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Molecular Force Fields of Ethylene, Allene, Formaldehyde, Ketene, and Diazomethane

Charles Edward Bailey
University of Tennessee - Knoxville

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To the Graduate Council:

I am submitting herewith a dissertation written by Charles Edward Bailey entitled "Molecular Force Fields of Ethylene, Allene, Formaldehyde, Ketene, and Diazomethane." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemistry.

William H. Fletcher, Major Professor

We have read this dissertation and recommend its acceptance:

Accepted for the Council:

Carolyn R. Hodges

Vice Provost and Dean of the Graduate School

(Original signatures are on file with official student records.)

December 20, 1958

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We have read this dissertation
and recommend its acceptance:

Alvin H. Nielsen

W. E. Deeds

Jerome F. Eastham

Accepted for the Council:

Dale Wantling
Dean of the Graduate School

MOLECULAR FORCE FIELDS OF ETHYLENE, ALLENE, FORMALDEHYDE, KETENE, AND DIAZOMETHANE

A DISSERTATION

Submitted to
The Graduate Council
of
The University of Tennessee
in
Partial Fulfillment of the Requirements
for the Degree of
Doctor of Philosophy

by

Charles Edward Bailey

March, 1959

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CHAPTER I

INTRODUCTION

A. Vibration-Rotation Spectra

Infrared and Raman spectra furnish one of the most powerful methods for studying the internal forces which act in molecules. The vibrational frequencies which are obtained from a study of the spectra are functions of the geometry and masses, which determine the kinetic energy of the system, and of the forces acting in the molecule, which determine the potential energy of the system. Therefore, if the geometry of a molecule is known, the vibrational frequencies of the molecule can be used to obtain information concerning the forces acting during the motions.

The first attempt to interpret infrared spectra in terms of internal forces was made by Bjerrum[1] in 1914. In a study of the spectrum of CO_2, Bjerrum concluded that the observed bands were caused by vibrational motions of the molecule and that the line broadening was due to simultaneous rotational transitions. He then attempted to account for the spectrum in terms of various potential functions. This work marks the first application of the central force field and the simple valence force field. The development of the field was handicapped by the lack of data and progress was slow during the next few years. However, the theory of diatomic molecular spectra was well developed during the period 1918-1930, and since that time, much progress has been made concerning the theory of polyatomic molecular spectra. Because of the increasing complexity which is encountered as larger molecules are treated, there is still much work to be done, both experimental and theoretical, before a complete understanding of the spectra of polyatomic molecules is achieved.

The theory of vibration-rotation spectra falls into three distinct parts: (1) the assignment of the observed bands, consisting of the fundamental frequencies and the overtone and combination bands, (2) the analysis of the rotational structure of the bands and determination of the rotational constants, and (3) the use of the fundamental frequencies to study the potential field of the molecule.

Since the fundamental frequencies are necessary in order to study the internal forces, the frequencies should be assigned with certainty. If the observed frequencies have been correctly assigned, the remaining difficulties encountered are (1) in almost all cases, the available data are insufficient to make anharmonicity corrections possible, and (2) resonance interactions may be present causing observed bands to be shifted from their unperturbed positions. Consequently, it is obvious that an exact potential energy function cannot be determined using the observed values of the fundamental frequencies. The error introduced by the failure to make anharmonicity corrections should not have an appreciable effect on how well a given potential energy function describes the system, but rather will cause the force constants determined using the observed frequencies to be lower than those which would be determined using harmonic frequencies. Conversely, band shifts arising from resonance interactions will cause apparent discrepancies in the force field, but these errors should not be large enough to greatly influence the success or failure of the particular field being used.

The need for accurate structural data for a molecule is an important requirement which seems to have suffered from a lack of emphasis. The geometrical parameters have an effect on the values of the force constants, and should be known accurately. Values of bond lengths and bond angles are obtained from electron diffraction studies, from high resolution infrared studies, and in recent years from microwave data. However, recent values which have been determined for these parameters indicate that many of the older data are questionable. In many cases, insufficient data requires that a value be assumed for one of the bond angles or bond lengths of a molecule in order to calculate its geometry. The errors arising from these inaccuracies in geometry are not very large, but it is necessary to recognize their presence. Considering the factors which affect the accuracy with which a suitable potential function will reproduce the observed frequencies, this author feels that the frequencies should be reproduced with an average error of less than 1 per cent if the band centers have been determined accurately.

B. The Potential Function Problem

The study of molecular potential functions is based on the assumption that the motions occurring during the vibrations are harmonic. This would be expected to be true if the motions in general involve small displacements of the atoms from their equilibrium positions. The success with which harmonic functions have met in describing the force fields of molecules confirms the validity of the approximation of harmonic motions.

Since a non-linear molecule containing N atoms possesses (3N-6) vibrational degrees of freedom (3N-5 for linear molecules), the potential energy of the system can be expressed in terms of (3N-6) independent coordinates. The remaining six degrees of freedom, the three degrees of translational freedom of the molecule as a whole and the three degrees of rotational freedom of the molecule as a whole, do not affect the potential energy. It has been found that the (3N-6) internal coordinates are most conveniently chosen as displacements of bond lengths and bond angles from their equilibrium positions, since these coordinates provide the most physically significant set by which the potential energy may be expressed. Obviously, these coordinates are unaffected by translations and rotations of the molecule as a whole.

If the (3N-6) internal displacement coordinates are designated by q_i, then the potential energy, V, can be expressed in the general quadratic form

$$2V = \sum_{i,j=1}^{3N-6} f_{ij} \Delta q_i \Delta q_j \qquad (1)$$

where the f_{ij}'s are the force constants. This expression of the potential energy represents the most general quadratic potential field which can be used to describe a molecule. The number of force constants which appear in the expression is $\frac{1}{2}(3N-6)(3N-5)$, which means that this many independent pieces of data would be required to evaluate the force constants of a molecule. Fortunately, this number of force constants applies only in the case of an unsymmetrical molecule, since the presence of symmetry in a molecule leads to relations between the force constants and consequently to a reduction in the number of independent force constants which have to be evaluated. In order to illustrate this point, the case of the non-linear XYZ molecule will be considered. The internal coordinates for this molecule are conveniently chosen as Δr_{XY}, Δr_{YZ}, and $\Delta\gamma$, where Δ indicates the change in the bond length or bond angle from its equilibrium position. The potential energy for this molecule

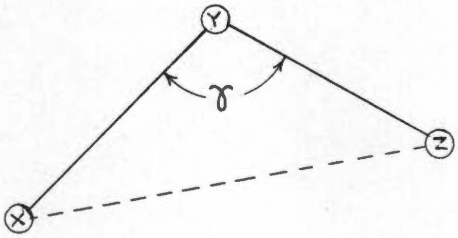

Figure 1. The Internal Coordinates of the Non-linear XYZ Molecule.

can then be written as

$$2V = f_1(\Delta r_{XY})^2 + f_2(\Delta r_{YZ})^2 + f_\gamma(\Delta\gamma)^2 + 2f_{12}(\Delta r_{XY}\Delta r_{YZ}) + 2f_{1\gamma}(\Delta r_{XY}\Delta\gamma)$$
$$+ 2f_{2\gamma}(\Delta r_{YZ}\Delta\gamma) , \quad (2)$$

where the f_i's are the principle force constants and the f_{ij}'s are the interaction constants. Thus, a total of six independent force constants are necessary to describe the potential field of this molecule. Now, assume that atoms X and Z are identical. This leads to a symmetrical, bent X_2Y molecule, and the equivalence of the two bonds leads to the relations

$$f_1 = f_2 \qquad \text{and} \qquad f_{1\gamma} = f_{2\gamma} . \quad (3)$$

Therefore, only four independent force constants are necessary to describe the potential field in this case. The simplification brought about by symmetry is perhaps better illustrated in the case of the ethylene molecule. If this molecule possessed no symmetry, 78 constants would be required to describe a general quadratic potential function; however, due to the high degree of symmetry, only 18 constants are necessary.

The (3N-6) fundamental frequencies of a molecule furnish just enough data to determine (3N-6) force constants. Even in view of the reduction in the number of force constants which symmetry brings about, the number of force constants arising when a general quadratic field is used is usually greater than (3N-6) and thus they cannot be determined. Additional data may be obtained from the frequencies of isotopic molecules,* however, since it has been shown[2] that isotopic substitution does not alter the force field to an appreciable extent. The use of isotopic data in the calculation of force constants is most useful when the relative mass changes occurring are large. This is because the frequencies are roughly proportional to the square roots of the reciprocal masses of the atoms which move during the vibrations, and a significant frequency shift is necessary to make the calculations reliable. For this reason, studies of hydrogen containing compounds and their deuterium analogs are of great importance. A comprehensive review on the use of deuterium in

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*The term "isotopic molecules" is used to define molecules which are identical except that one or more of the atoms of one molecule have been replaced by isotopic substitution; for example, CH_2O, CHDO, and CD_2O.

the analysis of molecular spectra has been given by Halverson.[3]

It would appear that if data were available for a series of isotopic molecules, for example, the seven $C_2H_nD_{4-n}$ (n = 0, 1, 2, 3, 4) molecules, one could determine an unique set of potential constants for a general quadratic field. However, as will be pointed out in a later chapter, a set of force constants which allows all of the observed frequencies to be calculated accurately for such a series of molecules is not necessarily unique. One reason for this is the fact that the observed frequencies must be used without being corrected for anharmonicity, or, if anharmonicity corrections are made, the correction is largely a matter of guesswork with the data which are presently available for most molecules. It should be pointed out that when data are used for such a series of molecules, the symmetry of the least symmetrical molecule determines the complexity of the solution for the force constants, and in general this increase in complexity makes the solution of the secular equation quite difficult without the aid of a computer.

The general quadratic potential function is arrived at by making no assumptions regarding the force field of the molecule other than requiring that it possess the same symmetry as the molecule. This field, in addition to usually containing more independent constants than can be evaluated, also does not give a clear description of the forces giving rise to the interaction constants. In order to decrease the number of force constants and to permit a clearer interpretation of the forces acting in a molecule to be made, various assumptions concerning the nature of the force field have been made, leading to a number of special force fields.

1. The Central Force Field

The central force field is based on the assumption that the forces acting in a molecule act along the lines connecting pairs of atoms and that every pair of atoms, both bonded and non-bonded, is connected by such a force. These forces are assumed to depend only on the distances between the atoms. For the non-linear XYZ molecule, the potential energy assuming a central force field can be written

$$2V = f_1(\Delta r_{XY})^2 + f_2(\Delta r_{YZ})^2 + f_3(\Delta r_{XZ})^2, \qquad (4)$$

where Δr_{XZ} represents the change in the distance between the non-bonded X and Z atoms and f_3 is the force constant associated with this change in distance. The number of force constants which are required when central forces are assumed is usually small compared with the number arising from a general quadratic force field treatment. The results obtained from the application of the central force field to a rather large number of molecules[4] have demonstrated that the field is not a satisfactory one.

The rather poor results obtained using the central force field are not surprising, since the field is the type that would result if the molecule were held together by purely ionic forces, and this is not the case. In particular, the field fails to account for the bending vibrations of linear molecules and the out-of-plane bending vibrations of planar molecules. This is readily seen by considering the bending motion for a linear XYZ molecule. A small bending motion does not alter any of the interatomic distances (to first order), and thus the central force field would predict a frequency of zero for the bending vibration. The distortion of an angle formed by two valence bonds from its equilibrium position would be expected to involve an increase in potential energy, so it is necessary that a suitable potential field include terms to account for this force.

2. The Simple Valency Force Field

The simple valency force field is similar to the central force field in its treatment of forces acting between bonded atoms, but forces between non-bonded atoms are not included. However, this field assumes that there is a force associated with the angle formed by valency bonds which opposes a change in the bond angle and that this force is proportional to the change in the bond angle. In treating the angular changes in this manner, this field can usually account for the bending vibrations of linear and planar molecules and thus is superior to the central force field in this respect. The potential energy for a non-linear XYZ molecule in terms of the simple valence force field is

$$2V = f_1(\Delta r_{XY})^2 + f_2(\Delta r_{XZ})^2 + f_\gamma(\Delta\gamma)^2, \qquad (5)$$

where $\Delta\gamma$ is the change in the XYZ angle from its equilibrium position. The simple valency force field has been applied to a large number of molecules,[5] and although the results obtained are in general superior to those obtained using the central force field, this field can at best be regarded as a rough approximation. Both the central force field and the simple valency force field are based on very simplified pictures of the potential field of a molecule, and the fact that the results obtained using these fields are rather poor is no surprise. Because of the simplicity of the assumed field in these cases, the number of potential constants in many cases is smaller than the number of fundamental frequencies which a molecule possesses and it is possible to generalize the field by including some additional terms in the potential energy expression. In this manner, a more suitable field should be obtained.

3. The Modified Valency Force Field

The simple valency force field can be looked upon as a special case of the general quadratic force field discussed earlier. If the interaction terms which are present in the potential energy expression based on a general quadratic potential function are neglected, then the expression for the potential energy reduces to that obtained using the simple valency force field.

In an effort to determine a more suitable potential function, it was, therefore, natural to modify the simple valency force field by including certain of the permitted interaction terms in the potential energy expression. This method, in general, allows a set of force constants to be evaluated which will reproduce the fundamental frequencies of a molecule fairly well and has been used rather widely in the determination of the force constants of molecules. However, it has not been possible to predict which cross terms should be important or to explain adequately the importance of those which have been found empirically to be necessary. The use of certain chosen interaction constants in the potential energy leads to the possibility that the solution for the force constants is not unique, since an equally good set of force constants might be determined by using a different set of interaction constants. Therefore, even though the modified valency force field will usually enable a suitable mathematical description of the field to be made, it does not provide a clear understanding of the internal forces and does not insure that the solution obtained is unique.

4. The Urey-Bradley Force Field

The Urey-Bradley force field may be considered as a simple valency force field modified to include central forces between non-bonded atoms or as a central force field modified to include forces which oppose changes in the angles formed by valence bonds. The potential energy for a non-linear XYZ molecule assuming a Urey-Bradley potential function is

$$2V = f_1(\Delta r_{XY})^2 + f_2(\Delta r_{YZ})^2 + f_\gamma(\Delta\gamma)^2 + f_3(\Delta r_{XZ})^2 + f_1'(\Delta r_{XY}) + f_2'(\Delta r_{YZ}) + f_\gamma'(\Delta\gamma) + f_3'(\Delta r_{XZ}) \; . \qquad (6)$$

The first three terms give the potential energy for a simple valency force field, while the fourth term takes into account the force acting between the non-bonded X and Z atoms. The linear terms are necessary when a Urey-Bradley force field is used because the set of internal coordinates used are linearly dependent. If the coordinates form a linearly independent set, as they do in all of the force fields previously described, the coefficients of the linear terms must vanish and therefore these terms have not been included in these cases. It should likewise be pointed out that the relations between the coordinates due to their linear dependence enables the coefficients of the linear terms to be related. Thus, f_1', f_2', and f_γ' can all be expressed in terms of f_3'. These linear terms necessitate that expressions for the redundancy conditions be correct to second order,[6] and when the redundancy is removed, it is found that the linear terms contribute to the quadratic portion of the potential energy expression. This will be described in more detail in Chapter II.

This type of field was first applied by Urey and Bradley[7] to tetrahedral XY_4 molecules, using a repulsive potential of Ar^{-n} between the non-bonded atoms. A and n are constants, and r is the distance between the non-bonded atoms. When this type of force field is used, the interaction terms arise because of the forces acting between non-bonded atoms. The number of independent force constants which arise when a Urey-Bradley field is used is smaller than the number when a general quadratic field is used. The Urey-Bradley force field, therefore, accounts for the interaction terms with a relatively small number of independent force constants and in a manner which is in accord with molecular structure, that is, in terms of van der Waals type forces acting between non-bonded atoms.

The Urey-Bradley force field has been found to be successful in its application to a considerable number of molecules.[8,9] A major difficulty encountered using the Urey-Bradley force field arises in connection with bending vibrations. In some cases, it is not possible to fit the bending frequencies. Consider the two rocking motions of the ethylene molecule shown below. The Urey-Bradley field requires that the same force constant describe both vibrations, but this does not permit the frequencies to be fitted. The fact that the same force constant does not describe both motions is not hard to understand, but it illustrates the failure of the field in the treatment of bending vibrations.

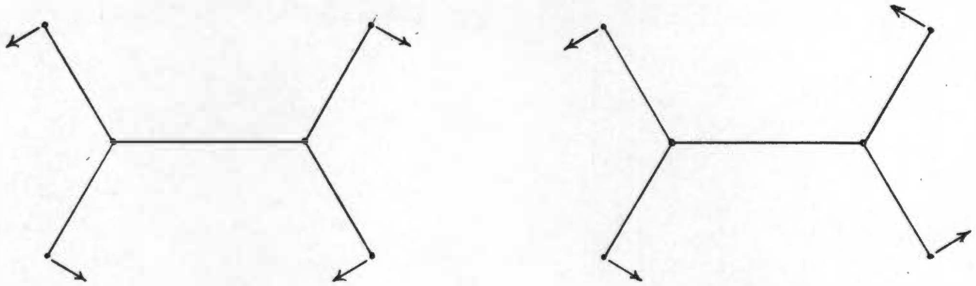

Figure 2. The Planar Rocking Motions of Ethylene.

5. The Orbital Valency Force Field

In an effort to extend the theory of bending vibrations, Linnett and Heath[10] developed the orbital valency force field. This field, basically a Urey-Bradley force field, attempts to interpret bending vibrations in terms of the changes in electronic overlap of the bonding orbitals in the molecule. In order to keep the decrease in electronic overlap at a minimum during a vibration, the orbitals of any particular atom are permitted to rotate. No changes in hybridization are allowed, so the orbitals of an atom maintain their positions with respect to each other, that is, they rotate as a unit. The first application of this field was to planar XY_3 molecules, and it was found that it was unnecessary to introduce a separate bending constant to account for the out-of-plane bending motion. Since different constants are necessary to account for the planar and non-planar bending modes if orbital rotation is not considered, this is strong evidence for the validity of the concept. In extending the orbital valency force field to tetrahedral XY_4 molecules, Linnett, Heath, and Wheatley[11,12,13] found that it was necessary, in the case of methane, to take into account changes in hybridization in order to explain the force constants. However, for most molecules, it is not possible to account for changes in hybridization.

A very interesting application of the orbital valency field to molecules possessing double bonds followed.[14] The formaldehyde and ethylene molecules were treated, but the frequencies which were used for ethylene were incorrectly assigned and the force constants calculated are thus in error. The approach is interesting, however, and the application of the field to molecules possessing multiple bonds shows promise.

6. The Transferability of Force Constants

It has long been recognized that molecules possessing like groups of atoms exhibit similar chemical behavior. It has likewise been found that like groups in different molecules possess similar vibrational frequencies. This leads to the concept of characteristic frequencies. The C-H stretching frequency, for example, occurs in the 3000 cm.$^{-1}$ region of the spectrum, regardless of the molecule in which the group is located. Certainly the frequencies differ somewhat from molecule to molecule, but all occur in the same region.

The occurrence of characteristic frequencies encouraged consideration of the idea of transferring force constants from molecules for which they are known to similar molecules whose spectra have not been observed, thus permitting the calculation of the fundamental vibrational frequencies of these molecules. In comparing force constants determined for similar vibrational motions occurring in different molecules, it is not expected that they will be exactly equal. Likewise, when force constants are transferred from molecules for which they are known to a similar molecule and the frequencies of this molecule are calculated, the calculated frequencies are not expected to be exact. This is because the forces acting in a molecule are determined by the electronic configuration of the molecule, and the electronic configuration of a portion of a molecule will be affected to some extent by the structure of the rest of the molecule. However, when the correct potential field is used, the variation of force constants should furnish information concerning the electron densities of the bonds. When force constants are transferred from one molecule to another, it is essential that the same type of potential field be used for both molecules.

Bending force constants are much smaller than stretching force constants, and as a consequence are much more sensitive to the interaction constants employed in the potential function. As a consequence, the transferring of bending force constants is likely to be less successful than transferring of stretching force constants.

C. Statement of the Problem

The orbital valency force field has been applied to several molecules* possessing single bonds only,[10-15] but only to formaldehyde and ethylene[14] in the case of molecules possessing double bonds. The treatment of

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*The molecules studied include planar molecules like BF_3, tetrahedral molecules like CCl_4, and octahedral molecules like SF_6. In addition, several anions like $CO_3^=$ and ClO_4^- were studied.

ethylene is not satisfactory, however, because of the use of incorrectly assigned frequencies.

The purpose of this investigation was to test the orbital valency force field thoroughly by applying it to ethylene and allene, and to then apply the field to formaldehyde, ketene, and diazomethane. The ethylene and allene molecules should furnish a very real test of the field, for the two molecules are quite similar. Formaldehyde, ketene, and diazomethane should provide further information with which to determine if the orbital valency force field adequately describes the bending motions of molecules possessing multiple bonds.

In addition to testing the orbital valency force field, it was an aim of this investigation to determine whether or not a unique solution for the force constants is obtained when repulsive forces between non-bonded atoms are used to account for the interaction terms in the potential energy expression. This is an important consideration, and one on which little work has been carried out. The calculation of the force constants for the ethylene molecule has been reported using a general quadratic field,[16,17] and a comparison of the force constants obtained in this investigation with those obtained using a general quadratic field should be informative.

CHAPTER II

THEORETICAL DISCUSSION

A. Theory of Molecular Vibrations

The logical manner in which to account for the observed vibrational spectrum of a molecule would be to set up the wave equation for the molecular system and solve the equation. Even for the simplest molecules, this is a difficult job, and as larger molecules are treated, it becomes necessary to devise a method by which an approximate solution of the wave equation may be obtained. It has been shown by Born and Oppenheimer[18] that a good approximation to the solution of the wave equation can be obtained by first solving a wave equation for the electrons alone, holding the nuclei in fixed positions, and then solving a wave equation for the nuclei alone, in which a value of the energy obtained from the electronic wave equation enters as a potential function. This potential function is considered to be a function of the internuclear distances. It is apparent that when the vibrational wave equation is determined in this manner, the electronic state of the molecule must remain unchanged, since the assumed potential function would change if a change in the electronic state occurred.

The wave equation for the nuclei, when solved, should give the solution for the vibrational, rotational, and translational motions of the molecule. However, when no external fields are present, the translational energy can be separated exactly.[19] Therefore, the wave equation for vibration and rotation alone can be considered. The solution of this wave equation is difficult, and in studies of potential fields, the assumption that this wave equation can be separated into a vibrational wave equation and a rotational wave equation is usually made. The vibrational wave equation accounts for the vibrational motion of the non-rotating molecule, and the rotational wave equation accounts for the rotational motion of the molecule considered as a rigid body. The separation of rotation and vibration is based on the assumptions that the momenta of inertia of the molecule are constant and that the interaction of the angular momenta of rotation and vibration is negligible. It is recognized that the effective moments of inertia are functions of the vibrational state, and likewise that the moments of inertia vary with the rotational quantum number, since the molecule is not a rigid rotor. The interaction of angular momenta of vibration and rotation is usually quite small; however, in some cases, the interaction is significant, and the inclusion of the vibration-rotation interaction can be used to provide further information concerning the nature of the potential field.[20,21] Very accurate data are necessary in order that this type of calculation be reliable. It should be pointed out that the approximations made in order to separate vibration and rotation do not lead to any error in the determination of the force constants. This is true because the positions of the band centers, which are used in determining the force constants, are not affected by the assumptions made in separating rotation and vibration.* The occurrence of vibrational angular momentum and the changes in moments of inertia do affect the intensity and rotational line spacing of a vibration-rotation band, however, and it is these effects which can be used for a further study of the potential field. However, we are not concerned with these factors in this investigation.

The problem has now been reduced to that of the vibrational motions of a group of mass points, the nuclei, which exist in a stable equilibrium configuration under the influence of a potential field. The wave equation for the vibrational motions of such a system can be set up, and if it is assumed that the vibrational motions are harmonic, the wave equation is easily solved when the potential and kinetic energies of the system are expressed in normal coordinates. When normal coordinates are used, the wave equation can be factored to yield (3N-6) wave equations which are in the form of harmonic oscillator wave equations, each being associated with one of the normal coordinates. Therefore, the solution of the vibrational wave equation predicts (3N-6) normal modes of vibration which are harmonic in character.

The solution of the vibrational wave equation is quite easy when the normal coordinates are known. However, the normal coordinates are in general not known, and it is necessary to express the kinetic and potential energies in terms of a known coordinate system in order to

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*It is possible that neglecting the changes in moments of inertia and the coupling of angular momenta would cause the analysis of a band to be wrong. However, these effects do not cause any shift in the true band center, and if the band centers are chosen correctly, the force constants calculated from this information will be correct.

solve the equations of motion. After the force constants for the molecule have been determined, the normal coordinates can then be found if desired.

The wave equation can be set up in terms of a chosen coordinate system and solved. However, the treatment from this point is more easily carried out using classical mechanics, and since the results are known to be the same as those obtained using quantum mechanics, classical mechanics will be utilized. According to the laws of mechanics, particles which are held in stable equilibrium by a potential field can carry out vibrations about the equilibrium positions. If the displacements are small, the potential energy, V, can be expanded in a power series in the coordinates chosen to describe the system. Since a non-linear molecule has (3N-6) degrees of vibrational freedom, (3N-6) independent coordinates are required to describe the system. The (3N-6) internal coordinates are chosen in such a manner that they are unaffected by rotations or translations of the molecule as a whole, that is, they satisfy the Eckart conditions.[21]

The potential energy for small vibrations of the atoms about their equilibrium positions in a molecule containing N atoms can then be expanded in a Taylor series in the (3N-6) internal coordinates, the q_i's, as:

$$2V = 2V_o + 2\sum_{i=1}^{3N-6} \left(\frac{\partial V}{\partial q_i}\right)_o q_i + \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_o q_i q_j + \begin{array}{l}\text{cubic and}\\ \text{higher}\\ \text{order}\\ \text{terms}\end{array} . \quad (7)$$

The term V_o represents the potential energy of the molecule in its equilibrium configuration, and since only changes in potential energy are of importance, this term can be chosen as zero. In addition, when the atoms are all in their equilibrium positions, the potential energy must be at a minimum. This requires that the coefficients of the linear terms, the $(\frac{\partial V}{\partial q_i})_o$, must all be zero. If the amplitudes of vibration are small, then the cubic and higher order terms will be quite small in comparison to the quadratic terms and can be ignored without introducing appreciable error. By ignoring these forces, we assume that the internuclear forces are linear functions of the displacement coordinates, which is equivalent to assuming that the motions are harmonic. Although it is realized that the vibrations are not truly harmonic since the displacements are finite, the error introduced should not be large. Inclusion of the higher order terms would not only introduce additional unknowns in the potential energy expression, but also greatly increase the complexity of the solution for the force constants. Furthermore, the evaluation of the additional unknowns which are introduced by including these higher order terms is impossible in almost all cases because of insufficient data. The potential energy for small displacements can therefore be written as

$$2V = \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_o q_i q_j \quad . \qquad (8)$$

This expression is usually written in the form

$$2V = \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} f_{ij} q_i q_j \qquad f_{ij} = \left(\frac{\partial^2 V}{\partial q_i \partial q_j}\right)_o \qquad (9)$$

and the f_{ij}'s are called the force constants. The kinetic energy, T, of the system can be expressed as

$$2T = \sum_{i=1}^{3N-6} \sum_{j=1}^{3N-6} a_{ij} \dot{q}_i \dot{q}_j \quad , \qquad (10)$$

where the a_{ij}'s are functions of the masses of the atoms and the geometry of the molecule and the dots indicate the time derivative.

When the expressions given in (9) and (10) are introduced for the potential energy and the kinetic energy in the equations of motion in Lagrangian form, a series of (3N-6) differential equations of the form

$$\sum_{j=1}^{3N-6} (a_{ij}\ddot{q}_j + f_{ij}q_j) = 0 \qquad (11)$$

are obtained. These equations are in the form of the differential equation for an harmonic oscillator, and the solutions of these equations yield (3N-6) equations of the form

$$q_j = A_j \sin (\lambda^{\frac{1}{2}}t + \delta_j) , \qquad (12)$$

where $\lambda = 4\pi^2\nu^2$, ν being the frequency of oscillation, A_j is the amplitude of the motion, and δ_j is simply a phase constant. Now, if this value of q_j is substituted into Equation (11), the following equations are obtained.

$$\sum_{i=1}^{3N-6} (f_{ij} - a_{ij}\lambda) A_j = 0 . \qquad (13)$$

This is a set of (3N-6) simultaneous, linear, homogeneous equations in terms of the (3N-6) unknown amplitudes A_j, and for solution to exist which are non-trivial, that is, the A_j's not all equal to zero, it is necessary that the determinate of the coefficients must vanish. Therefore

$$\left| f_{ij} - a_{ij}\lambda \right| = 0 . \qquad (14)$$

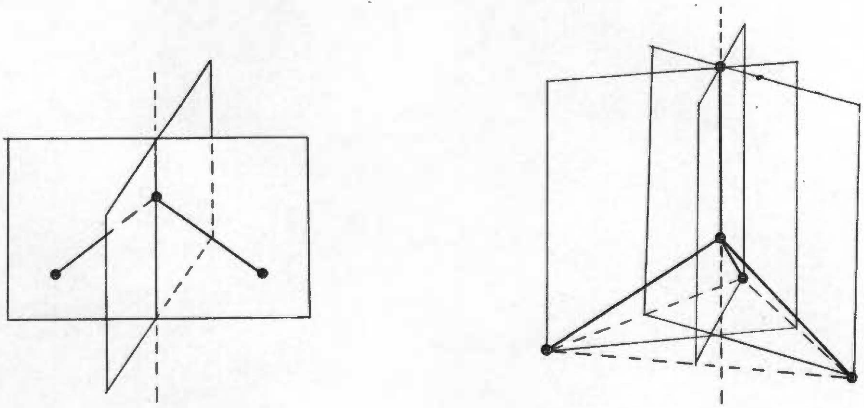
This is the secular determinant of order (3N-6), and is the equation which is used in order to calculate the force constants when the frequencies are known. This secular determinant can be expanded to give a polynomial equation in λ of the general form

$$\lambda^{(3N-6)} + C_1(\lambda)^{(3N-7)} + C_2\lambda^{(3N-8)} + ----- + C_{(3N-7)}\lambda + C_{(3N-6)} = 0 \quad (15)$$

where the C_i's are functions of the a_{ij}'s and the f_{ij}'s. Once the secular equation has been obtained, several standard methods are available for solving the equation for the force constants.[23] However, the solution of this equation is quite difficult when the order of the equation is large. In order to factor the secular equation to the maximum possible extent and thus simplify the solution of the equation for the force constants, group theoretical methods are utilized.

1. Group Theory

The application of group theory to the problem of molecular vibrations is based on the symmetry properties of molecules. Many common molecules, for example, H_2O and CH_3Cl, possess some symmetry. The geometrical structures of these two molecules are shown in Figure 3. Con-



(a) (b)

Figure 3. (a) The Structure of the H_2O Molecule; (b) The Structure of the CH_3Cl Molecule.

sider the H_2O molecule. It is readily seen that this molecule has two planes of symmetry, one coinciding with the plane of the molecule, and the other perpendicular to the plane of the molecule. In addition, the axis passing through the oxygen atom and the mid-point of the line connecting the hydrogen atoms is a twofold axis of symmetry, since a rotation of the molecule through 180° about this axis produces a configuration which is indistinguishable from the original configuration. The two planes of symmetry and the twofold axis of symmetry are examples of symmetry elements, and the reflection through a plane of symmetry or rotation about an axis of symmetry, which produce configurations which are indistinguishable from the original configuration, are the corresponding symmetry operations. The particular elements of symmetry which a molecule possesses determine the point group to which the molecule belongs, and every molecule can be assigned to one of a small number of point groups. The H_2O molecule belongs to the point group C_{2v}, since it possesses two planes of symmetry and a twofold axis of symmetry. The CH_3Cl molecule, shown in Figure 3 (b), possesses three planes of symmetry and a three-fold axis of symmetry, and belongs to the point group, C_{3v}. NH_3 and CH_3CN are examples of other molecules belonging to this point group.

The symmetry operations, when carried out on a molecule in its equilibrium configuration, produce configurations which are indistinguishable from the original configuration. Now, in order to determine the effect of the symmetry operations on the potential energy, the effect of the symmetry operations on a molecule in a given distorted configuration must be considered. When a symmetry operation is carried out on a molecule in a distorted configuration, the resulting configuration may be different from the original one, but the same interatomic distances and angles will occur in both configurations. Therefore, since the potential energy is assumed to depend only on the interatomic distances and angles, it must be invariant with respect to the symmetry operations. By a similar argument, it is readily shown that the kinetic energy is likewise invariant under the symmetry operations.

It has been pointed out previously that it is most convenient to express the potential energy in terms of changes in bond lengths and bond angles. However, in order to factor the secular equation to the maximum extent, it is necessary to use linear combinations of these internal coordinates. These linear combinations of the internal coordinates are called symmetry coordinates, and are chosen in such a manner that they are either unaltered (symmetric) or changed in sign (antisymmetric) by a given symmetry operation of the point group. The symmetry coordinates can then be divided into sets, or species, by determining how they transform under the group operations. The symmetry coordinates belonging to a particular species all transform in the same way under the group operations, while coordinates belonging to other species are transformed in a different way by at least one of the group operations. Therefore, no cross terms occur in either the kinetic or potential energies involving coordinates of different species, since if these terms were present, the kinetic and potential energies would be changed by one or more of the group operations.

The different species are designated by symbols such as A_1, A_2, B_1, and B_2 for point group C_{2v}, and A_1, A_2 and E for point group C_{3v}. The letters A and B represent non-degenerate species, while E represents a doubly-degenerate species. Species designated by the symbol A are symmetric with respect to a principle axis of symmetry, and the symbol B represents species which are antisymmetric with respect to a principle axis. Numerical subscripts are used to indicate whether the species are symmetric or antisymmetric with respect to either a two-fold axis perpendicular to the principal axis or to a vertical plane of symmetry. In addition, when a molecule possesses a center of symmetry, for example, C_2H_4, the subscripts g and u are employed to designate whether the species are symmetric or antisymmetric with respect to the center of symmetry.[24]

To illustrate the simplification of the secular equation which is brought about by the use of symmetry coordinates, consider the CH_3Cl molecule. The secular equation is of order nine, but when the proper symmetry coordinates are used, the equation is factored into three third-order factors, two of which are degenerate. The amount of work required to evaluate the force constants is therefore reduced greatly by the factoring of the equation.

In addition to factoring the secular equation, the application of group theory to molecular vibrations also enables the selection rules for infrared and Raman spectra to be determined, as well as further information concerning the nature of the vibrational modes. For a more general and detailed treatment of these subjects, the reader is referred to "Molecular Vibrations," by Wilson, Decius, and Cross.

2. The Form of the Secular Equation

The familiar $\mathfrak{F}$ and $\mathfrak{G}$ matrix method due to Wilson[25,26] was used to obtain the factored secular equation. The secular equation is given by

$$\left| \mathfrak{G}\mathfrak{F} - \lambda I \right| = 0 , \tag{16}$$

where

$$\mathfrak{G} = UBM^{-1}\tilde{B}\tilde{U} \tag{17}$$

and

$$\mathfrak{F} = UF\tilde{U}. \tag{18}$$

M^{-1} is the inverse of the diagonal matrix where elements are the atomic masses, B is the transformation matrix relating the internal coordinates to the Cartesian displacement coordinates, U is the orthogonal transformation relating the symmetry coordinates to the internal coordinates, and F is the potential energy matrix whose elements are the force constants. The roots of the secular equation, the λ_i, are related to the fundamental frequencies by

$$\lambda_i = 4\pi^2 c^2 \nu_i^2 , \tag{19}$$

where ν is the frequency in cm.$^{-1}$.

Rather than evaluating the transformation matrix B, it is usually more convenient to determine the $\mathfrak{G}$ matrix by expressing the internal coordinates in terms of $\vec{S}$ vectors. The $\vec{S}$ vectors are defined in the following manner. For a given internal coordinate R_k, a vector $\vec{S}_{kt}$ is defined for each atom t of the molecule so that for an arbitrary displacement $\vec{\rho}_t$ for each atom

$$R_k = \sum_{t=1}^{3N-6} \vec{S}_{kt} \cdot \vec{\rho}_t . \tag{20}$$

The physical meaning of the vector $\vec{S}_{kt}$ can be simply illustrated. If all of the atoms in the molecule are in their equilibrium positions, then the direction of $\vec{S}_{kt}$ is the direction in which a given displacement of atom t will produce the greatest change in R_k, and the magnitude of $\vec{S}_{kt}$ is equal to the increase in R_k which is brought about by a unit displacement of the atom in this direction. The vectors can usually be written down by inspection. The transformation to symmetry coordinates yields

$$\vec{\mathcal{S}}_{kt} = \sum_{i=1}^{3N-6} U_{ki}\vec{S}_{it} \tag{21}$$

and the elements of the $\mathcal{G}$ matrix are then given by

$$\mathcal{G}_{ki} = \sum_{t=1}^{3N-6} \mu_t \vec{\mathcal{S}}_{kt}\cdot\vec{\mathcal{S}}_{it} \quad , \tag{22}$$

where μ_t is the reciprocal mass of the atom t.

B. Interaction Terms in the Potential Energy Expression

In the discussion of potential fields in Chapter I, it was pointed out that it is usually necessary to introduce interaction terms into the potential energy expression in order to obtain a suitable description of the potential field of a molecule. When a valency force field is used, the nature of these cross terms is not well understood, and it is difficult to decide which of the permitted interaction terms should be included. The inclusion of the interaction terms can be justified on a physical basis by observing that a change in a bond length or a bond angle in a molecule will change the electronic configuration, and this may lead to changes in the other bond lengths and bond angles in the molecule. Thompson and Linnett[27] have explained the positive sign of the bond-bond interaction term in CO_2 in terms of resonance theory. According to their argument, if one of the bonds is lengthened, there is a tendency for the other bond to decrease in length and become stronger. Therefore, the interaction constant would be positive. A study[28] of the bond-bond interaction term in YXY molecules showed that the sign of the interaction term could be explained in terms of the change in one XY bond when the other XY bond was broken. If the bond length in the XY molecule is greater than the bond length in the YXY molecule, then the interaction constant would be expected to be negative, while if the bond length in the XY molecule is less than the bond length in the YXY molecule, the interaction constant would be expected to be positive. This relationship was found to exist in every case in a study of 10 molecules. However, in larger molecules, it is not possible to make such a simple interpretation of the interaction constants.

When a modified valency force field is used to describe the potential field of a molecule, the assumption that the interaction terms involving coordinates which are far apart from each other in a molecule are very small and can be neglected is usually employed. In addition, when molecules possessing C-H bonds are considered, the interactions involving the C-H stretching motions and other motions in the molecule are often ignored. This is due to the fact that when a frequency is widely separated from the other frequencies belonging to the same symmetry species, the interaction constants connecting this motion with the other motions have relatively little effect on the frequencies. When this reasoning is used in selecting the interaction constants to include in the potential energy expression, the resulting potential function usually furnishes an acceptable description of the potential field; that is, a set of force constants can be determined which will reproduce the observed frequencies of the molecule rather well. However, it is desirable to account for the interaction terms in a manner which would permit a more complete understanding of the forces acting in a molecule.

