

STRUCTURE AND MICROWAVE SPECTRUM
OF THE 2-CYANO-2-PROPYL RADICAL

by

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(ABSTRACT)

The rotational spectra of the 2-cyano-2-propyl and d^6 -2-cyano-2-propyl radicals were observed using a Stark modulated spectrometer. The radicals were generated in the gas phase by UV irradiation of sublimed azoisobisbutyronitrile. They were detectable in the cell for approximately one hour. Thirty-three transitions were assigned for $(CH_3)_2CCN$ and twenty-one for $(CD_3)_2CCN$. The rigid rotor rotational constants determined by calculation of the hypothetical unsplit rotational transitions are $A=8276.7$, $B=3919.7$, $C=2751.5$ Mhz for $(CH_3)_2CCN$ and $A=6241.3$, $B=3490.7$, $C=2372.6$ Mhz for $(CD_3)_2CCN$.

A program to calculate the fine splittings and hyperfine splittings due to the ^{14}N nucleus and six protons was written. The spin rotation constants determined for the two species were $E_{aa}=-69.9$, $E_{bb}=-36.1$, $E_{cc}=2.7$ Mhz and $E_{aa}=-55.4$, $E_{bb}=-32.6$ Mhz for $(CH_3)_2CCN$ and $(CD_3)_2CCN$ respectively. The hyperfine coupling constants for ^{14}N are identical for both isotopic species and were found to be $T_{aa}=-17.2$, $T_{bb}=-17.1$ and $T_{cc}=34.4$ Mhz. The proton and deuteron hyperfine splittings were not resolved. The structural parameters determined from an $\langle r_0 \rangle$ fit of the moments are $r_{CN}=1.18A$, $r_{CC}=1.42A$, $r_{CMe}=1.50A$ and $\angle CMe=119.3^\circ$. The C_4N skeletal framework was found to be planar.

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Dedication
to
(my parents)

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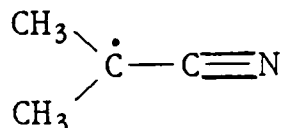
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Chapter I

Introduction

The purpose of this work was to characterize the molecular and electronic structure of the 2-cyano-2-propyl radical,



by using data obtained from the rotational spectra of the protonated and fully deuterated species. The analysis of two isotopic species was necessary in order to determine the four important structural parameters. The use of two isotopic species also serves to confirm the assignment as well as the fine and hyperfine coupling constants.

Analysis of the fine and hyperfine spectral splittings allowed the components of the spin-rotation and dipole-dipole tensors to be determined. Using these values, the hypothetical unsplit rotational transition frequencies were calculated and the principal moments of inertia determined. From the six moments, four highly correlated structural parameters were obtained.

The planarity of the non-hydrogen skeleton of the molecule was established by the fit of the fine splitting parameters and the

magnitude of the moment differences. If only diagonal components of the spin-rotation tensor are needed in the fit, a planar structure is most probable. The position of the orbital of the unpaired electron relative to the molecular plane can be determined by examining the relative magnitudes of the fine splitting parameters.

Spin density on the nitrogen atom can be estimated by considering the magnitudes of the dipole-dipole coupling constants. The magnitude of the Fermi contact parameter is related to the hybridization of the orbital which the lone electron occupies when it is on the nitrogen nucleus.

Hyperfine splittings due to the six protons or deuterons were not resolved in this study. These components could have been assigned using a computer program written for the study if the splittings had been resolvable. This program considers the interaction of six equivalent spin $\frac{1}{2}$ nuclei and a separate nonequivalent spin 1 nucleus. This assignment could further substantiate assumptions made by Endo² and White³ where the spins of the six nuclei were handled as a single nucleus with a spin equal to the vector sum of all the individual nuclei.

Chapter II

Review of Prior Research

This chapter will review three related topics; the development of high resolution spectroscopy of paramagnetic species, previous studies of the 2-cyano-2-propyl radical that are relevant to this work and previous high resolution studies of several multinuclear-spin free radicals. The particular radicals of interest are NH_2^1 , CF_2^2 , and $(\text{CF}_3)_2\text{NO}^3$.

Identification of the stable free radical triphenylmethyl in the early 1900's gave impetus to the study and characterization of these novel chemical species.⁴ Due to the short lifetime of most radicals their study remains a formidable task. A number of simple free radicals, mostly diatomics, were identified in flames and discharges by recording their emission spectra.

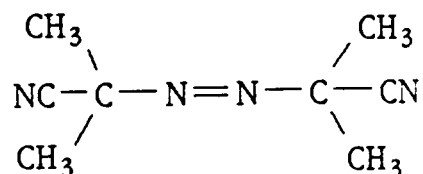
In the 1920's and 1930's, the new quantum theory provided spectroscopists with a sound theoretical basis for assigning and interpreting spectra. Development of radar during World War II led to the new spectroscopic method of Electron Spin Resonance. This technique has been successfully applied to examine a number of free radicals trapped in inert matrices. Carrington⁵ successfully applied it to gas

phase diatomic and linear triatomic free radicals. The hyperfine coupling constants obtained from these investigations provide information on transient molecules that is unobtainable from traditional optical spectroscopy.

Microwave spectroscopy has improved the precision with which molecular parameters can be determined. It has been applied to a number of molecules, most of which are stable. Townes¹ succeeded in detecting rotational transitions of the OH radical in 1955. Nine years later, Powell and Lide² successfully observed and characterized the SO radical using microwave spectroscopy.

In the past twenty years, many other techniques have been developed to characterize radical species spectroscopically. New infrared, laser and fluorescence techniques along with improvements in microwave hardware have advanced this type of spectroscopic study to the point where the limiting factors are generation of the radical or developing the theoretical basis for assigning and interpreting the spectra. Developing the theory for a spectroscopic investigation is especially difficult with a radical possessing many coupled nuclear spins.

The 2-cyano-2-propyl radical has been widely used in initiating free radical polymerization. It is produced by the thermal or photolytic decomposition of azobisisobutyronitrile.

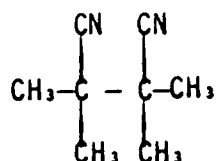


The proximity of the CN triple bond with the lone electron makes the lifetime in solution of this radical similar in magnitude to the benzyl

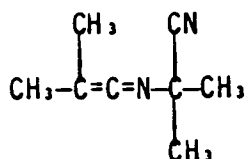
radicals.¹⁰

Most interest in this radical has been concerned with its properties in solution. Numerous studies have been performed on its lifetime in different solutions and its reactivity with a number of monomers. No gas phase studies were performed, hence only a few sources concerning this radical were relevant to this study.

The 2-cyano-2-propyl radical is known to recombine to form the dimer:



and other minor products that form less readily.⁹ This includes a keteneimine compound



which dissociates back into the radical and eventually forms the stable dimer.¹⁰ The recombination rate of the radical in 100°C biphenyl solution has been monitored by ESR by Kerr et al.¹¹ The second order rate constant was found to be $5.5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$. With a starting concentration of $5 \times 10^{-7} \text{ M}$, over half of the radical species remained after 20 minutes. Other work¹² has presented rate constants an order of magnitude less for the recombination of the free radical than that reported by Kerr.

Other ESR studies of the 2-cyano-2-propyl radical in liquid and solid states have yielded much information concerning the electronic nature of the species.^{13,14} The Fermi contact parameters for nitrogen and protons were found to be 9.5 ± 2 and 59.0 ± 6 Mhz, respectively.¹⁰ The study of this radical in the solid state yielded data concerning the anisotropic coupling of the nitrogen nucleus. The parallel dipolar coupling constant was found to be 13 ± 2 gauss (36 ± 6 Mhz), which indicated a spin density on the nitrogen nucleus of approximately 0.3.¹⁴

A theoretical study was performed on a series of α -substituted isopropyl and cyclopropyl free radicals.¹⁵ This study included the 2-cyano-2-propyl radical. The calculations were performed using a Restricted Hartree Fock basis set at a 3-21G level of theory and the "MONSTERGAUSS" program.¹⁶ The calculations found all α -substituted isopropyl radicals to be nonplanar. The 2-cyano-2-propyl radical deviated the least from planarity with an out of plane angle of 12.7° . The same calculations determined the isopropyl radical to deviate from planarity by 23.1° , however, this radical has been experimentally determined to be planar.¹⁷ For this reason, the author believes that the most probable structure for the 2-cyano-2-propyl radical is planar (with the exception of the out of plane protons). This can be rationalized by the cyano group being a π -acceptor. Donation of the unpaired electron into the π^* orbital on the cyano group would favor a planar structure.

Structural parameters reported from this theoretical structure were $r_{C-Me} = 1.51 \text{ \AA}$ and $r_{C-CN} = 1.41 \text{ \AA}$. The other structural parameters were not reported. The total energy (without nuclear repulsion considered) was

calculated to be -208.20846 Hartrees. Spin densities on each atom were not reported.

The NH_2 radical has been characterized by Curl and coworkers¹ using a microwave-optical double resonance technique. The theory for hyperfine splitting due to two equivalent protons and one nitrogen (^{14}N) was examined in detail. Expressions for the matrix elements of the hyperfine Hamiltonian were derived in this paper. This particular study is important to radical spectroscopists since it considers two different types of nuclei involved in hyperfine splitting. It was found experimentally that two equivalent protons each with $\frac{1}{2}$ spin could be treated theoretically as a single 1-spin system. With this assumption, a satisfactory spectral fit with reasonable structural and spectroscopic parameters was obtained.

Endo² and coworkers analyzed the rotational spectrum of the trifluoromethyl radical. The theory for the hyperfine structure due to three equivalent fluorine nuclei ($\frac{1}{2}$ spin) was developed and the matrix elements of the hyperfine Hamiltonian were derived. The off diagonal elements in the quantum number K (quantum number for the angular momentum about the symmetry axis) were neglected in the hyperfine energy matrix which resulted in no systematic errors in calculated and observed lines. Matrix elements diagonal in K are identical to those for a single nucleus with a spin equal to that of the sum of the three component spins (here $3 \times \frac{1}{2} = 3/2$). An excellent spectral fit justified this approximation.

White has taken Endo's approximation one step further.³ In the analysis of the bistrifluoromethyl nitroxide radical $(\text{CF}_3)_2\text{NO}$, the two

trifluoromethyl groups were treated as two equivalent 3/2 spin systems. This work extends Endo's approximation to multiple "group spin" systems.

White's approximation is used in this study to characterize the hyperfine coupling of the protons on the two equivalent methyl groups. The matrix elements derived by Curl for the NH_2 radical are used to calculate the hyperfine splitting due to the ^{14}N nucleus in the 2-cyano-2-propyl radical.

Chapter III

Review of Theoretical Concepts

This chapter is composed of four parts. The first part will address the theory used in deriving the pertinent equations involving the fine and hyperfine splitting in free radicals. The second and third parts will deal with the description of the moments of inertia and the asymmetric rigid rotor respectively. The final section will discuss the symmetry of asymmetric rotor rotational energy levels.

Coupling Theory

It has been shown that an angular momentum eigenfunction $|jm\rangle$ spans an irreducible representation $D^{(j)}$ of R_3 , the infinite rotation group.^{21,22,23} In other words, if one rotates the coordinate system but not the angular momentum state $|jm\rangle$, its $(2j+1)$ states in the new coordinate system may be expressed as a linear combination of the $(2j+1)$ states of the previous coordinate system.

$$[3.1] \quad D(\alpha\beta\gamma)|jm\rangle = \sum_{m=j}^j |jm'\rangle D_{mm}^{(j)}(\alpha\beta\gamma)$$

where m' refers to the new coordinate system, the $d_{m,m}^{(j)}(\alpha\beta\gamma)$ are the

coefficients depending on j , m and m' and on α , β , and γ , the Euler angles of rotation.

This property is similar to that of the spherical harmonics $Y_m^l(\theta, \phi)$, where we can say that $2l+1$ orthonormalized functions $Y_m^l(\theta, \phi)$ form an invariant subspace under the set of operators $D(\alpha\beta\gamma)$. Premultiplying both sides of equation 3.1 with $\langle jm|$, integrating and applying the orthonormality of the angular momentum eigenfunctions, the matrix elements of the coordinate transformation can be expressed as

$$d_{mm'}^{(l)}(\alpha\beta\gamma) = \langle jm' | D(\alpha\beta\gamma) | jm \rangle \quad [3.2]$$

Thus, for a given j , there are $(2j+1)^2$ elements in the matrix which describe this transformation. The general matrix of this kind is called the Wigner rotation matrix.

The direct product of two independent sets of states $|j_1, m_1\rangle$ and $|j_2, m_2\rangle$ consist of $(2j_1+1)(2j_2+1)$ product functions $|j_1, m_1\rangle |j_2, m_2\rangle$ all of which are eigenfunctions of the operators j_{1z} , j_{2z} , j_1^2 and j_2^2 . These product functions are not necessarily eigenfunctions of j^2 ($j^2 = j_1^2 + j_2^2$). However, there exists a unitary transformation that transforms this set of product functions into another orthogonal set of $(2j_1+1)(2j_2+1)$ states which are eigenfunctions of j^2 along with j_2^2 , j_1^2 and j_z ($j_z = j_{1z} + j_{2z}$). The matrix elements connecting these two schemes are the Clebsch-Gordon Coefficients.²⁴

$$|j_1 m_1\rangle |j_2 m_2\rangle \rightarrow \text{Clebsch-Gordon Coefficients} \rightarrow |j j_z m\rangle \quad [3.3]$$

or

$$j_1^2 j_2^2 j_{1z} j_{2z} \rightarrow \text{Clebsch Gordon Coefficients} \rightarrow j_1^2 j_2^2 j^2 j_z \quad [3.4]$$

Clebsch-Gordon coefficients are often called vector-coupling (or VC) coefficients and will be referred to as VC coefficients in this thesis. Equation 3.3 can be written in a more explicit form describing the coupled states and VC coefficients.

$$|j_1 j_2 j m\rangle = \sum_{m_1 m_2} C_{m_1 m_2 m}^{j_1 j_2 j} |j_1 m_1\rangle |j_2 m_2\rangle \quad [3.5]$$

For convenience, $|j_1 m_1\rangle |j_2 m_2\rangle$ can be written as $|j_1 m_1 j_2 m_2\rangle$. Multiplying both sides of Equation 3.5 by this quantity and integrating over all possible states, the expression for the VC coefficient is found.

$$C_{m_1 m_2 m}^{j_1 j_2 j} = \langle j_1 m_1 j_2 m_2 | j_1 j_2 j m \rangle \quad [3.6]$$

From this, one observes that the coefficients are actually scalar products of the states $|j_1 m_1 j_2 m_2\rangle$ and the state $|j_1 j_2 j m\rangle$. The geometrical interpretation of this result is that one can regard the state $|j_1 j_2 j m\rangle$ as a vector in a $(2j_1+1)(2j_2+1)$ subspace spanned by the orthogonal product states ($|j_1 m_1 j_2 m_2\rangle$). This means the contribution of a state, $|j_1 m_1 j_2 m_2\rangle$, to this vector is the projection of a vector on this state, or the scalar product of the two states. Using this concept, equation 2 can be rewritten as

$$|j_1 j_2 j m\rangle = \sum_{m_1 m_2} |j_1 m_1 j_2 m_2\rangle \langle j_1 m_1 j_2 m_2 | j_1 j_2 j m \rangle \quad [3.7]$$

This can also be found by using the identity operator expressed as

$$E = \sum_{m_1 m_2} |j_1 m_1 j_2 m_2\rangle \langle j_1 m_1 j_2 m_2| \quad [3.8]$$

and applying it to one side of the expression

$$|j_1 j_2 j m\rangle = |j_1 j_2 j m\rangle \quad [3.9]$$

In order to evaluate the VC coefficients, their properties must first be examined. The coefficient vanishes unless $m_1 + m_2 = m$ and $(j_1 + j_2) \geq j \geq |j_1 - j_2|$ (this is called the triangle condition). This arises as a consequence of rules for vector addition of angular momenta. The coefficients are also real and form an orthogonal matrix.

The symmetry of the VC coefficients can be used to simplify their evaluation. For example:

$$\langle j_1 m_1 j_2 m_2 | j_1 j_2 j_3 m_3 \rangle = (-1)^{j_2 + m_2} \left(\frac{j_3 + 1}{2j_1 + 1} \right)^{1/2} \langle j_2 - m_2 j_3 m_3 | j_2 j_3 j_1 m_1 \rangle \quad [3.10]$$

which indicates a relationship between two VC coefficients differing only in the order or sign of their constituent and their m values. This and similar relationships reduce the number of coefficients it is necessary to tabulate.

Wigner has introduced a symbol that has very simple symmetry properties and is very closely related to the VC coefficients.¹⁹ This is called a 3-J symbol and is defined by

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = (-1)^{j_1 - j_2 - m_3} (2j_3 + 1)^{-1/2} \langle j_1 m_1 j_2 m_2 | j_3 j_3 m_3 \rangle \quad [3.11]$$

An even permutation of columns results in an unchanged value for the symbol,

$$\begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_3 & j_1 \\ m_2 & m_3 & m_1 \end{pmatrix} = \begin{pmatrix} j_3 & j_1 & j_2 \\ m_3 & m_1 & m_2 \end{pmatrix} \quad [3.12]$$

and an odd permutation results in a symbol multiplied by the factor $(-1)^{j_1 + j_2 + j_3}$

$$(-1)^{j_1 + j_2 + j_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} = \begin{pmatrix} j_2 & j_1 & j_3 \\ m_2 & m_1 & m_3 \end{pmatrix} \quad [3.13]$$

The practical and computational advantages of the 3-J symbols are obvious due to the simplicity of these relationships.

The relationship connecting elements of the rotation matrix is now addressed. It can be shown that²⁵

$$\begin{aligned} d_{m'_1 m_1}^{(j_1)}(\alpha\beta\gamma) d_{m'_2 m_2}^{(j_2)}(\alpha\beta\gamma) &= \sum_j \langle j_1 m'_1 j_2 m'_2 | j_3 j_3 (m'_1 + m'_2) \rangle \\ &\times \langle j_1 m_1 j_2 m_2 | j_3 j_3 (m_1 + m_2) \rangle d_{(m'_1 + m'_2), (m_1 + m_2)}^{(j_3)}(\alpha\beta\gamma) \end{aligned} \quad [3.14]$$

Hence, if one takes any element of matrix $D^{(j_1)}(\alpha\beta\gamma)$, and

multiplies it by any element of matrix $D^{(j_2)}(\alpha\beta\gamma)$, the result can be expressed as a linear combination of the matrices $D^j(\alpha\beta\gamma)$ where j can have values of $|j_1 - j_2|$ up to $j_1 + j_2$. Equation 3.14 can be expressed in a computationally more convenient form if the VC coefficient are replaced by 3-J symbolism.

$$d_{m'_1 m_1}^{(j_1)}(\alpha\beta\gamma) d_{m'_2 m_2}^{(j_2)}(\alpha\beta\gamma) = \sum_j (2j+1) \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -(m'_1 + m'_2) \end{pmatrix} \times \begin{pmatrix} j_1 & j_2 & j \\ m_1 & m_2 & -(m_1 + m_2) \end{pmatrix} d_{(m'_1 + m'_2), (m_1 + m_2)}^{(j)}(\alpha\beta\gamma) \quad [3.15]$$

When these angular momenta couple form a resultant total angular momentum j , the order of the coupling can be carried out in several different ways. The order of the coupling determines the phase of the resulting vector. Associated with each of the different coupling schemes are intermediate values of angular momentum which result in the same final total angular momentum. These states are independent and must be distinguishable by these intermediate j values and mode of coupling. It follows from the development of the VC coefficients that each mode of coupling must be related by a unitary transformation.

If one couples j_1 and j_2 together first, then couples the resulting vector $j_{1,2}$ with the remaining vector j_3 , the state is symbolized by $|(j_1 j_2) j_{1,2} j_3 jm\rangle$. Similarly, if j_2 and j_3 are coupled together first the corresponding symbol is $|j_1 (j_2 j_3) j_{2,3} jm\rangle$. Following the argument developed for two angular momenta, one can write²⁶

$$|(j_1 j_2) j_1 j_2 j_3 m\rangle \rightarrow \text{transformation coefficients} \rightarrow |j_1 (j_2 j_3) j_2 j_3 m\rangle \quad [3.16]$$

$$|(j_1 j_2) j_1 j_2 j_3 m\rangle = \sum_{\text{expansion coefficient}} \langle (j_1 j_2) j_1 j_2 j_3 j' | j_1 (j_2 j_3) j_2 j_3 j' \rangle |j_1 (j_2 j_3) j_2 j_3 m\rangle \delta_{j j'} \delta_{m m'} \quad [3.17]$$

where the expansion coefficient is merely the scalar product between kets taken from the coupling schemes. These coefficients are independent of M and vanish unless $J=J'$ and $M=M'$. They are often called recoupling coefficients since they describe the transformation between two different coupling schemes.

These expansion coefficients have certain symmetry properties that may be utilized to simplify their evaluation. A short hand notation can be employed similar to the 3-J symbolism. It is the 6-J symbolism. It is related to the expansion coefficients by the following expression²⁷

$$\left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j & j_{23} \end{matrix} \right\} = (-1)^{j_1 + j_2 + j_3 + j} [(2j_{12} + 1)(2j_{23} + 1)]^{-1/2} \langle (j_1 j_2) j_1 j_2 j_3 j | j_1 (j_2 j_3) j_2 j_3 j \rangle \quad [3.18]$$

It should be noted that a 6-J symbol is denoted by a brace and a 3-J symbol by parenthesis.

A 6-J symbol is unaltered in value by the interchange of any two rows or columns or by switching the upper and lower members of any two rows.

$$\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{matrix} \right\} = \left\{ \begin{matrix} j_4 & j_5 & j_3 \\ j_1 & j_1 & j_6 \end{matrix} \right\} = \left\{ \begin{matrix} j_2 & j_1 & j_3 \\ j_5 & j_4 & j_6 \end{matrix} \right\} \quad [3.19]$$

The triangle condition holds for any possible row in a 6-J symbol. The symbol can also be expressed in terms of 3-J symbols

$$\left\{ \begin{matrix} j_1 & j_2 & j_3 \\ j_4 & j_5 & j_6 \end{matrix} \right\} = \sum_{\text{all } n, m_1, m_2} (-1)^{j_4 + j_5 + j_6 + n_1 + n_2 + n_3} \begin{pmatrix} j_1 & j_2 & j_3 \\ m_1 & m_2 & m_3 \end{pmatrix} \times \begin{pmatrix} j_1 & j_5 & j_6 \\ m_1 & n_5 & -n_6 \end{pmatrix} \begin{pmatrix} j_4 & j_2 & j_6 \\ -n_4 & m_2 & m_6 \end{pmatrix} \begin{pmatrix} j_4 & j_5 & j_6 \\ m_4 & -n_5 & m_3 \end{pmatrix} \quad [3.20]$$

Just as recoupling of three angular momenta could be described using the 6-J symbolism, the recoupling of four leads to the 9-J symbol. Following the line of reasoning used to obtain the 3-J and 6-J symbols, any state in a particular coupling scheme can be expressed.²⁸

$$|(j_1 j_2) j_{12} (j_3 j_4) j_{34} j m\rangle = \sum_{j_{13}} \langle (j_1 j_2) j_{12} (j_3 j_4) j_{34} j | (j_1 j_3) j_{13} (j_2 j_4) j_{24} j \rangle |(j_1 j_3) j_{13} (j_2 j_4) j_{24} j m\rangle \quad [3.21]$$

expansion coefficient

The expansion, or recoupling, coefficients are independent and possess certain symmetry properties. Wigner has replaced the coefficients with closely related properties with greater symmetry. Nine angular momenta are required in order to define them, thus they are called 9-J symbols and are defined by the following relationship.²⁹

$$\langle (j_1 j_2) j_{12} (j_3 j_4) j_{34} j | (j_1 j_3) j_{13} (j_2 j_4) j_{24} j \rangle = [(2j_{14} + 1)(2j_{34} + 1)(2j_{13} + 1)(2j_{24} + 1)]^{1/2} \times \left\{ \begin{matrix} j_1 & j_2 & j_{12} \\ j_3 & j_4 & j_{34} \\ j_{13} & j_{24} & j \end{matrix} \right\} \quad [3.22]$$

An even permutation of rows or columns or a transposition results

in an unchanged value for the 9-J symbol. An odd permutation of rows or columns results in a factor of $(-1)^{\sum \text{all } j}$ multiplying the symbol. The 9-J symbols can be expressed in terms of the 6-J symbols and ultimately in terms of the 3-J symbols.

Having reviewed the method used to describe the coupling of angular momenta and their behavior upon coordinate transformation, the effect of the symmetrization upon operations will be considered. In particular, the transformation properties of operators under coordinate rotations will be addressed.

It is known that functions which transform under coordinate rotations transform into linear combinations of a closed set of functions. This concept can be applied to operators as well.³⁰

Many operators that occur in spectroscopy are built from products of components of simpler operators. They are called compound operators or, in this discussion, compound irreducible tensor operators. Irreducible tensor operators have been defined such that under coordinate transformations they behave identically to angular momenta. For this reason, building compound irreducible tensor operators is the same as coupling angular momenta.

An irreducible tensor operator ("ITO") of rank K is a set of $2K+1$ operators, T_q^K (where q can have values of K to $-K$), which under a coordinate rotation transform according to the relation³¹

$$D(\alpha\beta\gamma)T_q^K D^{-1}(\alpha\beta\gamma) = \sum_{q'} T_{q'}^K d_{q'q}^{(K)}(\alpha\beta\gamma) \quad [3.23]$$

Under coordinate rotation $D(\alpha\beta\gamma)$, the operator T_q^K is transformed

into a linear combination of the $2K+1$ operators, with the expansion coefficients being elements of the Wigner rotation matrices. Note that the definition concerns itself only with the transformation properties of the operators and not with the detailed form.

In order to utilize the transformation properties of coupled angular momenta, the operators which eventually give us the desired quantities must be written in irreducible tensor form.

Simple examples of rewriting the operators into the necessary form will be informative. For example, many operators are scalar, $k=0$, and only one operator spans the D^0 representation.

$$D(\alpha\beta\gamma)T_0^0D^{-1}(\alpha\beta\gamma) = T_0^0d_{00}^0 = T_0^0 \cdot 1 = T_0^0 \quad [3.24]$$

For $k=1$, there are three component operators, T_1^1 , T_0^1 and T_{-1}^1 which form a first rank irreducible operator. Under coordinate transformation, they must transform into one another.

$$D(\alpha\beta\gamma)T_0^1D^{-1}(\alpha\beta\gamma) = T_{-1}^1d_{-10}^1 + T_0^1d_{00}^1 + T_1^1d_{01}^1 \quad [3.25]$$

These three component operators span the representation and they constitute a vector operator. The simplest example of a vector operator is the position operator \underline{r} , having components r_x , r_y and r_z .³² These components do not, however, transform according to Equation 3.23, thus they do not satisfy the definition of an irreducible tensor operator. The component operators r_x , r_y , r_z do not span $D^{(1)}$ in the standard form. The transformation coefficients in Equation 3.1 are elements of

the Wigner rotation matrices, which are defined in terms of a transformation of a standard set of basis functions. A suitable orthogonal transformation of the set $\{r_x, r_y, r_z\}$ will result in another set that spans $D^{(1)}$ in the appropriate standard form.

$$z \equiv T_0^1, \quad -2^{-1/2}(x + iy) \equiv T_1^1, \quad 2^{-1/2}(x - iy) \equiv T_{-1}^1 \quad [3.26]$$

These operators are proportional to the spherical harmonics $Y_m^1(\theta, \phi)$. This is not surprising considering the way irreducible tensor operators are defined in Equation 3.23. This fact will also help in writing operators into irreducible tensor operator form when the rank is greater than 0.

Given two irreducible tensor operators of rank k_1 and k_2 spanning $D^{(k_1)}$ and $D^{(k_2)}$, a direct product can be defined consisting of all the $(2k_1 + 1)(2k_2 + 1)$ possible products $T_q^{k_1} T_q^{k_2}$. A linear combination of these products will span the irreducible representation contained in the product representation $D^{(k_1)} \times D^{(k_2)}$.³³

A simple example at this point will be informative. Consider the direct product of two first rank irreducible tensor operators, a compound operator made up of two 1st rank irreducible tensor operator. The direct product will span the representation:

$$D^1 \otimes D^1 = D^2 + D^1 + D^0 \quad [3.27]$$

In other words, one second rank, one first rank and one scalar tensor operator are formed.

$$\mathbf{T}^1 \otimes \mathbf{T}^1 = \mathbf{T}^2 + \mathbf{T}^1 + \mathbf{T}^0 \quad [3.28]$$

Referring back to the theory developed for coupling angular momenta, the correct linear combination of the three tensor operators on the right of Equation 3.28 is given by the VC coefficients of $|j_1, m_1\rangle$ and $|j_2, m_2\rangle$ where $j_1 = j_2 = 1$.^{3,4}

It has been shown that the \mathbf{T}_q^k behave under coordinate rotations in the same way as the spherical harmonics, Y_q^k , and therefore the same as the states $|kq\rangle$.^{2,4} This allows the coupling of commuting tensor operators to be mathematically identical to the coupling of angular momenta. Thus, only transformational and group theoretical properties of the states or operators are needed.

Having outlined the theory for the coupling for several angular momenta and compound operators, it remains only to examine the procedures used to generate the necessary angular momenta matrix elements. First, a theorem which allows one to separate the physical part of the problem from the geometric aspect is introduced. This is called the Wigner-Eckert Theorem.^{3,5} An operator \mathbf{T}_q^k operating on a state $|\alpha j m\rangle$ transforms under rotations as follows.

$$\begin{aligned} \mathbf{D}(\alpha\beta\gamma)[\mathbf{T}_q^k|\alpha\beta\gamma\rangle] &= \mathbf{D}(\alpha\beta\gamma)\mathbf{T}_q^k\mathbf{D}^{-1}(\alpha\beta\gamma)\mathbf{D}(\alpha\beta\gamma)|\alpha j m\rangle \\ &= \sum_{q'} d_{qq'}^k(\alpha\beta\gamma)\mathbf{T}_{q'}^k \times \sum_{m'} d_{mm'}^j(\alpha\beta\gamma)|\alpha j m'\rangle \\ &= \sum_{q'm'} d_{q'q}^{(k)}(\alpha\beta\gamma)d_{mm'}^{(j)}(\alpha\beta\gamma)\mathbf{T}_{q'}^k|\alpha j m'\rangle \end{aligned} \quad [3.29]$$

The $(2k+1)(2j+1)$ products $\mathbf{T}_q^k|\alpha j m\rangle$ transform under rotation as bases for

the direct product representation $D^{(k)} \times D^{(j)}$. This representation can be broken up into subspaces.

$$D^{(k)} \otimes D^{(j)} = D^{(k+j)} + \dots + D^{(k-j)} \quad [3.30]$$

The linear combination of the products $T_q^k |\alpha_j m\rangle$ that transforms according to a particular component $|\beta_{JM}\rangle$ ($J=k+j \dots |k-j|$) of the $2J+1$ functions that are basis for a particular representation D^J are given by the V-C coefficients

$$|\beta_{JM}\rangle = \sum \langle kqjm | kjJM \rangle T_q^k |\alpha_j m\rangle \quad [3.31]$$

which can be rewritten as

$$T_q^k |\alpha_j m\rangle = \sum_{JM} \langle kqjm | kjJM \rangle |\beta_{JM}\rangle \quad [3.32]$$

multiplying both sides of Equation 3.32 by $\langle \alpha' j' m' |$

$$\langle \alpha' j' m' | T_q^k |\alpha_j m\rangle = \sum_{JM} \langle kqjm | kjJM \rangle \langle \alpha' j' m' | \beta_{JM}\rangle \quad [3.33]$$

Due to the orthogonality of angular momentum eigenfunctions, the summation vanishes except when $J=j'$ and $M=m'$. This makes the value of the summation independent of m' . Thus, Equation 3.33 can be written

$$\langle \alpha' j' m' | T_q^k |\alpha_j m\rangle = \langle kqjm | k j j' m' \rangle \langle \alpha' j' || T_q^k || \alpha_j \rangle \quad [3.34]$$

where $\langle \alpha' j' || T_q^k || \alpha_j \rangle$ is equal to $\langle \alpha' j' m' | \beta_{j' m'} \rangle$ and is called the reduced matrix element. Equation 3.34 shows that the matrix elements of an

irreducible tensor operator can be factored into a coupling constant and a term independent of magnetic quantum numbers.

The VC coefficient in Equation 3.34 can be replaced with the 3-J symbolism to give an expression which will appear in many matrix elements in this study.

$$\langle \alpha' j' m' | T_q^k | \alpha j m \rangle = (-1)^{k-j+m'} (2j'+1)^{1/2} \begin{pmatrix} j' & k & j \\ -m & q & m \end{pmatrix} \langle \alpha' j' || T^k || \alpha j \rangle \quad [3.35]$$

If the value of one reduced matrix element $\langle \alpha' j' || T^k || \alpha j \rangle$ is known, then all of the rest can be evaluated. The values of the reduced matrix elements of pertinent operators (I, L and S) have been evaluated.³⁶

Now that the Wigner-Eckert theorem has been introduced, all tools necessary to generate the matrix elements of ITO's are present. The basic steps for deriving the formulas are as follows.³⁷

- 1) Functions are constructed such that they form standard basis functions for the full rotation group.
- 2) All operators are written in irreducible tensor operator form.
- 3) The Wigner-Eckert theorem is employed to factor matrix elements into the reduced matrix element (physical component) and the 3-J symbolism (the geometrical component).
- 4) If the operator is compound, the reduced matrix element of the operator is expressed in terms of the component operators. In doing this, 6-J and 9-J symbols are often introduced to signify the recoupling of several component operators.

This method and the theory behind it is best understood by use of

examples. For this reason, the expressions for matrix elements of the fine and hyperfine Hamiltonians for this system will be derived, not merely shown, in Chapter 4. Useful relations employed in these derivations are outlined in Appendix A.

Moments of Inertia

The classical angular momentum \mathbf{P} of a rigid system of point masses is given by

$$\mathbf{P} = \underline{\mathbf{I}} \cdot \boldsymbol{\omega} \quad [3.36]$$

where $\boldsymbol{\omega}$ is the angular velocity and $\underline{\mathbf{I}}$ is the inertial tensor. The elements of this tensor are:³⁰

$$I_{xx} = \sum_i m_i (y_i^2 + z_i^2) \quad [3.37]$$

$$I_{yy} = \sum_i m_i (z_i^2 + x_i^2) \quad [3.38]$$

$$I_{zz} = \sum_i m_i (x_i^2 + y_i^2) \quad [3.39]$$

$$I_{xy} = I_{yx} = - \sum_i m_i x_i y_i \quad [3.40]$$

$$I_{zx} = I_{xz} = - \sum_i m_i x_i z_i \quad [3.41]$$

$$I_{zy} = I_{yz} = - \sum_i m_i y_i z_i \quad [3.42]$$

where the summation is over all particles in the system, m_i is the mass of the i^{th} particle and x_i , y_i and z_i are its cartesian coordinates in the center of mass coordinate system. By rotation of the center of mass coordinate system, the products of inertia I_{xy} , I_{xz} , I_{yz} can be reduced

to zero, leaving only nonzero diagonal elements. These elements are called the principal moments of inertia and are the roots of the cubic equation

$$\begin{vmatrix} I_{xx} - I & I_{xy} & I_{xz} \\ I_{yx} & I_{yy} - I & I_{yz} \\ I_{zx} & I_{zy} & I_{zz} - I \end{vmatrix} = 0 \quad [3.43]$$

The axes of this new coordinate system in which the inertial tensor is diagonal are normally designated by a, b and c, and the principal moments by I_A , I_B and I_C . By convention, the largest moment is designated I_C , the smallest I_A and the intermediate I_B .

