APPENDIX A. Description of the rotor program, iar95.exe.

The "internal axis rotor" program, *iar95.exe*, has been written in the C programming language to calculate rotational transition energies and intensities between one or two states each having a rotational Hamiltonian of the general form,

$$\hat{H}_{rot} = A\hat{P}_a^2 + B\hat{P}_b^2 + C\hat{P}_c^2 + \sum_g D\hat{P}_g + \sum_{g \neq g'} E\hat{P}_g\hat{P}_{g'} \tag{D.1}$$

The program calculates transition intensities between the eigenstates of Eq. (D.1) following the formalism developed in Appendix B. Furthermore, the program uses no symmetry to obtain the eigenvalues and eigenvectors of Eq (D.1) and does not impose any selection rules on the calculation of transition intensities. The reason for this approach is a result of the relaxation of the selection rules that occur with the symmetry reduction of the Hamiltonian as discussed in Ref. 2. The program also allows for inertial axis rotation defined in terms of the Euler angles, , , and of one or both states prior to diagonalization of the Hamiltonian matrix. Rotational perturbations arising from inertial axis reorientation are thereby treatable when only one state's Euler angle(s) are non-zero. When the Euler angles in both states are identical but non-zero, non-principal methods (internal axis methods) are applicable and provide a useful and convenient method for the treatment of perturbations terms like those given in Eq. (D.1) that do not lie along the principal axes. The program operates in five phases.

Phase I is the parameter input and assigned line input phase.

Phase II is applied twice, once for each state, and calculates the Hamiltonian matrix for each J block. This consists of the matrix elements for all operators in Eq. (D.1) having non-zero parameter values. Operators for which $g = c$ in Eq. (D.1) are treated as purely imaginary elements. Each matrix is diagonalized to give the eigenvalues and eigenvectors which are then saved to file with the corresponding quantum numbers. The eigenvectors also are used to calculate the derivatives of the expectation values of each operator in Eq. (D.1) with respect to its corresponding parameter. These also are saved to file to be used later in a least squares analysis phase (Phase 4). When the internal axis method is employed, the derivatives with respect to A, B, and C are back-transformed to the principal axis derivatives to eliminate from the least squares fit the additional (and unnecessary) cross term parameters.

Having the eigenvectors (real and possible imaginary), quantum numbers and derivatives for each eigenvalue in each electronic state, Phase III calculates the transition intensities between the levels of each state according to the selection rules J = -1 (P), 0 (Q) and +1 (R) in the sequence R(0), P(1), Q(1), R(1),   Q(J_{max}). The eigenvalues, eigenvectors, quantum numbers (JK_aK_c) and derivatives of each J block for each state are first read from files. Intensities between all permutations of the K sublevels within the value of the K_{order} are then calculated. The a-, b- and c-type sums are performed individually and the band type components are scaled according to the

transition moment projection factors calculated in Phase I. The band type components are then summed, squared (squared modulus when complex) and multiplied by a Boltzmann factor. The quantum numbers of the calculated line are compared with those observed. When a match is found or the calculated line intensity exceeds a predefined minimum intensity cutoff, the observed and calculated transition energies, intensity, associated quantum numbers and band type are saved to disk. The sum of all such lines constitutes the final line set.

When no linear least squares analysis is desired, Phase IV reads the line set and orders all lines according to the calculated transition energies and writes out a formatted lineset for input into the analysis program, *jb95.exe*. The program then terminates.

Phase V performs a linear least squares fit analysis (LSF) of the adjustable parameters (specified on input) in order to minimize the sum of the observed minus calculated energy differences. The phase operates in two nested cycles. The outer cycle (slowest varying) calls Phases II and III repeatedly until the cycle count specified on input is exceeded. Exact energies and derivatives are therefore used in the LSF analysis based on the best fit parameters from the previous cycle. The inner cycle utilizes the old derivatives and new parameters to obtain new but approximate calculated energies. The new energy differences (OMC) are then used to determine whether additional assigned lines will be accepted in the next inner cycle. If no additional lines are accepted based on the rejection level specified on input, the inner cycle terminates.

Phase V terminates with an error if a) the number of fitted parameters exceeds the number of observed lines accepted in the fit; b) linear dependence is found when solving the system of equations; or c) a negative A, B or C parameter is generated. Otherwise Phase V logs the best fit parameters and standard deviation of each parameter as well as the overall OMC standard deviation for all accepted lines.

