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HYPERFINE STRUCTURE IN THE ROTATIONAL SPECTRUM OF ASYMMETRIC-TOP MOLECULES CONTAINING TWO IDENTICAL QUADRUPOLAR NUCLEI

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CHAPTER I

INTRODUCTION

The theory leading up to the study of the hyperfine structure of the asymmetric rotor spectrum has been developed over a period of 40 years. The theory of the rotational spectrum of an asymmetric rotor was presented in complete form by King, Hainer and Cross (1), including discussions of wavefunction symmetry and a perturbation method of obtaining rotational energy. In a second paper on the asymmetric rotor, Cross, Hainer and King discussed the selection rules for the rotor (2). The method used in this work for obtaining the rotational energy levels of the rotor differed from that of the above authors in that the Hamiltonian matrix for each J level was diagonalized by a computer to obtain energy eigenvalues instead of using second-order perturbation theory.

In 1936 Casimir (3) treated the interaction between a quadrupolar nucleus and atomic electrons for a single atom and this was extended to the case of a single quadrupolar nucleus in a symmetric-top molecule by Low and Townes (4). The case of two quadrupolar nuclei in a symmetric rotor was treated by Bardeen and Townes (5) using the vector coupling algebra developed by Racah (6), (7), (8) a few years before to couple the spins of the nuclei. Bersohn (9) derived expressions for treating the quadrupole interaction of two or more nuclei in terms of the algebra of irreducible tensor operators which was also developed by Racah in the above papers. More recently Flygare and Gwinn (10) developed expressions for diagonal and off-diagonal matrix elements of the quadrupole Hamiltonian for an asymmetric rotor in terms of parameters which are explicitly evaluated in this work.

The purpose of this research is to completely develop and test the theory of the quadrupole interaction in an asymmetric rotor molecule containing two identical quadrupolar nuclei. The observed spectra of such molecules contains transition patterns displaying varying degrees of asymmetry. The diagonal matrix elements of the quadrupole Hamiltonian obtained in the theory when applied to a molecule through first-order perturbation theory lead only to predicted patterns which are symmetric for even-τ transitions. Thus, it was hoped, the derivation of off-diagonal matrix elements and their application through second-order perturbation theory would lead to a theoretical explanation of the slightly asymmetric patterns in even-τ transitions. The off-diagonal elements involve the off-diagonal element of the quadrupole coupling constant tensor, $\chi_{x'y'}$, (as well as the diagonal elements), and accurate predictions of asymmetric transition patterns should lead to a determination of this otherwise unobtainable physical parameter. This component of the tensor is related through a transformation to the angle between the molecular symmetry axis and the z-principal axis of the dyadic. (See Figure 7).

The quadrupole moment of bromine is large enough to lead to second-order, asymmetric effects of a magnitude which should be easily measurable, e.g., 0.5 to 1 MHz. Originally it was intended to observe the spectra of asymmetric-tops containing bromine such as CH_2Br_2 and CF_2Br_2. However, these molecules were found to have high-J transitions of large intensity in the same region as the desirable low-J, low intensity transitions. Both these molecules possess two sets of identical nuclei. The Exclusion Principle applied to them results in many more allowable states than would exist in a molecule with just one pair of identical nuclei. The complication of the resulting spectrum of both molecules prevented assignment of either spectrum.

Attention was then directed at $S^{32}C\ell_2^{35}$ for two main reasons, even though the quadrupole moment of chlorine is considerably smaller than that of bromine: (1) The only previously published work on $SC\ell_2$ in the microwave region was done in this laboratory by J. T. Murray (11). There was therefore a certain degree of familiarity with the behavior of the molecule. Also the spectrum of $SC\ell_2$ in the microwave region had been assigned in this laboratory on basically the same apparatus as was to be used in this work. (2) Murray's work had analyzed the quadrupole spectrum of the molecule to first-order and thus predicted symmetric patterns of transitions. Several transitions had been observed to be asymmetric, and, it was hoped that employing second-order theory would lead to a better determination of the diagonal elements of the coupling constant tensor as well as a first determination of the off-diagonal element.

Chapter II contains a description of the general experimental setup of the microwave spectrometer as well as a fairly detailed treatment of the Waveform Eductor, a new piece of apparatus in this laboratory, which was used in data taking.

Chapter III discusses the theoretical development of the quadrupole interaction in the asymmetric-top with two identical nuclei. Parts of this theory may be found in many references, however the entire theory with a computer program for calculations is presented here.

The analysis of experimental data is presented in Chapter IV, followed by a discussion comparing the observed spectrum of $SC\ell_2$ with the theoretical predictions in Chapter V. The Appendices contain derivations, examples and programming necessary for a complete presentation of the problem.

CHAPTER II

EXPERIMENTAL APPARATUS AND TECHNIQUES

The apparatus used in this work involved a Stark-modulated spectrometer which has been described in various forms by several authors (12), (13). An important difference in this work, however, is that data was taken with the aid of a Princeton Applied Research Corporation Waveform Eductor, a device designed to extract repetitive waveforms from noise.

This chapter will provide a description of the apparatus from the point of view of subsystems, a more detailed discussion of the Eductor, and a section on preparation and use of the sample of $SC\ell_2$.

Equipment Layout

Figure (1) shows the general layout of the apparatus involved in the microwave spectrometer. It has been divided into four main sections or subsystems which will be described below.

The Microwave System - Number One

Microwave energy is provided by a reflex klystron which may be electrically swept rapidly, or mechanically or electrically tuned slowly over the frequency range of interest. After passing through monitoring equipment the energy enters the absorption cell through hermetically sealed mylar windows.

The cell is about seventeen feet of rectangular hollow waveguide in which a conducting plate is supported by teflon strips. The plate

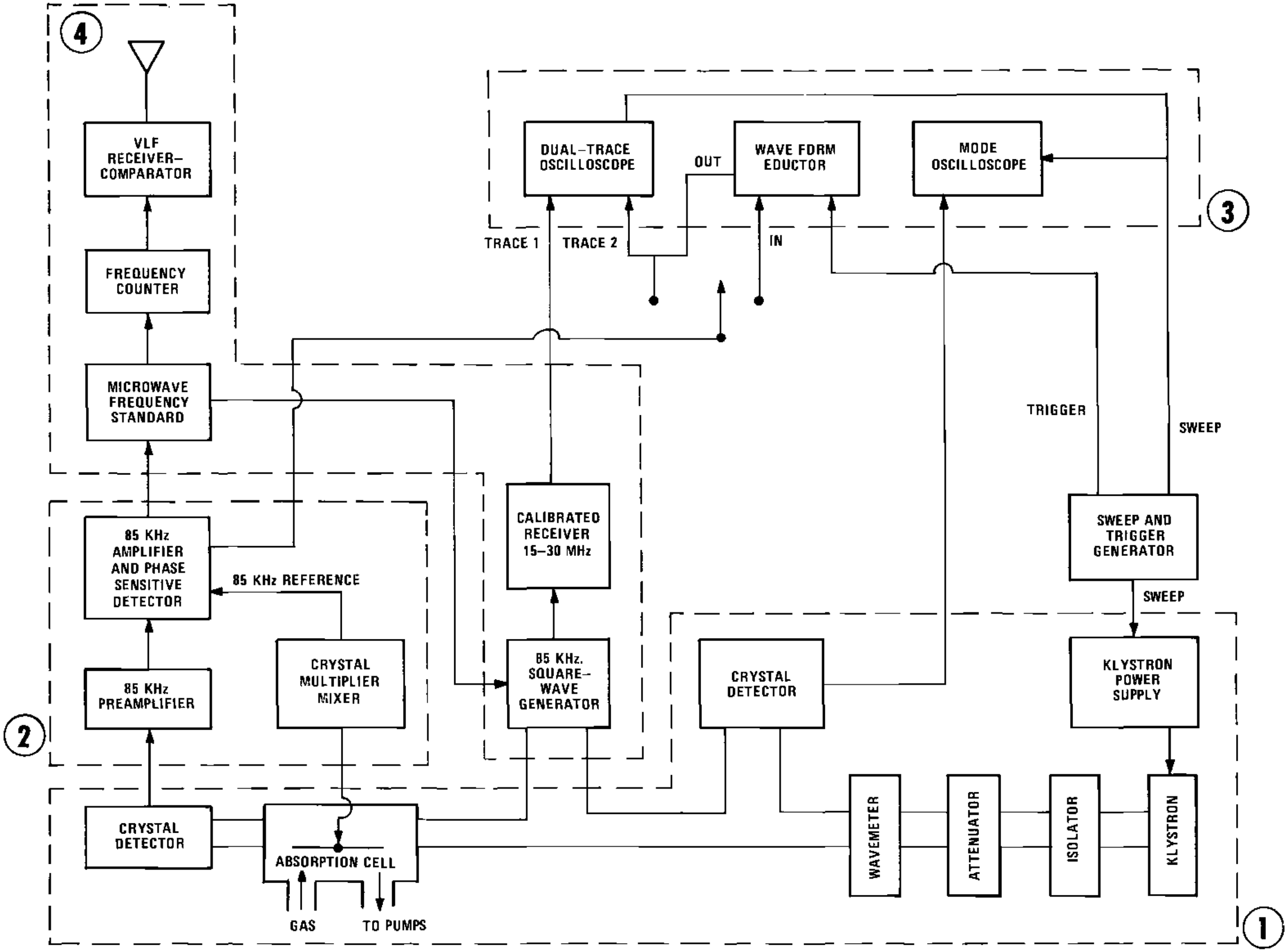

Figure 1. Block Diagram of the Microwave Spectrometer.

is parallel to the broad dimension of the waveguide and, with the sides of the guide, forms the load capacitor for the Stark voltage generator. The gas to be investigated is admitted into the guide at one end. It may be kept at low pressure - typically in the range 30 to 70 microns - by pumps attached to the guide, and at low temperature by placing dry ice on the guide. The net energy coming out of the absorption cell passes through another mylar window into a crystal detector.

The Stark Modulation System - Number Two

An 85 kHz square wave voltage is applied between the conducting plate and the walls of the absorption cell by the Stark square wave generator. If the amount of incoming microwave energy absorbed by the gas is different for the Stark-field-on case and the Stark-field-off case, the microwave power at the detector will fluctuate at the rate of 85 kHz. The magnitude and phase of the detected signal, with respect to the original 85 kHz signal from the generator, is determined by phase comparator circuitry in the 85 kHz receiver. This has been well described by Reinhart (14). Absorptions which occur during the field-on half-cycle of the square wave produce a negative output signal, while those occurring during the field-off half-cycle produce a positive output. Thus the spectrum of the molecule resulting from the Stark effect can be distinguished from the field-free spectrum.

It should be noted that the amplitude of the square wave is variable from zero to one thousand volts, so the magnitude of the Stark effect is controllable. This, plus the different polarity of the field-on and field-off signals, would lead one to hope that he might eliminate the Stark effect from consideration. One would hope to move the Stark spectrum far enough away from the field-free spectrum so that the Stark spectrum could be neglected. In some transitions the Stark voltage could not be increased enough to accomplish this because the cell would arc-over past a certain voltage.

The amplified output of the phase sensitive detector is sent to the spectrum display apparatus.

The Spectrum Display System - Number Three

The output of the phase sensitive detector may be applied to one channel of the dual-trace oscilloscope directly, or it may be analyzed by the Waveform Eductor and then applied to the oscilloscope. (The operation of the Eductor will be explained in more detail below).

The oscilloscope is swept horizontally on both traces by the same sweep generator that sweeps the klystron. The amplitude of the sweep may be altered, thus changing the frequency range over which the klystron is swept. The slope of the sawtooth sweep may be inverted to change the direction of the sweep in terms of frequency. The need for this arises because in sweeping over the absorption line the slight time delay suffered by the line in the lock-in output filter causes a small displacement of the line peak from its true position. Inversion of the sawtooth causes the apparent displacement of the line to be of the same magnitude but in the opposite direction. Data taking involves both types of readings.

The other trace of the dual-trace oscilloscope displays a frequency marker which is produced by the Frequency Measurement System.

The Frequency Measurement System - Number Four

Frequencies are measured by mixing the output of the klystron and a Micro-Now frequency multiplier chain. The fundamental frequency of the multiplier chain may be set to any frequency in the interval 4.979 MHz to 5.006 MHz. This frequency is measured by a Hewlett-Packard frequency counter. The counter operates by counting the oscillations of the input signal over a very exact time gate which is determined by an internally generated 1 MHz frequency from a crystal controlled oscillator. The frequency of the oscillator in the frequency counter is checked continuously by comparison with a frequency received from WWVB or WWVL in Boulder, Colorado. The beat note between the reference frequency and the oscillator frequency is plotted by a VLF comparator and allows an immediate estimate of the accuracy of the counter.

As is described by Reinhart (15), strong harmonics of the multiplier chain are found at about every 50 MHz. Some multiple of this is mixed with the klystron frequency to produce a beat note. When the beat frequency coincides with the frequency at which the receiver is set, the receiver produces an audio signal which is displayed on one trace of the dual-trace oscilloscope along with the signal from the absorption cell. The position of the marker was varied in this experiment by changing the fundamental frequency of the multiplier chain. The oscilloscope display looked like Figure (2).

The Waveform Eductor

A simplified block diagram of the Eductor is shown in Figure (3). It consists of four main subsystems, the signal input channel, the memory, the timing and control system, and the signal output channel.

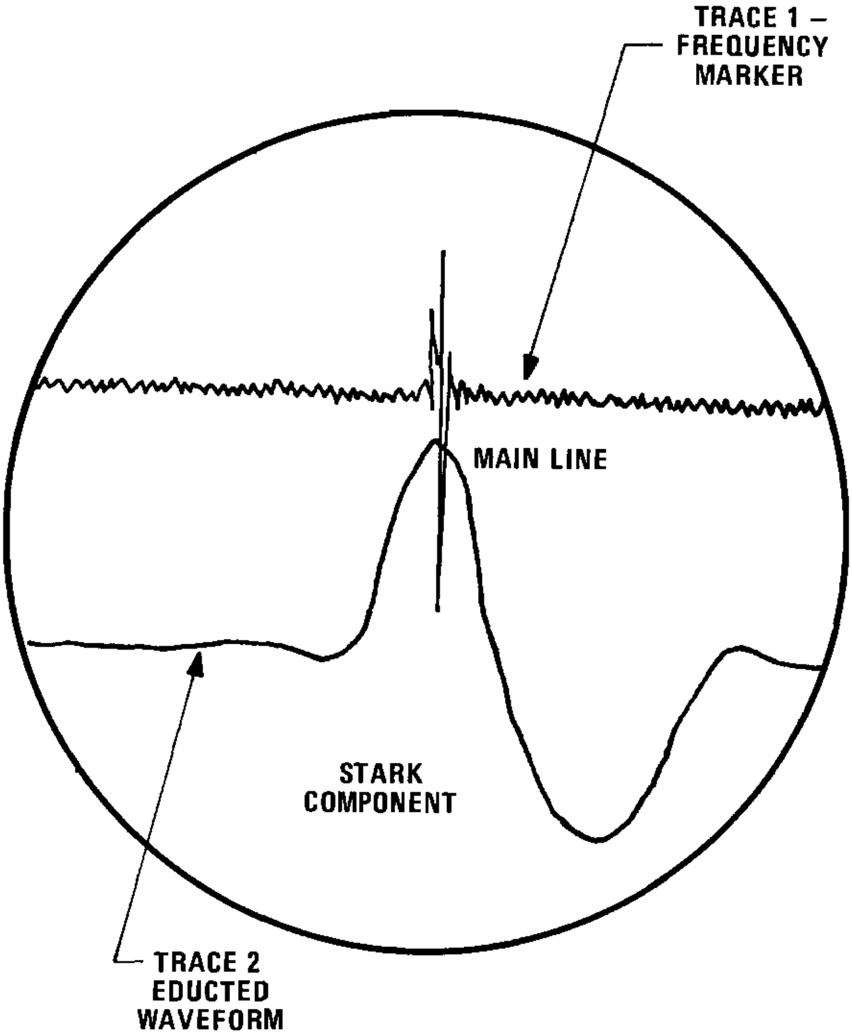

Figure 2. Dual-Trace Oscilloscope Display for Data Taking.

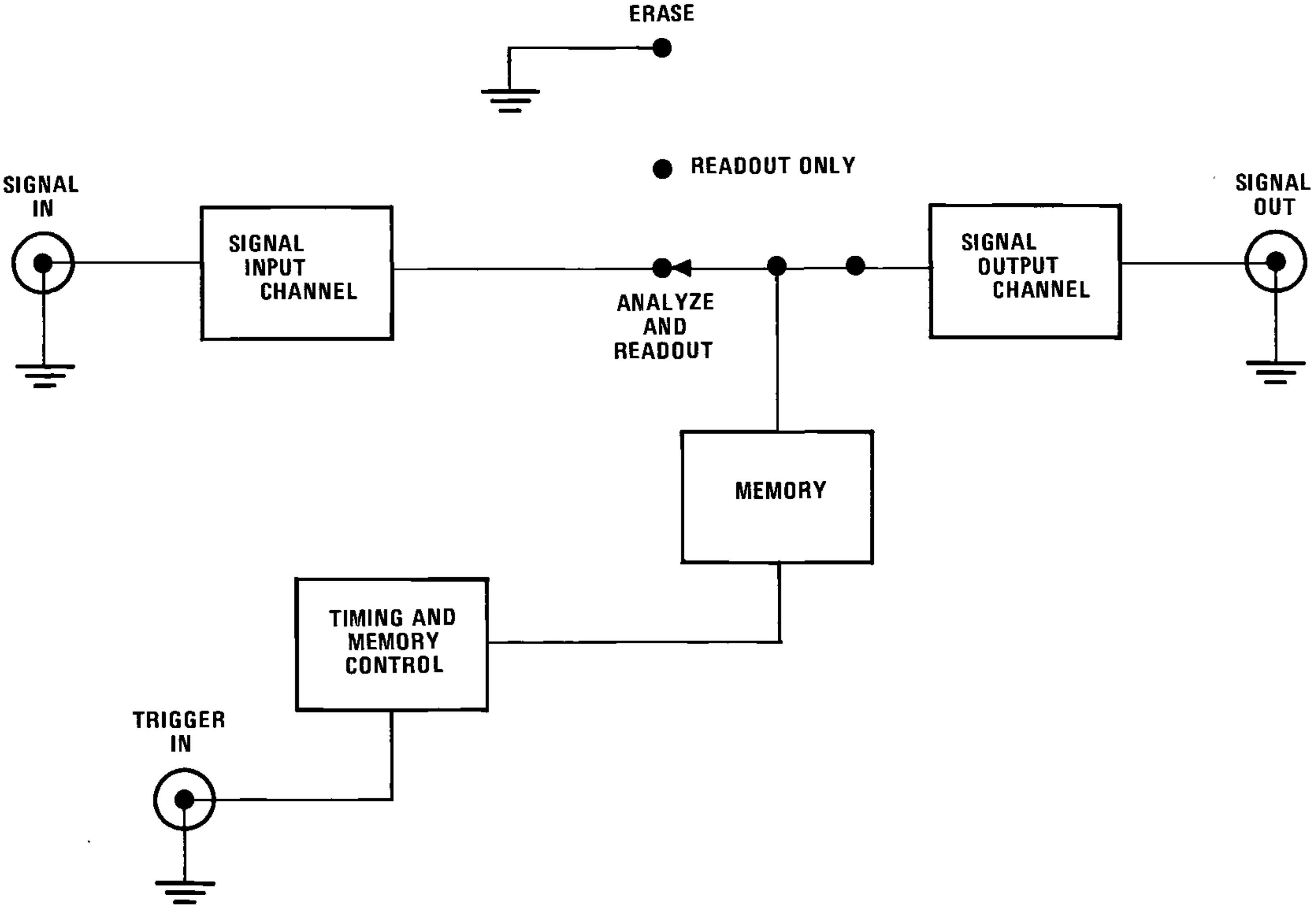

Figure 3. Block Diagram of the Waveform Eductor.

