

1984

The Intermolecular Force Field of Acetylene-HCl: The Normal Coordinate and Centrifugal Distortion Analysis of Two Weakly Bound Rigid Rods

Rebecca S. Lee

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The Intermolecular Force Field of Acetylene-HCl:
The Normal Coordinate and Centrifugal Distortion
Analysis of Two Weakly Bound Rigid Rods
(TITLE)

BY

Rebecca S. Lee

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SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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CHARLESTON, ILLINOIS

1984
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The Intermolecular Force Field of Acetylene-HCl: The Normal
Coordinate and Centrifugal Distortion Analysis
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By

Rebecca S. Lee

Submitted in
partial fulfillment of the requirements
for the degree of Master of Science in Chemistry
at the Graduate School of Eastern Illinois University
Charleston, Illinois

1984

ABSTRACT

In order to determine the intermolecular force field of $C_2H_2 \cdots HCl$, a normal coordinate analysis appropriate for two weakly bound rigid rods is developed. An exact centrifugal distortion analysis is then carried out on the microwave spectrum of this "T"-shaped hydrogen-bonded π complex. The distortion constants and published matrix-isolated vibrational frequencies are employed in the normal coordinate analysis to obtain the intermolecular force field and refinements in the structural parameters. The following van der Waals force field is found to reproduce the existing spectroscopic constants of $C_2H_2 \cdots H^{35}Cl$:

f_{ij}	Mode	$\Gamma(C_{2v})$	$C_2H_2 \cdots H^{35}Cl$
f_{11} (mdyne/A)	H-bond stretch	A_1	0.0630
f_{22} (mdyne A)	in-plane HCl libration	B_1	0.0522
f_{23} (mdyne A)	in-plane interaction	B_1	0.0302
f_{33} (mdyne A)	C_2H_2 libration	B_1	0.0454
f_{44} (mdyne A)	out-of-plane HCl libration	B_2	0.0544

This study permits the first opportunity to ascertain the effect of complexation on monomer properties in $C_2H_2 \cdots HX/DX$ where $X = F, Cl$. A more accurate description of the quadrupole coupling constant acknowledging the effects of vibrational averaging of the projection operator and changes in $(\partial^2 V / \partial z^2)$ indicate that hydrogen bonding decreases $(\partial^2 V / \partial z^2)$ by 7.8% for Cl in $C_2H_2 \cdots HCl$ and 10% for deuterium in $C_2H_2 \cdots DF$. In the course of this study, D_{HF} and r_{HF} , the spin-spin coupling constant and the H-F bond length, were obtained for the complex. Comparison with r_{HF} in free HF indicates that complexation causes an increase in bond length by 1%.

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INTRODUCTION

Van der Waals complexes have long been the object of considerable study. It has been within the past twenty to thirty years that spectroscopy has advanced such that the spectra of van der Waals complexes can be recorded. The motivation for the spectroscopic study of van der Waals complexes is a description of the forces that hold them together. This study is concerned with extracting a description of the intermolecular force field of the van der Waals complex acetylene-HCl. Determination of the force field will involve an analysis of microwave data obtained previously by A. C. Legon¹ and co-workers at the University of Illinois and infrared data obtained by Lester Andrews² and co-workers at the University of Virginia. The methods used to extract the force field as well as a discussion of the results of the analysis will follow. An experimental section will not be included as the author did not participate in the collection of either the microwave or infrared data. This introduction will serve to acquaint the reader with the study of van der Waals molecules by a discussion of major experimental methods employed in their study. Major emphasis will be placed on those methods which deal with the determination of the intermolecular force fields of van der Waals complexes.

A discussion of van der Waals complexes must begin with some clarification of the terminology involved. Van der Waals complexes are weakly bound aggregates composed of two or more subunits. For the purposes of this study, the term "complex" will be used to describe a dimer whose subunits may vary. These subunits can take the form of noble gas atoms, or

diatomic or polyatomic molecules. Examples of some types of van der Waals complexes are Ar_2 ,³ $(\text{N}_2)_2$,⁴ $\text{He}\cdots\text{I}_2$,⁵ $\text{CH}_3\text{C}_2\text{H}\cdots\text{HF}$.⁶ A fairly complete listing (as of November 1983) of van der Waals complexes that have been studied may be found in Reference 7. Additional new complexes studied include $\text{HCN}\cdots\text{CO}_2$,⁸ $\text{NH}_3\cdots\text{C}_2\text{H}_2$,⁹ $\text{Ar}\cdots\text{NCCN}$,¹⁰ $\text{Ar}\cdots\text{HCN}$,¹¹ and $\text{H}_2\text{O}\cdots\text{CO}_2$.¹²

The types of interactions between the subunits may also vary. They may be dispersion interactions as in the case of Ar_2 ,³ hydrogen bonded π complexes such as $\text{CH}_3\text{C}_2\text{H}\cdots\text{HF}$ ⁶ (the hydrogen atom is pointed directly at the π bond along a line perpendicular to and bisecting the π bond), and charge-transfer complexes such as $\text{C}_6\text{H}_6\cdots\text{I}_2$.¹³ It is the variety of interactions that leads to the intense study of these complexes. The characterization of the strengths of these interactions are of great interest to the scientific community.

These complexes have been studied directly via spectroscopy¹⁴⁻¹⁹ and also indirectly through many physical properties. Their existence has been determined by their effects on spectra and physical properties. The earliest work on van der Waals complexes evolved as a consequence of their effect on many physical properties. With the advent of spectroscopy, more accurate detection and quantitative information about these complexes became available. Table I lists the major spectroscopic methods used to study van der Waals complexes as well as physical properties affected by these complexes. With recent advances in technology, spectroscopy has become the principal tool used in the study of these complexes and thus will be the focus of the introduction.

The amount and type of information available from spectroscopy varies with the type of method. Of the various spectroscopic methods, nuclear magnetic resonance, mass spectroscopy, electron, neutron and x-ray diffrac-

Table I. Methods of Investigating van der Waals Complexes

<u>Spectroscopy</u>	<u>Physical Properties</u>
Electron Diffraction	Solubility
Neutron Diffraction	Density
X-Ray Diffraction	Viscosity
Laser Induced Fluorescence	Heats of Reaction
Mass Spectroscopy	Conductivity
NMR	Melting Point
UV-Visible	Molar Refraction
Raman	Diamagnetic susceptibility
Infrared	Dielectric constant
Molecular Beams	
Microwave	

tion are marginal in terms of detection and quantitative information on van der Waals complexes, particularly hydrogen bonded complexes.

In nuclear magnetic resonance (NMR), the anomalous chemical shifts of certain protons are indicative of their participation in hydrogen bonding, a type of van der Waals interaction.¹⁴ The merging of signals in the NMR can be an indication of formation and dissociation of van der Waals complexes. The fact that this can be observed indicates a short life time relative to the time scale of the experiment. The line widths of NMR signals, which are a function of relaxation times T_1 and T_2 (longitudinal and transverse relaxation time), are affected by complexation.¹⁴ Formation of complexes tends to freeze the immediate environment of a molecule, thus requiring more time for nuclei in an upper energy state to transfer their energy to the surrounding lattice of electrons and nuclei. As these relaxation times increase, the line width increases. Thus examination of the NMR can reveal the existence of van der Waals complexes.

Mass spectroscopy has been used to detect and measure concentrations of van der Waals complexes. Leckenby and Robbins have studied concentrations of both rare gas and polyatomic van der Waals dimers.^{20,21} Their instrumentation, designed to distinguish between true dimers formed and those produced as a result of ion-atom interactions within the spectrometer, determined dimer concentrations which are in reasonable agreement with calculated values.^{21,22} This method will be shown later, used in conjunction with molecular beams to provide a powerful tool in the investigation of van der Waals complexes.

Neutron and X-ray diffraction can also indirectly yield information on van der Waals interactions within the structure of a crystal. Bombardment of the crystal with neutrons and X-rays can yield information particularly on the location of hydrogen atoms. The location of the

hydrogen atom can yield information as to whether it is involved in hydrogen bonding. It is also possible to determine hydrogen bond distances in complexes found in crystals.¹⁴ Electron diffraction studies can also yield information on van der Waals complexes.¹⁸ The interference pattern obtained when an electron beam is crossed into a molecular beam containing rare gas van der Waals molecules can be analyzed for the vibrationally averaged separation distance between the subunits of the complex.²³⁻²⁶ This method can be expected to yield even more information in future studies as more extensive van der Waals complexes are studied.

Laser induced fluorescence and UV-visible spectroscopy are other more substantial sources of information on van der Waals complexes. The vacuum ultraviolet spectrum of gaseous argon is a classic example of ultraviolet spectroscopy of van der Waals complexes.³ Additional structures that appear in the line spectra of argon are due to transitions between the vibrational and rotational levels of the rare gas van der Waals complex Ar_2 . Thus, the molecular potential function and the dissociation energy of the complex can be calculated from the vibrational fine structure observed. Laser induced fluorescence provides vibronic spectra which can be used to characterize the various electronic states of van der Waals complexes. Smalley and coworkers have measured the laser induced fluorescence spectrum of $\text{He}\cdots\text{I}_2$ and analyzed the vibronic structure for information on the electronic states of the complex.⁵

Of the spectroscopic methods listed in Table 1, molecular beams, Raman, infrared and microwave spectroscopy provide data that can be analyzed to yield the intermolecular force field of a van der Waals complex. Raman spectroscopy has the potential to yield force field data, but its potential has yet to be realized due to difficulty in data analysis. The scattering

due to van der Waals complexes is weak and often obscured by the scattering due to the subunits.¹⁶

Molecular beams, infrared and microwave spectroscopy are the three major sources of force field data for van der Waals complexes. The remainder of this section will detail how these three methods are used to study van der Waals complexes for the purpose of obtaining the intermolecular force field.

Infrared spectroscopy is generally used when the force field of a molecule is under investigation. By using what is known as a normal coordinate analysis,²⁷⁻²⁹ it is possible to relate the force constants to the observed vibrational frequencies. However, due to the nature of van der Waals complexes, it is necessary to depart from the usual infrared techniques to obtain their spectra. This is due to the fact that van der Waals complexes are weakly bound species; i.e., the intermolecular bonds are weaker, hence the force constants for these bonds are smaller. Recalling that the vibrational frequencies are a function of k , the force constant, it is evident that van der Waals frequencies will be significantly smaller than those in conventional molecules. Another factor to be considered is the very small change in dipole moment due to van der Waals vibration. This will result in very weak transitions as the intensity is a function of the change in dipole moment.

Despite these limitations, the infrared spectra of van der Waals molecules have been observed. Two approaches have been used to obtain the spectra of these complexes--matrix isolation studies and LPLS (long path length spectroscopy).

LPLS (long path length spectroscopy) provides a means of obtaining infrared spectra for complexes whose monomers possess no dipole moment. This can be achieved by the modulation of an electric dipole induced by

the proximity of a van der Waals partner (or collision partner). If the incoming monomer has a quadrupole moment, it will induce a dipole moment in the target monomer. It is also possible that upon collision, electron density between the two monomers will overlap and become distorted, giving rise to a dipole in the complex. The dipole created as a result of these effects is then altered by the van der Waals vibration and can interact with the incident radiation, thus giving rise to an infrared spectrum.

In order to achieve sufficient concentrations so as to record a spectrum, conditions must be optimum for dimer formation. The gas samples are cooled to very low temperatures (less than 100K) to achieve this.³⁰ Large amounts of gas samples are required to obtain a sufficient optical density of dimer to record the weak spectrum. To further optimize conditions for recording the infrared spectrum, an extremely long path length cell is used. Early LPLS experiments involved cells up to 220m in length.³¹ These cells were constructed out of steel drums that literally stretched the length of a city block.³² The LPLS cell designed by Blickens-derfer, et. al.³³ avoided this by the use of White optics which permit multiple transversals in a cell a fraction of the length of the earliest LPLS cells. This LPLS cell (located at Indiana University) will generate variable path lengths up to 230m in a 38m cell.³³

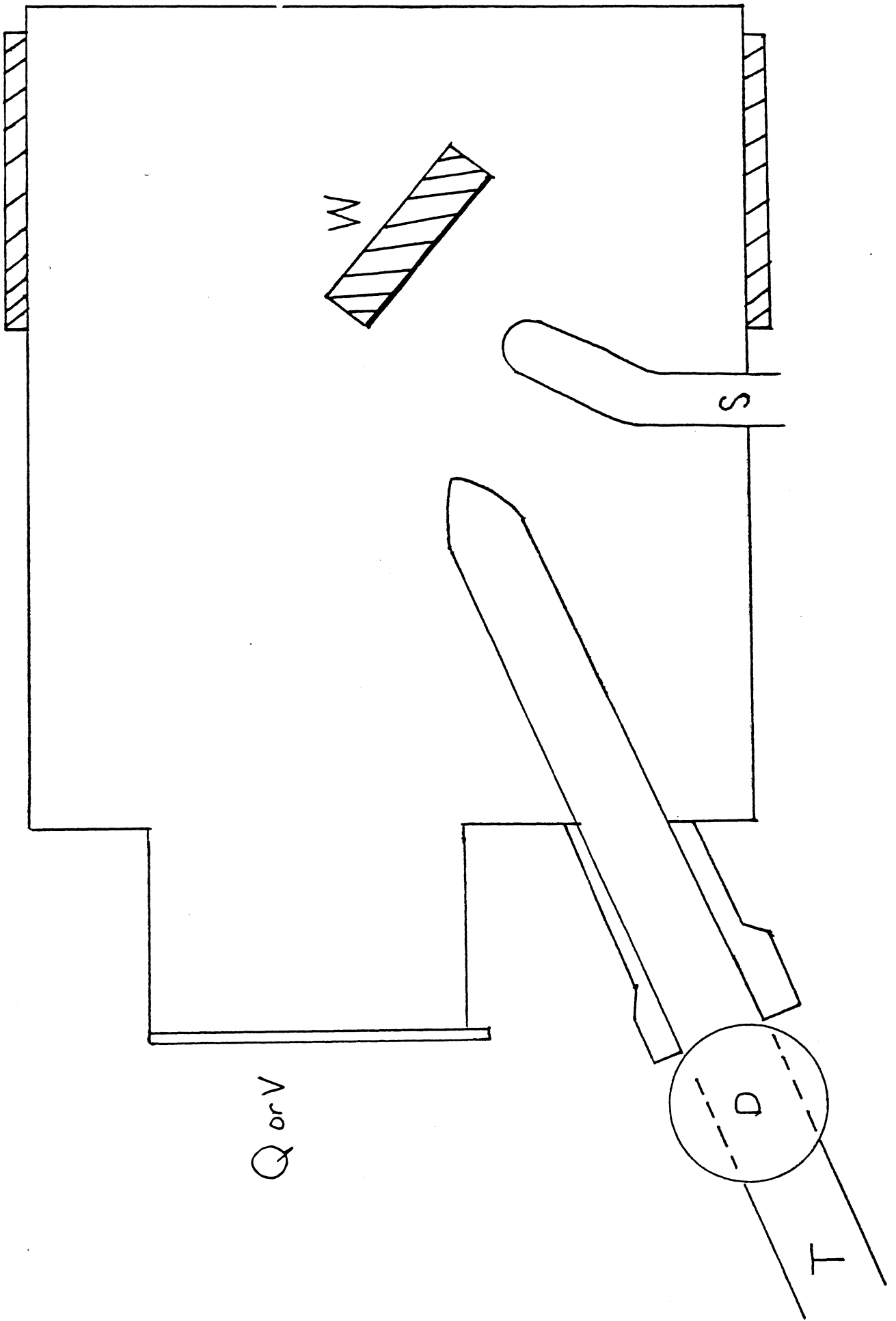
The data obtained from LPLS can be analyzed for force constants. Primarily, the rotational fine structure is analyzed to determine molecular geometry and energy levels of van der Waals complexes. These spectra are characteristically complex with many unresolved features due to the large Boltzmann population of excited van der Waals modes. Moreover the spectral lines are typically broad due to the relatively short lifetime of weak complexes in a static gas; i.e. typical collision energies are sufficient to dissociate them.

Another direct source of vibrational frequencies for complexes is matrix isolation infrared spectra. This method was developed for the study of reactive, unstable species by Pimentel and coworkers.³⁴ It has most recently been used by L. Andrews to study van der Waals complexes.

In the technique employed by Andrews,^{35,36} the monomers of interest are diluted with argon and sprayed onto a cold CsI window in a vacuum. This entire assembly resides inside a vacuum vessel maintained at 14K. Infrared spectroscopy can be done during or after the deposition of the monomer/argon samples. The vacuum cell used by Andrews is shown in Fig. (1.1).

The argon serves to trap and contain species which might not otherwise survive in order to obtain spectra. Argon is not a unique choice as a matrix. Becker and Pimentel have detailed the desired criteria for a matrix.³⁵ In order for a matrix to be useful, it must be chemically inert with respect to the species it will contain. The matrix must accommodate and contain the trapped species. This factor will be influenced greatly by temperature. Another property of matrices which is also influenced by temperature is its light scattering ability. A matrix should not scatter a large amount of incident light and should be transparent in the region of interest. The matrix must also be involatile so as to be used in a vacuum at temperatures below 100K. Another characteristic is the mole ratio of matrix to monomer, M/A.³⁵ This must be determined so as to properly isolate the species to prevent any undesired reactions. Undesired encounters and subsequent reactions are usually limited when the number of nearest neighbors is kept at two or lower. This corresponds to a M/A of 100/1. This will vary, however, according to matrix and monomer studied. The study of vibrational modes in an argon matrix permits infrared active van der Waals

Fig. [1.1] Vacuum Cell utilized by L. Andrews for argon matrix isolated vibrational spectroscopy. The sample is delivered from a gas spray (S) onto the cold CsI window (W). This cell is also designed for argon photolysis experiments by using (D) as the discharge cavity and (T) as the discharge tube. The vacuum port (V) is replaced with a quartz window (Q) during this experiment.



modes to be assigned and characterized. However, the method does have its drawbacks. The matrix atoms may perturb the local force field of the complex which will be reflected in the frequencies observed and in the force constants obtained from these frequencies. The effect of the matrix is to shift the frequencies to a lower value, the shift being roughly 10% of their gas phase values.³⁶ The use of force constants obtained from a matrix isolation infrared spectrum should be done with the above consideration.

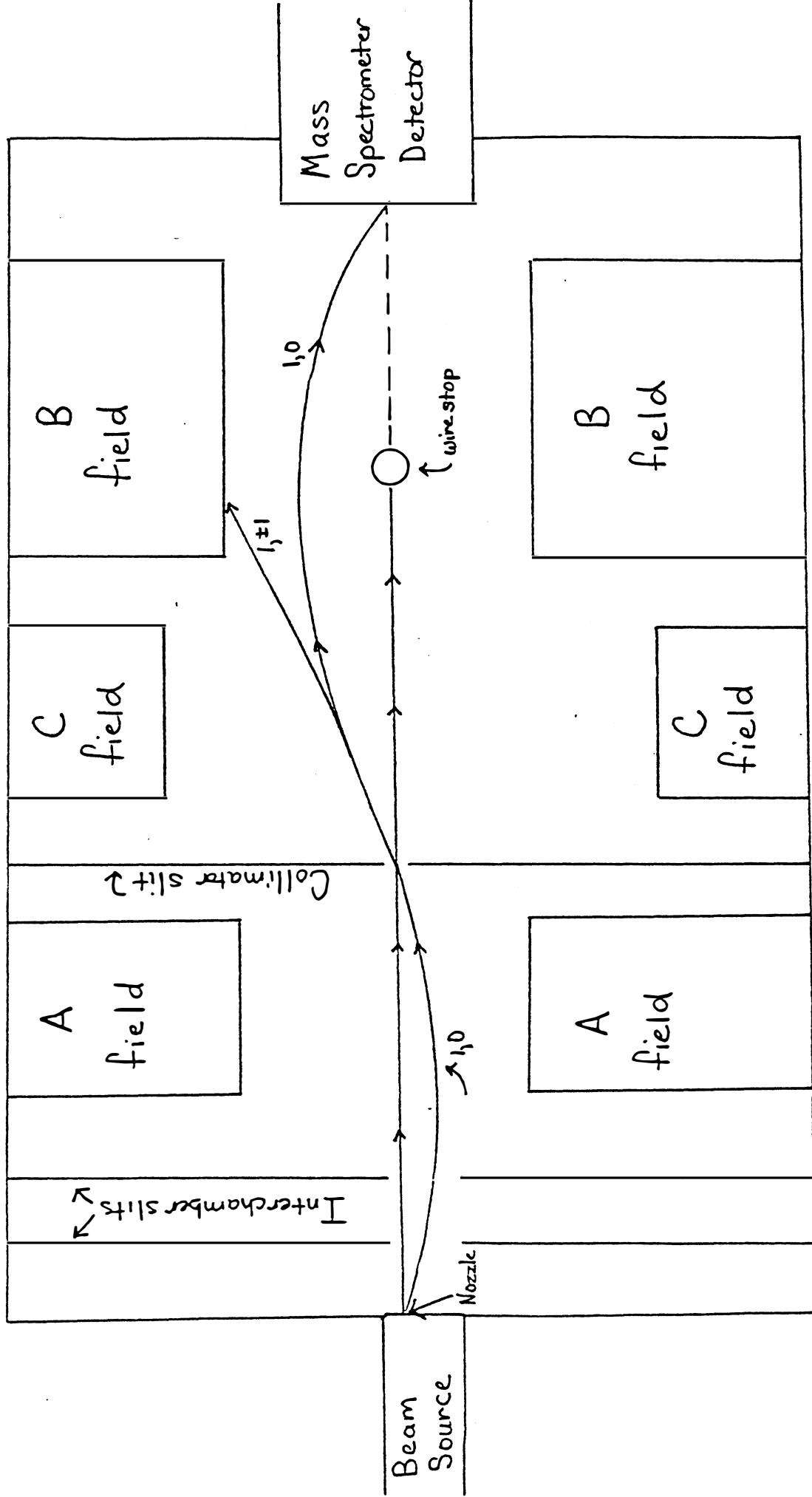
There do exist two spectroscopic methods where it is possible to obtain gas phase data to determine intermolecular force fields for van der Waals complexes. Molecular Beams and microwave spectroscopy provide rotational spectra which can be analyzed for the effects of centrifugal distortion. The results of the centrifugal distortion analysis can be used to obtain an intermolecular force field.

Molecular beams encompass a wide range of experimental methods. A classic discussion of the field can be found in Reference 37. The specific method employed in van der Waals molecules is known as molecular beam electric double resonance spectroscopy. This method, employed by Klemperer, utilizes a supersonic nozzle to deliver the gas samples into the spectrometer where they expand adiabatically. The spectrometer, a Rabi-type molecular beam instrument, involves the use of three electric fields, two inhomogeneous reflecting fields (A & B), separated by a homogeneous field (C). As the molecular beam leaves the nozzle, it enters the first reflecting field at an angle and is deflected slightly. The amount of deflection will depend on the field-induced effective molecular dipole moment, which is also a function of the rotational state of the molecule.³⁷ Thus molecules in different J states will be deflected by different amounts. This deflected

beam then passes through a collimator in the center of the spectrometer and enters the C field. This homogeneous field can oscillate at a given frequency, in this case in the microwave-radio frequency region of the spectrum. As the C field oscillates, transitions between energy levels in the molecule occur when the oscillator frequency is in resonance with the energy level spacings of the molecule. The beam is then passed through another reflecting field, the B field, which focuses the beam onto the detector according to the same principle that applies to the A field. Resonance is detected as a decrease in intensity at the detector, which is a mass spectrometer in the instrument used by Klemperer³⁸ (see Fig (1.2)).

Resonance between the oscillating electric field (C) and the rotational energy levels of a complex gives rise to transitions in the microwave-radio frequency region of the electromagnetic spectrum. Analysis of the rotational spectrum can yield valuable information about complexes provided certain assumptions are made regarding the monomers. In order for the analysis of the rotational spectrum of a van der Waals complex to be tractable, the structure, electrical, and magnetic properties of the monomers are commonly assumed to be unaffected by complexation. This permits the structure, electrical and magnetic properties of the complex to be extracted from the spectrum. When the spectrum is analyzed under these circumstances, the distortion of the complex due to rotation can also be detected. This contribution to the overall rotational spectrum, known as centrifugal distortion, yields distortion constants which can be used to obtain an intermolecular force field. The force constants obtained in this manner are as accurate as the data from which they were obtained. It should be noted that the accuracy of the force field obtained in this manner is generally subject to approximations made in the calculation as opposed to

Fig. [1.2] Diagram of Molecular Beam Electric Double Resonance Spectrometer used by W. Klemperer. Illustrated is the method by which molecules in the $J=0, K=0$ state are selected from the beam by the electrostatic fields.



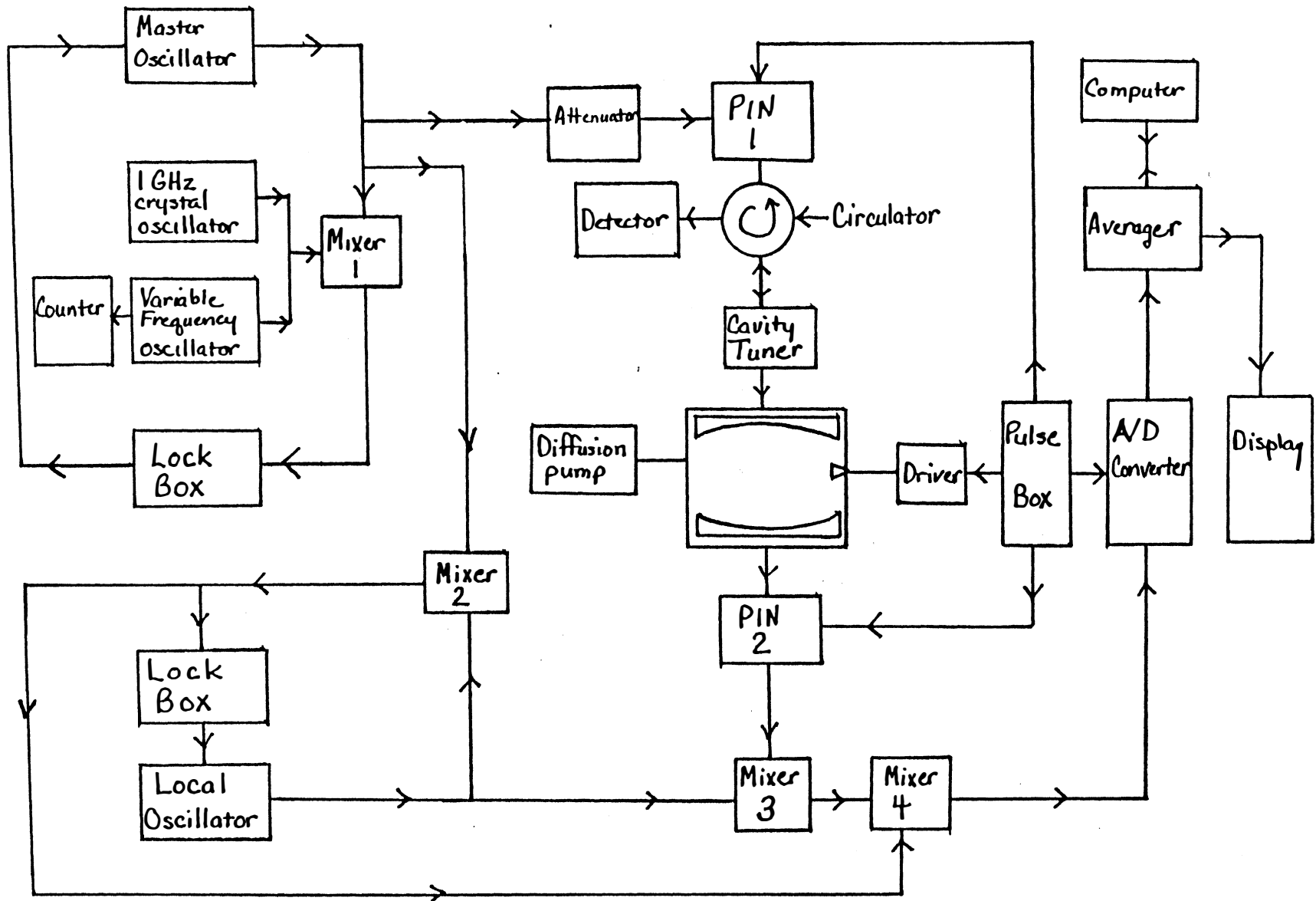
experimental uncertainty, since the method yields rotational frequencies with precisions of 10 kHz.

