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THE TRANSFERABILITY OF FORCE CONSTANTS
AMONG OLEFINS

BY

JOHN MARTIN COMERFORD

A THESIS

PRESENTED IN PARTIAL FULFILLMENT OF

THE REQUIREMENTS FOR THE DEGREE

OF

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AT

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ABSTRACT

A normal coordinate analysis of the in-plane vibrations of ethylene was performed using a modified valence force field, a modified Urey-Bradley force field and a hybrid orbital force field. The B_{2u} species of isobutene was also analyzed. An attempt was made to transfer force constants from ethylene and thereby solve the A_1 species of isobutene, but a solution could not be obtained. This suggests that simple transference of force constants is not feasible in this case.

The potential energy distributions obtained for ethylene are discussed. The normal coordinates calculated in this work are appended.

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THE TRANSFERABILITY OF FORCE CONSTANTS
AMONG OLEFINS

BY

JOHN MARTIN COMERFORD

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CHAPTER I
INTRODUCTION

The objective of this study was to study possible relationships between force constants in olefinic type molecules and to investigate the effect of the molecular environment on isolated C=C bonds in different olefins.

Although a few vibrational studies of ethylene have been reported, very little work on force constant calculations for more complicated olefins are available. Furthermore, differences in the results obtained by different workers for ethylene exists. These differences can be attributed to differences in frequency assignments, in choice of coordinates, in assumed potential fields, or some combination of these factors. Thus it was deemed necessary to perform normal coordinate calculations on the in-plane vibrations of ethylene and isobutene. It is hoped that the results of this study may provide methods for transferring force constants between molecules which would then permit prediction of properties such as vibrational frequencies, bond energies, etc. in more complicated olefinic type molecules.

A computer program was used to perform normal coordinate analyses which provide a "best fit" set of force constants (in the least square sense) to the

observed frequencies of each molecule. The force fields used for the calculations were the modified valence force field (MVFF), the Urey Bradley force field (UBFF) and the hybrid orbital force field (HOFF). Some modifications in each case were made to reduce the number of force constants which had to be calculated and thus allow the computer program to converge.

The roots of the set of equations of the type

$$\left| GF - \lambda E \right| = 0 \quad (1)$$

yield the vibrational frequencies of a molecule since

$$\lambda = 4 \pi^2 c^2 v^2 \quad (2)$$

where G is the kinetic energy matrix and F is the potential energy matrix. v is the frequency of vibration, c is the velocity of light and λ represents the roots of equation (1).

One of the underlying assumptions of this type of calculation is that the molecular force field or potential energy function is understood. Since the number of independent constants or force constants necessary to describe the potential energy depends on the type of function chosen, one frequently must choose a potential energy function which can be solved with the data available.

One of the simplest and most widely used force fields is the general valence force field (GVFF), which assumes that if a bond changes its length due to vibration, there is a force tending to restore it to its equilibrium length which is proportional to the change. A similar restoring force is assigned to bond angle changes. This means that on the basis of the GVFF the potential energy function may be written as:

$$V = \sum_a \frac{1}{2} k_a \Delta R_a^2 + \sum_m \frac{1}{2} k_m \Delta \angle_m^2 \quad (3)$$

where ΔR_a is the change in the length of the bond "a" and \angle_m is the change in bond angle of the angle "m". The summations are over all bond angles and bond lengths.

The GVFF includes all possible cross terms to account for interactions between terms. In most cases it is necessary to limit the number of cross terms introduced into the GVFF since, even with the use of isotopes, the number of observed frequencies are frequently too few to solve for all of the force constants. It must be admitted, however, that there is no sure way of knowing which are the proper cross terms to use and which should be omitted.

Another type of potential function, introduced by H. C. Urey and C. A. Bradley (28), should be mentioned here. They superimposed on the GVFF a repulsion potential of the form:

$$V' = a/R^n \quad (4)$$

between non-bonded atoms, R being the distance between non-bonded atoms and a and n being constants. The effect of the Urey-Bradley field is to take into account the Van der Waals repulsive forces between non-bonded atoms.

A third type of field, the HOFF, was proposed by Mills (21) and considers that changes in bond hybridization are accompanied by changes in bond length. Hence changing the hybridization ratios during bending creates a secondary interaction with the stretching vibration.

CHAPTER II
METHOD OF CALCULATION

A. Description of the Method

The potential energy of a molecule may be written in terms of internal coordinates, R_i , which are measurements of changes in the bond lengths and interbond angles from the equilibrium configuration of the molecule (so that $R_i = 0$ at equilibrium). The potential energy expression is thus:

$$V = V_0 + \sum_i \left(\frac{\partial V}{\partial R_i} \right) R_i + \frac{1}{2} \sum_i \sum_j \left(\frac{\partial^2 V}{\partial R_i \partial R_j} \right) R_i R_j + \frac{1}{6} \sum_i \sum_j \sum_k \left(\frac{\partial^3 V}{\partial R_i \partial R_j \partial R_k} \right) R_i R_j R_k + \dots (5)$$

V_0 defines the potential energy at equilibrium and is taken as zero. In the second term, since $(\partial V / \partial R_i)$ is to be taken in the equilibrium position it is zero by definition. The coefficients of the third term are what are known as the harmonic force constants and are defined by $F_{ij} = (\partial^2 V / \partial R_i \partial R_j)$.

The coefficients of higher order terms are known as anharmonic force constants and are not treated in this work.

For symmetric molecules, symmetry coordinates may be used instead of internal coordinates to define the potential energy function. The symmetry coordinates, S_i , are related to internal coordinates, R_j , by means of the elements of a transformation matrix, U_{ij} , according to the equation:

$$S_i = \sum_j U_{ij} R_j \quad (6)$$

or in matrix notation

$$S = U R \quad (7)$$

The symmetry coordinates of any molecule may be classified into symmetry species.

Wilson, Decius and Cross (30) and Herzberg (15) described the following procedure for calculation of force constants.

Defining the potential and kinetic energy by:

$$2V = \sum_i \sum_j F_{ij} R_i R_j \quad (8)$$

$$2T = \sum_i \sum_j G_{ij} \dot{R}_i \dot{R}_j \quad (9)$$

or in matrix notation

$$2V = R' F R \quad (10)$$

$$2T = \dot{R}' G^{-1} \dot{R} \quad (11)$$

Where F is the force constant matrix defined above and the elements of the G^{-1} matrix are functions of atomic masses and equilibrium geometry of the molecule. The values of F and G depend on the coordinates chosen and in general there will be non-zero off diagonal terms in the expression for both V and T . The primes denote matrix transposes and $\dot{R} = (\partial R_i / \partial t)$ where t is time. A column matrix of normal coordinates, Q can be defined

by
$$R = L Q \quad (12)$$

where L transforms R to normal coordinates, i.e.

$$Q_j = \sum_i L_{ij} R_i \quad (13)$$

The transformation matrix L is chosen such that

$$2V = Q' \Lambda Q \quad (14)$$

and
$$2T = \dot{Q}' E \dot{Q} \quad (15)$$

where E is the identity matrix and Λ is a diagonal matrix of the frequency parameters, $\lambda_k = 4\pi^2 c^2 v^2$.

In terms of normal coordinates the expressions for both V and T have zero coefficients for all cross terms and unity coefficients for all diagonal terms.

Substitution of equation (12) into equations (10) and (11) and comparing the results with equations (14) and (15) yields

$$L' F L = \Lambda \quad (16)$$

and
$$L' G^{-1} L = E \quad (17)$$

Combination of these two equations gives the expression

$$F L = G^{-1} L \Lambda \quad (18)$$

or
$$G F L = L \Lambda \quad (19)$$

Consider a single column of the L matrix denoted by L_i and let the corresponding frequency parameter be λ_i . Equation (19) can then be written in the form

$$(G F - \lambda_i E) L_i = 0 \quad (20)$$

where
$$G F = (G F)_{ji} = \sum_k G_{jk} F_{ki} .$$

A necessary and sufficient condition that non-trivial solutions (i.e. $L \neq 0$) for equation (20) exist is that

$$|G F - \lambda E| = 0 \quad (21)$$

Equation (21) is called the secular equation. Expansion of it leads to a polynomial equation in λ which can be solved if the elements of G and F are known. The secular equation can be factored in terms of symmetry coordinates so that cross terms of F and G matrices of different symmetry species are always zero. This, of course, means that a set of equations with $(3N-6)$ unknowns reduces to several smaller problems which are correspondingly simpler to solve.

After solving for the λ 's using equation (21) one may substitute them back into equation (20) and solve for the L's.

Desius (9) published "A Tabulation of General Formulas for Inverse Kinetic Energy Matrix Elements in Acyclic Molecules". Selected portions of these tables later appeared in the book by Wilson, Desius and Cross (30). General formulas for deriving the G matrix elements are given in terms of internal coordinates of the bond stretching and angle bending types, together with a torsional type of coordinate. Using the tables of Desius internal coordinates are chosen for a molecule by selecting convenient bond lengths, bond angles and torsional angles in the molecule. Symmetry coordinates are then set up such that

they are linear combinations of the internal coordinates. The symmetry coordinates are not necessarily unique, but must be normalized, orthogonal and of the form

$$S_j = \sum_k U_{jk} r_k \quad (22)$$

where S_j is the j th symmetry coordinate, r_k the k th internal coordinate and U_{jk} the appropriate coefficient for r_k . The condition of normalization is satisfied when

$$\sum_k U_{jk} U_{jk} = 1 \quad (23)$$

and the condition of orthogonality is satisfied when

$$\sum_k U_{jk} U_{ik} = 0 \quad (24)$$

where $j \neq i$.

It is not necessary to actually calculate the symmetry coordinates (S_j); only the coefficients, U_{jk} , in equation (22) are needed. Thus a U matrix composed of the elements U_{jk} shown in equation (22) is generated. The G matrix in symmetry coordinates may then be calculated using the equation

$$G = U g U' \quad (25)$$

where g is a general kinetic energy matrix in terms of internal coordinates whose elements are calculated using the formulas given by Desius (9). U' is the transpose matrix of U .

In order to simplify the calculation of the G matrix for the in-plane symmetry species of ethylene and isobutene,

two computer programs were written. The first program, called WORK4, calculates the g matrix, or the kinetic energy matrix, based on internal coordinates. The input data used are the five bond lengths and the six bond angles described in figure I. The program also needs the atomic weights of carbon and the four elements or chemical moieties shown in Figure I as R_1 , R_2 , R_3 , and R_4 .

The second program, called WORK3, uses as in-put data the U matrix appropriate to each symmetry species and the g matrix generated by program WORK4. WORK3 calculates the G matrix for the species according to the equation

$$U g U' = G \quad (26)$$

where U' is U transpose.

For both WORK4 and WORK3 the format for the in-put data, a sample problem, and the programs are given in Appendix I.

B. Force Constant Refinement

Using equations (20) and (21) one can calculate the λ 's and L's if G and F are known. In practice F is not known and the λ 's are observed values. Wilson, Desius and Cross (30) have employed perturbation theory to solve the equation $|G F - \lambda E| = 0$ by a force constant refinement procedure. In this procedure an initial set of force constants, F, are used to calculate frequencies (λ 's) and to calculate the transformation matrix L. The force constants are then adjusted to obtain better values for λ 's.

The changes in frequencies were shown to be (30):

$$\Delta \lambda_i = \sum_{jk} L_{ji} L_{ki} \Delta F_{ik} \quad (27)$$

where L_{ji} and L_{ki} are the transformation coefficients.

Thus in matrix notation

$$\Delta \Lambda = J \Delta F \quad (28)$$

where $\Delta \Lambda$ is a column matrix of $\Delta \lambda$'s, ΔF is a column matrix ΔF_{jk} and J is the Jacobian matrix whose elements are the products of L_{ji} and L_{ki} . Thus equation (28) forms the basis of the iteration method.

A computer program by W. T. Thompson and C. S. Shoup was written for performing force constant refinements on the IBM 7090 computer. The program was subsequently revised by H. Kimmel for the IBM 7040 (16) then by this

author for the PDP 10 time sharing system used by Personal Products Company, a division of Johnson and Johnson. The modified program, shown in Appendix II is summarized below.

An assumed set of F 's (i.e. the F matrix) is used to calculate λ^0 's and a set of transformation coefficients, L^0 's. If $\Delta \lambda_i = \lambda_i - \lambda^0_i$, set $\Delta \Lambda = J \Delta F$ where the matrix J is computed from the L 's (J is Jacobian matrix whose elements are products $L_{ji} L_{hi}$). It is possible (though not necessarily true) that ΔF can be found which directly satisfies $\Delta \Lambda = J \Delta F$. It is usually necessary to compute the correction to F^0 so that the difference between observed and calculated frequency parameters, $\Delta \Lambda$, are minimized. Let $r = J \Delta F - \Delta \Lambda$ where r represents the error in the solution to $\Delta \Lambda = J \Delta F$ for each correction to F^0 . The solution ΔF is obtained by a least squares method.

If the weighted square error, S , in the solution of equation $\Delta \Lambda = J \Delta F$ is defined as $S = r' W r$ where the matrix W is a diagonal matrix of the weight $W_i = 1/\lambda_i^2$, then the solution ΔF that minimizes S can be determined by forming the equations

$$J' W J \Delta F = J' W \Delta \Lambda$$

the solution for this equation is

$$\Delta F = (J' W J)^{-1} J' W \Delta \Lambda \quad (29)$$

and the ΔF 's can be used to form a new set of force constants by

$$F(\text{new}) = F(\text{old}) + \Delta F \quad (30)$$

The calculation is then repeated using $F(\text{new})$ as the F^0 . This iteration procedure is repeated until $\Delta F = 0$ or is negligibly small.

The dispersion of each refined force constant is calculated by the relation

$$\sigma^2(F) = (J' W J)^{-1} \sigma^2$$

where $\sigma^2 = (\Delta \Lambda') W (\Delta \Lambda) / (N - P)$

N being the number of fundamental frequencies used in the calculation and P the number of refined force constants. The diagonal elements of $\sigma^2(F)$ give the uncertainties obtained by the equation.

$$\sigma^2(F) = (J' W J)^{-1} \sigma^2$$

when a large number of independently observed frequencies are being used to determine a small number of force constants, i.e. $(N-P)$ is not too small a number and when the relationship $\Delta \Lambda = J \Delta F$ is valid.

Equations (29) and (30) show that in the iteration process it is necessary to obtain the inverse of a matrix. Not all matrices have an inverse. A matrix with no inverse is known as a singular matrix, in which case the determinant of the matrix is equal to zero. Since a computer carries a finite number of significant figures, it is

necessary to decide what constitutes a determinant close enough to zero that it should be considered zero and computation should be halted. The penalty paid for trying to calculate an inverse for a matrix which truly has no inverse is generally that the program enters a loop which it can not finish and continues trying to find the inverse of the matrix until the program is halted manually. A second possibility is that the program generates a meaningless result. We have found that, in general, when using the PDP-10 computer (made by Digital Equipment Corp.). A determinant less than 10^{-30} is close enough to zero to consider it zero and an inverse should not be attempted.

C. Available Structural Data and Frequency Assignments

Table I shows the atomic weights used in this work, and in figure I (page 23) the bond lengths and bond angles used for each molecule are presented together with a general diagram of the molecule.

TABLE I

ATOMIC WEIGHTS USED

Element	Atomic weight	Reference
carbon	12.01115	(13)
deuterium	2.0147	(14)
hydrogen	1.00797	(13)

Bartell, et al. (3) did an electron diffraction study of the structures of C_2H_4 and C_2D_4 and compared their results to the results of earlier workers. Table II summarizes their results. The C-D bond length appears to be shorter than the C-H bond length, but one would expect the opposite to be true based on our understanding of steric hindrance.

TABLE II

ELECTRON DIFFRACTION STUDY OF C₂H₄ AND C₂D₄

(Bartell, Roth and Hollowell (3))

C₂H₄

C-H bond length	1.1030	± 0.0018	(angstroms)
C=C bond length	1.3369	± 0.0016	(angstroms)
H-C-H angle	117.2	± 1.2	(degrees)

C₂D₄

C-D bond length	1.099	± 0.003	(angstroms)
C=C bond length	1.338	± 0.003	(angstroms)
D-C-D angle	117.1	± 1.6	(degrees)

The uncertainties reported for the C-H and C-D bond lengths, however, suggest that the relative distance could be reversed and indicate that the C-H measurement is more reliable. Considering the uncertainties in the C=C measurements and the bond angles for both molecules, one is again lead to the conclusion that there is little to choose between them but the data from the C₂H₄ molecule seems more reliable. In view of this we have used the measurements reported for C₂H₄ and applied them to both isotopic species as shown in Figure I.

The structure of Isobutylene was obtained from microwave data reported by Scharpen and Laurie (19).

The frequency assignments for ethylene were reported by Gallaway and Baker (12) and by Cyvin and Cyvin (6) and their results are shown in Table III for the in-plane symmetry species. Since there is a discrepancy between the two papers for both the B_{1g} and B_{2u} symmetry species, both sets of data were used and force constants are reported for each set.

TABLE III

ASSIGNMENTS FOR IN-PLANE VIBRATIONS OF ETHYLENE

Symmetry	Description	C_2H_4		C_2D_4	
		Ref. (12)	Ref. (6)	Ref. (12)	Ref. (6)
A_{1g}	C-H stretch	3019.3	3026.4	2252	2260
	CH ₂ sym bend	1342.4	1342.4	981	985
	C=C stretch	1623.3	1622.6	1515	1518
B_{3u}	C-H sym stret	2989.4	2989.5	2200.2	2200.2
	CH ₂ asym bend	1443.9	1443.5	1077.9	1077.9
B_{1g}	C-H stretch	3069	3102.5	2304	2310
	CH ₂ rock	1055	1236	860	1011
B_{2u}	C-H stretch	3105.5	3105.5	2343	2343
	CH ₂ rock	995	810.3	740	584

The vibrational spectrum for isobutylene is reported in the literature (24). In Table IV their assignments for the in-plane vibrations of the C_4H_8 and C_4D_8 molecules are given.

TABLE IV

Frequency Assignments for the In-Plane
Vibrations of Isobutylene

<u>Species</u>	<u>Description</u>	<u>C_4H_8</u>	<u>C_4D_8</u>
A ₁	C-H stretch	2984.9	2226.2
	C-C stretch	803.0	705.0
	CH ₂ wag	1416.0	1047.6*
	skeletal bend	383.0	322.6
	C=C stretch	1658.0	1613.4
B ₂	C-H stretch	3083.5	2305.5
	C-C stretch	1281.0	1267.0
	CH ₂ wag	973.0	767.0
	skeletal bend	418.0	353.0

(* indicates the value was calculated by Pathak and Fletcher. (24))

D. The G Matrix

In the normal coordinate treatment of a molecule the kinetic energy is expressed by the G matrix and is a function of the atomic masses and molecular configuration. Once a set of bond lengths and bond angles is chosen, the G matrix may be calculated most conveniently by using a set of tabulated equations such as the set provided by Desius. (9). Several authors have chosen different sets of bond lengths and bond angles as described below and have therefore developed different G matrices to describe the kinetic energy of the A_{1g} species of the ethylene molecule.

Arnett and Crawford (1), for example, choose a set of interatomic relationships involving the five interatomic distances between bonded atoms plus the following seven angles: The two HCH angles; the two angles between the C=C bond and the bisectors of the HCH angles; the two angles between the C=C bond and the HCH planes caused by rotation about a common axis which includes the C atoms. Table V gives the G matrix for the A_{1g} species of ethylene which is calculated by using the internal coordinates suggested by Arnett and Crawford.

TABLE V

Arnett and Crawford G Matrix for Ethylene

<u>A_{1g} Symmetry Species</u>			
1.0373	-0.0868	-0.1047	
	0.1655	0.2010	Normal Ethylene (C ₂ H ₄)
		2.0718	
0.5417	-0.0870	-0.1048	
	0.1655	0.2008	Deuterated Ethylene (C ₂ D ₄)
		1.2351	

Morino, Kuchitsu and Shimanouchi (22) choose internal coordinates for the molecule CF₂=CF₂ which could be applied directly to ethylene. The coordinates chosen involved the five bond lengths, the six bond angles of the planar molecule and two non-bonded distances. The non-bonded distances chosen were the distances between the F atoms in each CF₂ group and the distance between the C and F atoms not bonded directly.

Shimanouchi et al. calculated a G matrix for C₂F₂ which can be used for C₂H₂ by substituting the appropriate bond lengths, bond angles and atomic masses. Table VI shows the G matrix for the A_{1g} species of ethylene which was arrived at by applying the geometry of ethylene and

and deuterated ethylene (Figure I) to the G matrix formula.

Table VI.