Rigid Assymmetric Rotor

If a molecule possesses no equivalent or zero moments of inertia, it is classified as an asymmetric top molecule. The rotational Hamiltonian for such a molecule is given by³⁹

$$H_r = (1/2) \left(\frac{P_a^2}{I_a} + \frac{P_b^2}{I_b} + \frac{P_c^2}{I_c} \right) \quad [3.44]$$

where the P_g are the components of angular momentum along the principal interital axes ($g=a,b,c$). To simplify the Hamiltonian, rotational constants are introduced.

$$A = \frac{h}{8\pi^2 I_a} \quad [3.45]$$

$$B = \frac{h}{8\pi^2 I_b} \quad [3.46]$$

$$C = \frac{h}{8\pi^2 I_c} \quad [3.47]$$

The rigid rotor Hamiltonian is now written

$$H_r = \frac{4\pi^2}{h} [AP_a^2 + BP_b^2 + CP_c^2] \quad [3.48]$$

For an asymmetric top molecule, the energy levels (except for the lowest states) cannot be expressed in a single algebraic form like those for a symmetric top molecule. They must be obtained by diagonalization of the energy matrix. A description of the rotation used to designate the energy levels of an asymmetric top molecule relative to those of a symmetric top molecule will be informative.

For a prolate symmetric top molecule having $B=C \neq A$, Equation 3.48 simplifies to

$$H_r = \frac{4\pi^2}{h} [BP^2 + (A - B)P_a^2] \quad [3.49]$$

and

$$E_r = hBJ(J + 1) + h(A - B)K^2 \quad [3.50]$$

where J is the quantum number related to the total angular momentum and K is that related to the projection of the total angular momentum on the symmetry axis of the molecule. J can have any nonnegative value and K can have values ranging from $-J$ to $+J$.

Similarly, an expression for an oblate top molecule having $A=B \neq C$ is

$$E_r = hBJ(J+1) + h(C-B)K^2 \quad [3.51]$$

For an asymmetric top molecule B can have values ranging from A to C , depending on the asymmetry of the molecule. An asymmetry parameter is introduced to help describe the energy of this type of rotor.

$$\kappa = \frac{2B - A - C}{A - C} \quad [3.52]$$

Note that $\kappa = -1$ corresponds to the molecule being a prolate symmetric top, $B=C$ and $\kappa = 1$ to its being an oblate symmetric top, $B=A$. These are the two limiting cases for κ .

In symmetric top molecules, the energy levels corresponding to $-K$ and K are degenerate due to the energy expression containing only K^2 terms. For the symmetric rotor there are $J+1$ energy levels for a given value of J . These levels are not degenerate in asymmetric molecules and there will be $2J+1$ levels for a particular J value.

For an asymmetric top molecule, J and its projection M on an axis fixed in space are constants of motion and are good quantum numbers. The K quantum number is not and cannot be used to specify a rotational state. However, rotational energy levels for an asymmetric rotor are designated or indexed by a superscript giving the value of J and subscripts giving those of K (K_{-1}) for the limiting prolate case and K (K_1) for the limiting oblate case. An alternate method involves the subscripting of J with τ where τ is defined by

$$\tau = K_{-1} - K_1 \quad [3.53]$$

τ has values ranging from $-J$ to J with increasing energy.

For the rigid asymmetric rotor, Equation 3.48 can be rearranged to give⁴¹

$$H_r = \frac{4\pi^2}{h} \left[\frac{1}{2} (A + C)P^2 + \frac{1}{2} (A - C)H(\kappa) \right] \quad [3.54]$$

where

$$H(\kappa) = P_a^2 + \kappa P_b^2 - P_c^2 \quad [3.55]$$

and

$$P^2 = P_a^2 + P_b^2 + P_c^2 \quad [3.56]$$

The Hamiltonian cannot be solved directly and a general closed expression for the wavefunctions cannot be obtained. The asymmetric rotor wavefunctions must be expressed as linear combinations of symmetric top function

$$\Psi_{(a)} = \sum_n c_n \Psi_{(s)N} \quad [3.57]$$

where $\Psi_{(s)n}$ is a normalized set of orthogonal symmetric top wavefunctions.

Using $H\Psi_a = E\Psi_a$ with Ψ_a given by Equation 3.57 yields

$$\sum_n c_n H \Psi_n = E \sum_n c_n \Psi_n \quad [3.58]$$

Multiplication by Ψ_m^* and integrating gives

$$\sum_n c_n \int \Psi_m^* H \Psi_n d\tau = E \sum_n c_n \int \Psi_m^* \Psi_n d\tau \quad [3.59]$$

Incorporation of the orthogonality of the symmetric top wavefunctions leads to a set of equations. The criteria for having a solution for this set of equations is that the determinant vanishes.

$$|(m|H|n) - E\delta_{mn}| = 0 \quad [3.60]$$

Knowing the matrix elements $(m|H|n)$, one can solve for the energies of an asymmetric rotor. The nonvanishing matrix elements are

$$(JKM|P_z|JKM) = Kh \quad [3.61]$$

$$(JKM|P^2|JKM) = J(J+1)h^2 \quad [3.62]$$

$$(JKM|P_z^2|JKM) = K^2h^2 \quad [3.63]$$

$$(JKM|P_y^2|JKM) = (JKM|P_x^2|JKM) = \frac{1}{2} [J(J+1) - K^2]h^2 \quad [3.64]$$

$$\begin{aligned}
 (JKM|P_y^2|JK \pm 2M) &= -(JKM|P_x^2|JK \pm 2M) = \\
 \frac{1}{4} \{[J(J+1) - K(K \pm 1)][J(J+1) - (K \mp 1)(K \mp 2)]\}^{1/2} \hbar^2 & \quad [3.65]
 \end{aligned}$$

The matrix is diagonal in J but has off-diagonal elements in K . It is Hermitian, thus $H_{K, K+2} = H_{K+2, K} = H_{-K, -K-2} = H_{-K-2, -K}$. The matrix is diagonal in J so each J block may be solved separately. This procedure is explained in detail in a variety of sources.^{38, 40}

Symmetry of the Asymmetric Rotor Wavefunction.

The symmetry of the total wavefunction depends on the combined symmetries of each of the component functions.

$$\Psi_T = \Psi_e \Psi_v \Psi_r \Psi_n \quad [3.66]$$

where Ψ_T is the total wavefunction, Ψ_e , Ψ_v , Ψ_r and Ψ_n are the electronic, vibrational, rotational and nuclear functions, respectively.

The asymmetric rotor functions are distinguished by their behavior with respect to a 180° rotation about the three principal axes (C_2^a , C_2^b , C_2^c). The C_2^c and C_2^a operations are all that need be considered since C_2^b is equivalent to the other two carried out in succession. There are four different types of rotational levels, ++, +-, -+, -- where the first sign refers to the behavior of the corresponding wavefunction with respect to the C_2^c operation and the second with respect to the C_2^a .⁴²

For a C_{2v} molecule, if the a axis (corresponding to the least moment of inertia) is the C_2 axis, the rotational eigenfunctions belong

to type A or B for ++, -+ or +-, -- levels respectively. A type rotational levels are considered symmetric and B type are considered antisymmetric. The parity classifications of the rotational levels of a nonplanar molecules are not of interest in this work and will not be discussed.⁴¹

The symmetry of the total wavefunction is also effected by the nuclear spin quantum numbers, I_i . If two (or more) identical nuclei exchange upon a C_2 rotation, the total wavefunction must obey Bose-Einstein statistics if I for a single nucleus is integer or Fermi-Dirac statistics if I is half integer. For I being an integer, the total wavefunctions is symmetric with respect to rotation about the symmetry axis. If I is half integer, the wavefunction is antisymmetric.

There are $(2I+1)^2$ total spin functions for two identical nuclei, $(I+1)(2I+1)$ are symmetric and $I(2I+1)$ antisymmetric. For two $3/2$ spin nuclei (which obey Fermi Dirac statistics) the symmetric spin functions ($I=3,1$) combine only with the antisymmetric rotational levels and antisymmetric spin functions ($I=2,0$) combine only with the symmetric rotational levels when the molecule is in a totally symmetric vibronic and electronic state.

Chapter IV

Matrix Elements of the Hamiltonian

Using the theory outlined in the previous section, the Hamiltonian and appropriate matrix elements for the analysis of the microwave spectrum of the 2-cyano-2-propyl radical were developed. Hund's coupling case b applies to this molecule as it does to all nonlinear radicals.⁴³ For an asymmetric top radical, the electron spin angular momentum \underline{S} couples to the molecular rotation angular momentum \underline{N} to give a resulting momentum \underline{J} . This results in a doubling of each rotational line producing fine structure in the observed spectrum.

If there exists at least one nucleus with nonzero spin in the molecule, its nuclear spin \underline{I} will couple with \underline{J} resulting in a total angular momentum \underline{F} . When several such nuclei are present in the molecule, the introduction of intermediate angular momentum vectors \underline{F}_j is necessary. Hence, the coupling scheme for the 2-cyano-2-propyl radical is

$$\underline{N} + \underline{S} = \underline{J}; \quad \underline{I} + \underline{I}_N = \underline{E}_1; \quad \underline{E}_1 + \underline{I}_H = \underline{F}$$

where \underline{I}_N is the nuclear spin state of the ^{14}N nucleus and \underline{I}_H is the

total nuclear spin state of the six protons. ^{14}N is taken as the first nucleus coupled with \underline{j} strictly for convenience. The order in which different nuclei are coupled into the system will not effect the calculated splitting.¹ Splitting of the rotational lines due to nuclear spin is referred to as hyperfine splitting.

The Hamiltonian needed to analyze the spectrum of the 2-cyano-2-propyl radical is

$$\mathbf{H} = \mathbf{H}_{rot} + \mathbf{H}_{sr} + \mathbf{H}_{hf}^N + \mathbf{H}_{hf}^H \quad [4.1]$$

where the terms on the right describe molecular rotations, spin-rotation coupling, ^{14}N hyperfine interactions and ^1H hyperfine interactions, respectively. \mathbf{H}_{rot} is the asymmetric rotor Hamiltonian which was discussed earlier. The remaining three will be addressed separately.

Spin Rotation

Unpaired electrons produce three types of fine structure interactions. These are spin-orbit, spin-rotation and spin-spin. Spin-spin interactions apply only to molecules with more than one unpaired electron. The spin orbit interaction is generally several orders of magnitude smaller than spin-rotation interaction in an asymmetric top radical.⁴³ This makes spin-rotation the predominant term in the fine splitting of the 2-cyano-2-propyl radical rotational spectrum.

The Hamiltonian for spin-rotation is given by⁴⁴

$$\mathbf{H}_{sr} = (1/2) \sum_{\alpha, \beta} \epsilon_{\alpha\beta} (\mathbf{N}_\alpha \mathbf{S}_\beta + \mathbf{S}_\beta \mathbf{N}_\alpha) \quad [4.2]$$

where $\alpha, \beta = X, Y, Z$. This can be rewritten in terms of spherical tensors^{4,5}

$$H_{sr} = (1/2) \sum_{k=0}^2 [T_p^k(\epsilon) T^k(N, S) + T^k(N, S) T^k(\epsilon)] \quad [4.3]$$

where

$$T_p^k(N, S) = (-1)^p (2k+1)^{1/2} \sum_{p_1 p_2} T_{p_1}^1(N) T_{p_2}^1(S) \begin{pmatrix} 1 & 1 & k \\ p_1 & p_2 & -p \end{pmatrix} \quad [4.4]$$

where $T_p^k(\epsilon)$ is an irreducible tensor of rank k composed of the spin rotation coupling constants. $T^k(\epsilon)$ is a second rank tensor and in general will have nine components. In a molecule with no symmetry, only six components are independent. The number of independent components decreases with increasing molecular symmetry. A molecule possessing C_{2v} symmetry will have a tensor where only the diagonal elements remain.

The matrix elements of the Hamiltonian are evaluated using Hund's case b basis functions $|NKSJM_J\rangle$. No contributions due to \underline{I} or \underline{F} are present in the functions since spin-rotation interaction is independent of nuclear spins. The rotational parts of these functions are the symmetric top functions which simultaneously diagonalize the N^2 and N_z operators. They can be expressed by the Wigner rotation matrix of rank N .

$$|NKM\rangle = \left[\frac{(2N+1)}{8\pi} \right]^{1/2} D_{mk}^{(N)*}(\omega) \quad [4.5]$$

An anomalous sign arises between the commutation relations of angular momentum operators that are molecule fixed and those that are space-fixed. Transforming all molecule-fixed components (q) of angular momenta to space-fixed components (p) alleviates this difficulty. This is done using the Wigner rotation matrix.

$$T_p^k(\epsilon) = \sum_q d_{pq}^{(k)*}(\omega) T_q^k(\epsilon) \quad [4.6]$$

Using the spherical tensor operator given in equation 4.3 and the tensor relations given in Appendix A, the spin rotation matrix elements can be written.

$$\begin{aligned} \langle N'K'SJ'M'_J | H_{sr} | NKSJM_J \rangle &= \delta_{JJ'} \delta_{M'_J M_J} \sum_{k=0}^2 (2k+1)^{1/2} [S(S+1)(2S+1)(2N+1)(2N'+1)]^{1/2} \\ &\times \left\{ \begin{matrix} 1 & 1 & k \\ N' & N & N \end{matrix} \right\} (-1)^{J+S+N} (1/2) \left\{ (-1)^k [N(N+1)(2N+1)]^{1/2} \left\{ \begin{matrix} 1 & 1 & k \\ N' & N & N \end{matrix} \right\} \right\} \\ &\times \sum_q (-1)^{N'-K'} \left(\begin{matrix} N' & k & N \\ -K' & q & K \end{matrix} \right) T_q^k(\epsilon) \end{aligned} \quad [4.7]$$

This equation indicates the spin-rotation Hamiltonian has non-vanishing matrix elements where $\Delta N=0, \pm 1$ and $\Delta K=0, \pm 1, \pm 2$. The matrix is diagonal in J. In a molecule possessing C_{2v} symmetry, $\Delta K=\pm 1$ also vanish.⁴⁶

Derivation of the spin-rotation matrix elements has been reported in several different publications, (Cook and DeLucia⁴⁷ is one of the better). Thus only an outline was presented here. Other Hamiltonian matrix elements where the derivation is more informative and less well

known will be derived in greater detail.

Hyperfine Coupling

Interactions involving nuclear spin angular momentum are usually very small and can only be observed using a high resolution instrument. In free radicals, the most important hyperfine interactions are magnetic which are due to the coupling between unpaired electrons and the nuclear spin in the molecule. This type of coupling can occur with any nucleus having nonzero spin, unlike nuclear quadrupole coupling which requires the nucleus to have a spin greater than $\frac{1}{2}$. Nuclear quadrupole due to ^{14}N coupling will also be present in the 2-cyano-2-propyl radical, but the magnitude of its splitting will be below the resolution of the microwave spectrometer used in this study. Nuclear spin-rotation and nuclear spin-nuclear spin interaction will also be unresolved since they are several orders of magnitude smaller than other hyperfine couplings.⁴⁸

The magnetic interactions of the unpaired electron and nuclear spins is composed of two terms. The first term is the interaction of electron orbital angular momentum \underline{L} and nuclear spin angular momentum \underline{I} . This interaction does not exist in nonlinear radicals⁴⁹ and will not be discussed further. The second term arises from the interaction of the electron spin angular momentum \underline{S} and nuclear spin angular momentum \underline{I} . It is composed of two parts, the Fermi contact interaction and the dipole-dipole interaction. The operators are given respectively as:

$$H_F = a_F \mathbf{S} \cdot \mathbf{I}$$

[4.8]

$$H_{DD} = \mathbf{S} \cdot \underline{\mathbf{I}} \cdot \mathbf{I} \quad [4.9]$$

where $\underline{\mathbf{I}}$ denotes a second rank traceless tensor.

The Fermi contact interaction is due to the finite probability of finding the lone electron at the nucleus being considered, thus the Fermi contact parameter a_F is proportional to the expectation value of the unpaired electron at this nucleus, $|\psi(0)|^2$. Hence, it is proportional to the S character of the orbital that the electron occupies. The parameter can be written:

$$a_F = (8\pi/3)g_s g_N \beta_N |\psi(0)|^2 \quad [4.10]$$

The remainder of the Fermi contact Hamiltonian is $\mathbf{S} \cdot \mathbf{I}$. These are vector operators and can be written in spherical tensor notation. Using the states from Hund's case b coupling ($\underline{\mathbf{N}} + \underline{\mathbf{S}} = \underline{\mathbf{J}}$, $\underline{\mathbf{J}} + \underline{\mathbf{I}}_N = \underline{\mathbf{F}}_1$) and considering only the ^{14}N nucleus, the matrix elements are initially expressed as:

$$\langle N'K'S'J'I_N F_1 M'_{F_1} | T^1(\mathbf{S}) \cdot T^1(\mathbf{I}) | NK S J I_N F_1 M_{F_1} \rangle$$

Operators $T^1(\mathbf{S})$ and $T^1(\mathbf{I})$ commute because their eigenfunctions are independent, i.e. they refer to different parts of the system. The scalar product of two vectors is a scalar thus, part A.6.3 of Appendix A applies to this case. The matrix elements now may be written

$$\langle N'K'SJ I_N F_1 M'_{F_1} | T^1(\mathbf{S}) \cdot T^1(\mathbf{I}) | NKSJ I_N F_1 M_{F_1} \rangle = (-1)^{J+I_N+F_1} \delta_{F_1 F_1} \delta_{M'_{F_1} M_{F_1}} \quad [4.11]$$

$$\left\{ \begin{matrix} F_1 & I_N & J' \\ 1 & J & I_N \end{matrix} \right\} \sum_{N''K''} \langle N'K'SJ || T^1(\mathbf{S}) || N''K''SJ \rangle \langle N''K''I_N || T^1(\mathbf{I}) || NKI_N \rangle$$

where the terms after the 6-J symbol are the reduced matrix elements. The second reduced matrix element will be zero unless $N''=N$ and $K''=K$ and can be written

$$\langle N''K''I_N || T^1(\mathbf{I}) || NKI_N \rangle \equiv \langle I_N || T^1(\mathbf{I}) || I_N \rangle \delta_{N''N} \delta_{K''K} \quad [4.12]$$

$$= [I_N(I_N + 1)(2I_N + 1)]^{1/2}$$

The first reduced matrix elements in Equation 4.11 involves a tensor operator working only on part two of a coupled state, as in A.6.4 of Appendix A. This reduced matrix element can now be written

$$\langle N'K'SJ || T^1(\mathbf{S}) || KNSJ \rangle = (-1)^{N+S+J'+1} [(2J+1)(2J'+1)]^{1/2} \left\{ \begin{matrix} S & J' & N \\ J & S & 1 \end{matrix} \right\} \quad [4.13]$$

$$\times \langle K'N'S || T^1(\mathbf{S}) || KNS \rangle$$

and

$$\langle K'N'S || T^1(\mathbf{S}) || KNS \rangle = [S(S+1)(2S+1)]^{1/2} \quad [4.14]$$

Combining equations 4.11-4.14, the matrix element expression for the Fermi contact parameter for the nitrogen nucleus is obtained.

$$\begin{aligned}
\langle N'K'SJ'I_N F_1 M'_{F_1} | \mathbf{H}_F | NKSJ'I_N F_1 M_{F_1} \rangle &= \delta_{F_1 F_1} \delta_{M'_{F_1} M_{F_1}} \delta_{N' N} \delta_{K' K} (-1)^{J+I+F} (-1)^{N+S+J'+1} \\
& [(2J+1)(2J'+1)I_N(I_N+1)(2I_N+1)S(S+1)(2S+1)]^{1/2} \quad [4.15] \\
& \left\{ \begin{matrix} F_1 & I_N & J' \\ 1 & J & I_N \end{matrix} \right\} \left\{ \begin{matrix} S & J' & N \\ J & S & 1 \end{matrix} \right\} a_F(I_N)
\end{aligned}$$

The second set of nuclei considered in the hyperfine splitting of the 2-cyano-2-propyl radical are the six equivalent hydrogens. The hyperfine splitting of six equivalent nuclei with $\frac{1}{2}$ spins has been addressed by White³. It was found that the hyperfine matrix elements of six equivalent spins can be handled in the same way as a single nucleus with a spin of the vector sum of the original six. The assumptions and reasoning behind this is detailed in Appendix E. The proton hyperfine coupling is calculated for total spin states of 0,1,2, and 3.

For the Fermi interactions for the protons, a different coupled state, $|NKSJ'I_N F_1 I_H M_F\rangle$, and a slightly different operator, $[a_F \cdot \mathbf{T}'(S) \cdot \mathbf{T}'(I_H)]$, are used to formulate the matrix elements. Following the same logic as that for the nitrogen nucleus, one obtains an expression differing only in the first reduced matrix element of Equation 4.11. The new reduced matrix element will add a factor of

$$(-1)^{J'+F_1+I_N+1} [(2F_1+1)(2F_1+1)]^{1/2} \left\{ \begin{matrix} I_N & J' & F_1 \\ 1 & F_1 & J \end{matrix} \right\}$$

to the original element expression. The second reduced matrix element now refers to the proton spin state rather than the nitrogen spin resulting in changing I_N to I_H in the expression. The final expression

for the Fermi contact matrix elements of the protons is:

$$\begin{aligned}
 & \langle N'K'SJ'I_NF_1I_HFM_F | a_F \cdot T^1(\mathbf{S}) \cdot T^1(\mathbf{I}) | NKSJI_NF_1I_HFM_F \rangle = (-1)^{2F_1+F+2J'+S+N+I_N+I_H} \\
 & \times [(2F_1+1)(2F_1+1)(2J+1)(2J'+1)I_H(I_H+1)(2I_H+1)]^{1/2} \begin{Bmatrix} F & I_H & F_1 \\ 1 & F_1 & I_H \end{Bmatrix} \\
 & \times \begin{Bmatrix} I_N & J' & F_1 \\ 1 & F_1 & J \end{Bmatrix} \begin{Bmatrix} N & J' & S \\ 1 & S & J \end{Bmatrix} a_F(I_H)
 \end{aligned} \tag{4.16}$$

Dipole-dipole interactions arise from the interaction of two dipoles (electron and nuclear spins); consequently the interaction depends upon their mutual orientation and a tensoral quantity is required to describe it. Dipole-dipole matrix elements are slightly more involved. The $\mathbf{S} \cdot \mathbf{I} \cdot \mathbf{I}$ operator can be rewritten using spherical tensors.

$$H_{DD} = [\mathbf{I}^2 \times T^1(\mathbf{S})]^1 \cdot T^1(\mathbf{I}) \tag{4.18}$$

The matrix elements for the second nucleus were not rigorously derived for the Fermi contact term. The dipole-dipole matrix elements are now derived in order to clarify how one obtains the matrix expressions for the second nucleus. The coupled state used is $|NKSJI_NF_1I_HFM_F\rangle$. Equation 4.18 is applied to this coupled state. The two operators, $T^1(\mathbf{I})$ and $[\mathbf{I}^2 \times T^1(\mathbf{S})]^1$, operate on different parts of this state, thus they commute. The expression for the scalar product of commuting tensor operators, A.6.3 of Appendix A is once again applicable.

$$\begin{aligned}
 & \langle N'K'SJ'I_NF_1FM'_F | [\mathbf{I}^2 \times T^1(\mathbf{S})]^1 \cdot T^1(\mathbf{I}) | NKSJI_NF_1FM_F \rangle = \delta_{F'F} \delta_{M'_F M_F} (-1)^{F_1+I_N+F} \\
 & \begin{Bmatrix} F & I_N & F_1 \\ 1 & F_1 & I \end{Bmatrix} \langle N'K'SJ'I_NF_1 | | [\mathbf{I}^2 \times T^1(\mathbf{S})]^1 | | NKSJI_NF_1 \rangle \langle I_H | | T^1(\mathbf{I}) | | I_H \rangle
 \end{aligned} \tag{4.19}$$

The first reduced matrix element is defined by

$$\langle I_H || T^1(\mathbb{I}) || I_H \rangle = [I_H(I_H+1)(2I_H+1)]^{1/2} \quad [4.20]$$

Since both operators are independent of I_N , they can now be treated as a single operator in a coupled scheme. Using A.6.4, the second reduced matrix element can be rewritten as:

$$\begin{aligned} \langle N'K'SJ' I_N F_1 || [T^2 \times T^1(S)]^1 || NKSJ I_N F_1 \rangle &= (-1)^{J'+I_N+F_1+1} \\ &[(2F_1+1)(2F_1+1)]^{1/2} \left\{ \begin{matrix} J' & F_1 & I_N \\ F_1 & J & 1 \end{matrix} \right\} \langle N'K'SJ' || [T^2 \times T^1(S)]^1 || NKSJ \rangle \end{aligned} \quad [4.21]$$

The two operators operate on different systems, thus A.6.2 can be applied to Equation 4.21. This results in

$$\begin{aligned} \langle N'K'SJ' || [T^2 \times T^1(S)]^1 || NKSJ \rangle &= \langle N'K' || T^2 || NK \rangle \langle S || T^1(S) || S \rangle \\ &\times [(2J'+1)(2J+1)]^{1/2} \left\{ \begin{matrix} N' & N & 1 \\ S & S & 1 \\ J' & J & 2 \end{matrix} \right\} \end{aligned} \quad [4.22]$$

The first reduced matrix element in Equation 4.22 is simply defined as

$$\langle S || T^1(S) || S \rangle = [S(S+1)(2S+1)] \quad [4.23]$$

The components of angular momentum in the second reduced matrix element

of 4.22 are defined in the molecule fixed coordinate system. They are transformed into space fixed coordinates in the same manner shown earlier with the spin-rotation interaction (Equation 4.6). Including this transformation, the second reduced matrix element is rewritten ' ,

$$(N'K' || \underline{T}^2 D_q^2 || NK) = [(2N' + 1)(2N + 1)]^{1/2} (-1)^{N'-K'} \begin{pmatrix} N' & 2 & N \\ -K' & q & K \end{pmatrix} T_q^k(\Delta K) \quad [4.24]$$

The dipole-dipole matrix elements for the second nuclei can then be written

$$\begin{aligned} < N'K'SJ'I_N F_1 F_M F | H_{DD} | NKSJ'I_N F_1 F_M F > = (-1)^{2F_1 + F + J' + N' + I_N + I_H + K'} \\ & \times [I_H(I_H + 1)(2I_H + 1)S(S + 1)(2S + 1)(2N' + 1)(2N + 1)(2J + 1)(2J' + 1)(2F_1 + 1)(2F_1 + 1)]^{1/2} \\ & \left\{ \begin{matrix} I_N & J' & F_1 \\ 1 & F_1 & J \end{matrix} \right\} \left\{ \begin{matrix} F & I_H & F_1 \\ 1 & F_1 & I_H \end{matrix} \right\} \left\{ \begin{matrix} N' & N & 1 \\ S & S & 1 \\ J' & J & 2 \end{matrix} \right\} \sum_q (-1)^{N'-K'} \begin{pmatrix} N' & 2 & N \\ -K' & q & K \end{pmatrix} T_q^2(\Delta K) \end{aligned} \quad [4.25]$$

where

$$g_{SgN\beta\beta} T_0^2(C) = \frac{T_{zz}}{2} = -\frac{(T_{yy} + T_{xx})}{2} \quad [4.26]$$

$$g_{SgN\beta\beta} T_{\pm 1}^2(C) = \mp(1/\sqrt{6})(T_{zz} \pm iT_{yz}) \quad [4.27]$$

$$g_{SgN\beta\beta} T_{\pm 2}^2(C) = (1/\sqrt{24})(T_{xx} - T_{yy} \pm 2iT_{xy}) \quad [4.28]$$

The dipole-dipole matrix element expression for the first nuclei is found in a similar fashion

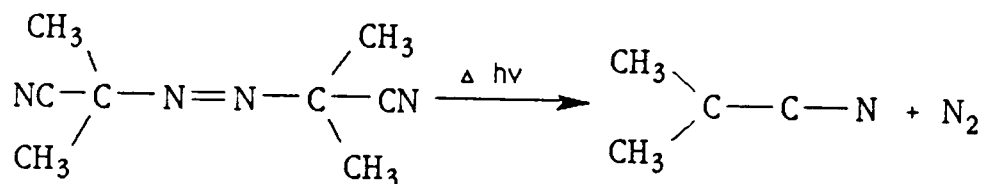
$$\begin{aligned} \langle N'K'SJ'I_NF_1M'_{F_1} | \mathbf{H}_{DD} | NKSJ'I_NF_1M_{F_1} \rangle &= (-1)^{F_1+J+N+I_N+K'} \\ & [(2J'+1)(2J+1)(2N'+1)(2N+1)S(S+1)(2S+1)I_N(I_N+1)(2I_N+1)]^{1/2} \\ & \left\{ \begin{matrix} F & I_N & J' \\ 1 & J & I_N \end{matrix} \right\} \left\{ \begin{matrix} N' & N & 2 \\ S & S & 1 \\ J' & J & 1 \end{matrix} \right\} \begin{pmatrix} N' & 2 & N \\ -K & \Delta K & K \end{pmatrix} T_q^2(\Delta K) \end{aligned} \quad [4.29]$$

The selection rules for the hyperfine matrix elements are $\Delta N=0, \pm 2$; $\Delta K=0, \pm 1, \pm 2$ and $\Delta J=0, \pm 1$. The algebraic expressions for the specific 3-J, 6-J and 9-J symbols used in the fine and hyperfine coupling expressions are listed in Appendix B, C and D respectively.

A computer program was written to calculate the contributions of the fine and hyperfine interactions to the splitting of rotational transition. A detailed description of the program with a copy of the written code and a sample output is included in Appendix F.

Chapter V
Experimental

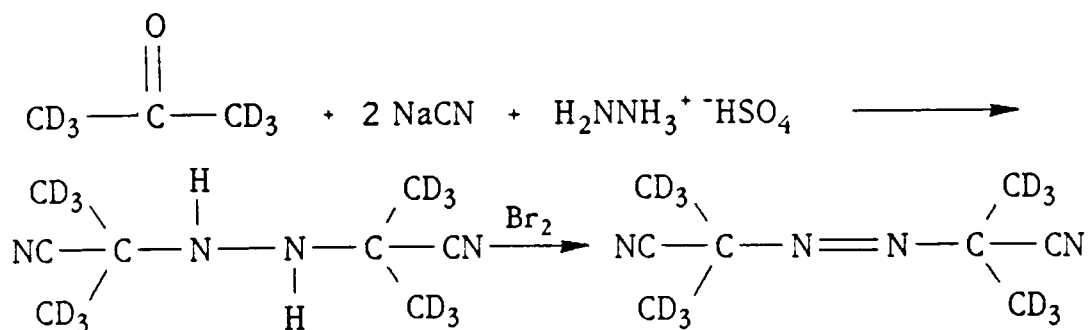
The thermolysis and photolysis of azoisobisbutyronitrile (AIBN) to generate the 2-cyano-2-propyl radical has been used for many years by polymer chemists to initiate free radical polymerizations.



The same reaction is used to generate the radical for spectroscopic characterization.

The starting compound (Aldrich Chemical Co.) was recrystallized from cold methanol to insure purity. The melting point of the resulting crystals was 104°C, agreeing well with that reported by Aldrich.

The fully deuterated analog was synthesized from d^6 -acetone (Aldrich Chemical Co.) using the following reaction⁵⁰



The final product was recrystallized twice from cold methanol. The melting point was 104°C. Proton NMR of the final compound indicated that no detectable exchange of methyl deuterons with other protons had occurred.

Thermogravimetric Analysis-Mass Spectrometry was performed on the proton sample to determine the temperature at which AIBN evaporated and the resulting decomposition products which would be present. At atmospheric pressure, the compound evaporated at 127°C. The mass spectrum shown in Figure 5.1, contained the radical ion peak but no molecular (AIBN) ion peak. This suggests that thermolysis occurs at or below 127°C.

The 2-cyano-2-propyl radical has been shown to have a significant lifetime in solution.¹¹ Its lifetime in the gas phase has not been measured. A lifetime study of the radical was necessary in order to establish its presence in the microwave cell for a suitable length of time.

The first attempt at establishing a lifetime for the radical was performed using Electron Paramagnetic Resonance. This was not successful due to the lack of intense lines. In the gas phase, orbital angular momentum is quenched and the electron spin angular momentum S

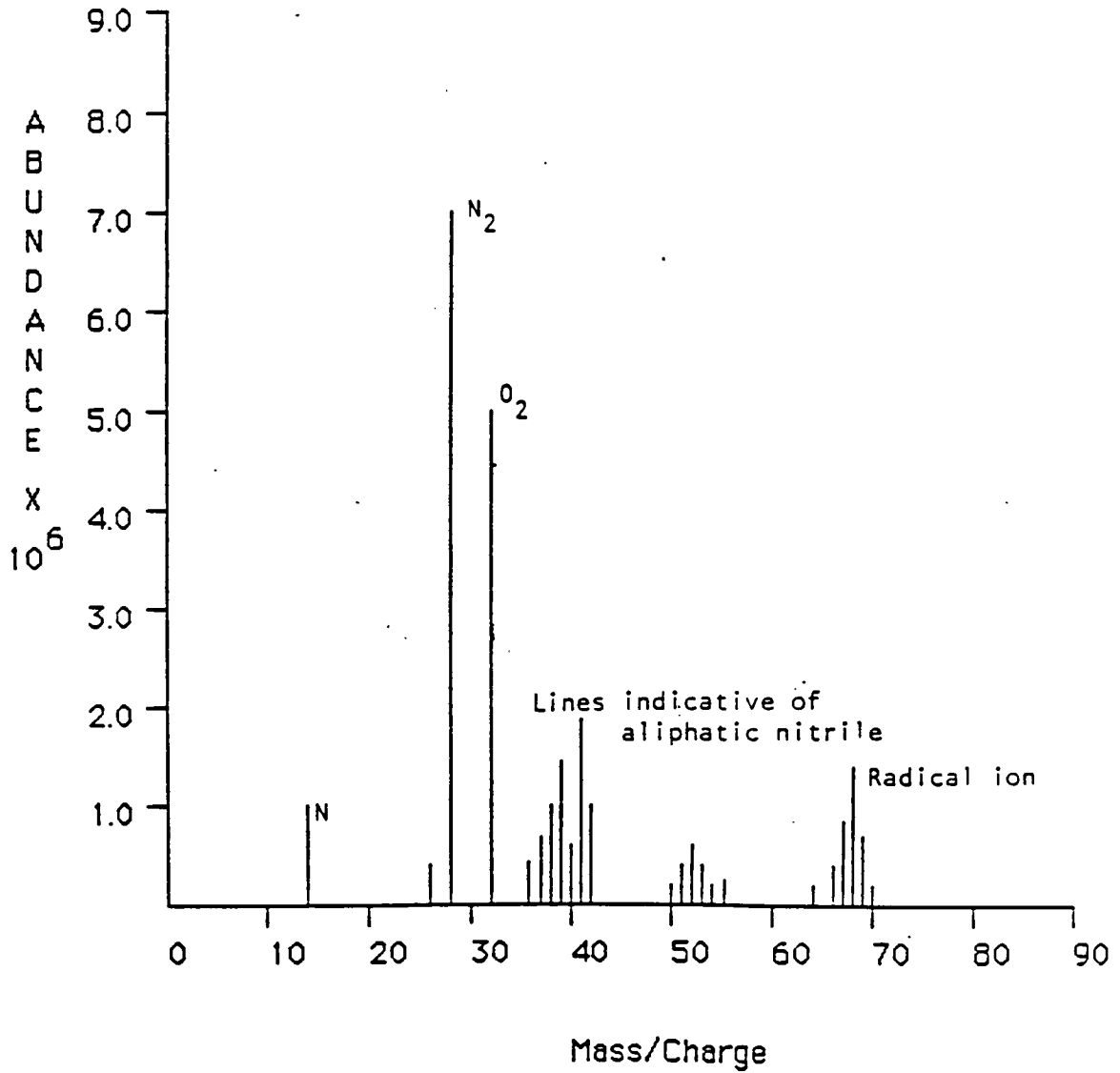


Figure 5.1 Thermogravimetric Analysis/Mass Spectrum of AIBN (sample evaporated at 127^o C)

decouples from the molecular frame work due to rotation of the molecule. Thus, only magnetic dipole transitions are possible. This results in numerous lines of extremely low intensity. For this reason, very few nonlinear radicals have been studied in the gas phase with EPR.⁵¹ This is also the reason why no reproducible signal was obtained for the 2-cyano-2-propyl radical in the gas phase.

