech}^2 (A_T \phi_m^{-\frac{1}{2}}) \right] \times \left[\sum_k m_{km}^{o\,2} Z_{kki} + 2 \sum_k \sum_{l>k} m_{km}^o m_{lm}^o Z_{kli} \right] \quad \text{(II,40)}$$

where $A_T = 937.492/T$.

The partial derivatives of the elements of the L matrix, $(\partial L_{km} / \partial C_i)$ are very difficult to evaluate in closed form for any but the smallest matrices. For this reason they are most easily evaluated numerically. The approximation used here is

$$\partial L_{km} / \partial C_i \approx \Delta L_{km} / \Delta C_i = \frac{1}{2 \Delta C_i} L_{km}(C_1, \ldots, C_i + \Delta C_i, \ldots, C_m) - L_{km}(C_1 \ldots, C_i - \Delta C_i, \ldots, C_m) \quad \text{(II,41)}$$

$\partial t_{\alpha\beta\gamma\delta} / \partial C_i$

The derivatives of the centrifugal distortion parameters, $(\partial t_{\alpha\beta\gamma\delta} / \partial C_i)$, are the most easily evaluated. From equations (I,46) and (II,15)

$$t_{\alpha\beta\gamma\delta} = \sum_j \sum_k \sum_i \left[J_{\alpha\beta}(j)\right]^0 \left[J_{\gamma\delta}(k)\right]^0 Z_{jki} C_i \quad \text{(II,42)}$$

and thus

$$\partial t_{\alpha\beta\gamma\delta} / \partial C_i = \sum_j \sum_k \left[J_{\alpha\beta}(j)\right]^0 \left[J_{\gamma\delta}(k)\right]^0 Z_{jki} \quad \text{(II,43)}$$

or since $Z_{jki} = Z_{kji}$

$$\partial t_{\alpha\beta\gamma\delta} / \partial C_i = \sum_j \left[J_{\alpha\beta}(j)\right]^0 \left[J_{\gamma\delta}(j)\right]^0 Z_{jji} + \sum_j \sum_{k>j} \left[\left[J_{\alpha\beta}(j)\right]^0 \left[J_{\gamma\delta}(k)\right]^0 + \left[J_{\alpha\beta}(k)\right]^0 \left[J_{\gamma\delta}(j)\right]^0 Z_{jki} \right] \quad \text{(II,43')}$$

The P Matrix

The assumption of equation (II,8) is that the elements of the P matrix are known. That is, for each set $(\alpha_j, X_{j1}, X_{j2}, \ldots, X_{jm})$ the variance of y_j, σ_j^2 is known and that the general variance, σ^2, is known, where $p_j \sigma_j^2 = \sigma^2$. In reality these quantities are not known but can be estimated. Since the quantity of interest is $\hat{C}ov(\hat{\beta})$ and not σ^2, only the relative values of the p_j and not their absolute values are important. Thus an arbitrary value of σ^2, $\tilde{\sigma}^2$, may be chosen to relate the p_j's.

If the variance of a function of the quantity of interest is known, a truncated Taylor series is used to determine the variance of the quantity of interest.

That is if

$$f = f(x_1, x_2, \ldots, x_l)$$

$$= f^0(\mu_1, \mu_2, \ldots, \mu_l) + \sum_{i=1}^{l} (\partial f / \partial x_i)_{\mu} (x_i - \mu_i),$$

and $\bar{f}(x_1, \ldots, x_l) = f(\mu_1, \ldots, \mu_l)$,

then $\sigma_f^2 = E\left[(f-\bar{f})^2\right]$

$$= E\left[\left(\sum_i \left(\partial f/\partial x_i\right)_{\mu} (x_i - \mu_i)\right)^2\right]$$

$$= E\left\{\sum_i \left(\partial f/\partial x_i\right)^2 (x_i - \mu_i)^2 + \sum_i \sum_{j\neq i} \left(\partial f/\partial x_i\right)\left(\partial f/\partial x_j\right)(x_i-\mu_i)(x_j-\mu_j)\right\}$$

If the x_i are independently distributed

$$E\left[\sum_i \sum_{j\neq i} \left(\partial f/\partial x_i\right)\left(\partial f/\partial x_j\right)(x_i-\mu_i)(x_j-\mu_j)\right]$$

$$= 0.$$

Then

$$\sigma_f^2 = E\left[\sum_i \left(\partial f/\partial x_i\right)^2 (x_i - \mu_i)^2\right]$$

$$= \sum_i \left(\partial f/\partial x_i\right)^2 E\left[(x_i - \mu_i)^2\right]$$

$$\sigma_f^2 = \sum_i \left(\partial f/\partial x_i\right)^2 \sigma_{x_i}^2 \qquad \text{(II,44)}$$

Frequency Data

Since ϕ_j rather than ω_j is used in the least squares procedure, it is necessary to express $\sigma_{\phi_j}^2$ in terms of $\sigma_{\omega_j}^2$.

$$\phi_j = 1/(5.88852 \times 10^{-7} \omega_j^2)$$

So that

$$\partial \phi_j / \partial \omega_j = - 3.39644 \times 10^6 \omega_j^{-3}$$

where μ_j is assumed to be the observed ω_j. Then

$$\sigma^2_{\phi_j} = (\partial \phi_j / \partial \omega_j)^2 \sigma^2_{\omega_j}$$

$$\sigma^2_{\phi_j} = 1.15358 \times 10^{13} \omega_j^{-6} \sigma^2_{\omega_j} \qquad \text{(III,45)}$$

and if $\sigma^2_{\omega_j} = 0.1$ and $\omega_j = 1000$ cm^{-1} then

$\sigma^2_{\phi^*} \approx 10^{-6}$ where ϕ^* is the ϕ corresponding to 1000 cm^{-1}. Since $\bar{\sigma}^2$ is arbitrary, it can be chosen so that it corresponds to a fixed $\sigma^2_{\omega_j}$ of 0.1 and to $\omega_j = 1000$ cm^{-1} i.e., $\sigma^2_{\phi^*}$. If another value of $\sigma^2_{\omega_j}$

is used, equation (II,45) may be used to calculate the corresponding $\bar{\sigma}^2 = \sigma^2_{\phi^*}$.

The elements of the P matrix, p_j, for frequency data are defined by the equation

$$p_1 \sigma^2_{\phi_1} = p_2 \sigma^2_{\phi_2} = \ldots = \sigma^2_{\phi^*} = \bar{\sigma}^2$$

$$p_1 C \omega_1^{-6} = p_2 C \omega_2^{-6} = \ldots = C(1000)^{-6}$$

Then

$$p_1 = \omega_1^6 / 10^{18}$$

$$p_2 = \omega_2^6 / 10^{18}$$

$$p_j = \omega_j^6 / 10^{18} \qquad \text{(II,46)}$$

Mean Square Amplitude Data

The least squares analysis used for electron diffraction data results in values for the root mean square amplitude l_j and its estimated standard error σ_{l_j}.

$$\langle r_j^2 \rangle = l_j^2$$

so

$$(\partial \langle r_j^2 \rangle / \partial l_j) = 2l_j$$

where μ_j is chosen as l_j.

Then

$$\sigma^2_{\langle r_j^2 \rangle} = 4l_j^2 \sigma^2_{l_j} \qquad \text{(II,47)}$$

and

$$p_1 4l_1^2 \sigma^2_{l_1} = p_2 4l_2^2 \sigma^2_{l_2} = \ldots = \bar{\sigma}^2$$

from which

$$p_j = \bar{\sigma}^2 / (4 \langle r_j^2 \rangle \sigma^2_{l_j}) \qquad \text{(II,48)}$$

Centrifugal Distortion Data

For simple diatomic molecules centrifugal distortion data has been reported to within one percent, but for larger molecules it has proven difficult to obtain better than ten percent agreement. For this reason $0.01t^2_{\alpha\beta\gamma\delta}$ has been rather pessimistically chosen for the variance of $t_{\alpha\beta\gamma\delta}$. Then since

$$p_1 \sigma^2 t_{aaaa} = p_2 \sigma^2 t_{bbbb} = \cdots = \bar{\sigma}^2$$

$$p_j = \bar{\sigma}^2/(0.01t^2_{\alpha\beta\gamma\delta}) \qquad (II,49)$$

It should be mentioned that if the estimated p_j's are chosen generally to be higher than the true p_j's, an upper limit on $Cov(\hat{\beta})$ will usually be obtained, which is to be desired for most purposes.

Computer Program

A FORTRAN II program based on this model has been written for the I.B.M. 7094. The program has the following limitations. No more than 60 independent compliance constants, C_i's, can be determined at one time. No compliance matrix or secular determinant may be larger than 30 x 30 and no more than 30 observables may correspond to a given secular determinant or compliance matrix at one time. However, it is possible to repeat compliance matrices so that the same one may be used for various sets of data and there is no limit on how much total information may be used. The above restrictions may be modified simply by changing the DIMENSION statements of the program but one must be careful not to exceed the capacity of the machine being used.

The program has been written so that it is possible to modify the p_j's calculated above if some better estimates of the variances or standard errors are available.

III. APPLICATIONS OF THE MODEL

The model described in Section Two has been applied to three molecules; Nitrogen Dioxide, NO_2; Sulfur Dioxide, SO_2; and Dinitrogen Tetroxide, N_2O_4 .

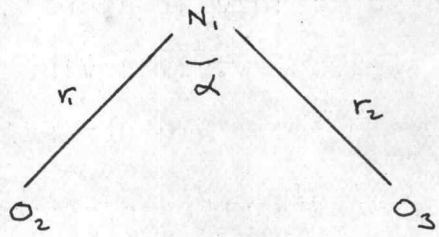
Nitrogen Dioxide

NO_2 was selected for analysis because an electron diffraction study yielding both structural parameters and mean square amplitudes of vibration was recently completed at Oregon State University. In 1964 Dr. Jerome S. Blank completed his electron diffraction analysis which yielded the following parameters for $^{14}N^{16}O_2$ at 380° Kelvin: the bonded N-O distance 1.202 $\pm$ .0013Å , the non-bonded O...O distance 2.213 $\pm$ .0050Å , the N-O root mean square amplitude 0.0382 $\pm$ .0025Å^2, and the O...O root mean square 0.0470 $\pm$ .0050 (3,22-69).

The vibration frequencies observed by Arakawa and Nielsen (1,413-427) for $^{14}N^{16}O_2$ are $\nu_1 = 1319.7$ cm^{-1} , $\nu_2 = 749.8$ cm^{-1} and $\nu_3 = 1617.75$ cm^{-1} . For $^{15}N^{16}O_2$

they are $\nu_1 = 1306.5\ cm^{-1}$, $\nu_2 = 740.15\ cm^{-1}$ and $\nu_3 = 1580.32\ cm^{-1}$.

The compliance constants to be calculated are those corresponding to the commonly used valence force field. The internal coordinates chosen for this analysis are $S_1 = \Delta r_1$, $S_2 = \Delta r_2$, and $S_3 = r^e \Delta \alpha$ where r^e is the equilibrium N-O distance, included in the angle coordinate to give all compliance constants the units Å/millidyne. The following diagram illustrates the numbering of the atoms and of the coordinates



Since both $^{14}N^{16}O_2$ and $^{15}N^{16}O_2$ have C_{2v} symmetry it is possible to construct by the technique of Wilson, Decius, and Cross (23,102-145) the symmetry coordinates:

$$S_r^{(A_1)} = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2),\ S_\alpha^{(A_1)} = r^e \Delta \alpha\ ,$$

and

$$S_r^{(B_1)} = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2)$$

Thus the U matrix in the transformation S = US is

$$U = \begin{vmatrix} 1/\sqrt{2} & 1/\sqrt{2} & 0 \\ 0 & 0 & 1 \\ 1/\sqrt{2} & -1/\sqrt{2} & 0 \end{vmatrix}$$

In order to calculate the frequencies and mean square amplitudes it is necessary to first calculate the G or K matrix elements. A program based on one written by J.H. Schactschneider was used to determine the G matrix elements for the $^{14}N^{16}O_2$ and $^{15}N^{16}O_2$ molecules. Since there are no redundant coordinates these G matrices may be directly inverted to give the corresponding K matrices. The needed G , $\hat{G}$, K , and $\hat{K}$ matrices for the two molecules are tabulated below.

