Normal Coordinate Analysis of the Vibrations of Polyatomic Molecules

By

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TO MY PARENTS
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## TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>iii</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>vii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>ix</td>
</tr>
<tr>
<td>SYMBOLS</td>
<td>xi</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>xiv</td>
</tr>
<tr>
<td>CHAPTERS:</td>
<td></td>
</tr>
<tr>
<td>1. INTRODUCTION</td>
<td>1</td>
</tr>
<tr>
<td>1. Vibrational Spectra and Molecular Structure</td>
<td>2</td>
</tr>
<tr>
<td>2. Fundamental Problem in the Calculation of the Force Field</td>
<td>3</td>
</tr>
<tr>
<td>Isotopic substitution</td>
<td>4</td>
</tr>
<tr>
<td>3. Normal Coordinate Analysis</td>
<td>5</td>
</tr>
<tr>
<td>Brief review of previous work</td>
<td>5</td>
</tr>
<tr>
<td>Scope of the present work</td>
<td>9</td>
</tr>
<tr>
<td>2. GENERAL ASPECTS IN THE CALCULATION OF FORCE CONSTANTS</td>
<td>12</td>
</tr>
<tr>
<td>1. The Nature of the Normal Vibrations</td>
<td>12</td>
</tr>
<tr>
<td>2. The Harmonic Force Field</td>
<td>13</td>
</tr>
<tr>
<td>3. The Vibrational Secular Equation</td>
<td>15</td>
</tr>
<tr>
<td>4. Valence Displacement Coordinates</td>
<td>17</td>
</tr>
<tr>
<td>5. Symmetry Coordinates</td>
<td>18</td>
</tr>
<tr>
<td>6. Sources of Additional Observed Data</td>
<td>19</td>
</tr>
<tr>
<td>7. Anharmonicity</td>
<td>21</td>
</tr>
<tr>
<td>8. Modified Force Fields</td>
<td>23</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS (CONTINUED)

<table>
<thead>
<tr>
<th>CHAPTERS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td></td>
</tr>
<tr>
<td>FORCE CONSTANTS REFINEMENT PROCEDURE</td>
<td>25</td>
</tr>
<tr>
<td>1. Successive Diagonalization Procedure</td>
<td>26</td>
</tr>
<tr>
<td>2. Perturbation Procedure</td>
<td>28</td>
</tr>
<tr>
<td>3. Discussion of the Procedure</td>
<td>32</td>
</tr>
<tr>
<td>4</td>
<td></td>
</tr>
<tr>
<td>STATISTICAL ERROR ANALYSIS</td>
<td>36</td>
</tr>
<tr>
<td>1. Variance-Covariance Matrix for Observed Frequency Parameters</td>
<td>36</td>
</tr>
<tr>
<td>2. Variance-Covariance Matrix for Force Constants Parameters</td>
<td>39</td>
</tr>
<tr>
<td>3. Variance-Covariance Matrix for the Normal Coordinates Transformation Matrices $L$ and $L^{-1}$</td>
<td>44</td>
</tr>
<tr>
<td>4. Approximate Dispersions for $L$ and $L^{-1}$</td>
<td>46</td>
</tr>
<tr>
<td>5. Error Analysis for Dipole Moment Derivatives</td>
<td>48</td>
</tr>
<tr>
<td>6. Variance-Covariance Matrix for $(\partial p/\partial Q)$</td>
<td>49</td>
</tr>
<tr>
<td>7. Approximate Analysis of the Dispersions of $\partial p/\partial Q_i$</td>
<td>52</td>
</tr>
<tr>
<td>8. Variance-Covariance Matrix for $p_j$</td>
<td>54</td>
</tr>
<tr>
<td>5</td>
<td></td>
</tr>
<tr>
<td>NORMAL COORDINATES OF ETHYLENE</td>
<td>57</td>
</tr>
<tr>
<td>1. Geometrical Aspects of the Ethylene Molecule Structural Parameters</td>
<td>57</td>
</tr>
<tr>
<td>2. Symmetry Aspects of the Ethylene Molecule</td>
<td>60</td>
</tr>
<tr>
<td>3. Normal Vibrations</td>
<td>65</td>
</tr>
<tr>
<td>4. The Inverse Kinetic Energy Matrix $G$</td>
<td>65</td>
</tr>
<tr>
<td>5. The Force Field of Ethylene</td>
<td>67</td>
</tr>
<tr>
<td>6. Experimental Data</td>
<td>75</td>
</tr>
<tr>
<td>7. Force Constants Refinement</td>
<td>76</td>
</tr>
<tr>
<td>8. Coriolis Coupling Coefficient $\zeta_{7,10}$</td>
<td>82</td>
</tr>
<tr>
<td>CHAPTERS:</td>
<td>Page</td>
</tr>
<tr>
<td>-----------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>6 UNCERTAINTIES IN THE NORMAL COORDINATES TRANSFORMATION MATRIX</td>
<td>83</td>
</tr>
<tr>
<td>1. Description of the Problems</td>
<td>84</td>
</tr>
<tr>
<td>2. Presentation of the Results</td>
<td>85</td>
</tr>
<tr>
<td>3. Discussion of Results</td>
<td>85</td>
</tr>
<tr>
<td>4. Sensitivity of the $\mathbf{L}$ Matrix Coefficients</td>
<td>102</td>
</tr>
<tr>
<td>5. Coriolis Coupling Coefficients $\zeta^\text{(x)}_{7,10}$</td>
<td>105</td>
</tr>
<tr>
<td>7 ANALYSIS OF THE INFRARED INTENSITIES OF ETHYLENE</td>
<td>109</td>
</tr>
<tr>
<td>1. Results</td>
<td>110</td>
</tr>
<tr>
<td>2. Discussion</td>
<td>124</td>
</tr>
<tr>
<td>3. Conclusion</td>
<td>131</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>APPENDICES</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1 UNITS AND NOTATION</td>
<td>134</td>
</tr>
<tr>
<td>1. Dimensions and Units</td>
<td>134</td>
</tr>
<tr>
<td>2. Notes on Matrix Notation</td>
<td>136</td>
</tr>
<tr>
<td>3. Transformation Factors for $\frac{\partial p}{\partial S_j}$'s Into Arnett and Crawford Symmetry Coordinates System</td>
<td>141</td>
</tr>
<tr>
<td>2 TABLES</td>
<td>143</td>
</tr>
<tr>
<td>3 COMPUTER PROGRAMS</td>
<td>150</td>
</tr>
</tbody>
</table>

<p>| BIBLIOGRAPHY                                    | 191  |
| BIOGRAPHICAL SKETCH                            | 196  |</p>
<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$X$ matrix for the ethylene molecule</td>
<td>58</td>
</tr>
<tr>
<td>2</td>
<td>Internal displacement coordinates for ethylene</td>
<td>61</td>
</tr>
<tr>
<td>3</td>
<td>Character table for point group $D_{2h}$. Cartesian and internal coordinate analysis for the ethylene molecule</td>
<td>63</td>
</tr>
<tr>
<td>4</td>
<td>Symmetry coordinates for ethylene molecule</td>
<td>64</td>
</tr>
<tr>
<td>5</td>
<td>Factorized form of $F$ and $G$ matrices, expressed in terms of symmetry coordinates</td>
<td>68</td>
</tr>
<tr>
<td>6</td>
<td>Symmetrized $G$ elements for $C_2H_4$</td>
<td>69</td>
</tr>
<tr>
<td>7</td>
<td>Numerical values of symmetrized $G$ elements for $C_2H_4$ and $C_2D_4$</td>
<td>70</td>
</tr>
<tr>
<td>8</td>
<td>Force constants in valence displacement coordinates for ethylene</td>
<td>71</td>
</tr>
<tr>
<td>9</td>
<td>Two sets of initial valence force constants for ethylene</td>
<td>72</td>
</tr>
<tr>
<td>10</td>
<td>Symmetrized $F$ elements for ethylene</td>
<td>74</td>
</tr>
<tr>
<td>11</td>
<td>Observed and calculated fundamental frequencies obtained from the force constant refinement calculation (M27)</td>
<td>77</td>
</tr>
<tr>
<td>12</td>
<td>Final valence force constants $\phi_i$ for ethylene and their dispersions $[\sigma(\phi_i)]$</td>
<td>78</td>
</tr>
<tr>
<td>13</td>
<td>Initial (M) and final (M27) symmetrized $F$ matrix for ethylene</td>
<td>79</td>
</tr>
<tr>
<td>14</td>
<td>Elements of $L$ and $L^{-1}$ matrices and their dispersions for $C_2H_4$ resulting force constant set M27</td>
<td>80</td>
</tr>
<tr>
<td>15</td>
<td>Summary of problems studied to determine $\tilde{L}$ matrix sensitivity for the in-plane vibrations of ethylene</td>
<td>86</td>
</tr>
<tr>
<td>TABLE</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>16</td>
<td>CALCULATED CORIOLIS COUPLING COEFFICIENT $\zeta_7^{(x)}$ FOR ETHYLENE FROM DIFFERENT PROBLEMS</td>
<td>106</td>
</tr>
<tr>
<td>17</td>
<td>SYMMETRY FORCE CONSTANTS FOR THE $B_{2u}$ SYMMETRY SPECIES OF ETHYLENE</td>
<td>108</td>
</tr>
<tr>
<td>18</td>
<td>HARMONIC FREQUENCIES AND DISPERSIONS; EXPERIMENTAL INTENSITIES, STANDARD DEVIATION, DEGREE OF MIXING AND DISPERSIONS</td>
<td>111</td>
</tr>
<tr>
<td>19</td>
<td>DIPOLE MOMENT DERIVATIVES WITH RESPECT TO NORMAL COORDINATES</td>
<td>112</td>
</tr>
<tr>
<td>20</td>
<td>INVERSE EIGENVECTORS AND THEIR DISPERSIONS FOR SYMMETRY SPECIES $B_{1u}$, $B_{2u}$ AND $B_{3u}$ OF ETHYLENE</td>
<td>114</td>
</tr>
<tr>
<td>21</td>
<td>VALUES OF $p_j$ FOR $B_{1u}$, $B_{2u}$, $B_{3u}$ SYMMETRY SPECIES OF $C_2H_4$ AND $C_2D_4$</td>
<td>122</td>
</tr>
<tr>
<td>22</td>
<td>VALUES OF $p_j$ FOR $B_{2u}$, $B_{3u}$ AND $B_{1u}$ SYMMETRY SPECIES OF $C_2H_4$ AND $C_2D_4$ IN THE COORDINATE SYSTEM OF ARNETT AND CRAWFORD</td>
<td>123</td>
</tr>
<tr>
<td>23</td>
<td>PREFERRED VALUES FOR THE $p_j$'s AND SIGN CHOICES; ANALYSIS OF THE TOTAL DISPERSIONS $\sigma(p_j)$</td>
<td>128</td>
</tr>
<tr>
<td>24</td>
<td>TOTAL BOND MOMENT DERIVATIVES WITH RESPECT TO THE CH-BOND, r, AND CCH-ANGLE, $\alpha$</td>
<td>130</td>
</tr>
<tr>
<td>25</td>
<td>OBSERVED FUNDAMENTAL WAVE NUMBER ($\nu$), ESTIMATED ANHARMONICITY CONSTANTS ($\chi$) AND RESULTING HARMONIC FREQUENCIES ($\omega$) FOR $C_2H_4$ AND $C_2D_4$</td>
<td>144</td>
</tr>
<tr>
<td>26</td>
<td>OBSERVED AND CALCULATED WAVE NUMBERS FOR $C_2H_3D$, $C_2HD_3$, AND CIS, TRANS AND GEM $C_2H_2D_2$</td>
<td>146</td>
</tr>
<tr>
<td>27</td>
<td>SYMMETRY FORCE CONSTANTS FOR PROBLEMS C, AND Cy. IN-PLANE IN THE COORDINATE SYSTEM OF THE PRESENT WORK</td>
<td>149</td>
</tr>
</tbody>
</table>
LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>The equilibrium configuration and valence internal coordinates of ethylene. The z-axis perpendicular to the plane, in a right-hand system.</td>
<td>59</td>
</tr>
<tr>
<td>2</td>
<td>Normal vibrations of ethylene.</td>
<td>66</td>
</tr>
<tr>
<td>3</td>
<td>Display graph for the $A_g$ symmetry force constants for ethylene.</td>
<td>87</td>
</tr>
<tr>
<td>4</td>
<td>Display graph for the $B_{1g}$ symmetry force constants for ethylene.</td>
<td>88</td>
</tr>
<tr>
<td>5</td>
<td>Display graph for the $B_{2u}$ symmetry force constants for ethylene.</td>
<td>89</td>
</tr>
<tr>
<td>6</td>
<td>Display graph for the $B_{3u}$ symmetry force constants for ethylene.</td>
<td>90</td>
</tr>
<tr>
<td>7</td>
<td>Display graph for the diagonal valence force constants for ethylene.</td>
<td>91</td>
</tr>
<tr>
<td>8</td>
<td>Display graph for the stretch-stretch interaction valence force constants for ethylene.</td>
<td>92</td>
</tr>
<tr>
<td>9</td>
<td>Display graph for the bend-bend interaction valence force constants for ethylene.</td>
<td>93</td>
</tr>
<tr>
<td>10</td>
<td>Display graph for the stretch-bend interaction valence force constants for ethylene.</td>
<td>94</td>
</tr>
<tr>
<td>11</td>
<td>Display graph for the $A_g$ symmetry eigenvector 1 of the normal coordinates transformation matrix.</td>
<td>95</td>
</tr>
<tr>
<td>12</td>
<td>Display graph for the $A_g$ symmetry eigenvector 2 of the normal coordinates transformation matrix.</td>
<td>96</td>
</tr>
<tr>
<td>13</td>
<td>Display graph for the $A_g$ symmetry eigenvector 3 of the normal coordinates transformation matrix.</td>
<td>97</td>
</tr>
<tr>
<td>14</td>
<td>Display graph for the $B_{1g}$ symmetry eigenvectors 4 of the normal coordinates transformation matrix.</td>
<td>98</td>
</tr>
<tr>
<td>FIGURE</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>Display graph for the B\textsubscript{2u} symmetry eigenvectors of the normal coordinates transformation matrix</td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Display graph for the B\textsubscript{3u} symmetry eigenvectors of the normal coordinates transformation matrix</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Display graph for the B\textsubscript{2u} symmetry elements of the inverse normal coordinates transformation matrix</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>Display graph for the B\textsubscript{3u} symmetry elements of the inverse normal coordinates transformation matrix</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>Display graph for dp/dS\textsubscript{q} for various choices of sign in dp/dQ\textsubscript{i}'s for C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}D\textsubscript{4}</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>Display graph for dp/dS\textsubscript{10} for various choices of sign in dp/dQ\textsubscript{i}'s for C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}D\textsubscript{4}</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>Display graph for dp/dS\textsubscript{11} for various choices of sign in dp/dQ\textsubscript{i}'s for C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}D\textsubscript{4}</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>Display graph for dp/dS\textsubscript{12} for various choices of sign in dp/dQ\textsubscript{i}'s for C\textsubscript{2}H\textsubscript{4} and C\textsubscript{2}D\textsubscript{4}</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>Charge distortion diagram of the B\textsubscript{2u}, B\textsubscript{3u} and B\textsubscript{1u} symmetry coordinates of ethylene</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>Flowchart diagram for W transformation matrix, program WMAT</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>Flowchart for the force constants refinement procedure, program CHARLY</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>Flowchart diagram for the normal coordinate transformation variance-covariance matrix, program VARCO</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>Flowchart diagram for the reduction of intensity data, program DIPOLE</td>
<td></td>
</tr>
</tbody>
</table>
SYMBOLS

I. Matrices and Vectors

1. Subscripted Capital Italic Letters

A ~ Normal equation matrix
B ~ Transformation matrix from cartesian to internal coordinates
C ~ Orthogonal transformation matrix of H
C^{(q)} ~ Kinetic matrix for calculated coriolis coupling coefficients
D ~ Orthogonal transformation matrix of G
E ~ Unit matrix
F ~ Force constants matrix
G ~ Inverse kinetic energy matrix
H ~ Transformed F matrix
J ~ Jacobian matrix
K ~ Dipole moment derivatives matrix
L ~ Transformation matrix from normal coordinates to internal or symmetry coordinates
M ~ Diagonal matrix of the atomic masses
P ~ Weight matrix; momenta matrix
Q ~ Normal coordinates vector
R ~ Internal coordinates vector
S ~ Symmetry coordinates vector
U ~ Transformation matrix from internal to symmetry coordinates
W ~ Orthogonal transformation matrix for F
X ~ Cartesian coordinates vector
2. Other Symbols

S ~ Wilson's vector
ε ~ Error vector
μ ~ Total bond moment vector
Γ ~ Eigenvalues of G
ζ ~ Coriolis coupling coefficient matrix
Δ ~ Frequency parameters matrix
Σ{ } Variance-covariance matrix
σ{ } Dispersion matrix

II. General Symbols

1. Capital Italic Letters

A,B Symmetry species
F Stretch-bend interaction force constants
F Symmetry force constant
G Out-of-plane bending-out-of-plane bending interaction force constant
H Bending-bending interaction force constant
K Stretching-stretching interaction force constant
N Avogadro's number
Qi Normal coordinate
Ri Internal coordinate
Si Symmetry coordinate
T Kinetic energy; torsion-torsion interaction force constant
V Potential energy; variance
W Weight
2. **Small Italic Letters**

- c: Velocity of light
- d: Weight of internal coordinate; degeneracy of normal mode
- i,j,k: Matrix elements subindices
- m: Number of force constants
- n: Number of observed data
- p: Dipole moment
- r: Bond length
- t,u,v: Subindices
- x,y,z: Cartesian coordinates

3. **Capital Greek Letters**

- \( \Gamma \): Intensity
- \( \chi \): Reducible representation of point group

4. **Small Greek Letters**

- \( \alpha, \beta \): Angles
- \( \phi \): Generalized force constant parameter
- \( \zeta \): Coriolis coupling coefficients
- \( \lambda \): Frequency parameter
- \( \mu \): Reduced mass
- \( \nu \): Observed frequency
- \( \pi \): Universal constant
- \( \rho \): Correlation coefficients
- \( \sigma \): Dispersion; standard deviation
- \( \tau \): Torsional coordinate
- \( \theta \): Out-of-plane bending coordinate
- \( \omega \): Harmonic frequency
NORMAL COORDINATE ANALYSIS OF THE VIBRATIONS OF POLYATOMIC MOLECULES

By

Gustavo E. Sanchez

June, 1971

Molecular properties, such as valence force constants and dipole moment derivatives, can be obtained from the analysis of experimental vibrational spectrum of molecules. The frequency and intensity of the observed absorption bands are related to the force constants and dipole moment derivatives through well-known mathematical formulations. The present study deals with this interpretation of the experimental data (based on the harmonic approximation) and presents a detailed statistical error analysis of the uncertainties in the calculated values from the experimental data, particularly as applied to ethylene.

The mathematical calculations are presented in matrix form as a useful introduction to the calculations involved. Computer programs already available have been revised for use in the IBM 360 computer and additional programs have been written to perform most of the calculations.

The theory has been applied to the ethylene molecule to produce a consistent set of force constants parameters which reproduce the
observed frequencies for all seven denterated derivatives of ethylene and also the coriolis coupling coefficient \( \zeta_{7,10} \). Since no further experimental data are yet available for ethylene, the force field proposed in this study is expected to be as complete as can be expected at the present moment. This set of force constants argues with a previous set obtained by Machida, except in the infrared \( A_{1g} \) symmetry block.

Our primary purpose was to study the sensitivity of the normal coordinate transformation matrix \( L \), taking into consideration the main factors involved in the determination of the \( L \) coefficients; namely, sensitivity towards the assumptions and errors in the field, towards weights of observed parameters and towards the number of isotopic species used to evaluate \( F \) and hence \( L \). The results of this study showed that although the diagonal elements \( L_{ii} \) are well determined and insensitive towards changes in the factors mentioned above, the off-diagonal elements \( L_{ij} \) are not well determined by the observed data and large fluctuations in their values are possible, as measured by the large dispersions obtained for those coefficients.

The new \( L^{-1} \) transformation matrix calculated in the present work has been used for the reduction of the earlier experimental intensity data to obtain new values for the experimental dipole moment derivatives with respect to symmetry coordinates, \( (\partial \mu / \partial S_j) \). The error analysis was extended to these values and showed that the principle of isotopic invariance could not be applied to choose signs for the dipole moment derivatives with respect to the normal coordinates, \( (\partial \mu / \partial Q_i) \). Nevertheless, based on the agreement with calculated values obtained from the CNDO/2 technique, we
were able to make an assignment of preferred signs (the (-) and (+) combinations, respectively, for the $B_{2u}$ and $B_{3u}$ symmetry classes) that is consistent with isotopic invariance.

The results for the dipole moment derivatives ($\partial p/\partial S_j$) for the ethylene molecule from the present study are consistent with similar results for other hydrocarbons. The apparent anomaly in the earlier results appears now to have been due to uncertainties in the earlier normal coordinate transformation and to insufficient appreciation of the magnitudes of the experimental errors.
CHAPTER 1

INTRODUCTION

Infrared spectroscopy has an important place in the solution of structural problems and in the study of molecular properties of polyatomic molecules, as confirmed by the large number of papers found in the literature. Although it is not our purpose to give a review of the many topics in this field, some of the most relevant publications dealing with the relation between the observed vibrational spectrum and molecular properties, such as force constants and electron distribution within a molecule, may be usefully mentioned here. Mills (1) has treated the calculation of force constants in one of the best introductions to the subject; he outlines the problem of obtaining the force field, the various physical considerations involved, and the main computational features of the procedure most often used. In a similar approach, Overend (2) has presented the most important aspects of the interpretation of infrared vibrational intensities, the basic theory, and the main difficulties in obtaining dipole moment derivatives from intensities. These two chapters provide the basic background for the present study.

Barrow (3) and King (4) have written well-known textbooks of molecular spectroscopy which provide a basic, broader introduction to the subject and are most relevant in relating the vibrational problem to the broad area of spectroscopy and in presenting the basic physico-chemical approach.
For our purpose the most useful reference for the understanding of the methods used in the present work is the book by Wilson, Decius and Cross (5) to which we will refer time and again when the basic principles and procedures are applied to the treatment of molecular vibrations. There is, finally, the classic reference book by Herzberg (6), with which the reader is assumed to be familiar.

In this thesis, we shall summarize the basic mathematical formulas and physical principles involved in obtaining the force field and normal coordinates associated with the vibrational spectrum of the molecule, and used in the interpretation of the intensities of the infrared bands. We shall attempt to put in one place all the information needed for such calculations in a way so as to be useful to a student interested in beginning research in this field. For this reason we have reproduced some basic material that can already be found in the references given above.

1. Vibrational Spectra and Molecular Structure

The frequencies of the observed vibration-rotation absorption spectrum of a molecule are directly related to the vibrational and rotational motions of the nuclei in explicit expressions for the potential and kinetic energies of the molecule, and so depend on the atomic masses, the equilibrium configuration of the molecule, and the force field holding the atoms in the molecule together as a result of the electrostatic interaction among nuclei and electrons.

Before any attempt is made to evaluate a force field from the observed spectrum of a molecule, the atomic masses and equilibrium
geometry of the molecule must be known. Microwave spectra or electron and x-ray diffraction techniques generally provide this information with a high degree of accuracy for most simple molecules of interest. The force field which tends to restore the equilibrium configuration after any distortion is not known in advance, and finding the force constants that determine this potential field constitutes the first step in the quantitative analysis of the observed vibration frequencies.

Two experimental quantities, frequency and intensity, for each vibrational degree of freedom, are measured in the infrared and Raman spectra from which the vibrational information is obtained. The frequencies are functions of force constants, molecular geometry and masses as described above, and are associated with characteristic modes of vibration described in terms of normal coordinates. The absorption intensities yield information about the transition dipole moment or, for harmonic oscillators, about the derivatives \( \partial p / \partial q_i \) of the dipole moment \( p \) with respect to the \( i^{th} \) normal coordinate \( q_i \). The transformation relating the normal coordinates of the molecule to the internal coordinates is determined by the potential field and masses and geometry of the molecule. The internal coordinates are more easily visualized than the normal coordinates, and the dipole moment gradients \( \partial p / \partial q_i \) can be expressed in terms of these internal coordinates, \( \partial p / \partial r_k \), using the normal coordinate transformation.

2. **Fundamental Problem in the Calculation of the Force Field**

The molecule has a total of \( 3N \) degrees of freedom, where \( N \) is the number of atoms in the molecule; of these 3 are translational
and 3 are rotational degrees of freedom (or two rotational modes for linear molecules) and the remaining 3N-6 (or 3N-5) internal coordinates describe the vibrational motions. In general, there are 3N-6 observed fundamental frequencies, \( \nu_i \); one for each vibrational degree of freedom.

The total number of independent force constants, needed for these 3N-6 degrees of freedom, is \( \frac{1}{2} (3N-6)(3N-5) \) (see, for instance Herzberg (6)). This complete set of force field parameters in terms of internal displacement coordinates, \( R_k \), is known as the general force field (G.F.F.) and is described briefly in Chapter 2. There are, then, generally many more unknown force constants than observed fundamental frequencies and the G.F.F. cannot be determined unless extra data can be obtained and/or extra assumptions, reducing the number of unknown parameters, can be made regarding the force field.

Isotopic substitution

The total vibrational energy of the molecule is the sum of the kinetic and potential energies. The Born-Oppenheimer approximation (7) allows separation of the nuclear and electronic motions and the expression of the potential energy as a function of the electronic structure, determined by the charges and not the masses of the atoms. When one or more atoms in the molecule are substituted by an isotope, the force field is not affected since the charges in the atoms remain the same; the vibrational kinetic energy, on the other hand, does depend on the masses so that the frequency of the observed fundamentals does change from one isotopic derivative to another. In this fashion, a different set of observed fundamental frequencies can be used from each isotopic
derivative of the parent molecule to provide extra data in determining the force field and, hence, in closing the gap between the number of observed frequencies and the number of force constants in the G.F.F.

But even when enough frequencies from isotopic molecules are available so that it would seem that the problem of evaluating the force constants is mathematically determined, it may not be sufficient since the new data are not completely independent: there exists a set of sum and product rules relating the frequencies of different isotopic derivatives; these rules were worked out by Teller and Redlich (8) and later generalized by Brodersen and Langseth (9). This problem of isotopic substitution is treated at length by Wilson, Decius and Cross (10).

In Chapter 2, we shall discuss briefly the use of other sources of additional observed data relating to the force field such as the coriolis coupling coefficients, centrifugal distortion constants and, hypothetically, the mean square amplitudes of vibration. Furthermore, the use of the symmetry properties of the molecule identifies symmetrically equivalent force constants in the G.F.F., reducing the number of force constant parameters.

3. **Normal Coordinate Analysis**

**Brief review of previous work**

The normal coordinate analysis of the vibrations of polyatomic molecules has been applied for many years, but it is true, to a large extent, that only with the availability of modern computers has the application to complex molecules been possible. Although there are
not well-determined separate areas of application of the results of normal coordinate analyses, it is safe to define the following three different applications: to the assignment of the observed fundamental frequencies, to the precise determination of the force field, and to the analysis of intensities. These topics are related among themselves, and only a few references are given as an example of the applications rather than a review of such an extensive field.

**Vibrational assignment.**—The assignment of the vibrational frequencies of the observed Raman and infrared spectra is not an easy task but the fate of any vibrational analysis depends upon its successful solution. Hadzi (11) discusses the main principles near the invariance of observed frequencies for different chemical groups, while King and Crawford (12) have provided a mathematical method to study the dependency of the frequency of a given chemical functional group upon the molecular framework to which it is attached. The general independence of group vibrations has been well established and is continuously used in the assignment of the observed frequencies in the spectra of complex molecules. It constitutes one of the most versatile tools that chemists have in deducing the structure of such complex molecules.

**Force constants.**—The determination of the harmonic force field has been discussed by Mills (1), and different simplified model force fields have been suggested and used to represent the "unique" force field (G.F.F.). For example, Overend and Scherer (13) have applied the Urey-Bradley force field to several molecules and studied the transferability of force constants of a particular chemical group from one
molecule to another. Although a great deal of effort has been dedicated to the determination of the force constants of polyatomic molecules, they still remain undetermined in general, except for the simplest molecules. The lack of sufficient independent data and the complexity of the calculation of the force field from the frequencies makes the problem almost an impossible one except perhaps for triatomic molecules and a few larger molecules with a high degree of symmetry, such as methane, and perhaps benzene and halogen derivatives of all these. As we shall see, however, not all the force constants in the G.F.F. can be determined even for ethylene.

In recent years, serious attempts have been made to obtain the more general anharmonic force field. Overend (14) presents a review of the most significant work done toward this goal. The anharmonic potential constants have been calculated for CO$_2$ (15) and HCN (16) by Overend and coworkers; the same group has applied their method to larger molecules, such as methyl halides (17) and BF$_3$ (18), but without as much success as for the triatomic molecules.

In brief, a comprehensive review of the work done in force constants calculations, and the theory behind the general quartic force field is highly desirable; the current available literature is either theoretical in nature as Nielsen's work (19) or presented in separate papers and difficult to assimilate.

**Intensity analysis.**—The experimental determination of the intensity of infrared absorption bands and the basic theory behind the reduction of intensity data to obtain dipole moment derivatives with respect to symmetry coordinates has been reviewed by Overend (2);
typical of early studies to solve problems of the measurement and interpretation of intensities were those by Crawford and coworkers: the first paper (20) deals with theory of the interpretation of intensities while the use of isotopic species is discussed in the second paper of the series (21). The difficulties associated with obtaining the dipole moment derivatives ($\partial \mu / \partial S_j$) with respect to the symmetry coordinate, $S_j$, are not only those from the experimental measurement of the intensity and the difficulty in finding the correct normal coordinate transformation matrix but also those from the assignment of even relative signs for $\partial \mu / \partial Q_i$ and then in the interpretation of the $\partial \mu / \partial S_j$'s. These topics have been discussed for ethylene (22), for ethane (23) and for halogen derivatives of methane (24), among other polyatomic molecules, by Crawford and coworkers. 

The problem of the assignment of signs for $\partial \mu / \partial S_j$ and of the interpretation of the dipole moment derivatives was discussed for ethylene by Coulson and Stephen (25) using approximate quantum-mechanical calculations. From this study and others many doubts arose about the experimental basis for the assignment of signs from raw intensity data. In recent years, more refined approximate molecular orbital techniques, such as the CNDO/2 (complete neglect of differential overlap) method, as developed by Pople and Segal (26) have been used by Segal and Klein (27) in the theoretical calculation of dipole moment derivatives and found especially helpful for the understanding of the signs of $\partial \mu / \partial S_j$ and their interpretation. For example, the experimental values for the dipole moment derivatives for $F_2$CO reported by Hopper et al. (28) have been successfully compared with theoretical values from CNDO
calculations by Segal, Bruns and Person (29) (as corrected by McKean et al. (30)). On the other hand, CNDO calculations of the dipole moment derivatives of HCN by Segal and Klein (27) and by Bruns and Person (31) showed large divergences from the experimental values given by Hyde and Hornig (32). However, the bad agreement between the experimental dipole derivatives and those theoretical values from CNDO calculations could possibly be explained as due to the large dispersions on the experimental values. Such an explanation seems valid for the case of CH$_3$F, as found in the error analysis of the dipole moment derivatives given by Russell, Needham and Overend (33).

Since the use of the CNDO/2 method to calculate the dipole moment derivatives has only recently been introduced, additional tests of its validity, at least for predicting the signs of the dipole moment derivatives, are necessary.

Scope of the present work

The ethylene molecule is one of the cases in which the assignment of the relation signs of the dipole moment derivatives reported by Golike et al. (22) is in disagreement with the values calculated from the CNDO method by Segal and Klein (27). We have therefore applied the statistical error analysis developed by Russell, Needham and Overend (33) to the experimental values reported for the dipole moment derivatives of ethylene, in order to see whether the difference between the experimental and the calculated values can be explained by experimental errors. Ethylene is, then, a test of the ability of the CNDO technique to predict at least correct signs for the dipole moment derivatives.
Since the earlier work on the vibrational frequencies of ethylene by Arnett and Crawford (34) and the partial determination of its potential function by Crawford et al. (35) the ethylene molecule has been completely reinvestigated many times. Scherer and Overend (36) applied the Urey-Bradley force field to calculate ethylene frequencies and Cyvin and Cyvin (37) estimated corrected harmonic frequencies and calculated a modified harmonic force field for the molecule.

