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# Computer Simulation of the Rotational Spectrum of a Symmetric Top Molecule

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Wells,

W. Scott

1977

COMPUTER SIMULATION OF THE ROTATIONAL SPECTRUM  
OF A SYMMETRIC TOP MOLECULE

A Thesis

Presented to

the Faculty of the Department of Chemistry

Western Kentucky University

Bowling Green, Kentucky

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

by

W. Scott Wells

May 1977

COMPUTER SIMULATION OF THE ROTATIONAL SPECTRUM  
OF A SYMMETRIC TOP MOLECULE

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COMPUTER SIMULATION OF THE ROTATIONAL SPECTRUM OF A SYMMETRIC TOP MOLECULE

W. Scott Wells

49 pages

Directed by: Dr. Earl F. Pearson

Department of Chemistry

Western Kentucky University

Given the proper equations and the appropriate set of selection rules, a computer can be programmed to simulate the spectrum of a molecule. This study deals with the rotational spectrum of a symmetric top molecule. The program itself was written in several subroutine blocks. By doing this the computing time was reduced by 70% over similar programs.

The program can be used to simulate the spectrum of a molecule if the transition polarization type and the rotational constants are known. However, if the type of transition polarization or constants is unknown, the program can be used as a tool for data determination.

#### ACKNOWLEDGEMENT

I would like to thank Dr. Earl Pearson for his guidance and extreme patience in assisting me in this study. I wish to express my gratitude to the entire faculty for help given. I want also to thank Mrs. Jean Almand of the Western Kentucky Science Library for her assistance.

Anything man can conceive in his mind, he can accomplish. . . impossibles are as impossible as thinking makes them so.

W. Scott Wells

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## INTRODUCTION

The purpose of this work has been to write a more efficient program to simulate the rotational spectrum of a symmetric top molecule. Subroutines are used to divide the program into sections which will permit more efficient operation. Subroutines were written for two different polarization bands, parallel and perpendicular--and for six different plot types.

The program is useful as an informational device for giving data on the excited state of a molecule and also as a teaching tool.

## I. THEORETICAL

### A. Classification of Symmetric Top Molecules

#### 1. Symmetry

A symmetric top molecule can be identified in two ways. One is by its symmetry operations. If a molecule has symmetry of  $C_n$  where  $n \geq 3$ , that is, a molecule with an axis of three-fold or greater symmetry, it is a symmetric top molecule. Secondly, a symmetric top molecule can also be defined by its moments of inertia, identified as:

$$I = \sum_i m_i r_i^2 \quad \text{Eqn. (1)}$$

where  $r_i$  is the distance of the  $i^{\text{th}}$  particle from the center of mass of the molecule. A molecule has three moments of inertia, corresponding to three mutually perpendicular axes, A, B, C, passing through the center of mass. A symmetric top molecule has two equal moments of inertia and one unique moment of inertia. Those molecules with  $I_A < I_B = I_C$  are called prolate symmetric tops and those with  $I_A = I_B < I_C$  are called oblate symmetric tops. (See Fig. 1)<sup>(1)</sup>

#### 2. Inertial Constants

There are inertial constants called rotational constants designated A, B, C, corresponding to each of these moments of inertia.

$$A = \frac{h}{8\pi^2 I_A} \quad B = \frac{h}{8\pi^2 I_B} \quad C = \frac{h}{8\pi^2 I_C} \quad \text{Eqn. (2)}$$

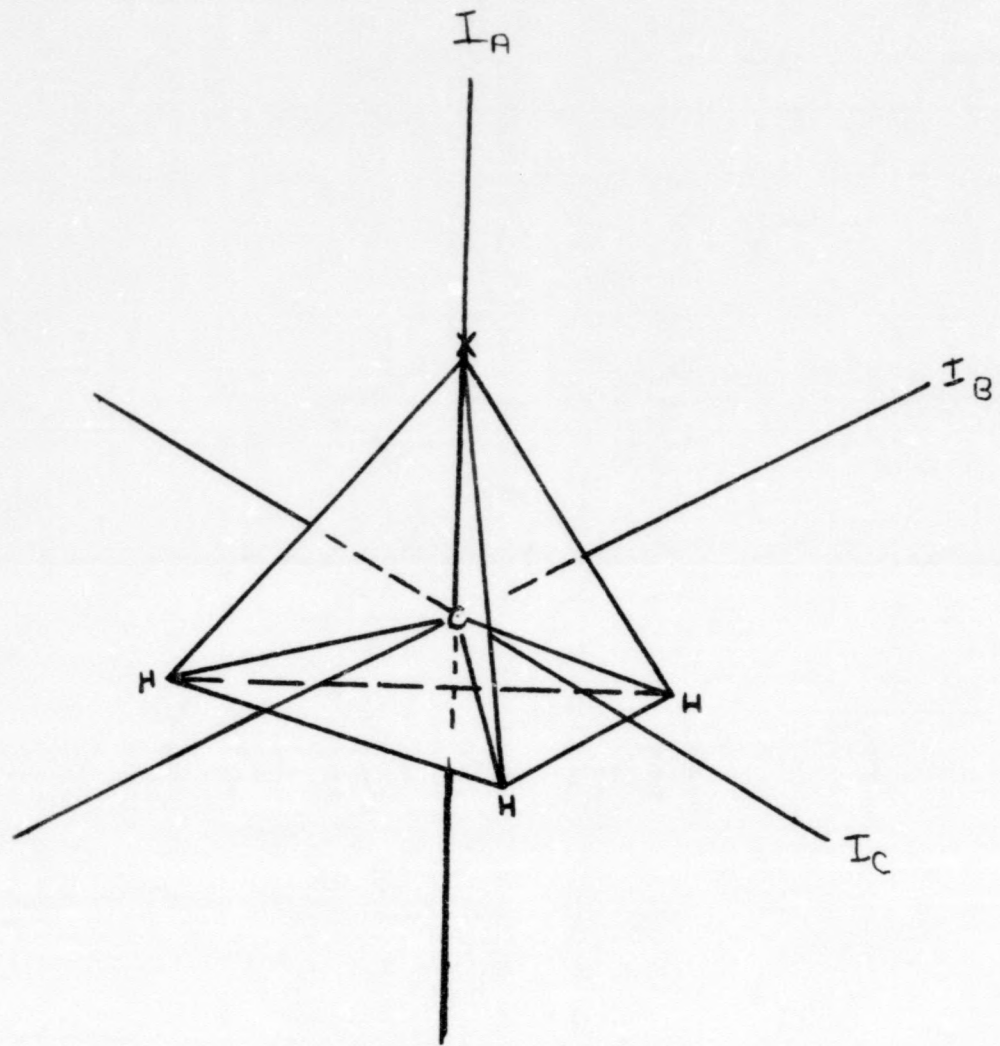
These constants are used in calculating the rotational energy of the molecule.

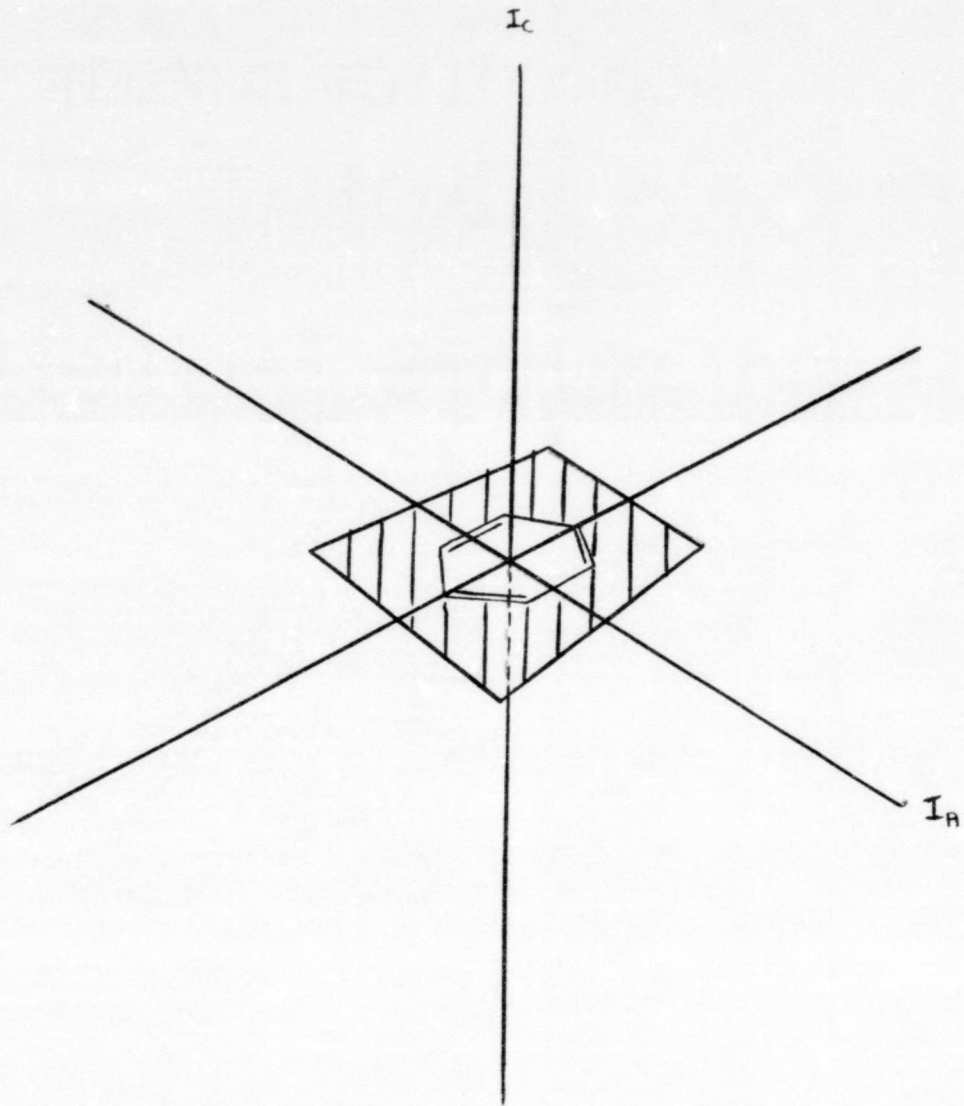
Figure 1. Examples of Symmetric Top Molecule

$$I_A \neq I_B = I_C$$

(a) Prolate Symmetric Top  $I_A < I_B = I_C$

(b) Oblate Symmetric Top  $I_A = I_B < I_C$





There are molecules which have two equal moments of inertia but do not meet the symmetry requirements of a three-fold or higher axis of rotational symmetry. These "accidental" symmetric top molecules are less important than molecules that meet the symmetry requirements since they are rarely encountered.