A successful lifetime study was performed using gas phase infrared spectroscopy (Figure 5.2). An apparent ketene-imine ($-C=C=N$) peak normalized with respect to the C-H stretch was used to monitor radical concentration in the IR cell at 130°C. Absence of a N-H, C N or C-N stretch in the spectra confirmed the ketene-imine peak was due to the radical.

The ketene-imine peak was observed in the IR spectrum for approximately 60 minutes before a reduction in its intensity became apparent. This coincided with the cyano ($C\equiv N$) stretch becoming stronger due to the recombination of the radical into 2-2'-dimethyl,2-2'-dicyanopropane. Extrapolating from this study, once the radical is generated in the microwave cell, spectra of it could be obtained for at least 45 minutes. The IR experiment was repeated on the fully deuterated species with identical results other than expected peak shifts from D replacement.

The microwave spectrometer used in this study consisted of a standard Stark cell (three meters in length), a computer controlled Hewlett Packard 8673B oscillator and a Princeton Applied Research lock-in amplifier. The Stark modulation frequency used was 35Khz with a field strength of 750V. Lower Stark fields were attempted but resulted

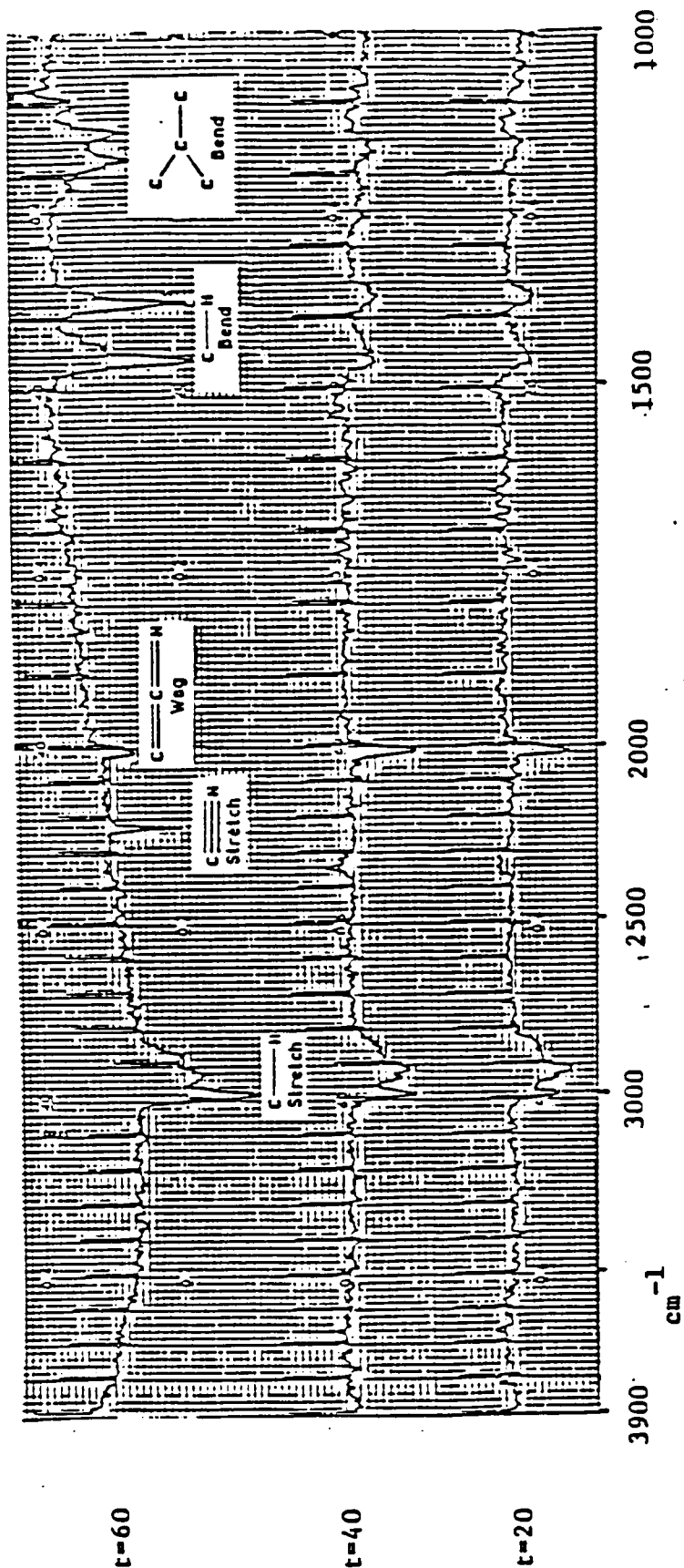


Figure 5.2 Infrared Spectrum of Sublimed AIBN versus time
(temperature of cell 130°C)

in a reduction in intensity of the microwave lines.

The cell is connected to a vacuum manifold through which the sample is introduced. For this study, the cell was heated to 110°C to prevent sample condensation in the cell. A schematic of the Stark cell is shown in Figure 5.3.

Thermal generation of the radical was attempted but due to the higher vacuum in the manifold of the Stark system as compared to that in the IR cell in earlier studies, the AIBN sublimed at 100°C. The resulting spectrum consisted of methanol (solvent used for recrystallizing original compound) and ammonia (impurity believed to be present in cell prior to this study). This sample was frozen from the microwave cell and analyzed. It was determined that the AIBN had not dissociated into the radical. The absence of any observable rotational transitions (other than methanol or ammonia) indicated that the AIBN molecule has no strong microwave lines, thus will not interfere with the observation of the radical spectrum. This absence of any observable radical spectrum indicated that UV photodissociation would be necessary to generate an adequate concentration of the radical in the microwave cell.

Sublimed AIBN was passed through a quartz adaptor and photolyzed using a 140 watt Hg UV lamp before entering the microwave cell (Figure 5.4). The spectrum was obtained using sample pressures ranging from 50 to 100 microns. It consisted of many lines which could not be attributed to methanol or ammonia. These lines disappeared after approximately two hours (depending on sample pressure in the microwave cell) indicating their transient nature.

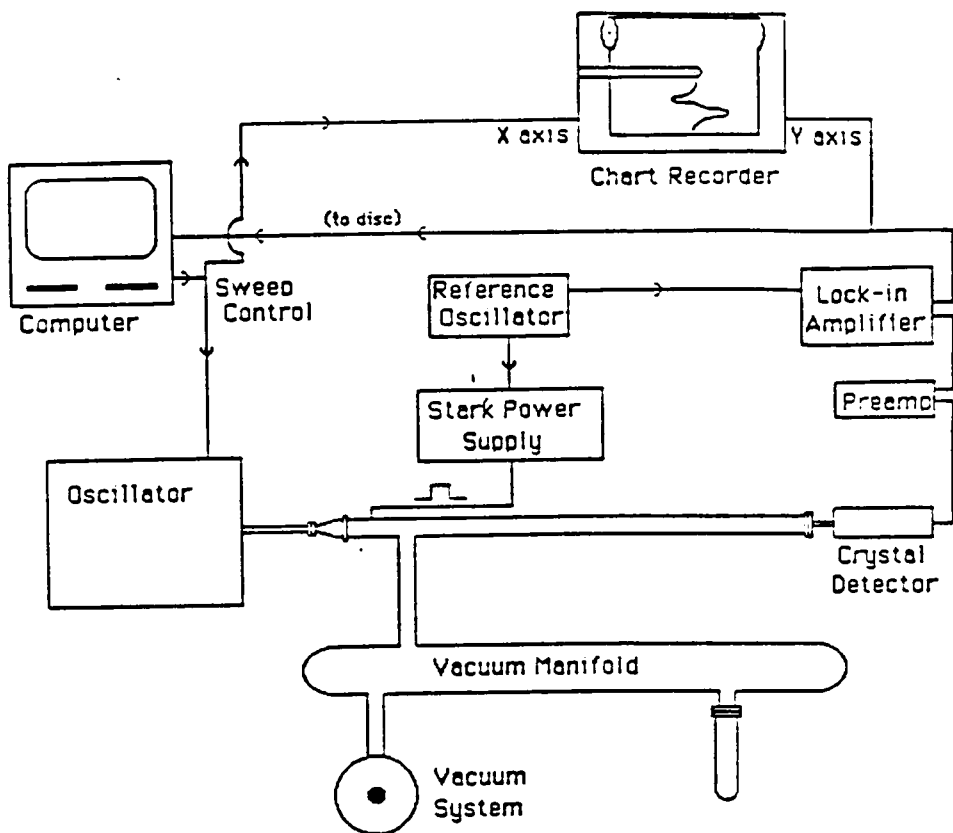


Figure 5.3 Schematic of Stark Modulated Spectrometer System

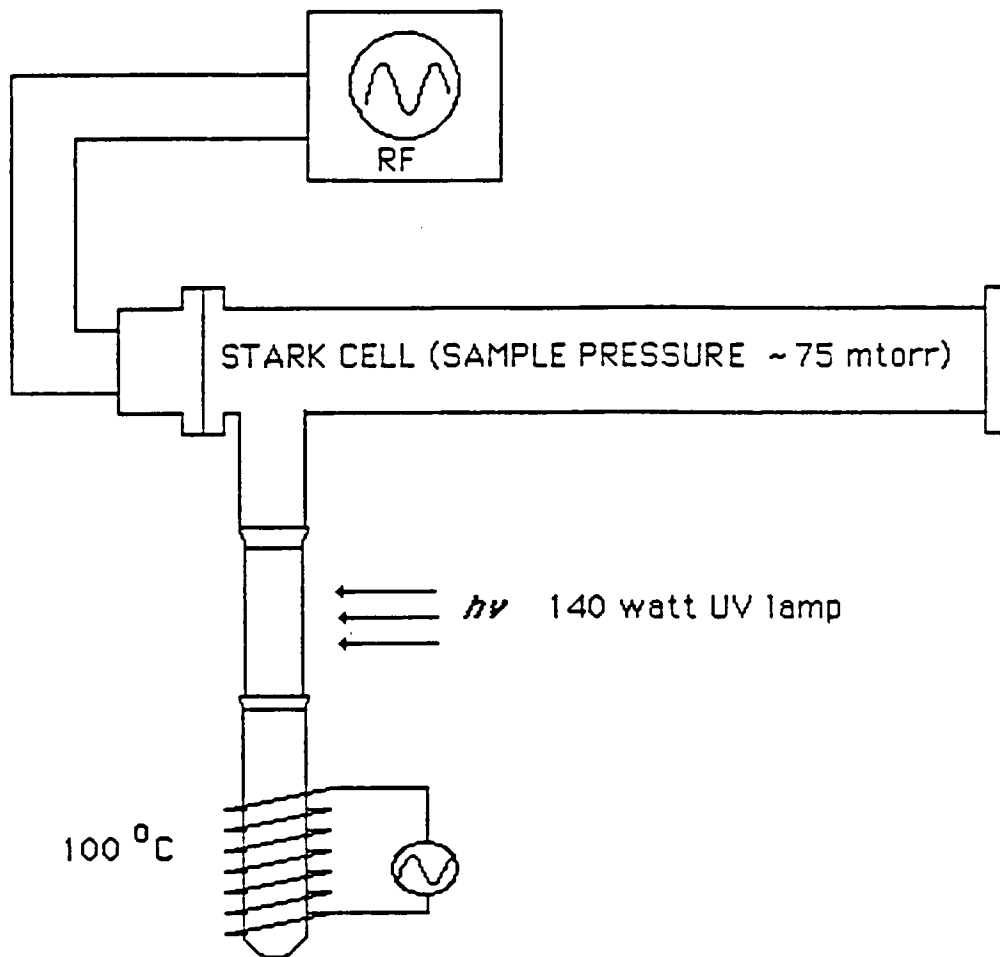


Figure 5.4 Radical Generation Apparatus for Microwave Spectroscopy

The lines were broad (4-5 Mhz) due in part to the relatively high pressure in the cell and in part due to unresolved hyperfine structure. Some of the lines exhibited fine structure which was impossible to assign due to noise in the spectrometer system and the possibility of vibrational satellites resulting from relatively high sample temperatures.

Chapter VI

Results

The observed microwave spectrum consisted of many lines which were due to methanol and ammonia in addition to those of the radical. A spectrum of methanol at 100°C was obtained in the same cell used for the observation of the radical spectrum. This spectrum of pure methanol was compared to the radical spectrum to insure that methanol lines were not erroneously assigned to the radical. Ammonia lines appeared in both the methanol and radical spectra. It is not known how the ammonia was introduced into the cell but once in the cell it is exceptionally difficult to completely remove. As with methanol, however, the lines were well cataloged and presented no problem other than to mask out an occasional weak radical transition.

The dimerized radical (2,3 dicyano-2,3-dimethylbutane), $(\text{CH}_3)_2\text{CNC-CCN}(\text{CH}_3)_2$, is not commercially available so the compound's microwave spectrum was not directly observed. A rigid rotor calculation using a model structure of the gauche form (the only conformer with a dipole moment) was performed to ascertain the general nature of its microwave spectrum. No spectral patterns of the types predicted were observed in the spectrum. This led to the conclusions that either this compound

was not present in the cell or, more likely, it has a trans conformation and exhibits no rotational spectrum.

It is beneficial to have a reasonable initial structure when making an assignment of a microwave spectrum. Since no previous molecular structure determination of the radical had been performed, a theoretical study was employed to obtain an initial structure. A previous theoretical study¹⁵ was performed using a Restricted Hartree-Fock basis set at a 3-21G level. This work was discussed in Chapter II.

Gaussian 80⁶⁰ calculations were performed using an Unrestricted Hartree-Fock basis set at STO-3G and 4-31G levels. In the calculations, r_{CH} was fixed to 1.09Å and angle CCH and angle HCH were set to 109.467°. All other structural parameters were allowed to vary to obtain the lowest energy. The CCMe angle, r_{CN} , r_{CC} , r_{CMe} and the out of plane angle were set as computer program variables. The relative methyl group conformations were systematically varied on successive calculations.

Six different calculations were performed using the STO-3G basis sets: the three relative methyl conformations (staggered, eclipsed and doubly eclipsed) each with planar and nonplanar carbon-nitrogen skeletal networks as initial structures. The nonplanar cases started with an out of plane angle of 10°. Only one of the six calculations resulted in a final nonplanar structure. This nonplanar case had staggered methyl groups and a nonplanar structure as a starting point. The resulting energy was 0.3 Hartrees (180 kilocalories per mole) larger than any of the other five. This calculation is believed to have encountered a false minimum resulting in an erroneous structure.

At a 4-31G level of theory, calculations were performed on the

three methyl conformations but only the staggered form was started with both planar and nonplanar structures. All four calculations resulted in a planar structure with computational oscillations around the three bond lengths allowed to vary. The oscillations were on the order of .02Å. The final structure was taken to be the average of these bond lengths. The energy difference between methyl conformations was theoretically determined to be 120 cal/mole. Structural parameters from the calculations are summarized in Table 6.1 and Fig. 6.1.

The 4-31G structure was used as the initial structure to provide a basis for assigning the microwave spectrum. At best, only three structural parameters can be obtained from the initial fit since the spectrum of a single isotopic species provided only three moments of inertia. Initially, the C-C-Me angle was set to be 120.55 and r_{CN} , r_{CC} and r_{CMe} were systematically varied until the calculated rigid rotor rotational lines were brought into proximity with the observed lines. Once this initial fit of the spectrum was obtained, fine and hyperfine splitting was considered.

The largest splitting of the 2-cyano-2-propyl rotational lines is due to the spin rotation interaction (fine splitting). Lines with no hyperfine structure exist for $I_N = I_H = 0$. These lines can be assigned to determine the spin-rotation splitting and the relevant constants involved. Again, a reasonable starting point is needed.

It has been shown by Curl⁶¹ that the spin-rotation constants ($\epsilon_{aa}, \epsilon_{bb}, \epsilon_{cc}$) are proportional to the corresponding rotational constants of the molecule. These constants are often reported normalized with respect to the rotational constant. Molecules of like symmetry have

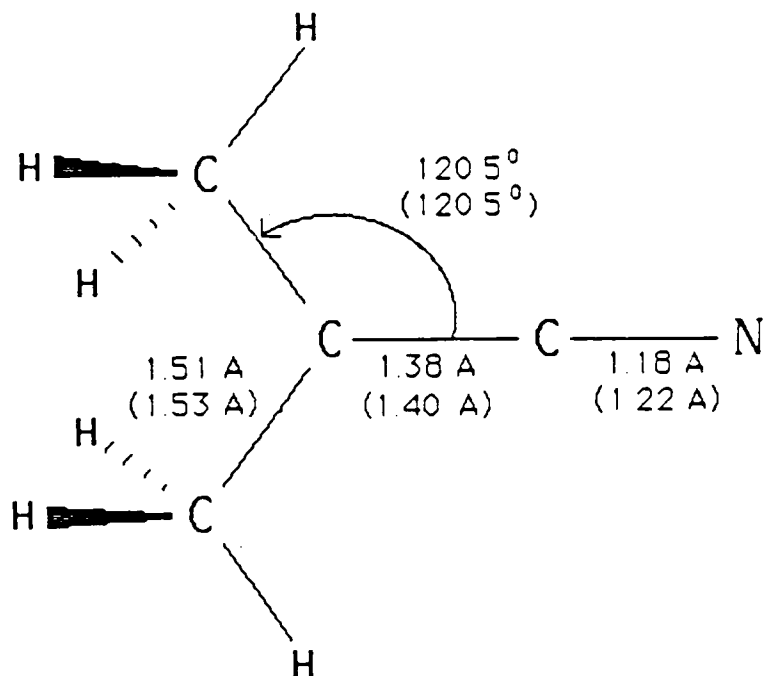


Figure 6.1 Theoretical Structural Parameters for the 2-cyanopropyl Radical using 4-31G(STO-3G) Basis Sets

Table 6.1

Final Theoretical Structural Parameters Calculated
With Gaussian 80

Basis Set	STO-3G	4-31G
$r_{\text{C-N}}$	1.21 Å	1.18 Å
$r_{\text{C-C}}$	1.40 Å	1.38 Å
$r_{\text{C-CH}_3}$	1.53 Å	1.51 Å
$r_{\text{C-H}}$	(1.09 Å)*	(1.09 Å)
$\angle \text{CCN}$	180°	180°
$\angle (\text{Me})\text{CC}$	120.55	120.55
$\angle \text{CCH}$	(109.5°)	(109.5°)

*Quantities in the parenthesis were not allowed to vary

normalized spin-rotation constants similar in magnitude. The initial estimates for the spin-rotation constants of the 2-cyano-2-propyl radical were taken to be the average value of the observed normalized spin-rotation constants for several molecules possessing C_{2v} symmetry multiplied by the rotational constant of the radical as determined from the theoretical study. These parameters are listed in Table 6.2. The magnitude of the ϵ 's were systematically varied until the calculated splittings agreed with those observed in the spectrum.

Hyperfine interactions for the two different types of nuclei were considered separately. Solution ESR work has shown the Fermi contact parameters to be 59.0 and 9.5 Mhz for ^1H and ^{14}N nuclei, respectively.¹¹ It was found that the calculated hyperfine splitting was not sensitive to changes in these parameters, so their values were not varied in the hyperfine fit. Dipole-dipole coupling parameter T_{cc} can be estimated from the spin density on the nucleus of interest.¹² ESR studies estimate the spin density on the ^{14}N to be 0.3. Using the equation

$$T_{cc} \cong \left(\frac{4}{5}\right) g_s g_n \beta \beta_n \langle r^{-3} \rangle \quad [6.1]$$

an initial value of T_{cc} could be estimated. For a radical with the unpaired electron in an out of plane p orbital, the relative values of the diagonal components of the dipole-dipole tensor can be expressed as

$$(1/2)T_{cc} \cong -T_{aa} \cong -T_{bb} \quad [6.2]$$

Thus all diagonal components of the ^{14}N hyperfine tensor can be

Table 6.2

Normalized Spin Rotation Constants
For C_{2v} Symmetry Molecules

	$E_{aa}/A \times 10^2$	$E_{bb}/B \times 10^2$	$E_{cc}/C \times 10^2$	
NH_2	-1.3046	-0.3488	0.0049	[52]
PH_2	-3.0782	-1.0145	-0.0056	[53]
NF_2	-1.3501	-0.7822	0.0443	[54]
CH_2F	-0.57	-0.6003	0.0051	[55]
CH_2Cl	-1.1478	-1.4900	0.0785	[56]
NO_2	2.2536	0.0593	-0.7742	[57]

estimated from the spin density on the nitrogen nucleus.

The protons behave differently compared to the nitrogen nucleus. Their dipole-dipole coupling is mainly ascribed to the interaction of the protons with the unpaired electron localized on the atom to which the protons are attached. Most proton hyperfine coupling has been measured in molecules where the electron is predominantly localized on the atom to which the proton is attached (NH_2 , PH_2 , CH_2F , etc.). Hyperfine splitting calculations using the dipole-dipole coupling parameters for PH_2^{\bullet} (which would be expected to be larger than those in the 2-cyano-2-propyl radical) and the Fermi contact parameter from ESR studies of the 2-cyano-2-propyl radical resulted in a calculated splitting of less than 1 Mhz. This is too small to be resolved with the spectrometer system using the conditions present in this study.

The observed spectrum did not indicate otherwise. The broadening of observed transitions can be attributed to this unresolved hyperfine splitting. Dipole-dipole coupling constants for the protons could not be determined from this study.

Once initial values for all relevant parameters were obtained, a first fit was achieved by varying three bond lengths, r_{CN} , r_{CC} , $r_{\text{C-Me}}$ until calculated lines were brought into proximity of observed lines. Differences in calculated lines from fine and hyperfine splitting were compared to observed splittings in the spectrum. Fine and hyperfine coupling constants were varied until calculated splitting matched these observed. The assigned transitions are listed in Table 6.3. Initial and final fine and hyperfine coupling constants are listed in Table 6.4.

Table 6.3
 $(\text{CH}_3)_2\text{CCN}$ ASSIGNED TRANSITIONS

$N(K_1, K_{-1}) - N(K_1, K_{-1})$	J-J	$F_1 - F_1$	Obs Freq(Mhz)	C-0(Mhz)
3(1,3) - 2(1,2)	2.5-1.5	3.5-2.5	18118.0	-1.3
	3.5-2.5	2.5-1.5	18159.0*	-1.9
		3.5-2.5	18159.0*	-1.8
		4.5-3.5	17590.9	1.7
3(0,3) - 2(0,2)	2.5-1.5	1.5-0.5	19314.3	-0.6
		2.5-1.5	19306.9	1.9
	3.5-2.5	2.5-1.5	19242.0	-0.6
		3.5-2.5	19242.0	-0.6
3(2,2) - 2(2,1)	2.5-1.5	1.5-0.5	20086.2	-0.4
		2.5-1.5	20074.9	-0.1
		3.5-2.5	20009.6	-1.9
	3.5-2.5	2.5-1.5	20019.1*	-2.4
		3.5-2.5	20019.1*	-0.7
3(2,1) - 2(2,0)	2.5-1.5	1.5-0.5	20839.9	1.0
		2.5-1.5	20805.0	0.5
	2.5-2.5	2.5-1.5	20786.3*	1.7
		3.5-2.5	20786.3*	-0.1
3(1,2) - 2(1,1)	2.5-1.5	1.5-0.5	21659.8	-1.9
		3.5-2.5	21558.0	-1.8
	3.5-2.5	2.5-1.5	21612.2	1.5
		3.5-2.5	21616.6	-0.3
		4.5-3.5	21487.4	-1.6

*adjacent lines unresolved

Table 6.3

(cont.)

4(1,4) - 3(1,3)	3.5-2.5	2.5-1.5	24117.2	0.9
		3.5-2.5	24071.5	-1.8
		4.5-3.5	24019.7	1.9
	4.5-3.5	3.5-2.5	24031.1*	0.5
		4.5-3.5	24031.1*	-1.1
		5.5-4.5	23792.5	-1.9
4(0,4) - 3(0,3)	3.5-2.5	2.5-1.5	25031.0	0.6
		3.5-2.5	24994.4	1.6
		4.5-3.5	24913.3	1.9
	4.5-3.5	3.5-2.5	24961.0*	0.3
		4.5-3.5	24961.0*	-1.9

Table 6.4
Initial and Final Fine and
Hyperfine Coupling Constants
of $(\text{CH}_3)_2\text{CCN}$

<u>parameter</u>	<u>initial value(Mhz)</u>	<u>final value(Mhz)</u>
E_{aa}	-79.5	-69.9 \pm .1
E_{bb}	-26.5	-36.1 \pm .1
E_{cc}	0.9	2.7 \pm .1
$a_F(^{14}\text{N})$	9.5	9.5 ^a
$T_{aa}(^{14}\text{N})$	-19.0	-17.2 ^b \pm .1
$T_{bb}(^{14}\text{N})$	-19.0	-17.1 ^b \pm .1
$T_{cc}(^{14}\text{N})$	38.0	34.3 \pm .1
$a_F(^1\text{H})$	59.0	(-) ^c
$T_{aa}(^1\text{H})$	- 1.0	(-) ^c
$T_{bb}(^1\text{H})$	- 4.46	(-) ^c
$T_{cc}(^1\text{H})$	5.46	(-) ^c

a) Not varied in fit of data

b) T_{aa} and T_{bb} values can be reversed and identical splitting will result

c) Proton hyperfine splitting not resolved in this study

From the observed lines and calculated splittings, a back calculation was performed to obtain hypothetical unsplit rotational transitions. These are referred to as centerline frequencies and are listed in Table 6.5.

Using a program developed by Kirchoff⁶⁴ (see CDANAL in Appendix F), the centerline frequencies were fit in order to determine the experimental rotational constants. If a sufficient number of observed transitions are available, this program allows the observed transitions to be fit to a maximum of 13 spectral constants (3 rotation constants and 10 centrifugal constants). A rigid rotor fit (using only the three rotational constants to fit the transitions) was performed due to the relatively small number and the low J values (where centrifugal distortion will be minimal) of the rotational transitions assigned.

Rotational constants obtained from this spectral fit were used to determine an experimental structure. The initial (from the theoretical structure) and final rotational constants are listed in Table 6.6. A structure fitting program developed by Schwendeman⁶⁵ (see STRFTQ in Appendix F) was used to vary r_{CN} , r_{CC} and r_{C-Me} through a least squares reduction scheme to best fit the observed moments. These final structural parameters, with an assumed C-C-CH₃ angle of 120.55, are listed in Table 6.7.

The microwave spectrum of the fully deuterated species of the 2-cyano-2-propyl radical was experimentally obtained. This experiment was performed in order to better characterize the structure of the radical and to confirm the original assignment of the fully protonated species. The hyperfine splitting due to the six deuterium atoms will be

Table 6.5
Theoretical Unsplit Rotational Transitions
of $(\text{CH}_3)_2\text{CCN}$

<u>Transition</u>	<u>Frequency(Mhz)</u>
3(1,3)-2(1,2)	18189.9±2.0
3(0,3)-2(0,2)	19274.1±2.0
3(2,2)-2(2,1)	20044.5±2.0
3(2,1)-2(2,0)	20814.9±2.0
3(1,2)-2(1,1)	21642.9±2.0
4(1,4)-3(1,3)	24063.6±2.0
4(0,4)-3(0,3)	24992.7±2.0

Table 6.6

Initial and Final Rotational Constants
for $(\text{CH}_3)_2\text{CCN}$

	Initial	Experimental
A	8274.7Mhz	8276.7 \pm 3Mhz
B	3807.7Mhz	3919.7 \pm .8Mhz
C	2696.5Mhz	2751.5 \pm .4Mhz
K	-0.602	-0.577

Table 6.7
Structural Parameters of $(\text{CH}_3)_2\text{CCN}$
Prior to $(\text{CD}_3)_2\text{CCN}$ Study
($\angle\text{CCMe} = 120.55^\circ$ assumed)

Parameter	Value
r_{CN}	$1.19\text{\AA} \pm 0.01$
r_{CC}	$1.38\text{\AA} \pm 0.01$
r_{CMe}	$1.48\text{\AA} \pm 0.01$
r_{CH}	(1.09\AA)
$\angle\text{CCMe}$	120.55°
$\angle\text{CCH}$	109.5°

smaller than those due to the protons, thus its spectrum can be analyzed in the same manner as used for the protonated radical.

The structure from the proton species study was used as an initial structure for assigning this spectrum. In order for an assignment to be made, four structural (r_{CC} , r_{CN} , r_{CCH_3} , CCMe angle) parameters were varied until the calculated rotational transitions were brought into the vicinity of observed lines. Hyperfine and fine splittings were then added to these lines and compared with those observed in the spectrum.

It must be recognized, in order to fit the deuterated radical spectrum that the fine splittings observed for the protonated species will not be identical to those for the deuterated case. Fine splittings are proportional to the rotational constants. Deuterium substitution significantly changes all three moments of inertia in the 2-cyano-2-propyl radical. This means that the fine splitting parameters will change upon deuteration of the species. However, the normalized fine splitting parameters will not. An initial estimate of the fine splitting parameters for the deuterium species can be calculated from the normalized parameters taken from the proton species.

With these fine splitting parameters and the initial structure from the protonated species, the spectrum of $(CD_3)_2CCN$ was assigned in the same manner described for $(CH_3)_2CCN$. The assigned lines are listed in Table 6.8. Initial and final fine splitting parameters are found in Table 6.9. Hyperfine splitting parameters for the two species were identical, as expected. Using the assigned lines, the fine and the hyperfine splitting parameters for $(CD_3)_2CCN$, the centerlines (listed in

Table 6.8
 $(\text{CD}_3)_2\text{CCN}$ ASSIGNED TRANSITIONS

$N(K_1, K_{-1}) - N(K_1, K_{-1})$	J-J	$F_1 - F_1$	Obs Freq(Mhz)	C-0(Mhz)
3(1,2) - 2(1,1)	2.5-1.5	1.5-0.5	19077.5	1.9
		2.5-1.5	19068.3	0.1
	3.5-2.5	3.5-2.5	18977.6	0.0
		2.5-1.5	19141.2	-1.4
		3.5-2.5	19041.2	1.1
		2.5-1.5	20824.1	-2.0
4(1,4) - 3(1,3)	3.5-2.5	4.5-3.5	20726.0	1.6
		4.5-3.5	20504.1	-0.3
	4.5-3.5	21370.7	0.0	
4(0,4) - 3(0,3)	3.5-2.5	2.5-1.5	21370.7	0.0
		3.5-2.5	21341.2	-1.1
		4.5-3.5	21253.9	0.4
	4.5-3.5	3.5-2.5	21307.0	0.5
		5.5-4.5	21065.3	1.4
		2.5-1.5	23290.0	-2.2
4(2,3) - 3(2,2)	3.5-2.5	3.5-2.5	23232.4	0.4
		4.5-3.5	23134.5	-1.2
		4.5-3.5	23210.9	-0.2
	4.5-3.5	3.5-2.5	23210.9	-0.2
		4.5-3.5	23205.1	-1.1
		2.5-1.5	23891.2*	-1.4
4(3,2) - 3(3,1)	3.5-2.5	3.5-2.5	23891.2*	-1.4
		4.5-3.5	23891.2*	-2.0
	4.5-3.5	4.5-3.5	23884.0	1.8
		5.5-4.5	23750.0	1.9

*adjacent lines unresolved

Table 6.9
Final and Initial
Fine Splitting Parameters
for $(\text{CD}_3)_2\text{CCN}$

	<u>Initial</u> *(Mhz)	<u>Final</u> (Mhz)
E_{aa}	-52.7	-55.4 \pm .1
E_{bb}	-32.1	-32.6 \pm .1
E_{cc}	2.3	2.4 \pm .1

* initial values were obtained by taking the normalized spin-rotation constants of $(\text{CH}_3)_2\text{CCN}$ and multiplying them by the theoretical rotational constants of $(\text{CD}_3)_2\text{CCN}$.

Table 6.10

Theoretical Unsplit Rotational
Transitions of $(\text{CD}_3)_2\text{CCN}$

Transition	Frequency(Mhz)
3(1,2)-2(1,1)	19063.8±2.0
4(1,4)-3(1,3)	20769.6±2.0
4(0,4)-3(0,3)	21332.6±2.0
4(2,3)-3(2,2)	23233.2±2.0
4(3,2)-3(3,1)	23897.2±2.0

Table 6.10) were calculated and fit using CDANAL to determine the experimental rotational constants. These constants, along with those from the protonated species, are listed in Table 6.11.

With a total of six experimental moments from two isotopic species, it is theoretically possible to determine a maximum of six structural parameters using STRFTQ. If linear dependencies exist in a structure fit, then some structural parameters must be held constant at a reasonable value while others are fit to the moments. This is the case for the 2-cyano-2-propyl radical and r_{CH} and HCH angle which were held constant at 1.09Å and 109.467°, respectively. Since this occurred for the fitting of the radical, four structural parameters were determined giving a unique structure which reproduces the six experimental moments. It should be emphasized that this structure is a unique structure for these assumed parameters and only this combination of these four parameters fit the experimental moments. Table 6.11 compares experimental rotational constants with those calculated from the final structure. Good agreement of these constants confirms the original assignment of $(\text{CH}_3)_2\text{CCN}$. A summary of the final structure is given in Table 6.12 and Figure 6.2.

Nonplanar structures were considered and their fit to experimental data was attempted. No reasonable nonplanar structure could be fit to the experimental moments. The spin rotation splitting parameters indicate a planar structure (no off diagonal elements necessary in the fit of either species). For these reasons, it is believed that the molecule is planar.

Table 6.11

Comparison of Experimental Rotational
 Constants and Those Calculated From
 the Final Structure

		<u>Experimental</u> (Mhz)	<u>Calculated</u> (Mhz)	<u>Difference</u>
(CH ₃) ₂ CCN	A	8276.7±3.0	8273.8	2.9
	B	3919.7±0.8	3918.9	0.8
	C	2751.6±0.4	2751.9	0.3
(CD ₃) ₂ CCN	A	6241.3±2.7	6240.6	0.7
	B	3490.3±0.9	3490.4	0.1
	C	2372.5±0.5	2372.7	0.2

Table 6.12

Final Structural Parameters

r_{CN}	$1.22 \pm .01 \text{ \AA}$
r_{CC}	$1.40 \pm .01 \text{ \AA}$
r_{CCH_3}	$1.50 \pm .01 \text{ \AA}$
$\angle \text{CCCH}_3$	$119.3^\circ \pm .2$

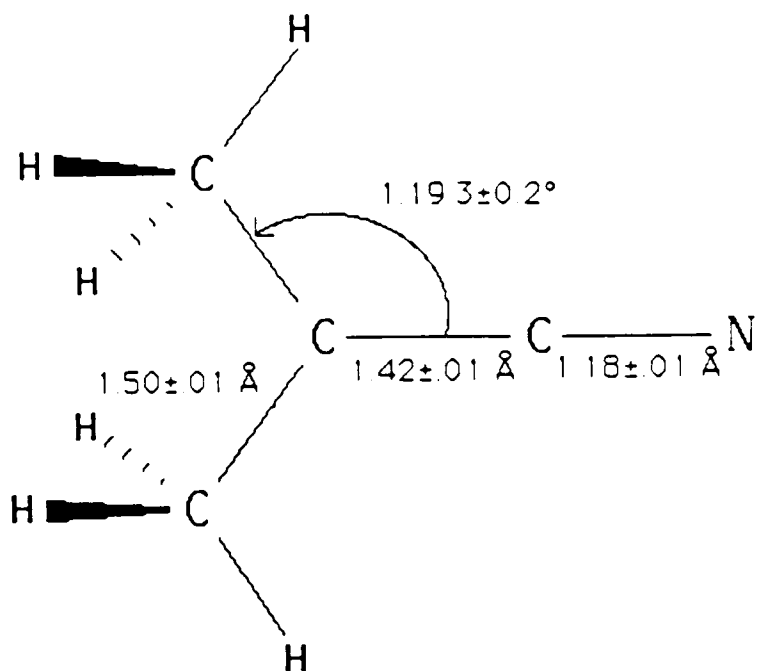


Figure 6.2 Final Structure Parameters Determined from the Experimental Moments of Inertia of Both Isotopic Species

Discussion

The H and D hyperfine splittings were too small to be resolved under the conditions used in this study. This is not surprising considering proton hyperfine splitting observed for similar molecules.^{55,66,67}

Hyperfine splittings due to protons have been observed in spectroscopic studies of CH_3O ⁶⁶ and CH_2F ⁵⁵ radicals. Both compounds exhibit large proton Fermi contact parameters (-55.55 and -60.7Mhz, respectively) explained by the lone electron hyperconjugating to the s orbital on the hydrogen. Proton dipole-dipole interactions are very small in the CH_3O radical, probably due to the lone electron being primarily localized on the oxygen nucleus. The proton dipole-dipole parameters of CH_2F were larger due to the spin density (greater than 0.8) on the C atom. The observed proton hyperfine splitting in CH_2F is less than 10Mhz. The observed splittings in CH_3O are so small that they were only resolved using a laser technique with high sensitivity and resolution (laser magnetic resonance).⁶⁸ The CH_3O radical also exhibits electron orbit-nuclear spin interactions which contribute to the observed splittings, making the splittings larger than if only Fermi contact and dipole-dipole interactions were present.