$^{14}N^{16}O_2$

G	S_1	S_2	S_3
S_1	0.133890	-0.049603	-0.051343
S_2		0.133890	-0.051343
S_3			0.366987

$\hat{G}$	$S_r^{(A_1)}$	$S_\alpha^{(A_1)}$	$S_r^{(B_1)}$
$S_r^{(A_1)}$	0.084287	-0.072609	0
$S_\alpha^{(A_1)}$		0.366987	0
$S_r^{(B_1)}$			0.183494

K			
	9.875847	4.426048 9.875847	2.000894 2.000894 3.284759

$\hat{K}$			
	14.301895	2.829692 3.284759	0 0 5.449799

$^{15}N^{16}O_2$

$\hat{G}$			
	0.082839	-0.067783 0.350903	0. 0. 0.175451

$\hat{K}$			
	14.337863	2.769625 3.384803	0. 0. 5.699597

Also needed to calculate the mean square amplitudes is the V matrix defined by equation (I,31) , R = VS , where S is the vector of internal coordinates used to define K and C and R the vector of interatomic distance displacement coordinates. In the present case

$$R = \begin{vmatrix} \Delta r_1 \\ \Delta r_2 \\ \Delta R(0\ldots0) \end{vmatrix}$$

and thus from simple geometrical considerations

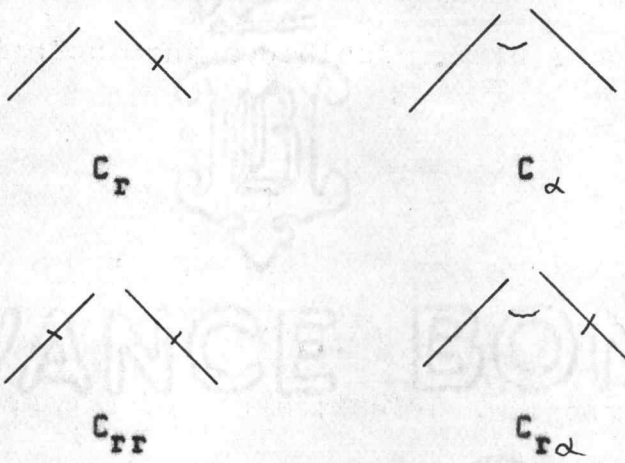
$$V = \begin{vmatrix} 1.0 & 0. & 0. \\ 0. & 1.0 & 0. \\ 0.920549 & 0.920549 & 0.390627 \end{vmatrix}$$

The compliance matrix corresponding to the internal coordinates is

C	S_1	S_2	S_3
S_1	C_r	C_{rr}	$C_{r\alpha}$
S_2		C_r	$C_{r\alpha}$
S_3			C_α

where the four independent constants C_r , C_α , C_{rr} , and $C_{r\alpha}$ are coefficients of terms of the form $\frac{1}{2} \mathcal{F}_r^2$,

$\frac{1}{2} \mathcal{F}_\alpha^2$, $\mathcal{F}_r \mathcal{F}_{r'}$ and $\mathcal{F}_r \mathcal{F}_\alpha$ respectively in the expansion of the potential energy. These constants may be represented pictorially as follows:



The compliance matrix corresponding to the symmetry coordinates S has the form

$\hat{C}$	$S_r^{(A_1)}$	$S_\alpha^{(A_1)}$	$S_r^{(B_1)}$
$S_r^{(A_1)}$	$C_r^{(A_1)}$	$C_{r\alpha}^{(A_1)}$	0
$S_\alpha^{(A_1)}$		$C_\alpha^{(A_1)}$	0
$S_r^{(B_1)}$			$C_r^{(B_1)}$

where

$$C_r^{(A_1)} = C_r + C_{rr}$$

$$C_\alpha^{(A_1)} = C_\alpha$$

$$C_{r\alpha}^{(A_1)} = \sqrt{2}\ C_{r\alpha}$$

$$C_r^{(B_1)} = C_r - C_{rr}$$

The observed data and the various required supplementary information tabulated earlier were used to prepare input cards for the 7094 FORTRAN II program based on the model described in Section Two. The program was processed at Western Data Processing Center at the University of California at Los Angeles.

Since there are eight observed parameters and only four independent constants to be determined, various combinations of data were used to observe how the compliance constants and their estimated errors varied. The constants determined using the whole of the data might be called the "best" or "most compatible" constants and serve as the standard to which the constants determined using less information are compared.

The following tables list for each set of data the compliance constants, their estimated errors, the observed

parameters and those calculated for each set of constants. In all cases the iteration procedure was said converged when

$$\Delta C_i = 0.00005\, C_i . \qquad i = 1,2,3,4 .$$

Trial one includes all of the data; the $^{14}NO_2$ frequencies, the $^{15}NO_2$ frequencies, and the two mean square amplitudes. These constants are then the "most compatible" constants. Trial two uses the $^{14}NO_2$ and $^{15}NO_2$ frequencies only. Trial three uses the $^{14}NO_2$ frequencies and the two mean square amplitudes. Trial four uses only the $^{15}NO_2$ frequencies and the two mean square amplitudes. In each case it is necessary to have at least five pieces of data in order to estimate the errors.

TABLE I.

NO_2 COMPLIANCE CONSTANTS AND ESTIMATED ERRORS

	Trial 1	Trial 2	Trial 3	Trial 4
C_r	0.1011 ± .0003	0.1011 ± .0004	0.1006 ± .0001	0.1009 ± .00002
C_α	0.9368 ± .0144	0.9367 ± .0203	0.9748 ± .0448	0.9701 ± .0431
C_{rr}	-0.0181 ± .0003	-0.0181 ± .0004	-0.0184 ± .0001	-0.0184 ± .00002
$C_{r\alpha}$	-0.0339 ± .0051	-0.0339 ± .0072	-0.0477 ± .0179	-0.0473 ± .0185

OBSERVED AND CALCULATED PARAMETERS

$N^{14}O_2$ Frequencies (cm^{-1})

Observed	Trial 1	Trial 2	Trial 3	Trial 4
749.8	750.0	750.0	749.8	751.2*
1319.7	1319.8	1319.8	1319.7	1317.4*
1617.75	1616.96	1616.96	1617.75	1616.17*

$N^{15}O_2$ Frequencies

Observed	Trial 1	Trial 2	Trial 3	Trial 4
740.15	739.96	739.96	738.70*	740.15
1306.5	1306.4	1306.4	1308.2*	1306.5
1580.32	1581.13	1581.1	1582.3*	1580.32

$N^{14}O_2$ Mean Square Amplitudes at 380°K

Observed	Trial 1	Trial 2	Trial 3	Trial 4
0.001459	0.001509	0.001509*	0.001506	0.001508
0.002209	0.002300	0.002300*	0.002207	0.002209

* Not used for fitting in this trial.

Comparison of the results of trials two through four with trial one gives some idea of the utility of the model when less than the full complement of one kind of data is available. The starred (*) values in the table are those calculated using the compliance constants determined using the unstarred values. These were calculated at a different time using a slightly different approach to setting up the data. Thus there are some round-off errors which show up as slight inconsistencies in the outputs of the two models.

In all cases it is apparent that the use of less than the full amount of data has little significant effect on the compliance constants and the estimated errors. The general increase in the magnitude of the estimated errors for the compliance constants can mostly be attributed to the decrease in the number of degrees of freedom. The change in the compliance constants is generally significant only in the off-diagonal terms C_{rr} and $C_{r\alpha}$; the diagonal constants C_r and C_α are apparently quite stable.

At this time it should prove useful to compare the results of trial one with those of Blank (3,130) who used a cruder weight matrix in a similar least squares program for the same data.

	Blank	Trial 1
C_r	0.1010 ± .0003	0.1011 ± .0003
C_{rr}	-0.0181 ± .0003	-0.0181 ± .0003
C_α	0.9424 ± .0134	0.9368 ± .0144
$C_{r\alpha}$	-0.0358 ± .0048	-0.0339 ± .0051

It can be easily seen that except for minor inconsistencies which may probably be ascribed to the slight difference in G matrices they are in close agreement.

To test whether changes in the weight (P) matrix have a significant effect on the compliance constants a series of trials were run in which the whole of the data was used, but where the weight of the mean square amplitude data relative to the frequency data was varied. Letting $\overline{P}$ represent the weights calculated using equation (II,48) the matrices $\overline{P}_5 = 10^{-2}\overline{P}$, $\overline{P}_6 = 10^{-1}\overline{P}$, $\overline{P}_7 = 10\overline{P}$, $\overline{P}_8 = 10^{2}\overline{P}$ are the weight matrices used with the mean square amplitude data of trials five, six, seven, and eight respectively. The results are given in the following table.

TABLE II.

	Trial 1	Trial 5	Trial 6	Trial 7	Trial 8
C_r	0.1011 ±.0003	0.1011 ±.0003	0.1011 ±.0003	0.1011 ±.0003	0.1010 ±.0003
C_α	0.9368 ±.0144	0.9367 ±.0144	0.9367 ±.0144	0.9373 ±.0147	0.9420 ±.0170
C_{rr}	-0.0181 ± .0003	-0.0181 ± .0003	-0.0181 ± .0003	-0.0181 ± .0003	-0.0181 ± .0003
$C_{r\alpha}$	-0.0339 ± .0051	-0.0339 ± .0051	-0.0339 ± .0051	-0.0341 ± .0052	-0.0358 ± .0061

$N^{14}O_2$ Frequencies (cm^{-1})

Observed	Trial 1	Trial 5	Trial 6	Trial 7	Trial 8
749.8	750.0	750.0	750.0	750.0	750.1
1319.7	1319.8	1319.8	1319.8	1319.8	1319.7
1617.75	1616.96	1616.96	1616.96	1616.96	1616.97

$N^{15}O_2$ Frequencies (cm^{-1})

Observed	Trial 1	Trial 5	Trial 6	Trial 7	Trial 8
740.15	739.96	739.96	739.96	739.95	739.89
1306.5	1306.4	1306.4	1306.4	1306.4	1306.5
1580.32	1581.13	1581.13	1581.13	1581.13	1581.13

$N^{14}O_2$ Mean Square Amplitudes

Observed	Trial 1	Trial 5	Trial 6	Trial 7	Trial 8
0.001459	.001509	0.001510	0.001510	0.001509	0.001509
0.002209	.002300	0.002301	0.002301	0.002300	0.002288

The results of Table II indicate that at least for NO_2 the model is not particularly sensitive to the weight matrix. The fact that the estimated errors for trial one are, in general, less than those for the other trials indicates that the P matrix elements as estimated by equation (II,45) are probably representative.

While this work was in progress a paper by Bird, et al (2,3378-3390) appeared reporting the centrifugal distortion constants as well as other parameters. These data were not included in the determination of the compliance constants since the vibrational data was used in the microwave analysis and thus the data was not independent.

Sulfur Dioxide

SO_2, like NO_2 is a simple triatomic. It was selected for study because there is considerable infrared and microwave data available in the literature including centrifugal distortion parameters. The infrared spectrum of various isotopically substituted SO_2 molecules has been studied by Polo and Wilson (18,900-903). The microwave spectrum was studied by Kivelson (10,904-908).

The structure used in the calculations is that of Kivelson: the S-O distance equal to 1.4321 Å and the O-S-O angle equal to 119.536^0. The observed vibration frequencies are $\nu_1 = 1151.4 \pm .3$, $\nu_2 = 517.8 \pm .3$, and $\nu_3 = 1360.5 \pm .5$ for $S^{16}O_2$, $\nu_1 = 1122.0 \pm 1$, $\nu_2 = 506.8 \pm .5$, and $\nu_3 = 1341.1 \pm .5$ for $S^{16}O^{18}O$, and $\nu_3 = 1316.0 \pm .5$ for $S^{18}O_2$. The observed centrifugal distortion constants for $S^{16}O_2$ are $\tau_{aaaa} = -10.1557$ Mc., $\tau_{bbbb} = -0.035615$ Mc., $\tau_{aabb} = 0.46436$ Mc., and $\tau_{abab} = 0.048496$ Mc., where a, b, and c refer to the cartesian coordinates chosen so that $I_{aa} \leq I_{bb} \leq I_{cc}$.

The internal coordinates for SO_2 are the same as those for NO_2 and further since $S^{16}O_2$ and $S^{18}O_2$ have C_{2v} symmetry the same symmetry coordinates may be used for these molecules. The G and K matrices and the J vectors were calculated using these coordinates in conjunction with the Kivelson structure. The G and K (and $\hat{G}$ and $\hat{K}$, where applicable) matrices are tabulated below.

$S^{16}O_2$

$\hat{G}$

0.078353	-0.038472	0.
	0.218362	0.
		0.109181

$\hat{K}$

13.971410	2.461563	0.
	5.013244	0.
		9.159103

$S^{16}O^{18}O$

G

0.93767	-0.015414	-0.027204
	0.086808	-0.027204
		0.211403

K

11.631725	2.640951	1.836653
	12.603370	1.961687
		5.219084

$S^{18}O_2$

$\hat{G}$

0.071394	-0.038472	0.
	0.204444	0.
		0.102222

$\hat{K}$

15.587422	2.933241	0.
	5.443292	0.
		9.782630

In order to be used in the model, the centrifugal constants, $\tau_{\alpha\beta\gamma\delta}$ (Mc.), must be converted into the corresponding parameters, $t_{\alpha\beta\gamma\delta}$ using equation (I,45). In general this has the form

$$t_{\alpha\beta\gamma\delta} = -32\,\pi^4 h^{-3} N^{-2} \times 10^{-37} \times (I^0_{\alpha\alpha}\ I^0_{\beta\beta}\ I^0_{\gamma\gamma}\ I^0_{\delta\delta})\,\tau_{\alpha\beta\gamma\delta} \qquad \text{(III,1)}$$

$$= -2.953006 \times 10^{-3} \times (I^0_{\alpha\alpha}\ I^0_{\beta\beta}\ I^0_{\gamma\gamma}\ I^0_{\delta\delta})\,\tau_{\alpha\beta\gamma\delta} \qquad \text{(III,1')}$$

where $I^0_{\alpha\alpha}$, $I^0_{\beta\beta}$, $I^0_{\gamma\gamma}$, and $I^0_{\delta\delta}$, have the units a.m.u. $\mathring{A}^2$.

For $S^{16}O_2$ $I_{aa} = 8.3167$, $I_{bb} = 48.911$, and $I_{cc} = 57.3077$ so that $t_{aaaa} = 143.473$, $t_{bbbb} = 605.843$, $t_{aabb} = -227.643$ and $t_{abab} = 23.7740$.

In order to calculate the t's using equation (I,46), the $J_{\alpha\beta}$ and $J_{\gamma\delta}$ vectors are required. The vectors needed in the case of SO_2 are J_{aa}, J_{bb}, and J_{ab}. These vectors are tabulated below.

	J_{aa}	J_{bb}	J_{ab}
S_1	5.807315*	34.209288	-11.412138
S_2	5.807316*	34.209288	11.412138
S_3	-9.965164	19.935862	0.

* These values differ because of round-off error introduced in their calculation.

As in the case of NO_2 there is enough data so that various combinations can be used to observe the variance in the compliance constants, their errors, and the parameters. For SO_2 there are eleven pieces of data and still only four constants to be determined. In trial one all of the data was used; the seven observed frequencies and the four centrifugal distortion parameters. These are the "most compatible" constants. In trial two only the frequency data was used. In trial three the $S^{16}O_2$ frequencies were combined with the four centrifugal distortion parameters and in trial four the $S^{16}O^{18}O$ frequency data was combined with distortion parameters. In trial five the one $S^{18}O_2$ frequency was used with the centrifugal distortion data. The results of these trials are tabulated in Table III.

TABLE III.