#### B. Energy Levels

Figure 2 represents a typical potential energy curve for two electronic states of a molecule.<sup>(2)</sup> In general, the potential energy curve for each electronic state of a molecule has a different shape and, in the case of stable states, there is a minimum in the curve at the equilibrium bond distance.

As a result of the relatively large difference in their energies, a transition between two different electronic states usually falls in the visible or ultraviolet regions. The spectrum consists of a group of bands resulting from transitions between various vibrational levels. Under high resolution each band in the vapor shows a rotational structure caused by transitions between the individual rotational levels associated with each vibrational level.<sup>(3)</sup>

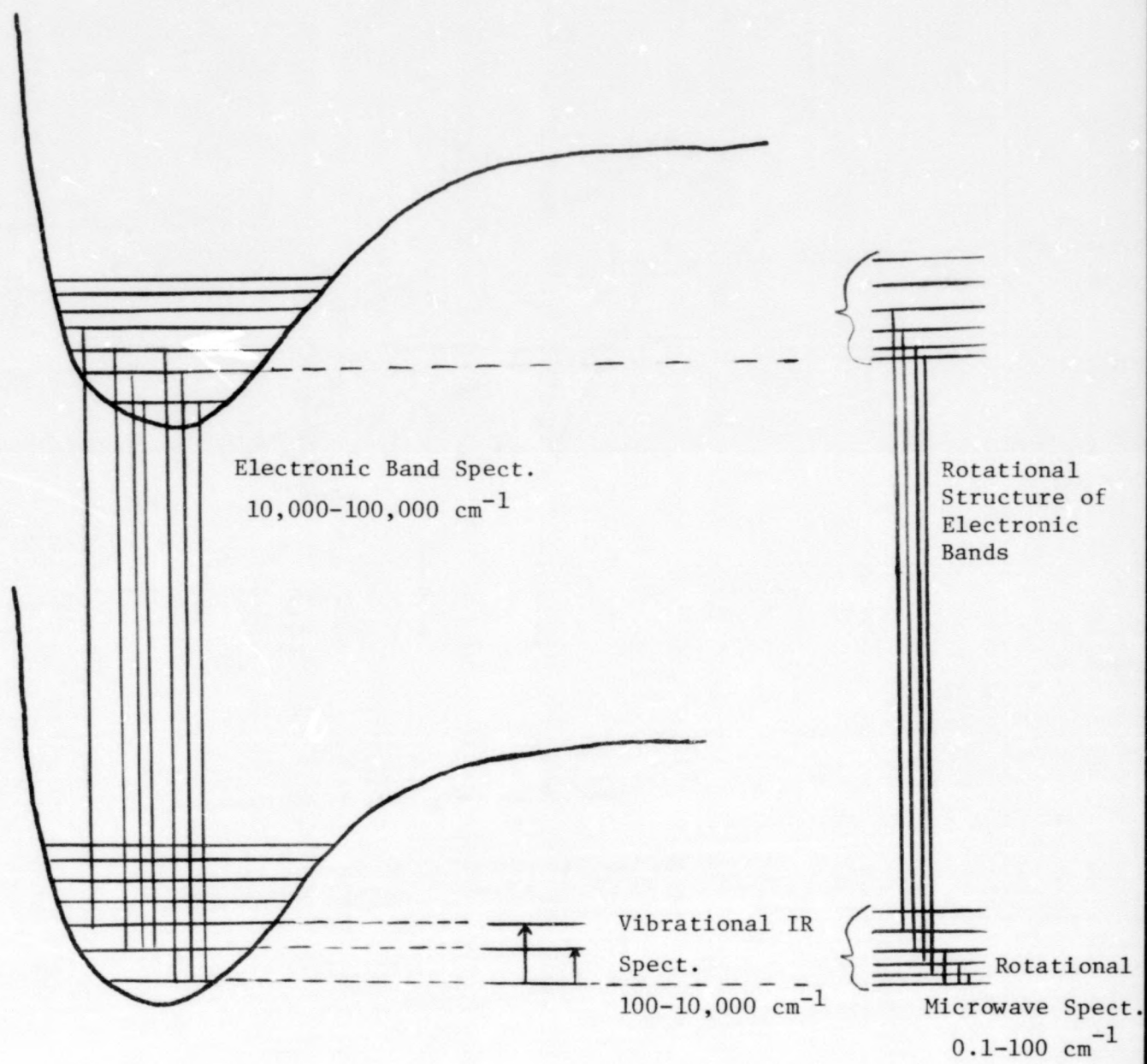
The rotational energy of a rigid symmetric top molecule is given by:

$$F(J,K) = BJ(J+1) + (A-B)K^2 \pm 2A\zeta K \quad \text{Eqn. (3)}$$

$J$  is the total angular momentum quantum number and  $K$  is the component of the total angular momentum, ( $J$ ) on the unique axis (top axis). The value of  $J$  must be greater than or equal to  $K$ .  $J$  can assume the values of:  $J = K, K + 1, K + 2, \dots$ ; for  $K = 0, 1, 2, 3 \dots$ .  $A$  and  $B$  are the rotational constants as defined above and the constant  $\zeta$  (zeta) is the angular momentum (vibrational or electronic) in addition to the angular momentum about the unique axis.

Figure 2. Vibrational and Rotational Structure in an Electronic Transition. The rotational levels associated with a typical vibrational level in each electronic state are shown on an expanded energy scale at the right. The lower state is assumed to be the ground state.





The term  $\pm 2A\zeta K$  gives a splitting of the energy levels which increase linearly with increasing  $K$ . The (-) sign in this term applies when the vibrational angular momentum has the same direction as the rotational angular momentum, whereas the (+) sign applies if they are in directions opposite to one another.<sup>(4)</sup> For convenience we shall distinguish the two levels as  $+\ell$  and  $-\ell$  levels. A schematic energy-level diagram is given in Figure 2. Each level is double degenerate because of the two possible directions of  $K$ , i.e. "clockwise" or "counterclockwise" direction.<sup>(5)</sup>

The energy level diagrams of prolate and oblate symmetric top molecules are different. Figure 3a represents the energy level diagram of a prolate symmetric top molecule,<sup>(6)</sup> that is, one with  $I_A < I_B = I_C$ . Figure 3b is the energy level diagram for an oblate symmetric top ( $I_A = I_B < I_C$ ). For a rigid rotor, the energy spacing for the lines can be written as  $BJ(J+1)$  and the degeneracy as  $(2J+1)$ . The number  $2J+1$  arises from the states with angular momentum components of  $J, J-1, J-2, \dots, 0, -1, -2, \dots, -J$  times  $h/2\pi$  that would appear if an external field were applied. The energy level pattern and degeneracy are shown in Figure 4.<sup>(7)</sup>

### C. Boltzman Distribution

The population of a specific state with energy  $\epsilon_i$  compared to that of the lower state with energy  $\epsilon_0$  can be calculated from the Boltzman distribution:

$$N = N_0 e^{(\epsilon_i - \epsilon_0)/kt} \quad \text{Eqn. (4)}$$

In view of the  $2J + 1$  degeneracy described above, the Boltzman distribution expression for the population of a rotational energy level is:

$$N_J = (2J+1)N_0 e^{(\epsilon_i - \epsilon_0)/kt} \quad \text{Eqn. (5)}$$

Figure 3. The rotational energy-level patterns for (a) prolate and  
(b) oblate symmetric top molecule.

J

9

8

7

6

5

4

3

2

1

K=

0

—

—

—

—

—

—

—

2

—

—

—

—

—

—

—

—

1

(a)

J

9

8

7

6

5

4

3

2

1

K=

0

—

—

—

—

—

—

—

—

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—

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1

(b)