The spin density of the methyl carbons in the 2-cyano-2-propyl radical is estimated to be 0.17. This value was obtained using the atomic spin densities obtained from a 4-31G calculations. Considering this value relative to that of the CH_2F radical, it would be expected that the hyperfine splittings due to the methyl protons of the 2-cyano-2-propyl radical would be very small.

The nitrogen hyperfine coupling was well resolved. The Fermi contact parameter taken from EPR studies¹¹ indicates very little s character in the unpaired electron orbital on the nitrogen nucleus. The relations $T_{aa} + T_{bb} + T_{cc} = 0$ accurately describes the relative magnitudes of the coupling constants. This suggests that the lone electron occupies a P π orbital perpendicular to the molecular plane. The relative value of T_{aa} and T_{bb} could not be explicitly determined. Identical calculated splitting resulted when their values were exchanged.

The T_{cc} value indicates an approximate spin density on the nitrogen of .32, agreeing well with that value obtained from solid state EPR of 0.3.¹¹ This indicates that the unpaired electron spends a substantial amount of time on the nitrogen. This could lead to the occurrence of some double bond character between the two non-methyl carbons due to resonance with the carbon-nitrogen triple bond. This resonance would also result in a reduction of the bond order of the carbon-nitrogen bond.

The spin-rotation constants are responsible for the largest part of the splitting of rotational lines. Strict interpretation of three parameters includes assumptions concerning other electronic constants and contributions from excited states⁴³, however some information may be

obtained from them. A satisfactory fit of the spin-rotation splitting of the lines was achieved for both isotopic species by considering only diagonal elements of the spin-rotation tensor. Calculated splittings were very sensitive to the magnitude of the off-diagonal elements and no satisfactory fit could be obtained using any off-diagonal component of substantial magnitude. This suggests a planar structure for the carbon-nitrogen skeletal network.

The general trend $\epsilon_{aa} < \epsilon_{bb} < \epsilon_{cc}$ observed in other free radicals was found to hold. The magnitude of ϵ_{cc} indicates that the unpaired electron occupies the p orbital perpendicular to the plane of the molecule where no one electron excitation can induce a C component.⁴³

The predominant reason for performing this work was to determine the structure of the radical. Two isotopic species were studied and six moments of inertia were obtained. Four structural parameters which were highly correlated were determined. The lack of any single atom isotopic substitutions and the correlation of the structural parameters prevented the use of a Kraitchman analysis. Thus, only an $\langle r_0 \rangle$ structure was determined. The use of some assumed structural parameters was necessary to obtain a statistically relevant fit. These parameters were r_{CH} , CCH angle and HCH angle.

The experimentally determined length of the CN bond is longer than a typical CN triple bond but shorter than a CN double bond. Similarly, the observed CC bond length is shorter than an aliphatic CC single bond but longer than a normal double bond. These are shown in Table 6.13. These determined distances coupled with the estimated spin density on the nitrogen nucleus indicate significant resonance of the unpaired

Table 6.13
 Comparison Of r_{CN} and r_{CC} Of
 $(\text{CH}_3)_2\text{CCN}$ With Other Compounds

Parameter	Compound	Distance (Å)	
$\text{C}\equiv\text{N}$	CH_3CN	1.157	[58]*
	$\text{CH}_3\text{CH}_2=\text{C}-\text{C}\equiv\text{N}$	1.157	
	CN radical	1.177	
r_{CN}	$(\text{CH}_3)_2\text{CCN}$	1.22	This study
C=N	$(\text{CH}_3\text{SO}_2)_2\text{C}-\text{C}=\text{N}-\text{CH}_3$	1.34	
	$\text{HC}=\text{NNH}$	1.34	
	$(\text{CH}_3\cdot\text{C}=\text{NOH})_2$	1.27	
C-C	C_2H_6	1.536	
	$(\text{CH}_3)_2\text{CCH}_2$	1.53	
	CH_3CN	1.458	
r_{CC}	$(\text{CH}_3)_2\text{CCN}$	1.40	This study
C=C	C_2H_4	1.33	
	CH_2CCH_2	1.309	
	$\text{CH}_2\text{CHCHCH}_2$	1.34	

*all bond lengths other than r_{CN} and r_{CC} from this study were taken from this source.

electron with the CN triple bond. This type of structure was predicted by Kerr et al. from EPR data and Huckel calculations.¹¹

The planar carbon-nitrogen skeleton also agrees with the result of the theoretical calculations. This is also in agreement with the general trends observed for similar organic radicals that have been characterized with spectroscopic means. The methyl⁶⁹, monofluoromethyl⁶³, ethyl¹⁷, and isopropyl¹⁷ radicals have been shown to be planar. This is indicative of sp^2 hybridization on the center carbon atom.

A characteristic of sp^2 hybridization is the occurrence of bond angles of approximately 120° about the central carbon atom. The slight derivation from this value by the C-C-Me angle is attributed to the steric interaction between the methyl groups. It is not expected that this angle will be less than 118° however, since the corresponding angle is bistrifluormethyl nitroxide radical was found to be 117.2° .³ Hence, the value for this angle agrees well with other experimental measurements.

Consideration of the inertial defect also provides information concerning the structure of the molecule. If a molecule is planar and rigid in its equilibrium configuration, the moments are related by

$$I_a + I_b - I_c = 0 \quad [6.3]$$

where c is the principal axis perpendicular to the molecular plane. For a nonrigid molecule vibrational effects will result in a modification of this relationship to

$$I_a + I_b - I_c = \Delta \quad [6.4]$$

where Δ is nonzero and is called the inertial defect. It is generally very small except in molecules with heavy atoms.

The plane of symmetry of the 2-cyano-2-propyl radical contains all atoms with the exception of two pairs of hydrogen atoms lying above and below the plane. For a nonplanar molecule of this type, the moments are related by⁷⁰

$$|I_a + I_b - I_c| = \sum_i 4m_i c_i^2 - \Delta \quad [6.5]$$

where the m_i are the masses of the out of plane atoms and the c_i 's are their perpendicular distances from the ab plane. The summation is over all pairs of atoms lying out of the ab plane.

The inertial defect for the radical should be small, thus the original assignment can be checked by comparing the difference, $I_a + I_b - I_c$ with the theoretical value of the summation in Equation 6.3. These values agree well with one another. The inertial defect can also be compared with that in a similar molecule, acetone, as shown in Table 6.14. These values, for both the deuterated and protonated species, agree very well.

Table 6.14

Comparison of Theoretical and Experimental
 Inertial Defects of the 2-Cyano-2-Propyl Radical
 with that of Acetone

	2-Cyano-2-Propyl Radical		Acetone ¹¹
	Calculated $\sum 4m_i c_i^2$ (amu·Å ²)	Experimental $I_a + I_b - I_c$ (amu·Å ²)	Experimental $I_a + I_b - I_c$ (amu·Å ²)
H	6.583	6.3	6.3
D	13.166	12.8	12.4

Conclusions

Two isotopic species of the 2-cyano-2-propyl radical were characterized using microwave spectroscopy. The assignment of their spectra resulted in the calculation of six principal moments of inertia. These moments were used to determine four structural parameters.

Analysis of the fine and hyperfine splittings provided the 3 spin-rotation coupling constants and the 4 hyperfine coupling constants of the nitrogen atom in the molecule. From these parameters, the nature of the unpaired electron and the spin density on the nitrogen nucleus could be estimated.

Proton and deuteron hyperfine coupling was not resolved due to experimental conditions used in this study. These splittings could probably be resolved using a flow technique with reduced sample pressures where line widths would be well below 1Mhz. This would allow the assignment of the hyperfine splitting of the protons and deuterons and determine the nature of the interaction of the lone electron with these six equivalent nuclei. This would also confirm the methods of Endo² and White³ in handling multinuclear-spin radicals as valid or invalid.

Appendix A

Useful Relations in Spherical Tensor Methods

This section utilizes concepts of irreducible tensor operators and coupling of angular moments discussed in Chapter III to obtain relations useful in deriving matrix elements in Chapter IV. The derivation of each relation listed below can be found in Edmonds^{2,6} and have been tabulated by Hirota.^{4,3}

- 1) Spherical tensor rotation of a vector r

$$r_0 = Z \quad [A.1.1]$$

$$r_{\pm} = \mp 2^{1/2}(x \pm iy) \quad [A.1.2]$$

- 2) Coupling of two tensor operators (T and U couple to give Q)

$$Q_m^l = (-1)^{l_1 - l_2 - m} (2l + 1)^{1/2} \sum_{m_1 m_2} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & m \end{pmatrix} T_{m_1}^{l_1} U_{m_2}^{l_2} \quad [A.2]$$

- 3) Scalar product of two tensors

$$\mathbf{T} \cdot \mathbf{U} = \sum_q (-1)^q T_q^k U_{-q}^k \quad [A.3]$$

- 4) The Wigner-Eckert Theorem

$$\langle r^j m' | T_q^k | r^j m \rangle = (-1)^{j' - m'} \begin{pmatrix} j' & k & j \\ -m' & q & m \end{pmatrix} \langle r^j || T^k || r^j \rangle \quad [A.4]$$

where $\langle r' j' || T^K || r j \rangle$ is the reduced matrix element

- 5) Computation of the reduced matrix elements:
Choose m, m' and q so as to give a trivial value for $\langle r', j, m' | T^K | r, j, m \rangle$ and divide it by

$$(-1)^{j-m'} \begin{pmatrix} j & k & j \\ -m' & q & m \end{pmatrix}$$

example:

$$\langle S || T^1(S) || s \rangle = [S(S+1)(2S+1)]^{1/2} \quad [A.5.1]$$

$$\langle J' K' || D_q^k(\theta\phi) || J K \rangle = [(2J'+1)(2J+1)]^{1/2} (-1)^{J-K'} \begin{pmatrix} J' & k & J \\ -K' & q & K \end{pmatrix} \quad [A.5.2]$$

- 6) Matrix Elements of coupled tensor operators.

- a) Noncommuting tensor operators operating on the same system

$$\begin{aligned} \langle r' j' || X^k || r j \rangle &= (2K+1)^{1/2} (-1)^{K+j+j'} \sum_{r'' j''} \begin{Bmatrix} k_1 & k_2 & J \\ j & j' & K \end{Bmatrix} \\ &\times \langle r' j' || T^{k_1} || r'' j'' \rangle \langle r'' j'' || T^{k_2} || r j \rangle \end{aligned} \quad [A.6.1]$$

- b) Tensor operators operating on different system:

$$\begin{aligned} \langle r' j' j_2 J' || X^k || r j j_2 J \rangle &= \sum_{r''} \langle r' j_1 || T^{k_1} || r'' j_1 \rangle \langle r'' j_2 || U^{k_2} || r j_2 \rangle \\ &\times [(2J'+1)(2J+1)(2K+1)]^{1/2} \begin{Bmatrix} j_1 & j_1 & k_1 \\ j_2 & j_2 & k_2 \\ J' & J & K \end{Bmatrix} \end{aligned} \quad [A.6.2]$$

c) Scalar product of two commuting tensor operators:

$$\begin{aligned} \langle r'j'j'_2J'M' | \mathbf{T}^k \cdot \mathbf{U}^k | rj_1j_2JM \rangle &= \delta_{JJ'} \delta_{MM'} (-1)^{j'_1+j'_2+J} \left\{ \begin{matrix} J & j'_2 & j'_1 \\ k & j_1 & j_2 \end{matrix} \right\} \\ &\times \sum_{r''} \langle r'j'_1 | | \mathbf{T}^k | | r''j_1 \rangle \langle r''j'_2 | | \mathbf{U}^k | | rj_2 \rangle \end{aligned} \quad [A.6.3]$$

d) Single operator in a coupled scheme (only operating on one part of system)

$$\begin{aligned} \langle r'j'j'_2J' | | \mathbf{T}^k | | rj_1j_2J \rangle &= \delta_{j'_2j_2} (-1)^{j'_1+j_2+J+k} [(2J'+1)(2J+1)]^{1/2} \left\{ \begin{matrix} j'_1 & J' & j_2 \\ J & j_1 & k \end{matrix} \right\} \\ &\times \langle r'j'_1 | | \mathbf{T}^k | | rj_1 \rangle \end{aligned} \quad [A.6.4]$$

Appendix B

Selected Wigner 3-j Symbols

$$\begin{pmatrix} J+1 & J & 1 \\ M & -M-1 & 1 \end{pmatrix} = (-1)^{J-M-1} \left[\frac{(J-M)(J-M+1)}{(2J+3)(2J+2)(2J+1)} \right]^{1/2}$$

$$\begin{pmatrix} J+1 & J & 1 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M-1} \left[\frac{(J+M+1)(J-M+1)2}{(2J+3)(2J+2)(2J+1)} \right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ M & -M-1 & 1 \end{pmatrix} = (-1)^{J-M} \left[\frac{(J-M)(J+M+1)2}{(2J+2)(2J+1)2J} \right]^{1/2}$$

$$\begin{pmatrix} J & J & 1 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M} \frac{M}{[(2J+1)(J+1)J]^{1/2}}$$

$$\begin{pmatrix} J+2 & J & 2 \\ M & -M-2 & 2 \end{pmatrix} = (-1)^{J-M} \left[\frac{(J-M-1)(J-M)(J-M+1)(J-M+2)}{(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)} \right]^{1/2}$$

$$\begin{pmatrix} J+2 & J & 2 \\ M & -M-1 & 1 \end{pmatrix} = 2(-1)^{J-M} \left[\frac{(J+M+2)(J-M+2)(J-M+1)(J-M)}{(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)} \right]^{1/2}$$

$$\begin{pmatrix} J+2 & J & 2 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M} \left[\frac{6(J+M+2)(J+M+1)(J-M+2)(J-M+1)}{(2J+5)(2J+4)(2J+3)(2J+2)(2J+1)} \right]^{1/2}$$

$$\begin{pmatrix} J+1 & J & 2 \\ M & -M-2 & 2 \end{pmatrix} = 2(-1)^{J-M+1} \left[\frac{(J-M-1)(J-M)(J-M+1)(J+M+2)}{(2J+4)(2J+3)(2J+2)(2J+1)2J} \right]^{1/2}$$

$$\begin{pmatrix} J+1 & J & 2 \\ M & -M & 1 \end{pmatrix} (-1)^{J-M+1} 2(J+2M+2) \left[\frac{(J-M+1)(J-M)}{(2J+4)(2J+3)(2J+2)(2J+1)2J} \right]^{1/2}$$

$$\begin{pmatrix} J+1 & J & 2 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M+1} 2M \left[\frac{6(J+M+1)(J-M+1)}{(2J+4)(2J+3)(2J+2)(2J+1)2J} \right]^{1/2}$$

$$\begin{pmatrix} J & J & 2 \\ M & -M-2 & 2 \end{pmatrix} = (-1)^{J-M} \left[\frac{6(J-M-1)(J-M)(J+M+1)(J+M+2)}{(2J+3)(2J+2)(2J+1)2J(2J-1)} \right]^{1/2}$$

$$\begin{pmatrix} J & J & 2 \\ M & -M-1 & 1 \end{pmatrix} = (-1)^{J-M} (1+2M) \left[\frac{6(J+M+1)(J-M)}{(2J+3)(2J+2)(2J+1)2J(2J-1)} \right]^{1/2}$$

$$\begin{pmatrix} J & J & 2 \\ M & -M & 0 \end{pmatrix} = (-1)^{J-M} \frac{2[3M^2 - J(J+1)]}{[(2J+3)(2J+2)(2J+1)2J(2J-1)]^{1/2}}$$

Appendix C
Selected Wigner 6-j Symbols

$$s = a + b + c$$

$$\left\{ \begin{matrix} a & b & c \\ 1 & c-1 & b-1 \end{matrix} \right\} = (-1)^s \left[\frac{s(s+1)(s-2a-1)(s-2a)}{(2b-1)2b(2b+1)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 1 & c-1 & b \end{matrix} \right\} = (-1)^s \left[\frac{2(s+1)(s-2a)(s-2b)(s-2c+1)}{2b(2b+1)(2b+2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 1 & c-1 & b+1 \end{matrix} \right\} = (-1)^s \left[\frac{(s-2b-1)(s-2b)(s-2c+1)(s-2c+2)}{(2b+1)(2b+2)(2b+3)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 1 & c & b \end{matrix} \right\} = (-1)^{s+1/2} \frac{[b(b+1) + c(c+1) - a(a+1)]}{[2b(2b+1)(2b+2)2c(2c+1)(2c+2)]^{1/2}}$$

$$\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b-2 \end{matrix} \right\} = (-1)^s \left[\frac{(s-2)(s-1)s(s+1)(s-2a-3)(s-2a-2)(s-2a-1)(s-2a)}{(2b-3)(2b-2)(2b-1)2b(2b+1)(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b-1 \end{matrix} \right\} = (-1)^{s/2} \left[\frac{(s-1)s(s+1)(s-2a-2)(s-2a-1)(s-2a)(s-2b)(s-2c+1)}{(2b-2)(2b-1)2b(2b+1)(2b+2)(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} a & b & c \\ 2 & c-2 & b \end{matrix} \right\} = (-1)^s \left[\frac{6s(s+1)(s-2a-1)(s-2b-1)(s-2a)(s-2b)(s-2c+1)(s-2c+2)}{(2b-1)2b(2b+1)(2b+2)(2b+3)(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{array}{ccc} a & b & c \\ 2 & c-2 & b+1 \end{array} \right\} = (-1)^s 2 \left[\frac{(s+1)(s-2a)(s-2b-2)(s-2b-1)(s-2b)}{2b(2b+1)(2b+2)(2b+3)(2b+4)} \right]^{1/2} \\ \times \left[\frac{(s-2c+1)(s-2c+2)(s-2c+3)}{(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{array}{ccc} a & b & c \\ 2 & c-2 & b+2 \end{array} \right\} = (-1)^s \left[\frac{(s-2b-3)(s-2b-2)(s-2b-1)(s-2b)}{(2b+1)(2b+2)(2b+3)(2b+4)(2b+5)} \right]^{1/2} \\ \times \left[\frac{(s-2c+1)(s-2c+2)(s-2c+3)(s-2c+4)}{(2c-3)(2c-2)(2c-1)2c(2c+1)} \right]^{1/2}$$

$$\left\{ \begin{array}{ccc} a & b & c \\ 2c-1 & b-1 & \end{array} \right\} = (-1)^s \frac{4[(a+b)(a-b+1) - (c-1)(c-b+1)][s(s+1)(s-2a-1)(s-2a)]^{1/2}}{[(2b-2)(2b-1)2b(2b+1)(2b+2)(2c-2)(2c-1)2c(2c+1)(2c+2)]^{1/2}}$$

$$\left\{ \begin{array}{ccc} a & b & c \\ 2 & c-1 & b \end{array} \right\} = (-1)^s \frac{2[(a+b+1)(a-b) - c^2 + 1][6(s+1)(s-2a)(s-2b)(s-2c+1)]^{1/2}}{[(2b-1)2b(2b+1)(2b+2)(2b+3)(2c-2)(2c-1)2c(2c+1)(2c+2)]^{1/2}}$$

$$\left\{ \begin{array}{ccc} a & b & c \\ 2 & c-1 & b+1 \end{array} \right\} = (-1)^s 4[(a+b+2)(a-b-1) - (c-1)(b+c+2)] \\ \times \frac{[(s-2b-1)(s-2b)(s-2c+1)(s-2c+2)]^{1/2}}{[2b(2b+1)(2b+2)(2b+3)(2b+4)(2c-2)(2c-1)2c(2c+1)(2c+2)]^{1/2}}$$

$$X = b(b+1) + c(c+1) - a(a+1)$$

$$\left\{ \begin{array}{ccc} a & b & c \\ 2 & c & b \end{array} \right\} = (-1)^s \frac{2[3X(X-1) - 4b(b+1)c(c+1)]}{[(2b-1)2b(2b+1)(2b+2)(2b+3)(2c-1)2c(2c+1)(2c+2)(2c+3)]^{1/2}}$$

Appendix D
Selected Wigner 9-j Symbols

$$\Gamma(abc) = a(a+1) + b(b+1) - c(c+1)$$

$$\left\{ \begin{matrix} N & N & 2 \\ S & S & 1 \\ J & J & 1 \end{matrix} \right\} = \frac{\sqrt{3} [\Gamma(NSJ)\Gamma(NJS) + (2/3)N(N+1)\Gamma(SJN)]}{[40N(N+1)(2N-1)(2N+3)S(S+1)(2S+1)J(J+1)(2J+1)]^{1/2}}$$

$$\left\{ \begin{matrix} N & N & 2 \\ S & S & 1 \\ J-1 & J & 1 \end{matrix} \right\} = \left[\frac{(N-S+J)(N+S-J+1)(-N+S+J)(N+S+J+1)}{30N(N+1)(2N-1)(2N+1)(2N+3)S(S+1)(2S+1)J(2J-1)(2J+1)} \right]^{1/2}$$

$$(\Gamma(SNJ)(2N-1)(2N+3) + \frac{1}{2N+1} N^2(2N-1)(N+S+J+2)(N-S+J+1) - (N+1)^2(2N+3)(N+S-J)(-N+S+J+1)) \left[\frac{1}{4N(N+1)} \right]$$

$$\left\{ \begin{matrix} N-2 & N & 2 \\ S & S & 1 \\ J+1 & J & 1 \end{matrix} \right\} = - \left[\frac{(J+S+N+1)(-J+S+N)(J-S+N)(J+S-N+1)}{16(N-1)N(2N-3)(2N-1)(2N+1)S(S+1)(2S+1)} \right]^{1/2}$$

$$\left[\frac{(-J+S+N-2)(-J+S+N-1)(J+S-N+2)(J+S-N+3)}{(J+1)(2J+1)(2J+3)} \right]^{1/2}$$

$$\left\{ \begin{matrix} N-2 & N & 2 \\ S & S & 1 \\ J & J & 1 \end{matrix} \right\} = - \left[\frac{(J+S+N+1)(-J+S+N)(J-S+N)(J+S-N+1)}{16(N-1)N(2N-3)(2N-1)(2N+1)S(S+1)(2S+1)} \right]^{1/2}$$

$$\left[\frac{(J+S+N)(J-S+N-1)(-J+S+N-1)(J+S-N+2)}{J(2J-1)(2J+1)} \right]^{1/2}$$

$$\left\{ \begin{matrix} N-2 & N & 2 \\ S & S & 1 \\ J-1 & J & 1 \end{matrix} \right\} = - \left[\frac{(J+S+N+1)(-J+S+N)(J-S+N)(J+S-N+1)}{16(N-1)N(2N-3)(2N-1)(2N+1)S(S+1)(2S+1)} \right]^{1/2} \\ \left[\frac{(J+S+N-1)(J+S+N)(J-S+N-2)(J-S+N-1)}{J(2J-1)(2J+1)} \right]^{1/2}$$

Appendix E

Hyperfine Coupling of the Protons on Two Equivalent Methyl Groups

The hyperfine coupling of six equivalent $\frac{1}{2}$ spin nuclei has been determined for the two equivalent trifluoromethyl groups in bistrifluoromethyl nitroxide radical.³¹ The matrix elements developed for the hyperfine analysis of the six protons on the two methyl groups on the 2-cyano-2-propyl radical were taken primarily from this study. A brief description of the theory used in the previous study follows.

The trifluoromethyl radical was the first molecule with three equivalent nuclei of nonzero spin and Hund's b type coupling to have its rotational spectrum assigned.² In this spectrum, hyperfine splittings due to three equivalent fluorine nuclei were observed. Matrix elements were derived for their hyperfine analysis. A fit of the spectrum determined that the hyperfine splitting was not dependent on the elements off diagonal in K. In fact, an excellent fit was obtained when these off diagonal elements were set to zero.

It has been shown by Bowater et al.¹⁹ that having only matrix elements diagonal in K is the same as considering the behavior of all nuclear spins as being equivalent to a single nucleus with a spin equal to the sum of all the nuclei (i.e., $3(\frac{1}{2})=1(3/2)$).

Following this, White has shown that the number of states of the following two representations must be the same³

$$\sum_{j=|j_1-j_2|}^{j_1+j_2} (2j+1) = (2j_1+1)(2j_2+1) \quad [E.1]$$

where j_1 and j_2 commute. This has also been determined empirically by spectroscopists before the advent of quantum mechanics. This is called the addition rules of angular moments.

If different angular momenta operators (i.e., nuclear spins) refer to different particles or different properties of the same particle, they commute. A state vector such as $V(j_1 m_1 j_2 m_2)$ may be split into a sum of products of factors relating separate parts of the system.

$$V(j_1 m_1 j_2 m_2) = \sum_{\alpha_1 \alpha_2} V_1(\alpha_1 j_1 m_1) V_2(\alpha_2 j_2 m_2) \quad [E.2]$$

These state vectors are linear combinations of the basis elements of the product representation $D^{(j_1)} \times D^{(j_2)}$. The representation of dimension $(2j_1+1)(2j_2+1)$ is reducible. The representation is made up of a number of invariant irreducible subspaces each of which represents a particular value of j . With this, we can consider the nuclear spins of the two identical nuclei to be the sum of the individual spins. This concept was used to characterize proton hyperfine splitting in NH_2^{\cdot} , PH_2^{\cdot} and other radicals. This can be extended to consider groups with resultant spins equal to that of a single nuclei. This was done to assign the hyperfine splitting of fluorine nuclei in bistrifluoromethyl nitoxide

radical and also be used to characterize the proton hyperfine splitting in the 2-cyano-2-propyl radical.

Appendix F

Computer Programs

Moment of Inertia

The program which calculates the principal moments of inertia of a molecule was developed by R.A. Beaudet and N.R. Pauley at University of Southern California. Bond lengths, bond angles and atomic masses are read in as data. The bond lengths and angles are referenced to three arbitrary atoms; 1 is the origin, 2 is the positive x axis and 3 lies in the positive xy quadrant. With all atoms defined in terms of this initial coordinate system, the center of mass is calculated and then taken to be the new origin. This new center of mass coordinate system is then transformed to the principal axis coordinate system. The coordinate of each atom of the molecule in the final coordinate system are used to calculate the principal moments of inertia and rotational constants.

Asymmetric Rotor

This program is a modification of one developed by R.A. Beaudet at USC to calculate the frequencies of rotational transition for a molecule given its rotational constants and dipole selection rules. The transition frequencies are calculated by taking the energy differences between two appropriate levels. Relative intensities and line strengths may also be calculated given the components and magnitude of the dipole moment in the molecules. The data that is required by the program are: dipole selection rules, magnitude of the dipole moment, upper and lower frequency limits and limits on J quantum numbers (maximum $J=80$).

CDANAL (Semirigid Rotor Fit Program)

This program, developed by Kirchoff, performs an iterative least squares fit of the centrifugal distortion constants in the Watson formulation. With P^4 and P^6 (first and second order centrifugal distortion), there are ten independent centrifugal distortion terms using this formulation. Adding to this the three rotational constant, there are a maximum of thirteen parameters which can be fit to the spectrum.

For a rigid rotor fit, only the rotational constants are varied. This is often done in molecules where a small number of rotational transitions are assigned. This is valid if the assigned transitions are low in J where the centrifugal distortion is minimal.

The necessary input data consist of the approximate rotational constants, dipole moment, selection rules, experimental frequencies with the $J, K_{-1}, +K_1$ quantum numbers and the number and type of distortion constants to be included in the fit.

STRFTQ

This program was written by Schwendeman⁶⁵ at Michigan State University to adjust internal coordinates of a molecule to fit its experimentally determined moments of inertia by an iterative least squares procedure. Depending on the number of isotopically substituted species studies and the number of experimental moments obtained, values of some structural are assumed and not used in the fit. The program computes the final coordinates of each atom, in the molecule, the moments of inertia, planar second moments and rotational constants. The final coordinates of each atom are used to determine final bond lengths and angles.

The necessary input consists of a trial set of internal coordinates, atomic number of each atom, experimental rotational constants, structural parameters to be fit and necessary constraints of the fit (assumed bond lengths, bond angles, etc.)

Gaussian 80

Gaussian 80 is a further development of Gaussian 70 and Gaussian 76. It is a general purpose program for ab initio molecular orbital calculations. Basis sets involving s, p and d type gaussian functions can be used and Restricted Hartree-Fock, Unrestricted Hartree-Fock and Restricted Open Shell Hartree-Fock wavefunctions are available when using this program. The program calculates the one and two electron integrals and then determines the Hartree-Fock single determinant wave functions and the total energy. This is followed by Mulliken population analysis calculation of electric dipole moment and spin densities on each nucleus in the molecule. The program can be used for geometric optimization by calling a sub-program that computes the first derivative of Hartree-Fock energy with respect to the nuclear coordinates.

The input necessary for the program include specification of the quantum mechanical procedure to be used (Hartree-Fock, etc.), specification of the basis set (STO-3G, etc.), optimization method employed and relative positions of atoms in the molecule (using the same method as in moment of inertia program). The user must specify which bond lengths and angles are to be fixed and those that are varied. Sample input with the program used to call Gaussian 80 are given. An abbreviated listing of resulting output, reproduction of initial data and final data from the last iteration, are also listed.

Gaussian 80 Control Program
with Sample Data

```

READ GAUSS80 JCL      A1 IRSPEC 05/06/88 10:37:50
//A513XJDG JOB 20F93,GRAYBEAL,REGION=1500K,TIME=120
/*LONGKEY BUTANE
/*PRIORITY IDLE
/*JOBPARM LINES=30
//STEP1 EXEC PGM=G82
//STEPLIB DD DSN=A51003.G82A.EXE,DISP=SHR
//INT DD UNIT=3380,SPACE=(6233,(3000,3000),,,ROUND),
// DCB=(RECFM=FT,BLKSIZE=23472),
// DISP=(NEW,DELETE),VOL=SER=WORK02
//D2E DD UNIT=3380,SPACE=(6233,(3000,3000),,,ROUND),
// DCB=(RECFM=FT,BLKSIZE=23472),
// DISP=(NEW,DELETE),VOL=SER=WORK03
//RWF DD UNIT=3380,SPACE=(6233,(3000,3000),,,ROUND),
// DCB=(RECFM=FT,BLKSIZE=23472),
// DISP=(NEW,DELETE),VOL=SER=WORK03
//CHK DD UNIT=SYSDA,SPACE=(6233,(100,30)),
// DCB=(RECFM=F,BLKSIZE=1024),
// DISP=(NEW,DELETE),VOL=SER=WORK03
//FT06F001 DD SYSOUT=A
//FT07F001 DD SYSOUT=B
//SNAPDD DD DUMMY
//SYSDUMP DD SYSOUT=A
//FT05F001 DD *
# HF/4-31G OPT=FP

```

(CH3)2-C-CN RADICAL OPTIMIZATION WITH METHYL GROUP OPTIMIZATION

```

0 2
C
C 1 1.404172
C 1 1.520108 2 120.546
N 2 1.21682 1 180. 3 0.
C 1 1.520108 2 120.546 3 OOPA
H 5 1.09 1 109.5 2 0.
H 5 1.09 1 109.5 2 120.
H 5 1.09 1 109.5 2 240.
H 3 1.09 1 109.5 2 HANGLE
X 9 1.09 3 109.5 1 HANGLE
H 3 1.09 9 109.5 10 120.
H 3 1.09 9 109.5 10 240.
HANGLE=1.111
OOPA=189.84

```

Gaussian 80 Abbreviated Output

```
*****
GAUSSIAN 82  IBM-MVS-G82REVVH/C2  7 SEPTEMBER 1984
8-MAY-1988 17:28:28
*****
```

```
-----
# HF/4-31G OPT=FP
-----
```

```
1//1,2;
2//2;
3/5=1,11=9,25=11,30=1/1,2,3,11;
4//1;
5//1,2;
6//1;
1//2;
2//2;
3/5=1,11=9,25=11,30=1/1,2,11;
4/5=5/1;
5//1,2;
1//2(-4);
2//2;
3/5=1,11=9,25=11,30=1,39=1/1,3;
6//1;
99//99;
```

```
-----
(CH3)2-C-CN RADICAL OPTIMIZATION WITH METHYL GROUP OPTIMIZATION
-----
```

```
SYMBOLIC Z-MATRIX:
```

```
CHARGE = 0 MULTIPLICITY = 2
```

C							
C	1	1.40417					
C	1	1.52011	2	120.546			
N	2	1.21682	1	180.	3	0.	0
C	1	1.52011	2	120.546	3	OOPA	0
H	5	1.09	1	109.5	2	0.	0
H	5	1.09	1	109.5	2	120.	0
H	5	1.09	1	109.5	2	240.	0
H	3	1.09	1	109.5	2	HANGLE	0
X	9	1.09	3	109.5	1	HANGLE	0
H	3	1.09	9	109.5	10	120.	0
H	3	1.09	9	109.5	10	240.	0

```
VARIABLES
```

```
OOPA 189.84
HANGLE 1.111
```

```
FLETCHER-POWELL TOTAL OPTIMIZATION PROGRAM. INITIALIZED AT 17:29:11 ON 5/08/88
-----
```

Z-MATRIX (ANGSTROMS AND DEGREES)										
CD	CENT	ATOM	N1	LENGTH	N2	ALPHA	N3	BETA	J	
1	1	C								
2	2	C	1	1.404172 (1)						
3	3	C	1	1.520108 (2)	2	120.546 (12)				
4	4	N	2	1.216820 (3)	1	180.000 (13)	3	0.0 (22)	0	
5	5	C	1	1.520108 (4)	2	120.546 (14)	3	189.840 (23)	0	
6	6	H	5	1.090000 (5)	1	109.500 (15)	2	0.0 (24)	0	
7	7	H	5	1.090000 (6)	1	109.500 (16)	2	120.000 (25)	0	
8	8	H	5	1.090000 (7)	1	109.500 (17)	2	240.000 (26)	0	
9	9	H	3	1.090000 (8)	1	109.500 (18)	2	1.111 (27)	0	
10		X	9	1.090000 (9)	3	109.500 (19)	1	1.111 (28)	0	
11	10	H	3	1.090000 (10)	9	109.500 (20)	10	120.000 (29)	0	
12	11	H	3	1.090000 (11)	9	109.500 (21)	10	240.000 (30)	0	

Z-MATRIX ORIENTATION:

CENTER NUMBER	ATOMIC NUMBER	COORDINATES (ANGSTROMS)		
		X	Y	Z
1	6	0.0	0.0	0.0
2	6	0.0	0.0	1.404172
3	6	1.309150	0.0	-0.772564
4	7	0.000000	0.0	2.620992
5	6	-1.289890	0.223730	-0.772564
6	1	-2.113149	0.366524	-0.072597
7	1	-1.189310	1.109394	-1.399927
8	1	-1.493447	-0.644072	-1.399927
9	1	2.144602	-0.019922	-0.072763
10	-1	1.763558	-0.053140	0.947924
11	1	1.357919	0.909311	-1.371627
12	1	1.362545	-0.869443	-1.427788

DISTANCE MATRIX (ANGSTROMS):

	1	2	3	4	5
1 C	0.0				
2 C	1.404172	0.0			
3 C	1.520108	2.540089	0.0		
4 N	2.620992	1.216820	3.637320	0.0	
5 C	1.520108	2.540089	2.608652	3.637320	0.0
6 H	2.145929	2.603956	3.512324	3.443132	1.090000
7 H	2.145929	3.241633	2.804753	4.337396	1.090000
8 H	2.145929	3.241633	2.943291	4.337396	1.090000
9 H	2.145929	2.604045	1.090000	3.443259	3.513521
10 X	2.002878	1.822395	1.780279	2.431484	3.515720
11 H	2.133576	3.221156	1.090000	4.314139	2.799962
12 H	2.156626	3.260745	1.090000	4.359481	2.942747
	6	7	8	9	10
6 H	0.0				

7	H	1.779646	0.0				
8	H	1.779646	1.779646	0.0			
9	H	4.275253	3.761873	3.922541	0.0		
10	X	4.030687	3.947572	4.058287	1.090000	0.0	
11	H	3.745719	2.555232	3.247166	1.780279	2.543849	
12	H	3.929963	3.229324	2.865006	1.780279	2.543849	
		11	12				
11	H	0.0					
12	H	1.779646	0.0				

INTERATOMIC ANGLES:

C2-C1-C3=120.546	C1-C2-N4=180.	C2-C1-C5=120.546
C3-C1-C5=118.1963	C1-C5-H6=109.5	C1-C5-H7=109.5
H6-C5-H7=109.4424	C1-C5-H8=109.5	H6-C5-H8=109.4424
H7-C5-H8=109.4424	C1-C3-H9=109.5	C3-H9-X10=109.5
C1-C3-H11=108.5333	H9-C3-H11=109.5	C1-C3-H12=110.3465
H9-C3-H12=109.5	H11-C3-H12=109.4424	

FINAL ITERATION

FLETCHER-POWELL OPTIMIZATION TERMINATED.
FORCES BELOW THRESHOLD AFTER 2 STEPS.