G Matrix for Ethylene Calculated from G Matrix for C₂F₄

(From Shimanouchi et al. (22))

A _{1g} Symmetry Species			
1.0373	-0.0868	-0.1283	
	0.1665	0.2462	Normal Ethylene (C ₂ H ₄)
		3.3402	
0.5153	-0.0868	-0.1283	
	0.1665	0.2462	Deuterated Ethylene (C ₂ D ₄)
		1.7744	

Kilpatrick and Pitzer (18) used the same internal coordinates for ethylene as were used in this work. The five bond lengths were used together with the six bond angles of the planar figure of the molecule. A torsional angle was used to describe the out of plane bending of the molecule, however, the out of plane motions were not considered in this work. Because of a lack of structural data, Kilpatrick and Pitzer assumed that the bond angles were 120 degrees. Using our program for calculation of the G matrix and applying the structural data used by

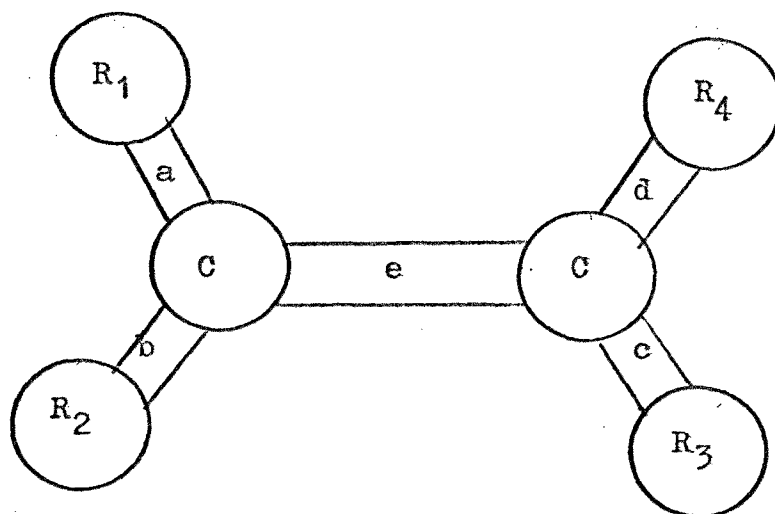
Kilpatrick and Pitzer, we were able to exactly repeat their calculation of the G matrix for the A_{1g} species. Table VII shows the results of our G matrix calculation using the structure shown in Figure I.

TABLE VII

<u>G Matrix Used for Ethylene A_{1g} Species</u>			
1.0373	-0.0868	0.0740	
	0.1665	-0.1421	Normal Ethylene (C_2H_4)
		1.1134	
0.5415	-0.0868	0.0671	
	0.1665	-0.1289	Deuterated Ethylene (C_2D_4)
		0.5077	

Any set of force constants which are calculated depend on both the field which is being considered and the potential energy equation which is being assumed. The kinetic energy is described by the G matrix, and as pointed out, is different when different internal coordinates are used to calculate it.

FIGURE I

STRUCTURAL DATA USED

	Ethylene	Deuterated Ethylene	Isobutene
R ₁	hydrogen	deuterium	methyl
R ₂	hydrogen	deuterium	methyl
R ₃	hydrogen	deuterium	hydrogen
R ₄	hydrogen	deuterium	hydrogen
a	1.1030 Å	1.1030 Å	1.507 Å
b	1.1030 Å	1.1030 Å	1.507 Å
c	1.1030 Å	1.1030 Å	1.088 Å
d	1.1030 Å	1.1030 Å	1.088 Å
e	1.3369 Å	1.3369 Å	1.330 Å
R ₁ CC	121.4°	121.4°	122.35°
R ₂ CC	121.4°	121.4°	122.35°
R ₃ CC	121.4°	121.4°	120.75°
R ₄ CC	121.4°	121.4°	120.75°
R ₁ CR ₂	117.2°	117.2°	115.3°
R ₃ CR ₄	117.2°	117.2°	118.5°

CHAPTER III
VIBRATIONAL AND STRUCTURAL DATA

A. Previous Work

The fundamental principles upon which the normal coordinate analysis of molecules rests have been discussed in detail by Wilson, Desius and Cross (30) and summarized in Chapter II. Both prior to and subsequent to that writing a number of authors described the analysis of the in-plane vibrations of the molecules which are treated in this work. Kilpatrick and Pitzer (18), for example, published an analysis of all vibrations of ethylene, propylene, cis-2-butene, trans-2-butene, and isobutene. In their work symmetry coordinates were used to set up the inverse kinetic energy matrices (G matrix) and the potential energy matrices (F matrix) for each symmetry species. The symmetry coordinates and resulting F and G matrices are presented in table form by Kilpatrick and Pitzer.

Arnett and Crawford (1) developed a set of symmetry coordinates for ethylene based on a somewhat different set of internal coordinates from those chosen by Kilpatrick and Pitzer. The different symmetry coordinates lead to a different G matrix which Arnett and Crawford used to calculate the non-planar fundamental vibrational frequencies of ethylene.

Using the same symmetry coordinates as Arnett and Crawford, Crawford, Lancaster, and Inskeep (5) calculated a set of force constants which are satisfactory for the planar vibrations of ethylene and several of its deuterated isotopes.

The out-of-plane vibrations of ethylene were treated by Dowling (10) using appropriate internal coordinates to describe the vibrations.

More recently Cyvin and Cyvin (6,7) derived a set of normal frequencies for ethylene and deuterated ethylene by a systematic correction of the observed frequencies for anharmonicity. A set of force constants was then calculated which reproduce the derived frequencies. The mean amplitudes of vibrations were also reported by these authors.

Fletcher and Thompson (11) reported force constants for ethylene and deuterated ethylene which were based on yet another set of symmetry coordinates and using the HOFF.

B. Evaluation of Some of the Previous Work

The most difficult problem in attempting to reconcile all of the available work on ethylene is that the selection of different sets of internal coordinates lead to different sets of symmetry coordinates, and, as we will show later, these lead to different G matrices.

Some authors scale their force constants, others do not. That is, when developing the general G matrix to be used in equation (25) it is convenient to multiply those interactions between a bond stretching coordinate and an angle bending coordinate by an arbitrary constant bond length. Likewise, interactions between two angle bending coordinates may be multiplied by the square of the arbitrary constant. By doing this all of the force constants calculated have the same dimensions (millidynes/angstrom), if bond lengths are expressed in angstroms and masses of atoms are expressed in atomic weight units. It is mathematically equivalent and more convenient in our work if the scaling factors are applied to the U matrix elements rather than directly to the g matrix. The resulting G matrix is the same in either case. We have, therefore, chosen to multiply bond stretching-angle bending interactions by the length of the C-H bond in ethylene ($1.1030 \overset{\circ}{\text{A}}$) and to multiply coordinates involving only angle bending by the square of that distance.

The same constant was used regardless of which molecule was being treated.

It is well known that the observed frequencies of vibration are not harmonic vibrations. Two semi-empirical approaches have been used to correct for this difficulty. In one approach the masses of the atoms are adjusted and the calculation of the G matrix is done in the usual way but using the "harmonic masses". In a second approach the observed frequencies are adjusted and the calculation is done in the usual way to obtain a set of force constants which best fit the "harmonic frequencies". Neglecting to correct for anharmonicity can lead to errors in the calculated frequencies. In this work, however, it was not possible to correct for anharmonicity.

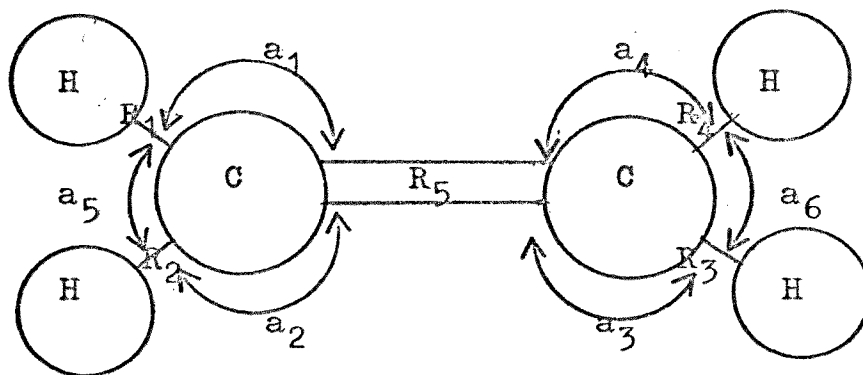
CHAPTER IV
RESULTS OF CALCULATIONS

A. The Ethylene Molecule

Ethylene belongs to the point group D_{2h} . The nine in-plane vibrations are factored into four symmetry species, i.e., the A_{1g} symmetry species which contains three vibrations and the B_{1g} , B_{2u} , and B_{3u} symmetry species, each of which contains two vibrations. If all possible interactions between vibrations are considered, then for a given symmetry species containing n vibrations, there will be $(\frac{1}{2}n)(n+1)$ independent force constants, e.g. for the A_{1g} species of ethylene, there will be six force constants for the three vibrations.

The internal and symmetry coordinates used for ethylene were the same as those used by Kilpatrick and Pitzer (18) and are shown in Figure II.

Figure II
Symmetry Coordinates of Ethylene



Symmetry Type

Coordinate

A_{1g}

$$S_1 = \frac{1}{2} (R_1 + R_2 + R_3 + R_4)$$

$$S_2 = \frac{1}{2} (a_1 + a_2 + a_3 + a_4)$$

$$S_3 = R_5$$

B_{1g}

$$S_4 = \frac{1}{2} (R_1 - R_2 + R_3 - R_4)$$

$$S_5 = \frac{1}{2} (a_1 - a_2 + a_3 - a_4)$$

B_{2u}

$$S_6 = \frac{1}{2} (R_1 - R_2 - R_3 + R_4)$$

$$S_7 = \frac{1}{2} (a_1 - a_2 - a_3 + a_4)$$

B_{3u}

$$S_8 = \frac{1}{2} (R_1 + R_2 - R_3 - R_4)$$

$$S_9 = \frac{1}{2} (a_1 + a_2 - a_3 - a_4)$$

A.1 The Valence Force Field

Two isotopic species of ethylene, C_2H_4 and C_2D_4 were used and the usual assumption was made that the force constants appropriate to each species were identical. This assumption provided enough data so that only one a priori assumption about force constants being constrained to zero or to some constant value was necessary for the A_{1g} symmetry species.

The several frequency assignments found in the literature and reported in this work in Table III are in agreement for the A_{1g} and B_{3u} species of ethylene. An initial set of force constants was obtained for the calculations from preliminary trials. The calculated force constants and dispersions for the A_{1g} species were obtained from the several runs shown in Table VIII holding different constants invariant during each run. The results of the three runs indicate that the initial assumption, i.e. the C-H stretch-bend interaction constant is negligible, is a valid one. In addition, the results suggest that the data obtained from run 3 give good agreement between the observed and calculated frequencies (Table IX).

Table VIII

FORCE CONSTANTS FOR A_{1g} SPECIES OF ETHYLENE

Description Of Vibration	Starting Values	Result of Run 1		Result of Run 2		Result of Run 3	
		Force Constant	σ	Force Constant	σ	Force Constant	σ
CH stretch	5.500	5.568	0.770	5.568	0.829	5.568	0.765
CC stretch	10.634	10.197	0.964	10.197	0.928	10.197	0.938
CH ₂ sym. bend	0.812	1.453	0.143	1.454	0.153	1.454	0.148
CH stretch - bend interact.	0.000	0.000*	-----	0.000	5.635	0.000	1.686
CC stretch - bend interact.	1.833	1.834	3.383	1.834	1.065	1.834*	-----
CH stretch- CC stretch interact.	1.020	1.448	0.285	1.448*	-----	1.448	3.785

(* denotes that the force constant was held invariant during the run.)

TABLE IX
OBSERVED AND CALCULATED FREQUENCIES FOR A_{1g} SPECIES OF ETHYLENE

Description of Vibration	Observed Frequency	Calculated Frequency	Percent Error
C-H stretch	3026.4	3085.2	1.9%
C=C stretch (C_2H_4)	1622.0	1653.5	1.9%
H _C H bend	1342.2	1368.3	1.9%
C-D stretch	2260.0	2211.3	-2.2%
C=C stretch (C_2D_4)	1518.0	1485.3	-2.2%
D _C D bend	985.0	963.8	-2.2%

The uniformity of error in the deuterated and undeuterated species suggests that some type of systematic error may be involved. A possible explanation for this is the need for correcting the data for anharmonicity effects.

In the B_{3u} species there are two vibrations to be considered and thus three force constants are needed (i.e. two diagonal force constants and one interaction force constant). Table X presents the force constants found for the B_{3u} species of ethylene together with a description of the vibrations being treated.

Table X

Force Constants for the B_{3u} Species of Ethylene

Description of Vibration	Observed Frequency	Calculated Frequency	Percent Error	Force Constant	ρ^2
CH stretch	2989.5	2990.4	0.0	4.723	0.224
CH ₂ bend	1443.5	1451.7	0.6	1.339	0.161
CD stretch	2200.2	2197.8	-0.1	-----	-----
CD ₂ bend	1077.9	1056.8	-2.0	-----	-----
Stretch bend interaction	-----	-----	---	0.797	0.286

Cyvin and Cyvin (6) and Gallaway and Barker (12) reported frequency assignments for the B_{1g} and B_{2u} species of ethylene. Since the assignments are somewhat different, both sets of reported frequencies were used and the force constants obtained are shown in Table XI. For each of these symmetry species there are only two fundamental vibrations and thus only three force constants are needed for each species. Since four observed frequencies are available for each species (two for the C_2H_4 molecule and two for the C_2D_4 molecule) it was possible in each case to compute a set of force constants without using any constraints.

In both the B_{1g} and B_{2u} symmetry species the calculated frequencies are in closer agreement to the observed frequencies when Cyvin and Cyvin's data are used than when Gallaway and Barker's data are used. In addition, the calculated dispersions are lower for both the B_{1g} species and the B_{2u} species when Cyvin and Cyvin's observed frequencies are used. This suggests that the frequency assignments of Cyvin and Cyvin may be the more reliable data. This conclusion is in agreement with the results obtained from the Teller-Redlick Product Rule Calculations (30).

The Product Rule is based on the assumption that the potential force field of a molecule is unaffected by isotopic substitution. Thus, if one takes a ratio of the

Table XI

Force Constants For Ethylene
MVFF

Observed Frequency	Ref.	Description of Vibration	Calculated Frequency	Force Constant	Dispersion (ω^2)
B _{1g} Species					
3102.5	(6)	CH str.	3102.7	5.124	0.017
1236.0	(6)	CH ₂ rock	1238.6	0.534	0.004
2310.0	(6)	CD str.	2309.6		
1011.0	(6)	CD ₂ rock	1006.1		
		str.-rock interaction		0.131	0.023
3069.0	(12)	CH str.	3069.2	4.897	0.024
1055.0	(12)	CH ₂ rock	1058.7	0.398	0.005
2304.0	(12)	CD str.	2303.6		
860.0	(12)	CD ₂ rock	852.9		
		str.-rock interaction		-0.078	0.027
B _{2u} Species					
3105.5	(6)	CH str.	3105.6	4.353	0.185
810.3	(6)	CH ₂ rock	813.1	0.964	0.169
2345.0	(6)	CD str.	2344.9		
584.0	(6)	CD ₂ rock	576.1		
		str.-rock interaction		-1.507	0.185
3105.5	(12)	CH str.	3105.8	4.444	0.688
995.0	(12)	CH ₂ rock	1005.1	1.085	0.622
2345.0	(12)	CD str.	2344.2		
740.0	(12)	CD ₂ rock	712.4		
		str.-rock interaction		-1.371	0.735

product of frequencies for the substituted molecule to that for the normal molecule, the ratio should be independent of the force field (i.e., the terms cancel out) and a function only of the molecular geometry. The G matrix is a convenient representation of the geometry and it has been shown that (8A) for a given symmetry species

$$\frac{\text{Det } G'}{\text{Det } G} = \frac{\prod \nu_i'}{\prod \nu_i}$$

where Det G represents the determinant of the factored G matrix for the symmetry species and the prime denotes the isotopic substituted molecule. The frequencies are assumed to be harmonic.

The results of the calculations for the B_{1g} and B_{2u} symmetry species are shown in Table XII. It is seen that the data of Cyvin and Cyvin is in almost exact agreement with the calculated ratios for the B_{1g} species and in better agreement for the B_{2u} species than the data of Gallaway and Barker.

TABLE XII

PRODUCT RULE - RATIO OF PRODUCTS OF FREQUENCIES

Symmetry Species	$\frac{ G' }{ G }$	Cyvin and Cyvin	Gallaway and Barker
B_{1g}	0.6091	0.6090	0.6120
B_{2u}	0.5350	0.5443	0.5616

It is also interesting to note that the vibrations in the B_{1g} species are apparently harmonic ones whereas in the B_{2u} species anharmonicity effects may be significant. (Small differences between calculated and observed ratios are usually observed and are attributed to the fact that the observed frequencies and harmonic frequencies are not the same, i.e., the vibrations are not strictly harmonic.)

The normal coordinates for all symmetry species, based on the MVFF, were calculated using the frequency data of Cyvin and Cyvin. They are listed in Appendix III.

A.2 The Urey Bradley Field

Morino, Kuchitsu and Shimanouchi (22) presented a normal coordinate treatment of the $\text{CF}_2 = \text{CF}_2$ and $\text{CF}_2 = \text{CH}_2$ molecules. Their treatment was based on a potential function of the Urey Bradley (28) type, in which the stretching of bonds, the changes in bond angles and non-bonded interactions are considered. A set of equations was presented which relate symmetry force constants of those molecules to the Urey Bradley force constants enabling one to calculate the symmetry force constants directly from Urey Bradley force constants.

Using the structure of ethylene presented in Figure I, it is possible to calculate the relationships between the symmetry force constants and the Urey Bradley Force Constants (22). These equations have been presented in tabular form in Table XIII. The physical significance of the Urey Bradley constants is:

K_{CH} is the C-H stretching force constant

K_{CC} is the C=C stretching force constant

$H_{\text{H-C-H}}$ is the H-C-H angle bending force constant

H_{CCH} is the C-C-H angle bending force constant

F'_{CH} and F_{CH} are CH non-bonded interaction constants

F'_{HH} and F_{HH} are HH non-bonded interaction constants

and Kappa is the intramolecular tension constant. The usual assumption is that $F'_{\text{CH}} = 0.1F_{\text{CH}}$ and $F'_{\text{HH}} = 0.1F_{\text{HH}}$.

Table XIII

Relationship Between Symmetry Force Constants and Urey-Bradley Force Constants
Ethylene

Designation (and Coordinate) of Symmetry Force Constant	Symmetry Species	K_{CH}	K_{CC}	H_{HCH}	H_{CCH}	F_{CH}	F'_{CH}	F_{HH}	F'_{HH}	κ
CH str. (F1, 1)	A _{1g}	1.000	1.000	0.333	0.821	0.920	0.379	1.460		
CC str. (F2, 2)						4.201	1.000			
CH ₂ rock (F3, 3)						0.253	-0.807	0.090	-0.243	2.4863
CH str. (F4, 4)	B _{1g}	1.000			1.231	0.921	0.379		0.540	
CH ₂ rock (F5, 5)						0.379	-1.211			
CH str. (F6, 6)	B _{2u}	1.000			1.231	0.921	0.379		0.540	
CH ₂ rock (F7, 7)						0.379	-1.211			
CH str. (F8, 8)	B _{3u}	1.000		0.333	0.821	0.921	0.379	1.460		
CH ₂ rock (F9, 9)						0.253	-0.807	0.090	-0.243	2.486
(F1, 3)						-0.341	-0.448	0.513	0.513	
(F1, 2)	A _{1g}					1.967	-0.616			
(F2, 3)						-0.728	-0.554			
(F4, 5)						0.591	0.777			
(F6, 7)	B _{1g}					0.591	0.777			
(F8, 9)						-0.341	-0.448	0.513	0.513	

It should be noted that if F'_{CH} is equal to $0.1 F_{CH}$, then according to Table XIII the ratio of interaction force constants is given by

$$\frac{F_{12}}{F_{23}} = -2.40$$

this is significantly different from the ratio 0.79 found in the calculation of the valence force field directly as shown in Table VIII.

The computer program allows one to use a Urey Bradley Field by including in the input data a transformation matrix obtained from the appropriate relationships between Urey Bradley force constants and symmetry force constants (Table XIII). The Urey Bradley constants can then be calculated directly using the program in the usual way.

Six different attempts to obtain a set of force constants for ethylene using the Urey Bradley field all ended in ill conditioned solutions (negative Eigenvalues). A seventh attempt converged after nineteen iterations. In Table XIV the starting values for the nine Urey Bradley constants have been listed and those values which were held invariant during the run have been indicated.