The coriolis coupling interaction between the \( \nu_7 \) and \( \nu_{10} \) fundamentals of ethylene was measured by Smith and Mills (38) who used it for the determination of the symmetry force constants for the \( B_{2u} \) species; Kuchitsu, Oka and Morino (39) recalculated the force field to obtain the \( L^{-1} \) matrix, the coriolis coupling coefficient and the contributions to the inertial defect from individual modes of the ethylene molecule, using the model proposed by Mann et al. (40). Machida (41) treated the problem of anharmonicity and published a set of quartic force constants together with a refined harmonic force field, and Machida and Overend (42) calculated the anharmonicity constants. Finally, Machida et al. (43) have used a semi-empirical ASMO-SCF calculation to try to obtain all diagonal force constants in the internal coordinate system described by Machida (41). However, although these later treatments obtained modified values for normal coordinates from those given by Arnett and Crawford, no one has used them to recalculate the \( \partial \mu_j/\partial S_i \)'s for ethylene.

We shall discuss here the main factors involved in the refinement of the harmonic force constants by the least-square method (Chapter 3); and we have reinvestigated the statistical error analysis given by
Russell, Needham and Overend (33) for the force constants, normal coordinates transformation matrices and dipole moment derivatives in Chapter 4. Our calculation of the best general force field for ethylene is reported in Chapter 5, together with the normal coordinates transformation matrices. Chapter 6 presents a study of the sensitivity of the \( L \) matrices to the choice of initial force constants and to the observed frequency parameters. Finally, the intensities reported by Golike et al. (22) are reduced to the new \( \partial p/\partial \xi_j \) values using the new \( L^{-1} \) matrices, an error analysis is presented for the dipole moment derivatives and the results are compared to the calculated CNDO values in Chapter 7. Although definite answers still cannot readily be formulated from our results, a satisfying picture of the ethylene molecule is emerging.
CHAPTER 2

GENERAL ASPECTS IN THE CALCULATION OF FORCE CONSTANTS

1. The Nature of the Normal Vibrations

The normal coordinates have often been taken as a mere theoretical device to explain the complicated motions of the atoms in the molecule. This is not so, but, on the contrary, they have a very solid basis in the dynamical principles controlling the mechanics of small vibrations. Normal coordinates, and normal vibrations, are in fact the logical physical picture behind the vibrating system and are amply justified by simple treatments in classical and quantum mechanics, such as that by Eyring, Walter and Kimball (44). A complete mathematical treatment presented by Herzberg (45) is very illuminating in this respect and the essential considerations are stated here as an introduction to the origin of the vibrational equation.

Consider an \(N\)-atomic molecule, in which the nuclei are point masses elastically bonded and their equilibrium configuration referred to a coordinate system that translates and rotates with the molecule. The bonds create restoring forces between the nuclei when these are displaced from their equilibrium positions. A normal vibration arises when all nuclei are simultaneously displaced along their respective normal coordinates and then released; each nucleus carries out a simple harmonic motion about its equilibrium position with the same frequency of oscillation and, in general, with a definite phase relationship with respect to the other
nuclei. The frequency of this simple harmonic motion for all nuclei is a normal frequency, and, in general, there are \( 3N-6 \) of these normal frequencies; one for each of the \( 3N-6 \) vibrational degrees of freedom of the molecule. The form of the normal vibration may be described by a linear combination of the internal coordinates associated with the displacement of the nuclei along bonds or bond angles and constitute the normal coordinate of each normal vibration. In general, any arbitrary vibrational motion of the molecule may be represented as a superposition of normal vibrations with suitable amplitudes. Furthermore, two normal vibrations of different frequencies are orthogonal to each other, and the set of normal coordinates can be made an orthonormal set.

2. The Harmonic Force Field

In any physical system, the first step in solving the equations of motion is to derive expressions for the kinetic and potential energy in terms of a convenient set of coordinates describing the system. The calculation is basically similar in any complete basis set of coordinates and, for the vibrational problem, it is convenient to define \( 3N-6 \) internal displacement coordinates \( R_i \) (\( 3N-5 \) for linear molecules) which rotate and translate with the molecule (46). By displacement coordinates, we mean the displacement from the equilibrium configuration of the molecule.

The potential energy as a function of internal displacement coordinates can be expanded in a Taylor series about the equilibrium configuration (47):

\[
V = V_e + \sum_i \left( \frac{\partial V}{\partial R_i} \right)_e \Delta R_i + \frac{1}{2} \sum_i \sum_j \left( \frac{\partial^2 V}{\partial R_i \partial R_j} \right)_e \Delta R_i \Delta R_j + \cdots \quad \text{terms of higher order}.
\]  

(2-1)
The first term, $V_e$, represents an arbitrary energy of the equilibrium configuration and can be assumed to be zero. The second term represents the derivative of the potential energy with respect to each of the coordinates, $R_i$, evaluated at the equilibrium configuration of each coordinate. Since the potential energy is a minimum at the equilibrium configuration the coefficients $\left(\frac{\partial V}{\partial R_i}\right)_e$ are all zero. The third term, involving the second derivatives of the potential energy with respect to the coordinates evaluated at the equilibrium configuration, represent the harmonic restoring forces:

$$F_{ij} = \left(\frac{\partial^2 V}{\partial R_i \partial R_j}\right)_e.$$  \hspace{1cm} (2-2)

Here $F_{ij}$ is the Hooke's law force constant meaning the force restoring the molecule to equilibrium from a distortion measured by the two displacement coordinates $\Delta R_i$ and $\Delta R_j$.

For small displacements, the cubic, quartic and higher order terms in the potential energy are indeed small compared to the harmonic terms. These anharmonic terms of the potential can be neglected in a first harmonic approximation to the true potential energy of the molecule. When the higher order terms in Eq. (2-1) are ignored, the force field is said to be harmonic and in this approximation the potential energy is simply

$$2V = \sum_i \sum_j F_{ij} \Delta R_i \Delta R_j.$$  \hspace{1cm} (2-3)

The kinetic energy depends only on the masses and geometry of the molecule and can be given in similar form (44):
Here, $M_{ij}$ are coefficients depending on the masses and molecular geometry and $\dot{R}_i$ and $\dot{R}_j$ are the time derivatives of the internal displacement coordinates. A more convenient form for the kinetic energy can be given in terms of the momenta $P_i$ defined as

$$P_i = \sum_j M_{ij} \dot{R}_j,$$  \hspace{1cm} (2-5)

and the coefficients $G_{ij}$ related to $M_{ij}$:

$$2T = \sum_i \sum_j G_{ij} P_i P_j. \hspace{1cm} (2-6)$$

3. The Vibrational Secular Equation

The complete mathematical method to obtain the vibrational secular equation is found in Wilson, Decius and Cross (5) and many other references (48). Here we will give the basic formulation in matrix form given by Mills (1) for reference in the following chapters. Short notes on matrix notation and properties are given in Appendix 1. Eqs. (2-3) through (2-6), in matrix notation, are as follows:

$$2V = R' F R$$ \hspace{1cm} (2-7)

$$2T = R' M \ddot{R} = \dot{P}' G P$$ \hspace{1cm} (2-8)

$$P = M \ddot{R}.$$ \hspace{1cm} (2-9)
The relationship between the "inverse kinetic energy" matrix, \( \mathcal{G} \), and \( \mathbf{M} \) is given by

\[
\mathcal{G} = \mathbf{M}^{-1} .
\] (2-10)

We define a column vector \( \mathbf{Q} \) of the \( 3N-6 \) normal coordinate, \( Q_i \). This column vector is related to the column vector, \( \mathbf{R} \), of internal displacement coordinates, \( \Delta R_i \), through the transformation matrix \( \mathbf{L} \)

\[
\mathbf{R} = \mathbf{L} \mathbf{Q} .
\] (2-11)

Here, the elements \( L_{ij} \) are the derivatives \( (\partial R_i / \partial Q_j) \).

In terms of these normal coordinates, the potential and kinetic energies take the form:

\[
2V = \mathbf{Q}' \mathbf{A} \mathbf{Q}
\] (2-12)

and

\[
2T = \mathbf{Q}' \mathbf{\dot{Q}} .
\] (2-13)

\( \mathbf{A} \) in Eq. (2-12) is a diagonal matrix of the frequency parameters \( \lambda_k \); the parameter \( \lambda_k \) is related to the wave number \( \omega_k \) by:

\[
\lambda_k = 4\pi^2 c^2 \omega_k^2
\] (2-14)

where \( \omega_k \) is taken in \( \text{cm}^{-1} \) and \( c \) is the velocity of light.
Substitution of Eq. (2-11) in Eqs. (2-7) and (2-8) and comparing the results with Eqs. (2-12) and (2-13) gives

\[ L' F L = \Lambda \]  
and

\[ L' G L = E, \]

where \( E \) is the unit matrix.

From these two equations, the vibrational secular equation is obtained as

\[ (G F - \Lambda)L = 0, \]

which is the typical equation of an eigenvalue-eigenvector problem whose characteristic equation is given by the determinantal form

\[ |G F - \Lambda| = 0. \]

4. Valence Displacement Coordinates

From the physico-chemical point of view, the force constant parameters \( F_{ij} \) are easily visualized in terms of valence bonds and angles. Wilson, Decius and Cross (49) define five valence displacement coordinates as bond stretching, valence angle bending, out-of-plane bending, torsion and linear valence angle bending.

There, the analytical expressions for the valence displacement coordinates in terms of cartesian coordinates are given. For our
purpose, we express the internal displacement coordinate vector in
terms of a set of 3N cartesian coordinates through the transformation
\( B \) as

\[
\tilde{R} = B \tilde{X}
\]  
(2-19)

where \( \tilde{X} \) is a 3N vector of the cartesian displacement coordinates.
Since the kinetic energy is easier to construct in cartesian coordinates,
the appropriate formula for the inverse kinetic energy matrix \( G \) is given
by

\[
G = B \tilde{M}^{-1} B'
\]  
(2-20)

where \( \tilde{M}^{-1} \) is a diagonal matrix of the reciprocal of the masses. The
expressions for the \( G_{ij} \) elements are given by Wilson, Decius and Cross
(49) and by Decius (50) in a tabulated form.

The relationship \( \tilde{\sim} \) between the 3N cartesian coordinates and
the 3N-6 valence displacement coordinates, taking into account the
Sayvetz-Eckart conditions is treated by Herzberg (45) and can be found
in many other references (48,49).

5. Symmetry Coordinates

The vibrational secular equation (2-17) is greatly simplified
by the use of molecular symmetry since the secular equation factors
into smaller symmetry blocks and each block can be treated separately.
Wilson, Decius and Cross (51) treat the problem at length and we have
followed their method in the analysis of the ethylene molecule in
Chapter 5.
The symmetry coordinates are, in general, constructed as a linear combination of the valence displacement coordinates

$$ S = U R $$

(2-21)

where $U$ is an orthogonal transformation matrix.

Sometimes, in order to make full use of the symmetry of the molecule, it is convenient to introduce more than $3N-6$ valence displacement coordinates. The equations expressing the relations between the resulting dependent set of coordinates are called redundancy conditions, with zero roots in the secular equation. The problem of constructing a complete basic set of symmetry coordinates exactly orthogonal to the redundant condition is often not obvious and has been treated by Sun, Parr and Crawford (52) and later by Crawford and Overend (53).

6. Sources of Additional Observed Data

As mentioned in Chapter 1, the main problem in obtaining the potential function of a molecule in the most general form (G.F.F.) is the lack of sufficient data to fix the force field. The use of the observed fundamental frequencies of isotopic derivatives (i.e., when an atom of the parent molecule is replaced by an isotopic atom of the same element), had been the main source of information since it is assumed that the force field is changed by negligible amounts (54). Nevertheless, due to the Teller-Redlich product rule (8) and Brodersen's complete isotopic rule (9) limit the availability of the observed frequencies of the isotopic derivatives to fix the force field of a given molecule, additional data are necessary as stated by Mills (55).
One extra source of information about the vibrational force field can be data from the study of vibration-rotation interaction. The most complete theoretical treatment of the coupling of rotation with vibration is that given by Nielsen (19) and in a less sophisticated fashion by Herzberg (56). The basic relationships between the coriolis coupling constants and the force constants have been well established by several authors, as reviewed by Mills (57) while those of the centrifugal distortion constants have been treated by Kivelson and Wilson (58). The experimental determination of both coriolis coupling and centrifugal distortion constants is a rather difficult matter; data have been measured for only a very few molecules. The coriolis coefficients may be determined by the analysis of high resolution infrared spectra and the reader is referred to the discussion of the experimental problem by Allen and Cross (59) and to Boyd and Longuet-Higgins (60) and Meal and Polo (61) for the relationship between the coriolis coupling coefficients and the force constants. Mills (55) has discussed the use of coriolis coupling and centrifugal distortion constants in obtaining force constants for methane and ethylene (38).

Another type of experimental data that may be helpful in the determination of the force field is the mean-square amplitudes of vibration from electron diffraction work. Cyvin (62) has treated the meaning and determination of the mean-square amplitudes of vibration and their relation to the force field; again, only a few molecules have been studied with the degree of accuracy needed to be useful in the calculation of the force constants; in fact, in many cases the known force field is used to determine the mean amplitudes of vibration rather than vice versa.
Calculated coriolis coupling coefficients.--The basic formulas for the calculation of the coriolis coupling coefficients from any assumed potential field have been given by Meal and Polo (61). In matrix form, the coriolis \( \zeta \) coefficients are given by

\[
\zeta^{(\alpha)} = \tilde{L}^{-1} C^{(\alpha)} (\tilde{L}^{-1})',
\]

where \( \alpha \) is either \( x \), \( y \) or \( z \); the elements of the \( \tilde{C}^{\alpha} \) matrix are defined in terms of the Wilson's \( S \) vectors (49) and \( \tilde{L}^{-1} \) is the inverse transformation matrix from internal displacement coordinates to normal coordinates, according to Eq. (2-11):

\[
\tilde{Q} = \tilde{L}^{-1} \tilde{R}
\]

where \( \tilde{Q}^{(\alpha)} \) matrix is given by the expression (61)

\[
\tilde{C}^{\alpha} = \tilde{D} \tilde{M}^{\alpha} \tilde{D}'
\]

where \( \tilde{D} \) depends only on the masses and equilibrium geometry of the molecule, in the same fashion as in the expression for the inverse kinetic energy matrix \( \tilde{G} \). \( \tilde{D} \) is defined by Meal and Polo (61).

7. Anharmonicity

The potential field given by Eq. (2-3) represents a harmonic potential in which higher order terms (in other words, the anharmonic part of the potential) of the Taylor expansion of Eq. (2-1) have been neglected. The normal frequencies obtained as roots of the vibrational
secular determinant of Eq. (2-18) are harmonic frequencies, $\omega_i$. The observed fundamental frequencies, $\nu_i$, depend not only upon the quadratic coefficients, but, to a lesser extent, upon the anharmonic terms of the potential. It is, then, important to correct the observed fundamental frequencies for anharmonicity before using them to fix the harmonic force field; in principle, this can be accomplished accurately if all overtones and combination bands are known so that anharmonicity corrections are known. This information is rarely available, however, and an approximate method has been proposed by Dennison (63) and Hansen and Dennison (64).

The method, based on the Redlich-Teller product rule (8), defines the anharmonicity correction factor, $x$, through the equation

$$\nu_i = (1 - x_i)\omega_i$$  \hspace{1cm} (2-25)

where $\nu_i$ and $\omega_i$ are the observed fundamental and harmonic normal frequencies, respectively.

The method has been discussed by Mills (1) and applied to the ethylene molecule by Cyvin and Cyvin (37); it should be pointed out that the method is only approximate for polyatomic molecules (55) and anharmonicity constitutes the largest uncertainty in the calculation of force constants. Other additional data, such as coriolis coupling coefficients and centrifugal distortion constants, are anharmonic in nature and, in general, no procedure exists to correct them for anharmonicity as pointed out by Mills (55).
8. Modified Force Fields

Even when all different sources of data mentioned above are used, one finds that the G.F.F. (even with the symmetry) cannot be fixed in general. Thus we try to deduce it from simplified model force fields where certain assumptions are made regarding the nature of the force field. Wilson, Decius and Cross (54) present a discussion of different assumptions generally made to develop model force fields, and Aldous and Mills (65) make a helpful comparison of several of the simplified models with the G.F.F.

One of the simplest model fields is the valence force field (V.F.F.), which assumes that there are no interaction terms in the potential. It is a greatly simplified model often used in the rough or first order assignment of frequencies. Herzberg (66) gives a presentation of this model and discusses its applications.

The modified valence force field (M.V.F.F.) introduces some (but not all) interaction force constants to the V.F.F., still leaving the problem determined. In fact, the number of interaction force constants added to the V.F.F. is often chosen to be sufficient to fit the available independent data and the criterion for the validity of the assumptions is always the ability to predict the observed data. The M.V.F.F. has been successfully used by many authors for molecules in which no extra data can be obtained to fit the G.F.F. (66).

The Urey-Bradley force field (U.B.F.F.) named after its first proponents (67), includes the repulsion interaction between non-bonded atoms to calculate the interaction terms to be added to the V.F.F. It has been extensively used by Simanouti (68) and others, and by Scherer and Overend (13, etc.) in many systems.
The change in hybridization in the orbitals expected during a vibration (47) has been the theoretical basis for another model, the hybrid-orbital force field (H.O.F.F.) proposed and investigated by Aldous and Mills (65). The concept of orbital-following rehybridization, upon which this model is based, established that the central atom of a bending coordinate could "follow" the distortion caused by the vibration by partially rotating the orbitals in the process.

Although these simplified models are not, by any means, the only ones in existence, they are widely known and used with relative success. The reader is referred to the original references for the detailed understanding of the methods.

In the present study, we use a M.V.F.F. for ethylene as complete and close to the G.F.F. as the availability of experimental data permit. We discuss the assumptions made for the force field of ethylene in Chapter 5.
CHAPTER 3
FORCE CONSTANTS REFINEMENT PROCEDURE

As discussed in the previous chapter, the solution of the vibrational secular equation, Eq. (2-17) presents three major difficulties: first, lack of sufficient experimental data to fix a unique G.F.F.; second, computational difficulties since the force constants are rather complicated functions of the frequencies; third, the problem of anharmonicity, arising from the neglect of the anharmonic terms in the potential functions, introduces a further degree of uncertainty in the knowledge of experimental frequencies of the molecule and thus in the calculation of the harmonic potential. Here, in this chapter, we shall discuss some details connected with the computational problem.

A force constant refinement procedure using first order perturbation methods has been mathematically formulated by King (69) but the original treatment of the present technique is due to Mann, Shimanouchi, Meal and Fano (40) and has been widely used since the application of digital computers to the vibrational problem. Further developments have been published by Overend and Scherer (13), by Mills (55), and by Duinker (70), among others. Computer programs by Schachtschneider and Snyder (71) are widely available.

In this chapter, the method is outlined briefly and the relevant features of the calculation are discussed in order to stress the importance of key factors that determine the results. A minimum of mathematical
procedures are included when convenient for the understanding of the method.

1. Successive Diagonalization Procedure

Although the frequency parameters, $\lambda^0_1$, are obtained by finding the eigenvalues of $G_F$ in the secular equation, (2-17), it is convenient not to try to find the eigenvector matrix of the unsymmetric matrix $G_F$ directly through diagonalization but to break down the problem into steps as follows:

1. The first step in the calculation is to obtain the inverse kinetic energy matrix $G$ by the Wilson method (49). Since $G$ is a real symmetric matrix, it can be diagonalized by an orthogonal transformation $D$

$$G \sim D = \sim \Gamma $$

or

$$D'G\sim = \Gamma = \sim \Gamma^{1/2} \Gamma^{1/2}.$$

Here $D$ is an orthogonal matrix of the eigenvectors of $G$ and $\Gamma$ is a diagonal matrix of the eigenvalues of $G$. The diagonalization is carried out in the computer by the Jacobi diagonalization procedure found in standard mathematical textbooks (72).

2. A similarity transformation matrix $W$ is constructed such that

$$W^{-1} = \sim D \Gamma^{-1/2} $$

or

$$W = \sim \Gamma^{+1/2} D'.$$
Eq. (3-2) can be rewritten as

\[ \Gamma^{+1/2} D' G D \Gamma^{-1/2} = E ; \]  

(3-5)

substituting Eqs. (3-3) and (3-4) in Eq. (3-5) we obtain, since \( \bar{W}^{-1} = \bar{W}' \),

\[ \bar{W} G \bar{W}' = E . \]  

(3-5a)

Thus \( \bar{W} \) is a unitary transformation for \( G \) (73). The \( \bar{W} \) matrix is calculated by the computer using the WMAT program obtained from the University of Minnesota (71); the flowchart is given in Appendix 3.

3. An initial force constant matrix \( \bar{F} \) is constructed from values of the force constants transferred from related molecules or taken from the literature. \( \bar{F} \) is a real symmetric matrix; we apply the similarity transformation \( \bar{W} \) to the \( \bar{F} \) matrix

\[ \bar{W} \bar{F} \bar{W}' = \bar{H} \]  

(3-6)

The transformed \( \bar{F} \) matrix, \( \bar{H} \), is symmetric and can also be diagonalized by the Jacobi method:

\[ \bar{H} \bar{C} = \bar{C} \bar{A} \]  

(3-7)

Here \( \bar{C} \) is an orthogonal matrix of the eigenvectors of \( \bar{H} \), and \( \bar{A} \) is a diagonal matrix of the eigenvalues of \( \bar{H} \).

Since \( \bar{W} \) is a similarity transformation taking \( \bar{G} \) to the identity matrix \( \bar{F} \) and \( \bar{F} \) to \( \bar{H} \), the eigenvalues of \( \bar{H} \) are the same as the eigenvalues of \( \bar{G} \bar{F} \) (74).
4. Once the eigenvalues of $G_{F}$ are obtained, the normal co-
ordinate transformation matrix $L$ is also calculated

$$L = W C .$$ (3-8)

Obviously, we cannot find the absolute value of the $L_{ij}$ co-
efficients but rather their ratio. To normalize the matrix $C$ to unity
is equivalent to normalizing the $L_{ij}$ coefficients to the condition

$$L L' = C .$$ (3-9)

The inverse normal coordinate transformation matrix $L^{-1}$ can be calcu-
lated from $C$ and $W$ since both are orthogonal.

From Eq. (3-8)

$$L^{-1} = (W C)^{-1} = C^{-1} W^{-1} = C' W'$$ (3-10)

An equivalent method of calculating $L^{-1}$ is obtained from

Eq. (2-24)

$$L' F L = A$$ (3-11)

Multiplying from the left by $(L')^{-1}$ and from the right by
$A^{-1}$, and taking the transpose,

$$L^{-1} = (F L A^{-1})'$$ (3-12)

2. Perturbation Procedure

5. The relationship between the frequency parameters $\lambda_i$ and
the force constants $F_{jk}$ can be expanded in a Taylor series

$$
\Delta \lambda_j = \sum \frac{\partial \lambda_j}{\partial F_{jk}} \Delta F_{jk} + \frac{1}{2} \sum \left( \frac{\partial^2 \lambda_j}{\partial F_{jk} \partial F_{km}} \right) \Delta F_{jk} \Delta F_{km}
$$

We assume that the quadratic (and higher terms) should be very small compared to the first term, so that, in matrix form,

$$
\Delta \lambda = J_{\lambda} \Delta F
$$

Here, $J_{\lambda}$ is the Jacobian matrix of the first partial derivatives of the frequencies with respect to the force constants ($J_{i,j} = \partial \lambda_i / \partial F_{jk}$) (75); $\Delta F$ is the column vector of the corrections to be made to the force constants and $\Delta \lambda$ is a vector defined by

$$
\Delta \lambda_i = (\lambda_i^0 - \lambda_i)
$$

where $\lambda_i^0$ is the observed and $\lambda_i$ is the first calculated value of the frequency parameter.

(Other experimental parameters such as coriolis coupling coefficients and centrifugal distortion constants can be introduced at this stage. Mills (75) has a complete treatment for this case. It is omitted here since the complete treatment is parallel to the single problem of the frequencies above.)

With this provision, we define a vector of residuals $\varepsilon$ from Eq. (3-14)

$$
J_{\lambda} \Delta F - \Delta \lambda = \varepsilon
$$

(3-16)
6. Assume that the error (random, or that due to the anharmonicity in the observed frequencies) in the experimental measurement of the $i^{th}$ observed frequency is $\sigma_i$. We define a statistical weight $W_i$ as

$$ \sigma_i^2 W_i = \sigma_2^2 W_2 = \ldots = \sigma_1^2 W_1 = \sigma^2 $$

(3-17)

where $\sigma$ is the variance of an observation of unit weight and constitutes a scaling factor, which in general is not known as discussed in the next chapter.

We define a weight matrix $P$ as a diagonal matrix whose elements are

$$ P_{ii} = W_i = \frac{\sigma^2}{\sigma_i^2} $$

(3-18)

and the variance $V$ of the agreement between observed and calculated frequency parameters is defined as

$$ V = \sum_i W_i (\lambda_i^0 - \lambda_i)^2 $$

(3-19)

or, in matrix notation,

$$ V = \Delta \Lambda' \, P \, \Delta \Lambda $$

(3-20)

7. The Gauss method (31) of least squares, based on the minimization of the variance $V$, states that the best set of force constants will be the one that has the minimum variance.

The minimization of $V$ in Eq. (3-20) is equivalent to the minimization of the quadratic form
\[ V = \varepsilon' P \varepsilon \]  
(3-21)

where \( \varepsilon \) is defined in Eq. (3-16). \( V \) then can be written as

\[ V = (J \Delta F - \Delta \Lambda)' P (J \Delta F - \Delta \Lambda) \]

\[ = (J \Delta F)' P (J \Delta F) + \Delta \Lambda' P \Delta \Lambda \]

\[ -(J \Delta F)' P \Delta \Lambda - \Delta \Lambda' P (J \Delta F) \]

\[ = \Delta F' J' P J \Delta F - \Delta F' J' P \Delta \Lambda \]

\[ + \Delta \Lambda' P (\Delta \Lambda - J \Delta F) \]

\[ = \Delta F' (J' P J \Delta F - J' P \Delta \Lambda) - \Delta \Lambda' P \varepsilon \]  
(3-22)

The minimization of \( V \) requires that

\[ dV = 0 = 2(\Delta F') (J' P J \Delta F - J' P \Delta \Lambda) \]

(3-23)

where \( \Delta \Lambda P \varepsilon \) has vanished since it is a real constant. This gives us

\[ J' P J \Delta F - J' P \Delta \Lambda = 0 \]

(3-24)

We define the normal equation matrix \( \Lambda \) as

\[ \Lambda = J' P J \]

(3-25)

and the normal equation vector \( \Xi \) as

\[ \Xi = J' P \Delta \Lambda \].  
(3-26)

The force constant correction vector \( \Delta F \), for the first order
perturbation, is then obtained from the above definitions in Eq. (3-24)

\[ \Delta_\sim F = X \sim, \quad (3-27) \]

or

\[ \Delta F = A^{-1} X \sim. \quad (3-28) \]

The inversion of the normal equation matrix \( A \) is the single most important step in this part of the calculation and will be discussed later.

8. A new set of force constants is obtained by adding the set of corrections \( \Delta_\sim F \) to the original values

\[ F_{\text{new}} = F_{\text{old}} + \Delta F \sim. \quad (3-29) \]

The cycle is re-entered at step 3 of the procedure and the perturbation cycle repeated until convergence is obtained. The criterion for convergence is a rather arbitrary choice of how good a fit between observed and calculated values is desired. Mills (55) discusses this point at length.

The refinement procedure is done by computer techniques and the flowchart is presented in Appendix 3.

3. Discussion of the Procedure

The force constant refinement procedure gives the "best" set of values of force constants that give "good" agreement between all observed data available and the calculated values from this set of force constants. This criterion may not be sufficient to give a unique solution to the force field, so that the set of force constants should
be regarded as a possible solution rather than the solution to the problem. This uncertainty implies that, even in the best of cases, in which more independent data are available than the number of force constants to be fixed, the final set of force constants from the refinement cannot be said to be unique since no criterion exists in the procedure to decide about the uniqueness of the force field in question (65).

Eq. (3-28) gives the corrections to be applied to the initial set of force constants in terms of the inverse normal equation matrix $A^{-1}$. We have pointed out there the importance of this inversion step: the inverse matrix, $A^{-1}$, exists only if $A$ is not singular; i.e., only if the determinant of $A$ is different from zero. In the case that $A$ is indeed singular, the perturbation procedure diverges and there is no solution possible for the problem. In the case that $A$ is nearly singular it is possible to obtain convergence and large errors are introduced in calculating $A^{-1}$ and corresponding errors are introduced in the force constants corrections; in this case $A$ is said to be ill-conditioned and there is no physical meaning of the results. It is important, then, that some tests for singularity should be made on $A$ at each stage of the refinement procedure. Mills (57) has suggested several tests for singularity, as described below.

First, since $A$ is a symmetric positive matrix, the product of the diagonal terms should be of the same order of magnitude as the value of the determinant of the matrix. Second, if one or more diagonal elements of $A$ are nearly zero, at least one diagonal element of $A^{-1}$ would be unusually large producing a correspondingly large correction in at least one force constant. Third, the variance in Eq. (3-21) is expected
to be smaller or equal to $V$ of Eq. (3-20); i.e.,

$$\varepsilon' P \varepsilon \leq \Delta A' P \Delta A. \quad (3-30)$$

The two sides of the equation are equal if convergence is obtained.

One of these tests for singularity should be applied in order to detect an ill-conditioned $A$ matrix.

The nature of the singularity or near singularity of $\sim A$ can be studied from the definition of $A$ by Eq. (3-25).

First, it has been assumed in Eq. (3-14) that a linear relationship exists between the differences in observed and calculated frequency parameters, $\Delta \sim A$, and the corrections to the force constants, $\Delta \sim F$, by neglecting higher terms in the Taylor expansion of Eq. (3-13). If we have started with a bad set of force constants, large corrections would have been necessary, so that the linear relationship of Eq. (3-14) no longer would be expected to hold. The Jacobian $J$ will not define the normal equation $A$ properly, and ill-conditioned behavior is expected. This situation can be detected by the test provided by Eq. (3-30).

Second, the Jacobian $J$ is defined as a matrix of whose elements are the partial derivatives

$$J_{ij} = \sum_k \frac{\partial \sim \lambda_i}{\partial \sim F_{jk}}. \quad (3-31)$$

If it happens that one frequency is largely insensitive to changes in the force constants an entire row of the Jacobian will have small values and $J' P J$ will have at least one diagonal element $(J' P J)_{ii}$ that is very small compared to the other diagonal elements. Again, the $A$ matrix
is expected to be ill-conditioned. This condition can be detected by the second test.

Third, we note that the weight matrix $P$ is not important in the determination of $\Delta F$ as can be shown from Eq. (3-28)

$$\Delta F = (J' \ P \ J)^{-1} J' \ P \ \Delta \Lambda$$  \hspace{1cm} (3-32)

For the case in which the number of independent data parameters $\lambda_i$ is the same as the number of force constants to be fixed, $J$ is a square matrix and does have an inverse; Eq. (3-32) can be written, then, as

$$\Delta F = J^{-1} P^{-1} (J')^{-1} J' \ P \ \Delta \Lambda$$  \hspace{1cm} (3-33)

or

$$\Delta F = J^{-1} \ \Delta \Lambda$$  \hspace{1cm} (3-34)

which is similar to Eq. (3-14).

Then, we can adjust the matrix $P$ in order to prevent any anomalies in the $\Delta \Lambda$ matrix without affecting the force constant corrections. As we will discuss in the next chapter, the matrix $P$ is very important in determining the dispersions of the force constants. When a dispersion is large, $P$ gives a criterion as to which force constant should be constrained to avoid near singularity in the normal equation matrix. The choice of weights will be discussed in the next chapter.
CHAPTER 4

STATISTICAL ERROR ANALYSIS

The theory of statistical error analysis applied to physical problems has been presented in several standard books (76,77) and applied to the problem of normal coordinate analysis more recently by Russell, Needham and Overend (33). For the following sections, it is advisable to be familiar with the treatment presented in the references given above. We intend to reproduce the basic formulation used in the present work since the understanding of dispersions is important in the interpretation of the results in Chapter 6.

1. Variance-Covariance Matrix for Observed Frequency Parameters

The least-square treatment for adjusting an initial set of force constants to observed frequency parameters, described in the previous chapter, provides the basic formulation for the statistical error analysis of the final set of force constants and any other quantities calculated from them, such as calculated frequency parameters and $L$ and $L^{-1}$ transformation matrices.