FINAL POOL OF VARIABLES:

NAME	VALUE	INCREMENT
----	-----	-----
OOPA	180.07314	1.00000
HANGLE	0.00475	1.00000

FINAL OPTIMIZED VALUE = -0.2090751355912D+03

Z-MATRIX (ANGSTROMS AND DEGREES)

CD	CENT	ATOM	N1	LENGTH	N2	ALPHA	N3	BETA	J
-----	-----	-----	-----	-----	-----	-----	-----	-----	-----
1	1	C							
2	2	C	1	1.404172 (1)					
3	3	C	1	1.520108 (2)	2	120.546 (12)			
4	4	N	2	1.216820 (3)	1	180.000 (13)	3	0.0 (22)	0
5	5	C	1	1.520108 (4)	2	120.546 (14)	3	180.073 (23)	0
6	6	H	5	1.090000 (5)	1	109.500 (15)	2	0.0 (24)	0
7	7	H	5	1.090000 (6)	1	109.500 (16)	2	120.000 (25)	0
8	8	H	5	1.090000 (7)	1	109.500 (17)	2	240.000 (26)	0
9	9	H	3	1.090000 (8)	1	109.500 (18)	2	0.005 (27)	0
10		X	9	1.090000 (9)	3	109.500 (19)	1	0.005 (28)	0
11	10	H	3	1.090000 (10)	9	109.500 (20)	10	120.000 (29)	0
12	11	H	3	1.090000 (11)	9	109.500 (21)	10	240.000 (30)	0

Z-MATRIX ORIENTATION:

CENTER NUMBER	ATOMIC NUMBER	COORDINATES (ANGSTROMS)		
		X	Y	Z
1	6	0.0	0.0	0.0
2	6	0.0	0.0	1.404172
3	6	1.309150	0.0	-0.772564
4	7	0.000000	0.0	2.620992
5	6	-1.309148	0.001671	-0.772564
6	1	-2.144698	0.002738	-0.072597
7	1	-1.360270	0.891560	-1.399927
8	1	-1.362541	-0.888085	-1.399927
9	1	2.144700	-0.000085	-0.072597
10	-1	1.763794	-0.000227	0.948682
11	1	1.360137	0.889908	-1.399911
12	1	1.360156	-0.889738	-1.400151

DISTANCE MATRIX (ANGSTROMS):

	1	2	3	4	5
1 C	0.0				
2 C	1.404172	0.0			
3 C	1.520108	2.540089	0.0		
4 N	2.620992	1.216820	3.637320	0.0	
5 C	1.520108	2.540089	2.618299	3.637320	0.0
6 H	2.145929	2.603956	3.524064	3.443132	1.090000
7 H	2.145929	3.241633	2.883446	4.337396	1.090000
8 H	2.145929	3.241633	2.884478	4.337396	1.090000
9 H	2.145929	2.603956	1.090000	3.443132	3.524064
10 X	2.002740	1.821659	1.780279	2.430553	3.522168
11 H	2.145148	3.241109	1.090000	4.337000	2.882293
12 H	2.145246	3.241278	1.090000	4.337194	2.883342
	6	7	8	9	10
6 H	0.0				
7 H	1.779646	0.0			
8 H	1.779646	1.779646	0.0		
9 H	4.289400	3.852486	3.853712	0.0	
10 X	4.039719	4.008868	4.009767	1.090000	0.0
11 H	3.851325	2.720407	3.251805	1.780279	2.543849
12 H	3.852651	3.251729	2.722698	1.780279	2.543849
	11	12			
11 H	0.0				
12 H	1.779646	0.0			

INTERATOMIC ANGLES:

C2-C1-C3=120.546	C1-C2-N4=180.	C2-C1-C5=120.546
C3-C1-C5=118.908	C1-C5-H6=109.5	C1-C5-H7=109.5
H6-C5-H7=109.4424	C1-C5-H8=109.5	H6-C5-H8=109.4424
H7-C5-H8=109.4424	C1-C3-H9=109.5	C3-H9-X10=109.5
C1-C3-H11=109.4385	H9-C3-H11=109.5	C1-C3-H12=109.4463

H9-C3-H12=109.5 H11-C3-H12=109.4424
 SYMMETRY TURNED OFF BY EXTERNAL REQUEST.
 STOICHIOMETRY C4H6N(2)
 FRAMEWORK GROUP C1[X(C4H6N)]
 DEG. OF FREEDOM 27
 FULL POINT GROUP C1 NOP 1
 ROTATIONAL CONSTANTS (GHZ): 8.2766091 3.8073717 2.6965881
 ISOTOPES: C-12,C-12,C-12,N-14,C-12,H-1,H-1,H-1,H-1,H-1,H-1
 STANDARD BASIS: 4-31G (S, S=P, 6D, 7F)
 57 BASIS FUNCTIONS 124 PRIMITIVE GAUSSIANS
 19 ALPHA ELECTRONS 18 BETA ELECTRONS
 NUCLEAR REPULSION ENERGY 147.5309522840 HARTREES
 RAFFENETTI 2 INTEGRAL FORMAT.
 TWO-ELECTRON INTEGRAL SYMMETRY IS TURNED OFF.

ALPHA MOLECULAR ORBITAL COEFFICIENTS

		1	2	3	4	5
EIGENVALUES --		-15.58805	-11.27978	-11.24966	-11.22572	-11.22562
1	1 C 1S	-0.00017	-0.99330	-0.01235	-0.00018	0.00349
2	2S (I)	-0.00104	-0.05939	-0.00433	-0.00007	0.00143
3	2PX (I)	-0.00000	0.00000	0.00000	-0.00099	-0.00005
4	2PY (I)	-0.00000	-0.00001	0.00000	0.00001	-0.00001
5	2PZ (I)	0.00059	-0.00092	-0.00129	0.00001	-0.00029
6	2S (O)	0.02984	0.05036	0.03179	0.00025	-0.00504
7	2PX (O)	-0.00000	-0.00001	-0.00000	0.01148	0.00058
8	2PY (O)	-0.00000	-0.00000	-0.00002	-0.00004	0.00004
9	2PZ (O)	0.01777	0.00596	0.02483	-0.00050	0.00972
10	2 C 1S	0.00057	-0.01176	0.99344	0.00015	-0.00286
11	2S (I)	0.00062	0.00227	0.05502	-0.00008	0.00158

. . .CONTINUING. . .

BETA MOLECULAR ORBITAL COEFFICIENTS.

		1	2	3	4	5
EIGENVALUES --		-15.55170	-11.27642	-11.25384	-11.22982	-11.22972
1	1 C 1S	-0.00017	-0.01407	-0.99386	-0.00032	0.00922
2	2S (I)	-0.00100	0.00295	-0.05731	-0.00006	0.00178
3	2PX (I)	-0.00000	-0.00000	0.00000	-0.00099	-0.00003
4	2PY (I)	-0.00000	-0.00000	-0.00001	0.00001	-0.00001
5	2PZ (I)	0.00061	0.00147	-0.00088	0.00001	-0.00029
6	2S (O)	0.02930	-0.03101	0.05367	0.00019	-0.00561
7	2PX (O)	-0.00000	0.00000	-0.00001	0.01163	0.00040
8	2PY (O)	-0.00000	0.00002	-0.00000	-0.00004	0.00004
9	2PZ (O)	0.01742	-0.02509	0.00755	-0.00034	0.00970
10	2 C 1S	0.00057	-0.99285	0.01465	0.00005	-0.00154
11	2S (I)	0.00092	-0.05763	0.00375	-0.00006	0.00163
12	2PX (I)	0.00000	-0.00000	0.00000	-0.00026	-0.00001

. . .CONTINUING. . .

ALPHA DENSITY MATRIX.

		1	2	3	4	5
1	1 C 1S	1.02805				

2		2S (I)	-0.00995	0.11912				
3		2PX (I)	-0.00001	0.00001	0.19538			
4		2PY (I)	-0.00016	0.00022	0.00053	0.31279		
5		2PZ (I)	0.00480	-0.00249	-0.00001	-0.00022	0.18471	
6		2S (O)	-0.15415	0.16846	0.00005	0.00131	-0.04603	
7		2PX (O)	-0.00000	0.00001	0.13511	0.00085	-0.00002	
8		2PY (O)	-0.00018	0.00028	0.00067	0.29355	-0.00031	
9		2PZ (O)	0.00107	-0.01081	-0.00002	-0.00061	0.08842	
10	2	C 1S	0.00958	-0.02236	0.00000	0.00005	-0.04776	
11		2S (I)	-0.02037	0.03184	-0.00000	-0.00010	0.07836	

. . .CONTINUING. . .

BETA DENSITY MATRIX.

				1	2	3	4	5
1	1	C 1S		1.02170				
2		2S (I)		-0.00189	0.10613			
3		2PX (I)		-0.00000	-0.00000	0.16302		
4		2PY (I)		0.00007	-0.00015	-0.00050	0.01866	
5		2PZ (I)		0.00684	-0.00886	-0.00000	0.00020	0.14043
6		2S (O)		-0.10232	0.08150	0.00004	-0.00011	-0.04434
7		2PX (O)		-0.00000	0.00001	0.09758	-0.00043	-0.00001
8		2PY (O)		0.00002	-0.00004	-0.00033	0.00823	0.00010
9		2PZ (O)		0.00888	-0.02842	-0.00001	0.00007	0.05426
10	2	C 1S		0.00918	-0.02245	0.00000	-0.00003	-0.04239
11		2S (I)		-0.01940	0.03149	-0.00000	0.00006	0.07085

. . .CONTINUING. . .

FULL MULLIKEN POPULATION ANALYSIS.

				1	2	3	4	5
1	1	C 1S		2.04975				
2		2S (I)		-0.00225	0.22525			
3		2PX (I)		0.0	0.0	0.35841		
4		2PY (I)		0.0	0.0	0.0	0.33146	
5		2PZ (I)		0.0	0.0	0.0	0.0	0.32514
6		2S (O)		-0.04735	0.20283	0.0	0.0	0.0
7		2PX (O)		0.0	0.0	0.13231	0.0	0.0
8		2PY (O)		0.0	0.0	0.0	0.17159	0.0
9		2PZ (O)		0.0	0.0	0.0	0.0	0.08113
10	2	C 1S		0.00000	-0.00047	0.0	0.0	-0.00225
11		2S (I)		-0.00042	0.00952	0.0	0.0	0.03302

. . .CONTINUING. . .

GROSS ORBITAL POPULATIONS:

				TOTAL	ALPHA	BETA	SPIN
1	1	C 1S		1.99628	0.99839	0.99790	0.00049
2		2S (I)		0.57277	0.30090	0.27187	0.02902
3		2PX (I)		0.66092	0.35199	0.30894	0.04305
4		2PY (I)		0.52829	0.48273	0.04556	0.43717
5		2PZ (I)		0.62667	0.34304	0.28364	0.05940
6		2S (O)		0.58486	0.40142	0.18344	0.21798

7		2PX (O)	0.30033	0.17444	0.12590	0.04854
8		2PY (O)	0.43656	0.40029	0.03626	0.36403
9		2PZ (O)	0.19207	0.12376	0.06831	0.05544
10	2	C 1S	1.99623	0.99786	0.99837	-0.00052
11		2S (I)	0.63900	0.29309	0.34591	-0.05282
12		2PX (I)	0.49779	0.13211	0.36568	-0.23357
13		2PY (I)	0.53829	0.13909	0.39920	-0.26011
14		2PZ (I)	0.79986	0.37116	0.42870	-0.05754
15		2S (O)	0.41345	0.12316	0.29028	-0.16712
16		2PX (O)	0.43635	0.12139	0.31496	-0.19357
17		2PY (O)	0.47269	0.12082	0.35187	-0.23105
18		2PZ (O)	0.08864	-0.02434	0.11299	-0.13733
19	3	C 1S	1.99661	0.99823	0.99838	-0.00016
20		2S (I)	0.54603	0.26725	0.27878	-0.01153
21		2PX (I)	0.61793	0.29265	0.32528	-0.03263
22		2PY (I)	0.64800	0.31711	0.33089	-0.01379
23		2PZ (I)	0.64246	0.30981	0.33265	-0.02284
24		2S (O)	0.82461	0.39843	0.42617	-0.02774
25		2PX (O)	0.32187	0.14435	0.17752	-0.03317
26		2PY (O)	0.45223	0.21347	0.23875	-0.02528
27		2PZ (O)	0.41508	0.19592	0.21915	-0.02323
28	4	N 1S	1.99770	0.99898	0.99872	0.00026
29		2S (I)	0.76814	0.39962	0.36852	0.03110
30		2PX (I)	0.60502	0.43332	0.17170	0.26161
31		2PY (I)	0.59490	0.49031	0.10459	0.38572
32		2PZ (I)	0.85556	0.45143	0.40414	0.04729
33		2S (O)	1.16286	0.64302	0.51985	0.12317
34		2PX (O)	0.48307	0.32799	0.15508	0.17290
35		2PY (O)	0.44419	0.35402	0.09017	0.26384
36		2PZ (O)	0.46486	0.22696	0.23790	-0.01094
37	5	C 1S	1.99661	0.99823	0.99838	-0.00016
38		2S (I)	0.54603	0.26725	0.27879	-0.01154
39		2PX (I)	0.61794	0.29265	0.32528	-0.03263
40		2PY (I)	0.64801	0.31710	0.33091	-0.01381
41		2PZ (I)	0.64246	0.30981	0.33265	-0.02284
42		2S (O)	0.82451	0.39837	0.42614	-0.02777
43		2PX (O)	0.32190	0.14437	0.17753	-0.03317
44		2PY (O)	0.45231	0.21351	0.23880	-0.02529
45		2PZ (O)	0.41510	0.19593	0.21917	-0.02324
46	6	H 1S (I)	0.53259	0.26856	0.26403	0.00453
47		1S (O)	0.27991	0.14317	0.13673	0.00644
48	7	H 1S (I)	0.53178	0.27666	0.25512	0.02154
49		1S (O)	0.29040	0.15480	0.13560	0.01920
50	8	H 1S (I)	0.53174	0.27660	0.25513	0.02147
51		1S (O)	0.29009	0.15456	0.13553	0.01904
52	9	H 1S (I)	0.53258	0.26856	0.26402	0.00454
53		1S (O)	0.27990	0.14317	0.13673	0.00643
54	10	H 1S (I)	0.53184	0.27695	0.25489	0.02206
55		1S (O)	0.29014	0.15473	0.13541	0.01932
56	11	H 1S (I)	0.53167	0.27630	0.25537	0.02094

57		1S (O)	0.29029	0.15458	0.13571	0.01887	
CONDENSED TO ATOMS (ALL ELECTRONS)							
		1	2	3	4	5	6
1	C	5.323396	0.338401	0.283818	-0.045385	0.283942	-0.042721
2	C	0.338401	5.004613	-0.048275	0.634607	-0.048250	-0.002251
3	C	0.283818	-0.048275	5.105907	0.000130	-0.046292	0.002670
4	N	-0.045385	0.634607	0.000130	6.786501	0.000132	0.000147
5	C	0.283942	-0.048250	-0.046292	0.000132	5.105879	0.392474
6	H	-0.042721	-0.002251	0.002670	0.000147	0.392474	0.509255
7	H	-0.050082	0.001425	-0.000717	0.000009	0.387922	-0.023468
8	H	-0.049780	0.001430	-0.000840	0.000009	0.387954	-0.023443
9	H	-0.042721	-0.002250	0.392482	0.000147	0.002670	-0.000094
10	H	-0.051844	0.001341	0.388158	0.000008	-0.000782	-0.000040
11	H	-0.048269	0.001511	0.387781	0.000009	-0.000774	-0.000028
		7	8	9	10	11	
1	C	-0.050082	-0.049780	-0.042721	-0.051844	-0.048269	
2	C	0.001425	0.001430	-0.002250	0.001341	0.001511	
3	C	-0.000717	-0.000840	0.392482	0.388158	0.387781	
4	N	0.000009	0.000009	0.000147	0.000008	0.000009	
5	C	0.387922	0.387954	0.002670	-0.000782	-0.000774	
6	H	-0.023468	-0.023443	-0.000094	-0.000040	-0.000028	
7	H	0.535350	-0.029973	-0.000034	0.002151	-0.000403	
8	H	-0.029973	0.534813	-0.000034	-0.000392	0.002081	
9	H	-0.000034	-0.000034	0.509089	-0.023397	-0.023377	
10	H	0.002151	-0.000392	-0.023397	0.536759	-0.029978	
11	H	-0.000403	0.002081	-0.023377	-0.029978	0.533411	
TOTAL ATOMIC CHARGES.							
		1					
1	C	5.898755					
2	C	5.882302					
3	C	6.464822					
4	N	7.376314					
5	C	6.464875					
6	H	0.812501					
7	H	0.822178					
8	H	0.821826					
9	H	0.812480					
10	H	0.821984					
11	H	0.821963					
ATOMIC SPIN DENSITIES.							
		1	2	3	4	5	6
1	C	1.430874	0.051047	-0.066848	-0.011931	-0.066694	-0.003555
2	C	0.051047	-1.248938	0.005335	-0.148609	0.005328	0.001139
3	C	-0.066848	0.005335	-0.170396	-0.000120	0.005015	-0.000094
4	N	-0.011931	-0.148609	-0.000120	1.435493	-0.000120	0.000049
5	C	-0.066694	0.005328	0.005015	-0.000120	-0.170561	0.007282
6	H	-0.003555	0.001139	-0.000094	0.000049	0.007282	0.009434
7	H	-0.018635	-0.000015	0.000440	0.000037	0.014285	-0.001657
8	H	-0.018429	-0.000017	0.000344	0.000037	0.014321	-0.001626

9	H	-0.003554	0.001136	0.007281	0.000049	-0.000094	-0.000002
10	H	-0.019799	-0.000003	0.015077	0.000040	0.000421	-0.000002
11	H	-0.017361	-0.000028	0.013595	0.000034	0.000363	-0.000000
		7	8	9	10	11	
1	C	-0.018635	-0.018429	-0.003554	-0.019799	-0.017361	
2	C	-0.000015	-0.000017	0.001136	-0.000003	-0.000028	
3	C	0.000440	0.000344	0.007281	0.015077	0.013595	
4	N	0.000037	0.000037	0.000049	0.000040	0.000034	
5	C	0.014285	0.014321	-0.000094	0.000421	0.000363	
6	H	-0.001657	-0.001626	-0.000002	-0.000002	-0.000000	
7	H	0.055369	-0.010358	-0.000004	0.001911	-0.000626	
8	H	-0.010358	0.055021	0.000002	-0.000623	0.001835	
9	H	-0.000004	0.000002	0.009431	-0.001797	-0.001482	
10	H	0.001911	-0.000623	-0.001797	0.056508	-0.010355	
11	H	-0.000626	0.001835	-0.001482	-0.010355	0.053831	

DIPOLE MOMENT (DEBYE): X= 0.0018 Y=-0.0145 Z=-4.0337 TOTAL= 4.0337
 FERMI CONTACT ANALYSIS (ATOMIC UNITS).

1	
1	C 0.280471
2	C -0.272268
3	C -0.067675
4	N 0.239584
5	C -0.067751
6	H 0.003663
7	H 0.018617
8	H 0.018555
9	H 0.003667
10	H 0.019129
11	H 0.018046

1|0|IBM-VT-MVS1|FOPT|UHF|4-31G|C4H6N1(2)|GRAYBEAL|8-MAY-1988|1|/# HF/4-31G OPT=FP|(CH3)2-C-CN RADICAL OPTIMIZATION WITH METHYL GROUP OPTIMIZATION||0,2|C|C,1,1.404172|C,1,1.520108,2,120.546|N,2,1.21682,1,180.,3,0.,0|C,1,1.520108,2,120.546,3,OOPA,0|H,5,1.09,1,109.5,2,0.,0|H,5,1.09,1,109.5,2,120.,0|H,5,1.09,1,109.5,2,240.,0|H,3,1.09,1,109.5,2,HANGLE,0|X,9,1.09,3,109.5,1,HANGLE,0|H,3,1.09,9,109.5,10,120.,0|H,3,1.09,9,109.5,10,240.,0||OOPA=180.073138|HANGLE=0.00475||VERSION=IBM-MVS-G82REVH/C2|HF=-209.0751356|S2=1.126|S2-1=0.|S2A=0.852|RMSD=0.117D-09|RMSF=0.381D-05|DIP=4.03374|PG=C01|@

EVERYBODY NEEDS BEAUTY AS WELL AS BREAD, PLACES TO PLAY IN AND PRAY IN,
 WHERE NATURE MAY HEAL AND CHEER AND GIVE STRENGTH TO BODY AND SOUL ALIKE.

-- JOHN MUIR

TOTAL JOB TIME: 0 DAYS 1 HOURS 48 MINUTES 48.55 SECONDS
 8-MAY-1988 22:19:42
 GAUSSIAN 82 DONE

HYPERFINE

This computer program was written to calculate splittings from spin-rotation, Fermi contact and dipole-dipole interactions. Rather than tediously deriving every possible nonzero diagonal and off diagonal matrix element expression, matrix elements were calculated numerically using the expressions for each interaction defined in Chapter 3 and a hierarchy of subroutines and user-defined functions. Thus, the programming logic is easier to follow and the program itself is less susceptible to programmer error.

Data input for the program includes maximum and minimum N values (molecular rotation quantum number), spin-rotation constants and hyperfine coupling constants for both the ^{14}N and ^1H nuclei. The FINE, taken from a similar program written by Richard White³, subroutine calculates the spin rotation matrix elements. This entire matrix is then diagonalized by the Jacobi method using the HDIAG subroutine. XORDER orders the diagonal elements of the matrix in ascending order. XORDER and HDIAG were taken from the asymmetric rotor computer program written by R.A. Beaudet. Resulting eigenvalues are assigned to specific quantum numbers N, K and J by a subroutine called JASSIN.

The hyperfine matrix elements are calculated by a subroutine (HYPER) which calls four other subroutines. The four are FERMI, DIPOLE, FERMIH and DIPOLH and they calculate each contribution corresponding to the Fermi and dipole-dipole interaction of the ^{14}N nucleus and ^1H nuclei, respectively. All four terms are added together for each matrix element. The matrix is diagonalized in the same manner as the spin-rotation matrix. A subroutine called FASSIN assigns the diagonalized

elements to a specific set of quantum numbers, N , K , J , F_1 and F .

ELEVEL combines the values of the fine and the hyperfine energy matrices for each I_N , I_H and F with the same J , N and K . Subroutine FREQP takes the appropriate differences between the energy levels to calculate the splittings. A later version of this program incorporated rigid rotor rotational frequencies to predict the microwave spectrum.

The program increments the spin of the nitrogen (0 and 1) and protons (0,3) to consider the coupling of all possible spin states. The first iteration calculates only the spin-rotation interaction as a results of both spins being zero. Hyperfine splitting due to the ^{14}N nucleus can be evaluated when $I_H=0$ and $I_N=1$. Proton hyperfine coupling is calculated for spins of 0,1,2 and 3. The assumptions and reasoning behind this were detailed earlier. The program listing, a sample data and a sample output are given.

The first data read in after the header are the minimum and maximum rotational angular momenta quantum numbers (2 and 4 in the printed data file). In the program, these have the variable names NMIN and NMAX. The second line of numbers are the spin-rotation constants and are named EAA, EBB, ECC, EAB, EBA, respectively. These correspond to the subscripted E_{XX} values given in the thesis text.

The third and fourth lines of numbers are the ^{14}N and proton hyperfine coupling constants. The last number in each line is the Fermi contact parameter for each nucleus and the preceding four are the dipole-dipole coupling parameters. These are given in the following order from left to right: T_{aa} , T_{bb} , T_{cc} , T_{ab} where T refers to the nitrogen dipole-dipole tensor and H to the proton dipole-dipole tensor.

These numbers are given variable names from the above description.

The remaining numbers are the $N(K_1, K_{-1}) - N'(K'_1, K'_{-1})$ of a transition of interest with the calculated rigid rotor frequency. This was used in later adaptation of the program in order to reproduce the spectrum of the 2-cyano-2-propyl radical. This part may be skipped by deleting several lines in the FREQP subroutine.

Hyperfine Computer Program Listing

```

IMPLICIT REAL (A-H,O-Z)
REAL J1,J,N,GS,GB,BETA,BETAN
INTEGER ARANK,FM,F1M,JM,UFM,UF1M,UJM,UK,UKO,UKP,UN,POWR,IH,IN
INTEGER DNPKE
CHARACTER*4 IDENT(20)
C THIS PORTION OF THE PROGRAM IS THE MAIN PROGRAM WHICH CONTROLS
C EXECUTION OF THE SUBROUTINES AND READS IN ALL DATA
DIMENSION EJ(1:4,2:4,0:4,0:4),EF(0:10,0:5,1:4,2:4,0:4,0:4)
C THE DATA IS NOW READ IN. THE FIRST CARD IS AN IDENTIFICATION CARD
C WHICH MAY HAVE ANY INFORMATION THE USER WISHES TO USE TO LABEL THE
C OUTPUT. FORMAT IS 18A4. THE SECOND CARD CONTAINS THE MINIMUM AND
C MAXIMUM VALUES OVER WHICH N, THE ROTATIONAL QUANTUM NUMBER, VARIES
C FORMAT IS 2I5. THE THIRD CARD CONTAINS THE SPIN ROTATION COUPLING
C CONSTANTS IN MHZ. THE FORMAT IS 2F10.2. THE FINAL CARD CONTAINS
C THE HYPERFINE INTERACTION CONSTANTS IN MHZ. THE FORMAT IS 4F10.2.
C PROGRAM WAS ALTERED TO INCLUDE ALL N14 COUPLING AS OF 7-14-87
C THREE CARDS WERE ADDED TO INCLUDE THE APPROPRIATE CONSTANTS
READ (7,10) (IDENT(I),I=1,18)
10 FORMAT (18A4)
WRITE (6,10) (IDENT(I),I=1,18)
c read in the maximum and minimum values of the molecular rotational
c quantum numbered desired for the calculation.
READ (7,20) NMIN,NMAX
WRITE (6,20) NMIN,NMAX
20 FORMAT (2I5)
25 FORMAT (5F10.2)
c read in the spin-rotation parameters
READ (7,25) EAA,EBB,ECC,EAB,EBA
WRITE (6,25) EAA,EBB,ECC,EAB,EBA
30 FORMAT (5F10.2)
c read in the hyperfine splitting parameters for the nitrogen nucleus
c in the order of aa, bb, cc, ab, and Fermi Contact Parameter
READ (7,30) TA,TB,TC,TAB,AF
WRITE (6,30) TA,TB,TC,TAB,AF
c read in the hyperfine splitting parameters for the protons in the
c same order as those for the nitrogen nucleus
READ (7,30) HA,HB,HC,HAB,HAF
WRITE (6,30) HA,HB,HC,HAB,HAF
C THE FINE STRUCTURE ENERGY LEVELS ARE CALCULATED FIRST. THE LOOP
C OVER J IS BEGUN AT JMIN AND GOES TO JMAX.
C ONLY ALTERATION IN FINE ENERGY ROUTINE IS TO INCLUDE MATRIX
C ELEMENTS OFF DIAGONAL IN K BY 1, THOSE IN 2 WERE PREVIOUSLY
C INCLUDED.
DO 50 J=ABS(NMIN-0.5),NMAX+0.5
ARANK=2*(2*J+1)
NM=ABS(J-0.5)
NP=J+0.5

```

```

S=0.5
CALL FINE (ARANK, J, EAA, EBB, ECC, EAB, EBA, NM, NP, EJ, NMIN, NMAX)
50 CONTINUE
C THE HYPERFINE ENERGY LEVELS ARE NOW CALCULATED. THE LOOP IS OVER
C ALL VALUES OF I SINCE THE TRANSITION SPLITTINGS ARE CALCULATED IN
C THIS LOOP. THE LOOP OVER F IS BEGUN AT FMIN AND GOES TO FMAX.
C THE TOTAL ANG. MOM. IS NOW 'F', WHICH IS F1+IN, WHERE F1=J+IH

DO 90 IN=0,1
DO 80 IH=0,3
IF (NMIN .LT. 5) THEN
  FMIN=.5
ELSE
  FMIN=(NMIN-4.5)
ENDIF
DO 70 F=.5,(NMAX+IH+IN+.5)
ARANK=0
J1=F+I+1
NM=NMIN
FM=F-0.5
DO 60 J=ABS(F-I),F+I
ARANK=2*(2*J+1)+ORDER
IF ((J+0.5) .LE. NMIN) GOTO 60
IF (J .LE. J1) THEN
  J1=J
  NM=J+0.5
END IF
IF ((J-0.5) .LT. NMAX) THEN
  NP=J-0.5
ELSE
  NP=NMAX
END IF
60 CONTINUE
  NM1=NM-1
  CALL HYPER(F, IN, IH, ARANK, TA, TB, TC, TAB, AF, HA, HB, HC, HAB, HF, NMIN,
  1NMAX, EF)
  CALL ELEVEL (F, IN, IH, NMIN, NMAX, EF, EJ)
70 CONTINUE
  CALL FREQP(NMIN, NMAX, IN, IH, EF, EJ)
80 CONTINUE
90 CONTINUE
END
SUBROUTINE FINE (ARANK, J, EAA, EBB, ECC, EAB, EBA, NM, NP, E, NMIN, NMAX)
IMPLICIT REAL (A-H, O-Z)
REAL J
C THIS SUBROUTINE CALCULATES THE MATRIX ELEMENTS FOR THE SPIN
C ROTATION INTERACTION. THE RANK OF THE MATRIX IS 2*(NM+NP+1) WHERE
C NM=J-.5 AND NP=J+.5. THE MATRIX ELEMENTS ARE STORED IN THE ARRAY
C NAMED A. THE DIAGONALIZED MATRIX ELEMENTS WHICH ARE THE ENERGY

```

```

C   LEVELS ARE ASSIGNED TO ENERGY LEVELS USING J,N,KP,KO AS THE
C   INDICES AND ARE STORED IN THE ARRAY LABELED EJ.
      INTEGER DK,ARANK
      DIMENSION Q(1000,1000),E(1:4,2:4,0:4,0:4)
C   WRITE (6,5) NM,NP,NMIN,NMAX
      5 FORMAT (41H SUBROUTINE FINE WAS CALLED N NP NMIN NMAX, 415.1)
      DO 10 L=1,2*(NM+NP+1)
      DO 10 M=1,2*(NM+NP+1)
      Q(L,M)=0.0
10  CONTINUE
      L=0
      DO 150 NPRIME =NM,NP
      DO 150 KPRIME=-NPRIME,NPRIME
      M=0
      L=L+1
      DO 150 N=NM,NP
      NPN=NPRIME-N
      IF (NPN) 20,20,140
20  DO 135 K=-N,N
      KM=KPRIME-K
      M=M+1
C   WRITE (6,23) J,NPRIME,KPRIME,N,K,L,M
      23 FORMAT (6H FINE ,5F5.1,2I5)
      IF (M.LT.L) GOTO 135
      IF (N) 30,120,30
30  DK=ABS(KPRIME-K)
      IF (DK .GT. 2) GOTO 120
      IF (DK .EQ. 1) GOTO 112
C   SINCE THE MATRIX IS HERMITIAN ONLY THOSE MATRIX ELEMENTS TO THE
C   RIGHT OF THE MAIN DIAGONAL ARE CALCULATED. THE NEXT LINE
C   DETERMINES IF THE CHANGE IN N IS POSITIVE (NOT CALCULATED), ZERO
C   OR NEGATIVE AND DIRECTS THE PROGRAM TO THE APPROPRIATE STATEMENT
C   STATEMENT.
      IF (NPN) 40,80,150
C   THE CHANGE IN K IS NOW DETERMINED AND THE APPROPRIATE MATRIX
C   ELEMENT IS CALCULATED.
C   PROGRAM WAS ALTERED FROM ORIGINAL FORM TO CALCULATE THE ELEMENTS
C   OFF DIAGONAL IN K BY 1 ( FOR CS SYMMETRY MOLECULES) FINE SUBROUTIN
40  IF (ABS(KM).EQ.1) GOTO 45
      IF (KM) 50,60,70
C   LINES 45-47 ARE FOR MOLECULES OF CS SYMMETRY, WHERE K IS OFFDIAG BY 1
45  IF (KM) 47,60,48
47  B=(N+K)*(N+K-1)
      Q(L,M)=- (N-2*K+1)*(SQRT(B))*(EAB+EBA)/(8*N)
C   WRITE (6,125) Q(L,M),EAB,EBA,J,N,NPRIME,K,KPRIME
      GOTO 130
48  B=(N-K)*(N-K-1)
      Q(L,M)=- (N+2*K+1)*(SQRT(B))*(EAB+EBA)/(8*N)
C   WRITE (6,125) Q(L,M),EAB,EBA,J,N,NPRIME,K,KPRIME
      GOTO 130

```

```

50 B=(N+K)*(N+K-1)*(N+K-2)*(N-K+1)
   Q(L,M)=(EBB-ECC)*SQRT(B)/(8*N)
   GOTO 130
60 B=N*N-K*K
   Q(L,M)=(EBB+ECC)/2.0-EAA)*K*SQRT(B)/(2*N)
   GOTO 130
70 B=(N-K)*(N-K-1)*(N-K-2)*(N+K+1)
   Q(L,M)=(ECC-EBB)*SQRT(B)/(8*N)
   GOTO 130
80 IF (ABS(KM).EQ.1) GOTO 85
   IF (KM) 90,100,110
85 IF (KM) 87,100,88
87 B=(N*(N+1)-K*(K-1))
   Q(L,M)=(N*(N+1)+.75-J*(J+1))*(2*K-1)*(SQRT(B
1))* (EAB+EBA)/(8*N*(N+1))
   GOTO 130
88 B=(N*(N+1)-K*(K+1))
   Q(L,M)=(N*(N+1)+.75-J*(J+1))*(2*K+1)*(SQRT(B
1))* (EAB+EBA)/(8*N*(N+1))
   GOTO 130
90 B=(N*(N+1)-K*(K-1))*(N*(N+1)-(K-1)*(K-2))
   Q(L,M)=(ECC-EBB)*(N*(N+1)+0.75-J*(J+1))*SQRT(B)/(8*N*(N+1))
   GOTO 130
100 Q(L,M)=(EAA*K*K+(EBB+ECC)*(N*(N+1)-K*K)/2.0)*(J*(J+1)-N*(N+1
1-0.75)/(2.0*N*(N+1))
   GOTO 130
110 B=(N*(N+1)-K*(K+1))*(N*(N+1)-(K+1)*(K+2))
   Q(L,M)=(ECC-EBB)*(N*(N+1)+0.75-J*(J+1))*SQRT(B)/(8*N*(N+1))
   GOTO 130
120 Q(L,M)=0.0
125 FORMAT (15H FINE ELEMENT =,3F10.2,1F5.1,4I5)
C 130 WRITE (6,125) Q(L,M),J,N,NPRIME,K,KPRIME
130 Q(M,L)=Q(L,M)
   GOTO 150
135 CONTINUE
140 M=2*N+1
150 CONTINUE
   CALL HDIAG (Q,L,1,L)
   CALL XORDER(Q,L,L)
   CALL JASSIN(NM,NP,Q,L,E)
   RETURN
   END
SUBROUTINE HDIAG(H,N,IEGEN,NX)
C THIS SUBROUTINE WAS TAKEN FROM THE ASYMMETRIC ROTOR PROGRAM
C WRITTEN BY ROBERT A. BEAUDET. MIHDI3, FORTRAN II DIAGONALIZATION
C OF A REAL SYMMETRIC MATRIX BY THE JACOBI METHOD. MAY 19, 1959
C CALLING SEQUENCE FOR DIAGONALIZATION. CALL HDIAG(H,N,IEGEN,U,NR)
C WHERE H IS THE ARRAY TO BE DIAGONALIZED. N IS THE ORDER OF THE
C MATRIX, H. U IS THE UNITARY MATRIX USED FOR FORMATION OF THE
C EIGENVECTORS. NR IS THE NUMBER OF ROTATIONS. IEGEN MUST BE SET