A signal consisting of a repetitive waveform plus noise is applied to the signal input channel where it is amplified and prefiltered to remove high frequency components which are beyond the 1 per cent of sweep time resolution capability of the instrument. The signal is again amplified and applied across a changeable time-constant RC-circuit. The "analyze and readout" position of the signal mode switch then causes the signal to be applied to the signal bus of the memory subsystem, which is a common line for the 100 channel capacitor memory.

The memory subsystem shown in Figure (4) includes 100 capacitor memory channels each of which consists of a five microfarad capacitor, one end of which is grounded and the other end of which is connected to the signal bus through a field-effect transistor gate. During a sweep the Timing and Memory Control Subsystem consecutively opens each of the gates for 1 per cent of the sweep time, and the memory capacitors charge toward the average level of the signal in that particular frequency interval. After several sweeps have occurred each capacitor will be charged to the average of that voltage applied to the time-constant resistor over the appropriate intervals, and the repetitive portion of the input signal will have been stored as 100 consecutive voltage levels or pedestals. It is this series of pedestals which is coupled to the signal output channel during each sweep.

During any given sweep, the signal on the signal bus at any instant will be the voltage to which the "on" memory capacitor is charged at that instant. This signal, which comprises the memory

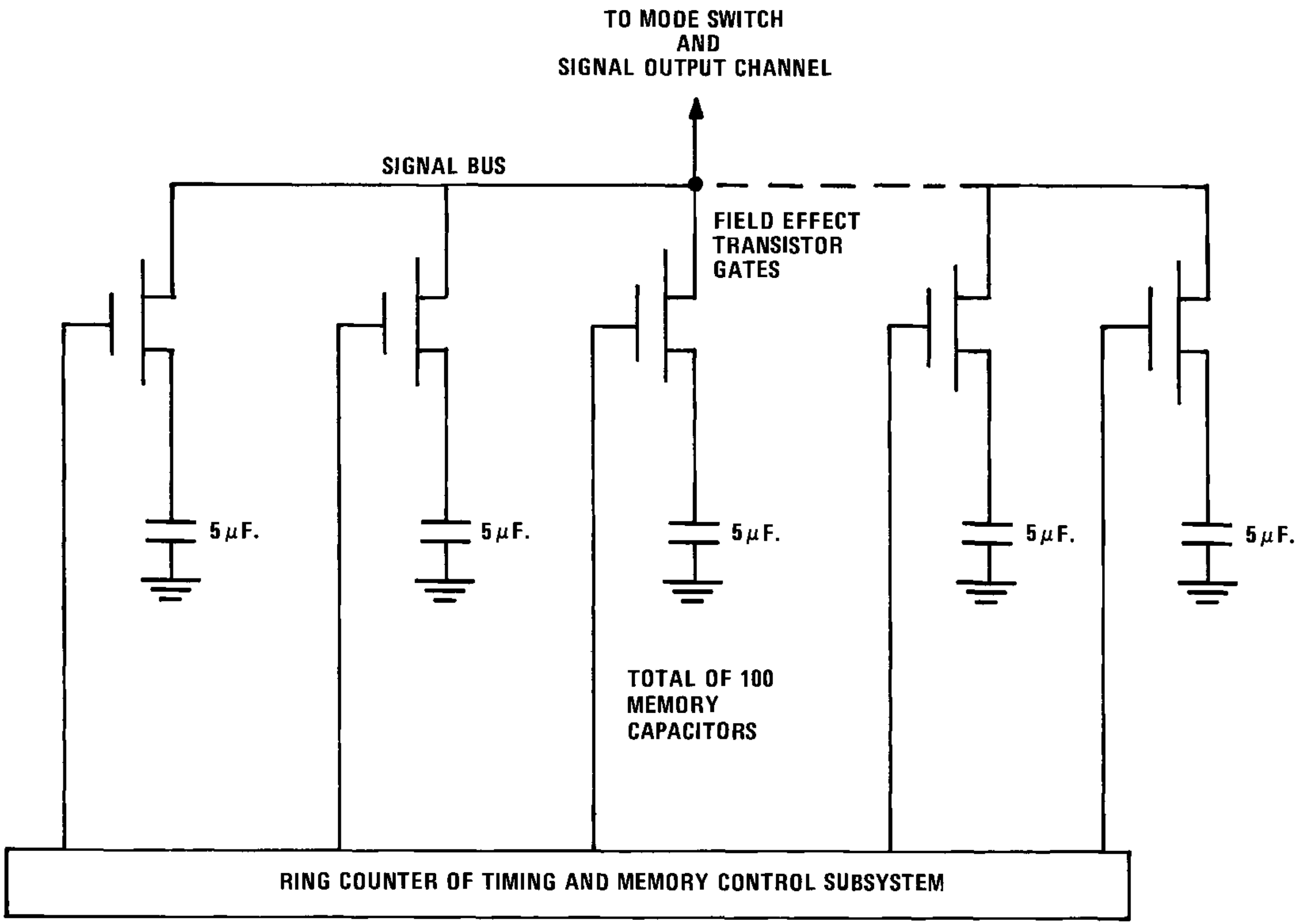

Figure 4. The Memory Subsystem of the Waveform Eductor.

contents, is applied to the input of the Signal Output Channel as the sweep advances. The signal is then amplified and then may or may not be smoothed at the choice of the operator. The smoother is a series of two filters which integrate or smooth out the output signal so that it is no longer pedestaled but continuous. Finally the output signal is amplified and displayed on the dual-trace oscilloscope.

The Timing and Memory Control system steps the memory, triggers the sweep, and determines the sweep duration among other functions. The stepping of the memory is provided by a ring counter which sequentially unlocks the memory gates. A clock oscillator provides the ring counter drive and determines the sweep time. One may vary the frequency of the clock oscillator manually so that the oscillator period is maintained at 1/100 of the selected sweep time. The oscillator is turned on and off by logic circuits which sense the operating condition at any moment, such as the state of the trigger circuits, whether or not delay has been selected, and whether or not sweep is occurring. An external trigger is provided by the sweep generator in Figure (1) which coincides with the frequency used to sweep the klystron and the various oscilloscopes. The trigger pulse may be delayed by a selected time which, in effect, selects the portion of the sweep range to be analyzed by the Eductor. The trigger pulse is applied to a trigger gate which advances the ring counter and starts the sweep.

Because the random noise has been averaged out, the frequencies of lines which were difficult to see in the lock-in output are easily measured in the Eductor output. The Eductor will respond to effects which take a long time relative to the sweep time such as klystron frequency drifts arising from temperature variations. The amount of response is dependent on the value of the time-constant resistance in the Signal Input Channel. It was decided to have this time constant as small as possible so that such effects would average out over the repetitions involved in taking data.

Sample Preparation and Use

The commercially prepared sample of $SC\ell_2$ used in gathering data for this work was found to decompose in the bottle as well as in the waveguide while the experiment was in progress. A discussion of the dissociation of the molecule may be found in a paper by Lowry, McHatton and Jones (16). As a result certain techniques for sample preparation and use were arrived at which will be mentioned here.

It was found advisable to prepare the sample by pumping on the commercial liquid for several minutes with the vacuum pump attached to the waveguide. The liquid was kept at dry ice temperature during this process. This appeared to remove gaseous decomposition products of the sample which had previously formed. However, it is thought that* the primary decomposition process in $SC\ell_2$ at dry ice temperature and low pressure obeys the equation $2SC\ell_2 \rightarrow S_2C\ell_2 + C\ell_2$, so that prolonged pumping will remove the chlorine from the right-hand side of this equation, thus forcing the decomposition of $SC\ell_2$, and leaving the undesirable impurity $S_2C\ell_2$. Therefore it is not

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*A private communication from Dr. D. J. Royer, Department of Chemistry, Georgia Institute of Technology.

recommended that the sample be distilled to half its original volume as suggested by Murray (11). Fractional distillation of the commercial liquid would be feasible because of the large differences in boiling points of $SC\ell_2$, $S_2C\ell_2$ and $C\ell_2$. This would increase the initial concentration of $SC\ell_2$ in the sample but the dissociation process quoted above would still occur, resulting in the problems mentioned in Chapter IV.

The distilled sample was admitted to the cell, which was surrounded by dry ice, by opening the stopcock of the sample holder while the pump was on and the liquid still at dry ice temperature. The sample was slowly allowed to warm up to room temperature by lowering the dry ice away from the holder. ($SC\ell_2$ has a very low vapor pressure at dry ice temperature). After a fairly strong absorption line had appeared on the dual-trace oscilloscope, the pump was shut off and the sample shut off and placed back in the dry ice.

The pressure in the cell rose as the $SC\ell_2$ decomposed as explained above. The cell had to be pumped out when the pressure reached 90 or 100 microns to prevent arcing of the Stark cell at high voltages. The sample had to be replaced about every hour because of decomposition, depending on how much was initially admitted to the guide.

CHAPTER III

THEORY

The total Hamiltonian operator for a molecule including a quadrupole interaction may be written

$$H = H_{e\ell} + H_{vib} + H_{rot} + H_Q ,$$

where the $H_{e\ell}$ and H_{vib} are operators concerned with electronic and vibrational energies. In the microwave region only H_{rot}, the rotational Hamiltonian, and any interactions which may be treated as perturbations on the rotational Hamiltonian such as H_Q, the quadrupole Hamiltonian, need be considered. The object of this chapter will be to apply second-order, non-degenerate perturbation theory to the calculation of the rotational plus quadrupole interaction energy of an asymmetric rotor molecule with two identical quadrupolar nuclei. This will involve determining a form of the asymmetric-top wavefunction and calculating the quadrupole matrix elements between different rotational states of the molecule.

The asymmetric-top theory outlined here may be found in detail in several references (17), (18). The quadrupole interaction theory presented employs the notation used by Wolf (19) with regard to the symbols of vector algebra, but follows the general development of Flygare and Gwinn (20).

Asymmetric-Top Theory

The rotational Hamiltonian for the symmetric-top is given by (21)

$$H_S = \frac{P^2 - P_{z'}^{\,2}}{2I_B} + \frac{P_{z'}^{\,2}}{2I_{z'}}$$

where P and $P_{z'}$ are operators for the total and z′- (or symmetry-axis) component of angular momentum of the rotor, respectively. The quantities I_B and $I_{z'}$ are principal moments of inertia, usually chosen so that

$$I_{x'} = I_{y'} = I_B \ ,$$

and if $I_B > I_{z'}$ then $I_{z'} = I_A$ otherwise $I_{z'} = I_C$.

The eigenstates of the Hamiltonian operator may be taken to be eigenfunctions of the three commuting observables P^2, $P_{z'}$ and P_Z, where P_Z is the operator for the space-fixed Z-component of angular momentum. Thus one obtains

$$\Psi_S = \Psi_S\ (J,K,M) \ ,$$

where

$$P^2\ \Psi_S\ (J,K,M) = J(J+1)\hbar^2\ \Psi_S\ (J,K,M) \ ,$$

$$P_{z'}\ \Psi_S\ (J,K,M) = K\ \hbar\ \Psi_S\ (J,K,M) \ ,$$

and

$$P_Z \Psi_S (J,K,M) = M\hbar \Psi_S (J,K,M) .$$

The Hamiltonian for the asymmetric-top has the form

$$H_A = \frac{P_{x'}^2}{2I_A} + \frac{P_{y'}^2}{2I_B} + \frac{P_{z'}^2}{2I_C}$$

where $I_A < I_B < I_C$. Now, however, $P_{z'}$ does not commute with the Hamiltonian and P^2, P_Z and H_A must be taken as a complete set of commuting observables. Wang (22) has suggested that in order to solve the resulting Schrodinger equation,

$$H_A \Psi_A = E \Psi_A$$

the asymmetric-top wavefunction should be expanded as a linear combination of symmetric-top wavefunctions. When this is done the resulting wavefunction is an eigenfunction of P^2 and P_Z with the same eigenvalues as listed above for a symmetric-top function, that is, J and M retain their identity as good quantum numbers. So the asymmetric wavefunction may be written

$$\Psi_A (J,\tau,M) = \sum_{K=-J}^{J} a_{K\tau} \Psi_S(J,K,M)$$

where τ is related to the Hamiltonian operator's eigenvalue, and the $a_{K\tau}$ are the expansion coefficients. When one requires that the above wavefunction be an eigenfunction of the H_A operator, one obtains by orthonormality of the eigenfunctions 2J+1 simultaneous equations for the $a_{K\tau}$'S for each value of J. The matrix obtained from these equations is called the rotational Hamiltonian matrix and when it is diagonalized it yields 2J+1 eigenvalues for H_A which are enumerated by τ, the largest eigenvalue being assigned $\tau = J$, the next largest being assigned the value $\tau = J-1$ and so forth. The matrix elements of H_A may be obtained from angular momentum algebra (23).

Quadrupole-Interaction Theory

The average orientation of a non-spherical charged nucleus with respect to the electronic bonds in the molecule will determine the magnitude of a small quadrupolar energy correction to the rotational energy of the molecule.

The Hamiltonian Operator

The electrostatic interaction between a nucleus and the electrons in a molecule is given by (24)

$$H = - \sum_{i,j} \frac{e^2}{|\vec{r}_{ei} - \vec{r}_{pj}|} ,$$

where e is the electronic charge, $\vec{r}_{ei}$ is the position vector of the ith electron in a space-fixed frame, and $\vec{r}_{pj}$ is the position vector vector of the jth proton in a space-fixed frame. The sum is over all the protons in the nucleus and all the molecular electrons.

It may be shown (25) that

$$\frac{1}{|\vec{r}_{ei} - \vec{r}_{pj}|} = \sum_{\ell=0}^{\infty} (r_{ei})^{-(\ell+1)} (r_{pj})^{\ell} P_{\ell}(\cos\theta) ,$$

$$(|\vec{r}_{pj}| < |\vec{r}_{ei}|) ,$$

where $P_{\ell}(\cos\theta)$ is a Legendre polynomial and θ is the angle between $\vec{r}_{ei}$ and $\vec{r}_{pj}$. Thus one obtains

$$H = -e^2 \sum_{i,j,\ell} (r_{ei})^{-(\ell+1)} (r_{pj})^{\ell} P_{\ell}(\cos\theta) .$$

The term with $\ell=2$ is called the quadrupole interaction term of the series, therefore one has

$$H_Q = -e^2 \sum_{i,j} \frac{r_{pj}^{\ 2}}{r_{ei}^{\ 3}} P_{\ell}(\cos\theta) .$$

The spherical harmonics, $C_m^{(\ell)}(\varphi,\theta)$, are such that (26)

$$P_{\ell}(\cos\theta) = \sum_{m=-\ell}^{\ell} (-1)^m C_m^{(\ell)} (\varphi_i,\theta_i) C_{-m}^{(\ell)} (\varphi_j,\theta_j) ,$$

where φ_i and θ_i are the polar coordinates of $\vec{r}_{ei}$, and φ_j and θ_j are the polar coordinates of $\vec{r}_{pj}$. The quadrupole Hamiltonian then becomes

$$H_Q = - \sum_{m=-2}^{2} (-1)^m \sum_i \frac{e}{r_{ei}^3} C_m^{(2)}(\varphi_i,\theta_i) \sum_j e\, r_{pj}^2\, C_{-m}^{(2)} (\varphi_j,\theta_j) .$$

From the theory of spherical tensor operators (27) one has that the dot product of two such operators is defined by

$$A \circ B = \sum_{m=-\ell}^{\ell} (-1)^m A_m^{(\ell)} B_{-m}^{(\ell)} .$$

So that one can express the Hamiltonian operator as

$$H_Q = A \cdot B = \sum_{m=-2}^{2} (-1)^m A_m^{(2)} B_{-m}^{(2)} ,$$

where

$$A_m^{(2)} = -\sum_i \frac{e}{(r_{ei})^3} C_m^{(2)}(\varphi_i,\theta_i) , \qquad (1)$$

and

$$B_m^{(2)} = \sum_j e\, r_{pj}^2\, C_m^{(2)}(\varphi_j,\theta_j) .$$

Matrix Elements of the Hamiltonian

The quadrupole interaction is an internal interaction which, as explained above, will involve the nuclear orientation and the electronic environment of the nucleus. The former is related to the nuclear spin vector $\vec{I}$ and the latter to the rotational angular momentum vector $\vec{J}$. Thus a total molecular wavefunction is needed involving rotation of the molecule and spin of the nuclei. An asymmetric rotor state function will then be written

$$\Psi_A\ (J,\tau,I,F,M)\ ,$$

where

$$\vec{I}_1 + \vec{I}_2 = \vec{I}\ ,$$

and $\vec{I}_1$ and $\vec{I}_2$ are the spins of the two quadrupolar nuclei, and

$$\vec{J} + \vec{I} = \vec{F}\ .$$

Since the operator for $\vec{F}$, the total angular momentum vector, commutes with the quadrupole Hamiltonian, there are no matrix elements of the quadrupole Hamiltonian between states of different $\vec{F}$. The matrix elements to be considered then are of the form $\langle J'\tau'I'F\ M'|A\cdot B|J\tau IFM\rangle$.