We define the variance-covariance matrix (76) for any observed parameters $\lambda_i$ as
\[
\Sigma(\lambda) = \begin{bmatrix}
\sigma_i^2(\lambda_i) & \rho_{12}\sigma_1\sigma_2 & \cdots & \rho_{1n}\sigma_1\sigma_n \\
\rho_{21}\sigma_2\sigma_1 & \sigma_2^2(\lambda_2) & \cdots & \rho_{2n}\sigma_2\sigma_n \\
\vdots & \vdots & \ddots & \vdots \\
\rho_{n1}\sigma_n\sigma_1 & \rho_{n2}\sigma_n\sigma_2 & \cdots & \sigma_n^2(\lambda_n)
\end{bmatrix}
\]  

(4-1)

where the diagonal terms of the variance-covariance matrix \( \Sigma(\lambda) \) are

\[
\sigma_i^2(\lambda_i) = \text{variance of } \lambda_i,
\]

and the off-diagonal terms are

\[
\rho_{ij}\sigma_i\sigma_j = \rho_{ij}(\lambda_i,\lambda_j) \sigma_i(\lambda_i) \sigma_j(\lambda_j) = \text{covariance of } \lambda_i, \lambda_j.
\]  

(4-2)

We define, furthermore,

\[
\sigma_i(\lambda_i) = \text{dispersion of } \lambda_i
\]

\[
\rho_{ij} = \text{correlation coefficient between } \lambda_i \text{ and } \lambda_j
\]

(4-3)

The variance is assumed to have finite values and the correlation coefficient is interpreted as a measure of the stochastic independence of the parameters \( \lambda_i \) and \( \lambda_j \), being zero when the variables are stochastically independent.

In the least-square procedure, we have defined a diagonal matrix \( P \), whose elements \( W_i \) are defined by Eq. (3-18) as
\[ \sigma^2 W_1 = \sigma^2 W_2 = \cdots = \sigma^2 W_i = \bar{\sigma}^2 \]  

(4-4)

where \( \bar{\sigma}^2 \) is the standard deviation of an observed frequency of unit weight, and, in general, not known. We assume that \( \sigma^2 \) is the dispersion \( \sigma^2 \{\lambda_i\} \) as described in Eqs. (4-1), (4-2) and (4-3). If we consider the frequencies to be stochastically independent (i.e., \( \rho_{ij} = 0 \)), we can see that the variance-covariance matrix for the observed frequency parameters is related to the \( P \) matrix

\[
P = \begin{bmatrix}
W_1 & 0 \\
W_2 & \ddots \\
0 & \ddots & W_1
\end{bmatrix} = \bar{\sigma}^2 \begin{bmatrix}
\frac{1}{\sigma^2\{\lambda_1\}} & 0 \\
0 & \frac{1}{\sigma^2\{\lambda_2\}} \\
\frac{1}{\sigma^2\{\lambda_1\}} & \ddots & \ddots & \frac{1}{\sigma^2\{\lambda_1\}}
\end{bmatrix}
\]  

(4-5)

By comparison with Eq. (4-1)

\[
\Sigma\{\lambda\} = \frac{1}{\bar{\sigma}^2} P^{-1}
\]  

(4-6)

or

\[
\tilde{P} = \bar{\sigma}^2 [\Sigma\{\lambda\}]^{-1}.
\]  

(4-7)

Replacing Eq. (4-7) in the definition of the normal equation matrix and vector in the least-square procedure, Eqs. (3-25) and (3-26), we have

\[
\tilde{A} = J^T \bar{\sigma}^2 [\Sigma\{\lambda\}]^{-1} J
\]  

(4-8)
and
\[ X = J' \sigma^2 [\Sigma(\lambda)]^{-1} \Delta \Lambda \] (4-9)

and substituting in Eq. (3-27) we have
\[ J' \sigma^2 [\Sigma(\lambda)]^{-1} \Delta \Lambda F = J' \sigma^2 [\Sigma(\lambda)]^{-1} \Delta \Lambda \] (4-10)

Since \( \sigma^2 \) is a constant it commutes with \( J' \) and may be eliminated from both sides of the Eq. (4-10). The solution for the force constant correction vector is thus seen to be independent of the unknown scaling factor \( \sigma^2 \) of the variance-covariance matrix \( \Sigma(\lambda) \).

2. Variance-Covariance Matrix for Force Constants Parameters

**Formulation.**—Since the "best" least-square values of the force constants have been obtained as solutions to the normal equations, the variance-covariance matrix for the force constants \( \Sigma(\lambda) \) is proportional to the inverse normal equation matrix \( A^{-1} \), the proportionality constant being the scaling factor \( \sigma^2 \):

\[ \Sigma(F) = \sigma^2 A^{-1} \] (4-11)

The proof is given by Hamilton (76), based on statistical theory of the expectation value of \( \Delta \Lambda F \) vector, and it can be shown (76) that the value of \( \sigma^2 \) is given by

\[ \sigma^2 = \frac{\varphi_p \varphi_p}{n-m} = \frac{\nu}{n-m} \] (4-12)

\( \nu \) being the variance defined by Eq. (3-20) in the least-square method; 

\( n \) is the number of observed data and \( m \) the number of force constants.
to be fixed. Replacing the value of $\sigma^2$ from Eq. (4-12) in Eq. (4-11)

$$\Sigma[F] = \frac{V}{n-m} A^{-1} \quad (4-13)$$

The dimension of the variance-covariance matrix $\Sigma[F]$ is $m \times m$, as is the dimension of the $A^{-1}$ matrix, and can be visualized as follows:

$$A = J' P J \quad (4-14)$$

from the definition of the normal equation matrix.

The Jacobian matrix $J$ is defined as

$$J_{ij} = \sum_k \delta \lambda_i / \delta F_{jk} \quad (4-15)$$

and since there are $n$ frequency parameters and $m$ force constant parameters, the dimension of $A^{-1}$ can be visualized as follows:

$$\begin{pmatrix} A \end{pmatrix} = \begin{pmatrix} J' \end{pmatrix} \begin{pmatrix} P \end{pmatrix} \begin{pmatrix} J \end{pmatrix} \quad (4-16)$$

The dispersions of the force constants are then given by

$$\sigma_i \{ F_i \} = \left[ \frac{V}{n-m} A_{ii}^{-1} \right]^{1/2} \quad (4-17)$$

and the correlation coefficients

$$\rho_{ij} \{ F_i F_j \} = \rho_{ij} = A_{ij}^{-1} / \sigma_i \sigma_j \quad (4-18)$$
Discussion.--It is important to understand the role played by the dispersion in the error treatment of the normal coordinate analysis. From the definition of the dispersion of the force constant parameters in Eq. (4-17) as the square root of the diagonal terms of the variance-covariance matrix $\Sigma(F)$ in Eq. (4-13), several important features can be discussed. By substituting Eq. (4-14) in Eq. (4-13) and the definition of the variance $V$ of Eq. (3-19) we obtain

$$
\Sigma(F) = \sum \frac{W_i (\lambda_i^0 - \lambda_i)}{n-m} \{J \, P \, J'\}^{-1}.
$$  \hspace{1cm} (4-19)

First, the choice of weights $W_i$, both in the variance $V$ and the weight matrix $P$, is important in the magnitude of the dispersions. We have pointed out that the results of the force constant refinement procedure are insensitive to the choice of weights as expressed by Eq. (3-34). The dispersions, on the other hand, do depend on them and it is easily visualized when the weights are considered as the dispersions of the observed frequency parameters, or, since they are experimental quantities, as standard deviations. The choice of weights is a rather arbitrary matter, and only a brief discussion of the points of view presented by Russell, Needham and Overend (33) and those by Mills (57) are summarized here since they differ in their approach.

It is agreed that the main experimental uncertainties in our knowledge of the observed frequency parameters arise from anharmonicity. The calculated frequencies are harmonic while the observed frequencies are anharmonic in nature. Even if anharmonicity corrections are estimated and applied to the observed frequencies, still the largest degree of uncertainty would be due to the anharmonicity correction.
since no exact correction procedure exists and, in the best of cases as the Dennison method, the corrected observed frequencies are only approximate. Mills (57) argues that the relative errors in the derived harmonic stretching frequencies are less than the relative errors in the harmonic bending frequencies. When no corrections for anharmonicity are made, the errors in the stretching frequencies are larger than those of the bending frequencies. For these reasons, the weights should be inversely proportional to the magnitude of \( \lambda \), and weights as \( 1/\lambda \) or \( 1/\lambda^2 \) should be considered, so as to give larger weights to the lower frequencies.

Russell, Needham and Overend (33), on the other hand, argue that although the harmonic corrections to the stretching frequencies are larger than those to the bending frequencies, they are much more regular and equal weights for the observed frequencies should be preferred in the least-square calculation. Since the choice of weights is scaled by the factor \( \sigma^{-2} \), the equal weights are taken as 1.0.

For this last case, the weight matrix becomes the unit matrix and Eq. (4-19) reduces to

\[
\sum \{ F \} = \frac{\Sigma (\lambda_i^o - \lambda_i)^2}{n-m} (J' J')^{-1}
\]  

(4-20)

It is easily seen that the magnitudes of the diagonal elements of \( \sum \{ F \} \) would be larger here for the stretching frequencies than for the case where the weights are \( 1/\lambda \) or \( 1/\lambda^2 \); for frequencies about 2000 cm\(^{-1}\) the weights in all three cases would be about equal; for bending frequencies, the weights here would be smaller than for weights of \( 1/\lambda \) or \( 1/\lambda^2 \). In Chapter 6, results with weights 1.0 and \( 1/\lambda \) are presented and discussed.
Second, the magnitude of $\Sigma [F_{ii}]$ depends on the variance as a scaling factor which would be smaller in magnitude the more precise the choice of the force constant parameters in their ability to predict the observed frequencies; the dispersion in this case would be smaller correspondingly.

Finally, the statistical factor $n-m$ deserves consideration. The larger the difference between the number of observed data, $n$, and the number of force constants, $m$, to be fixed in the least-square treatment, the smaller the dispersions in the force constants will be. For the case $n \leq m$, no statistical method can be applied since the problem is undetermined or only exactly determined. When the problem is overdetermined, the statistical method is valid, but the question arises as to how small the term $n-m$ can be and yet the treatment can have statistical validity. From this point of view, the method favors the use of as many observed data as possible and so it is desirable to include all isotopic frequencies available. Here again, the results, using 2 or 7 isotopic molecules of ethylene in the determination of the force field, are presented in Chapter 6.

To conclude, it is worth pointing out once more that the magnitudes of the dispersions cannot be regarded as absolute values of the errors of the calculated force constant parameters but rather that they are only a measure of the goodness of fit of the calculated values to the observed data and, hence, only the relative values of the dispersions, within a given set, have significance.
3. Variance-Covariance Matrix for the Normal Coordinates

Transformation Matrices $L$ and $L^{-1}$

The $L$ matrix is formed by the eigenvectors of $G F$, as given by Eq. (2-17), and assuming linear propagation of errors, the dispersions in the $L$ and $L^{-1}$ coefficients can be obtained by a treatment similar to that for the force constants. Russell, Needham and Overend (33) have presented the basic formulation. We reproduce here the formulas in our notation with the assumption that errors due to the geometry and masses of the molecule (the $G$ matrix) are negligible (i.e., $\Sigma[G] = 0$) in comparison to the errors in the force field (the $F$ matrix).

The variance-covariance matrices for $L$ and $L^{-1}$ can then be expressed as

\[
\Sigma\{L\} = J_1 \Sigma\{F\} J_1^{-1}
\]  
(4-21)

and

\[
\Sigma\{L^{-1}\} = J_2 \Sigma\{F\} J_2^{-1}
\]  
(4-22)

Here $\Sigma\{F\}$ is the variance-covariance matrix for the force constants and $J_1$ and $J_2$ are Jacobians defined as

\[
J_{1n}^{ij} = \partial L_{ij} / \partial F_n
\]

and

\[
J_{2n}^{ij} = \partial L_{ij}^{-1} / \partial F_n
\]  
(4-23)

The analytical formulation for the Jacobian elements has been given by Miyazawa and Overend (78) in terms of the $L_{ij}$ coefficients themselves.
The dispersions $\sigma_{ij}$ and the correlation coefficients $\rho_{ij\kappa\lambda}$ are given by

$$
\sigma_{ij} = (\Sigma[L]_{gg})^{1/2}, \quad g = (i-1)P + j \quad (4-26)
$$

$$
\rho_{ij\kappa\lambda} = (\Sigma[L]_{gr}r_{ij\kappa\lambda})/\sigma_{ij}\sigma_{\kappa\lambda}, \quad r = (k-1)P + \ell \quad (4-27)
$$

and for $L^{-1}$ matrix,

$$
\sigma^{-1}_{ij} = (\Sigma[L^{-1}]_{tt})^{1/2}, \quad t = (i-1)S + j \quad (4-28)
$$

$$
\rho^{-1}_{ij\kappa\lambda} = (\Sigma[L^{-1}]_{tu}r_{ij\kappa\lambda})/\sigma_{ij}\sigma_{\kappa\lambda}, \quad u = (k-1)S + \ell \quad (4-29)
$$

where $S$ is the number of internal coordinates and $P$ the number of normal coordinates.

The size of the variance-covariance matrices $\Sigma[L]$ and $\Sigma[L^{-1}]$ can be visualized as follows: the transformation matrix $L$, as defined by Eq. (2-11), will have dimensions $S \times P$:
There are then \((S \times P)_{ij}\) elements and the Jacobian \(J_{ij}\) of Eq. (4-21) will have dimensions \(m \times (S \times P)\). The dimensions of \(\Sigma\{L\}\) will be, then,

\[
\begin{bmatrix}
\Sigma\{L\} \\
J_{ij}
\end{bmatrix}
= \begin{bmatrix}
S_{xP} \\
m
S_{xP}
\end{bmatrix}
\begin{bmatrix}
L_{ij}
\\
\Sigma\{F\}
\\
J_{ij}^{-1}
\end{bmatrix}
\]

which means that the order of \(\Sigma\{L\}\) is \((SxP)\times(SxP)\) which is quite large even for small molecules and makes the use of symmetry imperative to reduce the size of such a cumbersome matrix.

Many elements of \(\Sigma\{L\}\) will be reduced to zero but the nonzero elements will be distributed blockwise depending on the symmetry of the molecule. For ethylene for example there are 9 in-plane vibrations and 9 internal and 9 normal coordinates which determine the dimensions of \(\Sigma\{L\}\) to be 81 \(\times\) 81. By use of symmetry however, it would be reduced to a matrix of 21 \(\times\) 21. The determination of the nonzero elements in the reduced matrix \(\Sigma\{L\}\) is not simple and it is explained, for the case of methyl fluoride, by Russell, Needham and Overend (33).

4. Approximate Dispersions for \(L\) and \(L_{ij}^{-1}\)

In some problems, when the number of observed data is barely larger than the number of force constants to be fixed, the statistical treatment is not justified and an approximate treatment based on first order perturbation theory is preferable (33).

Assuming that the \(L_{ij}\) and \(L_{ij}^{-1}\) coefficients are essentially independent of the uncertainties in the geometry a Taylor expansion
of these coefficients about the values, $L_{ij}^0$, calculated using the preferred least-square values, of the force constants give

$$L_{ij} = L_{ij}^0 + \sum_{k, \ell} \left( \frac{\partial L_{ij}}{\partial F_{k\ell}} \right) \Delta F_{k\ell} + \text{higher order terms} \quad (4-32)$$

or

$$L_{ij}^{-1} = L_{ij}^0 + \sum_{k, \ell} \left( \frac{\partial L_{ij}^{-1}}{\partial F_{k\ell}} \right) \Delta F_{k\ell} + \text{higher order terms} \quad (4-33)$$

Here $\Delta F$ is taken as a measure of the uncertainty in the force constants and can be taken to be the dispersions $\sigma(F_{k\ell})$ of Eq. (4-17).

Neglecting the higher order terms in Eqs. (4-32) and (4-33) for a first order perturbation approximation, the upper limits of the dispersions of the $L$ and $L^{-1}$ matrices are given by

$$\Delta L = J_1 \Delta F \quad (4-34)$$

$$\Delta L^{-1} = J_2 \Delta F \quad (4-35)$$

Here $\Delta F$ is a diagonal matrix of the dispersions $\sigma(F_{ij})$ and the coefficients of Taylor expansions are the Jacobian matrices $J_1$ and $J_2$ of Eq. (4-23).

The approximate values of the dispersions, $\sigma(L)$ and $\sigma(L^{-1})$, are given by

$$\sigma(L) = J_1 \sigma(F) \quad (4-36)$$

and

$$\sigma(L^{-1}) = J_2 \sigma(F) \quad (4-37)$$
Here $\sigma[F]$ is a diagonal matrix of the dispersions for the force constant parameters. These dispersions are subject to the same factors that affect the force constant dispersions as discussed earlier. The approximate dispersions can be considered upper-limit errors since the linear relationships of Eqs. (4-36) and (4-37) do not consider the off-diagonal terms in the dispersion-correlation coefficient matrix of the force constants.

The computer program used for the calculation of the dispersions $\sigma[L]$ and $\sigma[L^{-1}]$ is given in Appendix 3.

5. Error Analysis for Dipole Moment Derivatives

As mentioned in Chapter 1, the experimental techniques used in measuring, and the theory used in interpreting the intensities of the infrared vibration bands have been summarized in a review by Overend (2). The details of the interpretation of intensities in terms of the bond-moment hypothesis have been discussed by Kagel (79). In this section, the basic formulas of the treatment of intensity data are given in order to facilitate the understanding of the origin of the error analysis of the dipole moment derivatives in terms of symmetry coordinates.

The relationship between the intensity $\Gamma_i$ of an infrared absorption band and the dipole moment derivative in terms of normal coordinates is given by

$$\Gamma_i = \frac{\pi N}{3c^2} \frac{d_i}{\omega_i} \left(\frac{\partial \nu}{\partial Q_i}\right)^2$$

(4-38)
Here $N$ is Avogadro's number, $c$ the velocity of light, $d_i$ the degeneracy of the vibrational mode $i$, $\omega_i$ the frequency, $p$ the total dipole moment and $Q$ the normal coordinate associated with the vibrational normal mode $i$.

The magnitude of the dipole moment derivative with respect to the normal coordinate $Q_i$ is:

$$\left| \frac{\partial p}{\partial Q_i} \right| = \left( \frac{3c^2}{4\pi} \right)^{1/2} \left( \frac{\omega_i}{d_i} \right)^{1/2} i^{1/2}$$  \hspace{1cm} (4-39)

The dipole moment derivatives with respect to defined symmetry coordinates can be obtained from the derivatives with respect to normal coordinates through the inverse transformation matrix $L^{-1}$, according to the formula

$$p_j = \frac{\partial p}{\partial S_j} = \sum_i (L^{-1})_{ij} \left| \frac{\partial p}{\partial Q_i} \right|$$  \hspace{1cm} (4-40)

Since only the magnitude and not the sign of $\frac{\partial p}{\partial Q_i}$ is known from Eq. (4-39), different values for $p_j$'s are obtained by considering all possible combinations of signs for the $\frac{\partial p}{\partial Q_i}$'s involved in the summation of Eq. (4-40).

The units for the intensities $\Gamma_i$ and dipole moment derivatives are given in Appendix 1.

6. **Variance-Covariance Matrix for ($3p/3Q$)**

The dipole moment derivatives with respect to the normal coordinates as given by Eq. (4-39) are linear functions of two stochastically
independent variables, namely $\omega_i^{1/2}$ and $I_i^{1/2}$. The variance-covariance matrix for $\partial p/\partial Q_i$ as proposed by Russell, Needham and Overend (33) is not properly defined and should be considered rather as the variance-covariance matrix for $(\partial p/\partial Q_i)^2$ and not $\partial p/\partial Q_i$. The latter can be derived from multivariate analysis as

$$\Sigma\{\partial p/\partial Q\} = C \omega^{1/2} \Gamma^{-1/2} \Sigma\{\Gamma\} (\omega^{-1/2})' (C')' + C \omega^{1/2} \Gamma^{-1/2} \Sigma\{\omega\} (\omega^{-1/2})' (\Gamma^{1/2})' (C')'.$$

Here, $C$ is a diagonal matrix of elements defined as

$$C_{ii} = \left(\frac{3c^2}{4\pi d_i}\right)^{1/2}.$$

$\omega^{1/2}$ and $\Gamma^{-1/2}$ are diagonal matrices also, whose elements are the square roots of the frequencies, $\omega_i$, and the intensities, $I_i$, respectively. Similar definitions are applied to the inverse matrices $\omega^{-1/2}$ and $\Gamma^{-1/2}$. Here $\Sigma\{\omega\}$ is the variance-covariance matrix for the harmonic frequencies, [Eq. (4-6)], which are uncorrelated quantities whose covariances vanish since the correlation coefficients, $\rho_{ij}$, defined in Eq. (4-2) are zero for two stochastically independent variables. Thus, $\Sigma\{\omega\}$ is a diagonal matrix and $[\Sigma\{\omega\}]^{1/2}$ is the dispersion in the harmonic frequencies, according to Eq. (4-3):

$$[\Sigma\{\omega\}_{ii}]^{1/2} = \sigma_{\omega_i}.$$

The variance-covariance matrix for the intensities, $\Sigma\{\Gamma\}$, has been defined by Russell, Needham and Overend (33) in terms of two
quantities: the error in the experimental measurement of the intensity, $\Delta \Gamma$, and the error in the separation of two overlapped bands, $\Delta S$, called the degree of mixing of the intensities. The variance terms of $\Sigma \{\Gamma\}$ are given by

$$\Sigma \{\Gamma\}_{ii} = (\Delta \Gamma_i)^2 + \sum_j (\Delta S_{ij})^2$$  \hspace{1cm} (4-44)$$

where $j$ is summed over all bands overlapping the $i^{th}$ fundamental.

The covariances or off-diagonal terms of $\Sigma \{\Gamma\}$ are defined as zero for nonoverlapping bands and as $-1$ for the overlapped bands when the total intensity is known exactly since both bands would be totally correlated.

In terms of the degree of mixing, the covariances can be defined as (33)

$$\Sigma \{\Gamma\}_{ij} = - (\Delta S_{ij})^2.$$  \hspace{1cm} (4-45)$$

The dispersions in the intensities are given as the square roots of the variance terms of $\Sigma \{\Gamma\}$

$$\sigma_{\{\Gamma\}} = [\Sigma \{\Gamma\}_{ii}]^{1/2}$$  \hspace{1cm} (4-46)$$

and the off-diagonal terms are the correlation coefficients for the intensities

$$\rho_{ij}\{\Gamma\} = \Sigma \{\Gamma\}_{ij}/\sigma_{\{\Gamma\}_i}\sigma_{\{\Gamma\}_j}.$$  \hspace{1cm} (4-47)$$

Finally, the dispersions in $\partial p/\partial Q_i$ are obtained from the diagonal terms of $\Sigma \{\partial p/\partial Q_i\}$ of Eq. (4-41) as
\[
\sigma_{\partial p/\partial \Omega_i} = [\Sigma \sigma_{\partial p/\partial \Omega_i}]^{1/2}
\]  \hspace{1cm} (4-48)

or, in analytical form, as

\[
\sigma_{\partial p/\partial \Omega_i} = \frac{1}{2} C_{i} \omega_{i}^{1/2} \frac{\sigma(T_{i})}{\Gamma_{i}^{1/2}} + \frac{1}{2} C_{i} \Gamma_{i}^{1/2} \frac{\sigma(\omega_{i})}{\omega_{i}^{1/2}}
\]  \hspace{1cm} (4-49)

7. Approximate Analysis of the Dispersions of \( \partial p/\partial \Omega_i \)

Many times the errors in the intensity are not determined accurately enough to justify the rigorous treatment described in the previous section and an approximate analysis of the dispersions is desirable. The total derivative of Eq. (4-39) gives

\[
d\left(\frac{\partial p}{\partial \Omega_i}\right) = \left(\frac{\pi N}{3c^2d_i}\right)^{1/2} \omega_{i}^{1/2} \frac{\Gamma_{i}^{-1/2}}{2} d\Gamma_{i} + \left(\frac{\pi N}{3c^2d_i}\right)^{1/2} \Gamma_{i}^{-1/2} \frac{1}{2} \omega_{i}^{-1/2} d\omega.
\]  \hspace{1cm} (4-50)

The approximate dispersions are, then,

\[
\Delta(\partial p/\partial \Omega_i) = \frac{1}{2} C_{i} \omega_{i}^{1/2} \Delta(\Gamma_{i}) + \frac{1}{2} C_{i} \Gamma_{i}^{1/2} \Sigma(\omega_{i})
\]  \hspace{1cm} (4-51)

where \( C_{i} \), \( \Delta(\omega_{i}) \) and \( \Delta(\Gamma_{i}) \) are approximated by Eqs. (4-42), (4-43) and (4-46), respectively.

It should be pointed out that the dispersions given by (4-51) are essentially those defined in (4-49).

**Discussion.**—The dispersions of the dipole moment derivatives \( \sigma(\partial p/\partial \Omega_i) \) are quantities that depend on the dispersions of both frequencies and intensities, \( \sigma(\omega_{i}), \sigma(\Gamma_{i}). \) It is important, then, to understand the criteria used in estimating these latter quantities.
First, the harmonic frequencies are subject to errors introduced by anharmonicity corrections. Since the anharmonicity is larger for larger frequencies it seems that the dispersions should be proportional to the magnitude of the frequencies. Aldous and Mills (65) consider these dispersions \( \sigma(\omega_i) \) to be \( 0.01 \omega_i \) and this criterion is used for our calculations.

Second, the dispersions in the intensities \( \sigma(\Gamma_i) \) as defined by Eq. (4-46) are determined by the errors in the intensity measurements \( \Delta \Gamma_i \), and the degree of mixing of two overlapped bands \( \Delta S_{ij} \). The errors \( \Delta \Gamma_i \) are usually determined as the standard deviation of the intensity measurements from the Beer's law plots but, in some cases, the measurement of the intensity is particularly difficult and a somewhat larger error is determined by several authors. (See, for instance, Nyquist et al. (23).) The error in the separation of two overlapped bands is a much more difficult problem, and has been treated by Dickson et al. (24).

The difficulty in the determination of \( \Delta S \) has been described by Russell, Needham and Overend (33) as follows: "This separation is a major source of error, demanding, as it usually does, a keen eye, a sharp pencil, a certain artistic talent, and simple faith in the symmetry of vibration-rotation bands and the cooperation of nature."

In a somewhat more quantitative way, Dickson et al. (24) give the following criterion for estimating the dispersions in \( \Gamma_i \): the error due to the separation of a pair of overlapping bands is taken as \( \pm 0.20\% \Gamma_i \) for each of the overlapped bands. Furthermore, they estimate dispersions as equal to upper-limit errors, higher than the
standard errors derived in the following way: "(a) 2% of the band area (i.e., one percent of $|\partial p/\partial Q|$), (b) twice the standard error of the Beer's law plot, or (c) the separation error when this is dominant."

The errors in the frequencies and intensities are taken as the dispersions $\sigma(\omega_i)$ and $\sigma(\Gamma_i)$ for the calculation of the dispersion of $\partial p/\partial Q_i$, $\sigma(\partial p/\partial Q_i)$ in Eq. (4-49) or in the approximate dispersion of Eq. (4-51).

8. Variance-Covariance Matrix for $p_j$

Since $p_j$ is obtained from the $\partial p/\partial Q_i$ through the transformation $L^{-1}$, the variance-covariance matrix of $p_j$ can be expressed as

$$
\Sigma(p_j) = (L^{-1})' \Sigma(\partial p/\partial Q) L^{-1} + K \Sigma(L^{-1})K' .
$$

(4-52)

Here $\Sigma(\partial p/\partial Q)$ is the variance-covariance matrix of Eq. (4-48) and $\Sigma(L^{-1})$ the variance-covariance matrix of the inverse normal coordinates transformation matrix $L^{-1}$ given by Eq. (4-22). $K$ is a matrix constructed from the elements of $\partial \mu/\partial Q_i$; the dimensions of $K$ are $m \times (m \times n)$ where $m$ is the number of normal coordinates and $n$ the number of internal coordinates, since the dimension of $\Sigma(L^{-1})$ is $(m \times n) \times (m \times n)$ as described before. Since the dimensions of $\Sigma(p_j)$ are $m \times m$, the dimensions of the triple product $K \Sigma(L^{-1})K'$ are $m \times m$ also. When symmetry is applied, extreme caution should be used in the construction of matrix $K$ since $\Sigma(L^{-1})$ has only some blocks with nonzero elements as discussed in the section of the variance-covariance matrix for $L$ and $L^{-1}$. The matrix $K$ is constructed from the values of $(\partial p/\partial Q_i)$ in a rather cumbersome fashion explained by Russell, Needham and Overend (33).
The dispersions of \( p_j \) are obtained from Eq. (4-52) as

\[
\sigma(p_j) = \left[ \Sigma(p_j) \right]^{1/2}
\]  

(4-53)

and are independent of the choice of sign for the \( \partial p/\partial Q_i \)'s.

The approximate treatment of the dispersions \( \sigma(p_j) \) can be obtained from first order perturbation theory as in the previous sections:

\[
\Delta(p_j) = \sum_i \left[ \left( \frac{L^{-1}}{L} \right)_{ij} \cdot \Delta(\partial p/\partial Q_i) + (\partial p/\partial Q_i) \cdot \Delta(L^{-1})_{ij} \right]
\]  

(4-54)

and, by approximating the \( \Delta \)'s in the above expression to the dispersions of the terms involved, we have that the approximate dispersions of \( p_j \), \( \sigma(p_j) \) are given by

\[
\sigma(p_j) = \sum_i \left[ \left( \frac{L^{-1}}{L} \right)_{ij} \cdot \sigma(\partial p/\partial Q_i) + (\partial p/\partial Q_i) \cdot \sigma(L^{-1})_{ij} \right].
\]  

(4-55)

The dispersions of \( p_j \), obtained either from Eq. (4-53) or Eq. (4-55) can be analyzed in terms of the different contributions from the dispersions \( \partial p/\partial Q_i \) and the dispersions of \( L^{-1} \). Since these dispersions are obtained from the dispersions of the intensities and frequencies and force constants, respectively, the total dispersion of \( p_j \) can be broken down in contributions from the dispersions of the intensities, frequencies and force constants:

\[
\sigma(p_j) = \sigma(\text{intensities}) + \sigma(\text{frequencies}) + \sigma(\text{force constants}).
\]  

(4-56)

This analysis has been applied to the ethylene case in Chapter 7.
The complete error treatment presented in this chapter has been programmed for use in the IBM 360 computer and the programs are presented in Appendix 3. In the following chapters, the force constant refinement procedure, the reduction of the intensity data and the complete error analysis are applied to the ethylene molecule and the results discussed there.
CHAPTER 5
NORMAL COORDINATES OF ETHYLENE

In this chapter, the normal coordinate analysis for the vibrational modes of ethylene is presented. The molecular geometry, internal coordinates and inverse kinetic energy matrix given in this chapter have been used throughout the calculations in Chapter 6. The symmetry properties and corresponding \( U \) matrix transformation applied to the \( G \) and \( F \) matrices are discussed.

1. Geometrical Aspects of the Ethylene Molecule Structural Parameters

The equilibrium bond lengths and angles for \( \text{C}_2\text{H}_4 \) have been taken to be the values reported by Allen and Plyler (80) and have also been used by Machida (41):

- carbon-carbon double bond \((r_{\text{C-C}})\): 1.337 Å
- carbon-hydrogen bond \((r_{\text{C-H}})\): 1.086 Å
- carbon-carbon hydrogen angle \((< \text{CCH})\): 121°19'

From these values, the cartesian coordinates, given in Table 1, are calculated; the numbering of the atoms and the equilibrium configuration of the ethylene molecule are given in Figure 1.

The atomic masses for hydrogen, deuterium and carbon, respectively, are:
### Table 1

**X Matrix for the Ethylene Molecule**

<table>
<thead>
<tr>
<th>Atom</th>
<th>Cartesian Coordinate, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>X</td>
</tr>
<tr>
<td>1</td>
<td>0.6685</td>
</tr>
<tr>
<td>2</td>
<td>-0.6685</td>
</tr>
<tr>
<td>3</td>
<td>1.2330</td>
</tr>
<tr>
<td>4</td>
<td>-1.2330</td>
</tr>
<tr>
<td>5</td>
<td>-1.2330</td>
</tr>
<tr>
<td>6</td>
<td>1.2330</td>
</tr>
</tbody>
</table>
Figure 1. The equilibrium configuration and valence internal coordinates of ethylene. The z-axis perpendicular to the plane, in a right-hand system.

\[ R = 1.337 \ \text{Å} \]
\[ r_1 = r_2 = r_3 = r_4 = 1.086 \ \text{Å} \]
\[ a_1 = a_2 = a_3 = a_4 = 121° \ 19' \]
\[ m_H = 1.008141 \text{ a.m.u.} \]
\[ m_D = 2.014741 \text{ a.m.u.} \]
\[ m_C = 12.003844 \text{ a.m.u.} \]

**Internal displacement coordinates.**—The description of the internal coordinates, valence, bonds and angles of ethylene is given by Machida (41) and described in Figure 1. The valence displacement coordinates are summarized in Table 2. The bending coordinates are weighted by 1Å so that the coordinates describing bending of the CCH\(_3\) angle \( \alpha \), is \( d\Delta \alpha \), with \( d = 1\)Å so that the force constants are all in the same units (mdyn/Å) as described in Appendix 1. This set of internal coordinates is different from the set used by Arnett and Crawford (34) and by Cyvin and Cyvin (37) in the weighing of the bending coordinates; differences occur here in the magnitudes of the G and F matrix elements from earlier workers (41,34) are introduced as discussed in Wilson, Decius and Cross (49).