TABLE XIV

UREY BRADLEY FORCE CONSTANTS USED AS STARTING VALUES
FOR ETHYLENE

Force Constant	Run						
	1	2	3	4	5	6	7
K_{CH}	4.80	4.80	4.80	4.80	4.80	4.80	4.80
K_{CC}	10.50	8.00	10.50	10.50	8.00	8.00	8.00
H_{HCH}	0.40	0.40	0.40	0.40	0.40	0.40	0.40
H_{CCH}	0.22	0.22	0.22	0.22	0.22	0.22	0.22
F_{CH}	0.70	0.40	0.70	0.70	0.40	0.40	0.40
F'_{CH}	-0.07	0.20	-0.07	$-0.1F_{CH}^*$	0*	0.20	0*
F_{HH}	0.10	-0.10	0.10	0.10	0.20	0*	0.20
F'_{HH}	-0.01	-0.10	-0.01	$-0.1F_{HH}^*$	0*	0*	0*
Kappa	0.01	0.10	0*	0.01	0.01	0.10	0*

* Held invariant during the run.

The results of run seven have been tabulated in Table XV. The observed frequencies used were those reported by Cyvin and Cyvin (6) since the work with the VFF and the Teller-Redlich Product Rule suggested that these were the more reliable values. The average percent error in the calculated frequencies is 4.17%. The normal coordinates were calculated and are listed in Appendix III.

Table XV

Urey Bradley Force Constants for Ethylene

Observed Frequency	Calculated Frequency	Percent Error	Description of Force Constant	Force Constant	Dispersion (σ^2)
3026.4	3053.7	0.9	CH stretch	5.214	0.390
1622.6	1689.5	4.1	CC stretch	10.585	2.686
1342.2	1304.2	-2.8	HCH bend	2.715	0.298
3102.5	3109.8	0.2	CCH bend	0.439	0.101
1236.0	1098.9	-11.1	C...H repulsion	-0.267	0.273
3105.3	3073.8	-1.0	H...H repulsion	0.037	0.307
810.3	870.2	7.4			
2989.5	2983.8	-0.2			
1443.5	1497.1	3.7			
2260.0	2333.9	3.3			
1518.0	1482.7	-2.3			
985.0	881.8	-10.5			
2310.0	2356.1	2.0			
1011.0	893.5	-12.6			
2345.0	2294.6	-2.1			
584.0	623.7	6.8			
2200.2	2164.8	-1.6			
1077.9	1103.9	2.4			
				Average:	0.676

Average: 4.2

A.3 The Hybrid Orbital Force Field

Using an Hybrid Orbital Field (HOFF) model the in-plane vibrations of ethylene were investigated. According to the HOFF for ethylene (11) the CH stretching force constant in the B_{1g} symmetry species is equal to the corresponding force constant in the B_{2u} symmetry species. Furthermore, the CH stretch- CH_2 rock interaction force constants in the B_{1g} and B_{2u} symmetry species are equal and these force constants are equal to 1.85 times the CH stretch- CH_2 bend interaction force constants in the A_{1g} and B_{3u} symmetry species.

In the first two runs the frequencies taken from both Gallaway and Barker (12) and from Cyvin and Cyvin (6) were used and the CH stretch-C=C stretch interaction was constrained to zero. In a third run Cyvin and Cyvin's observed frequencies were used and allowed to vary. Tables XVI, XVII and XVIII summarize the results of the three runs. The normal coordinates, based on the HOFF, are listed in Appendix III.

The data indicate that Cyvin and cyvin's frequency assignments are more reliable than those of Gallaway and Barker since the average percent error in the calculated frequencies is lower using Cyvin and Cyvin's data. This

is in agreement with the results of the MVFF and Product Rule Calculations. When Cyvin and Cyvin's data were used and the CH stretch-CC stretch interaction constant was calculated, the value of 1.541 was obtained. However, the dispersion associated with that value was 1.338, nearly as high as the value itself. This suggests that the value might be zero and is certainly not well defined by the calculation. Comparing the runs using Cyvin and Cyvin's data (Table XVII and Table XVIII), it was found that the average percent error in the calculated frequencies was 0.9% when the interaction between the CH stretch and CC stretch was not constrained to zero and 1.0% when interaction was held at zero. The average dispersion of all force constants was 0.155 in the run in which the interaction was constrained to zero (Table XVII). Yet when the interaction force constant was allowed to vary (Table XVIII) the average of the resulting dispersions of all the force constants was 0.251. With these results there does not seem to be any way to choose between the results in Table XVII and Table XVIII.

Table XVI

Force Constants For Ethylene Using HOFF Model and Galloway and Barker's Assignments

Observed Frequency	Calculated Frequency	Percent Error	Description of Force Constant	Force Constant	Dispersion (cm^{-2})
3026.4	3303.0	0.2	CH stretch	5.116	0.207
1622.6	1667.0	2.7	CC stretch	8.784	0.506
1342.2	1378.2	2.6	CH ₂ deformation	1.377	0.708
3069.0	3098.1	0.9	CH stretch	5.135	0.186
1055.0	1053.0	-0.2	CH ₂ rock	0.388	0.013
3105.5	3110.9	0.2	CH ₂ rock	0.586	0.024
995.0	1011.0	1.6	CH stretch	5.124	0.186
2989.5	3011.5	0.7	CH ₂ deformation	1.128	0.043
1443.5	1452.9	0.6	CH str.-rock interaction	0.086	0.161
2260.0	2264.3	0.2	CC str.-rock interaction	0.492	0.112
1518.0	1462.8	-3.6	CH str.-CC str. interact.	0.0	*
985.0	954.2	-3.1			
2304.0	2306.6	0.1			
860.0	861.5	0.2			
2345.0	2314.2	-1.3			
740.0	727.1	-1.7			
2200.2	2183.3	-0.8			
1077.9	1071.4	-0.6			
				Average:	0.215

(* indicates that the force constant was held invariant during the run.)

Average: 1.2

Table XVII

Force Constants for Ethylene Using HOFF Model and Cyvin and Cyvin's Assignments
(CH str.-CC str. interaction = 0)

Observed Frequency	Calculated Frequency	Percent Error	Description of Force Constant	Force Constant	Dispersion (cm^{-2})
3026.4	3303.2	0.2	CH stretch	5.114	0.191
1622.6	1667.1	2.7	CH str.-rock interaction	0.900	0.139
1342.2	1378.2	2.7	CC stretch	8.785	0.469
3102.5	3108.2	0.2	CC str.-rock interaction	0.491	0.103
1236.0	1237.4	0.1	CH ₂ deformation	1.377	0.066
3105.5	3118.7	0.4	CH stretch	5.162	0.170
810.3	811.1	0.1	CH ₂ rock	0.535	0.018
2989.5	3011.4	0.7	CH ₂ rock	0.379	0.184
1443.5	1442.0	0.6	CH stretch	5.123	0.172
2260.0	2264.5	0.2	CH ₂ deformation	1.128	0.039
1518.0	1462.7	-3.6	CH str.-CC str. interact.	0.0	*
985.0	954.2	-3.1			
2310.0	2320.2	0.4			
1011.0	1009.7	-0.1			
2345.0	2319.5	-1.1			
584.0	583.4	-0.1			
2200.2	2183.4	-0.8			
1077.9	1071.4	-0.6			
				Average:	0.155

(* indicates that the force constant was held invariant during the run.)

Average: 1.0

Table XVIII

Force Constants for Ethylene Using HOFF Model and Cyvin and Cyvin's Assignments

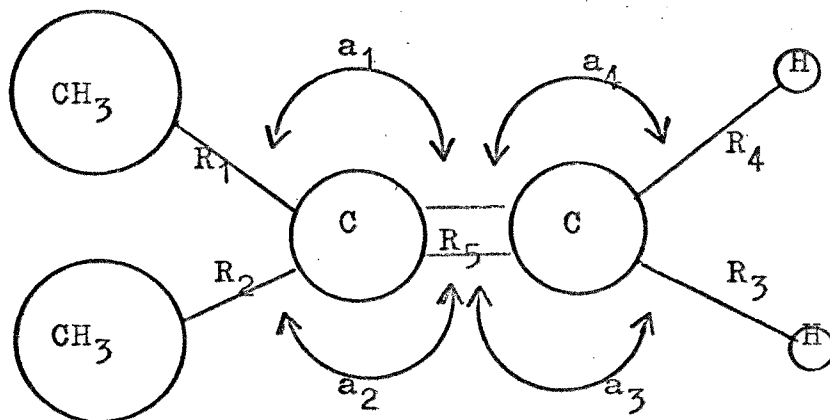
Observed Frequency	Calculated Frequency	Percent Error	Description of Force Constant	Force Constant	Dispersion (cm^{-1})
3024.6	3085.0	1.9	CH stretch	5.559	0.311
1622.6	1654.0	1.9	CC stretch	8.454	0.439
1342.2	1368.2	1.9	CH ₂ deformation	1.403	0.055
3102.5	3107.0	0.1	CH stretch	5.192	0.148
1236.0	1235.3	-0.1	CH ₂ rock	0.535	0.015
3105.5	3126.6	0.7	CH ₂ rock	0.384	0.022
810.3	810.8	0.1	CH stretch	5.111	0.154
2989.5	3010.5	0.7	CH ₂ deformation	1.132	0.036
1443.5	1452.4	0.6	CH str.-rock interact.	0.126	0.130
2260.0	2211.5	-2.1	CC str.-rock interact.	0.591	0.119
1518.0	1485.4	-2.1	CH str.-CC str. interact.	1.541	1.338
985.0	963.9	-2.1			
2310.0	2311.3	0.1			
1011.0	1011.5	0.1			
2345.0	2323.6	-0.9			
584.0	583.7	-0.1			
2220.2	2184.2	-0.7			
1077.9	1071.0	-0.6			
				Average:	0.251
				Average:	0.9

B. The Isobutene Molecule

Since this investigation is primarily concerned with the C=C bond and the effects of (1) bonds adjacent to the double bond and (2) the masses connected to the double bond, the calculation for isobutene can be simplified by treating the two methyl groups as point groups. In this treatment isobutene belongs to the point group C_{2v} . The in-plane vibrations of isobutene are factored into two symmetry species, i.e. the A_1 symmetry species (5 vibrations) and the B_2 symmetry species (4 vibrations).

The internal symmetry coordinates used for Isobutene were the same as those by Kilpatrick and Pitzer (18) and are shown in Figure III.

FIGURE III
INTERNAL SYMMETRY COORDINATES OF ISOBUTENE



Symmetry Type

Coordinate

A_1	$S_1 = \frac{1}{2} (R_1 + R_2)$
	$S_2 = \frac{1}{2} (R_3 + R_4)$
	$S_3 = R_5$
	$S_4 = a_1 + a_2$
	$S_5 = a_3 + a_4$
B_2	$S_6 = \frac{1}{2} (R_1 - R_2)$
	$S_7 = \frac{1}{2} (R_3 - R_4)$
	$S_8 = \frac{1}{2} (a_1 - a_2)$
	$S_9 = \frac{1}{2} (a_3 - a_4)$

B.1 The Valence Force Field

To consider all of the interaction force constants in addition to the five principle force constants of the A_1 species, a total of fifteen force constants would be needed. An additional 10 force constants are needed for the B_2 species. Since data from only two isomers are available, it is clearly impossible to consider all interaction force constants.

Since the B_2 species needs fewer force constants than the A_1 species it was thought that the best approach would be to solve the B_2 species first then transfer those force constants to the A_1 species. The frequency assignments used were taken from Pathak and Fletcher (24) since only these authors reported assignments for normal isobutene (C_4H_8) and deuterated isobutene (C_4D_8).

Kilpatrick and Pitzer (18) reported observed frequencies for normal isobutene, and a more recent paper by Nakamuar (23) gave the observed spectra, but no assignments were made. Tentative assignments of the observed data were made based on the previous assignments and on assignments of related molecules.

Pathak and Fletcher, however, have reported the assignment of both normal isobutene and the totally deuterated isobutene, C_4D_8 . However, the assignment of the

C-C stretch and the CH_2 wag vibrations in the B_2 species are reversed from the assignments of the earlier workers. Data for isobutene D_2 and isobutene D_6 would be useful in resolving the conflict; but they are not available. Since only Pathak and Fletcher's data are available for the deuterated species, it is necessary to use their assignments.

The interaction force constant between the C-H stretching vibration and the CH_2 rock was held invariant at zero since the data from the A_1 species of ethylene suggested that there was little or no interaction. All other interaction force constants were assumed to be zero with the exception of the C-H stretch skeletal rock interaction and the C-C stretch-skeletal rock interaction.

Table XIX shows the results found for the B_2 species. The program did not converge on a single set of force constants, but rather oscillated between two possible solutions and was halted after 24 iterations.

The two sets of force constants from the B_2 species were averaged and the resulting set was used as starting values for the A_1 species of Isobutene. If it is assumed that the interaction force constant between vibrations which do not have a common atom is zero, and that the interaction force constant between the C-H stretch and

the CH_2 scissors is zero (because of the results of the A_{1g} species of ethylene), there are five principle force constants and five interaction force constants to be solved for. Using the frequencies from both the normal and deuterated molecules, there are only ten observed frequencies. All attempts to obtain a set of force constants for the A_1 species of isobutene failed because of ill conditioned solutions. The calculated normal coordinates are given in Appendix III.

The failure to obtain a good set of force constants for the A_1 species is due to the lack of sufficient data to completely define the potential field. Data from other Isotopic Species are needed and/or a systematic method of constraining force constants is necessary to calculate force constants for the A_1 symmetry species.

Table XIX

Force Constants Found for the B₂ Species of Isobutene

Description of Vibration	Observed Frequency	Calculated Frequency (% Error)		Solution I	Solution II	Force Constant	Force Constant	Dispersion (σ^2)
		Solution I	Solution II					
CH stretch	3083.5	3089.3 (0.2)	3080.0 (-0.1)			5.058	4.955	0.453
CC stretch	1281.0	1293.9 (1.0)	1296.0 (1.2)			4.882	5.065	0.377
CH ₂ rock	973.0	952.5 (-2.1)	951.8 (-2.2)			0.642	0.665	0.065
skeletal bend	418.0	414.0 (-1.0)	415.4 (-0.6)			0.382	0.384	0.066
CD stretch	2305.5	2305.6 (0.0)	2312.7 (0.3)					
CC stretch	1267.0	1263.6 (-0.3)	1260.9 (-0.5)					
CD ₂ rock	767.0	757.0 (-1.3)	758.7 (-1.1)					
skeletal bend	353.0	353.6 (0.6)	352.8 (-0.3)					
CH stretch - skeletal bend interaction						-0.102	0.084	0.706
CC stretch - skeletal bend interaction						-0.284	-0.430	0.356

B.2 The Hybrid Orbital Field

Several attempts were made using the HOFF to transfer the force constants found for ethylene to isobutene. These attempts failed to produce a consistent set of force constants and suggest strongly that the force constants can not be transferred a priori. It would seem that the HOFF would be the most appropriate field to use because the physical significance of the field suggests relationships between force constants and therefore reduces the number of unknowns (11).

CHAPTER V
DISCUSSION OF RESULTS

A. Force Constants in Relation to Bond Lengths

An important feature of force constants is the relation they bear to bond lengths. R.M. Badger (2) suggested that for diatomic molecules the force constant increases as the equilibrium bond length becomes shorter, and proposed the empirical relationship:

$$k = A / (R_e - B)^3$$

where k is the force constant, R_e is the equilibrium bond length and A and B are constants appropriate for the atoms forming the diatomic molecule. Badger also found that his equation was quite successful with C-H, C-O, C-S and S-O linkages in triatomic molecules.

Linnett (20) reviewed various empirical relations between bond lengths and force constants and reported that the most satisfactory relation (mainly because of its simplicity) was that proposed by C.H. Douglas Clark (8), i.e.

$$k R_e^6 = C$$

where C is a constant.

Both Badger's and Clark's equations imply that the C-H stretching force constant should be the same in each of the symmetry species of a given molecule since the equilibrium bond distance does not change. We have found

that with ethylene this is only a first order approximation. Table XX lists the C-H stretch force constants and the corresponding dispersions found for each of the in-plane species of ethylene using the VFF. The data show that differences in force constants as high as 28% occur.

TABLE XX
C-H Stretch Force Constants for Ethylene
(VFF)

Species	Force Constant	σ^2
A _{1g}	5.568	0.765
B _{1g}	5.124	0.017
B _{2u}	4.353	0.185
B _{3u}	4.723	0.224
Average	4.942	

Using the data from the A_{1g} symmetry species of ethylene and substituting the appropriate values into the Douglas Clark equation, one can calculate the constant C. Using this calculated value and the C-H equilibrium distance one may then calculate a force constant for the C-H stretch of isobutene. The value calculated is 6.07. If, however, the average value of the four force constants is used, one obtains 5.39. Although we do not have reliable data for the C-H stretch force constant of isobutene, the data we do have suggests that either 4.9 or

5.0 are appropriate values for the B₂ species. This seems to suggest that there is considerable uncertainty about the validity of transferring force constants in this manner.

B. Structural Data and Force Constants

The structural data shown in Figure 1 suggests that the H-C-H angle in ethylene is slightly smaller than the H-C-H angle in isobutene. Since the isobutene H-C-H angle is closer to the tetrahedral angle as a first approximation one might expect less resistance to angle bending in the isobutene molecule and therefore a lower force constant. The data presented in Table XXI shows the H-C-H force constant found for each symmetry species of ethylene using the VFF. Clearly the value of about 0.6 found for the B_2 species of isobutene is very much lower than the A_{1g} or B_{3u} values for ethylene and slightly higher than the B_{1g} value.

TABLE XXI

H-C-H Rock Force Constant for Ethylene
(VFF)

Species	Force Constant	σ^2
A_{1g}	1.454	0.148
B_{1g}	0.534	0.004
B_{2u}	0.964	0.169
B_{3u}	1.339	0.161

It is interesting, although perhaps a coincidence, that when the C-H stretch force constants and the CH₂ rock force constants for the two molecules are compared, the agreement is good if the B_{1g} species of ethylene is compared to the B₂ species of isobutene.

C. Potential Energy Distribution

From equation (27) it follows that

$$\lambda_i = \sum_{j,k} L_{ji} L_{ki} F_{ik}$$

or in matrix form

$$\Lambda = J F$$

Since the potential energy is given by

$$2 V = \sum_i \lambda_i Q_i^2$$

it can be shown (17) that the potential energy distribution (P.E.D.) is given by

$$\text{P.E.D.} = J F \Lambda^{-1}$$

Thus the P.E.D. is a matrix which shows the contribution of each force constant to each of the observed frequencies. Tables XXIII through XXIV give the potential energy distributions obtained for ethylene for each of the three force fields used. The observed frequencies shown in the tables were taken from Cyvin and Cyvin (6) since their data seemed to be more reliable than the previously reported frequencies, as discussed earlier. The P.E.D. shown in Table XXIV for the Hybrid Orbital Force Field was taken from the calculation in which $F(1,2)$ was allowed to vary. The P.E.D. obtained from the run was nearly the same as the one obtained from the run in which the $F(1,2)$ constant was constrained to zero.

