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The transferability of force constants among olefins

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THE TRANSFERABILITY OF FORCE CONSTANTS AMONG OLEFINS

BY

JOHN MARTIN COMERFORD

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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 feasable in this case.

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

APPROVAL OF THESIS

THE TRANSFERABILITY OF FORCE CONSTANTS AMONG OLEFINS

BY

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FOR

DEPARTMENT OF CHEMICAL ENGINEERING

NEWARK COLLEGE OF ENGINEERING

BY

FACULTY COMMITTEE

APPROVED: ______________________

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NEWARK, NEW JERSEY

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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. Futhermore, 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

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

yield the vibrational frequencies of a molecule since

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

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 choosen, 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:

$$V = \sum_a \tfrac{1}{2} k_a \Delta R_a^2 + \sum_m \tfrac{1}{2} k_m \Delta \measuredangle_m^2 \tag{3}$$

where ΔR_a is the change in the length of the bond "a" and $\measuredangle_m$ 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:

$$V' = a/R^n \tag{4}$$

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:

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

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 defination. 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:

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

or in matrix notation

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

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:

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

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

or in matrix notation

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

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

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

$$R = L Q \qquad (12)$$

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

$$Q_j = \sum_i L_{ij} R_i \tag{13}$$

The transformation matrix L is chosen such that

$$2V = Q' \Lambda Q \tag{14}$$

and

$$2T = \dot{Q}' E \dot{Q} \tag{15}$$

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

$$L' F L = \Lambda \tag{16}$$

and

$$L' G^{-1} L = E \tag{17}$$

Combination of these two equations gives the expression

$$F L = G^{-1} L \Lambda \tag{18}$$

or

$$G F L = L \Lambda \tag{19}$$

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

$$(G F - \lambda_i E) L_i = 0 \tag{20}$$

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

$$|G F - \lambda E| = 0 \tag{21}$$

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 choosen 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

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

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

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

and the condition of orthogonality is satisfied when

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

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

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

where g is a general kinetic energy matrix in terms of internal coordinates whose elements are calculated using the formulas gives 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 assording to the equation

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

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 $|GF - \lambda E| = 0$ 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):

$$\Delta \lambda_i = \sum_{jk} L_{ji} L_{ki} \Delta F_{ik} \tag{27}$$

where L_{ji} and L_{ki} are the transformation coefficients. Thus in matrix notation

$$\Delta \Lambda = J \Delta F \tag{28}$$

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^o's and a set of transformation coefficients, L^o's. If $\Delta\lambda i = \lambda i - \lambda^o i$, 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^o so that the difference between observed amd 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^o. 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

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

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

$$F_{(new)} = F_{(old)} + \Delta F \tag{30}$$

The calculation is then repeated using F (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 σ^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 matricies 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 C_2H_4 AND C_2D_4

(Bartell, Roth and Hollowell (3))

C_2H_4		
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)
C_2D_4		
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 C_2H_4 molecule seems more reliable. In view of this we have used the measurements reported for C_2H_4 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

Species	Description	C_4H_8	C_4D_8
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 choosen, 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 choosen different sets of bond lengths and bond angles as described below and have therefore developed different G matricies 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

A_{1g} Symmetry Species

1.0373	-0.0868	-0.1047	
	0.1655	0.2010	Normal Ethylene (C_2H_4)
		2.0718	

0.5417	-0.0870	-0.1048	
	0.1655	0.2008	Deuterated Ethylene (C_2D_4)
		1.2351	

Morino, Kuchitsu and Shimanouchi (22) choose internal coordinates for the molecule $CF_2{=}CF_2$ which could be applied directly to ethylene. The coordinates choosen involved the five bond lengths, the six bond angles of the planar molecule and two non-bonded distances. The non-bonded distances choosen were the distances between the F atoms in each CF_2 group and the distance between the C and F atoms not bonded directly.

Shimanouchi et al. calculated a G matrix for C_2F_2 which can be used for C_2H_2 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 C_2F_4

(From Shimanouchi et al. (22))

A_{1g} Symmetry Species

1.0373	-0.0868	-0.1283	
	0.1665	0.2462	Normal Ethylene (C_2H_4)
		3.3402	
0.5153	-0.0868	-0.1283	
	0.1665	0.2462	Deuterated Ethylene (C_2D_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

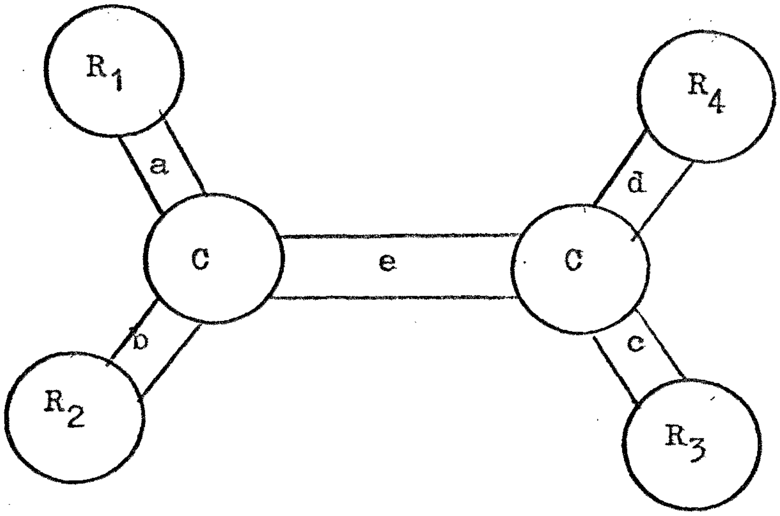
G Matrix Used for Ethylene A_{1g} Species

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_1CC	121.4°	121.4°	122.35°
R_2CC	121.4°	121.4°	122.35°
R_3CC	121.4°	121.4°	120.75°
R_4CC	121.4°	121.4°	120.75°
R_1CR_2	117.2°	117.2°	115.3°
R_3CR_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 matricies (G matrix) and the potential energy matricies (F matrix) for each symmetry species. The symmetry coordinates and resulting F and G matricies 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 choosen 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 anharmoncity. 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 matricies.

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, choosen to multiply bond stretching-angle bending interactions by the length of the C-H bond in ethylene (1.1030 Å) 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

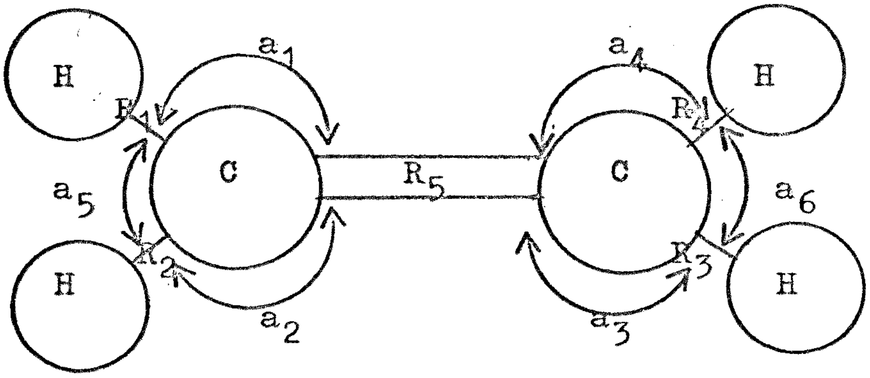
A. The Ethylene Molecule

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^2	Force Constant	σ^2
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 explaination 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	σ^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 suggest that the frequency assignments of Cyvin abd Cyvin may be the more reliable data. This conslusion 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 (σ^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

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

where Det G represents the determinent 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	$\frac{\lvert G' \rvert}{\lvert G \rvert}$	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 $CF_2 = CF_2$ and $CF_2 = CH_2$ 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_{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 $F'_{CH} = 0.1F_{CH}$ and $F'_{HH} = 0.1F_{HH}$.