1. Interaction Terms Arising From Forces Between Non-bonded Atoms

The proposal by Urey and Bradley that forces between non-bonded atoms be included in the potential energy expression furnishes a method by which interaction terms can be introduced which is consistent with theoretical considerations and which permits the interaction constants to be interpreted more clearly. As a first approximation, the interaction between two non-bonded atoms in a molecule may be considered the same as the interaction between two corresponding inert gas atoms. For example, in the ethylene molecule, the forces acting between a carbon atom and a hydrogen atom to which it is not bonded can be considered in terms of the forces acting between a helium atom and a neon atom separated by the same distance as the carbon and hydrogen atoms in the molecule. It is recognized that this is a very rough approximation, but the forces acting in the two cases should be of essentially the same form.

It has been found[29,30] that the potential energy between two like inert gas atoms can be expressed by

$$V = \frac{a}{R^{12}} - \frac{b}{R^{6}} , \qquad (23)$$

where a and b are positive constants and R is the distance between the two atoms. The first term corresponds to a repulsion between the two atoms, while the second term corresponds to an attraction between the atoms. Although later work[31] has led to the expression of the repulsion term in the form of an exponential in R, the above expression is exact enough for the present work. In the molecules which are studied in this problem, the distances between the non-bonded atoms are of the order of 2Å, and at this distance, the repulsive term in the potential energy expression, $\frac{a}{R^{12}}$, is the predominant one. Therefore, the potential energy can be written approximately as

$$V = \frac{a}{R^{12}} \quad . \tag{24}$$

The contribution to the potential energy for a small change in the equilibrium distance between two non-bonded atoms in a molecule can be written as

$$\Delta V = -B\Delta R + A\Delta R^2 \,, \tag{25}$$

where

$$B = -\left(\frac{\partial V}{\partial R}\right), \qquad A = \tfrac{1}{2}\left(\frac{\partial^2 V}{\partial R^2}\right), \tag{26}$$

and R is the distance between the two atoms. Utilizing the expression for the potential energy given in Equation (2~~3~~4), it is found that

$$\frac{B}{R_e} = \frac{2}{13} A \,, \tag{27}$$

where R_e is the equilibrium distance between the non-bonded atoms. The use of the potential energy in the form given by Equation (24) enables the constants B and A to be related, and thus only one constant is introduced into the potential energy expression for the molecule for each pair of non-bonded atoms which are assumed to repel each other.

The necessity of including the linear term, $-B\Delta R$, in the potential energy expression has been questioned. Torkington[32] states that the constant B cannot appear in the secular equation because the linear terms in the internal coordinates must vanish in order that the equilibrium configuration of the molecule be stable. The requirement that the linear terms must vanish is correct; however, when the coordinates which are used to describe the repulsions between non-bonded atoms are expressed in terms of the set of independent internal coordinates of the molecule, the linear term is found to introduce quadratic contributions to the potential energy. In order to illustrate this point, the non-linear XYZ molecule will be considered. The geometry of the XYZ molecule is shown in Figure 4. The potential energy of the molecule, based on a Urey-Bradley force field, is

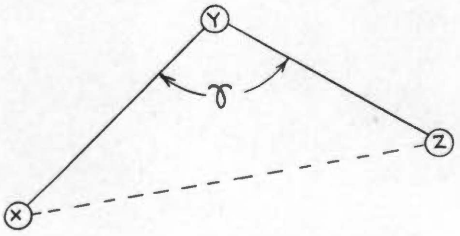


Figure 4. The Geometry of the Non-linear XYZ Molecule.

$$2V = k_1(\Delta r_1)^2 + k_2(\Delta r_2)^2 + k_\gamma(\Delta\gamma)^2 + B_1(\Delta r_1) + B_2(\Delta r_2) + B_\gamma(\Delta\gamma) - 2B(\Delta R_1) + 2A(\Delta R_1)^2, \qquad (28)$$

where the last two terms account for the repulsion between the non-bonded X and Z atoms. The coordinate ΔR is a function of the other coordinates, and in order to remove this redundancy, the transformation expressing ΔR as a function of Δr_1, Δr_2, and $\Delta\gamma$ is desired. The important point to be observed is that the transformation must include second-order terms, because of the presence of the linear term $-2B(\Delta R_1)$. Employing the law of cosines, the equilibrium distance between the two non-bonded atoms can be written as

$$R_e^2 = r_1^2 + r_2^2 - 2r_1 r_2 \cos\gamma , \tag{29}$$

where the subscript e indicates the equilibrium value. The change in the distance R produced by infinitesimal changes in the bond lengths and bond angle is then given by

$$(R_e + \Delta R)^2 = (r_1 + \Delta r_1)^2 + (r_2 + \Delta r_2)^2 - 2(r_1 + \Delta r_1)(r_2 + \Delta r_2) \cos(\gamma + \Delta\gamma) . \tag{30}$$

For small changes in γ, the term $\cos(\gamma + \Delta\gamma)$ can be expressed in the form

$$\cos(\gamma + \Delta\gamma) = \cos\gamma - \frac{\cos\gamma}{2}\Delta\gamma^2 - \sin\gamma\,\Delta\gamma , \tag{31}$$

which is correct to second order in $\Delta\gamma$. When this value is substituted into Equation (30), the equation becomes

$$2R_e\Delta R + \Delta R^2 = (2r_1 - 2r_2 \cos\gamma)\Delta r_1 + (2r_2 - 2r_1 \cos\gamma)\Delta r_2 + 2r_1 r_2 \sin\gamma\,\Delta\gamma + \Delta r_1^2 + \Delta r_2^2 + r_{1e}r_2 \cos\gamma\,(\Delta\gamma)^2 - 2\cos\gamma\,\Delta r_1\Delta r_2 + 2r_2 \sin\gamma\,\Delta r_1\Delta\gamma + 2r_1 \sin\gamma\,\Delta r_2\Delta\gamma . \tag{32}$$

The cubic terms which arise have been ignored. When Equation (32) is solved for ΔR, and the resulting expression is simplified, ΔR is found to be

$$\Delta R = \cos\phi\,\Delta r_1 + \cos\theta\,\Delta r_2 + \frac{r_1\,r_2}{R_e}\sin\gamma\ \Delta\gamma + \frac{1}{2R_e}\sin^2\phi\ \Delta r_1^2$$

$$+ \frac{1}{2Re}\sin^2\theta\ \Delta r_2^2 - \frac{r_1\,r_2}{2Re}\cos\phi\ \cos\theta\ \Delta\gamma^2 - \frac{1}{Re}\sin\phi\ \overset{\sin\theta}{\wedge}\ \Delta r_1\Delta r_2$$

$$+ \frac{1}{Re}\,r_2\ \sin\phi\ \cos\theta\ \Delta r_1\Delta\gamma + \frac{1}{Re}\,r_1\ \sin\theta\ \cos\phi\ \Delta r_2\Delta\gamma\,. \quad (33)$$

When this value of ΔR is substituted into the potential energy expression given by Equation (28), the potential energy becomes

$$2V = \left[k_1 \overset{-}{\cancel{+}} \frac{B}{R_e}\sin^2\phi + 2A\cos^2\phi\right]\Delta r_1^2 + \left[k_2 - \frac{B}{Re}\sin^2\theta + 2A\cos^2\theta\right]$$

$$\Delta r_2^2 + \left[k_\gamma + \frac{B}{R_e}\,r_1\,r_2\ \cos\phi\ \cos\theta + 2A\,r_1\,r_2\ \sin\phi\ \sin\theta\right]\Delta\gamma^2$$

$$+\left[\frac{2B}{R_e}\sin\phi\ \sin\theta + 4A\cos\phi\ \cos\theta\right]\Delta r_1\Delta_2$$

$$+\left[-\frac{2B}{R_e}\,r_2\ \sin\phi\ \cos\theta + 4A\,r_{1e}\sin\phi\ \cos\phi\right]\Delta r_1\Delta\gamma$$

$$+\left[-\frac{2B}{R_e}\,r_1\ \sin\theta\ \cos\phi + 4A\,r_2\sin\phi\ \cos\theta\right]\Delta r_2\Delta\gamma$$

$$+\left[B_1 - 2B\cos\phi\right]\Delta r_1 + \left[B_2 - 2B\cos\theta\right]\Delta r_2$$

$$+\left[B_\gamma - \frac{2B}{R_e}\,r_1\,r_2\ \sin\gamma\right]\Delta\gamma\,. \quad (34)$$

? 34

The last three terms in Equation (11) must vanish in order that the equilibrium configuration be stable, and this condition allows B_1, B_2, and B_γ to be evaluated in terms of B. These ~~terms~~ [illegible] are not important in the XYZ molecule, but in more complicated molecules such as ethylene, they must be determined in order that their contribution to the potential energy during the out-of-plane vibrational motions can be determined. This contribution during non-planar modes arises because the changes in the Δr's and the ΔR's are not in the same ratio for planar and non-planar motions.

Equations (33) and (34) show how the quadratic contributions to the potential energy arise from the linear term $-B\Delta R$, and it is apparent that Torkington is wrong in his statement that such terms do not occur. The problem of including linear terms in the potential energy expression when redundant coordinates are used is discussed by Wilson, Decius and Cross.[33] p.172 These authors point out that when a completely general quadratic field is used, it appears to be unnecessary to introduce linear terms into the potential energy expression when redundant coordinates are used, since the lack of data makes it impossible to evaluate the constants arising from these terms. However, when forces between non-bonded atoms are considered, it is possible to relate the coefficients of the linear terms to the coefficients of the quadratic terms, and these terms should be included.

2. Repulsive Forces Between Non-bonded Hydrogen Atoms

The molecules which are studied in this investigation, C_2H_4, C_3H_4, CH_2O, CH_2CO, and CH_2N_2, all possess hydrogen atoms between which repulsive forces would be predicted on the basis of the potential field assumed. The hydrogen atoms are small, and the force of repulsion between non-bonded hydrogen atoms might be expected to be small. Linnett and Wheatley[13] found that it was possible to ignore the hydrogen-hydrogen repulsion in CH_4, and it was likewise found that this repulsion could be ignored in treating CH_2O.[14] Further evidence that the hydrogen-hydrogen repulsion is small compared to the repulsion between a hydrogen atom and a carbon or oxygen atom is obtained from a consideration of the magnitude of the helium-helium and neon-neon repulsion forces. Considering only the repulsive portion of the potential energy between inert gas atoms,[34] it is found that the contribution to the potential energy, $\frac{1}{2}(\frac{\partial^2 V}{\partial R^2})$, for a small change in the distance between two neon atoms is 10 times as great as that for two helium atoms which are the same distance apart as the neon atoms. The potential energy contribution when a neon atom and a helium atom are considered will lie between these two values, and will be considerably greater than the value for the helium-helium case.

For these reasons, it has been assumed that the repulsive force between non-bonded hydrogen atoms can be ignored. It is desirable to ignore this repulsion because when this is done, only one type of repulsion must be considered in each of the molecules treated. This leads to a simple secular determinant which can be solved in a straightforward manner, whereas if another constant is introduced into the potential energy expression, the solution of the secular equation becomes much more difficult.

C. Theory of Bending Vibrations in Terms of the Orbital Valency Force Field

The orbital valency force field was proposed by Heath and Linnett[10] in 1948 in an attempt to extend the theory of bending vibrations. The field is based on the assumptions that the bond-forming orbitals of an atom are fixed at definite angles with respect to each other, and that the most stable bond is formed between two atoms when the overlap of the bonding orbitals is a maximum. Using such a picture, it is possible to consider an angular distortion in terms of the change in overlap of the bonding orbitals which is brought about by the distortion. Furthermore, use of this concept accounts for the fact that during some of the vibrational motions, rotation of the bonding orbitals of an atom will lead to a decrease in the potential energy, and this rotation must be taken into account in determining the potential energy expression.

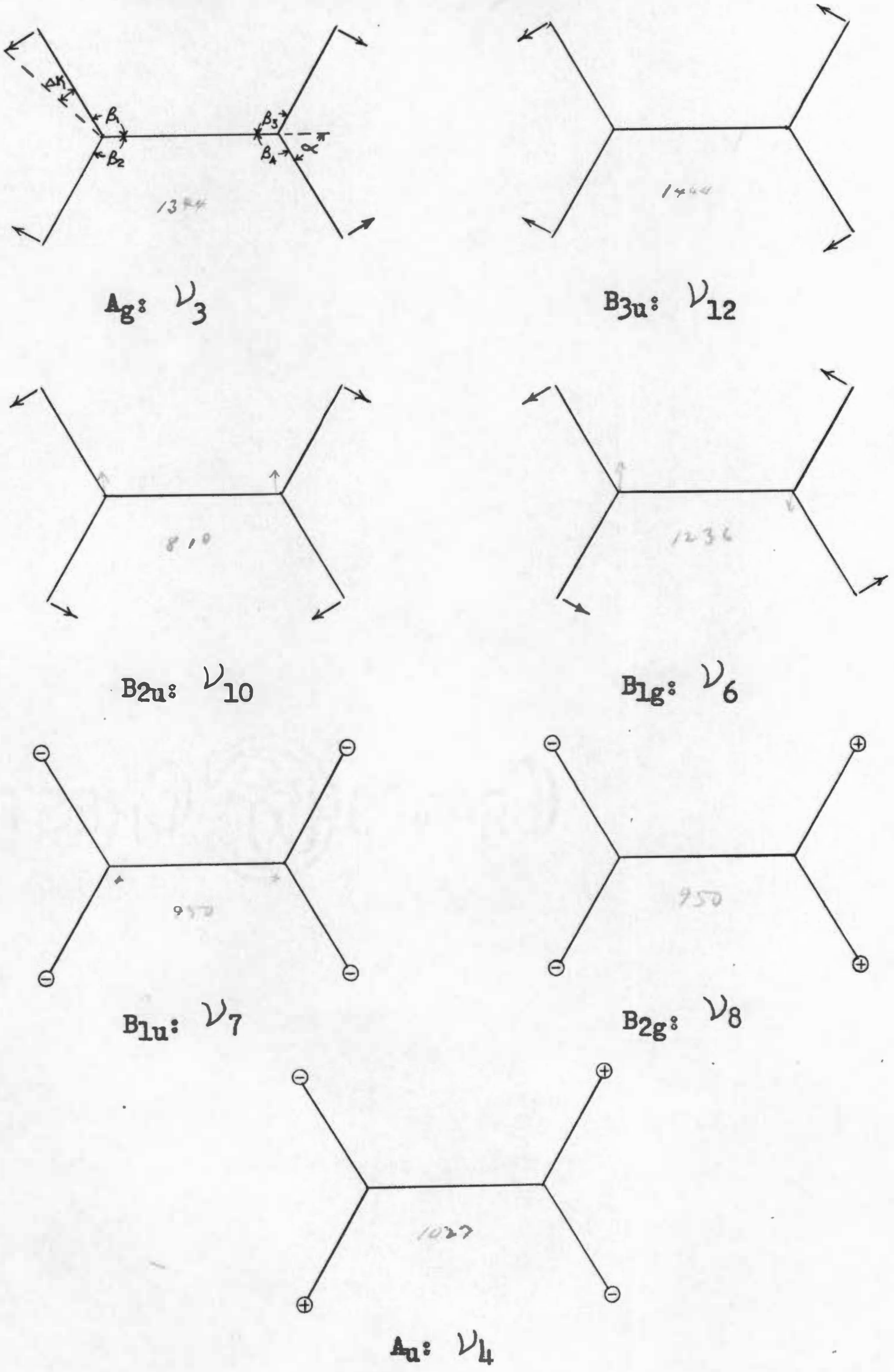
When this field was applied to a group of planar XY_3 molecules, it was found that only one force constant was necessary to describe the planar bending mode and the non-planar bending mode. This is a consequence of the fact that if the bending orbitals of the molecule are symmetrical about the bond axes, then the restoring force associated with a given angular distortion in the plane is the same as the restoring force associated with an equivalent distortion out of the plane. When a valency force field is used, it is necessary to introduce a separate bending constant for the out-of-plane motion, and the fact that the orbital valency force field is able to account for both motions using only one constant indicates that the concept is valid. The orbital valency force field was next applied to a group of eight tetrahedral halides,[11] and the results obtained were quite good. However, when the field was applied to CH_4,[13] it was found to be unsatisfactory. The force constant associated with the bending of a C-H bond was found to be 1.35×10^5 dynes cm.$^{-1}$ when the doubly-degenerate bending frequency was used and 0.86×10^5 dynes cm.$^{-1}$ when the triply degenerate bending frequency was used. The orbital valency force field requires that these constants be the same, and is unable to account for the large difference. In an attempt to explain this difference, the possibility of changes in hybridization of the carbon orbitals during the vibrations was considered. If changes in hybridization of the carbon orbitals can occur during a vibration in such a manner that the orbitals can follow the movements of the hydrogen atoms, then the change in hybridization may lead to a decrease in the potential energy. An examination of the wave functions of the carbon orbitals revealed that a change in hybridization which would permit orbital following can occur during the triply-degenerate bending motion, but that no change in hybridization is possible during the doubly-degenerate bending motion. This explains why the bending constant associated with the doubly-degenerate vibration is larger than the bending constant associated with the triply-degenerate vibration. It should be emphasized that orbital following arises from a change in hybridization, and is quite different from the orbital rotation which is permitted in using the orbital valency force field. Orbital following involves a change in the angles between the bonding orbitals of an atom, while orbital rotation involves a rotation in which the bonding orbitals of an atom rotate as a unit, retaining their original configuration with respect to each other. In general, it is not possible to account for changes in hybridization because of lack of sufficient data, but it is necessary to realize that such changes may occur. *

The orbital valency force field was then applied to formaldehyde and ethylene,[14] molecules which contain double bonds. Unfortunately, the frequencies which were used for ethylene were incorrectly assigned, and the force constants obtained were incorrect. No further applications of the orbital valency force field to molecules possessing multiple bonds have been reported.

In this investigation, the orbital valency force field has been applied to ethylene, allene, formaldehyde, ketene, and diazomethane. The manner in which the potential energy expressions for the bending motions of these molecules were obtained will now be presented.

1. Ethylene

The ethylene molecule, C_2H_4, belongs to the point group V_h. It possesses 12 fundamental vibrational modes, 7 of which involve bending motions. The bending vibrations are shown in Figure 5, along with the species to which they belong. Now it is necessary to consider the structure of the bonding orbitals in the molecule. The carbon-carbon double bond is made up of a σ bond and a π bond, while only σ bonds are formed between the carbon and hydrogen atoms. It is desired to associate force constants with the changes in orbital overlap which occur during the bending motions, and in order to accomplish this, the molecular orbitals are considered as being formed by the overlapping of the directed atomic orbitals of the atoms comprising the molecule. The ethylene molecule, based on this model, is shown in Figure 6. The teardrop-shaped orbitals represent σ orbitals and these are cylindrically symmetric with respect to the bond axes. The circular orbitals represent π orbitals, and these orbitals are also cylindrically symmetric with respect to their axes. The orbital valency force field constants are determined on the basis of the changes in orbital overlap which would occur in this model when orbital rotation is permitted. It is recognized that this model does not give a true picture of the orbital structure of a molecule, but



Ag: ν_3 B3u: ν_{12}

B2u: ν_{10} B1g: ν_6

B1u: ν_7 B2g: ν_8

Au: ν_4

Figure 5. The Bending Vibrations of Ethylene.

it is as close an approximation as can be made at this time.

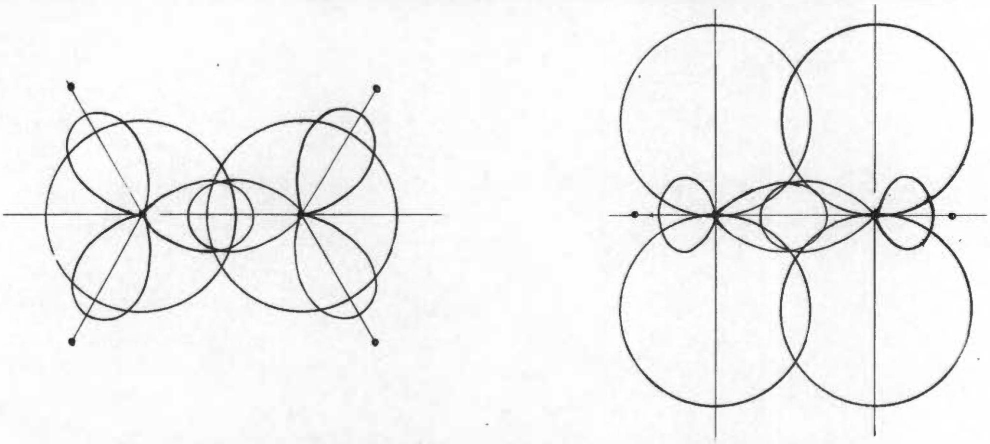


Figure 6. The Orbital Model of Ethylene.

The variation of the potential energy when a C-H bond is distorted is defined as

$$2V = K_H\ (\Delta\kappa)^2, \qquad (35)$$

where $\Delta\kappa$ is the angle formed found by the C-H bond axis in its equilibrium position and the line connecting the carbon and hydrogen atoms in the distorted position. The σ bonds are symmetrical about their axes, so the potential energy change produced by a bending of the C-H bond in the plane of the molecule is the same as that for the bending of the bond through the same angle perpendicular to the plane of the molecule. The bending vibrations are pictured in Figure 5, and the potential energy associated with each of the motions will now be determined.

a. <u>The A_g and B_{3u} bending vibrations</u>. From an examination of the orbital structure shown in Figure 6, it is clear that no orbital rotation can occur in the A_g and B_{3u} bending modes. Therefore, the potential energy expression for these motions can be written as

$$2V = K_H \sum_{i=1}^{4} (\Delta\beta_i)^2, \qquad (36)$$

where $\Delta\beta$ represents the change in an HCC angle. It is clear that $\Delta\beta$ is equal to the angular distortion of the C-H bond, so it is correct to express the potential energy in terms of the $\Delta\beta$'s.

b. The B_{2u} bending vibration. In the B_{2u} rocking motion, orbital rotation may occur. If the orbitals of the carbon atoms are allowed to rotate in the direction in which the hydrogen atoms to which they are bonded have been displaced, the potential energy of the motion will be decreased if the increase in orbital overlap of the C-H σ bonds is greater than the decrease in orbital overlap of the C-C σ bond. The magnitude of the angle through which the orbitals rotate is determined in the following manner. The potential energy of the vibrational motion before orbital rotation is permitted is

$$2V = K_H \sum_{i=1}^{4} (\Delta\beta_i)^2 \tag{37}$$

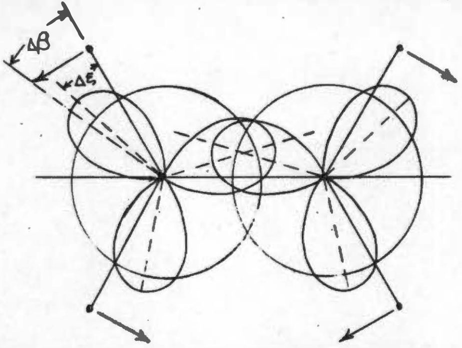
and is seen to be the same as the potential energy for the A_g and B_{3u} vibrations. This expression would be correct if the carbon-carbon bond were so strong that no orbital rotation would occur. This bond is not infinitely strong, however, so orbital rotation will occur. The orbitals of each carbon atom are now allowed to rotate through an angle, $\Delta\xi$, in order to minimize the potential energy. The orbital picture after this rotation occurs is shown in Figure 7.

The overlap of the π bond is unaffected by this rotation. The overlap of the carbon-carbon σ bond is decreased, however, and this will cause an increase in potential energy. The potential energy after the orbital rotation is actually, the force const for C-H bond overlap

takes care of decrease in k due to less rehybridization in C-H σ bond overlap

$$2V = \underline{\underline{K_H}} \sum_{i=1}^{4} (\Delta\beta_i - \Delta\xi)^2 + k_\sigma^u (\Delta\xi)^2, \tag{38}$$

where k_σ^u is the force constant associated with the bending of the carbon-carbon σ bond in the manner shown in Figure 7. The orbitals will rotate



Note the σ bonds of both C atoms rotate, & it is this "manner" which defines k^u_σ. Not same as Ket.(?)

Figure 7. The Effect of Orbital Rotation During the B_{2u} Vibration of Ethylene.

until the potential energy is a minimum. Therefore, Δξ can be determined by minimizing V with respect to Δξ.

$$\frac{\partial V}{\partial(\Delta\xi)} = 0 = -K_H \sum_{i=1}^{4} (\Delta\beta_i - \Delta\xi) + k_\sigma^u (\Delta\xi). \tag{39}$$

When this expression is solved for Δξ, one obtains

$$\Delta\xi = \frac{K_H}{4K_H + k_\sigma^u} \sum_{i=1}^{4} (\Delta\beta_i). \checkmark \tag{40}$$

It is readily seen that if the carbon-carbon σ bond were infinitely strong ($k_\sigma^u = \infty$), Δξ would be zero and no orbital rotation would occur. Substitution of the value of Δξ given by Equation (40) into Equation (38), followed by a straightforward simplification, gives the potential energy as

$$2V = \frac{3K_H^2 + K_H k_\sigma^u}{4K_H + k_\sigma^u} \sum_{i=1}^{4} (\Delta\beta_i)^2 - \frac{2\,K_H^2}{4K_H + k_\sigma^u} \sum_{\substack{i,j \\ i \neq j}}^{4} \Delta\beta_i \Delta\beta_j. \tag{41}$$

This expression gives the potential energy for the B_{2u} rocking motion in terms of the $\Delta\beta_i$'s, the changes in the H-C-C angles. In order to obtain the $\mathfrak{F}$ matrix element for this mode, the potential energy matrix determined by Equation (41) must be symmetrized. The correct symmetry coordinate for the B_{2u} motion, in terms of the $\Delta\beta_i$'s, is $\frac{1}{2}(\Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4)$. However, because of the fact that the potential energy is written as a sum of squares before orbital rotation is taken into account, any sign associated with the angular displacements disappears and is not recovered in subsequent manipulations. Consequently, the proper symmetry coordinate to use in order to obtain the B_{2u} $\mathfrak{F}$ matrix element is the sum of the $\Delta\beta_i$'s, $\frac{1}{2}(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4)$. When the symmetrization is carried out, the diagonal $\mathfrak{F}$ matrix element for the B_{2u} bending vibration is found to be

$$\frac{K_H k_\sigma^u}{4K_H + k_\sigma^u} \; . \tag{42}$$

Symmetrization of the matrix determined by Equation (42) using the other three orthogonal linear combinations of the $\Delta\beta_i$'s, which correspond to the A_g, B_{3u}, and B_{1g} bending vibrations, yields three diagonal $\mathfrak{F}$ elements which are just K_H. This fact indicates that the rotation of the orbitals in the manner permitted during the B_{2u} vibration cannot occur during the A_g, B_{3u}, or B_{1g} vibrations. The correct elements for A_g and B_{3u} is K_H, because no orbital rotation in any manner is possible during these motions. However, in the B_{1g} rocking motion, the orbitals can rotate in a different manner from the motion of the B_{2u} rocking vibration, and this rotation must be considered independently in order to determine the correct $\mathfrak{F}$ matrix element for the B_{1g} rocking motion.

c. The B_{1g} bending vibration. The B_{1g} bending vibration is also a rocking motion of the CH_2 groups. However, in this case, the two ends rock in the same circular direction. Again it is possible for orbital rotation to occur, but the effect on the carbon-carbon σ bond is different from that in the B_{2u} vibration. The potential energy for the motion before orbital rotation is taken into account is

$$2V = K_H \sum_{i=1}^{4} (\Delta\beta_i)^2 \ . \tag{43}$$

The orbitals of each carbon atom are now allowed to rotate through an angle $\Delta\xi$. The orbital picture after rotation is shown in Figure 8.

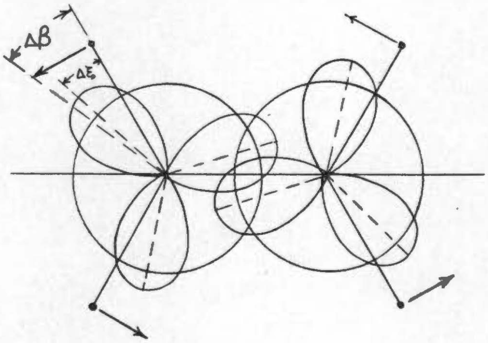
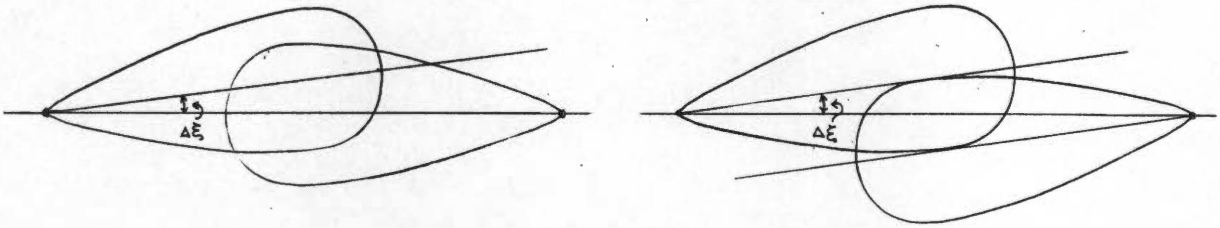


Figure 8. The Effect of Orbital Rotation During the B_{1g} Vibration of Ethylene.

The potential energy after the rotation is

$$2V = K_H \sum_{i=1}^{4} (\Delta\beta_i - \Delta\xi)^2 + k_\sigma^g (2\Delta\xi)^2 \ . \tag{44}$$

k_σ^g is defined as the force constant which is associated with the change in overlap which occurs when one of the carbon σ orbitals is rotated through a unit angle. Therefore, when each of the carbon σ orbitals is rotated through an angle, $\Delta\xi$, in the same circular direction, the potential energy is $k^g\,(2\Delta\xi)^2$. Figure 9 illustrates this point. k^g_σ is



(a) (b)

Figure 9. The Change in Overlap of the σ Orbitals During the B_{1g} Vibration of Ethylene

defined as the constant which is associated with the change in overlap occurring during the motion shown in Figure 9 (a). Therefore, the potential energy for this motion is $2V = k^g_\sigma\,(\Delta\xi)^2$. Figure 9 (b) shows the change in orbital overlap which occurs in the B_{2u} motion, and if the force associated with the change in orbital overlap is linear, the potential energy for this motion, assuming infinitesinal displacements, is $2V = k^g_\sigma\,(2\Delta\xi)^2$. This constant was defined in this manner so that it would be the same as the corresponding constant in allene, which will be discussed later. This definition of k^g_σ differs from the way k^g_σ was defined by Linnett,[14] and the constant defined in this investigation is equal to $\frac{1}{4}$ of the constant as defined by Linnett.

When the potential energy given in Equation (44) is minimized with respect to $\Delta\xi$, the value of $\Delta\xi$ is found to be

$$\Delta\xi = \frac{K_H}{4K_H + 4k^g_\sigma} \sum_{i=1}^{4} (\Delta\beta_i). \qquad (45)$$

When this value of $\Delta\xi$ is substituted into Equation (44), the potential energy becomes

$$2V = \frac{3K_H^2 + 4K_H k_\sigma^g}{4K_H + 4k_\sigma^g} \sum_{i=1}^{4} (\Delta\beta_i)^2 - \frac{K_H^2}{4K_H + 4k_\sigma^g} \sum_{\substack{i,j \\ i \neq j}}^{4} (\Delta\beta_i \Delta\beta_j) , \quad (46)$$

When the matrix determined by this expression is symmetrized, the $\mathcal{F}$ matrix element for the B_{3u} rocking motion is found to be

$$\frac{K_H k_\sigma^g}{K_H + k_\sigma^g} . \quad (47)$$

d. <u>The B_{1u} and B_{2g} bending vibrations</u>. These vibrational motions involve out-of-plane distortions, and the π bonds have to be considered. The B_{1u} wagging motion is one in which all four hydrogen atoms move in the same direction, perpendicular to the plane of the molecule. In the B_{2g} wagging motion, the hydrogen atoms all move perpendicular to the plane of the molecule, but the two ends wag in opposite directions. The coordinates used in expressing the potential energy are the two angles formed by the CH_2 planes and the axis of the molecule. Figure 10 shows the change in overlap in the σ and π bonds brought about by the orbital

this motion defines k_π^u

k_π^g

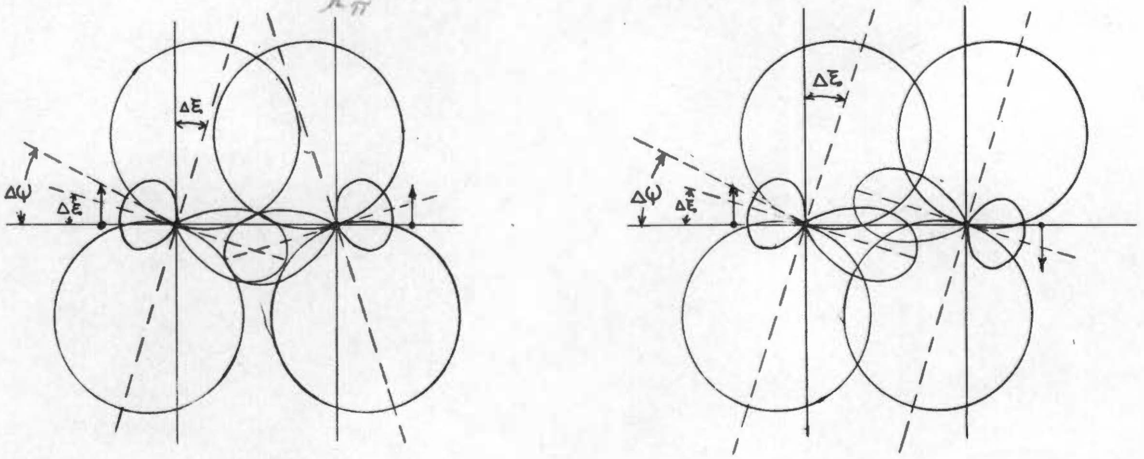


Figure 10. The Effect of Orbital Rotation During the B_{1u} and B_{2g} Vibrations of Ethylene.

rotation occurring during the motions.

Consider the B_{1u} vibrational motion. The potential energy for the bending of the C-H bonds before taking orbital rotation into account is

$$2V = K_H \sum_{i=1}^{4} (\Delta \kappa_i)^2 = 2K_H \sum_{i=1}^{2} (\cos\alpha \, \Delta\psi_i)^2 \quad . \qquad (48)$$

Inspection of Figure 10 shows that the change in orbital overlap occurring in the carbon-carbon σ bond is the same as it was in the B_{2u} vibration; therefore, k_σ^u is the constant associated with the change in overlap of the σ bond. A new constant must be introduced to account for the overlap change occurring in the π bond. In order to express this constant in such a way that it will be the same as the corresponding constant in allene, it is defined in the following manner. k_π^u is the force constant associated with the change in overlap of the π bond when the orbitals of one of the carbon atoms rotates through a unit angle. Therefore, if the orbitals of both the carbon atoms are now permitted to rotate through an angle $\Delta\xi$, in the manner shown in Figure 10, the potential energy for the B_{1u} vibration becomes

$$2V = 2K_H \sum_{i=1}^{2} (\cos\alpha \, \Delta\psi_i - \cos\alpha \, \Delta\xi)^2 + k_\sigma^u (\Delta\xi)^2 + k_\pi^u (2\Delta\xi)^2 . \qquad (49)$$

The manner in which k_π^u has been defined differs from the way Linnett[14] defined this constant, the constant defined here being equal to $\frac{1}{4}$ of the constant as defined by Linnett. When the potential energy is minimized with respect to $\Delta\xi$, one obtains

$$\Delta\xi = \frac{2K_H \cos^2\alpha}{4K_H \cos^2\alpha + (k_\sigma^u + 4k_\pi^u)} \sum_{i=1}^{2} (\Delta\psi_i)^2 . \qquad (50)$$

When this value of $\Delta\xi$ is substituted into Equation (49), the potential energy becomes

$$2V = \frac{2K_H \cos^2\alpha \left[2K_H \cos^2\alpha + (k_\sigma^u + 4k_\pi^u)\right]}{4K_H \cos^2\alpha + (k_\sigma^u + k_\pi^u)} \sum_{i=1}^{2} (\Delta\psi_i)^2$$

$$- \frac{4K_H^2 \cos^4\alpha}{4K_H \cos^2\alpha + (k_\sigma^u + k_\pi^u)} \sum_{\substack{i,j \\ i \neq j}}^{2} \Delta\psi_i \, \Delta\psi_j . \qquad (51)$$

When the above expression is symmetrized, the $\mathfrak{F}$ matrix element for the B_{1u} vibration is found to be

$$\frac{2K_H \cos^2\alpha \, (k_\sigma^u + 4k_\pi^u)}{4K_H \cos^2\alpha + (k_\sigma^u + 4k_\pi^u)} . \qquad (52)$$

The potential energy for the bending of the C-H bonds in the B_{2g} vibrational motion before orbital rotation is taken into account is the same as that for the B_{1u} vibration given in Equation (48),

$$2V = 2K_H \sum_{i=1}^{2} (\cos\alpha \, \Delta\psi_i)^2 . \qquad (53)$$

Now, the orbitals of the two carbon atoms are allowed to rotate as shown in Figure 10. The constant associated with the change in overlap of the σ orbitals between the carbon atoms is k_σ^g, the same as the constant associated with the σ orbitals in the B_{1g} motion. The overlap change of the π bond is different in this case than in the B_{1u} motion, and a new constant must be introduced to account for this motion. k_π^g is defined as the force constant associated with the change in overlap of the

π orbitals which occurs when the orbitals of each carbon atom rotate through equal angles in the same circular direction, as shown in Figure 10.