Phase III is called on termination of Phase V to calculate transition energies based on the old derivatives and new parameters. The line set is ordered and written out in a format for input to the analysis program, *jb95.exe*.

APPENDIX B. Matrix elements and transition intensity calculation used in *iar95.exe*.

Hamiltonian matrix elements

The symmetric rotor functions, $|JK$, provide a convenient basis set for the Hamiltonian given in Eq. D.1. The matrix elements that form the Hamiltonian matrix are given by[2]

$$\langle JK|\hat{H}_{rot}|JK\rangle = \frac{(B+C)}{2}J(J+1) + [A - \frac{(B+C)}{2}]K^2 + D_aK \tag{B.5}$$

$$\langle JK|\hat{H}_{rot}|JK\pm1\rangle = \frac{D_b}{2}[J(J+1) - K(K\pm1)]^{1/2} \tag{B.6}$$

$$\langle JK|\hat{H}_{rot}|JK\pm2\rangle = \frac{(B-C)}{4}\{[J(J+1) - K(K\pm1)][J(J+1) - (K\pm1)(K\pm2)]\}^{1/2} \tag{B.7}$$

$$\langle JK|\hat{H}_{rot}|JK\pm1\rangle = i\frac{D_y}{2}[J(J+1) - K(K\pm1)]^{1/2} \tag{B.8}$$

Transition intensities

In isotropic magnetic field free space, the intensity, *I*, of a given rovibronic line may be written as

$$I = I_0\ g_N\ S(J'K_aK_c:J''K_aK_c)\ \exp\left(\frac{-E(J''K_aK_c)}{kT_{rot}}\right) \tag{5.17}$$

where g_N is the nuclear spin weighting factor. *S* is the line strength factor given by

$$S(J'K_aK_c:J''K_aK_c) = \sum_{M'M''}\left[\langle J'K_aK_cM|\,\hat{\mu}\,|J''K_aK_cM\rangle\right]^2 \tag{5.18}$$

where JK_aK_c are the asymmetric rotor wavefunctions labeled with the total angular momentum quantum number *J* and the prolate and oblate symmetric top quantum numbers K_a and K_c. $\hat{\mu}$ is the electric dipole moment operator and the sum is over all magnetic sublevels, *M*, of both states. *S* may be redefined in terms of the space-fixed **Z** component of $\hat{\mu}$ as

$$S(J'K_aK_c:J''K_aK_c) = 3\sum_{M'M''}\left|\langle J'K_aK_cM|\hat{\mu}_Z|J''K_aK_cM\rangle\right|^2 \tag{5.19}$$

which becomes

$$S(J'K_aK_c:J''K_aK_c) = 3\sum_{M'M''}\left[\langle J'K_aK_cM|\sum_q D_{0q}^{1*}\ \hat{\mu}(1,q)|J''K_aK_cM\rangle\right]^2 \tag{5.20}$$

when the dipole moment is expressed in spherical tensor form and referenced to the molecular fixed frame. The eigenfunctions of the rotational Hamiltonian may always be expanded in a basis of symmetric top functions, $|JKM\rangle$, or in terms of the rotation matrices, D_{MK}^{J*}, by

$$|JK_aK_cM\rangle = \sum_K c_K |JKM\rangle = \left(\frac{2J+1}{8\pi^2}\right)^{1/2} \sum_K c_K D_{MK}^{J*} \tag{5.21}$$

Substitution of Eq. (5.21) into Eq. (5.20) gives

$$S(J'K_aK_c:J''K_aK_c) =$$

$$3\frac{(2J''+1)(2J'+1)}{(8\pi^2)^2} \sum_{M'M''} \left[\sum_{K'K''} c_{K'}^* c_{K''} \sum_q \mu(1,q) \int D_{MK}^{J'} D_{0q}^{1*} D_{MK}^{J''*} d\Omega \right]^2 = \tag{5.22}$$

$$3\frac{(2J''+1)(2J'+1)}{(8\pi^2)^2} \sum_{M'M''} \left[\left[\sum_{K'K''} c_{K'} c_{K''}^* \sum_q \mu^*(1,q) \int D_{MK}^{J'*} D_{0q}^{1} D_{MK}^{J''} d\Omega \right]^*\right]^2 =$$