An alternative method developed by T. J. Balle and W. H. Flygare at the University of Illinois offers an even more precise determination of the rotational frequencies of a complex. This method (Flygare-Balle method) also involves obtaining the rotational spectrum of a complex, but the manner in which it is obtained offers greater accuracy.

The rotational spectrum is obtained using a pulsed nozzle, Fabry Perot cavity spectrometer. The theory of this spectrometer has been described in detail elsewhere.⁴⁰⁻⁴³ The gas samples of monomer/carrier gas are pulsed through a supersonic nozzle, causing the gas samples to expand adiabatically into a vacuum. This technique favors low rotational gas temperatures which lead to dimer formation. The gas molecules/dimers expand between two mirrors in a Fabry Perot cavity and are subjected to a microwave pulse which enters the cavity through one of the mirrors. This pulse, containing frequencies over a range of 1 MHz, is the monochromatic radiation that emerges from the source compressed over time. As this pulse travels through the gas sample, it is possible for resonance to occur between frequencies of this pulse and frequencies due to transitions between energy levels in the gas sample. After the pulse has dissipated, molecular coherent emission due to free inductive decay occurs and is detected using a super heterodyne detector. These data are digitized, stored and later corrected for background. This cycle is repeated until a sufficient number of pulses is obtained. These data are averaged and the frequency spectrum is obtained by a fourier transform. A diagram of the spectrometer is shown in Fig (1.3).

The rotational spectra obtained in this manner for complexes has been analyzed under the same constraints as in molecular electric double resonance. The electrical and magnetic properties of complexes as well as

Fig. [1.3] Block Diagram of the major components of the Flygare-Balle
Microwave Fourier transform spectrometer.



molecular structure can be determined from the spectrum. Distortion of molecular structure due to rotation can also be detected in the spectral analysis to yield distortion constants to be analyzed for force constants. The intermolecular force field determined here will have uncertainty due to model approximations. The experimental uncertainty in frequencies measured on the Flygare-Balle spectrometer is reported as 5-10 kHz; however, it resolves hyperfine structure more completely than the spectrometer used by Klemperer.

The major spectroscopic methods for obtaining data for the extraction of intermolecular force fields have been described briefly to acquaint the reader with the field. Of the methods described, this study will use matrix isolation infrared data and microwave data from a Flygare-Balle spectrometer to obtain the intermolecular force field of the van der Waals complex $C_2H_2 \cdot HCl$. The next section will detail how these data will be analyzed to yield force constants. It will also be shown that a knowledge of the vibrational force field will permit the first microwave determination of changes in monomer properties due to complex formation.

METHODS

A. Normal Coordinate Analysis of Two Weakly Bound Rigid Rods

In a description of forces between atoms in a molecule or between monomers in a complex, it is extremely important to understand the nature of the motions or degrees of freedom within the molecule or complex, i.e. vibrations. These motions can be directly tied to the force field within a molecule or complex. The magnitude and frequencies of the vibrations of a molecule or complex can be analyzed for the force field of a particular molecule or complex. The method of analysis of the vibrational frequencies, known as a Normal Coordinate Analysis, permits the extraction of a force field based on knowledge of vibrational frequencies and structure of the molecule or complex. This section will develop the concepts of a Normal Coordinate Analysis for a chemically bound molecule and for the case of two weakly bound rigid rods (ex: $C_2H_2 \cdot \cdot H^{35}Cl$).

In a normal coordinate analysis, the potential energy of the molecule or complex undergoing vibrations can be written in terms of two types of coordinates, internal coordinates and normal coordinates. Internal coordinates are changes in bond angles or bond lengths, i.e. changes in structural parameters defined with respect to an internal molecular frame whose linear combinations give rise to the vibrational motion of a molecular complex. The choice of internal coordinates for a given molecule or complex is not unique. However the selection of internal coordinates is generally made such that the force field obtained can be related to properties of interest within the molecule or complex. Internal coordinates must also be invariant

to translations and rotations of the active molecule. This constraint must be met such that the potential function written in terms of these coordinates will not be affected by translations or rotations of the entire molecule. The number of internal coordinates may not necessarily coincide with the number of vibrations of a given molecule. This is quite common in highly symmetric molecules such as chloroform⁴⁴ where in one choice of internal coordinates, there are ten internal coordinates and only nine possible modes of vibration.

The second type of coordinates that can be used to write the potential function of a vibrating molecule or complex are called normal coordinates. The value of normal coordinates lies in the fact that the potential and kinetic energies of vibration can be written without off-diagonal cross terms. Normal coordinates are also very concise in that a normal coordinate will encompass all the displacements of the atoms during a vibration. Since the mechanics of complex vibrational motions are best described in terms of normal coordinates while the molecular force field and potential energy are most conveniently written in terms of internal coordinates and the kinetic energy in terms of Cartesian displacement coordinates, transformations between these coordinates would be desirable.

Using internal coordinates (due to their physical significance and the ease in their use), the potential energy of a nonlinear molecule in a harmonic approximation can be written in the following manner:

$$2\underline{V} = \underline{R}' \underline{f} \underline{R} \quad (1)$$

where \underline{R} is a vector of $3N-6$ (where N equals the number of atoms) internal coordinates and \underline{f} is the Wilson symmetric square \underline{f} or force constant matrix of order $3N-6$. The kinetic energy of a vibrating nonlinear molecule can

also be written in matrix notation:

$$2T = \dot{\underline{X}}' \underline{M} \dot{\underline{X}} \quad (2)$$

where $\dot{\underline{X}}$ is a $3N-6$ vector whose elements are the derivatives of the cartesian displacement coordinates (Cartesian displacement coordinates are coordinates which can be used to describe the displacements of the atoms in a convenient coordinate system) and M is a square diagonal matrix of order $3N-6$ whose elements are the masses of all the atoms in the molecule, each being present three times.

It is possible to convert between the Cartesian displacement coordinates and internal coordinates via eqn (3). Here \underline{R} and \underline{X} are defined as before

$$\underline{R} = \underline{B} \underline{X} \quad (3)$$

and \underline{B} is a rectangular matrix of $3N-6 \times 3N$ whose elements are defined below. Since \underline{B} is rectangular, it is not possible to invert \underline{B} and convert

$$B_{ij} = \partial R_i / \partial X_j \quad (4)$$

directly to internal coordinates unless the Eckart conditions are incorporated into \underline{B} . The Eckart conditions⁴⁵⁻⁴⁷ (zero net translation or rotation of the molecule in a vibration) add 6 additional rows to the \underline{B} matrix corresponding to the 3 degrees of translation and 3 degrees of rotation in the case of a nonlinear molecule.

Having the ability to convert from Cartesian displacement coordinates to internal coordinates, it is now possible to write eqn (2) in internal coordinates. Using eqn (3), the kinetic energy is written as:

$$2T = \dot{\underline{R}}' \underline{K} \dot{\underline{R}} \quad (5)$$

where \underline{K} is a symmetric square matrix of order $3N-6$ as defined below:

$$\underline{K} = [\underline{B} \underline{M}^{-1} \underline{B}']^{-1} = \underline{G}^{-1} \quad (6)$$

The \underline{K} matrix is the inverse of the Wilson \underline{G} matrix, a symmetric square matrix of order $3N-6$.

Having expressed the potential and kinetic energies as a function of the internal coordinates in the limit of a harmonic oscillator model, it is now possible to construct an equation of motion using Lagrange's equation, eqn (7), in a form appropriate for internal coordinates:²⁷

$$\frac{\partial}{\partial t} \left(\frac{\partial T}{\partial \dot{R}_i} \right) + \frac{\partial V}{\partial R_i} = 0 \quad (7)$$

where i denotes the i th internal coordinate. Substitution of eqns (5) and (1) and simplification of i equations yields i second order differential equations to be solved simultaneously.

$$\underline{f} \underline{R} + \underline{K} \underline{\ddot{R}} = 0 \quad (8)$$

An appropriate solution to eqn (8) involves expressing the elements of the \underline{R} matrix, $R_i(t)$ in terms of a cosine function. Expressions for these elements are shown below along with the appropriate derivatives with respect to time.

$$R_i(t) = \ell_{ij} \cos(2\pi\nu_j t + \theta) \quad (9)$$

$$\dot{R}_i(t) = -2\pi\nu_j \ell_{ij} \sin(2\pi\nu_j t + \theta) \quad (10)$$

$$\ddot{R}_i(t) = -4\pi^2 \nu_j^2 \ell_{ij} (\cos 2\pi\nu_j t + \theta) \quad (11)$$

ℓ refers to the amplitude of the function and its subscripts i and j refer to the number of internal coordinates and the number of vibrations respec-

tively. θ is the phase factor of the wave function and ν is the frequency of the j th vibration. The solution of eqn (8) using eqns (9) - (11) yields $3N-6$ eqns of the form of eqn (12), where $\lambda_j = 4\pi^2\nu_j^2$.

$$[f_{ij} - \lambda_j K_{ij}]l_{ij} = 0 \quad (12)$$

The $3N-6$ equations in the form of eqn (12) can be cast in a matrix form and a solution obtained by left multiplying the terms within the brackets by $\underline{K}^{-1}(\underline{G})$.

$$[\underline{f} - \underline{\Lambda} \underline{K}] \underline{L} = 0 \quad (13)$$

$$[\underline{G} \underline{f} - \underline{\Lambda}] \underline{L} = 0 \quad (14)$$

$$\underline{G} \underline{f} \underline{L} = \underline{L} \underline{\Lambda} \quad (15)$$

In eqn (15), \underline{L} and $\underline{\Lambda}$ are matrices of order $3N-6$ whose elements are the terms l_{ij} and λ_j that appeared in eqn (12). The matrices \underline{G} and \underline{f} are as defined earlier.

The significance of eqn (15) is immediately evident. The frequencies of the vibrations of a molecule or a complex can be determined if the \underline{f} and \underline{G} matrices are known and their product can be diagonalized. Before the method of solving eqn (15) is discussed, it would be appropriate to discuss the nature of the \underline{G} and \underline{f} matrices in more detail.

The \underline{f} Matrix. The \underline{f} matrix is a symmetric (Hermitian) square matrix of order $3N-6$ whose elements are the force constants that describe the vibrations of a molecule or a van der Waals complex.

The structure of the \underline{f} matrix consists of diagonal and off-diagonal elements. The diagonal elements are the force constants that relate how much force is required to cause a change in a given internal coordinate. The off-diagonal elements are called interaction constants; these relate

how the change in bond length or bond angle can affect the force required to change other bond lengths or bond angles in the molecule or complex. The assignment of non-zero values to interaction constants is not a simple process for most molecules and complexes. There do exist a few general guidelines in the determination of non-zero interaction constants. One consideration which is important is the relative proximity of the two motions. It is highly unlikely that a change in bond length would affect a change in bond angle more than three or four atoms away. However, this type of rationale must be invoked with caution. Another guideline is that there must be a one-to-one correspondence between the \underline{f} matrix elements and \underline{G} -matrix elements. If any \underline{G} -matrix element is zero, then its corresponding \underline{f} -matrix element must be so.

Using the guidelines mentioned previously, the density of the \underline{f} -matrix would be reduced to the diagonal elements and some selected interaction constants. At this point, the non-zero elements in the \underline{f} matrix are determined by the description of the forces within a molecule or complex. There exist three general approximations to the description of forces within a molecule or complex: the central forces approximation, the valence force approximation and the Urey-Bradley approximation.

The central forces approximation considers all forces acting within a molecule or complex to be acting along lines joining pairs of atoms.²⁸ In this level of approximation, the forces acting on an atom are the total of the attractions and repulsions of other atoms to which it is bonded. The forces vary according to the distances between the atoms along lines (bond lengths) which join these atoms. This approximation is the least sophisticated of the three descriptions of forces within a molecule or complex in that it very poorly describes the forces involved

in bending vibrations. The only advantage to this description lies in the fact that the number of force constants is less than the number of normal vibrations, thus making the problem soluble.

The valence force approximation is an improvement on the central force description in that it contains a more refined description of the forces involved in changing a bond angle. This idea, first proposed by Bjerrum, states that restoring forces act along every valence bond in a molecule and in bonds that join at a common atom to form a bond angle.⁴⁸ In addition to its improved description of the forces, it also has the advantage that the number of force constants used is often less than the number of normal vibrational frequencies, once again making the problem soluble. Due to these advantages, the valence force description is considered the first level of approximation in any normal coordinate analysis.

The most refined description of forces within a molecule or complex is the Urey-Bradley approximation. The Urey-Bradley description builds upon the valence force description by acknowledging the contribution of non-bonding interactions to the forces within a molecule. The density of the \underline{f} matrix under the Urey-Bradley approximation is the maximum permitted by the number of experimental frequencies available. This description is the most refined and complete of the three approximations.

In the description of the \underline{f} matrix, it has been shown that the forces used to describe the vibrations of a molecule or complex can be modified through the use of diagonal and off-diagonal elements to reproduce the normal vibrational frequencies. However, the vibrational frequencies are not solely dependent on the forces within a given molecule or a complex. The equilibrium geometry of a molecule or a complex also makes a significant contribution to the normal frequencies through the \underline{G} matrix, which will be described in the next section.

The \underline{G} Matrix. The \underline{G} matrix is the inverse of the kinetic energy matrix in eqn (6). By taking the inverse of eqn (6), it is possible to define \underline{G} in the following manner:

$$\underline{G} = \underline{B} \underline{M}^{-1} \underline{B}' \quad (16)$$

where \underline{B} is the rectangular matrix ($3N-6 \times 3N$) that transforms cartesian displacement coordinates into internal coordinates, \underline{B}' denotes B-transpose and \underline{M} is a diagonal square matrix of order $3N$ where the mass of each atom appears three times.

In the case of most chemically bound molecules, however, it is not necessary to revert to eqn (16) to derive the \underline{G} matrix. Each \underline{G} matrix element is composed of two \underline{B} matrix elements which in turn coorespond to two internal coordinates. There are many combinations of internal coordinates that occur frequently in chemically bound molecules, thus general formulas for these elements are available.^{28,49} For more geometrically complete molecules of low symmetry, the \underline{G} matrix elements are constructed by deriving the \underline{B} matrix using eqn (16). This approach has also been employed on many occasions to derive the \underline{G} matrix for van der Waals complexes. The derivation of the \underline{B} matrix utilizes the s-vector method, simultaneously developed by Wilson⁵⁰ and Eliashevich,⁵¹ which will be discussed in the next section.

The "s" Vector Method--Derivation of B

In the derivation of the \underline{B} matrix using the "s" vector method, eqn (17) is the point from which the derivation begins. This equation states that for a given set of Cartesian displacement coordinates there exist coefficients B_{ti} that will properly mix these displacements such that the summation of the product of these two quantities will generate R_t , one of the $3N-6$ internal coordinates.

This equation is then rewritten such that the three Cartesian displacement coordinates used to describe each atom α 's displacement are replaced by a vector, ρ_α , whose components along the three axes of the Cartesian frame are the Cartesian displacement coordinates of the atom α . The elements

$$R_t = \sum_{i=1}^3 B_{ti} X_i \quad t = 1, 2, \dots, 3N-6 \quad (17)$$

B_{ti} , every three being associated with an atom α , are also converted into a vector, $s_{t\alpha}$, which cares about an internal coordinate t and an atom α . Thus eqn (17) can be rewritten in the following manner:

$$R_t = \sum_{\alpha=1}^N s_{t\alpha} \cdot \rho_\alpha \quad (18)$$

where R_t is now expressed as the summation of the dot products of these vectors.

The advantages to eqn (18) in relation to deriving \underline{B} are not immediately clear. There is no need to define a reference frame for the Cartesian displacement coordinates. There are also definite rules for quantifying the vectors $s_{t\alpha}$. In physical terms, $s_{t\alpha}$ is defined in the following manner: all atoms except the α th atom are at equilibrium such that the vector displacement of atom α is in the direction that will produce the greatest increase in R_t and the magnitude of $s_{t\alpha}$, $|s_{t\alpha}|$, is equal to the increase in R_t due to a unit displacement of α in the direction of maximum increase of R_t .²⁸ In terms of the derivation of B-matrix elements, when the vector $s_{t\alpha}$ is resolved in the same Cartesian frame as the Cartesian displacement coordinates, the components along the three axes are the \underline{B} matrix elements.

The $s_{t\alpha}$ vectors have been worked out for the four most frequently encountered internal coordinates in chemically bound molecules.^{28,29} The $s_{t\alpha}$ vectors for bond stretching and bond bending will be described in

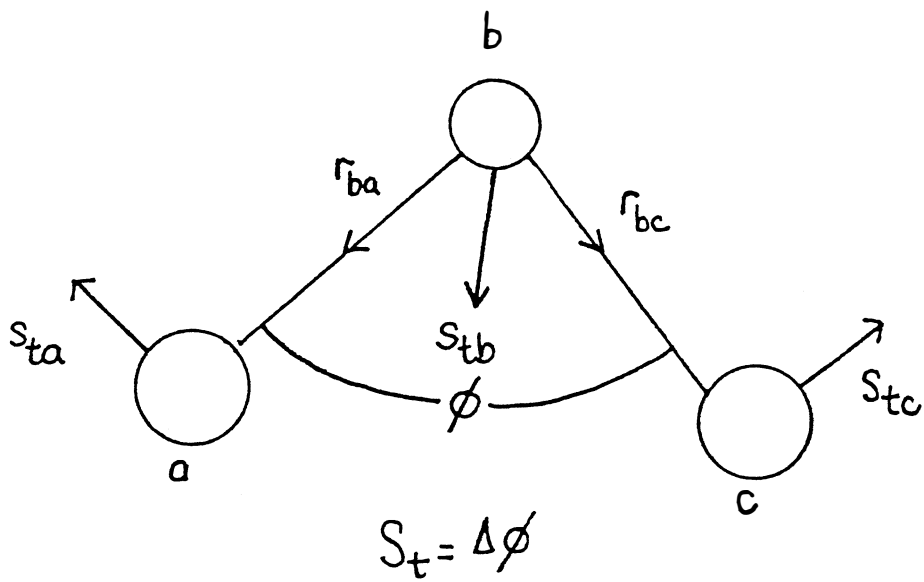
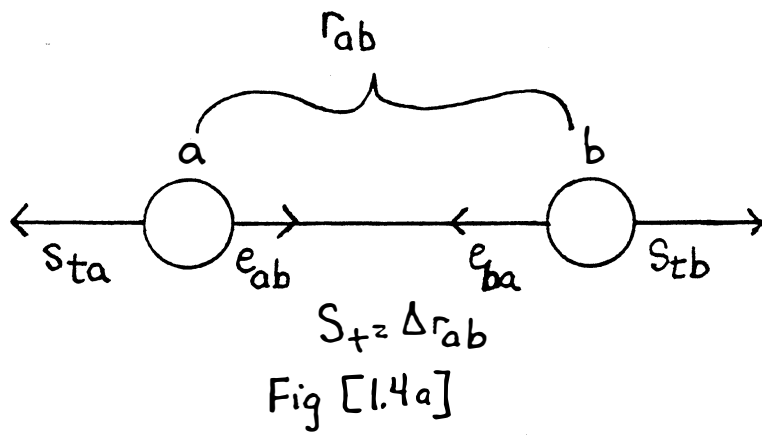
detail. The derivation of the $s_{t\alpha}$ vectors necessary to describe torsion and out-of-plane bending can be found in detail elsewhere.^{28,29}

To illustrate the construction of an $s_{t\alpha}$ vector appropriate for bond stretching, it will be informative to use a simple diatomic molecule as only two atoms are only involved in stretching a bond (see Fig. 1.4a). It is clear from Fig. (1.4a) that the optimum direction for each atom to move so as to increase the bond length is away from the other atom along a line joining the two atoms. The magnitude of the $s_{t\alpha}$ vector appropriate for each atom has previously been defined as the increase in the internal coordinate due to a unit displacement in the most effective direction. If e_{ab} represents a unit vector from atom a to atom b along the bond joining atoms a and b, then the magnitude of the vector s_{ta} is equal to $-e_{ab}$ or in terms of the unit vector from atom b to atom a, e_{ba} . The magnitude of the vector s_{tb} is equivalent to $-e_{ba}$ or e_{ab} .

The construction of the $s_{t\alpha}$ vectors appropriate for the valence angle bending involves three atoms and hence a triatomic molecule like that shown in Fig (1.4b) will be used in the illustration. If construction of the $s_{t\alpha}$ vectors for atoms a and c, s_{ta} and s_{tc} , are considered first, the direction of these vectors will be perpendicular and outward from r_{ba} and r_{bc} respectively. The distances r_{ba} and r_{bc} correspond to the bond lengths between atoms b and a and atoms b and c respectively. The direction of these vectors perpendicular to r_{ba} and r_{bc} will result in the longest increase to the angle defined by r_{ba} and r_{bc} . The magnitudes of s_{ta} and s_{tc} can be calculated by recognizing that an infinitesimal unit displacement in the directions of s_{ta} and s_{tc} will increment ϕ by $1/r_{ba}$ and $1/r_{bc}$ respectively, thus the magnitudes of s_{ta} and s_{tc} are $1/r_{ba}$ and $1/r_{bc}$ respectively.

Fig. [1.4a] Diatomic Molecule-Illustration of $s_{t\alpha}$ vectors for bond stretching.

Fig [1.4b] Triatomic Molecule-Illustration of $s_{t\alpha}$ vectors for valence angle bending.



Calculation of the vector s_{tb} can be simplified by invoking constraints which must be followed in the construction of these vectors. These constraints are known as the Eckart conditions and state that during a vibration the center of mass of the molecule or complex must not shift and that no angular momentum must be imparted to the molecule.⁴⁵⁻⁴⁷ When the Eckart Conditions are invoked in the calculation of the $s_{t\alpha}$ vectors these constraints take the following form:⁵²

$$\sum_{\alpha} s_{t\alpha} = 0 \quad (19)$$

$$\sum_{\alpha} R_{\alpha} \times s_{t\alpha} = 0 \quad (20)$$

where R_{α} is a vector which defines the atom α 's equilibrium position relative to an arbitrary origin and the \times denotes the cross product.

Using eqn (19), it is now possible to determine the magnitude and direction of s_{tc} for the valence angle bending case. The magnitude of s_{tc} must be equivalent to $-(|s_{ta}| + |s_{tb}|)$ since all $s_{t\alpha}$ vectors must obey the constraint of eqn (19). The direction of s_{tc} downward between r_{bc} and r_{ba} is a consequence of eqn (19) such that the center of mass does not shift due to the motions of atoms a and c.

Having derived the $s_{t\alpha}$ vectors for two of the most common coordinates, the components of these vectors resolved into a cartesian reference frame become the elements of the B matrix necessary to calculate G. If the B matrix is not to be utilized in another calculation, the $s_{t\alpha}$ vectors can be utilized directly to calculate the matrix elements of G in the following manner:

$$G_{tt'} = \sum_{\alpha=1}^N \frac{1}{m_{\alpha}} s_{t\alpha} \cdot s_{t'\alpha} \quad \begin{array}{l} N = \text{number of atoms} \\ t, t' = 1, 2, 3 \dots 3N-6 \end{array} \quad (21)$$

where t, t' denote the vibrational modes, N is the number of atoms in the molecule and the dot denotes the scalar product.

This approach is generally the method of choice for all chemically bound molecules and a variety of van der Waals complexes. When this approach is utilized on van der Waals complexes, the internal coordinates of the monomers as well as those of the complex must be considered. This leads to a \underline{G} matrix whose elements are not easily calculated and requires a more elaborate force field (\underline{f} matrix). There have been two occasions where this difficulty has been circumvented. In the calculation of vibrational frequencies of carboxylic acid dimers, Halford⁵³ and Pitzer⁵⁴ have used a "rigid monomer" model to construct the \underline{G} matrix in which only the internal coordinates of the dimer were used. This method led to a much smaller \underline{G} matrix and a smaller number of force constants. The justification for the "rigid monomer" method was that the vibrational frequencies of the monomer were several orders of magnitude larger than the vibrational frequencies of the dimer. This statement is equivalent to saying that the "exact" \underline{G} matrix, one that is constructed using both monomer and dimer internal coordinates, can be factored into two blocks. The two blocks correspond to one which is concerned primarily with the high frequency modes of the monomers and one that is concerned with the low frequency dimer modes. Halford and Pitzer did not, however, begin with the "exact" \underline{G} matrix and block factor it into high and low frequency blocks. Their method, involving a \underline{G} matrix based solely on the internal coordinates of the dimer, achieved the same results as the factoring of the "exact" \underline{G} matrix into high and low frequency blocks.

Since the "rigid monomer" model was first introduced by Halford and Pitzer, it has been rarely used in the analysis of complexes. The large

variety of complexes studied with the advent of Molecular beam electric resonance and pulsed nozzle fourier-transform microwave spectroscopy whose intermolecular force fields have characterized via a normal coordinate analysis have used "exact" \underline{G} -matrices calculated using the s-vector method.^{55,56} The \underline{G} matrices calculated for these complexes have all shown the feature of being blocked off into high and low frequency blocks.

In the study of the intermolecular force field of acetylene-HCl, the "exact" \underline{G} matrix will approximately factor into high and low frequency blocks. Based on this assumption, the \underline{G} matrix is calculated considering only the internal coordinates of the complex and assuming the monomers to be "rigid rods". A description of how the \underline{G} matrix is calculated in the "rigid rod" approximation will be discussed in the next section.

Calculation of the \underline{G} Matrix for Two Weakly Bound Rigid Rods

In the calculation of the \underline{G} matrix for two weakly bound rigid rods, it is necessary to define the rod system and discuss how the degrees of freedom a rod possesses can be utilized to construct internal coordinates for a nonlinear rigid rod complex.

Figure (1.5) shows two rods in an orientation exactly like that of acetylene-HCl (Figure (1.6)). The arrows and coordinates illustrate the fact that a rod requires 5 coordinates to describe its location relative to a reference frame, 3 cartesian coordinates (x,y,z) and two angles (θ, ϕ). If two rods are brought together in an arrangement such as in Figure (1.5), the resulting nonlinear rod complex can easily be shown to have three degrees of rotation and three degrees of translation. In analogy to the treatment used to calculate the number of normal vibrations in a nonlinear molecule, if the number of rods is multiplied by the number of coordinates necessary to describe each rod's location in space and then

Fig [1.5] The ten degrees of freedom and rod displacement coordinates of a two rod "T"-shaped complex and their respective C_{2v} symmetry types.