```

```

C      UNEQUAL TO ZERO IF ONLY EIGENVALUES ARE TO BE COMPUTED.  IEGEN
C      MUST BE SET EQUAL TO ZERO IF EIGENVALUES AND EIGENVECTORS ARE TO
C      BE COMPUTED.  SUBROUTINE PLACES COMPUTER IN FLOATING TRAP MODE.
C      THE SUBROUTINE OPERATES ONLY ON THE ELEMENTS OF H THAT ARE TO THE
C      RIGHT OF THE MAIN DIAGONAL.  THUS, ONLY A TRIANGULAR SECTION NEED
C      BE STORED IN THE ARRAY H.
      IMPLICIT REAL (A-H,O-Z)
      DIMENSION H(1000,1000),X(1000),IQ(1000)
      CALL XUFLOW
C      WRITE(6,5)
      5 FORMAT (26H SUBROUTINE HDIAG IS CALLED)
      IF (IEGEN) 15,10,15
10     DO 14 I=1,N
        DO 14 J=1,N
          IF (I-J) 12,11,12
11     CONTINUE
        GOTO 14
12     CONTINUE
14     CONTINUE
15     NR=0
        IF (N-1) 1000,1000,17
C      SCAN FOR LARGEST OFF DIAGONAL ELEMENT IN EACH ROW.  X(I) CONTAINS
C      LARGEST ELEMENT IN ITH ROW.  IQ(I) HOLDS SECOND SUBSCRIPT DEFINING
C      POSITION OF ELEMENT.
17     NMI1=N-1
        DO 30 I=1,NMI1
          X(I)=0.0
          IPL1=I+1
          DO 30 J=IPL1,N
            IF (X(I)-ABS(H(I,J))) 20,20,30
20     X(I)=ABS(H(I,J))
          IQ(I)=J
30     CONTINUE
C      SET INDICATOR FOR SHUTOFF.  RAP=2**-27, NR=NO. OF ROTATIONS
      RAP=0.745058059D-08
      HDTEST=1.0D38
C      FIND MAXIMUM OF X(I)S FOR PIVOT ELEMENT AND TEST FOR END OF
C      PROBLEM.
40     DO 70 I=1,NMI1
        IF (I-1) 60,60,45
45     IF (XMAX-X(I)) 60,70,70
60     XMAX=X(I)
        IPIV=I
        JPIV=IQ(I)
70     CONTINUE
C      IF MAX. X(I) EQUAL TO ZERO, IF LESS THAN HDTEST, REVISE HDTEST
      IF (XMAX) 1000,1000,80
80     IF (HDTEST) 90,90,85
85     IF (XMAX-HDTEST) 90,90,148
90     HDIMIN=ABS(H(1,1))

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```

DO 110 I=2,N
  IF (HDIMIN-ABS(H(I,I))) 110,110,100
100 HDIMIN=ABS(H(I,I))
110 CONTINUE
  HDTEST=HDIMIN*RAP
C   RETURN IF MAX. H(I,J) LESS THAN (2**-27)*ABS(H(K,K)-MIN)
  IF (HDTEST-XMAX) 148,1000,1000
148 NR=NR+1
C   COMPUTE TANGENT SINE AND COSINE, H(I,I), H(J,J)
  DENOM=(ABS(H(IPIV,IPIV)-H(JPIV,JPIV))+SQRT((H(IPIV,IPIV)-H(JPIV
1,JPIV))**2+4.0*H(IPIV,JPIV)**2))
  IF (DENOM .EQ. 0.0) GOTO 150
149 TANG=SIGN(2.,(H(IPIV,IPIV)-H(JPIV,JPIV)))*H(IPIV,JPIV)/(ABS
1(H(IPIV,IPIV)-H(JPIV,JPIV))+SQRT((H(IPIV,IPIV)-H(JPIV,JPIV))
2**2+4.0*H(IPIV,JPIV)**2))
  GOTO 151
150 TANG=0.0
151 COSINE=1.0/SQRT(1.0+TANG**2)
C   WRITE (6,151) COSINE
  SINE=TANG*COSINE
C   WRITE (6,151) SINE
  HII=H(IPIV,IPIV)
  H(IPIV,IPIV)=COSINE**2*(HII+TANG*(2.0*H(IPIV,JPIV)+TANG*H(JPIV,J
1PIV)))
  H(JPIV,JPIV)=COSINE**2*(H(JPIV,JPIV)-TANG*(2.0*H(IPIV,JPIV)-TANG
1*HII))
  H(IPIV,JPIV)=0.0
C   PSEUDO RANK THE EIGENVALUES.  ADJUST SINE AND COS FOR COMPUTATION
C   OF H(IK) AND U(IK).
  IF (H(IPIV,IPIV)-H(JPIV,JPIV)) 152,153,153
152 HTEMP=H(IPIV,IPIV)
  H(IPIV,IPIV)=H(JPIV,JPIV)
  H(JPIV,JPIV)=HTEMP
C   RECOMPUTE SINE AND COS
  HTEMP=SIGN(1.0,-SINE)*COSINE
  COSINE=ABS(SINE)
  SINE=HTEMP
153 CONTINUE
C   INSPECT THE IQS BETWEEN I+1 AND N-1 TO DETERMINE WHETHER A NEW
C   MAXIMUM VALUE SHOULD BE COMPUTED SINCE THE PRESENT MAXIMUM IS
C   IN THE I OR J ROW.
  DO 350 I=1,NMI1
  IF (I-IPIV) 210,350,200
200 IF (I-JPIV) 210,350,210
210 IF (IQ(I)-IPIV)230,240,230
230 IF (IQ(I)-JPIV)350,240,350
240 K=IQ(I)
250 HTEMP=H(I,K)
  H(I,K)=0.0
  IPL1=I+1

```

```

X(I)=0.0
C SEARCH IN DEPLETED ROW FOR NEW MAXIMUM
DO 320 J=IPL1,N
IF (X(I)-ABS(H(I,J)))300,300,320
300 X(I)=ABS(H(I,J))
IQ(I)=J
320 CONTINUE
H(I,K)=HTEMP
350 CONTINUE
X(IPIV)=0.0
X(JPIV)=0.0
C CHANGE THE OTHER ELEMENTS OF H.
DO 530 I=1,N
IF (I-IPIV)370,530,420
370 HTEMP=H(I,IPIV)
H(I,IPIV)=COSINE*HTEMP+SINE*H(I,JPIV)
IF (X(I)-ABS(H(I,IPIV)))380,390,390
380 X(I)=ABS(H(I,IPIV))
IQ(I)=IPIV
390 H(I,JPIV)=-SINE*HTEMP+COSINE*H(I,JPIV)
IF (X(I)-ABS(H(I,JPIV)))400,530,530
400 X(I)=ABS(H(I,JPIV))
IQ(I)=JPIV
GOTO 530
420 IF (I-JPIV)430,530,480
430 HTEMP=H(IPIV,I)
H(IPIV,I)=COSINE*HTEMP+SINE*H(I,JPIV)
IF (X(IPIV)-ABS(H(IPIV,I)))440,450,450
440 X(IPIV)=ABS(H(IPIV,I))
IQ(IPIV)=I
450 H(I,JPIV)=-SINE*HTEMP+COSINE*H(I,JPIV)
IF (X(I)-ABS(H(I,JPIV)))400,530,530
480 HTEMP=H(IPIV,I)
H(IPIV,I)=COSINE*HTEMP+SINE*H(JPIV,I)
IF (X(IPIV)-ABS(H(IPIV,I)))490,500,500
490 X(IPIV)=ABS(H(IPIV,I))
IQ(IPIV)=I
500 H(JPIV,I)=-SINE*HTEMP+COSINE*H(JPIV,I)
IF (X(JPIV)-ABS(H(JPIV,I))) 510,530,530
510 X(JPIV)=ABS(H(JPIV,I))
IQ(JPIV)=I
530 CONTINUE
C TEST FOR COMPUTATION OF EIGENVECTORS.
IF (IEGEN) 40,540,40
540 DO 550 I=1,N
550 CONTINUE
GOTO 40
1000 RETURN
END

```



```

SUBROUTINE XORDER(ARRAY,LIMIT,NX)
C THIS SUBROUTINE IN ADDITION TO HDIAG WERE TAKEN FROM THE
C ASYMMETRIC ROTOR PROGRAM WRITTEN BY ROBERT A. BEAUDET.
  IMPLICIT REAL (A-H,O-Z)
C ROBERT A. BEUDET AI06 ENERGY DIAGONALIZATION
C THIS SUBROUTINE ARRANGES THE EIGENVALUES AND EIGENVECTORS
C IN INCREASING ORDER. HDIAG IS NOT DEPENDABLE IN DOING THIS.
  DIMENSION ARRAY(1000,1000)
C WRITE (6,5)
  5 FORMAT (27HSUBROUTINE XORDER IS CALLED)
  30 IF (LIMIT-1) 220,220,40
  40 DO 210 KTEST=2,LIMIT
  50 DO 200 JTEST=2,KTEST
    ITEST=KTEST+2-JTEST
    ITESTM=ITEST-1
    IF (ARRAY(ITEST,ITEST)-ARRAY(ITESTM,ITESTM)) 60,210,210
  60 XCHAN=ARRAY(ITEST,ITEST)
    ARRAY(ITEST,ITEST)=ARRAY(ITESTM,ITESTM)
    ARRAY(ITESTM,ITESTM)=XCHAN
    DO 70 L=1,LIMIT
  70 CONTINUE
  200 CONTINUE
  210 CONTINUE
  220 RETURN
  END
SUBROUTINE JASSIN(NM,NP,D,L,C)
C THIS SUBROUTINE ASSIGNS THE ORDERED EIGENVALUES TO ENERGY LEVELS
C USING THE VALUES OF J,N,KP,KO AS SUBSCRIPTS AND STORES THEM IN
C THE ARRAY EJ.
  IMPLICIT REAL (A-H,O-Z)
  DIMENSION D(1000,1000),C(1:4,2:4,0:4,0:4)
C WRITE (6,4)
  4 FORMAT (27HSUBROUTINE JASSIN IS CALLED)
  DO 1 LP=1,L
C WRITE (6,20) LP,D(LP,LP)
  1 CONTINUE
  LINDEX=1
  DO 10 N=NM,NP
    IF (N .LT. 2) GOTO 5
    IF (N .GT. 4) GOTO 5
    DO 3 K=0,N
      KO=N-K
C WRITE (6,20) NM,N,K,KO,C(NM,N,K,KO)
      C(NM,N,K,KO)=D(LINDEX,LINDEX)
C WRITE (6,3) NM,N,K,KO,C(NM,N,K,KO)
      LINDEX=LINDEX+1
      IF (K .EQ. N) GOTO 3
      KP=K+1
      C(NM,N,KP,KO)=D(LINDEX,LINDEX)
C WRITE(6,20) NM,N,KP,KO,C(NM,N,KP,KO)

```

```

    LINDEX=LINDEX+1
3  CONTINUE
    GOTO 10
5  LINDEX=2*N+1
10 CONTINUE
20 FORMAT ( 2HD(, I2, 2H)=, E10.2)
    RETURN
    END
    SUBROUTINE HYPER(F, IN, IH, ARANK, TA, TB, TC, TAB, AF, HA, HB, HC, HAB, HAF,
INMIN, NMAX, EF)
C   THIS SUBROUTINE CALCULATES THE HYPERFINE MATRIX ELEMENTS. HDIAG
C   IS THEN CALLED WHICH DIAGONALIZES THE MATRIX. XORDER ORDERS THE
C   DIAGONALIZED MATRIX A AND FASSIGN THEN ASSIGNS THESE EIGENVALUES
C   TO THE ARRAY EF USING I, F, J, N, KP, KO AS THE ASSIGNMENT INDICES.

C   THIS SUBROUTINE CALCULATES THE MATRIX ELEMENTS NUMERICALLY BY
C   USING PERTINENT 3-J, 6-J AND 9-J FUNCTIONS.
    IMPLICIT REAL (A-H, O-Z)
    REAL J, JP, JF1, N, NP, K, KP, S, NLOW, PF1, PJ, PN, PK, PKO, PKP, PNL
    INTEGER DJ, DNMAX, DN, DFIJ, ADK, ARANK, FM, IH, IN, IHN, L, M, PF1M, PJM
    DIMENSION Q(1000, 1000), EF(0:10, 0:5, 1:4, 2:4, 0:4, 0:4)
    S=.5
5  FORMAT (6H HYPER, 9F5.1, 2I5, 1F14.6)
6  FORMAT (11H HYPER IHIN, 2I5)
    WRITE (6, 6) IH, IN
7  IF (F .LT. IH) THEN
    FIHDF=.5
    ELSE
    FIHDF=ABS(F-IH)
    ENDIF
11 L=0
    DO 301 F1P=FIHDF, F+IH
    DO 301 JP=ABS(F1P-IN), F1P+IN
    IF (JP .LT. 1) THEN
        NLOW=1
    ELSE
        NLOW=(JP-0.5)
    ENDIF
    DO 301 NP=NLOW, JP+0.5
    DO 301 KP=-NP, NP
    M=0
    L=L+1
C   WRITE (6, 5) F, F1P, JP, NP, KP, L, M
    DO 300 F1=FIHDF, F+IH
    DO 300 J=ABS(F1-IN), F1+IN
    IF (J .LT. 1) THEN
        NLOW1=1
    ELSE
        NLOW1=(J-0.5)
    ENDIF

```

```

DO 300 N=NLOW1,J+0.5
C   NPN=(NP-N)
C   IF (NPN) 12,12,
DO 300 K=-N,N
M=M+1
12 FORMAT (13H AT HYPER F =,1F5.1)
C   WRITE (6,12) F
IF (M .LT. L) GOTO 300
IF (IN) 200,210,200
200 IF (IH) 220,230,220
210 IF (IH) 240,250,240
C IN AND IH NOT EQUAL TO 0
220 Q(L,M)=AF*FERMI(N,NP,K,KP,S,J,JP,REAL(IN),F1,F1P)+FERMIH(N,NP,K,
1KP,S,J,JP,REAL(IN),F1,F1P,REAL(IH),F)*HAF-DIPOLE(N,NP,K,KP,S,J,
1JP,REAL(IN),F1,F1P,REAL(IH),F,TC,TA,TB,TAB)-DIPOLH(N,NP,K,KP,S,
1J,JP,REAL(IN),F1,F1P,REAL(IH),F,HC,HA,HB,HAB)
C   WRITE(6,5) F,F1P,JP,NP,KP,F1,J,N,K,IH,IN,Q(L,M)
GOTO 300
225 FORMAT (27HTHE VALUES M,L,Q(L,M) HYPER,2I5,1F10.2)
C IN NOT EQUAL TO ZERO AND IH EQUAL 0
230 Q(L,M)=AF*FERMI(N,NP,K,KP,S,J,JP,REAL(IN),F1,F1P)-DIPOLE(N,NP,K,
1KP,S,J,JP,REAL(IN),F1,F1P,REAL(IH),F,TC,TA,TB,TAB)
C   WRITE(6,5) F,F1P,JP,NP,KP,F1,J,N,K,IH,IN,Q(L,M)
GOTO 300
C IN EQUAL TO 0, IH NOT
240 Q(L,M)=FERMIH(N,NP,K,KP,S,J,JP,REAL(IN),F1,F1P,REAL(IH),F)*HAF-
1DIPOLH(N,NP,K,KP,S,J,JP,REAL(IN),F1,F1P,REAL(IH),F,HC,HA,HB,HAB)
C   WRITE(6,5) F,F1P,JP,NP,KP,F1,J,N,K,IH,IN,Q(L,M)
GOTO 300
C IH,IN=0
250 Q(L,M)=0
C   WRITE(6,5) F,F1P,JP,NP,KP,F1,J,N,K,IH,IN,Q(L,M)
C   GOTO 300
C 299 M=2*N+1+M
300 CONTINUE
301 CONTINUE
CALL HDIAG(Q,L,1,L)
CALL XORDER(Q,L,L)
C   DO 305 IL=0,L
C   WRITE (6,304) F,L,IL,Q(IL,IL)
C 304 FORMAT (6H HYPER,1F5.1,2I5,1F20.10)
C 305 CONTINUE
FM=F-0.5
CALL FASSIN(F,IN,IH,NMIN,NMAX,Q,EF)
410 RETURN
END
SUBROUTINE FASSIN(F,IN,IH,NMIN,NMAX,A,P)
C   THIS SUBROUTINE ASSIGNS THE DIAGONALIZED MATRIX ELEMENTS TO
C   THE VARIOUS VALUES OF I,F,J,N,KP,KO. THIS SUBROUTINE CONSIDERS
C   ALL POSSIBLE PERMUTATION OF QUANTUM NUMBERS F1,J,N THAT WOULD

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C RESULT IN THE VALUE F BEING CONSIDERED. THE SUBROUTINE ASSUMES
C ROTATION > SPINROTATION >NUCLEAR-ELECTRON SPIN ENERGY ORDER.
C WITH THI,, THE DIAGONALIZED MATRIX LEMENTS WHICH HAVE BEEN
C ORDERED CAN BE ASSIGNED TO THE CORRECT QUANTUM NUMBERS,
  IMPLICIT REAL (A-H,O-Z)
  REAL J,NLOWF
  INTEGER FM,F1M,JM,N,K,KO,KP
  DIMENSION A(1000,1000),P(0:10,0:5,1:4,2:4,0:4,0:4)
  5 FORMAT (27HSUBROUTINE FASSIN IS CALLED,3F5.1,6I5)
10 LINDEX=1
  IF (F .LT. IH) THEN
    FIHDF=.5
  ELSE
    FIHDF=(F-IH)
  ENDIF
  6 FORMAT (8H F1 LOOP,3F5.1,6I5)
  DO 20 F1=FIHDF,F+IH
  DO 20 J=(ABS(F1-IN)),(F1+IN)
  IF (J .LT. 1) THEN
    NLOWF=1
  ELSE
    NLOWF=INT(J-.5)
  ENDIF
  DO 20 N=NLOWF,INT(J+.5)
  7 FORMAT (8H NJ LOOP,3F5.1,6I5)
  8 FORMAT (6H N IFS,3F5.1,6I5)
  IF (N .LT. NMIN) GOTO 19
  IF (N .GT. NMAX) GOTO 19
  DO 20 K=0,N
  9 FORMAT (7H K LOOP,3F5.1,6I5)
  KO=N-K
  KP=K+1
C WRITE (6,9) F,F1,J,N,K,KO,KP,IH,IN
  FM=INT(F-.5)
  F1M=INT(F1-.5)
  JM=INT(J-.5)
  P(FM,F1M,JM,N,K,KO)=A(LINDEX,LINDEX)
12 FORMAT (11H AT FASSIN ,3F5.1,3I5,1F20.10)
C WRITE (6,12)F,F1,J,N,K,KO,A(LINDEX,LINDEX)
  LINDEX=LINDEX+1
  IF (K .EQ. N) GOTO 20
  P(FM,F1M,JM,N,KP,KO)=A(LINDEX,LINDEX)
C WRITE (6,12)F,F1,J,N,KP,KO,A(LINDEX,LINDEX)
  LINDEX=LINDEX+1
  GOTO 20
19 LINDEX=LINDEX+2*N+1
20 CONTINUE
30 RETURN
  END

```

```

SUBROUTINE ELEVEL(F, IN, IH, NMIN, NMAX, P, E)
C THIS SUBROUTINE COMBINES THE ENERGY LEVELS DETERMINED FROM
C SUBROUTINES HYPER AND FINE AND STORES THEM IN ARRAY EF.
IMPLICIT REAL (A-H, O-Z)
INTEGER FM, F1M, JM, UFM, UF1M, UJM, UN, N, KO, K, KP
REAL J
DIMENSION P(0:10, 0:5, 1:4, 2:4, 0:4, 0:4), E(1:4, 2:4, 0:4, 0:4)
C WRITE (6, 5) IN
5 FORMAT(14H AT ELEVEL IN=, I5)
10 IF ((F-IH) .LT. 0) THEN
    F1MIN=.5
    ELSE
    F1MIN=(F-IH)
ENDIF
DO 20 F1=F1MIN, (F+IH)
DO 20 J=ABS(F1-IN), F1+IN
IF (J .LT. 1) THEN
    NLOWA=1
    ELSE
    NLOWA=INT(J-.5)
ENDIF
DO 20 N=NLOWA, INT(J+.5)
IF (N .LT. NMIN) GOTO 20
IF (N .GT. NMAX) GOTO 20
DO 20 K=0, N
KO=N-K
KP=K+1
FM=INT(F-.5)
F1M=INT(F1-.5)
JM=INT(J-.5)
C WRITE (6, 13) F, F1, J, N, K, KO, E(JM, N, K, KO), P(FM, F1M, JM, N, K, KO)
13 FORMAT (3F5.1, 3I5, 2F25.10)
P(FM, F1M, JM, N, K, KO)=P(FM, F1M, JM, N, K, KO)+E(JM, N, K, KO)
C WRITE (6, 15) F, F1, J, N, K, KO, P(FM, F1M, JM, N, K, KO)
15 FORMAT (3F5.1, 3I5, 1F20.10)
IF (K .EQ. N) GOTO 20
C WRITE (6, 13) F, F1, J, N, KP, KO, E(JM, N, K, KO), P(FM, F1M, JM, N, KP, KO)
P(FM, F1M, JM, N, KP, KO)=P(FM, F1M, JM, N, KP, KO)+E(JM, N, KP, KO)
C WRITE (6, 15) F, F1, J, N, KP, KO, P(FM, F1M, J, N, KP, KO)
20 CONTINUE
30 RETURN
END
SUBROUTINE FREQP(NMIN, NMAX, IN, IH, P, E)
IMPLICIT REAL (A-H, O-Z)
REAL UJ, J1, J, GS, GB, BETA, BETAN
INTEGER ARANK, FM, F1M, JM, UFM, UF1M, UJM, UK, UKO, UKP, UN, POWR, IH, IN
INTEGER DNP KP
CHARACTER*4 IDENT(20)
DIMENSION E(1:4, 2:4, 0:4, 0:4), P(0:10, 0:5, 1:4, 2:4, 0:4, 0:4)
WRITE (6, 4) IH, IN

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4 FORMAT (37H THE FOLLOWING ARE TRANSITIONS OF IH=,1I5,8H AND IN=,
1I5)
  IF (IN) 50,5,50
5 IF (IH) 50,7,50
7 DO 45 ITRANS=1,7
  READ (7,10) UN,UK,UKO,N,K,KO,ROTA
C  WRITE (6,10) UN,UK,UKO,N,K,KO
C  IF (((-1)**UK).NE.((-1)**IH).OR.((-1)**K).NE.((-1)**IH)) GOTO 45
10 FORMAT (6I5,1F8.2)
  DO 40 UJ=ABS(UN-.5),(UN+.5)
  UJM=INT(UJ-.5)
  DO 35 J=ABS(N-.5),(N+.5)
  JM=INT(J-.5)
13 FORMAT (2F5.1)
C  WRITE (6,13) UJ,J
  IF ((INT(UJ-J)) .EQ. 1) GOTO 25
15 FORMAT (I2,1H(,I2,1H,,I2,2H)-,I2,1H(,I2,1H,,I2,1H),5X,F4.1,1H-,
1F4.1,5X,F12.5)
20 GOTO 35
25 FREQ=(E(UJM,UN,UK,UKO)-E(JM,N,K,KO))+ROTA
  WRITE(6,15) UN,UK,UKO,N,K,KO,UJ,J,FREQ
35 CONTINUE
40 CONTINUE
45 CONTINUE
  GOTO 105
C PRINT OUT HYPERFINE SPLITTING FREQUENCIES, IH OR IN NE TO 0
50 DO 100 ITRANS=1,7
  READ (7,10) UN,UK,UKO,N,K,KO,ROTA
C  WRITE (6,10) UN,UK,UKO,N,K,KO
C  IF (((-1)**UK).NE.((-1)**IH).OR.((-1)**K).NE.((-1)**IH)) GOTO 100
  DO 95 UJ=ABS(UN-.5),(UN+.5)
  UJM=INT(UJ-.5)
  DO 90 UF1=(UJ-IN),(UJ+IN)
  IF (IN .EQ. 0) GOTO 90
  UF1M=INT(UF1-.5)
  IF (UF1 .LT. IH) THEN
    UFL=.5
  ELSE
    UFL=(UF1-IH)
  ENDIF
  DO 85 UF=UFL,UF1+IH
  UFM=INT(UF-.5)
  DO 80 J=ABS(N-.5),(N+.5)
  JM=INT(J-.5)
C  WRITE (6,13) UJ,J
  IF ((INT(ABS(UJ-J))).NE.1) GOTO 80
  DO 75 F1=(J-IN),(J+IN)
  F1M=INT(F1-.5)
  IF (INT(ABS(UF1-F1)).NE.1) GOTO 75
  IF (F1 .LT. IH) THEN

```

```

      FL=.5
      ELSE
      FL=(F1-IH)
    ENDIF
    DO 70 F=FL,F1+IH
    FM=INT(F-.5)
    IF (INT(ABS(UF-F)).NE.1) GOTO 70
    FREQ=(P(UFM,UF1M,UJM,UN,UK,UKO)-P(FM,F1M,JM,N,K,KO))+ROTA
    WRITE (6,60) UN,UK,UKO,N,K,KO,UJ,J,UF1,F1,UF,F,FREQ
60  FORMAT (I2,1H(,I2,1H,,I2,2H)-,I2,1H(,I2,1H,,I2,1H),2X,1F4.1,
      11H-,1F4.1,2X,1F4.1,1H-,1F4.1,2X,1F4.1,1H-,1F4.1,5X,1F12.5)
C 60  FORMAT (6I5,6F5.1,1F20.10)
70  CONTINUE
75  CONTINUE
80  CONTINUE
85  CONTINUE
90  CONTINUE
95  CONTINUE
100 CONTINUE
105 RETURN
    END

C  FUNCTIONS DEFINED TO CALCULATE THE CONTRIBUTION OF THE FERMI CONTACT,
C  DIPOLE-DIPOLE, AND QUADRUPOLE CONTRIBUTION OF ROTATIONAL ENERGY.
C  FERMI,DIPOLE AND QUAD APPLY TO N14, FERMIH AND DIPOLH THE PROTONS
C
      REAL FUNCTION FERMI(N,NP,K,KP,S,J,JP,IN,F1,F1P)
      REAL J,JP,NP,N,J6DIAG,J6ODJ1,IN
      INTEGER POWR
      S=.5
12  FORMAT (15HFERMI IS CALLED)
      POWR=(INT(N+S+JP))
      IF (F1 .NE. F1P) GOTO 30
      IF (N .NE. NP) GOTO 30
      IF (K .NE. KP) GOTO 30
      IF (J .NE. JP) GOTO 20
      FERMI=(((2*J+1)**2)*S*(S+1)*(2*S+1)*IN*(IN+1)*(2*IN+1))**.5*
1J6DIAG(F1,REAL(IN),J)*J6DIAG(REAL(N),S,J)*((-1)**(POWR))
      GOTO 40
20  IF (J.GT.JP) GOTO 21
      FERMI=(((2*JP+1)*S*(S+1)*(2*S+1)*IN*(IN+1)*(2*IN+1)/(2*J+1))**.5
1*J6ODJ1(F1,REAL(IN),JP)*J6ODJ1(REAL(N),S,JP)*((-1)**(POWR))
      GOTO 40
21  FERMI=(((2*J+1)*S*(S+1)*(2*S+1)*IN*(IN+1)*(2*IN+1)/(2*JP+1))**.5
1*J6ODJ1(F1,REAL(IN),J)*J6ODJ1(REAL(N),S,J)*((-1)**(POWR))
      GOTO 40
30  FERMI=0.0
40  RETURN
    END

C
      REAL FUNCTION FERMIH(N,NP,K,KP,S,J,JP,IN,F1,F1P,IH,F)

```

```

REAL J,JP,JF1,IH,IN,N,NP,J6DIAG,J6ODJ1,J6ODJF
12 FORMAT (34H FERMIH N NP K KP J JP F1 F1P IH S,11F5.1)
FERFAC=((-1)**(INT(2*F1+F+2*JP+S+N+IN+IH+2)))
C WRITE (6,12)N,NP,K,KP,J,JP,F1,F1P,IH,S,FERFAC
DJ=(J-JP)
DF1=(F1-F1P)
S=.5
IF (DJ .GT. 0 .AND. DF1 .LT. 0) THEN
    JF1=1
    ELSE IF (DJ .LT. 0 .AND. DF1 .GT. 0) THEN
        JF1=-1
    ELSE
        JF1=0
ENDIF
50 IF (N .NE. NP) GOTO 100
IF (K .NE. KP) GOTO 100
IF (J .NE. JP) GOTO 75
IF (F1 .NE. F1P) GOTO 60
C WRITE (6,12) F,IH,F1
FERMH=FERFAC*(((2*F1+1)**2)*((2*J+1)**2)*S*(S+1)*(2*S+1)*IH*(IH
1+1)*(2*IH+1))**.5
C WRITE (6,53) FERMH
53 FORMAT (25H PRE SUBROUTINE FACTOR IS,1F10.5)
FH=FERMH*J6DIAG(F,REAL(IH),F1)
FIH=FH*J6DIAG(REAL(IN),J,F1)
FERMIH=FIH*J6DIAG(REAL(N),S,J)
GO TO 110
C F1 OFF DIAGONAL BY ONE
60 IF (F1 .LT.F1P) THEN
    PASS=F1
    F1=F1P
    F1P=PASS
ENDIF
C A FACTOR OF 2*F1P+1 WAS TAKEN OUT THAT CANCELLED WITH PART OF THE
C J6ODJ1 EXPRESSION, INORDER TO PREVENT 0 DENOMINATOR IN J6ODJ1
FERMIH=FERFAC*(((2*J+1)**2)*(2*F1+1)*S*(S+1)*(2*S+1)*IH
1*(IH+1)*(2*IH+1)/(2*FP+1))**.5*J6ODJ1(F,REAL(IH),F1)*
2J6ODJ1(REAL(IN),J,F1)*J6DIAG(N,S,J)
GOTO 110
C J OFF DIAGONAL BY ONE
75 IF (J .LT. JP) THEN
    PASS=J
    J=JP
    JP=PASS
END IF
IF (F1 .NE. F1P) GOTO 85
FERMIH=FERFAC*(((2*J+1)*((2*F1+1)**2)*S*(S+1)*(2*S+1)*IH/(2*JP+1)*
1*(IH+1)*(2*IH+1))**.5*J6DIAG(F,REAL(IH),F1)*J6ODJ1(REAL(IN),F1,J)*
2J6ODJ1(REAL(N),S,J)/((2*JP+1)**.5)

```



```

      GOTO 110
C BOTH F1 AND J ARE OFF DIAGONAL BY ONE
  85 IF (JF1) 90, 95, 91
C   F1+1,J-1
  90 FERMIH=FERFAC*((2*J+1)*(2*F1+1)*S*(S+1)*(2*S+1)
    1*IH*(IH+1)*(2*IH+1)**.5*J6ODJ1(F,REAL(IH),F1)*
    2J6ODJ1(N,S,J)*J6ODJF(REAL(IN),J,F1)
      GOTO 110
C   F1-1,J+1
  91 FERMIH=FERFAC*((2*J+1)*(2*F1+1)*S*(S+1)*(2*S+1)
    1*IH*(IH+1)*(2*IH+1)**.5*J6ODJ1(F,REAL(IH),F1)
    2*J6ODJ1(N,S,J)*J6OJFP(REAL(IN),F1,J)
      GOTO 110
C J-1,F1-1 OR J+1,F1+1
  95 IF (F1 .LT. F1P) THEN
      PASS=F1
      F1=F1P
      F1P=PASS
      ENDIF
      FERMIH=FERFAC*((2*J+1)*(2*F1+1)*S*(S+1)*(2*S+1)
    1*IH*(IH+1)*(2*IH+1)**.5*J6ODJ1(F,REAL(IH),F1)*
    2J6ODJF(REAL(IN),J,F1)*J6ODJ1(REAL(N),S,J)
      GOTO 110
 100 FERMIH=0.0
 105 FORMAT (9H FERMIH =,F40.20)
C 110 WRITE (6,105) FERMIH
 110 RETURN
      END
C
C
      REAL FUNCTION DIPOLE(N,NP,K,KP,S,J,JP,IN,F1,F1P,IH,F,TC,TA,TB,TAB)
      REAL J,JP,JF1,IN,IH,N,NP,K,KP,J6DIAG,J9DIAG,J3DIAG,J3ODK1
      REAL J3ODK2,J3ODN2,J6ODJ1,J9ODJ1,J9ODJN,J9OJPN,J9ODN2,J6OJFP
      REAL J6ODJF
      INTEGER DNP KP,DKAY,POWR
C   WRITE (6,12)
  12 FORMAT (16HDIPOLE IS CALLED)
      POWR=INT(JP+IN+F1)
      DIPFAC=(-1)**INT(POWR)*(5**.5)
      DKAY=INT((ABS(K-KP))-2)
      DNP KP=INT(NP-KP)
      DN=INT(N-NP)
      DJ=INT(J-JP)
      IF (DN .GT. 0 .AND. DJ .LT. 0) THEN
          NJ=1
      ELSE IF (DN .LT. 0 .AND. DJ .GT. 0) THEN
          NJ=-1
      ELSE
          NJ=0
      END IF