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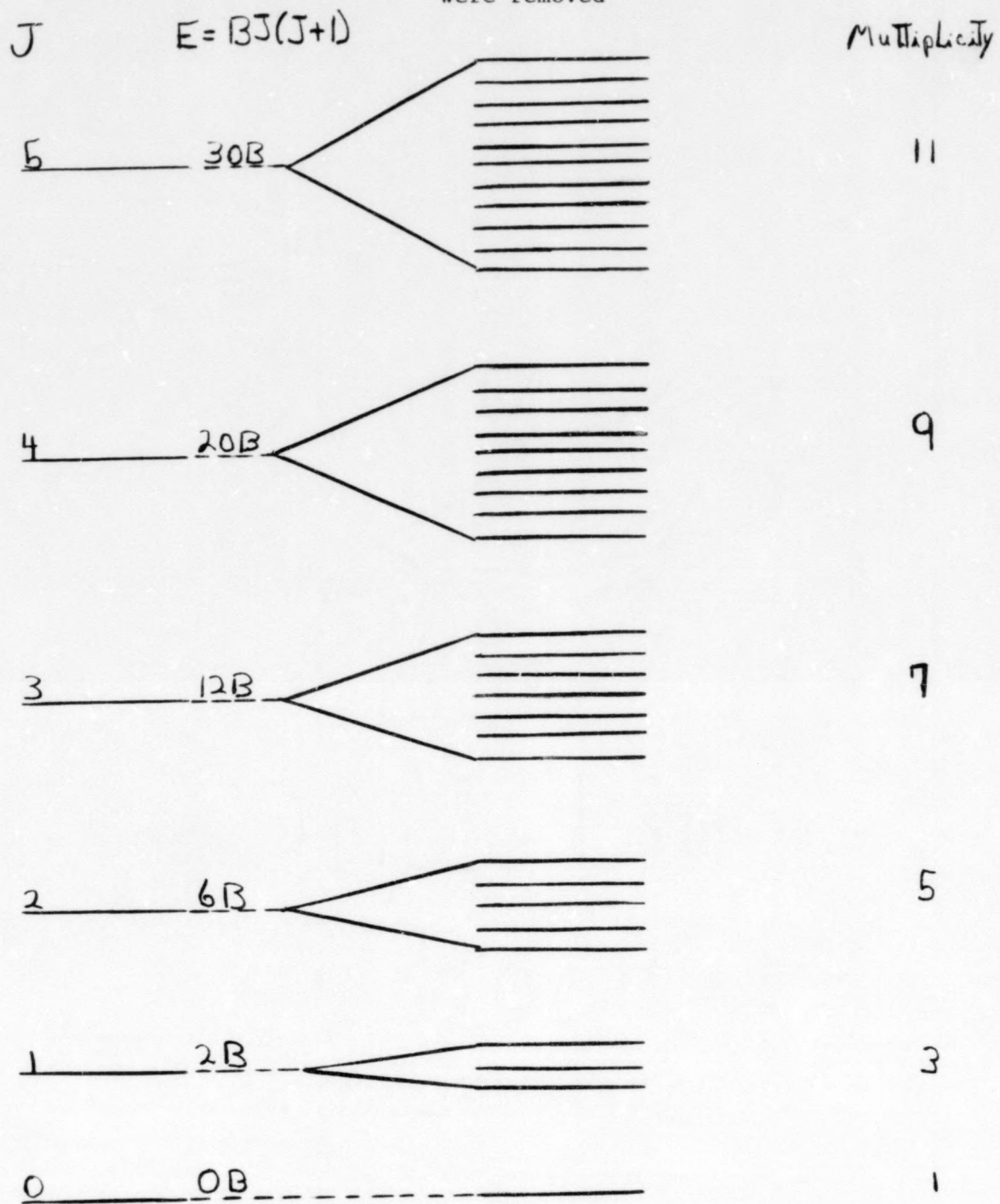
—

—

2

Figure 4. A representation of the energy-level of a molecule. The multiplicity of each rotational level is indicated by the number of levels that would appear if the degeneracy were removed.

Energy pattern if  
 $2J+1$  degeneracy  
were removed



#### D. Selection Rules

For a vibration to be IR-active, its motion must cause a change in the dipole moment. When the molecule is excited, the change in the dipole moment may be either parallel or perpendicular to the top axis of symmetry.<sup>(8)</sup> (See Figure 5).

If the change in the dipole moment (transition moment) is parallel to the top axis, the rotational quantum numbers for the excited state are found from the following set of selection rules:

$$\Delta K = 0, \quad \Delta J = 0, \quad \pm 1 \quad \text{for } K \neq 0 \quad \text{Eqn. (6)}$$

$$\Delta K = 0, \quad \Delta J = \pm 1 \quad \text{for } K = 0 \quad \text{Eqn. (7)}$$

and if the change in dipole is perpendicular to the top axis, the selection rules are:

$$K = \pm 1, \quad \Delta J = 0, \quad \pm 1 \quad \text{Eqn. (8)}$$

If the transition moment has a component both in the direction of and perpendicular to the top axis, as would be expected for an accidentally symmetric top, both sets of transitions may occur.<sup>(9)</sup>

Figure 6 shows the possible transitions between a ground state and an excited state for a prolate symmetric top molecule.<sup>(10)</sup>

#### E. Rotational Spectrum

The excited state values and the excited state energy level for J and K can be obtained from the ground state by using the various selection rules. (See Equation 3). Once this energy has been calculated, the frequency of a transition can be calculated as the difference in the energy between the excited state and the ground state.

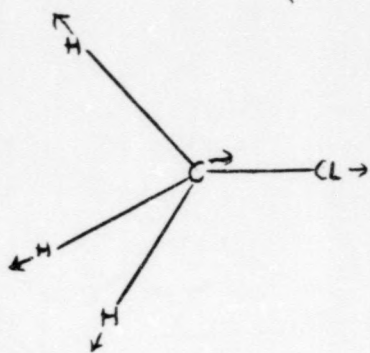
$$\nu = F(J', K') - F(J'', K'') \quad \text{Eqn. (9)}$$

Here J' and K' represent the excited state values of J and K and J'' and K'' represent the ground state values.

Figure 5. Vibrations of symmetric top molecules that leads to (a) parallel absorption bands (b) perpendicular absorption bands.



(a)



(b)

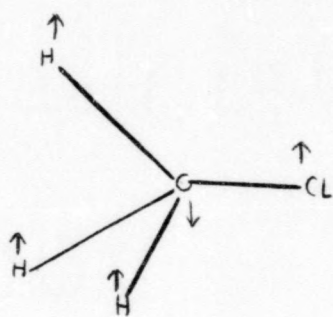
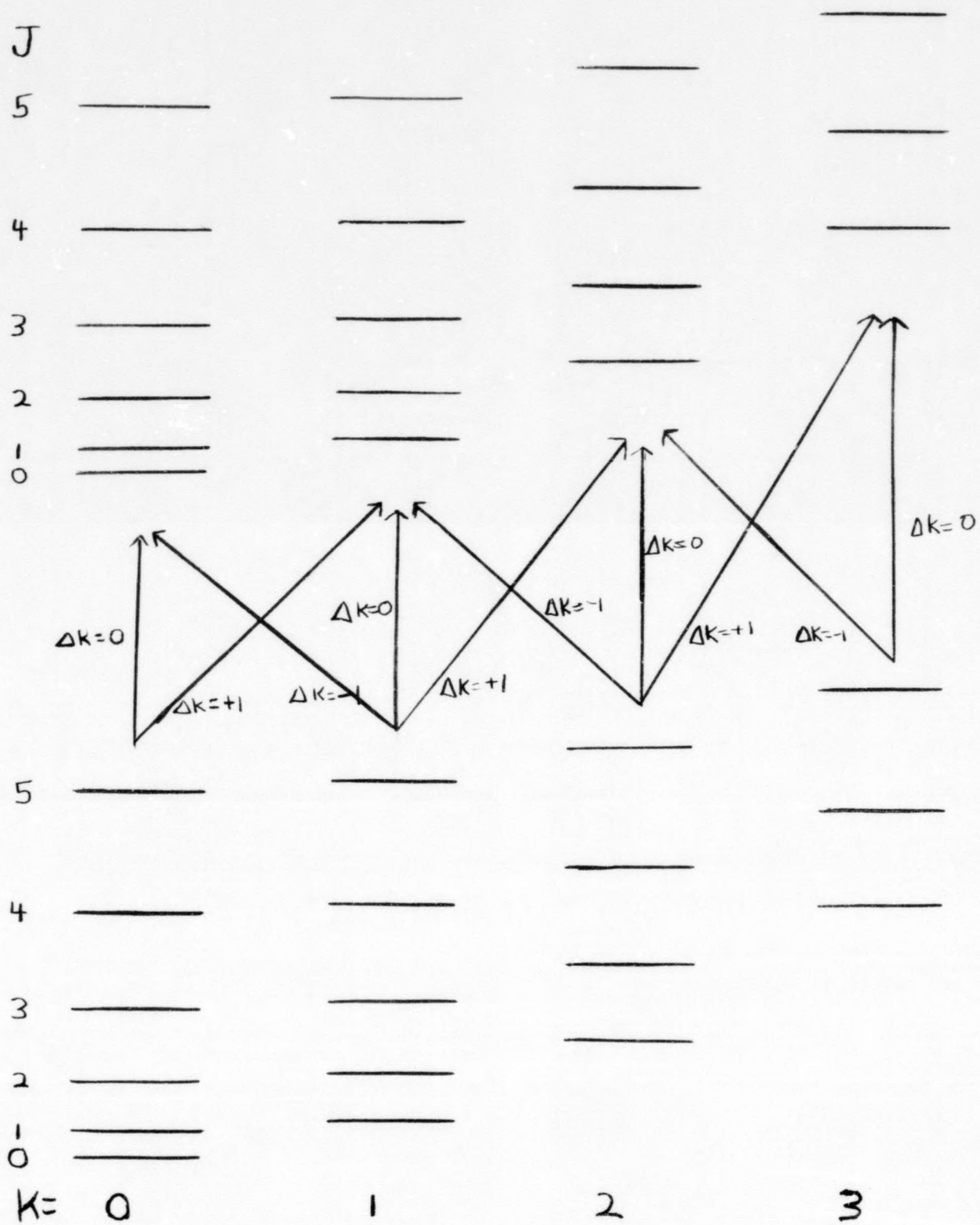


Figure 6. The energy levels of a prolate symmetric top molecule and the possible transitions.



Neglecting distortions, the difference between the excited state energy and ground state energy is equal to  $2B(J+1)$ .<sup>(11)</sup> This formula represents a simple series of equi-distant lines. The quantum number  $K$  drops out entirely and the spectrum is the same as would be obtained for one value of  $K$  only, that is, the various sets of levels lie vertically above one another<sup>(12)</sup> as shown in Figure 8.

Figure 7 illustrates the transitions giving rise to each line in the spectrum.<sup>(13)</sup> The separation of successive lines is  $2B$ . If this transition is measured, the moment of inertia about an axis perpendicular to the symmetry axis can be calculated from Equation 2.