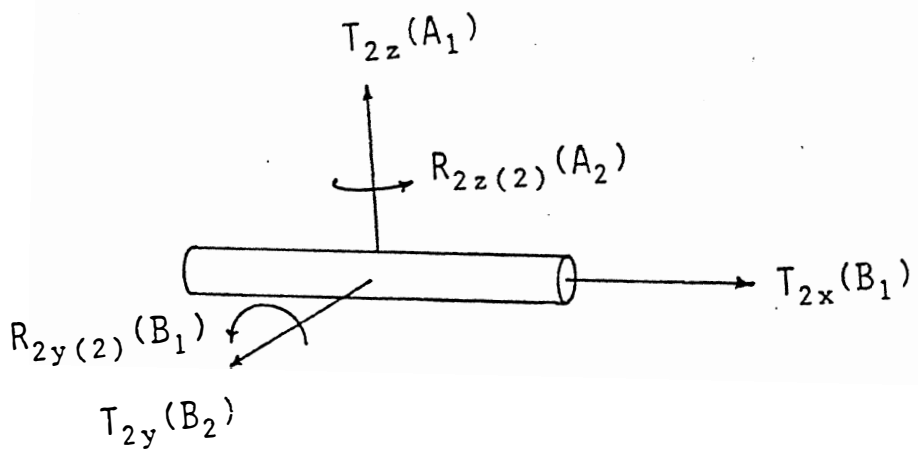
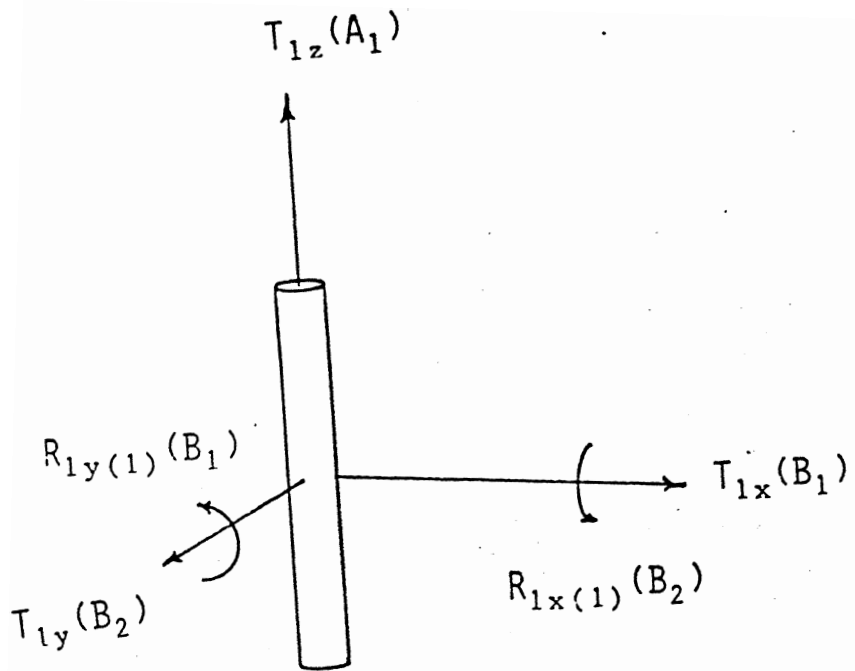
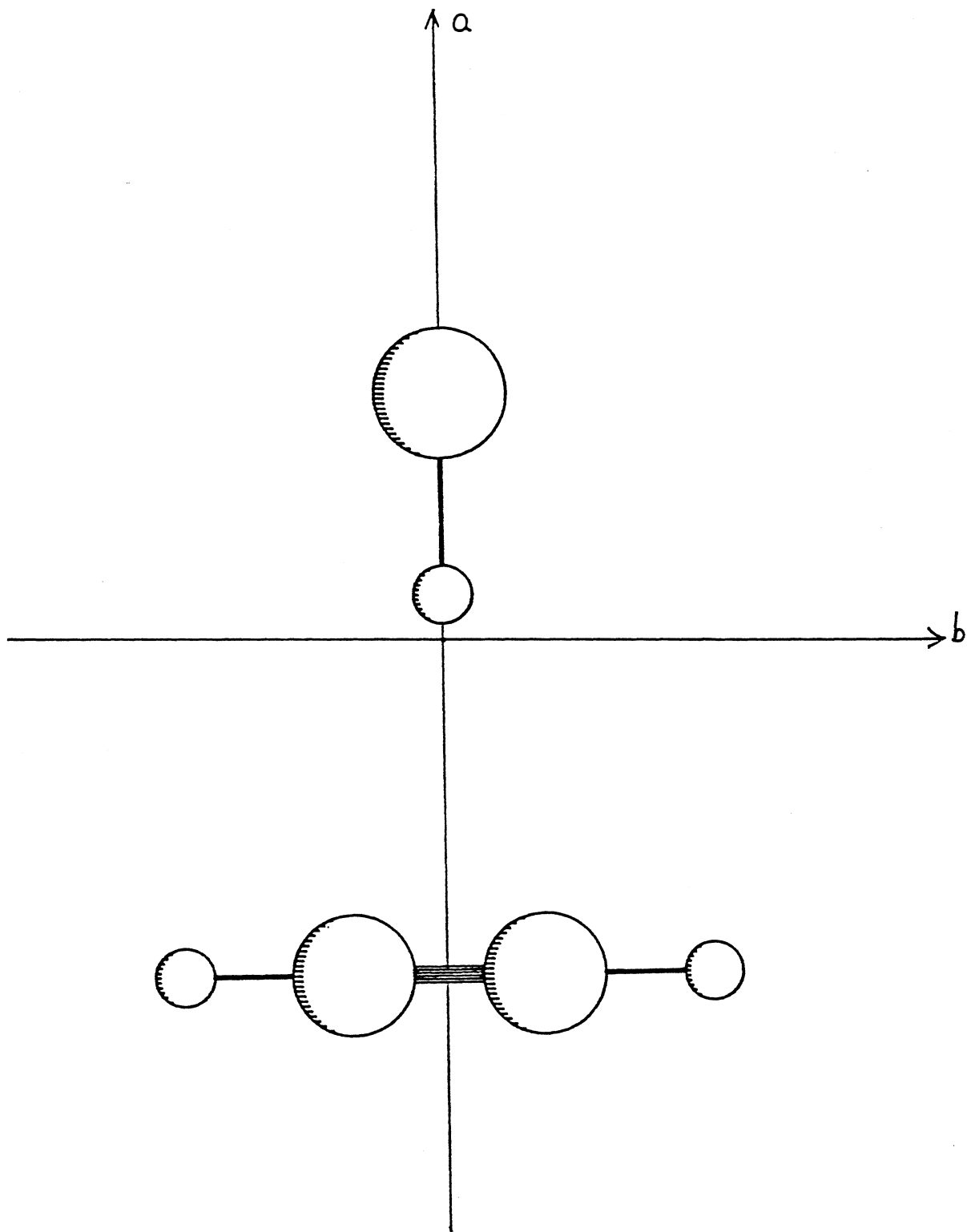


Fig. [1.6] Equilibrium Structure of Acetylene-HCl.



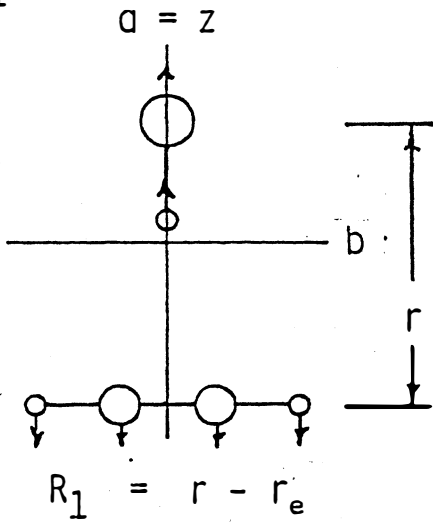
the number of translations and rotations possible for a nonlinear rod system is subtracted from the product, it is possible to obtain the number of normal vibrations for a nonlinear rod complex, $5\rho-6$ (where ρ is the number of rods in the complex). For the nonlinear complex shown in Figure (1.5) there exist 4 normal vibrations.

In describing the normal modes of a rigid rod system, it is necessary as in a chemically bound molecule to choose a set of coordinates in which to construct the kinetic and potential energies of the rod complex. Internal coordinates are chosen for their physical significance and these are illustrated for a nonlinear two-rod system in Figure (1.7). Figure (1.7a) shows R_1 , which is equivalent to a change in distance between centers of mass of the monomers. R_1 is very similar to a change in bond length in chemically bound molecules. The three remaining internal coordinates, R_2-R_4 are librations or rotations of the rods about their centers of mass which give rise to an incrementation of an angle. Librations are somewhat similar to valence bond angle displacements in chemically bound molecules. Each libration in Figure (1.7b-d) shows displacement of both rods. This is due to the fact that in order for the librational modes to be considered proper internal coordinates, these motions must in no way shift the center of mass or impart angular momentum to the complex. Thus, for each libration or rotation of a rod about its center of mass as in Figure (1.4b), there is a simultaneous counter rotation of the other rod about the first rod's center of mass. This "Eckart" counter rotation of the other rod guarantees that no angular momentum is imparted to the complex. Implicit also in Figures (1.7b-d) is the fact that either one or both of the rods must also be translated such that the center of mass of the complex remains unchanged.

At this point, the number of normal modes and the internal coordinates for a nonlinear weakly bound complex of two rods of uniform mass distribu-

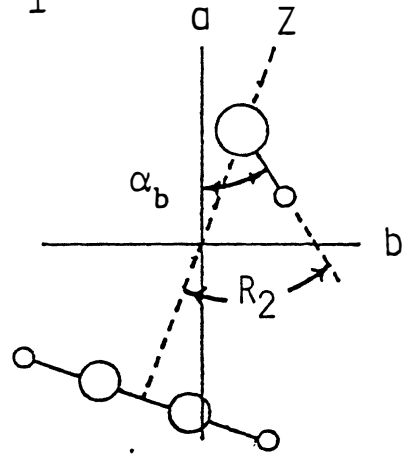
Fig. [1.7a-d] The van der Waals internal coordinates of a two rod complex of C_{2v} symmetry. The angles α_b and α_c are the instantaneous angles made by HCl with the (a) inertial axis in the [a,b] and [a,c] planes respectively. The Eckart displacements shown are deliberately exaggerated to permit definition of various structural parameters.

$R_1(A_1)$



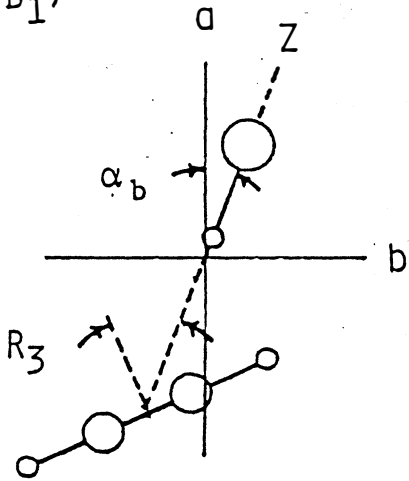
a.

$R_2(B_1)$



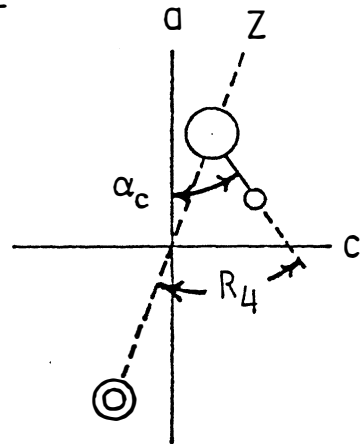
b.

$R_3(B_1)$



c.

$R_4(B_2)$



d.

tion has been developed. It is evident, though, that the van der Waals complex for which this concept is being developed ($C_2H_2 \cdots HCl$) is composed of two rod-like monomers whose mass distribution is not uniform. It becomes necessary to try to construct internal coordinates for a rod system where the rods' mass distribution is not uniform.

The "rigid rod" approach has been modified for this in the following manner. If these rods are constructed of discrete point masses corresponding to atoms, it is possible to write rod displacement operators for the rotation or translation of the ρ th rod in an inertial frame.²⁸ Translations of the ρ th rod can be expressed as:

$$T_{\rho g} = \frac{1}{m_{\rho}} \sum_{i=1}^N m_i [\Delta g_i] \quad g = x, y, z \quad (22)$$

where Δg_i represents the cartesian displacement of the ρ th rod composed of N atoms and a total mass m_{ρ} . Rotations of the ρ th rod about the X axis can be described by eqn (23):

$$R_{\rho x} = \frac{1}{I_{\rho x}} \sum_{i=1}^N m_i \{z_i [\Delta y_i] - y_i [\Delta z_i]\} \quad (23)$$

where x, y, z can be taken in cyclic order for rotation about the y and z axes and $I_{\rho x}$ is the moment of inertia of the ρ th rod about the x axis. In this approximation the monomers are replaced with inertially equivalent rigid rods. Therefore, at the time scale of the van der Waals motions, the rods are inertially equivalent to the monomers averaged over their high frequency ground state vibrations. This separation of high and low frequency modes is then analogous to the "rigid rotor" approximation in which rotational constants correspond to a vibrationally averaged moment of inertia. In constructing the coordinates of each of the atoms of each

rod, vibrational ground state structural parameters are therefore used for the calculations of interatomic distances and equilibrium parameters are used for the internal coordinates of the complex.

With the ability to write the rotation or translation of a rod in terms of atomic displacements in a cartesian frame, these rigid rod displacement operators are then used to construct internal coordinates that conform to the Eckart Constraints. The rotations and translations are written such that each rod is rotated and/or translated to give maximum incrementation to the internal coordinates in a manner similar to that used in the s-vector method outlined previously. For the case of a "T"-shaped rod complex of C_{2v} symmetry such as $C_2H_2 \cdot HCl$, the following equations developed by Henderson describe the internal coordinates of the complex in terms of rigid rod displacement operators.⁵⁷

$$R_1 = T_{1z} - T_{2z} \quad (24)$$

$$R_2 = R_{1y1} - R_{2y1} + C_2 T_{1x} \quad (25)$$

$$R_3 = R_{2y2} - R_{1y2} + C_3 T_{2x} \quad (26)$$

$$R_4 = R_{1x1} - R_{2x1} + C_4 T_{1y} \quad (27)$$

The subscripts differ slightly from the notation presented earlier (see eqn (23)). The additional subscript is required to encode specific information about the axis of rotation, i.e., R_{2x1} is the rotational operator which will give rise to rotation of rod 2 about the center of mass of rod 1 in the x-plane. The coefficients of the translation operators guarantee the condition of zero net translation of the complex.

When these operators are summed, the x,y,z components of each atom are used to construct a B-matrix of order $5\rho-6$ by $3N$ where ρ and N are as

defined earlier. The B matrix is then used with the M matrix as defined earlier to construct the G matrix according to eqn (16).

It is clear that while the construction of the f matrix is not significantly altered by whether the species being studied is a complex or chemically bound molecule, the G matrix is significantly affected. Having discussed the methods available to handle the special case of a G matrix for a van der Waals complex and the nature of f and G matrices in general, it would now be appropriate to discuss the solution of eqn (15).

Solution of the Secular Eqn

As stated earlier, if the product Gf could be determined and diagonalized, it would be possible to determine the elements of Λ, which contain the normal frequencies. It turns out that while it is possible to

$$\underline{L}' \underline{G} \underline{f} \underline{L} = \underline{\Lambda} \quad (28)$$

obtain the product Gf, it is not possible to diagonalize it using algorithms for Hamiltonian matrices. The f and G matrices are both square symmetric matrices, but their product Gf is not symmetric, i.e. Hermitian. If a matrix is not Hermitian, it cannot be diagonalized using the algorithms appropriate for diagonalizing Hamiltonian matrices. To bypass this difficulty, it is necessary to construct a similar matrix, H, using G and f. The first step in this procedure is to diagonalize G, which is Hermitian, and obtain the transformation matrix A and the D matrix, a diagonal matrix whose elements are the square root of the eigenvalues of G. Equation (29)

$$\underline{A}' \underline{G} \underline{A} = \underline{D} \underline{D} \quad (29)$$

can be rearranged and used to rewrite eqn (15). It should be noted in eqn (31) that the L matrix can easily be recovered and defined in eqns (32) and (33).

$$\underline{D}^{-1} \underline{A}' \underline{G} \underline{A} \underline{D}^{-1} = \underline{E} \quad (30)$$

$$\underline{C}' [\underline{D}' \underline{A}' \underline{G} \underline{A} \underline{D}^{-1} \underline{D} \underline{A}' \underline{f} \underline{A} \underline{D}] \underline{C} = \underline{\Lambda} \quad (31)$$

$$\underline{L} = \underline{A} \underline{D} \underline{C} \quad (32)$$

$$\underline{L}^{-1} = \underline{C}' \underline{D}' \underline{A}' \quad (33)$$

It can be shown that since eqn (34) is true that eqn (31) reduces to eqn (35). Replacing \underline{G} with its new definition (eqn (29)), it is possible

$$\underline{A} \underline{D}^{-1} \underline{D} \underline{A}' = \underline{E} \quad (34)$$

$$\underline{C}' [\underline{D}^{-1} \underline{A}' \underline{G} \underline{f} \underline{A} \underline{D}] \underline{C} = \underline{\Lambda} \quad (35)$$

to define the new similar matrix, \underline{H} .

$$\underline{C}' [\underline{D}^{-1} \underline{A}' \underline{A} \underline{D} \underline{D} \underline{A}' \underline{f} \underline{A} \underline{D}] \underline{C} = \underline{\Lambda} \quad (36)$$

$$\underline{C}' [\underline{E} \underline{D} \underline{A}' \underline{f} \underline{A} \underline{D}] \underline{C} = \underline{\Lambda} \quad (37)$$

$$\underline{C}' [\underline{D} \underline{A}' \underline{f} \underline{A} \underline{D}] \underline{C} = \underline{\Lambda} \quad (38)$$

$$\underline{H} = \underline{D} \underline{A}' \underline{f} \underline{A} \underline{D} \quad (39)$$

The solution to the secular equation (15) not only provides frequencies for the normal modes of vibration but a means of transforming the internal coordinates of a molecule or complex into the normal coordinates of the molecule or complex. If the normal coordinates of a molecule or complex are defined as elements of the $3N-6$ dimensional column vector \underline{Q} , then the eigenvector matrix of the secular eqn, the \underline{L} matrix, can be used to convert \underline{R} into \underline{Q} . A more detailed proof can be found in reference (5).

$$\underline{R} = \underline{L} \underline{Q} \quad (40)$$

A normal coordinate analysis can be used in two directions--to determine the force field of a molecule or complex if the normal mode frequencies are available or to determine frequencies if a force field is available. Both approaches depend also on a knowledge of structural parameters of the molecule or complex.

In the situation where the force field is being sought, it may be necessary to supplement the experimental data in order to obtain the most accurate and refined force field. The most common source of data to supplement vibrational spectra is from a centrifugal distortion analysis of the microwave spectrum. In section B, the microwave spectrum and the phenomenon known as Centrifugal Distortion will be investigated to ascertain how they can be used to determine force constants for both chemically bound molecules and van der Waals complexes.

B. The Microwave Spectrum and Centrifugal Distortion Analysis of van der Waals Complexes

To clearly understand how the microwave spectrum can be used as a means of supplementing vibrational data for the determination of the force field of a chemically bound molecule or complex, it will be necessary to first present a brief summary of the basic principles of rotational spectroscopy. This summary will serve to introduce the nature of rotational spectroscopy and provide a basis upon which the topic of Centrifugal Distortion can be developed.

In the description of a rotating nonlinear molecule or complex, the dynamics can be described to a first approximation by assuming that the bonds connecting atoms in a molecule or complex are not distorted during rotation. This approximation, known as the rigid rotor approximation, can be used to calculate the components of the angular momentum vector \underline{P} in both a molecular fixed frame (xyz) and in the principal inertial frame

(abc) of the molecule or complex. The components of angular momentum in the molecular and principal inertial frames are operators which can be interconverted via a direction cosine transformation.⁵⁸

$$(P_a \ P_b \ P_c) = (P_x \ P_y \ P_z) \underline{C} \quad (41)$$

The angular momentum operators along with the moments of inertia in the principal inertial frame can be used to construct the rigid rotor Hamiltonian:

$$H_r = \frac{P_a^2}{2I_{aa}} + \frac{P_b^2}{2I_{bb}} + \frac{P_c^2}{2I_{cc}} \quad (42)$$

where $I_{aa} \leq I_{bb} \leq I_{cc}$ and the labels a, b, and c are given to the inertial axes according to the conventions described in Reference 58. Eqn (42) can now be inserted into the Schrödinger equation:

$$H\Psi = \left(\frac{P_a^2}{2I_{aa}} + \frac{P_b^2}{2I_{bb}} + \frac{P_c^2}{2I_{cc}} \right) \Psi = E\Psi \quad (43)$$

and consideration given to the wave functions or basis set appropriate to solve this eigenvalue problem.

The wave functions appropriate for the solution of eqn (43) will be functions in three angles θ , ϕ , and χ since it requires three angles to describe the molecule or complex's orientation relative to either the principal inertial frame or the molecular frame. The wave functions must also be eigenfunctions of the commuting angular momentum operators, P^2 , P_z , and P_c .⁵⁸

The exact form of the wave functions is given in detail elsewhere.^{59,60} It is sufficient to note that when these functions are employed in the eigenvalue equations involving the commuting angular momentum operators P^2 , P_z , and P_c the following eigenvalues result:⁵⁸

$$P^2\Psi(\theta,\phi,\chi) = \hbar^2J(J+1)\Psi(\theta,\phi,\chi) \quad (44)$$

$$P_z\Psi(\theta,\phi,\chi) = \hbar M\Psi(\theta,\phi,\chi), \quad (45)$$

$$P_c\Psi(\theta,\phi,\chi) = \hbar K\Psi(\theta,\phi,\chi) \quad (46)$$

In the solution of eqn (43), it will be advantageous to employ a matrix representation of the Hamiltonian. It becomes necessary then to determine the matrix elements of the angular momentum operators P_a^2 , P_b^2 , and P_c^2 using $\Psi(\theta,\phi,\chi)$. These matrix elements in the $\Psi(\theta,\phi,\chi)$ basis set can be constructed using the commutation relationships and the eigenvalue eqns (44) - (46). The details of the derivation of the matrix elements can be found in References 58 and 61.

The matrix representations of P_a^2 , P_b^2 , and P_c^2 are square, symmetric matrices of order $2J+1$. These matrices can be factored into blocks corresponding to a particular value of J . Each J block will be of order $2J+1$ with diagonal elements in J,K,M . In the matrix representations of P_a^2 and P_b^2 , the J blocks will also have off diagonal elements corresponding to $K\pm 2$.

The angular momentum matrices may be combined in accordance with eqn (43) to construct H_R , the Hamiltonian matrix appropriate for any type of rigid rotor. The Hamiltonian matrix is a square, symmetric matrix of order $2J+1$ and can also be factored into J blocks in a manner similar to that of P_a^2 , P_b^2 and P_c^2 . The internal structure of these J blocks consists of diagonal elements in J,K,M and off diagonal elements corresponding to $K\pm 2$. The matrix elements are functions of J , K and the moments of inertia expressed as rotational constants A,B,C . These rotational constants are defined as $\hbar^2/4\pi I_{gg}$ where $g = a,b,c$. The diagonal and off diagonal matrix elements for the rigid rotor Hamiltonian are given below in the prolate symmetric rotor basis:⁵⁸

$$\langle J, K, M | H_r | J, K, M \rangle = \frac{h(B+C)}{2} [J(J+1) - K^2] + hK^2A \quad (47)$$

$$\langle J, K, M | H_r | J, K \pm 2, M \rangle = \frac{h}{4} (B-C) [J(J+1) - K(K \pm 1)]^{\frac{1}{2}} [J(J+1) - (K \pm 1)(K \pm 2)]^{\frac{1}{2}} \quad (48)$$

It is possible by permuting A with B, B with C, and C with A to obtain the corresponding Hamiltonian in the oblate symmetric rotor basis.

It is evident from eqn (48) that in the limit of a symmetric rotor ($B = C$) the Hamiltonian matrix is diagonal and the diagonal elements give the energy levels of the symmetric rotor directly.

The discussion to this point has acknowledged the limiting cases of prolate and oblate symmetric rotors. The intermediate case, an asymmetric rotor, requires special consideration. There exists no general closed expression for the basis set of an asymmetric rotor, hence an appropriate choice of a basis set would be linear combinations of $\Psi(\theta, \phi, \chi)$, the symmetric rotor wave functions. The Hamiltonian constructed for an asymmetric rotor in this basis set is no longer diagonal. The off diagonal elements corresponding to $K \pm 2$ are now present.

To determine the energy levels of an asymmetric rotor, the Hamiltonian matrix is diagonalized:⁵⁸

$$\underline{U}' H_r \underline{U} = E \quad (49)$$

The transformation matrix, \underline{U} , yields the coefficients necessary to construct Ψ from the symmetric rotor wave functions.

Having described the methods necessary to obtain the energy levels of the three types of rotors, it is essential to describe the energy levels and selection rules appropriate to calculate the spectra of these rotors.

The energy levels for the symmetric rotors are given in detail in other sources.⁵⁸⁻⁶⁰ It is sufficient to recognize that the K-states in

the symmetric rotor are degenerate and that when the symmetry of these rotors is destroyed the degeneracy in the K-states is broken. This is due to the fact that as the molecule or complex becomes more asymmetric, off diagonal elements in K are no longer zero and thus mixing occurs between the K-states of a given J block. The notation used to identify the asymmetric top energy levels reveals this feature as each level is denoted J, K-prolate, K-oblate where K-prolate and K-oblate are the quantum numbers of the degenerate K levels that it is derived from (see Fig (1.8)).

The selection rules will also differ slightly between symmetric and asymmetric rotors. The details of the derivation of the selection rules are given elsewhere.^{59,60} The selection rules for a symmetric rotor are $\Delta J = \pm 1, 0$, $\Delta K = 0$. The situation differs slightly for an asymmetric rotor. The selection rules for J are still applicable, but the selection rules for K must acknowledge the fact that there are projections of the dipole moment of the molecule or complex along any one or all three inertial axes. These are given in Table II, where e and o refer to the evenness or oddness of the K-prolate, K-oblate quantum numbers.

Figure (1.9a) shows the stick representation of the spectrum of an asymmetric rotor. The transitions illustrated are R-branch, a-dipole transitions. The intensities are not drawn to scale.

Having discussed the dynamics of the rigid rotor, it is now appropriate to consider the effect of relaxing this constraint on the description of rotation for a chemically bound molecule or complex. In a non-rigid molecule or complex, rotation causes centrifugal distortions of bond lengths and bond angles which are opposed by the restoring forces of the bonds. It is possible to obtain molecular force constants from an analysis of the effects of these distortions on the rotational spectrum. This technique is known as a Centrifugal Distortion Analysis and will be discussed with

Fig. [1.8] Energy level diagram for the near prolate asymmetric rotor NSF. The energy levels in the limit of a rigid rotor are shown on the left and the energy levels acknowledging centrifugal distortion (calculated using a first order approximation from distortion constants in Reference 76) are shown on the left.

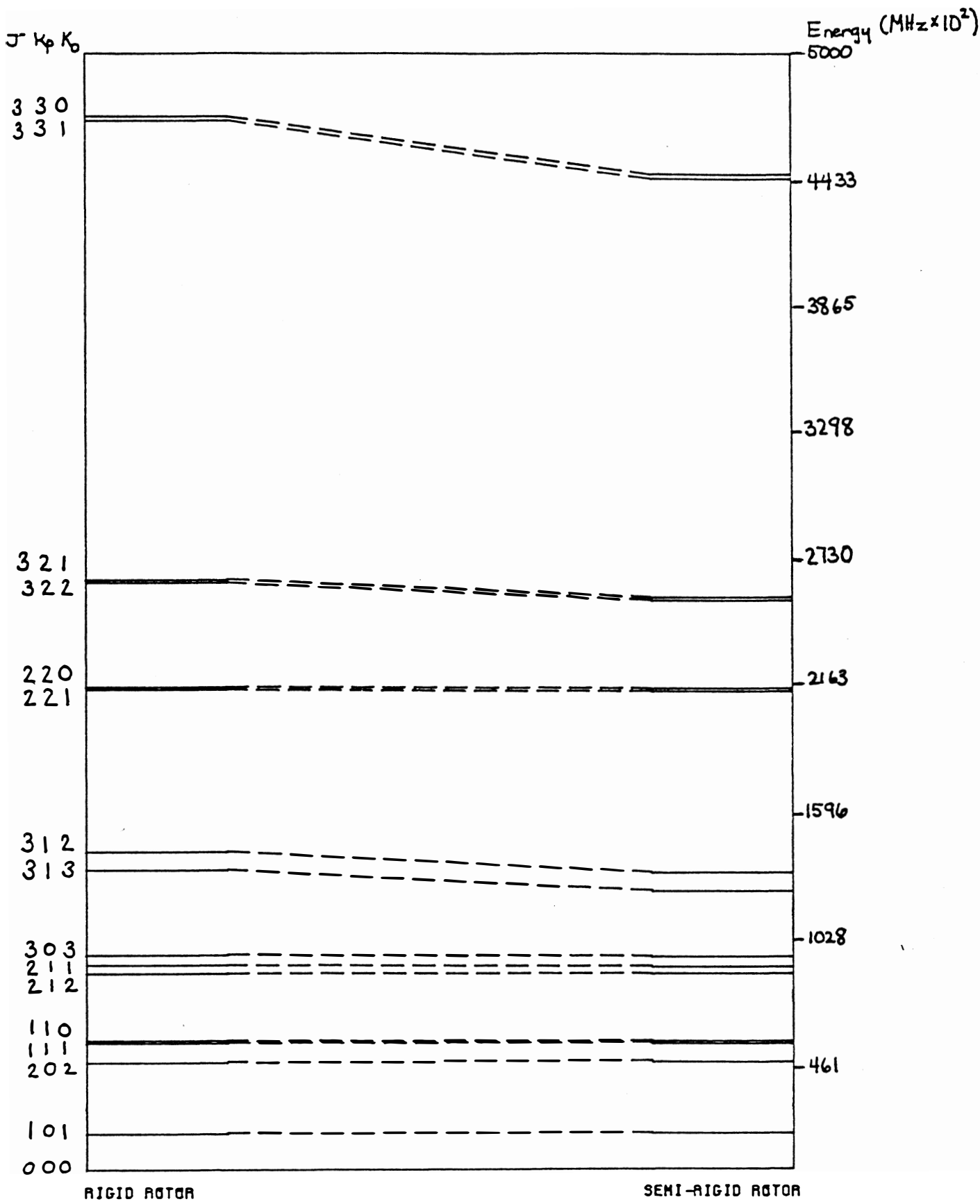


Fig. [1.9a] Spectrum of a near prolate asymmetric rigid rotor, NSF. Illustrated are selected R-branch, A-dipole transitions. The transitions are denoted 1-10 and the corresponding quantum labels are given below. The following spectroscopic constants were employed in the calculation of the spectrum:⁷⁶

A= 49719.5600 MHz

B= 8712.3300 MHz

C= 7393.1300 MHz

Fig. [1.9b] Spectrum of NSF acknowledging centrifugal distortion. The same transitions shown in Fig. [1.9a] were calculated with centrifugal distortion included. Centrifugal Distortion was treated as a first order correction using distortion constants from Reference 76. The effects of distortion are somewhat exaggerated to illustrate the effect more clearly.