According to Edmonds (28) this may be expressed as

$$\langle J'\tau'I'FM'|A\cdot B|J\tau IFM\rangle = (-1)^{J+I'+F}W(FI'J':2JI)$$

$$\langle J'\tau'||A||J\tau\rangle\ \langle I'||B||I\rangle\ , \qquad (2)$$

where W(FI'J':2JI) is a six-j symbol (see Wolf (29) or Edmonds p. 97). One notes that the right-hand side shows no M dependence since the interaction cannot depend on the orientation of the molecule with respect to a space-fixed frame. One may then write that (30)

$$\langle J'\tau'M'|A_0^{(2)}|J\tau M\rangle = (-1)^{J'-M'}\chi(J'2J;-M'0M)\ \langle J'\tau'||A||J\tau\rangle \ .$$

Here $\chi(J'2J;-M'0M)$ is a three-j symbol (see Wolf (31) or Edmonds p. 46). A property of the three-j symbol $\chi(j_1j_2j_3;\ m_1m_2m_3)$ however is that it is zero unless (32)

$$m_1 + m_2 + m_3 = 0$$

so the above expression becomes

$$\langle J'\tau'||A||J\tau\rangle = \frac{(-1)^{M-J'}\langle J'\tau'M|A_0^{(2)}|J\tau M\rangle}{\chi(J'2J;-M0M)} \qquad (3)$$

where, from equation (1),

$$A_0^{(2)} = -e\sum_i (r_{ei})^{-3}\ C_0^{(2)}(\varphi_{ei},\theta_{ei}) \ .$$

Now, it may be shown that (33)

$$A_0^{(2)} = \frac{1}{2}\frac{\partial^2 V}{\partial Z^2} = \frac{1}{2}V_{ZZ} \ ,$$

where Z is the space-fixed Z-axis. The field gradient coupling

$eq_{J'J}$ is defined as (34)

$$eq_{J'J} = \langle J'\tau'M'|V_{ZZ}|J\tau M\rangle,\ M' = M = J\ ,$$

$$= \langle J'\tau'J|V_{ZZ}|J\tau J\rangle\ .$$

One should note that since the reduced matrix element $\langle J'\tau||A||J\tau\rangle$ is independent of M' and M, any matrix element involving $A_0^{(2)}$ in equation (3) may be used in evaluating $\langle J'\tau'||A||J\tau\rangle$, so $eq_{J'J}$ will suffice. This gives

$$\langle J'\tau'||A||J\tau\rangle = \frac{(-1)^{J-J'}eq_{J'J}}{2\chi(J'2J;-J0J)}\ . \tag{4}$$

Now consider the second reduced matrix element in equation (2). The reduced matrix element of an operator B acting on an eigenvector $u(j_1m_1)$ in a scheme in which $u(j_1m_1)$ is coupled to $u(j_2m_2)$ is given by (35)

$$\langle j_1'j_2\ j'||B||j_1j_2j\rangle = (-1)^{j_1'+j_2+j+k}$$

$$[(2j+1)(2j'+1)]^{1/2}W(j_1'j'j_2:jj_1k)\ \langle j_1'||B||j_1\rangle\ ,$$

where k is the order of the tensor operator. Also the reduced matrix element of B operating on $u(j_2m_2)$ in a scheme in which $u(j_2m_2)$ is coupled to $u(j_1m_1)$ is given by (35)

$$\langle j_1 j_2' j' || B || j_1 j_2 j \rangle = (-1)^{j_1+j_2+j'+k}$$

$$[(2j+1)(2j'+1)]^{1/2} W(j_2' j' j_1 : j j_2 k) \ \langle j_2' || B || j_2 \rangle \ .$$

Thus, for nucleus one,

$$\langle I' || B || I \rangle = \langle I_1' I_2 I' || B || I_1 I_2 I \rangle =$$

$$(-1)^{I+1} [(2I+1)(2I'+1)]^{1/2} W(\tfrac{3}{2} I' \tfrac{3}{2} : I \tfrac{3}{2} 2) \ \langle \tfrac{3}{2} || B || \tfrac{3}{2} \rangle \ ,$$

and for nucleus two,

$$\langle I' || B || I \rangle = \langle I_1 I_2' I' || B || I_1 I_2 I \rangle =$$

$$(-1)^{I'+1} [(2I+1)(2I'+1)]^{1/2} W(\tfrac{3}{2} I' \tfrac{3}{2} : I \tfrac{3}{2} \ 2) \ \langle \tfrac{3}{2} || B || \tfrac{3}{2} \rangle \ . \qquad (5)$$

Applying Edmond's equation 5.4.1 (30) to the operator B gives

$$\langle j_1' m_1' | B_0^{(2)} | j_1 m_1 \rangle = (-1)^{j_1' - m_1'} \chi(j_1' 2 j_1 ; -m_1' 0 m_1) \ \langle j_1' || B || j_1 \rangle \ ,$$

so that

$$\langle \tfrac{3}{2} || B || \tfrac{3}{2} \rangle = \frac{(-1)^{m_1' - \frac{3}{2}} \langle \frac{3}{2} \ m_1' || B_0^{(2)} || \frac{3}{2} \ m_1 \rangle}{\chi(\frac{3}{2} \ 2 \ \frac{3}{2} ; -m_1' 0 m_1)}$$

Once again, the three-j symbol is non-zero only if $m_1{}' = m_1$. It can be shown (36) that for the state in which the nucleus has the maximum projection of its angular momentum along the Z-axis

$$B_0^{(2)} = \frac{eQ}{2}$$

where Q is known as the quadrupole moment of the nucleus. Thus one has

$$\langle \tfrac{3}{2}||B||\tfrac{3}{2}\rangle = \frac{\langle \frac{3}{2}\,\frac{3}{2}||B_0^{(2)}||\frac{3}{2}\,\frac{3}{2}\rangle}{\chi(\frac{3}{2}\;2\;\frac{3}{2};-\frac{3}{2}\;0\;\frac{3}{2})} = \sqrt{5}\,eQ \qquad (6)$$

Combining equations (2), (4), (5) and (6) above gives

$$\langle J'\tau'I'F|A\cdot B|J\tau IF\rangle = \frac{(-1)^{J+I'+F+1}}{2} W(FI'J':2JI)$$

$$W(\tfrac{3}{2}\;I'\;\tfrac{3}{2}:I\;\tfrac{3}{2}\;2)[(2I+1)(2I'+1)]^{1/2}(5)^{1/2}$$

$$\frac{[e^2(q_{J'J})_1Q_1(-1)^{I} + e^2(q_{J'J})_2Q_2(-1)^{I'}]}{\chi(J2J';\;J0-J)} \quad .$$

If I′ = I, I±2 the part in brackets becomes

$$(-1)^I[e^2(q_{J'J})_1Q_1 + e^2(q_{J'J})_2Q_2] = (-1)^I\chi^+ \;,$$

and if $I' = I \pm 1$ the part in brackets becomes

$$(-1)^{I}\ [e^2(q_{J'J})_1 Q_1 - e^2(q_{J'J})_2 Q_2] = (-1)^{I} \chi^{-} .$$

Thus, finally one obtains

$$\langle J'\tau'I'F|A\ B|J\tau IF\rangle = \frac{(-1)^{J+I'+F+1}}{2} W(FI'J':2JI)W(\tfrac{3}{2}I'\tfrac{3}{2}:I\tfrac{3}{2}2) \frac{[(2I+1)(2I'+1)]^{1/2}(5)^{1/2}\ \chi^{\pm}}{\chi(J2J';J0-J)} , \tag{7}$$

where the quantities $\chi^{\pm}$ depend on $I'-I$.

The Quantities $\chi^{\pm}$

Up to this time the discussion has been framed in terms of asymmetric-top wavefunctions. However, to evaluate $\chi^{\pm}$, which are functions of J, J', I, and I', one must go to a symmetric-top expansion of the wavefunction.

It should be noted first that the above definition of $(q_{J'J})$, the field gradient coupling constant, assumes $J \leq J'$ since if this were not true, the state on the left-hand side of the element could not exist, i.e., M' cannot be greater than J'. It turns out that $(q_{J'J})$ will be zero if $J > J'$. Likewise the three-j symbol in the denominator of equation (7) goes to zero if $J > J'$. Therefore the expression for the second-order quadrupole matrix element becomes indeterminate then if $J > J'$ because $M' > J'$. This difficulty is overcome by calculating

$$\langle J\tau IFM|A\cdot B|J'\tau'I'FM'\rangle \text{ for } M' = M = J'$$

instead of

$$\langle J'\tau'I'FM'|A\cdot B|J\tau IFM\rangle \text{ with } M' = M = J$$

if $J > J'$. The former must give the complex conjugate of the latter since the quadrupole interaction cannot depend on the orientation of the molecule relative to a space-fixed axis, and the quadrupole Hamiltonian is Hermitian.

The ZZ-term of the field gradient tensor is given by (37)

$$\frac{\partial^2 V}{\partial Z^2} = \alpha^2_{Zx'} \frac{\partial^2 V}{\partial x'^2} + \alpha^2_{Zy'} \frac{\partial^2 V}{\partial y'^2} + \alpha^2_{Zz'} \frac{\partial^2 V}{\partial z'^2} + 2\, \alpha_{Zx'}\, \alpha_{Zy'} \frac{\partial^2 V}{\partial x'\partial y'}$$

$$+ 2\, \alpha_{Zx'}\, \alpha_{Zz'} \frac{\partial^2 V}{\partial x'\partial z'} + 2\, \alpha_{Zy'}\, \alpha_{Zz'} \frac{\partial^2 V}{\partial y'\partial z'} \quad .$$

where the α_{ij}'s are the direction cosines relating the space-fixed Z-axis to the molecular principal axes indicated by primes. Using the abbreviation

$$V_{ab} = \frac{\partial^2 V}{\partial a \partial b}$$

the field gradient coupling constant becomes

$$q_{J'J} = \langle \alpha^2_{Zx'} \rangle V_{x'x'} + \langle \alpha^2_{Zy'} \rangle V_{y'y'} + \langle \alpha^2_{Zz'} \rangle V_{z'z'}$$

$$+ 2\langle \alpha_{Zx'} \alpha_{Zy'} \rangle V_{x'y'} + 2\langle \alpha_{Zx'} \alpha_{Zz'} \rangle V_{x'z'}$$

$$+ 2\langle \alpha_{Zy'} \alpha_{Zz'} \rangle V_{y'z'}$$

where the brackets mean the matrix element for the state M' = M = J.

The field gradient tensor in its molecular principal axis system may be obtained from the field gradient tensor expressed in its principal axis system by means of a similarity transformation (see Appendix B). When this is done for both nuclei it is found that

$$V_{x'x'}^{(1)} = V_{x'x'}^{(2)} = V_{x'x'} ,$$

$$V_{y'y'}^{(1)} = V_{y'y'}^{(2)} = V_{y'y'} ,$$

$$V_{z'z'}^{(1)} = V_{z'z'}^{(2)} = V_{z'z'} ,$$

$$V_{x'y'}^{(1)} = -V_{x'y'}^{(2)} = V_{x'y'} ,$$

$$V_{x'z'}^{(1)} = V_{x'z'}^{(2)} = 0$$

$$V_{y'z'}^{(1)} = V_{y'z'}^{(2)} = 0$$

where the superscripts refer to nucleus number. Thus the expression for $(q_{J'J})$ for nucleus one becomes

$$(q_{J'J})_1 = \langle\alpha^2_{Zx'}\rangle V_{x'x'} + \langle\alpha^2_{Zy'}\rangle V_{y'y'}$$

$$+ \langle\alpha^2_{Zz'}\rangle V_{z'z'} + 2\langle\alpha_{Zx'}\alpha_{Zy'}\rangle V_{x'y'} ,$$

and for nucleus two

$$(q_{J'J})_2 = \langle\alpha^2_{Zx'}\rangle V_{x'x'} + \langle\alpha^2_{Zy'}\rangle V_{y'y'}$$

$$+ \langle\alpha^2_{Zz'}\rangle V_{z'z'} -2\langle\alpha_{Zx'}\alpha_{Zy'}\rangle V_{x'y'} .$$

One obtains for $\chi^{\pm}$ then

$$\chi^{+} = 2[\langle\alpha^2_{Zx'}\rangle \chi_{x'x'} + \langle\alpha^2_{Zy'}\rangle \chi_{y'y'} + \langle\alpha^2_{Zz'}\rangle \chi_{z'z'}] ,$$

and

$$\chi^{-} = 4\langle\alpha_{Zx'}\alpha_{Zy'}\rangle \chi_{x'y'} ,$$

where

$$\chi_{ab} = e^2Q\, V_{ab} .$$

In order to evaluate the matrix elements of the direction cosines above the symmetric-top expansion of the asymmetric-top wavefunction was chosen,

$$\Psi_A(J\tau M) = \sum_{K=-J}^{J} a^J_{K\tau}\, \Psi_S(JKM) \quad ,$$

since a table of direction cosine matrix elements for a symmetric-top is available from Cross, Hainer and King (38). In terms of symmetric-top functions, the quantities $\chi^{\pm}$ become

$$\chi^+ = 2 \sum_{K'=-J'}^{J'} \sum_{K=-J}^{J} a^{J'}_{K'\tau'}\, a^{J}_{K\tau} \Big\{ \langle J'K'J|\alpha^2_{Zx'}|JKJ\rangle\, \chi_{x'x'}$$

$$+ \langle J'K'J|\alpha^2_{Zy'}|JKJ\rangle\, \chi_{y'y'} + \langle J'K'J|\alpha^2_{Zz'}|JKJ\rangle\, \chi_{z'z'} \Big\}$$

and

$$\chi^- = 4 \sum_{K'=-J'}^{J'} \sum_{K=-J}^{J} a^{J'}_{K'\tau'}\, a^{J}_{K\tau}\, \langle J'K'J|\alpha_{Zx'}\, \alpha_{Zy'}|JKJ\rangle\, \chi_{x'y'} \ .$$

Now, in general, if α and β are two operators

$$\langle n|\alpha\,\beta|n'\rangle = \sum_{n''} \langle n|\alpha|n''\rangle\langle n''|\beta|n'\rangle \ ,$$

where n'' ranges over all states linked to n and n', so that one obtains in this case

$$\chi^{+} = 2 \sum_{K'} \sum_{K} a^{J'}_{K'\tau'} a^{J}_{K\tau} \sum_{J''} \sum_{K''}$$

$$\left\{ \langle J'K'J | \alpha_{Zx'} | J''K''J \rangle \langle J''K''J | \alpha_{Zx'} | JKJ \rangle \chi_{x'x'} \right.$$

$$\left. + \text{ similar terms for } \chi_{y'y'} \text{ and } \chi_{z'z'} \right\} .$$

Likewise one obtains

$$\chi^{-} = 4 \sum_{K'} \sum_{K} a^{J'}_{K'\tau'} a^{J}_{K\tau} \sum_{J''} \sum_{K''}$$

$$\langle J'K'J | \alpha_{Zx'} | J''K''J \rangle \langle J''K''J | \alpha_{Zy'} | JKJ \rangle \chi_{x'y'}$$

Here the sums over J'' and K'' are over all states which may be linked to J and J'. It has been assumed here that $J' \geq J$ as explained above.

The above expressions for $\chi^{\pm}$ must now be evaluated using the table from Cross, Hainer and King. An example is done in Appendix D and the final results are written here for all cases. If $J' = J$, then

$$\chi^{+} = \frac{2}{(J+1)(2J+3)} \sum_{K} \Big[a^{J}_{K\tau} a^{J}_{K\tau'} [3K^2 - J(J+1)] \chi_{z'z'}$$

$$- \Big\{ a^{J}_{K\tau} a^{J}_{K+2\tau'} \frac{[(J-K)(J+K+1)(J-K-1)(J+K+2)]^{1/2}}{2}$$

$$+ a^{J}_{K\tau} a^{J}_{K-2\tau'} \frac{[(J+K)(J-K+1)(J+K-1)(J-K+2)]^{1/2}}{2} \Big\} (\chi_{x'x'} - \chi_{y'y'}) \Big] ,$$

$$\chi^{-} = \frac{2i}{(J+1)(2J+3)} \sum_{K} \left\{ a^{J}_{K\tau}\, a^{J}_{K+2\tau'} \left(-[(J-K)(J+K+1)(J-K-1)(J+K+2)]^{1/2} \right) \right.$$

$$\left. + a^{J}_{K\tau}\, a^{J}_{K-2\tau'}\, [(J+K)(J-K+1)(J+K-1)(J-K+2)]^{1/2} \right\} \chi_{x'y'} \quad ,$$

if J' = J+1, then

$$\chi^{+} = \frac{1}{(J+1)(J+2)(2J+3)^{1/2}} \sum_{K} \left\{ a^{J}_{K\tau}\, a^{J+1}_{K\tau'}\, [6K[(J+1)^{2}-K^{2}]^{1/2}] \chi_{z'z'} \right.$$

$$+ \left[a^{J}_{K\tau}\, a^{J+1}_{K+2\tau'}\, [(J-K)(J+K+1)(J+K+2)(J+K+3)]^{1/2} - a^{J}_{K\tau}\, a^{J+1}_{K-2\tau'} \right.$$

$$\left. \left. [(J+K)(J-K+1)(J-K+2)(J-K+3)]^{1/2} \right] (\chi_{x'x'} - \chi_{y'y'}) \right\} ,$$

$$\chi^{-} = \frac{2i}{(J+1)(J+2)(2J+3)^{1/2}} \sum_{K} \left\{ a^{J}_{K\tau}\, a^{J+1}_{K+2\tau'}\, [(J-K)(J+K+1)(J+K+2) \right.$$

$$\left. (J+K+3)]^{1/2} + a^{J}_{K\tau}\, a^{J+1}_{K-2\tau'} [(J+K)(J-K+1)(J-K+2)(J-K+3)]^{1/2} \right\} \chi_{x'y'} \; ,$$

if J' = J+2, then

$$\chi^{+} = \frac{2}{(J+2)(2J+3)(J+1)^{1/2}(2J+5)^{1/2}}$$

$$\sum_{K} \left\{ a^{J}_{K\tau}\, a^{J}_{K\tau'}\, 3[(J-K+1)(J+K+1)(J-K+2)(J+K+2)]^{1/2} \chi_{z'z'} \right.$$

$$- \left\{ a^{J}_{K\tau}\, a^{J+2}_{K+2\tau'}\, \frac{[(J+K+1)(J+K+2)(J+K+3)(J+K+4)]^{1/2}}{2} \right.$$

$$+ a_{K\tau}\, a_{K-2\tau'} \frac{[(J-K+1)(J-K+2)(J-K+3)(J-K+4)]^{1/2}}{2} \Big\} (\chi_{x'x'} - \chi_{y'y'}) \Big\} ,$$

$$\chi^{-} = \frac{-2i}{(J+2)(2J+3)(J+1)^{1/2}(2J+5)^{1/2}} \sum_{K} \Big\{ a^{J}_{K\tau}\, a^{J+2}_{K+2\tau'} [(J+K+1)(J+K+2)(J+K+3)$$

$$(J+K+4)]^{1/2} - a^{J}_{K\tau}\, a^{J+2}_{K-2\tau'} [(J-K+1)(J-K+2)(J-K+3)(J-K+4)]^{1/2} \Big\} \chi_{x'y'} .$$

Relative Intensities of Hyperfine Lines

The relative intensity of a rotational transition in a molecule is proportional to the square of the matrix element of the dipole moment operator between the initial and final states (39). The quadrupole interaction removes the degeneracy in previously degenerate levels of the asymmetric rotor. When the first-order quadrupole matrices are diagonalized the correct zero-order state function corresponding to a hyperfine level is given by

$$\Psi_A(E_{J_\tau}\epsilon) = \sum_{I} B_{\epsilon I}\, \Psi_A(E_{J_\tau} IFM_F) , \qquad (9)$$

where ϵ distinguishes different hyperfine levels and M_F is the space-fixed Z-component of $\vec{F}$, the total angular momentum. The functions $\Psi_A(E_{J_\tau} IFM_F)$ are those referred to on page (19), but M_F was suppressed before since the quadrupole interaction is internal and does not depend on the spatial orientation of the molecule. The $B_{\epsilon I}$ are the transformation coefficients between the I and ϵ representations.

The total intensity of a line, N, is obtained by summing over all possible values of M_F since the molecules are randomly distributed in spatial orientation (40) so that

$$N = \sum_{M_F^i \, M_F^f} [\langle E^i_{J_\tau} \, \epsilon^i | d^{(1)}_m | E^f_{J_\tau} \, \epsilon^f \rangle]^2 , \qquad (10)$$

where $d^{(1)}_m$ is a component of the spherical tensor operator of rank one representing the dipole moment of the molecule. The spherical tensor components are related to the rectangular components by the following

$$d^{(1)}_{\pm 1} = \mp \frac{q}{\sqrt{2}} \, (x \pm iy) \ ,$$

$$d^{(1)}_0 = qz \ .$$

Substituting (9) and (10) one obtains

$$N = \sum_{M_F^i \, M_F^f} [\sum_{I^i I^f} B^i_{\epsilon^i I^i} \, B^f_{\epsilon^f I^f}$$

$$\langle E^i_{J_\tau} \, I^i F^i M_F^i | d^{(1)}_m | E^f_{J_\tau} \, J^f F^f M_F^f \rangle] \ . \qquad (11)$$

In equation (11) the i and f refer to initial and final states respectively.