A complete rotational spectrum is obtained by superimposing all the "sub-bands" on one another. The sub-bands for a parallel transition can be seen in Figure 8. In a parallel transition, only levels of the same  $K$  value, that is--levels in the same vertical column, can combine with each other. (See Figure 6.) One row shows a sub-band with three simple branches, designated P, Q, R.<sup>(14)</sup> (See Equation 5 for selection rules.) The Q branch, corresponding to  $\Delta J = 0$  is missing in the first line of Figure 8 because of the restriction that if  $K = 0$  then  $\Delta J$  can assume only the values  $\pm 1$ . Also, because of the restriction that  $J \geq K$  more and more lines are missing from the sub-bands as  $K$  increases.

The spacing of the lines in the P and R branches is  $2B$ . This is determined by the moment of inertia about an axis perpendicular to the top axis.<sup>(15)</sup> This is exactly true only for a rigid molecule if  $B' = B''$  and  $A' = A''$ , where  $A''$  and  $B''$  are ground state A and B;  $A'$  and  $B'$  are the excited state A and B. In this case, all the lines of the Q branch will coincide.

Figure 7. Rotational energy levels.

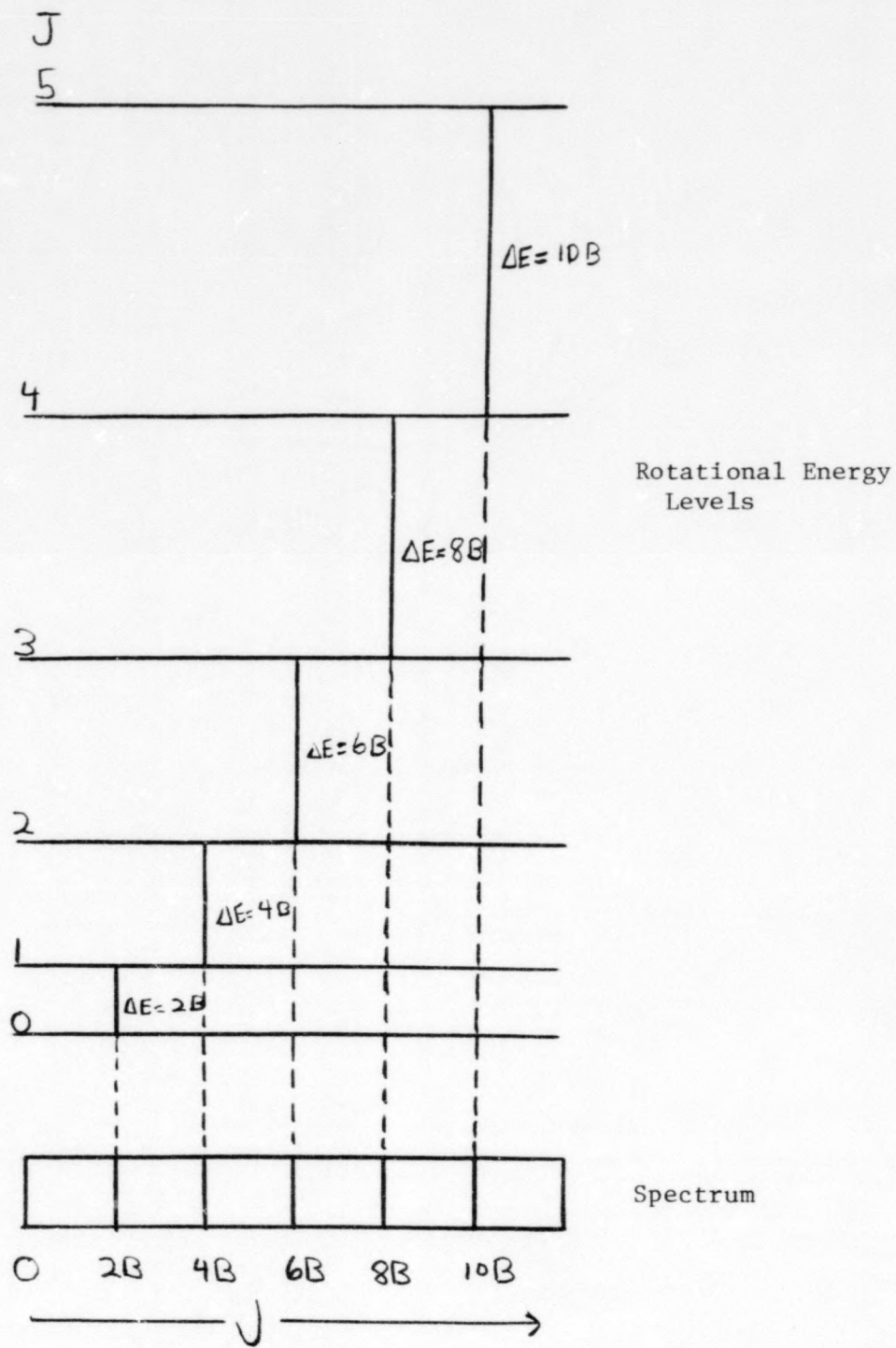
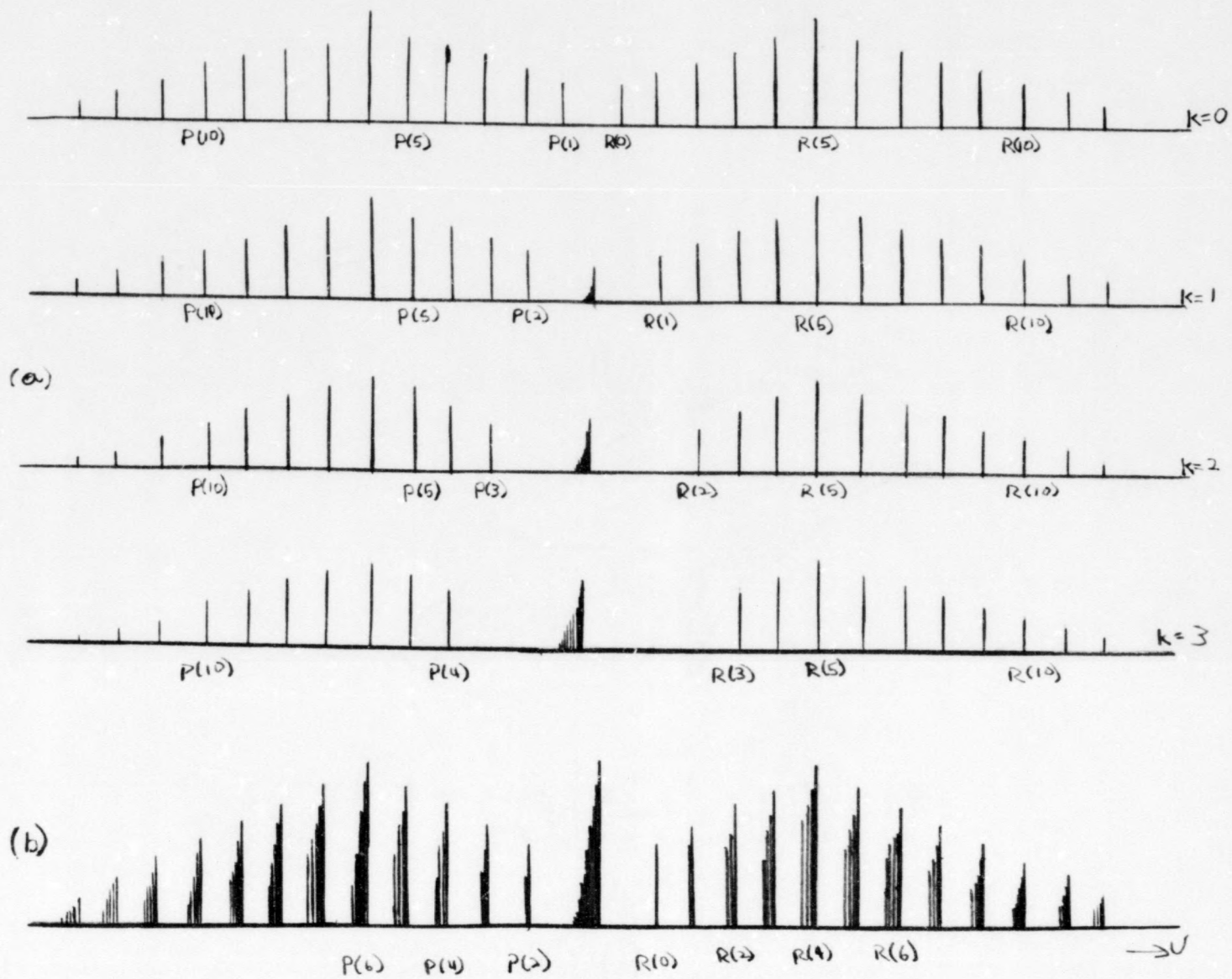


Figure 8. Sub-bands of a Parallel Band and Complete Parallel Band of a Symmetric Top Molecule.

The sub-bands of (a) are directly superimposed in (b). In both (a) and (b) a slight difference between  $A'-B'$  and  $A''-B''$  is assumed.





Generally, there is an interaction between rotation and vibration, causing a slight difference in  $A'$  and  $A''$  and  $B'$  and  $B''$ . Because of this, the lines of the P and R branches in each sub-band will no longer be equidistant but will converge and the lines of the Q branch will no longer coincide exactly, although in general they will not be resolved.<sup>(16)</sup> Also, as can be seen in Figure 8b, the sub-bands no longer coincide exactly.

The spectrum of a molecule which undergoes a perpendicular transition consists of two sub-bands, each with three branches. The sub-band corresponding to  $\Delta K = +1$  is identified as R form branches and the sub-bands corresponding to  $\Delta K = -1$  as P form branches. The branches arising from the various values of  $\Delta J$  are the same as before.  $\Delta J = -1$ , P-branch;  $\Delta J = 0$ , Q-branch;  $\Delta J = 1$ , the R-branch.