The orbitals of the carbon atoms are now permitted to rotate through an angle $\Delta\xi$, and the potential energy for the B_{2g} vibrational motion becomes

$$2V = 2K_H \sum_{i=1}^{2} (\cos\alpha\ \Delta\psi_i - \cos\alpha\ \Delta\xi)^2 + k^g_\sigma (2\Delta\xi)^2 + k^g_\pi (\Delta\xi)^2 \ . \qquad (54)$$

When the potential energy is minimized, $\Delta\xi$ is found to be

$$\Delta\xi = \frac{2K_H \cos^2\alpha}{4K_H \cos^2\alpha + (4k^g_\sigma + k^g_\pi)} \sum_{i=1}^{2} (\Delta\psi_i) \ . \qquad (55)$$

When this value of $\Delta\xi$ is substituted into Equation (54), the potential energy becomes

$$2V = \frac{2K_H \cos^2\alpha \left[2K_H \cos^2\alpha + (4k^g_\sigma + k^g_\pi)\right]}{4K_H \cos^2\alpha + (4k^g + k^g_\pi)} \sum_{i=1}^{2} (\Delta\psi_i)^2$$

$$- \frac{4K_H^2 \cos^4\alpha}{4K_H \cos^2\alpha + (4k^g_\sigma + k^g_\pi)} \sum_{\substack{i,j \\ i \neq j}}^{2} (\Delta\psi_i \Delta\psi_j) . \qquad (56)$$

The $\mathfrak{F}$ matrix element for the B_{2g} vibrational mode, determined by symmetrizing the above expression, is

$$\frac{2K_H \cos^2\alpha\ (4k^g_\sigma + k^g_\pi)}{4K_H \cos^2\alpha + (4k^g_\sigma + k^g_\pi)} \ . \qquad (57)$$

e. <u>The A_u vibration</u>. The vibrational motion belonging to A_u is the torsional motion, or twisting, of the CH_2 groups about the carbon-carbon axis. The coordinate used to describe this motion is the angle, τ, formed by the intersection of the two CH_2 planes. The potential energy for this motion before orbital rotation is taken into account is

$$2V = 4K_H \left(\sin\alpha \frac{\Delta\tau}{2}\right)^2 . \qquad (58)$$

$\frac{\Delta\tau}{2}$ because each CH_2 rotates only half the angle $\Delta\tau$

Now, each set of carbon orbitals are allowed to rotate about the carbon-carbon axis through an angle $\Delta\xi$. Only the π orbitals are affected by this rotation, and the potential energy after rotation is

$$2V = 4K_H \left(\sin\alpha \frac{\Delta\tau}{2} - \sin\alpha\, \Delta\xi\right)^2 + k_\pi^\tau \,(2\Delta\xi)^2, \qquad (59)$$

where k_π^τ is defined as the force constant associated with the change in overlap of the π orbitals when one of the orbitals rotates through a unit angle. In the torsional motion, both π orbitals rotate, and the contribution of this motion to the potential energy is $k_\pi^\tau\,(2\Delta\xi)^2$. $\Delta\xi$, evaluated by minimizing the potential energy with respect to $\Delta\xi$, is found to be

$$\Delta\xi = \frac{2K_H \sin^2\alpha}{4K_H \sin^2\alpha + k_\pi^\tau}\,\Delta\tau . \qquad (60)$$

When this value of $\Delta\xi$ is substituted into Equation (59), the potential energy for the A_u vibration becomes

$$2V = \frac{K_H \sin^2\alpha\, k_\pi^\tau}{K_H \sin^2\alpha + k_\pi^\tau}\,(\Delta\tau)^2 . \qquad (61)$$

Since $\Delta\tau$ is a symmetry coordinate, the $\mathcal{F}$ matrix element for the A_u vibrational motion is given by Equation (61).

2. Allene

The allene molecule, C_3H_4, is similar in some respects to ethylene. However, the CH_2 groups lie in planes which are perpendicular to each other in allene, while they are in the same plane in the ethylene molecule. In addition, allene possesses adjacent double bonds, whereas ethylene has only one double bond. The model of allene based on directed atomic orbitals is shown in Figure 11.

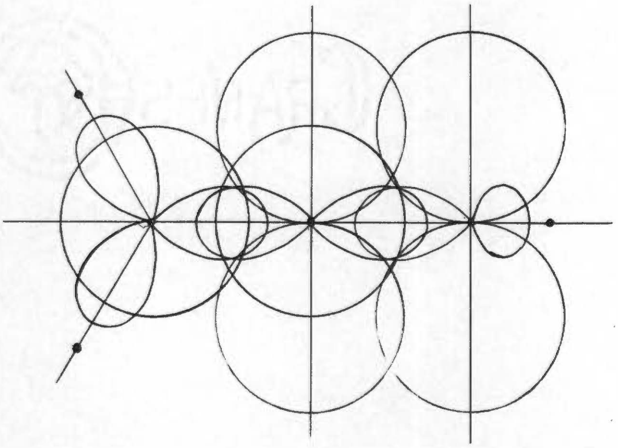
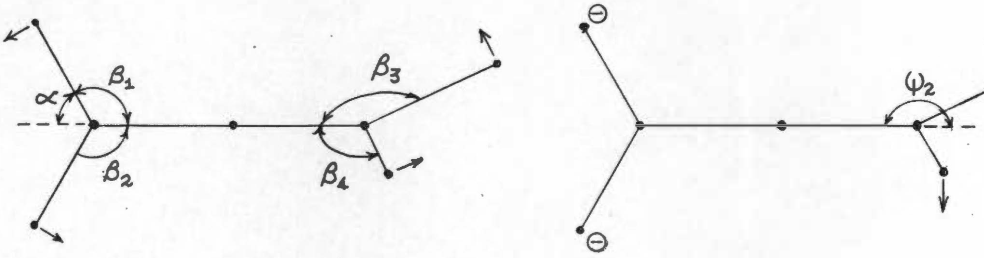


Figure 11. The Orbital Model of Allene.

There are four vibrational modes, one non-degenerate and three doubly-degenerate, in which orbital rotation can ease the bending motions. However, only three of these motions, the CH_2 rocking, the CH_2 wagging, and the torsion, can be considered as vibrations involving bending of the C-H bonds. The other vibration, the degenerate C-C-C chain bending motion, cannot be considered as a motion involving bending of the C-H bonds. As a consequence, the concept of orbital rotation cannot be applied to this motion in a simple manner.

a. The degenerate rocking and wagging vibrations of allene. The degenerate rocking and wagging vibrations of allene are shown in Figure 12. As for ethylene, K_H is defined as the force constant associated with the change in overlap which occurs when a C-H bond is distorted. Therefore, the potential energy for the degenerate rocking motion, shown



(a) (b)

Figure 12. (a) The Degenerate Rocking Motion of Allene.
(b) The Degenerate Wagging Motion of Allene.

in Figure 12 (a), before orbital rotation is taken into account, is

$$2V = k_H \sum_{i=1}^{4} (\Delta\beta_i)^2 \ . \tag{62}$$

Now, the orbitals of the carbon atoms are permitted to rotate so as to minimize the potential energy. Examination of Figure 11 shows that rotation of the orbitals of the terminal carbon atoms in this case would not affect the π bond overlap, but would decrease the overlap of the C-C σ bonds. If the orbitals of the central carbon atom are allowed to rotate, then the π bond overlap would be affected. If this rotation were permitted, then there would be two constants associated with the motion, and since neither can be determined from other vibrational motions, these constants could not be evaluated. Furthermore, allowing the orbitals of the central carbon atom to rotate would require that the magnitude of the angle of rotation would have to be assumed, since it cannot be evaluated directly. For these reasons, the orbitals of the central carbon atom are assumed to remain fixed during the vibrational motions.

The orbitals of the terminal carbon atoms are now allowed to rotate through an angle, $\Delta\xi$, about axes perpendicular to the respective CH_2 planes. The potential energy for the rocking motion then becomes

$$2V = K_H \sum_{i=1}^{4} (\Delta\beta - \Delta\xi)^2 + 2k_\sigma (\Delta\xi)^2, \qquad (63)$$

where k_σ is defined as the force constant associated with the change in overlap occurring in the carbon-carbon σ bond when the orbitals of one of the carbon atoms are allowed to rotate through a unit angle. This constant is equivalent to the constant k_σ^g used for ethylene. When the potential energy is minimized with respect to $\Delta\xi$, it becomes

$$2V = \frac{3K_H^2 + 2K_H k_\sigma}{4K_H + 2k_\sigma} \sum_{i=1}^{4} (\Delta\beta_i)^2 - \frac{K_H^2}{(4K_H + 2k_\sigma)} \sum_{\substack{i,j \\ i \neq j}}^{4} \Delta\beta_i \Delta\beta_j \, . \qquad (64)$$

The $\mathfrak{F}$ matrix element, obtained by symmetrizing the above expression, is

$$\frac{K_H k_\sigma}{2K_H + k_\sigma} \, . \qquad (65)$$

The degenerate wagging motion of the CH_2 groups is illustrated in Figure 12 (b). The potential energy for this motion, before orbital rotation is taken into account, is

$$2V = 2K_H \sum_{i=1}^{2} (\cos\alpha \, \Delta\psi_i)^2 \, . \qquad (66)$$

Now, the orbitals of the central carbon are assumed to remain fixed, but the orbitals of each of the terminal carbon atoms are allowed to rotate through an angle, $\Delta\xi$. Figure 13 shows the configuration of the orbitals

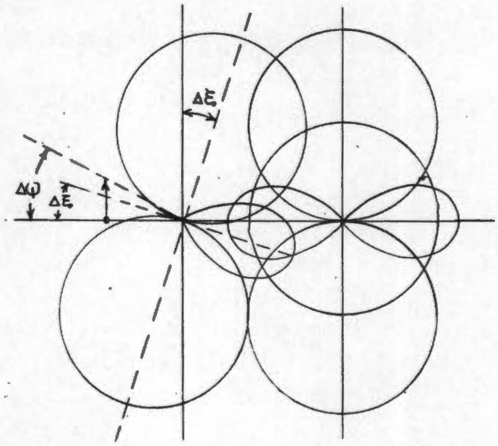


Figure 13. The Effect of Orbital Rotation During the Degenerate Wagging Motion of Allene.

of one of the end carbon atoms and the central atom after orbital rotation has occurred. The changes in orbital overlap are the same on both ends of the molecule. The potential energy after the orbital rotation is

$$2V = 2K_H \sum_{i=1}^{2} (\cos\alpha\,\Delta\psi_i - \cos\alpha\,\Delta\xi)^2 + 2k_\sigma (\Delta\xi)^2 + 2k_\pi (\Delta\xi)^2, \qquad (67)$$

where k_σ is the same as in the rocking motion just described, and k_π is defined as the force constant associated with the change in overlap in the π bond which occurs when one of the π orbitals is rotated through a unit angle, as shown in Figure 13. After minimizing with respect to $\Delta\xi$, the potential energy for the degenerate wagging motion becomes

$$2V = \frac{2K_H \cos^2\alpha \left[K_H \cos^2\alpha + (k_\sigma + k_\pi)\right]}{2K_H \cos^2\alpha + (k_\sigma + k_\pi)} \sum_{i=1}^{2} (\Delta\psi_i)^2$$

$$- \frac{2K_H^2 \cos^4\alpha}{2K_H \cos^2\alpha + (k_\sigma + k_\pi)} \sum_{\substack{i,j \\ i \neq j}}^{2} (\Delta\psi_i \Delta\psi_j) \,. \qquad (68)$$

The $\mathcal{F}$ matrix element for the degenerate wagging motion, obtained by symmetrizing the above expression, is

$$\frac{2K_H \cos^2\alpha \, (k_\sigma + k_\pi)}{2K_H \cos^2\alpha + (k_\sigma + k_\pi)} \, . \tag{69}$$

b. The B_1 vibration. The B_1 vibration in allene is the torsion, and is quite similar to the torsional motion in ethylene. The potential energy for this motion, before taking orbital rotation into account, is

$$2V = 4K_H \left(\sin\alpha \, \frac{\Delta\tau}{2}\right)^2 , \tag{70}$$

where $\Delta\tau$ is the change in the angle formed by the intersection of the two CH_2 planes. If the carbon orbitals of the terminal atoms are now permitted to rotate through an angle, $\Delta\xi$, the potential energy becomes

$$2V = 4K_H \left(\sin\alpha \frac{\Delta\tau}{2} - \sin\alpha \, \Delta\xi\right)^2 + 2k_\pi^\tau \, (\Delta\xi)^2 , \tag{71}$$

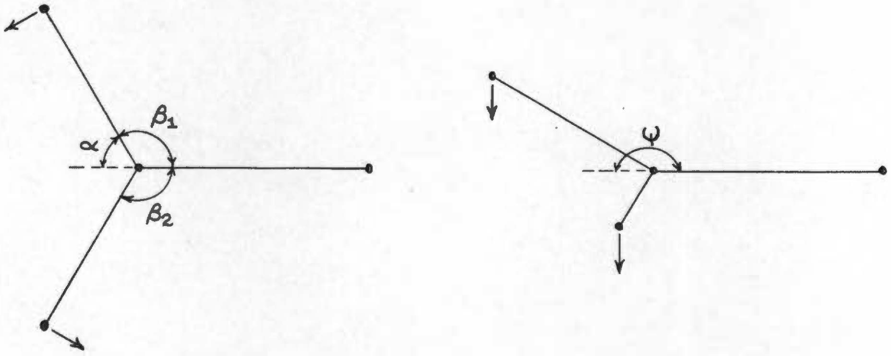
where k_π^τ is defined as the force constant associated with the change in overlap of the π orbitals when one set of carbon orbitals rotate through a unit angle. This definition of k_π^τ is the same as that for k_π^τ in ethylene. It should be noted, however, that there are two sets of overlapping π orbitals in allene. When the potential energy is minimized with respect to $\Delta\xi$, it becomes

$$2V = \frac{K_H \sin^2\alpha \, k_\pi^\tau}{2K_H \sin^2\alpha + k_\pi^\tau} \, (\Delta\tau)^2 \, . \tag{72}$$

Since $\Delta\tau$ is a symmetry coordinate, the $\mathfrak{F}$ matrix element for the B_1 vibrational motion appears directly in Equation (72).

3. Formaldehyde

In the formaldehyde molecule, CH_2O, there are only two vibrational motions in which orbital rotation can lead to a decrease in the potential energy. These motions are the planar rocking motion and the out-of-plane bending motion, and are shown in Figure 14. The orbital model of formaldehyde is shown in Figure 15. The potential energy for the planar rocking motion, before orbital rotation is taken into account, is



(a) (b)

Figure 14. (a) The Planar Rocking Motion of Formaldehyde.
(b) The Out-of-Plane Bending Motion of Formaldehyde.

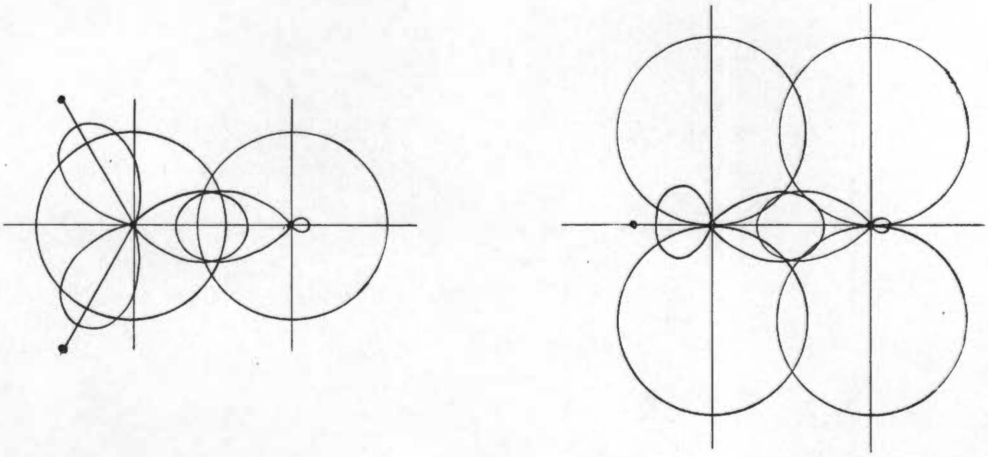


Figure 15. The Orbital Model of Formaldehyde.

$$2V = K_H \sum_{i=1}^{2} (\Delta\beta_i)^2, \tag{73}$$

where K_H is the force constant associated with the bending of a C-H bond. The orbitals of the carbon atom are now permitted to rotate through an angle, $\Delta\xi$, and the potential energy becomes

$$2V = K_H \sum_{i=1}^{2} (\Delta\beta_i - \Delta\xi)^2 + k_\sigma (\Delta\xi)^2 . \tag{74}$$

The constant, k_σ, is defined as the constant associated with the change in overlap in the C-O σ bond which occurs when the orbitals of the carbon atom are rotated. When the potential energy is minimized with respect to $\Delta\xi$, it becomes

$$2V = \frac{K_H (K_H + k_\sigma)}{2K_H + k_\sigma} \sum_{i=1}^{2} (\Delta\beta_i)^2 - \frac{K_H^2}{2K_H + k_\sigma} \sum_{\substack{i,j \\ i\neq j}}^{2} (\Delta\beta_i \Delta\beta_j) . \tag{75}$$

Symmetrization of this expression gives the $\mathcal{F}$ matrix element for the planar rocking motion, which is

$$\frac{K_H k_\sigma}{2K_H + k_\sigma} . \tag{76}$$

The behavior of the orbitals of the oxygen atom when the orbitals of the carbon atom rotate must be considered. The rotation of the carbon orbitals during the planar rocking motion does not affect the overlap of the π orbitals, but the overlap of the C-O σ bond is affected. The orbitals of the oxygen atom would be expected to rotate in such a way as to minimize the change in overlap. Therefore, the oxygen orbitals would be expected to rotate through the same angle as the orbitals of the carbon atom, as shown in Figure 16. The behavior of the oxygen orbitals is of importance because the k_σ which is determined from the planar rocking motion could be transferred to the out-of-plane motion if the C-O σ orbitals behave in the same manner during the two vibrations and therefore k_π could be determined.

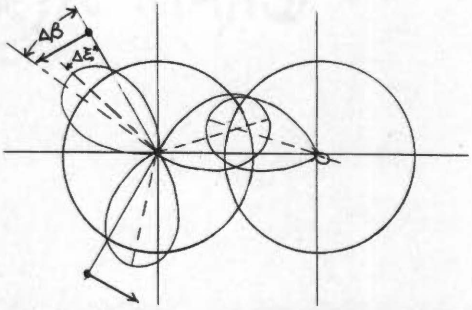


Figure 16. The Effect of Orbital Rotation During the Planar Rocking Vibration in Formaldehyde.

The potential energy for the out-of-plane bending vibration, before orbital rotation is taken into account, is

$$2V = 2K_H (\cos\alpha \; \Delta\psi)^2, \tag{77}$$

where ψ is the angle formed by the intersection of the CH_2 plane and the C-O bond axis. The orbitals of the carbon atom are now permitted to rotate through an angle, $\Delta\xi$, so as to minimize the potential energy. The orbital picture after this rotation has occurred is shown in Figure 17. Now, the orbitals of the oxygen atom are free to rotate so as to

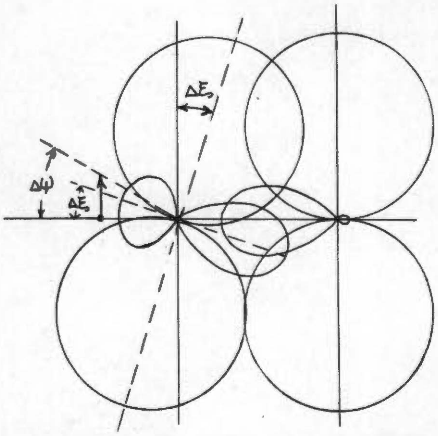


Figure 17. The Effect of Orbital Rotation of the Carbon Orbitals During the Out-of-Plane Bending Vibration of Formaldehyde.

minimize the decrease in overlap of the σ and π orbitals, but the way in which this rotation would occur is not clear. For this reason, the constant associated with the change in overlap occurring in the σ bond during the out-of-plane bending motion cannot be assumed to be the same as the constant associated with the change in overlap of the σ bond during the planar rocking motion. The potential energy for the out-of-plane vibration, after orbital rotation occurs, is

$$2V = 2K_H\,(\cos\alpha\ \Delta\psi - \cos\alpha\ \Delta\xi)^2 + (k'_\sigma + k_\pi)\,(\Delta\xi)^2 \qquad (78)$$

where k'_σ and k_π are defined as the constants associated with the change in overlap of the σ and π orbitals which is brought about by the rotation of the carbon and oxygen orbitals. When the potential energy is minimized with respect to $\Delta\xi$, it becomes

$$2V = \frac{2K_H\cos^2\alpha\ (k'_\sigma + k_\pi)}{2K_H\cos^2\alpha + (k'_\sigma + k_\pi)}\,(\Delta\psi)^2, \qquad (79)$$

and since $\Delta\psi$ is a symmetry coordinate, the $\mathcal{F}$ matrix element is given directly by (79).

Linnett, Heath and Wheatley have applied the orbital valency force field to formaldehyde,[14] and these authors assumed that the constants associated with the change in σ bond overlap in the planar and non-planar vibrational motions were the same. It is necessary to make this assumption in order to determine k_π, but the assumption does not appear to be justified. This means that the sum, $k'_\sigma + k_\pi$, can be determined, but the values of k'_σ and k_π cannot be obtained.

4. Ketene and Diazomethane

Ketene, CH_2CO, and diazomethane, CH_2N_2, are planar molecules belonging to the point group C_{2v}. Each molecule has four vibrational motions, the CH_2 rocking, the CH_2 wagging, the planar skeletal banding, and the non-planar skeletal bending, in which orbital rotation may lead to a decrease in the potential energy. However, the skeletal bending modes are equivalent to the degenerate skeletal bending vibration of allene, and the concept of orbital rotation cannot be successfully applied to these motions. Therefore, the concept of orbital rotation has been applied to the CH_2 rocking and CH_2 wagging motions only.

The orbital model of the CH_2CO molecule is shown in Figure 18. The bonding structure of ketene and diazomethane are similar, and the same model was used for diazomethane. The CH_2 rocking motion and the CH_2 wagging motions are shown in Figure 19. These vibrational motions are quite similar to the corresponding motions in formaldehyde. As was pointed out in the discussion of the CH_2O molecule, the orbitals of the oxygen atom are free to rotate when the orbitals of the carbon atom

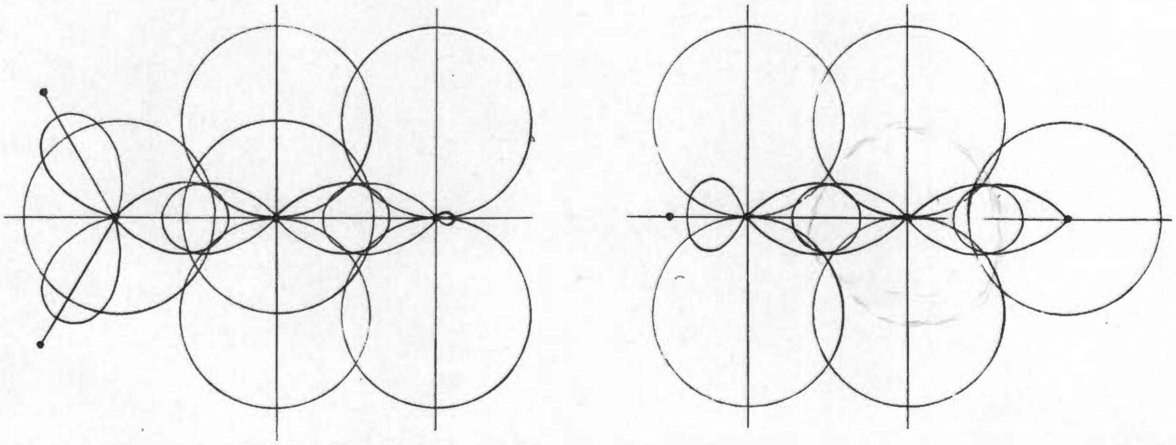
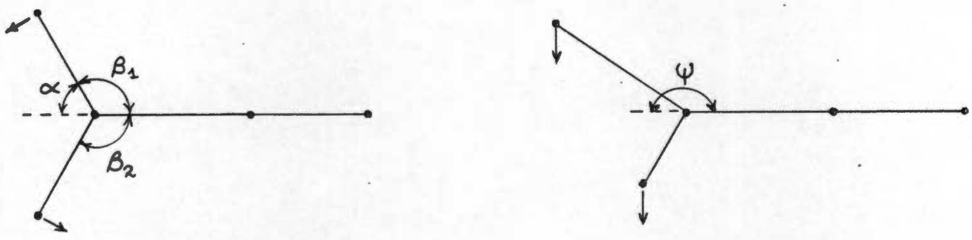


Figure 18. The Orbital Model of Ketene.



(a) (b)

Figure 19. (a) The CH_2 Rocking Motion of Ketene and Diazomethane.
(b) The CH_2 Wagging Motion of Ketene and Diazomethane.

rotate. However, it is impossible to determine how the oxygen orbitals rotate when the carbon orbitals rotate. In a similar manner, the rotation of the orbitals of the terminal carbon atom in ketene and diazomethane may cause a rotation of the orbitals of the central C and O atoms in ketene and of the N atoms in diazomethane. However, it is likewise impossible to take this rotation into account quantitatively. Therefore, the treatment of the CH_2 rocking and wagging motions in CH_2CO and CH_2N_2 is identical with that previously described for CH_2O, and the $\mathcal{F}$ matrix elements will be the same as those obtained for CH_2O. The $\mathcal{F}$ matrix element for the CH_2 wagging motion is given by Equation (76) as

$$\frac{K_H k_\sigma}{2K_H + k_\sigma}, \tag{80}$$

and the $\mathcal{F}$ matrix element for the CH_2 wagging motion, given by Equation (79), is

$$\frac{2K_H \cos^2\alpha\ (k'_\sigma + k_\pi)}{2K_H \cos^2\alpha + (k'_\sigma + k_\pi)}, \tag{81}$$

where K_H is the force constant associated with the bending of a C-H bond,

k_σ is the constant associated with the change in the C-C or C-N σ orbital overlap during the CH_2 rocking motion, and k'_σ and k_π are the constants associated with the change in the σ and π orbital overlaps during the CH_2 wagging motion.

It should be pointed out that the use of different constants to describe the change in σ orbital overlap in the rocking and wagging motions makes it impossible to evaluate k_π, but it appears that this distinction is necessary for CH_2CO and CH_2N_2, just as it was in the case of CH_2O. Furthermore, it should be noted that the neglect of the effect of the rotation of the orbitals of the central carbon and oxygen atoms in ketene and the two nitrogen atoms in diazomethane makes this treatment a very approximate one, and this fact must be borne in mind in interpreting the results for these molecules.

CHAPTER III

EVALUATION OF THE FORCE CONSTANTS

A. Anharmonicity Corrections

The force constants of a molecule are functions of the normal vibrational frequencies of the molecule, and these frequencies should be used in evaluating the force constants. The observed fundamental frequencies differ from the normal frequencies, primarily because of the cubic and higher order terms in the potential energy expression. In order to determine the normal frequencies, however, it is necessary to know the observed values of many combination and overtone bands. In general, not enough data are available to enable the normal frequencies of a polyatomic molecule to be determined, and this necessitates using the observed frequencies in evaluating the force constants.

Although the data for the molecules treated in this investigation are insufficient to permit precise anharmonicity corrections to be made, an attempt was made to correct the frequencies of ethylene and allene in order to enable better sets of force constants to be determined. Hansen and Dennison[35] have determined the normal frequencies of C_2H_6 and C_2D_6, using the known anharmonicity constants of CH_4 in conjunction with the available data for C_2H_6 and C_2D_6. The anharmonic constants which were determined for ethane were used as a guide in this investigation in determining anharmonic constants for ethylene and allene. However, it was found that the normal frequencies determined in this manner did not permit a better solution for the force constants to be obtained. The assumption was then made that all of the anharmonicity was present in the C-H and C-D stretching modes, but again it was found that no improvement in the solution for the force constants over that obtained using the observed frequencies could be achieved. One of the reasons why anharmonicity corrections do not lead to a better solution for the force constants for the ethylene molecule is the fact that the frequencies of species B_{1g} almost ~~obey the product~~ rule. This means that the C-H and C-D stretching frequencies of this species will be raised very little by making anharmonicity corrections, while the C-H and C-D stretching frequencies belonging to the other species are raised several per cent. This makes it impossible to fit the C-H and C-D stretching frequencies as well when anharmonicity corrections are made as they are fitted using the observed frequencies. Therefore, the values of the observed frequencies have been used in all of the calculations carried out in this investigation.

It should be emphasized that if the correct anharmonic constants could be obtained, the normal frequencies would permit a set of force constants to be obtained which would reproduce the normal frequencies exactly if a general quadratic field were used. The fact that making anharmonicity corrections for ethylene and allene does not permit a better set of force constants to be obtained can be attributed to the fact that we do not know the correct values of the anharmonic constants and to the restricted nature of the potential field assumed for these molecules.

B. Ethylene

The force constants for ethylene were determined using the frequencies of C_2H_4 and C_2D_4. The frequencies of the other isotopic ethylenes were then calculated using the force constants which were obtained from C_2H_4 and C_2D_4 in order to verify that the potential field was correct for all of the molecules. The frequencies of *cis*-, *trans*-, or *asym*.-$C_2H_2D_2$ could have been utilized directly in the calculations, but because of the reduction in symmetry brought about by the isotopic substitutions, the factored secular equations for the planar vibrations of these molecules contain a fifth-order and a fourth-order block, and the solution of these blocks was not practicable.

The $\mathfrak{F}$ and $\mathfrak{G}$ matrices for C_2H_4 and C_2D_4 are given in Appendix I. The algebraic equations obtained from expansion of the secular equations of C_2H_4 and C_2D_4 are

A_g: $\underline{C_2H_4}$

$$1.0335773\ f_1 + 0.1666138\ f_2 + 0.9737090\ f_3 - 0.9315736\ A = \sum_{i=1}^{3} \lambda_i \tag{82}$$

$$\begin{aligned} &0.1652682\ f_1f_2 + 1.0018657\ f_1f_3 + 0.1440822\ f_2f_3 - 0.5401301\ Af_1 \\ &- 0.4405429\ Af_3 - 1.9533690\ A^2 = \sum_{\substack{i,j=1 \\ i \neq j}}^{3} \lambda_i\lambda_j \end{aligned} \tag{83}$$

$$\begin{aligned} &f_1f_2f_3 - 4.0839156\ A^2f_1 - 0.8252451\ A^2f_2 - 9.3487955\ A^2f_3 \\ &+ 11.2263264\ A^3 = 6.9969850 \prod_{i=1}^{3} \lambda_i \end{aligned} \tag{84}$$

$\underline{C_2D_4}$

$$0.5379967\ f_1 + 0.1666138\ f_2 + 0.5416577\ f_3 - 0.9315736\ A = \sum_{i=1}^{3} \lambda_i' \tag{85}$$

$$0.0826976\ f_1f_2 + 0.2868723\ f_1f_3 + 0.0720965\ f_2f_3 - 0.8004645\ A^2 - 0.2702728\ Af_1 - 0.2204411\ Af_3 = \sum_{\substack{i,j=1\\ i\neq j}}^{3} \lambda_i'\lambda_j' \tag{86}$$

$$f_1f_2f_3 - 4.0839156\ A^2f_1 - 0.8252451\ A^2f_2 - 9.3487955\ A^2f_3 + 11.2263264\ A^3 = 27.9449039 \prod_{i=1}^{3} \lambda_i' \tag{87}$$

B_{3u}: $\underline{C_2H_4}$

$$1.0335773\ f_1 + 0.9737090\ f_3 + 0.1223893\ A = \sum_{i=11}^{12} \lambda_i \tag{88}$$

$$f_1f_{\cancel{2}_3} - 0.8252451\ A^2 = 0.9981378 \prod_{i=11}^{12} \lambda_i \tag{89}$$

$\underline{C_2D_4}$

$$0.5379967\ f_1 + 0.5416577\ f_3 + 0.1223893\ A = \sum_{i=11}^{12} \lambda_i' \tag{90}$$

$$f_1f_3 - 0.8252451\ A^2 = 3.4858728 \prod_{i=11}^{12} \lambda_i \tag{91}$$

B_{2u}: $\underline{C_2H_4}$

$$1.1168842\ f_1 + 0.9010814\ f_4 - 0.1223893\ A = \sum_{i=9}^{10} \lambda_i \tag{92}$$

$$f_1f_4 - 0.8252451\ A^2 = 0.9981378 \prod_{i=9}^{10} \lambda_i \tag{93}$$

$\underline{C_2D_4}$

$$0.6213036\ f_1 + 0.4690300\ f_4 - 0.1223893\ A = \sum_{i=9}^{10} \lambda_i' \tag{94}$$

$$f_1f_4 - 0.8252451\ A^2 = 3.4858728 \prod_{i=9}^{10} \lambda_i' \tag{95}$$

B_{1g}: $\underline{C_2H_4}$

$$1.1168842\ f_1 + 1.4951041\ f_5 - 0.5099101\ A = \sum_{i=5}^{6} \lambda_i \tag{96}$$

$$f_1 f_5 - 0.8252451\ A^2 = 0.6284995 \prod_{i=5}^{6} \lambda_i \tag{97}$$

$\underline{C_2D_4}$

$$0.6213036\ f_1 + 1.0630528\ f_5 - 0.5099101\ A = \sum_{i=5}^{6} \lambda_i' \tag{98}$$

$$f_1 f_5 - 0.8252451\ A^2 = 1.7190652 \prod_{i=5}^{6} \lambda_i' \tag{99}$$

B_{1u}: $\underline{C_2H_4}$

$$f_6 = 0.4950384\ (\lambda_7) \tag{100}$$

$\underline{C_2D_4}$

$$f_6 = 0.8650947\ (\lambda_7') \tag{101}$$

B_{2g}: $\underline{C_2H_4}$

$$f_7 = 0.3756577\ (\lambda_8) \tag{102}$$

$\underline{C_2D_4}$

$$f_7 = 0.5562060\ (\lambda_8') \tag{103}$$

A_u: $\underline{C_2H_4}$

$$f_8 = 0.8672844\ (\lambda_4) \tag{104}$$

$\underline{C_2D_4}$

$$f_8 = 1.7332392\ (\lambda_4')\ . \tag{105}$$

The unprimed λ's refer to C_2H_4, and the primed λ's refer to C_2D_4.*

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* $\lambda_i = \left(\frac{\nu_i}{1302.93}\right)^2$. The $\mathfrak{G}$ matrix was computed in atomic weight-Angstrom units and the force constants in these equations are expressed in dynes/cm. x 10^5 or in ergs/radian^2 x 10^{-11}. The factor, 1302.93, includes all of the constants involved in using these factors, when the ν_i are expressed in cm.$^{-1}$.

The f_i's in the above equations are the diagonal $\mathfrak{F}$ matrix elements and are defined by the following relations:

$$f_1 = K_{CH} + 1.33196\ A \tag{106}$$

$$f_2 = K_{CC} + 6.32571\ A \tag{107}$$

$$f_3 = K_H + 0.87773\ A \tag{108}$$

$$f_4 = \frac{K_H k_\sigma^u}{4K_H + k_\sigma^u} + 0.87773\ A \tag{109}$$

$$f_5 = \frac{K_H k_\sigma^g}{K_H + k_\sigma^g} + 0.87773\ A \tag{110}$$

$$f_6 = \frac{2K_H \cos^2\alpha(k_\sigma^u + 4k_\pi^u)}{4K_H \cos^2\alpha + (k_\sigma^u + 4k_\pi^u)} + 0.05573\ A \tag{111}$$

$$f_7 = \frac{2K_H \cos^2\alpha(4k_\sigma^g + k_\pi^g)}{4K_H \cos^2\alpha + (4k_\sigma^g + k_\pi^g)} + 0.05573\ A \tag{112}$$

$$f_8 = \frac{K_H \sin^2\alpha k_\pi^\tau}{K_H \sin^2\alpha + k_\pi^\tau} + 0.08361\ A\ . \tag{113}$$

There are nine constants to be evaluated, and twenty-four equations involving these constants. However, because of the product rule relationship, only seventeen of the equations are independent. In theory, nine of these equations should permit the constants to be calculated. However, due to inconsistencies in the equations, which are primarily caused by anharmonicity in the frequencies, all of the equations must be used in order to determine the best values for the constants.

The potential field assumed in this investigation is of such a nature that all of the off-diagonal elements in the $\mathfrak{F}$ matrices are either zero or contain terms which are functions of the constant A. This constant, A, is the force constant associated with the repulsive force between hydrogen atoms and carbon, oxygen, or nitrogen atoms to which they are not bonded. This points out the reason why it was desirable to neglect repulsive forces between two hydrogen atoms, because if these forces had been taken into account, the off-diagonal $\mathfrak{F}$ matrix elements would have contained two or three independent constants. This would have made it impractical to evaluate the force constants by the method which has been used. Fortunately, the hydrogen-hydrogen repulsions are indeed negligible.

The number of independent force constants in a species of order n is therefore (n + 1). These (n + 1) constants are the n diagonal $\mathfrak{F}$ matrix elements and the constant A. This means that if the value of A is fixed, the other n constants can be calculated using the frequencies of one molecule. Now, if data are available for an isotopic molecule, the constants can be evaluated in a similar fashion. The values of the constants obtained from both molecules can then be plotted against A, and the values of the constants which fit both molecules are easily determined from observing where the values of the constants coincide or lie close together.

The range of solutions for the force constants of species B_{3u}, B_{2u}, and B_{1g} were determined initially. Since each of these species is of order two, the solution of the equations was quite straightforward. The solution of the equations of species B_{3u} of C_2H_4 will be described to illustrate the way in which the solutions were obtained. Solution of Equation (88) for f_1 yields

$$f_1 = 0.9675135 \sum_{i=11}^{12} \lambda_i - 0.9420766\, f_3 - 0.1184133\, A. \qquad (114)$$

This value of f_1, when substituted into Equation (89), gives

$$f_3^2 - 1.0270009 \sum_{i=11}^{12} \lambda_i (f_3) + 0.1256939\, Af_3 + 0.8759852\, A^2$$

$$+ 1.0595081 \prod_{i=11}^{12} \lambda_i = 0. \tag{115}$$

When the numerical values of the λ_i's are substituted into Equations (114) and (115), they become

$$f_1 = 6.2809899 - 0.1184133\, A - 0.9420766\, f_3 \tag{116}$$

$$f_3^2 - 6.6671754\, f_3 + 0.1256939\, Af_3 + 0.8759852\, A^2 + 6.84621660 = 0. \tag{117}$$

For a given value of A, Equation (117) can be solved for f_3. Two values of f_3 are obtained, and the corresponding values of f_1 are then obtained from Equation (116). When the values of f_1 and f_3 are plotted against A, one obtains ellipses which permit f_1 and f_3 to be determined for any value of A for which real solutions exist. Similar calculations were carried out for species B_{3u} of C_2D_4, and for species B_{2u} and B_{1g} of C_2H_4 and C_2D_4. The results of these calculations for representative values of A are given in Table I.

The constant, f_1, is present in the equations for each of the three species. Therefore, six values of f_1 were obtained for each value of A. In Figure 20, the values of f_1 obtained from species B_{3u}, B_{2u} and B_{1g} of C_2H_4 and C_2D_4 are plotted against A. If the frequencies are harmonic and the force field assumed was exact, the six ellipses would intersect in a point. Although the ellipses do not intersect in a point, it is seen that for values of A between 0.00 and 0.70, the ellipses lie close together.