Table XXII

Potential Energy Distribution for Ethylene
[MVFF]

Symmetry Species	Observed Frequency	Force Constant					
		CH str. F(1,1)	CC str. F(2,2)	HCH bend F(3,3)	F(1,2)	F(1,3)	F(2,3)
A _{1g} [C ₂ H ₄]	3026.4	96.49	0.54	0.04	-2.78	0.00	F(2,3)
	1622.0	0.42	33.22	33.25	-1.44	0.00	-0.14
	1342.2	0.70	33.75	32.24	-1.87	0.00	31.67
A _{1g} [C ₂ D ₄]	2260.0	88.45	3.61	0.22	-6.87	0.00	-0.84
	1518.0	0.04	86.30	1.64	-0.69	0.00	-11.33
	985.0	0.19	9.28	66.35	-0.52	0.00	-23.65
B _{1g} [C ₂ H ₄]	3102.5	97.77	0.82	F(4,5)			
	1236.0	0.02	99.79	0.19	1.41		
	2310.0	94.14	3.14	-2.72			
B _{1g} [C ₂ D ₄]	1011.0	1.07	97.31	1.62			
		CH str.	HCH rock				
		F(4,4)	F(5,5)	F(4,5)			
B _{2u} [C ₂ H ₄]	3105.5	75.56	2.85	21.59			
	810.0	23.15	34.97	-41.87			
	2345.0	74.36	3.14	22.49			
B _{2u} [C ₂ D ₄]	584.0	23.28	34.82	-41.90			
		CH str.	HCH rock				
		F(6,6)	F(7,7)	F(6,7)			
B _{3u} [C ₂ H ₄]	2989.5	87.43	2.75	9.83			
	1443.5	14.45	65.96	-19.58			
	2200.2	83.50	4.37	12.12			
B _{3u} [C ₂ D ₄]	1077.9	16.38	63.21	-20.41			
		CH str.	HCH rock				
	F(8,8)	F(9,9)	F(8,9)				

Table XXIII

Potential Energy Distribution for Ethylene
[UBFF]

Symmetry Species	Observed Frequency	Force Constant						
		CH str.	CC str.	HCH bend	CCH bend	C...H Repulsion	H...H Repulsion	
A _{1g} [C ₂ H ₄]	3026.4	92.55	3.95		0.20	-1.72	1.08	
	1622.6	5.83	46.75	23.53	9.37	-14.46	-0.06	
	1342.2	0.57	40.78	39.96	15.92	-2.53	0.24	
A _{1g} [C ₂ D ₄]	2260.0	76.57	20.25	1.50	0.60	-0.10	0.99	
	1518.0	19.40	57.00	5.91	2.35	-15.29	0.04	
	985.0	0.00	9.97	62.38	24.84	-2.56	0.24	
B _{1g} [C ₂ H ₄]	3102.5	96.00			1.38	-2.62		
	1236.0	3.11			79.02	-17.87		
B _{1g} [C ₂ D ₄]	2310.0	94.33			4.17	-1.50		
	1011.0	5.63			76.01	-18.36		
B _{2u} [C ₂ H ₄]	3105.5	95.95			0.11	-3.94		
	810.3	1.31			81.46	-17.23		
B _{2u} [C ₂ D ₄]	2345.0	96.10			0.25	-3.65		
	584.0	1.62			81.00	-17.37		
B _{3u} [C ₂ H ₄]	2989.5	94.51		0.26	0.11	-4.05	1.07	
	1443.5	1.04		66.61	26.53	-5.71	0.11	
B _{3u} [C ₂ D ₄]	2200.2	94.01		0.78	0.31	-3.77	1.13	
	1077.9	2.07		65.72	26.18	-5.97	0.06	

Table XXIV

Potential Energy Distribution for Ethylene
[HOFF]

Symmetry Species	Observed Frequency	Force Constant										
		F(1,1)	F(2,2)	F(3,3)	F(4,4)	F(5,5)	F(7,7)	F(8,8)	F(9,9)	F(1,3) F(8,9) F(4,5) F(6,7)		
A _{1g} [C ₂ H ₄]	3026.4	95.81	0.48	0.18						0.38	-0.10	-3.05
	1622.6	0.06	26.78	58.77						0.17	-13.62	-0.59
	1342.2	2.61	61.49	18.13						-0.62	11.46	-5.69
A _{1g} [C ₂ D ₄]	2260.0	87.90	3.10	0.52						0.61	-0.44	-7.43
	1518.0	0.01	74.77	13.77						0.03	-11.01	-0.40
	985.0	0.97	7.42	81.19						-0.80	8.42	-1.20
B _{1g} [C ₂ H ₄]	3102.5				97.23	0.61						-2.16
	1236.0				0.36	97.97						-1.67
	2310.0				93.15	2.54						-4.30
B _{1g} [C ₂ D ₄]	1011.0				0.07	99.21						0.73
	3105.5				99.76		0.01					-0.24
	810.3				2.31		92.85					-4.83
B _{2u} [C ₂ D ₄]	2345.0				99.19		0.05					-0.77
	584.0				1.89		93.72					-4.39
	2989.5							99.02	0.36			0.62
B _{3u} [C ₂ H ₄]	1443.5							1.22	97.63			-1.14
	2200.2							97.93	1.02			1.04
	1077.9							2.27	96.18			-1.55

Where: F(1,1)= CH str.; F(2,2)= CC str.; F(3,3)= HCH bend; F(4,4)=F(6,6)= CH str.

F(5,5)= HCH rock; F(7,7)= HCH rock; F(8,8)= CH str.; and F(9,9)= HCH rock

It is interesting that in all three force fields the C=C stretching vibration is not a pure vibration in the normal molecule, i.e. the F(2,2) force constant accounts for only a portion of the 1622 cm^{-1} frequency. In the deuterated ethylene, however, there is a change in the potential energy distribution and the F(2,2) force constant accounts for most of the 1518 cm^{-1} frequency. This suggests that as the moieties attached to the C=C bond become heavier the C=C stretching vibration becomes less coupled to the HCH bending vibration. Unfortunately we were not able to obtain the potential energy distribution for the A_1 species of isobutene.

The situation is reversed, however, when one considers the C-H (C-D) stretching vibration. The F(1,1) force constant always accounts for more of the potential energy in the CH stretch than in the CD stretch vibration. The same is true for the F(4,4), F(6,6) and F(8,8) frequencies.

The data suggests, therefore, that when one goes from the C_2H_4 molecule to the C_2D_4 molecule there is a significant decrease in the C=C stretch-HCH bend coupling and a slight increase in the C=C stretch-C-H stretch coupling. Although the data from isobutene is not completely satisfactory because of the unresolved ambiguity in the two sets of results, the potential energy distribution

does show decrease in the purity of the C-D stretching vibration.

The Potential Energy Distributions for the B_2 species of isobutene are shown in Table XXV.

Table XXV

Potential Energy Distribution of Isobutene B₂ Species
[MVFF]

Observed Frequency	CH Stretch	C-C Stretch	Skeletal Bend	CH ₂ Rock	CH Stretch- Skel. Bend Interaction	C-C Stretch Skel Bend Interaction
3083.5	98.71	0.00	0.36	0.18	0.73	-0.01
1281.0	0.02	81.50	1.20	11.16	-0.02	-6.10
973.0	1.49	0.46	84.55	8.36	-1.37	-3.78
418.0	0.00	14.33	12.47	64.94	-0.01	-8.23
2305.5	96.90	0.01	1.11	0.64	1.27	-0.07
1267.0	0.13	76.23	2.69	12.06	-0.07	-8.82
767.0	3.11	0.29	76.91	14.87	-1.89	2.93
353.0	0.00	13.81	21.01	54.65	-0.04	-10.49

D. Comparison of Force Fields for Ethylene

It has been previously shown that, in principle, the most general harmonic valence force field (GVFF) is the best function to use as a description of the potential forces within a molecule because it considers all possible interactions. However in practice, there is usually insufficient data to completely define the field and the frequencies are usually not harmonic. This was the case for ethylene. There are several approaches available to get the best possible force field for ethylene. A modified valence force field (MVFF) was used where interaction force constants were constrained to a fixed value or zero a priori. This permitted the calculation of a set of force constants which were used to calculate vibrational frequencies with a reasonable accuracy. However, there is no physical basis to decide which interaction constants to constrain and which ones to vary. Thus the force constants obtained from the MVFF could not be used as a basis for obtaining force constants for more complicated olefins.

A second approach is to use a force field based on a physical model. The two models used in this study, as discussed previously, are the Urey-Bradley Force Field (UBFF) and the Hybrid Orbital Force Field (HOFF).

The results of this study indicate that the UBFF is not a useful model for ethylene. As seen in Table XV, the reproduction of the observed frequencies using UBFF is poorer than those obtained using the MVFF. Further, the dispersions for the repulsive force constants are larger than the force constants themselves. This rather limits the physical significance of the model. That is, it appears that non-bonded interactions make no significant contribution to the molecular force field of ethylene. Further evidence for this conclusion is shown in the tabulation of Potential Energy Distributions for the application of the UBFF to ethylene (Table XXIII). It is seen that the H...H repulsive force constant makes negligible or no contribution to the vibrational modes and the C...H repulsive force constant makes, at most, a minor contribution to the C=C stretching and CH₂ rocking modes.

The Hybrid Orbital Force Field reproduces the observed data as well as the MVFF and has the further advantage that there is a physical basis for constraining some of the force constants. It would thus appear to be an appropriate field to transfer some corresponding force constants to more complex olefins. However, the results of the work on isobutene apparently indicate that the HOFF is not, in its present form, a suitable model for transferring force constants in olefin-type molecules.

E. Future Work Needed

The frequency assignments by Pathak and Fletcher (24) for isobutene contradict the earlier assignments of Kilpatrick and Pitzer (18), as discussed earlier, and this difference must be completely resolved before one can have confidence in the normal coordinate analysis of isobutene. To clarify the situation the $\text{CH}_2=\text{C}-(\text{CD}_3)_2$ and $\text{CD}_2=\text{C}-(\text{CH}_3)_2$ molecules would be helpful. With the spectra of these isotopes it would be possible to clearly distinguish which assignments were correct.

Although the data obtained thus far suggests that it is not likely that one can transfer force constants directly from one olefin to another, to completely explore this question it is necessary to complete the normal coordinate analysis of other olefins, such as 2,3-dimethyl-2-butene, cis-2-butene, and trans-2-butene.

APPENDIX I

Programs WORK4 and WORK3

Program WORK4 Operating Instructions

This program generates the g matrix for an ethylene type molecule, using the structure of the molecule as input data.

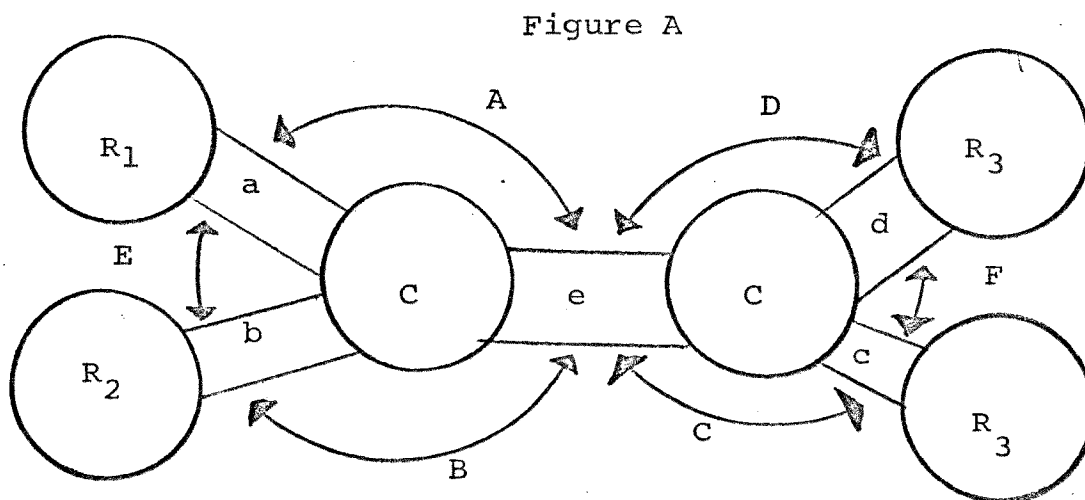
Input Data

Line 1 of the input data contains the bond distances (Å) a, b, c, d, e as shown in Figure A. Distances are separated by commas (Free format).

Line 2 contains the bond angles (degrees) A, B, C, D, E, F as shown in Figure A. Angles are separated by commas (Free format).

Line 3 contains the atomic weights of the moieties R_1, R_2, R_3, R_4 as shown in Figure A. Weights are separated by commas (Free format).

Line 4 contains the atomic weight of carbon (Free format).



Output

The resulting 12 by 12 matrix is written with 6 data points to a line - i.e. the matrix elements 1,1 through 1,6 are written on the first line. Elements 1,7 through 1,12 are on the second line. Line 3 contains elements 2,1 through 2,6, and elements 2,7 through 2,12 are on the next line, etc.

```

1      DIMENSION R1(5),B1(6),H1(4),GO(20,20)
999    READ(1,999)(R1(II),II=1,5)
      FORMAT(6F)
      READ(1,999)(B1(II),II=1,6)
      READ(1,999)(H1(II),II=1,4)
      A=1.0/R1(1)
      B=1.0/R1(2)
      C=1.0/R1(3)
      D=1.0/R1(4)
      E=1.0/R1(5)
      FF=COSD(B1(1))
      FG=COSD(B1(2))
      FH=COSD(B1(3))
      FI=COSD(B1(4))
      FJ=COSD(B1(5))
      FK=COSD(B1(6))
      FL=SIND(B1(1))
      FM=SIND(B1(2))
      FN=SIND(B1(3))
      FO=SIND(B1(4))
      FP=SIND(B1(5))
      FQ=SIND(B1(6))
      READ(1,999)FR
      FR=1/FR
      FS=1.0/H1(1)
      FT=1.0/H1(2)
      FU=1.0/H1(3)
      FV=1.0/H1(4)
      FW=(FJ-(FF*FG))/(FL*FM)
      FX=(FG-(FF*FJ))/(FL*FP)
      FY=(FF-(FG*FJ))/(FM*FP)
      FZ=(FK-(FI*FH))/(FO*FN)
      GO(1,1)=FR + FS
      GO(1,2)=FR * FJ
      GO(1,3)=0.0
      GO(1,4)=0.0
      GO(1,5)=FR*FF
      GO(1,6)=-E*FR*FL
      GO(1,7)=-((B*FP*((FF-(FJ*FG))/(FP*FM)))+
1(E*FL*((FJ-(FF*FG))/(FL*FM))))*FR
      GO(1,8)=-E*FR*FN
      GO(1,9)=E*FR*FO
      GO(1,10)=-B*FR*FP
      GO(1,11)=0.0
      GO(1,12)=0.0
      GO(2,2)=FR+FT
      GO(2,3)=0.0
      GO(2,4)=0.0
      GO(2,5)=FR*FG
      GO(2,6)=-((A*FP*((FG-(FJ*FF))/(FP*FL)))+
1(E*FM*((FJ-(FG*FF))/(FM*FL))))*FR
      GO(2,7)=-E*FR*FM
      GO(2,8)=E*FR*FN
      GO(2,9)=-E*FR*FO
      GO(2,10)=-A*FR*FP
      GO(2,11)=0.0
      GO(2,12)=0.0
      GO(3,3)=FU+FR
      GO(3,4)=FR*FK
      GO(3,5)=FR*FH
      GO(3,6)=-E*FR*FI

```

$G0(3,7) = E * FR * FM$
 $G0(3,8) = -E * FR * FN$
 $G0(3,9) = -((E * FN * ((FK - (FH * FI)) / (FN * FO))) +$
 $1(D * FQ * ((FH - (FK * FI)) / (FQ * FO))) * FR$
 $G0(3,10) = 0.0$
 $G0(3,11) = -D * FR * FQ$
 $G0(3,12) = 0.0$
 $G0(4,4) = FR + FV$
 $G0(4,5) = FR * FI$
 $G0(4,6) = E * FR * FL$
 $G0(4,7) = -E * FR * FM$
 $G0(4,8) = -((E * FO * ((FK - (FI * FH)) / (FO * FN))) +$
 $1(C * FQ * ((FI - (FK * FH)) / (FQ * FN))) * FR$
 $G0(4,9) = -E * FR * FO$
 $G0(4,10) = 0.0$
 $G0(4,11) = -C * FR * FQ$
 $G0(4,12) = 0.0$
 $G0(5,5) = FR + FR$
 $G0(5,6) = -A * FR * FL$
 $G0(5,7) = -B * FR * FM$
 $G0(5,8) = -C * FR * FN$
 $G0(5,9) = -D * FR * FO$
 $G0(5,10) = -((A * FL * ((FG - FF * FJ) / FL * FP)) +$
 $1(B * FM * ((FF - FG * FJ) / FM * FP)) * FR$
 $G0(5,11) = -((C * FN * ((FI - FH * FK) / FN * FQ)) +$
 $1(D * FO * ((FH - FI * FK) / FO * FQ)) * FR$
 $G0(5,12) = 0.0$
 $G0(6,6) = (E * E * FR) + (A * A * FS) + ((E * E + A * A - 2.0 * A * E * FF) * FR)$
 $G0(6,7) = (E * E * (FW)) * FR + (((E - (A * FF)) - (B * FG)) * E * FW)$
 $1 + ((FL * FN * (1.0 - (FW * FW))) + (FJ * FW)) * A * B * FR$
 $G0(6,8) = E * (((E - (C * FH)) * FR) + ((E - (A * FF)) * FR))$
 $G0(6,9) = -E * (((E - (C * FI)) * FR) + ((E - (A * FF)) * FR))$
 $G0(6,10) = (A * A * FX * FS) + (((A - (B * FJ)) - (E * FF)) * A * FX)$
 $1 + ((FP * FL * (1.0 - (FX * FX))) + (FG * FX)) * B * E * FR$
 $G0(6,11) = (((FN * FK) - FO) * C) + (((FO * FK) - FN) * D) *$
 $1(E * FR / FQ)$
 $G0(6,12) = 0.0$
 $G0(7,7) = (E * E * FR) + (B * B * FT) + ((E * E) + (B * B) - (2.0 * E * B * FG)) * FR$
 $G0(7,8) = -E * (((E - (C * FH)) * FR) + ((E - (B * FG)) * FR))$
 $G0(7,9) = E * (((E - (D * FI)) * FR) + ((E - (B * FG)) * FR))$
 $G0(7,10) = (B * B * FY) * FT + ((B - E * FG - A * FJ) * B * FY +$
 $1(FM * FP * (1.0 - (FY * FY)) + FF * FY) * E * A * FR$
 $G0(7,11) = ((FN * FK - FO) * C + (FO * FK - FN) * D) * (E * FR / FQ)$
 $G0(7,12) = 0.0$
 $G0(8,8) = (C * C * FU) + (E * E * FR) * ((C * C + E * E - 2.0 * C * E * FH) * FR)$
 $G0(8,9) = (E * E * FZ * FR) + ((E - C * FH - D * FI) * E * FZ +$
 $1(FN * FO * (1.0 - (FZ * FZ)) + FK * FZ) * C * D * FR$
 $G0(8,10) = ((FL * FJ - FM) * A + (FM * FJ - FL) * B) * (E * FR / FP)$
 $FW = (FH - (FI * FK)) / (FO * FQ)$
 $G0(8,11) = (D * D * FW * FS) + ((D - E * FI - C * FK) * D * FW +$
 $1(FO * FQ * (1.0 - (FW * FW)) + FH * FW) * E * C * FR$
 $G0(8,12) = 0.0$
 $G0(9,9) = D * D * FV + E * E * FR + ((D * D + E * E - 2.0 * D * E * FI) * FR)$
 $G0(9,10) = ((FL * FJ - FM) * A + (FM * FJ - FL) * B) * (E * FR / FP)$
 $FX = (FH - (FK * FI)) / (FQ * FO)$
 $G0(9,11) = (D * D * FX * FS) + ((D - C * FK - E * FI) * D * FX +$
 $1(FQ * FO * (1.0 - (FX * FX)) + FH * FX) * C * E * FR$
 $G0(9,12) = 0.0$
 $G0(10,10) = (A * A * FS) + (B * B * FT) + (A * A + B * B - 2.0 * A * B * FJ) * FR$
 $G0(10,11) = 0.0$
 $G0(10,12) = 0.0$

```
GO(11,11)=(D*D*FV)+(C*C*FL)+(D*D+C*C-2.0*D*C*FK)*FR
```

```
GO(11,12)=0.0
```

```
GO(12,12)=((A/FL)**2)*FS+((C/FN)**2)*FV+
```

```
1*((A/FL)-((FH/FN + FF/FL)*FE))*FR+
```

```
1*((C/FN)-((FF/FL + FH/FN)*FE))*FR
```

```
DO 10 JJJ=1,12
```

```
DO 10 III=JJJ,12
```

```
10 GO(III, JJJ)=GO(JJJ, III)
```

```
DO 20 III=1,12
```

```
WRITE(2,998)(GO(III, JJJ), JJJ=1,6)
```

```
WRITE(2,998)(GO(III, JJJ), JJJ=7,12)
```

```
998 FORMAT(6(F9.5, ','))
```

```
20 CONTINUE
```

```
END
```

WORK4 Sample Problem

The Ethylene Molecule (C_2H_4)

00010	1.1030, 1.1030, 1.1030, 1.1030, 1.3369	Input
00020	121.4, 121.4, 121.4, 121.4, 117.2, 117.2	
00030	1.00797, 1.00797, 1.00797, 1.00797	
00040	12.01115	
	1.07535, -0.03806, 0.00000, 0.00000, -0.04338, -0.05316,	O U T P U T
	0.12029, -0.05316, 0.05316, -0.06713, 0.00000, 0.00000,	
	-0.03806, 1.07535, 0.00000, 0.00000, -0.04338, 0.12029,	
	-0.05316, 0.05316, -0.05316, -0.06713, 0.00000, 0.00000,	
	0.00000, 0.00000, 1.07535, -0.03806, -0.04338, -0.05316,	
	0.05316, -0.05316, 0.12029, 0.00000, -0.06713, 0.00000,	
	0.00000, 0.00000, -0.03806, 1.07535, -0.04338, 0.05316,	
	-0.05316, 0.12029, -0.05316, 0.00000, -0.06713, 0.00000,	
	-0.04338, -0.04338, -0.04338, -0.04338, 0.16651, -0.06443,	
	-0.06443, -0.06443, -0.06443, 0.10193, 0.10193, 0.00000,	
	-0.05316, 0.12029, -0.05316, 0.05316, -0.06443, 1.03589,	
	-0.12072, 0.15200, -0.15200, -0.91517, -0.15790, 0.00000,	
	0.12029, -0.05316, 0.05316, -0.05316, -0.06443, -0.12072,	
	1.03589, -0.15200, 0.15200, -0.91517, -0.15790, 0.00000,	
	-0.05316, 0.05316, -0.05316, 0.12029, -0.06443, 0.15200,	
	-0.15200, 1.03589, -0.12072, -0.15790, -0.91517, 0.00000,	
	0.05316, -0.05316, 0.12029, -0.05316, -0.06443, -0.15200,	
	0.15200, -0.12072, 1.03589, -0.15790, -0.91517, 0.00000,	
	-0.06713, -0.06713, 0.00000, 0.00000, 0.10193, -0.91517,	
	-0.91517, -0.15790, -0.15790, 1.83034, 0.00000, 0.00000,	
	0.00000, 0.00000, -0.06713, -0.06713, 0.10193, -0.15790,	
	-0.15790, -0.91517, -0.91517, 0.00000, 1.83034, 0.00000,	
	0.00000, 0.00000, 0.00000, 0.00000, 0.00000, 0.00000,	
	0.00000, 0.00000, 0.00000, 0.00000, 0.00000, 2.41544,	

Program WORK3 Operating Instructions

This Program uses as starting data the U and g matrices and produces the G matrix needed for the normal coordinate analysis. The algorithm used for the calculation is

$$G = U g U'$$

where U' is U transpose. Subroutines ARRAY, GMPRD and GMTRA used in this program are taken from the IBM Scientific Subroutine Package.