$$3(2J''+1)(2J'+1) \times$$

$$\sum_{M'M''} \left[\left[\sum_{K'K''} c_{K'} c_{K''}^* \sum_q \mu^*(1,q)(-1)^{M'-K'} \begin{pmatrix} J'' & 1 & J' \\ M'' & 0 & -M' \end{pmatrix} \begin{pmatrix} J'' & 1 & J' \\ K'' & q & -K' \end{pmatrix}\right]^*\right]^2$$

where we have used the property that

$$D_{MK}^{J*} = (-1)^{M-K} D_{-M-K}^{J} \tag{5.23}$$

and the Wigner 3-J (W3J) symbol relation

$$\int D_{-M-K}^{J'} D_{0q}^{1} D_{MK}^{J''} d\Omega = 8\pi^2 \begin{pmatrix} J'' & 1 & J' \\ M'' & 0 & -M' \end{pmatrix} \begin{pmatrix} J'' & 1 & J' \\ K'' & q & -K' \end{pmatrix} \tag{5.24}$$

Rearranging Eq. (5.22) gives

$$S(J'K_aK_c:J''K_aK_c) =$$

$$(2J''+1)(2J'+1)\left[\left[\sum_{K'K''} c_{K'} c_{K''}^* \sum_q \mu^*(1,q)(-1)^{-K'} \begin{pmatrix} J'' & 1 & J' \\ K'' & q & -K' \end{pmatrix}\right]^*\right]^2 \tag{5.25}$$

Here, we have used the symmetry properties of the W3J symbols and the orthogonality relation

Finally, we express Eq. (5.25) in terms of the Clebsch-Gordan coefficients using

$$\begin{pmatrix} J'' & 1 & J' \\ K'' & q & -K' \end{pmatrix} = \frac{(-1)^{J'-J''+K'}}{\sqrt{2J'+1}} \langle J''K'',1q \mid J'K' \rangle \tag{5.27}$$

yielding

$$S(J'K_aK_c:J''K_aK_c) =$$

$$(2J''+1) \left[\sum_{K'K''} c^*_{K'} c_{K''} \sum_q \mu(1,q) \langle J''K'',1q \mid J'K' \rangle \right]^2 \tag{5.28}$$

Terms only contribute to the sum in Eq. (5.28) when $K - K = q$.

     The Cartesian component projections of the dipole moment operator are given in terms of the spherical tensor forms appearing in Eq. (5.28) as[6]

$$\hat{\mu}_z = \hat{\mu}(1,0) \tag{5.29}$$

$$\hat{\mu}_x = \frac{1}{\sqrt{2}} \left[\hat{\mu}(1,-1) - \hat{\mu}(1,1) \right] \tag{5.30}$$

$$\hat{\mu}_y = \frac{i}{\sqrt{2}} \left[\hat{\mu}(1,-1) + \hat{\mu}(1,1) \right] \tag{5.31}$$

As an example, consider a dipole moment lying in the **xz** plane and having a orientation angle, $_{TM}$ with respect to **z**. Then, $\hat{\mu}_x = \hat{\mu} \sin{}_{TM}$ and $\hat{\mu}_z = \hat{\mu} \cos{}_{TM}$, and for an R branch transition ($J - J = +1$), the line strength is obtained from

$$S(J'K_aK_c:J''K_aK_c) =$$

$$\left[\sum_{K''} \left\{ c'^*_{K''} c''_{K''} \langle J''K'',10 \mid J'K'' \rangle \cos\theta_{TM} + \right. \right.$$

$$\frac{1}{\sqrt{2}} \left[c'^*_{K''-1} c''_{K''} \langle J''K'',1-1 \mid J'K''-1 \rangle - \right.$$

$$\left. \left. \left. c'^*_{K''+1} c''_{K''} \langle J''K'',11 \mid J'K''+1 \rangle \right] \sin\theta_{TM} \right\} \right]^2 \tag{5.32}$$

$$\sum_{M'M''} \begin{pmatrix} J'' & 1 & J' \\ M'' & 0 & -M' \end{pmatrix} \begin{pmatrix} J'' & 1 & J' \\ M'' & 0 & -M' \end{pmatrix} =$$

$$\sum_{M'M''} \begin{pmatrix} J' & J'' & 1 \\ -M' & M'' & 0 \end{pmatrix} \begin{pmatrix} J' & J'' & 1 \\ -M' & M'' & 0 \end{pmatrix} = \frac{1}{3} \tag{5.26}$$