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}	Kappa
CH str. (F1,1)	A_{1g}	1.000				0.920	0.379	1.460		
CC str. (F2,2)			1.000			4.201	1.000			
CH_2 rock (F3,3)				0.333	0.821	0.253	-0.807	0.090	-0.243	2.4863
CH str. (F4,4)	B_{1g}	1.000				0.921	0.379		0.540	
CH_2 rock (F5,5)					1.231	0.379	-1.211			
CH str. (F6,6)	B_{2u}	1.000				0.921	0.379		0.540	
CH_2 rock (F7,7)					1.231	0.379	-1.211			
CH str. (F8,8)	B_{3u}	1.000				0.921	0.379	1.460		
CH_2 rock (F9,9)				0.333	0.821	0.253	-0.807	0.090	-0.243	2.486
(F1,3)	A_{1g}					-0.341	-0.448	0.513	0.513	
(F1,2)						1.967	-0.616			
(F2,3)						-0.728	-0.554			
(F4,5)	B_{1g}					0.591	0.777			
(F6,7)	B_{2u}					0.591	0.777			
(F8,9)	B_{3u}					-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 ninteen 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
3026.4	3053.7	0.9
1622.6	1689.5	4.1
1342.2	1304.2	-2.8
3102.5	3109.8	0.2
1236.0	1098.9	-11.1
3105.3	3073.8	-1.0
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:	4.2

Description of Force Constant	Force Constant	Dispersion (σ^2)
CH stretch	5.214	0.390
CC stretch	10.585	2.686
HCH bend	2.715	0.298
CCH bend	0.439	0.101
C...H repulsion	-0.267	0.273
H...H repulsion	0.037	0.307
	Average:	0.676

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. Futhermore, 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 Gallaway and Barker's Assignments

Observed Frequency	Calculated Frequency	Percent Error	Description of Force Constant	Force Constant	Dispersion (σ^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		Average:	0.215
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:	1.2			

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

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 (σ^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		Average:	0.155
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:	1.0			

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

Table XVIII

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

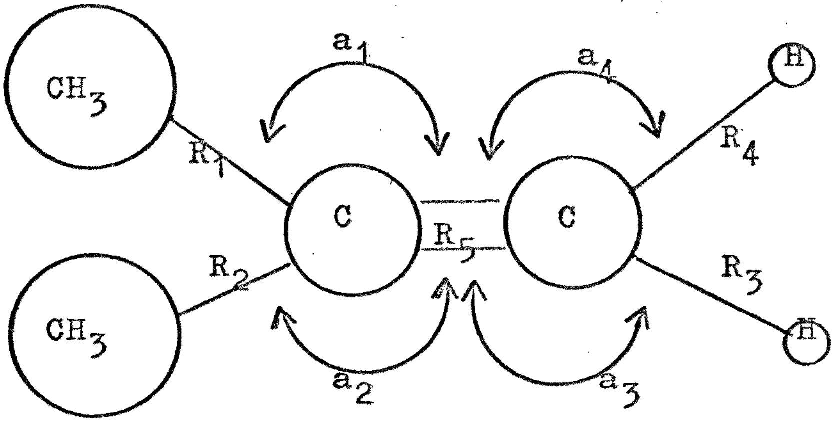
Observed Frequency	Calculated Frequency	Percent Error	Description of Force Constant	Force Constant	Dispersion (σ^2)
3024.6	3085.0	1.9	CH stretch	5.559	0.311
1622.6	1654.0	1.9	CC stretch	8.454	0.439
1342.2	1368.2	1.9	CH_2 deformation	1.403	0.055
3102.5	3107.0	0.1	CH stretch	5.192	0.148
1236.0	1235.3	-0.1	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		Average:	0.251
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:	0.9			

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 Constnats Found for the B_2 Species of Isobutene

Description of Vibration	Observed Frequency	Calculated Frequency (% Error)	Calculated Frequency (% Error)	Force Constant	Force Constant	Dispersion (σ^2)
		Solution I	Solution II	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 consistant 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 B_2 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 CH_2 rock force constants for the two molecules are compared, the agreement is good if the B_{1g} species of ethylene is compared to the B_2 species of isobutene.

C. Potential Energy Distribution

From equation (27) it follows that

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

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 XXII 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 form 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.	CC str.	HCH bend			
		F(1,1)	F(2,2)	F(3,3)	F(1,2)	F(1,3)	F(2,3)
$A_{1g}[C_2H_4]$	3026.4	96.49	0.54	0.04	-2.78	0.00	-0.14
	1622.0	0.42	33.22	33.25	-1.44	0.00	31.67
	1342.2	0.70	33.75	32.24	-1.87	0.00	-31.44
$A_{1g}[C_2D_4]$	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
		CH str.	HCH rock				
		F(4,4)	F(5,5)	F(4,5)			
$B_{1g}[C_2H_4]$	3102.5	97.77	0.82	1.41			
	1236.0	0.02	99.79	0.19			
$B_{1g}[C_2D_4]$	2310.0	94.14	3.14	-2.72			
	1011.0	1.07	97.31	1.62			
		CH str.	HCH rock				
		F(6,6)	F(7,7)	F(6,7)			
$B_{2u}[C_2H_4]$	3105.5	75.56	2.85	21.59			
	810.0	23.15	34.97	-41.87			
$B_{2u}[C_2D_4]$	2345.0	74.36	3.14	22.49			
	584.0	23.28	34.82	-41.90			
		CH str.	HCH rock				
		F(8,8)	F(9,9)	F(8,9)			
$B_{3u}[C_2H_4]$	2989.5	87.43	2.75	9.83			
	1443.5	14.45	65.96	-19.58			
$B_{3u}[C_2D_4]$	2200.2	83.50	4.37	12.12			
	1077.9	16.38	63.21	-20.41			

Table XXIII

Potential Energy Distribution for Ethylene
[UBFF]

Symmetry Species	Observed Frequency		Force Constant				
						C...H	H...H
		CH str.	CC str.	HCH bend	CCH bend	Repulsion	Repulsion
$A_{1g}[C_2H_4]$	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
$A_{1g}[C_2D_4]$	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
$B_{1g}[C_2H_4]$	3102.5	96.00			1.38	-2.62	
	1236.0	3.11			79.02	-17.87	
$B_{1g}[C_2D_4]$	2310.0	94.33			4.17	-1.50	
	1011.0	5.63			76.01	-18.36	
$B_{2u}[C_2H_4]$	3105.5	95.95			0.11	-3.94	
	810.3	1.31			81.46	-17.23	
$B_{2u}[C_2D_4]$	2345.0	96.10			0.25	-3.65	
	584.0	1.62			81.00	-17.37	
$B_{3u}[C_2H_4]$	2989.5	94.51		0.26	0.11	-4.05	1.07
	1443.5	1.04		66.61	26.53	-5.71	0.11
$B_{3u}[C_2D_4]$	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(6,6)	F(5,5)	F(7,7)	F(8,8)	F(9,9)	F(1,3) F(8,9) F(4,5) F(6,7)	F(2,3)	F(1,2)
$A_{1g}[C_2H_4]$	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
$A_{1g}[C_2D_4]$	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
$B_{1g}[C_2H_4]$	3102.5				97.23	0.61				-2.16		
	1236.0				0.36	97.97				-1.67		
$B_{1g}[C_2D_4]$	2310.0				93.15	2.54				-4.30		
	1011.0				0.07	99.21				0.73		
$B_{2u}[C_2H_4]$	3105.5				99.76		0.01			-0.24		
	810.3				2.31		92.85			-4.83		
$B_{2u}[C_2D_4]$	2345.0				99.19		0.05			-0.77		
	584.0				1.89		93.72			-4.39		
$B_{3u}[C_2H_4]$	2989.5							99.02	0.36	0.62		
	1443.5							1.22	97.63	-1.14		
$B_{3u}[C_2D_4]$	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 B_2 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. Futher, 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 CH_2 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 $CH_2=C-(CD_3)_2$ and $CD_2=C-(CH_3)_2$ 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 liketly 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

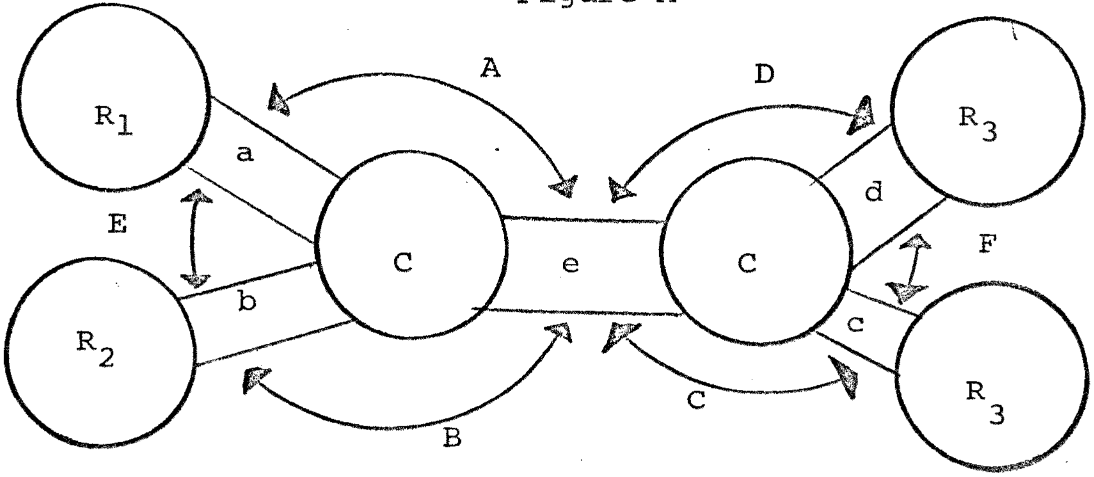
Line 1 of the input data contains the bond distances (Å) a,b,c,d,e as shown in Figure A. Distances are separated by commas (Free format).