Input Data

Line 1 contains the format to be used for inputing the U matrix.

Line 2 contains the format to be used for inputing the g matrix (always 6F if the g matrix was generated by program WORK4).

Line 3 contains the format to be used for outputing the G matrix.

Line 4 contains the dimensions of the U matrix (row,column) in free format.

Line 5 and following contain the elements of the U matrix, beginning with element 1,1 through 1,n then 2,1 through 2,n etc. The format must be in agreement with Line 1. As many lines as

are needed can be used for the U matrix (2 lines were used in the example shown).

After the U matrix, the dimensions of the g matrix follow in free format (row, column).

The g matrix follows in the format specified in Line 2.

Output

The resulting G matrix is written in the format specified in Line 3 beginning with element 1,1 through element 1,n then element 2,1 through element 2,n, etc.

Program: WORK3

```

      DIMENSION U(10,20),UA(200),G(20,20),GA(400),
1 UTR(200),G1(200),G2(20,20),G2A(400),FMT1(14),FMT2(14),
1 FMT3(14)
C      FORMAT FOR THE "U" MATRIX INPUT
      READ(1,900)(FMT1(I),I=1,14)
C      FORMAT FOR THE "G" MATRIX INPUT
      READ(1,900)(FMT2(I),I=1,14)
C      FORMAT FOR THE "G" MATRIX OUTPUT
      READ(1,900)(FMT3(I),I=1,14)
900    FORMAT(14A5)
C      DIMENSIONS OF "U" MATRIX (ROWS,COLUMNS)
      READ(1,999)NU1,NU2
999    FORMAT(2I)
      DO 3I=1,NU1,1
3      READ(1,FMT1)(U(I,J),J=1,NU2,1)
      CALL ARRAY(2,NU1,NU2,10,20,UA,U)
C      DIMENSION OF "G" MATRIS(ROW,COL.) AND # OF DATA /LINE
      READ(1,998)NG1,NG2
998    FORMAT(2I)
      IF(NG2 - 6)10,10,11
11     IF(NG2-12) 12,12,13
13     IF(NG2-18) 14,14,15
10     DO 4 I = 1,NG1
4      READ(1,FMT2)(G(I,J),J=1,NG2)
      GO TO 16
12     DO 80 I=1,NG1
      READ(1,FMT2)(G(I,J),J=1,6)
80     READ(1,FMT2)(G(I,J),J=7,NG2)
      GO TO 16
14     DO 81 I=1,NG1
      READ(1,FMT2)(G(I,J),J=1,6)
      READ(1,FMT2)(G(I,J),J=7,12)
81     READ(1,FMT2)(G(I,J),J=13,NG2)
      GO TO 16
15     DO 82 I=1,NG1
      READ(1,FMT2)(G(I,J),J=1,6)
      READ(1,FMT2)(G(I,J),J=7,12)
      READ(1,FMT2)(G(I,J),J=13,18)
82     READ(1,FMT2)(G(I,J),J=19,NG2)
16     CALL ARRAY(2,NG1,NG2,20,20,GA,G)
      CALL GMTRA(UA,UTR,NU1,NU2)
      CALL GMPRD(GA,UTR,G1,NG1,NG2,NU1)
      CALL GMPRD(UA,G1,G2A,NU1,NU2,NU1)
      CALL ARRAY(1,NU1,NU1,20,20,G2A,G2)
      DO 5 I=1,NU1,1
5      WRITE(2,FMT3)(G2(I,J),J=1,NU1,1)
      END

```

WORK3 Sample Problem

The Ethylene Molecule (C_2H_4) - B_{3u} Symmetry

		(12F)
		(6F)
		(1H, 12(FE.4, 2X))
		2, 12
		.5, .5, -.5, -.5, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0, 0.0
		0.0, 0.0, 0.0, 0.0, .5515, .5515, -.5515, -.5515, 0.0, 0.0, 0.0, 0.0
		12, 12
I N P U T		1.07535, -0.03806, 0.00000, 0.00000, -0.04338, -0.05316,
		0.12029, -0.05316, 0.05316, -0.06713, 0.00000, 0.00000,
		-0.03806, 1.07535, 0.00000, 0.00000, -0.04338, 0.12029,
		-0.05316, 0.05316, -0.05316, -0.06713, 0.00000, 0.00000,
		0.00000, 0.00000, 1.07535, -0.03806, -0.04338, -0.05316,
		0.05316, -0.05316, 0.12029, 0.00000, -0.06713, 0.00000,
		0.00000, 0.00000, -0.03806, 1.07535, -0.04338, 0.05316,
		-0.05316, 0.12029, -0.05316, 0.00000, -0.06713, 0.00000,
		-0.04338, -0.04338, -0.04338, -0.04338, 0.16651, -0.06443,
		-0.06443, -0.06443, -0.06443, 0.10193, 0.10193, 0.00000,
		-0.05316, 0.12029, -0.05316, 0.05316, -0.06443, 1.03589,
		-0.12072, 0.15200, -0.15200, -0.91517, -0.15790, 0.00000,
		0.12029, -0.05316, 0.05316, -0.05316, -0.06443, -0.12072,
		1.03589, -0.15200, 0.15200, -0.91517, -0.15790, 0.00000,
		-0.05316, 0.05316, -0.05316, 0.12029, -0.06443, 0.15200,
		-0.15200, 1.03589, -0.12072, -0.15790, -0.91517, 0.00000,
		0.05316, -0.05316, 0.12029, -0.05316, -0.06443, -0.15200,
		0.15200, -0.12072, 1.03589, -0.15790, -0.91517, 0.00000,
		-0.06713, -0.06713, 0.00000, 0.00000, 0.10193, -0.91517,
		-0.91517, -0.15790, -0.15790, 1.83034, 0.00000, 0.00000,
		0.00000, 0.00000, -0.06713, -0.06713, 0.10193, -0.15790,
		-0.15790, -0.91517, -0.91517, 0.00000, 1.83034, 0.00000,
		0.00000, 0.00000, 0.00000, 0.00000, 0.00000, 0.00000,
		0.00000, 0.00000, 0.00000, 0.00000, 0.00000, 2.41544,
O U T P U T		1.0373 0.0740
		0.0740 1.1134

APPENDIX II
Program CHEM2

Program CHEM2 Operating Instructions

This program adjusts an initial set of force constants until a least squares fit of the observed fundamental frequencies of a molecule is obtained. From one to three isotopic versions of a given molecule may be run simultaneously.

INPUT DATA

1. The first 4 lines contain alphanumeric information about the molecule to be used as a heading, punched in cols 1 to 78.
2. The 5th line contains the fixed point numbers defined below in the order given in successive 2 column fields beginning in col. 1. All fixed point numbers must be right justified.

IN	Number of symmetry coordinates.	Col. 1-2
IL	Number of internal coordinates.	Col. 3-4
IR	Number of cartesian coordinates.	Col. 5-6
IM	Number of principle force constants.	Col. 7-8
IH	Number of independent variable interaction force constants.	Col. 9-10
NISP	Number of isotopic molecules.	Col. 11-12
NI	The maximum number of iterations to be allowed is equal to $8*(NI - 1)$.	Col. 13-14
ISCF	If it is desired that the force constant corrections calculated at the end of each iteration be scaled down by some factor, a non-zero value is entered. The corrections will then each be scaled by a factor of $1/ISCF$ before being applied to the existing set of force constants.	Col. 15-16
IFFC	Number of force constants to be invariant in the iteration.	Col. 17-18
IW	Zero if the weighting factors in the variance are to be unity, otherwise non-zero.	Col. 19-20
ISYM	If the C matrices are to be entered in unsymmetrized form, a non-zero value is entered and the program will symmetrize them and print them out in symmetrized form. Otherwise a zero value is entered.	Col. 23-24

IDEG Number of coordinates in the degenerate species
 (the first set only) if coriolis constants are
 to be fitted. Otherwise zero. Col. 25-26
 LW Defines the method of weighting. Col. 27-28
 LW = 0 ; W(I) are all unity
 LW = 1 ; W(I) = 1/Lambda(I)
 LW = 2 ; W(I) = 1/Lambda(I)**2
 LW = 3 ; W(I) = 1/delta Lambda(i)**2
 The delta lambdas are defined by the elements of
 W(I). The uncertainties in Nus (wave numbers)
 and zetas are entered directly. Note that if
 LW = 3, IW cannot be zero.

3. The sixth line contains the number of symmetry species in the first up to the NISP-th isotopic derivative in successive two column fixed-point fields, beginning in Col. 1.
4. The seventh line contains the dimensions of the symmetry species of the first isotopic derivative in the order in which the symmetry blocks appear going down the principle diagonal of the G matrix. These numbers are in successive two column fixed point fields, beginning in Col. 1.
5. If there are more isotopic derivatives, lines similar to the previous card are included for each, in proper order.
6. The C matrix in index form, i.e. the value of a non-zero element of C appears in the first twelve columns in free format and is followed by the I and J indices of all elements of C with that value in successive free fields. There will be as many lines as there are different non-zero values of matrix elements. Zero elements need not be entered. The number of C

matrices will be equal to $IM+IH+IFFC$, and a blank card must follow each. Elements of the C matrices below the principal diagonal need not be entered explicitly. The C matrices are used to construct the interaction terms of the F matrix. A given C matrix contains the coefficients in the F matrix of the corresponding interaction constant. In the case of fixed force constants, if there are more than one of them, it is more efficient to put the values of the constant in a single C matrix and enter unity as the corresponding constant in the column of initial constants. Fixed principal as well as fixed interaction constants must always be entered via the C matrix.

7. The G matrix by indices for each isotopic species. Each G matrix is terminated by a blank card.
8. Observed frequencies in successive free fields beginning with column 1. Up to six frequencies may appear on a card, and they must be arranged in descending magnitude within each symmetry species. The symmetry species must be in the same order as in the F and G matrices. If an isotopic derivative is being used, all the frequencies for it follow the complete set for the normal molecule using the same rule for ordering.
9. If IW is non-zero lines for the altered weighting factors come next. Each of these lines contains an

altered weighting factor in floating point in columns 1-12, followed by two-column fixed point numbers I, J, K, etc. Beginning in column 13 and corresponding to the number of the frequencies in the column of observed frequencies to be given that weighting factor. A blank card follows the last card. If IW is zero, no data are entered here and no blank card.

10. The column of initial force constants follows. Each constant is punched on a separate line in free format followed by a comma. The 20 columns following the comma may contain alphanumeric information to label each constant. The order of the initial force constant must agree with the order of the C matrices.
11. A line with a non-zero fixed point number punched in columns 1-2 if this is the last set of data. If there are additional data sets to be run, a blank line is included here.

OUTPUT

All the input data is printed out except item 11. In item 2, the numbers printed have labels which omit the letter I which is the first letter in each variable name. The C matrices printed are the symmetrized ones whether or not the input C matrices were symmetrized. G matrix or matrices together with the determinant of each block for use with the product rule. Initially and after each iteration the F matrix, calculated frequencies with their observed values, errors and percent errors, the average percent error over all frequencies, the force constants used, the frequency Jacobian, and a singularity criterion for the product matrix, (J-transpose) (W) (J), are printed. This criterion is the ratio of the determinant of the matrix to the product of its diagonal elements. The nearer the criterion is to unity, the farther the matrix is from being singular provided it has no diagonal elements nearly zero. After each set of eight iterations, summaries of the force constants, calculated frequencies with their observed values and errors, the average percent error, and the variance is printed. When convergence occurs or when the maximum number of iterations has been reached, summaries as above for the last group of iterations are printed, followed by the L matrices, the P.E. distribution, the final calculated frequencies with their observed values, errors, percent errors, and dispersions, the final force constants with their dispersions, the variance and average percent error over all frequencies, and the correlation matrix for force constants.

STOPS

During execution of a given set of data, the program will stop and automatically proceed to the next set of data if one of the following situations is encountered.

1. None of the calculated frequencies or coriolis constants differ from their values in the preceding iteration by more than 0.01 percent.
2. The maximum number of iterations specified is reached.
3. A negative eigenvalue is calculated.
4. The average percent error exceeds fifty percent.
5. The singularity criterion is less than 0.001.

In cases 1 and 2 the final results are printed. In cases 3, 4, and 5, only the calculations for those iterations successfully completed are printed. In case 3, the negative eigenvalue is made positive and a message is printed giving its number. In case 5 the message - no inverse for this case- is printed.

```
00300      DIMENSION IDENT(13,4),VOBS(18),W(18),C(12,12,8),
00310      1Q(12,12),DK(14),TEMP(18,14),G(12,12,3),VN(18),XI(18),
00320      2EL(12,12,3),F(12,12),V(18),VYR(18,8),XXX(18,8),X(18),
00330      3TKR(14,8),AJ(18,14),DELK(14),SUMT(2,8),AJWJ(14,14),
00340      4INEG(18),ELIN(12,12,3),SIGK(14),SIGV(18),
00350      6KIDENT(33,3),NFAC(3),ID(8,3)
00360      DIMENSION FLMOBS(18),FLMC(18)
00370      COMMON D,EL,ELIN,AJWJ,C,AJ,G
00380      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IV,IB,ISYM,IDEG,N2,LW
00400      1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B3/VYR,TKR,XXX,SUMT/
00410      2B4/TEMP/B5/G/B6/XI,INEG/B7/F,H,DK/B8/IDENT,KIDENT,W,ID,NFAC/B9/
00420      3CZ,ZM/B10/SIGK,SIGV/B11/FLMOBS,FLMC
00430      C
00440      I      FORMAT(13A5)
00450      C
00460      C      READ IDENTIFICATION
00470      C
00480      1002      READ(1,1)((IDENT(I,J),I=1,13),J=1,4)
00490      C
00500      CALL LINK1
00510      CALL LINK2
00520      CALL LINK3
00530      C
00540      C      IS THIS THE LAST SET OF DATA
00550      C
00560      READ(1,2)NND
00570      2 FORMAT(24I2)
00580      IF (NND) 1001,1002,1001
00590      1001 CONTINUE
00600      END
```

```

00100      SUBROUTINE LINK1
00110      C      READ IN DATA
00120      C
00130          DIMENSION IDENT(13,4),VOBS(18),W(18),C(12,12,8),
00140          1Q(12,12),DK(14),TEMP(18,14),G(12,12,3),VNC(18),XI(18),
00150          2EL(12,12,3),F(12,12),V(18),VYR(18,8),XXX(18,3),X(18),
00160          3TKR(14,8),AJ(18,14),DELK(14),SUMT(2,8),AJWJ(14,14),
00170          4INEG(18),ELIN(12,12,3),SIGK(14),SIGV(18),
00180          6KIDENT(33,3),NFAC(3),ID(8,3)
00190          DIMENSION FLMOBS(18),FLMC(18)
00200          COMMON D,EL,ELIN,AJWJ,C,AJ,Q
00210          COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,LW
00230          1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B3/VYR,TKR,XXX,SUMT/
00240          2B4/TEMP/B5/G/B6/XI,INEG/B7/F,H,DK/B8/IDENT,KIDENT,W,ID,NFAC/B9/
00250          3CZ,ZM/B10/SIGK,SIGV/B11/FLMOBS,FLMC
00260      C
00270      C      READ MATRIX DIMENSIONS AND CHECK WORDS
00280      C
00290          READ(1,2)IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,
00300          1IB,ISYM,IDEG,LW,ISENT
00310          READ(1,2)(NFAC(I),I=1,NISP)
00320          DO 25 I=1,NISP
00330              K=NFAC(I)
00340              READ(1,2)(ID(J,I),J=1,K)
00350          25 CONTINUE
00360          2 FORMAT(24I2)
00370          IF(NI)4,3,4
00380          3 NII=1
00390          GO TO 420
00400          4 NII=NI
00410          420 CONTINUE
00420          IF (ISYM) 104,104,105
00430          105 ND=IL
00440          GO TO 106
00450          104 ND=IN
00460          106 IHT=IH+IFFC
00470          IF (IHT) 801,801,800
00480          800 DO 112 I=1,IHT
00490      C
00500      C      READ C MATRICES
00510      C
00520      C
00530          CALL READFL (TEMP,ND,ND,0)
00540          IF (ISYM) 109,109,110
00550          110 DO 108 J=1,IN
00560              DO 103 K=1,IL
00570                  ELIN(J,K,2)=0.
00580                  DO 108 L=1,IL
00590          108 ELIN(J,K,2)=ELIN(J,K,2)+ELIN(J,L,1)*TEMP(L,K)
00600              DO 111 J=1,IN
00610                  DO 111 K=1,IN
00620                      TEMP(J,K)=0.
00630                      DO 111 L=1,IL
00640          111 TEMP(J,K)=TEMP(J,K)+ELIN(J,L,2)*ELIN(K,L,1)
00650          109 DO 112 J=1,IN
00660              DO 112 K=1,IN
00670          112 C(J,K,1)=TEMP(J,K)
00710          801 CONTINUE
00750          DO 152 L=1,NISP
00760      C
00770      C      READ G MATRICES

```

```

00780 C
00790 ND=IN
00800 CALL READFL (TEMP,ND,ND,0)
00810 DO 152 I=1,ND
00820 DO 152 J=1,ND
00830 152 G(I,J,L)=TEMP(I,J)
00840 IF (ISCF) 82,81,82
00850 81 FNISP=NISP
00860 SCF=1./FNISP
00870 GOTO83
00880 82 XYZ=NISP*ISCF
00890 SCF=1./XYZ
00900 83 FLN2=SCF
00910 N2=NISP*(IN+IDEG)
00920 C
00930 C READ OBSERVED FREQUENCIES AND ZETA CONSTANTS
00940 C
00950 READ(1,118)(VOBS(I),I=1,N2)
00960 N3=NISP*IN
00970 DO901I=1,N3
00980 901 FLMOBS(I)=(VOBS(I)/1303.0)**2
00990 IF(IDEG)915,915,916
01000 916 KAP=N3+1
01010 DO912I=KAP,N2
01020 912 FLMOBS(I)=VOBS(I)
01030 118 FORMAT(6F)
01040 915 DO8J=1,N2
01050 8 W(J)=1.
01060 IF(LW)87,913,87
01070 87 CALL READDN(VN,N2)
01080 DO 89 I=1,N2
01090 IF(VN(I))88,89,88
01100 88 W(I)=VN(I)
01110 89 CONTINUE
01120 913 IF(LW-1)90,90,904
01130 904 IF(LW-1)905,905,910
01140 905 DO 907 I=1,N2
01150 907 W(I)=W(I)*1.0/ABS(FLMOBS(I))
01160 GOTO90
01170 910 IF(LW-2)906,906,908
01180 906 DO930I=1,N2
01190 930 W(I)=W(I)*1.0/FLMOBS(I)**2
01200 GOTO90
01210 908 DO909I=1,N3
01220 IF(VN(I))920,920,921
01230 920 W(I)=0.0
01240 GOTO909
01250 921 W(I)=(848904.5/(VOBS(I)*VN(I)))**2
01260 909 CONTINUE
01270 IF(IDEG)90,90,918
01280 918 DO911I=KAP,N2
01290 IF(VN(I))925,925,926
01300 925 W(I)=0.0
01310 GOTO911
01320 926 W(I)=1.0/VN(I)**2
01330 911 CONTINUE
01340 90 CONTINUE
01350 MPH=IH
01355 MPHT=MPH+IFFC
01360 N2G=IN*NISP
01380 DO 103 I=1,N2G