	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
C_r	0.10029 ±0.00007	0.1003 ±0.0001	0.1003 ±0.0004	0.1004 ±0.0003	0.0822 ±0.0144
C_α	1.2920 ±0.0181	1.2846 ±0.0255	1.2992 ±0.0283	1.3042 ±0.0299	1.3368 ±0.0903
C_{rr}	0.000098 ±0.000065	0.0001 ±0.0001	0.0002 ±0.0004	0.0002 ±0.0003	-0.0181 ±0.0144
$C_{r\alpha}$	-0.0378 ±0.0131	-0.0321 ±0.0177	-0.0435 ±0.0218	-0.0441 ±0.0217	-0.0277 ±0.0273

$S^{16}O_2$ Frequencies

	Observed	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
ν_1	1151.4	1151.4	1151.3	1151.4	1151.3*	1441.4*
ν_2	517.8	517.6	517.6	517.8	516.9*	507.8*
ν_3	1360.5	1360.4	1360.4	1360.5	1360.3*	1359.6*

$S^{16}O^{18}$ Frequencies

	Observed	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
ν_1	1122.0	1122.5	1122.7	1122.4*	1122.0	1328.5*
ν_2	506.8	507.3	507.2	507.6*	506.8	497.7*
ν_3	1341.1	1341.1	1341.0	1341.6*	1341.1	1417.6*

* Not used for calculation in this trial.

(TABLE III continued)

$S^{18}O_2$ Frequencies

	Observed	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
ν_1	...	1099.0*	1099.3*	1098.7*	1098.2*	1375.5*
ν_2	...	496.8*	496.6*	497.2*	496.3*	487.4*
ν_3	1316.0	1316.3	1316.3	1316.9	1316.2*	1316.0

$S^{16}O_2$ Centrifugal Distortion Constants

	Observed	Trial 1	Trial 2	Trial 3	Trial 4	Trial 5
t_{aaaa}	143.473	143.723	141.769*	145.867	146.510	143.473
t_{bbbb}	605.843	646.589	657.973*	632.988	633.380	605.843
t_{aabb}	-227.643	-199.979	-200.859*	-198.593	-199.253	-227.643
t_{abab}	23.774	26.098	26.099*	26.092	26.092	26.109

* Not used for calculation in this trial.

The same general remarks can be made for SO_2 that were made for NO_2 except for trial five. As long as a complete set of frequency data from either $S^{16}O_2$ or $S^{16}O^{18}O$ was used the parameters estimated using these compliance constants agree quite well with the parameters calculated using the whole of the data. This indicates that in order to get a reasonable set of constants it is necessary not only to have more data than constants but to have more than one piece of data bearing on a given constant. In trial five the one piece of frequency data is related only to the difference $C_r - C_{rr}$, thus the C_α and $C_{r\alpha}$ constants as well as the individual magnitudes of C_r and C_{rr} are determined only by the centrifugal distortion data which, of course, are subject to large error as previously mentioned.

Some remarks should also be made regarding the significance of the reported estimated errors. These errors only measure how well the determined constants fit the data that has been used in their determination. Thus they only have real significance when the conditions outlined in the previous paragraph are fulfilled.

The results of trial one may be compared with those obtained by inversion of the force constants determined by

Polo and Wilson (18,903) and Kivelson (10,907) using the same data.

	Polo, Wilson, and Kivelson	Trial 1
C_r	0.10035	0.10029 ± 0.00007
C_{rr}	0.00025	0.000098 ± 0.000065
$C_\perp$	1.2719	1.2920 ± 0.0181
$C_{r\alpha}$	-0.0239	-0.0378 ± 0.0131

These results apparently agree quite well.

As for NO_2 a series of trials were run in which the whole of the data was used and only the relative weights of the centrifugal distortion data relative to the frequency data was varied. Letting $\bar{P}$ equal the weight matrix calculated by equation (II,49), trial six uses $\bar{P}_6 = 10^{-2}\bar{P}$, trial seven uses $\bar{P}_7 = 10^{-1}\bar{P}$, trial eight uses $\bar{P}_8 = 10\bar{P}$, trial nine uses $\bar{P}_9 = 10^{2}\bar{P}$ and trial ten uses $\bar{P}_{10} = \bar{P}$. The results from trial ten differ from those of trial one because of round-off error. This is introduced because the U matrix was used explicity by the program to determine C, K and

$(L^{-1})^t$ in trial one whereas in trial ten the $\hat{G}$ and symmetrized Z matrix were input, and $(L^{-1})^t$ not determined. The results are presented in Table IV.

TABLE IV.

	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10
C_r	0.1004 ±.0002	0.1004 ±.0002	0.1004 ±.0002	0.1004 ±.0003	0.1004 ±.0002
C_α	1.3048 ±.0089	1.3048 ±.0092	1.3021 ±.0163	1.3019 ±.0202	1.3041 ±.0112
C_{rr}	0.00024 ±.00015	0.00024 ±.00016	0.00020 ±.00022	0.00019 ±.00028	0.00023 ±.00018
$C_{r\alpha}$	-0.0470 ±.0069	-0.0470 ±.0071	-0.0447 ±.0123	-0.0439 ±.0140	-0.0464 ±.0086

$S^{16}O_2$ Frequencies

Observed	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10
517.8	517.6	517.6	517.5	517.4	517.6
1151.4	1151.3	1151.3	1151.3	1151.3	1151.3
1360.5	1360.3	1360.3	1360.4	1360.5	1360.3

$S^{18}O_2$ Frequencies

Observed	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10
...	497.0	497.0	496.9	496.7	497.0
...	1098.2	1098.2	1098.4	1098.4	1098.3
1316.0	1316.3	1316.3	1316.3	1316.4	1316.3

$S^{16}O^{18}O$ Frequencies

Observed	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10
506.8	507.4	507.4	507.4	507.2	507.4
1120.0	1122.1	1122.1	1122.2	1122.2	1122.1
1341.1	1341.0	1341.0	1341.0	1341.1	1341.0

(TABLE IV continued)

$S^{16}O_2$ Centrifugal Distortion Parameters

Observed	Trial 6	Trial 7	Trial 8	Trial 9	Trial 10
143.473	147.243	147.220	146.439	146.227	147.031
605.843	626.084	626.220	630.891	632.999	627.334
-227.643	-198.078	-198.092	-198.569	-198.919	-198.205
23.774	26.098	26.098	26.097	26.093	26.098

The variance model assumed for centrifugal distortion data seems to be reasonable. The diagonal compliance constants are only slightly affected so that most of the effect shows up in the off-diagonal constants. The effect however on the calculated parameters appears to be consistently negligible.

The magnitudes of the estimated errors are strongly affected due to the fact that the major portion of the estimated variance contributed by the differences between the observed and calculated distortion parameters. Since the p_j's are used directly in this variance calculation the effect is obviously significant.

Dinitrogen Tetroxide

N_2O_4 was chosen to be the first practical application of the model, NO_2 and SO_2 having been chosen more to illustrate and test various aspects of the model than to yield any new information about the molecules.

The structure of N_2O_4 was determined by Darwin Smith (20,56-71) who found the molecule to be planar with the following parameters: N-O bonded distance equal to 1.177Å, the O...O distance across one end of the molecule equal to 2.173Å and the N-N distance equal to 1.752Å. The mean square amplitudes for these and the dependent distances are also reported.

The infrared and Raman spectra have been compiled and reported by Hisatsuni (8,18-60 and 9,1-47).

The compliance constants to be calculated are again those corresponding to the valence force field. The internal coordinates chosen for this are the following: $S_1 = \Delta r_1$, $S_2 = \Delta r_2$, $S_3 = \Delta r_3$, $S_4 = \Delta r_4$, $S_5 = r^e \Delta \alpha_1$, $S_6 = r^e \Delta \alpha_2$, $S_7 = r^e \Delta \beta_1$, $S_8 = r^e \Delta \beta_2$, $S_9 = \Delta R$, $S_{10} = r^e \Delta \tau$, $S_{11} = r^e \Delta \gamma_1$, and $S_{12} = r^e \Delta \gamma_2$.

Since this molecule has D_{2h} symmetry it is possible to construct the following symmetry coordinates.

A_g

$$S_r^{(A_g)} = \tfrac{1}{2}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$$

$$S_\alpha^{(A_g)} = \frac{r^e}{\sqrt{2}} (\Delta\alpha_1 + \Delta\alpha_2)$$

$$S_R^{(A_g)} = \Delta R$$

A_u

$$S_\tau^{(A_u)} = r^e \Delta\tau$$

B_{1g}

$$S_r^{(B_{1g})} = \tfrac{1}{2}(\Delta r_1 - \Delta r_2 + \Delta r_3 - \Delta r_4)$$

$$S_\beta^{(B_{1g})} = \frac{r^e}{\sqrt{2}} (\Delta\beta_1 - \Delta\beta_2)$$

B_{1u}

$$S_\gamma^{(B_{1u})} = \frac{r^e}{\sqrt{2}} (\Delta\gamma_1 + \Delta\gamma_2)$$

B_{2g}

$$S_\gamma^{(B_{2g})} = \frac{r^e}{\sqrt{2}} (\Delta\gamma_2 - \Delta\gamma_1)$$

B_{2u}

$$S_r^{(B_{2u})} = \tfrac{1}{2}(\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4)$$

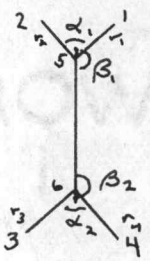
$$S_\beta^{(B_{2u})} = \frac{r^e}{\sqrt{2}} (\Delta\beta_1 + \Delta\beta_2)$$

B_{3u}

$$S_r^{(B_{3u})} = \tfrac{1}{2}(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$$

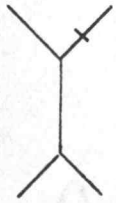
$$S_\alpha^{(B_{3u})} = \frac{r^e}{\sqrt{2}}(\Delta\alpha_1 - \Delta\alpha_2)$$

The numbering of the atoms and coordinates is defined in the following diagram.

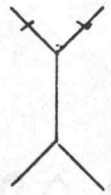


The $\Delta\tau$ coordinate displaces atom 2 and 4 up out of the paper and atom 1 and 3 into the paper. $\Delta\gamma_1$ is defined as atoms 1,2, and 6 coming up and atom 5 going down, $\Delta\gamma_2$ by atoms 3,4, and 5 coming up and 6 going down.

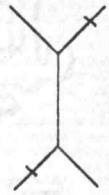
The following diagram illustrates pictorially the definition of the various compliance constants corresponding to the chosen set of internal coordinates.



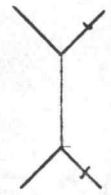
C_r



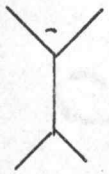
C_{rr}



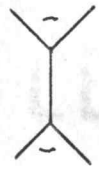
C'_{rr}



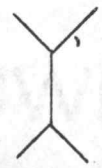
C''_{rr}



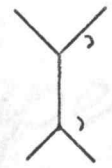
C_α



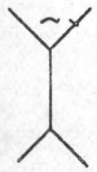
$C_{\alpha\alpha}$



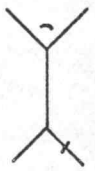
C_β



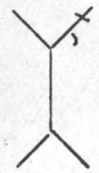
$C_{\beta\beta}$



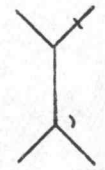
$C_{r\alpha}$



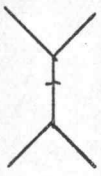
$C'_{r\alpha}$



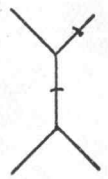
$C_{r\beta}$



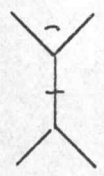
$C'_{r\beta}$



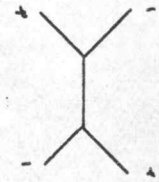
C_R



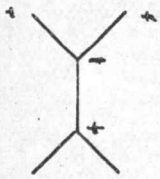
C_{Rr}



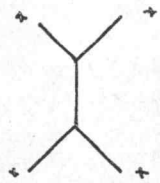
$C_{R\alpha}$



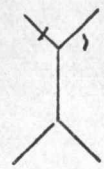
$C_\mathcal{L}$



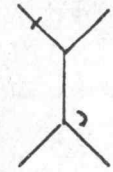
C_γ



$C_{\gamma\gamma}$



$-C_{r\beta}$



$-C'_{r\beta}$

The compliance constants corresponding to the chosen symmetry coordinates are

A_g

$$C_r^{(A_g)} = C_r + C_{rr} + C'_{rr} + C''_{rr}$$

$$C_\alpha^{(A_g)} = C_\alpha + C_{\alpha\alpha}$$

$$C_R^{(A_g)} = C_R$$

$$C_{r\alpha}^{(A_g)} = \sqrt{2}\ (C_{r\alpha} + C'_{r\alpha})$$

$$C_{Rr}^{(A_g)} = 2C_R$$

$$C_{R\alpha}^{(A_g)} = \sqrt{2}\ C_{R\alpha}$$

A_u

$$C_\tau^{(A_u)} = C_\tau$$

B_{1g}

$$C_r^{(B_{1g})} = C_r - C_{rr} - C'_{rr} + C''_{rr}$$

$$C_\beta^{(B_{1g})} = C_\beta - C_{\beta\beta}$$

$$C_{r\beta}^{(B_{1g})} = \sqrt{2}\ (C_{r\beta} - C'_{r\beta})$$

B_{1u}

$$C_{\gamma}^{(B_{1u})} = C_{\gamma} + C_{\gamma\gamma}$$

B_{2g}

$$C_{\gamma}^{(B_{2g})} = C_{\gamma} - C_{\gamma\gamma}$$

B_{2u}

$$C_{r}^{(B_{2u})} = C_{r} - C_{rr} + C'_{rr} - C''_{rr}$$

$$C_{\beta}^{(B_{2u})} = C_{\beta} + C_{\beta\beta}$$

$$C_{r\beta}^{(B_{2u})} = \sqrt{2}\ (C_{r\beta} + C'_{r\beta})$$

B_{3u}

$$C_{r}^{(B_{3u})} = C_{r} + C_{rr} - C'_{rr} - C''_{rr}$$

$$C_{\alpha}^{(B_{3u})} = C_{\alpha} - C_{\alpha\alpha}$$

$$C_{r\alpha}^{(B_{3u})} = \sqrt{2}\ (C_{r\alpha} - C'_{r\alpha})$$

Hisatsuni determined a set of force constants for the in-plane vibrations using frequency data for the

liquid. Since we wished to use the frequency data in conjunction with the gaseous mean square amplitude data we used the frequencies found for the gas phase. Hisatsuni's force constant matrix was inverted and transformed to give a set of compliance constants which would serve as starting values for our determination. In the following tables are listed the Hisatsuni compliance constants (trial one) and those constants determined, in the case of trial two, using just the frequency data and, in the case of trial three, the frequency data and three of the observed mean square amplitudes. The mean amplitudes corresponding to the N-O distance and O...O distance across the end of the molecule were discarded because their determination depended on knowing the correct structure for NO_2 which was in error at the time of Smith's analysis. The mean amplitude for the N-N distance was discarded because of poor resolution in the radial distribution curve. This left three amplitudes, those corresponding to the two across molecule O...O distances and that for the non-bonded N...O distance.