The out-of-plane valence coordinates were defined by Arnett and Crawford (34) as two out-of-plane bends and one torsion coordinate; on the other hand, Machida (41) chooses four equivalent torsion coordinates, introducing one redundant coordinate. Machida’s presentation is followed in this work.

2. **Symmetry Aspects of the Ethylene Molecule**

The ethylene molecule has the symmetry properties characteristic of the point group \( D_{2h} \). The simplification obtained by applying the symmetry properties to the normal coordinate analysis has been discussed in Chapter 3 and is applied here following the method given by Wilson, Decius and Cross (51).
### TABLE 2

INTERNAL DISPLACEMENT COORDINATES FOR ETHYLENE

<table>
<thead>
<tr>
<th>Coordinate</th>
<th>Atoms</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R^a$</td>
<td>1-2</td>
<td>$\Delta r_{C=C}$ stretching</td>
</tr>
<tr>
<td>$r_1$</td>
<td>1-3</td>
<td>$\Delta r_{C-H}$ stretching</td>
</tr>
<tr>
<td>$r_2$</td>
<td>2-4</td>
<td>$\Delta r_{C-H}$ stretching</td>
</tr>
<tr>
<td>$r_3$</td>
<td>2-5</td>
<td>$\Delta r_{C-H}$ stretching</td>
</tr>
<tr>
<td>$r_4$</td>
<td>1-6</td>
<td>$\Delta r_{C-H}$ stretching</td>
</tr>
<tr>
<td>$\alpha_1$</td>
<td>2-1-3</td>
<td>$d^b\Delta\alpha_1$, $&lt; H-C-C$ bending</td>
</tr>
<tr>
<td>$\alpha_2$</td>
<td>1-2-4</td>
<td>$d\Delta\alpha_2$, $&lt; H-C-C$ bending</td>
</tr>
<tr>
<td>$\alpha_3$</td>
<td>1-2-5</td>
<td>$d\Delta\alpha_3$, $&lt; H-C-C$ bending</td>
</tr>
<tr>
<td>$\alpha_4$</td>
<td>2-1-6</td>
<td>$d\Delta\alpha_4$, $&lt; H-C-C$ bending</td>
</tr>
<tr>
<td>$\tau_1$</td>
<td>3-1-2-4</td>
<td>$d\Delta\tau_1$, $&lt; H-C-C-H$ torsion</td>
</tr>
<tr>
<td>$\tau_2$</td>
<td>3-1-2-5</td>
<td>$d\Delta\tau_2$, $&lt; H-C-C-H$ torsion</td>
</tr>
<tr>
<td>$\tau_3$</td>
<td>6-1-2-4</td>
<td>$d\Delta\tau_3$, $&lt; H-C-C-H$ torsion</td>
</tr>
<tr>
<td>$\tau_4$</td>
<td>6-1-2-5</td>
<td>$d\Delta\tau_4$, $&lt; H-C-C-H$ torsion</td>
</tr>
</tbody>
</table>

*a Here $R$, $r$, $\alpha$, etc., symbolize displacement coordinates

$b$ $d = 1 \, \text{Å}$
The symmetry analysis is summarized in Table 3, using the character table for the point group $D_{2h}$ from Herzberg (81). The character of the reducible representations of the cartesian coordinates, $X_j$, and for the valence displacement coordinates $X_j(R)$, $X_j(r)$ and $X_j(\alpha)$ are obtained according to the formulas of Wilson, Decius and Cross (51) as: $n^\gamma$ the total number of degrees of freedom for each symmetry species; $n_v^\gamma$ the number of vibrational degrees of freedom, and $n^{\gamma(R)}$ the number of vibrational degrees of freedom for each type of valence displacement coordinates. It should be noted here, that the definition of cartesian coordinates (with the z-axis perpendicular to the plane of the $C_2H_4$ molecule, and the x-axis along the C=C bond as in Figure 1) determines the $B_1$, $B_2$ and $B_3$ classification as shown in Table 3. The symmetry coordinates have been given by Machida (41), but the numbering here has been changed to be consistent with that given by Arnett and Crawford (34). The symmetry coordinates we use are given in Table 4. The in-plane symmetry species are $A_{1g}$, $B_{1g}$, $B_{2u}$ and $B_{3u}$, while the out-of-plane symmetry coordinates correspond to the symmetry species $A_u$, $B_{1u}$, $B_{2g}$. The out-of-plane symmetry coordinates are expressed in terms of the valence displacement coordinates $\tau_1$, $\tau_2$, $\tau_3$ and $\tau_4$ by the following formulas (41):

$$\theta_1 = (\tau_2 + \tau_1 - \tau_3 - \tau_4)/2$$
$$\theta_2 = (\tau_2 - \tau_1 - \tau_3 + \tau_4)/2$$
$$\tau = (\tau_1 + \tau_2 + \tau_3 + \tau_4)/2$$

These coordinates are exactly orthogonal to the redundancy condition (41)
### TABLE 3

**CHARACTER TABLE FOR POINT GROUP D\textsubscript{2h}**

**CARTESIAN AND INTERNAL COORDINATE ANALYSIS FOR THE ETHYLENE MOLECULE**

<table>
<thead>
<tr>
<th>D\textsubscript{2h}</th>
<th>E</th>
<th>C\textsubscript{2}(z)</th>
<th>C\textsubscript{2}(y)</th>
<th>C\textsubscript{2}(x)</th>
<th>i</th>
<th>σ(xy)</th>
<th>σ(zx)</th>
<th>σ(yz)</th>
<th>n\textsuperscript{γ}</th>
<th>n\textsuperscript{ν}</th>
<th>n\textsuperscript{γ}\textsubscript{R}</th>
<th>n\textsuperscript{γ}\textsubscript{r}</th>
<th>n\textsuperscript{γ}\textsubscript{α}</th>
<th>n\textsuperscript{γ}\textsubscript{τ}</th>
</tr>
</thead>
<tbody>
<tr>
<td>A\textsubscript{1g}</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>3</td>
<td>3</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>A\textsubscript{1u}</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>B\textsubscript{1g}</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
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<td>R\textsubscript{z}</td>
<td>3</td>
<td>2</td>
<td>0</td>
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<td>1</td>
</tr>
<tr>
<td>B\textsubscript{2g}</td>
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<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
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<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
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<td>-1</td>
<td>1</td>
<td>-1</td>
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<td>R\textsubscript{x}</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B\textsubscript{1u}</td>
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<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>T\textsubscript{z}</td>
<td>2</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>B\textsubscript{2u}</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>T\textsubscript{y}</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>B\textsubscript{3u}</td>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>-1</td>
<td>T\textsubscript{x}</td>
<td>3</td>
<td>2</td>
<td>0</td>
<td>1</td>
<td>1</td>
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</table>

<table>
<thead>
<tr>
<th>X\textsubscript{j}</th>
<th>18</th>
<th>0</th>
<th>0</th>
<th>-2</th>
<th>0</th>
<th>6</th>
<th>2</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>X\textsubscript{j}\textsuperscript{(R)}</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>X\textsubscript{j}\textsuperscript{(r)}</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>X\textsubscript{j}\textsuperscript{(α)}</td>
<td>4</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*See text for description of X\textsubscript{j} and n\textsuperscript{γ}\textsuperscript{(R)}. 

---

*See text for description of X\textsubscript{j} and n\textsuperscript{γ}\textsuperscript{(R)}. 

---

*See text for description of X\textsubscript{j} and n\textsuperscript{γ}\textsuperscript{(R)}.
### Table 4

**Symmetry Coordinates for Ethylene Molecule**

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Coordinate</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>$S_1$</td>
<td>$R$</td>
</tr>
<tr>
<td></td>
<td>$S_2$</td>
<td>$(r_1 + r_2 + r_3 + r_4)/2$</td>
</tr>
<tr>
<td></td>
<td>$S_3$</td>
<td>$(\alpha_1 + \alpha_2 + \alpha_3 + \alpha_4)/2$</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>$S_4$</td>
<td>$\tau$</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>$S_5$</td>
<td>$(r_1 - r_2 + r_3 - r_4)/2$</td>
</tr>
<tr>
<td></td>
<td>$S_6$</td>
<td>$(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4)/2$</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>$S_7$</td>
<td>$(\theta_1 + \theta_2)/\sqrt{2}$</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>$S_8$</td>
<td>$(\theta_1 - \theta_2)/\sqrt{2}$</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>$S_9$</td>
<td>$(r_1 + r_2 - r_3 - r_4)/2$</td>
</tr>
<tr>
<td></td>
<td>$S_{10}$</td>
<td>$(\alpha_1 + \alpha_2 - \alpha_3 - \alpha_4)/2$</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>$S_{11}$</td>
<td>$(r_1 - r_2 - r_3 + r_4)/2$</td>
</tr>
<tr>
<td></td>
<td>$S_{12}$</td>
<td>$(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4)/2$</td>
</tr>
</tbody>
</table>

*The internal coordinates are given in Table 2.*
3. Normal Vibrations

The reducible representation spanned by the normal coordinates vector $Q$ is completely reduced under the symmetry operations of the point group $D_{2h}$. The structure of this representation is identical with that of a set of $3N-6$ cartesian displacement coordinates once the contribution from the translational and rotational modes have been subtracted (see Table 3). The reduced form of the vibrational normal coordinates is easily found by standard methods (51) for the in-plane vibrations:

$$\Gamma(Q) = 3A_{1g} + 2B_{1g} + 2B_{2u} + 2B_{3u};$$

(5-4)

and for the out-of-plane

$$\Gamma(Q) = A_{1u} + B_{2g} + B_{1u}.$$  

(5-5)

It is worth pointing out that only the $B_{2u}$, $B_{3u}$ and $A_{1u}$ modes are infrared active. The form of the normal vibrations is given by Herzberg (81) and reproduced here in Figure 2 for the sake of completeness.

4. The Inverse Kinetic Energy Matrix $G$

The $G$ matrix is constructed by the Wilson's method according to Eq. (2-20). Using the symmetry coordinates, the $12 \times 12$ $G$ matrix in terms of valence displacement coordinates is broken down to smaller blocks along the diagonal according to the transformation given by

$$S_{\text{red}} = (\tau_2 - \tau_1 + \tau_3 - \tau_4)/2$$

(5-3)
Figure 2. Normal vibrations of ethylene.
Eq. (2-21). Table 5 illustrates the form of the symmetrized matrix $G$.
The analytical formulas are given in Table 6 for $\text{C}_2\text{H}_4$; for other iso-
topes, the formulas given by Arnett and Crawford (34) can be applied
provided the correction due to the different weighting of the bending
symmetry coordinates is considered.

5. The Force Field of Ethylene

Force constants in valence displacement coordinates.--The most
general force field for ethylene would have $\frac{1}{2}(3N-6)(3N-5) = 66$ force
constants. Many of these force constants however are equivalent due
to the symmetry of the ethylene molecule. The G.V.F.F. may, then, be
described by 15 distinct in-plane force constants and 3 out-of-plane
force constants. Following the descriptions given by Machida (41) for
the quadratic force constants, $K$ represents a stretch-stretch inter-
action; $H$, bending-bending; $F$, stretching-bending; $G$, out-of-plane
bending-out-of-plane bending; $T$, torsion-torsion. In this form, the
G.V.F.F. of the ethylene is given in Table 8. Two initial sets of
numerical values for the valence force constants are used in the force
constant refinement presented here. The first labelled C in Table 9
is essentially the force field of Crawford, Lancaster and Inskeep (35)
reported by Machida (41) as set 1. The second (M in Table 9) is the
set force constants labelled set 2 by Machida (41). They are given
in Table 9 except for scaling in some of the force constants.

Force constants in symmetry coordinates.--Using the symmetry
coordinates given above, the $F$ matrix is transformed to a block form,
given by Table 5. The method for obtaining the symmetrized $F$ elements
TABLE 5

FACTORIZED FORM OF F AND G MATRICES, EXPRESSED
IN TERMS OF SYMMETRY COORDINATES
TABLE 6

SYMMETRIZED $G$ ELEMENTS FOR $C_2\text{H}_4^*$

<table>
<thead>
<tr>
<th>Species</th>
<th>Coordinate</th>
<th>$G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>$S_1$</td>
<td>$[2\mu_C, 2\mu_C, -2S\mu_C/r_o]$</td>
</tr>
<tr>
<td></td>
<td>$S_2$</td>
<td>$[\mu_H + 2C^2\mu_C, -2CS\mu_C/r_o]$</td>
</tr>
<tr>
<td></td>
<td>$S_3$</td>
<td>$[\text{Sym.}, (\mu_H + 2S^2\mu_C/r_o)]$</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td>$S_4$</td>
<td>$[4\mu_H/S^2r_o^2]$</td>
</tr>
<tr>
<td></td>
<td>$S_5$</td>
<td>$[\mu_H + 2S^2\mu_C, -2S\mu_C(2\rho-C)/r_o]$</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>$S_6$</td>
<td>$[\text{Sym.}, [\mu_H/2 + (2\rho-C)^2 2\mu_C]/r_o^2]$</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>$S_7$</td>
<td>$[2(2\mu_C + \mu_H)/S^2r_o^2]$</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>$S_8$</td>
<td>$[4(\mu_H/2 + (1+2\rho C)^2 \mu_C)/S^2r_o^2]$</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>$S_9$</td>
<td>$[\mu_H + 2S^2\mu_C, 2CS\mu_C/r_o]$</td>
</tr>
<tr>
<td></td>
<td>$S_{10}$</td>
<td>$[\text{Sym.}, 2(\mu_H/2 + \mu_C C^2)/r_o^2]$</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>$S_{11}$</td>
<td>$[\mu_H + 2C^2\mu_C, -2CS\mu_C/r_o]$</td>
</tr>
<tr>
<td></td>
<td>$S_{12}$</td>
<td>$[\text{Sym.}, (\mu_H + 2S^2\mu_C)r_o^2]$</td>
</tr>
</tbody>
</table>

*The symbols are defined as:

$\alpha = \text{equilibrium value of C-C-H angle}$

$C = \cos \alpha, \ S = \sin \alpha$

$\mu_C = \text{reciprocal mass of carbon atom}$

$\mu_H = \text{reciprocal mass of hydrogen atom}$

$r_o = \text{equilibrium C-H bond length; } \rho = \text{ratio of } r_o \text{ to C=C bond length}$
TABLE 7
NUMERICAL VALUES OF SYMMETRIZED G ELEMENTS FOR C\textsubscript{2}H\textsubscript{4} AND C\textsubscript{2}D\textsubscript{4} (UNITS ARE GIVEN IN APPENDIX 1)\textsuperscript{a}

<table>
<thead>
<tr>
<th>Species</th>
<th>C\textsubscript{2}H\textsubscript{4}</th>
<th>C\textsubscript{2}D\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(0.1666)</td>
<td>(0.1666)</td>
</tr>
<tr>
<td></td>
<td>(-0.0866)</td>
<td>(-0.0866)</td>
</tr>
<tr>
<td></td>
<td>(-0.1311)</td>
<td>(-0.1311)</td>
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<tr>
<td></td>
<td>(1.0369)</td>
<td>(0.5413)</td>
</tr>
<tr>
<td></td>
<td>(0.0681)</td>
<td>(0.0681)</td>
</tr>
<tr>
<td></td>
<td>(0.9441)</td>
<td>(0.5239)</td>
</tr>
<tr>
<td>(A\textsubscript{1g})</td>
<td>Sym.</td>
<td>Sym.</td>
</tr>
<tr>
<td>(A\textsubscript{1u})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B\textsubscript{1g})</td>
<td>(1.1135)</td>
<td>(0.6179)</td>
</tr>
<tr>
<td></td>
<td>(-0.2810)</td>
<td>(-0.2810)</td>
</tr>
<tr>
<td></td>
<td>(1.4906)</td>
<td>(1.0704)</td>
</tr>
<tr>
<td>(B\textsubscript{2g})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B\textsubscript{1u})</td>
<td>(3.6216)</td>
<td>(2.4701)</td>
</tr>
<tr>
<td>(B\textsubscript{2u})</td>
<td>(2.6918)</td>
<td>(1.5404)</td>
</tr>
<tr>
<td></td>
<td>(1.1135)</td>
<td>(0.6179)</td>
</tr>
<tr>
<td></td>
<td>(-0.0681)</td>
<td>(-0.0681)</td>
</tr>
<tr>
<td></td>
<td>(0.8792)</td>
<td>(0.4590)</td>
</tr>
<tr>
<td>(B\textsubscript{3u})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
|\(a\) Coordinates as in Table 6.
TABLE 8

FORCE CONSTANTS IN VALENCE DISPLACEMENT COORDINATES
FOR ETHYLENE

<table>
<thead>
<tr>
<th>Label</th>
<th>Definition*</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>$K(C=\text{C}, \text{C}=\text{C})$</td>
</tr>
<tr>
<td>$K_2$</td>
<td>$K(C-\text{H}_i, \text{C}-\text{H}_i)$</td>
</tr>
<tr>
<td>$K_3$</td>
<td>$K(C=\text{C}, \text{C}-\text{H}_i)$</td>
</tr>
<tr>
<td>$K_4$</td>
<td>$K(C-\text{H}_i, \text{C}-\text{H}_j)$ cis</td>
</tr>
<tr>
<td>$K_5$</td>
<td>$K(C-\text{H}_i, \text{C}-\text{H}_k)$ trans</td>
</tr>
<tr>
<td>$K_6$</td>
<td>$K(C-\text{H}<em>i, \text{C}-\text{H}</em>\gamma)$ gem</td>
</tr>
<tr>
<td>$H_1$</td>
<td>$H(\text{CCH}_i, \text{CCH}_i)$</td>
</tr>
<tr>
<td>$H_2$</td>
<td>$H(\text{CCH}_i, \text{CCH}_j)$ cis</td>
</tr>
<tr>
<td>$H_3$</td>
<td>$H(\text{CCH}_i, \text{CCH}_k)$ trans</td>
</tr>
<tr>
<td>$H_4$</td>
<td>$H(\text{CCH}<em>i, \text{CCH}</em>\gamma)$ gem</td>
</tr>
<tr>
<td>$F_1$</td>
<td>$F(\text{C}=\text{C}, \text{CCH}_i)$</td>
</tr>
<tr>
<td>$F_2$</td>
<td>$F(\text{C}-\text{H}_i, \text{CCH}_i)$</td>
</tr>
<tr>
<td>$F_3$</td>
<td>$F(\text{C}-\text{H}_i, \text{CCH}_j)$ cis</td>
</tr>
<tr>
<td>$F_4$</td>
<td>$F(\text{C}-\text{H}_i, \text{CCH}_k)$ trans</td>
</tr>
<tr>
<td>$F_5$</td>
<td>$F(\text{C}-\text{H}<em>i, \text{CCH}</em>\gamma)$ gem</td>
</tr>
<tr>
<td>$G_1$</td>
<td>$G(\theta_i, \theta_i)$</td>
</tr>
<tr>
<td>$G_2$</td>
<td>$G(\theta_i, \theta_j)$</td>
</tr>
<tr>
<td>$T$</td>
<td>$T(\tau, \tau)$</td>
</tr>
</tbody>
</table>

* See Machida, reference 41.
TABLE 9

TWO SETS OF INITIAL VALENCE FORCE CONSTANTS FOR ETHYLENE

ALL UNITS IN mdyn/Å

<table>
<thead>
<tr>
<th>Force Constant</th>
<th>C</th>
<th>M</th>
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</thead>
<tbody>
<tr>
<td>K₁</td>
<td>10.8956</td>
<td>11.7320</td>
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<tr>
<td>K₂</td>
<td>6.1262</td>
<td>5.3966</td>
</tr>
<tr>
<td>K₃</td>
<td>-0.0039</td>
<td>-0.1020</td>
</tr>
<tr>
<td>K₄</td>
<td>-0.0200</td>
<td>-0.0631</td>
</tr>
<tr>
<td>K₅</td>
<td>0.0496</td>
<td>0.0380</td>
</tr>
<tr>
<td>K₆</td>
<td>0.0429</td>
<td>-0.0559</td>
</tr>
<tr>
<td>H₁</td>
<td>1.0744</td>
<td>1.0184</td>
</tr>
<tr>
<td>H₂</td>
<td>0.0720</td>
<td>0.0119</td>
</tr>
<tr>
<td>H₃</td>
<td>0.0005</td>
<td>0.0650</td>
</tr>
<tr>
<td>H₄</td>
<td>0.3484</td>
<td>0.4340</td>
</tr>
<tr>
<td>F₁</td>
<td>0.9068</td>
<td>0.9139</td>
</tr>
<tr>
<td>F₂</td>
<td>0.1376</td>
<td>-0.1966</td>
</tr>
<tr>
<td>F₃</td>
<td>0.2310</td>
<td>-0.4138</td>
</tr>
<tr>
<td>F₄</td>
<td>-0.2310</td>
<td>-0.0395</td>
</tr>
<tr>
<td>F₅</td>
<td>-0.8651</td>
<td>-0.0302</td>
</tr>
<tr>
<td>G₁</td>
<td>0.1710</td>
<td>0.1734</td>
</tr>
<tr>
<td>G₂</td>
<td>0.0264</td>
<td>0.0265</td>
</tr>
<tr>
<td>T</td>
<td>0.1348</td>
<td>0.1370</td>
</tr>
</tbody>
</table>

ᵃC are for Arnett and Crawford given by Machida as set 1; M is Machida's set 2 (41).
from the valence force constants is given by Wilson, Decius and Cross (82) and the results for ethylene are given in Table 10.

It is readily seen that there are 18 unknown symmetry force constants to be fitted to the 12 observed fundamentals of \( \ce{C2H4} \). By using the 12 observed frequencies of \( \ce{C2D4} \), enough extra experimental data are available to determine all the force constants in each symmetry species, except for the \( A_{lg} \) block which has 6 symmetry force constants to be determined from the 3 fundamentals of \( \ce{C2D4} \) and the 3 fundamentals of \( \ce{C2H4} \). However, only 5 of these 6 frequencies are independent due to the isotope rule. In order to solve the problem of determining the force constants from the frequency data, a further restriction is introduced in the symmetrized force field. The usual restriction has been proposed by Crawford, Lancaster and Inskeep (35), adopted by Cyvin and Cyvin (37) and also by Kuchitsu et al. (39); the assumption is expressed as

\[
\frac{A_{lg}}{F_{23}} = \frac{B_{3u}}{F_{12}}. \tag{5-6}
\]

Some justification of this assumption is given by Arnett and Crawford in terms of the physical meaning of Eq. (5-6) but it remains strictly an assumption. We have adopted this same assumption with no further justification.

In terms of the valence force constants, Eq. (5-6) is found to be

\[
F_3 = -F_4. \tag{5-7}
\]
### TABLE 10

**Symmetrized F Elements for Ethylene**

(Units given in Appendix 1)

<table>
<thead>
<tr>
<th>Species</th>
<th>Coordinate</th>
<th>$F \sim$</th>
</tr>
</thead>
</table>
| $A_{1g}$ | $s_1$ | \[ K_1 \ 2K_3 \ 2F_1 \]
| $A_{1u}$ | $s_2$ | \[ K_2 + K_4 + K_5 + K_6 \ F_2 + F_3 + F_4 + F_5 \]
| $B_{1g}$ | $s_3$ | \[ H_1 + H_2 + H_3 + H_4 \]
| $B_{1u}$ | $s_4$ | \[ T \]
| $B_{2g}$ | $s_5$ | \[ K_2 - K_4 + K_5 - K_6 \ F_2 - F_3 - F_4 - F_5 \]
| $B_{2u}$ | $s_6$ | \[ H_1 - H_2 + H_3 - H_4 \]
| $B_{3u}$ | $s_7$ | \[ G_1 + G_2 \]
| $A_{1u}$ | $s_8$ | \[ G_1 - G_2 \]
| $B_{2g}$ | $s_9$ | \[ K_2 + K_4 - K_5 - K_6 \ F_2 + F_3 - F_4 - F_5 \]
| $B_{2u}$ | $s_{10}$ | \[ H_1 + H_2 - H_3 - H_4 \]
| $B_{3u}$ | $s_{11}$ | \[ K_2 - K_4 + K_5 + K_6 \ F_2 - F_3 + F_4 + F_5 \]
| $B_{3u}$ | $s_{12}$ | \[ H_1 - H_2 - H_3 + H_4 \]
From the definitions given in Table 8, $F_3$ and $F_4$ are then C-H stretching-HCC bending interaction terms for the CIS and TRANS configuration, respectively.

The numerical values of the symmetrized force constants evaluated to give the best fit to the frequency data of $C_2H_4$ and $C_2D_4$ with assumption of Eq. (5-6) of Table 9 are given in Table 27, Appendix 2 for set C and in Table 13 for set M.

6. Experimental Data

The observed fundamental frequencies for $C_2H_4$ and $C_2D_4$ in the gas phase have been reported (80,34,35) and values in the solid phase have been given by Dows (83). For the present work we have taken the experimental frequencies as listed by Machida (41) and given here in Table 11. Cyvin and Cyvin (37) have estimated the harmonic frequencies for both $C_2H_4$ and $C_2D_4$ from the observed fundamentals by using Dennison's anharmonicity corrections (64). However, this set (37) of harmonic frequencies does not appear to be entirely satisfactory because some of the anharmonicity constants have unexplained and unexpected negative values. Furthermore, the anharmonicity constants seem to be in contradiction with those obtained by Machida and Overend (42) from a more refined treatment. For these reasons we have used the anharmonic observed frequencies to fix the quadratic force field. We have to consider the rather large resulting frequency uncertainty in the error analysis discussed in the next chapter.

The observed frequencies for the other 5 isotopic species of ethylene are given in Appendix 2. The only other available experimental data useful for fixing the force constants of ethylene are the coriolis
coupling coefficient calculated by Smith and Mills (38) from an analysis of the coriolis interaction in ethylene between $v_7$ and $v_{10}$. In using this information we note that in our definition of cartesian coordinates (Figure 1) and the character table (Table 3) the direction of the coriolis rotation is about the x-axis. In the definition of axes used by Smith and Mills (38) the rotation was about the z-axis. They report $|\zeta(z)_{7,10}| = \zeta(x)_{7,10} = 0.44 \pm 0.02$. In the last section of this chapter, we give the value calculated from our force constants, and the formulas used for the calculations.

7. Force Constants Refinement

The refinement procedure described in Chapter 3 was applied using set M of Table 9, as the initial set $\{\phi_i\}$ together with the observed frequencies from all 7 isotopes (Table 11 and Table 26) with the weights for the frequencies chosen to be 1.0. The problem converged after 11 perturbations. The results are presented here in the following fashion: (a) the calculated frequencies are compared with the observed values for the fundamentals of $C_2H_4$ and $C_2D_4$ in Table 11; (b) the final set of valence force constants and their dispersions are given in Table 12; (c) the symmetrized force constants obtained from the refinement (M27) are presented in Table 13 along with the initial symmetrized force constants (set M); (d) finally, the $L$ and $L^{-1}$ transformation matrices for the force constants (M27) are given in Table 14.

This set of results (M27) has been chosen as the "best" set from all the different calculations that are reported in the next chapter. Discussion of these results will be presented in the next chapter.
TABLE 11

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OBTAINED
FROM THE FORCE CONSTANT REFINEMENT CALCULATION (M27)
FOR C\textsubscript{2}H\textsubscript{4} AND C\textsubscript{2}D\textsubscript{4}. UNITS ARE cm\textsuperscript{-1}

| Symmetry | Assignment | C\textsubscript{2}H\textsubscript{4} | | C\textsubscript{2}D\textsubscript{4} |
|----------|------------|----------------|----------------|
| A\textsubscript{1g} | \nu\textsubscript{1} | 3026.4         | 3016.40        | 2251.0        | 2246.12        |
|          | \nu\textsubscript{2} | 1622.6         | 1631.47        | 1515          | 1508.62        |
|          | \nu\textsubscript{3} | 1342.2         | 1349.85        | 981           | 980.94         |
| A\textsubscript{1u} | \nu\textsubscript{4} | 1023           | 1024.81        | 730.1         | 724.93         |
| B\textsubscript{1g} | \nu\textsubscript{5} | 3102.5         | 3094.57        | 2304          | 2293.06        |
|          | \nu\textsubscript{6} | 1222.0         | 1230.21        | 1009          | 1007.76        |
| B\textsubscript{1u} | \nu\textsubscript{7} | 949.3          | 967.67         | 728.1         | 799.17         |
| B\textsubscript{2g} | \nu\textsubscript{8} | 943            | 960.06         | 786.7         | 726.25         |
| B\textsubscript{2u} | \nu\textsubscript{9} | 3105.5         | 3109.77        | 2345          | 2329.36        |
|          | \nu\textsubscript{10} | 826.0          | 819.80         | 586           | 585.65         |
| B\textsubscript{3u} | \nu\textsubscript{11} | 2988.7         | 3004.63        | 2200.2        | 2189.83        |
|          | \nu\textsubscript{12} | 1443.5         | 1453.05        | 1077.9        | 1066.79        |
TABLE 12

FINAL VALENCE FORCE CONSTANTS $\phi_i$ FOR ETHYLENE AND THEIR DISPERSIONS [$\sigma(\phi_i)$]. UNITS ARE mdyn/Å

<table>
<thead>
<tr>
<th>Description</th>
<th>$\phi_i$</th>
<th>$\sigma(\phi_i)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_1$</td>
<td>10.9209</td>
<td>0.2230</td>
</tr>
<tr>
<td>$K_2$</td>
<td>5.0638</td>
<td>0.0288</td>
</tr>
<tr>
<td>$K_3$</td>
<td>0.1955</td>
<td>0.1747</td>
</tr>
<tr>
<td>$K_4$</td>
<td>-0.0324</td>
<td>0.0320</td>
</tr>
<tr>
<td>$K_5$</td>
<td>0.0627</td>
<td>0.0432</td>
</tr>
<tr>
<td>$K_6$</td>
<td>-0.0252</td>
<td>0.0679</td>
</tr>
<tr>
<td>$H_1$</td>
<td>0.9976</td>
<td>0.0346</td>
</tr>
<tr>
<td>$H_2$</td>
<td>-0.0138</td>
<td>0.0247</td>
</tr>
<tr>
<td>$H_3$</td>
<td>0.0438</td>
<td>0.0392</td>
</tr>
<tr>
<td>$H_4$</td>
<td>0.4202</td>
<td>0.0586</td>
</tr>
<tr>
<td>$F_1$</td>
<td>0.8253</td>
<td>0.0967</td>
</tr>
<tr>
<td>$F_2$</td>
<td>0.1557</td>
<td>0.2360</td>
</tr>
<tr>
<td>$F_3$</td>
<td>-0.2169</td>
<td>0.1512</td>
</tr>
<tr>
<td>$F_4$</td>
<td>0.2169</td>
<td>0.1512</td>
</tr>
<tr>
<td>$F_5$</td>
<td>0.2535</td>
<td>0.1070</td>
</tr>
<tr>
<td>$G_1$</td>
<td>0.1769</td>
<td>0.0052</td>
</tr>
<tr>
<td>$G_2$</td>
<td>0.0247</td>
<td>0.0025</td>
</tr>
<tr>
<td>$T$</td>
<td>0.1342</td>
<td>0.0032</td>
</tr>
</tbody>
</table>
**TABLE 13**