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 R1,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).

Figure A



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.

```
      DIMENSION R1(5),B1(6),H1(4),GO(20,20)
1     READ(1,999)(R1(II),II=1,5)
999   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
```

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

Input

```
  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,
```

OUTPUT

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, begining 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 begining 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),
     1UTR(200),G1(200),G2(20,20),G2A(400),FMT1(14),FMT2(14),
     1FMT3(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

INPUT

```
(12F)
(6F)
(1H ,12(F8.4,2X))
2,12
.5,.5,-.5,-.5,0,0,0,0,0,0,0,0
0,0,0,0,0,.5515,.5515,-.5515,-.5515,0,0,0
12,12
   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,
```

OUTPUT

```
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 sucessive 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 matricies. 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 intial 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.

```
      DIMENSION IDENT(13,4),VOBS(18).W(18),C(12.12.8).
     1Q(12,12),DK(14).TEMP(18.14).G(12,12,3),VN(18).XI(18).
     2EL(12,12,3).F(12,12).V(18),VYR(18.8),XXX(18,8).X(18).
     3TKR(14,8).AJ(18.14),DELK(14),SUMT(2.8),AJWJ(14.14),
     4INEG(18),ELIN(12,12,3).SIGK(14).SIGV(18).
     6KIDENT(33.3),NFAC(3),ID(8,3)
      DIMENSION FLMOBS(18),FLMC(18)
      COMMON D.EL.ELIN,AJWJ.C.AJ,G
      COMMON /B1/IN.IL.IR,IM,IH,NISP.NI,ISCF,IFFC.IW.IB,ISYM,IDEG,N2,LW
     1MPH.NUMB.ITER.NEG,MPHI,IHT,VAR/B2/VOBS.X.V/B3/VYR.TKR,XXX,SUMT/
     2B4/TEMP/B5/G/B6/XI,INEG/B7/F.H,DK/B8/IDENT,KIDENT,W.ID,NFAC/B9/
     3CZ,ZM/B10/SIGK,SIGV/B11/FLMOBS.FLMC
C
1        FORMAT(13A5)
C
C     READ IDENTIFICATION
C
1002     READ(1,1)((IDENT(I,J),I=1,13),J=1,4)
C
         CALL LINK1
         CALL LINK2
         CALL LINK3
C
C     IS THIS THE LAST SET OF DATA
C
         READ(1,2)NND
    2 FORMAT(24I2)
      IF (NND) 1001,1002,1001
 1001 CONTINUE
         END
```

```
        SUBROUTINE LINK1
C     READ IN DATA
C
       DIMENSION IDENT(13,4),VOBS(18),W(18),C(12,12,8),
     1Q(12,12),DK(14),TEMP(18,14),G(12,12,3),VN(18),XI(18),
     2EL(12,12,3),F(12,12),V(18),VYR(18,8),XXX(18,3),X(18),
     3TKR(14,8),AJ(18,14),DELK(14),SUMT(2,8),AJWJ(14,14),
     4INEG(18),ELIN(12,12,3),SIGK(14),SIGV(18),
     6KIDENT(33,3),NFAC(3),ID(8,3)
      DIMENSION FLMOBS(18),FLMC(18)
      COMMON D,EL,ELIN,AJWJ,C,AJ,Q
      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,LW
     1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B3/VYR,TKR,XXX,SUMT/
     2B4/TEMP/B5/G/B6/XI,INEG/B7/F,H,DK/B8/IDENT,KIDENT,W,ID,NFAC/B9/
     3CZ,ZM/B10/SIGK,SIGV/B11/FLMOBS,FLMC
C
C     READ MATRIX DIMENSIONS AND CHECK WORDS
C
        READ(1,2)IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,
     1IB,ISYM,IDEG,LW,ISENT
        READ(1,2)(NFAC(I),I=1,NISP)
      DO 25 I=1,NISP
      K=NFAC(I)
        READ(1,2)(ID(J,I),J=1,K)
   25 CONTINUE
    2 FORMAT(24I2)
      IF(NI)4,3,4
    3 NII=1
      GO TO 420
    4 NII=NI
  420 CONTINUE
      IF (ISYM) 104,104,105
  105 ND=IL
      GO TO 106
  104 ND=IN
  106 IHT=IH+IFFC
      IF (IHT) 801,801,800
  800 DO 112 I=1,IHT
C
C     READ C MATRICES
C
C
      CALL READFL (TEMP,ND,ND,0)
      IF (ISYM) 109,109,110
  110 DO 108 J=1,IN
      DO 108 K=1,IL
      ELIN(J,K,2)=0.
      DO 108 L=1,IL
  108 ELIN(J,K,2)=ELIN(J,K,2)+ELIN(J,L,I)*TEMP(L,K)
      DO 111 J=1,IN
      DO 111 K=1,IN
      TEMP(J,K)=0.
      DO 111 L=1,IL
  111 TEMP(J,K)=TEMP(J,K)+ELIN(J,L,2)*ELIN(K,L,1)
  109 DO 112 J=1,IN
      DO 112 K=1,IN
  112 C(J,K,I)=TEMP(J,K)
801     CONTINUE
      DO 152 L=1,NISP
C
C     READ G MATRICES
```

```
C
      ND=IN
      CALL READFL (TEMP,ND,ND,0)
      DO 152 I=1,ND
      DO 152 J=1,ND
  152 G(I,J,L)=TEMP(I,J)
      IF (ISCF) 82,81,82
   81 FNISP=NISP
      SCF=1./FNISP
      GOTO83
   82 XYZ=NISP*ISCF
      SCF=1./XYZ
   83 FLN2=SCF
      N2=NISP*(IN+IDEG)
C
C     READ OBSERVED FREQUENCIES AND ZETA CONSTANTS
C
        READ(1,118)(VOBS(I),I=1,N2)
      N3=NISP*IN
      DO901I=1,N3
  901 FLMOBS(I)=(VOBS(I)/1303.0)**2
      IF(IDEG)915,915,916
  916 KAP=N3+1
      DO912I=KAP,N2
  912 FLMOBS(I)=VOBS(I)
118     FORMAT(6F)
  915 DO8J=1,N2
    8 W(J)=1.
      IF(IW)87,913,87
   87 CALL READDM(VN,N2)
      DO 89 I=1,N2
      IF(VN(I))88,89,88
   88 W(I)=VN(I)
   89 CONTINUE
  913 IF(LW)90,90,904
  904 IF(LW-1)905,905,910
905     DO 907 I=1,N2
  907 W(I)=W(I)*1.0/ABS(FLMOBS(I))
      GOTO90
  910 IF(LW-2)906,906,908
  906 DO930I=1,N2
  930 W(I)=W(I)*1.0/FLMOBS(I)**2
      GOTO90
  908 DO909I=1,N3
      IF(VN(I))920,920,921
  920 W(I)=0.0
      GOTO909
  921 W(I)=(848904.5/(VOBS(I)*VN(I)))**2
  909 CONTINUE
      IF(IDEG)90,90,918
  918 DO911I=KAP,N2
      IF(VN(I))925,925,926
  925 W(I)=0.0
      GOTO911
  926 W(I)=1.0/VN(I)**2
  911 CONTINUE
   90 CONTINUE
        MPH=IH
        MPHT=MPH+IFFC
      N2G=IN*NISP
      DO 103 I=1,N2G
```

```
      103 INEG(I)=0
C
C         READ INITIAL FORCE CONSTANTS
C
          DO 77 I=1,IHT
77           READ(1,78)DK(I),(KIDENT(I,J),J=1,3)
78           FORMAT(1F,4A5)
C
C         LIST INPUT DATA
C
          CALL WINPI
       10 CONTINUE
             RETURN
             END
```