```

```

111 IF (NJ .NE. 0) GOTO 112
    IF (N .LT. NP) THEN
        PASS=NP
        NP=N
        N=PASS
    ENDIF
    IF (J .LT. JP) THEN
        PASS=NP
        NP=N
        N=PASS
    ENDIF
112 IF (F1 .NE. F1P) GOTO 200
    IF (J .NE. JP) GOTO 160
    IF (N .NE. NP) GOTO 120
113 DPFAC=DIPFAC*(((2*J+1)**2)*((2*N+1)**2)*S*(S+1)*(2*S+1)*IN*
    1(IN+1)*(2*IN+1)*J6DIAG(F1, IN, J)*J9DIAG(N, S, J))
    IF (K .NE. KP) GOTO 115
    DIPOLE=(DPFAC*((-1)**INT((DNPKP)))*J3DIAG(N, K)*TC)
C OFF DIAGONAL IN K BY 1
115 IF (DKAY .EQ. 0) GOTO 117
116 DIPOLE=(DPFAC*((-1)**(INT(DNPKP)))*J3ODK1(N, K)*TAB)
    GOTO 118
C OFF DIAGONAL IN K BY 2
117 DIPOLE=DPFAC*((-1)**(INT(DNPKP)))*J3ODK2(N, K)*(TA-TB)
118 RETURN
C
C OFF DIAGONAL IN N BY 2, AS WELL AS THE THREE DIFFERENT K ELEMENTS
120 DPFAC=DIPFAC*((2*J+1)**2*(2*N+1)*(2*NP+1)*J6DIAG(F1, IN, J)*
    1J9ODN2(N, S, J))*S*(S+1)*(2*S+1)*IN*(IN+1)*(2*IN+1)
    IF (K .NE. KP) GOTO 125
    DIPOLE=DPFAC*((-1)**(INT(DNPKP)))*J3ODN2(N, K)*TC
    RETURN
125 DIPOLE=0.000
137 RETURN
C
C J OFF DIAGONAL BY ONE, ALONG WITH OTHER OFFDIAGONALS OF N AND K
160 IF (N .NE. NP) GOTO 180
163 DPFAC=DIPFAC*((2*J+1)*((2*N+1)**2)*J6ODJ1(F1, REAL(IN), J)*
    1J9ODJ1(N, S, J))*S*(S+1)*(2*S+1)*IN*(IN+1)*(2*IN+1)
    IF (K .NE. KP) GOTO 165
    DIPOLE=DPFAC*((-1)**(INT(DNPKP)))*J3DIAG(N, K)*TC
    GOTO 175
165 IF (DKAY .EQ. 0) GOTO 172
170 DIPOLE=DPFAC*((-1)**(INT(DNPKP)))*J3ODK1(N, K)*TAB
    GOTO 175
172 DIPOLE=DPFAC*((-1)**(INT(DNPKP)))*J3ODK2(N, K)*(TA-TB)
175 RETURN
C
C N OFF DIAGONAL BY 2, LONG WITH J BY 1

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```

180 IF (NJ) 182, 181, 183
C N-2, J-1
181 DPFAC=DIPFAC*((2*J+1)*(2*N+1)*(2*NP+1)*J6ODJ1(F1, IN, J)*
1J9ODJN(N, S, J))*S*(S+1)*(2*S+1)*IN*(IN+1)*(2*IN+1)
GOTO 184
C N+2, J-1
182 DPFAC=DIPFAC*((2*J+1)*(2*N+1)*(2*NP+1)*J6ODJ1(F1, IN, J)*
1J9OJPN(NP, S, JP))*S*(S+1)*(2*S+1)*IN*(IN+1)*(2*IN+1)
GOTO 184
C N-2, J+1
183 DPFAC=DIPFAC*((2*J+1)*(2*N+1)*(2*NP+1)*J6ODJ1(F1, IN, J)*
1J9OJPN(N, S, J))*S*(S+1)*(2*S+1)*IN*(IN+1)*(2*IN+1)
184 IF (K .NE. KP) GOTO 200
DIPOLE=DPFAC*((-1)**(INT(DNPKP)))*J3ODN2(N, K)*TC
195 RETURN
200 DIPOLE=0.000
201 RETURN
END

C
C FUNCTION THAT CALCULATES THE PROTON CONTRIBUTION FROM DIPOLE-DIPOL
REAL FUNCTION DIPOLH(N, NP, K, KP, S, J, JP, IN, F1, F1P, IH, F, HC, HA, HB, HAB)
REAL J, JP, N, NP, IN, IH, K, KP, J6DIAG, J9DIAG, J3DIAG, J9ODN2
REAL J3ODK1, J3ODK2, J3ODN2, J9ODJ1, J9ODJN, J9OJPN, J6ODJ1
REAL J6ODJF, J6OJFP, S
INTEGER POWR, DNP KP, DKAY, DN, DJ, DF1, NJ, JF1
12 FORMAT (29H DIPOLH N K NP KP J JP F1 F1P, 8F5.1)
POWR=INT(2*F1+F+JP+S+NP+IN+IH)
DIPFAC=(-1)**(POWR)
DKAY=INT((ABS(K-KP))-2)
DNP KP=INT(NP-KP)
DN=INT(N-NP)
DJ=INT(J-JP)
DF1=INT(F1-F1P)
C WRITE (6, 12)N, K, NP, KP, J, JP, F1, F1P
IF (DN .GT. 0 .AND. DJ .LT. 0) THEN
NJ=1
ELSE IF (DN .LT. 0 .AND. DJ .GT. 0) THEN
NJ=-1
ELSE
NJ=0
ENDIF
203 IF (DJ .GT. 0 .AND. DF1 .LT. 0) THEN
JF1=1
ELSE IF (DJ .LT. 0 .AND. DF1 .LT. 0) THEN
JF1=-1
ELSE
JF1=0
ENDIF
IF (NJ .NE. 0) GOTO 205
IF (N .LT. NP) THEN

```

```

    PASS=NP
    NP=N
    N=PASS
ENDIF
IF (J .LT. JP) THEN
    PASS=JP
    JP=J
    J=PASS
ENDIF
205 IF (NF1 .NE. 0) GOTO 208
    IF (N .LT. NP) THEN
        PASS=NP
        NP=N
        N=PASS
    ENDIF
    IF (F1 .LT. F1P) THEN
        PASS=F1P
        F1P=F1
        F1=PASS
    ENDIF
208 IF (F1 .NE. F1P) GOTO 300
    IF (J .NE. JP) GOTO 250
    IF (N .NE. NP) GOTO 225
209 DPFAC=DIPFAC*(((2*F1+1)**2)*((2*J+1)**2)*S*(S+1)*(2*S+1)*IH*
    1(IH+1)*(2*IH+1)*((2*N+1)**2)**.5*J6DIAG(F,REAL(IH),F1)*
    2J6DIAG(REAL(IN),J,F1)*J9DIAG(N,S,J)
    IF (K .NE. KP) GOTO 210
    DIPOLH=DPFAC*J3DIAG(N,K)*((-1)**INT(DNPKP))*HC
    GOTO 224
210 IF (DKAY .EQ. 0) GOTO 220
215 DIPOLH=DPFAC*J3ODK1(N,K)*((-1)**INT(DNPKP))*HAB
    GOTO 224
220 DIPOLH=DPFAC*J3ODK2(N,K)*((-1)**INT(DNPKP))*(HA-HB)
221 FORMAT (9H ALL DIAG,1F20.10)
C 224 WRITE (6,221)DIPOLH
224 GOTO 395
C
C N OFF DIAGONAL BY 2
225 DPFAC=DIPFAC*(((2*F1+1)**2)*((2*J+1)**2)*S*(S+1)*(2*S+1)*IH*
    1(IH+1)*(2*IH+1)*(2*N+1)*(2*NP+1)**.5*J6DIAG(F,REAL(IH),F1)*
    2J6DIAG(REAL(IN),J,F1)*J9ODN2(N,S,J)
    IF (K .NE. KP) GOTO 230
C 229 WRITE (6,229) DNPKP,HC
229 FORMAT (9H DNPKP,HC,I5,1F5.1)
    DIPOLH=DPFAC*J3ODN2(N,K)*((-1)**INT(DNPKP))*HC
    GOTO 245
230 DIPOLH=0.000
239 FORMAT (7H N BY 2,1F20.10)
C 245 WRITE (6,239) DIPOLH

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245 GOTO 395
C
C J OFF DIAGONAL BY ONE
250 IF (N .NE. NP) GOTO 275
251 DPFAC=DIPFAC*(((2*F1+1)**2)*(2*J+1)*S*(S+1)*(2*S+1)*
1IH*(IH+1)*(2*IH+1)*(2*N+1)*(2*NP+1))**.5* J6DIAG(F,REAL(IH),F1)*
2J6ODJ1(REAL(IN),F1,J)*J9ODJ1(N,S,J)
IF (K .NE. KP) GOTO 255
DIPOLH=DPFAC*J3DIAG(N,K)*HC
GOTO 270
255 IF (DKAY .EQ. 0) GOTO 265
260 DIPOLH=DPFAC*J3ODK1(N,K)*HAB
GOTO 270
265 DIPOLH=DPFAC*J3ODK2(N,K)*(HA-HB)
269 FORMAT (7H J BY 1,1F20.10)
C 270 WRITE (6,269)DIPOLH
270 GOTO 395
C
C ELEMENTS OFF DIAGONAL IN J AND N SIMULTANEOUSLY
275 IF(NJ) 277, 276, 278
C IF N-2,J-1; 276 N-2,J+1;277 N+2,J-1; 278
276 DPFAC=DIPFAC*((2*F1+1)*(2*F1P+1)*(2*J+1)*S*(S+1)*
1(2*S+1)*IH*(IH+1)*(2*IH+1)*(2*N+1)*(2*NP+1))**.5*
2J6DIAG(F,REAL(IH),F1)*J6ODJ1(REAL(IN),F1,J)*J9ODJN(N,S,J)
GOTO 279
277 DPFAC=DIPFAC*((2*F1P+1)*(2*F1+1)*(2*J+1)*S*(S+1)*
1(2*S+1)*IH*(IH+1)*(2*IH+1)*(2*N+1)*(2*NP+1))**.5*
2J6DIAG(F,REAL(IH),F1)*J6ODJ1(REAL(IN),F1,J)*J9OJPN(N,S,J)
GOTO 279
278 DPFAC=DIPFAC*((2*F1P+1)*(2*F1+1)*(2*J+1)*S*(S+1)*
1(2*S+1)*IH*(IH+1)*(2*IH+1)*(2*N+1)*(2*NP+1))**.5*
2J6DIAG(F,REAL(IH),F1)*J6ODJ1(IH,F1,J)*J9OJPN(NP,S,JP)
IF (K .NE. KP) GOTO 280
279 DIPOLH=DPFAC*J3ODN2(N,K)*((-1)**(INT(DNPKP)))*HC
GOTO 295
280 DIPOLH=0.000
289 FORMAT (8H N AND J,1F20.10)
C 295 WRITE (6,289)DIPOLH
295 GOTO 395
C
C ELEMENTS OFF DIAGONAL IN F1
300 IF (J .NE. JP) GOTO 350
IF (N .NE. NP) GOTO 325
DPFAC=DIPFAC*((2*F1+1)*(2*J+1)*(2*JP+1)*(2*N+1)*(2*NP
1+1)*IH*(IH+1)*(2*IH+1)/(2*F1P+1))**.5*J6ODJ1(F,REAL(IH),F1)*
2J6ODJ1(REAL(IN),J,F1)*J9DIAG(N,S,J)*S*(S+1)*(2*S+1)
IF (K .NE. KP) GOTO 305
DIPOLH=DPFAC*J3DIAG(N,K)*((-1)**(DNPKP))*HC
GOTO 320
305 IF (DKAY .EQ. 0) GOTO 315

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310 DIPOLH=DPFAC*J3ODK1(N,K)*((-1)**(DNP KP))*HAB
    GOTO 320
315 DIPOLH=DPFAC*J3ODK2(N,K)*((-1)**(DNP KP))*(HA-HB)
317 FORMAT (8H F1 BY 1,1F20.10)
C 320 WRITE (6,317)DIPOLH
    320 GOTO 395
C
C ELEMENTS OFF DIAGONAL IN N AND F1
325 DPFAC=((2*F1+1)*(2*N+1)*(2*NP+1)*(2*J+1)*(2*JP+1)/(2*F1P+1))
    1**.5*J6ODJ1(F,REAL(IH),F1)*J6ODJ1(REAL(IN),J,F1)*
    2J9ODN2(N,S,J)*DIPFAC
    IF (K .NE. KP) GOTO 330
    DIPOLH=DPFAC*J3DIAG(N,K)*((-1)**(DNP KP))*HC
    GOTO 345
330 IF (DKAY .EQ. 0) GOTO 340
335 DIPOLH=DPFAC*J3ODK1(N,K)*((-1)**(DNP KP))*HAB
    GOTO 345
340 DIPOLH=DPFAC*J3ODK2(N,K)*((-1)**(DNP KP))*(HA-HB)
341 FORMAT (9H N AND F1,1F20.10)
C 345 WRITE (6,341)DIPOLH
    345 GOTO 395
C
C ELEMENTS OFF DIAGONAL IN J AND F1
350 IF (N .NE. NP) GOTO 375
    IF (JF1) 351, 352, 353
351 DPFAC=DIPFAC*((2*F1+1)*(2*N+1)*(2*NP+1)*(2*J+1)*
    1(2*JP+1))**.5*J6ODJ1(F,REAL(IH),F1)*J6OJFP(REAL(IN),F1,J)*
    2J9ODJ1(N,S,J)
    GOTO 354
352 DPFAC=DIPFAC*((2*F1+1)*(2*N+1)*(2*NP+1)*(2*J+1)*
    1(2*JP+1))**.5*J6ODJF(REAL(IN),J,F1)*J9ODJ1(N,S,J)*
    2J6ODJ1(F,REAL(IH),F1)
    GOTO 354
353 DPFAC=DIPFAC*((2*F1+1)*(2*N+1)*(2*NP+1)*(2*J+1)*
    1(2*JP+1))**.5*J6OJFP(REAL(IN),J,F1)*J9ODJ1(N,S,J)*
    2J6ODJ1(F,REAL(IH),F1)
354 IF (K .NE. KP) GOTO 355
    DIPOLH=DPFAC*J3DIAG(N,K)*((-1)**(DNP KP))*HC
    GOTO 370
355 IF (DKAY .EQ. 0) GOTO 365
360 DIPOLH=DPFAC*J3ODK1(N,K)*((-1)**(DNP KP))*HAB
    GOTO 370
365 DIPOLH=DPFAC*J3ODK2(N,K)*((-1)**(DNP KP))*(HA-HB)
369 FORMAT (9H J AND F1,1F20.10)
C 370 WRITE (6,369)F,F1P JP,NP,KP,F1,J,N,K,DIPOLH
    370 GOTO 395
C
C ELEMENTS OFF DIAGONAL IN J,N,AND F1
375 DPFAC=DIPFAC*((2*F1+1)*(2*N+1)*(2*NP+1)*(2*J+1)*
    1(2*JP+1))**.5*J6ODJ1(F,REAL(IH),F1)

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```

1(2*B*(2*B+1)*(2*B+2)*2*C*(2*C+1)*(2*C+2))**.5)
  J6DIAG=(-1)**(INT(A+B+C))*(J6DAG)
  GOTO 20
10   J6DIAG=0.0
C 20   WRITE (6,5) J6DIAG
20 RETURN
END

C
  REAL FUNCTION J3DIAG(A,B)
  DNOM=((2*A+3)*(2*A+2)*(2*A+1)*2*A*(2*A-1))
  IF (DNOM .LE. 0) GOTO 10
  J3DIAG=(-1)**(INT(B-A))*2*(3*B*B-A*(A+1))/((DNOM)**.5)
  GOTO 20
10   J3DIAG=0.0
15   FORMAT (8H J3DIAG=,1F10.3)
C 20   WRITE (6,15) J3DIAG
20   RETURN
END

C
C   A=J,B=K
  REAL FUNCTION J3ODN2(A,B)
  REAL J3DN2
  IF (A .EQ. 1) GOTO 10
  J3DN2=(6*(A+B+2)*(A+B+1)*(A-B+2)*(A-B+1))/
1((2*A+5)*(2*A+4)*(2*A+3)*(2*A+2)*(2*A+1))
C   WRITE (6,5) A,B,J3DN2
5   FORMAT(14H K AT J3ODN2 =,1F9.5)
  IF (J3DN2 .LT. 0) GOTO 10
  J3ODN2=(-1)**(INT(A-B))*((J3DN2)**.5)
  GOTO 20
10   J3ODN2=0.0
C 20   WRITE (6,5) J3ODN2
20   RETURN
END

C
  REAL FUNCTION J6ODJ1(A,B,C)
  REAL J6DJ1
C   WRITE (6,5) A,B,C
5   FORMAT (3F5.1)
  IF (B .LT. .1) GOTO 10
  J6DJ1=(2*(A+B+C+1)*(B+C-A)*(A+C-B)*(A+B-C+1))/((2*B)*(2*B+1)*
1(2*B+2)*(2*C)*(2*C+1))
C   WRITE (6,12) J6DJ1
12 FORMAT (8H J6DJ1 =,1F20.10)
  IF (J6DJ1 .LT. 0) GOTO 10
  J6ODJ1=((-1)**(INT(A+B+C)))*(J6DJ1**.5)
  GOTO 20
10   J6ODJ1=0.0
15 FORMAT (21H THE VALUE OF J6ODJ1=,1F9.5)
C 20   WRITE (6,15) J6ODJ1

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```

376 IF(JF1) 377, 378, 379
377 IF(NJ) 380, 381, 382
378 IF(NJ) 383, 384, 385
379 IF(NJ) 386, 387, 388
C J+1,J-1,N+1,F1-1; JF1=-1, NJ=-1
380 DPOFAC=0.0000
GOTO 389
C J-1,N-1,J+1,F-1 OR J+1,N+2,J+1,F-1 ; JF1=-1, NJ=0
381 DPOFAC=DPFAC*J6OJFP(REAL(IN),F1,J)*J9ODJN(N,S,J)
GOTO 389
C JF1=-1,NJ=1, N+2,J-1,F1+1
382 DPOFAC=DPFAC*J6OJFP(REAL(IN),J,F1)*J9OJPN(NP,S,JP)
GOTO 389
C JF1=0, NJ=-1, J-1,F1-1,N+2,J-1; J+1,F1+1,N+1,J-1
383 DPOFAC=DPFAC*J6ODJF(REAL(IN),J,F1)*J9OJPN(NP,S,JP)
GOTO 389
C JF1=0, NJ=0
384 DPOFAC=DPFAC*J6ODJF(REAL(IN),J,F1)*J9ODJN(N,S,J)
GOTO 389
C JF1=0, NJ=1; J-1,F1-1, N-2,J+1; J+1,F1+1,N-1,J+1
385 DPOFAC=DPFAC*J6ODJF(REAL(IN),J,F1)*J9OJPN(N,S,J)
GOTO 389
C JF1=1,NJ=-1; J-1,F+1,J-1,N+1
386 DPOFAC=DPFAC*J6OJFP(REAL(IN),J,F1)*J9OJPN(NP,S,JP)
GOTO 389
C JF1=1,NJ=0; J-1,F+1,J-1,N-1
387 DPOFAC=DPFAC*J6OJFP(REAL(IN),J,F1)*J9ODJN(N,S,J)
GOTO 389
C JF1=1,NJ=0; J-1,F+1,J+1,N-1
388 DPOFAC=0.000
389 IF (K .NE. KP) GOTO 390
DIPOLH=DPOFAC*J3DIAG(N,K)*((-1)**(INT(DNPKP)))*HC
391 FORMAT (7H F1 N J,1F20.10)
C WRITE (6,391)DIPOLH
GOTO 395
390 DIPOLH=0.000
C WRITE (6,394)DIPOLH
394 FORMAT (9H SKIP ALL,1F20.10)
395 RETURN
END
C THIS ENDS FUNCTIONS THAT CALCULATE MATRIX ELEMENTS
C
C
C FUNCTIONS DEFINING SPECIFIC 3J,6J AND 9J SYMBOLS
REAL FUNCTION J6DIAG(A,B,C)
REAL J6DAG
C WRITE (6,4) A,B,C
4 FORMAT(3F5.1)
5 FORMAT (23H THE VALUE OF J6DIAG IS,1F20.10)
J6DAG=(2*(B*(B+1)+C*(C+1)-A*(A+1)))/

```



```

20     RETURN
      END

C
C
      REAL FUNCTION J9DIAG(N,S,J)
      REAL N,S,J
      J9DIAG=((3)**.5)*((N*(N+1)+S*(S+1)-J*(J+1))*(N*(N+1)+J*(J+1)
1) -S*(S+1))+(2/3)*N*(N+1)*(S*(S+1)+J*(J+1)-N*(N+1)))/(40*N*(N+
21)*(2*N-1)*(2*N+1)*(2*N+3)*S*(S+1)*(2*S+1)*J*(J+1)*(2*J+1))**.5
C
      WRITE (6,5) J9DIAG
5      FORMAT (8H J9DIAG=,1F10.3)
      RETURN
      END

C SUBROUTINE FOR 9J WITH J-1
      REAL FUNCTION J9ODJ1(N,S,J)
      REAL J,N,S
      IF (J .EQ. .5) GOTO 10
5      FORMAT (6H N S J,3F5.1)
      NMERAT=((N-S+J)*(N+S-J+1)*(S+J-N)*(N+S+J+1))
      IF (NMERAT .LT. 0) GOTO 10
      DENOM=(30*N*(N+1)*(2*N-1)*(2*N+1)*(2*N+3)*S*(S+1)*
1(2*S+1)*J*(2*J-1)*(2*J+1))
      IF (DENOM .LE. 0) GOTO 10
      GAM=(S*(S+1)+N*(N+1)-J*(J+1))*(2*N-1)*(2*N+3)
      BTRM=(N**2*(2*N-1)*(N+S+J+2)*(N-S+J+1))
      LTRM=((N+1)**2*(2*N+3)*(N+S-J)*(S+J-N+1))
      J9ODJ1=((NMERAT)**.5)/((DENOM)**.5*4*N*(N+1))*(GAM+(
1BTRM-LTRM)/(2*N+1))
      GOTO 20
10 J9ODJ1=0.0
C 20 WRITE (6,25)J9ODJ1
C 25 FORMAT (8H J9ODJ1=,1F10.4)
C      WRITE (6,5) N,S,J
20     RETURN
      END

C SUBROUTINE FOR 9J WITH J+1, N-2
      REAL FUNCTION J9OJPN(N,S,J)
      REAL J,N,J9JPN,S
      IF (N .LE. 1) GOTO 10
      J9JPN=((J+S+N+1)*(S+N-J)*(J-S+N)*(J+S-N+1)*(S+N-J-2
1)*(S+N-J-1)*(J+S-N+2)*(J+S-N+3))/(16*(N-1)*N*(2*N-3)*(2*N-1)*(2*
2N+1)*S*(S+1)*(2*S+1)*(J+1)*(2*J+1)*(2*J+3))
      IF (J9JPN .LT. 0) GOTO 10
      J9OJPN=-(J9JPN**.5)
      GOTO 20
10 J9OJPN=0.0
15 FORMAT (8H J9OJPN=,1F10.4)
C 20 WRITE (6,15) J9OJPN

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```

20 RETURN
END
C SUBROUTINE FOR 9J WITH N-2
REAL FUNCTION J9ODN2(N,S,J)
REAL J9DN2,N,J
C WRITE (6,5) N,S,J
5 FORMAT(18HVALUE OF N,S,J ARE,3F5.1)
IF ((N .LE. 1) .OR. (J .LT. 1.0)) GOTO 10
J9DN2=((J+S+N+1)*(S+N-J)*(J+N-S)*(J+S-N+1)*(S+N+J)
1*(J+N-S-1)*(N+S-J-1)*(J+S-N+2))/((16*(N-1)*N*(2*N-3)*(2*N-1)*
2(2*N+1)*S*(S+1)*(2*S+1)*(J)*(2*J+1)*(2*J-1)))
C WRITE(6,7) J9DN2
7 FORMAT (8H J9ODN2=,1F10.4)
IF (J9DN2 .LT. 0) GOTO 10
J9ODN2=-(J9DN2**.5)
GOTO 20
10 J9ODN2=0.0
C 20 WRITE (6,7) J9ODN2
20 RETURN
END

C SUBROUTINE FOR 9J WITH J-1,N-2
REAL FUNCTION J9ODJN(N,S,J)
REAL N,S,J,J9DJN
IF ((N .LE. 1) .OR. (J .EQ. .5)) GOTO 10
J9DJN=((J+S+N+1)*(S+N-J)*(J+N-S)*(J+S-N+1)*(J+S+N
1-1)*(J+S+N)*(J-S+N-1)*(S-J+N-1)*(J+S-N+2))/((16*(N-1)*N*(2*N-3)*
2(2*N-1)*(2*N+1)*S*(S+1)*(2*S+1)*J*(2*J-1)*(2*J+1))
IF (J9DJN .LT. 0) GOTO 10
J9ODJN=-(J9DJN**(.5))
GOTO 20
10 J9ODJN=0.0
15 FORMAT (8H J9ODJN=,1F10.4)
C 20 WRITE (6,15) J9ODJN
20 RETURN
END

C SUBROUTINE FOR 6J WITH J-1,F-1
REAL FUNCTION J6ODJF(N,J,F)
REAL J6DJF,J,N
IF ((J .LT. .5) .OR. (F .LT. .5)) GOTO 10
J6DJF=(((N+J+F)*(N+J+F+1)*(J+F-N-1)*
1(J+F-N))/((2*J-1)*2*J*(2*J+1)*(2*F-1)*2*F*(2*F+1)))
IF (J6DJF .LT. 0) GOTO 10
J6ODJF=((-1)**(INT(N+J+F)))*(J6DJF**.5)
GOTO 20
5 FORMAT (22H THE VALUE OF J6ODJF =,1F9.5)
10 J6ODJF=0.0
C 20 WRITE (6,5) J6ODJF
20 RETURN

```


	-1.00		-4.46		5.46	0.00
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70

-59.0 proton hyperfine

$n, k_1, k_1-1, n', k_1', k_1'-1$, freq
for transitions so that the
spectrum can be reproduced
instead of only differences
being calculated

3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50

3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70
3	1	3	2	1	2	18189.90
3	0	3	2	0	2	19274.10
3	2	2	2	2	1	20044.50
3	2	1	2	2	0	20814.9
3	1	2	2	1	1	21642.9
4	1	4	3	1	3	24063.6
4	0	4	3	0	3	24992.70

Sample Output from Hyperfine

FINAL RUN

2 4

-69.90 -36.10 2.70 0.00 0.00

-15.90 -16.00 34.30 0.00 9.50

8.04 -16.00 13.92 0.00 -59.00

THE FOLLOWING ARE TRANSITIONS OF IH= 0 AND IN= 0

J'(K',K')-N(K,K)	J' - J	FREQ
3(0, 3)- 2(0, 2)	2.5- 1.5	19308.88670
3(0, 3)- 2(0, 2)	3.5- 2.5	19241.36720
3(2, 2)- 2(2, 1)	2.5- 1.5	20075.01560
3(2, 2)- 2(2, 1)	3.5- 2.5	20018.41410
3(2, 1)- 2(2, 0)	2.5- 1.5	20805.51170
3(2, 1)- 2(2, 0)	3.5- 2.5	20786.07420
4(0, 4)- 3(0, 3)	3.5- 2.5	25001.04690
4(0, 4)- 3(0, 3)	4.5- 3.5	24959.07810

N'(K'-K')-N(K,K)	J' - J	F1' - F1	F' - F	FREQ
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THE FOLLOWING ARE TRANSITIONS OF IH= 1 AND IN= 0

3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	1.5- 0.5	18206.68360
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	2.5- 1.5	18207.83590
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	3.5- 2.5	18207.65620
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	2.5- 1.5	18157.73440
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	3.5- 2.5	18157.31640
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	4.5- 3.5	18158.12500
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	1.5- 0.5	21646.81250
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	2.5- 1.5	21647.53910
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	3.5- 2.5	21647.12110
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	2.5- 1.5	21616.29690
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	3.5- 2.5	21616.46090
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	4.5- 3.5	21616.09770
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	2.5- 1.5	24069.36330
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	3.5- 2.5	24069.96870
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	4.5- 3.5	24069.41410
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	3.5- 2.5	24030.00780
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	4.5- 3.5	24030.05080
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	5.5- 4.5	24028.79300
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	1.5- 0.5	18206.68360
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	2.5- 1.5	18207.83590
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	3.5- 2.5	18207.65620
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	2.5- 1.5	18157.73440
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	3.5- 2.5	18157.31640

3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	4.5- 3.5	18158.12500
THE FOLLOWING ARE TRANSITIONS OF IH= 2 AND IN= 0				
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	1.5- 0.5	20077.04690
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	2.5- 1.5	20077.73830
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	3.5- 2.5	20076.05080
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	4.5- 3.5	20075.94920
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	1.5- 0.5	20017.94140
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	2.5- 1.5	20019.75780
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	3.5- 2.5	20018.91020
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	4.5- 3.5	20018.41800
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	5.5- 4.5	20019.58980
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	1.5- 0.5	20807.54690
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	2.5- 1.5	20808.51170
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	3.5- 2.5	20806.59370
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	4.5- 3.5	20805.65620
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	1.5- 0.5	20785.05860
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	2.5- 1.5	20787.41800
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	3.5- 2.5	20786.67190
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	4.5- 3.5	20786.21870
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	5.5- 4.5	20785.53120
4(0, 4)- 3(0, 3)	3.5- 2.5	3.5- 2.5	1.5- 0.5	24999.66800
4(0, 4)- 3(0, 3)	3.5- 2.5	3.5- 2.5	2.5- 1.5	25002.57030
4(0, 4)- 3(0, 3)	3.5- 2.5	3.5- 2.5	3.5- 2.5	25001.71870
4(0, 4)- 3(0, 3)	3.5- 2.5	3.5- 2.5	4.5- 3.5	25001.46870
4(0, 4)- 3(0, 3)	3.5- 2.5	3.5- 2.5	5.5- 4.5	25000.61330
4(0, 4)- 3(0, 3)	4.5- 3.5	4.5- 3.5	2.5- 1.5	24958.47270
4(0, 4)- 3(0, 3)	4.5- 3.5	4.5- 3.5	3.5- 2.5	24959.72660
4(0, 4)- 3(0, 3)	4.5- 3.5	4.5- 3.5	4.5- 3.5	24959.72270
4(0, 4)- 3(0, 3)	4.5- 3.5	4.5- 3.5	5.5- 4.5	24959.50780
4(0, 4)- 3(0, 3)	4.5- 3.5	4.5- 3.5	6.5- 5.5	24957.75000
3(0, 3)- 2(0, 2)	2.5- 1.5	2.5- 1.5	1.5- 0.5	19309.64840
3(0, 3)- 2(0, 2)	2.5- 1.5	2.5- 1.5	2.5- 1.5	19311.85550
3(0, 3)- 2(0, 2)	2.5- 1.5	2.5- 1.5	3.5- 2.5	19310.48830
3(0, 3)- 2(0, 2)	2.5- 1.5	2.5- 1.5	4.5- 3.5	19309.47660
3(0, 3)- 2(0, 2)	3.5- 2.5	3.5- 2.5	1.5- 0.5	19243.32810
3(0, 3)- 2(0, 2)	3.5- 2.5	3.5- 2.5	2.5- 1.5	19242.29690
3(0, 3)- 2(0, 2)	3.5- 2.5	3.5- 2.5	3.5- 2.5	19242.73440
3(0, 3)- 2(0, 2)	3.5- 2.5	3.5- 2.5	4.5- 3.5	19241.99610
3(0, 3)- 2(0, 2)	3.5- 2.5	3.5- 2.5	5.5- 4.5	19242.46870
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	1.5- 0.5	20077.04690
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	2.5- 1.5	20077.73830
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	3.5- 2.5	20076.05080
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	4.5- 3.5	20075.94920
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	1.5- 0.5	20017.94140
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	2.5- 1.5	20019.75780
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	3.5- 2.5	20018.91020
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	4.5- 3.5	20018.41800
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	5.5- 4.5	20019.58980
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	1.5- 0.5	20807.54690
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	2.5- 1.5	20808.51170

3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	3.5- 2.5	20806.59370
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	4.5- 3.5	20805.65620
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	1.5- 0.5	20785.05860
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	2.5- 1.5	20787.41800
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	3.5- 2.5	20786.67190
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	4.5- 3.5	20786.21870
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	5.5- 4.5	20785.53120

THE FOLLOWING ARE TRANSITIONS OF $I_H = 3$ AND $I_N = 0$

3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	1.5- 0.5	21651.11720
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	2.5- 1.5	21651.07810
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	3.5- 2.5	21650.13670
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	4.5- 3.5	21649.16020
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	5.5- 4.5	21647.14450
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	1.5- 0.5	21616.89840
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	2.5- 1.5	21618.82420
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	3.5- 2.5	21619.64450
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	4.5- 3.5	21617.76950
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	5.5- 4.5	21616.32030
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	6.5- 5.5	21617.74220
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	1.5- 0.5	24072.81640
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	2.5- 1.5	24070.95700
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	3.5- 2.5	24072.22660
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	4.5- 3.5	24071.62500
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	5.5- 4.5	24070.71480
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	6.5- 5.5	24069.66020
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	1.5- 0.5	24030.50390
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	2.5- 1.5	24032.26950
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	3.5- 2.5	24032.73050
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	4.5- 3.5	24030.84370
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	5.5- 4.5	24030.93750
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	6.5- 5.5	24031.22660
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	7.5- 6.5	24026.44920
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	1.5- 0.5	18213.40230
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	2.5- 1.5	18211.37110
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	3.5- 2.5	18209.98830
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	4.5- 3.5	18209.20310
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	5.5- 4.5	18208.16410
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	1.5- 0.5	18158.66800
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	2.5- 1.5	18159.49610
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	3.5- 2.5	18160.50780
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	4.5- 3.5	18159.32420
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	5.5- 4.5	18157.21480
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	6.5- 5.5	18160.49220
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	1.5- 0.5	21651.11720
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	2.5- 1.5	21651.07810
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	3.5- 2.5	21650.13670
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	4.5- 3.5	21649.16020
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	5.5- 4.5	21647.14450
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	1.5- 0.5	21616.89840
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	2.5- 1.5	21618.82420

3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	3.5- 2.5	21619.64450
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	4.5- 3.5	21617.76950
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	5.5- 4.5	21616.32030
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	6.5- 5.5	21617.74220
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	1.5- 0.5	24072.81640
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	2.5- 1.5	24070.95700
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	3.5- 2.5	24072.22660
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	4.5- 3.5	24071.62500
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	5.5- 4.5	24070.71480
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	6.5- 5.5	24069.66020
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	1.5- 0.5	24030.50390
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	2.5- 1.5	24032.26950
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	3.5- 2.5	24032.73050
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	4.5- 3.5	24030.84370
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	5.5- 4.5	24030.93750
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	6.5- 5.5	24031.22660
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	7.5- 6.5	24026.44920

THE FOLLOWING ARE TRANSITIONS OF IH= 0 AND IN= 1

4(0, 4)- 3(0, 3)	3.5- 2.5	2.5- 1.5	2.5- 1.5	25031.62500
4(0, 4)- 3(0, 3)	3.5- 2.5	3.5- 2.5	3.5- 2.5	25003.68360
4(0, 4)- 3(0, 3)	3.5- 2.5	4.5- 3.5	4.5- 3.5	24915.24220
4(0, 4)- 3(0, 3)	4.5- 3.5	3.5- 2.5	3.5- 2.5	24960.74610
4(0, 4)- 3(0, 3)	4.5- 3.5	4.5- 3.5	4.5- 3.5	24963.72660
4(0, 4)- 3(0, 3)	4.5- 3.5	5.5- 4.5	5.5- 4.5	24719.75000
3(0, 3)- 2(0, 2)	2.5- 1.5	1.5- 0.5	1.5- 0.5	19313.67970
3(0, 3)- 2(0, 2)	2.5- 1.5	2.5- 1.5	2.5- 1.5	19314.82810
3(0, 3)- 2(0, 2)	2.5- 1.5	3.5- 2.5	3.5- 2.5	19220.05860
3(0, 3)- 2(0, 2)	3.5- 2.5	2.5- 1.5	2.5- 1.5	19241.36720
3(0, 3)- 2(0, 2)	3.5- 2.5	3.5- 2.5	3.5- 2.5	19189.62890
3(0, 3)- 2(0, 2)	3.5- 2.5	4.5- 3.5	4.5- 3.5	19036.86330
3(2, 2)- 2(2, 1)	2.5- 1.5	1.5- 0.5	1.5- 0.5	20086.19140
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	2.5- 1.5	20075.97660
3(2, 2)- 2(2, 1)	2.5- 1.5	3.5- 2.5	3.5- 2.5	20007.73050
3(2, 2)- 2(2, 1)	3.5- 2.5	2.5- 1.5	2.5- 1.5	20016.69140
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	3.5- 2.5	20020.19920
3(2, 2)- 2(2, 1)	3.5- 2.5	4.5- 3.5	4.5- 3.5	19853.27340
3(2, 1)- 2(2, 0)	2.5- 1.5	1.5- 0.5	1.5- 0.5	20840.95310
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	2.5- 1.5	20805.51170
3(2, 1)- 2(2, 0)	2.5- 1.5	3.5- 2.5	3.5- 2.5	20740.25780
3(2, 1)- 2(2, 0)	3.5- 2.5	2.5- 1.5	2.5- 1.5	20788.04690
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	3.5- 2.5	20782.64450
3(2, 1)- 2(2, 0)	3.5- 2.5	4.5- 3.5	4.5- 3.5	20628.62500
4(0, 4)- 3(0, 3)	3.5- 2.5	2.5- 1.5	2.5- 1.5	25031.62500
4(0, 4)- 3(0, 3)	3.5- 2.5	3.5- 2.5	3.5- 2.5	25003.68360
4(0, 4)- 3(0, 3)	3.5- 2.5	4.5- 3.5	4.5- 3.5	24915.24220
4(0, 4)- 3(0, 3)	4.5- 3.5	3.5- 2.5	3.5- 2.5	24960.74610
4(0, 4)- 3(0, 3)	4.5- 3.5	4.5- 3.5	4.5- 3.5	24963.72660
4(0, 4)- 3(0, 3)	4.5- 3.5	5.5- 4.5	5.5- 4.5	24719.75000