```

```
01390      103 INEG(I)=0
01400      C
01410      C      READ INITIAL FORCE CONSTANTS
01420      C
01430      DO 77 I=1,IHT
01440      77      READ(1,78)DK(I),(KIDENT(I,J),J=1,3)
01450      78      FORMAT(1F,4A5)
01460      C
01470      C      LIST INPUT DATA
01480      C
01490      CALL WINPI
01500      10 CONTINUE
01510      RETURN
01520      END
```

```

00100      SUBROUTINE LINK2
00110      C      CALCULATE EIGENVALUES OF G MATRICES
00120      C
00130          DIMENSION IDENT(13,4),VOBS(18),W(18),C(12,12,8),
00140          1Q(12,12),DK(14),TEMP(18,14),G(12,12,3),VN(18),XI(18),
00150          2EL(12,12,3),F(12,12),V(18),VYR(18,8),XXX(18,8),X(18),
00160          3TKR(14,8),AJ(18,14),DELK(14),SUMT(2,8),AJWJ(14,14),
00170          4INEG(18),ELIN(12,12,3),SIGK(14),SIGV(18),
00180          6KIDENT(33,3),NFAC(3),ID(8,3)
00190          DIMENSION FLMOBS(18),FLMC(18)
00200          COMMON D,EL,ELIN,AJWJ,C,AJ,Q
00210          COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IV,IB,ISYM,IDEG,N2,LW
00230          1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B3/VYR,TKR,XXX,SUMT/
00240          2B4/TEMP/B5/G/B6/XI,INEG/B7/F,F,DK/B8/IDENT,KIDENT,W,ID,NFAC/B9/
00250          3CZ,ZH/B10/SIGK,SIGV/B11/FLMOBS,FLMC
00260          DO 24 I=1,NZ
00270      24  VN(I)=FLMOBS(I)
00280          DO 33 L=1,NISP
00290          DO 20 I=1,IN
00300          DO 20 J=1,IN
00310      20  TEMP(I,J) = G(I,J,L)
00320          WRITE(2,600)L
00330      600  FORMAT (17HISOTOPIC SPECIES,14,///55X,8HC MATRIX//)
00340          CALL WTEMP(IN,IN)
00350      C
00360      C      EIGENVALUES OF G MATRICES BY FACTORED SYMMETRY SPECIES
00370      C
00380      92  ISC = 0
00390          DO 151 I=1,IN
00400          DO 151 J=1,IN
00410          AJWJ(I,J)=G(I,J,L)
00420      151  EL(I,J,L)=0.
00430          M=0
00440          N=0
00450          INI=IN*(L-1)
00460          K=NFAC(L)
00470          DO 32 IDX=1,K
00480          IF (IDX-1) 1000,26,27
00490      26  M=M+1
00500          GOT028
00510      27  M=M+ID(IDX-1,L)
00520      28  N=N+ID(IDX,L)
00530          LL=L
00540          CALL SYMAS (AJWJ,XI,ISC,INI,M,N,LL,G)
00550          DET=1.
00560          DO 29 J=M,N
00570          JI=J+INI
00580          DET=DET*XI(JI)
00590          DO 29 I=M,N
00600      29  G(I,J,L)=AJWJ(I,J)*SQRT(XI(JI))
00610      32  WRITE(2,601)IDX,DET
00620      601  FORMAT(1H1,30H DETERMINAT OF G MATRIX VLOCK,I3
00630          1,2H =,E14.6)
00640      33  CONTINUE
00650          NZG=IN*NISP
00660          DO 34 J=1,NZG
00670      34  XI(J)=1./XI(J)
00680          DO 555 I=1,IN
00690          DO 555 J=1,IN
00700          DO 555 L=1,NISP
00710      555  FITNCT(L,1)=0

```

00720 1000 CONTINUE
00730 RETURN
00740 END

```

00100      SUBROUTINE LINK3
00110      C      DO ITERATIONS
00120      C
00130          DIMENSION IDENT(13,4),VOBS(18),W(18),C(12,12,8),
00140          1Q(12,12),DK(14),TEMP(18,14),G(12,12,3),VN(18),XI(18),
00150          2EL(12,12,3),F(12,12),V(18),VYR(18,8),XXX(18,8),X(18),
00160          3TKR(14,8),AJ(18,14),DELK(14),SUMT(2,8),AJWJ(14,14),
00170          4INEG(18),ELIN(12,12,3),SIGK(14),SIGV(18),
00180          6KIDENT(33,3),NFAC(3),ID(8,3)
00190          DIMENSION FLMOBS(18),FLMC(18)
00200          COMMON D,EL,ELIN,AJWJ,C,AJ,Q
00210          COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,LW,
00230          1MPH,NUMB,ITER,NEG,MPHT,INT,VAR/B2/VOBS,X,V/B3/VYR,TKR,XXX,SUMT/
00240          2B4/TEMP/B5/G/B6/XI,INEG/B7/F,H,DK/B8/IDENT,KIDENT,W,ID,NFAC/B9/
00250          3CZ,ZM/B10/SIGK,SIGV/B11/FLMOBS,FLMC
00260      C
00270      C      START ITERATION
00280      C
00290          IF (NI) 4,3,4
00300          3 NII=1
00310          GO TO 5
00320          4 NII=NI
00330          5 ISENT=1
00340          ITER=-1
00350          ICOUNT=1
00360          DO 72 ITERX=1,NII
00370          DO 70 KOUNT=1,ICOUNT
00380          NUMB=KOUNT
00390          ITER=ITER+1
00440          CALL FCALC1
00445          IM=0
00450          DO 31 I=1,IN
00460          DO 31 J=1,IN
00470          31 TEMP(I,J)=F(I,J)
00480          IF(ITER)1000,36,37
00490          36 WRITE(2,602)
00500          602 FORMAT(1H1,51X,16HINITIAL F MATRIX/IH )
00510          GOTO38
00520          37 WRITE(2,603)ITER
00530          603 FORMAT(1H1,48X,22HF MATRIX FOR ITERATION,I3/IH )
00540          38 CALL WTEMP(IN,IN)
00550          NEG=0
00560          DO 30 L=1,NISP
00570          M=0
00580          N=0
00590          INI=IN+(L-1)
00600          K=NFAC(L)
00610          DO 45 IDX=1,K
00620          IF (IDX-1) 1000,40,41
00630          40 M=1
00640          GOTO42
00650          41 M=M+ID(IDX-1,L)
00660          42 N=N+ID(IDX,L)
00670          DO 43 I=M,N
00680          DO 43 J=M,N
00690          43 AJWJ(I,J)=F(I,J)
00700          LL=L
00710          CALL SYMAS (AJWJ,X,IN,INI,M,N,LL,G)
00720          45 CONTINUE
00730          30 CONTINUE
00740          IF(ISENT)931,931,932

```



```

00750 932 WRITE(2,853)ITER
00760 853 FORMAT(28H0EIGENVECTORS FROM ITERATIONI4)
00770 DO854K=1,NISP
00780 DO854I=1,IN
00790 854 WRITE(2,855) (EL(I,J,K),J=1,IN)
00800 855 FORMAT(1H01OF11.5)
00810 931 IF(NEG)76,46,76
00820 76 CALL WNUOUT(AVE)
00830 WRITE(2,610)NEG
00840 610 FORMAT(1H ,I3, " NEGATIVE EIGEN VALUES.")
00850 N2G=IN*NISP
00860 DO 121 I = 1,N2G
00870 IF (INEG(I)) 122,121,122
00880 122 WRITE(2,123)I
00890 123 FORMAT(1H ,I10)
00900 121 CONTINUE
00910 GO TO 1000
00920 46 N3=NISP*IN
00930 DO47I=1,N3
00940 VYR(I,KOUNT)=1303.0*SQRT(FLMC(I))
00950 47 XXX(I,KOUNT)=1303.0*(SQRT(FLMC(I))-SQRT(FLMOBS(I)))
00960 IF(IDEG)950,950,960
00970 960 KAP=N3+1
00980 DO965I=KAP,N2
00990 VYR(I,KOUNT)=FLMC(I)
01000 965 XXX(I,KOUNT)=X(I)
01010 950 DO48I=1,MPHT
01020 48 TKR(I,KOUNT)=DK(I)
01030 C
01040 C CALCULATE JACOBIAN (AJ) FROM EIGENVECTORS
01050 C
01060 49 DO 50 I=1,N2
01070 DO 50 J=1,MPHT
01080 50 AJ(I,J) = 0.0
01090 DO 51 L=1,NISP
01100 M=(L-1)*IN+1
01110 N=M+IN-1
01120 CALL EIGJAC (M,N,L)
01130 51 CONTINUE
01140 CALL WNUOUT (AVE)
01150 97 DO 55 I=1,N2
01160 Y1=0.
01170 DO 54 J=1,MPHT
01180 TEMP(I,J)=AJ(I,J)*DK(J)/FLMC(I)
01190 54 Y1=Y1+ABS(TEMP(I,J))
01200 DO55J=1,MPHT
01210 55 TEMP(I,J)=TEMP(I,J)*100.0/Y1
01220 IF(ITER)57,53,57
01230 53 WRITE(2,605)
01240 605 FORMAT(1H1,29X,"POTENTIAL ENERGY DISTRIBUTION",
01250 932H - CONTRIBUTION OF K(J) TO NU(I)/1H")
01260 CALL WTEMP(N2,MPHT)
01270 57 DO 98 I=1,N2
01280 DO 98 J=1,MPHT
01290 98 TEMP(I,J)=AJ(I,J)
01300 WRITE(2,604) ITER
01310 604 FORMAT(1H1,47X,23HJACOBIAN FROM ITERATION,I3/1H")
01320 CALL WTEMP(N2,MPHT)
01330 IF(AVE-100.)201,201,200
01340 200 WRITE(2,202)
01350 202 FORMAT(66H CALCULATION TERMINATED BECAUSE AVERAGE ERROR EXCEEDS 1

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01370      10 PER CENT)
01380      GO TO 1000
01390      C
01400      C      TRANSPOSE JACOBIAN AND FORM (JTRANSPOSE)(W)(J)INVERSE AS XNIT
01410      C
01420      201 DO 58 I=1,N2
01430          DO 58 J=1,MPH
01440          58 TEMP(I,J)=W(I)*AJ(I,J)
01450          DO 59 I=1,MPH
01460          DO 59 J=1,MPH
01470          AJWJ(I,J)=0.
01480          DO 59 K=1,N2
01490          59 AJWJ(I,J)=AJWJ(I,J)+AJ(K,I)*TEMP(K,J)
01500          IF(ISENT)933,933,934
01510      934      WRITE(2,856)ITER
01520          856 FORMAT(22HOMATRIX FROM ITERATIONI4)
01530          DO 456 I=1,MPH
01540          456      WRITE(2,855)(AJWJ(I,J),J=1,MPH)
01550          933 PROD=1.0
01560          DO 119 I=1,MPH
01570          119 PROD=PROD*AJWJ(I,I)
01580          WRITE(2,615)PROD
01590          615 FORMAT (1H0.46X,16HA(1,1)*...*A(N,N)=,E11.2)
01600          NEROR=0
01610          CALLINVERT(AJWJ,MPH,1.0E-03,NEROR,DET,PROD)
01620          IF(ISENT)935,935,936
01630      936      WRITE(2,857)ITER
01640          857 FORMAT(30H0INVERSE MATRIX FROM ITERATIONI4)
01650          DO858I=1,MPH
01660          858      WRITE(2,855) (AJWJ(I,J),J=1,MPH)
01670          935 CONTINUE
01680          IF(NEROR)75,63,75
01690          63 DO 64 I=1,N2
01700          IF (ABS((FLMC(I)-VN(I))/FLMC(I))-0.0001) 64,64,65
01710          64 CONTINUE
01720          WRITE(2,606)
01730          606 FORMAT(1H0.46X,27HTHIS IS THE FINAL JACOBIAN.)
01740          GO TO 73
01750          65      DO 66 I=1,N2
01760          66      VN(I)=FLMC(I)
01770          WRITE(2,120)PROD
01780          120      FORMAT(1H0.46X,24HDET(A)/A(1,1)*...*A(N,N) =,E11.2)
01790          DO 67 I=1,MPH
01800          DO 67 J=1,N2
01810          TEMP(J,I)=0
01820          DO 67 K=1,MPH
01830          67      TEMP(J,I)=TEMP(J,I)+AJWJ(I,K)*AJ(J,K)*W(J)
01840          DO 69 I=1,MPH
01850          DELK(I) = 0
01860          DO 68 J=1,N2
01870          68      DELK(I) = DELK(I)-TEMP(J,I)*(FLMC(J)-FLMOBS(J))
01880          69      DK(I)=DK(I)+DELK(I)
01890          IF(ISENT)70,70,937
01900          937      WRITE(2,860)ITER
01910          860      FORMAT(32HOPARAMETER INCREMENTS, ITERATIONI4)
01920          DO859 I=1,MPH
01930          859      WRITE(2,855) DELK(I)
01940          70      CONTINUE
01950          IF(NI)991,991,990
01960          990      ICOUNT=8
01970          ICOUNT=8

```

```
01980      M=ITER-NUMB+1
01990      CALL SUMS
02000      IF(ITER)71,72,71
02010      71      CALL WDKNUX(M)
02020      72      CONTINUE
02030      DO 56 I=1,MPH
02040      56      DK(I)=DK(I)-DELK(I)
02050      VAR=SUMT(2,NUMB)
02060      CALL STAT
02070      991     WRITE(2,607)
02080      607     FORMAT(1H1,10X,"DID NOT CONVERGE .....")
02090      GO TO 1000
02100      73      CALL SUMS
02110      M=ITER-NUMB+1
02120      CALL WDKNUX(M)
02130      VAR=SUMT(2,NUMB)
02140      CALL STAT
02150      74      WRITE(2,608)
02160      608     FORMAT(1H1,10X,"END OF CASE .....")
02170      GO TO 1000
02180      75      WRITE(2,609)
02190      609     FORMAT(32H NO INVERSE EXISTS FOR THIS CASE)
02200      1000    CONTINUE
02210      RETURN
02220      END
```

```

00100      SUBROUTINE SUMS
00110      C
00120      C      CALCULATES AVERAGE PER CENT ERROR AND VARIANCE
00130      C
00140      DIMENSION VOBS(18),X(18),V(18),VYR(18,8),XXX(18,8),TKR(14,8),
00150      1SUMT(2,8),IDENT(13,4),KIDENT(33,3),W(18),ID(8,3),NFAC(3)
00160      DIMENSION FLMOBS(18),FLMC(18)
00170      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYN,IDEG,N2,LW
00190      1MPH,NUMB,ITER,NEG,MPHT,INTI,VAR/B2/VOBS,X,V/B3/VYR,TKR,XXX,SUMT
00200      2/B8/IDENT,KIDENT,W,ID,NFAC
00210      COMMON /B11/FLMOBS,FLNC
00220      N3=NISP*IN
00230      KAP=N3+1
00240      XN=N2
00250      DO 1 I=1,NUMB
00260      SUM1=0.
00270      SUM2=0.
00280      DO 2 J=1,N3
00290      SUM1=SUM1+ABS(XXX(J,I)/VOBS(J))
00300      2 SUM2=SUM2+W(J)*((VYR(J,I)**2-VOBS(J)**2)/1303.0**2)**2
00310      IF(IDEG)5,5,4
00320      4 DO3J=KAP,N2
00330      SUM1=SUM1+ABS(XXX(J,I)/VOBS(J))
00340      3 SUM2=SUM2+W(J)*XXX(J,I)**2
00350      5 SUMT(1,I)=SUM1*100./XN
00360      1 SUMT(2,I)=SUM2
00370      RETURN
00380      END

```

```
00100      SUBROUTINE FCALCI
00110      C
00120      C      CALCULATES F MATRIX FROM Q, DK, AND C MATRICES
00130      C
00140      DIMENSION F(12,12),Q(12,12),C(12,12,8),
00150      1EL(12,12,3),ELIN(12,12,3),AJ(18,14),AJWJ(14,14),DK(14)
00160      COMMON D,EL,ELIN,AJWJ,C,AJ,C
00170      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IN,IB,ISYM,IDEG,N2,LV
00190      1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B7/F,H,DK
00200      DO 6 I=1,IN
00210      DO 6 J=1,IN
00220      F(I,J)=0.
00260      7 DO 3 K=1,IHT
00280      3 F(I,J)=F(I,J)+C(I,J,K)+DK(K)
00290      6 CONTINUE
00300      RETURN
00310      END
```

```
00100      SUBROUTINE WDKNUX(M)
00110      C
00120      C      PRINTS K, NU, AND X COLUMNS AFTER EACH SET OF EIGHT ITERATIONS.
00130      C      CALLS SUBROUTINES WDK, AND WNUX
00140      C
00150      DIMENSION VYR(18,8),XXX(18,8),TKR(14,8),SUMT(2,8)
00160      COMMON /B1/IN,IL,IR,IM,IN,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEQ,N2,LW
00180      IMPH,NUMB,ITER,NEG,MPHT,IHTI,VAR/B3/VYR,TKR,XXX,SUMT
00190      WRITE(2,449)M,ITER
00200      449 FORMAT(1H1,39X,25HK COLUMNS FROM ITERATIONS, I3,8H THROUGH, I3)
00210      CALL WDK(M)
00220      WRITE(2,450)N,ITER
00230      450  FORMAT(1H1,34X,19HNUS FROM ITERATIONS, I3,8H THROUGH, I3,
00240      917H PLUS NU OBSERVED)
00250      KC=0
00260      CALL WNUX(VYR,SUMT,M,KC)
00270      WRITE(2,451)M,ITER
00280      451  FORMAT(1H1,18X, 'X(NU CALC. - NU OBS.) COLUMNS FROM IT
00290      IERATIONS', I3,8H THROUGH, I3,24H FOLLOWED BY I NU OBSERVED)
00300      KC=1
00310      CALL WNUX(XXX,SUMT,M,KC)
00320      RETURN
00330      END
```

```
00100      SUBROUTINE WDK(M)
00110      C
00120      C      PRINTS K COLUMNS AFTER EACH SET OF EIGHTI ITERATIONS
00130      C
00140      DIMENSION VYR(18,8),XXX(18,8),TKR(14,8),SUMT(2,8)
00150      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,LW
00170      1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B3/VYR,TKR,XXX,SUMT
00180      WRITE(2,1)(J,J=M,ITER)
00190      WRITE(2,4)
00200      DO 3 JD=1,MPHT
00210      3  WRITE(2,2)JD,(TKR(JD,K),K=1,NUMB)
00220      1  FORMAT(1H0,I11,7I14)
00230      2  FORMAT(1H ,I2,8F14.7)
00240      4  FORMAT(1H )
00250      RETURN
00260      END
```

```
00100      SUBROUTINE WNUX(A,SUMT,M,KC)
00110      C
00120      C      PRINTS NU AND X COLUMNS AFTER EACH SET OF EIGHT ITERATIONS
00130      C
00140      DIMENSION A(18,8),SUMT(2,8),VOBS(18),X(18),V(18)
00150      DIMENSION FLMOBS(18),FLMC(18)
00160      COMMON /B1/IN,IL,IR,IM,II,NISP,NI,ISCF,IFFC,IV,IB,ISYM,IDEG,N2,LW
00180      1MPH,NUMB,ITER,NEG,MPHT,INT,VAR/B2/VOBS,X,V
00190      COMMON /B11/FLMOBS,FLMC
00200      JD=0
00210      WRITE(2,1)(JJJ,JJJ=M,ITER),JD
00220      1 FORMAT(1H0,I11,8I13/1H )
00230      DO 3 JD=1,N2
00240      4      WRITE(2,2)JD,(A(JD,K),K=1,NUMB),VOBS(JD)
00250      3 CONTINUE
00260      2 FORMAT(1H ,I2,9F13.5)
00270      IF(KC)9,10,9
00280      9      WRITE(2,11)
00290      11 FORMAT(1H0,45X,27HPER CENT ERROR AND VARIANCE)
00300      DO 12 JD=1,2
00310      12      WRITE(2,16)JD,(SUMT(JD,K),K=1,NUMB)
00320      16 FORMAT(1H ,I2,8F13.7)
00330      10 RETURN
00340      END
```



```

00100      SUBROUTINE INVERT(A,N, EPS,NEROR,DELTA,PROD)
00120      C      MATRIX INVERSION BY GAUSS-JORDAN ELIMINATION
00130
00140      DIMENSION A(14,14),B(14),C(14),LZ(14)
00150      DELTA = 1.0
00170      NEROR=0
00190      DO 10 J=1,N
00210      10  LZ(J)=J
00220      EPS=10.0**(-20)
00230      DO 20 I=1,N
00250      K=I
00270      Y=A(I,I)
00280      L=I-1
00300      LP=I+1
00310
00320      IF(N-LP)14,11,11
00340      11 DO 13 J=LP,N
00360      W=A(I,J)
00380      IF (ABS(W)-ABS(Y)) 13,13,12
00390      12 K=J
00400      Y=W
00410      13 CONTINUE
00420      14 DELTA=DELTA*Y
00430      DO 15 J=1,N
00440      C(J)=A(J,K)
00450      A(J,K)=A(J,I)
00460      A(J,I)=C(J)/Y
00470      A(I,J)=A(I,J)/Y
00480      15 B(J)=A(I,J)
00490      A(I,I)=1.0/Y
00500      J=LZ(I)
00510      LZ(I)=LZ(K)
00520      LZ(K)=J
00530      DO 19 K=1,N
00540      IF(I-K)16,19,16
00550      16 DO 18 J=1,N
00560      IF(I-J)17,18,17
00570      17 A(K,J)=A(K,J)-B(J)*C(K)
00580      18 CONTINUE
00590      19 CONTINUE
00600      20 CONTINUE
00610      WRITE(2,1) DELTA
00620      1  FORMAT (1H0.46X,7HDET(A)=,E11.2)
00630      PROD=DELTA/PROD
00640      WRITE(2,120) PROD
00650      120 FORMAT (1H0.46X,24HDET(A)/A(1,1)**A(N,N) =,E11.2)
00660      IF (ABS(PROD)-EPS) 80,80,81
00670      80  NEROR = 1
00690      GO TO 82
00710      81 DO 200 I=1,N
00720      IF(I-LZ(I))100,200,100
00730
00740      100 K=I+1
00760      IF(I-N)800,200,200
00780      800 DO 500 J=K,N
00790
00800      IF(I-LZ(J))500,600,500
00810      600 M=LZ(I)
00820      LZ(I)=LZ(J)
00830      LZ(J)=M
00840      DELTA=-DELTA