```
        SUBROUTINE LINK2
C      CALCULATE EIGENVALUES OF G MATRICES
C
        DIMENSION IDENT(13,4),VOBS(18),W(18),C(12,12,8),
     1Q(12,12),DK(14),TEMP(18,14),G(12,12,3),VN(18),XI(18),
     2EL(12,12,3),F(12,12),V(18),VYR(18,8),XXX(18,8),X(18),
     3TKR(14,8),AJ(18,14),DELK(14),SUMT(2,8),AJWJ(14,14),
     4INEG(18),ELIN(12,12,3),SIGK(14),SIGV(18),
     6KIDENT(33,3),NFAC(3),ID(8,3)
       DIMENSION FLMOBS(18),FLMC(18)
       COMMON D,EL,ELIN,AJWJ,C,AJ,Q
       COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,LW
     1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B3/VYR,TKR,XXX,SUMT/
     2B4/TEMP/B5/G/B6/XI,INEG/B7/F,H,DK/B8/IDENT,KIDENT,W,ID,NFAC/B9/
     3CZ,ZM/B10/SIGK,SIGV/B11/FLMOBS,FLMC
       DO 24 I=1,N2
    24 VN(I)=FLMOBS(I)
       DO 33 L=1,NISP
       DO 20 I=1,IN
       DO 20 J=1,IN
20        TEMP(I,J) = G(I,J,L)
          WRITE(2,600)L
   600 FORMAT (17H1ISOTOPIC SPECIES,I4,///55X,8HG MATRIX//)
       CALL WTEMP(IN,IN)
C
C      EIGENVALUES OF G MATRICES BY FACTORED SYMMETRY SPECIES
C
    92 ISC = 0
       DO 151 I=1,IN
       DO 151 J=1,IN
       AJWJ(I,J)=G(I,J,L)
   151 EL(I,J,L)=0.
       M=0
       N=0
       INI=IN*(L-1)
       K=NFAC(L)
       DO 32 IDX=1,K
       IF (IDX-1) 1000,26,27
    26 M=1
       GOTO28
    27 M=M+ID(IDX-1,L)
    28 N=N+ID(IDX,L)
       LL=1
       CALL SYMAS (AJWJ,XI,ISC,INI,M,N,LL,G)
       DET=1.
       DO 29 J=M,N
       JI=J+INI
       DET=DET*XI(JI)
       DO 29 I=M,N
    29 G(I,J,L)=AJWJ(I,J)*SQRT(XI(JI))
32        WRITE(2,601)IDX,DET
601       FORMAT(1H1,30H DETERMINAT OF G MATRIX VLOCK,I3
      1,2H =,E14.6)
    33 CONTINUE
       N2G=IN*NISP
       DO 34 J=1,N2G
    34 XI(J)=1./XI(J)
       DO 555 I=1,IN
       DO 555 J=1,IN
       DO 555 L=1,NISP
   555 ELIN(I,J,L)=0
```

```
00720    1000 CONTINUE
00730            RETURN
00740         END
```

```
         SUBROUTINE LINK3
C       DO ITERATIONS
C
        DIMENSION IDENT(13,4),VOBS(18),W(18),C(12,12,8),
       1Q(12,12),DK(14),TEMP(18,14),G(12,12,3),VN(18),XI(18),
       2EL(12,12,3),F(12,12),V(18),VYR(18,8),XXX(18,8),X(18),
       3TKR(14,8),AJ(18,14),DELK(14),SUMT(2,8),AJWJ(14,14),
       4INEG(18),ELIN(12,12,3),SIGK(14),SIGV(18),
       6KIDENT(33,3),NFAC(3),ID(8,3)
        DIMENSION FLMOBS(18),FLMC(18)
        COMMON D,EL,ELIN,AJWJ,C,AJ,Q
        COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,LW,
       1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B3/VYR,TKR,XXX,SUMT/
       2B4/TEMP/B5/G/B6/XI,INEG/B7/F,H,DK/B8/IDENT,KIDENT,W,ID,NFAC/B9/
       3CZ,ZM/B10/SIGK,SIGV/B11/FLMOBS,FLMC
C
C       START ITERATION
C
        IF (NI) 4,3,4
      3 NII=1
        GO TO 5
      4 NII=NI
      5 ISENT=1
        ITER=-1
        ICOUNT=1
        DO72ITERX=1,NII
        DO 70  KOUNT=1,ICOUNT
        NUMB=KOUNT
        ITER=ITER+1
        CALL FCALC1
          IM=0
        DO 31 I=1,IN
        DO 31 J=1,IN
     31 TEMP(I,J)=F(I,J)
        IF(ITER)1000,36,37
36        WRITE(2,602)
    602 FORMAT(1H1,51X,16HINITIAL F MATRIX/1H )
        GOTO38
37        WRITE(2,603)ITER
    603 FORMAT(1H1,48X,22HF MATRIX FOR ITERATION,I3/1H )
     38 CALL WTEMP(IN,IN)
        NEG=0
        DO 30 L=1,NISP
        M=0
        N=0
        INI=IN*(L-1)
        K=NFAC(L)
        DO 45 IDX=1,K
        IF (IDX-1) 1000,40,41
     40 M=1
        GOTO42
     41 M=M+ID(IDX-1,L)
     42 N=N+ID(IDX,L)
        DO 43 I=M,N
        DO 43 J=M,N
     43 AJWJ(I,J)=F(I,J)
        LL=L
        CALL SYMAS (AJWJ,X,IN,INI,M,N,LL,G)
     45 CONTINUE
     30 CONTINUE
        IF(ISENT)931,931,932
```

```
932     WRITE(2,853)ITER
  853 FORMAT(28H0EIGENVECTORS FROM ITERATIONI4)
      DO854K=1,NISP
      DO854I=1,IN
854     WRITE(2,855) (EL(I,J,K),J=1,IN)
  855 FORMAT(1H010F11.5)
  931 IF(NEG)76,46,76
76      CALL WNUOUT(AVE)
        WRITE(2,610)NEG
610     FORMAT(1H ,I3,' NEGATIVE EIGEN VALUES.')
      N2G=IN*NISP
      DO 121 I = 1,N2G
      IF (INEG(I)) 122,121,122
122     WRITE(2,123)I
123     FORMAT(1H ,I10)
  121 CONTINUE
      GO TO 1000
   46 N3=NISP*IN
      DO47I=1,N3
      VYR(I,KOUNT)=1303.0*SQRT(FLMC(I))
   47 XXX(I,KOUNT)=1303.0*(SQRT(FLMC(I))-SQRT(FLMOBS(I)))
      IF(IDEG)950,950,960
  960 KAP=N3+1
      DO965I=KAP,N2
      VYR(I,KOUNT)=FLMC(I)
  965 XXX(I,KOUNT)=X(I)
  950 DO48I=1,MPHT
   48 TKR(I,KOUNT)=DK(I)
C
C     CALCULATE JACOBIAN (AJ) FROM EIGENVECTORS
C
   49 DO 50 I=1,N2
      DO 50 J=1,MPHT
50      AJ(I,J) = 0.0
      DO 51 L=1,NISP
        M=(L-1)*IN+1
      N=M+IN-1
      CALL EIGJAC (M,N,L)
   51 CONTINUE
      CALL WNUOUT (AVE)
   97 DO 55 I=1,N2
      Y1=0.
      DO 54 J=1,MPHT
      TEMP(I,J)=AJ(I,J)*DK(J)/FLMC(I)
   54 Y1=Y1+ABS(TEMP(I,J))
      DO55J=1,MPHT
   55 TEMP(I,J)=TEMP(I,J)*100.0/Y1
      IF(ITER)57,53,57
53      WRITE(2,605)
605     FORMAT(1H1,29X,'POTENTIAL ENERGY DISTRIBUTION',
     932H - CONTRIBUTION OF K(J) TO NU(I)/1H )
      CALL WTEMP(N2,MPHT)
   57 DO 98 I=1,N2
      DO 98 J=1,MPHT
   98 TEMP(I,J)=AJ(I,J)
        WRITE(2,604) ITER
  604 FORMAT(1H1,47X,23HJACOBIAN FROM ITERATION,I3/1H )
      CALL WTEMP(N2,MPHT)
      IF(AVE-100.)201,201,200
200     WRITE(2,202)
  202 FORMAT(66H CALCULATION TERMINATED BECAUSE AVERAGE ERROR EXCEDES 1
```