Figure 9<sup>(17)</sup> shows a schematic energy-level diagram of the sub-bands of a perpendicular transition. From the diagram it can be seen that, as in a parallel band, there is an increasing number of lines missing near the origin of the sub-bands as  $K$  increases. In a perpendicular band there is no zero gap between the two branches.

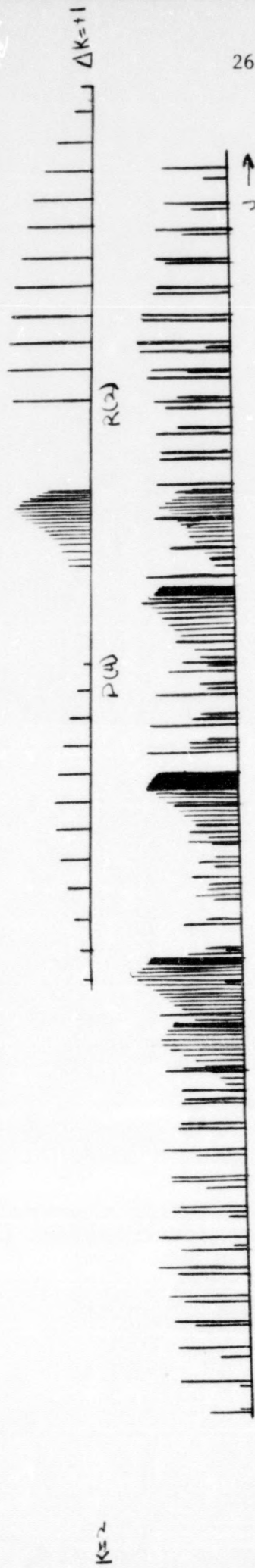
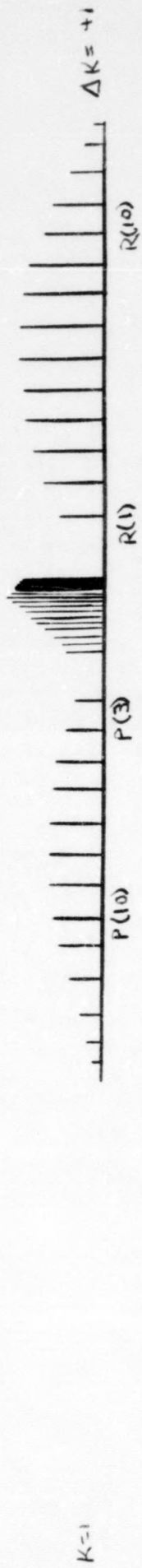
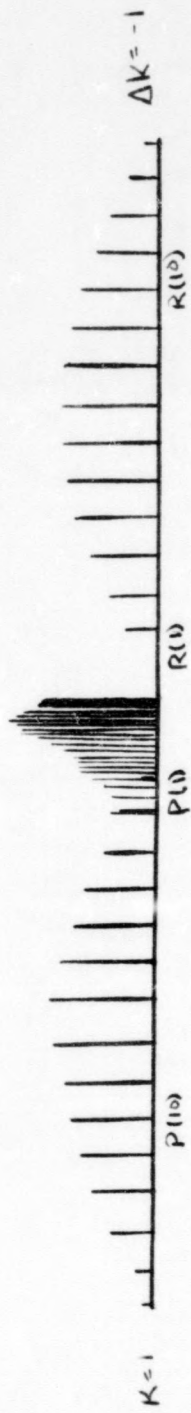
#### F. Intensity of a Transition

The intensity of a line can be calculated by a formula derived by Honl and London.<sup>(18)</sup> The intensity of a given transition in an absorption band is proportional to the product

$$I = CA_{jk} \nu g_{jk} e^{-E/kt} \quad \text{Eqn. (10)}$$

where  $C$  is a constant independent of  $J$  and  $K$  but is dependent on the vibrational transition;  $g_{jk}$  is a statistical weight factor. It assumes the value  $2J+1$  for  $K = 0$  and  $2(2J+1)$  for  $K \neq 0$ .  $\nu$  is the frequency calculated as the difference in excited state energy and ground state energy (Equation 3). The exponential represents the fraction of the molecules

Figure 9. Sub-bands of a perpendicular band.



in the level from which the transition originates (the Boltzman factor). The factor  $A_{jk}$  is represented by a set of equations which give the inherent strength of the transition. These equations are given in Table I.<sup>(19)</sup> In each factor the values of J and K are ground state values.

TABLE 1

## Hönl-London Intensity Factors

Parallel Transition

for $\Delta J = +1$	$A_{KJ} = \frac{(J+1)^2 - K^2}{(J+1)(2J+1)}$
$\Delta J = 0$	$A_{KJ} = \frac{K^2}{J(J+1)}$
$\Delta J = -1$	$A_{KJ} = \frac{J^2 - K^2}{J(2J+1)}$

Perpendicular Transition

for $\Delta J = +1$	$A_{KJ} = \frac{(J+2+K)(J+1+K)}{(J+1)(2J+1)}$
$\Delta J = 0$	$A_{KJ} = \frac{(J+1+K)(J+K)}{J(J+1)}$
$\Delta J = -1$	$A_{KJ} = \frac{(J-1+K)(J+K)}{J(2J+1)}$

For  $K \neq 0$  and  $\Delta K = +1$  the values given by the above formula have to be multiplied by 2. This latter fact compensates for the fact that the statistical weight for  $K=0$  is only half of the weight for  $K \neq 0$ .

For perpendicular rules the upper sign refers to  $\Delta K = +1$ , the lower to  $\Delta K = -1$ . In both cases  $K$  and  $J$  refer to the lower state.

## II. EXPERIMENTAL

The program written in this research was formulated in Fortran IV language and run on an IBM 370-165 computer. The program was divided into a main program with several subroutines in an effort to cut down on computer time and space. Two subroutines were written for the different polarizations, parallel and perpendicular bands. The subroutines are written and called in a manner such that only one polarization subroutine need be placed in the deck during any specific run, thus cutting down the number of cards that must be compiled. Subroutines were also written for several different plot types; linear display, log display, log-squared display, log-log display and exponential display. As before, the program is arranged so that only the cards for the plot type desired must be compiled.

Basically the program proceeds by the following format. (See Figure 10 for a flow chart). A test is performed to determine if the molecule is an oblate or prolate top molecule. J and K are initialized at the beginning of a loop. The ground state energy is calculated by use of Equation 3.

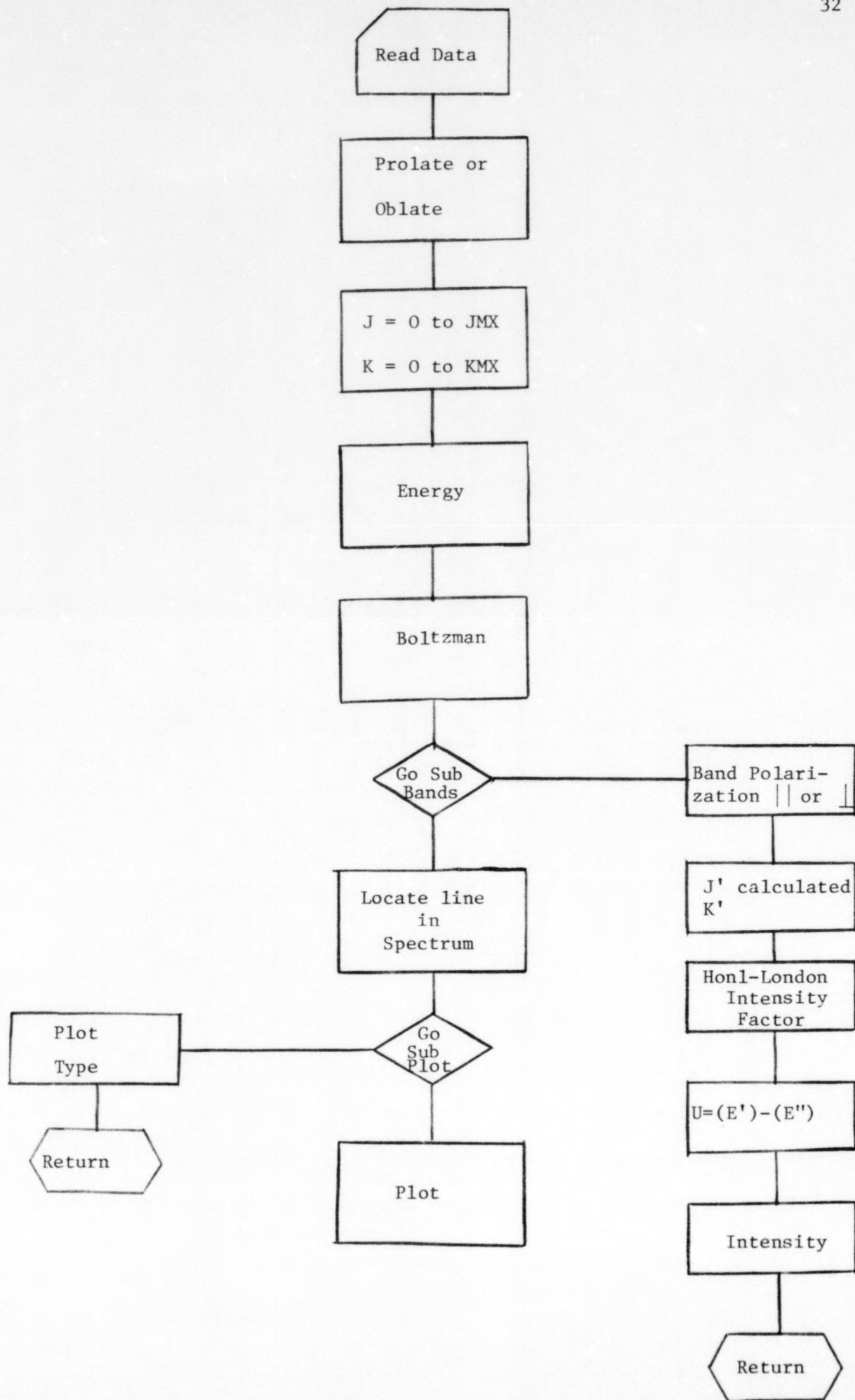
$$F(J,K) = BJ(J+1) + (A-B)^2 \pm 2A\zeta K \quad \text{Eqn. (3)}$$

A Boltzman factor is calculated using this ground state energy. Next, the subroutine for band polarization is called. In the subroutine the excited state values as a function of J and K are calculated, depending on the type of transition. (See Equations 6 and 7 for selection rules). In the respective subroutines the appropriate Honl-London line strengths are

calculated. (See Table 1). Next, the excited state energy is calculated. The frequency is calculated using Equation 9 as the difference between the excited state energy and the ground state energy. Finally, the intensity of the transition is calculated. Line intensities are taken as the product of the line strength, Boltzman factor and statistical weight applicable to each transition, and the line is then spread out. The contour is divided into a number of boxes, and each of these boxes is indexed. The intensity of the transition falling in a box can then be indexed by the box number and added to those already stored there. The process is applied to every possible transition for the ground state. Control is then returned to the main program. The program then locates the line frequency between a given maximum and minimum. Control is transferred to a subroutine for the plot type. Once the plot type is determined, control is again returned to the main program. All calculations being completed, the program now scales the intensity between a given maximum and minimum and the contour is printed by the computer.