For polarized electric fields such as are used in microwave spectroscopy one may choose the Z-axis to be the direction of polarization. Then using Edmonds' equation (41) one obtains

$$\langle E^i_{J_\tau}\ I^i F^i M_F{}^i | d_0^{(1)} | E^f_{J_\tau} I^f F^f M_F{}^f \rangle$$

$$= (-1)^{F^i - M_F{}^i}\ \chi(F^i 1 F^f; -M_F{}^i\ 0 M_F{}^f) \langle E^i_{J_\tau}\ I^i F^i || d || E^f_{J_\tau} I^f F^f \rangle\ .$$

Now, the reduced matrix element above is zero unless $I^i = I^f = I$ because d, the dipole moment of the molecule, does not involve the nuclear spin. Using Edmonds' equation (42) the reduced matrix element can be written

$$\langle E^i_{J_\tau}\ IF^i || d || E^f_{J_\tau}\ IF^f \rangle = (-1)^{J^i + I + F^f + 1} [(2F^i+1)(2F^f+1)]^{1/2}$$

$$W(J^i F^i I : F^f J^f 1)\ \langle E^i_{J_\tau} || d || E^f_{J_\tau} \rangle\ ,$$

where $\langle E^i_{J_\tau} || d || E^f_{J_\tau} \rangle$ is a further reduced matrix element which is the same for any pair of interacting J_τ levels. The intensity expression then becomes

$$N = \sum_{M_F{}^i M_F{}^f} [\sum_I B^i_{\epsilon^i I}\ B^f_{\epsilon^f I}\ (-1)^{F^i - M_F{}^i}$$

$$\chi(F^i 1 F^f;\ -M^i_F 0 M^f_F)\ (-1)^{J^i + I + F^f + 1}$$

$$[(2F^i+1)(2F^f+1)]^{1/2} W(J^i F^i I : F^f J^f 1) \langle E^i_{J_\tau} || d || E^f_{J_\tau} \rangle]^2\ .$$

This may be rearranged to give

$$N = \sum_{M_F^i\, M_F^f} [(-1)^{F^i - M_F^i + J^i + F^f + 1} \chi(F^i 1 F^f ; -M_F^i 0 M_F^f)$$

$$[(2F^i+1)(2F^f+1)]^{1/2} \langle E^i_{J_\tau} || d || E^f_{J_\tau} \rangle \sum_I B^i_{\epsilon^i I} \; B^f_{\epsilon^f I} (-1)^I$$

$$W(J^i F^i I : F^f J^f 1)]^2 ,$$

or finally,

$$N = \sum_{M_F^i\, M_F^f} \chi^2(F^i 1 F^f ; -M_F^i 0 M_F^f)$$

$$(2F^i+1)(2F^f+1) \langle E^i_{J_\tau} || d || E^f_{J_\tau} \rangle^2$$

$$[\sum_I B^i_{\epsilon^i I} \; B^f_{\epsilon^f I} (-1)^I W(J^i F^i I : F^f J^f 1)]^2 .$$

Using Edmonds' equation (43) one has that

$$\sum_{M_F^i\, M_F^f} \chi^2(F^i 1 F^f ; -M_F^i 0 M_F^f) = \frac{1}{3} ,$$

so that

$$N = \frac{(2F^i+1)(2F^f+1)}{3} \langle E^i_{J\tau} || d || E^f_{J\tau} \rangle^2$$

$$\left[\sum_I B^i_{\epsilon^i I} \; B^f_{\epsilon^f I} \; (-1)^I \; W(J^i F^i I : F^f J^f 1) \right]^2 . \qquad (12)$$

The quantity $\langle E^i_{J_\tau} || d || E^f_{J_\tau} \rangle$ as mentioned above is the same for all hyperfine lines associated with a particular J_τ transition so that the above equation gives relative intensities. A sample calculation of intensity may be found in Appendix C.

CHAPTER IV

DATA ANALYSIS

In order to test the second-order perturbation theory developed in other portions of this work, the measurements of J. T. Murray (11) on $SC\ell_2$ were repeated. It was hoped that the addition of the Waveform Eductor to the experimental equipment would result in more accurate measurement of the transition frequencies and quadrupole splittings. This would result in a better determination of the diagonal elements of the quadrupole coupling constant tensor, $\chi_{x'x'}$, $\chi_{y'y'}$, and $\chi_{z'z'}$, as well as a first determination of $\chi_{x'y'}$.

Data was taken on each quadrupole and main rotational line as discussed in Chapter II on page 9. Each group of data consisted of ten measurements of the line frequency taken with a positive-slope sweep and ten with a negative-slope sweep for the reason explained in Chapter II. A standard deviation for each data group was obtained with the formulae found in Beers (44). However, the rapid dissociation of $SC\ell_2$ into the products $S_2C\ell_2$ and $C\ell_2$, even at dry ice temperature, resulted in a rapid increase in pressure in the waveguide while data was being taken. Also, in several transitions an impurity line due to one or the other of the by-products fell in among the $SC\ell_2$ lines. Such a case is shown in Figures 5 and 6 where the graphical ammeter trace clearly demonstrates the growth of an impurity line near the high-frequency quadrupole lines as the intensity of the $SC\ell_2$ spectrum diminishes. Nave (45) has explained that the rapidly increasing

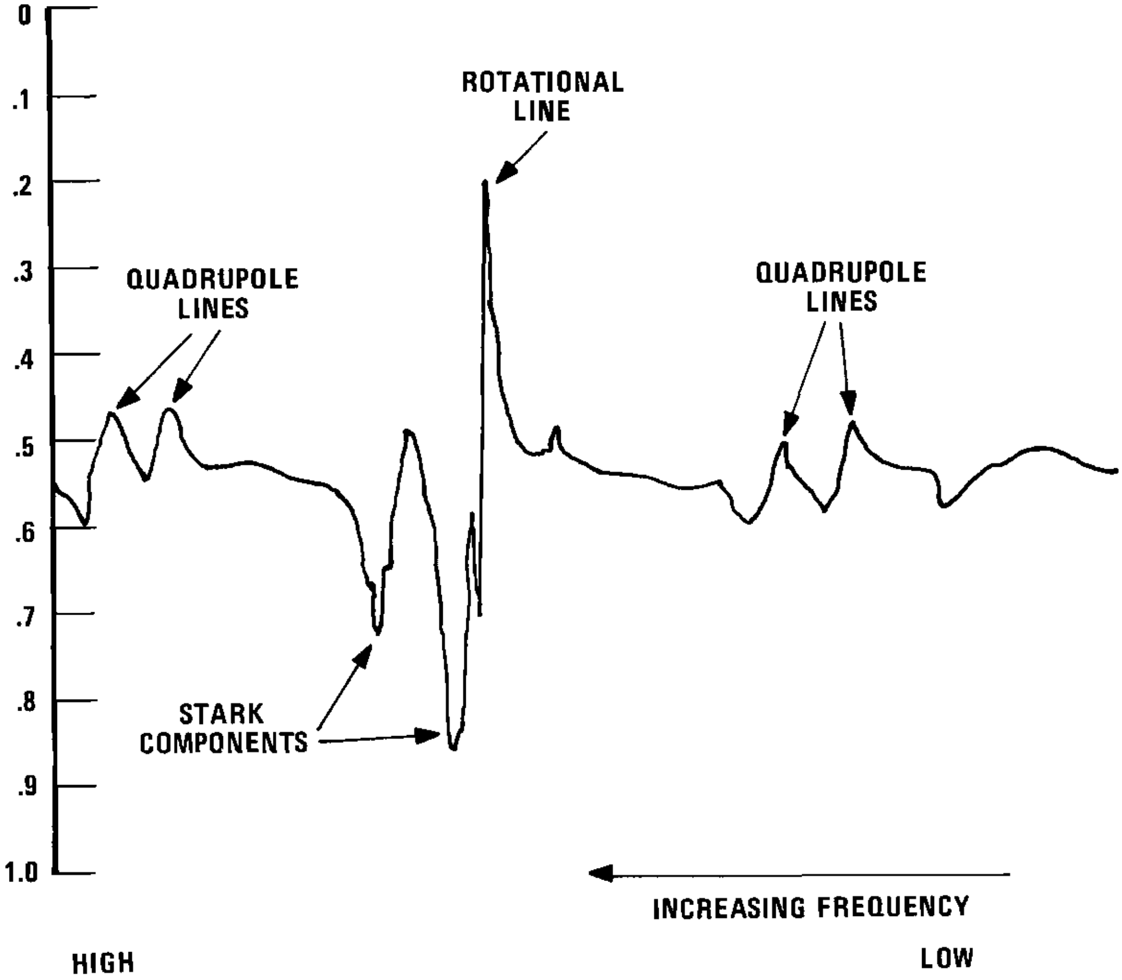

Figure 5. The $2_{-2} \rightarrow 2_0$ Transition in SCl_2 with a New Sample.

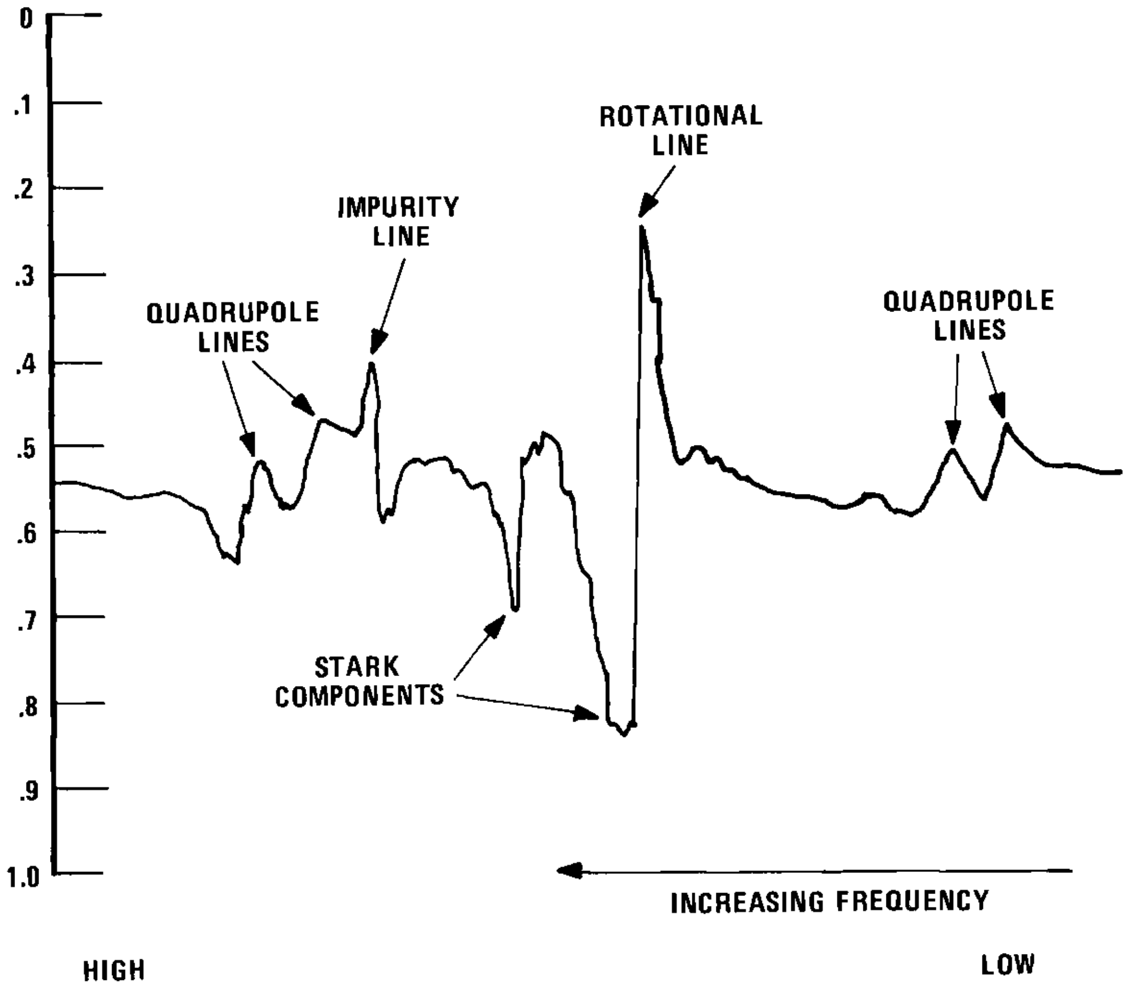

Figure 6. The $2_{-2} \rightarrow 2_0$ Transition in SCl_2 after Twenty Minutes.

pressure itself can result in different values of quadrupole splitting for different Stark voltages. (At times different voltages must be used for the two lines involved in a splitting to ensure that the Stark components of close-lying lines are displaced enough so as to not interfere with the main lines.) The presence of the impurity line(s) produces a similar effect, because the intensity of the impurity line increases as the dissociation progresses, i.e., as the pressure increases. The averaging effect of pressure broadening with such an impurity line will shift one of the two lines involved in a splitting more than the other, resulting in different values for the splitting at different pressures.

Since the effect of the impurity line described above acts independently on each of the two lines involved in determining a splitting the rules for calculating a standard error for the splitting assuming statistical independence may be employed (55). As the measurements in a data group were taken the pressure rose from about 10 to 15 microns to an equilibrium pressure of about 100 microns. The measurements of frequency within a data-group displayed a definite trend as expected due to the impurity lines. The average standard error for the four transitions is ± 0.05 MHz. This will be taken as the experimental error.

Table 1 lists experimentally measured and theoretically calculated splittings for four transitions in $SC\ell_2$. Several of the lines recorded by Murray were not used in this work because the intensities

Table 1. Quadrupole Splittings in MHz for the Rotational Spectrum of $S^{32}Cl_2^{35}$ Used to Determine $\chi_{x'x'}$, $\chi_{y'y'}$, $\chi_{z'z'}$ and $\chi_{x'y'}$.

Transition		Measurements			Calculations			Comparisons		
		Meas. Splitting	Average	Deviation	Cal. Split.	Average	Deviation			
$J_\tau \to J'_{\tau'}$	$\epsilon F \to \epsilon' F'$	$\Delta\nu^m$	A^m	$\Delta^m = \lvert\Delta\nu^m\rvert - A^m$	$\Delta\nu^c$	A^c	$\Delta^c = \lvert\Delta\nu^c\rvert - A^c$	$\Delta\nu^m - \Delta\nu^c$	$A^m - A^c$	$\Delta^m - \Delta^c$
0_0 1_0	00 01	-2.83	2.82	0.01	-2.82	2.82	0.00	-0.01	0.00	0.01
	22 21	2.79		-0.03	2.82		0.00	-0.03		-0.03
2_{-2} 2_0	21 22	-10.71	10.72	-0.01	-10.67	10.73	-0.06	-0.04	-0.01	0.05
	02 21	10.72		0.00	10.80		0.07	-0.08		-0.07*
	22 22	-12.97	13.12	-0.15	-12.96	13.12	-0.16	-0.01	0.00	0.01
	02 02	13.27		0.15	13.28		0.16	-0.01		-0.01
2_{-2} 3_{-2}	02 03	-4.29	4.31	-0.02	-4.22	4.26	-0.04	-0.07	0.05	0.02
	22 23	4.32		0.01	4.29		0.03	0.03		-0.02
4_{-4} 4_{-2}	24 24	-9.72	9.79	-0.07	-9.80	9.80	0.00	0.08	-0.01	-0.07*
	04 04	9.85		0.06	9.80		0.00	0.05		0.06*

---

*See Chapter V for a discussion of these splittings.

involved were calculated to be too small to be reliably measured. The data recorded by Murray for these lines may have been due to impurity lines. Several quantities are listed in the Table which are designed to illustrate different facets of the data. For example, the quantities entitled "Average", A^m and A^c, are the arithmetic averages of the absolute values of the splittings indicated, for the measured and calculated splittings, respectively. This quantity is the symmetric portion of the splitting, i.e., it is the portion which would be due to a first-order interaction only. The quantities $\Delta^m = |\Delta\nu^m| - A^m$ and $\Delta^c = |\Delta\nu^c| - A^c$ are measures of the deviation of the splitting from symmetry, i.e., measures of the asymmetry of the splitting.

The quadrupole splittings for the transitions listed in the Table were used as input for a computer program which calculated "best" values of $\chi_{x'x'}$, $\chi_{y'y'}$, and $\chi_{z'z'}$. The theory programmed was that explained by Clayton (46), and may be used only for the diagonal elements of the tensor, as it is essentially a least-squares fit of an overdetermined three-parameter system of linear equations. (The second-order effect is non-linear in the three diagonal elements as well as $\chi_{x'y'}$). An initial value of $\chi_{x'y'}$ was obtained from expression (15) in Appendix B with a value of β taken from a molecular structure table (47), and the values of $\chi_{x'x'}$ and $\chi_{z'z'}$ obtained by Murray. This value of $\chi_{x'y'}$ was adjusted in the computer program described in Appendix A until the best fit of the asymmetric patterns was obtained.

The values of the quadrupole coupling constants in the principal inertial system and in the principal dyadic system derived from the measurements in Table 1 are quoted here:

$$\chi_{x'x'} = -38.98 \text{ MHz} ,$$

$$\chi_{y'y'} = -8.87 ,$$

$$\chi_{z'z'} = 47.95 ,$$

$$\chi_{x'y'} = 64.3 \quad \text{(in magnitude)},$$

$$\beta = 51.6° ,$$

and,

$$\chi_{xx} = 47.85 \text{ MHz} ,$$

$$\chi_{yy} = 42.10 ,$$

$$\chi_{zz} = -89.94 .$$

The transformation between the two systems is explained in Appendix B.

CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The second-order theory applied to $SC\ell_2$ significantly improved the comparison between calculated and measured quadrupole splittings in the transitions indicated in Chapter IV. In the language of statistics, the average deviation between Murray's measurements and calculated first-order splittings was 0.054 MHz. and the standard deviation was 0.106 MHz. (48). The average deviation between the measurements in this work and the calculated second-order splittings is 0.010 MHz., and the standard deviation is 0.055 MHz., i.e., the standard deviation has been cut in half.

The values of $\chi_{x'x'}$, $\chi_{y'y'}$, and $\chi_{z'z'}$, derived from the data in Chapter IV better account for the symmetric portion of the splittings than the previously quoted values. The standard deviation between the averages (as defined in Chapter IV) of the splittings measured by Murray and the averages of the first-order splittings is 0.06 MHz. The standard deviation between the averages of the splittings measured in this work, labelled A^m in Table 1, and the averages of the second-order splittings, labelled A^c in Table 1, is 0.03 MHz.

The last column of Table 1 shows that the value of $\chi_{x'y'}$ quoted in Chapter IV accounts for the asymmetry in the splittings to within the estimated experimental error, 0.05 MHz., except for the three splittings indicated by asterisks. In these three splittings impurity lines were found quite close to the $SC\ell_2$ transition lines, and it is felt that this may well account for the deviations of these lines as explained in Chapter IV. It should be noted that the asymmetry of the splittings in $SC\ell_2$ is so small that the calculated splittings are not strongly dependent on the value of $\chi_{x'y'}$. Only in the $2_{-2} \rightarrow 2_0$ transition for the lines 22 → 22 and 02 → 02 does the asymmetry of the splitting become significantly more than the estimated experimental error. The particular value of $\chi_{x'y'}$ quoted here accounts for these asymmetries quite well. However, it should be noted that the uncertainty in the value of $\chi_{x'y'}$ produces a corresponding uncertainty in the angle β. The calculated β differs from half the $C\ell$-S-$C\ell$ bond angle measured by Murray, 102.8° (11), by only 0.2°. This is not a significant difference because of the uncertainty in β.

It is recommended that a second-order perturbation treatment as well as a quadrupole spectrum of an asymmetric rotor molecule containing identical bromine nuclei be undertaken. The asymmetry in the quadrupole splittings of such a molecule should be easily measurable and large enough to determine the $\chi_{x'y'}$ value for these nuclei with considerable accuracy.

APPENDIX A

COMPUTER CALCULATIONS

DESCRIPTION OF THE PROGRAM

An Algol computer program was written to calculate matrix elements of the form derived in Chapter III, in equation (7), for the quadrupole interaction of the asymmetric-top. The general structure of the program will be discussed here, and the program itself may be found on succeeding pages.

The program was divided into two blocks and information was transferred from block one to block two through three global parameters. The first block diagonalized the asymmetric-top rotational Hamiltonian using symmetric-top functions as basis functions. The block reads-in the rotational constants of the molecule, usually designated A,B, and C. The program computes the asymmetric-top Hamiltonian matrix elements and uses a double-precision procedure, called "DJACOBI", to produce eigenvalues and orthonormal eigenvectors of the Hamiltonian. This block also calculates the rotational symmetry of each asymmetric level.