TABLE I

FORCE CONSTANTS* FOR SPECIES B_{3u}, B_{2u} AND B_{1g} OF C_2H_4 AND C_2D_4 FOR ARBITRARY VALUES OF A

	C_2H_4			C_2D_4		
Species	A	f_1	f_3	A	f_1	f_3
B_{3u}	-2.40	3.7530	2.9851	-2.50	4.4114	2.7114
		2.8122	3.9837		2.7299	4.3815
	-1.00	5.0395	1.4436	-1.50	5.2543	1.6482
		1.3601	5.3493		1.6594	5.2188
	0.00	5.0860	1.2685	0.00	5.2737	1.2900
		1.1950	5.3987		1.2988	5.2380
	1.00	5.0215	1.2685	1.00	4.7167	1.6173
		1.2239	5.3987		1.6283	4.6848
	1.80	4.7064	1.5458	1.75	3.4573	2.6988
		1.4562	4.9957		2.7171	3.4339
	A	f_1	f_4	A	f_1	f_4
B_{2u}	-2.00	4.1439	1.3258	-2.00	4.1233	1.3507
		1.0696	5.1363		1.0197	5.4620
	-1.00	4.8177	0.6265	-1.00	4.8594	0.6367
		0.5055	5.9715		0.4806	6.4370
	0.00	5.0847	0.4313	0.00	5.2082	0.4356
		0.3480	6.3025		0.3288	6.8990
	1.50	4.9350	0.8207	1.50	5.2379	0.7876
		0.6621	6.1169		0.5946	6.9384
	3.14	2.8885	3.5803	3.592	3.1223	4.1359
	A	f_1	f_5	A	f_1	f_5
B_{1g}	-1.502	2.6074	1.9478	-0.953	2.6124	1.5268
	-0.50	4.6958	0.7293	-0.50	4.1883	0.8228
		0.9762	3.5079		1.4079	2.4479
	0.00	5.0467	0.6377	0.00	4.8677	0.6656
		0.8536	3.7700		1.1388	2.8449
	1.50	5.3044	0.9568	1.50	5.7105	0.8925
		1.2808	3.9625		1.5271	3.3375
	2.781	3.5850	2.6781	2.935	4.2075	2.4591

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*The units of A and f_1 are dynes/cm. x 10^5, and the units of f_3, f_4 and f_5 are ergs/radian^2 x 10^{-11}.

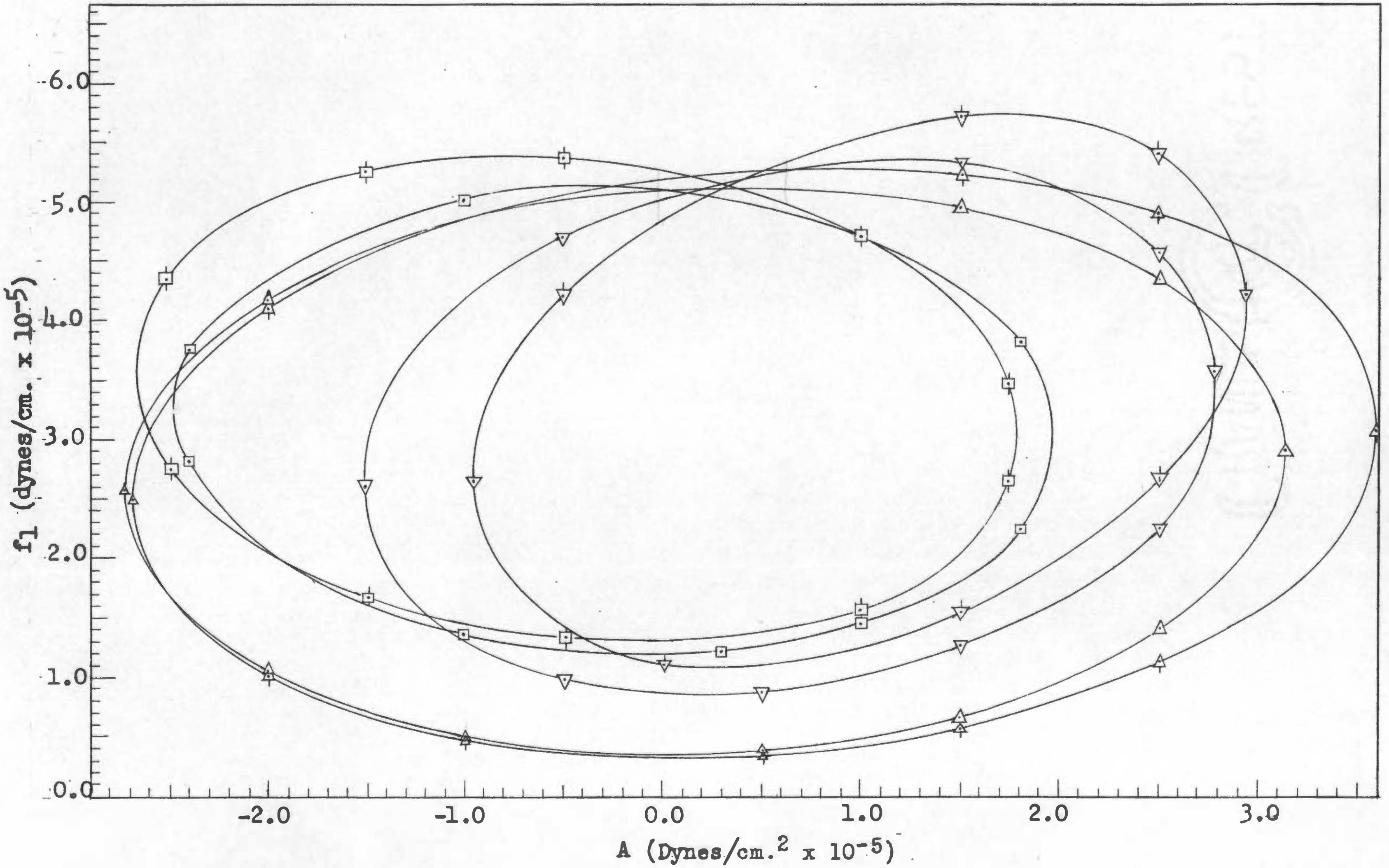


Figure 20. f_1 vs. A for Species B_{3u}, B_{2u}, and B_{1g} of C_2H_4 and C_2D_4.
□, B_{3u}, C_2H_4; □̍ , B_{3u}, C_2D_4; △ , B_{2u}, C_2H_4; △̍ , B_{2u}, C_2D_4; ▽ , B_{1g}, C_2H_4; ▽̍ , B_{1g}, C_2D_4.

Therefore, the value of A should lie in this range. The graphs of f_3, f_4, and f_5 against A are not reproduced in full. However, the two ellipses for each of these constants lie close together for A values from 0.00 to 0.70.

After the value of A was found to lie between 0.00 and 0.70, the equations for species A_g of C_2H_4 and C_2D_4 were solved. This species is third-order, and the solution for f_1, f_2, and f_3 for a given value of A is more difficult than the solution of the equations of species of second-order. Consider Equations (82), (83), and (84), which are for species A_g of C_2H_4. When Equation (82) is solved for f_1, one obtains

$$f_1 = 0.9675135 \sum_{i=1}^{3} \lambda_i + 0.9013100\ A - 0.1612011\ f_2 - 0.9420766\ f_3. \quad (118)$$

This value of f_1, when substituted into Equation (83), yields a second-order equation involving the constants f_2, f_3, and A. This equation was solved as a quadratic in f_3, yielding

$$f_3 = 0.5135005 \sum_{i=1}^{3} \lambda_i + 0.5145462\ A - 0.0917084\ f_2 \pm P, \quad (119)$$

where

$$P = \left[\begin{array}{l} 0.2636827 \left(\sum_{i=1}^{3} \lambda_i \right)^2 - 1.0595081 \sum_{\substack{i,j=1 \\ i \neq 1}}^{3} \lambda_i \lambda_j - 0.0252417 \sum_{i=1}^{3} \lambda_i\ A \\ + 0.0752299 \sum_{i=1}^{3} \lambda_i\ f_2 - 2.3206472\ A^2 + 0.1556967\ Af_2 - 0.0198164\ f_2^2 \end{array} \right]^{\frac{1}{2}} . \quad (120)$$

Equations (119), (120), and (84) were then used to solve for f_1, f_2, and f_3 for selected values of A. After a value of A had been chosen, an arbitrary value of f_2 was selected, and Equation (120) was solved for f_3. Equation (119) was then solved for f_1. The values of f_1, f_2, f_3, and A were then substituted into Equation (84), and the value of the left side of the equation, determined by the constants, was compared with the value of the right side of the equation, which is determined by the frequencies. Further values of f_2 were chosen until a set of constants was obtained which fit Equation (84). It was usually necessary to solve the equations for four or five values of f_2 for a given value of A before a satisfactory solution was obtained. The equations for species Ag of C_2D_4 were solved in the same manner. The results of the calculations are given in Table II.

Although there are six possible sets of solutions for f_1, f_2, and f_3 for a given value of A, it was not necessary to evaluate all of these sets. In general, only one set of constants could be obtained which was reasonable. However, in species A_g of C_2H_4, it was found that below an A value of 0.265, the solutions for the constants were imaginary. Thus, at A = 0.265, two sets of solutions coincided, and it was necessary to evaluate two sets of constants at higher A values. The results given in Table II, along with the values of the constants determined from the other species which are given in Table III, are shown in graphical form in Figures 21, 22, and 23. In addition, the magnitude of the change in the force constant which will produce a change of approximately 1 per cent in the corresponding frequencies is shown by a vertical line on the graphs. This enables a prediction of how well the frequencies will be fit by a set of force constants for any value of the constant A.

TABLE II

FORCE CONSTANTS* FOR SPECIES A_g OF C_2H_4 AND C_2D_4 FOR ARBITRARY VALUES OF A

Molecule	A	f_1	f_2	f_3
C_2H_4	0.2701	5.218	8.873	1.400
		5.220	8.414	1.475
	0.300	5.225	9.337	1.339
	0.350	5.238	9.758	1.302
	0.500	5.269	10.523	1.282
		5.268	7.705	1.764
	0.700	5.283	11.240	1.336
C_2D_4	0.100	5.317	8.020	1.536
	0.200	5.416	8.510	1.448
	0.300	5.517	8.899	1.399
	0.400	5.608	9.231	1.378
	0.700	5.802	10.153	1.417

*The units of A, f_1, and f_2 are dyne/cm. x 10^5, and the units of f_3 are ergs/radian^2 x 10^{-11}.

TABLE III

FORCE CONSTANTS* FOR SPECIES B_{3u}, B_{2u}, AND B_{1g} OF C_2H_4 AND C_2D_4 FOR ARBITRARY VALUES OF A BETWEEN 0.00 AND 0.80

	C_2H_4			C_2D_4		
Species	A	f_1	f_3	A	f_1	f_3
B_{3u}	0.000	5.0860	1.2685	0.000	5.2738	1.2900
	0.300	5.0215	1.2992	0.300	5.1631	1.3320
	0.500	4.9568	1.3428	0.500	5.0656	1.3837
	0.700	4.8731	1.4065	0.700	4.9461	1.4572
	A	f_1	f_4	A	f_1	f_4
B_{2u}	0.000	5.0847	0.4313	0.000	5.2082	0.4356
	0.300	5.1074	0.4439	0.300	5.2598	0.4454
	0.500	5.1086	0.4699	0.500	5.2817	0.4686
	0.700	5.0984	0.5095	0.700	5.2937	0.5049
	A	f_1	f_5	A	f_1	f_5
B_{1g}	0.000	5.0467	0.6377	0.000	4.8677	0.6656
	0.300	5.1877	0.6347	0.300	5.1521	0.6433
	0.500	5.2565	0.6515	0.500	5.3055	0.6496
	0.700	5.3060	0.6827	0.700	5.4334	0.6707

*The units of A, f_1, and f_2 are dynes/cm. x 10^5, and the units of f_3, f_4, and f_5 are ergs/radian^2 x 10^{-11}.

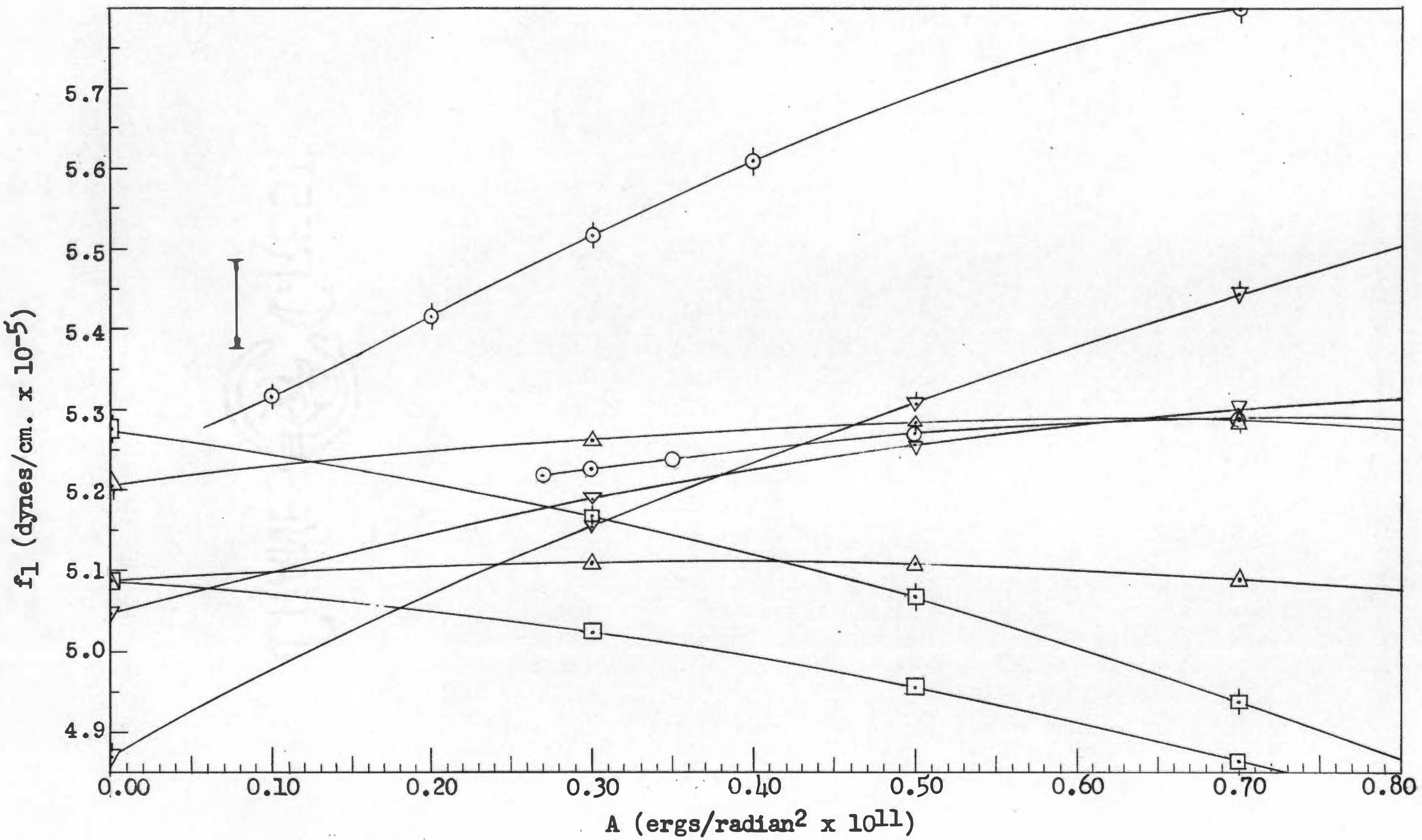


Figure 21. f_1 vs. A for Species A_g, B_{3u}, B_{2u}, and B_{1g} of C_2H_4 and C_2D_4. o, A_g, C_2H_4; ϕ , A_g, C_2D_4; □, B_{3u}, C_2H_4; ⌶ , B_{3u}, C_2D_4; △ , B_{2u}, C_2H_4; △ , B_{2u}, C_2D_4; ▽ , B_{1g}, C_2H_4; ▽ , B_{1g}, C_2D_4.

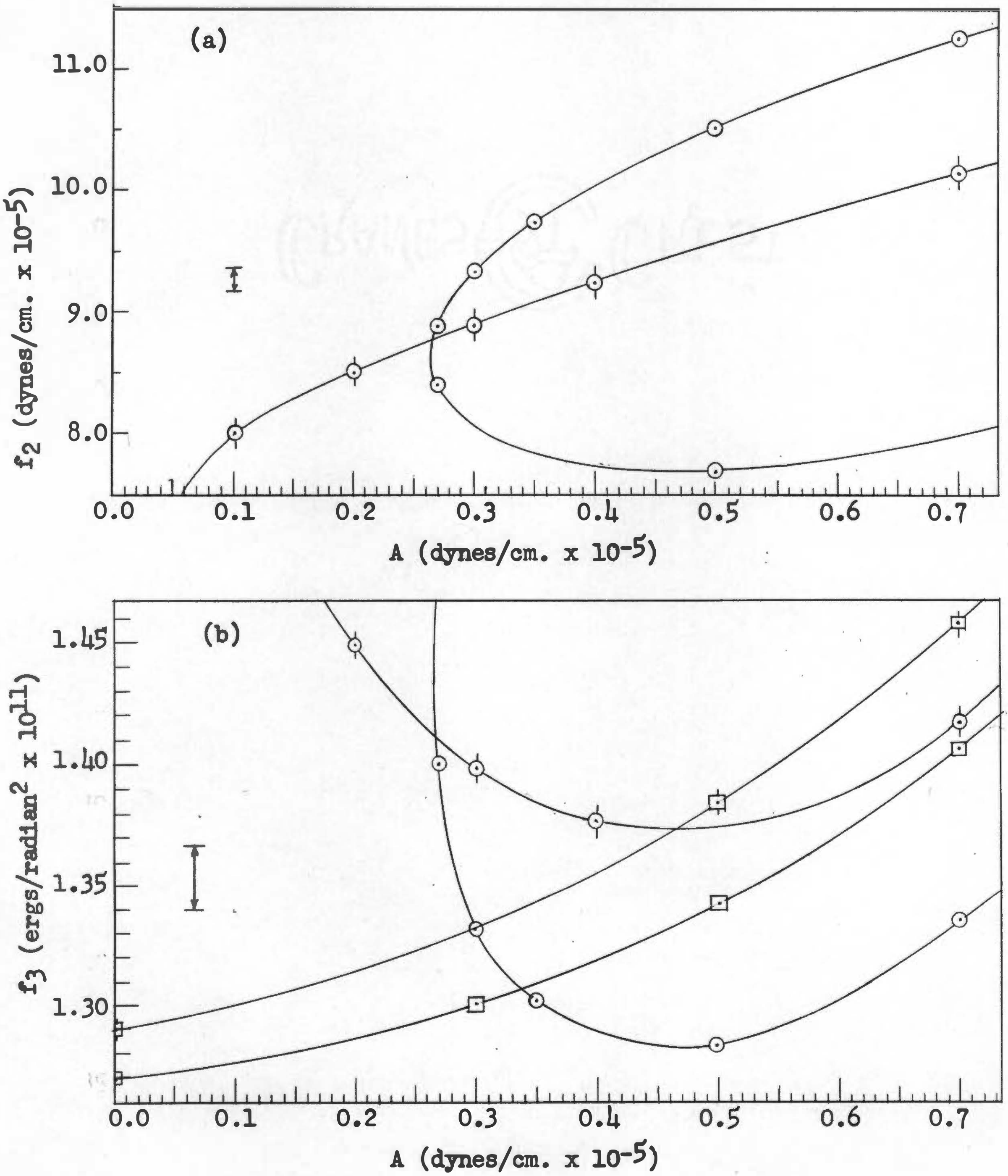


Figure 22. (a) f_2 vs. A for Species A_g of C_2H_4 and C_2D_4.
(b) f_3 vs. A for Species A_g and B_{3u} of C_2H_4 and C_2D_4. o, A_g, C_2H_4; ϕ , A_g, C_2D_4; □ , B_{3u}, C_2H_4; ⊓ , B_{3u}, C_2D_4.

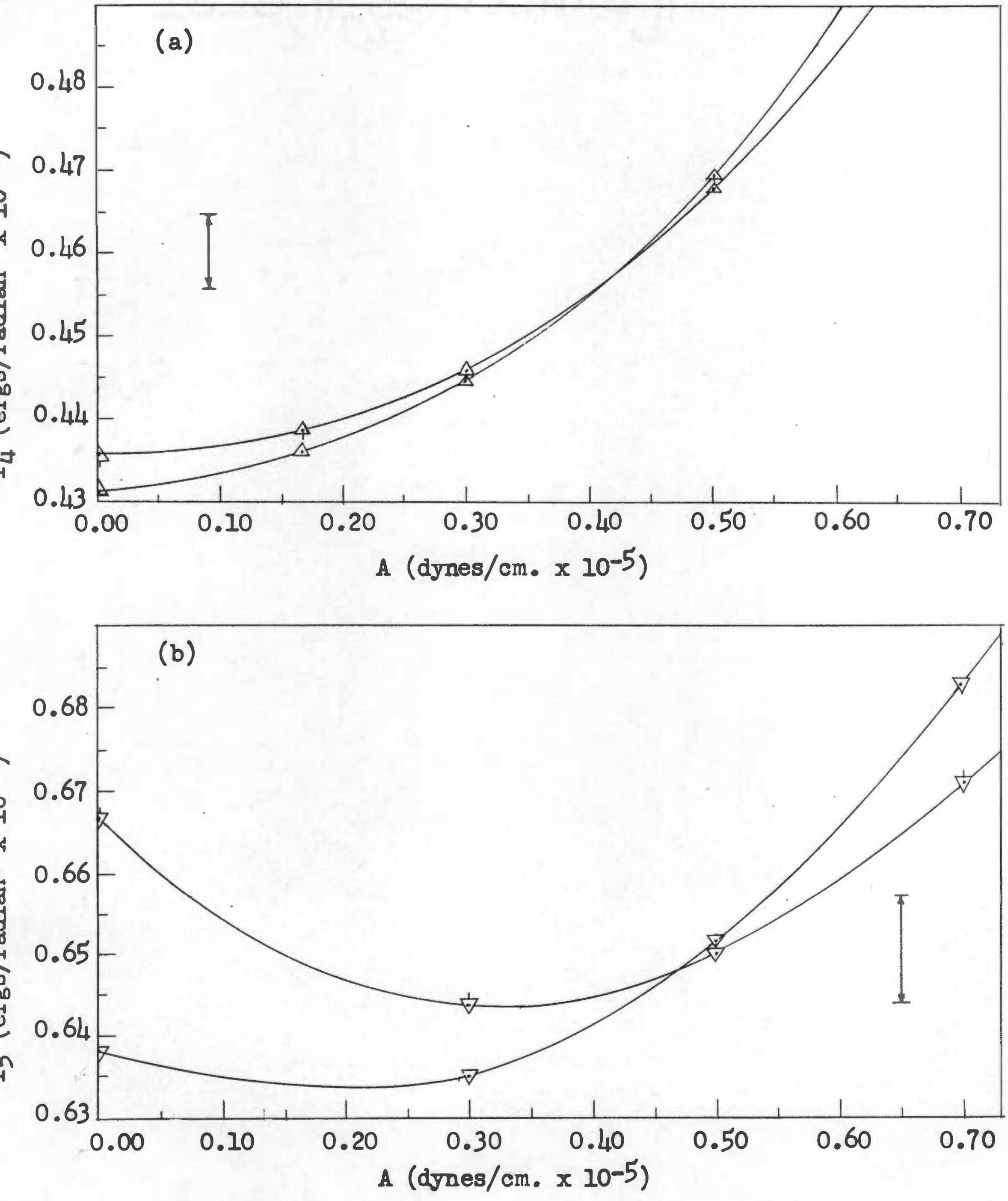


Figure 23. (a) f_4 *vs.* A for Species B_{2u} of C_2H_4 and C_2D_4.
(b) f_5 *vs.* A for Species B_{1g} of C_2H_4 and C_2D_4.
△ , B_{2u}, C_2H_4; △ , B_{2u}, C_2D_4; ▽ , B_{1g}, C_2H_4;
▽ , B_{1g}, C_2D_4.

From inspection of Figures 21, 22, and 23, it is apparent that the best set of force constants occurs for a value of A between 0.27 and 0.33. Furthermore, the solution in this range of A is unique, because at higher and lower values of A, the differences in the force constants are considerably larger. From inspection of the figures, the best value of A was found to be 0.317. The values of the other force constants were obtained by taking the average value of each constant at A = 0.317. This set of constants was then substituted into the secular equations of C_2H_4 and C_2D_4, and the frequencies of these molecules were calculated. Very slight adjustments were made in the constants in order to improve the agreement between calculated and observed frequencies. The constants f_6, f_7, and f_8, associated with the one-dimensional species, were calculated quite simply using Equations (100)-(105). The values of the constants are given in Table IV, designated as Set I.

The limited range of A for which an acceptable solution for the force constants can be obtained is determined primarily by f_1, f_2, and f_3, since the values of f_4 and f_5 for C_2H_4 and C_2D_4 remain close together throughout the range of A from 0.00 to 0.70. It was observed from Figure 22b. that if f_3 were different in species A_g and B_{3u}, a better set of constants could be obtained. Such a difference would occur if a repulsive force were included between hydrogen atoms on opposite ends of the molecule. Although this force was assumed to be negligible, a set of force constants, designated as Set II, were chosen assuming f_3 for species Ag and B_{3u} to be different. The best value of A

TABLE IV

FORCE CONSTANTS FOR ETHYLENE

Constant	Set I	Set II
A	0.3170 x 10^5 dynes/cm.	0.2680 x 10^5 dynes/cm.
f_1	5.1673	5.1550
f_2	9.2550	8.8489
f_3^{Ag}	1.3370 x 10^{-11} ergs/radian^2	1.4030 x 10^{-11} ergs/radian^2
f_3^{B3u}	1.3370	1.3094
f_4	0.4462	0.4421
f_5	0.6394	0.6384
f_6	0.2635	0.2635
f_7	0.1995	0.1995
f_8	0.5389	0.5389
K_{CH}	4.7451 x 10^5 dynes/cm.	
K_{CC}	7.2498	
K_H	1.0588 x 10^{-11} ergs/radian^2	
k_{σ}^{u}	0.7985	
k_{σ}^{g}	0.5481	
k_{π}^{u}	0.0298	
k_{π}^{g}	-1.6385	
k_{π}^{τ}	1.4087	

for this set of constants was found to be 0.268. This set of constants is given in Table IV, and in Table V, the calculated frequencies of the isotopic ethylenes for both sets of constants are given, along with the observed frequencies. The frequencies of C_2H_3D and C_2HD_3 were obtained for the Set I constants only. The secular determinants of these molecules contain a 9 x 9 block, and the roots of these determinants were obtained by use of a digital computer. The roots (frequencies) of the secular determinants of the other molecules were obtained by direct expansion when the determinant was third or lower order. For determinant of higher order, the iteration procedure described by Fletcher and Crawford[36] was used.

The constants of Set II reproduce the frequencies somewhat better than those of Set I, but the improvement is not great enough to justify including a force of repulsion between hydrogen atoms on opposite ends of the molecule. It is interesting to note that the best possible frequency fit for C_2H_4 and C_2D_4 would have an average error of 0.28 per cent in each frequency, due to the failure of the observed frequencies to fit the product rule. The average error in the frequencies calculated for C_2H_4 and C_2D_4 using the Set II constants is 0.40 per cent, so these constants are almost as good as the best possible set of constants which could be determined using a completely general quadratic field.

The overall agreement of the calculated frequencies with the observed frequencies is slightly better than that obtained by Lancaster, Inskeep, and Crawford.[16] These investigators used a completely general quadratic field, and the fact that the results presented in this disserta-

TABLE V

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF THE ISOTOPIC ETHYLENES

Molecule	Species and Freq.	No.	Obs. Freq. (cm.$^{-1}$)	Calc. Freq. Set I	% Diff.	Calc. Freq. Set II	% Diff.
C_2H_4	A_g	1	3018.5	3000.1	-0.60	3000.5	-0.61
		2	1622.5	1607.8	-0.91	1623.6	+0.07
		3	1343.5	1344.6	+0.08	1343.2	-0.02
	A_u	4	1027[a]	1027.0	0.00	1027.0	0.00
	B_{1g}	5	3108	3099.8	-0.26	3102.0	-0.19
		6	1236[b]	1239.8	+0.31	1240.9	+0.40
	B_{1u}	7	949.2	950.5	+0.11	950.5	+0.11
	B_{2g}	8	950	949.6	-0.04	949.6	-0.04
	B_{2u}	9	3105.5	3123.5	+0.58	3120.3	+0.48
		10	810.3	811.0	+0.09	811.3	+0.12
	B_{3u}	11	2989.5	3033.2	+1.46	3102.0	-0.19
		12	1443.5	1463.6	+1.39	1441.0	+0.40
Average Per Cent Error					0.49		0.32
C_2D_4	A_g	1	2260	2186.7	-3.24	2192.6	-2.98
		2	1517.5	1531.0	+0.89	1516.8	-0.05
		3	984.5	969.3	-1.54	984.5	+0.01
	A_u	4	c	726.5	- -	726.5	- -
	B_{1g}	5	2305	2305.1	0.00	2311.6	+0.29
		6	1011.1[d]	1008.1	-0.30	1006.9	-0.41
	B_{1u}	7	720	719.0	-0.14	719.0	-0.14
	B_{2g}	8	780	780.4	+0.05	780.4	+0.05
	B_{2u}	9	2345	2323.6	-0.91	2322.3	-0.97
		10	584	583.4	-0.10	583.3	-0.12
	B_{3u}	11	2200.2	2200.6	+0.12	2195.5	-0.21
		12	1077.9	1078.5	+0.06	1071.2	-0.62
Average Per Cent Error					0.61		0.48

TABLE V

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF THE ISOTOPIC ETHYLENES (Continued)

Molecule	Species and Freq.	No.	Obs. Freq. (cm.$^{-1}$)	Calc. Freq. Set I	% Diff.	Calc. Freq. Set II	% Diff.
asym.-$C_2H_2D_2$	A_1	1	3019	3016.9	-0.10	3013.3	-0.19
		2	1585	1584.2	-0.05	1583.4	-0.10
		3	1032	1017.3	-1.42	1025.8	-0.59
		11	2231	2194.3	-1.64	2194.0	-1.66
		12	1384	1394.9	+0.79	1387.0	+0.21
	B_1	5	2335	2314.6	-0.87	2317.4	-0.75
		6	1150[e]	1149.2	-0.06	1149.4	-0.05
		9	3095	3111.7	+0.54	3111.2	+0.52
		10	676[e]	673.0	-0.43	672.9	-0.46
	B_2	7	752	750.4	-0.21	Same	
		8	944	950.0	+0.63	Same	
	A_2	4	890[f]	889.5	-0.05	Same	
Average Per Cent Error					0.56		0.45
cis-$C_2H_2D_2$	A_1	1	2300	2248.9	-2.22	2251.8	-2.10
		2	1567[b]	1566.1	-0.06	1563.3	-0.24
		3	1215[b]	1209.7	-0.44	1219.4	+0.36
		9	3058.7	3067.4	+0.28	3065.6	+0.23
		10	646	651.3	+0.82	652.1	+0.95
	B_1	5	3056	3067.8	+0.39	3065.8	+0.32
		6	1039.3	1048.0	+0.83	1045.9	+0.63
		11	2254	2255.7	+0.08	2254.8	+0.04
		12	1342	1348.5	+0.50	1341.5	-0.04
	A_2	4	c	985.1	- -	Same	
		8	763[b]	759.0	-0.53	Same	
	B_2	7	842.5	842.7	+0.03	Same	
Average Per Cent Error					0.52		0.46

TABLE V

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF THE ISOTOPIC ETHYLENES (Continued)

Molecule	Species and Freq.	No.	Obs. Freq. (cm.$^{-1}$)	Calc. Freq. Set I	% Diff.	Calc. Freq. Set II	% Diff.
	A_g	1	2284.5	2243.6	-1.79	2250.2	-1.50
		2	1570.8	1565.1	-0.36	1562.5	-0.53
		3	1285.7	1286.2	+0.04	1291.5	+0.45
		5	3045	3053.4	+0.28	3054.8	+0.32
		6	1003.5	1003.1	-0.04	1007.7	+0.42
trans- $C_2H_2D_2$	B_u	9	3064.9	3081.4	+0.53	3076.4	+0.37
		10	660^e	661.9	+0.30	661.8	+0.27
		11	2271	2261.0	-0.44	2256.4	-0.64
		12	1298.8	1307.9	+0.69	1299.0	+0.01
	A_u	4	988	989.9	+0.20	Same	
		7	726.3	722.1	-0.59	Same	
	B_g	8	864^b	869.1	+0.58	Same	
Average Per Cent Error					0.48		0.49
C_2HD_3	A'	1	2280	2252.8	-1.19		
		2	1547	1549.7	+0.17		
		3	1046.9	1045.2	-0.17		
		5	2332	2315.1	-0.72		
		6	999	992.7	-0.63		
		9	3047	3067.7	+0.62		
		10	609.7	618.3	+1.40		
		11	2222	2193.8	-1.27		
		12	1289	1292.0	+0.23		
	A"	4	764	763.7	-0.04		
		7	723.4	722.0	-0.15		
		8	918.0	922.4	+0.40		
Average Per Cent Error					0.58		

TABLE V

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF THE ISOTOPIC ETHYLENES (Continued)

Molecule	Species and	Freq. No.	Obs. Freq. (cm.$^{-1}$)	Calc. Freq. Set I	% Diff.
C_2H_3D	A'	1	3002	3014.7	+0.42
		2	1605	1590.5	-0.90
		3	1290	1289.1	-0.06
		5	3061.3	3068.0	+0.23
		6	1128.5	1129.5	+0.09
		9	3103	3113.7	+0.34
		10	713[e]	719.7	+0.94
		11	2276.1	2252.4	-1.04
		12	1401.5	1417.4	+1.13
	A"	4	1000.4	1002.6	+0.22
		7	807.6	806.7	-0.12
		8	943.7	950.0	+0.66
Average Per Cent Error					0.51

[a] Calculated by Arnett and Crawford.

[b] Liquid phase Raman data.

[c] Not observed.

[d] Calculated from $\nu_6 + \nu_{10} = 1595.1$ cm.$^{-1}$.

[e] Band center uncertain.

[f] Calculated from $\nu_4 + \nu_6 = 2040$ cm.$^{-1}$.

tion are better than the results obtained using a general quadratic field points out the difficulty of obtaining the best solution for the force constants by direct solution of the equations involving the force constants and frequencies. It should be pointed out that Lancaster, Inskeep, and Crawford corrected the frequencies for anharmonicity by assuming all of the anharmonicity occurred in the C-H and C-D stretching modes. Their results were presented in terms of the observed frequencies, however, and could be compared directly with the results obtained in this investigation. Sverdlov[17] has also reported a determination of the force constants for ethylene using a general quadratic field. The overall agreement between observed and calculated frequencies obtained by Sverdlov is slightly better than the results obtained in this investigation, but the difference is small. It can therefore be concluded that the force field assumed for the ethylene molecule in the present investigation is quite satisfactory, and little improvement is possible using a more general field. The frequencies calculated for C_2H_3D and C_2HD_3, given in Table V, are the first reported for these molecules, and confirm the assignment of the fundamental frequencies.

An interesting pattern was noted in the difference in the calculated and observed C-H and C-D stretching frequencies. In almost all cases, the calculated values for C-H stretching modes were higher than the observed values, while the calculated values for C-D stretching modes were lower than the observed values. In particular, the calculated values of symmetric C-D stretching modes were much lower than the observed values. This pattern is in line with the expectation that the C-H stretching vibrations would be more anharmonic than the C-D stretching vibrations.

C. Allene

The secular equations of C_3H_4 and C_3D_4 factor into two third-order blocks, one doubly degenerate fourth-order block, and one first-order block. The $\mathfrak{F}$ and $\mathfrak{G}$ matrices for these molecules are given in Appendix I. The algebraic equations obtained by expansion of the secular equations for species A_1, B_1, and B_2 of C_3H_4 and C_3D_4 are:

A_1: <u>C_3H_4</u>

$$1.0375398\ f_1 + 0.0833069\ f_2 + 0.9738883\ f_3 - 0.4075018\ A = \sum_{i=1}^{3} \lambda_i \qquad (121)$$

$$0.0826341\ f_1f_2 + 1.0056180\ f_1f_3 + 0.0723109\ f_2f_3 - 0.2556926\ Af_1 -$$

$$0.2350480\ Af_3 - 0.8133496\ A^2 = \sum_{\substack{i,j=1\\ i\neq j}}^{3} \lambda_i \lambda_j \qquad (122)$$

$$f_1f_2f_3 - 1.8832896\ A^2f_1 - 0.7586240\ A^2f_2 - 4.8240414\ A^2f_3 +$$

$$5.2505789\ A^3 = 13.9427816 \prod_{i=1}^{3} \lambda_i \qquad (123)$$

<u>C_3D_4</u>

$$0.5419592\ f_1 + 0.0833069\ f_2 + 0.5402188\ f_3 - 0.4075018\ A = \sum_{i=1}^{3} \lambda_i' \qquad (124)$$

$$0.0413488\ f_1f_2 + 0.2879466\ f_1f_3 + 0.0361833\ f_2f_3 - 0.1279445\ Af_1 -$$

$$0.1176143\ Af_3 - 0.2436946\ A^2 = \sum_{\substack{i,j=1\\ i\neq j}}^{3} \lambda_i' \lambda_j' \qquad (125)$$

$$f_1f_2f_3 - 1.8832896\ A^2f_1 - 0.7586236\ A^2f_2 - 4.8240411\ A^2f_3 +$$

$$5.2505792\ A^3 = 55.6811474 \prod_{i=1}^{3} \lambda_i' \qquad (126)$$

B_2: <u>C_3H_4</u>

$$1.0375398\ f_1 + 0.2499207\ f_2' + 0.9738883\ f_3 - 0.4075018\ A =$$

$$\sum_{i=5}^{7} \lambda_i \qquad (127)$$

$$0.2555026\ f_1f_2' + 1.0056180\ f_1f_3 + 0.2345742\ f_2'f_3 - 0.2556925\ Af_1 +$$

$$0.0201709\ Af_2'' - 0.2350480\ Af_3 - 2.0226665\ A^2 = \sum_{\substack{i,j=5\\ i\neq j}}^{7} \lambda_i \lambda_j \qquad (128)$$

$$f_1f_2'f_3 - 1.8832896\ A^2f_1 - 0.7586240\ A^2f_2' - 4.8240414\ A^2f_3 +$$

$$5.2505789\ A^3 = 4.1792582 \prod_{i=5}^{7} \lambda_i \qquad (129)$$

<u>C_3D_4</u>

$$0.5419592\ f_1 + 0.2499207\ f_2' + 0.5402188\ f_3 - 0.4075018\ A =$$

$$\sum_{i=5}^{7} \lambda_i' \qquad (130)$$

$$0.1316467\ f_1f_2' + 0.2879466\ f_1f_3 + 0.1261912\ f_2'f_3 - 0.1279445\ Af_1 +$$

$$0.0201709\ Af_2' - 0.1176143\ Af_3 - 0.9186097\ A^2 = \sum_{\substack{i,j=5\\ i\neq j}}^{7} \lambda_i' \lambda_j' \qquad (131)$$

$$f_1f_2'f_3 - 1.8832896\ A^2f_1 - 0.7586236\ A^2f_2' - 4.8240411\ A^2f_3 +$$

$$5.2505792\ A^3 = 15.1664058 \prod_{i=5}^{7} \lambda_i' \qquad (132)$$

B_1: <u>C_3H_4</u>

$$f_4 = 0.8366495 \quad (\lambda_4) \qquad (133)$$

$\underline{C_3D_4}$

$$f_4 = 1.6720135 \quad (\lambda_4') . \tag{134}$$

The f_i's in the above equations are the diagonal $\mathfrak{F}$ matrix elements and are defined by the following relations:

$$f_1 = K_{CH} + 1.37978\ A \tag{135}$$

$$f_2 = K_{CC} + k_{CC}^{CC} + 3.17241\ A \tag{136}$$

$$f_2' = K_{CC} - k_{CC}^{CC} + 3.17241\ A \tag{137}$$

$$f_3 = K_H + 0.82139\ A \tag{138}$$

$$f_4 = \frac{K_H \sin^2\alpha\ k_\pi^\tau}{2K_H \sin^2\alpha + k_\pi^\tau} + 0.08179\ A . \tag{139}$$

The equations for the fourth-order degenerate block were not obtained explicitly because the solution of a fourth-order set is impractical. The diagonal elements of this block are:

$$f_1 = K_{CH} + 1.37978\ A \qquad \text{(CH stretching)} \tag{140}$$

$$f_5 = \frac{K_H k_\sigma}{2K_H + k_\sigma} + 0.81239\ A \qquad \text{(CH}_2\text{ rocking)} \tag{141}$$

$$f_6 = K \qquad \text{(CCC bending)} \tag{142}$$

$$f_7 = \frac{2K_H \cos^2\alpha\,(k_\sigma + k_\pi)}{2K_H \cos^2\alpha + (k_\sigma + k_\pi)} + 0.06155\ A . \qquad \text{(CH}_2\text{ wagging)} \tag{143}$$

The equations for species A_1 contain four independent constants, f_1, f_2, f_3, and A. The equations of species B_2 likewise contain four independent constants, f_1, f_2', f_3, and A. Thus, if the value of A is fixed, the three frequencies of C_3H_4 or C_3D_4 belonging to each species enable the values of the other three constants to be determined. The equations for each species were solved for the f_i's for values of A ranging from 0.00 to 0.70, since the results obtained for ethylene indicated that the best solution for the constants would lie in this range. The equations were solved in the same manner as has been described for the equations of species A_g of C_2H_4. The values of the constants obtained are given in Table VI. In Figures 24 and 25, the values of f_1, f_2, f_2', and f_3 are plotted against A. The vertical lines indicate the change in the force constant which will cause a change of approximately 1 per cent in the corresponding frequencies.