Following the compliance constant table is a table giving the observed data and that calculated for each of the three sets of constants.

In the cases of trials two and trial three the computer selected which of the constants were significant (see Appendix III). Those listed with the value 0. were judged insignificant or indeterminant.

TABLE V.

IN-PLANE CONSTANTS

	Trial 1[a]	Trial 2	Trial 3
C_r	0.0989	0.0986 ± .0003	0.0986 ± .0003
C_{rr}	-0.0053	-0.0094 ± .0003	-0.0094 ± .0003
C'_{rr}	-0.0001	0.	0.
C''_{rr}	0.0017	0.	0.
C_α	0.9252	0.9903 ± .0181	0.9906 ± .0158
$C_{\alpha\alpha}$	0.0004	0.	0.
C_β	0.6135	0.6111 ± .0114	0.6111 ± .0100
$C_{\beta\beta}$	-0.2069	-0.1837 ± .0111	-0.1838 ± .0097
$C_{r\alpha}$	-0.0336	-0.0535 ± .0077	-0.0536 ± .0067
$C'_{r\alpha}$	-0.0005	0.	0.
$C_{r\beta}$	-0.0405	-0.0473 ± .0021	-0.0473 ± .0018
$C'_{r\beta}$	0.0137	0.	0.
C_R	0.7491	0.8134 ± .0457	0.8152 ± .0396
C_{Rr}	0.0241	0.0232 ± .0025	0.0232 ± .0021
$C_{R\alpha}$	-0.0173	0.	0.

(a) Inverted Hisatsuni force constants

(Table V continued)

IN-PLANE FREQUENCIES AND MEAN SQUARE AMPLITUDES

$N^{14}_2O_4$ Frequencies (cm^{-1})

	Observed	Trial 1	Trial 2	Trial 3
A_{1g}				
ν_3	260	267	260	260
ν_2	812	809	813	813
ν_1	1373	1370	1371	1371
B_{1g}				
ν_6	480	479	481	481
ν_5	1710	1721	1710	1710
B_{2u}				
ν_{10}	385	387	381	381
ν_9	1748	1755	1746	1746
B_{3u}				
ν_{12}	750	753	750	750
ν_{11}	1261	1254	1261	1261

$N^{15}_2O_4$ Frequencies (cm^{-1})

	Observed	Trial 1	Trial 2	Trial 3
A_{1g}				
ν_3	260	266	258	258
ν_2	800	800	801	801
ν_1	1350	1347	1352	1352
B_{1g}				
ν_6	478	475	477	477
ν_5	1670	1682	1671	1671

(Table V continued)

	Observed	Trial 1	Trial 2	Trial 3
B_{2u}				
ω_{10}	377	386	381	381
ω_{9}	1707	1717	1709	1709
B_{3u}				
ω_{12}	739	744	739	739
ω_{11}	1251	1241	1251	1251

$N_2^{14}O_4$ Mean Square Amplitudes

	Observed	Trial 1	Trial 2	Trial 3
N-O	.001747	...	.001457*	.001457*
N-N	.005625	...	.004479*	.004486*
$O_1 \cdots O_2$	.002430	...	.002117*	.002116*
N...O	.006053	...	.005464*	.005470
$O_2 \cdots O_3$	.009178	...	.008786*	.008793
$O_1 \cdots O_4$	.005432	...	.005519*	.005524

* Not used for fitting in this trial.

As before the results of trial three can be called the "most compatible" constants. These constants are only slightly different from those of trial two while in all cases the estimated errors are reduced, indicating that while the mean amplitudes did not give us enough information to determine any other constants, they did increase our confidence in those which could be determined.

The difference between trial one (Hisatsuni's values) and trial three are noticeable mostly for the diagonal constants C_α and C_R. These differences are probably due to Hisatsuni's use of the liquid frequencies combined with the fact that a slightly different G matrix was used here. The other differences observed for the other constants may be due to the reasons above as well as to round-off error in the inversion.

In the following table the compliance constants for the out-of-plane modes are determined. The wag (γ) constants are calculated from observed frequencies and the torsion constant from a frequency estimated from thermal data, since the torsional mode is both infrared and Raman inactive. These constants are determined separately from the in-plane constants because there are no constants common to both the in-plane and out-of-plane blocks. The in-plane constants were determined together

since all blocks have at least four constants in common (C_r , C_{rr} , C'_{rr} , and C''_{rr}) , and thus a representative fit could not be determined using only the separated symmetry blocks. Also all of the in-plane constants are involved in the mean amplitude fitting.

It would also be incorrect to estimate the errors in the out-of-plane constants using a $\tilde{\sigma}^2$ calculated from derivations in both the in-plane and out-of-plane frequencies, since there is no relationship between them.

The out-of-plane constants are themselves determined in two sets: C_γ and $C_{\gamma\gamma}$ together; and C_τ by itself for the same reasons.

There is no error estimate for the C_τ constant because there is only one observation. This, however, does not mean there is no error in the calculated C_τ .

TABLE VI.

OUT-OF-PLANE CONSTANTS

Torsion

$C_{\tau} = 199.3$

Frequency

50 cm^{-1}

Out-of-Plane Wags

$C_{\gamma} = 5.7051 \pm .0421$

$C_{\gamma\gamma} = 0.6734 \pm .0421$

			Frequencies (cm^{-1})	
			Observed	Calculated
$N^{14}_2O_4$	ω_8	B_{2g}	675	668
$N^{15}_2O_4$	ω_8	B_{2g}	641	649
$N^{14}_2O_4$	ω_7	B_{1u}	430	430
$N^{14}_2O_4$	ω_7	B_{1u}	420	420

In the course of the calculations on N_2O_4, J.C. Decius (7) noted that some of the odd band shapes observed in the infrared spectrum might be explained in terms of a torsional angle dependence of the kinetic energy matrix, G.

In the following paragraphs I will give a brief resume of the resulting theory and then show the application to N_2O_4.

The effect can most simply be explained in terms of an "anharmonicity" constant, $X_{kk'}$, in the expansion vibrational energy of the molecule,

$$E_{vib} = hc \left[\sum_k \omega_k (V_k + \tfrac{1}{2}) + \sum_k \sum_{k'} X_{kk'} \times (V_k + \tfrac{1}{2})(V_k + \tfrac{1}{2}) \right] \text{ where } 1 \leq k \leq k' \leq 3N-6 .$$

It should be noted that while this equation is identical with that used for non-harmonic potentials, we here are considering harmonic potentials, and $X_{kk'}$ is really a coupling due only to torsion (τ) angle.

There are two ways of simply treating the effect on the vibrational energy. The first is a perturbation

treatment in which the $X_{kk'}$ are explicity evaluated and the second a more straight forward technique involving evaluating G for different values of τ and using these G's together with the equilibrium potential constants to calculate the vibrational frequencies.

In the perturbation technique the kinetic energy term, 2T , is expanded in matrix notation as follows in

$$2T = p^t(G^o + G'\tau + \tfrac{1}{2}G''\tau^2)p \qquad \text{(III,2)}$$

where

$$G^o = G(\tau \text{ equil})$$

$$G' = \frac{\partial G(\tau)}{\partial \tau} \tau\text{equil}$$

$$G'' = \frac{\partial^2 G(\tau)}{\partial \tau^2} \tau\text{equil}$$

and the potential energy is left in usual form

$$2V = S^t F S \qquad \text{(III,3)}$$

where the S are internal symmetry coordinates and p their associated momenta.

Using the usual notation for the transformation to internal coordinates

$$S = LQ \quad \text{and} \quad p' = p'L^{-1}$$

yields the following two equations for $2V$ and $2T$

$$2V = Q^t \Lambda Q \tag{III,4}$$

$$2T = p^t p + p^t L^{-1} G^1 (L^{-1})^t p\, \tau + \tfrac{1}{2} p^t L^{-1} G'' (L^{-1})^t p\, \tau^2 \tag{III,5}$$

If we let

$$\Gamma' = L^{-1} G^1 (L^{-1})^t$$

and

$$\Gamma'' = L^{-1} G'' (L^{-1})^t$$

(III,5) may be rewritten as

$$2T = p^t p + p^t \Gamma' p \tau + \tfrac{1}{2} p^t \Gamma'' p^2 \tau^2 \tag{III,6}$$

In order to find the contributions to the $X_{kk'}$ terms using perturbation theory it is convenient to write (III,6) in summation notation

$$2T = \Sigma p_k^2 + \tau \sum_k \sum_{k'} p_k \Gamma'_{kk'} p_{k'}$$

$$+ \tfrac{1}{2} \tau^2 \sum_k \sum_{k'} p_k \Gamma''_{kk'} p_{k'} \tag{III,7}$$

We first treat the τ^2 term in (III,7) .

For $k = k'$ first order perturbation theory results in an energy contribution

$$(\Gamma''_{kk}/4F_\tau)(hc)^2 \omega_\tau \omega_k (V_k + \tfrac{1}{2})(V_\tau + \tfrac{1}{2})$$

which leads to a contribution to $X_{k\tau}$ of

$$X^{(1)}_{k\tau} = \omega_k \Gamma''_{kk}(\omega_\tau/8V_0) \quad \text{(III,8)}$$

where V_0 is the rotational barrier height in wave numbers.

For $k \neq k'$ second order theory gives an energy correction cubic in the vibrational quantum numbers and thus not affecting the X_{kk} terms.

For the two cases involving the τ term we find for $k = k'$ a second order correction

$$-\tfrac{1}{4}(\Gamma'_{kk})^2(\omega_k^2/V_0)(V_k + \tfrac{1}{2})^2$$

which vanishes unless τ is totally symmetric.

For $k \neq k'$ there are contributions to both kinds of anharmonicity constants. They are

$$X_{kk'} = \tfrac{1}{4}(\Gamma'_{kk'})^2(\omega_\tau^2/V_0)\frac{\omega_k \omega_{k'}(\omega_k^2 + \omega_{k'}^2 - \omega_\tau^2)}{\left[(\omega_k + \omega_{k'})^2 - \omega_\tau^2\right]\left[(\omega_k - \omega_{k'})^2 - \omega_\tau^2\right]}$$

where $k \neq k' \neq \tau$ (III,9)

and

$$X_{k\tau}^{(2)} = \tfrac{1}{4}(\omega_\tau\,\omega_k/V_0)\sum_{k'}(\Gamma_{kk'})^2 \times$$

$$\frac{\omega_{k'}^2(\omega_k^2 - \omega_{k'}^2 + \omega_\tau^2)}{\left[(\omega_k+\omega_\tau)^2 - \omega_{k'}^2\right]\left[(\omega_k-\omega_\tau)^2 - \omega_{k'}^2\right]} \qquad \text{(III,10)}$$

$$X_{k\tau} = X_{k\tau}^{(1)} + X_{k\tau}^{(2)}$$

where $X_{k\tau}^{(1)}$ and $X_{k\tau}^{(2)}$ are defined by equations (III,8) and (III,10) respectively.

The vibrational energy for a particular mode perturbed by the frequency interactions may be written as

$$E_k = \left[\omega_k + \sum_{k'} X_{kk'}(V_{k'} + \tfrac{1}{2})\right](V_k + \tfrac{1}{2})$$

Then for a fundamental transition the observed frequency $\nu_k(cm^{-1})$ is given by

$$\nu_k = \left[\omega_k + \Sigma X_{kk'}(V_{k'} + \tfrac{1}{2})\right](V_k + 1 + \tfrac{1}{2} - V_k - \tfrac{1}{2})$$

$$= \omega_k + \Sigma X_{kk'}(V_{k'} + \tfrac{1}{2}) \qquad \text{(III,11)}$$

which has an obvious dependence on the quantum numbers corresponding to the other normal modes.

In order to evaluate these terms for N_2O_4 the following terms will be required

$$V_o = 1014 \text{ cm}^{-1}$$

$$\omega_\tau = 61 \text{ cm}^{-1}$$

(this ω_τ was calculated from V_o), the G , G' , and G" matrices, Γ' and Γ'' and the frequencies for the other modes.

G , G' , and G''

Using the symmetry coordinates previously defined for the V_h symmetry only the following G elements are found to depend on τ (5)

$$G_{r\beta} = -\sqrt{2}\ \mu_N \sin\frac{\alpha}{2}\ \cos\frac{\alpha}{2} + \frac{r}{R}(1 \pm \cos\tau)$$

$$G_{r\gamma} = \sqrt{2}\ \frac{r}{R}\ \mu_N\ \sin\frac{\alpha}{2}\ \sin\tau$$

$$G_{\beta} = \mu_N\left[\frac{r^2}{R^2} + \left(\frac{r}{R} + \cos\frac{\alpha}{2}\right)^2 \pm \frac{2r}{R}\left(\frac{r}{R} + \cos\frac{\alpha}{2}\right)\cos\tau\right] + \tfrac{1}{2}\mu_o$$

$$G_{\beta\gamma} = -\frac{r}{R}\ \mu_N\left(\frac{2r}{R} + \cos\frac{\alpha}{2} + \sec\frac{\alpha}{2}\right)\sin\tau$$

$$G_{\gamma} = \mu_N\left[\frac{r^2}{R^2} + \left(\frac{r}{R} + \sec\frac{\alpha}{2}\right)^2 \mp \frac{2r}{R}\left(\frac{r}{R} + \sec\frac{\alpha}{2}\right)\cos\tau\right]$$
$$+ \tfrac{1}{2}\ \mu_o \sec^2\frac{\alpha}{2}$$

where the upper sign in $\pm$ or $\mp$ refers to B_1 , the lower to B_2 . Note that $G_{r\gamma}$ and $G_{\beta\gamma}$ are zero for $\tau = 0$, thus allowing the further factoring into the g and u blocks seen for V_h . The G' and G'' are blocked according to the more general V symmetry as will be shown later.