THE FOLLOWING ARE TRANSITIONS OF IH= 1 AND IN= 1

3(1, 2)- 2(1, 1)	2.5- 1.5	1.5- 0.5	1.5- 0.5	21652.85160
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3(1, 2)- 2(1, 1)	2.5- 1.5	1.5- 0.5	2.5- 1.5	21648.37890
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	1.5- 0.5	21643.87890
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	2.5- 1.5	21646.81250
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	3.5- 2.5	21647.51560
3(1, 2)- 2(1, 1)	2.5- 1.5	3.5- 2.5	2.5- 1.5	21646.84370
3(1, 2)- 2(1, 1)	2.5- 1.5	3.5- 2.5	3.5- 2.5	21646.81250
3(1, 2)- 2(1, 1)	2.5- 1.5	3.5- 2.5	4.5- 3.5	21678.28520
3(1, 2)- 2(1, 1)	3.5- 2.5	2.5- 1.5	1.5- 0.5	21609.44140
3(1, 2)- 2(1, 1)	3.5- 2.5	2.5- 1.5	2.5- 1.5	21616.25000
3(1, 2)- 2(1, 1)	3.5- 2.5	2.5- 1.5	3.5- 2.5	21616.47660
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	2.5- 1.5	21616.45700
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	3.5- 2.5	21616.25000
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	4.5- 3.5	21616.36720
3(1, 2)- 2(1, 1)	3.5- 2.5	4.5- 3.5	3.5- 2.5	21616.25000
3(1, 2)- 2(1, 1)	3.5- 2.5	4.5- 3.5	4.5- 3.5	21616.25000
3(1, 2)- 2(1, 1)	3.5- 2.5	4.5- 3.5	5.5- 4.5	21439.67190
4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	1.5- 0.5	24071.26950
4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	2.5- 1.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	3.5- 2.5	24069.93750
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	2.5- 1.5	24070.57030
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	3.5- 2.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	4.5- 3.5	24069.74220
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	3.5- 2.5	24069.75000
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	4.5- 3.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	5.5- 4.5	23991.39450
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	2.5- 1.5	24082.35160
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	3.5- 2.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	4.5- 3.5	24030.08590
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	3.5- 2.5	24030.03520
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	4.5- 3.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	5.5- 4.5	24030.26560
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	4.5- 3.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	5.5- 4.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	6.5- 5.5	23812.41020
3(1, 3)- 2(1, 2)	2.5- 1.5	1.5- 0.5	1.5- 0.5	18214.61720
3(1, 3)- 2(1, 2)	2.5- 1.5	1.5- 0.5	2.5- 1.5	18209.10550
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	1.5- 0.5	18204.68750
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	2.5- 1.5	18207.11330
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	3.5- 2.5	18207.94530
3(1, 3)- 2(1, 2)	2.5- 1.5	3.5- 2.5	2.5- 1.5	18207.11720
3(1, 3)- 2(1, 2)	2.5- 1.5	3.5- 2.5	3.5- 2.5	18207.11330
3(1, 3)- 2(1, 2)	2.5- 1.5	3.5- 2.5	4.5- 3.5	18238.73050
3(1, 3)- 2(1, 2)	3.5- 2.5	2.5- 1.5	1.5- 0.5	18151.37890
3(1, 3)- 2(1, 2)	3.5- 2.5	2.5- 1.5	2.5- 1.5	18157.16410
3(1, 3)- 2(1, 2)	3.5- 2.5	2.5- 1.5	3.5- 2.5	18157.40620
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	2.5- 1.5	18157.35550
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	3.5- 2.5	18157.16410
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	4.5- 3.5	18157.14450
3(1, 3)- 2(1, 2)	3.5- 2.5	4.5- 3.5	3.5- 2.5	18157.16410
3(1, 3)- 2(1, 2)	3.5- 2.5	4.5- 3.5	4.5- 3.5	18157.16410

3(1, 3)- 2(1, 2)	3.5- 2.5	4.5- 3.5	5.5- 4.5	17980.55470
THE FOLLOWING ARE TRANSITIONS OF IH= 2 AND IN= 1				
3(2, 1)- 2(2, 0)	2.5- 1.5	1.5- 0.5	1.5- 0.5	20805.78520
3(2, 1)- 2(2, 0)	2.5- 1.5	1.5- 0.5	2.5- 1.5	20806.86330
3(2, 1)- 2(2, 0)	2.5- 1.5	1.5- 0.5	3.5- 2.5	20806.97660
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	1.5- 0.5	20805.51170
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	2.5- 1.5	20805.83590
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	3.5- 2.5	20805.92190
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	4.5- 3.5	20806.55470
3(2, 1)- 2(2, 0)	2.5- 1.5	3.5- 2.5	1.5- 0.5	20805.61330
3(2, 1)- 2(2, 0)	2.5- 1.5	3.5- 2.5	2.5- 1.5	20805.51170
3(2, 1)- 2(2, 0)	2.5- 1.5	3.5- 2.5	3.5- 2.5	20805.51170
3(2, 1)- 2(2, 0)	2.5- 1.5	3.5- 2.5	4.5- 3.5	20805.53520
3(2, 1)- 2(2, 0)	2.5- 1.5	3.5- 2.5	5.5- 4.5	20805.00780
3(2, 1)- 2(2, 0)	3.5- 2.5	2.5- 1.5	1.5- 0.5	20786.07420
3(2, 1)- 2(2, 0)	3.5- 2.5	2.5- 1.5	2.5- 1.5	20786.12500
3(2, 1)- 2(2, 0)	3.5- 2.5	2.5- 1.5	3.5- 2.5	20786.21090
3(2, 1)- 2(2, 0)	3.5- 2.5	2.5- 1.5	4.5- 3.5	20786.89450
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	1.5- 0.5	20786.87500
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	2.5- 1.5	20786.07420
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	3.5- 2.5	20786.07420
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	4.5- 3.5	20786.08590
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	5.5- 4.5	20785.94530
3(2, 1)- 2(2, 0)	3.5- 2.5	4.5- 3.5	2.5- 1.5	20786.23830
3(2, 1)- 2(2, 0)	3.5- 2.5	4.5- 3.5	3.5- 2.5	20786.07420
3(2, 1)- 2(2, 0)	3.5- 2.5	4.5- 3.5	4.5- 3.5	20786.07420
3(2, 1)- 2(2, 0)	3.5- 2.5	4.5- 3.5	5.5- 4.5	20786.05080
3(2, 1)- 2(2, 0)	3.5- 2.5	4.5- 3.5	6.5- 5.5	20674.34370
4(0, 4)- 3(0, 3)	3.5- 2.5	2.5- 1.5	1.5- 0.5	25001.04690
4(0, 4)- 3(0, 3)	3.5- 2.5	2.5- 1.5	2.5- 1.5	25001.07030
4(0, 4)- 3(0, 3)	3.5- 2.5	2.5- 1.5	3.5- 2.5	25001.16410
4(0, 4)- 3(0, 3)	3.5- 2.5	2.5- 1.5	4.5- 3.5	25001.54690
4(0, 4)- 3(0, 3)	3.5- 2.5	3.5- 2.5	1.5- 0.5	25002.26170
4(0, 4)- 3(0, 3)	3.5- 2.5	3.5- 2.5	2.5- 1.5	25001.04690
4(0, 4)- 3(0, 3)	3.5- 2.5	3.5- 2.5	3.5- 2.5	25001.04690
4(0, 4)- 3(0, 3)	3.5- 2.5	3.5- 2.5	4.5- 3.5	25001.05080
4(0, 4)- 3(0, 3)	3.5- 2.5	3.5- 2.5	5.5- 4.5	25001.13670
4(0, 4)- 3(0, 3)	3.5- 2.5	4.5- 3.5	2.5- 1.5	25001.55080
4(0, 4)- 3(0, 3)	3.5- 2.5	4.5- 3.5	3.5- 2.5	25001.04690
4(0, 4)- 3(0, 3)	3.5- 2.5	4.5- 3.5	4.5- 3.5	25001.04690
4(0, 4)- 3(0, 3)	3.5- 2.5	4.5- 3.5	5.5- 4.5	25001.05080
4(0, 4)- 3(0, 3)	3.5- 2.5	4.5- 3.5	6.5- 5.5	25009.60160
4(0, 4)- 3(0, 3)	4.5- 3.5	3.5- 2.5	1.5- 0.5	24972.53910
4(0, 4)- 3(0, 3)	4.5- 3.5	3.5- 2.5	2.5- 1.5	24959.07810
4(0, 4)- 3(0, 3)	4.5- 3.5	3.5- 2.5	3.5- 2.5	24959.07810
4(0, 4)- 3(0, 3)	4.5- 3.5	3.5- 2.5	4.5- 3.5	24959.12110
4(0, 4)- 3(0, 3)	4.5- 3.5	3.5- 2.5	5.5- 4.5	24959.21090
4(0, 4)- 3(0, 3)	4.5- 3.5	4.5- 3.5	2.5- 1.5	24959.98830
4(0, 4)- 3(0, 3)	4.5- 3.5	4.5- 3.5	3.5- 2.5	24959.07810
4(0, 4)- 3(0, 3)	4.5- 3.5	4.5- 3.5	4.5- 3.5	24959.07810

4(0, 4)- 3(0, 3)	4.5- 3.5	4.5- 3.5	5.5- 4.5	24959.10550
4(0, 4)- 3(0, 3)	4.5- 3.5	4.5- 3.5	6.5- 5.5	24959.54690
4(0, 4)- 3(0, 3)	4.5- 3.5	5.5- 4.5	3.5- 2.5	24959.21870
4(0, 4)- 3(0, 3)	4.5- 3.5	5.5- 4.5	4.5- 3.5	24959.07810
4(0, 4)- 3(0, 3)	4.5- 3.5	5.5- 4.5	5.5- 4.5	24959.07810
4(0, 4)- 3(0, 3)	4.5- 3.5	5.5- 4.5	6.5- 5.5	24959.17190
4(0, 4)- 3(0, 3)	4.5- 3.5	5.5- 4.5	7.5- 6.5	24721.13670
3(0, 3)- 2(0, 2)	2.5- 1.5	1.5- 0.5	1.5- 0.5	19311.49610
3(0, 3)- 2(0, 2)	2.5- 1.5	1.5- 0.5	2.5- 1.5	19312.27340
3(0, 3)- 2(0, 2)	2.5- 1.5	1.5- 0.5	3.5- 2.5	19312.57810
3(0, 3)- 2(0, 2)	2.5- 1.5	2.5- 1.5	1.5- 0.5	19308.88670
3(0, 3)- 2(0, 2)	2.5- 1.5	2.5- 1.5	2.5- 1.5	19309.37890
3(0, 3)- 2(0, 2)	2.5- 1.5	2.5- 1.5	3.5- 2.5	19309.64060
3(0, 3)- 2(0, 2)	2.5- 1.5	2.5- 1.5	4.5- 3.5	19310.18360
3(0, 3)- 2(0, 2)	2.5- 1.5	3.5- 2.5	1.5- 0.5	19308.91410
3(0, 3)- 2(0, 2)	2.5- 1.5	3.5- 2.5	2.5- 1.5	19308.88670
3(0, 3)- 2(0, 2)	2.5- 1.5	3.5- 2.5	3.5- 2.5	19308.88670
3(0, 3)- 2(0, 2)	2.5- 1.5	3.5- 2.5	4.5- 3.5	19309.01950
3(0, 3)- 2(0, 2)	2.5- 1.5	3.5- 2.5	5.5- 4.5	19242.48440
3(0, 3)- 2(0, 2)	3.5- 2.5	2.5- 1.5	1.5- 0.5	19241.36720
3(0, 3)- 2(0, 2)	3.5- 2.5	2.5- 1.5	2.5- 1.5	19241.69140
3(0, 3)- 2(0, 2)	3.5- 2.5	2.5- 1.5	3.5- 2.5	19241.73050
3(0, 3)- 2(0, 2)	3.5- 2.5	2.5- 1.5	4.5- 3.5	19242.47270
3(0, 3)- 2(0, 2)	3.5- 2.5	3.5- 2.5	1.5- 0.5	19241.85160
3(0, 3)- 2(0, 2)	3.5- 2.5	3.5- 2.5	2.5- 1.5	19241.36720
3(0, 3)- 2(0, 2)	3.5- 2.5	3.5- 2.5	3.5- 2.5	19241.36720
3(0, 3)- 2(0, 2)	3.5- 2.5	3.5- 2.5	4.5- 3.5	19241.41410
3(0, 3)- 2(0, 2)	3.5- 2.5	3.5- 2.5	5.5- 4.5	19241.55470
3(0, 3)- 2(0, 2)	3.5- 2.5	4.5- 3.5	2.5- 1.5	19241.47660
3(0, 3)- 2(0, 2)	3.5- 2.5	4.5- 3.5	3.5- 2.5	19241.36720
3(0, 3)- 2(0, 2)	3.5- 2.5	4.5- 3.5	4.5- 3.5	19241.36720
3(0, 3)- 2(0, 2)	3.5- 2.5	4.5- 3.5	5.5- 4.5	19241.34770
3(0, 3)- 2(0, 2)	3.5- 2.5	4.5- 3.5	6.5- 5.5	19035.43750
3(2, 2)- 2(2, 1)	2.5- 1.5	1.5- 0.5	1.5- 0.5	20076.48050
3(2, 2)- 2(2, 1)	2.5- 1.5	1.5- 0.5	2.5- 1.5	20076.50780
3(2, 2)- 2(2, 1)	2.5- 1.5	1.5- 0.5	3.5- 2.5	20076.62500
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	1.5- 0.5	20075.01560
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	2.5- 1.5	20075.43750
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	3.5- 2.5	20075.43360
3(2, 2)- 2(2, 1)	2.5- 1.5	2.5- 1.5	4.5- 3.5	20076.19140
3(2, 2)- 2(2, 1)	2.5- 1.5	3.5- 2.5	1.5- 0.5	20075.08200
3(2, 2)- 2(2, 1)	2.5- 1.5	3.5- 2.5	2.5- 1.5	20075.01560
3(2, 2)- 2(2, 1)	2.5- 1.5	3.5- 2.5	3.5- 2.5	20075.01560
3(2, 2)- 2(2, 1)	2.5- 1.5	3.5- 2.5	4.5- 3.5	20075.03520
3(2, 2)- 2(2, 1)	2.5- 1.5	3.5- 2.5	5.5- 4.5	20074.32420
3(2, 2)- 2(2, 1)	3.5- 2.5	2.5- 1.5	1.5- 0.5	20018.41410
3(2, 2)- 2(2, 1)	3.5- 2.5	2.5- 1.5	2.5- 1.5	20018.50780
3(2, 2)- 2(2, 1)	3.5- 2.5	2.5- 1.5	3.5- 2.5	20018.55080
3(2, 2)- 2(2, 1)	3.5- 2.5	2.5- 1.5	4.5- 3.5	20019.22660
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	1.5- 0.5	20019.16410

3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	2.5- 1.5	20018.41410
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	3.5- 2.5	20018.41410
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	4.5- 3.5	20018.44140
3(2, 2)- 2(2, 1)	3.5- 2.5	3.5- 2.5	5.5- 4.5	20018.30080
3(2, 2)- 2(2, 1)	3.5- 2.5	4.5- 3.5	2.5- 1.5	20018.56250
3(2, 2)- 2(2, 1)	3.5- 2.5	4.5- 3.5	3.5- 2.5	20018.41410
3(2, 2)- 2(2, 1)	3.5- 2.5	4.5- 3.5	4.5- 3.5	20018.41410
3(2, 2)- 2(2, 1)	3.5- 2.5	4.5- 3.5	5.5- 4.5	20018.38670
3(2, 2)- 2(2, 1)	3.5- 2.5	4.5- 3.5	6.5- 5.5	19907.10160
3(2, 1)- 2(2, 0)	2.5- 1.5	1.5- 0.5	1.5- 0.5	20805.78520
3(2, 1)- 2(2, 0)	2.5- 1.5	1.5- 0.5	2.5- 1.5	20806.86330
3(2, 1)- 2(2, 0)	2.5- 1.5	1.5- 0.5	3.5- 2.5	20806.97660
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	1.5- 0.5	20805.51170
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	2.5- 1.5	20805.83590
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	3.5- 2.5	20805.92190
3(2, 1)- 2(2, 0)	2.5- 1.5	2.5- 1.5	4.5- 3.5	20806.55470
3(2, 1)- 2(2, 0)	2.5- 1.5	3.5- 2.5	1.5- 0.5	20805.61330
3(2, 1)- 2(2, 0)	2.5- 1.5	3.5- 2.5	2.5- 1.5	20805.51170
3(2, 1)- 2(2, 0)	2.5- 1.5	3.5- 2.5	3.5- 2.5	20805.51170
3(2, 1)- 2(2, 0)	2.5- 1.5	3.5- 2.5	4.5- 3.5	20805.53520
3(2, 1)- 2(2, 0)	2.5- 1.5	3.5- 2.5	5.5- 4.5	20805.00780
3(2, 1)- 2(2, 0)	3.5- 2.5	2.5- 1.5	1.5- 0.5	20786.07420
3(2, 1)- 2(2, 0)	3.5- 2.5	2.5- 1.5	2.5- 1.5	20786.12500
3(2, 1)- 2(2, 0)	3.5- 2.5	2.5- 1.5	3.5- 2.5	20786.21090
3(2, 1)- 2(2, 0)	3.5- 2.5	2.5- 1.5	4.5- 3.5	20786.89450
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	1.5- 0.5	20786.87500
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	2.5- 1.5	20786.07420
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	3.5- 2.5	20786.07420
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	4.5- 3.5	20786.08590
3(2, 1)- 2(2, 0)	3.5- 2.5	3.5- 2.5	5.5- 4.5	20785.94530
3(2, 1)- 2(2, 0)	3.5- 2.5	4.5- 3.5	2.5- 1.5	20786.23830
3(2, 1)- 2(2, 0)	3.5- 2.5	4.5- 3.5	3.5- 2.5	20786.07420
3(2, 1)- 2(2, 0)	3.5- 2.5	4.5- 3.5	4.5- 3.5	20786.07420
3(2, 1)- 2(2, 0)	3.5- 2.5	4.5- 3.5	5.5- 4.5	20786.05080
3(2, 1)- 2(2, 0)	3.5- 2.5	4.5- 3.5	6.5- 5.5	20674.34370

THE FOLLOWING ARE TRANSITIONS OF IH= 3 AND IN= 1

4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	1.5- 0.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	2.5- 1.5	24069.82030
4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	3.5- 2.5	24070.14450
4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	4.5- 3.5	24070.12500
4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	5.5- 4.5	24070.46480
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	1.5- 0.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	2.5- 1.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	3.5- 2.5	24069.77340
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	4.5- 3.5	24069.95700
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	5.5- 4.5	24070.15230
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	6.5- 5.5	24069.76560
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	1.5- 0.5	24070.08200
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	2.5- 1.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	3.5- 2.5	24069.73440

4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	4.5- 3.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	5.5- 4.5	24069.80470
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	6.5- 5.5	24069.69140
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	7.5- 6.5	23991.58200
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	1.5- 0.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	2.5- 1.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	3.5- 2.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	4.5- 3.5	24030.13280
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	5.5- 4.5	24030.34770
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	6.5- 5.5	24030.42970
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	1.5- 0.5	24031.37500
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	2.5- 1.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	3.5- 2.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	4.5- 3.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	5.5- 4.5	24030.03520
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	6.5- 5.5	24029.89060
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	7.5- 6.5	24030.58980
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	2.5- 1.5	24030.59370
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	3.5- 2.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	4.5- 3.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	5.5- 4.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	6.5- 5.5	24029.98440
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	7.5- 6.5	24030.32030
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	8.5- 7.5	23810.82420
3(1, 3)- 2(1, 2)	2.5- 1.5	1.5- 0.5	1.5- 0.5	18208.12500
3(1, 3)- 2(1, 2)	2.5- 1.5	1.5- 0.5	2.5- 1.5	18209.99220
3(1, 3)- 2(1, 2)	2.5- 1.5	1.5- 0.5	3.5- 2.5	18210.93750
3(1, 3)- 2(1, 2)	2.5- 1.5	1.5- 0.5	4.5- 3.5	18210.66410
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	1.5- 0.5	18207.33980
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	2.5- 1.5	18207.86720
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	3.5- 2.5	18208.41020
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	4.5- 3.5	18208.28120
3(1, 3)- 2(1, 2)	2.5- 1.5	2.5- 1.5	5.5- 4.5	18208.94140
3(1, 3)- 2(1, 2)	2.5- 1.5	3.5- 2.5	1.5- 0.5	18207.11330
3(1, 3)- 2(1, 2)	2.5- 1.5	3.5- 2.5	2.5- 1.5	18207.11330
3(1, 3)- 2(1, 2)	2.5- 1.5	3.5- 2.5	3.5- 2.5	18207.22270
3(1, 3)- 2(1, 2)	2.5- 1.5	3.5- 2.5	4.5- 3.5	18207.41020
3(1, 3)- 2(1, 2)	2.5- 1.5	3.5- 2.5	5.5- 4.5	18207.71870
3(1, 3)- 2(1, 2)	2.5- 1.5	3.5- 2.5	6.5- 5.5	18239.31250
3(1, 3)- 2(1, 2)	3.5- 2.5	2.5- 1.5	1.5- 0.5	18157.16410
3(1, 3)- 2(1, 2)	3.5- 2.5	2.5- 1.5	2.5- 1.5	18157.58980
3(1, 3)- 2(1, 2)	3.5- 2.5	2.5- 1.5	3.5- 2.5	18157.73050
3(1, 3)- 2(1, 2)	3.5- 2.5	2.5- 1.5	4.5- 3.5	18157.85940
3(1, 3)- 2(1, 2)	3.5- 2.5	2.5- 1.5	5.5- 4.5	18158.23830
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	1.5- 0.5	18157.16410
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	2.5- 1.5	18157.16410
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	3.5- 2.5	18157.23440
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	4.5- 3.5	18157.42580
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	5.5- 4.5	18157.60940
3(1, 3)- 2(1, 2)	3.5- 2.5	3.5- 2.5	6.5- 5.5	18157.31250

3(1, 3)- 2(1, 2)	3.5- 2.5	4.5- 3.5	1.5- 0.5	18157.22270
3(1, 3)- 2(1, 2)	3.5- 2.5	4.5- 3.5	2.5- 1.5	18157.16410
3(1, 3)- 2(1, 2)	3.5- 2.5	4.5- 3.5	3.5- 2.5	18157.16410
3(1, 3)- 2(1, 2)	3.5- 2.5	4.5- 3.5	4.5- 3.5	18157.17580
3(1, 3)- 2(1, 2)	3.5- 2.5	4.5- 3.5	5.5- 4.5	18157.24610
3(1, 3)- 2(1, 2)	3.5- 2.5	4.5- 3.5	6.5- 5.5	18157.15230
3(1, 3)- 2(1, 2)	3.5- 2.5	4.5- 3.5	7.5- 6.5	17982.51560
3(1, 2)- 2(1, 1)	2.5- 1.5	1.5- 0.5	1.5- 0.5	21647.71090
3(1, 2)- 2(1, 1)	2.5- 1.5	1.5- 0.5	2.5- 1.5	21649.32420
3(1, 2)- 2(1, 1)	2.5- 1.5	1.5- 0.5	3.5- 2.5	21649.07420
3(1, 2)- 2(1, 1)	2.5- 1.5	1.5- 0.5	4.5- 3.5	21649.02730
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	1.5- 0.5	21647.03910
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	2.5- 1.5	21647.47270
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	3.5- 2.5	21648.07420
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	4.5- 3.5	21647.58980
3(1, 2)- 2(1, 1)	2.5- 1.5	2.5- 1.5	5.5- 4.5	21648.36330
3(1, 2)- 2(1, 1)	2.5- 1.5	3.5- 2.5	1.5- 0.5	21646.81250
3(1, 2)- 2(1, 1)	2.5- 1.5	3.5- 2.5	2.5- 1.5	21646.81250
3(1, 2)- 2(1, 1)	2.5- 1.5	3.5- 2.5	3.5- 2.5	21646.91800
3(1, 2)- 2(1, 1)	2.5- 1.5	3.5- 2.5	4.5- 3.5	21647.10940
3(1, 2)- 2(1, 1)	2.5- 1.5	3.5- 2.5	5.5- 4.5	21647.35160
3(1, 2)- 2(1, 1)	2.5- 1.5	3.5- 2.5	6.5- 5.5	21678.77730
3(1, 2)- 2(1, 1)	3.5- 2.5	2.5- 1.5	1.5- 0.5	21616.25000
3(1, 2)- 2(1, 1)	3.5- 2.5	2.5- 1.5	2.5- 1.5	21616.64060
3(1, 2)- 2(1, 1)	3.5- 2.5	2.5- 1.5	3.5- 2.5	21616.80080
3(1, 2)- 2(1, 1)	3.5- 2.5	2.5- 1.5	4.5- 3.5	21616.87500
3(1, 2)- 2(1, 1)	3.5- 2.5	2.5- 1.5	5.5- 4.5	21617.25000
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	1.5- 0.5	21616.25000
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	2.5- 1.5	21616.25000
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	3.5- 2.5	21616.30860
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	4.5- 3.5	21616.51170
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	5.5- 4.5	21616.71480
3(1, 2)- 2(1, 1)	3.5- 2.5	3.5- 2.5	6.5- 5.5	21616.34770
3(1, 2)- 2(1, 1)	3.5- 2.5	4.5- 3.5	1.5- 0.5	21616.31250
3(1, 2)- 2(1, 1)	3.5- 2.5	4.5- 3.5	2.5- 1.5	21616.25000
3(1, 2)- 2(1, 1)	3.5- 2.5	4.5- 3.5	3.5- 2.5	21616.25000
3(1, 2)- 2(1, 1)	3.5- 2.5	4.5- 3.5	4.5- 3.5	21616.25390
3(1, 2)- 2(1, 1)	3.5- 2.5	4.5- 3.5	5.5- 4.5	21616.33980
3(1, 2)- 2(1, 1)	3.5- 2.5	4.5- 3.5	6.5- 5.5	21616.23050
3(1, 2)- 2(1, 1)	3.5- 2.5	4.5- 3.5	7.5- 6.5	21441.53910
4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	1.5- 0.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	2.5- 1.5	24069.82030
4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	3.5- 2.5	24070.14450
4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	4.5- 3.5	24070.12500
4(1, 4)- 3(1, 3)	3.5- 2.5	2.5- 1.5	5.5- 4.5	24070.46480
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	1.5- 0.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	2.5- 1.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	3.5- 2.5	24069.77340
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	4.5- 3.5	24069.95700
4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	5.5- 4.5	24070.15230

4(1, 4)- 3(1, 3)	3.5- 2.5	3.5- 2.5	6.5- 5.5	24069.76560
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	1.5- 0.5	24070.08200
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	2.5- 1.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	3.5- 2.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	4.5- 3.5	24069.73440
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	5.5- 4.5	24069.80470
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	6.5- 5.5	24069.69140
4(1, 4)- 3(1, 3)	3.5- 2.5	4.5- 3.5	7.5- 6.5	23991.58200
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	1.5- 0.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	2.5- 1.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	3.5- 2.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	4.5- 3.5	24030.13280
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	5.5- 4.5	24030.34770
4(1, 4)- 3(1, 3)	4.5- 3.5	3.5- 2.5	6.5- 5.5	24030.42970
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	1.5- 0.5	24031.37500
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	2.5- 1.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	3.5- 2.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	4.5- 3.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	5.5- 4.5	24030.03520
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	6.5- 5.5	24029.89060
4(1, 4)- 3(1, 3)	4.5- 3.5	4.5- 3.5	7.5- 6.5	24030.58980
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	2.5- 1.5	24030.59370
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	3.5- 2.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	4.5- 3.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	5.5- 4.5	24029.98050
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	6.5- 5.5	24029.98440
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	7.5- 6.5	24030.32030
4(1, 4)- 3(1, 3)	4.5- 3.5	5.5- 4.5	8.5- 7.5	23810.82420

Bibliography

- 1) Cook, J.M., Hills, G.W. and Curl, R.F., J. Chem. Phys. 67, 1450 (1977).
- 2) Y. Endo, C. Yamada, S. Saito and E. Hirota, J. Chem. Phys. 77, 3376, (1982).
- 3) White, R.M., Dissertation at VPI&SU 1986.
- 4) G. Herzberg, "Spectra to Structures of Simple Free Radicals, An Introduction to Molecular Spectroscopy", Cornell Press, NY, 1971.
- 5) Carrington, A. "Microwave Molecular Spectra", Academic Press, London, 1974.
- 6) Gordy, W. and Cook, R.L., "Microwave Molecular Spectra", Interscience Publishers, NY, 1970.
- 7) Townes, C.H. and Schaulow, A.C., "Microwave Spectroscopy", McGraw Hill, NY, 1955.
- 8) Dousmanis, G.C., Sanders, T.C., Towner, C.H., Phys. Rev. 100, 1735, (1955).
- 9) Powell, F.X., Lide, D.R., J. Chem. Phys. 41, 1413, (1964).
- 10) Tulât-Erben, M. and Bywater, S., J. Am. Chem. Soc. 77, 3710, (1955).
- 11) Bullock, A.J., Burnette, G.M., Kerr, C.M.L., European Polymer Journal, 7, 1011-1019, (1971).
- 12) Bichutinski, A.A., Prokofiev, A.I. and Shabalkin, V.A., Russ J. Phys. Chem. 38, 534, (1964).
- 13) Livingston, R., Zeldes, H. J. Mag. Res., 1(1), 169-77 (1969).
- 14) Moriuchi, S., Junkichi, S., Molecular Physics, 21(2) 369-371 (1971).

- 15) Lien, M.H., Hopkinson, A.C., *Journal of Computational Chemistry*, 6(4) 274-281 (1985).
- 16) Peterson, M.R., Puirier, R.A., MONSTERGAUSS, University of Toronto (1980).
- 17) Criller, D., Marriott, P.R., Preston, K.F., *J. Chem. Phys.* 71, 3703, (1979).
- 18) Bowater, I.C., Brown, J.M., and A. Carrington, "Proc. R. Soc. London, Sev, A333, 265, (1973).
- 19) Wigner, E.P. (1940), "On the Matrices Which Reduce the Kronecker Products of Representations of Spin-Rotation Groups", Reprinted in "Quantum Theory of Angular Momentum", L.C. Biedenharn and H. VanDam, Editors, Academic Press N.Y., 1965.
- 20) Buckmaster, H.A., Chatterjee, R. and Shing, *Phys. Stat. Sol.A.* 13(9) 1972.
- 21) Wigner, E.P. "Group Theory and its Application to Quantum Mechanics of Atomic Spectra", Academic Press, NY, 1959.
- 22) V. Heine "Group Theory in Quantum Mechanics", Pergamon, Oxford, 1960.
- 23) M. Tinkham, "Group Theory and Quantum Mechanics", McGraw Hill, New York, 1964.
- 24) Silver, B.L. "Irreducible Tensor Methods, An Introduction for Chemists", Academic Press, New York, 1976.
- 25) Silver, p.40.
- 26) Edmunds, A.R. "Angular Momentum in Quantum Mechanics", Princeton University Press, Princeton, 1957, p.91.
- 27) Wigner, E.P. "Group Theory", Academic Press, 1959.
- 28) Edmonds, p.100.
- 29) Silver, p.84.
- 30) Dirac, P.A.M., "Principles of Quantum Mechanics", Oxford, 1947.
- 31) Silver, p.52.
- 32) Condon and Shortly, "Theory of Atomic Spectra, Cambridge, 1955.
- 33) Silver, p.58.
- 34) Silver, p.58

- 35) Eckert, C., "The Application of Group Theory to Quantum Dynamic of Monatomic Systems", Rev. Mod. Physics, 2, 305-380 (1930).
- 36) Edmonds, p.76.
- 37) Silver, p.88
- 38) Gordy, W., and Cook, R.L., p.8.
- 39) Harmony, M.D. "Introduction to Molecular Energies and Spectra", Holt, Rhinehart and Winston, New York, (1972).
- 40) Townes, C.H. and Schawlow, A.C., p.26.
- 41) King, G.W., Harrier, R.M., Cross, P.C., J. Chem. Phys. 11, 27, (1943).
- 42) Herzberg, G. "Electronic Spectra of Polyatomic Molecules", Van Nostrand Rneinhold, New York, 1966.
- 43) Hirota, E., "High Resolution Spectroscopy of Transient Molecules", Springer-Verlag, New York, 1985, p.20.
- 44) Van Vleck, J.H., Rev. Mod. Phys., 23, 213, (1951).
- 45) Hirota, E., p.26.
- 46) Brown, J.M. and T.J. Sears, J. Mol. Spectrosc. 75, 111, (1979).
- 47) Cook, R.L. and Delucia, F.C., Am. J. Phys., 39, 1433, (1971).
- 48) Hirota, E. p.34.
- 49) Curl, R.L., Private Communication.
- 50) Rabjohn, J. (Chief Editor) "Organic Synthesis, Collective Volume 4", John wiley & Sons, New York, 1963, p.274, 66.
- 51) wertz, J.E. and Bolton, J.R., "Electron Spin Resonance", Chapman and Hall, New York, 1986, p.349.
- 52) Hills, G.W., Cook, J.M., J. Molec. Spectosc. 94, 456 (1982).
- 53) Davies, P.B., Russell, D.K., Thrush, B.A. and Radford, H.E., Chem. Phys. 44, 42 (1979).
- 54) Brown, R.D., Burden, F.R., Godfrey, P.D. and Gillard, I.R., J. Mole. Spectrosc. 52, 301, (1974).
- 55) Endo, Y., Yamada, C., Saito, S. and Hirota, E., J. Chem. Phys. 79 1605 (1983).

- 56) Endo, Y., Saito, S., Hirota, E., Canadian J. Physics, 62, 1347 (1984).
- 57) Bowman, W.C., DeLucia, F.C., J. Chem. Phys. 75, 5256, (1981).
- 58) Sutton, L.E. (Chief Editor), "Tables of Interatomic Distances and Configurations in Molecules and Ions", Burlington House, London, 1965.
- 59) Swalen, J.D., Constain, C.C., J. Chem. Phys. 31(6) 1562 (1959).
- 60) Gaussian 80, Binkley, J.U.S., Whiteside, R.A., Krishnan, R., Seeger, R., DeFrees, D.J., Schlegel, H.B., Topiol, S., Kann, L.R. and Pople, J.A., Dept. of Chemistry, Carnegie Mellon Univ., (1980).
- 61) Curl, R.F., Mol. Phys. 9, 585, (1965).
- 62) Morton, J.R., Preston, K.F., J. Mag. Res. 30, 577, (1978).
- 63) Endo, Y., Saito, S. Hirota, E. J. Molec. Spectrosc. 97, 204 (1983).
- 64) Kirchoff, W.H. J. Molec. Spectrosc., 41, 333 (1972).
- 65) Schwendemann, R.H. "Critical Evaluation of Chemical and Physical Structural Information", National Academy of Sciences, Washington, D.C. 1974.
- 66) Y. Endo, S. Saito, E. Hirota: J. Chem. Phys. 81, 122 (1984).
- 67) Russell, D.K., Radford, H.E., J. Chem. Phys. 72, 2750 (1980).
- 68) H.E. Radford, D.K. Russell, J. Chem. Phys. 66, 2222 (1977).
- 69) Yamada, Y. Hirota, E., Kawaguchi, K., J. Chem. Phys. 75, 5256 (1981).
- 70) Laurie, V.W., J. Chem. Phys. 28 704 (1958).
- 71) Swalen, J.C., Constain, C.C., J. Chem. Phys. 31(6), 1562 (1959).

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