INITIAL (M) AND FINAL (M27) SYMMETRIZED F MATRIX FOR ETHYLENE

**UNITs ARE mdyn/Å**

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>M</th>
<th>M27</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>M</td>
<td>M27</td>
</tr>
<tr>
<td>A1g</td>
<td>11.7320</td>
<td>10.9210</td>
</tr>
<tr>
<td></td>
<td>-0.2040</td>
<td>0.3911</td>
</tr>
<tr>
<td></td>
<td>1.8378</td>
<td>1.6506</td>
</tr>
<tr>
<td></td>
<td>5.3156</td>
<td>5.0689</td>
</tr>
<tr>
<td>Sym.</td>
<td>-0.6801</td>
<td>0.4092</td>
</tr>
<tr>
<td></td>
<td>1.5293</td>
<td>1.4480</td>
</tr>
<tr>
<td>A1u</td>
<td>0.1370</td>
<td>0.1342</td>
</tr>
<tr>
<td>B1g</td>
<td>5.5536</td>
<td>5.1841</td>
</tr>
<tr>
<td></td>
<td>0.2079</td>
<td>0.3361</td>
</tr>
<tr>
<td>Sym.</td>
<td>0.6375</td>
<td>0.6350</td>
</tr>
<tr>
<td>B1u</td>
<td>0.1999</td>
<td>0.2016</td>
</tr>
<tr>
<td>B2g</td>
<td>0.1469</td>
<td>0.1522</td>
</tr>
<tr>
<td>B2u</td>
<td>5.3514</td>
<td>4.9940</td>
</tr>
<tr>
<td></td>
<td>-0.5407</td>
<td>-0.5316</td>
</tr>
<tr>
<td>Sym.</td>
<td>0.5313</td>
<td>0.5196</td>
</tr>
<tr>
<td>B3u</td>
<td>5.3658</td>
<td>5.0083</td>
</tr>
<tr>
<td></td>
<td>0.2265</td>
<td>0.4092</td>
</tr>
<tr>
<td>Sym.</td>
<td>1.3755</td>
<td>1.3878</td>
</tr>
</tbody>
</table>

*a* Coordinates as defined in Table 10.
### Table 14

Elements of $L$ and $L^{-1}$ matrices and their dispersions for $C_2H_4$ resulting force constant set M27

<table>
<thead>
<tr>
<th>Species</th>
<th>$L_{ji}$</th>
<th>$\sigma(L_{ji})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>-0.1121 1.0127 0.1607</td>
<td>0.0231 0.0207 0.2033</td>
</tr>
<tr>
<td></td>
<td>0.3464 0.0221 0.1756</td>
<td>0.0103 0.0720 0.0554</td>
</tr>
<tr>
<td></td>
<td>-0.1846 -0.1046 0.9420</td>
<td>0.0134 0.0307 0.0059</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td></td>
<td>2.1469</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>1.0541 -0.2105</td>
<td>0.0063 0.1552</td>
</tr>
<tr>
<td></td>
<td>-0.0492 1.2026</td>
<td>0.0022 0.0004</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td></td>
<td>1.6407</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td></td>
<td>1.9031</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>1.0493 -0.1629</td>
<td>0.0064 0.0528</td>
</tr>
<tr>
<td></td>
<td>0.1114 0.9234</td>
<td>0.0047 0.0007</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>1.0107 0.1848</td>
<td>0.0185 0.1415</td>
</tr>
<tr>
<td></td>
<td>-0.1244 0.9539</td>
<td>0.0083 0.0015</td>
</tr>
</tbody>
</table>

Coordinates as defined in Table 10.
<table>
<thead>
<tr>
<th>Species</th>
<th>$L^{-1}_{ij}$</th>
<th>$\sigma(L^{-1})_{ij}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>0.1051 -0.9621 -0.0862</td>
<td>0.0183 0.0330 0.2202</td>
</tr>
<tr>
<td></td>
<td>-2.6039 -0.2038 0.2022</td>
<td>0.0269 0.0723 0.0577</td>
</tr>
<tr>
<td></td>
<td>-0.0862 -0.5328 -0.9474</td>
<td>0.0885 0.0273 0.0169</td>
</tr>
<tr>
<td>$A_{1u}$</td>
<td></td>
<td>0.4658</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>0.9565 0.0391</td>
<td>0.0216 0.1082</td>
</tr>
<tr>
<td></td>
<td>0.1674 0.8384</td>
<td>0.0020 0.0001</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td></td>
<td>0.6095</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td></td>
<td>0.5255</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>0.9355 -0.1128</td>
<td>0.0094 0.0608</td>
</tr>
<tr>
<td></td>
<td>0.1651 1.0630</td>
<td>0.0042 0.0005</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>0.9664 0.1260</td>
<td>0.0278 0.1591</td>
</tr>
<tr>
<td></td>
<td>-0.1873 1.0239</td>
<td>0.0079 0.0010</td>
</tr>
</tbody>
</table>
8. Coriolis Coupling Coefficient $\zeta_{7,10}^{(x)}$

The coriolis coupling coefficients are obtained from Eq. (2-22)

$$\zeta^{(x)} = \zeta^{-1} \zeta^{\alpha} (L^{-1}),$$

(5-8)

where $\zeta^{\alpha}$ is defined by Eq. (2-24) and depends on the geometry and masses of the molecule only. For the $\zeta_{7,10}^{(x)}$ coefficient of ethylene we obtain from Eq. (5-8)

$$\zeta_{7,10}^{(x)} = L^{-1} C_{7,9}^{(x)} L^{-1} + L^{-1} C_{7,10}^{(x)} L^{-1}$$

(5-9)

The $C_{7,9}^{(x)}$ and $C_{7,10}^{(x)}$ elements in the coordinate system we are using are given as:

$$C_{7,9}^{(x)} = -2/(2\mu_C + \mu_H)r_o^2 = 1.46372,$$

and

$$C_{7,10}^{(x)} = -2C/(2\mu_C + \mu_H)r_o^2 s = 0.89054.$$

(5-10)

The symbols in Eqs. (5-10) are defined in the footnote of Table 6. The $L^{-1}$, $L^{-1}$, $L^{-1}$ elements are given in Table 14.

We obtain then for our calculated value of $\zeta_{7,10}^{(x)}$ a value of $0.430 \pm 0.004$ to be compared with the observed value of $0.440 \pm 0.02$.

The coriolis coupling coefficients are dimensionless.
In the discussion presented in Chapter 3, it has been pointed out that the choice of the initial set of force constants, the choice of the weights used for the observed data in the least-squares refinement, and the number of isotopic species providing frequency data are three of the important factors to be considered in analyzing the force constants calculated by the refinement procedure. Furthermore, it has been said there that the final set of force constants obtained from the perturbation may not be unique just because it fits the observed data even when there are more independent frequencies than force constants to be fixed. These comments about the uncertainties in force constants imply that the $L$ and $L^{-1}$ matrices obtained in the calculation may also be subject to the same uncertainties.

In Chapter 4, we have outlined an error analysis procedure which gives the dispersions for the calculated force constants, for the $L$ and $L^{-1}$ matrices, for calculated frequency and coriolis parameters, etc. These dispersions are interpreted as a semi-quantitative measure of the uncertainties in the calculated values, so that the smaller the dispersion, the more reliable the calculated value.

The treatment has been applied to the 9 in-plane vibrations of ethylene since the 3 out-of-plane modes each factor by symmetry to a one-by-one matrix for which there is only one force constant to be fixed and one observed frequency for each out-of-plane symmetry.
species, leaving the out-of-plane problem completely determined. The results for the out-of-plane force constants and $L$ and $L^{-1}$ elements were given in Chapter 5.

The results of these sensitivity studies are presented in Progress Reports No. 1, 2 and 3 as computer output since they are rather lengthy and not absolutely necessary for the presentation and discussion of the problems treated in this chapter.

1. Description of the Problems

In order to investigate the sensitivity of the $L$ matrix elements to the choice of different initial force fields, three different sets have been considered. The first, proposed by Crawford et al. (35), is called set C (Table 9); the second, proposed by Machida (41), is here called set M (Table 9) and the third was given by Cyvin and Cyvin (37) and is called set Cy here. The symmetry force constants for the three initial sets are given in Tables 13 and 27.

In order to study the effect on the $L$ matrix of the different statistical weights for the observed frequencies, we made calculations using weights of $1/\lambda_1$ and 1.0; the weight $1/\lambda_1^2$ was considered also, but unsuccessfully, since none of the problems converged when this weight ($1/\lambda_1^2$) was used. The choice of weights has been discussed in Chapter 4.

The number of isotopic molecules used was either 2 ($C_2H_4$ and $C_2D_4$) or 7, including data from all partially denterated ethylenes (from Table 26). The frequencies proposed by Cyvin and Cyvin (37) were used (Table 25) with the Cy initial force constants and also with the C initial force constants.
In order to classify the different sets of results, a summary is presented and labelled in Table 15.

2. Presentation of the Results

For each of the 12 problems defined in Table 15, a set of results is obtained that is equivalent to those presented in the previous chapter for problem M27; namely, calculated frequencies, valence force constants and their dispersions, symmetry force constants and the transformation matrices $L$ and $L^{-1}$ with dispersions.

These results are presented here in display graphs in Figures 3-16, for symmetry force constants (Figures 3-6), valence force constants (Figures 7-10) and the $L$ matrix elements (Figures 11-16). The actual numerical values are available elsewhere as computer output (laboratory reports No. 1, 2 and 3 by Gustavo E. Sanchez). On each of the figures the vertical line represents the dispersion.

3. Discussion of Results

Symmetry force constants.—The $A_{1g}$ symmetry block of ethylene contains six force constants. Figure 3 presents the results for all problems described in Table 15. While the diagonal force constants do not fluctuate too badly, the off-diagonal values do. As discussed elsewhere, there are not enough independent observed data for this symmetry species to fix the $A_{1g}$ force field uniquely, so that it remains undetermined. The constraint $F_{23}^R = F_{12}^{3u}$ imposed on the force field, as explained in Chapter 5, makes the problem determined but it is difficult to assess the validity of the assumption. Recently, McKean and Duncan (84) have used $C^{13}$ isotopic derivatives of ethylene
TABLE 15

SUMMARY OF PROBLEMS STUDIED TO DETERMINE $\mathbf{L}$ MATRIX SENSITIVITY FOR THE IN-PLANE VIBRATIONS OF ETHYLENE

<table>
<thead>
<tr>
<th>Problem Label</th>
<th>Initial Force Constant</th>
<th>Frequency Data Used$^a$</th>
<th>Weight</th>
<th>Number of Isotopic Molecules</th>
<th>Variance$^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>M</td>
<td>C</td>
<td>Obs.</td>
<td>1.0</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Cy</td>
<td></td>
<td>Harm.</td>
<td></td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>CIH</td>
<td>C</td>
<td>Harm.</td>
<td>1/λ</td>
<td>2</td>
<td>0.0</td>
</tr>
<tr>
<td>C2</td>
<td>C</td>
<td>Obs.</td>
<td>1.0</td>
<td>2</td>
<td>0.0012</td>
</tr>
<tr>
<td>CI</td>
<td>C</td>
<td>Obs.</td>
<td>1/λ</td>
<td>2</td>
<td>0.0013</td>
</tr>
<tr>
<td>C3</td>
<td>C</td>
<td>Obs.</td>
<td>1/λ$^2$</td>
<td>2</td>
<td>div.</td>
</tr>
<tr>
<td>M2</td>
<td>M</td>
<td>Obs.</td>
<td>1.0</td>
<td>2</td>
<td>0.0012</td>
</tr>
<tr>
<td>M1</td>
<td>M</td>
<td>Obs.</td>
<td>1/λ</td>
<td>2</td>
<td>div.</td>
</tr>
<tr>
<td>M3</td>
<td>M</td>
<td>Obs.</td>
<td>1/λ$^2$</td>
<td>2</td>
<td>div.</td>
</tr>
<tr>
<td>Cl7</td>
<td>C</td>
<td>Obs.</td>
<td>1/λ</td>
<td>7</td>
<td>div.</td>
</tr>
<tr>
<td>M17</td>
<td>M</td>
<td>Obs.</td>
<td>1/λ</td>
<td>7</td>
<td>0.0194</td>
</tr>
<tr>
<td>C27</td>
<td>C</td>
<td>Obs.</td>
<td>1.0</td>
<td>7</td>
<td>div.</td>
</tr>
<tr>
<td>M27</td>
<td>M</td>
<td>Obs.</td>
<td>1.0</td>
<td>7</td>
<td>0.0530</td>
</tr>
</tbody>
</table>

$^a$Obs. = Observed from Tables 11 and 26.

Harm. = "Harmonic" from Cyvin and Cyvin (37).

$^b$Variance is defined by Eq. (3-19).

"div." means the problem diverged in the perturbation force constant refinement, so that no results were obtained.
Figure 3. Display graph for the $A_g$ symmetry force constants for ethylene.
Figure 4. Display graph for the $B_{1g}$ symmetry force constants for ethylene.
Figure 5. Display graph for the $B_{2u}$ symmetry force constants for ethylene.
Figure 6. Display graph for the $B_{3u}$ symmetry force constants for ethylene.
Figure 7. Display graph for the diagonal valence force constants for ethylene.
Figure 8. Display graph for the stretch-stretch interaction valence force constants for ethylene.
Figure 9. Display graph for the bend-bend interaction valence force constants for ethylene.
Figure 10. Display graph for the stretch-bend interaction valence force constants for ethylene.
Figure 11. Display graph for the $A_g$ symmetry eigenvector 1 of the normal coordinates transformation matrix.
Figure 12. Display graph for the $A_g$ symmetry eigenvector 2 of the normal coordinates transformation matrix.
Figure 13. Display graph for the $A_g$ symmetry eigenvector 3 of the normal coordinates transformation matrix.
Figure 14. Display graph for the $B_{1g}$ symmetry eigenvectors of the normal coordinates transformation matrix.
Figure 15. Display graph for the $B_{2u}$ symmetry eigenvectors of the normal coordinates transformation matrix.
Figure 16. Display graph for the $B_{3u}$ symmetry eigenvectors of the normal coordinates transformation matrix.
to determine the $A_{1g}$ symmetry force field but they constrained $F_{23}^{Ag}$ to zero and no basic differences from our results are reported by them.

The $B_{1g}$, $B_{2u}$, $B_{3u}$ symmetry species (Figures 4-6) each contain 3 symmetry force constants so that enough independent frequency data apparently are available for a unique determination of the force constants. Nevertheless, the off-diagonal terms, in general, seem to be ill-determined as judged by the fluctuations in the values. Only for the $B_{1g}$ species do the values for all three force constants seem to be well-defined.

In order to try to understand the behavior of the symmetry force constants, we have analyzed them to obtain the values of the valence force constants presented in Figures 7 through 10. The relationships among valence force constants and symmetry force constants are given in Table 10 of Chapter 5, while the definitions of the valence force constants are given in Table 8 of the same chapter. The stretching-stretching interaction force constants, $K_1$, of Figure 8 are all small nearly zero, with large dispersions. Problem CIH, in which harmonic frequencies were used, shows the largest deviation which is not surprising since the uncertain anharmonicity corrections are towards higher stretching frequencies and correspondingly higher force constants. Nevertheless, the fluctuations in values for the $K_1$ constants seem to be of little importance compared to those of $K_2$, the C-H stretching-stretching diagonal force constant (Figure 7). This fact accounts for the good behavior of the symmetry force constants $F_{22}^{A_{1g}}$, $F_{11}^{B_{1g}}$, $F_{11}^{B_{2u}}$ and $F_{11}^{B_{3u}}$ for all problems with the exception of problems Cy, and CIH for which harmonic frequencies were used.
Similarly, the bending-bending interaction force constants $H_1$ (Figure 9) are nearly zero, with large dispersions; $H_1$ is the largest value of all $H_i$ (Figure 7) and hence determines the symmetry force constants $A_{1g}, B_{1g}, B_{2u}$ accounting for the good behavior of these force constants. The anharmonicity of the bending frequencies is not as prominent so that results from problems Ck and CjH do not differ very much from the other values.

Finally, the stretch-bend interaction force constants, $F_i$, determine the value of the off-diagonal symmetry force constants. The $F_i$'s (Figure 10) have large dispersions and this fact is reflected in the fluctuations of the off-diagonal terms of the symmetry force constants.

Normal coordinates transformation matrix.---Figures 11 through 16 are display graphs of the $L$ matrix elements. In general, the diagonal elements of the $L$ matrix also seem to be well-determined and insensitive to the changes in the off-diagonal terms of the potential function. They have small dispersions and, in general, the value is almost constant for all cases considered. The off-diagonal values, though, are much more sensitive toward the indeterminacy of the off-diagonal terms in the potential function, or in other words, towards the stretch-bend interaction constants that carry the largest dispersions in the force field.

4. Sensitivity of the $L$ Matrix Coefficients

In Chapter 4, the dispersions for the force constants and $L$ matrix have been discussed and the true meaning of the dispersions has been presented. A large dispersion in the $L$ coefficients is
interpreted as high sensitivity to the uncertainty in the frequencies and thus in the force constants, while a small dispersion in a given coefficient is evidence of the insensitivity of that coefficient toward changes in the force field. Several factors are involved in the determination of the dispersions for the force constants according to Eq. (4-19). By assuming linear propagation of errors, the L coefficients are subject to the same uncertainties as the force constants, as given by Eqs. (4-21) and (4-22). Thus, as for the dispersion of the force constants the most important factors affecting the determination of the dispersions in L are the choice of initial set of force constants, the choice of weights in the observed data used for the force constant refinement procedure, and the number of isotopic species whose frequencies are included in the least-square method.

From Figures 12 through 16 the general feature is that the diagonal terms carry a much smaller dispersion than do the off-diagonal terms, so that the diagonal L elements are virtually independent of the uncertainty in the force field. The off-diagonal terms, on the other hand, are highly sensitive to the factors mentioned above.

A similar consideration can be applied to the pair of problem C2 and Cl, M and M2, M17 and M27 in which the basic difference is in the weight used for the observed data, namely, 1.0 and 1/\(\lambda\) respectively for each pair. The results are not dependent on the choice of weights but larger dispersions are obtained for weights of 1/\(\lambda_i^2\). Those problems in which 1/\(\lambda_i^2\) were used as weight diverged, showing that the normal equation matrix \(A\) becomes ill-conditioned when the weights are too small for the larger frequencies, making it much more difficult for the calculation to converge.
As for the number of isotopic molecules whose frequencies are included, problems M17 and M27 have data from isotopic species providing a total of 63 observed frequencies. However, the Brodersen and Langseth (9) treatment of the complete isotope rule suggests that no extra information is introduced by these extra data that is not contained in the data from \(\text{C}_2\text{H}_4\) and \(\text{C}_2\text{D}_4\) so that the refinement procedure is statistical in nature and the larger the number of observed data, the better the behavior of the statistically determined quantities. This fact is reflected in the smaller dispersions for problems M17 and M27 compared to the other problems.

Finally, it should be pointed out once more that the final set of force constants as it comes out of the refinement procedure, as discussed in Chapter 3, is not necessarily unique just because it fits the observed data, even when the problem is completely determined by more independent data than force constants. The \(\mathbf{L}\) matrix is subject to the same consideration and arguments about the uniqueness of the calculated \(\mathbf{L}\) transformation matrix are hard to prove. Nevertheless, the reasonable behavior of the \(\mathbf{L}\) coefficients gives us enough confidence to believe that unique \(\mathbf{L}\) matrices have, in fact, been determined within the dispersions. It is seen from the figures that the diagonal terms of the \(\mathbf{L}\) transformations are well behaved and the off-diagonal coefficients in certain cases [like those of the \(E_{1g}\) symmetry species (Figure 14)] are well determined. The worst case occurs for the \(A_{1g}\) symmetry species, but then again it is this species which cannot be properly determined because of the lack of sufficient data to fix all six force constants in that force field.
5. Coriolis Coupling Coefficients $\zeta_{7,10}^{(x)}$

As pointed out by Smith and Mills (38) the coriolis coupling coefficient $\zeta_{7,10}^{(x)}$ between $v_1$ and $v_{10}$ provides an extra piece of information for the determination of the force constants of the $B_{2u}$ symmetry species to which $v_{10}$ belongs. The value of $\zeta_{7,10}^{(x)}$ is calculated by Eq. (5-9). Table 16 presents the calculated values of $\zeta_{7,10}^{(x)}$ for problems C, M, Cy, ClH, C2, M17 and M27.

Since the $L_{77}^{-1}$ coefficient is determined from the G matrix element of the $B_{1u}$ species and since the values of $C_{7,9}^{(x)}$ and $C_{7,10}^{(x)}$ depend only on the geometry and masses of the molecule from which we assume no significant errors, the approximate uncertainty in the calculated value in $\zeta_{7,10}^{(x)}$ can be obtained from

$$\Delta \zeta_{7,10}^{(x)} = (L_{77}^{-1} C_{7,9}^{(x)}) \Delta L_{10,9}^{-1} + (L_{77}^{-1} C_{7,10}^{(x)}) \Delta L_{10,110}^{-1} \quad (6-1)$$

We approximate $\Delta L_{10,9}^{-1}$ and $\Delta L_{10,110}^{-1}$ by the dispersions in those elements and since the first is much larger than the second, the dispersion in $L_{10,9}^{-1} [\sigma(L_{10,9}^{-1})]$ determines the approximate dispersion in $\zeta_{7,10}^{(x)}$.

The experimental value for $\zeta_{7,10}^{(x)}$ given by Smith and Mills (38) is $0.44 \pm 0.02$. We have also included in Table 16 the result calculated by Kuchitsu, Oka and Morino (39), labelled KOM.

From Table 16 we see that the coriolis coupling coefficient does help determine the value for $L_{10,9}^{-1}$. It is easily seen that $L_{10,9}^{-1}$ cannot be negative, as in problem C, since a negative value predicts a value for the coriolis coupling coefficient that is much too high.
# TABLE 16

**CALCULATED CORIOLIS COUPLING COEFFICIENT**

\(\zeta(x)\) **FOR ETHYLENE FROM DIFFERENT PROBLEMS**

<table>
<thead>
<tr>
<th>Problem(^a)</th>
<th>(L^{-1}_{10,9})</th>
<th>(\sigma(L^{-1}_{10,9}))</th>
<th>(L^{-1}_{10,10})</th>
<th>(\sigma(L^{-1}_{10,10}))</th>
<th>(\zeta(x)_{7,10})</th>
<th>(\Delta\zeta_{7,10})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>-0.147</td>
<td>0.175</td>
<td>1.358</td>
<td>0.044</td>
<td>0.692</td>
<td>0.180</td>
</tr>
<tr>
<td>M</td>
<td>0.160</td>
<td>0.168</td>
<td>1.064</td>
<td>0.019</td>
<td>0.435</td>
<td>0.187</td>
</tr>
<tr>
<td>Cy(^b)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.492</td>
<td></td>
</tr>
<tr>
<td>CIH</td>
<td>0.064</td>
<td>0.062</td>
<td>1.069</td>
<td>0.083</td>
<td>0.524</td>
<td>0.145</td>
</tr>
<tr>
<td>C2</td>
<td>0.380</td>
<td>0.058</td>
<td>1.007</td>
<td>0.024</td>
<td>0.298</td>
<td>0.082</td>
</tr>
<tr>
<td>M17</td>
<td>0.218</td>
<td>0.008</td>
<td>1.055</td>
<td>0.001</td>
<td>0.378</td>
<td>0.009</td>
</tr>
<tr>
<td>M27</td>
<td>0.165</td>
<td>0.004</td>
<td>1.063</td>
<td>0.0</td>
<td>0.430</td>
<td>0.005</td>
</tr>
<tr>
<td>KOM(^b)</td>
<td>0.119</td>
<td>0.983</td>
<td></td>
<td></td>
<td>0.440</td>
<td></td>
</tr>
<tr>
<td>Experimental(^c)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.440</td>
<td>0.02</td>
</tr>
</tbody>
</table>

\(^a\)See Table 15 for definitions.

\(^b\)The values Cy\(^*\) and Morino\(^*\) are those of References (85) and (39). No errors are given for these values by their authors.

\(^c\)From Smith and Mills (38).
Similarly, those values of $\zeta_{7,10}^{(x)}$ calculated from problems CIH, C2, M17 are in poorer agreement with the experimental value than are those from M and M27 both of which predict $\zeta_{17,10}^{(x)}$ within the experimental error.

Since the force constants of $B_{2u}$ symmetry determine the values of $L$ and $L^{-1}$, for that symmetry species the coriolis coupling coefficient does help to fix the value of the force constants for the $B_{2u}$ symmetry species. Transforming Eq. (2-15) we obtain

$$F = (L^{-1})' \Lambda L^{-1}$$

and, for the present case

$$F_{B_{2u}}^{9,10} = L_{99}^{-1} L_{910}^{-1} \lambda_9 + L_{10,9}^{-1} L_{10,10}^{-1} \lambda_10.$$ 

Since the diagonal terms of the $L^{-1}$ matrix are well determined from any set of force constants (Figure 15) and $L_{10,9}^{-1}$ is determined from the coriolis coupling coefficient as described above, $F_{B_{2u}}^{9,10}$ is therefore determined more exactly. Table 17 gives the values of the force constants for the $B_{2u}$ symmetry species for problems C, M, Cy, M, CIH, C2, M17 and M27. We include here also the values reported by Kuchitzu, Oka and Morino (39), labelled KOM, and those reported by Smith and Mills (38), labelled SM. All literature values have been corrected from the coordinate system reported by the authors to the coordinate system used in this work, for comparison purposes.

The agreement between sets M, M27, KOM and SM, which all reproduce the coriolis coupling coefficient, is quite satisfying. This is one of the reasons for choosing set M27 as the best of our results to be presented in Chapter 5, besides the fact that the weights and number of isotopes used make it preferable to the other sets.
### TABLE 17

**SYMMETRY FORCE CONSTANTS FOR THE B$_{2u}$ SYMMETRY SPECIES OF ETHYLENE**

<table>
<thead>
<tr>
<th>Problem $^b$</th>
<th>$B_{2u}^{F_{11}}$</th>
<th>$B_{2u}^{F_{22}}$</th>
<th>$B_{2u}^{F_{12}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>6.014</td>
<td>0.797</td>
<td>1.465</td>
</tr>
<tr>
<td>M</td>
<td>5.351</td>
<td>0.531</td>
<td>-0.541</td>
</tr>
<tr>
<td>CIH</td>
<td>5.687</td>
<td>0.460</td>
<td>0.039</td>
</tr>
<tr>
<td>C2</td>
<td>4.364</td>
<td>1.138</td>
<td>-1.621</td>
</tr>
<tr>
<td>M17</td>
<td>4.875</td>
<td>0.610</td>
<td>-0.820</td>
</tr>
<tr>
<td>M27</td>
<td>4.994</td>
<td>0.520</td>
<td>-0.532</td>
</tr>
<tr>
<td>KOM</td>
<td>5.498</td>
<td>0.492</td>
<td>-0.303</td>
</tr>
<tr>
<td>SM</td>
<td>5.05</td>
<td>0.48</td>
<td>-0.27</td>
</tr>
</tbody>
</table>

$^a$Values leading to agreement with the experimental value of $\zeta_{7,10}$ are underlined.

$^b$Defined in Table 15.
CHAPTER 7

ANALYSIS OF THE INFRARED INTENSITIES OF ETHYLENE

As pointed out in Chapter 1, the problem of interpreting the infrared intensities is manifold (2): the experimental measurement of the intensities; finding the correct $L^{-1}$ transformation matrix, as described in the previous chapter; and the assignment of signs to the dipole moment derivatives, $\partial p/\partial Q_i$, as expressed in Eq. (4-38), only the absolute values are obtained, [Eq. (4-39)]. It is, then, a difficult problem to ascertain the sign of this derivative. The interpretation of these intensity data in terms of pure stretches and bends (the symmetry coordinates $S_j$) is carried out through Eq. (4-40), which can be rewritten as

$$\frac{\partial p}{\partial S_j} = \sum_i (\partial p/\partial Q_i)(\partial Q_i/\partial S_j) = \sum_i (L^{-1})_{ij}(\partial p/\partial Q_i)$$  \hspace{1cm} (7-1)$$

and leads to as many sets of possible values for the derivative with respect to the $j$ symmetry coordinate, $\partial p/\partial S_j$, as there are possible sign combinations for the individual $\partial p/\partial Q_i$'s.

Although it has been previously demonstrated that the signs and approximate magnitudes of the $\partial p/\partial S_j$'s may be calculated by the CNDO method (25) for a large number of molecules, the results for ethylene (29) were apparently an exception as mentioned in Chapter 1. Since a complete error analysis, proposed by Russell, Needham and Overend (33), as given in Chapter 4, may be expected to be helpful
in understanding the discrepancies between the experimental values and the calculated CNDO values, it has been applied to the ethylene molecule in this study.

The experimental study of the infrared vibrational intensities was reported by Golike et al. (22). They were able to choose a set of signs for the dipole moment derivatives by making intensity studies of $\text{C}_2\text{H}_4$, $\text{C}_2\text{D}_4$ and all three $\text{C}_2\text{H}_2\text{D}_2$ molecules since the $\partial p/\partial S_j$ is expected to be invariant toward isotopic substitution (21). However, the values chosen by Golike et al. (22) had sign relationships that did not seem reasonable to them, and that approximate quantum-mechanical calculations by Coulson and Stephen (25) could not justify. Hence, we have reinvestigated the interpretation of the experimental intensities, in the light of a complete error analysis, in order to compare our results with the more recent theoretical values reported by Segal and Klein (27).

1. Results

Table 18 presents the experimental data needed in the calculations of the $\partial p/\partial Q_i$'s, namely, the harmonic frequencies, $\omega_i$, and their dispersions $\sigma(\omega_i)$ [taken as 0.01 $\omega_i$ according to Mills' criterion (65)], the intensities, $\Gamma$, and standard errors, $\Delta \Gamma$, as given by Golike et al. (22), the degree of mixing, $\Delta S$, for overlapped bands and measured experimentally by the same authors, and, finally, the dispersions in the intensities, $\sigma(\Gamma)$, calculated from Eq. (4-45) in the fashion described in Chapter 4.

Table 19 gives the values for $\partial p/\partial Q_i$ obtained in this work using the harmonic frequencies from Table 11 (Chapter 5), and these are
TABLE 18

HARMONIC FREQUENCIES\(^a\) AND DISPERSIONS;\(^b\) EXPERIMENTAL
INTENSITIES, STANDARD DEVIATION, DEGREE OF MIXING\(^c\)
AND DISPERSIONS\(^d\)

<table>
<thead>
<tr>
<th>Symmetry and Mode</th>
<th>(\omega) (\text{cm}^{-1})</th>
<th>(\sigma(\omega)) (\text{cm}^{-1})</th>
<th>(\Gamma) (\text{cm}^2/\text{mole})</th>
<th>(\Delta\Gamma) (\text{cm}^2/\text{mole})</th>
<th>(\Delta S) (\text{cm}^2/\text{mole})</th>
<th>(\sigma(\Gamma)) (\text{cm}^2/\text{mole})</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{C}_2\text{H}_4)</td>
<td>(\nu_9)</td>
<td>3109.77</td>
<td>31.0</td>
<td>801.8</td>
<td>20.6</td>
<td>16.0</td>
</tr>
<tr>
<td>(\nu_{10})</td>
<td>819.80</td>
<td>8.2</td>
<td>65.4</td>
<td>2.0</td>
<td>32.7</td>
<td>32.71</td>
</tr>
<tr>
<td>(\nu_{11})</td>
<td>3004.63</td>
<td>30.0</td>
<td>452.0</td>
<td>22.4</td>
<td>16.0</td>
<td>27.53</td>
</tr>
<tr>
<td>(\text{B}_3\text{u})</td>
<td>(\nu_{12})</td>
<td>1453.05</td>
<td>14.5</td>
<td>676.1</td>
<td>5.6</td>
<td>0.0</td>
</tr>
<tr>
<td>(\text{B}_1\text{u})</td>
<td>(\nu_7)</td>
<td>967.67</td>
<td>9.7</td>
<td>84.02</td>
<td>8.0</td>
<td>0.0</td>
</tr>
<tr>
<td>(\text{C}_2\text{D}_4)</td>
<td>(\nu_9)</td>
<td>2329.36</td>
<td>23.2</td>
<td>520.7</td>
<td>4.7</td>
<td>26.0</td>
</tr>
<tr>
<td>(\nu_{10})</td>
<td>585.65</td>
<td>5.8</td>
<td>7.3</td>
<td>7.3</td>
<td>7.3</td>
<td>14.6</td>
</tr>
<tr>
<td>(\nu_{11})</td>
<td>2189.83</td>
<td>21.9</td>
<td>364.4</td>
<td>2.0</td>
<td>17.3</td>
<td>19.3</td>
</tr>
<tr>
<td>(\text{B}_3\text{u})</td>
<td>(\nu_{12})</td>
<td>1066.79</td>
<td>10.7</td>
<td>481.4</td>
<td>4.8</td>
<td>0.0</td>
</tr>
<tr>
<td>(\text{B}_1\text{u})</td>
<td>(\nu_7)</td>
<td>799.17</td>
<td>8.0</td>
<td>5794.0</td>
<td>52.0</td>
<td>0.0</td>
</tr>
</tbody>
</table>

\(^a\)Harmonic frequencies of problem M27, Table 11.
\(^b\)Dispersions \(\sigma(\omega_i)\) taken as 0.01 \(\omega_i\) according to Mills (65).
\(^c\)Values from Golike et al. (22). See text, Chapter 4.
\(^d\)Dispersions calculated from Eq. (4-45). See reference (33).
TABLE 19
DIPOLE MOMENT DERIVATIVES WITH RESPECT TO NORMAL COORDINATES
ALL UNITS IN Debye/Å. (a.m.u)$^{1/2}$

| Symmetry and Mode | $|\partial \mu / \partial Q_1|$ | $\sigma(\partial \mu / \partial Q_1)$ | $|\partial \mu / \partial Q_1|^a$ | $\sigma(\partial \mu / \partial Q_1)^b$ |
|-------------------|-----------------|-----------------|-----------------|-----------------|
|                   | This work       | Golike et al.   |                  |                  |
| $C_2H_4$          |                 |                 |                  |                  |
| $v_9$             | 0.7883          | 0.0512          | 0.8037          | 0.0258          |
| $B_{2u}$          |                 |                 |                  |                  |
| $v_{10}$          | 0.1131          | 0.0255          | 0.1120          | 0.0644          |
| $v_{11}$          | 0.5847          | 0.0491          | 0.5912          | 0.0258          |
| $B_{3u}$          |                 |                 |                  |                  |
| $v_{12}$          | 0.4881          | 0.0207          | 0.4804          | 0.0051          |
| $B_{1u}$          |                 |                 |                  |                  |
| $v_7$             | 1.3863          | 0.0285          | 1.3730          | 0.0129          |
| $C_2D_4$          |                 |                 |                  |                  |
| $v_9$             | 0.5483          | 0.0426          | 0.5551          | 0.0064          |
| $B_{2u}$          |                 |                 |                  |                  |
| $v_{10}$          | 0.0320          | 0.0121          | 0.0322          | 0.0644          |
| $v_{11}$          | 0.4463          | 0.0338          | 0.4392          | 0.0039          |
| $B_{3u}$          |                 |                 |                  |                  |
| $v_{12}$          | 0.3545          | 0.0157          | 0.3502          | 0.0039          |
| $B_{1u}$          |                 |                 |                  |                  |
| $v_7$             | 1.0462          | 0.0476          | 0.9930          | 0.0103          |

*a*The values of Golike et al. (22) are reported in e.s.u./cm gr$^{1/2}$ and here reduced to Debyes Å$^{-1}$ (a.m.u.$)^{1/2}$. See Appendix 1.