Taking the partial derivatives with respect to gives the following results.

$$G'_{r\beta} = -\sqrt{2}\,\mu_N \sin\frac{\alpha}{2}\frac{r}{R}(\mp \sin\tau)$$

$$= \sqrt{2}\,\mu_N \sin\frac{\alpha}{2}\frac{r}{R}(\pm \sin\tau)$$

$$G''_{r\beta} = \sqrt{2}\,\mu_N \sin\frac{\alpha}{2}\frac{r}{R}(\pm \cos\tau)$$

$$G'_{r\gamma} = \sqrt{2}\,\frac{r}{R}\,\mu_N \sin\frac{\alpha}{2}\cos\tau$$

$$G''_{r\gamma} = -\sqrt{2}\,\frac{r}{R}\,\mu_N \sin\frac{\alpha}{2}\sin\tau$$

$$G'_{\beta} = \mu_N \frac{2r}{R}\left(\frac{r}{R} + \cos\frac{\alpha}{2}\right)\sin\tau$$

$$G''_{\beta} = \mu_N \frac{2r}{R}\left(\frac{r}{R} + \cos\frac{\alpha}{2}\right)\cos\tau$$

$$G'_{\beta\gamma} = -\frac{r}{R}\,\mu_N\left(\frac{2r}{R} + \cos\frac{\alpha}{2} + \sec\frac{\alpha}{2}\right)\cos\tau$$

$$G''_{\beta\gamma} = \frac{r}{R}\,\mu_N\left(\frac{2r}{R} + \cos\frac{\alpha}{2} + \sec\frac{\alpha}{2}\right)\sin\tau$$

$$G'_{\gamma} = \pm\mu_N \frac{2r}{R}\left(\frac{r}{R} + \sec\frac{\alpha}{2}\right)\sin\tau$$

$$G''_{\gamma} = \pm\mu_N \frac{2r}{R}\left(\frac{r}{R} + \sec\frac{\alpha}{2}\right)\cos\tau$$

Since all other partials are equal to zero, the G' and G'' matrices are factored into B_1 and B_2 blocks.

For example

G'	S_r	S_β	S_γ
	0	$G'_{r\beta}$	$G'_{r\gamma}$
		G'_β	$G'_{\beta\gamma}$
			G'_γ

Since G is symmetric, G' and G" are also symmetric. Using the following quantities

$$r = 1.177\text{A}^{\circ}$$

$$R = 1.752\text{A}^{\circ}$$

$$\sin\frac{\alpha}{2} = 0.92321$$

$$\cos\frac{\alpha}{2} = 0.3843$$

$$\sec\frac{\alpha}{2} = 2.6021$$

$$\mu_N = 0.0713$$

we can now evaluate the derivatives

$G'_{r\beta} = 0$ $\qquad$ $G''_{r\beta} = \pm 0.0625$

$G'_{r\gamma} = 0.0625$ $\qquad$ $G''_{r\gamma} = 0$

$G'_\beta = 0$ $\qquad$ $G''_\beta = 0.1011$

$G'_{\beta\gamma} = -0.2073$ $\quad$ $G''_{\beta\gamma} = 0$

$G'_{\gamma} = 0$ $\quad$ $G''_{\gamma} = \pm 0.3136$

In order to now evaluate Γ' and Γ'' we need the L^{-1} elements corresponding to the B_1 and B_2 blocks of G' and G''. The L^{-1} matrices are output by the program for the final set of compliance constants. For $^{14}N_2O_4$ they are

B_1

L^{-1}	S_r	S_β	S_γ
Q_6	2.7845	3.1056	0.
Q_5	-2.2489	0.0918	0.
Q_7	0.	0.	1.2000

B_2

L^{-1}	S_r	S_β	S_γ
Q_{10}	0.9209	5.3511	0.
Q_9	-2.3808	-0.2763	0.
Q_8	0.	0.	0.8697

Using these matrices we can now evaluate the corresponding Γ' and Γ'' matrices using the equations

$$\Gamma' = L^{-1}G'(L^{-1})^t$$

$$\Gamma'' = L^{-1}G''(L^{-1})^t$$

B_1

$$\Gamma' = \begin{vmatrix} 0. & 0. & -0.5636 \\ & 0. & -0.1914 \\ & & 0. \end{vmatrix}$$

$$\Gamma'' = \begin{vmatrix} 0.1342 & -0.4487 & 0. \\ & -0.0265 & 0. \\ & & +0.4515 \end{vmatrix}$$

B_2

$$\Gamma' = \begin{vmatrix} 0. & 0. & -0.9144 \\ & 0. & -0.0796 \\ & & 0. \end{vmatrix}$$

$$\Gamma'' = \begin{vmatrix} 2.2788 & 0.6626 & 0. \\ & -0.0743 & 0. \\ & & -0.2371 \end{vmatrix}$$

For purpose of calculation we will use the frequencies calculated from the most compatible compliance constants for the B_1 and B_2 blocks. The other frequencies are not required since the corresponding Γ','' matrices vanish.

B_1

$\omega_6 = 481\ cm^{-1}$ (β mode)

$\omega_5 = 1710\ cm^{-1}$ (r mode)

$\omega_7 = 430\ cm^{-1}$ (γ mode)

B_2

$\omega_{10} = 381\ cm^{-1}$ (β mode)

$\omega_9 = 1746\ cm^{-1}$ (r mode)

$\omega_8 = 668\ cm^{-1}$ (γ mode)

Using equations (III,8) and (III,10) together with the above tabulated quantities, we find the following results for the $X_{k\tau}$ terms

B_1

$X_{6\tau}^{(1)} = 0.4853$ $\quad X_{6\tau}^{(2)} = -23.0372$ $\quad X_{6\tau} = -22.5519$

$X_{5\tau}^{(1)} = -0.3407$ $\quad X_{5\tau}^{(2)} = 0.0616$ $\quad X_{5\tau} = -0.2791$

$X_{7\tau}^{(1)} = 1.4598$ $\quad X_{7\tau}^{(2)} = 21.6976$ $\quad X_{7\tau} = 23.1572$

B_2

$X_{10\tau}^{(1)} = 6.5281$ $\quad X_{10\tau}^{(2)} = -7.3684$ $\quad X_{10\tau} = -0.8403$

$X_{9\tau}^{(1)} = -0.9752$ $\quad X_{9\tau}^{(2)} = 0.0260$ $\quad X_{9\tau} = -0.9492$

$X_{8\tau}^{(1)} = -1.1908$ $\quad X_{8\tau}^{(2)} = 4.2316$ $\quad X_{8\tau} = 3.0408$