The eigenvalues, eigenvectors, and symmetries are transferred to the second block which calculates the appropriate diagonal and off-diagonal matrix elements for the quadrupole Hamiltonian. The input parameters of the second block include four components of the coupling constant tensor, $\chi_{x'x'}$, $\chi_{y'y'}$, $\chi_{z'z'}$ and $\chi_{x'y'}$, which are related to the field gradient tensor as explained in Chapter III.

One may proceed in two ways with the elements from block two. The elements themselves may be placed into a rotational plus quadrupole Hamiltonian matrix, which will in general be complex, and the matrix may be diagonalized giving the actual frequencies of the perturbed lines. Or perturbation theory may be employed to give successive corrections to the rotational energy. In this work, both methods were tried on the $J_\tau = 2_{-2}$ to $J'_{\tau'} = 2_0$ transition and found to agree to within 0.001 MHz., which, it is felt, justified the use of perturbation theory on the entire spectrum. In either case, one must determine which levels a particular J_τ rotational level will interact with. This is arrived at by symmetry arguments.

For $SC\ell_2$, the identification of the rotational constants

$$A = \frac{h}{8\pi^2 I_A}$$

$$B = \frac{h}{8\pi^2 I_B}$$

and

$$C = \frac{h}{8\pi^2 I_C}$$

and the fact that $I_A < I_B < I_C$ dictates that the principal inertial axes of the molecule be drawn as in Figure 7. The relation between the abc axes shown inthe figure and the $x'y'z'$ referred to in other parts of this work is

$$x' \leftrightarrow a$$

$$y' \leftrightarrow b$$

$$z' \leftrightarrow c$$

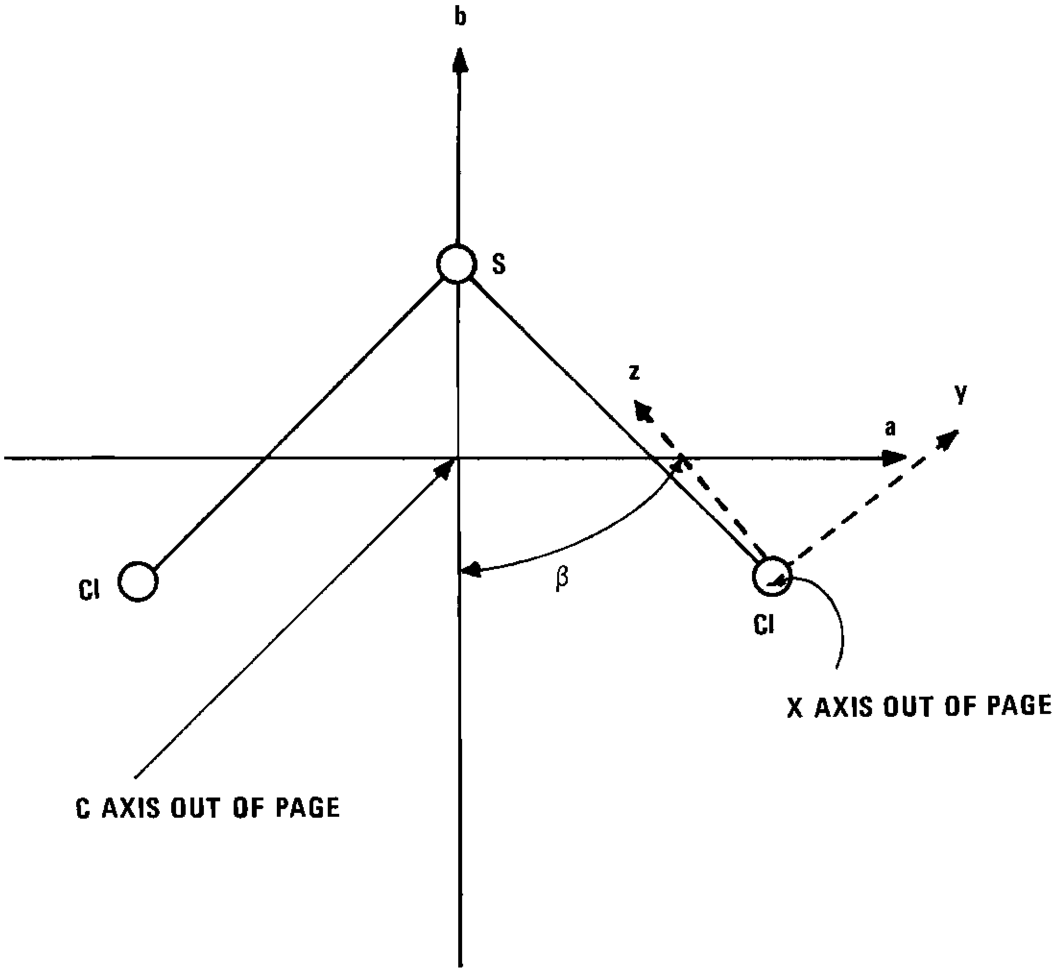

Figure 7. Principal Inertial Axes and Principal Axes for the Field-Gradient Dyadic in SCl_2.

The wavefunctions of a planar asymmetric-top molecule belong to a point symmetry group called the four group which has the four operators E, C_2^a, C_2^b, and C_2^c. Here E is the identity operator and the C_2^i operations indicate a rotation of the molecule through 180° about the superscripted axis. The four non-degenerate representations of the group, define four species of wavefunctions labeled A, B_a, B_b, and B_c with symmetries as shown in the table below. The plus and minus signs indicate symmetry and anti-symmetry with respect to the given group operation, respectively. Clayton shows this explicitly in his thesis (49).

Table 2. Species of Wavefunctions Under Operations of the Four-Group.

Species	E	C_2^c	C_2^b	C_2^a
A	+	+	+	+
B_c	+	+	-	-
B_b	+	-	+	-
B_a	+	-	-	+

The rotational symmetry of the rotational Hamiltonian is species A. The quadrupole Hamiltonian contains terms of symmetry A and B_c. Now, for a non-zero result for rotational or quadrupole matrix elements, the integrand must have symmetry A which means that the product of wavefunctions must have symmetry A or B_c. The program only considers interactions between states satisfying the above symmetry relations.

The Exclusion Principle applied to the total wavefunction for the asymmetric-top, i.e., electronic, vibrational, rotational, and spin parts, states that the entire function must be anti-symmetric with respect to interchange of identical nuclei of spin 3/2. For a symmetric electronic and vibrational state, such as the ground state, this means that the rotational times spin parts must be anti-symmetric with respect to interchange of identical nuclei. This interchange can be accomplished by operating on the rotational functions with the C_2^b operation of the four group, and interchanging the spins of the nuclei. As explained in Clayton (50), rotational states with even τ values are symmetric with respect to C_2^b and states with odd τ values are anti-symmetric. This means that the spin functions for the above states must be anti-symmetric and symmetric respectively to satisfy the Exclusion Principle. Now, one has from Edmonds (51) that, if $u(I_1I_2I)$ are the spin eigenvectors for the two nuclei system,

$$u(I_1I_2I) = (-1)^{I_1+I_2-I}u(I_2I_1I) \ ,$$

and in the case $I_1 = I_2 = 3/2$, one obtains

$$u(I_1I_2I) = (-1)^{3-I}u(I_2I_1I) \ .$$

Therefore requiring $u(I_1I_2I)$ to be symmetric with respect to interchange of identical nuclei is the same as saying I may be only 3 or 1. Likewise, requiring anti-symmetry is the same as saying I may be only 2 or 0.

To summarize then, states with even τ may have I values of only 2 or 0, and states with odd τ may have I values of only 3 or 1. This information is included in the program and greatly reduces the number of elements that must be calculated.

In this program, the perturbation theory approach was chosen. The general perturbation formula to second-order is (52)

$$E_n = E_n^{rot} + H_{nn}^{Q} + \sum_{m \neq n} \frac{H_{nm}^{Q} H_{mn}^{Q}}{E_n^{rot} - E_m^{rot}} , \qquad (13)$$

where E_n^{rot} is the rotational energy of the state n, and H_{nn}^{Q} is the first-order correction of the quadrupole interaction which is just the diagonal matrix element H_{nn}^{Q} itself. The second-order correction is given by the sum, where H_{nm}^{Q} is the off-diagonal quadrupole matrix element linking states n and m (which may be complex), and the sum extends over all the appropriate states determined by the above symmetry considerations. One notes the difference in rotational energies in the denominator of the summand. Interactions between rotational levels separated by more than 20,000 MHz. were not considered because of this term.

It is found that, for states with even τ values, the F = J levels may be obtained in two ways, i.e., with I = 2 or I = 0, and for odd τ levels, the F = J and F = J±1 states may be obtained in two ways, i.e., with I = 3 or I = 1. The first-order quadrupole interaction removes the degeneracy of these rotational states and new zero-order wavefunctions may be found which correspond to the non-degenerate perturbed states. For the even τ levels the new zero-order wavefunctions are of the form

$$\Psi_A(J\tau\epsilon J) = \frac{1}{\sqrt{2}} \; [\Psi_A(J\tau 2J) \pm \Psi_A(J\tau 0J)] \tag{14}$$

where $\Psi_A(J\tau IF)$ are the functions discussed above and in Chapter III. Here ϵ is a pseudo-spin parameter discussed in Robinson and Cornwell (53). Non-degenerate second-order perturbation theory may be applied if the new zero-order wavefunctions are used.

First-order perturbation theory gives a symmetric transition frequency pattern for even τ values, and for odd τ values the pattern is unsymmetrical. This work examined only the more symmetric even τ patterns and, as a result, the computer program assumes new zero-order wavefunctions of the above form. In the computer output the quantity written in the column labelled "ENERGY CORRECTION" is the term in the summand of equation (13) corresponding to the matrix element H^Q_{nm}. In the position labelled "CORRECTION FOR STATE WITH NON-ZERO FIRST-ORDER SPLITTING" the appropriate summand term appears for F = J assuming the J_τ level is of even τ, i.e., the new zero-order wavefunction is used in calculating this correction assuming τ is even. If τ is not even, the energy correction column will not be meaningful and a 2 by 2 matrix must be diagonalized to obtain the correct zero-order wavefunctions and the correct energies. It was found that in $SC\ell_2$, the second-order correction for the F = J levels was the same for both F = J states since only one of the two asymmetric functions in equation (14) gave non-zero matrix elements with other $J'_{\tau'}$ states and this fact is also incorporated into the computer program. If both asymmetric functions were to contribute to the off-diagonal elements, the correction would not be the same for both F = J states and considerably more programming would be involved.

The machine only calculates matrix elements if J′ ≥ J because of the problems indicated in Chapter III on page 28, so if a certain J level interacts with a lower J′ level the machine inverts the roles of the two states and, in effect, calculates the set of complex conjugate elements. One should understand that, if this is the case, the number in the position "CORRECTION FOR STATE WITH NON-ZERO FIRST-ORDER SPLITTING" will be the correction for the F = J′ state, not the F = J state. In these cases, one must calculate the appropriate F = J correction using the matrix element and the correct zero-order F = J wavefunctions.

The program itself is profusely commented to make it easier to locate any particular section of programming.