	J	K(-1)	K(+1)		J	K(-1)	K(+1)
1.	1	0	1		2	0	2
2.	1	1	1		2	1	2
3.	1	1	0		2	1	1
4.	2	1	2		3	1	3
5.	2	0	2		3	0	3
6.	2	1	1		3	1	2
7.	1	0	1		2	2	0
8.	2	0	2		3	2	1
9.	2	1	1		3	3	0
10.	2	1	2		3	3	1

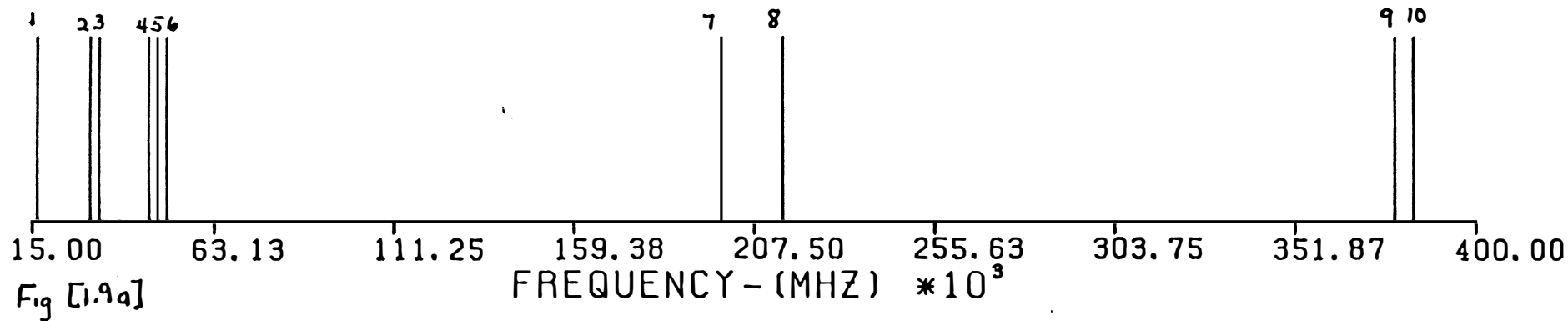
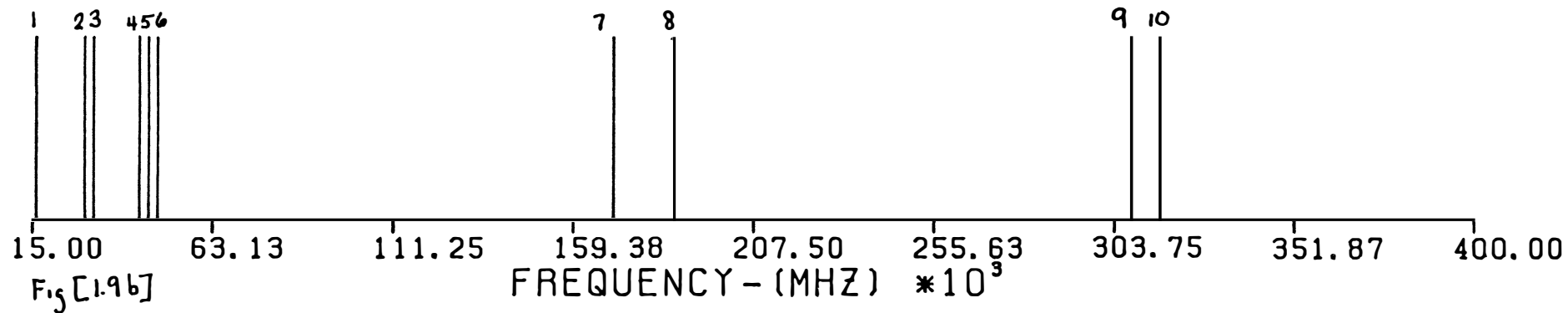


Table II. Selection Rules for an Asymmetric Rotor

A-dipole	$ee \longleftrightarrow eo$
	$oo \longleftrightarrow oe$
B dipole.	$oo \longleftrightarrow ee$
	$eo \longleftrightarrow oe$
C dipole	$ee \longleftrightarrow oe$
	$eo \longleftrightarrow oo$

respect to an asymmetric rotor in the next section.

Centrifugal Distortion

The effects of distortion and the subsequent restoring forces on a chemically bound molecule or complex can be described by an appropriate Hamiltonian:⁶²

$$H = \frac{1}{2} \sum_{\alpha, \beta} \mu_{\alpha\beta} P_{\alpha} P_{\beta} + V \quad (50)$$

where $\alpha, \beta = x, y, z$ (molecular fixed frame), $\mu_{\alpha\beta}$ are elements of the inverse of the moment of inertia tensor, P_{α} and P_{β} are components of the total angular momentum along the α and β axes in the molecular fixed frame and V is the potential energy in the limit of a harmonic oscillator.

$$V = \frac{1}{2} \sum_{ij}^{3N-6} f_{ij} R_i R_j \quad (51)$$

In this definition f_{ij} are elements of the \underline{f} matrix and \underline{R} is a vector whose elements are the internal coordinates of the molecule or complex (see Methods Section, Part A). The subscripts i and j are used to denote the $3N-6$ internal coordinates.

The elements $\mu_{\alpha\beta}$ can be approximated in a Taylor series expansion about $\mu_{\alpha\beta}^e$ where $\mu_{\alpha\beta} = f(R_i)$. The value of $\mu_{\alpha\beta}^e$ occurs when all r_i 's are zero (no rotation). At $\mu_{\alpha\beta}^e$, the moment of inertia tensor, \underline{I} , is diagonal and the elements of $\underline{\mu}$ are the inverse of the elements of \underline{I} . The series can be truncated at the linear term since all R_i 's are assumed to be very small.

$$\mu_{\alpha\beta} = \mu_{\alpha\beta}^e + \sum_i \mu_{\alpha\beta}^{(i)} R_i + \dots \quad (52)$$

$$\mu_{\alpha\beta}^{(i)} = \left(\frac{\partial \mu_{\alpha\beta}}{\partial R_i} \right)_e \quad (53)$$

This result can be used in conjunction with Hamilton's equation of motion:

$$\dot{p} = \frac{\partial H}{\partial R_i} \quad (54)$$

to express the relationship between the distorting forces of rotation and the restoring forces at equilibrium:

$$\frac{1}{2} \sum_{\alpha, \beta} \frac{\partial \mu_{\alpha\beta}}{\partial R_i} P_\alpha P_\beta + \frac{\partial V}{\partial R_i} = 0 \quad i = 1, 2, \dots, 3N-6 \quad (55)$$

when vibration is neglected. Upon substitution, eqn (55) becomes:

$$\frac{1}{2} \sum_{\alpha, \beta} \mu_{\alpha\beta}^{(i)} P_\alpha P_\beta + \sum_j f_{ij} R_j = 0 \quad (56)$$

which when solved for R_j for all $3N-6$ internal coordinates has the general form:

$$R_j = -\frac{1}{2} \sum_{i, \alpha, \beta} (f^{-1})_{ji} \mu_{\alpha\beta}^{(i)} P_\alpha P_\beta \quad (57)$$

where $(f^{-1})_{ji}$ is the ij th element of the inverse of the \underline{f} matrix.

Eqn (57) is valuable since both the potential energy and $\mu_{\alpha\beta}$ can now be expressed in terms of the components of angular momentum, P_α and P_β .

$$V = \frac{1}{8} \sum_{\substack{i, j, \alpha, \beta \\ \gamma, \delta}} \mu_{\alpha\beta}^{(i)} (f^{-1})_{ij} \quad (58)$$

$$\mu_{\alpha\beta} = \mu_{\alpha\beta}^e - \frac{1}{2} \sum_{i, j, \alpha, \beta, \gamma, \delta} \mu_{\alpha\beta}^{(i)} (f^{-1})_{ij} \mu_{\alpha\beta}^{(i)} P_\gamma P_\delta \quad (59)$$

The subscripts $\alpha, \beta, \gamma, \delta$ represent x, y, z in cyclic order.

These results are substituted into eqn (50) and the expression simplified to obtain:

$$H = \frac{1}{2} \sum_{\alpha, \beta} \mu_{\alpha\beta}^e P_{\alpha} P_{\beta} - \frac{1}{8} \sum_{\substack{i, j \\ \alpha, \beta, \gamma, \delta}} \mu_{\alpha\beta}^{(i)} (f^{-1})_{ij} \mu_{\gamma\delta} P_{\alpha} P_{\beta} P_{\gamma} P_{\delta} \quad (60)$$

This expression can be further simplified by substitution of the following expression:⁶²

$$\tau_{\alpha\beta\gamma\delta} = -\frac{1}{2} \sum_{i, j} \mu_{\alpha\beta}^{(i)} (f^{-1})_{ij} \mu_{\gamma\delta}^{(i)} \quad (61)$$

to obtain:

$$H = \frac{1}{2} \sum_{\alpha, \beta} \mu_{\alpha\beta}^e P_{\alpha} P_{\beta} + \frac{1}{4} \sum_{\alpha, \beta, \gamma, \delta} \tau_{\alpha\beta\gamma\delta} P_{\alpha} P_{\beta} P_{\gamma} P_{\delta} \quad (62)$$

It should be observed that the first term in the Hamiltonian is H_r , the rigid rotor Hamiltonian. The second term corresponds to H_D , the distortion Hamiltonian.

In order to evaluate H_D , it is necessary to discuss the calculation of $\tau_{\alpha\beta\gamma\delta}$. The $\tau_{\alpha\beta\gamma\delta}$'s, known as distortion constants, require knowledge of both the (\underline{f}^{-1}) matrix and $\mu_{\alpha\beta}^{(i)}$. The (\underline{f}^{-1}) matrix can be obtained by inversion of the \underline{f} matrix (the elements of (\underline{f}^{-1}) are not the same as the inverses of the elements of the \underline{f} matrix). The partial derivatives, $\mu_{\alpha\beta}^{(i)}$, can be obtained by writing the product of $\underline{\mu}$ and \underline{I} expressed as matrices:

$$\underline{\mu} \underline{I} = \underline{E} \quad (63)$$

where \underline{E} is the unit matrix. Taking the partial derivatives in eqn (63) with respect to R_i at equilibrium, a set of $3N-6$ equations result which

can be solved for $\mu_{\alpha\beta}^{(i)}$. This result is given below:

$$\left(\frac{\partial \mu_{\alpha\beta}}{\partial R_i} \right)_e = - \left(\frac{\partial I_{\alpha\beta}}{\partial R_i} \right) \frac{1}{I_{\alpha\alpha}^e I_{\beta\beta}^e} \quad (64)$$

Utilizing the following expression for $\partial I_{\alpha\beta} / \partial R_i$:

$$J_{\alpha\beta} = \frac{\partial I_{\alpha\beta}}{\partial R_i} \quad (65)$$

it is possible to rewrite eqn (60) in the following manner:

$$\tau_{\alpha\beta\gamma\delta} = -\frac{1}{2} (I_{\alpha\alpha}^e I_{\beta\beta}^e I_{\gamma\gamma}^e I_{\delta\delta}^e)^{-1} = [J_{\alpha\beta}]_e^i (f^{-1})_{ij} [J_{\gamma\delta}]_e^i \quad (66)$$

The values for the inertial derivatives, $J_{\alpha\beta}$, are evaluated at equilibrium for the i th internal coordinate.

When $\tau_{\alpha\beta\gamma\delta}$ is expressed as in eqn (65), the (f^{-1}) matrix and values for $I_{\alpha\alpha}^e$ (the moment of inertia about the α axis at equilibrium) and $[J_{\alpha\beta}]_e$ are required for its calculation. The moments of inertia can be calculated at equilibrium in the principal inertial frame using the equation below:

$$I_{\alpha\alpha}^e = \sum_{\ell=1}^N m_{\ell} (\beta_{\ell}^2 + \gamma_{\ell}^2) \quad (67)$$

where α, β , and γ are x, y, z taken in cyclic order. Obtaining $[J_{\alpha\beta}]_e$ is possible by two approaches; both of which will be discussed in the next section.

Calculation of $J_{\alpha\beta}$ --The Inertial Derivatives

The inertial derivatives are actually elements of the \underline{J} matrix which is a 3-dimensional matrix of order $3 \times 3 \times 3N-6$. Each cross section corresponds to derivatives of the moment of inertia tensor calculated for an appropriate

change in an internal coordinate. The change in a given internal coordinate cannot be made arbitrarily. It must be made such that the Eckart conditions are satisfied³ (see Methods Section, Part A). Kivelson and Wilson have obtained general analytical expressions for the matrix elements of each cross section. These expressions are given below:^{62,63}

$$J_{\alpha\alpha}^i = \frac{2}{\Delta R_i} \sum_{\ell=1}^N m_{\ell} (\beta_{\ell} \Delta \beta_{\ell} + \gamma_{\ell} \Delta \gamma_{\ell}) \quad (68)$$

$$J_{\alpha\beta}^i = - \frac{2}{\Delta R_i I_{\gamma\gamma}} \left\{ I_{\alpha} \sum_{\ell=1}^N m_{\ell} \beta_{\ell} \Delta \alpha_{\ell} + I_{\beta} \sum_{\ell=1}^N m_{\ell} \alpha_{\ell} \Delta \beta_{\ell} \right\} \quad (69)$$

where $I_{\gamma\gamma}$ is defined according to eqn (66) and $I_{\alpha} = \sum_{s=1}^N m_s \alpha_s^2$.

There are specific guidelines associated with the use of these equations. The coordinates of the atoms not involved in incrementing ΔR must be equilibrium values in the principal inertial frame. The locations of the atoms must be changed so as to increment the internal coordinate R_i . The advantage to the Wilson method is that these displacements of the atoms can be arbitrary. The axis system can even be translated such that the displacements can be calculated conveniently (note: They must be translated back to the principal inertial frame for use in eqns (68) - (69)). This is due to the fact that the Eckart Conditions are built into these eqns. Inherent in eqns (68) - (69) are translations and rotational terms that will convert any arbitrary displacement to an "Eckart allowed" displacement, provided the coordinates are in the principal inertial frame. As stated earlier, this method is appropriate for both chemically bound molecules and complexes and can be used with distortion constants to determine force constants for a nonlinear rigid rod system.

An alternative matrix method determines $J_{\alpha\beta}$ from readily available matrices. This method generates a column of a cross section of the \underline{J}

matrix according to the following eqn:⁶⁴

$$J_{\alpha\beta} = 2 \underline{G}^{-1} \underline{B} \underline{I}^{\alpha} \underline{I}^{\beta} \underline{X} \quad (70)$$

where \underline{G} and \underline{B} are as defined earlier (see Methods Section, Part A), \underline{X} is a 3N-dimensional column vector of the equilibrium coordinates of all the atoms in the principal inertial frame, \underline{I}^{α} and \underline{I}^{β} are auxiliary matrices of order 3N with the following matrices repeated N times along the diagonal:⁶⁵

$$i^x = \begin{vmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & -1 & 0 \end{vmatrix} \quad i^y = \begin{vmatrix} 0 & 0 & -1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{vmatrix} \quad i^z = \begin{vmatrix} 0 & 1 & 0 \\ -1 & 0 & 0 \\ 0 & 0 & 0 \end{vmatrix} \quad (71)$$

The Eckart considerations are consolidated in the construction of \underline{B} (see Methods Section, Part A).

It is now possible to calculate $\tau_{\alpha\beta\gamma\delta}$ and thus H_D for a chemically bound molecule, complex, and a nonlinear rigid rod complex in a classical sense. If the components of angular momentum are regarded as operators, the quantum mechanical Hamiltonian is obtained. The resulting distortion Hamiltonian, H_D , can be treated as a correction or perturbation to the rigid rotor Hamiltonian. The order of the correction (first, second, etc.) is that required to bring the calculated spectrum into agreement with the observed spectrum. The order generally indicates the magnitude of the effect the perturbation has on a given system. In the next section, the first order perturbation or correction due to centrifugal distortion will be discussed.

First Order Perturbation Treatment of Centrifugal Distortion

Using the quantum mechanical Hamiltonian (eqn (62) where the components of angular momentum are construed to be operators), the calculation of H_D will involve averaging H_D over the asymmetric rotor wave functions. This

discussion will serve to illustrate the pertinent points of this averaging to determine H_D to first order. More detailed discussions can be found in References 62, 66, 67.

The number of terms in the summation over $\alpha, \beta, \gamma, \delta$ in eqn (72) and

$$H_D = \frac{1}{4} \sum_{\alpha, \beta, \gamma, \delta} \tau_{\alpha\beta\gamma\delta} P_\alpha P_\beta P_\gamma P_\delta \quad (72)$$

hence the number of terms to average can be reduced by invoking the commutation rules of the angular momentum operators.⁶⁸ The commutation rules reduce the summation to eighty-one terms. It is also possible to reduce this further by recognizing that many of the remaining taus are equal (see eqn (66)). It also can be shown that many of these terms will not contribute to the first order correction.⁶²

$$\tau_{\alpha\beta\gamma\delta} = \tau_{\gamma\delta\beta\alpha} = \tau_{\gamma\beta\delta\alpha} = \tau_{\delta\beta\gamma\alpha} = \tau_{\beta\delta\gamma\alpha} \quad (73)$$

Another reduction occurs due to group theoretical considerations.

The product of the angular momentum operators averaged over the asymmetric rotor wave functions must be invariant to the symmetry operations of the point group to which the wave functions belong (D_2). This means that this product must belong to the totally symmetric representation A. This requirement must be met such that the integral does not go to zero. The angular momentum operators P_a, P_b, P_c transform as the irreducible representations $B_1, B_2, \text{ and } B_3$ respectively.^{58,62} Thus any term in the summation that contains an odd power of an angular momentum operator will, when averaged, vanish because the product of these operators will not transform as the symmetric representation A. This will reduce the number of terms in the summation to twenty-one (many of which are still equivalent to each other) for any asymmetric rotor.⁶⁶

Alternatively, this reduction can be made if the point group of the molecule or complex is considered. For the molecules or complexes of orthorhombic symmetry (C_{2v} , D_{2h} , D_2 point groups), the taus that multiply terms which contain odd powers of angular momentum vanish since H_r and H_D must be invariant to the symmetry operations of the point group of the molecule. This also yields twenty-one non-vanishing terms in H_D . For molecules of nonorthorhombic symmetry there are, in addition to the other twenty-one, terms whose angular momentum operators will generate $K\pm 1$ and $K\pm 3$ terms in H_D .⁶⁶ These terms will become significant only if H_D is treated as a second order perturbation.⁶⁶

The twenty-one remaining terms can be arranged into nine different groups, since several of these terms can be grouped under the same tau. The nine taus are given below:⁶²

$$\tau_{\alpha\alpha\alpha\alpha}, \tau_{\alpha\alpha\beta\beta} = \tau_{\beta\beta\alpha\alpha}, \tau_{\alpha\beta\alpha\beta} = \tau_{\alpha\beta\beta\alpha} = \tau_{\beta\alpha\beta\alpha} = \tau_{\beta\alpha\alpha\beta} \quad (74)$$

where $\alpha, \beta = x, y, \text{ or } z$.

The nine remaining groups can be reduced still further by utilizing the commutation rules for angular momentum and the following eqn:^{58,66}

$$(P_\alpha P_\beta + P_\beta P_\alpha)^2 = 2(P_\alpha^2 P_\beta^2 + P_\beta^2 P_\alpha^2) + 3 P_\gamma^2 - 2 P_\alpha^2 - 2 P_\beta^2 \quad (75)$$

where $\alpha \neq \beta \neq \gamma$ and α, β, γ are x, y, z taken in cyclic order. It should be noted that $P_\alpha P_\beta$ does not commute, therefore, there will be four P^4 terms which can be grouped under $\tau_{\alpha\beta\alpha\beta}$. If the right hand side of eqn (75) is substituted for these P^4 terms, it is possible to eliminate the $\tau_{\alpha\beta\alpha\beta}$ terms. The P^2 terms from the substitution are absorbed along with the associated $\tau_{\alpha\beta\alpha\beta}$ coefficients into H_r . The taus are combined with the rotational constants to define new effective rotational constants. Of the coefficients of the six remaining groups in H_D , three are now linear

combinations of taus. The new coefficients are denoted by $\tau'_{\alpha\alpha\beta\beta}$. The Hamiltonian corrected to first order for centrifugal distortion is shown below:

$$H = H_r + H_D \quad (76)$$

$$H_r = A'P_\alpha^2 + B'P_\beta^2 + C'P_\gamma^2 \quad (77)$$

$$H_D = \frac{1}{4} \sum_{\alpha,\beta} \tau'_{\alpha\alpha\beta\beta} P_\alpha^2 P_\beta^2 \quad (78)$$

The coefficients, $\tau'_{\alpha\alpha\beta\beta}$, and corrected rotational constants are defined in Table III.

Using eqn (78), the first order distortion energy can be written as an average over the asymmetric rotor wave functions:

$$E_D = 1/8 \sum_{\alpha,\beta} \tau'_{\alpha\alpha\beta\beta} \langle P_\alpha^2 P_\beta^2 + P_\beta^2 P_\alpha^2 \rangle \quad (79)$$

The integrals can be expressed as a function of $\langle P_z^n \rangle$ ($n=2,4$), the square of the rigid rotor energy, E_r^2 , and P^2 (the square of the total angular momentum). By use of commutation relationships developed by Wilson,⁶⁷ E_r^2 can be eliminated from these integrals. The details of the substitution of E_r^2 can be found in References 24 and 19. For this discussion, it is necessary to note that E_r^2 introduces additional terms, P_α^2 , which can be absorbed into H_r . This results in a redefinition of the effective rotational constants. The details of the subsequent calculation of E_D are given in References 67 and 62. The resulting expression defines the energy of a semirigid asymmetric rotor:

$$E = E_r + E_D \quad (80)$$

$$E_D = -d_J J^2 (J+1)^2 - d_{JK} (J+1) \langle P_z^2 \rangle - d_K \langle P_z^4 \rangle - d_{EJ} E_r J (J+1) - d_{EK} E_r \langle P_z^2 \rangle \quad (81)$$

Table III. Coefficients in H_D , the Distortion Hamiltonian

$$\tau'_{xxxx} = \hbar^4 \tau_{xxxx} \qquad \tau'_{xxzz} = \hbar^4 (\tau_{xxzz} + 2\tau_{xzxz})$$

$$\tau'_{yyyy} = \hbar^4 \tau_{yyyy} \qquad \tau'_{xxyy} = \hbar^4 (\tau_{xxyy} + 2\tau_{xyxy})$$

$$\tau'_{zzzz} = \hbar^4 \tau_{zzzz} \qquad \tau'_{yyzz} = \hbar^4 (\tau_{yyzz} + 2\tau_{yzyz})$$

$$A' = A + \frac{\hbar^4}{4} (3\tau_{xyxy} - 2\tau_{xzxz} - 2\tau_{yzyz})$$

$$B' = B + \frac{\hbar^4}{4} (3\tau_{yzyz} - 2\tau_{xyxy} - 2\tau_{yzyz})$$

$$C' = C + \frac{\hbar^4}{4} (3\tau_{xzxz} - 2\tau_{xyxy} - 2\tau_{yzyz})$$

where J is the rotational quantum number, the lower case d 's are Watson distortion coefficients defined in Table IV and $\langle P_z^n \rangle$ ($n=2,4$) is defined below:

$$\langle P_z^n \rangle = \sum_K a^n K^n \quad (82)$$

where the coefficients a are the elements of the transformation matrix of the rigid rotor.

Table IV gives the distortion coefficients and definitions of the rotational constants for the energy of a semirigid corrected to first order.^{66,67}

This discussion of the first order correction to the energy is appropriate for any molecule. The situation simplifies greatly for a planar molecule. In this case τ_{xyxy} and τ_{yzyz} are equal to zero. Thus, there are seven nonzero taus, four of which are independent (τ_{xxxx} , τ_{zzzz} , τ_{xxzz} , τ_{xzxz}). The three remaining taus are linear combinations of the independent taus and also dependent on the equilibrium rotational constants. If the equilibrium rotational constants are not available, the effective rotational constants can be utilized:⁶²

$$\tau_{yyyy} = (C'/A')^4 \tau_{zzzz} + \frac{2 C'^4}{A'^2 B'^2} \tau_{xxzz} + (C'/B')^4 \tau_{xxxx} \quad (83)$$

$$\tau_{xxyy} = (C'/B')^2 \tau_{xxxx} + (C'/A')^2 \tau_{xxzz} \quad (84)$$

$$\tau_{yyzz} = (C'/A')^2 \tau_{zzzz} + (C'/B')^2 \tau_{zzxx} \quad (85)$$

These taus can be used in the previous discussion to determine the first order correction to the energy.

Table IV. Distortion Coefficients and Rotational Constants
of the First-Order Energy Expression

$$A = A' + 16 R_6$$

$$B = B' - (16 R_6 (A' - C')) / (B' - C')$$

$$C = C' + (16 R_6 (A' - B')) / (B' - C')$$

$$d_J = D_J - \frac{2\delta_J(B + C)}{B - C} - 2R_6$$

$$d_{JK} = D_{JK} - 2\sigma\delta_J + 4(R_5 + 2\sigma R_6) \frac{B + C}{B - C} + 12R_6$$

$$d_K = D_K + 4\sigma(R_5 + 2\sigma R_6) - 10R_6$$

$$d_{EJ} = \frac{4\delta_J}{B - C}$$

$$d_{EK} = \frac{-8(R_5 + 2\sigma R_6)}{B - C}$$

$$\sigma = \frac{2A - B - C}{B - C}$$

$$D_J = -1/32 \{ 3\tau_{xxxx} + 3\tau_{yyyy} + 2(\tau_{xxyy} + 2\tau_{xyxy}) \} \hbar^4$$

$$D_K = D_J - 1/4 \{ \tau_{zzzz} - (\tau_{xxzz} + 2\tau_{xzxz}) - (\tau_{yyzz} + 2\tau_{zyyz}) \} \hbar^4$$

$$D_{JK} = -D_J - D_K - 1/4 \tau_{zzzz} \hbar^4$$

$$R_5 = -1/32 \{ \tau_{xxxx} - \tau_{yyyy} - 2(\tau_{xxzz} + 2\tau_{xzxz}) + 2(\tau_{yyzz} + 2\tau_{zyyz}) \} \hbar^4$$

$$R_6 = 1/64 \{ \tau_{xxxx} + \tau_{yyyy} - 2(\tau_{xxyy} + 2\tau_{xyxy}) \} \hbar^4$$

$$\delta_J = -1/16 \{ \tau_{xxxx} - \tau_{yyyy} \} \hbar^4$$

For the case of the "T"-shaped planar complex of C_{2v} symmetry, $C_2H_2 \cdots HCl$, further simplification is possible. Using the internal coordinates shown in Fig. (1.4) and eqn (67), it can be shown that J_{zz}^i vanishes for these internal coordinates. It is evident from eqn (65) that this will cause two of the four independent taus to vanish. Thus, for $C_2H_2 \cdots HCl$, this clearly permits a fit of the two remaining independent taus, τ_{xxxx} and τ_{xzxz} , and three rotational constants to the six observed line centers using a first order approximation of centrifugal distortion.