Using equation (III,9) leads to the following results

B_1

$X_{67} = X_{76} = -26.8672$

$X_{57} = X_{75} = 0.0100$

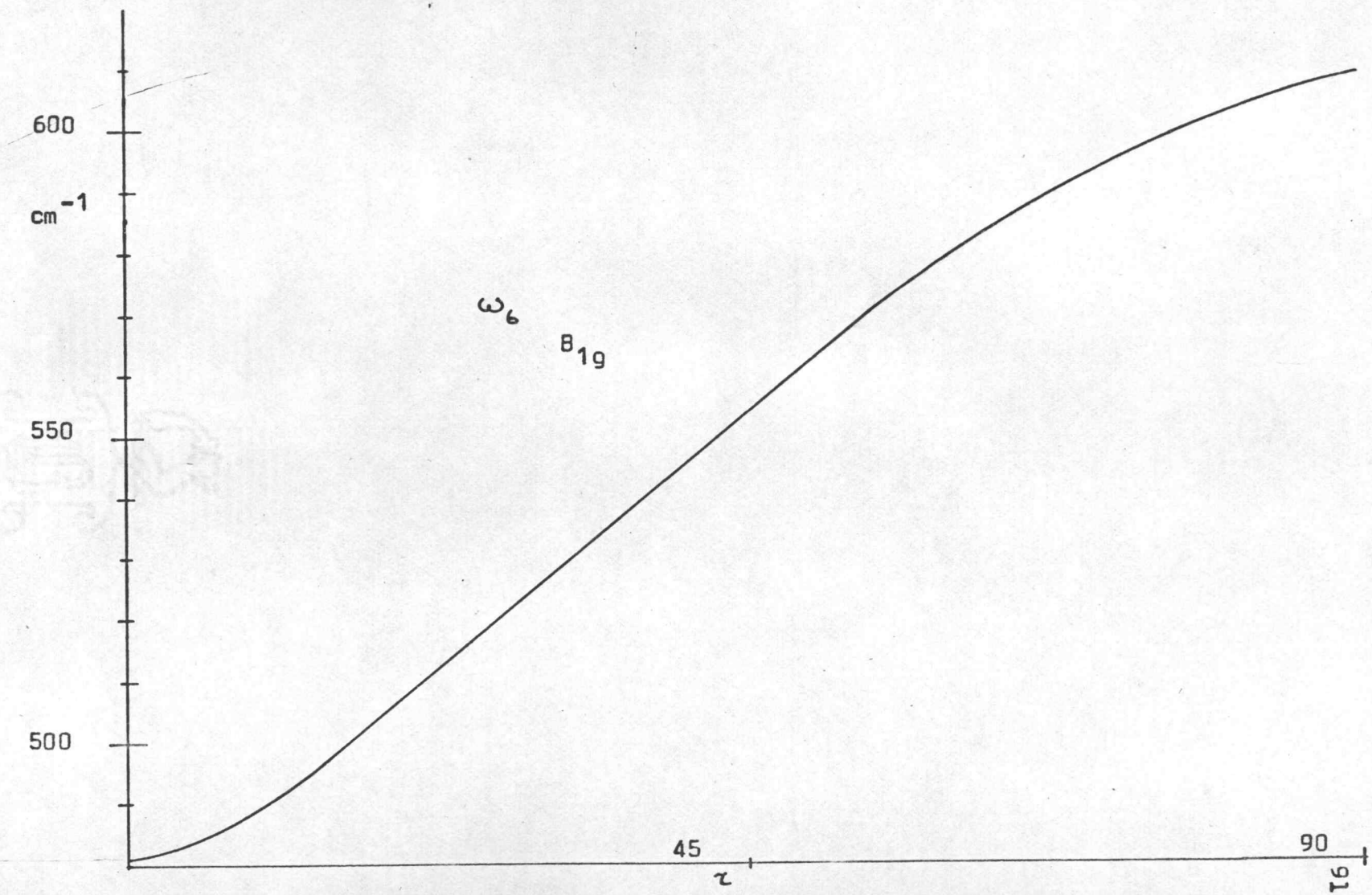
B_2

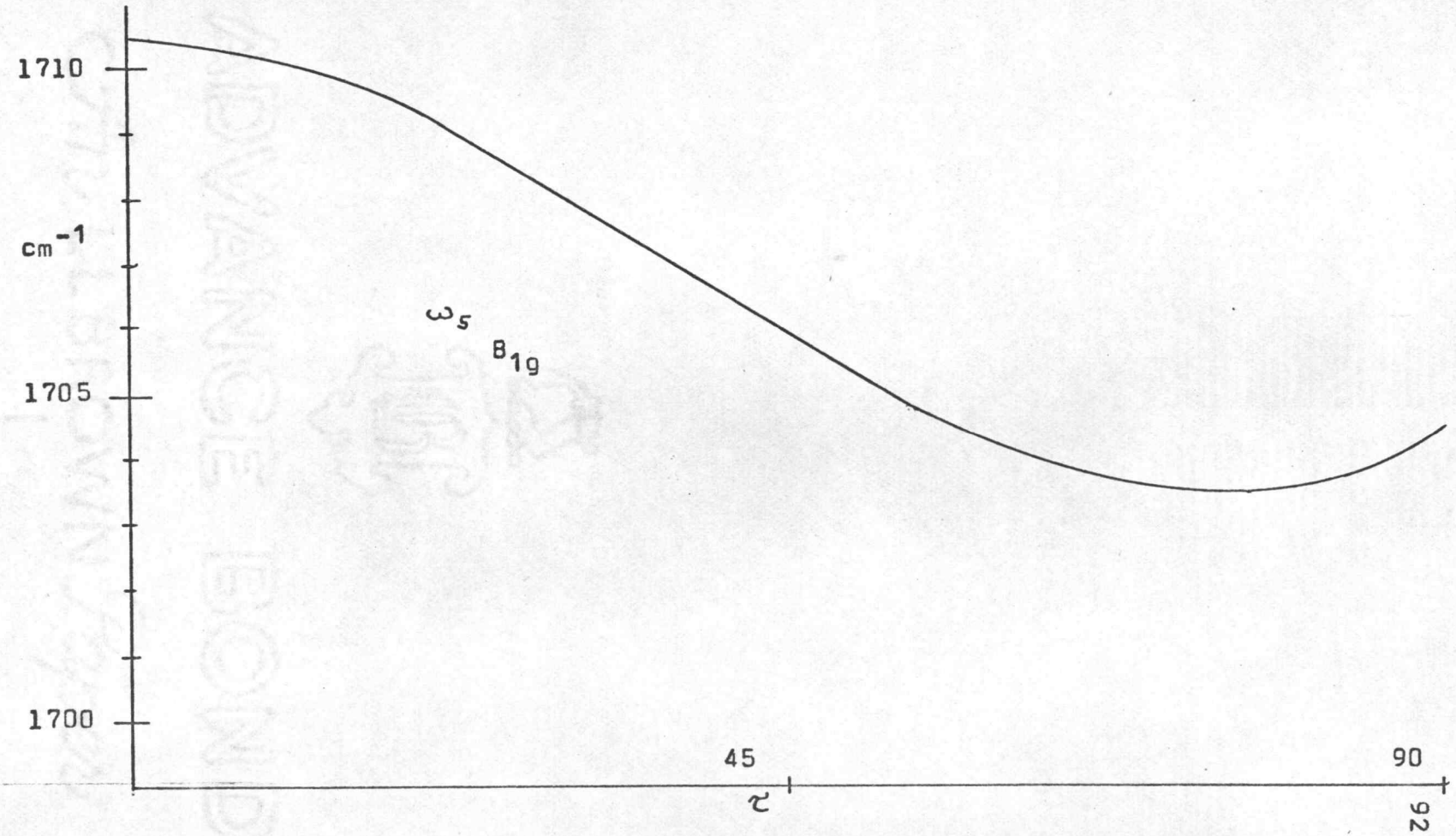
$X_{10,8} = X_{8,10} = 1.3300$

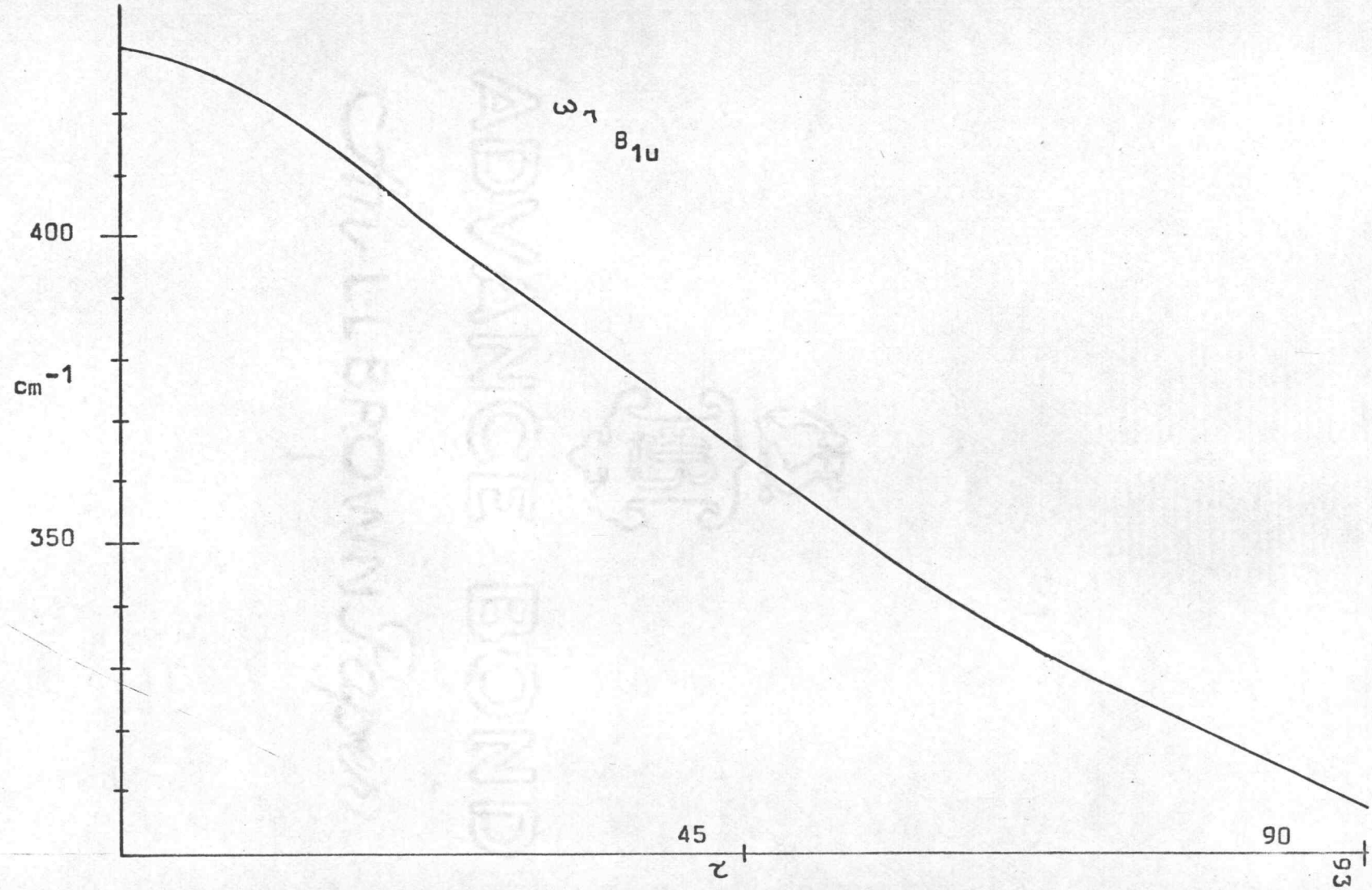
$X_{98} = X_{89} = 0.0032$

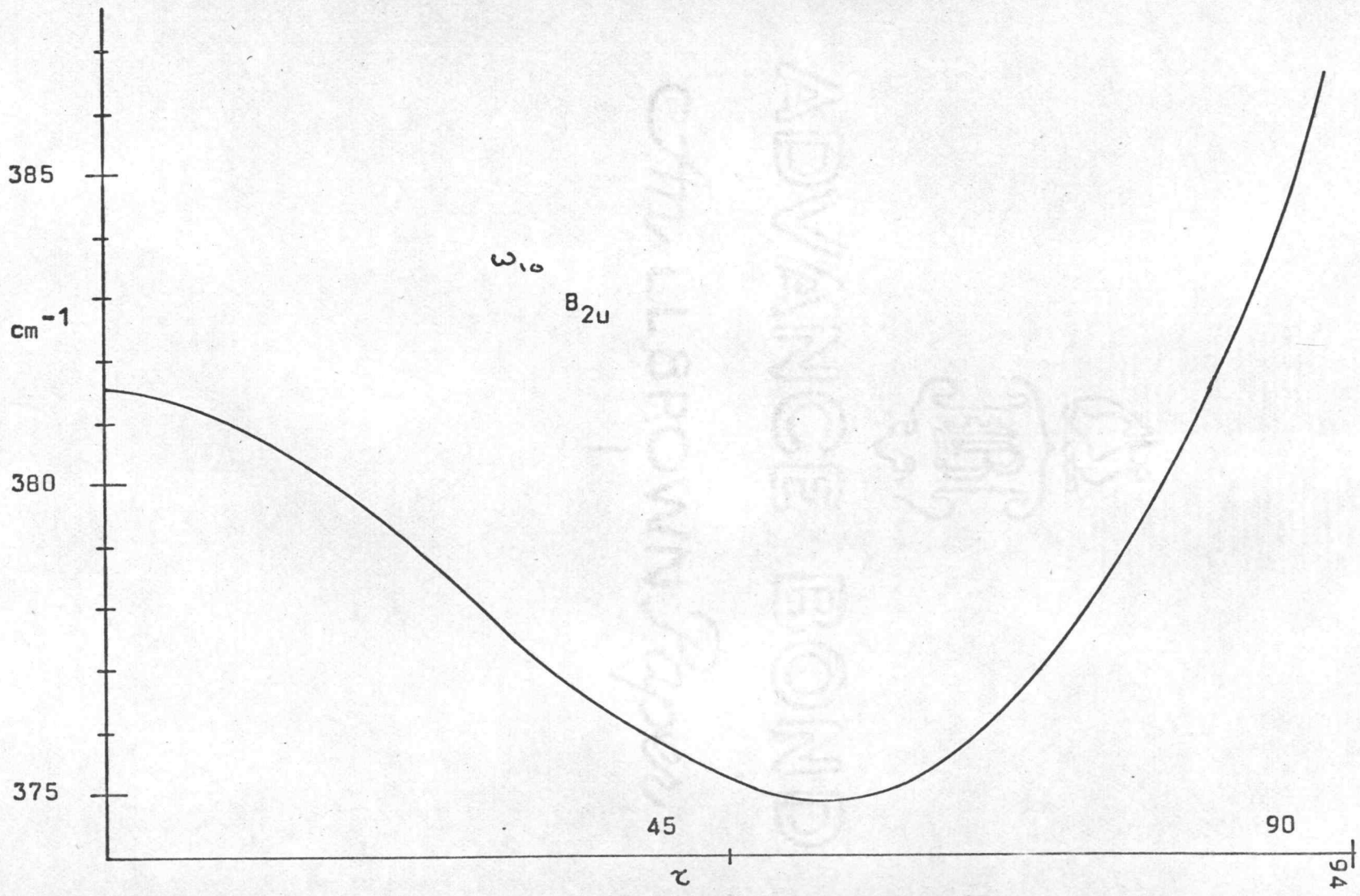
It should be noted that both the magnitude and sign of $X_{6\tau}$ and X_{67} are strongly dependent on the ω_τ value used. Since ω_τ is not observed directly the value used is subject to large error. This could lead to a large error in prediction of the shape of the observed band as the quantum levels above the ground state are only significantly occupied for the τ vibration.

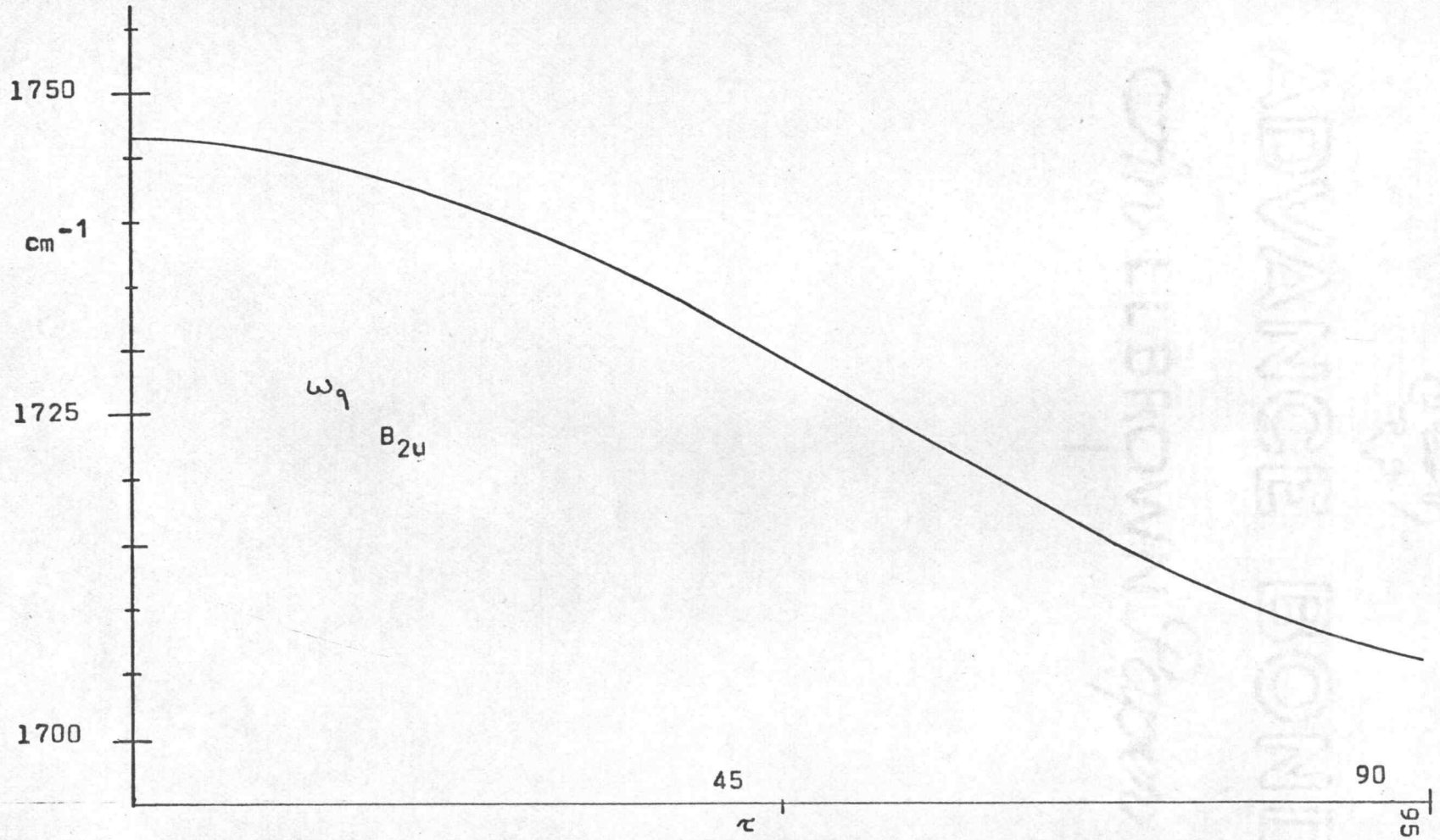
In the more straight-forward technique which is in reality a Born-Oppenheimer type treatment, the G matrix program was used to evaluate the G elements corresponding to the B_1 and B_2 blocks for values of τ between zero and ninety degrees. These G's were then used to find the K matrices and the secular equation solved assuming no change in the C matrices. The frequencies are plotted on the following pages as a function of τ.