CARD IMAGES OF THE PROGRAM

```
BEGIN
COMMENT BEGINNING OF PROGRAM TO COMPUTE THE FIRST- AND SECOND-ORDER MATR
IX ELEMENTS OF THE QUADRUPOLE HAMILTONIAN;
COMMENT THE DATA CARDS MUST BE AS FOLLOWS:
         CARD 1 MUST CONTAIN THE ROTATIONAL CONSTANTS A,B,C AND
              THE NUMBER OF J LEVELS TO BE DIAGONALIZED, N, ALL IN
              FREE-FIELD READ.
         CARDS 2 THROUGH N+1 EACH CONTAIN ONE J-VALUE FOR DIAGONAL-
              IZATION.
         CARD N+2 CONTAINS XAA,XBB,XCC,AND XAB IN FREE-FIELD READ.
         CARD N+3 CONTAINS THE NUMBER OF J-T LEVELS FOR WHICH THE FIRST
              AND SECOND ORDER CORRECTIONS ARE TO BE CALCULATED,P.
         CARDS N+4 THROUGH N+4+P EACH CONTAIN ONE J-T PAIR OF NUMBERS
              FOR WHICH CALCULATIONS ARE MADE;
FILE IN BAL (2,10);
FILE OUT LAB 16(2,15);
ARRAY E[0:19,0:19],CM[-19:19,-19:19,-19:19];
INTEGER ARRAY RS[0:19,0:19];
 BEGIN
 COMMENT BEGINNING OF FIRST BLOCK WHICH CALCULATES ASYMMETRIC-TOP ENERGY
 LEVELS AND NORMALIZED EIGENVECTORS IN TERMS OF SYMMETRIC-TOP EIGENVECT
 ORS;
 INTEGER I,J,K,N,M,P1,P2,NN,II,JJ,G,H,NM,JI,KI;
 REAL AA,BB,CC,CL;
 ARRAY AD[0:15],B[0:15,0:15];
 ARRAY A,AH,AL,BH,BL[0:15,0:15];
INTEGER PROCEDURE MIN(P1,P2);
COMMENT CALCULATES THE MINIMUM OF TWO NUMBERS;
VALUE P1,P2;
INTEGER P1,P2;
              IF P1 < P2 THEN MIN ← P1 ELSE MIN ← P2;
PROCEDURE MATRIXPRINT (N,M,A);
COMMENT PRINTS OUT AN N BY M MATRIX A;
VALUE N,M;
INTEGER N,M;
ARRAY A[0,0];
        BEGIN
```

```
        INTEGER MIN1;
        FORMAT OUT FMT (/,"ROW",I3,X2,"COL",I3,5F20.8);
        LIST ROW ( I,J,FOR K←J STEP 1 UNTIL MIN1 DO A[I,K] );
              FOR I ← 1 STEP 1 UNTIL N DO
        BEGIN
              MIN1 ← 5;
              J ← 1;
              WHILE J ≤ M DO
        BEGIN
              WRITE (LAB,FMT,ROW);
              J ← K;
              MIN1 ← MIN(J+4,M)
        END
        END
        END MATRIXPRINT;
PROCEDURE EAGLE(N,A);
VALUE N;
INTEGER N;
ARRAY A[0,0];
        BEGIN
ALPHA SYMM;
REAL TRA,TRD;
ARRAY REF,USE,USO[0:34,0:34],X,GOOF[0:34],T[0:11];
INTEGER ARRAY ID[0:34,0:34];
INTEGER ARRAY C2A,C2B,C2C[0:15];
FORMAT OUT FMT1(/,X6,"J",X6,"T",X9,"ROTATIONAL LEVEL",X6,"SYMMETRY");
FORMAT OUT FMT2(/,X5,I2,X5,I2,X4,F20.8,X10,A2);
FORMAT OUT GOOFF("VECTOR CHECK BY SUM OF PRODUCTS FOR ROW",I2,F12.8);
FORMAT OUT CHECK("TRA=",F13.4,X9,"TRD=",F13.4,X9,"DIFF=",F7.4);
LIST SNAFU(TRA,TRD,TRA-TRD);
LIST GOOFU (I,GOOF[I]);
PROCEDURE     DJACOBI(OPT,N,AH,AL,BH,BL) ; %
VALUE         OPT,N ; %
INTEGER       OPT,N ; %
REAL ARRAY    AH,AL,BH,BL[0,0] ; %
%
%             THIS PROCEDURE TRANSFORMS THE N-TH ORDER DOUBLE
```

```
%   PRECISION REAL SYMMETRIC MATRIX A INTO A DIAGONAL MATRIX
%   WHOSE ELEMENTS A[I,I], I = 1,2,...,N, CONTAIN THE EIGENVAL-
%   UES OF A IN DESCENDING ORDER OF MAGNITUDE. THE EIGENVECTOR
%   ASSOCIATED WITH THE I-TH EIGENVALUE IS STORED IN THE I-TH
%   COLUMN OF THE DOUBLE PRECISION MATRIX B. TWO OPERATIONS ARE
%   PERFORMED DEPENDING ON THE VALUE OF THE OPTION PARAMETER OPT:
%
%   IF OPT = 1, BOTH EIGENVALUES AND EIGENVECTORS ARE PRODUCED.
%
%   IF OPT = 2, ONLY EIGENVALUES ARE PRODUCED.
%
BEGIN %
INTEGER PROCEDURE DCOMPARE(XH,XL,YH,YL) ; %
VALUE   XH,XL,YH,YL ; %
REAL    XH,XL,YH,YL ; %
%
%       THIS PROCEDURE COMPARES THE DOUBLE PRECISION REAL NUMBERS
%   X = (XH,XL) AND Y = (YH,YL). THE PROCEDURE IDENTIFIER IS ASSIGNED
%   THE VALUE -1, 0, +1 ACCORDINGLY AS X <, =, > Y.
%
BEGIN %
REAL    ZH,ZL ; %
        DOUBLE(XH,XL,YH,YL,-,←,ZH,ZL) ; %
        DCOMPARE ← SIGN(ZH) ; %
END DCOMPARE ; %
INTEGER       I,K,L,M,KL,KM,P ; REAL DELH,DELL,EH,EL ; %
REAL      X,Y,QH,QL,RH,RL,SH,SL,TH,TL,VH,VL,WH,WL,ZH,ZL,MLH,MLL,MMH,MML;
REAL ARRAY    MXH,MXL[0:N], CON[0:7] ; %
INTEGER ARRAY KX[0:N] ; %
DEFINE        D = DOUBLE # , Q = QH,QL # , DEL = DELH,DELL # , %
              STU = STEP 1 UNTIL # , R = RH,RL # , %
              STW = STEP 1 WHILE # , S = SH,SL # , %
              IDO1 = FOR I ← 1 STU N DO # , T = TH,TL # , %
              IDO2 = FOR I ← 1 STW I ≤ N DO # , V = VH,VL # , %
              IDO3 = FOR I ← 1 STW I < L DO # , W = WH,WL # , %
              IDO4 = FOR I ← L+1 STW I < M DO # , Z = ZH,ZL # , %
              IDO5 = FOR I ← M+1 STW I ≤ N DO # , ML = MLH,MLL # , %
```

```
                    IDO6 = FOR I ← 1 STW I < N DO # , MM = MMH,MML # , %          00011200
                    KDO1 = FOR K ← I+1 STU N DO # , %                             00011300
                    KDO2 = FOR K ← I+1 STW K ≤ N DO # , %                         00011400
                    BII = BH[I,I],BL[I,I] # , ALI = AH[L,I],AL[L,I] # , %         00011500
                    BIK = BH[I,K],BL[I,K] # , BKI = BH[K,I],BL[K,I] # , %         00011600
                    MXI = MXH[I],MXL[I] # ,   AIM = AH[I,M],AL[I,M] # , %         00011700
                    ALM = AH[L,M],AL[L,M] # , ALL = AH[L,L],AL[L,L] # , %         00011800
                    AMM = AH[M,M],AL[M,M] # , AIL = AH[I,L],AL[I,L] # , %         00011900
                    BIL = BH[I,L],BL[I,L] # , BIM = BH[I,M],BL[I,M] # , %         00012000
                    AMI = AH[M,I],AL[M,I] # , AIK = AH[I,K],AL[I,K] # , %         00012100
                    LMX = MXH[L],MXL[L] #, MXM = MXH[M],MXL[M] # ; %              00012200
LABEL               L1,L2,RET1,RET2 ; %                                           00012300
DEFINE              SETUP = %                                                     00012400
          BEGIN %                                                                 00012500
                    X ← (1.0)×ZH ; P ← 0 ; %                                      00012600
                    P ← X.[8:2] ; P.[45:1] ← X.[2:1] ; %                          00012700
                    Y ← X ; Y.[3:6] ← Y.[2:6] ; Y ← Y×CON[P] ; %                  00012800
          END # ; %                                                               00012900
%                                                                                 00013000
DEFINE              ITER = Y ← (0.5)×(Y + X/Y) # ; %                              00013100
%                                                                                 00013200
DEFINE              DSQRT1 = %                                                    00013300
          BEGIN IF ZH = 0 THEN GO TO L1 ; %                                       00013400
                SETUP ; ITER ; ITER ; ITER ; ITER ;                               00013500
                D(Z,Y,0,/,Y,0,-,,0.5,×,Y,0,+,←,S) ; GO TO RET1 ; %                00013600
                L1: SH ← SL ← 0 ; %                                               00013700
                RET1:                                                             00013800
          END # ,                                                                 00013900
%                                                                                 00014000
                DSQRT2 = %                                                        00014100
          BEGIN IF ZH = 0 THEN GO TO L2 ; %                                       00014200
                SETUP ; ITER ; ITER ; ITER ; ITER ;                               00014300
                D(Z,Y,0,/,Y,0,-,,0.5,×,Y,0,+,←,T) ; GO TO RET2 ; %                00014400
                L2: TH ← TL ← 0 ; %                                               00014500
                RET2: %                                                           00014600
          END # ; %                                                               00014700
%                                                                                 00014800
```

```
          CON[0] ←  2.697398@-06 ; CON[1] ←  1.603683@-06 ;
          CON[2] ←  7.6294@-06 ; CON[3] ←  4.536465@-06 ;
          CON[4] ←  2.137099@+23 ; CON[5] ←  1.270727@+23 ;
          CON[6] ←  7.555786@+22 ; CON[7] ←  4.482697@+22 ;
          IF (OPT ≠ 2) THEN %
          IDO1 %
     BEGIN %
          D(1,0,←,BII) ; %
          KDO1 BEGIN BH[I,K] ← BL[I,K] ← BH[K,I] ← BL[K,I] ← 0 END ;
     END ; %
          QH ← QL ← 0 ; L ← 1 ; %
          IDO2 %
     BEGIN %
          MMH ← MML ← 0 ; KM ← N ; %
          KDO2
     BEGIN
          D(AIK,←,W) ; WH ← ABS(WH) ; %
          IF WH > MMH THEN %
          BEGIN D(W,←,MM) ; KM ← K END ; %
     END ; %
          D(MM,←,MXI) ; KX[I] ← KM ; %
          IF MMH > QH THEN %
          BEGIN D(MM,←,Q) ; L ← I END ; %
     END ; %
          M ← KX[L] ; %
          D(ALL,←,R) ; RH ← ABS(RH) ; %
          D(AMM,←,Z) ; ZH ← ABS(ZH) ; %
          EH ← 1.0@-20 ; EL ← 0 ; D(R,Z,+,←,R) ; D(Q,R,+,←,Q) ; %
          D(ABS(RH),RL,ABS(QH),QL,-,←,DEL) ; DELH ← ABS(DELH) ; %
          WHILE DCOMPARE(DELH,DELL,EH,EL) > 0 DO %
     BEGIN %
          D(ALM,ALM,+,←,Q) ; D(ALL,AMM,-,←,R) ; %
          D(R,R,×,Q,Q,×,+,4,0,×,←,Z) ; DSQRT1 ; %
          ZH ← ABS(RH) ; ZL ← RL ; %
          D(Z,S,/,,0.5,+,←,Z) ; DSQRT2 ; %
          D(0,0,Q,+,S,T,×,/,←,S) ; %
          IF RH< 0 THEN %
```

```
        BEGIN ZH←TH ; ZL←TL ; TH←SH ; TL←SL ; SH←ZH ; SL←ZL END ;
        IF (OPT ≠ 2) THEN %
        ID02 %
    BEGIN %
        D(BIL,←,Q) ; D(BIM,←,R) ; %
        D(T,Q,×,S,R,×,+,←,BIL) ; D(T,R,×,S,Q,×,-,←,BIM) ; %
    END ; %
        MLH ← MLL ← MMH ← MML ← 0 ; KL ← KM ← N ; %
        ID03 %
    BEGIN %
        D(AIL,←,Q) ; D(AIM,←,R) ; %
        D(T,Q,×,S,R,×,+,←,V) ; D(V,←,AIL) ; %
        D(T,R,×,S,Q,×,-,←,Z) ; D(Z,←,AIM) ; %
        ZH ← ABS(ZH) ; VH ← ABS(VH) ; D(MXI,←,W) ; %
        IF (ZH > WH) OR (VH > WH) THEN %
        IF (ZH > VH) THEN%
        BEGIN D(Z,←,MXI) ; KX[I] ← M END ELSE %
        BEGIN D(V,←,MXI) ; KX[I] ← L END %
    END ; %
        ID04 %
    BEGIN %
        D(ALI,←,Q) ; D(AIM,←,R) ; %
        D(T,Q,×,S,R,×,+,←,V) ; D(V,←,ALI) ; %
        D(T,R,×,S,Q,×,-,←,Z) ; D(Z,←,AIM) ; %
        IF ABS(VH) > MLH THEN %
        BEGIN MLH ← ABS(VH) ; MLL ← VL ; KL ← I END ; %
        IF ABS(ZH) > MXH[I] THEN %
        BEGIN MXH[I] ← ABS(ZH) ; MXL[I] ← ZL ; KX[I] ← M END %
    END ; %
        ID05 %
    BEGIN
        D(ALI,←,Q) ; D(AMI,←,R) ; %
        D(T,Q,×,S,R,×,+,←,V) ; D(V,←,ALI) ; %
        D(T,R,×,S,Q,×,-,←,Z) ; D(Z,←,AMI) ; %
        IF ABS(VH) > MLH THEN %
        BEGIN MLH ← ABS(VH) ; MLL ← VL ; KL ← I END ; %
        IF ABS(ZH) > MMH THEN %
```

```
                  BEGIN MMH ← ABS(ZH) ; MML ← ZL ; KM ← I END ; %
          END ; %
                  D(ML,←,LMX) ; KX[L] ← KL ; %
                  D(MM,←,MXM) ; KX[M] ← KM ; %
                  D(ALL,←,Q) ; D(AMM,←,R) ; D(ALM,←,Z) ; %
                  D(T,S,×,←,V) ; D(T,T,×,←,T) ; D(S,S,×,←,S) ; %
                  D(T,S,-,Z,×,R,Q,-,V,×,+,←,ALM) ; D(2,0,Z,×,V,×,←,V) ; %
                  D(T,Q,×,S,R,×,+,V,+,←,ALL) ; %
                  D(T,R,×,S,Q,×,+,V,-,←,AMM) ; D(ML,←,Q) ; %
                  ID06 IF (RH ← MXH[I] > QH) THEN %
                  BEGIN QH ← RH ; QL ← RL ; L ← I END ; %
                  M ← KX[L] ;
                  D(ALL,←,R) ; RH ← ABS(RH) ;
                  D(AMM,←,Z) ; ZH ← ABS(ZH) ;
                  D(R,Z,+,←,R) ; D(Q,R,+,←,Q) ; %
                  D(ABS(RH),RL,ABS(QH),QL,-,←,DEL) ; DELH ← ABS(DELH) ; %
          END ; %
                  FOR I ← 1 STEP 1 UNTIL N DO %
                  FOR K ← 1 STEP 1 UNTIL I-1 DO %
                  IF K ≠ I THEN AH[I,K] ← AL[I,K] ← AH[K,I] ← AL[K,I] ← 0 ;
END DJACOBI ; %
PROCEDURE SORTR(AD,B,N);
VALUE N;
INTEGER N;
ARRAY AD[0],B[0,0];
          BEGIN
          INTEGER I,J,K;
          REAL T;
                  FOR J ← 1 STEP 1 UNTIL N-1 DO
                  FOR I ← 1 STEP 1 UNTIL N-J DO
                  IF AD[I] ≥ AD[I+1] THEN
          BEGIN
                  T ← AD[I];
                  AD[I] ← AD[I+1];
                  AD[I+1] ← T;
                  FOR K ← 1 STEP 1 UNTIL N DO
          BEGIN
```

```
      T ← B[K,I];
      B[K,I] ← B[K,I+1];
      B[K,I+1] ← T;
END;
END;
END OF SORTR;
      FOR I ← 2 STEP 1 UNTIL N DO
      FOR J ← 1 STEP 1 UNTIL I-1 DO A[I,J] ← A[J,I];
      FOR I ← 1 STEP 1 UNTIL N DO FOR J ← 1 STEP 1 UNTIL N DO
BEGIN
      REF[I,J] ← A[I,J];
      IF I = J THEN ID[I,J] ← 1;
      IF I ≠ J THEN ID[I,J] ← 0
END;
      MATRIXPRINT(N,N,A);  COMMENT PRINTS INPUT MATRIX;
      FOR I←1 STEP 1 UNTIL N DO
      FOR J ← 1 STEP 1 UNTIL N DO
BEGIN
      AH[I,J] ← A[I,J];
      AL[I,J] ← 0.00;
END;
      TRA ← 0.00;
      FOR I ← 1 STEP 1 UNTIL N DO
      TRA ← TRA + A[I,I];
      DJACOBI(1,N,AH,AL,BH,BL); COMMENT CALCULATES EIGENVALUES
      AND EIGENVECTORS;
      FOR I ← 1 STEP 1 UNTIL N DO
      AD[I] ← ((AA+BB)/2)×((N-1)/2)×((N+1)/2) + (CC-(AA+BB)/2)
      ×AH[I,I]; COMMENT CONVERTS EIGENVALUES TO ROTATIONAL
      ENERGY LEVELS;
      SORTR(AD,BH,N); COMMENT SORTS ENERGY LEVEL MATRIX;
      FOR I ← 1 STEP 1 UNTIL N DO
      AH[I,I] ← (AD[I]-((AA+BB)/2)×((N-1)/2)×((N+1)/2))/
      (CC-(AA+BB)/2);
      WRITE(LAB,FMT1);
      FOR I ← N STEP -1 UNTIL 1 DO
BEGIN
```

```
      C2C[I] ← (-1)*(ENTIER((I-1)/2) + JI);
      C2A[I] ← (-1)*(ENTIER(I/2));
      C2B[I] ← C2C[I]×C2A[I];
END;
      FOR I ← N STEP -1 UNTIL 1 DO
BEGIN
COMMENT THIS SECTION OF PROGRAMMING STORES THE ROTATIONAL
SYMMETRIES OF THE ASYMMETRIC WAVEFUNCTIONS;
      IF C2C[I] = 1 AND C2A[I] = 1 AND C2B[I] = 1 THEN
BEGIN
      SYMM ← " A";
      RS[(N-1)/2,I-1] ← 1;
END;
      IF C2C[I] = -1 AND C2A[I] = 1 AND C2B[I] = -1 THEN
BEGIN
      SYMM ← "BA";
      RS[(N-1)/2,I-1] ← 2;
END;
      IF C2C[I] = -1 AND C2A[I] = -1 AND C2B[I] = 1 THEN
BEGIN
      SYMM ← "BB";
      RS[(N-1)/2,I-1] ← 3;
END;
      IF C2C[I] = 1 AND C2A[I] = -1 AND C2B[I] = -1 THEN
BEGIN
      SYMM ← "BC";
      RS[(N-1)/2,I-1] ← 5;
END;
      WRITE(LAB,FMT2,(N-1)/2,-((N-1)/2) - 1 + I,AD[I],SYMM);
END;
      MATRIXPRINT(N,N,BH); COMMENT PRINTS OUT EIGENVECTOR
      MATRIX;
      COMMENT NEXT SECTION OF PROGRAMMING CHECKS NORMALIZATION
      AND ORTHOGONALITY ON THE EIGENVECTORS;
      TRD ← 0.00;
      FOR I ← 1 STEP 1 UNTIL N DO
      TRD ← TRD + AH[I,I];
```

```
      IF ABS(TRA - TRD) > 1@-6 THEN                             00033400
      WRITE(LAB,CHECK,SNAFU);                                   00033500
      FOR K ← 1 STEP 1 UNTIL N DO                               00033600
BEGIN                                                           00033700
      FOR I ← 1 STEP 1 UNTIL N DO                               00033800
BEGIN                                                           00033900
      GOOF[I] ← 0.0;                                            00034000
      FOR J ← 1 STEP 1 UNTIL N DO                               00034100
      GOOF[I] ← GOOF[I] + (REF[I,J] - AH[K,K]×ID[I,J])×BH[J,K]; 00034200
      IF GOOF[I] > 1@-6 THEN                                    00034300
      WRITE(LAB,GOOFF,GOOFO)                                    00034400
END;                                                            00034500
END;                                                            00034600
END EAGLE;                                                      00034700
 COMMENT THE ACTUAL BODY OF BLOCK ONE NOW BEGINS;               00034800
 WRITE (LAB[NO]);                                               00034900
 READ(BAL,/,AA,BB,CC,NN);                                       00035000
 CL←(AA-BB)/(2×(CC)-(AA+BB));                                   00035100
 FOR NM ← 1 STEP 1 UNTIL NN DO                                  00035200
BEGIN                                                           00035300
 READ(BAL,/,JI);                                                00035400
 FOR G←1 STEP 1 UNTIL 2×(JI)+1 DO                               00035500
BEGIN                                                           00035600
 COMMENT THE NEXT SECTION OF PROGRAMMING FORMS THE ASYMMETRIC   00035700
 HAMILTONIAN MATRIX WHICH WILL BE DIAGONALIZED BY THE ABOVE     00035800
 PROCEDURES;                                                    00035900