```
          10 PER CENT)
           GO TO 1000
C
C          TRANSPOSE JACOBIAN AND FORM (JTRANSPOSE)(W)(J)INVERSE AS XNIT
C
      201 DO 58 I=1,N2
          DO 58 J=1,MPH
       58 TEMP(I,J)=W(I)*AJ(I,J)
          DO 59 I=1,MPH
          DO 59 J=1,MPH
          AJWJ(I,J)=0.
          DO 59 K=1,N2
       59 AJWJ(I,J)=AJWJ(I,J)+AJ(K,I)*TEMP(K,J)
          IF(ISENT)933,933,934
 934        WRITE(2,856)ITER
      856 FORMAT(22H0MATRIX FROM ITERATIONI4)
          DO 456 I=1,MPH
 456        WRITE(2,855)(AJWJ(I,J),J=1,MPH)
      933 PROD=1.0
          DO 119 I=1,MPH
      119 PROD=PROD*AJWJ(I,I)
            WRITE(2,615)PROD
      615 FORMAT (1H0,46X,16HA(1,1)***A(N,N)=,E11.2)
          NEROR=0
          CALLINVERT(AJWJ,MPH,1.0E-03,NEROR,DET,PROD)
          IF(ISENT)935,935,936
 936        WRITE(2,857)ITER
      857 FORMAT(30H0INVERSE MATRIX FROM ITERATIONI4)
          DO858I=1,MPH
 858        WRITE(2,855) (AJWJ(I,J),J=1,MPH)
      935 CONTINUE
            IF(NEROR)75,63,75
       63 DO 64 I=1,N2
          IF (ABS((FLMC(I)-VN(I))/FLMC(I))-.0001) 64,64,65
       64 CONTINUE
            WRITE(2,606)
      606 FORMAT(1H0,46X,27HTHIS IS THE FINAL JACOBIAN.)
            GO TO 73
 65         DO 66 I=1,N2
 66         VN(I)=FLMC(I)
            WRITE(2,120)PROD
 120        FORMAT(1H0,46X,24HDET(A)/A(1,1)***A(N,N) =,E11.2)
            DO 67 I=1,MPH
            DO 67 J=1,N2
            TEMP(J,I)=0
            DO 67 K=1,MPH
 67         TEMP(J,I)=TEMP(J,I)+AJWJ(I,K)*AJ(J,K)*W(J)
            DO 69 I=1,MPH
            DELK(I) = 0
            DO 68 J=1,N2
 68         DELK(I) = DELK(I)-TEMP(J,I)*(FLMC(J)-FLMOBS(J))
  69        DK(I)=DK(I)+DELK(I)
            IF(ISENT)70,70,937
 937        WRITE(2,860)ITER
 860        FORMAT(32H0PARAMETER INCREMENTS, ITERATIONI4)
            DO859 I=1,MPH
 859        WRITE(2,855) DELK(I)
 70         CONTINUE
            IF(NI)991,991,990
 990        ICOUNT=8
            ICOUNT=8
```

```
          M=ITER-NUMB+1
          CALL SUMS
          IF(ITER)71,72,71
   71     CALL WDKNUX(M)
   72     CONTINUE
          DO 56 I=1,MPH
   56     DK(I)=DK(I)-DELK(I)
          VAR=SUMT(2,NUMB)
          CALL STAT
   991    WRITE(2,607)
   607    FORMAT(1H1,10X,'DID NOT CONVERGE ..........')
          GO TO 1000
   73     CALL SUMS
          M=ITER-NUMB+1
          CALL WDKNUX(M)
          VAR=SUMT(2,NUMB)
          CALL STAT
   74     WRITE(2,608)
   608    FORMAT(1H1,10X,'END OF CASE ..........')
          GO TO 1000
   75     WRITE(2,609)
   609    FORMAT(32H NO INVERSE EXISTS FOR THIS CASE)
   1000   CONTINUE
          RETURN
          END
```

```
            SUBROUTINE SUMS
C
C           CALCULATES AVERAGE PER CENT ERROR AND VARIANCE
C
      DIMENSION VOBS(18),X(18),V(18),VYR(18,8),XXX(18,8),TKR(14,8),
     1SUMT(2,8),IDENT(13,4),KIDENT(33,3),W(18),ID(8,3),NFAC(3)
      DIMENSION FLMOBS(18),FLMC(18)
      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,LW
     1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B3/VYR,TKR,XXX,SUMT
     2/B8/IDENT,KIDENT,W,ID,NFAC
      COMMON /B11/FLMOBS,FLMC
      N3=NISP*IN
      KAP=N3+1
      XN=N2
      DO 1 I=1,NUMB
      SUM1=0.
      SUM2=0.
      DO 2 J=1,N3
      SUM1=SUM1+ABS(XXX(J,I)/VOBS(J))
    2 SUM2=SUM2+W(J)*((VYR(J,I)**2-VOBS(J)**2)/1303.0**2)**2
      IF(IDEG)5,5,4
    4 DO3J=KAP,N2
      SUM1=SUM1+ABS(XXX(J,I)/VOBS(J))
    3 SUM2=SUM2+W(J)*XXX(J,I)**2
    5 SUMT(1,I)=SUM1*100./XN
    1 SUMT(2,I)=SUM2
        RETURN
        END
```

```
      SUBROUTINE FCALC1
C
C     CALCULATES F MATRIX FROM Q, DK, AND C MATRICES
C
      DIMENSION F(12,12),Q(12,12),C(12,12,8),
     1EL(12,12,3),ELIN(12,12,3),AJ(18,14),AJWJ(14,14),DK(14)
      COMMON D,EL,ELIN,AJWJ,C,AJ,Q
      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,L
     1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B7/F,H,DK
      DO 6 I=1,IN
      DO 6 J=1,IN
      F(I,J)=0.
    7 DO 3 K=1,IHT
    3 F(I,J)=F(I,J)+C(I,J,K)*DK(K)
    6 CONTINUE
      RETURN
      END
```

```
        SUBROUTINE WDKNUX(M)
C
C       PRINTS K, NU, AND X COLUMNS AFTER EACH SET OF EIGHT ITERATIONS.
C       CALLS SUBROUTINES WDK,AND WNUX
C
      DIMENSION VYR(18,8),XXX(18,8),TKR(14,8),SUMT(2,8)
      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,LW
     1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B3/VYR,TKR,XXX,SUMT
        WRITE(2,449)M,ITER
  449 FORMAT(1H1,39X,25HK COLUMNS FROM ITERATIONS,I3,8H THROUGH,I3)
      CALL WDK(M)
        WRITE(2,450)N,ITER
  450   FORMAT(1H1,34X,19HNUS FROM ITERATIONS,I3,8H THROUGH,I3,
     917H PLUS NU OBSERVED)
      KC=0
      CALL WNUX(VYR,SUMT,M,KC)
        WRITE(2,451)M,ITER
  451   FORMAT(1H1,18X,'X(NU CALC. - NU OBS.) COLUMNS FROM IT
     1ERATIONS',I3,8H THROUGH,I3,24H FOLLOWED BY NU OBSERVED)
      KC=1
      CALL WNUX(XXX,SUMT,M,KC)
      RETURN
      END
```

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

```
        SUBROUTINE WNUX(A,SUMT,M,KC)
C
C       PRINTS NU AND X COLUMNS AFTER EACH SET OF EIGHT ITERATIONS
C
      DIMENSION A(18,8),SUMT(2,8),VOBS(18),X(18),V(18)
      DIMENSION FLMOBS(18),FLMC(18)
      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,LW
     1MPH,NUMB,ITER,NEG,MPHT,INT,VAR/B2/VOBS,X,V
      COMMON /B11/FLMOBS,FLMC
      JD=0
        WRITE(2,1)(JJJ,JJJ=M,ITER),JD
    1 FORMAT(1H0,I11,8I13/1H )
      DO 3 JD=1,N2
4       WRITE(2,2)JD,(A(JD,K),K=1,NUMB),VOBS(JD)
    3 CONTINUE
    2 FORMAT(1H ,I2,9F13.5)
      IF(KC)9,10,9
9       WRITE(2,11)
   11 FORMAT(1H0,45X,27HPER CENT ERROR AND VARIANCE)
      DO 12 JD=1,2
12      WRITE(2,16)JD,(SUMT(JD,K),K=1,NUMB)
   16 FORMAT(1H ,I2,8F13.7)
   10 RETURN
      END
```

```
         SUBROUTINE INVERT(A,N,EPS,NEROR,DELTA,PROD)
C      MATRIX INVERSION BY GAUSS-JORDAN ELIMINATIION

      DIMENSION A(14,14),B(14),C(14),LZ(14)
         DELTA = 1.0
      NEROR=0
      DO 10 J=1,N
   10 LZ(J)=J
         EPS=10.0**-20
      DO 20 I=1,N
      K=I
      Y=A(I,I)
         L=I-I
      LP=I+1

      IF(N-LP)14,11,11
   11 DO 13 J=LP,N
      W=A(I,J)
      IF (ABS(W)-ABS(Y)) 13,13,12
   12 K=J
      Y=W
   13 CONTINUE
   14 DELTA=DELTA*Y
      DO 15 J=1,N
      C(J)=A(J,K)
      A(J,K)=A(J,I)
      A(J,I)=-C(J)/Y
      A(I,J)=A(I,J)/Y
   15 B(J)=A(I,J)
      A(I,I)=1.0/Y
      J=LZ(I)
      LZ(I)=LZ(K)
      LZ(K)=J
      DO 19 K=1,N
      IF(I-K)16,19,16
   16 DO 18 J=1,N
      IF(I-J)17,18,17
   17 A(K,J)=A(K,J)-B(J)*C(K)
   18 CONTINUE
   19 CONTINUE
   20 CONTINUE
         WRITE(2,1) DELTA
    1 FORMAT (1H0,46X,7HDET(A)=,E11.2)
      PROD=DELTA/PROD
         WRITE(2,120) PROD
  120 FORMAT (1H0,46X,24HDET(A)/A(1,1)***A(N,N) =,E11.2)
      IF (ABS(PROD)-EPS) 80,80,81
 80      NEROR = 1
      GO TO 82
   81 DO 200 I=1,N
         IF(I-LZ(I))100,200,100