Figure 10. Flow Chart for the final program.





### III. RESULTS

The original program used in this work was written by Pearson.<sup>(20)</sup> It included large portions which were not used in all simulations but were read and compiled, resulting in increased computing time. The primary objective of this research was to write a program from which could be obtained an acceptable contour and at the same time eliminate those portions which were not necessary for the spectrum under study. It was anticipated that by writing the program into subroutines, computing time could be significantly reduced. By eliminating unneeded calculations and by writing into separate subroutine blocks those portions not used in a particular contour simulation, the computing time was reduced 70 percent.

In order to substantiate that the program written in the research correctly produces the spectrum of a molecule, contours simulated with this program were compared to contours reported in the literature by Duncan<sup>(21)</sup> and Pearson.<sup>(22)</sup>

Duncan reported the spectrum of boron trifluoride. The constants used by him and used in this work are given in Table 2, and comparison spectra are shown in Figures 11 and 12. Figure 11 gives the contour simulated in this research and an observed spectrum of  $\text{BF}_3$ . Figure 12 compares contours produced by this work and those by Duncan and Pearson.

Comparison was made with the rotational contour of the perpendicular band of deuterated ethane done by Pearson. (See Figures 12, 13 and 14 and Table 3). The spectrum has the appearance of a parallel band. However, as pointed out by Pearson, no set of constants could be made to give the correct contour when parallel selection rules were used.<sup>(23)</sup>

Figure 11.  $\text{BF}_3$  spectrum (a) observed (b) calculated

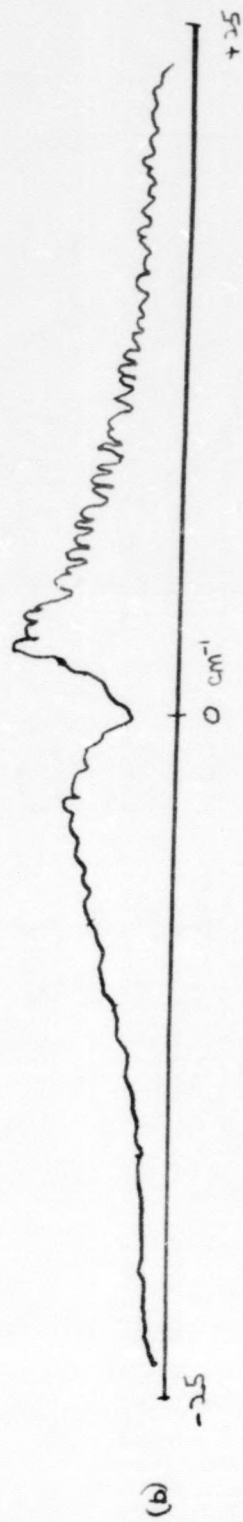
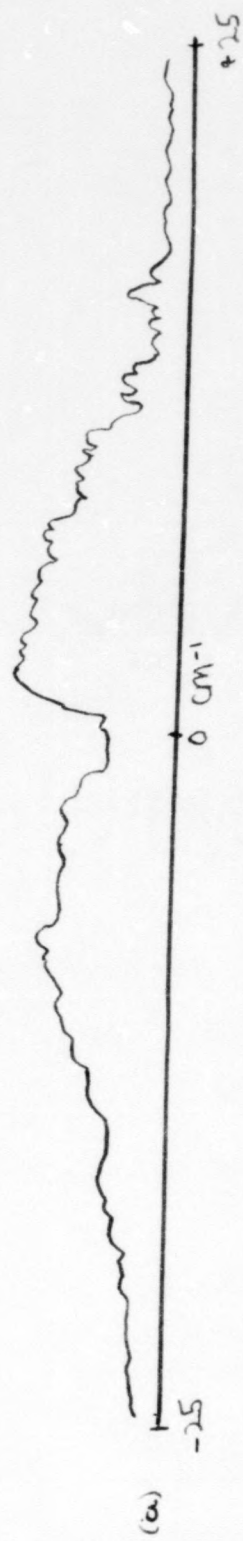


Figure 12.  $\text{BF}_3$  Spectrum (a) Duncan's work  
(b) Pearson's work  
(c) this work

(a)



(b)



(c)

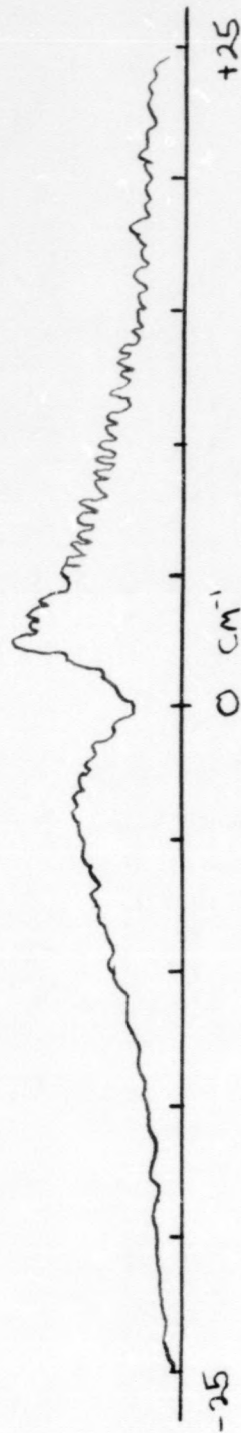


Table 2 gives the constants used to produce the ethane  $d_6$  contour. In Figures 13 and 14 a comparison between this work, Pearson's work and an observed spectrum can be seen.

TABLE 2  
Rotational Constants for  $\text{BF}_3$

<u>Constants</u>	<u>Ground State</u>	<u>Excited State</u>
A	0.17635	0.17575
B*	0.35270	0.35150
$\zeta$	- - - -	+0.81

\*B = C

TABLE 3  
Ground and Excited State Constants for  
Ethane  $d_6$

<u>Constant</u>	<u>Ground State</u>	<u>Excited State</u>
A	1.3416 $\text{cm}^{-1}$	1.3300 $\text{cm}^{-1}$
B*	0.45973 $\text{cm}^{-1}$	.46366 $\text{cm}^{-1}$
$\zeta$	- - - - -	0.32388