For more asymmetric molecules and lighter molecules, centrifugal distortion cannot be treated as a first order correction. For discussions of the treatment of centrifugal distortion as a higher order effect, references 62 and 69 are helpful.

While the centrifugal distortion analysis of the microwave spectrum and a normal coordinate analysis of the vibrational spectrum are the primary sources of information about molecular force fields, nuclear quadrupole coupling constants can be used to supplement the force field of those van der Waals complexes possessing nuclei with a quadrupole. Vibrational averaging of structural parameters of complexes over the appropriate wave functions also provides an additional source of information about the force field. The next two sections briefly describe these secondary sources--the nuclear quadrupole coupling constants and the vibrationally averaged structure.

C. Nuclear Quadrupole Coupling Constants and the van der Waals Force Field

In the previous discussions, the nuclei in a molecule or a complex have been described as discrete point charges. A more accurate description, however, recognizes that each nucleus possesses a rotating charge distribution which may or may not be spherically symmetric. This section will briefly illustrate how this description of the nucleus will affect the rotational spectrum and how information from this spectrum can be analyzed to yield force constants for complexes.

In the refined description of the nucleus, the nuclear charge distribution is no longer fixed in space but is spinning. This motion, known as nuclear spin, gives rise to a quantized angular momentum $|\underline{I}| = \sqrt{I(I+1)}\hbar$, where I is the nuclear spin quantum number, a property of the nucleus. There exist $2I+1$ allowed orientations of the angular momentum vector, I , in the nucleus. For the values of $I > \frac{1}{2}$, the nuclear charge distribution is no longer spherically symmetric. In cases of nonspherical nuclear charge distribution, the nuclear spin may couple with the rotational motions of the molecule causing small splittings in the rotational energies.

The energy due to this coupling is a function of the nuclear charge density and the electrostatic potential at the nucleus due to the surrounding electric field of the electrons. To define the energy, it is convenient to expand the electric potential as a Taylor series in three dimensions:

$$V = V_0 + \frac{x\partial V_0}{\partial x} + \frac{y\partial V_0}{\partial y} + \frac{z\partial V_0}{\partial z} \dots \dots \dots \quad (86)$$

integrate over the nuclear volume with the charge density, $\rho = f(x,y,z)$ and neglect those terms that are independent of the nuclear orientation and are due to the nuclear dipole moment (zero in absence of an applied field):⁵⁹

$$E_Q = 1/6 \rho [(3x^2 - r^2) \frac{\partial^2 V}{\partial x^2} + (3y^2 - r^2) \frac{\partial^2 V}{\partial y^2} + (3z^2 - r^2) \frac{\partial^2 V}{\partial z^2} + 6xy \frac{\partial^2 V}{\partial x \partial y} + 6yz \frac{\partial^2 V}{\partial y \partial z} + 6zx \frac{\partial^2 V}{\partial z \partial x}] dV \quad (87)$$

where x, y, z are coordinates in a Cartesian reference frame with the nucleus at the origin.

The matrix representation of eqn (87) is the dot product of the quadrupole moment tensor and the electric field gradient:⁵⁹

$$E_Q = -1/6 \underline{Q} : \nabla \underline{E} \quad (88)$$

where ∇E is the electric field gradient due to the electrons of a molecule. By defining Q and ∇E as operators, the quadrupole Hamiltonian may be written:⁵⁹

$$H_Q = -1/6 \underline{Q} : \nabla \underline{E} \quad (89)$$

The details of the solution of H_Q are discussed by Casimir.⁷⁰ The solution, E_Q , is given below for a linear molecule:⁵⁹

$$E_Q = (1/2)(eqQ/(I(2I-1)J(2J-1)))(3/4C(C+1)-I(I+1)J(J+1)) \quad (90)$$

where Q , the nuclear quadrupole moment, reveals how much the nuclear charge distribution deviates from spherical symmetry. When Q is positive, the nuclear charge distribution is extended along the nuclear z -axis; if Q is negative, the nuclear charge distribution is flattened against the nuclear z -axis.⁵⁹

The quantity C is defined as:⁵⁹

$$C = F(F+1) - I(I+1) - J(J+1) \quad (91)$$

where $F = I + J$, the nuclear spin and rotational quantum numbers. In eqn (90), e is the charge on an electron, q is the electric field gradient

at the nucleus due to an axially symmetric charge distribution:

$$q = \int \rho \frac{(3\cos^2\theta - 1)}{r^3} d\tau = \left(\frac{\partial^2 V}{\partial z^2} \right) \quad (92)$$

where r and θ are coordinates that define the orientation of the symmetric charge density, ρ , along the z axis. It should be noted that ρ is defined so as to include all the charge density outside of the nucleus. It includes the contributions due to valence electrons and charge distributions associated with neighboring atoms or molecules. A more detailed discussion which describes a more quantitative means of calculating the electric field gradient can be found in Reference 85.

It is evident that the nuclear spin angular momentum, I , can couple to the angular momentum of a molecule or complex through the electric field gradient of the molecule. This coupling will cause splitting in the rotational levels in the molecule or complex.⁶⁰ This splitting will cause a single transition in the spectrum to become a series of closely spaced lines known as nuclear spin hyperfine structure.

The collection of terms, eqQ , is referred to as the nuclear quadrupole coupling constant and has been obtained accurately for a number of molecules, ex: free HCl, $\chi_{\text{O}}^{\text{HCl}} = eqQ/h = -67.61893 \text{ MHz}$.⁷¹ However, in the hydrogen bonded complex $\text{C}_2\text{H}_2 \cdots \text{HCl}$, it is logical to expect slight changes in the electric field gradient about HCl, $\partial^2 V / \partial z^2$, due to alteration of the charge density ρ (as defined in eqn (92)) due to hydrogen bond formation. Since the nuclear quadrupole coupling constant is a function of $\partial^2 V / \partial z^2$, changes in eqn (90) due to complexation give rise to χ_{HCl} , the nuclear quadrupole constant for HCl in $\text{C}_2\text{H}_2 \cdots \text{HCl}$. It should also be observed that in $\text{C}_2\text{H}_2 \cdots \text{HCl}$ the librational modes of the HCl subunit will cause its electric field gradient to be displaced by some angle α away from the (a) inertial axis (see Fig (1.7)). The observed spectrum thus yields an effective nuclear

quadrupole constant which is the vibrationally averaged projection of χ_{HCl} on the (a) inertial axis:¹

$$\chi_{aa} = \chi_{\text{HCl}} \langle 3/2 \cos^2 \alpha - 1/2 \rangle \quad (93)$$

In the situation where the in-plane and out-of-plane librational amplitudes are not equivalent, there exists a corresponding anisotropy in the nuclear quadrupole tensor ($\chi_{bb} \neq \chi_{cc}$). This results in the following expressions for the vibrationally averaged cosine of the angle of the projections on the inertial axes:¹

$$\langle \cos^2 \alpha_b \rangle = \frac{\chi_{aa} + \frac{1}{2} \chi_{\text{HCl}}}{\chi_{aa} + \chi_{bb} + \chi_{\text{HCl}}} \quad (94)$$

$$\langle \cos^2 \alpha_c \rangle = \frac{\chi_{aa} + \frac{1}{2} \chi_{\text{HCl}}}{\chi_{aa} + \chi_{cc} + \chi_{\text{HCl}}} \quad (95)$$

where χ_{gg} ($g = a, b, c$) is the vibrationally averaged projection of the nuclear quadrupole coupling constant on the inertial axis and χ_{HCl} is as defined earlier.

An alternative way of calculating $\langle \cos^2 \alpha_c \rangle$ and $\langle \cos^2 \alpha_b \rangle$ involves the normal mode wave function, $\Psi(Q)$:

$$\langle \cos^2 \alpha_g \rangle = \int_{-\infty}^{\infty} \Psi^*(Q) \cos^2 \alpha_g \Psi(Q) dQ \quad g = b, c \quad (96)$$

To determine the value of this integral, it will be necessary to obtain expression for $\Psi(Q)$ and define the operator, $\cos^2 \alpha_g$, in terms of Q , the normal coordinate. Closed analytical expressions for the solution of these integrals are derived in Appendix V.

The normalized ground state harmonic wave function for the i th normal

mode, $\Psi_0(Q_i)$ is:⁷²

$$\Psi_0(Q_i) = \frac{\gamma_i^{1/4}}{\pi} \exp(-(\gamma_i Q_i)/2) \quad (97)$$

where γ_i is defined as:⁷²

$$\gamma_i = \frac{4\pi^2 c \omega_i}{h} \quad (98)$$

ω_i is the i th normal mode frequency and c and h are the speed of light and Planck's constant respectively.

It is obvious from eqn (98) that the force field can be used to determine ω_i via a normal coordinate analysis and subsequently determine $\Psi_0(Q_i)$. A normal coordinate analysis may also be used to express the operator, $\cos^2 \alpha_g$, in terms of Q_i . Unless the angle formed by the projection of the monomer and the g inertial axis is a normal coordinate, it will be necessary to write α_g as a function of a convenient internal coordinate, R_i . With α_g expressed as $f(R_i)$, the elements of the \underline{L} matrix can be used to transform the R_i into Q_i according to eqn (40).

Thus, the nuclear quadrupole coupling constants can be used to calculate the vibrationally averaged projection operator, which is also a function of $\Psi_0(Q_i)$, the normal mode wave functions calculated via a knowledge of the force field. It is now apparent that if χ_{HCl} is known, librational force constants can be obtained from eqns (94) - (95) via χ_{bb} and χ_{cc} . Conversely, knowledge of the force field will permit determination of χ_{HCl} via eqns (94) - (95) using χ_{bb} and χ_{cc} .

Comparison of χ_{HCl} with χ_{HCl}^0 , the nuclear quadrupole coupling constant of the free monomer, will make it possible to infer changes in the electric field gradient at chlorine due to complexation via eqn (92).

Another source that may be employed in the acquisition of the force field in the vibrationally averaged structure. This method, utilized

specifically for complexes, is an additional source of information and will be discussed in the next section.

D. Vibrationally Averaged Structure

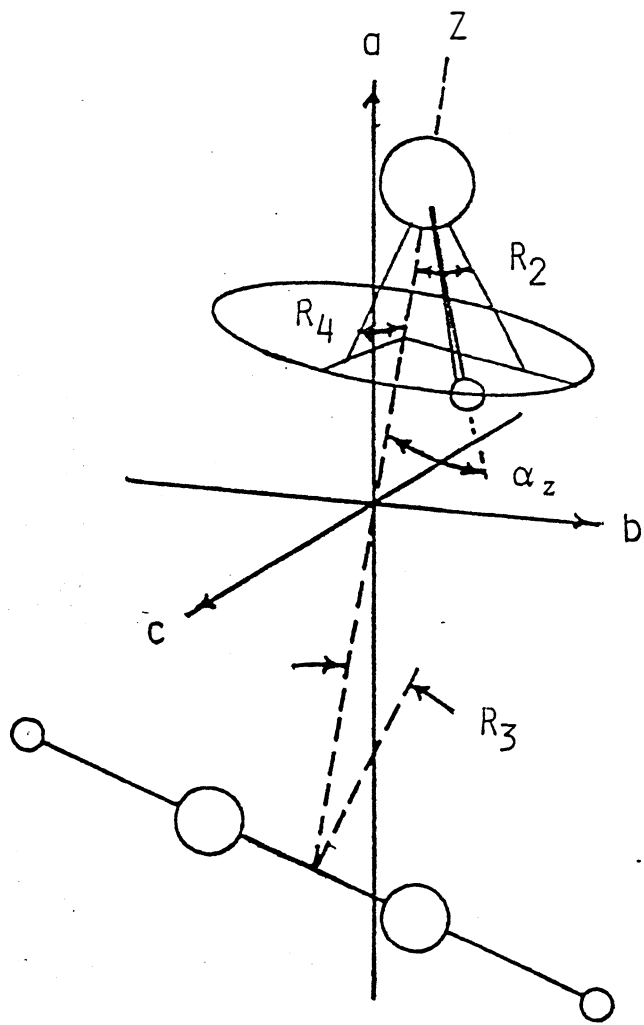
The vibrationally averaged structure refers to the instantaneous structural parameters averaged over the vibrational ground state motion and characterize the experimentally observed moments of inertia.

In order to describe the vibrationally averaged structure of a "T"-shaped planar complex of C_{2v} symmetry such as $C_2H_2 \cdot HCl$, it should be acknowledged that the monomers are undergoing large amplitude excursions from their equilibrium positions while in the vibrational ground state. The position and orientation of the monomers during these excursions can be described relative to a convenient xyz frame by the following structural parameters, r , R_3 , α_x and α_y (see Fig. (1.10)).

The derivation of inertial equations that will relate these structural parameters to the observed rotational constants will involve some approximation about the nature of the monomers and their motions. It will be assumed that the structure of the monomers will remain unchanged upon complexation. The linear combinations of the in-plane and out-of-plane librational motions of the HCl subunit give rise to a precessional motion whose period is less than the rotational period of the complex. Thus, the inertial equations for the vibrationally averaged structure describe the rods as masses distributed over the vibrationally averaged motions of the complex as opposed to the rigid point mass structure used previously.^{1,73} Hence, the vibrationally averaged structure can be described effectively by three parameters, r , R_3 and α_2 .

The above approximations and the parallel axis theorem were used to obtain eqns for the instantaneous inertial tensor elements, which were then averaged over the zero point motion to yield the non-zero inertial

Fig. [1.10] Instantaneous Structure of Acetylene-HCl.



tensor elements:

$$I_{xx} = \mu R_0^2 + I_{AC} \langle \sin^2 R_3 \rangle + \frac{1}{2} I_{HCl} (1 + \langle \cos^2 \alpha_z \rangle) \quad (99)$$

$$I_{yy} = \mu R_0^2 + I_{AC} + \frac{1}{2} I_{HCl} (1 + \langle \cos^2 \alpha_z \rangle) \quad (100)$$

$$I_{zz} = I_{AC} \langle \cos^2 \theta \rangle + I_{HCl} (1 + \langle \cos^2 \alpha_z \rangle) \quad (101)$$

$$I_{xz} = I_{AC} \langle \cos R_3 \sin R_3 \rangle \quad (102)$$

where μ is the pseudodiatom reduced mass ($m_{AC} m_{HCl} / (m_{AC} + m_{HCl})$), $R_0^2 = \langle r^2 \rangle$, the square of the distance between the centers of mass of the monomers averaged over the ground state, I_{AC} and I_{HCl} are the moments of inertia of C_2H_2 and HCl in their respective ground states, and α_z is the instantaneous angle HCl makes with the z axis defined in terms of α_x and α_y :

$$\langle \cos^2 \alpha_z \rangle = \left\langle \frac{\cos^2 \alpha_x \cos^2 \alpha_y}{\cos^2 \alpha_x + \cos^2 \alpha_y - \cos^2 \alpha_x \cos^2 \alpha_y} \right\rangle \quad (103)$$

The inertial tensor calculated from eqns (99) - (102) can be diagonalized via a direction cosine transformation to obtain the principal moments of inertia.

Examination of eqs (99)-(101) clearly show that the rotational constants are insensitive to the value of α_z , therefore, $\langle \cos^2 \alpha_z \rangle$ is obtained from the normal mode wave functions that reproduce the vibrational spectrum. This will permit a fit of the remaining structural parameters, $R_0 = [\langle r^2 \rangle]^{1/2}$ and $R_3^* = \text{Arccos}[\langle \cos^2 R_3 \rangle]^{1/2}$. Conversely, it is also possible to determine these parameters by averaging over their ground state wave functions, $\Psi_0(Q) = f(\omega_i)$, determined by the molecular force field via a normal coordinate analysis (see Methods Section, Part C).

In summary, the methods outlined in this section have demonstrated that the vibrational spectrum, centrifugal distortion constants, nuclear quadrupole coupling tensor elements and the vibrationally averaged structure are intimately related to the intermolecular force field through an appropriate normal coordinate analysis.

A rigid rod mode has been developed to determine the Wilson \underline{f} matrix that will reproduce the observed spectroscopic constants of $C_2H_2 \cdots HCl$.⁵⁷ The result of the application of this method, obtained using Fortran codes in Appendices I and II, will be presented in the next section.

RESULTS

The determination of the intermolecular force field of $C_2H_2 \cdots HCl$ involves the use of methods detailed in the previous section. The experimental data employed in these methods were obtained previously by Legon¹ and Andrews.² The data consist of two R-branch transitions ($J=1 \rightarrow 2$ and $J=2 \rightarrow 3$), nuclear quadrupole coupling constants, and normal mode frequencies of the complex. This section will detail the outcome of this application.

A. Centrifugal Distortion Analysis

Assuming the structures of the monomers to be unaffected by centrifugal distortion, the matrix representation of the semi-rigid asymmetric rotor Hamiltonian was constructed in accord with eqn (76). Due to planarity and the symmetry of the complex, only two linearly independent distortion constants and three rotational constants were needed to fit the observed quadrupole hyperfine band origins. Using the FORTRAN code in Appendix I, A, B, C, τ_{xxxx} and τ_{xzxz} were obtained and are reported in Table V with precisions of \pm one standard deviation. The calculated band origins are presented in Table VI in addition to the observed band origins and the earlier results of Legon.¹

B. Vibrationally Averaged Structure

The structural parameters of $C_2H_2 \cdots HCl$ may be determined from the rotational constants (see Table V) via eqns (99) - (102). Since examination of eqns (99) - (101) indicated that the moments of inertia were very

Table V. Spectroscopic Constants of $C_2H_2 \cdot HCl$ ^a(MHz)

	$C_2H_2 \cdot H^{35}Cl$	$C_2H_2 \cdot H^{37}Cl$
A	35975.6333 (48.4)	35966.2663 (13.6)
B	2482.1065 (11)	2425.4201 (3)
C	2307.3064 (8)	2258.2295 (2)
τ_{xxxx}	-0.03789 (1)	-0.03628 (3)
τ_{yyyy}	-0.02835 (1)	-0.02732 (1)
τ_{xxyy}	-0.03278 (1)	-0.03148 (1)
τ_{xzzz}	-1.0238 (8)	- .9806 (2)

^aNumbers in parentheses represent one standard deviation in the fit

Table VI. Observed and Calculated Line Centers for $C_2H_2 \cdots HCl$

Isotope	Transition		Observed (MHz)	This Work	Resd (KHz)	Legon, ¹ et al	Resd (KHz)
$C_2H_2 \cdots H^{35}Cl$	1_{01}	2_{02}	9578.417	9578.417	0	9578.417	0
	1_{10}	2_{11}	9749.571	9749.571	0	9749.555	16
	1_{11}	2_{12}	9404.613	9404.613	0	9404.629	-16
	2_{02}	3_{03}	14365.489	14365.489	0	14365.489	0
	2_{11}	3_{12}	14623.430	14623.430	0	14623.441	-11
	2_{12}	3_{13}	14106.064	14106.064	0	14106.054	10
$C_2H_2 \cdots H^{37}Cl$	1_{01}	2_{02}	9366.936	9366.936	0	9366.936	0
	1_{10}	2_{11}	9530.606	9530.606	0	9530.591	15
	1_{11}	2_{12}	9200.670	9200.670	0	9200.685	-15
	2_{02}	3_{03}	14048.429	14048.429	0	14048.429	0
	2_{11}	3_{12}	14295.038	14295.038	0	14295.048	-10
	2_{12}	3_{13}	13800.202	13800.202	0	13800.192	10

weakly dependent on $\langle \cos^2 \alpha_z \rangle$, this value was determined from the librational amplitude by approximately $\langle \cos^2 \alpha_z \rangle \cong \langle \cos^2 \alpha \rangle$ (see Results Section, part D). The validity of this approximation can be demonstrated by considering the magnitude of the Eckart counter-rotation necessary to offset the librational motion of the HCl subunit. For an in-plane libration of HCl about its center of mass of 35° , the Eckart counterrotation of the complex required to bring the z-axis into the (a) inertial frame is $.2^\circ$. This approximation can also be demonstrated to be reasonable when the magnitude of I_{xz} is considered relative to the diagonal inertial tensor elements.

Given the moments of inertia of the subunits (see Table VII) and the value of $\langle \cos^2 \alpha \rangle = 17.1^\circ$, $R_3^* = \text{Arccos}[\cos^2 R_3]^{1/2}$ and R_0 were determined from the rotational constants by an iterative fit of eqns (99) - (102). The vibrationally averaged structure of $\text{C}_2\text{H}_2 \cdot \text{HCl}$ is reported in Table VIII along with the earlier structure proposed by Legon.

C. Van der Waals Force Field

The van der Waals force field can be completely specified by four force constants and one interaction constant that couples the in-plane librational modes of the complex. The centrifugal distortion analysis provided two linearly independent taus which can be calculated from a knowledge of the force constants. The analysis of the nuclear quadrupole hyperfine structure yielded tensor elements which were used with a knowledge of the electric field gradient to calculate vibrationally averaged projection operators $\langle \cos^2 \alpha_b \rangle$ and $\langle \cos^2 \alpha_c \rangle$. These operators can also be determined from the force field when calculated from the normal mode wave functions (see Methods Section, part C). In order to completely determine the force field, it was necessary to supplement these values

Table VII. Spectroscopic and Molecular Constants of C₂H₂ and HCl

C ₂ H ₂		
B ₀ (MHz) ^a	35273.820	
B _e (MHz) ^b	35455.374	
r ₀ (C-C) (Å) ^c	1.20858 (5)	
r ₀ (C-H) (Å) ^c	1.05706 (10)	
r _e (C-C) (Å) ^b	1.20241 (9)	
r _e (C-H) (Å) ^b	1.06250 (10)	
Q (esu-cm ²) ^d	8.0 (16) × 10 ⁻²⁶	
	H ³⁵ Cl	H ³⁷ Cl
B ₀ (MHz) ^e	312989.297	312519.121
B _e (MHz) ^e	317557.115	317076.601
r ₀ (Å) ^f	1.28387	1.28386
r _e (Å) ^e	1.2745991	1.2745991
χ ₀ (MHz) ^g	-67.61893	-53.294
μ (D) ^h	1.07	1.07

^aReference 77^bReference 78^cCalculated from B₀ values in Reference 77 via least squares fit^dReference 79^eReference 80^fCalculated from Reference 80^gReference 71^hReference 81

Table VIII. The Vibrationally Averaged Structure of $C_2H_2 \cdot H^{35}Cl$

	This Work	Legon ¹ et.al.
R_0 (A)	3.660 (5) ^a	3.663
R_3^* (deg)	9.3 (4) ^a	not determined
α_b^* (deg)	12.6 ^b	15.7
α_c^* (deg)	11.7 ^b	15.0

^aDetermined from rotational constants

^bDetermined from normal mode wavefunctions, uncertainties described in Discussion Section

determined from the microwave spectrum with normal mode frequencies from an argon matrix infrared study.²

Since frequencies of the van der Waals modes may be shifted 5 to 10% from their gas phase values by matrix effects, a corresponding uncertainty in the force field is expected.³⁶

The distortion constants, normal mode frequencies and projection operators are not all linearly dependent on the force field. Recalling eqn (66), it is clear that the distortion constants are linear functions of the elements of the inverse force constant matrix, while the vibrationally averaged projection operators and normal mode frequencies are to first order linear functions of the \underline{f} matrix elements. Due to this incompatibility in dependence on the force field, a simultaneous fit of the force field to these five values was not possible using the usual Jacobian method.⁷⁴

The \underline{f} matrix of $C_2H_2 \cdot \cdot HCl$, however, factors into A_1 , B_2 and B_2 symmetry blocks of order 1,2,1 respectively. This clearly permits two of the five force constants to be determined independently. The force constants f_{11} and f_{44} correspond to the elements of the A_1 and B_2 symmetry blocks, while f_{22} , f_{23} and f_{33} comprise the B_1 symmetry block.

Consideration of the inertial derivatives, evaluated under the rigid rod approximation using a "T"-shaped geometry and $r_e = R_0$, indicated that τ_{xxxx} was a function of f_{11}^{-1} only. Since f_{11} is independent of the rest of the \underline{f} matrix, $f_{11}^{-1} = 1/f_{11}$, and may therefore be determined directly.

The value of f_{44} can also be determined independently by means of the secular eqn (15) since the normal mode ω_4 is the only mode of B_2 symmetry.

The remaining force constants, f_{22} , f_{23} and f_{33} , were determined iteratively from $\omega_2 = 240 \text{ cm}^{-1}$, τ_{xzxz} , and $\langle \cos^2 \alpha_b \rangle$. The normal mode fre-

Table IX. Normal Coordinate Analysis of $C_2H_2 \cdots H^{35}Cl$

f_{11} (mdyne/A)	0.0630 (2)
f_{22} (mdyne A)	0.0522
f_{23} (mdyne A)	0.0302
f_{33} (mdyne A)	0.0454
f_{44} (mdyne A)	0.0544
ω_1 (cm^{-1})	84.2
ω_2 (cm^{-1})	240.0
ω_3 (cm^{-1})	58.2
ω_4 (cm^{-1})	240.0
χ^{HCl} (Mhz)	-62.3

quencies ω_2 and ω_4 are degenerate as they are reported as unresolved features in the argon matrix study of Andrews, et. al.² The vibrationally averaged projection operator was determined from the electric field gradient and the nuclear quadrupole tensor elements as described in Part C, Methods Section. The iterative process was deemed necessary due to the nonlinear dependence of τ_{xzxz} on these force constants.

The complete force field and calculated normal mode frequencies from a rigid rod normal coordinate analysis are given in Table IX. Appendix III details the matrices and eqns used in this calculation. No uncertainties in the force field and normal mode frequencies are cited as the uncertainty due to matrix effects is expected to be larger than the uncertainties in the spectroscopic constants.

D. Effects of Hydrogen Bonding on Monomer Properties

The symmetry of the complex afforded the opportunity to investigate the effect of hydrogen bonding, i.e., complexation on the monomer properties, specifically the bond length in $C_2H_2 \cdots HF$ and the electric field gradient at a quadrupolar nucleus in $C_2H_2 \cdots DF$ and $C_2H_2 \cdots HCl$. It had been common practice prior to this study to assume the electric and structural properties of the monomers remained unchanged upon complexation.

Since ω_4 is the only mode of B_2 symmetry, the vibrationally averaged projection operator, $\langle \cos^2 \alpha_c \rangle$, can be calculated from ω_4 via the normal mode wave function Ψ_4 (see Part C, Methods Section).

The projection operator can also be determined from the electric field gradient and the nuclear quadrupole tensor elements via eqn (95). With the value of $\langle \cos^2 \alpha_c \rangle$ and the nuclear quadrupole tensor elements, a value for the electric field gradient at Cl in the complex can now be obtained via eqn (95). This permits calculation of $\langle \cos^2 \alpha_b \rangle$ via eqn (94),

which can be used in obtaining the force constants of the B_1 symmetry block. Knowledge of the electric field gradient also permits calculation of $\langle \cos^2 \alpha \rangle$ from χ_{aa} :¹

$$\chi_{HC1} = \frac{\chi_{aa}}{2} [3 \langle \cos^2 \alpha \rangle - 1]^{-1} \quad (104)$$

This value can be utilized in the determination of the vibrationally averaged structure (see Part B, Results Section).

This same approach may be invoked for $C_2H_2 \cdots DF$ to determine the electric field gradient at deuterium. The spectrum, obtained by Read,⁷³ reveals that $\chi_{bb} = \chi_{cc}$, thus $\langle \cos^2 \alpha_b \rangle = \langle \cos^2 \alpha_c \rangle$ as determined by eqns (94) - (95). With normal mode frequencies available from an argon matrix study,² $\langle \cos^2 \alpha_c \rangle = \langle \cos^2 \alpha_b \rangle$ can be obtained from the normal mode wave functions (see Methods Section, Part C). The projection operator $\langle \cos^2 \alpha \rangle$ can be written as a function of these components (see Appendix IV):

$$\langle \cos^2 \alpha \rangle = \left\langle \frac{\cos^2 \alpha_b \cos^2 \alpha_c}{\cos^2 \alpha_b + \cos^2 \alpha_c - \cos^2 \alpha_b \cos^2 \alpha_c} \right\rangle \quad (105)$$

and employed in eqn (106):

$$\chi_{DF} = \frac{\chi_{aa}}{2} [3 \langle \cos^2 \alpha \rangle - 1]^{-1} \quad (106)$$

to obtain χ_{DF} . The values for χ_{DF} , χ_{HC1} and their respective electric field gradients are cited in Tables X - XI. Their uncertainties are governed by the same considerations involved for the force field.