  100 K=I+1
      IF(I-N)800,200,200
  800 DO 500 J=K,N

      IF(I-LZ(J))500,600,500
  600 M=LZ(I)
      LZ(I)=LZ(J)
      LZ(J)=M
      DELTA=-DELTA
```

```
      DO 700 L=1,N
      C(L)=A(I,L)
      A(I,L)=A(J,L)
  700 A(J,L)=C(L)
  500 CONTINUE
  200 CONTINUE
   82 RETURN
      END
```

```
         SUBROUTINE SYMAS(A,Z,ISC,INI,MMM,NNN,L,G)
C
C          CALCULATES EIGENVECTORS AND EIGENVALUES OF FACTORED A MATRIX
C       CORRESPONDING TO G OR GF).  EIGENVALUES ARE STORED IN Z AND
C       EIGENVECTORS (OF GF) ARE STORED IN D(FACTORED).
C
      DIMENSION EL(12,12,3),ELIN(12,12,3),AJWJ(14,14),C(12,
     112,8),AJ(18,14),Q(12,12),VOBS(18),X(18),V(18),TEMP(18,14),XI(18),
     2INEG(18),G(12,12,3),Z(18),A(14,14),XNIT(14,14)
      DIMENSION FLMOBS(18),FLMC(18)
      COMMON D,EL,ELIN,AJWJ,C,AJ,Q
      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,L
     1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B4/TEMP/B6/XI,INEG
      COMMON /B11/FLMOBS,FLMC
      LL=L
      M=MMM
      N=NNN
      IF(ISC)1,4,1
C          CHECK FOR (1X1) SPECIES
    1 IF(N-M)145,142,145
  142 INM=INI+M
      Z(INM)=G(M,M,LL)*A(M,M)*G(M,M,LL)
      IF (Z(INM)) 143,144,144
  143 NEG=NEG+1
      INEG(NEG)=INM
      Z(INM)=-Z(INM)
  144 FLMC(INM)=Z(INM)
      X(INM)=FLMC(INM)-FLMOBS(INM)
      EL(M,M,LL)=G(M,M,LL)
      ELIN(M,M,LL)=1./EL(M,M,LL)
      RETURN
  145 DO 2 I=M,N
      DO 2 J=M,N
      EL(I,J,LL)=0.
      DO 2 K=M,N
    2 EL(I,J,LL)=EL(I,J,LL)+A(I,K)*G(K,J,LL)
      DO 3 I=M,N
      DO 3 J=M,N
      A(I,J)=0.
      DO 3 K=M,N
    3 A(I,J)=A(I,J)+G(K,I,LL)*EL(K,J,LL)
C         A IS NOW (GTRANSPOSE)(F)(G) WHERE G IS DEFINED IN MAIN PROGRAM
C         AFTER STATEMENT NO. 32.
C         CALCULATE EIGENVALUES -
    4 IF(N-M)5,6,5
    6 INM=INI+M
      Z(INM)=A(M,M)
      A(M,M)=1.
      RETURN
    5 E=0.
      DO 101 I=M,N
  101 E=E+ABS(A(I,I))
      R=N-M+1
      E=E/(5.*R)
      DO 102 I=M,N
      DO 102 J=M,N
      IF(I-J)103,104,103
  104 XNIT(I,J)=1.
      GO TO 102
  103 XNIT(I,J)=0.
  102 CONTINUE
```

```
  105 M2=M+1
      DO 106 J=M2,N
      L=J-1
      DO 106 I=M,L
      IF (ABS(A(I,J))-E) 106,106,126
  126 IF(A(I,I)-A(J,J))107,125,107
  125 QX=A(I,J)
      GO TO 109
  107 QX=A(I,J)/(2.*(A(I,I)-A(J,J)))
      IF (ABS(QX)-0.41421) 108,109,109
  108 S=2.*QX/(1.+(QX*QX))
      CO=(1.-(QX*QX))/(1.+(QX*QX))
      GO TO 110
  109 S=.70710678
      CO=.70710678
      IF(QX)111,110,110
  111 S=-S
  110 CC=CO*CO
      SS=S*S
      CS=CO*S
      QX=A(I,J)*(CC-SS)+CS*(A(J,J)-A(I,I))
      R=A(I,I)*CC+A(J,J)*SS+2.*CS*A(I,J)
      A(J,J)=SS*A(I,I)+CC*A(J,J)-(2.*CS*A(I,J))
      A(I,J)=QX
      A(I,I)=R
      A(J,I)=A(I,J)
      DO 112 K=M,N
      IF(K-I)113,114,113
  113 IF(K-J)115,114,115
  115 R=A(I,K)*CO+A(J,K)*S
      A(J,K)=A(J,K)*CO-A(I,K)*S
      A(K,J)=A(J,K)
      A(I,K)=R
      A(K,I)=A(I,K)
  114 R=XNIT(K,I)*CO+XNIT(K,J)*S
      XNIT(K,J)=XNIT(K,J)*CO-XNIT(K,I)*S
  112 XNIT(K,I)=R
  106 CONTINUE
      DO 116 J=M2,N
      L=J-1
      DO 116 I=M,L
      IF (ABS(A(I,J))-E) 116,116,105
  116 CONTINUE
      IF(E-1.0E-010)117,117,118
  118 E=E/10.
      GO TO 105
  117 DO 119 I=M,N
      INII=INI+I
      Z(INII)=A(I,I)
      DO 119 J=M,N
  119 A(I,J)=XNIT(I,J)
      IF(ISC)120,122,120
  120 DO 121 I=M,N
      INII=INI+I
      IF (Z(INII)) 140,141,141
  140 Z(INII)=-Z(INII)
      NEG=NEG+1
      INEG(INII)=1
  141 FLMC(INII)=Z(INII)
      DO 121 J=M,N
      TEMP(I,J)=0
```

```
      EL(I,J,LL)=0.
      DO 121 K=M,N
      INK=INI+K
      TEMP(I,J)=TEMP(I,J)+A(K,I)*XI(INK)*G(J,K,LL)
  121 EL(I,J,LL)=EL(I,J,LL)+G(I,K,LL)*A(K,J)
C     EL IS NOW THE MATRIX OF EIGENVECTORS OF GF.
      DO 135 J=M,N
      DO 135 I=M,N
      K=INI + I
      IF (I-N) 139,135,135
  139 IF(FLMC(K)-FLMC(K+1))137,135,135
  137 R=FLMC(K)
      FLMC(K)=FLMC(K+1)
      FLMC(K+1)=R
      IT=INEG(K)
      INEG(K)=INEG(K+1)
      INEG(K+1)=IT
      DO 138 L=M,N
      R=EL(L,I,LL)
      EL(L,I,LL)=EL(L,I+1,LL)
      EL(L,I+1,LL)=R
      R=TEMP(I,L)
      TEMP(I,L)=TEMP(I+1,L)
  138 TEMP(I+1,L)=R
  135 X(K)=FLMC(K)-FLMOBS(K)
      DO136 I=M,N
      DO136 J=M,N
  136 EL IN(I,J,LL)=TEMP(I,J)
  122 RETURN
      END
```

```
      SUBROUTINE WINPI
C
C     PRINTS INPUT DATA
C
      DIMENSION IDENT(13,4),NFAC(3),VOBS(18),W(18),C(12,12,8),
     1Q(12,12),DK(14),TEMP(18,14),G(12,12,3),EL(12,12,3),F(12,12),
     2V(18),X(18),AJ(18,14),AJWJ(14,14),ELIN(12,12,3),KIDENT(33,3)
     3,ID(8,3)
      DIMENSION FLMOBS(18),FLMC(18)
      COMMON D,EL,ELIN,AJWJ,C,AJ,Q
      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,L
     1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B4/TEMP/B5/G/B7/F,H,D
     2/B8/IDENT,KIDENT,W,ID,NFAC
      COMMON /B11/FLMOBS,FLMC
C
        WRITE(2,1)((IDENT(I,J),I=1,13),J=1,4)
1       FORMAT(1H1,22X,13A5/(1H ,22X,13A5))
        WRITE(2,7)IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,
     1IB,ISYM,IDEG,LW
    7 FORMAT(1H0,4X,1HN,4X,1HL,4X,1HR,4X,1HM,4X,1HH,2X,4HNISP,
     13X,2HNI,2X,3HSCF,2X,3HFFC,3X,1HW,4X,1HB,3X,3HSYM,2X,
     24HIDEG,2X,2HLW/I6,13I5)
        WRITE(2,2)
2       FORMAT(1H1,'      ISOTOPE      NO. FACTORS      FACTOR DI
     1MENSIONS          FOFI-428')
      DO 3 I=1,NISP
      K=NFAC(I)
        WRITE(2,4)I,K,(ID(J,NTINUE
4       7I3)
        WRITE(2,T (1H0,56X,5HINPUT/1H0)
        WRITE(2,34)
   34 FORMAT (1H0,55X,10HG MATRICES)
      DO 13 L=1,NISP
      DO 14 I=1,IN
      DO 14 J=1,IN
   14 TEMP(I,J)=G(I,J,L)
        WRITE(2,17)L
17      FORMAT(1H1,5            CALL WTE
   13 CONTINUE
      DO 35 I=1,IN
      DO 35 J=1,IM
   35 TEMP(I,J)=Q(I,J)
        WRITE(2,36)
36      FORMAT(1H1,58X,1HQ)
      CALL WTEMP(IN,IM)
      IF (MPHT-IM) 56,56,55
55      WRITE(2,38)
   38 FORMAT (1H1,55X,10HC MAFATRICES)1,IHT
      DO 39 640            DO 39 J=1,IN
   39 TEMP(I,J)=C(I,J,L)
        WRITE(2,40)L
40      FORMAT(1H1,59X,I2)
      CALL WTEMP(IN,IN)
   37 CONTINUE
56      WRITE(2,48)
   48 FORMAT (1H1,2H I,9X,2HM1,12X,2HM2,12X,2HM3,12X,2HM4//)
        WRITE(FA2,43)
43      E(2,43)
FORMAT(1H1,3H  I,6X,4HVOBS,10X,1HW,12X,1HK)
      IMAX=AMAX0(N2,MPHT)
      DO 44 I=1,IMAX
```