\*B = C



Figure 13.  $C_2D_6$  spectrum (a) observed  
(b) calculated from this work

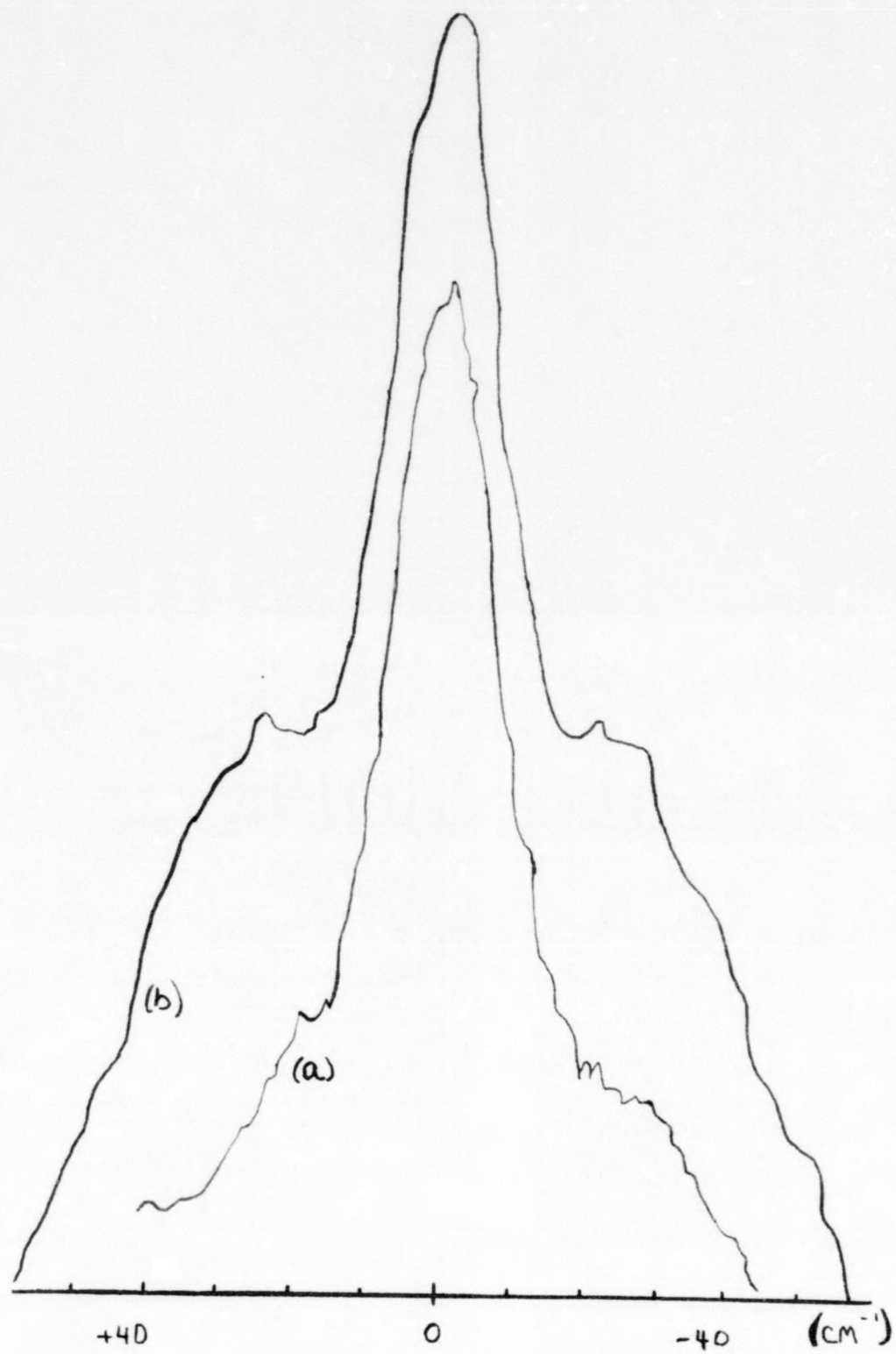
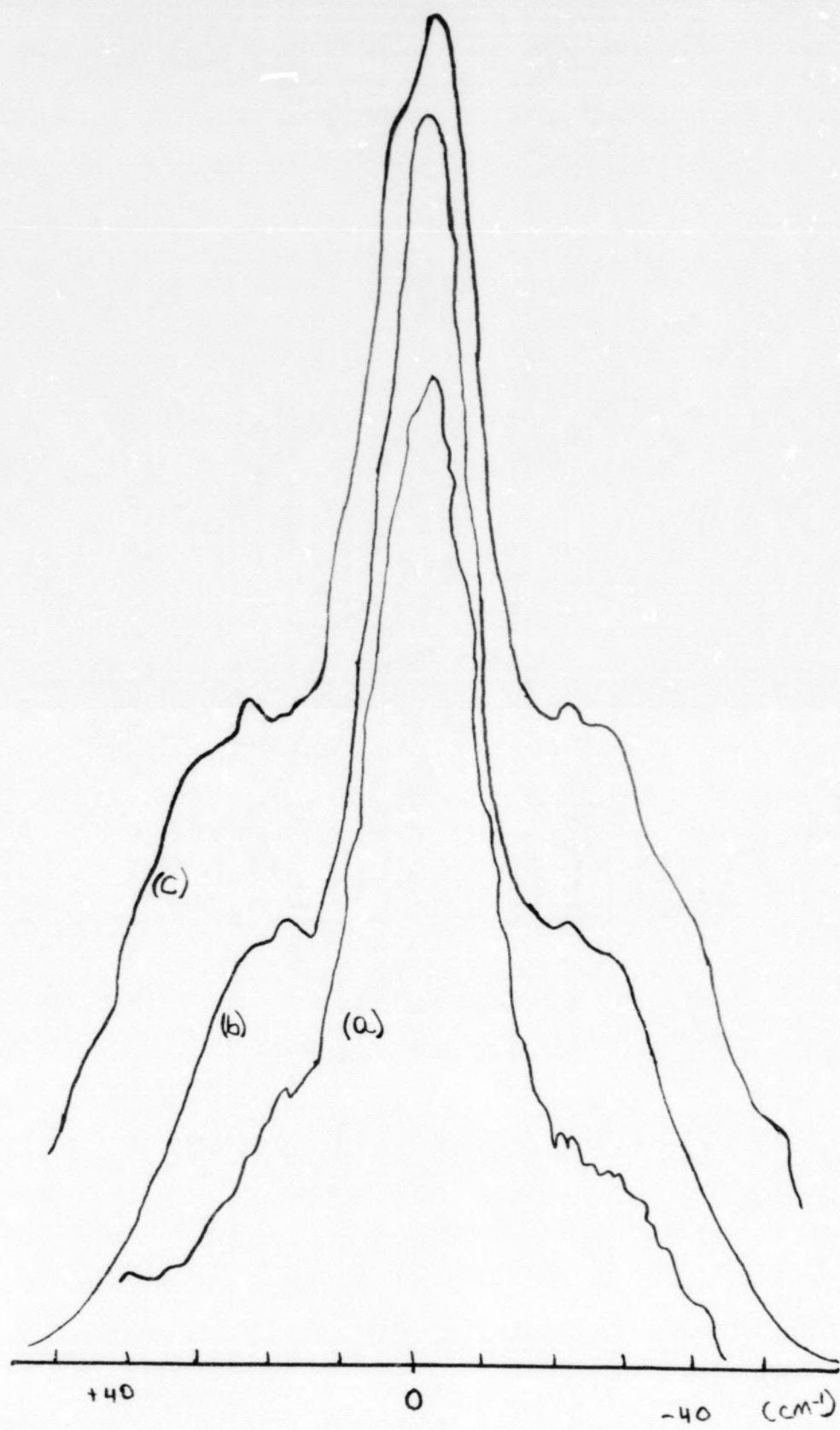


Figure 14.  $C_2D_6$  Spectrum (a) observed  
(b) Pearson's work  
(c) this work



The comparison with previous calculations shown in Figures 11 through 14 attests to the validity of the contours produced by this program. The usefulness of the program is not limited only to contour simulation. It can be used to substantiate experimental data. The contour program can be used in this manner to confirm such things as the type of polarization of the transition and the geometry of the excited and ground electronic states of the molecule. For the spectrum to be correctly produced, the proper selection rules and inertial constants must be used. Once these have been determined the comparison with experimental data is possible.

The program also has possible use as an instructional tool for observing the effects of changing such variables as the type of polarization transition. Contours could be produced for different temperatures and used in classroom discussion. A third possible instructional use could be to ascertain what effect changing the geometry would have on the contour, i.e. changing the moment of inertia due to assumed changes on bond lengths and/or bond angles.

## LIST OF REFERENCES

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2. G. King, "Spectroscopy and Molecular Research," p. 198, Holt, Rinehart and Winston, Inc., New York (1964).
3. See Reference 2, p. 198.
4. G. Herzberg, "Molecular Spectra and Molecular Structure," Vol. II, p. 403, D. Van Nostrand Company, Inc., New York, N. Y. (1945).
5. See Reference 1, p. 52.
6. See Reference 4, p. 25.
7. See Reference 1, p. 52.
8. See Reference 1, p. 150
9. See Reference 2, p. 414.
10. See Reference 4, p. 417
11. See Reference 4, p. 31.
12. See Reference 4, p. 418.
13. See Reference 1, p. 55.
14. See Reference 4, p. 416.
15. See Reference 4, p. 417.
16. See Reference 4, p. 426.
17. See Reference 4, p. 425.
18. See Reference 4, p. 421.
19. See Reference 4, p. 422.
20. E. Pearson, Thesis, p. 72.
21. J. L. Duncan, J. Mol. Spectry., 22, 247 (1967)

22. See Reference 20, p. 63.
23. See Reference 20, p. 67.

A. Program

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DIMENSION Z(50000), V(200), TITLE(100) $ DIMENSION G(1000) $
100 FORMAT(3F10.5) $ 1 FORMAT(5HSMAX=,F10.5,10X,5HSMIN-,F10.5) $
2 FORMAT(3F10.7,3E10.3,F10.5) $ 3 FORMAT(3F10.3,2F10.5,2F10.3) $
4 FORMAT(8I5,F10.5) $ 5 FORMAT(19A4,/) $ 6 FORMAT(4A1, 19A4) $
7 FORMAT(23H GROUND STATE CONSTANTS) $ 8 FORMAT(3H A=,F8.5,4H B=,F8.5,
4H C=,F8.5,6H DK = 3E10.3,16H DJK =,E10.3,6H DJ = E10.3,8H
ZETA = 1F10.5//) $ 9 FORMAT(23HEXCITED STATE CONSTANTS/) $ 10 FORMAT
(8H FVIB =, F10.3,12H INTERVAL =,F10.5,14H LINE WIDTH =,F 110.5, 8H
TEMP =,F10.3,9H DELTA =,F7.5,11H DELTA K =,I1,17H JMX =,I3//) $
11 FORMAT( 1E10.3,1F8.2,2X,102A1) $ 12 FORMAT(1PE10.3,10X102A1) $
13 FORMAT(1H2, 1X) $ 14 FORMAT(15HDLINEAR DISPLAY) $ 15 FORMAT
(12HDLOG DISPLAY) $ 16FORMAT(20HDLOG SQUARED DISPLAY) $ 17 FORMAT
(16HDLOG-LOG DISPLAY) $ 18 FORMAT(20HDEXPONENTIAL DISPLAY) $ 19
FORMAT(1H1,//////////) $ 20 FORMAT(23H FREE INTERNAL ROTATION//)
$ 21 FORMAT(6X,3HJ'',6X,2H4',6X,3hK'',6X,2HK',6X,4HKI'',6X,3HKI',16X,
2H V,6X,5HBLZMN,10X,4HAINT,10X,4HFREQ/) $ 22 FORMAT(F9.1,F8.1,F9.1,
F8.1,F10.1,F9.1,F8.1,F12.5,2F16.5) $ C $ READ INPUT DATA $ 23 READ
(5,4)NSETS $ 24 READ(5,6)KSTAR,KZERO,KDOT,KBLANK,(TITLE(I),=I,19) $
25 READ(5,2)A,B,C,DK,DJK,DJ $ 26 READ(5,2)AE,BE,CE,DKE,DJKE,DJE,ZETA
$ 27 READ(5,3)FVIB,FMN,FMX,DF,W,T,XXI $ 28 READ(5,4)ISWE,ISWO,JSWE,
JSWO,JMX,JDEL,KDEL,KSEL,DELTA $ 29 READ(5,4)ISIG5,ISIG6,INRO $ 30
WRITE(6,5)(TITLE(I),I=L,19) $ C $ WRITE INPUT DATA $ 31 WRITE(6,7)
$ 32 WRITE(6,8)A,B,C,DK,DJK,DJ WRITE(6,9) $ 33 WRITE(6,8)AE,BE,CE,
DKE,DJKE,DJE,ZETA $ 34 WRITE(6,10)FVIB,DF,W,T,DELTA,KSEL,JMX $ C $
CLEARING STORAGE SPACE $ DO 35 I = 1,200 $ 35V(I)=0.0 $ DO36I=1,50000
$ 36 Z(I)=0.0 $ DO 37 I=1,100 $ 37 TITLE(I)=0.00 $ C $ GAUSSIAN