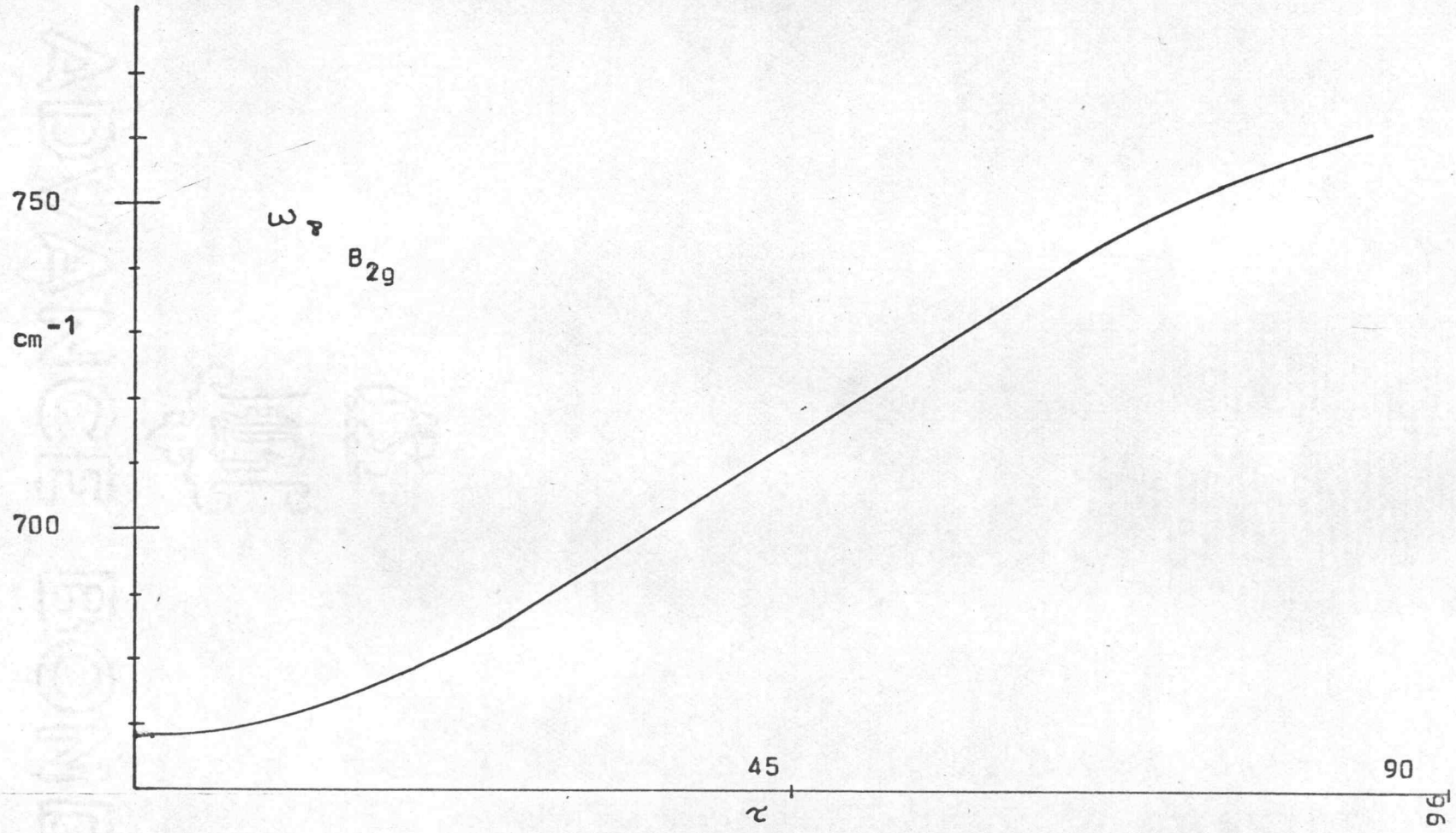

600
cm-1
550
500
ω6
B1g
45
90
z
91


1710
cm-1
1705
1700
ω5
B1g
45
90
τ
92


$^3\pi^*$ B_{1u}
400
cm^{-1}
350
45
90
τ
93


385
cm-1
380
375
3,0
B2u
45
90
τ
94


1750
cm-1
1725
1700
ω9
B2u
45
90
τ
95


750
700
cm -1
3 B2g
45
90
χ

In the Born-Oppenheimer treatment the total energy of the high frequency modes serves as the potential energy to the low frequency mode. A classical perturbation argument leads to a equation similar to (III,10) which is dependent on the curvature of the frequency curves at the origin. J.C. Decius has used this equation to determine the $X_{k\tau}$ values for the affected modes. These are tabulated below with the corresponding results from the straight perturbation theory.

	Born-Oppenheimer	Perturbation
$X_{6\tau}$	6.85	-22.55
$X_{5\tau}$	negligible	- 0.28
$X_{7\tau}$	-8.7	23.16
$X_{10\tau}$	-0.57	-0.84
$X_{9\tau}$	-0.953	-0.949
$X_{8\tau}$	2.8	3.04

These results for the Born-Oppenheimer treatment are valid only near the origin $\tau = 0$. The behavior seen on the graphs beyond the origin would probably be described by a further expansion of the perturbation arguments to terms in τ^3 , etc. Comparison of the results of the

results of the two treatments points to an apparent failure of the Born-Oppenheimer theory for the ω_6 and ω_7 frequencies. This failure is due in part to the absence of ω_τ in the denominator of the resulting equation and in part to a Fermi resonance effect which does not allow correct assignment of the bands on an harmonic oscillator model.

The theoretically more reliable perturbation results should prove quite useful for purposes of resolving structural and assignment questions. This is true because L^{-1}, G' and G'' are not particularly sensitive to the potential constants used or to structure (with the exception of the equilibrium value of τ) thus allowing semi-quantitative evaluation of Γ' and Γ'' from transferred compliance constants and preliminary structural information. This theory also explains some of the obvious anomalies previously observed in the spectra of X_2Y_4 molecules (very assymmetric bands, doublets where there should be singlets, etc.) which have proved difficult to reconcile with predictions based on an unperturbed model.

CONCLUSIONS

The model developed in Section Two and illustrated in Section Three is not intended to be used or interpreted blindly. For the small molecules, NO_2 and SO_2, it was possible to run various combinations of data and weights and to observe the effects on the compliance constants. In the practical case this sort of operation is not usually possible. Indeed, the motivation behind the model was to use data from the electron diffraction and microwave experiments to replace infrared and Raman frequencies where they are unavailable in the literature or difficult to get by experiment. Since usually the frequency data is known to much higher precision than either the mean square amplitude or the centrifugal distortion data, the best results are obtained when there is sufficient frequency data. The results obtained when the other data provides the major portion of the constants can at best only be said to be rough estimates. Of course, these estimates are considerably better than nothing at all.

As previously mentioned in discussions of the results for NO_2 and SO_2, the weight estimates (p_i) obtained in Section Two seem to be reasonable and not particularly critical. However, it should be remarked that if better

estimates than $\sigma^2 = 0.1(cm^{-1})^2$ for frequency data are known these should be used, since then the model will be definitely representative of the data. Also mentioned in those discussions was the necessity of having more than one piece of data bearing on a given constant in order to have some confidence in that constant and its estimated error. This is especially important in the case of the larger molecules where there might be some tendency just to total the number of observed data and note that this total is larger than the number of constants being determined. It is quite possible that some of the constants are insensitive to this data and thus indeterminate.

It is necessary that one understand not only limitations of the data but also those of the model. These mostly are related to the approximations used in various places in its derivation. The first approximation is that expressed in equation (II,13) involving the use of the truncated Taylor series, which is only valid when terms involving the second derivatives are small compared to those involving the first derivatives. The second is in the evaluation of the partial derivatives of the mean square amplitudes where the derivative is calculated numerically and is thus subject to a Taylor series type error. The third is in the least squares model which assumes that the p_i are known exactly; where, of course,

we only are able to estimate them. The fourth is in the use of equation (II,21) to evaluate the derivates of phi. This equation ignores the off-diagonal terms of the $\Delta \Phi$ matrix and thus can lead to improper values for the first derivatives if these off-diagonal terms are significant.

A final difficulty lies in the possibility of multiple solutions. The algebraic form of the exact solution of the secular determinant shows that in general more than one solution exists. In the present work everything depends upon the initial approximation used. Physical intuition is at present the only guide here.

If the model is used with knowledge of the limitations mentioned in the above paragraphs, it is possible to use it to find a reasonable set of constants and further to use these constants to give good estimates of isotopic frequencies, mean square amplitudes, and centrifugal distortion data which have not yet been observed. These constants and other data output from the model may also be used, as for N_2O_4, to derive further effects dependent on the force field and geometry of the molecules.

Such a model as this should serve as a useful tool in the utilization of all observed data to determine what

could not be determined using simply one kind of data. As further kinds of data become available there is no reason why these cannot be fit into the model, it only being necessary to be able to evaluate the derivatives and the weights (ρ_i's) as well as the functions themselves.

BIBLIOGRAPHY

1. Arakawa, Edward T. and Alvin H. Nielsen. Infrared spectra and molecular constants of $N^{14}O_2$ and $N^{15}O_2$. Journal of Molecular Spectroscopy 2: 413-427. 1958.

2. Bird, George et al. Microwave spectrum of NO_2 : Fine structure and magnetic coupling. The Journal of Chemical Physics 40:3378-3390. 1964.

3. Blank, Jerome S. A structure investigation of nitrogen dioxide, I. Geometry and amplitudes of vibration, II. Quadratic potential constants. Ph.D. thesis. Corvallis, Oregon State University, 1964. 137 numb. leaves.

4. Cyvin, S.J. Vibrational mean amplitude matrices, I. Secular equations involving mean amplitudes of vibration, and approximate computation of mean square amplitude matrices. Spectrochimica Acta 15: 828-834. 1959.

5. Cyvin, S.J. Associate Professor, Institute of Theoretical Chemistry, Technical University of Norway, Trondheim, Norway. Private communication. Corvallis. 1965.

6. Decius, J.C. Compliance matrix and molecular vibrations. Journal of Chemical Physics 38:241-248. 1963.

7. Decius, J.C. Professor, Department of Chemistry, Oregon State University, Corvallis, Oregon. Private communication. Corvallis. 1965.

8. Hisatsuni, I.C. The spectra of nitrogen oxides, I. The spectrum of N_2O_4. Manhattan, 1959. 60 numb. leaves. (Kansas State University. Dept. of Chemistry. Scientific report no. 1 on Air Force Contract AF 19(604)-2255).

9. _____. The spectra of nitrogen oxides, II. The Urey-Bradley force constants in N_2O_4 and the infrared spectrum of solid $N^{15}_2O_4$. Manhattan, 1960. 47 numb. leaves. (Kansas State University. Dept. of Chemistry. Scientific report no. 2 on Air Force Contract AF 19(604)-2255).

10. Kivelson, D. The determination of the potential constants of SO_2 from centrifugal distortion effects. Journal of Chemical Physics 22:904-908. 1954.

11. Kivelson, D. and E.B. Wilson, Jr. Theory of centrifugal distortion constants of polyatomic rotor molecules. Journal of Chemical Physics 21:1229-1236. 1953.

12. Mann, D.E. et al. Normal coordinate analysis of halogenated ethylenes, I. General methods. Journal of Chemical Physics 27:43-51. 1957.

13. Mood, Alexander M. and Franklin A. Graybill. Introduction to the theory of statistics. New York, McGraw-Hill, 1963. 443 p.

14. Morino, Yonezo, Kozo Kuchitsu, and Takehiko Shimanouchi. The mean amplitudes of thermal vibrations in polyatomic molecules, I. $CF_2 = CF_2$ and $CH_2 = CF_2$. Journal of Chemical Physics 20: 726-733. 1952.

15. Morino, Yonezo et al. The mean amplitudes of thermal vibrations in polyatomic molecules, II. An approximate method for calculating mean square amplitudes. Journal of Chemical Physics 21:1927-1933. 1953.

16. Overend, John and J.R. Scherer. Transferability of Urey-Bradley force constants, I. Calculation of force constants on a digital computer. Journal of Chemical Physics 32:1289-1295. 1960.

17. Polo, S.R. Matrices D^{-1} and G^{-1} in the theory of molecular vibrations. Journal of Chemical Physics 24:1133-1138. 1956.

18. Polo, S.R. and M. Kent Wilson. Infrared spectrum of $S^{16}O^{18}O$ and the potential constants of SO_2. Journal of Chemical Physics 22:900-903. 1954.

19. Schactschneider, J.H. Vibrational analysis of polyatomic molecules, III. Vibrational secular equation programs. Emeryville, California. Shell Oil Co. 1962. 70 numb. leaves. (Shell technical report no. 263-62).

20. Smith, Darwin. Some electron diffraction studies, I. Electron diffraction studies of some heavy metal hexafluorides. II. The molecular structure of N_2O_4. III. Applications of the method of least squares in electron diffraction investigations. Ph.D. thesis. Pasadena, California Institute of Technology, 1959. 90 numb. leaves.

21. Sukolnikoff, I.S. (ed.) Introduction to the theory of probability and statistics. New York, John Wiley, 1950. 238 p.

22. Wilson, E. Bright, Jr. A method of obtaining the expanded secular equation for the vibration frequencies of a molecule. Journal of Chemical Physics 7: 1047-1052. 1939.

23. Wilson, E. Bright, Jr., J. C. Decius, and Paul C. Cross. Molecular vibrations. New York, McGraw-Hill, 1955. 388 p.

APPENDIX

APPENDIX I

The B Matrix

In order to calculate frequencies, mean square amplitudes, and centrifugal distortion constants, one needs to have the K matrix, the V matrix, and the $J_{\alpha\beta}$ vectors. These quantities are all related to the B matrix where B is the transformation matrix relating internal displacement coordinates, S_t, the cartesian displacement coordinates, ξ_i

$$S = B\,\xi . \qquad (A1,1)$$

The elements of the B matrix are normally defined using the s vector technique (23,55-63) in which S_t is defined by the equation

$$S_t = \sum_{\alpha=1}^{N} s_{t\alpha}\,\rho_\alpha \qquad (A1,2)$$

where ρ_α is the vector

$$\rho_\alpha = \begin{vmatrix} \xi_{3\alpha-2} \\ \xi_{3\alpha-1} \\ \xi_{3\alpha} \end{vmatrix} \qquad (A1,3)$$

and the $S_{t\alpha}$ is a vector defined on an atom α so that its direction is that which will produce the maximum

increase in S_t and its magnitude is the increase in S_t produced by a unit displacement of atom α in this most effective direction.

Comparison of equations (A1,1) and (A1,2) shows that the three elements of the $s_{t\alpha}$ vector are $B_{t,3\alpha-2}$, $B_{t,3\alpha-1}$, and $B_{t,3\alpha}$. Therefore definition of the s vectors for the various internal coordinates gives the elements of B. Methods for construction of the s vectors are described in Wilson, Decius, and Cross (23,55-63).

The B matrix will then have 3N columns where N is the total number of atoms and the same number of rows as there are internal coordinates.