Consideration of $C_2H_2 \cdots HF$ permitted an opportunity to obtain an estimate of bond elongation upon complexation. Since both hydrogen and fluorine possess spins of $\frac{1}{2}$ the spectrum of $C_2H_2 \cdots HF$ will possess fine structure

Table X. Spectroscopic and Molecular Constants of C₂H₂··HF/DF

	C ₂ H ₂ ··HF	C ₂ H ₂ ··DF
ω_4 (cm ⁻¹) ^a	382.0	284.4
$b_{\text{HF/DF}}$ (MHz)	616365.5 ^b	325584.98 ^c
B (MHz) ^d	4719.9790	4698.4312
G_{44} ^e (amu A ²) ⁻¹	1.22895	0.65354
χ_{aa} (KHz) ^d	---	282.6
χ_{DF} (KHz) ^f	---	354.238
χ^{DF} (KHz) ^e	---	315.73
D_{aa} (KHz) ^d	-237.2	---
D^{HF} (KHz) ^f	-286.75	---
D^{HF} (KHz) ^e	-277.3	---

^aReference 2^bReference 82^cReference 83^dReference 73^eThis work^fReference 84

Table XI. Effect of Hydrogen Bonding on HX Properties

		Complex	bound HX/DX	free HX/DX
$\left(\frac{\partial^2 V}{\partial Z^2}\right)^{Cl}$	$(10^{13} \frac{\text{volt}}{\text{cm}^2})$	$C_2H_2 \cdots H^{35}Cl$	1.79	1.94
$\left(\frac{\partial^2 V}{\partial Z^2}\right)^D$	$(10^{13} \frac{\text{volt}}{\text{cm}^2})$	$C_2H_2 \cdots DF$	0.208	0.233
$r_{HF} (A^\circ)$		$C_2H_2 \cdots HF$	0.936	0.92559

related to the interaction of the magnetic moment of fluorine with the magnetic moment of hydrogen in HF. An analysis of this hyperfine structure yields D_{aa} , the vibrationally averaged projection of the spin-spin interaction of HF on the (a) inertial axis, defined in the following manner:⁷³

$$D_{aa} = D_{HF}/2 [3 \langle \cos^2 \alpha \rangle - 1] \quad (107)$$

where D_{HF} is defined as:⁴

$$D_{HF} = -2g_F g_H \mu_N^2 / R^3 \quad (108)$$

where g_F , g_H are the nuclear g-factors, μ_N is the nuclear magneton and R is the H-F bond length. A knowledge of D_{aa} and $\langle \cos^2 \alpha \rangle$ permit calculation of D_{HF} and via eqn (108), the H-F bond length in the complex. These results are reported in Tables X-XI subject to uncertainty due to matrix effects.

DISCUSSION

Examination of the results of this study clearly reveals a significant improvement in the description of $C_2H_2 \cdot \cdot HCl$. Comparison of the spectra given in Table VI indicates that for the transitions observed the effects of centrifugal distortion can be properly accounted for by an exact asymmetric top first order perturbation treatment as opposed to the approximate symmetric top treatment proposed by Legon.¹ This calculation also yielded spectroscopic constants which were used to further characterize the complex in terms of its vibrationally averaged structure and intermolecular force field.

The rotational constants obtained from the centrifugal distortion analysis permitted a complete description of the structural parameters of the rigid rod model. Using inertial eqns derived to describe the complex as a weakly bound nonlinear rigid rod system, it was possible to obtain the refined structure in Table VIII.

The description of the intermolecular force field based on the available data served as the incentive for the development of the rigid rod normal coordinate analysis. This description, neglecting anharmonicity and off-diagonal elements coupling the high and low frequency blocks of the exact Gf matrix, permitted characterization of the intermolecular force field of the complex. The neglect of off-diagonal elements that couple the high and low frequency blocks of the Gf matrix will introduce uncertainty into the force field, tending to overestimate the normal mode frequencies by several percent.⁵⁴ A measure of the self consistency of this calculation can be demonstrated by using normal mode wave functions

to calculate $\langle \cos^2 R_3 \rangle$:

$$\langle \cos^2 R_3 \rangle = \int_{-\infty}^{\infty} \Psi^*(Q_2) \Psi^*(Q_3) \cos^2 R_3 \Psi(Q_2) \Psi(Q_3) dQ_2 dQ_3 \quad (109)$$

where $\Psi(Q_2)$ and $\Psi(Q_3)$ are defined in terms of ω_2 and ω_3 respectively (see Methods Section, Part C). This vibrationally averaged projection operator was also obtained from the (A) rotational constant via eqn (101). The value $R_3^* = \text{Arccos}[\cos^2 R_3]^{1/2} = 9.3^\circ$ evaluated from (A) can be compared to $R_3^* = 8.2^\circ$ obtained from the integration over the normal mode wave functions. The discrepancy can be attributed to model dependent effects and matrix perturbations of the force field as well as the uncertainty in the (A) rotational constant.

This method permits a very important advance in the knowledge of the complexes in that it is now possible to estimate the effects of complexation on monomer properties such as bond length and the electric field gradient at a quadrupolar nucleus. Examination of Tables X-XI reveals a decrease in the electric field gradient due to complexation. This decrease can be attributed to an increase in charge separation due to hydrogen bonding. In $C_2H_2 \cdots HCl$, this causes the H-Cl bond to become more ionic. As the ionic character increases, the electric charge density immediately surrounding the atom tends to become more spherically symmetric thus decreasing the amount of interaction between the spinning nuclear charge and the rotating molecule. The observed increases in H-F bond length and ionic character of the HCl monomer are clearly consistent with the reported red shift of the HX stretching frequencies, e.g. 208 cm^{-1} for HF.^{75,2}

The importance of the methods developed in the course of this study cannot be overemphasized. It is evident that these methods will permit

the opportunity of further refinements of intermolecular force fields of complexes as well as gas phase vibrational spectra and vibrationally excited rotational spectra become available. In addition, the description of the van der Waals vibrations in terms of rigid subunits can clearly be generalized and extended to further understand the electrical properties and dynamics of other van der Waals molecules.

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Appendix I

FITSPECT-Jacobian Fitting Program to Calculate Spectrum


```

C ANYFIT BY REBECCA LEE 14 APR 83 00000070
C THIS PROGRAM IS DESIGNED FOR THE GENERAL PURPOSE OF JACOBIAN FITTING 00000080
C THE ALGORITHM USED IS OUTLINED BY NYUNYONG KIM, J. CHEM. ED., 7, 2 (1970) 00000090
C P. 120-122. THE FITTING ROUTINE IS GENERAL AND REQUIRES NO ADAPTATION 00000100
C FROM APPLICATION TO APPLICATION. THE USER MUST SUPPLY BOTH AN OUTPUT 00000110
C SUBROUTINE CUSTOMIZED TO OUTPUT THE DATA IN THE DESIRED FORMAT, AND 00000120
C AN 'FSUB' SUBROUTINE THAT MAY EITHER SERVE AS AN INTERFACE BETWEEN 00000130
C THE SUBROUTINE THAT CALCULATES THE NUMBERS THAT ARE TO BE USED IN 00000140
C FITTING PROCESS OR WILL ACTUALLY DO THE CALCULATIONS ITSELF. THIS 00000150
C IS DEPENDENT ON THE COMPLEXITY OF THE CALCULATIONS INVOLVED. 00000160
C THERE ARE THREE STOCK SUBROUTINES THAT ACCOMPANY THIS PACKAGE 00000170
C MATOUT=SUBROUTINE THAT OUTPUTS JACOBIAN MATRIX WHEN FIT CONVERGES 00000180
C MMULT=MATRIX MULTIPLICATION SUBROUTINE 00000190
C MTRXIN=MATRIX INVERSION SUBROUTINE 00000200
C N=NUMBER OF PARAMETERS M=NUMBER OF EXPERIMENTALS 00000210
C A=ARRAY OF PARAMETERS TO BE FITTED 00000220
C Y=ARRAY OF EXPERIMENTAL VALUES YL=ARRAY TO STORE THE EXP. LABELS 00000230
C TITLE=WHERE HEADING STORED STAR=LINE OF STARS FOR FORMAT 00000240
C E=ERROR ARRAY XJ=JACOBIAN ARRAY 00000250
C XJT=TRANSPOSE OF XJ XJP=XJ*XJT, INVERSE ALSO STORED HERE 00000260
C XJTE=XJT*E VRP=VARIANCE OF PARMS ARRAY 00000270
C F,FP=CALCULATED VALUES ARRAY (FP HOLDS THE NEW CALC VALUES IN IT) 00000280
C DLA=ARRAY TO HOLD ADJUSTMENTS TO PARAMETER ARRAY 00000290
C ISDE=SWITCH TO GET STD DEV OF PARMS (IF DESIRED=1) 00000300
C ITC=ULTIMATE HIGHEST NUMBER OF CYCLES FITTING PROGRAM IS PERMITTED 00000310
C ITC IS FAILSAFE LIMIT IN CASE FIT GETS OUT OF HAND 00000320
C IMPLICIT REAL*(8(A-H,I-Z)) 00000330
C DIMENSION A(50),Y(50),YL3L(50,15),TITLE(15),STAR(18),E(50) 00000340
C DIMENSION XJ(50,50),XJT(50,50),XJP(50,50),XJTE(50),AP(50) 00000350
C DIMENSION VRP(50),F(50),FP(50),DLA(50) 00000360
C*****INITIALIZE MATRICES*****00000370
K=1 00000380
MDIM=50 00000390
DO 40 IN=1,MDIM 00000400
AP(IN)=0.000 00000410
E(IN)=0.000 00000420
F(IN)=0.000 00000430
FP(IN)=0.000 00000440
XJTE(IN)=0.000 00000450
Y(IN)=0.000 00000460
DLA(IN)=0.000 00000470
A(IN)=0.000 00000480
VRP(IN)=0.000 00000490
DO 5 IM=1,7 00000500
YL3L(IN,IM)=0.000 00000510
CONTINUE 00000520
40 CONTINUE 00000530
DO 45 I1=1,MDIM 00000540
DO 45 IJ=1,MDIM 00000550
XJ(I1,IJ)=0.000 00000560
XJT(I1,IJ)=0.000 00000570
XJP(I1,IJ)=0.000 00000580
45 CONTINUE 00000590
C*****READ IN PARAMETERS, TITLE, EXPERIMENTAL VALUES, LABELS, ETC*****00000600
READ (5,30) TITLE 00000610
READ (5,30) STAR 00000620
READ (5,10) N,M,ITC,ISDE 00000630
DO 15 I=1,N 00000640
READ (5,20) A(I) 00000650
15 CONTINUE 00000660

```

```

DD 25 J=1,M                                00000670
READ (5,24) Y(J),(YLBL(J,IJ),IJ=1,7)      00000680
25 CONTINUE                                  00000690
C*****FITTING LDDP*****00000700
  ICHK=0                                     00000710
  WRITE (6,30) TITLE                         00000720
  WRITE (6,29)                               00000730
29 FORMAT (1H,'FORCE CONSTANTS IN PROPER CGS UNITS') 00000740
100 CALL FSUB (MDIM,N,M,A,F)                00000750
  DD 50 IE=1,M                               00000760
  E(IE)=Y(IE)-F(IE)                         00000770
50 CONTINUE                                  00000780
C*****CALCULATE VARIANCE OF OVERALL FIT, REGRESSION, STD ERROR OF PARMS****00000790
  RM2=0.000                                  00000800
  DD 85 NP=1,M                               00000810
  QM=M                                        00000820
  QN=N                                        00000830
  RM2=(E(NP)**2)+RM2                         00000840
85 CONTINUE                                  00000850
  VARP=DSQRT(RM2/(QM-QN))                   00000860
  IF (ISDE.NE.1) GO TO 95                   00000870
  IF (ICLK.EQ.0) GO TO 95                   00000880
  DD 90 NV=1,N                               00000890
  VRP(NV)=DSQRT((VARP**2)*XJP(NV,NV))      00000900
90 CONTINUE                                  00000910
95 WRITE (6,30) STAR                         00000920
110 CALL OUTPUT (N,M,A,F,Y,YLBL,E,VRP,ICLK,VARP,RM2) 00000930
C*****TEST FOR DIVERGENCE-CONVERGENCE*****00000940
  IF (ICLK.EQ.0) GO TO 121                  00000950
  IF (VARP.GT.VAR) GO TO 150                00000960
120 IF ((ICLK.GT.ITC).OR.(VARP.GT.(VAR-1.00-0.4*VAR))) GO TO 250 00000970
121 VAR=VARP                                 00000980
  GO TO 300                                  00000990
250 WRITE (6,30) STAR                         00001000
  KL=0                                       00001010
  CALL MATOUT (MDIM,M,XJ,KL)                00001020
  GO TO 200                                  00001030
C*****JACOBIAN LDDP*****00001040
300 ICHK=ICLK+1                              00001050
  DD 60 K=1,N                               00001060
  TWA=0.000                                  00001070
  DD 303 MI=1,N                              00001080
  AP(MI)=A(MI)                              00001090
303 CONTINUE                                  00001100
  IF (AP(K)-0.000) 55,54,55                 00001110
55 TWA=AP(K)*1.00-06                        00001120
  GO TO 56                                   00001130
54 TWA=1.00-06                              00001140
56 AP(K)=AP(K)+TWA                          00001150
  CALL FSUB (MDIM,N,M,AP,FP)                00001160
  DD 65 IK=1,M                              00001170
  XJ(IK,K)=(FP(IK)-F(IK))/TWA              00001180
65 CONTINUE                                  00001190
60 CONTINUE                                  00001200
  DD 70 IR=1,M                              00001210
  DD 70 IC=1,M                              00001220
  XJT(IC,IR)=XJ(IR,IC)                    00001230
70 CONTINUE                                  00001240
  CALL MMULT(MDIM,N,M,N,XJT,XJ,XJP)        00001250
  CALL MTPXIN (MDIM,XJP,I)                  00001260

```



```

16 DD 20 L=1,N                                00001670
      SWAP=A( IROW,L)                          00001680
      A( IROW,L)=A( ICCLUM,L)                  00001690
20 A( ICOLUM,L)=SWAP                           00001900
C   DIVIDE PIVOT ROW BY PIVOT ELEMENT           00001910
17 PIVOT=A( ICOLUM,ICCLUM)                     00001920
      A( ICOLUM,ICOLUM)=1.000                 00001930
      DD 23 L=1,N                               00001940
23 A( ICCLUM,L)=A( ICCLUM,L)/PIVOT             00001950
C   REDUCE THE NON PIVOT ROWS                  00001960
      DD J L1=1,N                               00001970
          IF( L1-ICOLUM)26,3,26                00001980
26     T=A( L1,ICOLUM)                         00001990
          A( L1,ICOLUM)=0.000                 00002000
          DD 29 L=1,N                           00002010
29     A( L1,L)=A( L1,L)-A( ICOLUM,L)*T       00002020
      3 CONTINUE                               00002030
C   INTERCHANGE THE COLUMNS                   00002040
      DD 31 I=1,N                               00002050
          L=N-I+1                              00002060
          IF( IPV( L,1)-IPV( L,2))34,31,34     00002070
34     JROW=IPV( L,1)                          00002080
          JCCLUM=IPV( L,2)                    00002090
          DD 32 K=1,N                           00002100
              SWAP=A( K,JROW)                 00002110
              A( K,JROW)=A( K,JCCLUM)        00002120
              A( K,JCCLUM)=SWAP              00002130
32     CONTINUE                               00002140
31 CONTINUE                                   00002150
41 RETURN                                     00002160
      END                                       00002170
C                                               00002180
C           MATOUT                               00002190
C   WRITTEN BY REBECCA LEE 11 FEB 83 EASTERN ILLINOIS UNIVERSITY 00002200
C   THIS SUBROUTINE WILL PRINT OUT ANY SIZE MATRIX WITH NINE COLUMNS 00002210
C   ON A PAGE. THE CALLING SEQUENCE IS AS FOLLOWS: 00002220
C   CALL MATOUT (MDIM,NN,X) 00002230
C   WHERE: MDIM=DIMENSION OF THE MAIN ARRAY 00002240
C           NN=ORDER OF THE MATRIX TO BE PRINTED OR NUMBER OF ROWS 00002250
C           IN THE CASE OF A MATRIX WHICH IS NOT SQUARE 00002260
C           X=THE MATRIX TO BE PRINTED 00002270
C   SUBROUTINE MATOUT (MDIM,NN,W,KL) 00002280
      IMPLICIT REAL*8(A-H,O-Z) 00002290
      DIMENSION W(MDIM,MDIM) 00002300
      MC=0 00002310
      NN=9 00002320
      IF (KL.EQ.1) GO TO 1000 00002330
      IF (NN.LE.NN)GO TO 40 00002340
      NT=NN/NN 00002350
      DD 5 K=1,NT 00002360
          IF (K.EQ.1) GO TO 3 00002370
          IF (K.NE.1) GO TO 5 00002380
3         M=1 00002390
          GO TO 8 00002400
6         M=M+9 00002410
8         MC=MC+9 00002420
          WRITE (0,500) M,MC 00002430
900     FORMAT (1H,'J=',I3,' TO ',I3) 00002440
          DD 7 I=1,NN 00002450
          WRITE (0,599) (W(I,J),J=4,MC) 00002460
          ***** FORMAT (1H0,5(012.0,2X)) 00002470

```

```

5   CONTINUE .                                00002470
    NTP=NT*NN                                  00002480
    NTR=NON-NTP                                00002490
    NTP=NTP+1                                  00002500
    IF(NTR.EQ.0) GO TO 1000                    00002510
    IF(NTR.LT.NN) GO TO 30                     00002520
30  WRITE (6,900) NTP,NON                      00002530
    GO TO 50                                    00002540
50  DO 45 I=1,NON                               00002550
45  WRITE (6,999) (*(I,J),J=1,NON)           00002560
    RETURN                                      00002570
50  DO 50 I=1,NON                               00002580
50  WRITE (6,999) (*(I,J),J=NTP,NON)         00002590
1000 RETURN                                    00002600
    END                                         00002610
    SUBROUTINE FSUB (MDIM,N,A,A,F)             00002620
    IMPLICIT REAL*8 (A-H,O-Z)                 00002630
    DIMENSION A(MDIM),F(MDIM),FRQI(14)       00002640
C *****CALCULATION OF SPECTRUM VIA DPREP AND ROTCEN***** 00002650
    DO 15 J=1,14                                00002660
    FRQI(J)=0.000                               00002670
15  CONTINUE                                    00002680
    CALL DPREP(MDIM,A,FRQI)                     00002690
C *****PLACE DESIRED FREQUENCIES IN F ARRAY*****          00002700
    F(1)=FRQI(2)                                00002710
    F(2)=FRQI(5)                                00002720
    F(3)=FRQI(4)                                00002730
    F(4)=FRQI(6)                                00002740
    F(5)=FRQI(10)                               00002750
    F(6)=FRQI(8)                                00002760
    RETURN                                       00002770
    END                                         00002780
C
C          DPREP                                00002790
C
C   DEFINITION OF INTERNAL COORDINATES:       00002800
C   R1=HCL STRETCHING MOTION ALONG THE Z-AXIS 00002810
C   R2=HCL LIBRATIONAL MOTION IN THE XZ PLANE 00002820
C   R3=ACETYLENE BENDING MOTION IN THE XZ PLANE 00002830
C   R4=HCL LIBRATIONAL MOTION IN THE YZ PLANE 00002840
C   BENDING AND LIBRATION PIVOT PT IS THE C.O.F.MASS OF SUBUNIT 00002850
C
C   SUBROUTINE DPREP(IDIM,P,FRQ)               00002860
C   IMPLICIT REAL*8(A-H,O-Z)                   00002870
C   DIMENSION P(IDIM),F(3),TAU(7),FRQ(14)     00002880
C *****INITIALIZATION*****                   00002890
    DO 10 IJ=1,7                                 00002900
    TAU(IJ)=0.000                               00002910
10  CONTINUE                                    00002920
C *****PLACE TAUS IN TAU ARRAY TO SEND TO ROTCEN*****    00002930
C   NOTE TAUS MUST BE CONVERTED TO MHZ BEFORE THEY ARE SENT TO ROTCEN 00002940
C   TAU(1)=T-ZZZZ      TAU(2)=T-XXXX=TX4      TAU(3)=T-KXZZ 00002950
C   TAU(4)=T-XZZZ=TXZ  TAU(5)=T-YYYY=TY4      TAU(6)=T-YYXX=TX2Y2 00002960
C   TAU(7)=T-YYZZ      00002970
C *****                                           00002980
    A=P(1)                                       00002990
    B=P(2)                                       00003000
    C=P(3)                                       00003010
    TAU(2)=P(4)                                  00003020
    TAU(4)=P(5)                                  00003030
    TAU(5)=((P(3)/P(2))**4)*TAU(2)              00003040
    TAU(6)=((P(3)/P(2))**2)*TAU(2)              00003050
    CALL ROTCEN (A,B,C,TAU,FRQ)                 00003060

```

```

RETURN 00003070
END 00003080
C ROTCEN BY REBECCA LEE 00003090
C EASTERN ILLINOIS UNIVERSITY 00003100
C 12 MAR 83 00003110
C ROTCEN CALCULATES THE HAMILTONIAN FOR A SPECIFIC J-BLOCK AND WILL 00003120
C DIAGONALIZE IT AND OBTAIN THE ENERGY LEVELS FOR THAT STATE. IT HAS 00003130
C A SWITCH TO CALCULATE THE ENERGIES CORRECTED FOR CENTRIFUGAL 00003140
C DISTORTION. IT CALLS A SUBROUTINE (CDI) WHICH WILL CALCULATE THE 00003150
C DISTORTION ENERGIES ACCORDING TO A FIRST ORDER APPROXIMATION. IT 00003160
C WILL ADD THIS CORRECTION TO THE RIGID ROTOR ENERGY. ROTCEN ALSO 00003170
C CALCULATES THE SPECTRUM OF THE MOLECULE IN QUESTION ACCORDING TO 00003180
C SWITCH, Q AND R BRANCH TRANSITIONS WITH ANY COMBINATION OF A,B,C 00003190
C DIPOLE TRANSITIONS CAN BE DESIGNATED. THE APPROPRIATE DESIGNATIONS 00003200
C FOR THE SWITCHES WILL FOLLOW. THE SWITCHES ARE EITHER ONE OR ZERO 00003210
C WITH ONE AS THE VALUE TO OBTAIN THE DESIRED OPTION. THIS PROGRAM 00003220
C WAS WRITTEN WITH THE STRATEGIES PROVIDED BY DR. GILES HENDERSON. 00003230
C PROFESSOR OF PHYSICAL CHEMISTRY, EASTERN ILLINOIS UNIVERSITY. 00003240
C***** 00003250
SUBROUTINE ROTCEN (AP,BP,CP,TAU,FRQ) 00003260
IMPLICIT REAL*8(A-H,O-Z) 00003270
DIMENSION TAU(7),FRQ(20),H(21,21),EIVR(21,21),E(11,21),T(7) 00003280
DIMENSION KPN(11,21),KOQN(11,21),ISK(11,21) 00003290
NDM=11 00003300
MDIM=21 00003310
IGN=1 00003320
IGEN=0 00003330
IQND=1 00003340
C***** 00003350
C AP,BP,CP ARE THE EQUILIBRIUM CONSTANTS NORMALLY USED IN THE RIGID 00003360
C ROTOR HAMILTONIAN. A,B,C ARE THE SCRIPT CONSTANTS GIVEN IN EQN 8.4 00003370
C ON P. 222, GCRDY AND COOK. 00003380
C***** 00003390
ICEDS=1 00003400
JMAX=3 00003410
IQBR=0 00003420
IRBR=1 00003430
IAS=1 00003440
IBS=0 00003450
ICS=0 00003460
C*****TAU-T INTERFACE***** 00003470
DO 6 I=1,7 00003480
T(I)=TAU(I) 00003490
6 CONTINUE 00003500
C*****CALCULATE A,B,C***** 00003510
R5=(1.000/64.000)*(T(2)+T(5)-2.000*T(6)) 00003520
A=AP+16.000*R5 00003530
E=BP-((16.000*R6*(AP-CP))/(BP-CP)) 00003540
C=CP+((16.000*R6*(AP-BP))/(BP-CP)) 00003550
GO TO 12 00003560
9 A=AP 00003570
B=BP 00003580
C=CP 00003590
C*****INITIALIZE THE APRAYS***** 00003600
DO 5 I=1,20 00003610
FRQ(I)=0.000 00003620
5 CONTINUE 00003630
12 NMAX=JMAX + 1 00003640
NMAX=2*JMAX + 1 00003650
DO 13 NI=1,NMAX 00003660

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      DD 13 NJ=NI,NMAX                                00003670
      H(NI,NJ)=C.0DC                                  00003680
      EIVR(NI,NJ)=C.0DC                               00003690
      H(NJ,NI)=H(NI,NJ)                              00003700
      EIVR(NJ,NI)=EIVR(NI,NJ)                       00003710
13    CONTINUE                                       00003720
      DD 15 MI=1,MMAX                                00003730
      DD 15 MJ=1,NMAX                                00003740
      E(MI,MJ)=C.0DC                                 00003750
      KPGN(MI,MJ)=0                                  00003760
      KCGN(MI,MJ)=0                                  00003770
      ISM (MI,MJ)=0                                  00003780
15    CONTINUE                                       00003790
      JMAXD=0                                         00003800
C*****CALCULATE ASYMP=KAPPA, THE ASYMMETRY PARAMETER***** 00003810
      ASYMP=((2.0DC*BP)-AP-CP)/(AP-CP)                00003820
C*****CALCULATE THE HAMILTONIAN MATRIX FOR EACH J-STATE***** 00003830
      DD 500 M=1,MMAX                                00003840
      N=M-1                                           00003850
      NXN=2*N +1                                     00003860
      DD 40 II=1,NXN                                  00003870
      DD 40 IJ=II,NXN                                00003880
      K=II-(N+1)                                      00003890
      KP=IJ-(N+1)                                     00003900
      IF (ASYMP-0.0DC) 25,25,30                      00003910
25    IF (K.EQ.KP) H(II,IJ)=HPD(A,B,C,N,K)          00003920
      IF ((K+2).EQ.KP) H(II,IJ)=HPGD(A,B,C,N,K)    00003930
      IF ((K.NE.KP).AND.((K+2).NE.KP)) H(II,IJ)=0.0DC 00003940
      H(IJ,II)=H(II,IJ)                              00003950
      GO TO 40                                         00003960
30    IF (K.EQ.KP) H(II,IJ)=HOD(A,B,C,N,K)          00003970
      IF ((K+2).EQ.KP) H(II,IJ)=HOGD(A,B,C,N,K)    00003980
      IF ((K.NE.KP).AND.((K+2).NE.KP)) H(II,IJ)=0.0DC 00003990
      H(IJ,II)=H(II,IJ)                              00004000
      GO TO 40                                         00004010
40    CONTINUE                                       00004020
C*****DIAGONALIZE J BLOCK,ORDER. READ EIGENVALJES INTO E MATRIX***** 00004030
      CALL HDIAG (H,NXN,MDIM,IGEN,IORND,EIVR)        00004040
      DD 28 J=1,NXN                                   00004050
      E(M,J)=H(J,J)                                  00004060
28    CONTINUE                                       00004070
C*****REINITIALIZE H MATRIX***** 00004080
      DD 45 IL=1,21                                   00004090
      DD 45 LI=1,21                                   00004100
      H(IL,LI)=C.0DC                                 00004110
45    CONTINUE                                       00004120
C*****CONSTRUCT K-PROLATE,K-OBLATE LABELS***** 00004130
      IK=0                                             00004140
      L=0                                              00004150
      DD 29 KJ=1,NXN,2                                00004160
      IK=IK+1                                          00004170
      L=NXN+1-KJ                                       00004180
      KPGN(M,KJ)=KJ-IK                                  00004190
      KCGN(M,L)=KPGN(M,KJ)                             00004200
      IF (IK.EQ.KJ) GO TO 29                          00004210
      IF (IK.NE.KJ) KPGN(M,(KJ-1))=KPGN(M,KJ)        00004220
      KCGN(M,(L+1))=KPGN(M,KJ)                       00004230
29    CONTINUE                                       00004240
C*****CALCULATE ENERGIES WITH CENTRIFUGAL DISTORTION INCLUDED***** 00004250
      IF (ICEDS.EQ.1) CALL CDI (E,MDIM,NXN,T,EIVR,N,AP,CP) 00004260

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C*****SET UP SYMMETRY MATRIX*****00004270
  DJ 60 JS=1,NXN 00004280
  NP=KPCN(M,JS) 00004290
  KCP= KSYM(NP) 00004300
  NQ=KQCN(M,JS) 00004310
  KCL= KSYM(NQ) 00004320
  IF ((KCP.EQ.-1).AND.(KQU.EQ.1)) GO TO 50 00004330
  IF ((KCP.EQ.-1).AND.(KQJ.EQ.-1)) GO TO 51 00004340
  IF ((KCP.EQ.1).AND.(KQJ.EQ.1)) GO TO 52 00004350
  IF ((KCP.EQ.1).AND.(KQD.EQ.-1)) GO TO 53 00004360
50 ISM(M,JS)=7 00004370
  GO TO 60 00004380
51 ISM(M,JS)=10 00004390
  GO TO 60 00004400
52 ISM(M,JS)=16 00004410
  GO TO 60 00004420
53 ISM(M,JS)=41 00004430
60 CONTINUE 00004440
500 CONTINUE 00004450
C*****CALCULATE SPECTRUM*****00004460
  IF=0 00004470
  IF (IRBR.EQ.1) GO TO 200 00004480
600 IF (IQER.EQ.1) GO TO 300 00004490
  GO TO 1000 00004500
200 IF (IAS.EQ.1) GO TO 201 00004510
250 IF (IBS.EQ.1) GO TO 251 00004520
260 IF (ICS.EQ.1) GO TO 261 00004530
  GO TO 600 00004540
C*****A-DIPOLE SELECTION RULES*****00004550
201 ICHK=0 00004560
  DO 210 IG=1,JMAX 00004570
  IE=IG+1 00004580
  JE=IG-1 00004590
  NXN=2*J+1 00004600
  NXNE=2*IG+1 00004610
  DO 215 JG=1,NXN 00004620
  DO 220 JE=1,NXNE 00004630
  NS=ISM(IG,JG)+ISM(IE,JE) 00004640
  IF (NS.EQ.57) GO TO 235 00004650
  IF (NS.EQ.17) GO TO 235 00004660
  GO TO 220 00004670
235 DA=(E(IE,JE)-E(IG,JG)) 00004680
  ICHK=ICLK+1 00004690
  FRQ(ICLK)=DA 00004700
220 CONTINUE 00004710
215 CONTINUE 00004720
210 CONTINUE 00004730
  GO TO 250 00004740
C*****B-DIPOLE SELECTION RULES*****00004750
251 DG 254 LG=1,JMAX 00004760
  LE=LG+1 00004770
  JE=LG-1 00004780
  NEN=2*JB+1 00004790
  NBNE=2*LG+1 00004800
  DO 256 KG=1,NEN 00004810
  DO 257 KE=1,NBNE 00004820
  MS=ISM(LG,KG)+ISM(LE,KE) 00004830
  IF (MS.EQ.26) GO TO 253 00004840
  IF (MS.EQ.46) GO TO 255 00004850
  GO TO 257 00004860