From inspection of Figure 25 (a) and (b), it is apparent that the value of A lies close to 0.30, because in this region, the curves lie closest together. At lower and higher values of A, the curves rapidly diverge, so the solution for the constants at an A value close to 0.30 is unique. An interesting point is illustrated by Figure 25 (a). The difference in f_2 and f_2' is $2k_{CC}^{CC}$, where k_{CC}^{CC} is the interaction constant between the two CC double bonds. If k_{CC}^{CC} were zero, the four curves would be expected to lie close together at some value of A. It was found that this did not occur. However, the values of f_2 for species A_1 of C_3H_4 and C_3D_4 intersect at almost the same value of A at which the values of f_2' for species B_2 of C_3H_4 and C_3D_4 intersect. The values of f_2 and f_2' differ by about 0.86, leading to a value of k_{CC}^{CC} of about 0.43. This confirms the fact that the interaction constant must be included in the potential energy expression.

The value of A which would yield the best set of force constants was determined to be 0.290. The values of the other force constants for

TABLE VI

FORCE CONSTANTS* FOR SPECIES A_1 AND B_2 OF C_3H_4 AND C_3D_4 FOR ARBITRARY VALUES OF A

	C_3H_4				C_3D_4			
Species	A	f_1	f_2	f_3	A	f_1	f_2	f_3
A_1	0.150	5.0620	10.9650	1.1160	0.260	No real solutions		
	0.260	5.0752	10.2500	1.2087	0.270	5.1265	8.9591	1.4100
						5.1153	9.7850	1.2938
	0.300	5.0784	10.1052	1.2345				
					0.300	5.1177	10.2701	1.2392
	0.400	5.0831	9.8768	1.2908		5.1400	8.5332	1.4847
	0.500	5.0837	9.7730	1.3409	0.400	5.1358	11.0961	1.169
						5.1694	7.9520	1.620
	0.700	5.0726	9.8113	1.4320				
					0.700	5.191	12.339	1.145
						5.211	7.533	1.869
	A	f_1	f_2'	f_3	A	f_1	f_2'	f_3
B_2	0.000	5.068	8.940	1.280	0.000	No real solutions		
	0.300	5.1175	9.3211	1.2556	0.150	4.994	9.570	1.282
	0.400	5.1156	9.4340	1.2705	0.250	5.1926	9.2972	1.2871
	0.500	5.1035	9.5557	1.2940	0.300	5.2498	9.2433	1.2924
	0.700	5.0478	9.8470	1.3623	0.350	5.2932	9.2149	1.2997
					0.500	5.3597	9.2455	1.3319
					0.700	5.3202	9.5180	1.3964

*The units of A, f_1, f_2, and f_2' are dynes/cm. x 10^5, and the units of f_3 are ergs/radian^2 x 10^{-11}.

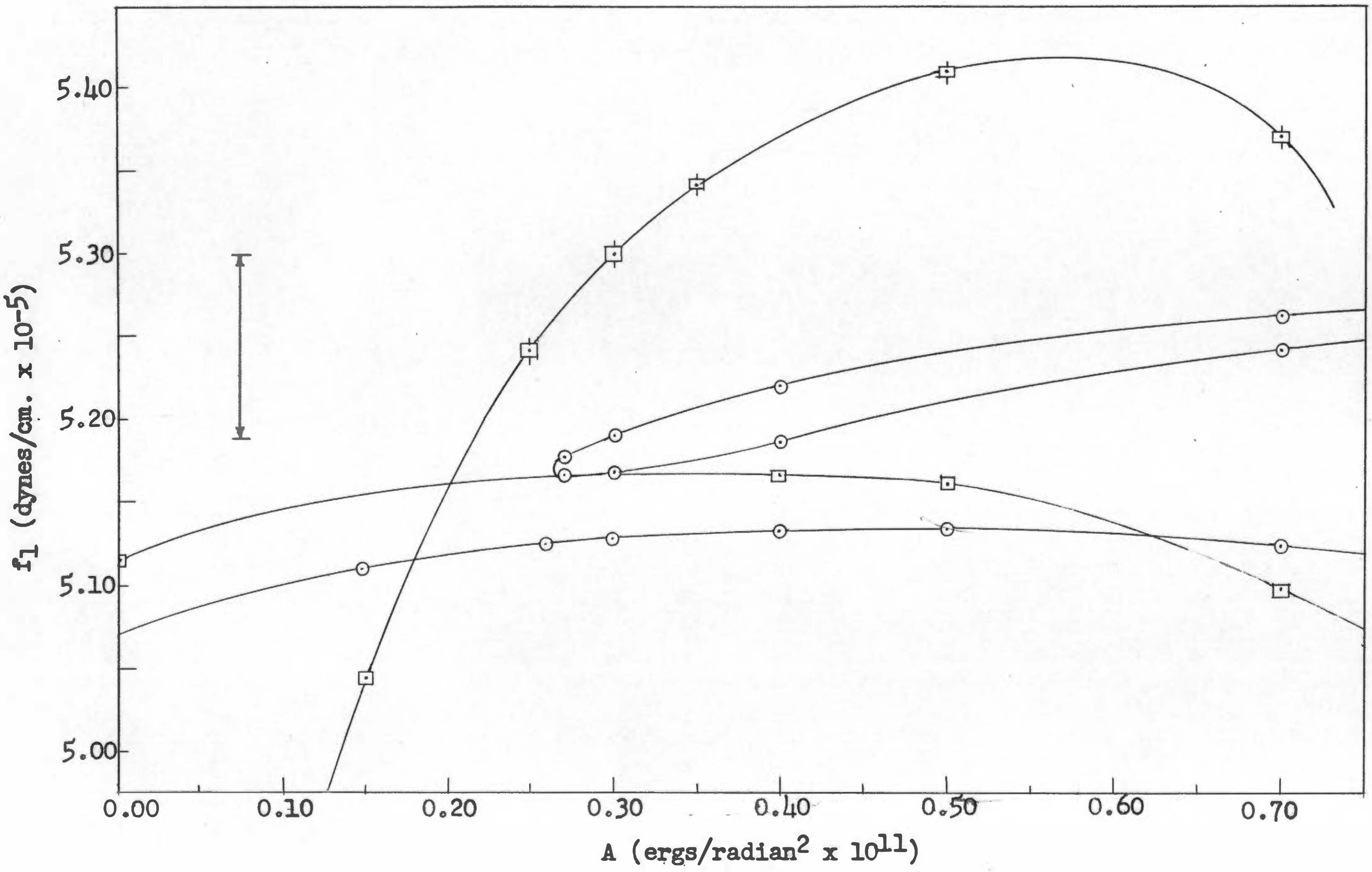


Figure 24. f_1 vs. A for Species A_1 and B_2 of C_3H_4 and C_3D_4.
o, A_1, C_3H_4; ϕ , A_1, C_3D_4; □ , B_2, C_3H_4; ⧮ , B_2, C_3D_4.

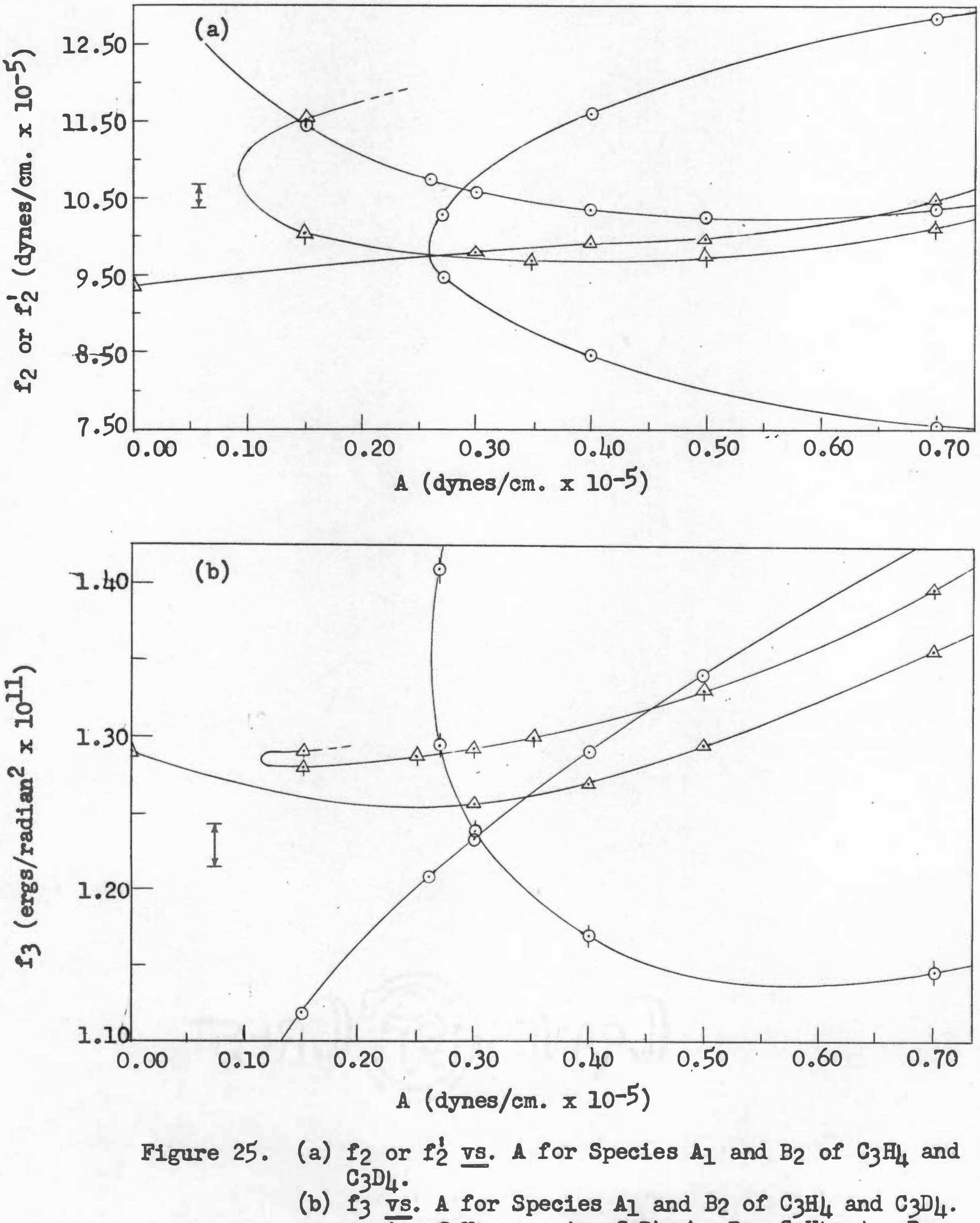


Figure 25. (a) f_2 or f_2' vs. A for Species A_1 and B_2 of C_3H_4 and C_3D_4.
(b) f_3 vs. A for Species A_1 and B_2 of C_3H_4 and C_3D_4.
o, A_1, C_3H_4; ϕ , A_1, C_3D_4; △, B_2, C_3H_4; ⍋ , B_2, C_3D_4.

species A_1 and B_2 were obtained with the aid of the figures, and are given in Table VII. The value of f_4 was obtained quite simply by solving Equations (133) and (134).

Species E is fourth-order, and it would be quite difficult to solve the equations of a fourth-order species in the way the equations of the third-order species were solved. However, the C-H stretching frequency in C_3H_4 and the C-D stretching frequency in C_3D_4 are both much higher than the other frequencies in the species, and therefore these frequencies can be factored off without appreciable effect on the force constants. After the C-H and C-D stretching frequencies were factored off by Wilson's method,[37] it was found that the reduced third-order $\mathfrak{F}$ matrix was diagonal, with elements f_5, f_6, and f_7. These constants were evaluated for C_3H_4 and C_3D_4. Two sets of real solutions were obtained for each molecule, and these sets are given in Table VIII. From inspection of Table VIII, it is clear that the two sets of constants for C_3H_4 agree equally well with the two sets for C_3D_4, so that either set could be considered as correct. An approximate average of each of these sets are given in Table VII, designated as Set I and Set II.

When the frequencies of species B_1 and B_2 of CH_2CCD_2 were calculated, it was found that the calculated frequencies were divided between the two species differently for the two sets of constants. The observed and calculated frequencies for C_3H_4, C_3D_4, and CH_2CCD_2 for both sets of force constants are given in Tables IX and X. It is seen from inspection of Tables IX and X that the two sets of constants yield frequencies which agree with the observed frequencies equally well. However, using the

TABLE VII

FORCE CONSTANTS* FOR ALLENE

Constant	Set I	Set II
A	0.2900	Same
f_1	5.1350	
f_2	10.1450	
f_2'	9.2820	
f_3	1.2550	
f_4	0.3707	
f_5	0.3420	0.5070
$f_6 = K_\epsilon$	0.3730	0.3683
f_7	0.2800	0.1880
K_{CH}	4.7349	Same
K_{CC}	8.7935	
k_{CC}^{CC}	0.4315	
K_H	1.0168	
k_τ	1.3090	
k_σ	0.2312	0.7308
k_π	0.2642	-0.4857

*The units of A, f_1, f_2, f_2', K_{CH}, K_{CC}, and k_{CC}^{CC} are dynes/cm. x 10^5, and the units of f_3, f_4, f_5, f_6, f_7, K_H, K_ϵ, k_τ, k_σ, and k_π are ergs/radian^2 x 10^{-11}.

TABLE VIII

FORCE CONSTANTS* FOR SPECIES E OF C_3H_4 AND C_3D_4 OBTAINED FROM REDUCED SECULAR DETERMINANT

Molecule	f_5	f_6	f_7
C_3H_4	0.3397	0.3685	0.2828
	0.5080	0.3660	0.1905
C_3D_4	0.3315	0.3781	0.2776
	0.5060	0.3706	0.1855

*The units of f_5, f_6, and f_7 are ergs/radian^2 x 10^{-11}.

TABLE IX

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF C_3H_4, C_3D_4, AND CH_2CCD_2 (SET I)

Species of D_{2d} and Freq. No.		C_3H_4			C_3D_4			CH_2CCD_2		
		Obs. Freq. (cm.$^{-1}$)	Calc. Freq.	% Diff.	Obs. Freq. (cm.$^{-1}$)	Calc. Freq.	% Diff.	Obs. Freq. (cm.$^{-1}$)	Calc. Freq.	% Diff.
A_1	1	2996	3012.9	+0.56	2195	2198.9	+0.18	3011	3012.4	+0.05
	2	1440	1454.1	+0.98	1228	1228.7	+0.06	1418	1429.3	+0.80
	3	1076	1077.8	+0.17	874	874.6	+0.06	924	926.3	+0.25
B_1	4	865	867.2	+0.26	615	613.4	-0.26	a	750.0	- -
B_2	5	3006.8	3011.9	+0.17	2230	2209.9	-0.90	2226	2204.7	-0.96
	6	1957	1957.1	+0.01	1921	1921.1	0.00	1942	1939.1	-0.15
	7	1398	1398.3	+0.02	1034	1019.1	-1.44	1176	1170.6	-0.46
E	8	3089.9	3096.0	+0.20	2325	2295.7	-1.05	2334	2295.7	-1.66
	9	1037.9	1033.0	-0.47	843.3	846.5	+0.38	1022	1031.0	+0.88
	10	845.2	838.9	-0.75	668.1	673.1	+0.75	670	688.0	+2.68
	11	352.0	353.4	+0.41	306	304.1	-0.61	327	319.8	-2.20
E	12							3100	3095.9	-0.13
	13							858	880.1	+2.58
	14							825	795.0	-3.63
	15							336	335.5	-0.16
Average Per Cent Error				0.36			0.53			1.11

[a] Not observed.

TABLE X

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF C_3H_4, C_3D_4, AND CH_2CCD_2 (SET II)*

Species of D_{2d} and Freq. No.		C_3H_4			C_3D_4			CH_2CCD_2		
		Obs. Freq. (cm.$^{-1}$)	Calc. Freq.	% Diff.	Obs. Freq. (cm.$^{-1}$)	Calc. Freq.	% Diff.	Obs. Freq.[a] (cm.$^{-1}$)	Calc. Freq.	% Diff.
E	8	3089.9	3096.7	+0.22	2325	2298.2	-1.15	2334	2298.2	-1.53
	9	1037.9	1031.1	-0.65	843.3	842.9	-0.05	858	878.2	+2.35
	10	845.2	839.8	-0.64	668.1	671.5	+0.51	825	794.4	-3.71
	11	352.0	352.7	+0.20	306	305.0	-0.32	327	324.0	-0.92
E	12							3100	3096.7	-0.11
	13							1022	1029.2	+0.71
	14							670	686.3	+2.43
	15							336	331.4	-1.38
Average Per Cent Error				0.35			0.45			1.05

*The frequencies for species A_1, B_1, and B_2 for Set II are identical with those given for Set I.

[a] It should be noted that the observed frequencies for species B_1 and B_2 of CH_2CCD_2 are assigned differently from the assignment used in Table IX.

Set I constants, the observed frequencies of species B_1 and B_2 of CH_2CCD_2 must be assigned as follows:

I. B_1: 2334 cm.$^{-1}$, 1022 cm.$^{-1}$, 670 cm.$^{-1}$, 327 cm.$^{-1}$
B_2: 3100 cm.$^{-1}$, 858 cm.$^{-1}$, 825 cm.$^{-1}$, 336 cm.$^{-1}$.

When the constants of Set II are used, the frequencies must be assigned as follows:

II. B_1: 2334 cm.$^{-1}$, 858 cm.$^{-1}$, 825 cm.$^{-1}$, 327 cm.$^{-1}$
B_2: 3100 cm.$^{-1}$, 1022 cm.$^{-1}$, 670 cm.$^{-1}$, 336 cm.$^{-1}$.

The assignment given by Schuler and Fletcher[38] is that shown in Set I. This assignment was made by use of the product rule and utilizing the frequencies calculated from a normal-coordinate treatment. The $\mathfrak{F}$ matrices of species B_1 and B_2 are identical, so the product of the frequencies of species B_1 divided by the product of the frequencies of species B_2 should be equal to the ratio $\left[|\mathfrak{G}|_{B_1}/|\mathfrak{G}|_{B_2}\right]^{\frac{1}{2}}$, which is 0.71662. The ratio of the products of the frequencies of Assignment I was found to be 0.72832, while that obtained using the frequencies of Assignment II was 0.75747. The ratio using the observed frequencies was expected to be larger than that predicted by theory, and this is seen to be true for both assignments. However, the value using Assignment I is 1.4 per cent higher than theory predicts, while the value using Assignment II is 5.8 per cent higher than predicted. On this basis alone, Assignment I would be favored. It should be noted, however, that the band centers of the 336 cm.$^{-1}$ and 327 cm.$^{-1}$ bands are not known with certainty, and a change of a few wave numbers in the values of these observed band centers could alter the ratio of the frequency products in such a manner as to favor Assignment

II. It should be pointed out that Assignment II was likewise ruled out in Schuler and Fletcher's work because only one set of force constants were determined by these investigators. This set of constants was equivalent to the Set I constants determined in the present work, and the fact that another set of constants would permit the frequencies to be assigned according to Assignment II was not apparent.

There are several reasons which favor Assignment II. The C-H stretching frequency and the CH_2 rocking frequency belong to species B_2. The CH_2 rocking frequency would be expected to occur at a higher frequency than the CD_2 rocking or the CH_2 or CD_2 wagging frequencies. This leads to the assignment of the 1022 cm.$^{-1}$ band as the CH_2 rocking frequency, and in Assignment II, this frequency is assigned to species B_2. Another point which favors Assignment II is illustrated by a comparison of the diagonal $\mathfrak{F}$ matrix elements corresponding to rocking and wagging vibrations. In both C_2H_4 and CH_2O, it was found that the elements corresponding to rocking motions were about 2.5 times those corresponding to wagging motions. This indicated that the ratio of f_5 to f_7 would be about 2.5. Inspection of Table VII shows that the ratio is 1.2 in Set I, and 2.70 in Set II, which indicates that the constants of Set II, associated with Assignment II, are correct. In addition, it was noted that f_6 is essentially the same in Set I and Set II, while large changes occur in f_5 and f_7. It is believed that the two sets of constants arise because of the interchange of the frequencies assigned to the CH_2 rocking and CH_2 wagging frequencies. Based on this idea, which will be discussed in more detail in Chapter IV, the set of constants in which f_5 is larger and f_7 smaller would be favored, and this is Set II.

The values of the orbital valency force constants, k_σ and k_π, which were obtained have been interpreted to favor the Set I constants. However, this evidence is questionable, and does not constitute a strong point. On the basis of the points discussed above, the assignment of the frequencies of species B_1 and B_2 of CH_2CCD_2 given by Assignment II is preferred, along with the force constants of Set II. The frequencies calculated for C_3H_4, C_3D_4, and CH_2CCD_2 using the constants of Set II are given along with the observed frequencies in Table X.

D. Formaldehyde

The $\mathfrak{F}$ and $\mathfrak{G}$ matrices for CH_2O and CD_2O are given in Appendix I. The algebraic equations obtained from expansion of the secular equations are:

A_1: <u>CH_2O</u>

$$1.0294386\, f_1 + 0.1458069\, f_2 + 0.9773168\, f_3 - 0.3869376\, A = \sum_{i=1}^{3} \lambda_i \tag{144}$$

$$0.1469742\, f_1f_2 + 1.0018655\, f_1f_3 + 0.1331234\, f_2f_3 - 0.2614682\, Af_1 + 0.0072278\, Af_2 - 0.2066674\, Af_3 - 1.2526544\, A^2 = \sum_{\substack{i,j=1 \\ i\neq j}}^{3} \lambda_i \lambda_j \tag{145}$$

$$f_1f_2f_3 - 1.8526558\, A^2f_1 - 0.7918953\, A^2f_2 - 4.5690106\, A^2f_3 + 5.1781226\, A^3 = 7.4585343 \prod_{i=1}^{3} \lambda_i \tag{146}$$

CD_2O

$$0.5338580\ f_1 + 0.1458069\ f_2 + 0.5452658\ f_3 - 0.3869376\ A = \sum_{i=1}^{3} \lambda_i' \qquad (147)$$

$$0.0747151\ f_1f_2 + 0.2868724\ f_1f_3 + 0.0701274\ f_2f_3 - 0.1308350\ Af_1 + 0.0072278\ Af_2 - 0.1034130\ Af_3 - 0.4806580\ A^2 = \sum_{\substack{i,j=1 \\ i \neq j}}^{3} \lambda_i \lambda_j \qquad (148)$$

$$f_1f_2f_3 - 1.8526558\ A^2f_1 - 0.7918953\ A^2f_2 - 4.5690106\ A^2f_3 - 5.1781226\ A^3 = 27.9159617 \prod_{i=1}^{3} \lambda_i' \qquad (149)$$

B_1:

$$1.1210228\ f_1 + 1.2123195\ f_4 - 0.3287272\ A = \sum_{i=4}^{5} \lambda_i \qquad (150)$$

$$f_1f_4 - 0.7918953\ A^2 = 0.7547609 \prod_{i=4}^{5} \lambda_i \qquad (151)$$

CD_2O

$$0.6254422\ f_1 + 0.7802680\ f_4 - 0.3287272\ A = \sum_{i=4}^{5} \lambda_i' \qquad (152)$$

$$f_1f_4 - 0.7918953\ A^2 = 2.2031396 \prod_{i=4}^{5} \lambda_i \qquad (153)$$

B_2: CH_2O

$$f_5 = 0.3834650 \quad (\lambda_6) \qquad (154)$$

CD_2O

$$f_5 = 0.6066758 \quad (\lambda_6'). \qquad (155)$$

The f_i are the diagonal elements of the $\mathcal{F}$ matrix and are defined by the following relations:

$$f_1 = K_{CH} + 1.35662\ A \qquad (156)$$

$$f_2 = K_{CO} + 3.01644\ A \qquad (157)$$

$$f_3 = K_H + 0.83374\ A \qquad (158)$$

$$f_4 = \frac{K_H k_\sigma}{2K_H + k_\sigma} + 0.83374\ A \qquad (159)$$

$$f_5 = \frac{2K_H \cos^2\alpha\ (k'_\sigma + k_\pi)}{2K_H \cos^2\alpha + (k'_\sigma + k_\pi)} + 0.04313\ A\,. \qquad (160)$$

The equations for each species were solved for arbitrary values of A between 0.00 and 1.00. The results of these calculations for species A_1 and B_1 of CH_2O and CD_2O are given in Table XI, and in Figures 26 and 27, the values of the constants are plotted against A. The vertical lines in the figures indicate the change in the force constants which will cause a change of approximately 1 per cent in the corresponding frequencies. It was found that for any A value between 0.39 and 0.51, the overall frequency fit was essentially the same. Varying A in this range causes the errors in the calculated frequencies to change, but the average error remains essentially the same. An A value of 0.470 was chosen to use in the calculations because this value of A would divide the error among all the frequencies. The values of the other constants were then obtained by taking the average values from the graphs at A = 0.470. The value of f_5 was determined by solving Equations (154) and (155).

The values of the force constants are given in Table XII, and in Table XIII the observed frequencies of CH_2O, CD_2O, and CHDO are given, along with the calculated frequencies obtained using the force constants given in Table XII. The frequency fit is quite good, although the frequencies of CHDO are not fitted as well as those of CH_2O and CD_2O.

TABLE XI

FORCE CONSTANTS* FOR SPECIES A_1 AND B_1 OF CH_2O AND CD_2O FOR ARBITRARY VALUES OF A

Species	CH_2O				CD_2O			
	A	f_1	f_2	f_3	A	f_1	f_2	f_3
A_1	0.300	No real solutions			0.200	4.210	12.850	1.594
	0.370	4.382	11.900	1.607	0.400	4.424	12.577	1.600
	0.400	4.380	12.087	1.592	0.500	4.480	12.576	1.616
	0.450	4.376	12.336	1.579	0.600	4.513	12.633	1.639
	0.500	4.370	12.538	1.575	0.800	4.524	12.857	1.711
	0.600	4.353	12.864	1.584				
	0.700	4.328	13.136	1.609				

Species	A	f_1	f_4	A	f_1	f_4
B_1	0.100	4.324	0.7760	0.100	4.369	0.8018
	0.200	4.351	0.7782	0.200	4.429	0.7965
	0.300	4.377	0.7810	0.300	4.482	0.7958
	0.400	4.397	0.7902	0.400	4.530	0.7997
	0.500	4.411	0.8037	0.500	4.572	0.8079
	0.600	4.421	0.8216	0.600	4.609	0.8203
	1.000	4.410	0.9405	1.000	4.706	0.9110

*The units of A, f_1, and f_2 are dynes/cm. x 10^5, and the units of f_3 and f_4 are ergs/radian^2 x 10^{-11}.

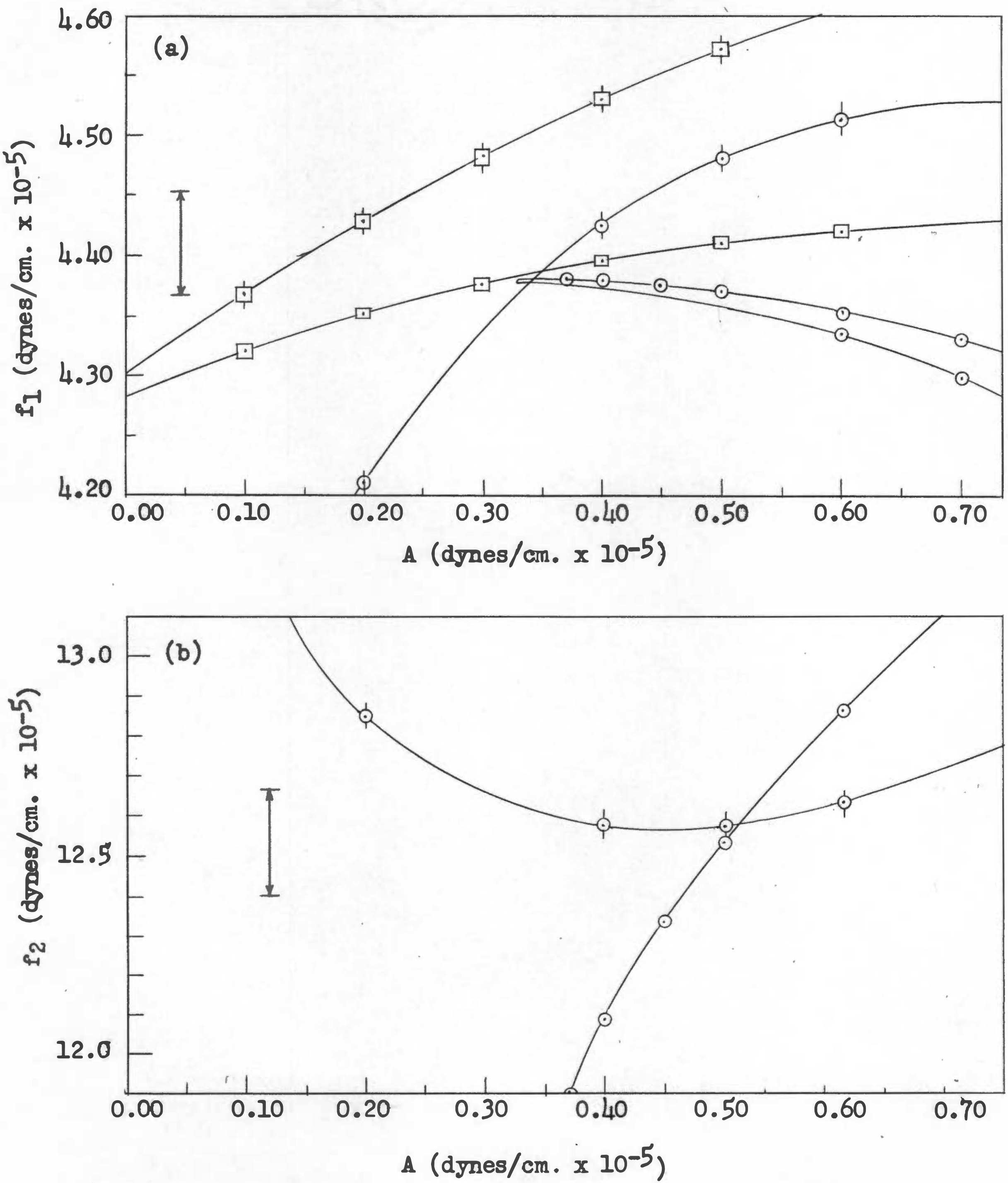


Figure 26. (a) f_1 *vs.* A for Species A_1 and B_1 of CH_2O and CD_2O.
(b) f_2 *vs.* A for Species A_1 of CH_2O and CD_2O.
o, A_1, CH_2O; ϕ , A_1, CD_2O; □ , B_1, CH_2O; ⊞ , B_1, CD_2O.

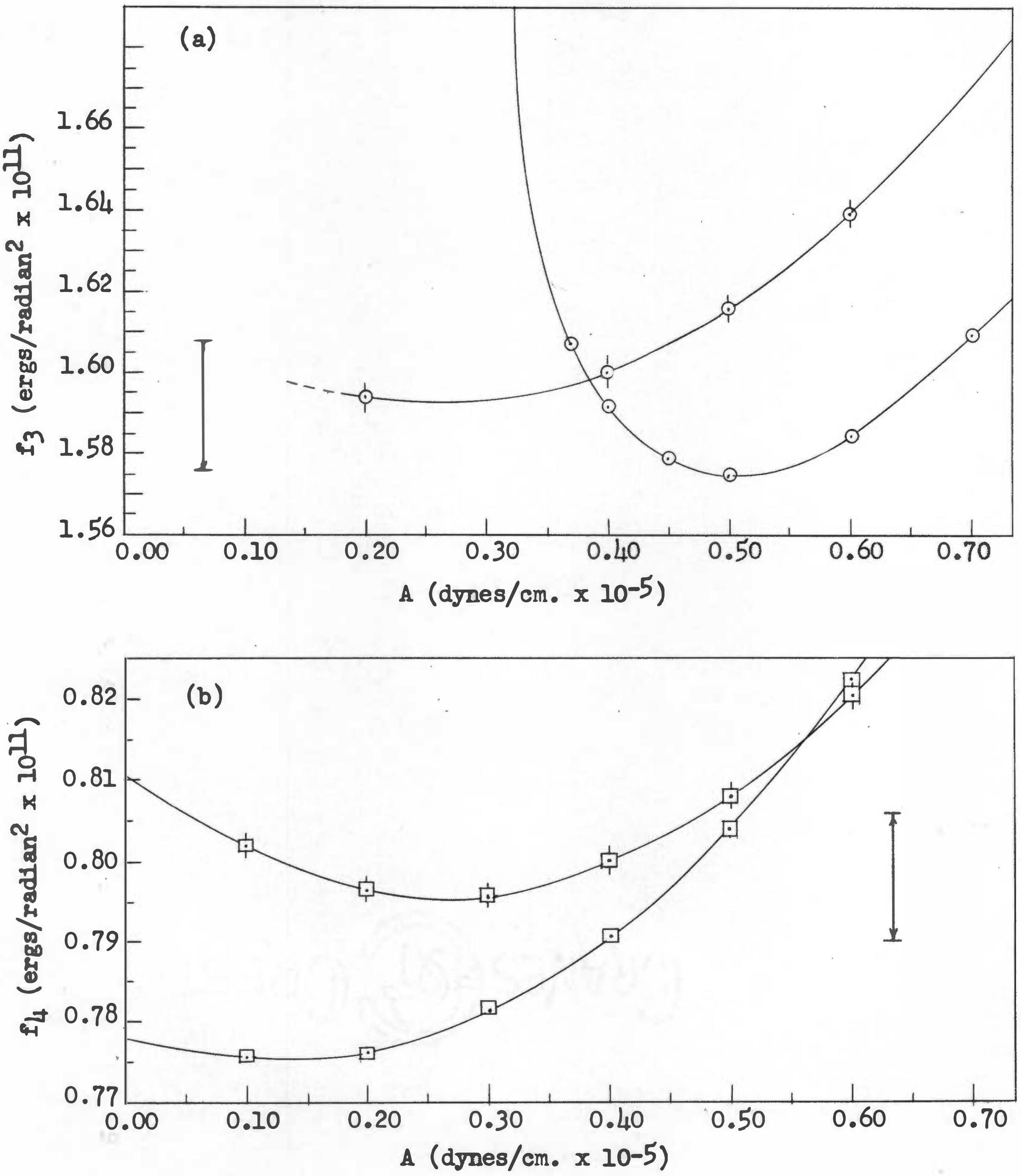


Figure 27. (a) f_3 vs. A for Species A_1 of CH_2O and CD_2O.
(b) f_4 vs. A for Species B_1 of CH_2O and CD_2O.
o, A_1, CH_2O; ϕ , A_1, CD_2O; □ , B_1, CH_2O;
⌷ , B_1, CD_2O.

TABLE XII

FORCE CONSTANTS FOR FORMALDEHYDE

Constant	Value
A	0.4700 x 10^5 dynes/cm.
f_1	4.4500
f_2	12.4950
f_3	1.5935 x 10^{-11} ergs/radian^2
f_4	0.8022
f_5	0.31103
K_{CH}	3.8124 x 10^5 dynes/cm.
K_{CO}	11.0773
K_H	1.2016 x 10^{-11} ergs/radian^2
k_σ	1.2463
$(k'_\sigma + k_\pi)$	0.6284

TABLE XIII

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF CH_2O, CD_2O, AND CHDO

Species of C_{2v} and Freq. No.		CH_2O			CD_2O			CHDO		
		Obs. Freq. (cm.$^{-1}$)	Calc. Freq.	% Diff.	Obs. Freq. (cm.$^{-1}$)	Calc. Freq.	% Diff.	Obs. Freq. (cm.$^{-1}$)	Calc. Freq.	% Diff.
A_1	1	2781.6	2804.2	+0.82	2056	2051.6	-0.22	2844.1	2843.8	-0.01
	2	1743	1753.7	+0.62	1700	1694.7	-0.31	2120.7	2093.3	-1.29
	3	1500	1502.1	+0.34	1106	1100.5	-0.50	1723.4	1720.0	-0.26
B_1	4	2866[a]	2880.0	+0.49	2160	2132.8	-1.26	1400	1397.6	-0.18
	5	1247.4	1250.1	+0.18	990	988.0	-0.20	1041	1029.2	-1.13
B_2	6	1167	1173.4	+0.55	938	932.9	-0.54	1074	1060.0	-1.30
Average Per Cent Error				0.50			0.51			0.70

[a] Band center uncertain.