```

```
00850      DO 700 L=1,N
00860      C(L)=A(I,L)
00870      A(I,L)=A(J,L)
00880      700 A(J,L)=C(L)
00890      500 CONTINUE
00900      200 CONTINUE
00910      82  RETURN
00920      END
```

```

00100      SUBROUTINE SYMAS(A,Z,ISC,INI,MMM,NNN,L,G)
00110      C
00120      C      CALCULATES EIGENVECTORS AND EIGENVALUES OF FACTORED A MATRIX
00130      C      CORRESPONDING TO G OR GF). EIGENVALUES ARE STORED IN Z AND
00140      C      EIGENVECTORS (OF GF) ARE STORED IN D(FACTORED).
00150      C
00160      DIMENSION EL(12,12,3),ELIN(12,12,3),AJWJ(14,14),C(12,
00170      112,8),AJ(18,14),Q(12,12),VOBS(18),X(18),V(18),TEMP(18,14),XI(18),
00180      2INEG(18),G(12,12,3),Z(18),A(14,14),XNIT(14,14)
00190      DIMENSION FLMOBS(18),FLMC(18)
00200      COMMON D,EL,ELIN,AJWJ,C,AJ,Q
00210      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IV,IB,ISYM,IDEG,N2,LV
00230      1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B4/TEMP/B6/XI,INEG
00240      COMMON /B11/FLMOBS,FLMC
00250      LL=L
00260      M=MMM
00270      N=NNN
00280      IF(ISC)1,4,1
00290      C      CHECK FOR (1X1) SPECIES
00300      1 IF(N-M)145,142,145
00310      142 INM=INI+M
00320      Z(INM)=G(M,M,LL)*A(M,M)*G(M,M,LL)
00330      IF(Z(INM))143,144,144
00340      143 NEG=NEG+1
00350      INEG(NEG)=INM
00360      Z(INM)=-Z(INM)
00370      144 FLMC(INM)=Z(INM)
00380      X(INM)=FLMC(INM)-FLMOBS(INM)
00390      EL(M,M,LL)=G(M,M,LL)
00400      ELIN(M,M,LL)=1./EL(M,M,LL)
00410      RETURN
00420      145 DO 2 I=M,N
00430      DO 2 J=M,N
00440      EL(I,J,LL)=0.
00450      DO 2 K=M,N
00460      2 EL(I,J,LL)=EL(I,J,LL)+A(I,K)*G(K,J,LL)
00470      DO 3 I=M,N
00480      DO 3 J=M,N
00490      A(I,J)=0.
00500      DO 3 K=M,N
00510      3 A(I,J)=A(I,J)+G(K,I,LL)*EL(K,J,LL)
00520      C      A IS NOW (GTRANSPOSE)(F)(G) WHERE G IS DEFINED IN MAIN PROGRAM
00530      C      AFTER STATEMENT NO. 32.
00540      C      CALCULATE EIGENVALUES -
00550      4 IF(N-M)5,6,5
00560      6 INM=INI+M
00570      Z(INM)=A(M,M)
00580      A(M,M)=1.
00590      RETURN
00600      5 E=0.
00610      DO 101 I=M,N
00620      101 E=E+ABS(A(I,I))
00630      R=N-M+1
00640      E=E/(5.*R)
00650      DO 102 I=M,N
00660      DO 102 J=M,N
00670      IF(I-J)103,104,103
00680      104 XNIT(I,J)=1.
00690      GO TO 102
00700      103 XNIT(I,J)=0.
00710      102 CONTINUE

```

```

00720      105 M2=M+1
00730      DO 106 J=M2,N
00740      L=J-1
00750      DO 106 I=M,L
00760      IF (ABS(A(I,J))-E) 106,106,126
00770      126 IF(A(I,I)-A(J,J))107,125,107
00780      125 QX=A(I,J)
00790      GO TO 109
00800      107 QX=A(I,J)/(2.*(A(I,I)-A(J,J)))
00810      IF (ABS(QX)-0.41421) 108,109,109
00820      108 S=2.*QX/(1.+(QX*QX))
00830      CO=(1.-(QX*QX))/(1.+(QX*QX))
00840      GO TO 110
00850      109 S=.70710678
00860      CO=.70710678
00870      IF(QX)111,110,110
00880      111 S=-S
00890      110 CC=CO*CO
00900      SS=S*S
00910      CS=CO*S
00920      QX=A(I,J)*(CC-SS)+CS*(A(J,J)-A(I,I))
00930      R=A(I,I)*CC+A(J,J)*SS+2.*CS*A(I,J)
00940      A(J,J)=SS*A(I,I)+CC*A(J,J)-(2.*CS*A(I,J))
00950      A(I,J)=QX
00960      A(I,I)=R
00970      A(J,I)=A(I,J)
00980      DO 112 K=M,N
00990      IF(K-I)113,114,113
01000      113 IF(K-J)115,114,115
01010      115 R=A(I,K)*CO+A(J,K)*S
01020      A(J,K)=A(J,K)*CO-A(I,K)*S
01030      A(K,J)=A(J,K)
01040      A(I,K)=R
01050      A(K,I)=A(I,K)
01060      114 R=XNIT(K,I)*CO+XNIT(K,J)*S
01070      XNIT(K,J)=XNIT(K,J)*CO-XNIT(K,I)*S
01080      112 XNIT(K,I)=R
01090      106 CONTINUE
01100      DO 116 J=M2,N
01110      L=J-1
01120      DO 116 I=M,L
01130      IF (ABS(A(I,J))-E) 116,116,105
01140      116 CONTINUE
01150      IF(E-1.0E-010)117,117,118
01160      118 E=E/10.
01170      GO TO 105
01180      117 DO 119 I=M,N
01190      INII=INI+I
01200      Z(INII)=A(I,I)
01210      DO 119 J=M,N
01220      119 A(I,J)=XNIT(I,J)
01230      IF(ISC)120,122,120
01240      120 DO 121 I=M,N
01250      INII=INI+I
01260      IF (Z(INII)) 140,141,141
01270      140 Z(INII)=-Z(INII)
01280      NEG=NEG+1
01290      INEG(INII)=1
01300      141 FL MC(INII)=Z(INII)
01310      DO 121 J=M,N
01320      TEMP(I,J)=0

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```

01330      EL(I,J,LL)=0.
01340      DO 121 K=M,N
01350      INK=INI+K
01360      TEMP(I,J)=TEMP(I,J)+A(K,I)*XI(INK)*G(J,K,LL)
01370      121 EL(I,J,LL)=EL(I,J,LL)+G(I,K,LL)*A(K,J)
01380      C      EL IS NOW THE MATRIX OF EIGENVECTORS OF GF.
01390      DO 135 J=M,N
01400      DO 135 I=M,N
01410      K=INI + I
01420      IF (I-N) 139,135,135
01430      139 IF(FLMC(K)-FLMC(K+1))137,135,135
01440      137 R=FLMC(K)
01450      FLMC(K)=FLMC(K+1)
01460      FLMC(K+1)=R
01470      IT=INEG(K)
01480      INEG(K)=INEG(K+1)
01490      INEG(K+1)=IT
01500      DO 138 L=M,N
01510      R=EL(L,I,LL)
01520      EL(L,I,LL)=EL(L,I+1,LL)
01530      EL(L,I+1,LL)=R
01540      R=TEMP(I,L)
01550      TEMP(I,L)=TEMP(I+1,L)
01560      138 TEMP(I+1,L)=R
01570      135 X(K)=FLMC(K)-FLMOBS(K)
01580      DO136 I=M,N
01590      DO136 J=M,N
01600      136 ELIN(I,J,LL)=TEMP(I,J)
01610      122 RETURN
01620      END

```

```

00100      SUBROUTINE WINPI
00110      C
00120      C      PRINTS INPUT DATA
00130      C
00140      DIMENSION IDENT(13,4),NFAC(3),VOBS(18),W(18),C(12,12,8),
00150      1Q(12,12),DK(14),TEMP(18,14),G(12,12,3),EL(12,12,3),F(12,12),
00160      2V(18),X(18),AJ(18,14),AJWJ(14,14),ELIN(12,12,3),KIDENT(33,3)
00170      3, ID(8,3)
00180      DIMENSION FLMOBS(18),FLMC(18)
00190      COMMON D,EL,ELIN,AJWJ,C,AJ,Q
00200      COMMON /B1/IN,IC,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,NZ,LI
00220      1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B4/TEMP/B5/G/B7/F,H,D
00230      2/B8/IDENT,KIDENT,W, ID,NFAC
00240      COMMON /B11/FLMOBS,FLMC
00250      C
00260      WRITE(2,1)((IDENT(I,J),I=1,13),J=1,4)
00270      1  FORMAT(1H1,22X,13A5/(1H,22X,13A5))
00280      WRITE(2,7)IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,
00290      1IB,ISYM,IDEG,LW
00300      7  FORMAT(1H0,4X,1HN,4X,1HL,4X,1HR,4X,1HM,4X,1HH,2X,4HNISP,
00310      13X,2HNI,2X,3HSCF,2X,3HFFC,3X,1HW,4X,1HB,3X,3HSYM,2X,
00320      24HIDEG,2X,2HLW/16,13I5)
00330      WRITE(2,2)
00340      2  FORMAT(1H1,          ISOTOPE          NO. FACTORS          FACTOR DI
00350      IMENSIONS          FOFI-428")
00360      DO 3 I=1,NISP
00370      K=NFAC(I)
00380      WRITE(2,4)I,K,(ID(J,NTINUE
00400      4  7I3)
00410      WRITE(2,T (1H0,56X,5HINPUT/1H0)
00430      WRITE(2,34)
00440      34  FORMAT (1H0,55X,10HC MATRICES)
00450      DO 13 L=1,NISP
00460      DO 14 I=1,IN
00470      DO 14 J=1,IN
00480      14  TEMP(I,J)=G(I,J,L)
00490      WRITE(2,17)L
00500      17  FORMAT(1H1,5-          CALL WTE
00520      13  CONTINUE
00530      DO 35 I=1,IN
00540      DO 35 J=1,IN
00550      35  TEMP(I,J)=Q(I,J)
00560      WRITE(2,36)
00570      36  FORMAT(1H1,58X,1HQ)
00580      CALL WTEMP(IN,IM)
00590      IF (MPHT-IM) 56,56,55
00600      55  WRITE(2,38)
00610      38  FORMAT (1H1,55X,10HC MATRICES)1,IHT
00630      DO 39 640          DO 39 J=1,IN
00650      39  TEMP(I,J)=C(I,J,L)
00660      WRITE(2,40)L
00670      40  FORMAT(1H1,59X,12)
00680      CALL WTEMP(IN,IN)
00690      37  CONTINUE
00700      56  WRITE(2,48)
00710      48  FORMAT (1H1,2H I,9X,2HM1,12X,2HM2,12X,2HM3,12X,2HM4//)
00720      WRITE(FA2,43)
00730      43  E(2,43)
          FORMAT(1H1,3H I,6X,4HVOBS,10X,1HW,12X,1HK)
00740      IMAX=AMAX0(NZ,MPHT)
00750      DO 44 I=1,IMAX

```

```
00760      IF (MPHT-1) 45,46,46
00770      46      WRITE(2,47)I,VOBS(I),W(I),DK(I),(KIDENT(I,J),J=1,3)
00780      GO TO 44
00790      45      WRITE(2,47)I,VOBS(I),W(I)
00800      44 CONTINUEFA
00810 TO 44
0047)I,VOBS(I),W(I)
00800      44 CONTINUE
00810      47      FORMAT(1H .I3.F11.3.F13.6.F13.5.4X.4A6)
00820      RETURN
00830      END
```

```
00100      SUBROUTINE READFL(D,M1,M2,IX)
00110      C
00120      C      READS MATRICES.
00130      C
00140      DIMENSION D(18,14),IH(15),JH(15)
00150      DO 10 I=1,M1
00160      DO 10 J=1,M2
00170      10 D(I,J)=0.
00180      5      READ(1,1)DH,(IH(I),JH(I),I=1,15)
00190      1      FORMAT(1F,30I)
00200      IF (FADH)2,3,2
00210      2 DO 6 K=1,15
00220      IF (IH(K))4,5,4
00230      4 I=IH(K)
00240      J=JH(K)
00250      6 D(I,J)=DH
00260      GO TO 5
00270      3 IF(IX)22,23,22
00280      23 DO 20 I=1,M1
00290      DO 20 J=1,M1
00300      IF (I=J) 21,20,21
00310      21 IF(D(I,J))11,20,11
00320      11 D(J,I)=D(I,J)
00330      20 CONTINUE
00340      22 RETURN
00350      END
```



```
00100      SUBROUTINE READDM (D,IR)
00110      C
00120      C      READS MASSES IN ATOMIC WEIGHT UNITS AND MODIFIED WEIGHT FACTOR
00130      C
00140      DIMENSION D(33),IH(24)
00150      DO 1 I=1,IR
00160      1 D(I)=0.
00170      2 READ(1,3)DH,(IH(I),I=1,24)
00180      3 FORMAT(1F,24I)
00190      IF(DH)4,7,4
00200      4 DO 6 K=1,24
00210      IF(IH(K))5,2,5
00220      5 IST=IH(K)
00230      6 D(IST)=DH
00240      GO TO 2
00250      7 RETURN
00260      END
```

```

00100 SUBROUTINE STAT
00110 C
00120 C CALCULATES AND PRINTS STATISTICAL ANALYSIS OF FINAL RESULTS
00130 C
00140 DIMENSION EL(12,12,3),ELIN(12,12,3),C(12,12,8),
00150 1AJWJ(14,14),AJ(18,14),Q(12,12),VOBS(18),X(18),V(18),TEMP(18,14),
00160 2F(12,12),DK(14),IDENT(13,4),KIDENT(33,3),W(18),
00170 3ID(8,3),NFAC(3),SIGK(14),SIGV(18)
00180 DIMENSION FLMOBS(18),FLMC(18)
00190 DIMENSION VYR(18,8),TKR(14,8),XXX(18,8),SUMT(2,8)
00200 COMMON D,EL,ELIN,AJWJ,C,AJ,Q
00210 COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,L
00230 1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B4/TEMP/B7/F,H,DK
00240 2/B8/IDENT,KIDENT,W,ID,NFAC/B10/SIGK,SIGV
00250 COMMON /B11/FLMOBS,FLMC
00260 COMMON /B3/VYR,TKR,XXX,SUMT
00270 C
00280 C PRINT EIGENVECTORS
00290 C
00300 WRITE(2,15)
00310 15 FORMAT (1H1,54X,10HL MATRICES)
00320 DO 1 L=1,NISP
00330 WRITE(2,2) L
00340 2 FORMAT(1H1,59X,I2)
00350 DO 3 I=1,IN
00360 DO 3 J=1,IN
00370 3 TEMP(I,J)=EL(I,J,L)
00380 CALL WTEMP(IN,IN)
00390 1 CONTINUE
00400 C
00410 C POTENTIAL ENERGY DISTRIBUTION
00420 C
00430 18 DO 24 I=1,N2
00440 Y1=0.
00450 DO 23 J=1,MPHT
00460 TEMP(I,J)=AJ(I,J)*DK(J)/FLMC(I)
00470 23 Y1=Y1+ABS(TEMP(I,J))
00480 DO 24 J=1,MPHT
00490 24 TEMP(I,J)=TEMP(I,J)*100./Y1
00500 WRITE(2,25)
00510 25 FORMAT(1H1,29X,44HPOTENTIAL ENERGY DISTRIBUTION - CONTRIBUTION,
00520 117H OF K(J) TO NU(I)/1H )
00530 CALL WTEMP(N2,MPHT)
00540 C
00550 C OVERALL DISPERSION(SIGMA) AND DISPERSIONS FOR FORCE CONSTANTS
00560 C AND FREQUENCIES
00570 C
00580 SIGMA=VAR
00590 DIF=N2-MPHT
00600 IF(DIF)26,26,27
00610 26 DIF=1.0
00620 27 SIGSQ=SIGMA/DIF
00630 SIGMA=SQRT(SIGSQ)
00640 DO 28 I=1,MPH
00650 28 SIGK(I)=SIGMA+SQRT(AJWJ(I,I))
00660 DO 29 I=1,N2
00670 DO 29 J=1,MPH
00680 TEMP(I,J)=0.
00690 DO 29 K=1,MPH
00700 29 TEMP(I,J)=TEMP(I,J)+AJ(I,K)*AJWJ(K,J)
00710 DO 31 I=1,N2

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```

00720      Y1=0.
00730      DO 30 K=1, MPH
00740      30 Y1=Y1+TEMP(I,K)*AJ(I,K)
00750      31 SIGV(I)=SIGMA*SQRT(Y1)
00760      N3=NISP*IN
00770      DO50I=1, N3
00780      50 SIGV(I)=84.8904.5/VYR(I,MUNB)*SIGV(I)
00790      C
00800      C      PRINT FINAL FREQUENCIES, FORCE CONSTANTS, AND DISPERSIONS
00810      C
00820      32      WRITE(2,33)
00830      33      FORMAT(1H1,3HNO.,2X,7HNU OBS.,6X,8HNU CALC.,7X,
00840      18HDELTA NU,
00850      94X,10HPCT. ERROR,4X,9HSIGMA(NU),6X,1HK,10X,8HSIGMA(K)/1H )
00860      AVE=0.
00870      DO 37 I=1, N2
00880      DIF=(X(I)/VOBS(I))*100.
00890      AVE=AVE+ABS(DIF)
00900      IF (I-MPHT) 34,34,36
00910      34      WRITE(2,35)I,VOBS(I),V(I),X(I),DIF,SIGV(I),
00920      9DK(I),SIGK(I),(KIDENT(I,J),J=1,3)
00930      GO TO 37
00940      35 FORMAT (1H ,12,F10.3,F16.7,3F13.5,4X,F10.7,F11.5,1X,4A6)
00950      36      WRITE(2,35)I,VOBS(I),V(I),X(I),DIF,SIGV(I)
00960      37 CONTINUE
00970      FN2=N2
00980      AVE=AVE/FN2
00990      WRITE(2,38)SIGMA,AVE
01000      38 FORMAT(1H0,20X,30HSQRT(SUM(W*(O-C)**2)/(NOI-AV))=F10.6,10X,
01010      925HAVERAGE PER CENT ERRDR = ,F10.6)
01020      C
01030      C      CORRELATION MATRICES
01040      C
01050      WRITE(2,39)
01060      39 FORMAT(1H1,40X,38HCORRELATION MATRIX FOR FORCE CONSTANTS/1H )
01070      DO 40 I=1, MPH
01080      DO 40 J=1, MPH
01090      40 TEMP(I,J)=AJWJ(I,J)*SIGSQ/(SIGK(I)*SIGK(J))
01100      CALL WTEMP(MPH,MPH)
01110      RETURN
01120      END

```

```

00100      SUBROUTINE EIGJAC (II,IE,L)
00110      C
00120      C      CALCULATES FREQUENCY JACOBIAN FROM EIGENVECTORS
00130      C
00140      DIMENSION EL(12,12,3),ELIN(12,12,3),AJWJ(14,14),
00150      IC(12,12,8),AJ(18,14),Q(12,12),VOBS(18),X(18),V(18)
00160      DIMENSION FLMOBS(18),FLMC(18)
00170      COMMON D,EL,ELIN,AJWJ,C,AJ,Q
00180      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,L1
00200      1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V
00210      COMMON /B11/FLMOBS,FLMC
00220      IG=0
00230      DO 2 I=II,IE
00240      IG=IG+1
00250      DO 2 J=I,IM
00260      DO 2 K=1,IN
00270      2  AJ(I,J)=AJ(I,J)+EL(K,IG,L)*EL(K,IG,L)*Q(K,J)
00280      IF(MPHT-IN)1000,1000,3
00290      3  IG=0
00300      DO 9 I=II,IE
00310      IG=IG+1
00320      DO 9 K=1,IN
00330      DO 9 IP=1,IN
00340      DO 9 J=1,IHT
00350      IMJ=IM+J
00360      9  AJ(I,IMJ)=AJ(I,IMJ)+EL(K,IG,L)*EL(IP,IG,L)*C(K,IP,J)
00370      1000 RETURN
00380      END