The G Matrix

When the B matrix elements have been defined it is quite simple to compute the elements of the G matrix. This matrix is defined by the equation

$$G = BM^{-1}B' \qquad (A1,4)$$

where M^{-1} is a 3N x 3N diagonal matrix whose elements have the form $(M^{-1})_{3i-2,3i-2} = (M^{-1})_{3i-1,3i-1} = (M^{-1})_{3i,3i} = \frac{1}{m_i}$ and m_i is the mass of atom i.

Since $\hat{S} = US$ it is also possible to find and use the symmetrized B matrix, $\hat{B}$, which may be used in the same way as B to find $\hat{G}$

$$\hat{G} = \hat{B}M^{-1}\hat{B}' \qquad (A1,5)$$

The K or $\hat{K}$ matrix can then usually be found simply by inverting the proper G matrix. This cannot be done however if there are redundant coordinates. For this case either the rows and columns corresponding to the redundant coordinates must be removed from the $\hat{G}$ matrix before inversion or the corresponding rows of $\hat{B}$ can be removed before using equation (A1,5). The latter technique is usually easier and has other advantages which will be discussed later.

The C^{α} Matrices

Other important matrices which may be directly calculated from the B matrices are the C^{α} matrices where α equals x, y, or z. These matrices are used in the computation of the Coriolis coupling coefficient matrices, ζ^{α}. The C^{α} matrices are defined generally by the operation

$$C^{\alpha} = BI^{\alpha}_{\mu}B' \qquad (A1,6)$$

where the non-zero elements of I_μ^α are

$$(I_\mu^x)_{3i-1,3i} = -(I_\mu^x)_{3i,3i-1} = 1/m_i \quad i=1,\ldots,N$$

for $\alpha = x$,

$$(I_\mu^y)_{3i,3i-2} = -(I_\mu^y)_{3i-2,3i} = 1/m_i \quad i=1,\ldots,N$$

for $\alpha = y$, and

$$(I_\mu^z)_{3i-2,3i-1} = -(I_\mu^z)_{3i-2,3i-2} = 1/m_i \quad i=1,\ldots,N$$

for $\alpha = z$.

If redundant coordinates are included in the internal coordinate B matrix normally the B matrix with the redundancies removed would be used to calculate the C^α matrices.

The $J_{\alpha\beta}$ Vectors

The calculation of the $t_{\alpha\beta\gamma\delta}$ parameters described in Section One requires the quantities of the form

$$J_{\alpha\beta}^{(i)} = (\partial I_{\alpha\beta} / \partial S_i)_{\underline{S}=\underline{0}}$$

evaluated with the molecule in a principal axis coordinate system and for cartesian displacements satisfying the Eckart conditions.

The elements of the moment of inertia matrix are

$$I_{xx} = \Sigma\, m_i(y_i^2 + z_i^2)$$

$$I_{yy} = \Sigma\, m_i(x_i^2 + z_i^2)$$

$$I_{zz} = \Sigma\, m_i(x_i^2 + y_i^2)$$

$$I_{xy} = -\Sigma\, m_i x_i y_i$$

$$I_{xz} = -\Sigma\, m_i x_i z_i$$

$$I_{yz} = -\Sigma\, m_i y_i z_i$$

Then for the derivative, for example, of I_{xy} with respect to S_k one has

$$(\partial I_{xy}/\partial S_i)_{\underline{S}=\underline{0}} = -\Sigma\, m_i \left[x_i (\partial y_i/\partial S_k)_{\underline{S}=\underline{0}} + y_i (\partial x_i/\partial S_k)_{\underline{S}=\underline{0}} \right] \qquad (A1,7)$$

and one is left with the problem of evaluating $(\partial y_i/\partial S_k)_{\underline{S}=\underline{0}}$ and $(\partial x_i/\partial S_k)_{\underline{S}=\underline{0}}$.

Referring to equation (A1,1) it can be easily seen that if B can somehow be inverted, an expression giving

as a function of S would be available. This cannot be done directly since B is non-square.

If, however, the origin of the position vectors describing the molecule is translated to the center of mass and if the molecule is then rotated to a principal axis system, it is possible to augment the B matrix in such a way that it may be inverted. This is done simply by combining the equation $S = B\xi$ with the equation

$$R = E_c \xi = \underline{0} \qquad (A1,8)$$

which expresses the Eckart conditions. For non-linear molecules R has six zero elements and E_c has the form

$$\begin{array}{ccccccccc}
m_1 & 0 & 0 & m_2 & \cdots & m_n & 0 & 0 \\
0 & m_1 & 0 & 0 & \cdots & 0 & m_n & 0 \\
0 & 0 & m_1 & 0 & \cdots & 0 & 0 & m_n \\
0 & -m_1z_1 & m_1y_1 & 0 & \cdots & 0 & -m_nz_n & m_ny_n \\
m_1z_1 & 0 & -m_1x_1 & m_2z_2 & \cdots & m_nz_n & 0 & -m_nx_n \\
-m_1y_1 & m_1x_1 & 0 & -m_2y_2 & \cdots & -m_ny_n & m_nx_n & 0
\end{array}$$

where x_i , y_i , z_i refer to those components of the position vectors in the principal axis system chosen.

For linear molecules E_c has the form

$$\begin{array}{ccccccc} m_1 & 0 & 0 & m_2 & \cdots & m_n & 0 & 0 \\ 0 & m_1 & 0 & 0 & \cdots & 0 & m_n & 0 \\ 0 & 0 & m_1 & 0 & \cdots & 0 & 0 & m_n \\ m_1 z_1 & 0 & 0 & m_2 z_2 & \cdots & m_n z_n & 0 & 0 \\ 0 & m_1 z_1 & 0 & 0 & \cdots & 0 & m_2 z_2 & 0 \end{array}$$

where z is the axis of the molecule.

Letting $\overline{S} = \begin{pmatrix} S \\ R \end{pmatrix}$ and $\overline{B} = \begin{pmatrix} B \\ E_c \end{pmatrix}$ we have

$$\overline{S} = \overline{B}\,\xi \qquad (A1,9)$$

where $\overline{B}$ is square if all redundancies have been removed. If the internal coordinates have been properly defined the $\overline{B}$ matrix should be invertable and after inversion one will have the equation

$$\xi = \overline{B}^{-1}\overline{S} \qquad (A1,10)$$

Now since

$$(\overline{B}^{-1})_{i,k} = \left(\frac{\partial \xi_i}{\partial S_k}\right)_{\underline{S}=\underline{0}} = \left(\frac{\partial \Delta\alpha_j}{\partial S_k}\right)_{\underline{S}=\underline{0}}$$

$$= \left(\frac{\partial \alpha_j}{\partial S_k}\right)_{\underline{S}=\underline{0}}$$

we have the quantities needed to evaluate (A1,7). It should be noted that these derivatives automatically satisfy the Eckart conditions and refer to the principal axis system.

Equation (A1,7) and others derived from the moment of inertia equations may now be used to evaluate the $J_{\alpha\beta}$ vectors for all α and β .

The V Matrix

The V matrix is the transformation from the internal coordinates, S , used to define the K and C matrices to the interatomic distance displacement coordinates, R

$$R = VS \ .$$

The elements of V are defined using a truncated Taylor series such that

$$\Delta R_{ij} = \sum_k \left(\partial R_{ij} / \partial S_k \right)_{\underline{S}=\underline{0}} S_k$$

Then if $\Delta R_{ij} = R_m$, $V_{mk} = \left(\partial R_{ij} / \partial S_k \right)_{\underline{S}=\underline{0}}$

where $\left(\partial R_{ij} / \partial S_k \right)$ are evaluated using the formulas

$$R_{ij}^2 = (x_i - x_j)^2 + (y_i - y_j)^2 + (z_i - z_j)^2$$

$$\left(\frac{\partial R_{ij}}{\partial S_k} \right)_{\underline{S}=\underline{0}} = \frac{1}{R_{ij}} \left[(x_i - x_j) \left(\frac{\partial x_i}{\partial S_k} - \frac{\partial x_j}{\partial S_k} \right) \right.$$

$$\left. + (y_i - y_j) \left(\frac{\partial y_i}{\partial S_k} - \frac{\partial y_j}{\partial S_k} \right) + (z_i - z_j) \left(\frac{\partial z_i}{\partial S_k} - \frac{\partial z_j}{\partial S_k} \right) \right]_{\underline{S}=\underline{0}}$$

where, for example

$$(\partial x_i / \partial s_k)_{\underline{S}=\underline{0}} = (\overline{B}^{-1})_{3i-2,k} \cdot$$

APPENDIX II

Solution of the Secular Equation

There are many ways to solve the secular equation (I,19).

$$K\mathbb{M} = \mathbb{M}\Phi$$

The technique presented here uses a subroutine based on Jacobi's method for solving real, symmetric matrices and has the following desirable characteristics. It is quite fast, being proportional to the dimension of the matrix cubed rather than to the fourth as is the case for the fastest methods for solving non-symmetric matrices. The resultant $\mathbb{M}$ matrix is automatically normalized so that $\mathbb{M}\mathbb{M}^t = K$, and it has no difficulty handling multiple roots.

The solution of (I,19) is accomplished by solving the symmetric matrices. First we consider the equation

$$KD = D\Gamma \qquad (A2,1)$$

where Γ is the diagonal eigenvalue matrix of K and D its eigenvector matrix. Since K is real and symmetric, D is orthogonal and the elements of Γ are real and positive. Therefore

$$K = D\Gamma D' \qquad (A2,2)$$

Let $W = D\Gamma^{\frac{1}{2}}$ then $K = WW'$. Next consider the solution of the secular equation for real symmetric matrix $H = W'CW$,

$$HS = S\underline{\Phi} \qquad (A2,3)$$

As before S is orthogonal and the elements of $\underline{\Phi}$ real and positive.

$$HS = S\underline{\Phi}$$

may be written as

$$W'CWS = S\underline{\Phi}$$

Multiplying on the left by W gives

$$WW'CWS = WS\underline{\Phi}$$

which is

$$KCWS = WS\underline{\Phi}$$

Comparison with (I,19) shows

$$M = WS \qquad (A2,4)$$

These matrices have the following properties

$$MM^t = WSS^tW^t = WW^t = K$$

$$M^tCM = S^tW^tCWS = S^tHS = \underline{\Phi}$$

as is desired.

Since $M = (L^{-1})^t$

$$L^{-1} = S^tW^t \qquad (A2,5)$$

and

$$L = W \Gamma^{-1} S \qquad (A2,6)$$

Solution using this technique thus greatly simplifies finding the desired $\underline{\Phi}$, M , L^{-1} and L matrices.

APPENDIX III

Multiple Regression

Often in the application of least squares models such as the one described in this thesis it is found that certain of the constants cannot be determined. This is usually due to one of two reasons; either the observed data is not sensitive to the particular constant, which leads to unusually large estimated errors and possible divergence or oscillation, or two constants are strongly correlated, which leads to near singularity of the S matrix and very large estimated errors and again possibly to divergence or oscillation. In order to obtain a reasonable and stable solution it is necessary for reason one to eliminate the indeterminant constants or for reason two to eliminate one of the strongly correlated pair. This may be done either by trial and error, i.e., by trying various sets of constants including some constants and excluding others or by setting up some criterion which will allow the computer to eliminate the offending constants.

The technique used here is a quite simple one based on the t test. The S matrix is inverted and the first $\hat{\beta}$ vector calculated. A vector t is then calculated using the formula

$$t_i = \left| \hat{\beta}_i / \sqrt{(S^{-1})_{ii} \hat{\sigma}^2} \right|$$

where $\hat{\sigma}^2$ is defined by equation (II,9'), m being the total number of constants minus those held fixed. These t elements are only calculated for those $\hat{\beta}$ which have not either been forced into the regression (usually diagonal constants and most important off-diagonal constants) or held constant, these constants being specified before the problem is begun. The set of calculated t's is then searched to find the minimum element. The t test is then used to determine whether the corresponding constant is significant, the criterion being determined by t table values, $t_\alpha(\text{d.f.})$, where α is the size of the test, i.e., the probability

$$\hat{\beta}_k / \sqrt{(S^{-1})_{kk} \hat{\sigma}^2} > t_\alpha(\text{d.f}) \text{ or } < -t_\alpha(\text{d.f.}) \text{ if } \beta_k = 0$$

and d.f. is the number of degrees of freedom, i.e., the number of pieces of data minus the total number of constants plus the number of constants being held fixed. If t_m is the minimum t value the test of significance is whether t_m is greater than $t_\alpha(\text{d.f.})$. If t_m is less than $t_\alpha(\text{d.f.})$ the corresponding constant, β_k, is judged as insignificant. The vector and the S^{-1} matrix are then modified using the following equations

$$\text{new } \hat{\beta}_i = \hat{\beta}_i - (S^{-1})_{im}\hat{\beta}_m/(S^{-1})_{mm}$$

$$\text{new } (S^{-1})_{ij} = (S^{-1})_{ij} - (S^{-1})_{im}(S^{-1})_{jm}/(S^{-1})_{mm} ,$$

the number of degrees of freedom increased by one and $\hat{\sigma}^2$ recalculated. The new t's are calculated and the above repeated until either all remaining constants are significant or there are no more to be tested, at which time control is returned to the main part of the program.

In our case since $\hat{\beta}_i$ is ΔC_i, $C_i + \Delta C_i$ is used in place of just $\hat{\beta}_i$ in the calculation of t_i. This is done so that some value other than zero may be used as a starting value for those constants which are to be tested. If the $\hat{\beta}_i$ is judged insignificant both C_i and ΔC_i are set equal to zero.

It is important to note some of the difficulties involved in using this technique to find the significant constants. The first is involved with the fact that the use of the t test assumes that β_i is normally distributed. Up to this time no assumption has been made about the distributions other than they have finite means and variances. It is difficult to predict the effect this has since a distribution function has not been

defined, but it can be hoped that the normal distribution is a reasonable assumption. There is also no good reason to assume that the t tests are independent, i.e., that we are not discarding a variable at one stage which may be significant at a later stage. This difficulty may be minimized by proper choice of which variables to force into the regression and which to hold fixed. Usually this decision is physically rather than statistically based.

The last difficulty lies in the interpretation of the final results. A constant is judged insignificant (or indeterminant) or significant on the basis of the data supplied to the model. There is no guarantee that if more or better data were available, one would have the same results or even the same constants in the final result.