```


256	DB=(E(LE,KE)-E(LG,KG))	00004870
257	CONTINUE	00004880
258	CONTINUE	00004890
254	CONTINUE	00004900
	GO TO 280	00004910
C*****L-DIPPLE SELECTION RULES*****		00004920
281	DO 290 IC=1,JMAX	00004930
	ID=IC+1	00004940
	JC=IC-1	00004950
	NCN=(2*JC)+1	00004960
	NCNE=2*IC+1	00004970
	DO 291 MG=1,NCN	00004980
	DO 292 ME=1,NCNE	00004990
	LS=ISM(IC,MG)+ISM(ID,ME)	00005000
	IF (LS.EQ.23) GO TO 293	00005010
	IF (LS.EQ.51) GO TO 293	00005020
	GO TO 292	00005030
293	DC=(E(ID,ME)-E(IC,MG))	00005040
292	CONTINUE	00005050
291	CONTINUE	00005060
290	CONTINUE	00005070
	GO TO 600	00005080
300	IF (IADS.EQ.1) GO TO 301	00005090
350	IF (IBDS.EQ.1) GO TO 351	00005100
360	IF (ICDS.EQ.1) GO TO 381	00005110
	GO TO 1000	00005120
C*****A-DIPPLE SELECTION*****		00005130
301	DO 311 IG=2,MX	00005140
	J=IG-1	00005150
	NXN=2*J+1	00005160
	DO 312 JG=1,NXN	00005170
	DO 313 JE=JG,NXN	00005180
	NS=ISM(IG,JG)+ISM(IG,JE)	00005190
	IF (NS.EQ.17) GO TO 314	00005200
	IF (NS.EQ.57) GO TO 314	00005210
	GO TO 313	00005220
314	DA=(E(IG,JE)-E(IG,JG))	00005230
313	CONTINUE	00005240
312	CONTINUE	00005250
311	CONTINUE	00005260
	GO TO 350	00005270
C*****B-DIPPLE SELECTION RULES*****		00005280
351	DO 353 LG=2,MX	00005290
	JB=LG-1	00005300
	NBN=2*JB+1	00005310
	DO 354 KG=1,NBN	00005320
	DO 355 KE=KG,NBN	00005330
	MS=ISM(LG,KG)+ISM(LG,KE)	00005340
	IF (MS.EQ.20) GO TO 356	00005350
	IF (MS.EQ.48) GO TO 356	00005360
	GO TO 355	00005370
356	DB=(E(LG,KE)-E(LG,KG))	00005380
355	CONTINUE	00005390
354	CONTINUE	00005400
353	CONTINUE	00005410
	GO TO 380	00005420
C*****C-DIPPLE SELECTION RULES*****		00005430
381	DO 383 IC=2,MX	00005440
	JC=IC-1	00005450
	NCN=(2*JC)+1	00005460

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      DD 384 MG=1,NCN                                00005470
      DC 385 ME=MG,NCN                                00005480
      LS=ISM(IC,MG)+ISM(IC,ME)                        00005490
      IF (LS.EQ.23) GO TO 386                          00005500
      IF (LS.EQ.51) GO TO 386                          00005510
      GO TO 385                                         00005520
386   DC=(E(IC,ME)-E(IC,MG))                          00005530
385   CONTINUE                                         00005540
384   CONTINUE                                         00005550
383   CONTINUE                                         00005560
1000  RETURN                                           00005570
      END                                              00005580
      FUNCTION KSYM (N)                                00005590
C*****CALCULATES THE EVEN OR ODDNESS OF THE QUANTUM NO. K*****00005600
      IMPLICIT REAL*8(A-H,O-Z)                          00005610
      KSYM=(-1)**N                                     00005620
      RETURN                                           00005630
      END                                              00005640
      FUNCTION HPD (A,B,C,N,K)                          00005650
C*****DIAGONAL MATRIX ELEMENT-RIGID ROTOR-PROLATE*****00005660
      IMPLICIT REAL*8(A-H,O-Z)                          00005670
      RN=N                                             00005680
      RK=K                                             00005690
      HPD=((B+C)/2.0D0)*(RN*(RN+1.0D0)-RK**2) + ((RK**2)*A) 00005700
      RETURN                                           00005710
      END                                              00005720
      FUNCTION HPOD (A,B,C,N,K)                          00005730
C*****OFF DIAGONAL MATRIX ELEMENT-RIGID ROTOR-PROLATE*****00005740
      IMPLICIT REAL*8(A-H,O-Z)                          00005750
      RN=N                                             00005760
      RK=K                                             00005770
      TA=DSQRT(RN*(RN+1.0D0)-RK*(RK+1.0D0))           00005780
      TB=USQRT(RN*(RN+1.0D0)-((RK+1.0D0)*(RK+2.0D0))) 00005790
      HPOD=((E-C)/4.0D0)*TA*TB                          00005800
      RETURN                                           00005810
      END                                              00005820
      FUNCTION HOD (A,B,C,N,K)                          00005830
C*****DIAGONAL MATRIX ELEMENT-RIGID ROTOR-OBLATE*****00005840
      IMPLICIT REAL*8(A-H,O-Z)                          00005850
      RN=N                                             00005860
      RK=K                                             00005870
      HOD=((A+B)/2.0D0)*(RN*(RN+1.0D0)-RK**2)+((RK**2)*C) 00005880
      RETURN                                           00005890
      END                                              00005900
      FUNCTION HODD (A,B,C,N,K)                          00005910
C*****OFF DIAGONAL MATRIX ELEMENT-RIGID ROTOR-OBLATE*****00005920
      IMPLICIT REAL*8(A-H,O-Z)                          00005930
      RN=N                                             00005940
      RK=K                                             00005950
      TA=DSQRT(RN*(RN+1.0D0)-RK*(RK+1.0D0))           00005960
      TB=USQRT(RN*(RN+1.0D0)-((RK+1.0D0)*(RK+2.0D0))) 00005970
      HODD=((A-B)/4.0D0)*TA*TB                          00005980
      RETURN                                           00005990
      END                                              00006000
      SUBROUTINE HDIAG(A,N,NDIM,IEGEN,IORD,EI,R)          00006010
                                                    00006020
                                                    00006030
                                                    00006040
A=MATRIX TO BE DIAGONALIZED                          00006050
NDIM=DIMENSION OF A                                  00006060

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```

S=A1J/ATCP                                00007270
D=D-S*S                                    00007280
IF(D.GE.DSTOP) GOTO 129                    00007290
C C C RECALCULATE DSTOP AND THRESH TO DISCARD ROUNDING ERRORS 00007300
C C C D=0.000                                00007310
C C C DD 128 JJ=2,N                            00007320
C C C DD 128 II=2, JJ                            00007330
C C C S=A(II-1, JJ)/ATCP                        00007340
120 D=S*S+D                                    00007350
DSTOP=(1.D-06)*D                            00007360
129 THRESH=DSQRT(D/AVGF)*ATCP                 00007370
130 CONTINUE                                    00007380
IF(IFLAG.NE.0) GOTO 115                      00007390
C C C ARRANGE THE EIGENVALUES IN THE ORDER OF INCREASING ENERGY. 00007400
C C C ARRANGE THE EIGENVECTORS IN THE SAME ORDER.                    00007410
C C C IF(IORD.EQ.0) RETURN                                          00007420
C C C NU=N                                                            00007430
C C C DD 11 I=1,N                                                    00007440
C C C IF(1.GE.NU) RETURN                                           00007450
C C C AMIN=A(I, I)                                                  00007460
C C C DD 10 J=I, NU                                                 00007470
C C C IF(A(J, J).GE.AMIN) GO TO 10                                  00007480
C C C IF EIGEN IS -1 , EXCLUDE UNCONVERGED EIGENVALUES FROM ORDERING. 00007490
C C C TE=DABS(EIVR(N, J))+DABS(EIVR(N-1, J))                        00007500
C C C IF((TE.GT..05).AND.(IEGEN.EQ.-1)) GO TO 15                  00007510
C C C II=I                                                            00007520
C C C AMIN=A(J, J)                                                  00007530
C C C A(J, J)=A(I, I)                                               00007540
C C C A(I, I)=AMIN                                                  00007550
16 DD 12 K=1, N                                                    00007560
TEMP=EIVR(K, II)                                                  00007570
EIVR(K, II)=EIVR(K, J)                                           00007580
12 EIVR(K, J)=TEMP                                                00007590
GO TO 10                                                            00007600
15 AM=A(J, J)                                                      00007610
A(J, J)=A(NU, NU)                                                00007620
A(NU, NU)=AM                                                      00007630
II=NU                                                              00007640
NU=NU-1                                                            00007650
GO TO 16                                                            00007660
10 CONTINUE                                                         00007670
11 CONTINUE                                                         00007680
RETURN                                                              00007690
END                                                                  00007700
C C C CD1                                                            00007710
C C C THIS SUBROUTINE CALCULATES THE ENERGY DUE TO CENTRIFUGAL    00007720
C C C DISTORTION BY A FIRST ORDER PERTURBATION METHOD. IT FOLLOWS  00007730
C C C A PROCEDURE AS OUTLINED BY WALTER GURDY & R.L. COOK IN CH. 8. 00007740
C C C 'MICROWAVE AND MOLECULAR SPECTRA'. THE PROCEDURE INVOLVES  00007750
C C C FIRST THE CALCULATION OF THE WILSON PARAMETERS, WHICH ARE    00007760
C C C EXPRESSED IN TERMS OF 7 TAUS. THE PLANARITY CONDITION HAS    00007770
C C C INVOKED IN THIS SITUATION. THERE ARE FOUR INDEPENDENT TAUS   00007780
C C C AND THREE TAUS WHICH CAN BE EXPRESSED IN TERMS OF THE OTHER  00007790
C C C FOUR. THESE WERE CALCULATED IN THE DRIVER. WITH THE CALCULATED 00007800
C C C WILSON PARAMETERS, THE WATSON DISTORTION PARAMETERS ARE THEN  00007810
C C C CALCULATED. THE AVERAGED VALUES PZ**2 AND PZ*** ARE CALCULATED 00007820
C C C

```


	WRITE (6,20)	00008470
20	FORMAT (1H0, ' EXPERIMENTAL', 33X, ' OBSERVED', 9X, ' CALCULATED', 12X,	00008480
	+ ' RESIDUAL')	00008490
	DO 45 I=1,M	00008500
	WRITE (6,25) (YLEL(I,IJ),IJ=1,7),Y(I),F(I),E(I)	00008510
25	FORMAT (1H .7A4,12X,F15.9,4X,F15.9,5X,F15.9)	00008520
-5	CONTINUE	00008530
	WRITE (6,30) RM2	00008540
30	FORMAT (1H0, ' RESIDUAL SUM OF SQUARES', D11.4)	00008550
	WRITE (6,35) VAR	00008560
35	FORMAT (1H . ' VARIANCE OF OVERALL FIT', D11.4)	00008570
	IF (ICLK.NE.0) GO TO 100	00008580
	WRITE (6,50)	00008590
50	FORMAT (1H . ' TRIAL GUESSES AND CALCULATED VALUES-FITTING BEGINS IN	00008600
	+ NEXT CYCLE')	00008610
100	RETURN	00008620
	END	00008630

Appendix II

NCOR-Normal Coordinate Analysis Program


```

      F(J,I)=F(I,J)                                00000670
90    CONTINUE                                     00000680
      CALL MATOUT (NDIM,NXN,F)                      00000690
***** GENERATE H-MATRIX*****                    00000700
      CALL MMULT (NDIM,NXN,NXN,NXN,A,D,AD)         00000710
      CALL MMULT (NDIM,NXN,NXN,NXN,F,D,FAD)       00000720
      DO 110 I=1,NXN                                00000730
      DO 110 J=1,NXN                                00000740
      AT(I,J)=A(J,I)                                00000750
110   CONTINUE                                     00000760
      CALL MMULT (NDIM,NXN,NXN,NXN,AT,FAD,ATFAD)   00000770
      CALL MMULT (NDIM,NXN,NXN,NXN,D,ATFAD,H)      00000780
      CALL DIAG (NDIM,H,NXN,IEIGN,C)              00000790
***** CALCULATION OF FREQUENCIES*****           00000800
      CS=2.997925D+10                               00000810
      PI=3.1415926D0                                00000820
      AV=6.022045D+23                              00000830
      CS=CS**2                                       00000840
      PI=4.0D0*(PI**2)                             00000850
      WRITE (6,150)                                 00000860
150   FORMAT (1H , 'FREQUENCIES (WAVE NUMBERS)', /) 00000870
      DO 130 I=1,NXN                                00000880
      FREQ=DSQRT(((H(I,I)*AV)/(CS*PI)))            00000890
      WRITE (6,170) I,FREQ                          00000900
170   FORMAT (1H ,13.2X,F20.4,2X, ' WAVE NUMBERS' ) 00000910
130   CONTINUE                                     00000920
***** CALCULATION OF L-INVERSE*****            00000930
      CALL MMULT(NDIM,NXN,NXN,NXN,J,C,C)          00000940
      CALL MMULT(NDIM,NXN,NXN,NXN,A,DC,ADC)       00000950
      CALL MTRXIN(NDIM,ADC,NXN)                   00000960
      CALL MATOUT (NDIM,NXN,ADC)                  00000970
      STOP                                         00000980
      END                                          00000990
*****                                           00001000
      SUBROUTINE MMULT(MDIM,NAR,NAC,NBC,A,B,C)     00001010
*****                                           00001020
      IMPLICIT REAL*8(A-H,O-Z)                   00001030
      DIMENSION A(MDIM,MDIM),B(MDIM,MDIM),C(MDIM,MDIM)
      DO 500 I=1,NAR                              00001050
      DO 500 J=1,NBC                              00001060
      C(I,J)=0.0D0                                00001070
      DO 500 K=1,NAC                              00001080
      C(I,J)=C(I,J)+A(I,K)*B(K,J)                00001090
500   CONTINUE                                   00001100
      RETURN                                     00001110
      END                                          00001120
*****                                           00001130
      SUBROUTINE MTRXIN(MDIM,A,N)                 00001140
*****                                           00001150
      IMPLICIT REAL*8(A-H,O-Z)                   00001160
      DIMENSION A(MDIM,MDIM),IPV(50,3)          00001170
      ! INITIALIZATION                            00001180
      DO 1 J=1,N                                  00001190
      ! IPV(J,3)=F                                00001200
      ! SEARCH FOR PIVOT ELEMENT                   00001210
      DO 5 I=1,N                                  00001220
      ! MAX=C.0D0                                  00001230
      DO 6 J=1,N                                  00001240
      ! IF(IPV(J,3)-1)7,J,7                        00001250
      ! DO 5 K=1,N                                  00001260

```

```

          IF(IPV(K,3)-1)9,5,9          00001270
          IF(AMAX-DABS(A(J,K)))11,5,5  00001280
11  IR0W=J                            00001290
          IC0LUM=K                    00001300
          AMAX=DABS(A(J,K))           00001310
          CONTINUE                    00001320
6  CONTINUE                          00001330
          IPV(IC0LUM,3)=IPV(IC0LUM,3)+1 00001340
          IPV(I,1)=IR0W              00001350
          IPV(I,2)=IC0LUM            00001360
C  INTERCHANGE ROWS TO PUT PIVOT ELEMENT ON DIAGONAL 00001370
          IF(IR0W-IC0LUM)16,17,16    00001380
16  DO 20 L=1,N                      00001390
          SWAP=A(IR0W,L)              00001400
          A(IR0W,L)=A(IC0LUM,L)      00001410
20  A(IC0LUM,L)=SWAP                00001420
C  DIVIDE PIVOT ROW BY PIVOT ELEMENT                00001430
17  PIVOT=A(IC0LUM,IC0LUM)          00001440
          A(IC0LUM,IC0LUM)=1.000     00001450
          DO 23 L=1,N                00001460
23  A(IC0LUM,L)=A(IC0LUM,L)/PIVOT  00001470
C  REDUCE THE NON PIVOT ROWS                        00001480
          DO 3 L1=1,N                00001490
          IF(L1-IC0LUM)26,3,26      00001500
26  T=A(L1,IC0LUM)                  00001510
          A(L1,IC0LUM)=0.000         00001520
          DO 29 L=1,N                00001530
29  A(L1,L)=A(L1,L)-A(IC0LUM,L)*T  00001540
          CONTINUE                    00001550
C  INTERCHANGE THE COLUMNS                        00001560
          DO 31 I=1,N                00001570
          L=N-I+1                    00001580
          IF(IPV(L,1)-IPV(L,2))34,31,34 00001590
34  JROW=IPV(L,1)                   00001600
          JC0LUM=IPV(L,2)            00001610
          DO 32 K=1,N                00001620
          SWAP=A(K,JROW)              00001630
          A(K,JROW)=A(K,JC0LUM)     00001640
          A(K,JC0LUM)=SWAP           00001650
32  CONTINUE                        00001660
31  CONTINUE                        00001670
41  RETURN                          00001680
          END                        00001690
C  MATOUT                                         00001700
C  WRITTEN BY REBECCA LEE 11 FEB 83 EASTERN ILLINOIS UNIVERSITY 00001710
C  THIS SUBROUTINE WILL PRINT OUT ANY SIZE MATRIX WITH NINE COLUMNS 00001720
C  ON A PAGE. THE CALLING SEQUENCE IS AS FOLLOWS: 00001730
C  CALL MATOUT (MDIM,NDN,X)              00001740
C  PARAMS: MDIM=DIMENSION OF THE MAIN ARRAY 00001750
C          NDN=ORDER OF THE MATRIX TO BE PRINTED OR NUMBER OF ROWS 00001760
C          IN THE CASE OF A MATRIX WHICH IS NOT SQUARE 00001770
C          X=THE MATRIX TO BE PRINTED    00001780
C          TITLE=TITLE OF MATRIX TO BE PRINTED 00001790
C  SUBROUTINE MATOUT (MDIM,NDN,X)        00001800
          IMPLICIT REAL*8(A-H,O-Z)      00001810
          DIMENSION *(MDIM,MDIM)       00001820
          MCE=0                          00001830
          NNE=9                           00001840
          IF (NDN.LE.9)GO TO 40         00001850
          NFE=NDN/NN                     00001860

```

```

      DO 5 K=1,N,T                                00001870
      IF (K.EQ.1) GO TO 3                          00001880
      IF (K.NE.1) GO TO 6                          00001890
      N=1                                           00001900
      GO TO 8                                       00001910
      M=M+3                                         00001920
      MC=MC+3                                       00001930
      WRITE (6,900) M,MC                           00001940
900  FORMAT (1H,'J=',I3,' TO ',I3)              00001950
      DO 7 I=1,NDN                                  00001960
      WRITE (6,999) (W(I,J),J=M,MC)               00001970
999  FORMAT (1H0.9(D12.5,2X))                    00001980
      CONTINUE                                       00001990
      NTP=NT*NN                                      00002000
      NTR=NCN-NTP                                    00002010
      NTP=NTP+1                                     00002020
      IF(NTR.EQ.0) GO TO 1000                      00002030
      IF(NTR.LT.NN) GO TO 30                       00002040
30   WRITE (6,900) NTP,NDN                        00002050
      GO TO 50                                      00002060
40   DO 45 I=1,NDN                                  00002070
45   WRITE (6,999) (W(I,J),J=1,NDN)              00002080
      RETURN                                       00002090
50   DO 60 I=1,NDN                                  00002100
60   WRITE (6,999) (W(I,J),J=NTP,NDN)            00002110
1000 RETURN                                       00002120
      END                                           00002130
C                                                     00002140
C                                                     00002150
C                                                     00002160
C   DIAG DIAGONALIZES HERMITIAN (REAL SYMMETRIC) MATRICES 00002170
C   BY THE JACOBI METHOD. THE CALLING SEQUENCE IS:       00002180
C                                                     00002190
C   CALL DIAG(NDIM,H,N,IGEN,U)                       00002200
C                                                     00002210
C   WHERE NDIM IS THE MATRIX DIMENSION                00002220
C   H=HERMITIAN MATRIX TO BE DIAGONALIZED            00002230
C   N =THE ORDER OF H                                 00002240
C   IGEN = 0 FOR BOTH EIGENVALUES AND EIGENVECTORS.  00002250
C   IGEN = 1 FOR ONLY EIGENVALUES                    00002260
C   AND U= EIGENVECTORS                              00002270
C                                                     00002280
C   THE EIGENVALUES ARE THE DIAGONAL ELEMENTS OF H   00002290
C   DIAG OPERATES ONLY ON THE ELEMENTS OF H THAT ARE TO THE 00002300
C   RIGHT OF THE MAIN DIAGONAL. THUS, ONLY A TRIANGULAR 00002310
C   SECTION MUST BE STORED IN THE ARRAY H.           00002320
C                                                     00002330
C   AUTHORS: F. CORBATO AND M. MERWIN (SEE K. WIBERG, "COMPUTER 00002340
C   PROGRAMS FOR CHEMISTS", BENJAMIN, 1955M PP.48-50). 00002350
C                                                     00002360
C                                                     00002370
C   SUBROUTINE DIAG (NDIM,H,N,IGEN,U)                00002380
C   IMPLICIT REAL*8(A-H,O-Z)                         00002390
C   DIMENSION H(NDIM,NDIM), J(NDIM,NDIM)            00002400
C   DIMENSION X(20), IQ(20)                          00002410
C                                                     00002420
C   INITIALIZE U                                      00002430
C   IF(IGEN.NE.0) GO TO 15                           00002440
C   DO 11 I=1,N                                       00002450
C   DO 11 J=1,N                                       00002460

```

	U(I,J)=0.000	00002470
	IF(I.EQ.J) U(I,J)=1.000	00002480
10	CONTINUE	00002490
15	NR=0	00002500
	IF(N.LE.1) RETURN	00002510
C		00002520
C	SCAN FOR LARGEST OFF-DIAGONAL ELEMENT IN EACH ROW	00002530
C	X(I) CONTAINS LARGEST ELEMENT IN THE ITH ROW	00002540
C	IQ(I) HOLDS SECOND SUBSCRIPT DEFINING POSITION OF ELEMENT	00002550
C		00002560
	NM11=N-1	00002570
	DO 30 I=1,NM11	00002580
	X(I)=0.000	00002590
	IPL1=I+1	00002600
	DO 30 J=IPL1,N	00002610
	IF(X(I).GT.DABS(H(I,J))) GO TO 30	00002620
	X(I)=DABS(H(I,J))	00002630
	IQ(I)=J	00002640
30	CONTINUE	00002650
C		00002660
C	SET INDICATOR FOR SHUT-OFF: RAP=2**-27. NR=ND OF ROTATIONS	00002670
C		00002680
	RAP=7.450580E00-S	00002690
	HDTEST=1.7038	00002700
C		00002710
C	FIND THE MAXIMUM OF X(I)'S FOR THE PIVOT ELEMENT	00002720
C	TEST FOR END OF PROBLEM	00002730
C		00002740
40	DO 70 I=1,NM11	00002750
	IF(I.LE.1) GO TO 60	00002760
	IF (XMAX.GE.X(I)) GO TO 70	00002770
60	XMAX=X(I)	00002780
	IPIV=I	00002790
	JPIV=IQ(I)	00002800
70	CONTINUE	00002810
C		00002820
C	IS MAX. X(I) EQUAL TO ZERO? IF LESS THAN HDTEST, REVISE HDTEST	00002830
C		00002840
	IF(XMAX.LE.0) RETURN	00002850
	IF(HDTEST.LE.0) GO TO 90	00002860
	IF(XMAX.GT.HDTEST) GO TO 140	00002870
90	HDIMIN=DABS(H(1,1))	00002880
	DO 110 I=2,N	00002890
	IF(HDIMIN.LE.DABS(H(I,1))) GO TO 110	00002900
	HDIMIN=DABS(H(I,1))	00002910
110	CONTINUE	00002920
	HDTEST=HDIMIN*RAP	00002930
C		00002940
C	RETURN IF MAX. H(I,J) LESS THAN (1**-27)*DABS (H(K,K)-MIN)	00002950
C		00002960
	IF(HDTEST.GE.XMAX) RETURN	00002970
140	NR=NR+1	00002980
C		00002990
C	COMPUTE TANGENT, SINE AND COSINE, H(I,I), H(J,J)	00003000
C		00003010
150	TANG=DSIGN(2.000,(H(IPIV,IPIV)-H(JPIV,JPIV)))*H(IPIV,JPIV)/	00003020
	+ (DABS(H(IPIV,IPIV)-H(JPIV,JPIV)) + DSQRT	00003030
	+ ((H(IPIV,IPIV)-H(JPIV,JPIV))**2 + 4.0 *H(IPIV,JPIV)**2))	00003040
	COSINE=1./DSQRT(1.0 +TANG**2)	00003050
	SINE=TANG*COSINE	00003060