```

```

00100      SUBROUTINE WNUOUT(AVE)
00120      C      WRITES NU OBS., NU CALC., X, PCT. ERROR, K AFTER EACH ITERATIO
00160      DIMENSION VOBS(18),X(18),V(18),F(12,12),DK(14),
00180      1IDENT(13,4),KIDENT(33,3),W(18),ID(8,3),NFAC(3)
00190      DIMENSION FLMOBS(18),FLMC(18)
00210      COMMON /B1/IN,IL,IR,IM, IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM, IDEG,N2,L
00240      1MPH,NUMB,ITER,NEG,MPHT,INT,VAR/B2/VOBS,X,V/B7/F,H,DK/B8/IDENT,
00260      2KIDENT,W,ID,NFAC
00280      COMMON /B11/FLMOBS,FLMC
00300      N3=NISP*IN
00310      DO 10 I=1,N3
00330      V(I)=1303.0*SQRT(FLMC(I))
00350      10 X(I)=1303.0*(SQRT(FLMC(I))-SQRT(FLMOBS(I)))
00370      N4=N3+1
00390      DO 11 I=N4,N2
00410      11 V(I)=FLMC(I)
00430      WRITE(2,1)ITER
00440      1      FORMAT(1H1,35X,16H ITERATION NUMBER,13)
00450      WRITE(2,2)
00460      2      FORMAT(1H0,3HND.,3X,7HNU OBS.,7X,8HNU CALC.,5X,8HDELTA NU,
00470      94X,10HPCT. ERROR,12X,3HND.,5X,1HK/1H )
00480      AVE=0.
00490      DO 3 I=1,MPHT
00500      PCT=X(I)*100./VOBS(I)
00510      WRITE(2,4)I,VOBS(I),V(I),X(I),PCT,I,DK(I),
00520      1(KIDENT(1,J),J=1,3)
00530      3 AVE=AVE+ABS(PCT)
00540      4      FORMAT (1H ,12,F13.3,3F13.5,12X,12,F13.7,2X,4A6)
00550      IF (N2-MPHT) 7,7,5
00560      5 II=MPHT+1
00570      DO 6 I=II,N2
00580      PCT=X(I)*100./VOBS(I)
00590      WRITE(2,4)I,VOBS(I),V(I),X(I),PCT
00600      6 AVE=AVE+ABS(PCT)
00610      7 FN2=N2
00620      AVE=AVE/FN2
00630      WRITE(2,8)AVE
00640      8      FORMAT(1H0,15HAVERAGE ERROR =,F10.5,9H PER CENT)
00650      RETURN
00660      END

```

```
00100      SUBROUTINE WTEMP(NR,NC)
00110      C      PRINTS UNSYMMETRIC MATRIX(60,60)
00120      C
00140      DIMENSION TEMP(18,14)
00150      COMMON/B4/TEMP
00160
00170      INC=1
00190      IL=9
00210      DO 1 I=1,3
00230      IF (NC-IL) 2,2,3
00250      2 IL=NC
00270      3      WRITE(2,4)(J,J=INC,IL)
00280      4 FORMAT (1H0,3HI/J,17,3I13,71H )
00290      DO 7 J=1,NR
00300      7      WRITE(2,10)J,(TEMP(J,K),K=INC,IL)
00310      10      FORMAT(1H ,I3,9F13.8)
00320      IF (NC-IL) 5,5,6
00330      6 INC=INC+9
00340      1 IL=IL+9
00350      5 RETURN
00360      END
```

CHEM2 Sample Problem

The Ethylene Molecule (C_2H_4) - B_{3u} Symmetry

INPUT

00010	ETHYLENE
00020	B3U SYMMETRY
00030	TWO ISOTOPES
00040	MVFF JOHN COMERFORD
00050	020000020302040000000000000002
00060	0101
00070	02
00080	02
00090	1.0,1,1
00100	
00110	1.0,2,2
00120	
00130	1.0,1,2
00140	
00150	1.0373,1,1
00160	1.1134,2,2
00170	0.0740,1,2
00180	
00190	0.5415,1,1
00200	0.6177,2,2
00210	0.0740,1,2
00220	
00230	2989.5,1443.5,2200.2,1077.9
00240	5.57, CH2 STR
00250	1.45, CH2 BEND
00260	0.00003, STR-BEND
00270	01

ETHYLENE
 B3U SYMMETRY
 TWO ISOTOPES

MVFF JOHN COMERFORD
 N L R M H NISP NI SCF FFC W B SYM IDEG LW
 2 0 0 2 3 2 4 0 0 0 0 0 0 0
 ISOTOPE NO. FACTORS FACTOR DIMENSIONS FOFI-4Z8
 1 1 2 2
 2 1 1 2

INPUT

G MATRICES

1

I/J 1 2
 1 1.03730000 0.07400000
 2 0.07400000 1.11340000

2

I/J 1 2
 1 0.54150000 0.07400000
 2 0.07400000 0.61770000

0

I/J 1 2
 1 0.00000000 0.00000000
 2 0.00000000 0.00000000

C MATRICES

1

I/J 1 2
 1 1.00000000 0.00000000
 2 0.00000000 0.00000000

2

I/J 1 2
 1 0.00000000 0.00000000
 2 0.00000000 1.00000000

3

I/J 1 2
 1 0.00000000 1.00000000

2 1.00000000 0.00000000

I M1

M2

M3

M4

I VOBS

W

K

I	VOBS	W	K	CH2	STR
1	2989.500	1.000000	5.57000	CH2	STR
2	1443.500	1.000000	1.45000	CH2	BEND
3	2200.200	1.000000	0.00003	STR-	BEND
4	1077.900	1.000000			

ISOTOPIC SPECIES 1

G MATRIX

I/J 1

2

1	1.03730000	0.07400000
2	0.07400000	1.11340000

DETERMINAT OF G MATRIX VLOCK, 1 = 0.114945E+01

ISOTOPIC SPECIES 2

G MATRIX

I/J 1

2

1	0.54150000	0.07400000
2	0.07400000	0.61770000

DETERMINAT OF G MATRIX VLOCK, 1 = 0.329009E+00

INITIAL F MATRIX

I/J 1

2

1	5.57000000	0.00003000
2	0.00003000	1.45000000

EIGENVECTORS FROM ITERATION 0

1.01812 -0.02701

0.10055 1.05038
 0.73485 -0.03875
 0.14147 0.77310

NO.	NU OBS.	NU CALC.	ITERATION NUMBER 0			CH2	STR
			DELTA NU	PCT. ERROR	NO. K		
1	2989.500	3134.88990	145.38992	4.86335	1	5.5700000	CH2 STR
2	1443.500	1650.15180	206.65176	14.31602	2	1.4500000	CH2 BEND
3	2200.200	2270.66840	70.46837	3.20282	3	0.0000300	STR- BEND
4	1077.900	1218.85000	140.95005	13.07636			

AVERAGE ERROR = 8.86464 PER CENT

POTENTIAL ENERGY DISTRIBUTION - CONTRIBUTION OF K(J) TO NU(I)

I/J	1	2	3
1	99.74663500	0.25325894	0.00010611
2	0.25336462	99.74653100	-0.00010614
3	99.04422800	0.95556625	0.00020539
4	0.95576757	99.04402800	-0.00020541

JACOBIAN FROM ITERATION 0

I/J	1	2	3
1	1.03657050	0.01011003	0.20474141
2	0.00072954	1.10329000	-0.05674141
3	0.53999849	0.02001296	0.20791315
4	0.00150145	0.59768697	-0.05991316

MATRIX FROM ITERATION 0

1.36608 0.02299 0.32437
 0.02299 1.57498 -0.09218
 0.32437 -0.09218 0.09196

A(1,1)**A(N,N) = 0.20E+00
 DET(A) = 0.19E-01
 DET(A)/A(1,1)**A(N,N) = 0.97E-01

INVERSE MATRIX FROM ITERATION 0
 7.13653 -1.67586 -26.85370
 -1.67586 1.06804 6.98217
 -26.85370 6.98217 112.59899

DET(A)/A(I,1)**A(N,N) = 0.97E-01

PARAMETER INCREMENTS, ITERATION 0

-0.65745
 -0.28530
 0.80243

F MATRIX FOR ITERATION 1

I/J	1	2
1	4.91255230	0.80245781
2	0.80245781	1.16470170

EIGENVECTORS FROM ITERATION 1

0.99280	0.22727
0.30572	-1.00992
0.71416	0.17743
0.28554	-0.73223

ITERATION NUMBER 1

NO.	NU OBS.	NU CALC.	DELTA NU	PC1. ERROR	NO.	K
1	2989.500	3038.54490	49.04497	1.64057	1	4.9125523
2	1443.500	1349.90510	-93.59488	-6.48389	2	1.1647017
3	2200.200	2229.51240	29.31244	1.33226	3	0.8024578
4	1077.900	984.27589	-93.62412	-8.68579		

AVERAGE ERROR = 4.53563 PER CENT

JACOBIAN FROM ITERATION 1

I/J	1	2	3
1	0.98564851	0.09346777	0.60704652
2	0.05165141	1.01993220	-0.45904654
3	0.51001756	0.08153493	0.40784431
4	0.03148241	0.53616503	-0.25984431

MATRIX FROM ITERATION 1

1.23528 0.20327 0.77445
 0.20327 1.34312 -0.51752
 0.77445 -0.51752 0.81309

A(I,1)**A(N,N) = 0.13E+01

DET(A) = 0.16E-01

DET(A)/A(1,1)**A(N,N) = 0.12E-01

INVERSE MATRIX FROM ITERATION 1
 51.31789 -35.24421 -71.31220
 -35.24421 25.19155 49.60381
 -71.31220 49.60381 100.72614

DET(A)/A(1,1)**A(N,N) = 0.12E-01

PARAMETER INCREMENTS, ITERATION 1
 -0.19793
 0.17992
 0.01140

F MATRIX FOR ITERATION 2

I/J 1 2
 1 4.71461790 0.81385520
 2 0.81385520 1.34462130
 EIGENVECTORS FROM ITERATION 2
 0.98617 0.25449
 0.33339 -1.00113
 0.70830 0.19953
 0.30815 -0.72301

ITERATION NUMBER 2
 NO. NU OBS. NU CALC. DELTA NU PCT. ERROR NO. K

NO.	NU OBS.	NU CALC.	DELTA NU	PCT. ERROR	NO.	K
1	2989.500	2991.15370	1.65368	0.05532	1	4.7146179
2	1443.500	1449.95950	6.45954	0.44749	2	1.3446213
3	2200.200	2199.02780	-1.17222	-0.05328	3	0.8138552
4	1077.900	1055.16830	-22.73174	-2.10889		

AVERAGE ERROR = 0.66624 PER CENT

JACOBIAN FROM ITERATION 2

I/J 1 2 3
 1 0.97253402 0.11114774 0.65755594
 2 0.06476595 1.00225220 -0.50955595
 3 0.50168589 0.09495917 0.43653030
 4 0.03981407 0.52274078 -0.28853031

MATRIX FROM ITERATION 2

1.20329 0.24146 0.81401
 0.24146 1.29914 -0.54699
 0.81401 -0.54699 0.96584

A(1,1)**A(N,N) = 0.15E+01
 DET(A) = 0.18E-01
 DET(A)/A(1,1)**A(N,N) = 0.12E-01

INVERSE MATRIX FROM ITERATION 2
 54.11349 -38.42178 -67.36671
 -38.42178 28.29108 48.40430
 -67.36671 48.40430 85.22542

DET(A)/A(1,1)**A(N,N) = 0.12E-01

PARAMETER INCREMENTS, ITERATION 2
 0.00890
 -0.00568
 -0.01604

F MATRIX FOR ITERATION 3

I/J 1 2
 1 4.72351770 0.79781851
 2 0.79781851 1.33893750
 EIGENVECTORS FROM ITERATION 3
 0.98734 0.24993
 0.32876 -1.00266
 0.70918 0.19638
 0.30493 -0.72437

NO.	NU OBS.	NU CALC.	ITERATION NUMBER 3		
			DELTA NU	PCT. ERROR	K
1	2989.500	2990.46240	0.96242	0.03219	1 4.7235177
2	1443.500	1451.69460	8.19463	0.56769	2 1.3389375
3	2200.200	2197.85700	-2.34292	-0.10649	3 0.7978185
4	1077.900	1056.74930	-21.15063	-1.96221	

AVERAGE ERROR = 0.66714 PER CENT

JACOBIAN FROM ITERATION 3

I/J 1 2 3

1	0.97483392	0.10808238	0.64919140
2	0.06246604	1.00531760	-0.50119140
3	0.50293669	0.09298142	0.43249862
4	0.03856328	0.52471855	-0.28449863

MATRIX FROM ITERATION 3

1	1.20864	0.23516	0.80809
2	0.23516	1.30632	-0.54276
3	0.80809	-0.54276	0.94064

A(1,1)**A(N,N)= 0.15E+01
 DET(A)= 0.18E-01
 DET(A)/A(1,1)**A(N,N) = 0.12E-01

INVERSE MATRIX FROM ITERATION 3

52.64814	-37.18441	-66.68547
-37.18441	27.26956	47.67971
-66.68547	47.67971	85.86385

DET(A)/A(1,1)**A(N,N) = 0.12E-01

PARAMETER INCREMENTS, ITERATION 3

0.00010
-0.00005
-0.00026

F MATRIX FOR ITERATION 4

I/J	1	2
1	4.72361800	0.79755893
2	0.79755893	1.33889070

EIGENVECTORS FROM ITERATION 4

0.98735	0.24986
0.32869	-1.00268
0.70919	0.19633
0.30488	-0.72439

NO.	NU OBS.	NU CALC.	DELTA NU	ITERATION NUMBER 4	PCT. ERROR	NO.	K
1	2989.500	2990.44090	0.94091	0.03147	1	4.7236180	CH2 STR
2	1443.500	1451.74690	8.24686	0.57131	2	1.3388907	CH2 BEND
3	2200.200	2197.83150	-2.36849	-0.10765	3	0.7975589	STR BEND

4 1077.900 1056.79200 -21.10795 -1.95825
 AVERAGE ERROR = 0.66717 PER CENT

JACOBIAN FROM ITERATION 4

I/J	1	2	3
1	0.97486775	0.10803721	0.64906698
2	0.06243223	1.00536270	-0.50106700
3	0.50295477	0.09295271	0.43243962
4	0.03854518	0.52474723	-0.28443964

MATRIX FROM ITERATION 4

1	2.0871	0.23507	0.80801
0	2.3507	1.30643	-0.54269
0	0.80801	-0.54269	0.94027

A(I,1)**A(N,N)= 0.15E+01

DET(A)= 0.18E-01

DET(A)/A(1,1)**A(N,N) = 0.12E-01

INVERSE MATRIX FROM ITERATION 4

52.62499	-37.16510	-66.67318
-37.16510	27.25378	47.66741
-66.67318	47.66741	85.87047

THIS IS THE FINAL JACOBIAN.

K COLUMNS FROM ITERATIONS 1 THROUGH 4

3 4

1	4.9125523	4.7146179	4.7235177	4.7236180
2	1.1647017	1.3446213	1.3389375	1.3388907
3	0.8024578	0.8138552	0.7978185	0.7975589

NUS FROM ITERATIONS 0 THROUGH 4 PLUS NU OBSERVED

125.

I	1	2	3	4
1	3038.54490	2991.15370	2990.46240	2990.44090
2	1349.90510	1449.95950	1451.69460	1451.74690
3	2229.51240	2199.02780	2197.85700	2197.83150
4	984.27589	1055.16830	1056.74930	1056.79200

X(NU CALC. - NU OBS.) COLUMNS FROM ITERATIONS 1 THROUGH 4 FOLLOWED BY NU OBSERVED

1	49.04497	1.65368	0.96242	0.94091	2989.50000
---	----------	---------	---------	---------	------------

2	-93.59488	6.45954	8.19463	8.24686	1443.50000
3	29.31244	-1.17222	-2.34292	-2.36849	2200.20000
4	-93.62412	-22.73174	-21.15063	-21.10795	1077.90000
PER CENT ERROR AND VARIANCE					
1	4.5356277	0.6662443	0.6671448	0.6671700	
2	0.0728163	0.0009800	0.0009508	0.0009507	

L MATRICES

1

I/J	1	2
1	0.98735390	0.24986441
2	0.32869014	-1.00267780

2

I/J	1	2
1	0.70919304	0.19632927
2	0.30488146	-0.72439439

POTENTIAL ENERGY DISTRIBUTION - CONTRIBUTION OF K(J) TO NU(I)

I/J	1	2	3
1	87.42564600	2.74622950	9.82812510
2	14.45187400	65.96422700	-19.58390000
3	83.50332300	4.37428620	12.12239200
4	16.38067400	63.20947600	-20.40985000
NO.	NU OBS.	NU CALC.	DELTA NU

SIGMA(K)

1	2989.500	2990.4409000	0.94091	0.03147	8.70225	4.7236180	0.22368	CH2	STR
2	1443.500	1451.7469000	8.24686	0.57131	16.04561	1.3388907	0.16097	CH2	BEND
3	2200.200	2197.8315000	-2.36849	-0.10765	11.67138	0.7975589	0.28573	STR-	BEND
4	1077.900	1056.7920000	-21.10795	-1.95825	12.60952				

AVERAGE PER CENT ERROR = 0.667170

SQRT(SUM(W*(O-C)**2)/(NO-NV)) = 0.030834

CORRELATION MATRIX FOR FORCE CONSTANTS

I/J	1	2	3
1	1.00000000	-0.98135449	-0.99182093
2	-0.98135447	1.00000000	0.98534037
3	-0.99182093	0.98534037	1.00000000

END OF CASE

APPENDIX III

Normal Coordinates of Ethylene
and Isobutene (B_2 Species only)

Ethylene - MVFF

	A_{1g}	
	(C_2H_4)	
1.01518	-0.03545	0.06447
-0.05635	0.23241	-0.33062
0.04002	0.61584	0.85589
	(C_2D_4)	
0.73554	-0.01072	0.01924
-0.10989	0.38050	-0.09818
0.07101	-0.13885	0.69525
	B_{1g}	
	(C_2H_4)	
1.05516		0.00516
-0.29882		1.29912
	(C_2D_4)	
0.78131		0.03533
-0.44209		1.04199
	B_{2u}	
	(C_2H_4)	
0.99296		0.35697
-0.40973		0.93242
	(C_2D_4)	
0.74376		0.25400
-0.32496		0.66023
	B_{3u}	
	(C_2H_4)	
0.98735		0.24986
0.32869		-1.00268
	(C_2D_4)	
0.70919		0.19635
0.30288		-0.72439

Ethylene - UBF

	A_{1g}	
	(C_2H_4)	
1.00480	-0.16282	0.03413
-0.14565	-0.32347	0.20163
0.17763	0.78481	0.68258
	(C_2D_4)	
0.68708	-0.26348	0.00110
-0.24799	-0.31695	0.06743
0.23057	0.34901	0.57683
	B_{1g}	
	(C_2H_4)	
1.05204		0.08123
-0.39157		1.27176
	(C_2D_4)	
0.78093		0.08860
-0.50983		1.01058
	B_{2u}	
	(C_2H_4)	
1.05437		0.04132
-0.10986		1.01254
	(C_2D_4)	
0.78525		0.03303
-0.12475		0.72522
	B_{3u}	
	(C_2H_4)	
1.01702		-0.05454
0.12893		1.04727
	(C_2D_4)	
0.73367		-0.05683
0.16046		0.76939

Ethylene - HOFF

	A_{1g}	
	(C_2H_4)	
1.01373	-0.09400	0.02842
-0.11937	-0.28248	0.26917
0.14413	0.91817	0.49958
	(C_2D_4)	
0.71126	-0.18867	-0.00343
-0.21238	-0.34183	0.06744
0.19518	0.36966	0.57702
	B_{1g}	
	(C_2H_4)	
1.05516	-0.00554	
-0.28564	1.29966	
	(C_2D_4)	
0.78552	0.02570	
-0.42715	1.04821	
	B_{2u}	
	(C_2H_4)	
1.05475	0.02998	
-0.04123	1.01764	
	(C_2D_4)	
0.78573	-0.01842	
-0.77025	0.73183	
	B_{3u}	
	(C_2H_4)	
1.01746	-0.04548	
0.11959	1.04838	
	(C_2D_4)	
0.73427	-0.04847	
0.15168	0.77116	

Isobutene - MVFF

$$B_2$$

$$(C_4H_8)$$

1.05511	-0.00660	-0.04227	-0.00033
0.00360	0.42588	0.02287	0.05867
0.12413	0.43504	0.27353	-0.34480
0.22987	0.18792	1.14409	0.19871

$$(C_4D_8)$$

0.78539	-0.01705	-0.04700	-0.00096
0.00819	0.41403	-0.01429	0.05030
0.17486	0.45462	0.28076	-0.27628
0.30221	0.28229	0.83982	0.22532

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