 KI ← -(JI-G+1);                                                00036000
 A[G,G]←(KI)*2;                                                 00036100
END;                                                            00036200
 FOR G←1 STEP 1 UNTIL 2×(JI)+1 DO                               00036300
 FOR H←G+1 STEP 1 UNTIL 2×(JI)+1 DO                             00036400
BEGIN                                                           00036500
 KI←-(JI-G+1);                                                  00036600
 IF H=G+2 THEN                                                  00036700
 A[G,H] ←-((CL)/2)×SQRT((JI-KI)×(JI-KI-1)×(JI+KI+2)             00036800
 ×(JI+KI+1))                                                    00036900
 ELSE A[G,H] ← 0.00;                                            00037000
```

```
        END;
         EAGLE(2×(JI)+1,A);
         COMMENT THESE STATEMENTS STORE THE THE RESULTS OF THE DIAG-
         ONALIZATION INTO THE ENERGY AND COEFFICIENT ARRAYS E AND CM;
         FOR II← 2×(JI) + 1 STEP -1 UNTIL 1 DO
         E[JI,II-1] ← AD[II];
         FOR II← 2×(JI) + 1 STEP -1 UNTIL 1 DO
         FOR JJ← 2×(JI) + 1 STEP -1 UNTIL 1 DO
         CM[JI,II-1,JJ-1]←BH[JJ,II];
        END;
 END OF BLOCK ONE;
 BEGIN
 COMMENT BEGINNING OF BLOCK TWO WHICH CALCULATES THE QUADRUPOLE MATRIX
 ELEMENTS AND THEIR ENERGY CORRECTIONS ACCORDING TO PERTURBATION THEORY;
 INTEGER W,EXP1,P,P1,P2,P3,P4,S,K,MIN3,F3,J,T,JP,TP,KA;
 REAL D1,D2,D3,J1,J2,J3,L1,L2,L3,SM1,M1,M2,M3,A,B,CHIXPXP,CHIYPYP,
 CHIZPZP,CHIXPYP;
 INTEGER ARRAY JA,TA[0:50];
 FORMAT OUT HEADING(/,X52,"MATRIX ELEMENT",//,X4,"JP",X3,"TP",X3,
 "IP",X3,"F",X4,"J",X4,"T",X4,"I",X18,"REAL VALUE",X5,"IM VALUE",
 X8,"ENERGY CORRECTION",X5,"SYMMETRY");
 FORMAT OUT EMIT(/,X9,"PROCESSOR TIME IS",F10.6,"MIN IO TIME IS",
 F10.6,"MIN");
INTEGER PROCEDURE MIN2(P1,P2,P3,P4);
COMMENT FINDS THE MINIMUM OF FOUR NUMBERS;
VALUE P1,P2,P3,P4;
INTEGER P1,P2,P3,P4;
        BEGIN
              IF P1≤P2 AND P1≤P3 AND P1≤P4 THEN MIN2 ← P1;
              IF P2≤P1 AND P2≤P3 AND P2≤P4 THEN MIN2 ← P2;
              IF P3≤P1 AND P3≤P2 AND P3≤P4 THEN MIN2 ← P3;
              IF P4≤P1 AND P4≤P2 AND P4≤P3 THEN MIN2 ← P4;
        END;
REAL PROCEDURE FACT(S);
COMMENT CALCULATES THE FACTORIAL OF S;
VALUE S;
INTEGER S;
```

```
              FACT ← IF S<0 THEN 0 ELSE IF S<2 THEN 1 ELSE FACT(S−1)×S;
REAL PROCEDURE DEL(D1,D2,D3);
VALUE D1,D2,D3;
REAL D1,D2,D3;
              DEL ← SQRT(FACT(D1+D2−D3)×FACT(D1−D2+D3)×FACT(−D1+D2+D3)/
              FACT(D1+D2+D3+1));
REAL PROCEDURE SUMK(J1,J2,J3,L1,L2,L3);
VALUE J1,J2,J3,L1,L2,L3;
REAL J1,J2,J3,L1,L2,L3;
        BEGIN
              SM1 ← 0;
              MIN3 ← MIN2(J1+J2−J3,J1+L2−L3,L1+J2−L3,L1+L2−J3);
              FOR K ← 0 STEP 1 UNTIL MIN3 DO
        BEGIN
              F3 ← FACT(K)×FACT(J1+J2−J3−K)×FACT(J1+L2−L3−K)
              ×FACT(L1+J2−L3−K)×FACT(−J1−L1+J3+L3+K)×FACT(−J2−L2+J3+L3
              +K)×FACT(L1+L2−J3−K);
              IF F3 > 0 THEN SM1 ← SM1 + (IF BOOLEAN(K) THEN −1 ELSE 1)
              ×FACT(J1+J2+L1+L2+1−K)/F3;
        END;
              SUMK ← SM1;
        END OF SUMK;
REAL PROCEDURE SIXJ(J1,J2,J3,L1,L2,L3); COMMENT CALCULATES WIGNER SIX−J
SYMBOLS;
VALUE J1,J2,J3,L1,L2,L3;
REAL J1,J2,J3,L1,L2,L3;
        BEGIN
              EXP1 ← J1+J2+L1+L2;
              IF ABS(J1+J2) ≥ J3 AND ABS(J1−J2) ≤ J3 THEN
              SIXJ ← (IF BOOLEAN(EXP1) THEN −1 ELSE 1)×DEL(J1,J2,J3)
              ×DEL(L1,L2,J3)×DEL(J1,L2,L3)×SUMK(J1,J2,J3,L1,L2,L3)
              ×DEL(L1,J2,L3) ELSE SIXJ ← 0;
        END;
REAL PROCEDURE SUMK2(J1,J2,J3,M1,M2,M3);
VALUE J1,J2,J3,M1,M2,M3;
REAL J1,J2,J3,M1,M2,M3;
        BEGIN
```

```
              SM1 ← 0;
              MIN3 ← MIN2(J1+J2-J3,J1-M1,J2+M2,100));
              FOR K ← 0 STEP 1 UNTIL MIN3 DO
        BEGIN
              F3 ← (FACT(K)×FACT(J1+J2-J3-K)×FACT(J1-M1-K)×
              FACT(J2+M2-K)×FACT(J3-J2+M1+K)×FACT(J3-J1-M2+K));
              IF F3 > 0 THEN SM1 ← SM1 + (IF BOOLEAN(K) THEN -1 ELSE 1)
              /F3;
        END;
              SUMK2 ← SM1;
        END OF SUMK2;
REAL PROCEDURE THREEJ(J1,J2,J3,M1,M2,M3); COMMENT CALCULATES THE WIGNER
THREE-J SYMBOL;
VALUE J1,J2,J3,M1,M2,M3;
REAL J1,J2,J3,M1,M2,M3;
        BEGIN
              EXP1 ← J1-J2-M3;
              IF M1+M2+M3 ≠ 0 THEN THREEJ ← 0 ELSE
              THREEJ ← (IF BOOLEAN(EXP1) THEN -1 ELSE 1)
              ×SQRT(FACT(J1+J2-J3)×FACT(J1-J2+J3)×FACT(-J1+J2+J3)
              ×FACT(J1+M1)×FACT(J1-M1)×FACT(J2+M2)×FACT(J2-M2)
              ×FACT(J3+M3)×FACT(J3-M3)/FACT(J1+J2+J3+1))
              ×SUMK2(J1,J2,J3,M1,M2,M3));
        END OF THREEJ;
COMMENT THE FOLLOWING TWO PROCEDURES DETERMINE THE VALUES OF THE
QUANTITIES X+ AND X- WHICH ARE FUNCTIONS OF J,T,JP,TP,I,AND IP.  THE
PHYSICAL CONSTANTS OF THE MOLECULE WHICH ENTER HERE, CHIXPXP,ETC.,
ARE THE POTENTIAL DERIVATIVES WITH RESPECT TO PRINCIPAL INERTIAL
AXES OF THE MOLECULE;
REAL PROCEDURE CHIPLUS(A,B,C,D,KA);
VALUE A,B,C,D,KA;
INTEGER A,B,C,D,KA;
        BEGIN
              IF ABS(A-B) = 0 THEN
         CHIPLUS ← ((2)/((B+1)×(2×(B)+3)))×((CM[B,B+D,B+KA]×CM[B,B+C,
            B+KA])×(3×(KA*2)-(B)×(B+1))×(CHIZPZP) - (CM[B,B+D,B+KA]×
            CM[B,B+C,B+KA+2])×SQRT((B-KA)×(B-KA-1)×(B+KA+1)×(B+KA+2))
```

```
            ×(CHIXPXP-CHIYPYP)/2 - (CM[B,B+D,B+KA]×CM[B,B+C,B+KA-2])
            ×SQRT((B+KA)×(B-KA+1)×(B+KA-1)×(B-KA+2))×(CHIXPXP-CHIYPYP)
            /2));
              IF ABS(A-B) = 1 THEN
         CHIPLUS ← (1/((B+1)×(B+2)×SQRT(2×B+3)))×(CM[B,B+D,B+KA]×
            CM[A,A+C,A+KA]×6×KA×SQRT(((B+1)*2)-(KA)*2)×
            CHIZPZP+CM[B,B+D,B+KA]×CM[A,A+C,A+KA+2]×SQRT((B-KA)×
            (B+KA+1)×(B+KA+2)×(B+KA+3))×(CHIXPXP-CHIYPYP)
            -CM[B,B+D,B+KA]×CM[A,A+C,A+KA-2]×SQRT((B+KA)×(B-KA+1)×(B-KA+
            2)×(B-KA+3))×(CHIXPXP-CHIYPYP));
              IF ABS(A-B) = 2 THEN
         CHIPLUS ← (2/(SQRT(B+1)×(B+2)×(2×B+3)×SQRT(2×B+5)))
            ×(CM[B,B+D,B+KA]×CM[A,A+C,A+KA]×3×SQRT((B+KA+1)×(B-KA+1)
            ×(B+KA+2)×(B-KA+2))×CHIZPZP-CM[B,B+D,B+KA]×CM[A,A+C,A+KA+2]
            ×SQRT((B+KA+1)×(B+KA+2)×(B+KA+3)×(B+KA+4))×(CHIXPXP
            -CHIYPYP)/2 - CM[B,B+D,B+KA]×CM[A,A+C,A+KA-2]×SQRT((B-KA+1)
            ×(B-KA+2)×(B-KA+3)×(B-KA+4))×(CHIXPXP-CHIYPYP)/2));
        END OF CHIPLUS;
REAL PROCEDURE CHIMINUS(A,B,C,D,KA);
VALUE A,B,C,D,KA;
INTEGER A,B,C,D,KA;
        BEGIN
              IF ABS(A-B) = 0 THEN
         CHIMINUS ← ((2)/((B+1)×(2×(B)+3)))×(CM[B,B+D,B+KA]
         ×CM[B,B+C,B+KA+2]×(-SQRT((B-KA)×(B+KA+1)×(B-KA-1)×(B+KA+2)))
         +CM[B,B+D,B+KA]×CM[B,B+C,B+KA-2]×SQRT((B+KA)×(B-KA+1)×(B+KA-1)
         ×(B-KA+2)))×CHIXPYP;
              IF ABS(A-B) = 1 THEN
         CHIMINUS ← (2/((B+1)×(B+2)×SQRT(2×B+3)))×(CM[B,B+D,B+KA]×
         CM[A,A+C,A+KA+2]×SQRT((B-KA)×(B+KA+1)×(B+KA+2)×(B+KA+3))×
         CHIXPYP + CM[B,B+D,B+KA]×CM[A,A+C,A+KA-2]×SQRT((B+KA)×(B-KA+1)
         ×(B-KA+2)×(B-KA+3))×CHIXPYP);
              IF ABS(A-B) = 2 THEN
         CHIMINUS ← (2/(SQRT(B+1)×(B+2)×(2×B+3)×SQRT(2×
         (B)+5)))×(CM[B,B+D,B+KA]×CM[A,A+C,A+KA+2]×(-SQRT((B+KA+1)×
         (B+KA+2)×(B+KA+3)×(B+KA+4))) + CM[B,B+D,B+KA]×CM[A,A+C,A+KA-2]
         ×SQRT((B-KA+1)×(B-KA+2)×(B-KA+3)×(B-KA+4)))×CHIXPYP;
```

```
        END OF CHIMINUS;
PROCEDURE MATRIXELEMENT(J,T,JP,TP);
COMMENT THIS PROCEDURE CALCULATES THE FIRST- AND SECOND-ORDER QUADRU-
POLE MATRIX ELEMENTS FOR THE ASYMMETRIC ROTOR AS WELL AS THEIR CONTRIBU-
TIONS TO THE SECOND-ORDER ENERGY CORRECTION;
VALUE J,T,JP,TP;
INTEGER J,T,JP,TP;
        BEGIN
        REAL ME,REP,IMA,PIMA,PREP,EC;
        INTEGER SS,SP,I,IP,F,R,RP,U,UP,FU,L,LP,FL;
        ALPHA SYM;
        LABEL FIRST,SECOND,THIRD,FOURTH,FIRSTP;
        FORMAT OUT ROW(/,X4,I1,X4,I2,X3,I1,X4,I1,X4,I1,X4,I2,X3,I1,X19,
        F11.6,F14.6,X7,F10.6,X10,A2),
        KROW(/,X5,"CORRECTION FOR STATE WITH NON-ZERO FIRST-ORDER SPLITT
ING IS",X22,F10.6,X10,A2),
        PROW(/,X4,I1,X4,I2,X3,I1,X4,I1,X4,I1,X4,I2,X3,I1,X19,F11.6,
        F14.6,X27,A2);
COMMENT DETERMINES THE SYMMETRY OF THE PRODUCT OF THE WAVEFUNCTIONS
INVOLVED IN THE MATRIX ELEMENT AND THUS THE SYMMETRY OF THE CONTRIBUT-
ING PART OF THE HAMILTONIAN;
              SYM←(IF RS[J,J+T]×RS[JP,JP+TP] = 5 OR
              RS[J,J+T]×RS[JP,JP+TP] = 6 THEN "BC" ELSE " A");
COMMENT THIS DETERMINES THE STEPPING RANGE ON I AND IP;
              SS←(IF RS[J,J+T] = 1 OR RS[J,J+T] = 3 THEN 2 ELSE 3);
              SP ← (IF RS[JP,JP+TP] = 1 OR RS[JP,JP+TP] = 3 THEN 2
              ELSE 3);
              FOR I ← SS STEP -2 WHILE I ≥ 0 DO
              FOR IP ← SP STEP -2 WHILE IP ≥ 0 DO
        BEGIN
COMMENT THIS DETERMINES THE STEPPING RANGE ON F;
              U←J+I;
              UP←JP+IP;
              IF UP≤U THEN
              FU←UP ELSE FU←U;
              L←ABS(J-I);
              LP←ABS(JP-IP);
```

```
      IF LP≤L THEN
      FL←L ELSE FL←LP;
      FOR F←FU STEP -1 UNTIL FL DO
BEGIN
      PREP←REP←0.00;
      PIMA←IMA←0.00;
      IF JP=J OR JP=J+1 OR JP=J+2 THEN
BEGIN
      IF IP=I+1 OR IP=I-1 THEN
      FOR KA←-(J) STEP 1 UNTIL J DO
      PIMA ← PIMA + (((-1)*(J+IP+F+I+1))/2)×SIXJ(F,IP,JP,2,J,I)
      ×SIXJ(3/2,IP,3/2,I,3/2,2)×SQRT((2×(I)+1)×(2×(IP)+1))
      ×SQRT(5)×CHIMINUS(JP,J,TP,T,KA)/(IF THREEJ(J,2,JP,J,0,-J)
       = 0.0 THEN 1 ELSE THREEJ(J,2,JP,J,0,-J));
      IF IP = I OR IP = I+2 OR IP = I-2 THEN
      FOR KA ← -(J) STEP 1 UNTIL J DO
      PREP ← PREP + (((-1)*(J+IP+F+I+1))/2)×SIXJ(F,IP,JP,2,J,I)
      ×SIXJ(3/2,IP,3/2,I,3/2,2)×SQRT((2×(I)+1)×(2×(IP)+1))
      ×SQRT(5)×CHIPLUS(JP,J,TP,T,KA)/(IF THREEJ(J,2,JP,J,0,-J)
       = 0.0 THEN 1 ELSE THREEJ(J,2,JP,J,0,-J));
END;
      IF JP = J-1 OR JP = J-2 THEN
BEGIN
      IF IP = I+1 OR IP = I-1 THEN
      FOR KA ← -(J) STEP 1 UNTIL J DO
      PIMA ← PIMA + (((-1)*(J+IP+F+I+2))/2)×SIXJ(F,IP,JP,2,J,I)
      ×SIXJ(3/2,IP,3/2,I,3/2,2)×SQRT((2×(I)+1)×(2×(IP)+1))
      ×SQRT(5)×CHIMINUS(JP,J,TP,T,KA)/(IF THREEJ(J,2,JP,J,0,-J)
       = 0.0 THEN 1 ELSE THREEJ(J,2,JP,J,0,-J));
      IF IP = I OR IP = I+2 OR IP = I-2 THEN
      FOR KA ← -(J) STEP 1 UNTIL J DO
      PREP ← PREP + (((-1)*(J+IP+F+I+1))/2)×SIXJ(F,IP,JP,2,J,I)
      ×SIXJ(3/2,IP,3/2,I,3/2,2)×SQRT((2×(I)+1)×(2×(IP)+1))
      ×SQRT(5)×CHIPLUS(JP,J,TP,T,KA)/(IF THREEJ(J,2,JP,J,0,-J)
       = 0.0 THEN 1 ELSE THREEJ(J,2,JP,J,0,-J));
END;
      IF J=JP AND T=TP THEN GO TO FIRST;
```

```
              IF ABS(E[J,J+T] - E[JP,JP+TP]) < 10×ABS(PREP) OR
              ABS(E[J,J+T] - E[JP,JP+TP]) < 10×ABS(PIMA) THEN
              GO TO FIRSTP ELSE GO TO SECOND;
FIRST:        REP ← PREP;
              IMA ← PIMA;
              EC ← SQRT((REP)*2 + (IMA)*2);
              GO TO THIRD;
FIRSTP:       REP ← PREP;
              IMA ← PIMA;
              WRITE(LAB,PROW,JP,TP,IP,F,J,T,I,REP,IMA,SYM);
              GO TO FOURTH;
SECOND:       IF F = J THEN
        BEGIN
              REP ← PREP/SQRT(2);
              IMA ← PIMA/SQRT(2);
              EC ← ((REP)*2 + (IMA)*2)/(E[J,J+T] - E[JP,JP+TP]);
              WRITE(LAB,KROW,EC,SYM);
              GO TO FOURTH;
        END ELSE
        BEGIN
              REP ← PREP;
              IMA ← PIMA;
              EC ← ((REP)*2 + (IMA)*2)/(E[J,J+T] - E[JP,JP+TP]);
              GO TO THIRD;
        END;
THIRD:        WRITE(LAB,ROW,JP,TP,IP,F,J,T,I,REP,IMA,EC,SYM);
FOURTH: END OF F LOOP;
        END OF I AND IP LOOP;
        END OF PROCEDURE MATRIXELEMENT;
COMMENT THIS IS THE BEGINNING OF THE BODY OF BLOCK TWO;
              WRITE(LAB[NO]);
              A ← TIME(2);
              B ← TIME(3);
              READ(BAL,/,CHIXPXP,CHIYPYP,CHIZPZP,CHIXPYP);
              READ(BAL,/,P);
              FOR W ← 1 STEP 1 UNTIL P DO
              READ(BAL,/,JA[W],TA[W]);
```

```
              CLOSE (BAL,RELEASE);                                       00063000
              FOR W ← 1 STEP 1 UNTIL P DO                                00063100
        BEGIN                                                            00063200
              WRITE(LAB,HEADING);                                        00063300
              JP ← J ← JA[W];                                            00063400
              TP ← T ← TA[W];                                            00063500
              MATRIXELEMENT(J,T,JP,TP);                                  00063600
        END;                                                             00063700
              FOR W ← 1 STEP 1 UNTIL P DO                                00063800
        BEGIN                                                            00063900
              J ← JA[W];                                                 00064000
              T ← TA[W];                                                 00064100
              FOR JP ← 0 STEP 1 UNTIL 5 DO                               00064200
              FOR TP ← JP STEP -1 UNTIL -(JP) DO                         00064300
        BEGIN                                                            00064400
              IF (J≠JP OR T≠TP) AND RS[J,J+T]×RS[JP,JP+TP] ≠ 2 AND       00064500
              RS[J,J+T]×RS[JP,JP+TP] ≠ 3 AND RS[J,J+T]×RS[JP,JP+TP]      00064600
               ≠ 10 AND RS[J,J+T]×RS[JP,JP+TP] ≠ 15 AND ABS(E[J,J+T]     00064700
               - E[JP,JP+TP]) ≤ 20000 AND JP≥J THEN                      00064800
        BEGIN                                                            00064900
              WRITE(LAB,HEADING);                                        00065000
              MATRIXELEMENT(J,T,JP,TP);                                  00065100
        END;                                                             00065200
              IF (J≠JP OR T≠TP) AND RS[J,J+T]×RS[JP,JP+TP] ≠ 2 AND       00065300
              RS[J,J+T]×RS[JP,JP+TP] ≠ 3 AND RS[J,J+T]×RS[JP,JP+TP]      00065400
               ≠ 10 AND RS[J,J+T]×RS[JP,JP+TP] ≠ 15 AND ABS(E[J,J+T]     00065500
               - E[JP,JP+TP]) ≤ 20000 AND JP≤J THEN                      00065600
        BEGIN                                                            00065700
              WRITE(LAB,HEADING);                                        00065800
              MATRIXELEMENT(JP,TP,J,T);                                  00065900
        END;                                                             00066000
        END;                                                             00066100
        END;                                                             00066200
              WRITE(LAB,EMIT,(TIME(2)-A)/3600,(TIME(3)-B)/3600);         00066300
 END;                                                                    00066400
END.                                                                     00066500
END;END.        LAST CARD ON OCRDING TAPE                                99999999
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APPENDIX B

TRANSFORMATION BETWEEN THE PRINCIPAL INERTIAL SYSTEM AND THE PRINCIPAL DYADIC SYSTEM FOR THE FIELD GRADIENT TENSOR

APPENDIX B

TRANSFORMATION BETWEEN THE PRINCIPAL INERTIAL SYSTEM AND THE PRINCIPAL DYADIC SYSTEM FOR THE FIELD GRADIENT TENSOR

For the asymmetric-top molecule, the principal inertial axes a,b, and c are chosen as in Figure 7 on page 52, and the nuclear or principal dyadic axes are labelled xyz on the same drawing. The angle β is not necessarily the bond angle, for the principal dyadic system is not necessarily the bond axis system.

In the principal dyadic system one first assumes that Laplace's equation holds at the nuclei, i.e.,

$$V_{xx} + V_{yy} + V_{zz} = 0 ,$$

and so the dyadic becomes

$$V' = \begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & -V_{xx}-V_{zz} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix}$$

To go from this to the principal inertial axis system a similarity transformation is used,

$$V = A^T V' A$$

where A is the matrix of direction cosines relating the two sets of axes, i.e., one may write