*b*These dispersions are essentially the errors of reference (22).
compared with the reported values of Golike et al. (22) as they used different frequencies in calculating $\frac{\partial p}{\partial q_1}$ from $\Gamma_1$ [Eq. (4-39)]. The values have been corrected to units of Debyes/Å (a.m.u.)$^{1/2}$ with the conversion factors given in Appendix 1.

Table 20 gives the elements of the $L^{-1}$ transformation matrix and their dispersions for the symmetry species of interest: $B_{1u}$, $B_{2u}$ and $B_{3u}$. Figures 17 and 18 are display graphs of these $L^{-1}_{ij}$ elements for the $B_{2u}$ and $B_{3u}$ classes, respectively. (Since $B_{1u}$ belongs to an out-of-plane mode which factors in a one by one matrix, it is determined exactly from the respective $G$ matrix element according to Eq. (3-9), and carries no significant error.) Problems C1H, M2, M17 and M27 were selected among those described in Table 15 as representative. The values reported by Golike et al. are included and labelled $G$ here. The dispersions are represented in the figures by a vertical line.

As it is easily seen from Table 20 and Figures 17 and 18, the diagonal elements, $L^{-1}_{ii}$, have smaller dispersions than the off-diagonal elements. By studying the Jacobian matrices that determine the variance-covariance matrix $\Sigma(L^{-1})$, [Eq. (4-22)], it is found that the off-diagonal elements, $L^{-1}_{ij}$, are more sensitive to the off-diagonal terms of the force constant matrix $F$ which carry larger dispersions, as discussed in Chapter 6.

Since the observed fundamentals for $C_2H_4$ are not known with the accuracy of those for $C_2D_4$, the dispersions are correspondingly larger.

Figures 9 through 22 are display graphs for the $(\partial p/\partial q_j)$'s using our coordinate system and the results of problems C1H, M2, M17 and M27, described in Table 15. The values of Golike et al., corrected to our coordinate system, are included and labelled $G$ here. Each figure presents
<table>
<thead>
<tr>
<th>Isotope</th>
<th>Symmetry</th>
<th>$L^{-1}_{ij}$</th>
<th>$\sigma(L^{-1}_{ij})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{C}_2\text{H}_4$</td>
<td>$B_{2u}$ Q₉</td>
<td>$s_9$ 0.9355 $s_{10}$ -0.1128</td>
<td>0.0094 0.0608</td>
</tr>
<tr>
<td></td>
<td>Q₁₀</td>
<td>0.1615 1.0630</td>
<td>0.0042 0.0005</td>
</tr>
<tr>
<td></td>
<td>$B_{3u}$ Q₁₁</td>
<td>$s_{11}$ 0.9664 $s_{12}$ 0.1260</td>
<td>0.0278 0.0079</td>
</tr>
<tr>
<td></td>
<td>Q₁₂</td>
<td>-0.1873 1.0239</td>
<td>0.1519 0.0010</td>
</tr>
<tr>
<td></td>
<td>$B_{1u}$ Q₇</td>
<td>$s_7$ 0.6095</td>
<td></td>
</tr>
<tr>
<td>$\text{C}_2\text{D}_4$</td>
<td>$B_{2u}$ Q₉</td>
<td>$s_9$ 1.2480 $s_{10}$ -0.1555</td>
<td>0.0862 0.4311</td>
</tr>
<tr>
<td></td>
<td>Q₁₀</td>
<td>0.2961 1.4801</td>
<td>0.0329 0.0041</td>
</tr>
<tr>
<td></td>
<td>$B_{3u}$ Q₁₁</td>
<td>$s_{11}$ 1.3194 $s_{12}$ 0.2016</td>
<td>0.2934 1.0927</td>
</tr>
<tr>
<td></td>
<td>Q₁₂</td>
<td>-0.3701 1.3783</td>
<td>0.0846 0.0129</td>
</tr>
<tr>
<td></td>
<td>$B_{1u}$ Q₇</td>
<td>$s_7$ 0.8058</td>
<td></td>
</tr>
</tbody>
</table>
Figure 17. Display graph for the $B_{2u}$ symmetry elements of the inverse normal coordinates transformation matrix.
Figure 18. Display graph for the $B_{3u}$ symmetry elements of the inverse normal coordinates transformation matrix.
Figure 19. Display graph for $dp/dS_9$ for various choices of sign in $dp/dQ_1$'s for $C_2H_4$ and $C_2D_4$. 
Figure 20. Display graph for $dp/dS_{10}$ for various choices of sign in $dp/dQ_i$'s for $C_2H_4$ and $C_2D_4$. 

[Graph showing values for $P_{10}$ versus $(debyes/Å)$. The graph includes symbols for $C_2H_4$, $C_2D_4$, and other chemical compounds.]
Figure 21. Display graph for $dp/dS_{11}$ for various choices of sign in $dp/dQ_1$'s for $C_2H_4$ and $C_2D_4$. 
Figure 22. Display graph for dp/dS₁₂ for various choices of sign in dp/dQ₁'s for C₂H₄ and C₂D₄.
the values of $p_j$ for the sign choices $(++)$ and $(+-)$ of the $(\partial p/\partial Q_i)'s$; also, the results for both $C_2H_4$ and $C_2D_4$ are included. The calculated dispersions are shown as vertical lines.

Finally, Table 21 gives the reduced $\partial p/\partial S_j$ values for the sign choices $(++) \equiv \partial p/\partial Q_9$ plus and $\partial p/\partial Q_{10}$ plus and $(+-)$ of the $\partial p/\partial Q_i$'s using Eq. (7-1) and the coordinate system and results of problem M27 (Chapter 5); the two other possible sign choices $(- -)$ and $(- +)$ are not included since the magnitudes are those of Table 21 for $(++)$ and $(+-)$, respectively, but with opposite signs. The dispersions, calculated using Eq. (4-5), are independent of the sign choice.

In order to compare our results to those reported by Golike et al. (22) it is necessary to correct the values of Table 21 to the coordinate system used by Golike et al.; namely, the symmetry coordinates defined by Arnett and Crawford (34); the transformation factors are given in Appendix 1. We present our recalculated values for $p_j (= \partial p/\partial S_j)$ in Table 22 (labelled M27) and those from Golike et al. (labelled G), together with the calculated values from CNDO method reported by Segal and Klein (27), for comparison. The underlined values, for the G set, are those selected by Golike et al. as the preferred choice while the underlined values of set M27 are our preferred values as we shall discuss in the next section.
### TABLE 21
VALUES OF $p_j$ FOR $B_{1u}$, $B_{2u}$, $B_{3u}$ SYMMETRY SPECIES OF
$C_2H_4$ AND $C_2D_4$. UNITS IN Debye/A$^a$

<table>
<thead>
<tr>
<th>$B_{2u}$</th>
<th>$\nu_9$</th>
<th>$\nu_{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sign choice of $\partial p/\partial Q_1$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ +</td>
<td>0.725</td>
<td>0.679</td>
</tr>
<tr>
<td>+ -</td>
<td>0.750</td>
<td>0.689</td>
</tr>
<tr>
<td>$\sigma(p_j)$</td>
<td>0.059</td>
<td>0.112</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$B_{3u}$</th>
<th>$\nu_{11}$</th>
<th>$\nu_{12}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>+ +</td>
<td>0.627</td>
<td>0.660</td>
</tr>
<tr>
<td>+ -</td>
<td>0.504</td>
<td>0.517</td>
</tr>
<tr>
<td>$\sigma(p_j)$</td>
<td>0.104</td>
<td>0.566</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>$B_{1u}$</th>
<th>$\nu_7$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>$\pm$</td>
<td>±0.845</td>
</tr>
<tr>
<td>$\sigma(p_j)$</td>
<td>0.017</td>
</tr>
</tbody>
</table>

$a$ Results from problem M27. Coordinate system as in Chapter 5.

$b$ The signs given are for $\partial p/\partial Q_9$ and $\partial p/\partial Q_{10}$ for the $B_{2u}$ class, etc.; two more sets for the signs for the $p_j$'s are obtained by multiplying each row by $-1$. 
<table>
<thead>
<tr>
<th></th>
<th>$B_{2u}$</th>
<th></th>
<th>$B_{3u}$</th>
<th></th>
<th>$B_{1u}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$P_9$</td>
<td>$P_{10}$</td>
<td>$P_{11}$</td>
<td>$P_{12}$</td>
<td>$P_{7}$</td>
</tr>
<tr>
<td>M27$^a$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2H_4$</td>
<td>$++$</td>
<td>0.725</td>
<td>0.163</td>
<td>0.627</td>
<td>0.254</td>
</tr>
<tr>
<td></td>
<td>$++$</td>
<td>0.750</td>
<td>0.007</td>
<td>0.504</td>
<td>-0.397</td>
</tr>
<tr>
<td></td>
<td>$+$ -</td>
<td>0.059</td>
<td>0.025</td>
<td>0.104</td>
<td>0.011</td>
</tr>
<tr>
<td>$C_2D_4$</td>
<td>$++$</td>
<td>0.679</td>
<td>0.137</td>
<td>0.660</td>
<td>0.210</td>
</tr>
<tr>
<td></td>
<td>$+$ -</td>
<td>0.689</td>
<td>0.075</td>
<td>0.517</td>
<td>-0.426</td>
</tr>
<tr>
<td></td>
<td>$\sigma{p_j}$</td>
<td>0.112</td>
<td>0.032</td>
<td>0.566</td>
<td>0.033</td>
</tr>
<tr>
<td>G$^c$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$C_2H_4$</td>
<td>$++$</td>
<td>0.736</td>
<td>0.405</td>
<td>0.554</td>
<td>0.370</td>
</tr>
<tr>
<td></td>
<td>$+$ -</td>
<td>0.770</td>
<td>0.101</td>
<td>0.611</td>
<td>-0.269</td>
</tr>
<tr>
<td></td>
<td>$\sigma{p_j}$</td>
<td>0.026</td>
<td>0.087</td>
<td>0.025</td>
<td>0.004</td>
</tr>
<tr>
<td>$C_2D_4$</td>
<td>$++$</td>
<td>0.704</td>
<td>0.294</td>
<td>0.606</td>
<td>0.361</td>
</tr>
<tr>
<td></td>
<td>$+$ -</td>
<td>0.711</td>
<td>0.172</td>
<td>0.599</td>
<td>-0.268</td>
</tr>
<tr>
<td></td>
<td>$\sigma{p_j}$</td>
<td>0.012</td>
<td>0.12</td>
<td>0.005</td>
<td>0.004</td>
</tr>
<tr>
<td>CNDO$^e$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-1.16</td>
<td>-0.41</td>
<td>0.67</td>
<td>0.09</td>
<td>-1.42</td>
</tr>
</tbody>
</table>

$^a$See text; $^b$ see footnote b, Table 21; $^c$ reference (22); $^d$ errors of reference (22); $^e$ reference (27).
2. Discussion

The values of $p_j$ of Golike et al. (22), labelled $G$ in Table 22 and Figures 19 through 22 in the previous section, have been accepted as correct (2), although the reasons for preferring the sign choices $(+ +)$ for the $B_{2u}$ symmetry class and $(+ -)$ for the $B_{3u}$ symmetry class were not conclusive, even as presented in that paper. As mentioned at the beginning of this chapter, this preferred set was chosen because of the apparent invariance of the $p_j$'s to isotopic substitution.

The results obtained in this study are based on the same intensity measurements of Golike (86), except that different values of the harmonic frequencies were used in obtaining the $(\partial p/\partial q_i)$'s and the inverse normal transformation matrix $L^{-1}$. In our case, we used the results from the force constants of problem M27 (Chapter 5). These new normal coordinates change the apparent isotopic invariance indicated by Golike et al., for the worse. The error analysis for the new $p_j$ values shows clearly that the total dispersion, $\sigma(p_j)$, is much too large to justify any choice of signs either in the $B_{2u}$ or in the $B_{3u}$ class on the basis of isotopic invariance, since the values of $p_j$ for $C_2H_4$ and $C_2D_4$ lie within the combined dispersions for both sign choices (Figures 19 through 22).

However the $p_{12}$ ($B_{3u}$) values lie outside the dispersions suggesting that the initial errors in Table 18 were underestimated for that class, and possibly for others as well. But even in this case (Figure 22), the difference between the $p_{12}$ values of $C_2H_4$ and $C_2D_4$ for both $(+ +)$ and $(+ -)$ choice are so small that no definite answer can be given.
Since it is not possible to choose a sign combination (++) or (+ -) based on the invariance of the \( p_j \)'s to isotopic substitution, and since the calculated values from CNDO have proven to be useful in predicting the correct sign for other molecules (29, 31), we have chosen the (- -) combination for the \( B_{2u} \) class (values underlined in Table 22, taken with opposite sign) and the (++) combination for the \( B_{3u} \) class (underlined values of Table 22) to be preferred on the basis of the agreement between experimental and calculated values. Based on the same argument, the (-) sign is preferred for \( p_7 \) since the calculated CNDO value predicts it to be negative.

Chosen on the above arguments, our preferred values for the \( p_j \)'s are presented in Table 23. The values there are the averages of the two values of \( p_j \) for \( C_2\text{H}_4 \) and \( C_2\text{D}_4 \). An analysis of the different contributions to the total dispersions in the \( p_j \)'s is presented in the same table to show the breakdown of the total dispersions into contributions from dispersions in the intensities, in the frequencies, and in the \( L^{-1} \) elements (the latter from dispersions in the force constants). These different contributions should be interpreted as the dispersions of \( p_j \) if only errors in the frequencies, the intensities or the force constants alone were considered. To obtain the total dispersion \( \sigma(p_j) \) from the contributions, the square root of the sum of the squares of the contributions should be taken. We see that the major contribution to the calculated dispersion is, in most cases, from the experimental error in the intensity measurement. The only exception is for the \( p_{10} \) value in which the uncertainty in the force constants, \( \sigma(f.c.) \), is the largest contribution. Since the force constants for the \( B_{2u} \)
class, to which $p_{10}$ belongs, predict the coriolis coupling coefficient, $\zeta_{7,10}^{(x)}$, as shown in Chapter 6, the dispersions in the $L^{-1}$ coefficients should be even smaller than the ones reported here from consideration of observed frequencies as the only observed data.

Although more accurate measurements of the intensities are desirable before final conclusions concerning the signs can be reached, based on isotopic invariance, the combinations $(- -)$ and $(+ +)$ for the $B_{2u}$ and $B_{3u}$ species, respectively, seem intuitively to be more consistent than do the alternatives. The reasons are presented below, using the charge distortion diagram of Figure 23 to visualize the argument.

For $s_{9}$ of the $B_{2u}$ class, the CH bonds stretch perpendicular to the C-C axis and a negative charge develops in the direction of motion of the H atoms; for $s_{10}$, the "rocking motion" of the CH$_2$, a positive charge develops in the direction of motion of the H atoms. These signs are consistent with those calculated for most hydrocarbons from the CNDO procedure. The signs are almost entirely due to rehybridization effects, but they are consistent.

In the $B_{3u}$ class, the $s_{11}$ motion stretches parallel to the C-C axis and a negative charge is again developed in the direction of motion of the H atoms; for $s_{12}$, the "scissors motion" of the CH$_2$, a positive charge is developed in the direction of motion of the H atoms as in the $p_{10}$ case. When the alternative sign choice $(+ +)$ and $(+ -)$ is assumed (as was done by Golike et al.) the positive charge is developed in different directions with respect to the motion of the H atoms for each class (22). It was this anomalous result that Golike et al. [and
Figure 23. Charge distortion diagram of the $B_{2u}$, $B_{3u}$ and $B_{1u}$ symmetry coordinates of ethylene.
TABLE 23

PREFERRED VALUES FOR THE $p_j$'s AND SIGN CHOICES;
ANALYSIS OF THE TOTAL DISPERSIONS $\sigma(p_j)$. UNITS IN Debye/Å

<table>
<thead>
<tr>
<th>Mode (sign choice)</th>
<th>$p_j$</th>
<th>$\sigma(p_j)$</th>
<th>$\sigma$(int.)</th>
<th>$\sigma$(freq.)</th>
<th>$\sigma$(f.c.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>9 (- -)</td>
<td>-0.70</td>
<td>0.06</td>
<td>0.04</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>10 (- -)</td>
<td>-0.15</td>
<td>0.02</td>
<td>0.03</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>11 (+ +)</td>
<td>+0.64</td>
<td>0.10</td>
<td>0.05</td>
<td>0.02</td>
<td>0.09</td>
</tr>
<tr>
<td>12 (+ +)</td>
<td>+0.23</td>
<td>0.01</td>
<td>0.01</td>
<td>0.01</td>
<td>0.00</td>
</tr>
<tr>
<td>7 (- )</td>
<td>-1.82</td>
<td>0.04</td>
<td>0.03</td>
<td>0.01</td>
<td>0.00</td>
</tr>
</tbody>
</table>
others (2,25,38] found hard to understand.

Figure 23 includes also our preferred values for \( p_j \)'s of
Table 23 and the calculated CNDO values, given in parentheses.

It is customary to reduce further the intensity data to
chemical bond parameters (2) using the geometrical relations given
by Golike et al. (22) in order to determine the change in dipole
moment when just one internal coordinate changes. It is not necessary
in our case to invoke the assumptions of the so-called "bond moment
hypothesis," as described by Overend (2) and by Hornig and McKean (87),
to compute these quantities. We can write the equations in terms of
the derivatives of the total dipole moment with respect to a CH-bond
distance, \( \partial p/\partial r \), and with respect to the CCH-angle, \( \partial p/\partial \alpha \), as follows,
assuming only that a change in \( r \) (or \( \alpha \)) develops a change in \( p \) along the
direction of the bond change

\[
\begin{align*}
(\partial p_y / \partial S_9) &= +2 \sin \alpha (\partial p / \partial r) \quad (7-2) \\
(\partial p_y / \partial S_{10}) &= +2 \sqrt{2} \cos \alpha (\partial p / \partial \alpha) \quad (7-3) \\
(\partial p_x / \partial S_{11}) &= +2 \cos \alpha (\partial p / \partial r) \quad (7-4) \\
(\partial p_x / \partial S_{12}) &= +\sqrt{2} \sin \alpha (\partial p / \partial \alpha) \quad (7-5) \\
(\partial p_z / \partial S_{7}) &= +2 \sqrt{2} (\partial p / \partial \alpha) \quad (7-6)
\end{align*}
\]

A positive value of the total moment vector, \( p \), corresponds
to a positive charge on the hydrogen atom. Table 24 presents the
values for \( \partial p / \partial r \) and \( \partial p / \partial \alpha \) obtained in this work (labelled M27)
compared to those predicted by Golike et al. (22) (labelled G) together
with those values calculated from the CNDO/2 values of the \( p_j \)'s. Our
<table>
<thead>
<tr>
<th></th>
<th>C^a</th>
<th>M27^b</th>
<th>CNDO^c</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>∂ρ/∂r</td>
<td>∂ρ/∂α</td>
<td>∂ρ/∂r</td>
</tr>
<tr>
<td>S9</td>
<td>-0.42</td>
<td>-0.41</td>
<td>-0.67</td>
</tr>
<tr>
<td>S10</td>
<td>+0.25</td>
<td>+0.10</td>
<td>+0.31</td>
</tr>
<tr>
<td>S11</td>
<td>-0.60</td>
<td>-0.61</td>
<td>-0.67</td>
</tr>
<tr>
<td>S12</td>
<td>-0.22</td>
<td>+0.19</td>
<td>+0.09</td>
</tr>
<tr>
<td>S7</td>
<td>±0.64</td>
<td>±0.64</td>
<td>+0.54</td>
</tr>
</tbody>
</table>

^a From reference (22), using their preferred values for p_j's.

^b This work, using our preferred values of p_j's.

^c Obtained from the calculated values for p_j of reference (27).

^d ∂ρ/∂α = μ_{CH}, if the bond moment hypothesis is made.
values for \( \partial p/\partial r \) and \( \partial p/\partial \alpha \) are also included in Figure 23 together with the calculated CNDO values given in parentheses there.

It is seen from Table 24 that all experimental and calculated values are in good agreement. It is worth stressing once more that our choice of \((- -)\) and \((+ +)\) for the sign combinations of \( \partial p/\partial q_i \)'s for the \( B_{2u} \) and \( B_{3u} \) classes, respectively, leads to a better picture of the ethylene molecule than the sign choices of Golike et al.; the \( \partial p/\partial \alpha \) values are consistent, as far as sign is concerned in our case, while those of set \( G \) have opposite signs, a fact which is difficult to understand from the chemical bond moment point of view. Furthermore, the magnitudes agree quite satisfactorily and are consistent with the isotopic invariances, and have given us confidence in the consistency of our final results.

3. Conclusion

The results presented in this chapter and in Chapters 5 and 6 for the molecular vibrational properties of ethylene are the most completely consistent set presently available to our knowledge. Obviously, the conclusions of this chapter are still subject to change when further experimental evidence becomes available. In particular, the force field presented in Chapter 5 could be improved, but mainly for the \( A_{1g} \) symmetry class, when further vibrational-rotational analysis provides additional data from coriolis coupling coefficients and/or centrifugal distortion constants. The interpretation of the intensities could be improved also if a more accurate experimental determination of the intensities were made. The transformation matrices \( L \) and \( L^{-1} \) are not expected to change.
much, even when further information is obtained, in the light of the analysis of Chapter 6; their dispersions, on the other hand, could be greatly reduced, simplifying the interpretation of the intensities. It seems to us that the mathematical machinery, within the harmonic approximation, is consistent in all its complex aspects and the error analysis is a powerful tool in the understanding of the significance of the calculated molecular properties from the experimental data. The series of programs used in all the calculations presented in this thesis can be applied to other polyatomic molecules and the results are confidently expected to be consistent.
APPENDICES
APPENDIX 1
UNITS AND NOTATION

1. Dimensions and Units

Coordinates.--All displacement coordinates, namely, cartesian coordinates vector $\mathbf{X}$, valence displacement coordinates vector $\mathbf{R}$, symmetry coordinates vector $\mathbf{S}$, are given in Å.

Masses.--Atomic masses and reduced masses are given in atomic mass units (a.m.u.) defined by

$$1 \text{ a.m.u.} = \frac{N}{1 \text{ mole}} \quad (A-1)$$

where $N$ is Avogadro's number $= 0.6023 \times 10^{24}$ a.m.u.

Inverse kinetic energy matrix $\mathbf{G}$.--The units of the diagonal elements are given in $(\text{a.m.u.})^{-1}$ when two valence bond coordinates are involved and in $(\text{a.m.u.} \times \text{Å}^2)^{-1}$ when two valence bond coordinates are involved. All other off-diagonal elements are in $(\text{a.m.u.} \times \text{Å})^{-1}$ when defined by one valence bond and one valence bond coordinates.

The same units apply to the elements of the $\mathbf{C}$ matrix of Eq. (3-38) in the determination of the coriolis coupling coefficient. (All coriolis coupling coefficients are dimensionless.)

Frequency parameters $\lambda$.--The dimensions of the observed and calculated frequency parameters are obtained from Eq. (2-14):
\[ \lambda_i = \frac{4\pi c^2}{N_0} \nu_i^2 \]  

(A-2)

where \( c \) is the velocity of light in cm/sec; the wave numbers \( \nu_i \) (or \( \omega_i \) for calculated frequencies) are given in cm\(^{-1}\); \( N_0 \) is Avogadro's number in a.m.u.; the units of \( \lambda_i \) are, then, mdyn Å\(^{-1}\) (a.m.u.)\(^{-1}\) since the value of \( c \) is \( 2.998 \times 10^{10} \) cm/sec

\[ \lambda_i = 5.88852 \times 10^{-7} (\nu_i^2) \text{mdyn Å}^{-1} \text{(a.m.u.)}^{-1}. \]  

(A-3)

Normal coordinate transformation matrix \( L \).—All normal coordinate transformation coefficients are given in (a.m.u.)\(^{-1/2}\) while those of the inverse transformation matrix \( L^{-1} \) are in (a.m.u.)\(^{1/2}\). The units of the normal coordinates vector \( Q \) are in (a.m.u.)\(^{1/2}\) Å.

Jacobi matrices.—The units of the Jacobian matrix \( J \) of elements \( (\partial L/\partial F) \) are (a.m.u.)\(^{-1}\) while those of \( J_1 \) and \( J_2 \) of elements \( (\partial L / \partial F) \) and \( (\partial L^{-1} / \partial F) \), respectively, are in units of (a.m.u.)\(^{-1}\) mdyn\(^{-1}\) Å and (a.m.u.) mdyn\(^{-1}\) Å.

Force constants.—All force constants have units of mdyn Å\(^{-1}\), either in symmetry or valence coordinates.

Intensities \( \Gamma_i \).—These have dimensions of cm\(^2\)/mol. The dimensions of the permanent dipole \( p \) are e.s.u. x cm and the units of the dipole derivatives with respect to the normal coordinate \( Q_j \) are obtained from Eq. (4-39)

\[ (\partial p / \partial Q_j)^2 = \frac{3c^2}{N_\pi} \omega_j \Gamma_j \]  

(A-4)
where \( c \), the velocity of light, has dimensions of cm/sec; \( \omega_j \), the harmonic wave number, is in cm\(^{-1}\), \( \Gamma_j \), the intensity, has units of cm\(^2\)/mol and \( N \), Avogadro's number, have units of gr/mol. Then, the units of \( \partial \rho / \partial Q_j \) are cm\(^{3/2}\) sec\(^{-1}\) gr\(^{-1/2}\). Since \( Q \) has units of gr\(^{1/2}\) cm, the units of the permanent dipole \( \rho \), are cm\(^{5/2}\) sec\(^{-1}\); which gives the relation

\[
1 \text{ e.s.u.} = \text{cm}^{3/2} \text{ sec}.
\]

To reduce to atomic masses, we divide by the factor \( \sqrt{N} \) (a.m.u.)\(^{1/2} \)/gr\(^{1/2}\) and the units of \( \partial \rho / \partial Q_j \) are then

\[
\frac{10^{-12}}{\sqrt{0.6023}} \text{ e.s.u. (a.m.u.)}^{-1/2}
\]

Since 1 Debye is \( 10^{-18} \) e.s.u. x cm, 1 Debye x A\(^{-1}\) is \( 10^{-10} \) e.s.u. All units for \( \rho_j = \partial \rho / \partial S_j \) are in Debye A\(^{-1}\). All units for bond moment derivatives \( \partial \rho / \partial r \) and \( \partial \rho / \partial \alpha \) are in Debye A\(^{-1}\).

### 2. Notes on Matrix Notation

**Definitions.**--A matrix \( A \) is defined as a two-dimensional array of real numbers, with \( n \) rows and \( m \) columns

\[
\begin{bmatrix}
A_{11} & \cdots & A_{1n} \\
A_{21} & \cdots & A_{2n} \\
\vdots & \ddots & \vdots \\
A_{m1} & \cdots & A_{mn}
\end{bmatrix}
\]

(A-6)
if \( n = m \), the matrix is said to be square. If \( n \neq m \), the matrix is rectangular. A vector is defined as a matrix with \( n = 1 \) (a column matrix). A diagonal matrix is a matrix \( \sim \) whose elements \( A_{ij} \) are given by

\[
A_{ij} = \delta_{ij} A_{ij} \quad \text{(A-7)}
\]

where \( \delta_{ij} \) is the Kronecker symbol, \( \delta_{ij} = 1 \) if \( i = j \); \( \delta_{ij} = 0 \) if \( i \neq j \).

The unit matrix \( \sim \) is a diagonal matrix of all elements equal to 1.

A constant matrix \( \sim \) is a diagonal matrix \( \sim \cdot E \). The inverse of matrix \( \sim \) is defined as \( \sim^{-1} \)

\[
\sim \sim^{-1} = \sim^{-1} \sim = E \quad \text{(A-8)}
\]

The determinant of matrix \( \sim \) is expressed as \( \text{det} |\sim| \); or simply \( |\sim| \) if the determinant is zero, the matrix is called singular. If the determinant does not vanish, the matrix is non-singular. Only square non-singular matrices possess an inverse.

The transpose of matrix \( \sim \), given by \( \sim' \) is obtained by interchanging rows and columns. If all elements of matrix \( \sim \) are real, \( \sim \) is called a real matrix. \( \sim \) is said to be symmetric if it is a square matrix of elements \( A_{ij} = A_{ji} \); then

\[
\sim = \sim' \quad \text{(A-9)}
\]

\( \sim \) is said to be orthogonal if it is a square matrix of elements \( A_{ij} = A'_{ij} \); then

\[
\sim = \sim^{-1} \quad \text{or} \quad \sim \sim' = E \quad \text{(A-10)}
\]
and since \( \det |A'| = \det |A| \),

\[
(\det |A|)^2 = 1 .
\]  

**(Properties)**—The transpose of a product of several matrices is obtained by inverting the order of the matrices in forming the product and taking the transpose of each

\[
(A B C)' = C' B' A' .
\]  

A similar rule applies for the inverse of a product of non-singular square matrices

\[
(\sim \sim \sim)^{-1} = \sim^{-1} \sim^{-1} \sim^{-1} .
\]

Only square matrices can be diagonal, constant, unit, inverse, symmetric and orthogonal. The transpose of a column matrix (a vector) is a row matrix (a row vector). The product of a matrix \( \sim \) and a vector \( \sim \) is a vector

\[
\begin{bmatrix}
+ & n & \uparrow \\
\sim & \downarrow & \sim
\end{bmatrix}
\begin{bmatrix}
+ & l & \uparrow \\
\sim & \downarrow & \sim
\end{bmatrix}
= \begin{bmatrix}
+ & l & \uparrow \\
\sim & \downarrow & \sim
\end{bmatrix}
\]

\[
\text{(A-13)}
\]

The product of a row vector and a column vector \( X \) is a one-by-one matrix, i.e., a single number
If $A$ is a square matrix and $V$ is a vector, the product

$$V' A V = a$$  \hspace{1cm} (A-15)$$

is a real number, and is called a quadratic form. If such a quadratic form is greater than zero for all real elements of vector $V$ ($a > 0$), $A$ is said to be positive definite.

If $A$ is a square matrix that can be expressed as

$$A D = D \Lambda$$  \hspace{1cm} (A-16)$$

$D$ is the matrix formed by the column of characteristic sign vectors of $A$ and $\Lambda$ is a diagonal matrix, the elements ($\lambda_{ii}$) are called the characteristic values of $A$ or eigenvalues of $A$.