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LINE SHAPE (NORMALIZED) $ NDF=((FMX-FMN)/DF+1.) $ XIN=(.91*W/DF)
$ IN=XIN $ FMN=FMN-0.5*DF $ SUM=1. $ DO431=1,IN $ AB=(IN-I+1)
$ 43 SUM=2.*EXP(-2.77*AB*AB*DF*DF/(W*W)+SUM $ V(IN+1)=1./SUM $
NDFW=IN+IN+1 $ DO50I=1,IN $ AB=(IN-I+1) $ V(I)=EXP(-2.77*AB*AB*DF*
DF/(W*W))/SUM $ I1=NDFW-I+1 $ 50 V(I1)=V(I) $ XSWE=ISWE $ XSWE=
ISWO $ KSWE= 1.375 $ XSWO= 1.000 $ C PROLATE OR PBLATE TOP $
IF(A-B)54,52,54 $ 52 BBAR=(C-B) $ GOTO55 $ 54 BBAR=(A-B) $ 55
IF(AE-BE)59,56,59 $ 56 BBARE=(CE-BE) $ AA=CE $ GOTO60 $ 59
BBARE=(AE-BE) $ AA=AE $ C CYCLE FOR J $ 60 CONTINUE $ C CYCLE
FOR K $ 64 DO 174M=1,JMX $ K=M-1 $ XK=K $ N=K+1 69 DO 173JJ=N,
JMX $ J=JJ-1 $ IF (J.EQ.0) GOTO 173 $ XJ=J $ IF (K)174,74,76 $
74 SWFK=XSWE $ GO TO 80 $ 76 DDT=K/3 $ LLL=DDT $ IF(LLL.EQ.DDT)
GO TO 79 $ 77 SWEK=XSWE+XSWE $ GO TO 80 $ 79 SWEK= XSWO + XSWO $
80 IF((J+1)/2-J/2) 81,81,82 $ 81 SWEJ= JSWE $ GO TO 83 $ 82 SWEJ=
JSWO $ 83 SWF=SWEJ*SWEK $ C GROUND STATE JANDK STORED $ XJ1=
XJ*XJ+XJ $ XJ2=XJ1*XJ1 $ XK1=XK*XK $ FREQ1=B*XJ*(XJ+1)+(A-B)
*XK*XK-KJ*XJ2-DJK*XJ1*XK1-DK*XK1*XK1 $ BLZMN= EXP((-FREQ1*1.43846)/T)
$ CALL BANDS (J,K,FREQ1,SWF,BLZMN,BBARE,AA,ZETA, $ ODJKE,DKE,FMN,DF,
IN,NDF,NDFW,I,XJ,XK,Z,V,DJE,BE,FVIB) $ 172 CONTINUE $ 173 CONTINUE
$ 174 CONTINUE $ 175 CONTINUE $ C PARAMETERS FOR CONTOUR $ 181
RFMN=FMN $ DO254NDX=1,ISIG6 $ IF(NDX.EQ.L.)GOTO178 $ WRITE(6,19)
$ 178 SMAX=Z(1) $ SMIN=SMAX $ DO180 I=1,NDF $ SMAX=AMAX1(Z(I),
SMAX) $ 180 SMIN=AMIN1(Z(I),SMIN) $ 186 FMN=RFMN-9.5*DF $ ICNT=10
$ IF(SMIN-1.)187,187,188 $ 187 SMIN=1. $ 188 IF(SMAX/SMIN-XXI)190,
190,189 $ 189 SMIN=SMAX?XXI $ 190 CONTINUE $ CALL PRINT(SMAX,
SMIN,YMAX,YMIN) $ 210 GOTO(211,213,215),ISIG6 $ 211 X=100. $ GOTO216
$ 213 X=200. $ GOTO216 $ 215 X=300. $ 216 SCALE=(X-1.)/(YMAX-YMIN)
$ ZERO=(X-SCALE*YMAX) $ DO2531=1,NDF $ 219 IF(Z(I)-1.)235,235,220 $

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220 GOTO(221,223,225,228,230),ISIG5 $ 221 Y=Z(I) $ GO TO 232 $
223 Y=ALOG(Z(I)) $ GO TO 232 $ 225 E=ALOG(Z(I)) $ Y=E*E $ GO
TO 232 $ 228 IF(Z(I)-3.)235,235,229 $ 229 Y=ALOG(ALOG(Z(I))) $
GO TO 232 $ 230 IF(Z(I)-SMIN) 235,235,231 $ 231 Y=EXP((Z(I)-
SMIN)/(SMAX-SMIN)) $ C LINEAR SCALING BETWEEN 1 AND X $ 232 NNN=
(SCALE*Y+ZERO+0.5) $ C PLOTTING $ ISIG2=1 $ IF(NNN)235,235,237
$ 235 NNN=1 $ GOTO242 $ 237 DO240II=1,3 $ 238 IF(NNN-100)241,
241,239 $ 239 NNN=NNN-100 $ 240 ISIG2=ISIG2+1 $ 241 GOTO(242,244,
246),ISIG2 $ 242 KKK=KDOT $ MMM=1 $ GOTO247 $ 244 KKK=KZERO $
MMM=2 $ GOTO247 $ 246 KKK=KSTAR $ MMM=3 $ 247 IF(ICNT-10)252,
248,248 $ 248 ICNT=0 $ FMN=FMN+10.*DF $ IF(MMM.NE.NDX)NNN=1 $
250 WRITE(6,11)Z(I),FMN,KDOT,(KBLAND,J=1,NNN),KKK $ GOTO253 $ 252
IF(MMM.NE.NDX)NNN=1 $ WRITE(6,12)(Z(I),KDOT,(KBLANK,J=1,NNN),KKK $
253 ICNT=ICNT+1 $ 254 CONTINUE $ NSETS=NSETS-1 $ IF(NSETS)258,258,
256 $ 256 WRITE(6,13) $ GOTO24 $ 258 STOP $ END $

```

#### BANDS

```

SUBROUTINE BANDS(J,K,FREQ1,SWF,BLZMN,BBARE,AA,ZETA, $ ODJKE,DKE,
FMN,DF,IN,NDF,NDFW,I,XJ,XK,Z,V,DJE,BE,FVIB) $ DIMENSIONZ(50000),
V(200),TITLE(100) $ 15 DO 175 I4=1,3,2 $ C PERPENDICULAR BANDS $
25 KE=K+2-I4 $ 26 IF (KE.LT.O) GO TO 170 $ 27 XKE=KE $ 30 DO
174N-=1,3 $ 35 JE=J+N-2 $ IF(KE.GT.JE) GO TO 174 $ 40 XJE=JE
$ IF(KE=K)50,175,90 $ 50 FREQ=2*AA*ZETA*XKE $ 55 IF(JE-J)60,70,
80 $ 60 AKJ=((XJ+XK-1.)*(XJ+XK))/XJ $ 65 GOTO 130 $ 70 AKJ=
((XJ-XK+1.)*(XJ+XK)*2.*XJ+1))/XJ*XJ+XJ $ 75 GOTO 130 $ 80 AKJ=
((XJ-XK+2.)*(XJ-XK+L.))/(XJ-1.) $ 85 GOTO 130 $ 90 FREQ=-2.*AA*
ZETA*XKE $ 95 IF(JE-J)100,110,120 $ 100 AKJ=((XJ-XK-1.)*(XJ-XK))/
XJ $ 105 GOTO 130 $ 110 AKJ=((XJ+XK-1.)*(XJ-XK)*(2.*XJ+1.))/
(XJ*XJ+XJ) $ 115 GOTO 130 $ 120 AKJ=((XJ+XK+2.)*(XJ+XK+1.))/
(XJ+1.) $ C EXCITED STATE FREQ. $ 130 XJE1=XJE*XJE+XJE $

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XJE2=XJE1*XJE1 $ XKE1=XKE*XKE $ FREQ2=BE*XJE1+BBARE*XKE1-DJE*XJE2-  
DJKE*XJE1*XKE1 $ 1-DKE*XKE1*XKE1+FREQ $ DELF=FREQ2-FREQ1+FVIB $  
C LOCATION OF LINR IN CONTOUR $ 140 I1=((DELF-FMN)/DF+1.) $ C  
ADD TO CONTOUR $ 145 IF (I1-IN)174,174,149 $ 149 CONTINUE $ 150  
IF(I1-NDF+IN)155,155,170 $ 155 DO 165I=1,NDFW $ 160 I2= I1+I-IN-1  
$ 165 Z(I2)=Z(I2)+SWF*AKJ*V(I)*BLZMN $ 170 CONTINUE $ 174 CONTINUE  
$ 175 CONTINUE $ 180 RETURN $ END $
```

PRINT

```
SUBROUTINE PRINT(SMAX,SMIN,YMAX,YMIN) $ YMAX=SMAX $ YMIN=SMIN $  
RETURN $ END.
```