```

H11=H(IPIV,IPIV)                                00003070
H(IPIV,IPIV)=COSINE**2*(H11+TANG*(2.*H(IPIV,JPIV)+TANG*
+ H(JPIV,JPIV)))                                00003080
H(JPIV,JPIV)=COSINE**2*(H(JPIV,JPIV)-TANG*(2.*H(IPIV,JPIV)-TANG*
+ H11))                                          00003100
H(IPIV,JPIV)=0.0000                              00003110
C                                                    00003120
C                                                    00003130
C PS=UDC RANK THE EIGENVALJES                    00003140
C - ADJUST SINE AND COS FOR COMPUTATION OF H(I,K) AND U(I,J) 00003150
C                                                    00003160
C IF(H(IPIV,IPIV).GE.H(JPIV,JPIV)) GO TO 153    00003170
C HTEMP=H(IPIV,IPIV)                             00003180
C H(IPIV,IPIV)=H(JPIV,JPIV)                     00003190
C H(JPIV,JPIV)=HTEMP                             00003200
C                                                    00003210
C RECOMPUTE SINE AND COSINE                      00003220
C                                                    00003230
C HTEMP=DSIGN(1.000,-SINE)*COSINE                00003240
C COSINE=DABS(SINE)                              00003250
C SINE=HTEMP                                      00003260
153 CONTINUE                                     00003270
C                                                    00003280
C INSPECT THE IQS BETWEEN I+1 AND N-1 TO DETERMINE 00003290
C WHETHER A NEW MAXIMUM VALUE SHOULD BE COMPUTED SINCE 00003300
C THE PRESENT MAXIMUM IS IN THE I OR J ROW.      00003310
C                                                    00003320
C DO 350 I=1,NM11                                00003330
C IF(I-IPIV) 210,350,200                         00003340
200 IF(I.EQ.JPIV) GO TO 350                       00003350
210 IF(IQ(I).EQ.IPIV) GO TO 240                  00003360
230 IF(IQ(I).NE.JPIV) GO TO 350                 00003370
240 K=IQ(I)                                       00003380
C HTEMP=H(I,K)                                    00003390
C H(I,K)=0.                                       00003400
C IPLI=I+1                                        00003410
C X(I)=0.0                                        00003420
C                                                    00003430
C SEARCH IN DEPLETED ROW FOR NEW MAXIMUM        00003440
C                                                    00003450
C DO 320 J=IPL1,N                                00003460
C IF(X(I).GT.DABS(H(I,J))) GO TO 320             00003470
C X(I)=DABS(H(I,J))                              00003480
C IQ(I)=J                                         00003490
320 CONTINUE                                     00003500
C H(I,K)=HTEMP                                    00003510
350 CONTINUE                                     00003520
C X(IPIV)=0.0                                    00003530
C X(JPIV)=0.0                                    00003540
C                                                    00003550
C CHANGE THE ORDER ELEMENTS OF H                00003560
C                                                    00003570
C DO 530 I=1,N                                    00003580
C IF(I-IPIV) 370,530,420                         00003590
370 HTEMP=H(I,IPIV)                              00003600
C H(I,IPIV)=COSINE*HTEMP + SINE*H(I,JPIV)      00003610
C IF (X(I).GE.DABS(H(I,IPIV))) GO TO 390        00003620
C X(I)=DABS(H(I,IPIV))                          00003630
C IQ(I)=IPIV                                     00003640
390 H(I,JPIV)=-SINE*HTEMP + COSINE*H(I,IPIV)   00003650
C IF (X(I).GE.DABS(H(I,JPIV))) GO TO 530       00003660

```

400	X(I)=DABS(H(I,JPIV))	00003670
	IC(I)=JPIV	00003680
	GO TO 530	00003690
420	IF(I-JPIV) 430,530,430	00003700
430	HTEMP=H(IPIV,I)	00003710
	H(IPIV,I)=COSINE*HTEMP + SINE*H(I,JPIV)	00003720
	IF (X(IPIV).GE.DABS(H(IPIV,I))) GO TO 450	00003730
	X(IPIV)=DABS(H(IPIV,I))	00003740
	IC(IPIV)=I	00003750
450	H(I,JPIV)=-SINE*HTEMP + COSINE*H(I,JPIV)	00003760
	IF (X(I)-DABS(H(I,JPIV))) 400,530,530	00003770
450	HTEMP=H(IPIV,I)	00003780
	H(IPIV,I)=COSINE*HTEMP + SINE*H(JPIV,I)	00003790
	IF (X(IPIV).GE.DABS(H(IPIV,I))) GO TO 500	00003800
	X(IPIV)=DABS(H(IPIV,I))	00003810
	IC(IPIV)= I	00003820
500	H(JPIV,I)= -SINE*HTEMP + COSINE*H(JPIV,I)	00003830
	IF (X(JPIV).GE.DABS(H(JPIV,I))) GO TO 530	00003840
	X(JPIV)=DABS(H(JPIV,I))	00003850
	IC(JPIV)= I	00003860
530	CONTINUE	00003870
C		00003880
C	TEST FOR COMPUTATION OF EIGENVECTORS	00003890
C		00003900
	IF(IGEN.NE.0) GO TO 40	00003910
	DO 550 I=1,N	00003920
	HTEMP=U(I,IPIV)	00003930
	U(I,IPIV)=COSINE*HTEMP + SINE*U(I,JPIV)	00003940
550	U(I,JPIV)= - SINE*HTEMP + COSINE*U(I,IPIV)	00003950
	GO TO 40	00003960
1000	RETURN	00003970
	END	00003980

Appendix III

Intermediate Matrices and Operators of the
Normal Coordinate Analysis of Acetylene-HCl
(CGS Units)

(B)-TRANSPOSE MATRIX

0	.7862E+08	.5027E+06	0
0	0	0	-.7865E+08
.2801E-01	0	0	0
0	-.5238E+08	.2673E+08	0
0	0	0	.5133E+08
.9720E+00	0	0	0
0	-.1017E+07	-.1055E+07	0
0	0	0	.1058E+07
-.3874E-01	.4615E+06	-.1169E+08	0
0	-.1211E+08	-.1256E+08	0
0	0	0	.1260E+08
-.4613E+00	.1999E+07	-.5061E+08	0
0	-.1211E+08	-.1256E+08	0
0	0	0	.1260E+08
-.4613E+00	-.1999E+07	.5061E+08	0
0	-.1017E+07	-.1055E+07	0
0	0	0	.1058E+07
-.3874E-01	-.4615E+06	.1169E+08	0

(G) -MATRIX

.3989E+23	0	0	0
0	.3758E+40	-.5472E+36	0
0	-.5472E+36	.4499E+39	0
0	0	0	.3759E+40

(L) -MATRIX

.1997E+12	0	0	0
0	.5995E+20	-.1280E+20	0
0	.4419E+19	.2075E+20	0
0	0	0	.6131E+20

ROTATION AND TRANSLATION OPERATORS
FOR ACETYLENE-HCL (CGS UNITS) IN
TERMS OF EQUILIBRIUM COORDINATES

DEFINITION OF ATOMS

(1)-H (4)-C (3RD QUADRANT)
 (2)-CL (5)-C (4TH QUADRANT)
 (3)-H (3RD QUADRANT) (6)-H (4TH QUADRANT)
 ROD 1=HCL ROD 2=ACETYLENE

DEFINITION OF OPERATORS

T =TRANSLATION OF ROD 1 IN Z-DIRECTION
 1Z

R =ROTATION OF ROD 1 ABOUT THE Y-AXIS WHICH RUNS THROUGH THE
 1Y2
 CENTER OF MASS OF ROD 2

OPERATORS

T =2.801E-02Z(1) + .9720Z(2)
 1Z

T =3.874E-02Z(3) + .4613Z(4) +.4613Z(5) + 3.874E-02Z(6)
 2Z

R =7.789E+07X(1) - 7.789E+07X(2)
 1Y1

R =1.017E+06X(3) - 4.615E+07Z(3) + 1.211E+07X(4) - 1.999E+06Z(4)
 2Y1
 + 1.211E+07X(5) + 1.999E+06Z(5) + 1.017E+06X(6) + 4.615E+06Z(6)

R =-1.169E+07Z(3) - 5.061E+07Z(4) + 5.061E+07Z(5) + 1.169E+07Z(6)
 2Y2

R =-5.027E+05X(1) + 2.801E+07X(2)
 1Y2

R =-7.789E+07Y(1) + 7.789E+07Y(2)
 1X1

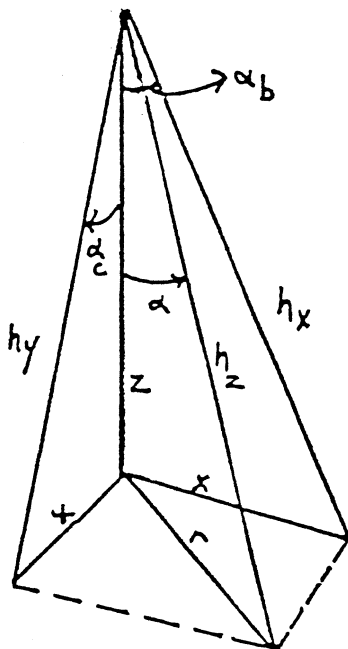
R =-1.058E+06Y(3) - 1.260E+07Y(4) - 1.260E+07Y(5) - 1.058E+06Y(6)
 2X1

Appendix IV

Derivation of $\langle \cos^2 \alpha \rangle = f(\langle \cos^2 \alpha_b \rangle, \langle \cos^2 \alpha_c \rangle)$

The angle made by the HCl subunit with the (a) inertial axis appears several times in the course of this study. However, experimental data permit the calculation of the projection of HCl on either the (b) or (c) inertial axis. Therefore, it would be desirable to write $\langle \cos^2 \alpha \rangle$ as a function of these two quantities, $\langle \cos^2 \alpha_b \rangle$ and $\langle \cos^2 \alpha_c \rangle$.

The figure below describes the necessary structural parameters employed in this derivation.



Inspection of the previous figure yields the following relationships:

$$\cos \alpha_b = z/hx \quad (A4-1)$$

$$\cos \alpha = z/hz \quad (A4-2)$$

$$\cos \alpha_c = z/hy \quad (A4-3)$$

By the pythagorean theorem, hx , hy , and hz can be replaced:

$$\cos \alpha_b = z/(x^2+z^2)^{1/2} \quad (A4-4)$$

$$\cos \alpha = z/(r^2+z^2)^{1/2} \quad (A4-5)$$

$$\cos \alpha_c = z/(y^2+z^2)^{1/2} \quad (A4-6)$$

If the expression for $\cos \alpha$ is squared, equation (A4-7) is obtained:

$$\cos^2 \alpha = z^2/(z^2+r^2) \quad (A4-7)$$

At this point, it is desirable to replace z^2 with expressions containing $\cos \alpha_b$ and $\cos \alpha_c$ (eqns (A4-4) and (A4-6)). In order to make this substitution, $\cos \alpha_b$ and $\cos \alpha_c$ must be squared and solved for z^2 . To easily solve eqns (A4-4) and (A4-6) for z^2 , the following substitutions are made:

$$x^2+z^2 = x^2/(\sin^2 \alpha_b) \quad (A4-8)$$

$$y^2 + z^2 = y^2 / (\sin^2 \alpha_c) \quad (A4-9)$$

and expressions for z^2 in terms of $\cos^2 \alpha_b$ and $\cos^2 \alpha_c$ are obtained using eqn (A4-10), a standard trigonometric identity:

$$\cos^2 \theta + \sin^2 \theta = 1 \quad (A4-10)$$

$$z^2 = x^2 \cos^2 \alpha_b / (1 - \cos^2 \alpha_b) \quad (A4-11)$$

$$z^2 = y^2 \cos^2 \alpha_c / (1 - \cos^2 \alpha_c) \quad (A4-12)$$

When equations (A4-11)-(A4-12) are substituted into the denominator and numerator of eqn (A4-7), the following expression results:

$$\cos^2 \alpha = \frac{y^2 \cos^2 \alpha_c / (1 - \cos^2 \alpha_c)}{(x^2 \cos^2 \alpha_b / (1 - \cos^2 \alpha_b)) + r^2} \quad (A4-13)$$

Close scrutiny of the figure on the first page of this appendix clearly indicates that x and y form the sides of a rectangle in which r is the diagonal. By the pythagorean theorem, it can be shown that:

$$r^2 = x^2 + y^2 \quad (A4-14)$$

Using eqn (A4-14) and simplifying, $\cos^2 \alpha$ is now defined in accordance with eqn (A4-15):

$$\cos^2 \alpha = \frac{y^2 (\cos^2 \alpha_c - \cos^2 \alpha_c \cos^2 \alpha_b)}{x^2 (1 - \cos^2 \alpha_c) + y^2 (1 - \cos^2 \alpha_b - \cos^2 \alpha_c - \cos^2 \alpha_b \cos^2 \alpha_c)} \quad (A4-15)$$

It is important that x^2 and y^2 be eliminated from eqn (A4-15), therefore, the following definitions of x^2 and y^2 in terms of $\tan^2 \alpha_b$ and $\tan^2 \alpha_c$ are used:

$$x^2 = z^2 \tan^2 \alpha_b \quad (\text{A4-16})$$

$$y^2 = z^2 \tan^2 \alpha_c \quad (\text{A4-17})$$

Substitution of eqns (A4-16)-(A4-17) yields the following expression:

$$\cos^2 \alpha = \frac{z^2 \tan^2 \alpha_c (\cos^2 \alpha_c - \cos^2 \alpha_c \cos^2 \alpha_b)}{z^2 \tan^2 \alpha_b (1 - \cos^2 \alpha_c) + z^2 \tan^2 \alpha_c (1 - \cos^2 \alpha_b - \cos^2 \alpha_c - \cos^2 \alpha_b \cos^2 \alpha_c)} \quad (\text{A4-18})$$

It is clear that z^2 factors out of eqn (A4-18), leaving only $\cos^2 \alpha$ as a function of $\cos^2 \alpha_b$, $\cos^2 \alpha_c$, $\tan^2 \alpha_b$, and $\tan^2 \alpha_c$. Recalling the definition of the tangent function, eqn (A4-19) :

$$\tan \theta = \sin \theta / \cos \theta \quad (\text{A4-19})$$

and eqn (A4-10), eqn (A4-18) can be rewritten:

$$\cos \alpha = \frac{\sin^2 \alpha_c (\cos^2 \alpha_c - \cos^2 \alpha_c \cos^2 \alpha_b)}{\cos^2 \alpha_c} \quad (\text{A4-20})$$

$$\frac{\sin^2 \alpha_b (1 - \cos^2 \alpha_c) + \sin^2 \alpha_c (1 - \cos^2 \alpha_b - \cos^2 \alpha_c - \cos^2 \alpha_b \cos^2 \alpha_c)}{\cos^2 \alpha_b \cos^2 \alpha_c}$$

The following eqns are the subsequent simplification of eqn (A4-20).

$$\cos^2 \alpha = \frac{\sin^2 \alpha_c (1 - \cos^2 \alpha_b)}{\sin^2 \alpha_b \sin^2 \alpha_c \cos^2 \alpha_c + \sin^2 \alpha_c \cos^2 \alpha_b (1 - \cos^2 \alpha_b - \cos^2 \alpha_c - \cos^2 \alpha_b \cos^2 \alpha_c)} \quad (\text{A4-21})$$

$$\cos^2 \alpha = \frac{\sin^2 \alpha_c \sin^2 \alpha_b \cos^2 \alpha_b \cos^2 \alpha_c}{\sin^2 \alpha_b \sin^2 \alpha_c \cos^2 \alpha_c + \sin^2 \alpha_c \cos^2 \alpha_b (1 - \cos^2 \alpha_b - \cos^2 \alpha_c - \cos^2 \alpha_b \cos^2 \alpha_c)} \quad (\text{A4-22})$$

$$\cos^2 \alpha = \frac{\sin^2 \alpha_b \cos^2 \alpha_b \cos^2 \alpha_c}{\sin^2 \alpha_b \cos^2 \alpha_c + \cos^2 \alpha_b (1 - \cos^2 \alpha_b - \cos^2 \alpha_c - \cos^2 \alpha_b \cos^2 \alpha_c)} \quad (\text{A4-23})$$

$$\cos^2 \alpha = \frac{\sin^2 \alpha_b \cos^2 \alpha_b \cos^2 \alpha_c}{\sin^2 \alpha_b \cos^2 \alpha_c + \cos^2 \alpha_b - \cos^4 \alpha_b - \cos^2 \alpha_b \cos^2 \alpha_c + \cos^4 \alpha_b \cos^2 \alpha_c} \quad (\text{A4-24})$$

$$\cos^2 \alpha = \frac{\sin^2 \alpha_b \cos^2 \alpha_b \cos^2 \alpha_c}{\sin^2 \alpha_b \cos^2 \alpha_c + \cos^2 \alpha_b (1 - \cos^2 \alpha_b) - \cos^2 \alpha_b \cos^2 \alpha_c (1 - \cos^2 \alpha_b)} \quad (\text{A4-25})$$

$$\cos^2 \alpha = \frac{\sin^2 \alpha_b \cos^2 \alpha_b \cos^2 \alpha_c}{\sin^2 \alpha_b (\cos^2 \alpha_b + \cos^2 \alpha_c - \cos^2 \alpha_b \cos^2 \alpha_c)} \quad (\text{A4-26})$$

$$\cos^2 \alpha = \frac{\cos^2 \alpha_b \cos^2 \alpha_c}{\cos^2 \alpha_b + \cos^2 \alpha_c - \cos^2 \alpha_b \cos^2 \alpha_c} \quad (\text{A4-27})$$

In order to obtain $\langle \cos^2 \alpha \rangle$, eqn (A4-27) is averaged over the ground state vibrational wave functions (see Methods section, Part C for a description of these wave functions):

$$\langle \cos^2 \alpha \rangle = \frac{\cos^2 \alpha_b \cos^2 \alpha_c}{\cos^2 \alpha_b + \cos^2 \alpha_c - \cos^2 \alpha_b \cos^2 \alpha_c} \quad (\text{A4-28})$$

It is assumed that the right hand side of eqn (A4-28) can be

written in terms of the individual vibrationally averaged projection operators:

$$\langle \cos^2 \alpha \rangle = \frac{\langle \cos^2 \alpha_b \rangle \langle \cos^2 \alpha_c \rangle}{\langle \cos^2 \alpha_b \rangle + \langle \cos^2 \alpha_c \rangle - \langle \cos^2 \alpha_b \rangle \langle \cos^2 \alpha_c \rangle} \quad (\text{A4-29})$$

so as to obtain $\langle \cos^2 \alpha \rangle$ as a function of $\langle \cos^2 \alpha_b \rangle$ and $\langle \cos^2 \alpha_c \rangle$.

Appendix V

Derivation of Solution to Integration of the Projection Operator $\langle \cos^2 \alpha_b \rangle$

The integration of $\langle \cos^2 \alpha_b \rangle$ involves averaging the operator $\cos^2 \alpha_b$ over the ground state vibrational wave functions. In order to accomplish this, the operator must be written as a function of Q_i , the normal coordinate. To write $\cos^2 \alpha_b = f(Q)$, the angle α_b must first be written as a function of R_i , an internal coordinate. Internal coordinates and normal coordinates are related through the following matrix equation:

$$\underline{R} = \underline{LQ} \tag{A5-1}$$

where \underline{L} is the eigenvector matrix of the secular equation:

$$\underline{GF} \underline{L} = \underline{L} \underline{\Lambda} \tag{A5-2}$$

For more details regarding \underline{L} and eqn (A5-2), see Methods section, Part A.

Examination of Fig [1.7b] clearly reveals that α_b is a function of R_2 :

$$\alpha_b = R_2 + \gamma \tag{A5-3}$$

where γ is the angle between the line joining the centers of mass of the two rods and the (a) inertial axis. The angle γ is a negative angle defined in accordance with vector conventions and angular momentum constraints. By the Eckart conditions

(see Methods section, Part A for a discussion of this topic), it is possible to relate R_2 to γ and thus obtain α_b solely as a function of R_2 :

$$R_2 I_{HCl} = -\gamma I_{yy}' \quad (A5-4)$$

$$\alpha_b = R_2 - R_2 (I_{HCl} / I_{yy}') \quad (A5-5)$$

where I_{yy}' is the moment of inertia about the y axis of the complex when R_2 is incremented. By the parallel axis theorem, it can be shown that the contribution of R_2 to I_{yy}' will be quite small; therefore, I_{yy}' can be approximated by I_{yy} :

$$I_{yy} = \mu R_0^2 + I_{Ac} + (1/2) I_{HCl} (1 + \cos^2 R_2) \quad (A5-6)$$

where I_{Ac} and I_{HCl} are the ground state moments of inertia (see Table VIII), R_0 is the distance between the centers of mass of the two rods and μ is the pseudodiatomic reduced mass equal to $(m_{Ac} m_{HCl}) / (m_{Ac} + m_{HCl})$. Anticipating the conversion from internal coordinates into normal coordinates, the last term of eqn (A5-6) is assumed constant in order to simplify the calculation. This approximation is valid as it can be shown that $\cos^2 R_2$ is constant to four figures over the integration limits.

It should also be noted that the internal coordinates R_2 and R_3 are both of B_1 symmetry and therefore are coupled.

It would be expected that any incrementation of R_3 could be expected to affect α_b . Examination of Fig [1.7c] and the Eckart conditions permit α_b to be expressed as a function of R_3 :

$$R_3 I_{Ac} = -\alpha_b I_{yy}' \quad (A5-7)$$

where I_{yy}' is approximated once again by I_{yy} . From Fig [1.7c], it is clear that R_2 is zero; therefore, the last term in eqn. (A5-6) vanishes.

Thus, α_b can be expressed as a function of R_2 and R_3 :

$$\alpha_b = R_2 (1 - (I_{HCl} / I_{yy})) + R_3 (-I_{Ac} / I_{yy}) \quad (A5-8)$$

and can be written as a function of Q via eqn (A5-1):

$$\alpha_b = \beta_2 Q_2 + \beta_3 Q_3 \quad (A5-9)$$

where β_2 and β_3 are defined in terms of the \underline{L} matrix elements and the ground state moments of inertia of the monomers:

$$\beta_2 = (1 - (I_{HCl} / I_{yy})) L_{22} - (-I_{Ac} / I_{yy}) L_{32} \quad (A5-10)$$

$$\beta_3 = (1 - (I_{HCl} / I_{yy})) L_{23} - (-I_{Ac} / I_{yy}) L_{33} \quad (A5-11)$$

Having defined α_b in terms of the normal coordinates Q_2 and Q_3 , it is possible to write the operator $\cos^2 \alpha_b$ in terms of Q_2 and Q_3 using the trigonometric identity, eqn (A5-12):

$$\cos(\theta + \phi) = \cos\theta \cos\phi + \sin\theta \sin\phi \quad (A5-12)$$

$$\cos^2 \alpha_b = [\cos \beta_2 Q_2 \cos \beta_3 Q_3 - \sin \beta_2 Q_2 \sin \beta_3 Q_3]^2 \quad (\text{A5-13})$$

$$\begin{aligned} \cos^2 \alpha_b = & \cos^2 \beta_2 Q_2 \cos^2 \beta_3 Q_3 - 2 \cos \beta_2 Q_2 \sin \beta_2 Q_2 \cos \beta_3 Q_3 \sin \beta_3 Q_3 \\ & + \sin^2 \beta_2 Q_2 \sin^2 \beta_3 Q_3 \end{aligned} \quad (\text{A5-14})$$

It is evident from symmetry considerations that the term $\cos \beta_i Q_i \sin \beta_i Q_i$ in eqn(A5-14) is an antisymmetric function and will vanish upon integration. Therefore, it is eliminated from eqn (A5-14) leaving the following expression:

$$\cos^2 \alpha_b = \cos^2 \beta_2 Q_2 \cos^2 \beta_3 Q_3 + \sin^2 \beta_2 Q_2 \sin^2 \beta_3 Q_3 \quad (\text{A5-15})$$

When eqn (A5-15) is integrated over the ground state vibrational wave functions, $\Psi(Q_i)$:

$$\Psi(Q_i) = (\gamma/\pi)^{1/4} \exp(-\gamma_i Q_i^2 / 2) \quad (\text{A5-16})$$

where γ_i is defined :

$$\gamma_i = 4\pi^2 c w_i / h \quad (\text{A5-17})$$

in terms of c , the speed of light, w_i , the i th normal mode frequency, the following integral is obtained:

$$\langle \cos^2 \alpha_b \rangle = \int_{-\infty}^{\infty} N_2 N_3 \exp(-\gamma_2 Q_2^2) \exp(-\gamma_3 Q_3^2) \cos^2 \alpha_b dQ_2 dQ_3 \quad (\text{A5-18})$$

where $\cos^2 \alpha_b$ is defined as in eqn (A5-15) and N_2 and N_3 are defined as:

$$N_2 = (\gamma_2/\pi)^{1/2} \quad (\text{A5-19})$$

$$N_3 = (\gamma_3/\pi)^{1/2} \quad (\text{A5-20})$$

Substitution of eqn (A5-15) permits eqn (A5-18) to be written as a sum of integrals:

$$\begin{aligned} \langle \cos^2 \alpha_b \rangle = & \int_{-\infty}^{\infty} N_2 N_3 \exp(-\gamma_2 Q_2^2) \exp(-\gamma_3 Q_3^2) \cos^2 \beta_2 Q_2 \cos^2 \beta_3 Q_3 dQ_2 dQ_3 \\ & + \int_{-\infty}^{\infty} N_2 N_3 \exp(-\gamma_2 Q_2^2) \exp(-\gamma_3 Q_3^2) \sin^2 \beta_2 Q_2 \sin^2 \beta_3 Q_3 dQ_2 dQ_3 \quad (\text{A5-21}) \end{aligned}$$

This sum can be rewritten as a sum of products of integrals :

$$\begin{aligned} \langle \cos^2 \alpha_b \rangle = & \int_{-\infty}^{\infty} N_2 \exp(-\gamma_2 Q_2^2) \cos^2 \beta_2 Q_2 dQ_2 \int_{-\infty}^{\infty} N_3 \exp(-\gamma_3 Q_3^2) \cos^2 \beta_3 Q_3 dQ_3 \\ & + \int_{-\infty}^{\infty} N_2 \exp(-\gamma_2 Q_2^2) \sin^2 \beta_2 Q_2 dQ_2 \int_{-\infty}^{\infty} N_3 \exp(-\gamma_3 Q_3^2) \sin^2 \beta_3 Q_3 dQ_3 \quad (\text{A5-22}) \end{aligned}$$

in which integration over the Q_2 space is separated from integration over the Q_3 space. The integrals involving $\sin^2 \beta_i Q_i$ can be rewritten in terms of $\cos^2 \beta_i Q_i$ using eqns (A5-23)-(A5-24):

$$N_2 \exp(-\gamma_2 Q_2^2) - N_2 \exp(-\gamma_2 Q_2^2) \cos^2 \beta_2 Q_2 dQ_2 \quad (\text{A5-23})$$

$$N_3 \exp(-\gamma_3 Q_3^2) - N_3 \exp(-\gamma_3 Q_3^2) \cos^2 \beta_3 Q_3 dQ_3 \quad (\text{A5-24})$$

The solution to eqn (A5-22) can be obtained numerically or by further simplification of the integrals so as to obtain expressions that can be evaluated by the use of tables. The later method will be used to evaluate the integrals to acquire $\langle \cos^2 \alpha_b \rangle$.

Examination of the integral tables yields two definite

integrals that can be used to solve the integrals in eqn (A5-22):

$$\int_0^{\infty} \exp(-a^2 x^2) dx = (1/2a) (\pi)^{1/2} \quad (A5-25)$$

$$\int_0^{\infty} \exp(-a^2 x^2) \cos bx \, dx = (1/2a) [(\pi)^{1/2} \exp(-b^2/4a^2)] \quad (A5-26)$$

However, the use of these integrals will involve making accommodations for their integration limits in eqn (A5-22). The actual integration will go from zero to infinity and the resulting area will be doubled to obtain the solution to eqn (A5-22). Another requirement involving use of these integrals is that $\cos^2 \beta_i Q_i$ be rewritten in a form appropriate for eqn (A5-26). In order to accomplish this, the following trigonometric identity is used:

$$\cos^2 \theta = (1/2) [1 + \cos 2\theta] \quad (A5-27)$$

These alterations and substitutions permit the solution of $\langle \cos^2 \alpha_b \rangle$ to be written in a closed analytical form:

$$\begin{aligned} \langle \cos^2 \alpha_b \rangle = & (1/2) [1 + \exp(-\beta_2^2/\gamma_2)] (1/2) [1 + \exp(-\beta_3^2/\gamma_3)] \\ & + (1/2) [1 - \exp(-\beta_2^2/\gamma_2)] (1/2) [1 - \exp(-\beta_3^2/\gamma_3)] \quad (A5-28) \end{aligned}$$

Multiplication of terms in eqn (A5-28) and simplification leads to the solution of $\langle \cos^2 \alpha_b \rangle$:

$$\langle \cos^2 \alpha_b \rangle = (1/2) [1 + \exp(-\beta_2^2/\gamma_2) \exp(-\beta_3^2/\gamma_3)] \quad (A5-29)$$