E. Ketene

The secular equations of CH_2CO and CD_2CO contain factors of fourth, third, and second order. The $\mathfrak{F}$ and $\mathfrak{G}$ matrices for these molecules are given in Appendix I. Rather than give the algebraic equations for each species, only the diagonal force constants of the $\mathfrak{F}$ matrix will be given. These constants are:

$$A_1:\quad f_1 = K_{CH} + 1.30884\ A \qquad \text{(CH stretching)} \tag{161}$$

$$f_2 = K_{CC} + 3.10229\ A \qquad \text{(CC stretching)} \tag{162}$$

$$f_3 = K_{CO} \qquad \text{(CO stretching)} \tag{163}$$

$$f_4 = K_H + 0.89672\ A \qquad \text{(CH}_2\text{ deformation)} \tag{164}$$

$$B_1:\quad f_5 = \frac{K_H k_\sigma}{2K_H + k_\sigma} + 0.89672\ A \qquad \text{(CH}_2\text{ rocking)} \tag{165}$$

f,

$$f_6 = K_\delta \qquad \text{(CCO bending)} \tag{166}$$

$$B_2:\quad f_7 = K_\epsilon \qquad \text{(CCO bending)} \tag{167}$$

$$f_8 = \frac{2K_H \cos^2\alpha\ (k'_\sigma + k_\pi)}{2K_H \cos^2\alpha + (k'_\sigma + k_\pi)} + 0.04682\ A\ . \qquad \text{(CH}_2\text{ wagging)} \tag{168}$$

The equations of species B_1 were solved initially for CH_2CO and CD_2CO. However, it was found that no reasonable solutions for the constants could be obtained for species B_1 of CD_2CO for A values between -0.20 and 0.70. Reasonable solutions for the constants for species B_1 of CH_2CO were obtained for A values from 0.20 to 0.50, however. Because of this difficulty, species A_1 was then considered. In order to reduce the fourth-order block to a third-order block, the CH and CD stretching frequencies were factored off by Wilson's method.[37] The resulting third-order secular determinants were expanded and the equations were solved for f_2, f_3, and f_4 for values of A between 0.20 and 0.45. It was found that below an A value of 0.30, the solutions for the equations for CH_2CO became imaginary, while above an A value of 0.25, the solutions for the equations of CD_2CO became imaginary. However, at an A value of 0.30, a set of constants was determined for CD_2CO which almost satisfied the equations, and which agreed quite well with the constants found using the CH_2CO data at A = 0.30. Therefore, the value of A was chosen as 0.30, which agrees with the A values obtained for ethylene and allene. The values of the diagonal constants of species A_1 were then obtained from graphs of the constants versus A.

After the value of A had been fixed by the results of species A_1, the constants for species B_1 were evaluated using the data for CH_2CO only. When the frequencies for CD_2CO were calculated, it was found that an appreciable error occurred only in ν_6 and ν_7, which belong to species B_1. It is clear that these observed frequencies cannot be fitted better without generalizing the potential field. The constants involved in species B_2, f_7 and f_8, were evaluated quite easily, since the species is second-order and the off-diagonal 3 element is zero. The force constants obtained are given in Table XIV, designated as Set I.

It was noted during the calculations that the values of f_2 and f_3 could be changed considerably without appreciably altering the frequency fit. Another set of force constants was obtained by trial and error in which the only significant changes were in f_2 and f_3. This set of constants is designated as Set II, and is given in Table XIV. By compari-

TABLE XIV

FORCE CONSTANTS FOR KETENE

Constant	Set I	Set II
A	0.300 x 10^5 dynes/cm.	0.300 x 10^5 dynes/cm.
f_1	5.3800	5.3800
f_2	11.0404	9.2500
$f_3 = K_{CO}$	12.3161	14.3000
f_4	1.1671 x 10^{-11} ergs/radian^2	1.1600 x 10^{-11} ergs/radian^2
f_5	0.4230	0.4230
$f_6 = K_\delta$	0.9110	0.9110
$f_7 = K_\epsilon$	0.71529	0.71529
f_8	0.11436	0.11436
K_{CH}	4.9874 x 10^5 dynes/cm.	4.9874 x 10^5 dynes/cm.
K_{CC}	10.1097	8.3193
K_H	0.8981 x 10^{-11} ergs/radian^2	0.8913 x 10^{-11} ergs/radian^2
k_σ	0.3717	0.3723
$(k'_\sigma + k_\pi)$	0.1338	0.1334

son with the Set I constants, it is seen that f_2 has been lowered about 16 per cent and f_3 has been raised about 16 per cent. In Table XV, the observed frequencies of CH_2CO, CD_2CO, and CHDCO are compared with the frequencies calculated using both sets of force constants. The constants of Set I are seen to yield somewhat better frequencies than those of Set II, but the difference is small.

The reason that f_2 and f_3 can be varied so much without affecting the frequency fit significantly is because the diagonal $\mathfrak{G}$ matrix elements corresponding to f_2 and f_3 are nearly the same, 0.166614 and 0.145807. This fact, along with the fact that the values of f_2 and f_3 are rather close, means that as long as the sum and product of f_2 and f_3 remain essentially constant, the frequency fit will remain essentially the same. Using the Set I constants, the sum and product of f_2 and f_3 are 23.36 and 135.97, while for the Set II constants, the sum and product of f_2 and f_3 are 23.55 and 132.28. The changes in the sum and product of f_2 and f_3 are small, so the calculated frequencies using the two different sets will differ only slightly. Therefore, the value of f_2 can be chosen from 9.25 to 11.04, with a corresponding value of f_3 from 14.30 to 12.32 without causing a significant change in the calculated frequencies.

TABLE XV

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF CH_2CO, CD_2CO, AND CHDCO

Molecule	Species and Freq.	No.	Obs. Freq. (cm.$^{-1}$)	Calc. Freq. Set I	% Diff.	Calc. Freq. Set II	% Diff.
CH_2CO	A_1	1	3069	3072.1	+0.10	3070.4	+0.04
		2	2151	2161.5	+0.49	2173.3	+1.04
		3	1388	1392.5	+0.33	1383.8	-0.30
		4	1120	1121.1	+0.10	1102.5	-1.56
	B_1	5	3166	3181.5	+0.50	Same	Same
		6	978	976.9	-0.10		
		7	588	588.7	+0.10		
	B_2	8	788	765.8	-1.80		
		9	528	543.9	+2.70		
Average Per Cent Error					0.69		0.90
CD_2CO	A_1	1	2265	2260.8	-0.18	2240.7	-1.08
		2	2119	2122.4	+0.16	2153.2	+1.60
		3	1228	1216.8	-0.92	1195.1	-2.69
		4	890	909.5	+2.19	903.8	+1.55
	B_1	5	2375	2368.1	-0.35	Same	Same
		6	798[a]	854.5	+7.00		
		7	530[b]	498.5	-5.60		
	B_2	8	712	695.8	-2.21		
		9	450[c]	460.3	+2.50		
Average Per Cent Error					2.35		2.73

TABLE XV

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF CH_2CO, CD_2CO, AND CHDCO (Continued)

Molecule	Species and Freq.	No.	Obs. Freq. (cm.$^{-1}$)	Calc. Freq. Set I	% Diff.	Calc. Freq. Set II	% Diff.
CHDCO	A'	1	3115	3131.3	+0.52	3130.6	+0.50
		2	2150	2147.4	-0.12	2167.7	+0.82
		3	1293	1292.1	-0.07	1278.3	-1.14
		4	1046	1086.5	+3.87	1073.3	+2.23
		5	2309	2305.4	-0.16	2296.2	-0.55
		6	d	869.4	- -	868.6	- -
		7	d	534.0	- -	534.0	- -
	A"	8	d	726.3	- -	726.3	- -
		9	508	511.6	+0.71	511.6	+0.71

[a] Calculated from product rule.

[b] Calculated from $2\nu_7 = 1060$ cm.$^{-1}$.

[c] Calculated from $2\nu_9 = 900$ cm.$^{-1}$.

[d] Not observed.

F. Diazomethane

The secular equations of CH_2N_2 and CD_2N_2 contain factors of fourth, third, and second-order, just as those of CH_2CO and CD_2CO. The $\mathfrak{F}$ and $\mathfrak{G}$ matrices for CH_2N_2 and CD_2N_2 are given in Appendix I. The diagonal elements of the $\mathfrak{F}$ matrix are:

$$A_1:\quad f_1 = K_{CH} + 1.27825\ A \qquad \text{(CH stretching)} \tag{169}$$

$$f_2 = K_{CN} + 3.04253\ A \qquad \text{(CN stretching)} \tag{170}$$

$$f_3 = K_{NN} \qquad \text{(NN stretching)} \tag{171}$$

$$f_4 = K_H + 0.93149\ A \qquad \text{(CH}_2\text{ deformation)} \tag{172}$$

$$B_1:\quad f_5 = \frac{K_H k_\sigma}{2K_H + k_\sigma} + 0.93149\ A \qquad \text{(CH}_2\text{ rocking)} \tag{173}$$

$$f_6 = K_\delta \qquad \text{(CCO bending)} \tag{174}$$

$$B_2:\quad f_7 = K_\epsilon \qquad \text{(CCO bending)} \tag{175}$$

$$f_8 = \frac{2K_N \cos^2\alpha\ (k'_\sigma + k_\pi)}{2K_H \cos^2\alpha + (k'_\sigma + k_\pi)} + 0.03879\ A\,. \qquad \text{(CH}_2\text{ wagging)} \tag{176}$$

The frequencies of species B_1 and B_2 of CD_2N_2 have not been determined satisfactorily, and this means that the value of the constant A must be determined from species A_1. The C-H and C-D stretching frequencies were factored off by Wilson's method,[37] and the resulting third-order determinants were solved for f_2, f_3, and f_4 for both CH_2N_2 and CD_2N_2. It was found that the constants did not agree at all well for positive values of A. In view of this, it was thought that factoring off the C-D stretching frequency was causing an error to be introduced into the equations, since the C-D stretching frequency is very close to the N-N stretching frequency. In order to check this, both of these frequencies were factored off, yielding a second-order determinant containing the constants f_2 and f_4. However, the values obtained were very nearly the same as those obtained when only the C-D stretching frequency was factored off.

The calculations were then extended to negative values of A, since it appeared that a satisfactory solution could be obtained at a negative value of A. It was found that at an A value between -0.25 and -0.30, the best solution could be obtained. In this region of A values, it was noted in the case of CD_2N_2 that the values of f_2 and f_4 obtained from the third-order determinant differed considerably from those obtained from the second-order determinant. The best value of A was determined to be -0.287, and because of the disagreement in f_2 and f_4 obtained from the third-order and second-order determinants, it was necessary to adjust the values of the other constants which were obtained from the graphs in order to obtain the best solution. The constants obtained are given in Table XVI, designated as Set I. The constants for species B_1 and B_2 were obtained by solving the equations of these species for CH_2N_2 only, since the correctness of the reported frequencies for CD_2N_2 is questionable.

In order to illustrate the impossibility of fitting the frequencies when a positive value of A is used, the values of the constants obtained from the CH_2N_2 equations for an A value of 0.35 are given in Table XVI, designated as Set II. In Table XVII, the calculated frequencies of CH_2N_2 and CD_2N_2 using both sets of constants are compared with the observed

TABLE XVI

FORCE CONSTANTS* FOR DIAZOMETHANE

Constant	Set I	Set II
A	-0.2870	0.3500
f_1	5.2000	5.3800
f_2	5.7000	4.3480
$f_3 = K_{NN}$	16.3800	16.9153
f_4	0.9800	1.2922
f_5	0.6475	0.6279
$f_6 = K_\delta$	0.4286	0.4298
$f_7 = K_\epsilon$	0.3669	0.3669
f_8	0.1615	0.1615
K_{CH}	5.5669	4.9326
K_{CN}	6.5732	3.2831
K_H	1.2473	0.9662
k_σ	6.8638	0.8781
$(k'_\sigma + k_\pi)$	0.2645	0.2402

*The units of A, f_1, f_2, K_{NN}, K_{CH}, and K_{CN} are dynes/cm. x 10^5, and the units of f_4, f_5, K_δ, K_ε, f_8, K_H, k_σ, and $(k'_\sigma + k_\pi)$ are ergs/radian^2 x 10^{-11}.

TABLE XVII

OBSERVED AND CALCULATED FUNDAMENTAL FREQUENCIES OF CH_2N_2 AND CD_2N_2

Molecule	Species and Freq.	No.	Obs. Freq. (cm.$^{-1}$)	Calc. Freq. Set I	% Diff.	Calc. Freq. Set II	% Diff.
CH_2N_2	A_1	1	3076	3032.4	-1.41	3062.6	-0.44
		2	2102	2110.4	+0.40	2100.4	-0.08
		3	1414	1409.5	-0.32	1411.5	-0.17
		4	852	832.3	-2.32	850.3	-0.20
	B_1	5	3185	3190.6	+0.18	3184.6	-0.01
		6	1111	1111.0	0.00	1111.0	0.00
		7	422	422.0	0.00	422.0	0.00
	B_2	8	898	898.0	0.00	898.0	0.00
		9	408	408.0	0.00	408.0	0.00
CD_2N_2	A_1	1	2241	2251.5	+0.47	2206.3	-1.55
		2	2088	2058.5	-1.42	2097.0	0.43
		3	1213	1209.7	-0.27	1060.9	-12.6
		4	662	685.8	+3.60	805.8	+21.7
	B_1	5	2406	2414.2	+0.34	2371.9	-1.43
		6	a	874.9	- -	889.8	- -
		7	a	390.9	- -	390.4	- -
	B_2	8	a	726.3	- -	726.3	- -
		9	a	387.6	- -	387.6	- -

[a] Not observed.

frequencies. From inspection of Table XVII, it is seen that the frequencies agree well for the Set I constants, while for the Set II constants, the calculated values of ν_3 and ν_4 of CD_2N_2 do not agree with the observed frequencies.

It should be pointed out that the negative value of A indicates that there is an attractive force acting between the hydrogen atoms and one of the nitrogen atoms in the molecule. The force field was set up assuming that a repulsive force exists between the central nitrogen atom and the hydrogen atoms. Therefore, the $\mathfrak{F}$ matrix is strictly correct only for positive values of the constant A, since the form of the repulsive potential differs from that for an attractive potential.

CHAPTER IV

DISCUSSION OF RESULTS

The discussion of the force constants which have been obtained can be divided into two parts. The first part deals with the evaluation of the $\mathfrak{F}$ matrix elements, and the second part deals with the interpretation of the values obtained for the constants comprising the $\mathfrak{F}$ elements.

A. The $\mathfrak{F}$ Matrix Elements

The potential field which has been assumed in this investigation is of such a form that all of the off-diagonal $\mathfrak{F}$ matrix elements are either zero or are functions of a single constant, A. Therefore, in an $\mathfrak{F}$ matrix of order n, there are (n + 1) independent constants which must be evaluated. Consider the $\mathfrak{F}$ matrix for a third-order species of a molecule. If the value of one of the four independent constants in this matrix is fixed, then the three frequencies of the molecule belonging to this species furnish sufficient data to enable the other three constants to be evaluated. However, there are six possible sets of solutions for the three constants, and the question as to which one of these sets of solutions is the correct one is of interest. It should be pointed out that the sets of solutions may be real or imaginary, but the sets of imaginary solutions will occur in pairs.

As an example, consider the CO_2 molecule. This molecule possesses two non-degenerate vibrational modes and one doubly-degenerate vibrational mode. Since each vibrational mode belongs to a different species, the $\mathfrak{F}$ and $\mathfrak{G}$ matrices for this molecule are diagonal. The three frequencies of the molecule are known, but it will be assumed that the frequencies have not been assigned to their respective species. If the elements of the $\mathfrak{F}$ matrix are designated f_1, f_2, and f_3, and the elements of the $\mathfrak{G}$ matrix are designated g_1, g_2, and g_3, the secular determinant will be

$$\begin{vmatrix} f_1g_1-\lambda & 0 & 0 \\ 0 & f_2g_2-\lambda & 0 \\ 0 & 0 & f_3g_3-\lambda \end{vmatrix} = 0. \qquad (177)$$

The six sets of solutions for the f_i's in this simple case are all real, and are given below.

	Set Number					
	I	II	III	IV	V	VI
f_1	$\frac{\lambda_1}{g_1}$	$\frac{\lambda_1}{g_1}$	$\frac{\lambda_2}{g_1}$	$\frac{\lambda_2}{g_1}$	$\frac{\lambda_3}{g_1}$	$\frac{\lambda_3}{g_1}$
f_2	$\frac{\lambda_2}{g_2}$	$\frac{\lambda_3}{g_2}$	$\frac{\lambda_1}{g_2}$	$\frac{\lambda_3}{g_2}$	$\frac{\lambda_1}{g_2}$	$\frac{\lambda_2}{g_2}$
f_3	$\frac{\lambda_3}{g_3}$	$\frac{\lambda_2}{g_3}$	$\frac{\lambda_3}{g_3}$	$\frac{\lambda_1}{g_3}$	$\frac{\lambda_2}{g_3}$	$\frac{\lambda_1}{g_3}$

From inspection of the six sets of solutions, it is seen that in this case, each constant is determined by one of the three frequencies, and that the six sets of solutions arise because of the six ways in which the three frequencies can be permuted. The correct solution is determined by properly assigning the frequencies to the different modes of motion.

In a third-order species, there will usually be off-diagonal elements in both the $\mathfrak{F}$ and $\mathfrak{G}$ matrices, and therefore the off-diagonal elements of the secular determinant will not vanish. This means that a diagonal force constant is no longer determined by one of the frequencies, but is influenced to some extent by all of the frequencies belonging to the species. This is expected, since it is recognized that the symmetry coordinates are usually only approximations of the normal coordinates. However, in spite of the fact that all of the frequencies are affected at least a little by each of the diagonal elements, there is still a one-to-one correspondence between frequencies and symmetry coordinates, and in a species with three vibrations there are six ways of forming this one-to-one correspondence. This reasoning applies to $\mathfrak{F}$ matrices of any order. Thus, if the matrix is of order n, there will be n! possible sets of solutions for the diagonal constants when the values of the off-diagonal constants are fixed. When the off-diagonal elements are small and the symmetry coordinates do not mix appreciably in the normal coordinates, this one-to-one correspondence has the same significance as in the case of carbon dioxide. If, however, two of the symmetry coordinates are mixed strongly in the normal coordinates, the significance of permuting the frequency assignments becomes difficult to interpret.

In many cases, one of the frequencies in a species can be assigned unambigiously to a motion described by a symmetry coordinate which approximates a normal coordinate closely. This is generally true when the species contains a C-H stretching vibration, and is responsible for the success of the factoring off of such frequencies. It is interesting to note that if a frequency is factored off from a third-order species, the number of sets of solutions for the diagonal constants is reduced from six to two. This reduction is brought about because the frequency which has been factored off has been associated with one of the force constants, and the two remaining frequencies can be permuted only two ways.

An indication of how well symmetry coordinates approximate the normal coordinates can be obtained from a study of the isotope shift which occurs when the hydrogen atoms in a molecule are replaced by deuterium atoms. If a vibrational mode is essentially a motion in which only the hydrogen atoms move, the band should be shifted by approximately $\frac{1}{\sqrt{2}}$ when the hydrogen atoms are replaced by deuterium atoms. On the other hand, if the vibrational mode is predominately a motion of other atoms or groups of atoms in the molecule, the isotope shift would be small. By inspection of the frequencies, it can be quickly determined whether the observed isotope shifts are close to that which would occur if the symmetry coordinates were the normal coordinates. If the isotope shifts are in the range which one would expect from a consideration of the symmetry coordinates, then these coordinates should be good approximations of the normal coordinates for both the light and heavy molecules.

Inspection of the frequencies of species A_g of C_2H_4 and C_2D_4 on page 84 reveals that the isotope shift is very nearly what one would expect if the symmetry coordinates were equal to the normal coordinates, while the frequencies of species A_1 of C_3H_4 and C_3D_4, given on page 99, indicate that the symmetry coordinates do not approximate the normal coordinates very well for at least one of the molecules.

The calculations carried out in determining the $\mathfrak{F}$ matrix elements of species A_1 of ketene illustrate an interesting point. If the product of one of the diagonal $\mathfrak{F}$ matrix elements and the corresponding $\mathfrak{G}$ matrix element is approximately the same as the product of another $\mathfrak{F}$ matrix element and the corresponding $\mathfrak{G}$ matrix element, then it is not possible to determine these diagonal $\mathfrak{F}$ elements accurately. In species A_1 of ketene, it was found that two of the diagonal $\mathfrak{F}$ matrix elements could be changed 15 per cent (one raised, the other lowered) without appreciable affect on the calculated frequencies. In order to determine the correct values of these constants, further independent data must be obtained, such as centrifugal distortion constants.

B. Results and Conclusions

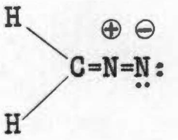
1. Repulsive Forces Between Non-bonded Atoms

The results obtained for ethylene, allene, formaldehyde and ketene show that there is an appreciable repulsion between the non-bonded carbon and hydrogen atoms in ethylene, allene, and ketene, and between the non-bonded oxygen and hydrogen atoms in formaldehyde. The repulsive forces between non-bonded hydrogen atoms has been found to be negligible, in agreement with the results obtained by Linnett, Heath and Wheatley[13,14] in their work on methane, formaldehyde, and ethylene. The results obtained for diazomethane indicate that there is a force of attraction rather than repulsion acting between the hydrogen atoms and one of the nitrogen atoms. This point will be discussed later.

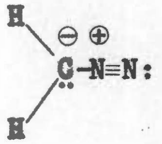
The values of the constant, $A = \frac{1}{2}\left(\frac{\partial^2 V}{\partial R^2}\right)$, which were obtained for ethylene, allene, formaldehyde, ketene, and diazomethane are 0.317, 0.290, 0.471, 0.300, and -0.287 x 10^5 dynes/cm., respectively. If the hydrogen atoms are considered as He atoms and the carbon and oxygen atoms are considered as Ne atoms, the force of repulsion based on a Lennard-Jones potential can be approximated by calculating the geometric mean of the He---He repulsion and Ne---Ne repulsion at the distances which separate the atoms in the molecules.[39] The results obtained for ethylene, allene, formaldehyde, ketene, and diazomethane are 0.26, 0.31, 0.65, 0.34, and 0.40 x 10^5 dynes/cm., respectively. The only significant fact obtained from these calculations is that the value of A for formaldehyde is expected to be considerably higher than the values for the other molecules, and this was found to be the case. The close agreement between the A values which were determined in this investigation and the calculated values obtained based on a Lennard-Jones potential may be rather fortuitous, because of the approximations involved, but it is interesting that the figures obtained from two entirely different sources agree as well as they do.

It was pointed out in Chapter II that it was necessary to include linear terms in the potential energy expression, because these terms give rise to quadratic terms when the redundancies in the coordinates are eliminated. These quadratic contributions, expressed in terms of B in the potential energy expressions, are quite small, and calculations carried out for ethylene, allene, and formaldehyde show that these terms can be neglected without appreciably affecting the best numerical values of the $\mathfrak{F}$ matrix elements. However, if these terms involving B are neglected, the values of the orbital valency force field constants are changed considerably in some instances, and it is therefore necessary to include these terms.

The negative value of the constant A which was obtained for diazomethane indicates that there is a net force of attraction between the hydrogen atoms and one of the nitrogen atoms. Therefore, the potential field used for diazomethane is incorrect, because terms accounting for an electrostatic interaction should be included. However, the fact that the potential field used is incorrect does not alter the conclusion that the attractive force exists. The explanation of the electrostatic attraction between the hydrogen atoms and one of the nitrogen atoms is not very clear. The two resonance forms which have been proposed for diazomethane are



and



.

(I) (II)

In order to account for an electrostatic attraction between the hydrogen atoms and one of the nitrogen atoms based on these resonance forms, one must conclude that the positive charges which are indicated are shielded quite well by the surrounding electrons, and the hydrogen nuclei are attracted by the net negative charge. Based on such a picture, structure (I) would be expected to be decidedly predominant.

It is interesting to note that although ketene and diazomethane are isoelectronic, no indication of attractive forces between the hydrogen atoms and the central carbon or oxygen atom in ketene was found. Although the electron distribution in ketene is the same as that shown in structure I of diazomethane, it is not surprising that no force of attraction between the hydrogen atoms and the central carbon or oxygen atom in ketene exists, because little localization of charge like that predicted for diazomethane is expected. Thus, even though diazomethane and ketene are similar in structure, it is understandable that the attractive force is found in diazomethane only. Further calculations using a potential function which takes this force into account should be carried out for diazomethane.

2. The Orbital Valency Force Constants

The force constants which were obtained in this investigation are summarized in Table XVIII. In the following discussion of these constants, the values obtained for diazomethane are not considered, since the values of the constants would be changed appreciably if the electrostatic attraction between the nitrogen atom and the hydrogen atoms had been taken into account. The values of the constants obtained for formaldehyde agree well with those obtained by Linnett, Heath, and Wheatley.[14] However, the values obtained for ethylene do not agree with the results obtained by these authors, due to revisions which have been made in frequency assignments and our redefinition of some of the force constants.

a. The stretching vibrations. The C-H bond stretching constant was found to be almost the same in ethylene and allene, and only slightly higher in ketene. For formaldehyde, the constant was found to be about 20 per cent lower than for the other molecules. This low value was expected, however, because the C-H stretching frequency in formaldehyde is

TABLE XVIII

SUMMARY OF FORCE CONSTANTS

	MOLECULE				
Constant	C_2H_4	C_3H_4	CH_2O	CH_2CO	CH_2N_2
A	0.317	0.290	0.470	0.300	-0.287
K_{CH}	4.745	4.735	3.812	4.987	5.567
K_{CC}	7.250	8.794		10.1-8.3	
k_{CC}^{CC}		0.432			
K_{CO}			11.077	12.3-14.3	
K_{CN}					6.573
K_{NN}					16.380
			x 10^5 dynes/cm.		
K_H	1.059	1.017	1.202	0.895	1.247
k_σ^u	0.799				
k_σ^g	0.548				
k_σ		0.731	1.246	0.372	6.864
k_π^g	-1.639				
k_π^u	0.030				
k_π		-0.486			
$(k_\sigma' + k_\pi)$			0.628	0.133	0.265
k_π^τ	1.409	1.309			
K_δ				0.911	0.429
K_ϵ		0.368		0.715	0.367
			x 10^{-11} ergs/radian^2		

much lower than in the other molecules. The C=C bond stretching constant for allene is larger than that for ethylene. For ketene, the value is about the same as that found in allene. The C=O bond stretching constant is larger in ketene than in formaldehyde, as was expected.

b. *The torsional vibrations*. The torsional modes in ethylene and allene are quite similar, even though there are two sets of overlapping π orbitals in allene and only one set in ethylene. The values of k_π^τ for ethylene and allene were found to be 1.409 and 1.309 x 10^{-11} ergs/radian^2, respectively. Although these constants differ by about 7 per cent, they would be brought into exact agreement by raising the frequency of the vibration in allene 1.8 per cent or by lowering the frequency in ethylene 1.8 per cent. Thus, the values of k_π^τ for ethylene and allene are in excellent agreement. It should be pointed out that the torsional vibration is the most clearly defined vibration in terms of the orbital valency force field, and the results indicate that the concepts are valid.

c. *The planar and non-planar bending vibrations*. The C-H bond bending constant, K_H, was found to be about the same in ethylene and allene. The value found for ketene is considerably lower than that for ethylene and allene, while the value for formaldehyde is much higher. It is interesting to note that when a large value of K_{CH} is obtained, the value of K_H is small. This can be explained qualitatively by a consideration of the effect of bond stretching and bending on the orbital overlap in σ bonds. The σ orbitals have cylindrical symmetry, and if the charge is concentrated near the bond axis, it may be expected to extend farther along the axis than if the charge is not concentrated near the bond axis. A long, thin σ orbital on the carbon atom would result in a smaller stretching constant than for a shorter but fatter orbital because the decrease in overlap is less for a given nuclear displacement in the case of the long thin orbital. When this same reasoning is applied to the angular distortion, we see that the long, thin orbital should indeed produce the larger force constant for an angular distortion.

The constants designated by k_σ are associated with the change in overlap of σ bonds during planar rocking vibrations. It was assumed that the π orbital overlap is not affected by these vibrations. This would be true if the P_z atomic orbitals retained their axial symmetry in the molecule, but they certainly do not do this. How much error this introduces in k_σ is impossible to tell.

The values which were found for k_σ^u and k_σ^g for ethylene are 0.799 and 0.548 x 10^{-11} ergs/radian^2, respectively. The values are reasonable, although the value of k_σ^u seems rather high, because the overlap change with which this constant is associated is small. However, the values of the rocking frequencies for species B_{2u} and B_{1g} are 810.3 cm.$^{-1}$ and 1236 cm.$^{-1}$, respectively, and the fact that the B_{2u} rocking frequency is fairly high shows that k_σ^u is fairly large. It should be pointed out that k_σ^g was defined so that the potential energy change arising from rotation of the σ orbitals during the B_{1g} rocking vibration is $k_\sigma^g(2\Delta\xi)^2$, where $\Delta\xi$ is the angle through which each of the σ orbitals rotate. On the basis of the change in orbital overlap, the value of k_σ^u would be expected to be smaller than $4k_{\sigma}^{g}$, but not necessarily smaller than k_{σ}^{g} itself. This is just what is found and the relative magnitudes are quite reasonable in terms of the physical picture.

In deriving the orbital valency force constants for allene which involve k_{σ} and k_{π}, the assumption was made that the orbitals of the central carbon atom remain fixed during the vibrational motions. Using this model, the value of k_{σ} for allene would be expected to be close to the value of k_{σ}^{g} for ethylene, and the value of k_{π} for allene would be expected to be close to the value of k_{π}^{u} for ethylene. However, k_{σ} is considerably larger than k_{σ}^{g}, while k_{π} is considerably smaller than k_{π}^{u}. The fact that k_{σ} of allene is larger than k_{σ}^{g} in ethylene is difficult to explain, because the possibility of a rotation of the orbitals of the central carbon atom in allene, which was not taken into account, would lead to the conclusion that k_{σ} would be equal to or less than k_{σ}^{g} in ethylene. However, the σ orbitals on the central carbon in allene arise from sp hybridization, while those in ethylene rise from sp^2 hybridization, and this may influence the values of the constants. It should be pointed out that although k_{σ} in allene is about 35 per cent larger than k_{σ}^{g} in ethylene, the values could be brought into exact agreement by raising the ethylene rocking frequency 8 per cent or lowering the allene rocking frequency 8 per cent. This illustrates the fact that the orbital valency force constants are much more sensitive to the values of the frequencies than are the $\mathcal{F}$ matrix elements or valence force constants. This must be borne in mind in concluding how well the orbital valency force constants for different molecules agree. The value of k_σ for formaldehyde, 1.25 x 10^{-11} ergs/radian^2, is quite high in comparison to the other values of k_σ. It is strange that the value is higher for formaldehyde than for the other molecules, because when the orbitals of the carbon atom rotate, the orbitals of the oxygen atom are completely free to rotate so as to minimize the potential energy. In ketene, k_σ was found to be 0.372 x 10^{-11} ergs/radian^2, considerably lower than the values for ethylene and allene.

The values of k^g_π and k^u_π for ethylene are -1.639 and 0.030 x 10^{-11} ergs/radian^2, respectively, while the value of k_π for allene is -0.486 x 10^{-11} ergs/radian^2. If we consider the allene model in which no rotation of the central carbon atom is permitted, k_π would be expected to have a value close to the value of k^u_π. However, the numerical values indicate that k_π for allene is more readily associated with the k^g_σ than with k^u_σ in ethylene. This appears to be anomalous and the significance of the results is not clear. However, if the orbitals of the central carbon atom in allene do rotate during the vibrational motions, then the assumption that k_σ is the same in the rocking and wagging motions will not be valid, and the true value of k_π cannot be determined.

Although the values of k_π for formaldehyde and ketene could not be determined, the results strongly indicate that k_π is negative for both molecules, because the value of $(k'_\sigma + k_\pi)$ is considerably smaller than k_σ, and the difference in k_σ and k'_σ is probably not large enough to allow k_π to be positive. These negative values of k_π are interesting, since they indicate that the rotation of the π orbitals decreases the potential energy and therefore stabilizes the molecule.

It does not seem profitable to speculate further on the significance of the orbital valency force constants obtained for the four molecules discussed above. Although the values obtained for some of the constants appear to be anamolous, it is very likely that a definite pattern and a clear interpretation can be deduced if more data for similar molecules are studied. Further work on this point is in progress at this time in this laboratory, although not by this author.

3. Ketene and Diazomethane

It is interesting to compare the electronic structure of ketene and diazomethane. These two molecules are isoelectronic and therefore must have the same orbital configurations. The bonding structure of ketene is clear. The terminal carbon atom has a set of trigonal sp^2 orbitals and one p_z orbital perpendicular to these. This atom forms a σ-and a π bond with the central carbon atom, which has a set of digonal (sp) orbitals and p_z and p_y orbitals perpendicular to the digonal axis. The central carbon atom forms a σ and a π bond with the p_x and p_y orbitals of the oxygen atom. The p_z orbital of the oxygen atom is already filled with its own electrons.

These same molecular orbitals can be constructed for diazomethane if an electron is shifted from the central nitrogen atom to the terminal nitrogen atom. This produces a formal negative charge on the terminal nitrogen atom, which can easily account for the attractive force which causes the value of the constant A to be negative. It is necessary to assume that the net positive charge on the central nitrogen atom is well shielded, so that there will be essentially no electrostatic repulsion between this atom and the hydrogen atoms. This is not unreasonable, and could be accounted for by the fact that the nitrogen atom is more electronegative than the carbon atom.

The agreement of the calculated frequencies with the observed frequencies was excellent for all of the molecules studied. The largest errors occurred in ν_6 and ν_7 of CD_2CO, which differed by 7 and 5.6 per cent from the "observed" frequencies. However, these large errors are not distressing, because of the uncertainty in the positions of ν_6 and ν_7. The value of ν_7 was obtained from a band located at 1060 cm.$^{-1}$, assigned as $2\nu_7$, and the value of ν_6 was then calculated using the product rule. Thus, neither band has been observed directly, and the possibility of a change of 6 per cent in the assigned positions of the band centers is not unreasonable. Errors of -2.3 per cent in ν_4 of CH_2N_2 and +3.6 per cent in ν_4 of CD_2N_2 were found. The assigned positions of these bands are reliable, and a better fit of these frequencies should be obtained. It is probable that if the electrostatic interaction between the hydrogen atoms and one of the nitrogen atoms were taken into account in the potential energy expression, better agreement would be obtained, because this would introduce off-diagonal terms in species A_1 of the $\mathcal{F}$ matrix linking the N-N stretching frequency with the other frequencies, as well as change the relative magnitudes of the other off-diagonal $\mathcal{F}$ elements.

CHAPTER V

SUMMARY

The orbital valency force field,[14] which is essentially a Urey-Bradley force field modified to interpret bending vibrations in terms of the changes in bonding orbital overlap which occur during the bending motions, has been applied to ethylene, allene, formaldehyde, ketene, and diazomethane. Each of these molecules possesses double bonds, and it was hoped that the bending force constants could be correlated with the changes in orbital overlap based on a model in which the molecular orbitals were assumed to be formed by overlapping directed atomic orbitals.

The vibrational potential energy expressions were simplified by assuming that the H----H repulsions in the molecules were negligible, and the results obtained show that this assumption was justified. Therefore, only the van der Waals repulsions between the H atoms and the nearest non-bonded C, N or O atoms were necessary. The fact that all of the off-diagonal elements in the $\mathcal{F}$ matrix of a molecule were either zero or functions of the same constant permitted a range of solutions for the force constants to be obtained independently for both the light molecule and the heavy molecule. The best solution for the force constants was obtained by plotting values of the diagonal $\mathcal{F}$ matrix elements *versus* the constant in the off-diagonal elements and determining the value of the constant in the off-diagonal elements for which the best agreement in the values of the diagonal elements for the light and heavy molecules was obtained.

It was shown that when the values of all but n independent force constants in a species of order n are fixed, the n! sets of solutions which exist for the n independent force constants arise because of the n! ways in which the n frequencies belonging to the species can be permuted. This correlation can be used to choose the correct set of force constants (if all but n of the constants have been fixed) when data are available for only one isotopic species.

The repulsive force between the non-bonded carbon and hydrogen atoms in ethylene, allene, and ketene, and the non-bonded oxygen and hydrogen atoms in formaldehyde were in agreement with the calculated repulsion based on a Lennard-Jones potential[29,30] in which the hydrogen atoms were considered as helium atoms and the carbon and oxygen atoms were considered as neon atoms. However, in diazomethane, it was found that an electrostatic attractive force exists between the hydrogen atoms and one of the nitrogen atoms (probably the terminal nitrogen atom) which is stronger than the repulsive force between the hydrogen atoms and the central nitrogen atom.

The agreement between the calculated frequencies and the observed frequencies for all the molecules is excellent, the average error in general being considerably less than 1 per cent.

The orbital valency force constants obtained for ethylene, allene, formaldehyde, and ketene were correlated in terms of the structures of the molecules. The force constants associated with the torsional vibrations of ethylene and allene were found to be quite similar, indicating that the concept of orbital overlap is quite good for this type of motion.

The agreement between the constants associated with the changes in orbital overlap of the σ and π bond orbitals which occur during planar and non-planar bending modes was not as good as in the case of the torsions. However, the agreement is as good as that found when corresponding bending force constants of different molecules obtained using a valency force field are compared. It is felt that the orbital valency force field provides a means of increasing our understanding of the nature of the forces acting during bending vibrations, and that further calculations utilizing data for similar molecules, in addition to refinements in the theory, will lead to a clear picture of bending vibrations.

APPENDICES

APPENDIX I

DETERMINATION OF THE $\mathfrak{F}$ AND $\mathfrak{G}$ MATRICES

The $\mathfrak{F}$ and $\mathfrak{G}$ matrices for the molecules studies in this investigation were determined by the method of Wilson, which has been described briefly in Chapter II, Section B. The determination of the $\mathfrak{F}$ matrix elements corresponding to motions during which orbital rotation occurs has been described in detail in Section C of Chapter II. In Section B of Chapter II, the way in which the contribution of the repulsive forces between non-bonded atoms to the potential energy is determined has been discussed. The $\mathfrak{G}$ matrices were determined using both the B and $\vec{S}$ matrices, in order to insure the accuracy of the results. In the following section, the determination of the $\mathfrak{F}$ and $\mathfrak{G}$ matrices is discussed.