Multiplying from the left Eq. (A-16) by $D^{-1}$

$$D^{-1} A D = \Lambda$$  \hspace{1cm} (A-17)$$

The transformation of $A$ affected by multiplying it from the right from the inverse of a matrix and from the left by the matrix, is called a similarity transformation and when the similarity transformation yields the eigenvalues of $A$, is said to be diagonalized by $D$. 
Any real symmetric matrix can be diagonalized, and the matrix $\Lambda$ that diagonalizes $A$ can be orthogonal. Then, an orthogonal transformation on a real symmetric matrix produces the eigenvalues of the matrix

$$D' \ A \ D = \Lambda . \quad (A-18)$$

If $A$ is symmetric and positive definite, its characteristic values are real positive, since

$$D^{-1} \ A \ D = D' \ A \ D = \Lambda . \quad (A-19)$$

If

$$A = B \ B' \quad (A-20)$$

for an arbitrary non-singular matrix $B$, then $A$ is symmetric positive definite.

The conditions under which two or more matrices can be simultaneously diagonalized by the same similarity transformation are that $A$, $B$, etc., are symmetric and commute with one another

$$A \ B = B \ A . \quad (A-21)$$

The eigenvalues matrix obtained through the similarity transformation of a product of two matrices is identical to the eigenvalue matrix obtained by two successive similarity transformations.

If

$$D' \ A \ B \ D = \Lambda \quad (A-22)$$

then

$$D' \ A \ D' \ B \ D = \Lambda \quad (A-23)$$

since

$$D \ D' = D \ D^{-1} = E . \quad (A-24)$$
3. Transformation Factors for \( \frac{\partial p}{\partial S_j} \)'s Into Arnett and Crawford Symmetry Coordinates System

From the definition of symmetry coordinates proposed by Arnett and Crawford (34) and those defined in Table 4, the following relationships are found:

\[
S_9^C = S_9^M \quad (A-25)
\]

\[
S_{10}^C = r_o \sqrt{2} S_{10}^M \quad (A-26)
\]

\[
S_{11}^C = S_{11}^M \quad (A-27)
\]

\[
S_{12}^C = r_o \sqrt{2} S_{12}^M \quad (A-28)
\]

\[
S_7^C = \frac{r_o \sin \alpha}{2} S_7^M \quad (A-29)
\]

Here, the superscript symbols C and M denote the symmetry coordinates for Arnett and Crawford and for this work, respectively; \( r_o \) is the CH-bond length and \( \alpha \) is the CCH-angle. From the above equations we can obtain relationships between \( \frac{\partial p}{\partial S_j} \)'s in both coordinates systems:

\[
(\frac{\partial p}{\partial S_j^C}) = (\frac{\partial p}{\partial S_j^M})(\frac{\partial S_j^M}{\partial S_j^C}) \quad (A-30)
\]

The partial derivatives \( \frac{\partial S_j^M}{\partial S_j^C} \) can be obtained by taking the partial derivatives in Eqs. (A-25) through (A-29). In this fashion we obtain:

\[
(\frac{\partial p}{\partial S_9})^C = (\frac{\partial p}{\partial S_9})^M \quad (A-31)
\]
These relationships are used in converting the values given in Table 21 to those of Table 22.
APPENDIX 2

TABLES
TABLE 25

OBSERVED FUNDAMENTAL WAVE NUMBER (ν), ESTIMATED ANHARMONICITY CONSTANTS (x) AND RESULTING HARMONIC FREQUENCIES (ω) FOR C₂H₄ AND C₂D₄. Ref. (37)

UNITS IN cm⁻¹

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Assignment</th>
<th>ν</th>
<th>x</th>
<th>ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁g</td>
<td>v₁</td>
<td>3026.4</td>
<td>0.1169</td>
<td>3426.9</td>
</tr>
<tr>
<td></td>
<td>v₂</td>
<td>1622.6</td>
<td>0.0069</td>
<td>1633.9</td>
</tr>
<tr>
<td></td>
<td>v₃</td>
<td>1342.2</td>
<td>-0.0353</td>
<td>1296.5</td>
</tr>
<tr>
<td>A₂u</td>
<td>v₄</td>
<td>1023</td>
<td>-0.0022</td>
<td>1024.7</td>
</tr>
<tr>
<td></td>
<td>v₅</td>
<td>3102.5</td>
<td>-0.0020</td>
<td>1096.2</td>
</tr>
<tr>
<td>B₁g</td>
<td>v₆</td>
<td>1222</td>
<td>0.0207</td>
<td>1262.1</td>
</tr>
<tr>
<td>B₁u</td>
<td>v₇</td>
<td>949.3</td>
<td>0.0112</td>
<td>959.9</td>
</tr>
<tr>
<td>B₂g</td>
<td>v₈</td>
<td>943</td>
<td>0.0212</td>
<td>967.6</td>
</tr>
<tr>
<td>B₂u</td>
<td>v₉</td>
<td>3105.5</td>
<td>0.0528</td>
<td>3278.5</td>
</tr>
<tr>
<td></td>
<td>v₁₀</td>
<td>826.0</td>
<td>0.02</td>
<td>826.8</td>
</tr>
<tr>
<td>B₃u</td>
<td>v₁₁</td>
<td>2988.7</td>
<td>0.0658</td>
<td>3199.9</td>
</tr>
<tr>
<td></td>
<td>v₁₂</td>
<td>1443.5</td>
<td>0.0317</td>
<td>1490.8</td>
</tr>
</tbody>
</table>
TABLE 25 (CONTINUED)

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Assignment</th>
<th>$\nu$</th>
<th>$x$</th>
<th>$\omega$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_{1g}$</td>
<td>$\nu_1$</td>
<td>2251</td>
<td>0.0873</td>
<td>2476.1</td>
</tr>
<tr>
<td></td>
<td>$\nu_2$</td>
<td>1515</td>
<td>0.0065</td>
<td>1527.9</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$</td>
<td>981</td>
<td>-0.0259</td>
<td>960.2</td>
</tr>
<tr>
<td>$A_u$</td>
<td>$\nu_4$</td>
<td>726.4</td>
<td>-0.0016</td>
<td>724.8</td>
</tr>
<tr>
<td></td>
<td>$\nu_5$</td>
<td>2304</td>
<td>-0.0015</td>
<td>2306.5</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>$\nu_6$</td>
<td>1009</td>
<td>0.0169</td>
<td>1028.4</td>
</tr>
<tr>
<td>$B_{1u}$</td>
<td>$\nu_7$</td>
<td>720.0</td>
<td>0.0085</td>
<td>726.2</td>
</tr>
<tr>
<td>$B_{2g}$</td>
<td>$\nu_8$</td>
<td>780</td>
<td>0.0176</td>
<td>799.1</td>
</tr>
<tr>
<td></td>
<td>$\nu_9$</td>
<td>2345</td>
<td>0.0399</td>
<td>2442.3</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>$\nu_{10}$</td>
<td>586</td>
<td>0.0144</td>
<td>593.9</td>
</tr>
<tr>
<td></td>
<td>$\nu_{11}$</td>
<td>2200.2</td>
<td>0.0484</td>
<td>2312.1</td>
</tr>
<tr>
<td>$B_{3u}$</td>
<td>$\nu_{12}$</td>
<td>1079.9</td>
<td>0.0236</td>
<td>1104.0</td>
</tr>
</tbody>
</table>
**TABLE 26**

OBSERVED AND CALCULATED WAVE NUMBERS FOR $C_2H_3D$, $C_2HD_3$ AND CIS, TRANS AND GEM $C_2H_2D_2$. UNITS IN cm$^{-1}$

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Observed $v_i$</th>
<th>Calculated $\omega_1$ M27</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_1$ ($C_2H_3D$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_9$</td>
<td>3103</td>
<td>3100.90</td>
</tr>
<tr>
<td>$v_5$</td>
<td>3063</td>
<td>3056.54</td>
</tr>
<tr>
<td>$v_1$</td>
<td>3002</td>
<td>3010.03</td>
</tr>
<tr>
<td>$v_{11}$</td>
<td>2274</td>
<td>2270.22</td>
</tr>
<tr>
<td>$v_{12}$</td>
<td>1605</td>
<td>1603.59</td>
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<td>$v_2$</td>
<td>1404</td>
<td>1413.70</td>
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<td>$v_3$</td>
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<td>1278.03</td>
</tr>
<tr>
<td>$v_6$</td>
<td>1129</td>
<td>1130.51</td>
</tr>
<tr>
<td>$v_{10}$</td>
<td>730</td>
<td>725.84</td>
</tr>
<tr>
<td>$C_1$ ($C_2HD_3$)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$v_9$</td>
<td>3045</td>
<td>3054.39</td>
</tr>
<tr>
<td>$v_5$</td>
<td>2280</td>
<td>2318.38</td>
</tr>
<tr>
<td>$v_1$</td>
<td>2232</td>
<td>2268.50</td>
</tr>
<tr>
<td>$v_{11}$</td>
<td>2222</td>
<td>2213.50</td>
</tr>
<tr>
<td>$v_2$</td>
<td>1546</td>
<td>1541.16</td>
</tr>
<tr>
<td>$v_{12}$</td>
<td>1289.5</td>
<td>1280.22</td>
</tr>
<tr>
<td>Symmetry</td>
<td>Observed $\nu_i$</td>
<td>$\omega_i$</td>
</tr>
<tr>
<td>-------------------</td>
<td>------------------</td>
<td>------------</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$ 1046.9</td>
<td>1039.93</td>
</tr>
<tr>
<td></td>
<td>$\nu_6$ 995.0</td>
<td>1000.68</td>
</tr>
<tr>
<td></td>
<td>$\nu_{10}$ 609.7</td>
<td>621.66</td>
</tr>
<tr>
<td>$\text{C}_{2h}$ (cis)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>$\nu_5$ 3035</td>
<td>3056.94</td>
</tr>
<tr>
<td></td>
<td>$\nu_1$ 2276</td>
<td>2268.21</td>
</tr>
<tr>
<td>$\text{Ag}$</td>
<td>$\nu_2$ 1567</td>
<td>1575.69</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$ 1282</td>
<td>1271.55</td>
</tr>
<tr>
<td></td>
<td>$\nu_6$ 1001</td>
<td>1012.58</td>
</tr>
<tr>
<td>$\text{B}_u$</td>
<td>$\nu_9$ 3065</td>
<td>3053.34</td>
</tr>
<tr>
<td></td>
<td>$\nu_{11}$ 2271</td>
<td>2272.29</td>
</tr>
<tr>
<td></td>
<td>$\nu_{12}$ 1300</td>
<td>1288.52</td>
</tr>
<tr>
<td></td>
<td>$\nu_{10}$ 678</td>
<td>677.72</td>
</tr>
<tr>
<td>$\text{C}_{2v}$ (trans)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$\text{A}_1$</td>
<td>$\nu_9$ 3058</td>
<td>3060.54</td>
</tr>
<tr>
<td></td>
<td>$\nu_1$ 2300</td>
<td>2291.36</td>
</tr>
<tr>
<td></td>
<td>$\nu_2$ 1567</td>
<td>1573.60</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$ 1215</td>
<td>1209.69</td>
</tr>
<tr>
<td></td>
<td>$\nu_{10}$ 646</td>
<td>657.19</td>
</tr>
<tr>
<td>Symmetry</td>
<td>Observed</td>
<td>$\omega_1$</td>
</tr>
<tr>
<td>----------</td>
<td>-----------</td>
<td>------------</td>
</tr>
<tr>
<td></td>
<td>$\nu_1$</td>
<td>$\omega_1$</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$\nu_5$</td>
<td>3056</td>
</tr>
<tr>
<td></td>
<td>$\nu_{11}$</td>
<td>2254</td>
</tr>
<tr>
<td></td>
<td>$\nu_{12}$</td>
<td>1344</td>
</tr>
<tr>
<td></td>
<td>$\nu_6$</td>
<td>1041</td>
</tr>
<tr>
<td>$C_{2u}$ (gem)</td>
<td>$\nu_1$</td>
<td>3019</td>
</tr>
<tr>
<td></td>
<td>$\nu_{11}$</td>
<td>2231</td>
</tr>
<tr>
<td>$A_1$</td>
<td>$\nu_2$</td>
<td>1585</td>
</tr>
<tr>
<td></td>
<td>$\nu_{12}$</td>
<td>1384</td>
</tr>
<tr>
<td></td>
<td>$\nu_3$</td>
<td>1032</td>
</tr>
<tr>
<td>$B_1$</td>
<td>$\nu_9$</td>
<td>3095</td>
</tr>
<tr>
<td></td>
<td>$\nu_5$</td>
<td>2335</td>
</tr>
<tr>
<td></td>
<td>$\nu_6$</td>
<td>1150</td>
</tr>
<tr>
<td></td>
<td>$\nu_{10}$</td>
<td>660</td>
</tr>
</tbody>
</table>
TABLE 27

SYMMETRY FORCE CONSTANTS FOR PROBLEMS C, Ref. (35),
AND Cy, Ref. (37). UNITS IN mdyn/Å. IN-PLANE
IN THE COORDINATE SYSTEM OF THE PRESENT WORK

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>$F_{ij}$</th>
<th>C</th>
<th>Cy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$F_{11}$</td>
<td>10.896</td>
<td>10.758</td>
</tr>
<tr>
<td></td>
<td>$F_{12}$</td>
<td>-0.0078</td>
<td>1.0027</td>
</tr>
<tr>
<td></td>
<td>$F_{13}$</td>
<td>1.8136</td>
<td>1.8225</td>
</tr>
<tr>
<td>$A_{1g}$</td>
<td>$F_{22}$</td>
<td>6.1978</td>
<td>6.7838</td>
</tr>
<tr>
<td></td>
<td>$F_{23}$</td>
<td>-0.7275</td>
<td>-0.1334</td>
</tr>
<tr>
<td></td>
<td>$F_{33}$</td>
<td>1.4953</td>
<td>1.3980</td>
</tr>
<tr>
<td></td>
<td>$F_{11}$</td>
<td>6.1529</td>
<td>5.1457</td>
</tr>
<tr>
<td></td>
<td>$F_{12}$</td>
<td>0.5407</td>
<td>0.2346</td>
</tr>
<tr>
<td></td>
<td>$F_{22}$</td>
<td>0.6545</td>
<td>0.6616</td>
</tr>
<tr>
<td>$B_{1g}$</td>
<td>$F_{11}$</td>
<td>6.0137</td>
<td>5.6874</td>
</tr>
<tr>
<td></td>
<td>$F_{12}$</td>
<td>1.4647</td>
<td>0.0394</td>
</tr>
<tr>
<td></td>
<td>$F_{22}$</td>
<td>0.7975</td>
<td>0.4599</td>
</tr>
<tr>
<td>$B_{2u}$</td>
<td>$F_{11}$</td>
<td>6.1395</td>
<td>5.8262</td>
</tr>
<tr>
<td></td>
<td>$F_{12}$</td>
<td>-0.7275</td>
<td>-0.1334</td>
</tr>
<tr>
<td></td>
<td>$F_{22}$</td>
<td>1.3503</td>
<td>1.3929</td>
</tr>
</tbody>
</table>
APPENDIX 3

COMPUTER PROGRAMS

The source of the programs described in this appendix is the
Program Manual of the Molecular Spectroscopy library of the University
of Minnesota, made available to us by Dr. J. Overend. Program WMAT
is described by Wu (73) while Program CHARLY has its origin in
Schachtschneider Programs (71) as modified by Needham (74) and by
Russell. Program CMAT is a new version of Program Zeta of the Program
Manual, while Program VARCO is based on Programs COVAR and COVARIN
written chiefly by Needham and Russell. Program Dipole is due origi­
nally to Kagel (79) and includes Programs TRANS and AMB5, described
by Kagel. All these programs have been revised and modified to fulfill
our needs and only those in which major modifications were made as to
constitute essentially new versions are listed in this appendix. A
brief description of INPUT/OUTPUT instructions, together with a self­
explanatory flowchart is given for Programs WMAT, CHARLY, CMAT, VARCO
and DIPOLE. All other programs used in the present work are due to
Schachtschneider (71).

Program WMAT

This program calculates the transformation matrix \( \mathbf{B} \) from a set
of cartesian coordinates to a set of valence internal coordinates, the
\( \mathbf{G} \) matrix of the inverse kinetic energy and uses the symmetry to give a
symmetrized \( \mathbf{G} \) matrix and calculates the transformation \( \mathbf{W} \) for use in
Program CHARLY.
INPUT: Cartesian coordinates
Valence internal coordinates
Atomic masses
U symmetry transformation matrix.

OUTPUT: B transformation matrix
G inverse kinetic energy matrix
Symmetrized G matrix
W transformation matrix.
Figure 24. Flowchart diagram for W transformation matrix, program WMAT.
**Program CHARLY**

This program calculates the frequencies, eigenvectors and potential energy distributions for a series of molecules and isotopes, from a given set of force constants. The force constants are adjusted to observed parameters (frequencies, coriolis coupling coefficients and centrifugal distortion constants) by the least-squares method described in Chapter 3. Finally, it calculates the variance-covariance matrix for the force constants and their dispersions.

**INPUT:** Initial set of force constants

W transformation matrices

Observed frequency parameters and weights

ζ matrix from CMAT for coriolis coupling coefficients

μ matrix for centrifugal distortion constants

**OUTPUT:** Transform F matrix, H

Calculated frequency parameters

Calculated coriolis coupling and centrifugal distortion constants

Jacobians

Normal equation matrix A

Force constants corrections for each cycle

Variance-covariance matrix for force constants
Figure 25. Flowchart for the force constants refinement procedure, program CHARLY.
Program CMAT

This program calculates the $\zeta$ matrix needed in the calculation of coriolis coupling coefficients from the atomic masses and molecular geometry. When the normal coordinate transformation matrix $L$ is known it calculates the $\zeta$ matrix of coriolis coupling coefficients. Since this version is essentially new, it is given here in full.
PROGRAM CMAT
COMBINATION OF THE PROGRAMS CMAT AND ZETA FROM MINNESOTA
COMPUTES C MATRIX AS PER CMAT AND ZETA MATRIX AS IN ZETA

DIMENSION XINL(45,45),TEMP(45,45),Z(45,45),NROWL(4),NCOLL(4),
2 DATINL(4),NRZ(75,3),NCZ(75,3),DATINB(4),C(45,45),WT(30),
1 U(45,45),NROWU(4),NCOLU(4),
2DATINU(4),CS(45,45),NROWC(75),NCOLC(75),DATINC(75)

2 COORDINATES='I4/' NO. OF SYMMETRIC COORDINATES='I4)
10 FORMAT (13)
308 FORMAT('ERROR IN L INVERSE PROBLEM' I8,' FIELD' I3,' HAD'2I3,F12.6)
430 FORMAT (4(2I3,F12.6))
451 FORMAT(4(' ZETA('I2,','I2,''))='F12.6,2X))
64 FORMAT('ZETA MATRIX',2X,A4,' COMPONENT' I4,' ELEMENTS')
904 FORMAT(4(' C('I2,','I2,''),'=F12.6,2X))
1900 FORMAT(I6,2013)
1903 READ 1904, (NROWB(L),NCOLB(L),DATINB(L),L=1,4)
1904 FORMAT (4(2I3,F12.6))
1930 FORMAT (6F12.6)
2021 FORMAT('OC MATRIX',2X,A4,' COMPONENT' I4,' ELEMENTS')
3001 FORMAT('ERROR IN B MATRIX, PROBLEM' I8,' FIELD' I3,' HAD'2I3,F12.6)
3076 FORMAT('ERROR IN U MATRIX, PROBLEM' I8,' FIELD' I3,' HAD'2I3,F12.6)
3997 FORMAT('OWEIGHTS OF ATOMS'//(10F12.6))
3998 FORMAT('OPUNCH C='I3,' ZETA CALC='I3,' ZETA PUNCH='I3,' INPUT PRI
2NT='I3)
3999 FORMAT('ONO. OF ISOTOPES='I4,'ONO. OF ATOMS='I4,'ONO. OF INTERNAL
4000 FORMAT('I PROBLEM' I8,' ISOTOPE' I3)
4001 FORMAT(3X,'O TITLE GOES HERE
4002 FORMAT('O',10F12.6//'',10F12.6))
4003 FORMAT('OU MATRIX'//)
4005 FORMAT('ONORMALIZED U MATRIX'//)
4007 FORMAT('OL INVERSE MATRIX'//)
DATA CO/" X ',' Y ',' Z '/
ISO=0
9 READ(5,10) IND
IF(IND+9)9,1895,9
1895 READ(5,1900) NOPROB,NISO,NOAT,NIC,NS,IFZ,IFPC,IFPZ,INPUT
READ(5,4001)
IF(NOPROB=7777) 1880,1881,1880
1881 STOP 1
1880 NA=3*NOAT
JERR=0

C READ B MATRIX
DO 1890 I = 1,NIC
DO 1890 J = 1,NA
1890 B(I,J) = 0.0
DO 1911 L = 1,4
  IF(NROWB(L)) 1912,3000,1907
1907 IF(NIC-NROWB(L)) 3000,1908,1908
1908 IF(NA-NCOLB(L)) 3000,1909,1909
1909 I = NROWB(L)
  J = NCOLB(L)
  B(I,J) = DATINB(L)
1911 CONTINUE
GO TO 1903
1912 IF(5+NROWB(L)) 3000,1990,3000
1990 IF(JERR) 2026,1995,2026
1995 ISO = 0

C READ AND NORMALIZE ORTHOGONAL U MATRIX
125 DO 127 I=1,NS
DO 127 J=1,NIC
127 U(I,J)=0.0
128 READ 1904, (NROWU(L),NCOLU(L),DATINU(L), L=1,4)
129 DO 135 L=1,4
   IF(NROWU(L))137,615,131
131 IF(NS-NROWU(L))615,132,132
132 IF(NIC-NCOLU(L))615,133,133
133 I=NROWU(L)
   J=NCOLU(L)
135 U(I,J)=DATINU(L)
136 GO TO 128
137 IF(3+NROWU(L))615,138,615
C
C NORMALIZE U MATRIX
138 DO 147 I=1,NS
141 US=0.0
142 DO 143 J=1,NIC
143 US=US+U(I,J)**2
   UN=SQRT (US)
145 DO 146 J=1,NIC
146 U(I,J)=U(I,J)/ UN
147 CONTINUE
   WRITE(6,4000)NOPROB,ISO
   WRITE(6,4001)
   WRITE(6,3998) IFPC,IFZ,IFPZ,INPUT
   WRITE(6,3999) NISO,NOAT,NIC,NS
C
C READ L INVERSE MATRIC IF Z MATRIX IS DESIRED
C SKIPS PRINTING B AND U MATRICES IF INPUT=0
   IF(INPUT.EQ.0) GO TO 25
   WRITE(6,4003)
   DO 4004 I=1,NIC
4004 WRITE(6,4002)(B(I,J),J=1,NA)
   WRITE(6,4005)
DO 4006 I=1,NS
4006 WRITE(6,4002)(U(I,J),J=1,NIC)
25 IF (IFZ.EQ.0) GO TO 1996
DO 26 I=1,NS
DO 26 J=1,NIC
26 XINL(I,J) = 0.0
30 READ(5,1904)(NROWL(L),NCOLL(L),DATINL(L), L=1,4)
DO 28 L=1,4
IF (NROWL(L))29,307,27
27 I = NROWL(L)
J = NCOLL(L)
28 XINL(I,J) = DATINL(L)
GO TO 30
29 IF (7 + NROWL(L))307,35,307
35 CONTINUE
IF (INPUT.EQ.0) GO TO 1996
WRITE(6,4007)
DO 4008 I=1,NS
4008 WRITE(6,4002) (XINL(I,J),J=1,NIC)
1996 ISO = ISO + 1
C
C READ MASS OF ATOMS
READ 1930, (WT(L), L = 1,NOAT)
WRITE(6,4000)NOPROB,ISO
WRITE(6,4001)
WRITE(6,3997)(WT(L),L=1,NOAT)
C
C COMPUTE C
1999 DO 2027 K = 1,3
IMAT = 0
DO 2010 I = 1,NIC
DO 2010 J = 1,NIC
C(I,J) = 0.0
DO 2010 L = 1,NOAT
\[ M = 3(L-1) + K \]


2001 \(N = M + 2\)
\(M = M + 1\)
GO TO 2010

2002 \(N = M - 1\)
\(M = M + 1\)
GO TO 2010

2003 \(N = M - 1\)
\(M = M - 2\)

2010 \(C(I, J) = C(I, J) + (B(I, M) \times B(J, N) - B(J, M) \times B(I, N)) / WT(L)\)

C SYMMETRIZE C MATRIX
DO 2100 I = 1, NS
DO 2100 J = I, NS
\(CS(I, J) = 0.0\)
DO 2100 M = 1, NIC
DO 2100 L = 1, NIC
\(CS(I, J) = CS(I, J) + U(I, M) \times C(M, L) \times U(J, L)\)
2100 \(CS(J, I) = -CS(I, J)\)

C PUNCH AND PRINT C MATRIX
420 \(LX = 0\)
DO 428 I = 1, NS
DO 428 J = 1, NS
IF \((0.000001 - \text{ABS}(CS(I, J))) = 0\)
424 \(LX = LX + 1\)
NRWLC(LX) = I
NCLC(LX) = J
DATINC(LX) = CS(I, J)
428 CONTINUE
IF (IFPC) 2020, 2025, 2020
2020 WRITE(7, 2021) CD(K)
429 \(LX = LX + 1\)
IF (LX.GT.75) GO TO 4051
NROWC(LX) = -2
NCOLC(LX) = 0
DATINC(LX) = 0.0
PUNCH 430, (NROWC(I),NCOLC(I),DATINC(I),I=1,LX)
LX=LX-1
2025 WRITE(6,2021) CO(K),LX
WRITE(6,4009)
WRITE(6,904) (NROWC(I),NCOLC(I),DATINC(I),I=1,LX)

C CALCULATES ZETA MATRIX
IF(IFZ.EQ.0) GO TO 2027
71 DO 73 I = 1,NS
DU 73 J = 1,NS
73 TEMP(I,J) = 0.0
DO 76 I = 1,NS
DO 76 J = 1,NS
DO 76 N = 1,NS
76 TEMP(I,J) = TEMP(I,J) +CS(I,N)*XINL(N,J)
DO 79 I = 1,NS
DU 79 J = 1,NS
79 Z(I,J) = 0.0
DO 82 I = 1,NS
DO 82 J = 1,NS
DO 82 N = 1,NS
82 Z(I,J) = Z(I,J) + XINL(N,I)*TEMP(N,J)

C WRITE ZETA MATRIZ
LX=0
DO 85 I=1,NS
DO 85 J=1,NS
IF(ABS(Z(I,J)).LT.1.E-6) GO TO 85
LX=LX+1
IF (LX.GT.75) GO TO 4052
NRZ(LX,K)=I
NCZ(LX,K)=J
DATZ(LX,K)=Z(I,J)
85 CONTINUE
NZ(K)=LX
2027 CONTINUE
IF (IFZ.EQ.0) GO TO 100
WRITE(6,4000)NOPROB,ISO
WRITE(6,4001)
DO 455 K=1,3
LX=NZ(K)
WRITE(6,64) CO(K),LX
WRITE(6,4009)
WRITE(6,451)(NRZ(L,K),NCZ(L,K),DATZ(L,K),L=1,LX)
IF (IFPZ.EQ.0) GO TO 455
LX=LX+1
NRZ(LX,K)=-10
NCZ(LX,K)=0
DATZ(LX,K)=0.0
WRITE(7,64)CO(K)
WRITE(7,430)(NRZ(L,K),NCZ(L,K),DATZ(L,K),L=1,LX)
455 CONTINUE
100 IF (NISO-ISO) 2026,2026,1996
2026 CONTINUE
GO TO 9
3000 WRITE(6,3001)NOPROB,L,NROWB(L),NCOLB(L),DATINB(L)
JERR = 1
GO TO 9
615 WRITE(6,3076) NOPROB,L,NROWU(L),NCOLU(L),DATINU(L)
JERR = 1
GO TO 9
307 WRITE(6,308 ) NOPROB,L,NROWL(L),NCO LL(L),DATINL(L)
GO TO 9
999 STOP
4051 WRITE(6,4053)
   GO TO 999
4052 WRITE(6,4054)
   GO TO 999
END
Program VARCO

This program calculates the inverse normal coordinate transformation matrix \( \tilde{L}^{-1} \), the variance-covariance matrices for \( \tilde{L} \) and \( \tilde{L}^{-1} \) and their dispersions. An option is available for an approximate analysis based on first order perturbation as described in Chapter 4.

**INPUT:**
- Variance-covariance matrix for force constants
- Force constants matrix \( \tilde{F} \)
- \( \tilde{L} \) transformation matrix
- Frequency parameters

**OUTPUT:**
- Jacobian matrices for \( \tilde{L} \) and \( \tilde{L}^{-1} \)
- Variance-covariance matrices for \( \tilde{L} \) and \( \tilde{L}^{-1} \)
- Dispersion-correlation coefficient matrices for \( \tilde{L} \) and \( \tilde{L}^{-1} \)
- Symmetrized eigenvectors and inverse eigenvectors and their dispersions
Figure 26. Flowchart diagram for the normal coordinate transformation variance-covariance matrix, program VARCO.
PROGRAM VARCO

THIS PROGRAM CALCULATE THE ERRORS IN
THE SYMMETRIZED EIGENVECTORS OF GF (L MATRIX)
AND SYMMETRIZED INVERSE EIGENVECTORS (L INVERSE MATRIX)

OUTPUT
1- JACOBIAN MATRIX IFJ=1
2- NORMAL COORDINATES VARIANCE COVARIANCE MATRIX FOR
L AND L INVERSE MATRIX
3- NORMAL COORDINATES DISPERSION CORRELATION
COEFFICIENTS MATRIX

AN OPTION (KS) IS USED FOR A COMPLETE CALCULATION
IF KS=1, THE COMPLETE VARIANCE-COVARIANCE MATRIX
IS CALCULATED.
IF KS=0, ONLY THE DISPERSIONS ARE CALCULATED.