```
00760           IF (MPHT-I) 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
0081 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
```

```
               SUBROUTINE READFL(D,M1,M2,IX)
      C
      C      READS MATRICES.
      C
             DIMENSION D(18,14),IH(15),JH(15)
             DO10I=1,M1
             DO 10 J=1,M2
          10 D(I,J)=0.
      5        READ(1,1)DH,(IH(I),JH(I),I=1,15)
      1        FORMAT(1F,30I)
             IF (FADH)2,3,2
           2 DO 6 K=1,15
             IF (IH(K))4,5,4
           4 I=IH(K)
             J=JH(K)
           6 D(I,J)=DH
             GO TO 5
           3 IF(IX)22,23,22
          23 DO 20 I=1,M1
             DO 20 J=1,M1
             IF (I-J) 21,20,21
          21 IF(D(I,J))11,20,11
          11 D(J,I)=D(I,J)
          20 CONTINUE
          22 RETURN
             END
```

```
        SUBROUTINE READDM (D,IR)
C
C       READS MASSES IN ATOMIC WEIGHT UNITS AND MODIFIED WEIGHT FACTOR
C
      DIMENSION D(33),IH(24)
      DO 1 I=1,IR
    1 D(I)=0.
2       READ(1,3)DH,(IH(I),I=1,24)
3       FORMAT(1F,24I)
      IF(DH)4,7,4
    4 DO 6 K=1,24
      IF(IH(K))5,2,5
    5 IST=IH(K)
    6 D(IST)=DH
      GO TO 2
    7 RETURN
      END
```

```
      SUBROUTINE STAT
C
C       CALCULATES AND PRINTS STATISTICAL ANALYSIS OF FINAL RESULTS
C
      DIMENSION EL(12,12,3),ELIN(12,12,3),C(12,12,8),
     1AJWJ(14,14),AJ(18,14),Q(12,12),VOBS(18),X(18),V(18),TEMP(18,14),
     2F(12,12),DK(14),IDENT(13,4),KIDENT(33,3),W(18),
     3ID(8,3),NFAC(3),SIGK(14),SIGV(18)
      DIMENSION FLMOBS(18),FLMC(18)
      DIMENSION VYR(18,8),TKR(14,8),XXX(18,8),SUMT(2,8)
      COMMON D,EL,ELIN,AJWJ,C,AJ,Q
      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,L
     1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B4/TEMP/B7/F,H,DK
     2/B8/IDENT,KIDENT,W,ID,NFAC/B10/SIGK,SIGV
      COMMON /B11/FLMOBS,FLMC
      COMMON /B3/VYR,TKR,XXX,SUMT
C
C       PRINT EIGENVECTORS
C
        WRITE(2,15)
   15 FORMAT (1H1,54X,10HL MATRICES)
      DO 1 L=1,NISP
        WRITE(2,2)L
2       FORMAT(1H1,59X,I2)
      DO 3 I=1,IN
      DO 3 J=1,IN
    3 TEMP(I,J)=EL(I,J,1)
      CALL WTEMP(IN,IN)
    1 CONTINUE
C
C     POTENTIAL ENERGY DISTRIBUTION
C
   18 DO 24 I=1,N2
      Y1=0.
      DO 23 J=1,MPHT
      TEMP(I,J)=AJ(I,J)*DK(J)/FLMC(I)
   23 Y1=Y1+ABS(TEMP(I,J))
      DO 24 J=1,MPHT
   24 TEMP(I,J)=TEMP(I,J)*100./Y1
        WRITE(2,25)
   25 FORMAT(1H1,29X,44HPOTENTIAL ENERGY DISTRIBUTION - CONTRIBUTION,
     117H OF K(J) TO NU(I)/1H )
      CALL WTEMP(N2,MPHT)
C
C       OVERALL DISPERSION(SIGMA) AND DISPERSIONS FOR FORCE CONSTANTS
C       AND FREQUENCIES
C
      SIGMA=VAR
      DIF=N2-MPHT
      IF(DIF)26,26,27
   26 DIF=1.0
   27 SIGSQ=SIGMA/DIF
      SIGMA=SQRT(SIGSQ)
      DO 28 I=1,MPH
   28 SIGK(I)=SIGMA*SQRT(AJWJ(I,I))
      DO 29 I=1,N2
      DO 29 J=1,MPH
      TEMP(I,J)=0.
      DO 29 K=1,MPH
   29 TEMP(I,J)=TEMP(I,J)+AJ(I,K)*AJWJ(K,J)
      DO 31 I=1,N2
```

```
      Y1=0.
      DO 30 K=1,MPH
   30 Y1=Y1+TEMP(I,K)*AJ(I,K)
   31 SIGV(I)=SIGMA*SQRT(Y1)
      N3=NISP*IN
      DO50I=1,N3
   50 SIGV(I)=848904.5/VYR(I,NUMB)*SIGV(I)
C
C          PRINT FINAL FREQUENCIES,FORCE CONSTANTS, AND DISPERSIONS
C
32          WRITE(2,33)
33          FORMAT(1H1,3HNO.,2X,7HNU OBS.,6X,8HNU CALC.,7X,
     18HDELTA NU,
     94X,10HPCT. ERROR,4X,9HSIGMA(NU),6X,1HK,10X,8HSIGMA(K)/1H )
      AVE=0.
      DO 37 I=1,N2
      DIF=(X(I)/VOBS(I))*100.
      AVE=AVE+ABS(DIF)
      IF (I-MPHT) 34,34,36
34          WRITE(2,35)I,VOBS(I),V(I),X(I),DIF,SIGV(I),
     9DK(I),SIGK(I),(KIDENT(I,J),J=1,3)
      GO TO 37
   35 FORMAT (1H ,I2,F10.3,F16.7,3F13.5,4X,F10.7,F11.5,1X,4A6)
36          WRITE(2,35)I,VOBS(I),V(I),X(I),DIF,SIGV(I)
   37 CONTINUE
      FN2=N2
      AVE=AVE/FN2
        WRITE(2,38)SIGMA,AVE
   38 FORMAT(1H0,20X,30HSQRT(SUM(W*(O-C)**2)/(NO-NV))=F10.6,10X,
     925HAVERAGE PER CENT ERROR = ,F10.6)
C
C          CORRELATION MATRICES
C
        WRITE(2,39)
   39 FORMAT(1H1,40X,38HCORRELATION MATRIX FOR FORCE CONSTANTS/1H )
      DO 40 I=1,MPH
      DO 40 J=1,MPH
   40 TEMP(I,J)=AJWJ(I,J)*SIGSQ/(SIGK(I)*SIGK(J))
      CALL WTEMP(MPH,MPH)
      RETURN
      END
```

```
      SUBROUTINE EIGJAC (II,IE,L)
C
C       CALCULATES FREQUENCY JACOBIAN FROM EIGENVECTORS
C
      DIMENSION EL(12,12,3),ELIN(12,12,3),AJWJ(14,14),
     1C(12,12,8),AJ(18,14),Q(12,12),VOBS(18),X(18),V(18)
      DIMENSION FLMOBS(18),FLMC(18)
      COMMON D,EL,ELIN,AJWJ,C,AJ,Q
      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,L
     1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V
      COMMON /B11/FLMOBS,FLMC
      IG=0
      DO 2 I=II,IE
      IG=IG+1
      DO 2 J=1,IM
      DO 2 K=1,IN
    2 AJ(I,J)=AJ(I,J)+EL(K,IG,L)*EL(K,IG,L)*Q(K,J)
      IF(MPHT-IM)1000,1000,3
    3 IG=0
      DO 9 I=II,IE
      IG=IG+1
      DO 9 K=1,IN
      DO 9 IP=1,IN
      DO 9 J=1,IHT
      IMJ=IM+J
    9 AJ(I,IMJ)=AJ(I,IMJ)+EL(K,IG,L)*EL(IP,IG,L)*C(K,IP,J)
 1000 RETURN
      END
```