A. Ethylene

The ethylene molecule, C_2H_4, belongs to the point group V_h. The internal coordinates and geometry of the molecule are shown in Figure 28. The potential energy of the molecule, before orbital rotation is taken into account, is

$$2V = K_{CH} \sum_{i=1}^{4} (\Delta r_i)^2 + K_{CC} (\Delta r_5)^2 + K_H \sum_{i=1}^{4} (\Delta \kappa_i)^2 + B_{CH} \sum_{i=1}^{4} (\Delta r_i) +$$

$$B_{CC} (\Delta r_5) + B_\kappa \sum_{i=1}^{4} (\Delta \kappa_i) - 2B \sum_{i=1}^{4} (\Delta R_i) + 2A \sum_{i=1}^{4} (\Delta R_i)^2 , \qquad \text{(A-1)}$$

where $\Delta\kappa$ is defined as the angular distortion of a C-H bond from its

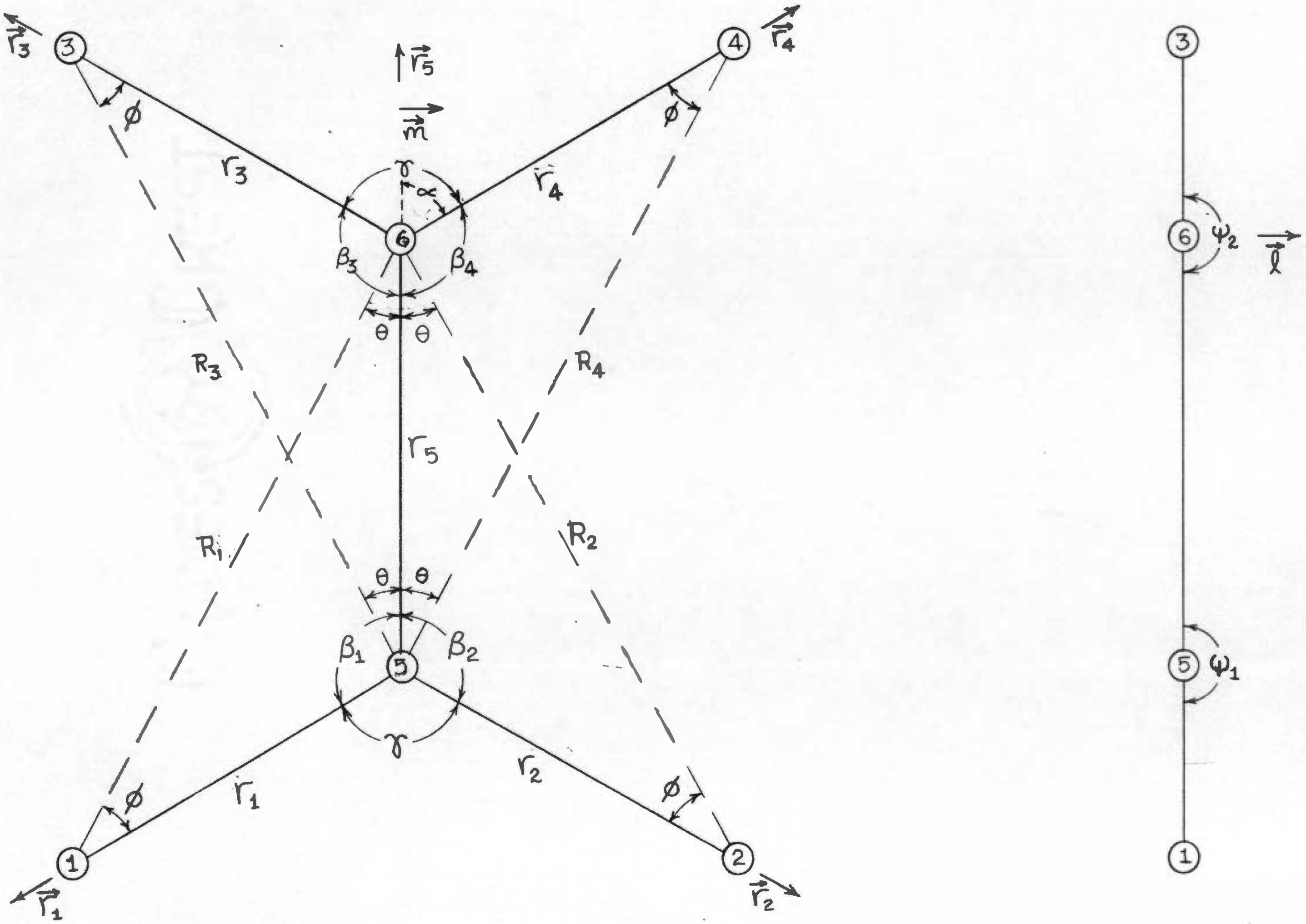


Figure 28. The Geometry of the Ethylene Molecule.

equilibrium position in any direction. K_{CH} and K_{CC} are the stretching force constants for the C-H and C-C bonds, respectively. The last two terms account for the repulsive forces between the non-bonded hydrogen and carbon atoms. Repulsive forces between hydrogen atoms have been assumed to be negligible. The linear terms in Δr_i and $\Delta\kappa$ are necessary in order to balance the linear term in ΔR_i, so that the equilibrium configuration will be stable.

It is desirable to express the potential energy in terms of the following set of internal coordinates (see Figure 28):

$$\begin{array}{ccc}
\Delta r_1 & \Delta r_5 & \Delta\beta_1 \\
\Delta r_2 & \Delta\psi_1 & \Delta\beta_2 \\
\Delta r_3 & \Delta\psi_2 & \Delta\beta_3 \\
\Delta r_4 & \Delta\tau & \Delta\beta_4 .
\end{array}$$

The meaning of the coordinates, except for $\Delta\tau$, is clear. $\Delta\tau$ is defined as the change in the angle formed by the intersection of the CH_2 planes caused by a twisting of the CH_2 groups about the symmetry axis of the molecule. In terms of these coordinates, the potential energy becomes

$$\begin{aligned}
2V = {} & K_{CH}\sum_{i=1}^{4}(\Delta r_i)^2 + K_{CC}(\Delta r_5)^2 + K_H\sum_{i=1}^{4}(\Delta\beta_i)^2 + 2K_H\cos^2\alpha\sum_{i=1}^{2}(\Delta\psi_i)^2 \\
& + K_H\sin^2\alpha\,(\Delta\tau)^2 + B_{CH}\sum_{i=1}^{4}(\Delta r_i) + B_{CC}(\Delta r_5) + B_\beta\sum_{i=1}^{4}(\Delta\beta_i) \\
& + B_\psi\sum_{i=1}^{2}(\Delta\psi_i) + B_\tau(\Delta\tau) - 2B\sum_{i=1}^{4}(\Delta R_i) + 2A\sum_{i=1}^{4}(\Delta R_i)^2 \qquad (A-2)
\end{aligned}$$

Again, it must be stressed that this expression gives the potential energy for the system before orbital rotation is taken into account. The modification in the potential energy brought about by orbital rotation must be determined for each vibrational motion during which orbital rotation occurs.

The symmetry coordinates, determined with the aid of group theory, are:

$$
\begin{array}{lll}
A_g: & S_{CH} & = \frac{1}{2}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4) \\
 & S_{CC} & = \Delta r_5 \\
 & S_\beta & = \frac{1}{2}(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4) \\
B_{3u}: & S'_{CH} & = \frac{1}{2}(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4) \\
 & S'_\beta & = \frac{1}{2}(\Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4) \\
B_{2u}: & S''_{CH} & = \frac{1}{2}(\Delta r_1 - \Delta r_2 - \Delta r_3 - \Delta r_4) \\
 & S''_\beta & = \frac{1}{2}(\Delta\beta_1 - \Delta\beta_2 + \Delta\beta_3 - \Delta\beta_4) \\
B_{1g}: & S'''_{CH} & = \frac{1}{2}(\Delta r_1 - \Delta r_2 - \Delta r_3 + \Delta r_4) \\
 & S'''_\beta & = \frac{1}{2}(\Delta\beta_1 - \Delta\beta_2 - \Delta\beta_3 + \Delta\beta_4) \\
B_{1u}: & S_\psi & = \frac{1}{\sqrt{2}}(\Delta\psi_1 + \Delta\psi_2) \\
B_{2g}: & S'_\psi & = \frac{1}{\sqrt{2}}(\Delta\psi_1 - \Delta\psi_2) \\
A_u: & S_\tau & = \Delta\tau .
\end{array}
$$

The coordinates which are used in describing the repulsion of the non-bonded hydrogen and carbon atoms, the ΔR_i, are expressed in terms of the internal coordinates in the manner described in Chapter II. The contribution of the repulsion terms to the potential energy for the planar motions is given in terms of the internal coordinates on page 145. After the modification of the potential energy brought about by orbital rotation is determined, the $\mathfrak{F}$ matrix is obtained by symmetrization. The

MATRIX OF CONTRIBUTION OF H---C REPULSION TO THE POTENTIAL ENERGY FOR PLANAR MOTIONS OF ETHYLENE

	Δr_1	Δr_2	Δr_3	Δr_4	Δr_5	$\Delta\beta_1$	$\Delta\beta_2$	$\Delta\beta_3$	$\Delta\beta_4$
Δr_1	$2A\cos^2\phi - \frac{B}{R_e}\sin^2\phi$				$2A\cos\phi\cos\theta + \frac{B}{R_e}\sin\phi\sin\theta$	$2Ar_{CH}\sin\phi\cos\phi - \frac{B}{R_e}r_{CC}\sin\phi\cos\theta$			
Δr_2		$2A\cos^2\phi - \frac{B}{R_e}\sin^2\phi$			$2A\cos\phi\cos\theta + \frac{B}{R_e}\sin\phi\sin\theta$		$2Ar_{CH}\sin\phi\cos\phi - \frac{B}{R_e}r_{CC}\sin\phi\cos\theta$		
Δr_3			$2A\cos^2\phi - \frac{B}{R_e}\sin^2\phi$		$2A\cos\phi\cos\theta + \frac{B}{R_e}\sin\phi\sin\theta$			$2Ar_{CH}\sin\phi\cos\phi - \frac{B}{R_e}r_{CC}\sin\phi\cos\theta$	
Δr_4				$2A\cos^2\phi - \frac{B}{R_e}\sin^2\phi$	$2A\cos\phi\cos\theta + \frac{B}{R_e}\sin\phi\sin\theta$				$2Ar_{CH}\sin\phi\cos\phi - \frac{B}{R_e}r_{CC}\sin\phi\cos\theta$
Δr_5					$8A\cos^2\theta - \frac{4B}{R_e}\sin^2\theta$	$2Ar_{CH}\sin\phi\cos\theta - \frac{B}{R_e}r_{CH}\sin\theta\cos\phi$	$2Ar_{CH}\sin\phi\cos\theta - \frac{B}{R_e}r_{CH}\sin\theta\cos\phi$	$2Ar_{CH}\sin\phi\cos\theta - \frac{B}{R_e}r_{CH}\sin\theta\cos\phi$	$2Ar_{CH}\sin\phi\cos\theta - \frac{B}{R_e}r_{CH}\sin\theta\cos\phi$
$\Delta\beta_1$						$2Ar_{CH}^2\sin^2\phi + \frac{B}{R_e}r_{CH}r_{CC}\cos\phi\cos\theta$			
$\Delta\beta_2$			SYMMETRIC				$2Ar_{CH}^2\sin^2\phi + \frac{B}{R_e}r_{CH}r_{CC}\cos\phi\cos\theta$		
$\Delta\beta_3$								$2Ar_{CH}^2\sin^2\phi + \frac{B}{R_e}r_{CH}r_{CC}\cos\phi\cos\theta$	
$\Delta\beta_4$									$2Ar_{CH}^2\sin^2\phi + \frac{B}{R_e}r_{CH}r_{CC}\cos\phi\cos\theta$

derivation of these elements has been given in detail in Chapter II, Section C. The complete $\mathfrak{F}$ matrix for ethylene is given on pages 148-150.

The $\mathfrak{G}$ matrices for C_2H_4, C_2D_4, cis-, trans-, and asym.-$C_2H_2D_2$, C_2H_3D, and C_2HD_3 have been determined. C_2H_4 and C_2D_4 belong to the point group V_h, and the $\mathfrak{G}$ matrices for these molecules will factor in the same way as the $\mathfrak{F}$ matrix. These $\mathfrak{G}$ matrices will factor into a 3 x 3 block, three 2 x 2 blocks, and three 1 x 1 blocks. Due to the reduction in symmetry brought about by isotopic substitution, the $\mathfrak{G}$ matrices for the other molecules will not factor so completely. Cis-$C_2H_2D_2$ and asym.-$C_2H_2D_2$ belong to the point group C_{2v}, trans-$C_2H_2D_2$ belongs to the point group C_{2h}, and C_2H_3D and C_2HD_3 belong to the point group C_s. On the following page, the correlation table showing how the species of the point groups of lower symmetry are related to the species of V_h is given. Inspection of this table shows how the $\mathfrak{G}$ matrices for the molecules factor.

The $\mathfrak{G}$ matrices for the ethylene molecules are given on pages 152-155. In order to give the necessary elements to form $\mathfrak{G}$ matrices for all of the isotopic ethylenes in a minimum space the 12 x 12 matrix has been split into sub-matrices as follows.

$$\begin{array}{|c|c|c|}
\hline
\mathfrak{G}_{11} & \mathfrak{G}_{12} & \\
\cline{1-2}
\mathfrak{G}_{21} & \mathfrak{G}_{22} & 0 \\
\hline
\multicolumn{2}{|c|}{0} & \mathfrak{G}_{33} \\
\hline
\end{array}$$

For those molecules with a high degree of symmetry, many of the off-diagonal elements vanish.

TABLE XVIII

NUMBER, SPECIES, AND ACTIVITY OF THE FUNDAMENTALS OF THE ISOTOPIC ETHYLENES AND THE CORRELATION TO POINT GROUP V_h

Group	Species	Correlation to V_h
C_{2h} (*trans*.-$C_2H_2D_2$)	$5A_g$ (R.) $2A_u$ (I. R.) B_g (R.) $4B_u$ (I. R.)	$3A_g$ (R.) + $2B_{1g}$ (R.) A_u (In.) + B_{1u} (I. R.) B_{2g} (R.) $2B_{2u}$ (I. R.) + $2B_{3u}$ (I. R.)
C_{2v} (*cis*.-$C_2H_2D_2$)	$5A_1$ (I. R., R.) $2A_2$ (R.) $4B_1$ (I. R., R.) $2B_2$ (I. R., R.)	$3A_g$ + $2B_{2u}$ A_u + B_{2g} $2B_{1g}$ + $2B_{3u}$ B_{1u}
C_{2v} (*asym*.-$C_2H_2D_2$)	$5A_1$ (I. R., R.) A_2 (R.) $4B_1$ (I. R., R.) $2B_2$ (I. R., R.)	$3A_g$ + $2B_{3u}$ A_u $2B_{1g}$ + $2B_{3u}$ B_{1u} + B_{2g}
C_s C_2H_3D and C_2HD_3	$9A'$ (I. R., R.) $3A''$ (I. R., R.)	$3A_g$ + $2B_{3u}$ + $2B_{2u}$ + $2B_{1g}$ A_u + B_{1u} + B_{2g}

$\mathcal{F}$ MATRIX FOR ETHYLENE (SPECIES A_g AND B_{3u})

$\mathcal{F}$	S_{CH}	S_{CC}	S_β	S'_{CH}	S'_β
S_{CH}	$K_{CH} + 2A\cos^2\phi - \frac{B}{R_e}\sin^2\phi$	$4A\cos\phi\cos\theta + \frac{2B}{R_e}\sin\phi\sin\theta$	$2Ar_{CH}\sin\phi\cos\phi - \frac{B}{R_e}r_{CC}\sin\phi\cos\theta$		
S_{CC}		$K_{CC} + 8A\cos^2\theta - \frac{4B}{R_e}\sin^2\theta$	$4Ar_{CH}\sin\phi\cos\theta - \frac{2B}{R_e}r_{CH}\sin\theta\cos\phi$		
S_β			$K_H + 2Ar_{CH}^2\sin^2\phi + \frac{B}{R_e}r_{CH}r_{CC}\cos\phi\cos\theta$		
S'_{CH}		(Symmetric)		$K_{CH} + 2Ar_{CH}^2\cos^2\phi - \frac{B}{R_e}\sin^2\phi$	$2Ar_{CH}\sin\phi\cos\phi - \frac{B}{R_e}r_{CC}\sin\phi\cos\theta$
S'_β					$K_H + 2Ar_{CH}^2\sin^2\phi + \frac{B}{R_e}r_{CH}r_{CC}\cos\phi\cos\theta$

$\mathcal{F}$ MATRIX FOR ETHYLENE (SPECIES B_{2u} AND B_{1g})

$\mathcal{F}$	S''_{CH}	S''_{β}	S'''_{CH}	S'''_{β}
S''_{CH}	$K_{CH} + 2A\cos^2\phi - \frac{B}{R_e}\sin^2\phi$	$2Ar_{CH}\sin\phi\cos\phi - \frac{B}{R_e}r_{CC}\sin\phi\cos\theta$		
S''_{β}		$\frac{k_H k^u_\sigma}{4k_H + k^u_\sigma} + 2Ar^2_{CH}\sin^2\phi + \frac{B}{R_e}r_{CH}r_{CC}\cos\phi\cos\theta$		
S'''_{CH}			$K_{CH} + 2A\cos^2\phi - \frac{B}{R_e}\sin^2\phi$	$2Ar_{CH}\sin\phi\cos\phi - \frac{B}{R_e}r_{CC}\sin\phi\cos\theta$
S'''_{β}				$\frac{k_H k^g_\sigma}{k_H + k^g_\sigma} + 2Ar^2_{CH}\sin^2\phi + \frac{B}{R_e}r_{CH}r_{CC}\cos\phi\cos\theta$

$\mathcal{F}$ MATRIX FOR ETHYLENE (SPECIES B_{1u}, B_{2g} AND A_u)

$\mathcal{F}$	S_ψ	S'_ψ	S_τ
S_ψ	$\frac{2K_H\cos^2\alpha(k_\sigma^u + 4k_\pi^u)}{4K_H\cos^2\alpha + (k_\sigma^u + 4k_\pi^u)}$ $+ \frac{2B}{R_e} r_{CH}r_{CC}\cos^3\alpha$		
S'_ψ		$\frac{2K_H\cos^2\alpha(4k_\sigma^g + k_\pi^g)}{4K_H\cos^2\alpha + (4k_\sigma^g + k_\pi^g)}$ $+ \frac{2B}{R_e} r_{CH}r_{CC}\cos^3\alpha$	
S_τ			$\frac{K_H\sin^2\alpha\, k_\pi^\tau}{K_H\sin^2\alpha + k_\pi^\tau} +$ $\frac{B}{R_e} r_{CH}r_{CC}\sin^2\alpha\cos\alpha$

The matrices given are $\mathfrak{G}_{11}$, $\mathfrak{G}_{22}$, $\mathfrak{G}_{33}$, and $\mathfrak{G}_{12}$. The matrix $\mathfrak{G}_{21}$ is easily obtained by taking the transpose of $\mathfrak{G}_{12}$. The symbols used in the $\mathfrak{G}$ matrices are defined as follows:

μ_i = reciprocal mass of i^{th} atom

α = equilibrium H-C-H angle

$\Sigma = \sin \alpha$

$\Gamma = \cos \alpha$

r = equilibrium bond length

$$\rho = \frac{r_{CH}}{r_{CC}} .$$

The geometrical parameters used for ethylene were those reported by Galloway and Barker,[40] and are given in Table XIX, along with the calculated values of other parameters which were used in the determination of the $\mathfrak{F}$ and $\mathfrak{G}$ matrices. After the work on the ethylene molecule had been completed, Allen[41] reported a new determination of the dimensions of the ethylene molecule based on high-resolution infrared studies. Allen reported the dimensions as:

$$r_{CH} = 1.086 \text{ Å}$$

$$r_{CC} = 1.337 \text{ Å}$$

$$\gamma = 117^\circ 22' .$$

These results differ from those given by Galloway and Barker, but the results obtained in this investigation using Galloway and Barker's dimensions should be close to those which would be obtained using the dimensions given by Allen. However, it should be emphasized that using the newer data would cause slight changes in the force constants.

The numerical $\mathfrak{G}$ matrices for the seven isotopic ethylene molecules are given on pages 157-160.

SYMBOLIC $\mathfrak{G}$ MATRIX FOR ETHYLENE ($\mathfrak{G}_{11}$)

$\mathfrak{G}_{11}$	S_{CH}	S_{CC}	S_{β}	S'_{CH}	S'_{β}
S_{CH}	$\frac{1}{4}(\mu_1+\mu_2+\mu_3+\mu_4) + 2\Gamma^2\mu_C$	$-2\Gamma\mu_C$	$\frac{2\Sigma\Gamma}{r_{CH}}\mu_C$	$\frac{1}{4}(\mu_1+\mu_2+\mu_3+\mu_4)$	0
S_{CC}		$2\mu_C$	$-\frac{2\Sigma}{r_{CH}}\mu_C$	0	0
S_{β}			$\frac{1}{4r_{CH}^2}(\mu_1+\mu_2+\mu_3+\mu_4) + \frac{2\Sigma^2}{r_{CH}^2}\mu_C$	0	$\frac{1}{4r_{CH}^2}(\mu_1+\mu_2-\mu_3-\mu_4)$
S'_{CH}		(Symmetric)		$\frac{1}{4}(\mu_1+\mu_2+\mu_3+\mu_4) + 2\Gamma^2\mu_C$	$\frac{2\Sigma\Gamma}{r_{CH}}\mu_C$
S'_{β}					$\frac{1}{4r_{CH}^2}(\mu_1+\mu_2+\mu_3+\mu_4) + \frac{2\Sigma^2}{r_{CH}^2}\mu_C$

SYMBOLIC $\mathcal{G}$ MATRIX FOR ETHYLENE ($\mathcal{G}_{22}$)

$\mathcal{G}_{22}$	S''_{CH}	S''_{β}	S'''_{CH}	S'''_{β}
S''_{CH}	$\frac{1}{4}(\mu_1+\mu_2+\mu_3+\mu_4)+2\Sigma^2\mu_C$	$-\frac{2\Sigma\Gamma}{r_{CH}}\mu_C$	$\frac{1}{4}(\mu_1+\mu_2-\mu_3-\mu_4)$	0
S''_{β}		$\frac{1}{4r^2_{CH}}(\mu_1+\mu_2+\mu_3+\mu_4)+$ $\frac{2\Gamma^2}{r^2_{CH}}\mu_C$	0	$\frac{1}{4r^2_{CH}}(\mu_1+\mu_2-\mu_3-\mu_4)$
S'''_{CH}			$\frac{1}{4}(\mu_1+\mu_2+\mu_3+\mu_4)+2\Sigma^2\mu_C$	$-\frac{2\Sigma(\Gamma+2\rho)}{r_{CH}}\mu_C$
S'''_{β}		(Symmetric)		$\frac{1}{4r^2_{CH}}(\mu_1+\mu_2+\mu_3+\mu_4)+$ $\frac{2(2\rho+\Gamma)^2}{r^2_{CH}}\mu_C$

SYMBOLIC $\mathcal{G}$ MATRIX FOR ETHYLENE ($\mathcal{G}_{12}$)

$\mathcal{G}_{12}$	S''_{CH}	S''_{β}	S'''_{CH}	S'''_{β}
S_{CH}	$\frac{1}{4}(\mu_1 - \mu_2 + \mu_3 - \mu_4)$	0	$\frac{1}{4}(\mu_1 - \mu_2 - \mu_3 + \mu_4)$	0
S_{CC}	0	0	0	0
S_{β}	0	$\frac{1}{4r_{CH}^2}(\mu_1 - \mu_2 + \mu_3 - \mu_4)$	0	$\frac{1}{4r_{CH}^2}(\mu_1 - \mu_2 - \mu_3 + \mu_4)$
S'_{CH}	$\frac{1}{4}(\mu_1 - \mu_2 - \mu_3 + \mu_4)$	0	$\frac{1}{4}(\mu_1 - \mu_2 + \mu_3 - \mu_4)$	0
S'_{β}	0	$\frac{1}{4r_{CH}^2}(\mu_1 - \mu_2 - \mu_3 + \mu_4)$	0	$\frac{1}{4r_{CH}^2}(\mu_1 - \mu_2 + \mu_3 - \mu_4)$

SYMBOLIC $\mathcal{G}$ MATRIX FOR ETHYLENE ($\mathcal{G}_{33}$)

$\mathcal{G}_{33}$	S_ψ	S'_ψ	S_τ
S_ψ	$\frac{1}{8(\Gamma r_{CH})^2}(\mu_1+\mu_2+\mu_3+\mu_4)$ $+\frac{1}{(\Gamma r_{CH})^2}\mu_C$	$\frac{1}{8(\Gamma r_{CH})^2}(\mu_1+\mu_2-\mu_3-\mu_4)$	$\frac{1}{4\sqrt{2}\Sigma\Gamma r_{CH}^2}(\mu_1-\mu_2-\mu_3+\mu_4)$
S'_ψ		$\frac{1}{8(\Gamma r_{CH})^2}(\mu_1+\mu_2+\mu_3+\mu_4)$ $+\frac{(2+8\Gamma\rho+8\Gamma^2\rho^2)}{2(\Gamma r_{CH})^2}\mu_C$	$\frac{1}{4\sqrt{2}\Sigma\Gamma r_{CH}^2}(\mu_1-\mu_2+\mu_3-\mu_4)$
S_τ	(Symmetric)		$\frac{1}{4(\Sigma r_{CH})^2}(\mu_1+\mu_2+\mu_3+\mu_4)$

TABLE XIX

GEOMETRICAL PARAMETERS AND CONSTANTS FOR ETHYLENE

Bond Lengths	Bond Angles	Atomic Masses	
$r_{CH} = 1.071$ Å	$\gamma = 120^\circ$	C	12.003804
$r_{CC} = 1.353$ Å	$\alpha = 60^\circ$	H	1.008142
		D	2.014735

Other Parameters

$\phi = 33^\circ 50'$

$\theta = 26^\circ 9'$

$R_e = 2.104$ Å

$\Gamma = \cos \alpha = 0.50000$

$\Sigma = \sin \alpha = 0.86603$

$\sin \phi = 0.55692$

$\cos \phi = 0.83057$

$\sin \theta = 0.44083$

$\cos \theta = 0.89759$

$$\rho = \frac{r_{CH}}{r_{CC}} = 0.791574$$

NUMERICAL $\mathcal{G}$ MATRICES FOR THE ISOTOPIC ETHYLENES

$\mathcal{G}$	S_{CH}	S_{CC}	S_β	S'_{CH}	S'_β	S''_{CH}	S''_β	S'''_{CH}	S'''_β
S_{CH}	1.0335773 0.5379967	-0.0833069	0.0673631						
S_{CC}		0.1666138	-0.1347261						
S_β			0.9737090 0.5416577						
S'_{CH}				1.0335773 0.5379967	0.0673631				
S'_β					0.9737090 0.5416577				
S''_{CH}						1.1168842 0.6213036	-0.0673631		
S''_β							0.9010814 0.4690300		
S'''_{CH}								1.1168842 0.6213036	-0.2806546
S'''_β									1.4951041 1.0630528

The matrix is symmetric. In blocks where two figures appear, the first is for C_2H_4, the second for C_2D_4.

NUMERICAL $\mathcal{G}$ MATRICES FOR THE ISOTOPIC ETHYLENES (Continued)

$\mathcal{G}$	S_{CH}	S_{CC}	S_{β}	S'_{CH}	S'_{β}	S''_{CH}	S''_{β}	S'''_{CH}	S'''_{β}
S_{CH}	0.7857890	-0.0833069	0.0673631	0 0 0.2477903		-0.2477903 0 0		0 0.2477903 0	
S_{CC}		0.1666138	-0.1347261						
S_{β}			0.7576833		0 0 0.2160257		-0.2160257 0 0		0 0.2160257 0
S'_{CH}				0.7857890	0.0673631	0 0.2477903 0		-0.2477903 0 0	
S'_{β}					0.7576833		0 0.2160257 0		-0.2160257 0 0
S''_{CH}						0.8690939	-0.0673631	0 0 0.2477903	
S''_{β}							0.6850556		0 0 0.2160257
S'''_{CH}								0.8690939	-0.2806546
S'''_{β}									1.2790784

The matrix is symmetric. In blocks where three figures appear, the first is for <u>cis</u>-$C_2H_2D_2$, the second for <u>trans</u>-$C_2H_2D_2$, and the third for <u>asym</u>.-$C_2H_2D_2$.

NUMERICAL $\mathcal{G}$ MATRICES FOR THE ISOTOPIC ETHYLENES (Continued)

$\mathcal{G}$	S_{CH}	S_{CC}	S_{β}	S'_{CH}	S'_{β}	S''_{CH}	S''_{β}	S'''_{CH}	S'''_{β}
S_{CH}	0.9096822 0.6618919	-0.0833069	0.0673631	0.1238952		0.1238952		-0.1238952	
S_{CC}		0.1666138	-0.1347261						
S_{β}			0.8656962 0.6496705		0.1080129		0.1080129		-0.1080129
S'_{CH}				0.9096822 0.6618919	0.0673631	-0.1238952		0.1238952	
S'_{β}					0.8656962 0.6496705		-0.1080129		0.1080129
S''_{CH}						0.9929891 0.7451988	-0.0673631	0.1238952	
S''_{β}							0.7930685 0.5770428		0.1080129
S'''_{CH}								0.9929891 0.7451988	-0.2806546
S'''_{β}									1.3870913 1.1710656

The matrix is symmetric.
In blocks where two figures
appear, the first is for
C_2H_3D, the second for C_2HD_3.

NUMERICAL $\mathcal{G}$ MATRICES FOR THE ISOTOPIC ETHYLENES (Continued)

$\mathcal{G}$	S_ψ	S'_ψ	S_τ
S_ψ	2.0200453[a] 1.1559428		
S'_ψ		2.6619976 1.7978951	
S_τ	(Symmetric)		1.1530243 0.5769544

[a] In blocks where two figures appear, the first is for C_2H_4, the second for C_2D_4.

$\mathcal{G}$	S_ψ	S'_ψ	S_τ
S_ψ	1.5879941	0[a] 0 0.4320512	0 0.3527685 0
S'_ψ		2.2299464	-0.3527685 0 0
S_τ	(Symmetric)		0.8649899

[a] In blocks where three figures appear, the first is for cis-$C_2H_2D_2$, the second for trans-$C_2H_2D_2$, and the third for asym.-$C_2H_2D_2$.

$\mathcal{G}$	S_ψ	S'_ψ	S_τ
S_ψ	1.8040196[a] 1.3719680	0.2160256	-0.1763843
S'_ψ		2.4459719 2.0139203	0.1763843
S_τ	(Symmetric)		1.0090073 0.7209727

[a] In blocks where two figures appear, the first is for C_2H_3D, the second for C_2HD_3.

B. Allene

C_3H_4 and C_3D_4 belong to point group D_{2d}. The geometrical structure and coordinates are shown in Figure 29. The potential energy was expressed in terms of the following set of internal coordinates:

Δr_1
Δr_2
Δr_3
Δr_4
Δr_5
Δr_6
$\Delta \epsilon_1$
$\Delta \epsilon_2$
$\Delta \psi_1$
$\Delta \psi_2$
$\Delta \beta_1$
$\Delta \beta_2$
$\Delta \beta_3$
$\Delta \beta_4$
$\Delta \tau$.

$\Delta \tau$ is defined as the change in the angle formed by the intersection of the two CH_2 planes caused by a twisting of the CH_2 groups about the symmetry axis of the molecule. The potential energy, before orbital rotation is taken into account, is

$$2V = K_{CH} \sum_{i=1}^{4} (\Delta r_i)^2 + K_{CC} \sum_{i=5}^{6} (\Delta r_i)^2 + 2k_{CC}^{CC} (\Delta r_5 \Delta r_6) + K_H \sum_{i=1}^{4} (\Delta \beta_i)^2$$

$$+ 2K_H \cos^2 \alpha \sum_{i=1}^{2} (\Delta \psi_i)^2 + K_H \sin^2 \alpha (\Delta \tau)^2 + K_\epsilon \sum_{i=1}^{2} (\Delta \epsilon_i)^2$$

$$+ B_{CH} \sum_{i=1}^{4} (\Delta r_i) + B_{CC} \sum_{i=5}^{6} (\Delta r_i) + B_H \sum_{i=1}^{4} (\Delta \beta_i) + B_\psi \sum_{i=1}^{2} (\Delta \psi_i)$$

$$+ B_\epsilon \sum_{i=1}^{2} (\Delta \epsilon_i) + B_\tau (\Delta \tau) - 2B \sum_{i=1}^{4} (\Delta R_i) + 2A \sum_{i=1}^{4} (\Delta R_i)^2 . \qquad \text{(A-3)}$$

K_{CH} and K_{CC} are the C-H and C-C bond stretching constants, K_H is the constant associated with the angular distortion of a C-H bond from its equilib-

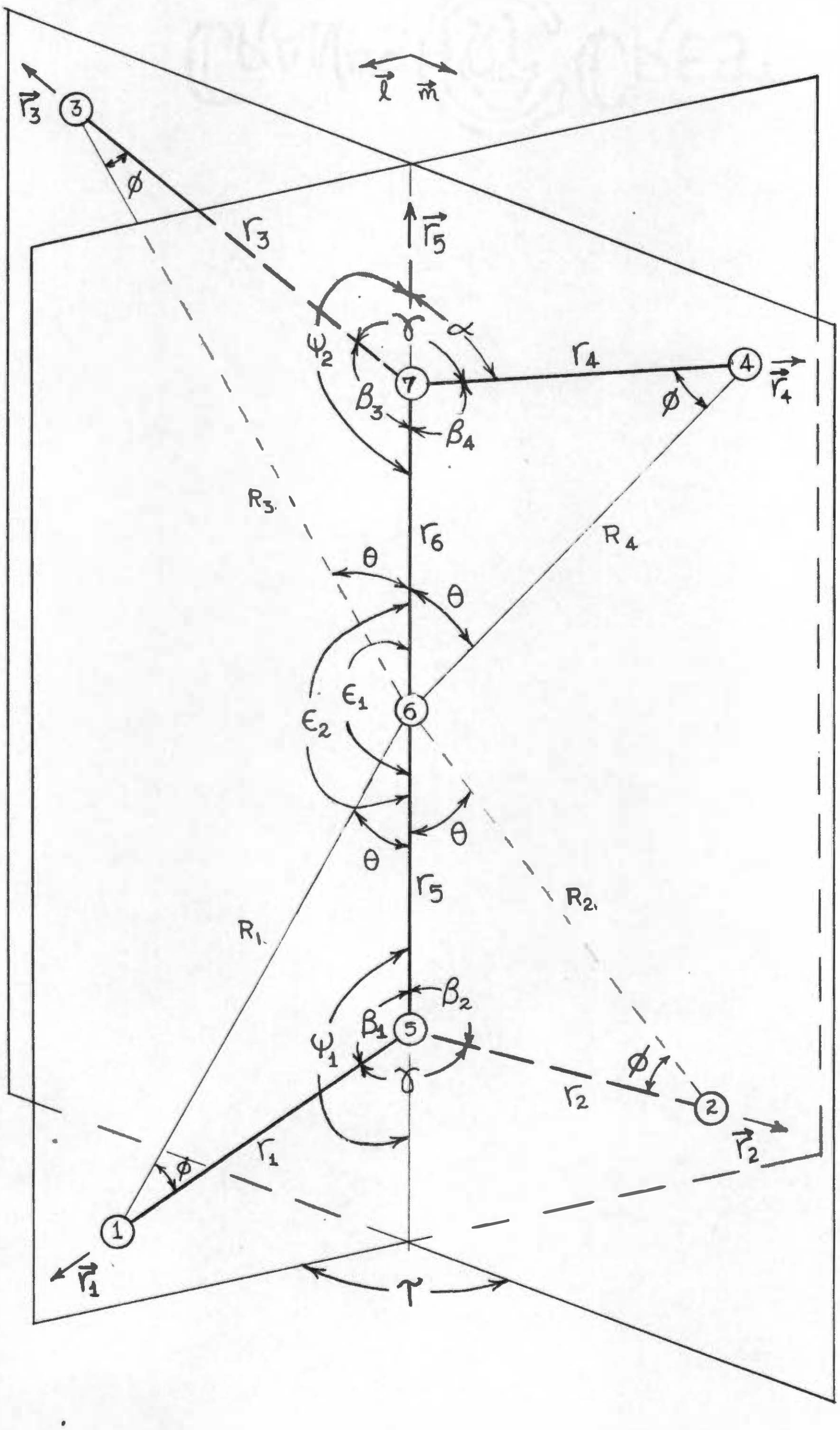


Figure 29. The Geometry of the Allene Molecule.

rium position, and K_ϵ is the constant associated with the bending of the C-C-C chain. The last two terms account for the repulsive forces between the hydrogen atoms and the central carbon atom. The constant k_{CC}^{CC} has been included to account for the interaction between the two C-C bonds, since this term was expected to be necessary, as indeed it is.

The symmetry coordinates which were used are:*

$$A_1:\quad S_{CH} = \tfrac{1}{2}(\Delta r_1 + \Delta r_2 + \Delta r_3 + \Delta r_4)$$

$$S_{CC} = \frac{1}{\sqrt{2}}(\Delta r_5 + \Delta r_6)$$

$$S_\beta = \tfrac{1}{2}(\Delta\beta_1 + \Delta\beta_2 + \Delta\beta_3 + \Delta\beta_4)$$

$$B_2:\quad S'_{CH} = \tfrac{1}{2}(\Delta r_1 + \Delta r_2 - \Delta r_3 - \Delta r_4)$$

$$S'_{CC} = \frac{1}{\sqrt{2}}(\Delta r_5 - \Delta r_6)$$

$$S'_\beta = \tfrac{1}{2}(\Delta\beta_1 + \Delta\beta_2 - \Delta\beta_3 - \Delta\beta_4)$$

$$B_1:\quad S_\tau = \Delta\tau$$

$$E:\quad S''_{CH} = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2) \qquad S'''_{CH} = \frac{1}{\sqrt{2}}(\Delta r_3 - \Delta r_4)$$

$$S''_\beta = \frac{1}{\sqrt{2}}(\Delta\beta_1 - \Delta\beta_2) \qquad S'''_\beta = \frac{1}{\sqrt{2}}(\Delta\beta_3 - \Delta\beta_4)$$

$$S_\epsilon = \Delta\epsilon_1 \qquad S'_\epsilon = \Delta\epsilon_2$$

$$S_\psi = \Delta\psi_1 \qquad S'_\psi = \Delta\psi_2$$

---

*The symmetry coordinates given for species E are actually those for point group C_{2v}. It is necessary to use these coordinates in order to factor the $\mathfrak{G}$ matrix of $C_3H_2D_2$. Although the correct symmetry coordinates for point group D_{2d} are made up of linear combinations of the coordinates given here, the $\mathfrak{G}$ matrices for C_3H_4 and C_3D_4 obtained using the above set of coordinates are correct.

After the ΔR_i's have been expressed in terms of the internal coordinates and the modification of the potential energy brought about by orbital rotation has been determined (see Chapter II), the $\mathfrak{F}$ matrix is obtained by symmetrization. The $\mathfrak{F}$ matrix for allene is given on pages 165-167.

The $\mathfrak{G}$ matrices for C_3H_4, C_3D_4, and H_2CCCD_2 were determined using both the B and $\vec{S}$ matrices. The $\vec{S}$ matrix is given on page 168 in order to illustrate the form of the matrix. The vectors $\vec{t}_1$ and $\vec{v}_5$ are defined by

$$\vec{t}_1 = \left(\frac{\Gamma}{r_{CH}} + \frac{1}{r_{CC}} \right) \vec{r}_1 \quad \text{and} \quad \vec{v}_5 = \left(\frac{\Gamma}{r_{CC}} + \frac{1}{r_{CH}} \right) \vec{r}_5 \,.$$

C_3H_4 and C_3D_4 belong to point group D_{2d}, while H_2CCCD_2 belongs to point group C_{2v}. The correlation of the species of the two groups is

D_{2d}	C_{2v}
$3A_1$ (R.) + $3B_2$ (I. R., R.)	$6A_1$ (R.)
B_1 (R.)	A_2 (R.)
$4E$ (I. R., R.)	$4B_1$ (I. R., R.) + $4B_2$ (I. R., R.),

and it is readily seen that the $\mathfrak{G}$ matrices for C_3H_4 and C_3D_4 will factor into one 1 x 1 block, two 3 x 3 blocks, and two (degenerate) 4 x 4 blocks, while for H_2CCCD_2, the matrix will factor into one 1 x 1 block, two 4 x 4 blocks, and one 6 x 6 block. The symbolic $\mathfrak{G}$ matrices are given on pages 169-171, and the numerical $\mathfrak{G}$ matrices are given on pages 172-173. The symbols used in the $\mathfrak{F}$ and $\mathfrak{G}$ matrices, along with the geometrical parameters, are given in Table XX.