GUSTAVO E. SANCHEZ FEB. 1970

INTEGER*2 INDEX
DIMENSION INDEX(30,30), IFUL(100), NR1(30), NR2(30), NR3(30), NR4(30),
1NBZ(30)
DIMENSION E(30,30), C(30,30), U(30,30), R(30,30), X(30),
1NROWU(4), NCOLU(4), DATINU(4), NROWZ(4), NCOLZ(4), DATINZ(4),
2NFZ(4), A(100,35), V(100,100), NR(900), NC(900), NA(900),
3NFSEUL35), Z(900), NISO(10), VE(900), RECURD(12)
DIMENSION F(30,30), S(30,30), B(100,35), Y(100,100), D(30,30)
EQUIVALENCE (E(1),R(1)), (D(1),S(1))
REAL*8 RECORD

1 FORMAT (I3)
2 FORMAT (I3, I6, 7I3, 2I2, I3, F12.6)
3 FORMAT (12A6)
4 FORMAT (24I3)
6 FORMAT (4(I3,F12.6))
7 FORMAT (4(3I3,F9.6))
8 FORMAT (43H JACOBIAN MATRIX (TRANSPOSED) FOR L MATRIX )
9 FORMAT (16HU FORCE CONSTANTI3/(10F12.6))
10 FORMAT(8H PROBLEM, 9H MOLECULE, 8H ISOTOPE, /(12A6), 1/13, 20H DEGREES OF FREEDOM )
11 FORMAT(44H VARIANCE-COVARIANCE FOR NORMAL COORDINATES/)  
12 FORMAT('O ROW', I3, ' CORRESPONDING TO ROW', I3, ' IN FULL MATRIX/' 
   2(10(1PE12.4)) )
13 FORMAT(72H DISPERSION-CORRELATION COEFFICIENTS MATRIX FOR NORMAL COORDINATE MAT. )
14 FORMAT(26H ERROR IN DIAGONAL ELEMENT, 3X, F12.6)
15 FORMAT(17H L INVERSE MATRIX, /(10F12.6))
16 FORMAT(22H U MATRIX ERROR FIELD, I3, 6H READS 214, F12.6)
17 FORMAT(22H Z MATRIX ERROR FIELD, I3, 6H READS 214)
19 FORMAT(24H JACOBIAN FOR L INVERSE )
24 FORMAT(31H FOR NORMAL COORDINATE MATRIX//)
25 FORMAT(56H SYMMETRIZED EIGENVECTORS AND THEIR DISPERSION
   15/26H NORMALIZATION CONSTANT = F12.6)
26 FORMAT(38H FOR INVERSE NORMAL COORDINATE MATRIX//)
27 FORMAT(13H EIGENVECTORS OF GF (L MATRIX) PRINTED IN ROWS//)
28 FORMAT(11H DISPERSION/ (10F12.6))
412 FORMAT('OU-MATRIX IFU=O'//)
700 FORMAT('INPUT INFORMATION FOR VARCO'//)
701 FORMAT('ONM =I4,' ' N1 =I4,' ' NS =I4,' ' NQ =I4,' ' NF =I4,' 
   ' NFS=I4,' ' KS =I4,' ' IFU=I4,' ' IFJ=I4/' 'ONDEFR=I4,' ' VAR=F12.6)
702 FORMAT('O', 10F12.6//', 10F12.6)
703 FORMAT('OU-MATRIX IFU=0'//)
704 FORMAT('OSYMMETRIZED Z FROM PROGRAM ZSYM'///)
705 FORMAT('ODISP. CORRLN. COEFT. MATRIX C'///)
706 FORMAT('OFORCE CONSTANT MATRIX F'///)
707 FORMAT('OCALCULATED FREQUENCY PARAMETER FROM CHARLY X(I) '///)
708 FORMAT('OEIGEN VECTORS OF GF (L MATRIX) PRINTED IN ROWS'///)
709 FORMAT('OL INVERSE MATRIX S(I,J)'///)
710 FORMAT(5(3I4, F12.6))
711 FORMAT('ONFSEL=2014')
712 FORMAT('O', I5, ' SYMMETRY BLOCKS OF SIZE'///(6(I3, ' X 'I3, 4X)) )
713 FORMAT('OADDRESSING ERROR FOR JACOBIAN L,M,N,I,J,,K,IJ ARE 8I4/
2 'ONR1, NR2,IFUL AND INDEX ARE'//)
714 FORMAT( 2014)
990 FORMAT(5H O.K.13)

C
90 READ 1,IND
   IF(IND+9) 90,100,90
C
C READ MOLECULE CONTROL CARD
100 READ 2,IND,NOPROB,NM,NI,NS,NQ,NF,NFS,KS,IFU,IFJ,NDEFR,VAR
   WRITE(6,700)
   WRITE(6,701) NM,NI,NS,NQ,NF,NFS,KS,IFU,IFJ,NDEFR,VAR
   IF(NOPROB=7777)102,103,102
102 READ 3, (RECORD(I), I=1,12)
   READ 4, (NISO(I), I=1,NM)
   READ(5,4) NOSB,(NBZ(I),I=1,NOSB)
   READ 4, (NFSEL(K), K=1,NFS)
   DO 611 I=1,10
   DO 611 J=1,10
   611 INDEX(I,J)=0
   WRITE(6,712) NOSB,(NBZ(I),NBZ(I),I=1,NOSB)
   WRITE(6,711) (NFSEL(I),I=1,NFS)
C
C SET MOLECULE AND ISOTOPE COUNTERS
NX=1
NIS=1
DEFR=NDEFR
SIGMA=VAR/DEFR
C
C READ U MATRIX
   IF (IFU) 105,125,105
105 DO 110 I=NS
   DO 110 J=NI
   110 U(I,J)=0.0
112 READ (5,6)(NROWU(L),NCOLU(L),DATINU(L),L=1,4)
DO 113 L=1,4
  IF (NROWU(L)) 114,600,115
115 IF(NS-NROWU(L)) 600,116,116
116 IF(NI-NCOLU(L)) 600,117,117
117 I=NROWU(L)
  J=NCOLU(L)
113 U(I,J)=DATINU(L)
  GO TO 112
114 IF(3+NROWU(L)) 600,118,600
C
C Normalize U matrix
118 DO 122 I=1,NS
  US=0.0
  DO 121 J=1,NI
121 US=US+U(I,J)**2
  UN=SQRT(US)
  DO 122 J=1,NI
122 U(I,J)=U(I,J)/UN
  WRITE(6,703)
  DO 803 I=1,NFS
803 WRITE(6,702) (U(I,J), J=1,NI)
125 CONTINUE
C
C Read symmetrized Z coefficients from program ZSYM
126 READ(5,7)(NROWZ(L), NCOLZ(L), NFZ(L), DATINZ(L), L=1,4)
  DO 130 L=1,4
130 IF (NROWZ(L)) 132,130,128
128 IF(NI-NROWZ(L)) 605,129,129
129 IF(NCOLZ(L)-NROWZ(L)) 605,131,131
131 IF(NF-NFZ(L)) 605,135,135
135 IF(DATINZ(L)) 133,134,133
134 DATINZ(L)=1.0
133 NOZ=NOZ+1
NR(NOZ)=NROWZ(L)
NC(NOZ)=NCOLZ(L)
NA(NOZ)=NFZ(L)
Z(NOZ)=DATINZ(L)
130 CONTINUE
GO TO 126
132 IF (2+NROWZ(L)) .GE. 605, 136, 605
136 NZ=NOZ
WRITE(6,700)
WRITE(6,704)
WRITE(6,710) (NR(I),NC(I),NA(I),Z(I), I=1,NZ)
C READ FORCE CONSTANTS COERROR MATRIX
READ(5,5)((C(I,J),J=1,NFS),I=1,NFS)
5 FORMAT (6F12.6)
WRITE(6,700)
WRITE(6,705)
DO 805 I=1,NFS
805 WRITE(6,702) (C(I,J),J=1,NFS)
C GENERATE ORIGINAL INVERSE NORMAL EQUATION MATRIX FROM FORCE
C CONSTANTS COERROR MATRIX (CHARLIE)
140 DO 142 J=1,NFS
X(J)=C(J,J)*C(J,J)/SIGMA
142 C(J,J)=X(J)
DO 144 I=1,NFS
DO 144 J=I,NFS
144 IF (I-J) .GE. 145, 144, 145
145 C(I,J)=C(I,J)*SQRT(X(I)*X(J))
C(J,I)=C(I,J)
144 CONTINUE
C READ FORCE CONSTANTS MATRIX
C READ CALCULATED FREQUENCY PARAMETERS
C READ EIGENVECTORS OF GF (L MATRIX)
C FROM CHARLY OUTPUT
236 READ(5,5)((F(I,J),J=1,NI),I=1,NI)
146 READ(5,5)(X(K),K=1,NS)
READ(5,5)((R(I,J),J=1,NS),I=1,NI)
C
C NOTE INDEXES REORDERED TO BE CONSISTENT WITH CHARLY PUNCH OUTPUT
WRITE(6,700)
WRITE(6,706)
DO 806 I=1,NI
806 WRITE(6,702) (F(I,J),J=1,NI)
WRITE(6,707)
WRITE(6,702) (X(K),K=1,NS)
WRITE(6,700)
WRITE(6,708)
DO 808 J=1,NS
808 WRITE(6,702) (R(I,J),I=1,NI)
C
C CALCULATE L INVERSE MATRIX
DO 201 I=1,NS
DO 201 J=1,NS
S(I,J) = 0.0
DO 202 K=1,NS
202 S(I,J) = S(I,J) + R(K,I)*F(K,J)
201 S(I,J) = S(I,J)/X(I)
WRITE(6,10) NOPROB,NX,NIS,(RECORD(I),I=1,12),NDEFR
WRITE(6,709)
DO 809 J=1,NQ
809 WRITE(6,702) (S(I,J),I=1,NS)
C
C CALCULATE JACOBIAN MATRIX
WRITE(6,10) NOPROB,NX,NIS,(RECORD(I),I=1,12),NDEFR
C
C SYMMETRIZE L AND L INVERSE MATRICES (IFU)
C NOSB = NO. OF SYMMETRY BLOCKS, SIZE OF BLOCK IS NBS X NBS
C JACOBIAN MATRIX REDUCES TO NS2 X NS AND VAR-COVAR MATRIX TO NS2 BY NS2
   NS2=0
   DO 1125 I=1,NOSB
1125 NS2=NS2+NBZ(I)**2
C
C NUMBER OF NON ZERO ELEMENTS IN THE MATRIX E D
   IF(IFU)30,29,30
30  DO 32 I=1,NS
    DO 32 J=1,NS
    E(I,J) = 0.0
32   D(J,I) = 0.0
    DO 31 I=1,NS
    DO 31 J=1,NS
    DO 31 K=1,NI
    D(J,I)=D(J,I)+U(I,K)*S(J,K)
31   E(I,J)=E(I,J)+U(I,K)*R(K,J)
29 CONTINUE
   DO 85 I = 1,NS2
   DO 85 J = 1,NFS
   B(I,J) = 0.0
85    A(I,J) = 0.
C
C A MATRIX OF INDEXES GENERATED 9X9 MATRIX REDUCED TO SYMMETRY BLOCKS
C CONTAINING NBSXNOSB TERMS FOR INDEXING JACOBIAN AND VAR-COVAR MATRICES
   IJ=0
   IF=0
   J1=1
   J2=NBZ(1)
   DO 88 K=1,NOSB
   DO 87 J=J1,J2
   NR1(J)= J1
   NR2(J)= J2
     NR3(J)= (J-1)*NBZ(K)+1
NR3(J)=IJ+1
NR4(J)=NR3(J) -1+NBZ(K)
DO 86 I=J1,J2
IJ=IJ+1
IF=IF+1
IFUL(J)=IF
86 INDEX(I,J)=IJ
87 IF=IF+NS-NBZ(K)
J1=J1+NBZ(K)
J2=J2+NBZ(K)
J2=J2+NBZ(K+1)
C
88 IF=IF+NBZ(K)
DO 39 NJ = 1,NZ
M = NA(NJ)
DO 34 I = 1,NFS
J = NFSEL(I)
IF (M-J) 34,33,34
34 CONTINUE
GO TO 39
33 N = I
L = NR(NJ)
M = NC(NJ)
IF (L-M) 81,80,81
80 RZ = Z(NJ)
GO TO 84
81 RZ = 2.*Z(NJ)
84 M1=NR1(M)
M2=NR2(M)
L1=NR1(L)
L2=NR2(L)
DO 38 J=L1,L2
DO 38 I=M1,M2
IJ=INDEX(I,J)
IF(IJ.EQ.0) GO TO 610
C
C  CALCULATE MOMENT MATRIX
47  WRITE (6,10) NOPROB,NX,NIS,(RECORD(I),I=1,12),NDEFR 
   WRITE (6,11) 
   DO 50 I=1,NS2 
   DO 50 J=1,NS2 
      V(I,J)=0.0 
      Y(I,J)=0.0 
   DO 49 K=1,NFS 
      IF(B(I,K).EQ.0.0) GO TO 49 
   DO 48 L=1,NFS 
      IF(B(J,L).EQ.0.0) GO TO 48 

DO 35 K=M1,M2 
   IF(J.EQ.K) GO TO 35 
   A(IJ,N)=E(I,K)*E(L,J)*E(M,K)*RZ/(X(J)-X(K)) +A(IJ,N) 
35  CONTINUE 
38  CONTINUE  
   DO 36 I=L1,L2 
   DO 36 J=M1,M2 
KJ=INDEX(J,I)  
   IF(KJ.EQ.0) GO TO 610 
   DO 37 K=M1,M2 
   IF(I.EQ.K) GO TO 37 
   B(KJ,N)=B(KJ,N)+E(L,I)*E(M,K)*D(K,J)*RZ/(X(I)-X(K)) 
37  CONTINUE 
36  CONTINUE 
39  CONTINUE  
44  WRITE (6,8) 
   DO 45 L=1,NFS 
45  WRITE (6,9) L,(A(K,L),K=1,NS2) 
   WRITE (6,19) 
   DO 207 L=1,NFS 
207  WRITE (6,9)NFSEL(L),(B(K,L),K=1,NS2) 
42  IF (KS) 47,72,47
Y(I,J) = Y(I,J) + B(I,K)*B(J,L)*C(K,L)

CONTINUE

DO 492 K=1,NFS
  IF(A(I,K).EQ.0.0) GO TO 492
  DO 491 L=1,NFS
    IF(A(J,L).EQ.0.0) GO TO 491
    V(I,J) = V(I,J) + A(I,K)*A(J,L)*C(K,L)
  491 CONTINUE
  492 CONTINUE

CONTINUE

DO 50 I=1,NS2
  MI=IFUL(I)
  WRITE(6,12)I,MI,(V(I,J),J=1,NS2)
  WRITE (6, 12) I ,MI, (V(I,J),J=1,NS2)

50 CONTINUE

C
C NORMALIZE THE MOMENT MATRIX.

WRITE (6,10) NOPROB,NX,NIS,(RECORD(I),I=1,12),NDEFR
WRITE (6,13)
DO 53 J=1,NS2
  IF (V(J,J)) 51,51,210

51 WRITE (6,14) J,V(J,J)
  V(J,J)=-V(J,J)

210 IF (Y(J,J)) 211,211,52

211 WRITE (6,14) J,Y(J,J)
  Y(J,J)=-Y(J,J)

52 V(J,J)=SQRT (V(J,J))
  Y(J,J)=SQRT (Y(J,J))

53 CONTINUE

DO 57 I=1,NS2
  DO 57 J=I,NS2
IF (I-J) .LT. 56, 257, 56
56  V(I,J)=V(I,J)/(V(I,I)*V(J,J))
   Y(I,J)=Y(I,J)/(Y(I,I)*Y(J,J))
257  V(J,I)=V(I,J)
   Y(J,I)=Y(I,J)
     DO 55 I=1,NS2
     MI=IFUL(I)
55  WRITE(6,12)I,MI,(V(I,J),J=1,NS2)
   WRITE (6,412)
   DO 255 I=1,NS2
   MI=IFUL(I)
255  WRITE(6,12)I,MI,(Y(I,J),J=1,NS2)
C
THE DIAGONAL TERMS ARE THE NORMAL COORDINATE DISPERSIONS.
   SIGMA = SQRT(SIGMA)
   DO 58 K = 1,NS2
      Y(K,K) = Y(K,K)*SIGMA
   58  V(K,K) = V(K,K)*SIGMA
      WRITE(6,25) SIGMA
      WRITE (6,24)
   DO 62 J = 1,NS
      K=NR3(J)
      L=NR4(J)
      WRITE(6,70)J,(E(I,J),I=1,NS)
62  WRITE(6,71)(V(I,I),I=K,L)
      WRITE (6,26)
   DO 215 J=1,NS
      K=NR3(J)
      L=NR4(J)
      WRITE(6,70)J,(D(J,I),I=1,NS)
215  WRITE(6,71)(Y(I,I),I=K,L)
      WRITE(7,10) NOPROB,NX,NIS,(RECORD(I),I=1,12),NDEFR
      WRITE(7,25) SIGMA
      WRITE(7,5) ((D(I,J),I=1,NS),J=1,NS)
GO TO 160
72 SIGMA = SQRT (SIGMA)
DO 75 J = 1, NS2
   VE(J) = 0.
   DO 73 K = 1, NS
   DO 73 L = 1, NS
   IF (A(J,K) .EQ. 0.0 .OR. A(J,L) .EQ. 0.0) GO TO 73
      VE(J) = VE(J) + A(J,K) * A(J,L) * C(K,L)
   CONTINUE
73 CONTINUE
75 VE(J) = SIGMA * SQRT (VE(J))
WRITE (6, 9) SIGMA
DO 78 J = 1, NS
   K = NR3(J)
   L = NR4(J)
   WRITE (6, 70) J, (E(I, J), I = 1, NS)
78 WRITE (6, 71) (VE(I), I = K, L)
160 IF (NIS - NISO(NX)) 163, 164, 165
163 NIS = NIS + 1
   GO TO 146
164 IF (NX - NM) 166, 90, 165
166 NX = NX + 1
   NIS = 1
   GO TO 236
600 WRITE (6, 16) L, NROWU(L), NCOLU(L), DATINU(L)
   GO TO 90
605 WRITE (6, 17) L, NROWZ(L), NCOLZ(L)
   GO TO 90
165 STOP 1
103 STOP 2
610 WRITE (6, 713) L, M, N, I, J, K, IJ, KJ
   WRITE (6, 714) (NR1(J), J = 1, NS)
   WRITE (6, 714) (NR2(J), J = 1, NS2)
   DO 715 I = 1, NS
715 WRITE(6,714) (INDEX(I,J),J=1,NS)
  STOP
  END
Program DIPOLE

This program calculates the $\partial p/\partial Q_j$'s from the experimental intensities and harmonic frequencies, and all the possible sets of $\partial p/\partial S_j$'s from the signs combinations of $\partial p/\partial Q_j$'s and the $L^{-1}$ transformation matrices. The error analysis of all quantities involved is also made.

INPUT:  
Intensities, $\Gamma$  
Standard error in $\Gamma$'s  
Frequencies, $\omega$  
Standard error in $\omega$'s  
Degree of mixing $\Delta S$ in the $\Gamma$'s  
Variance-covariance matrix for $L^{-1}$  
Dispersions in $L^{-1}$

OUTPUT:  
$\partial p/\partial Q_i$ and dispersion  
All possible sets of $\partial p/\partial S_j$  
Dispersions in $\partial p/\partial S_j$'s  
Analysis of the dispersions of $\partial p/\partial S_j$'s
Figure 27. Flowchart diagram for the reduction of intensity data, program DIPOL.E.
PROGRAM DIPOLE
THIS PROGRAM CALCULATES DIPOLE MOMENT DERIVATIVES RESPECT TO NORMAL
COORDINATES (DP/DQ) AND SYMMETRY COORDINATES (DP/DS).
THIS PROGRAM IS A MODIFICATION OF PROGRAM DIPOLE (NORMAL COORD.
PACKET, MOLECULAR STRUCTURE GROUP, U. OF MINNESOTA). IT'S NOT
LISTED IN THE BLUE BOOK. THIS VERSION INCLUDES PROGRAM ABMS (C
(CFR. KAGEL'S THESIS) AND PROGRAM TRANS.

DIMENSION C(90,90),EIGINV(30,30),D(30,30),PSP(30,30),PSL(30,30),
DP(30,30),P(30),G(30),FREQ(30),DFREQ(30),DEG(30),
DG(30),DS(30),DIG(30),PS(30),R(30),DIP(30),PSLS(30),PSPS(30),
3PSLT(30),RECORD(12),DDS(4),NSC(10),NISO(10),IDS(4),JDS(4)
DIMENSION GIG(30),DIPIN(30),PSINT(30)
REAL*8 RECORD

1 FORMAT (13)
2 FORMAT(I6,2I3,2I2)
3 FORMAT (12A6)
4 FORMAT (24I3)
5 FORMAT(6F12.6)
6 FORMAT(I5F4.1)
7 FORMAT(46H1 BAND AREAS, FREQUENCIES AND ERROR ESTIMATES !,4X,
*5H MODE,4X,12H FREQUENCY ,4X,12H DELTA ,4X,12H GAMMA ,
*4X,12H DELTA )
8 FORMAT(//,4X,I3,2X,4(4X,Fl2.6))
9 FORMAT(I5F4.1)
10 FORMAT(46H1 APPROXIMATE ANALYSIS OF DISPERSIONS IN DP/DS !,//,31H S
1HORT CALCULATION OPTION USED ,8HPROBLEM 16,///,5X,11H DISPERSION
2,5X,11H DISPERSION,5X,11H DISPERSION,///,5X,11H L INV TERM ,5X,11H D
3P/DQ TERM , 5X,11H TOTAL ,/)
11 FORMAT (3(4X,F12.6))
12 FORMAT (46H1 PROGRAM TRANS DP/DS WITH THEIR DISPERSIONS/
1 11H A IS DP/DS/
2 58H B IS DP/DS DISPERSION DUE TO UNCERTAINTIES IN INTENSITIES/
3 58H C IS DP/DS DISPERSION DUE TO UNCERTAINTIES IN FREQUENCIES/
462H D IS DP/DS DISPERSION DUE TO UNCERTAINTIES IN FORCE CONSTANTS/
5 55H E IS DP/DS DISPERSION DUE TO UNCERTAINTIES IN GEOMETRY/
6 22H F IS DP/DS DISPERSION/
7 46H G IS DP/DS DISPERSION CALCULATED BY FG METHOD/)
13 FORMAT (5H I, 5X, 2H A, 10X, 2H B, 10X, 2H C, 10X, 2H D, 10X, 2H E, 10X,
1 2H F, 10X, 2H G)
14 FORMAT (15, 7F12.6)
27 FORMAT (22HO ERROR IN PSL ELEMENTI3, 5X, F12.6)
33 FORMAT (43H1 DISPERSION-CORRELATION MATRIX FOR PROBLEM16//)
35 FORMAT (4H ROWI3/(10F12.8))
38 FORMAT (32H1 DP/DS AND DISPERSIONS MOLECULEI3, 8H ISOTOPEI3)
41 FORMAT (10X, I2, 6X, F8.4, 4X, F10.6)
50 FORMAT (54H1 L INVERSE TERM OF VARIANCE COVARIANCE MATRIX PROBLEM
16/)  
53 FORMAT (50HO DP/DQ TERM OF VARIANCE COVARIANCE MATRIX PROBLEM16//)
80 FORMAT (///, 10H1 PROBLEM 16, 5X, 3HNM= I3, 5X, 3HNS= I3, /)
130 FORMAT (30H1 GAMMAS AND DISPERSIONPROBLEM16)
131 FORMAT (8HO GAMMAS/(10F12.6))
132 FORMAT (12H DISPERSIONS /(10F12.6))
133 FORMAT (34H0 GAMMA VARIANCE COVARIANCE MATRIX)
136 FORMAT (34HO DP/DQ VARIANCE COVARIANCE MATRIX)
141 FORMAT (24H1 DP/DQ AND DISPERSIONS /)
142 FORMAT (6H DP/DQ/(10F12.6))
235 FORMAT (10F12.6)
90 READ 1, IND
   IF(IND+9) 90, 91, 90
C
READ MOLECULE CONTROL CARD
91 READ (5, 2) NOPROB, NM, NS, IFWF, IFSH
   IF(NOPROB-7777) 702, 703, 702
703 STOP
702 READ 3, (RECORD(I)), I=1, 12)
   WRITE (6, 80) NOPROB, NM, NS
   WRITE (6, 3) (RECORD(I), I=1, 12)
SET MOLECULE AND ISOTOPE COUNTERS
NX=1
READ(5,4)(NISO(I),I=1,NM)
100 READ(5,4)NSYM
READ(5,4)(NSC(I),I=1,NSYM)
ISO=1
NCOV=0
DO 109 I=1,NSYM
109 NCUN = NCON + NSC(I)*NSC(I)

READ INTENSITIES, FREQUENCIES, DEGENERACIES AND ERROR ESTIMATES
101 READ (5,5)(G(I),I=1,NS)
READ(5,5)(DG(I),I=1,NS)
READ(5,5)(FREQ(I),I=1,NS)
READ(5,6)(DEG(I),I=1,NS)
IF (IFWF)102,103,102
103 READ (5,5)(DFREQ(I),I=1,NS)
GO TO 104
102 DO 106 I=1,NS
106 DFREQ(I)=FREQ(I)*0.01
104 WRITE (6,7)
DO 98 I=1,NS
98 WRITE (6,8) I,FREQ(I),DFREQ(I),G(I),DG(I)

CALCULATE VARIANCE COVARIANCE MATRIX FOR INTENSITIES
READ DEGREE OF MIXING
DO 114 I = 1,NS
DS(I)=0.0
DO 114 J = 1,NS
114 DDG(I,J) = 0.0
116 READ(5,9) (IDS(L),JDS(L),DDS(L),L=1,4)
DO 119 L=1,4
IF (IDS(L)) 120, 120, 118
118 I = IDS(L)
   J = JDS(L)
   DDG(I,J) = -DDS(L)*DDS(L)
   DDG(J,I) = DDG(I,J)
119 DS(I) = -DDG(I,J) + DS(I)
   GO TO 116
120 DO 121 I=1,NS
   DDG(I,I) = DG(I)**2 + DS(I)
121 GIG(I) = SQRT(DDG(I,I))
   WRITE (6,133)
   DO 134 I = 1,NS
134 WRITE (6,235) (DDG(I,J), J=1,NS)
900 WRITE (6,130) NOPROB
   WRITE (6,131) (G(I), I=1,NS)
   WRITE(6,132) (GIG(I), I=1,NS)

C
C CALCULATE DP/DQ
   DO 105 I = 1,NS
   FREQ(I) = FREQ(I)/DEG(I)
   P(I) = 0.01288*SQT (0.001425*FREQ(I)*G(I))
105 R(I) = SQT (FREQ(I))
C
C CALCULATE DP/DQ VARIANCE COVARIANCE MATRIX
   DO 128 I=1,NS
   DO 128 J=1,NS
   DP(I,J) = 0.0
   DDG(I,J) = ABS(DDG(I,J))
   DP(I,J) = 0.16603E-04*0.001425*FREQ(I)*FREQ(J)*SQT(DDG(I,J))/(R(I)*R(J))
128 CONTINUE
IF(I-J) 129, 127, 129
127 DO 129 I=1,NS
   DIPIN(I) = SQRT(DP(I,I))
\text{DP}(i,i) = \text{DIPIN}(i) + 0.16602E-04 \times 0.001425 \times G(i) \times \text{DFREQ}(i) / \text{DEG}(i) \\
\text{DIP}(i) = \sqrt{\text{DP}(i,i)}

\text{CONTINUE}
\text{WRITE(6,136)}
\text{DO 137 I = 1,NS}
\text{WRITE(6,235)} (\text{DP}(i,j), j=1,NS)
\text{WRITE(6,142)} (\text{P}(i), i=1,NS)
\text{WRITE(6,132)} (\text{DIP}(i), i=1,NS)

\text{READ L INVERSE MATRIX, VARIANCE COVARIANCE AND DISPERSIONS}
\text{DO 602 I=1,NCON}
\text{DO 602 J=1,NCON}
\text{C}(i,j) = 0.0
\text{DO 603 I = 1,NS}
\text{DO 603 J = 1,NS}
\text{EIGINV}(i,j) = 0.0
\text{IF (IFSH)440,450,440}
\text{READ(5,5)}((\text{C}(i,j), j=1,NCON), i=1,NCON)
\text{READ(5,5)}((\text{D}(i,j), j=1,NS ), i=1,NS )
\text{READ(5,5)}((\text{EIGINV}(i,j), j=1,NS), i=1,NS)

\text{APPROXIMATE ANALYSIS (SHORT CALCULATION) OPTION. IFSH=1}
\text{IF (IFSH)148,149,148}
\text{DO 151 I=1,NS}
\text{DO 152 J=1,NS}
\text{PSL}(i,j) = 0.0
\text{MAX = 0}
\text{II = 1}
\text{MAX = MAX + NSC(II)}
\text{IF (I-MAX)155,155,156}
\text{MIN = MAX - NSC(II) + 1}
\text{NFIN = MAX}
\text{IB = II}
C DIM = NSC(II)
GO TO 157
156 II = II + 1
GO TO 154
157 MAX = 0
II = 1
158 MAX = MAX + NSC(II)
IF(J-MAX)159,159,160
159 MIN = MAX - NSC(II) + 1
MFIN = MAX
LDIM = NSC(II)
JB = II
GO TO 161
160 II = II + 1
GO TO 158
161 DO 153 N=NIN,NFIN
K = I + KDIM*(N-IB)
C
C CALCULATION OF L INVERSE TERM IN OP/OS VARIANCE COVARIANCE MATRIX
DO 150 M= MIN,MFIN
L = J + LDIM*(M-JB)
150 PSL(I,J) = PSL(I,J) + C(K,L)*P(N)*P(M)
153 CONTINUE
152 CONTINUE
151 CONTINUE
WRITE (6,50) NOPROB
DO 51 I = 1,NS
51 WRITE (6,235) (PSL(I,J),J=1,NS)
DO 56 I=1,NS
DO 57 J=1,NS
PSP(I,J) = 0.0
C
C CALCULATION OF DP/DQ TERM IN DP/DS VARIANCE COVARIANCE MATRIX
DO 25 K = 1,NS
DO 25 L = 1,NS
25 PSP(I,J) = PSP(I,J) + EIGINV(K,I)*EIGINV(L,J)*DP(K,L)
57 CONTINUE
56 CONTINUE
   WRITE (6,53) NOPROB
DO 54 I = 1,NS
54 WRITE (6,235) (PSP(I,J),J=1,NS)
955 DO 55 I = 1,NS
95 DO 55 J = 1,NS
55 PSL(I,J) = PSL(I,J) + PSP(I,J)
C
C CALCULATION OF DP/DS DISPERSION-CORRELATION COEFFICIENT MATRIX
DO 30 I = 1,NS
   IF(PSL(I,I)) 26,26,28
26 WRITE (6,27) I,PSL(I,I)
   JOKER = 1
GO TO 30
28 DIG(I) = SQRT (PSL(I,I))
   PSL(I,I) = DIG(I)
30 CONTINUE
   IF (JOKER) 45,300,45
300 DO 32 I = 1,9
32 DO 32 J = 1,9
   IF(I-J) 31,32,31
31 PSL(I,J) = PSL(I,J)/(DIG(I)*DIG(J))
32 CONTINUE
C
C APPROXIMATE ANALYSIS CALCULATION. DISPERSIONS(APPROX.) FOR DP/DS
148 DO 200 J=1,NS
149 PSLS(J)=0.
150 PSPS(J)=0.
DO 201 I=1,NS
151 PSLS(J)=PSLS(J)+D(I,J)*P(I)
201 PSPS(J)=PSPS(J)+EIGINV(I,J)*DIP(I)
200 PSLT(J) = PSLS(J) + PSPS(J)
    DO 206 J = 1, NS
    PSINT(J) = 0.
    DO 207 I = 1, NS
207 PSINT(J) = PSINT(J) + EIGINV(I, J) * DIPIN(I)
206 CONTINUE
    WRITE (6, 33) NOPROB
    IF (IFSH) 250, 232, 250
250 DO 252 I = 1, NS
252 DIG(I) = PSLT(I)
    WRITE (6, 10) NOPROB
    DO 170 I = 1, NS
170 WRITE (6, 11) PSLS(I), PSPS(I), PSLT(I)
    DO 172 I = 1, NS
172 PSL(I, I) = PSLT(I)
    DO 172 J = 1, NS
171 IF (I - J) 171, 172, 171
172 CONTINUE
232 DO 34 I = 1, NS
34 WRITE (6, 35) I, (PSIJ, J = 1, NS)
255 WRITE (6, 38) NX, ISO
C
C CALCULATION OF P(J) = DP/DS OFR VARIOUS SIGN CHOICES
    CALL SIGN (EIGINV, P, NS, PS)
C
C ANALYSIS OF THE DP/DS DISPERSIONS
    WRITE (6, 12)
    DO 60 I = 1, NS
60 DIP(I) = 0.0
    PSPS(I) = PSPS(I) - PSINT(I)
    WRITE (6, 13)
    DO 65 I = 1, NS
65 WRITE (6, 14) I, PS(I), PSINT(I), PSPS(I), PSLS(I), DIP(I), DIG(I),
IPS1T(I)

46 IF(NISO(NX)-ISO) 43,43,42

42 ISO = ISO+1
GO TO 101

43 IF(NM-NX) 45,45,44

44 NX = NX+1
GO TO 100

45 GO TO 90
END

SUBROUTINE SIGN(AL,X,N,Y)

DIMENSION AL(30,30),IS(12,100),S(12,100),Y(30),XS(30),X(30)

45 FORMAT (8I4)

46 FORMAT (32X,8F11.4//)

NM = N-1
NM2=2**NM
K=N
DO 1 J=1,NM2

1 IS(K,J)=J-1
2 K=K-1
IF (K) 3,5,3
3 DO 4 J=1,NM2

4 IS(K,J)=IS(K+1,J)/2
GO TO 2
5 DO 10 I=1,N
DO 10 J=1,NM2
IT=IS(I,J)/2
IF(2*IT-IS(I,J)) 7,6,7
6 IS(I,J)=1
GO TO 10
7 IS(I,J)=-1
10 S(I,J)=IS(I,J)

NM2=2**N-NM2
DO 40 J=1,NM2
DO 41 I=1,N

100 END
41 XS(I)=X(I)*S(I,J)
   DO 44 I=1,N
   Y(I)=0.
   DO 42 K=1,N
42 Y(I)=Y(I)+AL(K,I)*XS(K)
44 CONTINUE
   WRITE(6,45)(IS(I,J),I=1,N)
40 WRITE(6,46) (Y(I),I=1,N)
RETURN
END
/*
//GO.SYSIN DD *
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BIOGRAPHICAL SKETCH

Gustavo E. Sanchez was born May 17, 1941, at Cali, Colombia. In July, 1962, he graduated from Colegio Mayor de San Bartolome, Bogotá, Colombia. In June, 1966, he received the degree of Bachelor of Science from Universidad del Valle, Cali, Colombia. In September, 1966, he entered the Graduate School of the University of Florida on a Rockefeller Foundation fellowship. Since that time he has pursued his work toward the degree of Doctor of Philosophy.
I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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June, 1971

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Dean, Graduate School