```
        SUBROUTINE WNUOUT(AVE)
C       WRITES NU OBS., NU CALC., X, PCT. ERROR, K AFTER EACH ITERATIO
      DIMENSION VOBS(18),X(18),V(18),F(12,12),DK(14),
     1IDENT(13,4),KIDENT(33,3),W(18),ID(8,3),NFAC(3)
        DIMENSION FLMOBS(18),FLMC(18)
      COMMON /B1/IN,IL,IR,IM,IH,NISP,NI,ISCF,IFFC,IW,IB,ISYM,IDEG,N2,L
     1MPH,NUMB,ITER,NEG,MPHT,IHT,VAR/B2/VOBS,X,V/B7/F,H,DK/B8/IDENT,
     2KIDENT,W,ID,NFAC
      COMMON /B11/FLMOBS,FLMC
      N3=NISP*IN
        DO 10 I=1,N3
      V(I)=1303.0*SQRT(FLMC(I))
   10 X(I)=1303.0*(SQRT(FLMC(I))-SQRT(FLMOBS(I)))
      N4=N3+1
      DO11I=N4,N2
   11 V(I)=FLMC(I)
        WRITE(2,1)ITER
1       FORMAT(1H1,35X,16HITERATION NUMBER,I3)
        WRITE(2,2)
    2 FORMAT(1H0,3HNO.,3X,7HNU OBS.,7X,8HNU CALC.,5X,8HDELTA NU,
     94X,10HPCT. ERROR,12X,3HNO.,5X,1HK/1H )
      AVE=0.
      DO 3 I=1,MPHT
      PCT=X(I)*100./VOBS(I)
        WRITE(2,4)I,VOBS(I),V(I),X(I),PCT,I,DK(I),
     1(KIDENT(I,J),J=1,3)
    3 AVE=AVE+ABS(PCT)
    4 FORMAT (1H ,I2,F13.3,3F13.5,12X,I2,F13.7,2X,4A6)
      IF (N2-MPHT) 7,7,5
    5 II=MPHT+1
      DO 6 I=II,N2
      PCT=X(I)*100./VOBS(I)
        WRITE(2,4)I,VOBS(I),V(I),X(I),PCT
    6 AVE=AVE+ABS(PCT)
    7 FN2=N2
      AVE=AVE/FN2
        WRITE(2,8)AVE
    8 FORMAT(1H0,15HAVERAGE ERROR =,F10.5,9H PER CENT)
      RETURN
      END
```

```
        SUBROUTINE WTEMP(NR,NC)
C       PRINTS UNSYMMETRIC MATRIX(60,60)
C
      DIMENSION TEMP(18,14)
        COMMON/B4/TEMP

      INC=1
      IL=9
      DO 1 I=1,3
      IF (NC-IL) 2,2,3
    2 IL=NC
3       WRITE(2,4)(J,J=INC,IL)
    4 FORMAT (1H0,3HI/J,I7,8I13,/1H )
      DO 7 J=1,NR
7       WRITE(2,10)J,(TEMP(J,K),K=INC,IL)
10      FORMAT(1H ,I3,9F13.8)
      IF (NC-IL) 5,5,6
    6 INC=INC+9
    1 IL=IL+9
    5 RETURN
      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               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
                                                           Q
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
  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
                                   ITERATION NUMBER  0
 NO.   NU OBS.        NU CALC.     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(1,1)***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     PCT. ERROR               NO.     K

 1     2989.500    3038.54490      49.04497       1.64057                 1   4.9125523    CH2  STR
 2     1443.500    1349.90510     -93.59488      -6.48389                 2   1.1647017    CH2  BEND
 3     2200.200    2229.51240      29.31244       1.33226                 3   0.8024578    STR- BEND
 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(1,1)***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

 1     2989.500   2991.15370     1.65368     0.05532           1   4.7146179   CH2  STR
 2     1443.500   1449.95950     6.45954     0.44749           2   1.3446213   CH2  BEND
 3     2200.200   2199.02780    -1.17222    -0.05328           3   0.8138552   STR- BEND
 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
                                  ITERATION NUMBER  3
 NO.   NU OBS.        NU CALC.      DELTA NU     PCT. ERROR            NO.      K

  1      2989.500   2990.46240      0.96242      0.03219              1    4.7235177      CH2  STR
  2      1443.500   1451.69460      8.19463      0.56769              2    1.3389375      CH2  BEND
  3      2200.200   2197.85700     -2.34292     -0.10649              3    0.7978185      STR- BEND
  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
    1.20864     0.23516     0.80809
    0.23516     1.30632    -0.54276
    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
                                   ITERATION NUMBER  4
NO.   NU OBS.       NU CALC.      DELTA NU     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
     1.20871     0.23507     0.80801
     0.23507     1.30643    -0.54269
     0.80801    -0.54269     0.94027
                                                      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    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
             1                2                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
             1               2               3               4               0
 1    3038.54490      2991.15370      2990.46240      2990.44090      2989.50000
 2    1349.90510      1449.95950      1451.69460      1451.74690      1443.50000
 3    2229.51240      2199.02780      2197.85700      2197.83150      2200.20000
 4     984.27589      1055.16830      1056.74930      1056.79200      1077.90000
                        X(NU CALC. - NU OBS.) COLUMNS FROM ITERATIONS  1 THROUGH  4 FOLLOWED BY NU OBSERVED
             1               2               3               4               0
 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     PCT. ERROR     SIGMA(NU)       K           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
                     SQRT(SUM(W*(O-C)**2)/(NO-NV))=  0.030834          AVERAGE PER CENT ERROR =    0.667170
                                          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 - UBFF

A_{1g}

(C_2H_4)

$$\begin{matrix} 1.00480 & -0.16282 & 0.03413 \\ -0.14565 & -0.32347 & 0.20163 \\ 0.17763 & 0.78481 & 0.68258 \end{matrix}$$

(C_2D_4)

$$\begin{matrix} 0.68708 & -0.26348 & 0.00110 \\ -0.24799 & -0.31695 & 0.06743 \\ 0.23057 & 0.34901 & 0.57683 \end{matrix}$$

B_{1g}

(C_2H_4)

$$\begin{matrix} 1.05204 & 0.08123 \\ -0.39157 & 1.27176 \end{matrix}$$

(C_2D_4)

$$\begin{matrix} 0.78093 & 0.08860 \\ -0.50983 & 1.01058 \end{matrix}$$

B_{2u}

(C_2H_4)

$$\begin{matrix} 1.05437 & 0.04132 \\ -0.10986 & 1.01254 \end{matrix}$$

(C_2D_4)

$$\begin{matrix} 0.78525 & 0.03303 \\ -0.12475 & 0.72522 \end{matrix}$$

B_{3u}

(C_2H_4)

$$\begin{matrix} 1.01702 & -0.05454 \\ 0.12893 & 1.04727 \end{matrix}$$

(C_2D_4)

$$\begin{matrix} 0.73367 & -0.05683 \\ 0.16046 & 0.76939 \end{matrix}$$

Ethylene - HOFF

A_{1g}

(C_2H_4)

$$\begin{matrix} 1.01373 & -0.09400 & 0.02842 \\ -0.11937 & -0.28248 & 0.26917 \\ 0.14413 & 0.91817 & 0.49958 \end{matrix}$$

(C_2D_4)

$$\begin{matrix} 0.71126 & -0.18867 & -0.00343 \\ -0.21238 & -0.34183 & 0.06744 \\ 0.19518 & 0.36966 & 0.57702 \end{matrix}$$

B_{1g}

(C_2H_4)

$$\begin{matrix} 1.05516 & -0.00554 \\ -0.28564 & 1.29966 \end{matrix}$$

(C_2D_4)

$$\begin{matrix} 0.78552 & 0.02570 \\ -0.42715 & 1.04821 \end{matrix}$$

B_{2u}

(C_2H_4)

$$\begin{matrix} 1.05475 & 0.02998 \\ -0.04123 & 1.01764 \end{matrix}$$

(C_2D_4)

$$\begin{matrix} 0.78573 & -0.01842 \\ -0.77025 & 0.73183 \end{matrix}$$

B_{3u}

(C_2H_4)

$$\begin{matrix} 1.01746 & -0.04548 \\ 0.11959 & 1.04838 \end{matrix}$$

(C_2D_4)

$$\begin{matrix} 0.73427 & -0.04847 \\ 0.15168 & 0.77116 \end{matrix}$$

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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