$\mathcal{F}$ MATRIX FOR ALLENE (SPECIES A_1 AND B_2)

$\mathcal{F}$	S_{CH}	S_{CC}	S_{β}	S'_{CH}	S'_{CC}	S'_{β}
S_{CH}	$K_{CH}+2A\cos^2\phi - \frac{B}{R_e}\sin^2\phi$	$\frac{4}{\sqrt{2}}A\cos\phi\cos\theta - \frac{2B}{\sqrt{2}R_e}\sin\phi\sin\theta$	$2Ar_{CH}\sin\phi\cos\phi - \frac{B}{R_e}r_{CC}\sin\phi\cos\theta$			
S_{CC}		$K'_{CC} + 4A\cos^2\theta - \frac{2B}{R_e}\sin^2\theta$	$\frac{4}{\sqrt{2}}Ar_{CH}\sin\phi\cos\theta - \frac{2B}{\sqrt{2}R_e}r_{CH}\sin\theta\cos\phi$			
S_{β}			$K_H + Ar_{CH}^2\sin^2\phi + \frac{B}{R_e}r_{CH}r_{CC}\cos\phi\cos\theta$			
S'_{CH}				$K_{CH}+2A\cos^2\phi - \frac{B}{R_e}\sin^2\phi$	$\frac{4}{\sqrt{2}}A\cos\phi\cos\theta + \frac{2B}{\sqrt{2}R_e}\sin\phi\sin\theta$	$2Ar_{CH}\sin\phi\cos\phi - \frac{B}{R_e}r_{CC}\sin\phi\cos\theta$
S'_{CC}		(Symmetric)			$K''_{CC} + 4A\cos^2\theta - \frac{2B}{R_e}\sin^2\theta$	$\frac{4}{\sqrt{2}}Ar_{CH}\sin\phi\cos\theta - \frac{2B}{\sqrt{2}R_e}r_{CH}\sin\theta\cos\phi$
S'_{β}		$K'_{CC} = K_{CC} + k^{CC}_{CC}$ $K''_{CC} = K_{CC} - k^{CC}_{CC}$				$K_H + 2Ar_{CH}^2\sin^2\phi + \frac{B}{R_e}r_{CH}r_{CC}\cos\phi\cos\theta$

$\mathcal{F}$ MATRIX FOR ALLENE (SPECIES E)

$\mathcal{F}$	S''_{CH}	S''_{β}	S_{ϵ}	S_{ψ}
S''_{CH}	$K_{CH} + 2A\cos^2\phi - \frac{B}{R_e}\sin^2\phi$	$2Ar_{CH}\sin\phi\cos\phi - \frac{B}{R_e} r_{CC}\sin\phi\cos\Theta$		
S''_{β}		$\frac{K_H k_\sigma}{2K_H + k_\sigma} + 2Ar^2_{CH}\sin^2\phi + \frac{B}{R_e} r_{CH} r_{CC}\cos\phi\cos\Theta$		
S_{ϵ}			K_{ϵ}	
S_{ψ}		(Symmetric)		$\frac{2K_H\cos^2\alpha(k_\sigma + k_\pi)}{2K_H\cos^2\alpha + (k_\sigma + k_\pi)} + \frac{2B}{R_e} r_{CH} r_{CC}\cos^3\alpha$

$\mathcal{F}$ MATRIX FOR ALLENE (SPECIES A_2)

$\mathcal{F}$	S_τ
S_τ	$\frac{K_H \sin^2\alpha (k_\pi^\tau)}{2K_H \sin^2\alpha + k_\pi^\tau} +$ $\frac{B}{R_e} r_{CH} r_{CC} \sin^2 \alpha \cos \alpha$

$\mathcal{G}$ MATRIX FOR ALLENE

$\mathcal{G}$	S_τ
S_τ	$\frac{1}{4\Sigma r_{CH}^2} (\mu_1 + \mu_2 + \mu_3 + \mu_4)$

$\vec{S}$ MATRIX FOR ALLENE

$\vec{S}$	M_1	M_2	M_3	M_4	C_5	C_6	C_7
Δr_1	$\vec{r}_1$				$-\vec{r}_1$		
Δr_2		$\vec{r}_2$			$-\vec{r}_2$		
Δr_3			$\vec{r}_3$				$-\vec{r}_3$
Δr_4				$\vec{r}_4$			$-\vec{r}_4$
Δr_5					$-\vec{r}_5$	$\vec{r}_5$	
Δr_6						$-\vec{r}_5$	$\vec{r}_5$
$\Delta\beta_1$	$-\frac{1}{\Sigma r_{CH}}(\Gamma\vec{r}_1+\vec{r}_5)$				$\frac{1}{\Sigma}(\vec{t}_1+\vec{v}_5)$	$-\frac{1}{\Sigma r_{cc}}(\vec{r}_1+\Gamma\vec{r}_5)$	
$\Delta\beta_2$		$-\frac{1}{\Sigma r_{CH}}(\Gamma\vec{r}_2+\vec{r}_5)$			$\frac{1}{\Sigma}(\vec{t}_2+\vec{v}_5)$	$-\frac{1}{\Sigma r_{cc}}(\vec{r}_2+\Gamma\vec{r}_5)$	
$\Delta\beta_3$			$\frac{1}{\Sigma r_{CH}}(-\Gamma\vec{r}_3+\vec{r}_5)$			$-\frac{1}{\Sigma r_{cc}}(\vec{r}_3-\Gamma\vec{r}_5)$	$\frac{1}{\Sigma}(\vec{t}_3-\vec{v}_5)$
$\Delta\beta_4$				$\frac{1}{\Sigma r_{CH}}(-\Gamma\vec{r}_4+\vec{r}_5)$		$-\frac{1}{\Sigma r_{cc}}(\vec{r}_4-\Gamma\vec{r}_5)$	$\frac{1}{\Sigma}(t_4-v_5)$
$\Delta\epsilon_1$					$\frac{1}{r_{cc}}\vec{m}$	$-\frac{2}{r_{cc}}\vec{m}$	$\frac{1}{r_{cc}}\vec{m}$
$\Delta\epsilon_2$					$-\frac{1}{r_{cc}}\vec{l}$	$\frac{2}{r_{cc}}\vec{l}$	$-\frac{1}{r_{cc}}\vec{l}$
$\Delta\psi_1$	$-\frac{1}{2\Gamma r_{CH}}\vec{l}$	$-\frac{1}{2\Gamma r_{CH}}$			$\left(\frac{1}{\Gamma r_{CH}}+\frac{1}{r_{cc}}\right)\vec{l}$	$-\frac{1}{r_{cc}}\vec{l}$	
$\Delta\psi_2$			$\frac{1}{2\Gamma r_{CH}}\vec{m}$	$\frac{1}{2\Gamma r_{CH}}\vec{m}$		$\frac{1}{r_{cc}}\vec{m}$	$-\left(\frac{1}{\Gamma r_{CH}}+\frac{1}{r_{cc}}\right)\vec{m}$
$\Delta\tau$	$\frac{1}{2\Sigma r_{CH}^2}\vec{l}$	$-\frac{1}{2\Sigma r_{CH}^2}\vec{l}$	$\frac{1}{2\Sigma r_{CH}^2}\vec{m}$	$-\frac{1}{2\Sigma r_{CH}^2}\vec{m}$			

SYMBOLIC $\mathcal{G}$ MATRIX FOR ALLENE

$\mathcal{G}$	S_{CH}	S_{CC}	S_β	S'_{CH}	S'_{CC}	S'_β
S_{CH}	$\frac{1}{4}(\mu_1+\mu_2+\mu_3+\mu_4)$ $+ 2\Gamma^2\mu_C$	$-\frac{2\Gamma}{\sqrt{2}}\ \mu_C$	$\frac{2\Sigma\Gamma}{r_{CH}}\ \mu_C$	$\frac{1}{4}(\mu_1+\mu_2-\mu_3-\mu_4)$		
S_{CC}		μ_C	$-\frac{2\Sigma}{\sqrt{2}\ r_{CH}}\ \mu_C$			
S_β			$\frac{1}{4r_{CH}^2}(\mu_1+\mu_2+\mu_3+\mu_4)$ + $\frac{2\Sigma^2}{r_{CH}^2}\ \mu_C$			$\frac{1}{4r_{CH}^2}(\mu_1+\mu_2-\mu_3-\mu_4)$
S'_{CH}				$\frac{1}{4}(\mu_1+\mu_2+\mu_3+\mu_4)$ $+ 2\Gamma^2\ \mu_C$	$-\frac{2\Gamma}{\sqrt{2}}\ \mu_C$	$\frac{2\Sigma\Gamma}{r_{CH}}\ \mu_C$
S'_{CC}	(Symmetric)				$3\ \mu_C$	$-\frac{2\Sigma}{\sqrt{2}\ r_{CH}}\ \mu_C$
S'_β						$\frac{1}{4r_{CH}^2}(\mu_1+\mu_2+\mu_3+\mu_4)$ + $\frac{2\Sigma^2}{r_{CH}^2}\ \mu_C$

SYMBOLIC $\mathcal{G}$ MATRIX FOR ALLENE* (Continued)

$\mathcal{G}$	S''_{CH}	S''_{β}	S_{ϵ}	S_{ψ}
S''_{CH}	$\frac{1}{2}(\mu_1+\mu_2) + 2\Sigma^2\mu_C$	$-\frac{2\Sigma(\Gamma+\rho)}{r_{CH}}\mu_C$	$\frac{2\Sigma}{\sqrt{2}\, r_{CC}}\mu_C$	0
S''_{β}		$\frac{1}{2r^2_{CH}}(\mu_1+\mu_2) +$ $\frac{2(\Gamma+\rho)^2 + 2\rho^2}{r^2_{CH}}\mu_C$	$-\frac{2(\Gamma+3\rho)}{\sqrt{2} r_{CH} r_{CC}}\mu_C$	$\frac{2\rho^2}{\sqrt{2} r^2_{CH}}\mu_C$
S_{ϵ}	(Symmetric)		$\frac{6}{r^2_{CC}}\mu_C$	$-\frac{(1+3\rho\Gamma)}{\Gamma r_{CH} r_{CC}}\mu_C$
S_{ψ}				$\frac{1}{(\Gamma r_{CH})^2}(\mu_3+\mu_4) +$ $\frac{(1+\rho\Gamma)^2 + (\rho\Gamma)^2}{(\Gamma r_{CH})^2}\mu_C$

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*See footnote on page 163.

SYMBOLIC $\mathcal{G}$ MATRIX FOR ALLENE* (Continued)

$\mathcal{G}$	S'''_{CH}	S'''_{β}	S'_{ϵ}	S'_{ψ}
S'''_{CH}	$\frac{1}{2}(\mu_3+\mu_4) + 2\Sigma^2\mu_C$	$-\frac{2\Sigma(\Gamma+\rho)}{r_{CH}}\ \mu_C$	$\frac{2\Sigma}{\sqrt{2}r_{CC}}\ \mu_C$	0
S'''_{β}		$\frac{1}{2r_{CH}^2}(\mu_3+\mu_4) +$ $\frac{2(\Gamma+\rho)^2 + 2\ {}^2}{r_{CH}^2}\ \mu_C$	$-\frac{2(\Gamma+\rho)}{\sqrt{2}r_{CH}r_{CC}}\ \mu_C$	$\frac{2\rho^2}{\sqrt{2}r_{CH}^2}\ \mu_C$
S'_{ϵ}	(Symmetric)		$\frac{6}{r_{CC}^2}\ \mu_C$	$-\frac{(1+3\rho\Gamma)}{\Gamma r_{CH}r_{CC}}\ \mu_C$
S'_{ψ}				$\frac{1}{4(\Gamma r_{CH})^2}(\mu_1+\mu_2) +$ $\frac{(1+\Gamma\rho)^2 + (\rho\Gamma)^2}{(\Gamma r_{CH})^2}\ \mu_C$

*See footnote on page 163.

NUMERICAL $\mathcal{G}$ MATRICES FOR C_3H_4, C_3D_4 AND H_2CCCD_2

$\mathcal{G}$	S_{CH}	S_{CC}	S_β	S'_{CH}	S'_{CC}	S'_β
S_{CH}	1.0375398 0.7897495 0.5419592	-0.0616451	0.0694976	0 0.2477903 0		
S_{CC}		0.0833069	-0.0939185			
S_β			0.9738883 0.7570536 0.5402188			0 0.2168347 0
S'_{CH}				1.0375398 0.7897495 0.5419592	-0.0616451	0.0694976
S'_{CC}					0.2499207	-0.0939185
S'_β						0.9738883 0.7570536 0.5402188

The matrix is symmetric. In blocks where three figures appear, the first is for C_3H_4, the second for H_2CCCD_2, and the third for C_3D_4.

NUMERICAL $\mathcal{G}$ MATRICES FOR C_3H_4, C_3D_4 AND H_2CCCD_2 (Continued)

$\mathcal{G}$	S''_{CH}	S''_β	S_ϵ	S_ψ	S'''_{CH}	S'''_β	S'_ϵ	S'_ψ	S_τ
S''_{CH}	1.1129216 0.6173410 0.6173410	-0.1779829	0.0767107	0					
S''_β		1.2270786 0.7934091 0.7934091	-0.2503943	0.0687780					
S_ϵ			0.2918003	-0.2596961					
S_φ				2.1763349 2.1763349 1.3843400					
S'''_{CH}					1.1129216 1.1129216 0.6173410	-0.1779829	0.0767107	0	
S'''_β						1.2270786 1.2270786 0.7934091	-0.2503943	0.0687780	
S'_ϵ							0.2918003	-0.2596961	
S'_φ								2.1763349 1.3843400 1.3843400	
S_τ									1.1952437 0.8966626 0.5980813

The matrix is symmetric. In blocks where three figures appear, the first is for C_3H_4, the second for H_2CCCD_2, and the third for C_3D_4.

TABLE XX

GEOMETRICAL PARAMETERS FOR ALLENE

Bond Lengths[42]	Bond Angles[42]	Other Parameters
$r_{CH} = 1.069$ Å	$\gamma = 116°54'$	$\phi = 32°27'$
$r_{CC} = 1.309$ Å	$\alpha = 58°21'$	$\theta = 26°00'$
		$R_e = 2.07843$ Å
		$\Gamma = \cos\alpha = 0.52324$
		$\Sigma = \sin\alpha = 0.85218$
		$\sin\phi = 0.53662$
		$\cos\phi = 0.84382$
		$\sin\theta = 0.43831$
		$\cos\theta = 0.89882$
		$\rho = \frac{r_{CH}}{r_{CC}} = 0.816779$

C. Formaldehyde, Ketene, and Diazomethane

CH_2O, CH_2CO, and CH_2N_2 all belong to the point group C_{2v}. The geometrical structure of CH_2CO and CH_2N_2 is shown in Figure 30. If atom 5 is neglected, one obtains the CH_2O model. The internal coordinates used for CH_2CO and CH_2N_2 are:

$$\begin{array}{ccc} \Delta r_1 & \Delta r_4 & \Delta\delta \\ \Delta r_2 & \Delta\beta_1 & \Delta\epsilon \\ \Delta r_3 & \Delta\beta_2 & \Delta\psi \end{array} .$$

The potential energy for CH_2CO before orbital rotation is taken into account is

$$\begin{aligned} 2V = {} & K_{CH} \sum_{i=1}^{2} (\Delta r_i)^2 + K_{CC} (\Delta r_3)^2 + K_{CO} (\Delta r_4)^2 + K_H \sum_{i=1}^{2} (\Delta\beta_i)^2 \\ & + K_\delta (\Delta\delta)^2 + K_\epsilon (\Delta\epsilon)^2 + 2K_H \cos^2\alpha \, (\Delta\psi)^2 + B_{CH} \sum_{i=1}^{2} (\Delta r_i) + B_{CC} (\Delta r_3) \\ & + B_{CO} (\Delta r_4) + B_H \sum_{i=1}^{2} (\Delta\beta_i) + B_\delta (\Delta\delta) + B_\epsilon (\Delta\epsilon) + B_\psi (\Delta\psi) \\ & - 2B \sum_{i=1}^{2} (\Delta R_i) + 2A \sum_{i=1}^{2} (\Delta R_i)^2 \end{aligned} \qquad (A-4)$$

where K_{CH}, K_{CC}, and K_{CO} are the C-H, C-C, and C-O bond stretching constants, K_H is the constant associated with the angular distortion of a C-H bond from its equilibrium position, and K_ϵ and K_ψ are the constants associated with the planar and non-planar C-C-O bending. The last two terms account for the repulsive forces between the hydrogen atoms and the

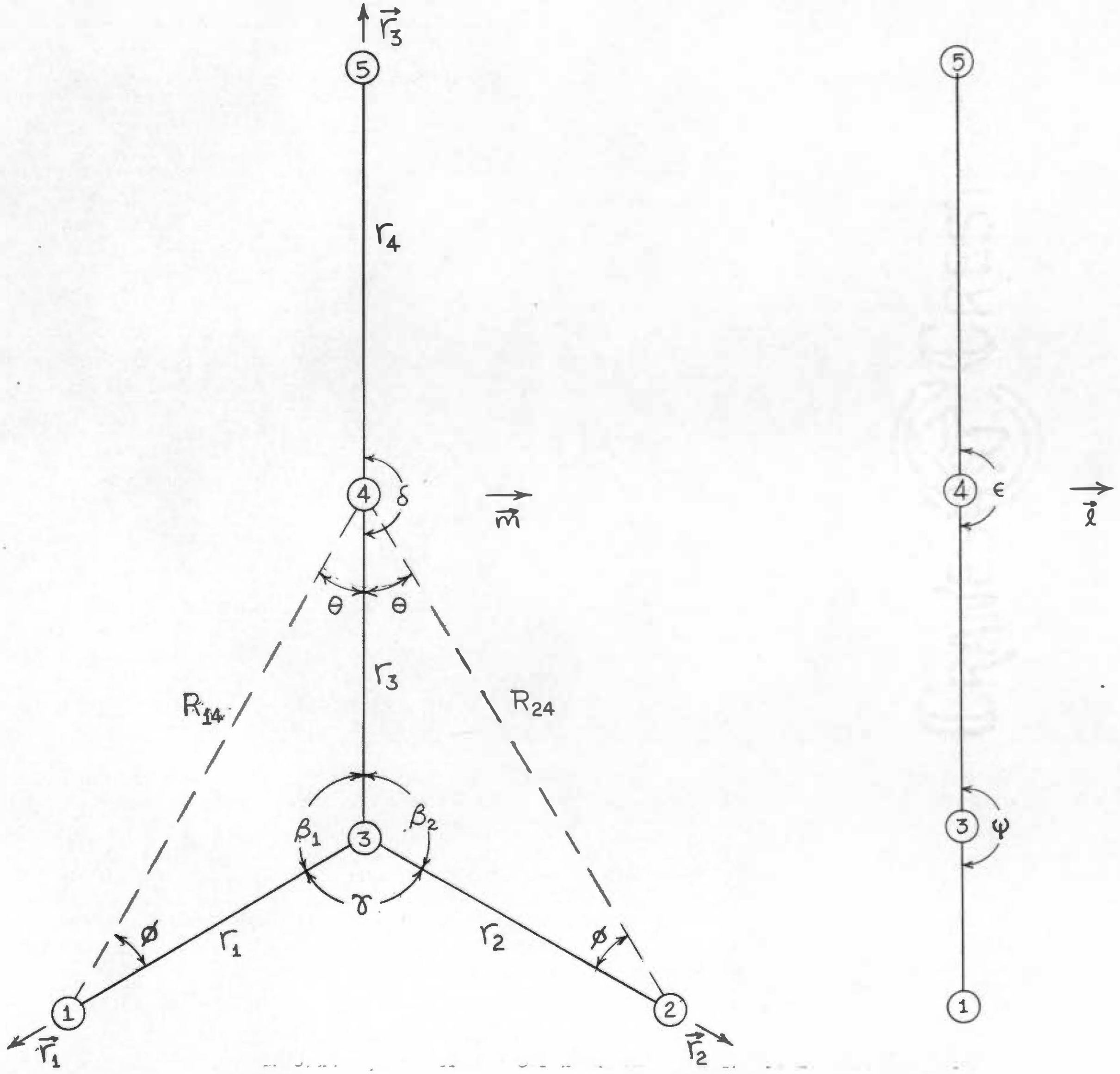

Figure 30. The Geometry of Ketene and Diazomethane.

central carbon atom. The potential energy expressions for CH_2N_2 and CH_2O can be obtained quite easily from Equation (A-4).

The symmetry coordinates used for CH_2CO are:

$$A_1:\quad S_{CH} = \frac{1}{\sqrt{2}}(\Delta r_1 + \Delta r_2)$$

$$S_{CC} = \Delta r_3$$

$$S_{CO} = \Delta r_4$$

$$S_{\beta} = \frac{1}{\sqrt{2}}(\Delta \beta_1 + \Delta \beta_2)$$

$$B_1:\quad S_{CH} = \frac{1}{\sqrt{2}}(\Delta r_1 - \Delta r_2)$$

$$S_{\beta}' = \frac{1}{\sqrt{2}}(\Delta \beta_1 - \Delta \beta_2)$$

$$S_{\delta} = \Delta \delta$$

$$B_2:\quad S_{\epsilon} = \Delta \epsilon$$

$$S_{\psi} = \Delta \psi$$

After the ΔR_i's have been expressed in terms of the internal coordinates and the modification of the potential energy brought about by orbital rotation has been determined (see Chapter II), the $\mathfrak{F}$ matrix is obtained by symmetrization. The $\mathfrak{F}$ matrix for CH_2CO is given on pages 178-179.

The $\mathfrak{F}$ matrix for CH_2N_2 can be obtained from the $\mathfrak{F}$ matrix of ketene by changing r_{CC} to r_{CN}, r_{CO} to r_{NN}, K_{CC} to K_{CN}, and K_{CO} to K_{NN}. The $\mathfrak{F}$ matrix for CH_2O can likewise be obtained from the $\mathfrak{F}$ matrix of ketene by deleting the rows and columns associated with S_{CO}, S_{δ}, and S_{ϵ}, and by changing r_{CC} to r_{CO} and K_{CC} to K_{CO}.

$\mathfrak{F}$ MATRIX FOR KETENE (SPECIES A_1)

$\mathfrak{F}$	S_{CH}	S_{CC}	S_{CO}	S_{β}
S_{CH}	$K_{CH} + 2A\cos^2\phi - \frac{B}{R_e}\sin^2\phi$	$\frac{4}{\sqrt{2}}A\cos\phi\cos\theta + \frac{2B}{\sqrt{2}R_e}\sin\phi\sin\theta$	0	$2Ar_{CH}\sin\phi\cos\phi - \frac{B}{R_e}r_{CC}\sin\phi\cos\theta$
S_{CC}		$K_{CC} + 4A\cos^2\theta - \frac{2B}{R_e}\sin^2\theta$	0	$\frac{4}{\sqrt{2}}Ar_{CH}\sin\phi\cos\theta - \frac{2B}{\sqrt{2}R_e}r_{CH}\sin\theta\cos\phi$
S_{CO}		(Symmetric)	K_{CO}	0
S_{β}				$K_H + 2Ar_{CH}^2\sin^2\phi + \frac{B}{R_e}r_{CH}r_{CC}\cos\phi\cos\theta$

$\mathcal{F}$ MATRIX FOR KETENE (SPECIES B_1 AND B_2)

$\mathcal{F}$	S'_{CH}	S'_{β}	S_{δ}	S_{ϵ}	S_{ψ}
S'_{CH}	$K_{CH} + 2A\cos^2\phi - \frac{B}{R_e}\sin^2\phi$	$2Ar_{CH}\sin\phi\cos\overset{\phi}{\theta} - \frac{B}{R_e} r_{CC}\sin\phi\cos\theta$	0		
S'_{β}		$\frac{K_H k_\sigma}{2K_H + k_\sigma} + 2Ar_{CH}^2\sin^2\phi + \frac{B}{R_e} r_{CH} r_{CC}\cos\phi\cos\theta$	0		
S_{δ}			K_{δ}		
S_{ϵ}		(Symmetric)		K_{ϵ}	0
S_{ψ}					$\frac{2K_H\cos^2\alpha(k'_\sigma + k_\pi)}{2K_H\cos^2\alpha + (k'_\sigma + k_\pi)} + \frac{2B}{R_e} r_{CH} r_{CC}\cos^3\alpha$

The symbolic $\mathfrak{G}$ matrices for formaldehyde, ketene and diazomethane are given on pages 181-184, and the numerical $\mathfrak{G}$ matrices are given on pages 185-187. The symbols used in the $\mathfrak{F}$ and $\mathfrak{G}$ matrices, along with the geometrical parameters for formaldehyde, ketene, and diazomethane, are given in Table XXI. The geometrical parameters used for formaldehyde were those reported by Davidson, Stoicheff, and Bernstein.[43] The values used for the bond lengths and angles in ketene were those reported by Arendale and Fletcher,[44] and the values used for diazomethane were taken from the values given by Fletcher and Garrett[45] and by Cox, Sheridan, and Thomas.[46]

SYMBOLIC $\mathcal{G}$ MATRIX FOR FORMALDEHYDE

$\mathcal{G}$	S_{CH}	S_{CO}	S_{β}	S'_{CH}	S'_{β}	S_{ψ}
S_{CH}	$\frac{1}{2}(\mu_1+\mu_2) + 2\Gamma^2\mu_C$	$-\frac{2\Gamma}{\sqrt{2}}\mu_C$	$\frac{2\Sigma\Gamma}{r_{CH}}\mu_C$	$\frac{1}{2}(\mu_1-\mu_2)$	0	0
S_{CO}		$\mu_C + \mu_O$	$-\frac{2\Sigma}{\sqrt{2}r_{CH}}\mu_C$	0	0	0
S_{β}			$\frac{1}{2r_{CH}^2}(\mu_1+\mu_2) + \frac{2\Sigma^2}{r_{CH}^2}\mu_C$	0	$\frac{1}{2r_{CH}^2}(\mu_1-\mu_2)$	0
S'_{CH}				$\frac{1}{2}(\mu_1+\mu_2) + 2\Sigma^2\mu_C$	$-\frac{2\Sigma}{r_{CH}}(\Gamma+\rho)\mu_C$	0
S'_{CO}		(Symmetric)			$\frac{1}{2r_{CH}^2}(\mu_1+\mu_2) + \frac{2\rho^2}{r_{CH}^2}\mu_O + \frac{2(\Gamma+\rho)^2}{r_{CH}^2}\mu_C$	0
S_{ψ}						$\frac{1}{4(\Gamma r_{CH})^2}(\mu_1+\mu_2) + \frac{(\rho\Gamma)^2}{(\Gamma r_{CH})^2}\mu_O + \frac{(1+\rho\Gamma)^2}{(\Gamma r_{CH})^2}\mu_C$

SYMBOLIC $\mathcal{G}$ MATRIX FOR KETENE

$\mathcal{G}$	S_{CH}	S_{CC}	S_{CO}	S_β	S'_{CH}	S'_β	S_δ
S_{CH}	$\frac{1}{2}(\mu_1+\mu_2)+2\Gamma^2\mu_C$	$-\frac{2\Gamma}{\sqrt{2}}\mu_C$	0	$\frac{2\Sigma\Gamma}{r_{CH}}\mu_C$	$\frac{1}{2}(\mu_1-\mu_2)$		
S_{CC}		$2\mu_C$	$-\mu_C$	$-\frac{2\Sigma}{\sqrt{2}r_{CH}}\mu_C$			
S_{CO}			$\mu_C+\mu_O$	0			
S_β				$\frac{1}{2r_{CH}^2}(\mu_1+\mu_2)$ $+\frac{2\Sigma^2}{r_{CH}^2}\mu_C$		$\frac{1}{2r_{CH}^2}(\mu_1-\mu_2)$	
S'_{CH}					$\frac{1}{2}(u_1+u_2)$ $+2\Sigma^2\mu_C$	$-\frac{2\Sigma(\Gamma+\rho)}{r_{CH}}\mu_C$	$\frac{2\Sigma}{\sqrt{2}r_{CC}}\mu_C$
S'_β		(Symmetric)				$\frac{1}{2r_{CH}^2}(\mu_1+\mu_2)+$ $\frac{2(\Gamma+\rho)^2+2\rho^2}{r_{CH}^2}\mu_C$	$-\frac{2}{\sqrt{2}r_{CH}}\left(\frac{\Gamma+2\rho}{r_{CC}}+\frac{\rho}{r_{CO}}\right)u_C$
S_δ							$\left(\frac{1}{r_{CC}}+\frac{1}{r_{CO}}\right)^2\mu_C+$ $\frac{1}{r_{CO}^2}\mu_O+\frac{1}{r_{CC}^2}\mu_C$

$= \frac{r_{CH}}{r_{CC}}$

SYMBOLIC $\mathcal{G}$ MATRIX FOR DIAZOMETHANE

$\mathcal{G}$	S_{CH}	S_{CN}	S_{NN}	S_β	S'_{CH}	S'_β	S_δ
S_{CH}	$\frac{1}{2}(\mu_1+\mu_2)+2\Gamma^2\ \mu_C$	$-\frac{2\Gamma}{\sqrt{2}}\ \mu_C$	0	$\frac{2\Sigma\Gamma}{r_{CH}}\ \mu_C$	$\frac{1}{2}(\mu_1-\mu_2)$		
S_{CN}		$\mu_C+\mu_N$	$-\mu_N$	$-\frac{2\Sigma}{\sqrt{2}r_{CH}}\ \mu_C$			
S_{NN}			$2\ \mu_N$	0			
S_β				$\frac{1}{2r_{CH}^2}(\mu_1+\mu_2)$ $+\frac{2\Sigma^2}{r_{CH}^2}\ \mu_C$		$\frac{1}{2r_{CH}^2}(\mu_1-\mu_2)$	
S'_{CH}					$\frac{1}{2}(\mu_1+\mu_2)$ $+\ 2\Sigma^2\ \mu_C$	$-\frac{2\Sigma(\Gamma+\rho)}{r_{CH}}\ \mu_C$	$\frac{2\Sigma}{\sqrt{2}r_{CN}}\ \mu_C$
S'_β		(Symmetric)				$\frac{1}{2r_{CH}^2}(\mu_1+\mu_2)+$ $\frac{2(\Gamma+\rho)^2}{r_{CH}^2}\mu_C+\frac{2\rho^2}{r_{CH}^2}\mu_N$	$-\frac{2(\Gamma+\rho)}{\sqrt{2}r_{CH}r_{CN}}\ \mu_C$ $-\frac{2\rho}{\sqrt{2}r_{CH}}\left(\frac{1}{r_{CN}}+\frac{1}{r_{NN}}\right)\ \mu_N$
S_δ						$\rho = \frac{r_{CH}}{r_{coc}}$	$\frac{1}{r_{CN}^2}\ \mu_C\ \frac{1}{r_{NN}^2}\ \mu_N\ +$ $\left(\frac{1}{r_{CN}}+\frac{1}{r_{NN}}\right)^2\ \mu_N$

SYMBOLIC $\mathcal{G}$ MATRIX FOR DIAZOMETHANE (Continued)

$\mathcal{G}$	S_ϵ	S_ψ
S_ϵ	$\frac{1}{r_{CN}^2}\mu_C + \frac{1}{r_{NN}^2}\mu_N + \left(\frac{1}{r_{CN}} + \frac{1}{r_{NN}}\right)^2 \mu_N$	$\frac{(1+\rho\Gamma)}{\Gamma r_{CH} r_{CN}}\mu_C + \frac{\rho\Gamma}{\Gamma r_{CH}}\left(\frac{1}{r_{CN}} + \frac{1}{r_{NN}}\right)\mu_N$
S_ψ	(Symmetric)	$\frac{1}{4(\Gamma r_{CH})^2}(\mu_1+\mu_2) + \frac{(1+\rho\Gamma)^2}{(\Gamma r_{CH})^2}\mu_C + \frac{(\rho\Gamma)^2}{(\Gamma r_{CH})^2}\mu_N$

SYMBOLIC $\mathcal{G}$ MATRIX FOR KETENE (Continued)

$\mathcal{G}$	S_ϵ	S_ψ
S_ϵ	$\frac{1}{r_{CC}^2}\mu_C + \frac{1}{r_{CO}^2}\mu_O + \left(\frac{1}{r_{CC}} + \frac{1}{r_{CO}}\right)^2 \mu_C$	$\frac{1}{\Gamma r_{CH}}\left(\frac{1+2\rho\Gamma}{r_{CC}} + \frac{\rho\Gamma}{r_{CO}}\right)\mu_C$
S_ψ	(Symmetric)	$\frac{1}{4(\Gamma r_{CH})^2}(\mu_1+\mu_2) + \frac{(1+\rho\Gamma)^2 + (\rho\Gamma)^2}{(\Gamma r_{CH})^2}\mu_C$

NUMERICAL $\mathcal{G}$ MATRICES FOR CH_2O, CD_2O AND CHDO

$\mathfrak{G}$	S_{CH}	S_{CO}	S_β	S'_{CH}	S'_β	S_φ
S_{CH}	1.0294386 0.7816483 0.5338580	-0.0559026	0.0649778	0 0.2477903 0		
S_{CO}		0.1458069	-0.0968306			
S_β			0.9773168 0.7612914 0.5452658		0 0.2160257 0	
S'_{CH}				1.1210228 0.8732325 0.6254422	-0.1847021	
S'_β					1.2123195 0.9962922 0.7802680	
S_φ						2.6078002 2.1280636 1.6483269

The matrix is symmetric. In blocks where three figures appear, the first is for CH_2O, the second for CHDO, and the third for CD_2O.

NUMERICAL $\mathcal{G}$ MATRICES FOR CH_2CO, CD_2CO AND CHDCO

$\mathcal{G}$	S_{CH}	S_{CC}	S_{CO}	S_β	S'_{CH}	S'_β	S_δ	S_ϵ	S_ψ
S_{CH}	1.0294536 0.7816633 0.5338730	-0.0559144	0	0.0649875	0 0.2477903 0				
S_{CC}		0.1666138	-0.0833069	-0.0968251					
S_{CO}			0.1458069	0					
S_β				0.9773041 0.7612784 0.5452528		0 0.2160257 0			
S'_{CH}					1.1210078 0.8732175 0.6254272	-0.1753363	0.0780283		
S'_β						1.1972607 0.9812350 0.7652094	-0.2497752		
S_δ							0.3135988		
S_ϵ								0.3135988	-0.2721616
S_ψ									2.5830277 2.1034934 1.6239587

The matrix is symmetric. In blocks where three figures appear, the first is for CH_2CO, the second for CHDCO, and the third for CD_2CO.

NUMERICAL $\mathcal{G}$ MATRICES FOR CH_2N_2, CD_2N_2 AND $CHDN_2$

$\mathcal{G}$	S_{CH}	S_{CN}	S_{NN}	S_β	S'_{CH}	S'_β	S_δ	S_ϵ	S_φ
S_{CH}	1.0250966 0.7773063 0.5295160	-0.0525685	0	0.0618901	0 0.2477903 0				
S_{CN}		0.1546972	-0.0713903	-0.0980791					
S_{NN}			0.1427806	0					
S_β				0.9738198 0.7593938 0.5449728		0 0.2144210 0			
S'_{CH}					1.1253648 0.9549784 0.6297842	-0.1748505	0.0798750		
S'_β						1.1693994 0.9549784 0.7405573	-0.2308964		
S_δ							0.2991858		
S_ϵ								0.2991858	-0.2686466
S_φ									2.8695536 2.3310780 1.7926020

The matrix is symmetric. In blocks where three figures appear, the first is for CH_2N_2, the second for $CHON_2$, and the third for CD_2N_2.

TABLE XXI

GEOMETRICAL PARAMETERS FOR FORMALDEHYDE, KETENE, AND DIAZOMETHANE

Parameter	CH_2O	CH_2CO	CH_2N_2
Bond Lengths (Å)	$r_{CH} = 1.071$	$r_{CH} = 1.071$	$r_{CH} = 1.075$
	$r_{CO} = 1.225$	$r_{CC} = 1.329$	$r_{CN} = 1.320$
		$r_{CO} = 1.150$	$r_{NN} = 1.120$
Bond Angles	$\gamma = 123°21'$	$\gamma = 123°20'$	$\gamma = 127°$
	$\alpha = 61°40'$	$\alpha = 61°40'$	$\alpha = 63°30'$
ϕ	33°08'	34°30'	35°22'
θ	28°33'	27°10'	28°07'
R_e	1.973 Å	2.065 Å	2.041 Å
$\Gamma = \cos\alpha$	0.47450	0.47460	0.44620
$\Sigma = \sin\alpha$	0.88025	0.88020	0.89493
$\sin\phi$	0.54654	0.56648	0.57888
$\cos\phi$	0.83743	0.82408	0.81541
$\sin\theta$	0.47783	0.45650	0.47145
$\cos\theta$	0.87845	0.88772	0.88189
	$\rho = \frac{r_{CH}}{r_{CO}} =$	$\rho = \frac{r_{CH}}{r_{CC}} =$	$\rho = \frac{r_{CH}}{r_{CN}} =$
	0.87429	0.80587	0.81439
		$\mu_O = 0.0625000$	$\mu_N = 0.0713903$

APPENDIX II

FREQUENCY DATA

The values of the fundamental frequencies of the isotopic ethylene molecules which were used in this investigation are, for the most part, the same as those given by Crawford, Lancaster and Inskeep.[16] However, slight changes in some of the band centers have been made on the basis of later values given by Courtoy and de Hemptinne,[47] Charette, Courtoy and de Hemptinne,[48] Stoicheff,[49] and by de Hemptinne and Charette.[50]

The frequencies of the isotopic allene molecules have been summarized by Fletcher and Shuler.[38] Slight adjustments in several band centers have been made on the basis of values reported by Rao, Nielsen and Fletcher,[42] by Overend and Thompson,[51] and by Evans, Wilmshurst and Bernstein.[52]

The frequencies of the isotopic formaldehyde molecules were taken from the values reported by Ebers and Nielsen,[53] by Davidson, Stoicheff and Bernstein,[43] and by Blau and Nielsen.[54] The frequencies of the isotopic ketene molecules which were used in this investigation are those given by Arendale and Fletcher,[44] and the frequencies of the isotopic diazomethane molecules which were used are those given by Fletcher and Garrett.[45]

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VITA

Charles Edward Bailey was born in Johnson City, Tennessee on May 25, 1932. He was educated in the public schools of South Carolina, Pennsylvania, and Tennessee. He was graduated from Science Hill High School in Johnson City in May, 1949. He entered East Tennessee State College the following September, and transferred to the University of Tennessee in 1951, where he received the Bachelor of Science degree in Chemistry in 1953 and the Master of Science degree in 1955.

The author is married to the former Della Ruth McKenzie.

He is a member of the American Chemical Society, Sigma Xi, and Phi Kappa Phi.