$$A = \begin{pmatrix} \cos(xa) & \cos(xb) & \cos(xc) \\ \cos(ya) & \cos(yb) & \cos(yc) \\ \cos(za) & \cos(zb) & \cos(zc) \end{pmatrix}$$

In the case of the systems in Figure 7 this becomes, for nucleus two,

$$A_2 = \begin{pmatrix} 0 & 0 & 1 \\ \cos\beta & \sin\beta & 0 \\ -\sin\beta & \cos\beta & 0 \end{pmatrix}$$

and for nucleus one,

$$A_1 = \begin{pmatrix} 0 & 0 & -1 \\ -\cos\beta & \sin\beta & 0 \\ \sin\beta & \cos\beta & 0 \end{pmatrix}$$

(The calculations for nucleus two will be outlined here and the changes for nucleus one will be indicated.)

From above one has

$$A_2^T = \begin{pmatrix} 0 & \cos\beta & -\sin\beta \\ 0 & \sin\beta & \cos\beta \\ 1 & 0 & 0 \end{pmatrix}$$

so that the expression for V in the principal inertial axis system becomes

$$V = \begin{pmatrix} 0 & \cos\beta & -\sin\beta \\ 0 & \sin\beta & \cos\beta \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} V_{xx} & 0 & 0 \\ 0 & -V_{xx}-V_{yy} & 0 \\ 0 & 0 & V_{zz} \end{pmatrix} \begin{pmatrix} 0 & 0 & 1 \\ \cos\beta & \sin\beta & 0 \\ -\sin\beta & \cos\beta & 0 \end{pmatrix}$$

Carrying out the indicated matrix multiplication gives

$$V = \begin{pmatrix} 0 & \cos\beta & -\sin\beta \\ 0 & \sin\beta & \cos\beta \\ 1 & 0 & 0 \end{pmatrix} \begin{pmatrix} 0 & 0 & V_{xx} \\ -(V_{xx}+V_{zz})\cos\beta & -(V_{xx}+V_{zz})\sin\beta & 0 \\ -V_{zz}\sin\beta & V_{zz}\cos\beta & 0 \end{pmatrix}$$

Thus, for nucleus two one obtains

$$V_{aa}^{(2)} = -(V_{xx} + V_{zz}) \cos^2\beta + V_{zz} \sin^2\beta$$

which may be written

$$V_{aa}^{(2)} = -(V_{xx} + 2V_{zz}) \cos^2\beta + V_{zz}$$

Likewise one has

$$V_{bb}^{(2)} = -(V_{xx} + V_{zz}) + (V_{xx} + 2V_{zz}) \cos^2\beta ,$$

and

$$V_{ab}^{(2)} = -(V_{xx} + 2V_{zz}) \sin\beta \cos\beta$$

Inverting this transformation gives

$$V_{xx} = -(V_{aa}^{(2)} + V_{bb}^{(2)})$$

and

$$V_{aa}^{(2)} - V_{bb}^{(2)} = -2(V_{xx} + 2V_{zz}) \cos^2\beta + (V_{xx} + 2V_{zz})$$

which may be written

$$V_{aa}^{(2)} - V_{bb}^{(2)} = -(V_{xx} + 2V_{zz}) \cos 2\beta \tag{15}$$

Now, one also has from above that

$$V_{ab}^{(2)} = -(V_{xx} + 2V_{zz}) \frac{\sin 2\beta}{2}$$

so that

$$\frac{2V_{ab}^{(2)}}{V_{aa}^{(2)} - V_{bb}^{(2)}} = \tan 2\beta$$

Finally, using the above expression for tan2β, one has

$$\cos 2\beta = \frac{V_{aa}^{(2)} - V_{bb}^{(2)}}{\left(4V_{ab}^{(2)2} + (V_{aa}^{(2)} - V_{bb}^{(2)})^2\right)^{1/2}}$$

But from equation (15) one has that

$$V_{aa}^{(2)} - V_{bb}^{(2)} = -(V_{xx} + 2V_{zz}) \cos 2\beta$$

so that

$$\left(4V_{ab}^{(2)} + (V_{aa}^{(2)} - V_{bb}^{(2)})^2\right)^{1/2} = -V_{xx} - 2V_{zz}$$

or

$$V_{zz} = \frac{1}{2}\left[V_{aa}^{(2)} + V_{bb}^{(2)} - \left(4V_{ab}^{(2)2} + (V_{aa}^{(2)} - V_{bb}^{(2)})^2\right)^{1/2}\right]$$

For nucleus one the results are

$$V_{aa}^{(1)} = V_{aa}^{(2)} ,$$

$$V_{bb}^{(1)} = V_{bb}^{(2)} ,$$

$$V_{ab}^{(1)} = -V_{ab}^{(2)} .$$

The inverted transformation for nucleus one gives

$$V_{xx}^{(1)} = V_{xx}^{(2)}$$

$$V_{zz}^{(1)} = V_{zz}^{(2)}$$

and $$\beta^{(1)} = -\beta^{(2)} .$$

APPENDIX C

SAMPLE INTENSITY CALCULATION FOR HYPERFINE LINES

APPENDIX C

SAMPLE INTENSITY CALCULATION FOR HYPERFINE LINES

According to equation (12) on page 39 of Chapter III, the intensity of a quadrupole line is given by

$$N = \frac{\langle E^{i}_{J_\tau} || d || E^{f}_{J_\tau} \rangle^{2}}{3} (2F^{i}+1)(2F^{f}+1)$$

$$\left[\sum_{I} B^{i}_{\epsilon^{i} I} \; B^{f}_{\epsilon^{f} I} \; (-1)^{I} W(J^{i}F^{i}I:F^{f}J^{f}1)\right]^{2} ,$$

where $\langle E^{i}_{J_\tau} || d || E^{f}_{J_\tau} \rangle$ is the same for all levels in a particular $J^{i}_{\tau^{i}} \leftrightarrow J^{f}_{\tau^{f}}$ transition. The expression for relative intensities is then

$$N = C(2F^{i}+1)(2F^{f}+1) \; \left[\sum_{I} B^{i}_{\epsilon^{i} I} \; B^{f}_{\epsilon^{f} I} \; (-1)^{I} W(J^{i}F^{i}I:F^{f}J^{f}1)\right]^{2},$$

where C is the same number for all lines in the transition.

Consider the line $\epsilon^{i}F^{i} = 2\ 1$ to $\epsilon^{f}F^{f} = 0\ 2$ in the $J^{\prime}_{\tau^{\prime}} = 2_{-2}$ to $J^{f}_{\tau^{f}} = 2_{0}$ transition. For even τ levels ϵ and I may have the values 0 and 2 only, as explained in Appendix A. Thus the expression above becomes

$$N = C[2(1)+1] \; [2(2)+1] \left[\sum_{I=0,2} B^{i}_{\epsilon^{i} I} \; B^{f}_{\epsilon^{f} I} \; W(2\ 1I:2\ 2\ 1)\right]^{2} .$$

The $B_{\epsilon I}$'s are the transformation coefficients between the I and ϵ representations, and, as explained in Appendix A on page 56 one has

$$B_{\epsilon 2} = \frac{1}{\sqrt{2}} \text{ and } B_{\epsilon 0} = \pm \frac{1}{\sqrt{2}} \text{ if } F = J .$$

The sign of the latter coefficient depends on the assignment of ϵ to the energy levels resulting from first-order splitting. The plus sign is always assigned to the higher energy level, and minus is assigned to the lower energy level, however the higher ϵ value is not always assigned to the higher energy, for example, in the $J_\tau = 2_0$ level. The assignment of ϵ is discussed further in a paper by Robinson and Cornwell (53).

In the case of the above line, one obtains

$$N = 15C[B^i_{20}\, B^f_{00}\, W(2\ 1\ 0:\ 2\ 2\ 1) + B^i_{22}\, B^f_{02}\, W(2\ 1\ 2:\ 2\ 2\ 1)]^2 .$$

Here the initial state is the $J^i_{\tau^i} = 2_{-2}$ state where $\epsilon = 2$ corresponds to the higher energy level, and the final state is the $J^f_{\tau^f} = 2_0$ state where $\epsilon = 0$ corresponds to the higher level. Therefore one has

$$B^i_{20} = \frac{1}{\sqrt{2}} , \quad B^i_{22} = \frac{1}{\sqrt{2}} ,$$

$$B^f_{00} = \frac{1}{\sqrt{2}} , \quad B^f_{02} = \frac{1}{\sqrt{2}} ,$$

and so

$$N = \frac{15C}{2} [W(2\ 1\ 0:\ 2\ 2\ 1) + W(2\ 1\ 2:\ 2\ 2\ 1)]^2$$

The values of the six-j symbols may be obtained from Rotenberg (54) giving

$$N = \frac{15C}{2} [\frac{\sqrt{7}}{(2)\sqrt{3}\,(5)}]^2 = \frac{7C}{40} \quad .$$

The example chosen here was for $F^i = J^i$ and F^f and $F^f = J^f$ which is probably the most complicated situation. For lines where $F \neq J$, the transformation coefficients are simply one since then ϵ is assigned the I value of the state.

APPENDIX D

SAMPLE CALCULATION OF χ^-

APPENDIX D

SAMPLE CALCULATION OF χ^-

In Chapter III the expression for χ^- is given as

$$\chi^- = 4\sum_{K'}\sum_{K} a^{J'}_{K'\tau'}\, a^{J}_{K\tau} \sum_{J''}\sum_{K''} \langle J'K'J|\alpha_{Zx'}|J''K''J\rangle$$

$$\langle J''K''J|\alpha_{Zy'}|JKJ\rangle\ \chi_{x'y'}$$

where the sums over J'' and K'' are over all states which may be linked to J and J'. The above expression is evaluated in this Appendix for one choice of the quantum numbers J and J' using the table of direction cosine matrix elements in the symmetric-top representation shown in Table 3. This is taken from Cross, Hainer and King (2) where it is explained that the total matrix element in each case is made up of a product of three elements from the table, i.e.,

$$\langle J'K'M'\ |\alpha_{Fg}|JKM\rangle = (\Phi_{Fg})_{J;J'}\cdot(\Phi_{Fg})_{J,K;J'K'}\cdot(\Phi_{Fg})_{J,M\ ;J'M'}\quad ,$$

where the F subscript refers to the space-fixed axis system, $F = (X,Y,Z)$, and the g subscript refers to the molecular principal axis system, $g = (x,y,z)$.

In the case above the elements are referred to the space-fixed Z axis, and, as mentioned in Chapter III, the elements for which M = J and $J' \geq J$ are the ones to be calculated. Thus the expression becomes

$$\langle J'K'J|\alpha_{Zg}|JKJ\rangle = (\Phi_{Zg})_{J;J'} \cdot (\Phi_{Zg})_{J,K;J',K'} \cdot (\Phi_{Zg})_{J,M_J;J',M_J} \ ,$$

where M = J.

Consider the case of $J' = J + 2$. The elements of the product of the two operators $\alpha_{Zx'}$ and $\alpha_{Zy'}$ may be divided into those diagonal in K and those off-diagonal in K, i.e.,

$$\langle J'KJ|\alpha_{Zx'}\,\alpha_{Zy'}|JKJ\rangle \ ,$$

and

$$\langle J'K'J|\alpha_{Zx'}\,\alpha_{Zy'}|JKJ\rangle$$

where $K' \neq K$. The first type are of the form

$$\langle J{+}2KJ|\alpha_{Zx'}|J{+}1\ K{+}1J\rangle\langle J{+}1\ K{+}1J|\alpha_{Zy'}|JKJ\rangle \ , \qquad (16)$$

and

$$\langle J{+}2KJ|\alpha_{Zx'}|J{+}1\ K{-}1J\rangle\langle J{+}1\ K{-}1J|\alpha_{Zy'}|JKJ\rangle \ . \qquad (17)$$

(One should note that the elements of the form

$$\langle J{-}1\ K{+}1J|\alpha_{Zg}|JKJ\rangle$$

Table 3. Matrix Elements of the Direction Cosine Operators in a Symmetric-Top Representation.

Matrix element factor	Value of J′		
	J+1	J	J-1
$(\Phi_{Fg})_{J,J'}$	$[4(J+1)\sqrt{(2J+1)(2J+3)}\,]^{-1}$	$[4J(J+1)]^{-1}$	$[4J\sqrt{4J^2-1}\,]^{-1}$
$(\Phi_{Fz})_{J,K;J'K}$	$2\sqrt{(J+K+1)(J-K+1)}$	$2K$	$-2\sqrt{J^2-K^2}$
$(\Phi_{Fy})_{J,K;J',K\pm1}$ $= \mp i(\Phi_{Fx})_{J,K;J',K\pm1}$	$\mp\sqrt{(J\pm K+1)(J\pm K+2)}$	$\sqrt{(J\mp K)(J\pm K+1)}$	$\mp\sqrt{(J\mp K)(J\mp K-1)}$
$(\Phi_{Zg})_{J,M;J',M}$	$2\sqrt{(J+M+1)(J-M+1)}$	$2M$	$-2\sqrt{J^2-M^2}$
$(\Phi_{Yg})_{J,M;J',M\pm1}$ $= \pm i(\Phi_{Xg})_{J,M;J',M\pm1}$	$\mp\sqrt{(J\pm M+1)(J\pm M+2)}$	$\sqrt{(J\mp M)(J\pm M+1)}$	$\mp\sqrt{(J\mp M)(J\mp M-1)}$

and

$$\langle J-1\ K-1J | \alpha_{Zg} | JKJ \rangle$$

must be zero because of the direction cosine factor

$$(\Phi_{Zg})_{J,M_J;J-1,M_J} = -2\ (J^2 - M\ ^2)^{1/2}$$

which is zero if $M = J$.)

To evaluate elements of the form (16) one has that

$$\langle J+2\ K\ J | \alpha_{Zx'} | J+1\ K+1\ J \rangle = \langle J+1\ K+1\ J | \alpha_{Zx'} | J+2\ K\ J \rangle^*$$

and

$$\langle J+1\ K+1\ J | \alpha_{Zx'} | J+2\ K\ J \rangle^*$$

$$= [(\Phi_{Zg})_{J+2,J+1} \cdot (\Phi_{Zg})_{J+2,K;J+1,K+1} \cdot (\Phi_{Zg})_{J+2,J;J+1,J}]^*$$

This element may be written

$$\langle \tilde{J}'\ K+1\ J | \alpha_{Zx'} | \tilde{J}\ K\ J \rangle^*$$

where $\tilde{J} = J + 2$ and $\tilde{J}' = \tilde{J} - 1$, so the appropriate column is the third column in the table. The element factors are

$$(\Phi_{Zg})_{J+2;J+1} = \frac{1}{4(J+2)\sqrt{2J+3}\sqrt{2J+5}} ,$$

$$(\Phi_{Zg})_{J+2,K;J+1,K+1} = \frac{1}{i}\sqrt{(J-K+2)(J-K+1)} ,$$

$$(\Phi_{Zg})_{J+2,J;J+1,J} = -4\sqrt{J+1}$$

Therefore one obtains

$$\langle J+2\ K\ J|\alpha_{Zx'}|J+1\ K+1\ J\rangle = \frac{(-i)\ \sqrt{J+1}\ \sqrt{(J-K+2)(J-K+1}}{(J+2)\ \sqrt{2J+2}\ \sqrt{2J+5}}$$

In the same manner one may obtain

$$\langle J+1\ K+1\ J|\alpha_{Zy'}|JKJ\rangle = \frac{-\sqrt{(J+K+1)(J+K+2)}}{2(J+1)\ \sqrt{2J+3}}$$

so that the product element (16) is given by

$$\frac{i\sqrt{(J-K+2)(J-K+1)(J+K+1)(J+K+2)}}{2\sqrt{J+1}\ \sqrt{2J+3}\ \sqrt{2J+5}}$$

The other element of the product operator diagonal in K, (17), turns out to be the negative of the above element, so the term in the sum of expression (13) which is diagonal in K is zero. The off-diagonal elements in K may be done in the same manner, giving the result quoted for χ^- in Chapter III.

APPENDIX E

MEASURED FREQUENCIES OF FOUR TRANSITIONS IN $S^{32}Cl_2^{35}$

Table 4.
Measured Frequencies of Four Transitions in $S^{32}C\ell_2{}^{35}$

Transition $J_\tau \rightarrow J'_{\tau'}$	ϵF	$\rightarrow \epsilon' F'$	Rotational Frequency ν_o (MHz)	Quadrupole Frequency ν(MHz)
$0_0 \quad 1_0$	00	01	17,044.20	17,041.37
	22	21		17,046.99
$2_{-2} \quad 2_0$	21	22	12,687.98	12,677.27
	02	21		12,698.70
	22	22		12,675.01
	02	02		12,701.25
$2_{-2} \quad 3_{-2}$	02	03	26,527.81	26,523.52
	22	23		26,532.13
$4_{-4} \quad 4_{-2}$	24	24	14,573.01	14,563.29
	04	04		14,582.86

LITERATURE CITED

1. G. W. King, R. M. Hainer, and P. C. Cross, "The Asymmetric Rotor I", The Journal of Chemical Physics, 11, 27 (1943).

2. P. C. Cross, R. M. Hainer, and G. W. King, "The Asymmetric Rotor II", The Journal of Chemical Physics, 12, 210 (1944).

3. H. B. G. Casimir, On the Interaction Between Atomic Nuclei and Electrons (Teyler's Tweede Genootschap, E. F. Bohn, Haarlem 1936).

4. W. Low and C. H. Townes, The Physical Review, 76, 1295 (1949).

5. J. Bardeen and C. H. Townes, "Calculation of Nuclear Quadrupole Effects in Molecules", The Physical Review, 73, 97 (1948).

6. G. Racah, "Theory of Complex Spectra I", The Physical Review, 61 186 (1942).

7. G. Racah, "Theory of Complex Spectra II", The Physical Review, 62, 438 (1942).

8. G. Racah, "Theory of Complex Spectra III", The Physical Review, 63, 367 (1943).

9. R. Bersohn, Unpublished Ph.D. Thesis, Harvard University (1949).

10. W. H. Flygare and W. D. Gwinn, "Electron Distribution in the C-Cℓ Bonds of $CH_2C\ell_2$ and Derivation of Matrix Elements Off-Diagonal in J for Two Quadrupolar Nuclei in an Asymmetric Rotor", The Journal of Chemical Physics, 36, 787 (1962).

11. J. T. Murray, Unpublished Thesis, Georgia Institute of Technology (1965).

12. M. W. Long, Unpublished Ph.D. Thesis, Georgia Institute of Technology (1959).

13. R. H. Hughes and E. B. Wilson, Jr., "A Microwave Spectrograph", The Physical Review, 71, 562 (1947).

14. P. B. Reinhart, Unpublished Ph.D. Thesis, Georgia Institute of Technology (1969) pp. 4-11.

15. Reinhart, op. cit., p. 14.

LITERATURE CITED
(continued)

16. T. M. Lowry, L. P. McHatton, and G. G. Jones, "The Properties of the Chlorides of Sulfur. Part I. Freezing Points", The Journal of the Chemical Society of London, 1421 (1929).

17. King, Hainer, and Cross, op. cit.

18. R. S. Mulliken, "Species Classification and Rotational Energy Level Patterns of Non-Linear Triatomic Molecules", The Physical Review, 59, 873 (1941).

19. A. A. Wolf, Unpublished Ph.D. Thesis, Georgia Institute of Technology, 1966, pp. 13-18.

20. Flygare and Gwinn, op. cit.

21. C. H. Townes and A. L. Schawlow, Microwave Spectroscopy (McGraw-Hill Book Company, New York, 1955), p. 50.

22. S. C. Wang, "On the Asymmetrical Top in Quantum Mechanics", The Physical Review, 34, 243 (1929).

23. Murray, op. cit., pp. 8-11.

24. J. D. Jackson, Classical Electrodynamics (John Wiley and Sons, Inc., New York, 1962), p. 98.

25. Jackson, op. cit., p. 69.

26. A. R. Edmonds, Angular Momentum In Quantum Mechanics (Princeton University Press, Princeton, 1965), p. 63.

27. Edmonds, op. cit., p. 72.

28. Edmonds, op. cit., p. 111.

29. Wolf, op. cit., p. 15.

30. Edmonds, op. cit., p. 75.

31. Wolf, op. cit., p. 14.

32. M. Rotenberg, R. Bivins, N. Metropolis, and J. K. Wooten, Jr., The 3-j and 6-j Symbols (The Technology Press, Massachusetts Institute of Technology, Cambridge, 1959), p. 3.

33. Edmonds, op. cit., p. 117.

34. Flygare and Gwinn, op. cit., p. 788.

LITERATURE CITED
(continued)

35. Edmonds, op. cit., p. 111.

36. Wolf, op. cit., p. 28.

37. J. K. Bragg, "The Interaction of Nuclear Electric Quadrupole Moments with Molecular Rotation in Asymmetric-Top Molecules I", The Physical Review, 74, 533 (1948).

38. Cross, Hainer, and King, op. cit., p. 212.

39. Townes and Schawlow, op. cit., p. 19.

40. Townes and Schawlow, op. cit., p. 21.

41. Edmonds, op. cit., p. 75.

42. Edmonds, op. cit., p. 111.

43. Edmonds, op. cit., p. 47.

44. Yardley Beers, Introduction to the Theory of Error (Addison-Wesley Publishing Company, Reading, Mass., 1957).

45. Carl R. Nave, Unpublished Ph.D. Thesis, Georgia Institute of Technology, 1966, pp. 66-67.

46. Lorimor Clayton, Unpublished Ph.D. Thesis, Georgia Institute of Technology, 1961, pp. 126-134.

47. H. J. M. Bowen, et al., Tables of Interatomic Distances and Configuration in Molecules and Ions (London: The Chemical Society, Burlington House, London, 1958), p. M71.

48. Murray, op. cit., p. 44.

49. Clayton, op. cit., pp. 94-97.

50. Clayton, op. cit., p. 97.

51. Edmonds, op. cit., p. 41.

52. H. Eyring, J. Walter, and G. E. Kimball, Quantum Chemistry (John Wiley and Sons, Inc., New York, 1944), p. 95.

53. G. W. Robinson and C. D. Cornwell, "The Interaction with Molecular Rotation of the Nuclear Electric Quadrupole Moments of Two Nuclei Having Spins 3/2", The Journal of Chemical Physics, 21 1436 (1953).

LITERATURE CITED
(continued)

54. Rotenberg, et al., *op. cit.*

55. John Mandel, *The Statistical Analysis of Experimental Data* (John Wiley and Sons, Inc., New York, 1964).

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