If the TM vector lies along the **x** axis, the cos θ_{TM} term in Eq. (5.32) vanishes. If it lies along the **z** axis, the sin θ_{TM} term vanishes. Additionally, when the eigenvector coefficients c appearing in Eq. (5.32) are obtained from diagonalization of a rigid rotor Hamiltonian matrix, the selection rules guarantee that at least one of these two terms will vanish when the sums are performed over K for a given transition. Both terms and their relative signs become important only when the symmetry of the rotational Hamiltonian is reduced to C_2 or C_1. When complex (real and imaginary) Hamiltonian matrices are diagonalized, separate sums are performed over the real and imaginary eigenvector coefficients. The line strength is obtained from the squared modulus of the real and imaginary summed values.

Linear least squares analysis

The linear least squares fitting algorithm used to fit N parameters of the rotational Hamiltonian (Eq. D.1) to the observed transition energies, E^{obs}, is based on a "chi-squared" minimization procedure where χ^2 is defined as

$$\chi^2 = \sum_i^N \left\{ E^{obs} - [E_i' - E_i'' + E_o] \right\}^2 \tag{E.2}$$

where E_i' and E_i'' are the upper and lower calculated state energies obtained from diagonalization Eq. (D.1) for each state. It is convenient to reexpress E_i' and E_i'' in terms of its parameters and derivatives as

$$E_i' = \sum_j^{M'} a_j' \frac{\partial E'}{\partial a_j'} \quad \text{and} \quad E_i'' = \sum_j^{M''} a_j'' \frac{\partial E''}{\partial a_j''} \tag{E.3}$$

for all M' and M'' terms in Eq. (D.1) where a_j are the parameters A, B, C, D or E and are linear functions of the energy, E. Substitution of Eq. (E.3) into Eq. (E.2) gives

$$\chi^2 = \sum_i^N \left\{ E_i^{o\beta\sigma} - \left[\sum_\kappa^{M'} \alpha_\kappa' \frac{\partial E'}{\partial \alpha_\kappa'} - \sum_\kappa^{M''} \alpha_\kappa'' \frac{\partial E''}{\partial \alpha_\kappa''} + \alpha_0 \right] \right\}^2 \tag{E.4}$$

where E^{ori} is defined as a_0. In order to evaluate $\dfrac{\partial E}{\partial a_k}$, we make use of a relation first introduced by Feynman[1],

$$\frac{\partial E}{\partial a_k} = \langle \Psi_i | \frac{\partial \hat{H}}{\partial a_k} | \Psi_i \rangle \tag{E.5}$$

where $\Psi_i = \sum_K c_{iK} |JK\rangle$ are the eigenfunctions of Eq. (D.1) expressed in a symmetric top basis.

The parameters, a_k, are desired such that the derivative of χ^2 with respect to all a_k is zero, *i.e.*,

$$0 = \sum_i^N \left\{ \left[E_i^{obs} - \left(\sum_k^{M'} a_k' \frac{\partial E_{ik}'}{\partial a_k'} - \sum_k^{M''} a_k'' \frac{\partial E_{ik}''}{\partial a_k''} + a_0 \right) \right] \frac{\partial E_{ij}}{\partial a_j} \right\} \tag{E.6}$$

$$\sum_j^{0,M',M''} \sum_i^N \frac{\partial E_i}{\partial a_j} \frac{\partial E_i^j}{\partial a_k} a_j = \sum_i^N E_i^{obs} \frac{\partial E_i}{\partial a_k} \tag{E.7}$$

for all $j = M'$ and M'' parameters and $\dfrac{\partial a_0}{\partial a_0} = 1$ giving a $M' + M'' + 1$ set of equations in unknown coefficients, a_k. Reversing the summation in Eq. (E.6) gives the *normal equations*. The *normal equations* are solved for the parameters, a_k, by a standard technique such as LU decomposition and backsubstitution also known as singular value decomposition.[2]

APPENDIX C. Rotor program, iar95.exe, sample input file and parameter description.

```
################################################################################
#                    IAR INPUT FILE : VERSION 2.0                 #
################################################################################
#------------------------------------------------------------------------------
# COMMENT LINE (< 200 CHARACTERS WITH NEW LINE END):
  2-METHYL NAPHTHALENE - E LINES
#------------------------------------------------------------------------------
#------------------------------------------------------------------------------
# OUTPUT FILENAME (EXTENSIONS WILL BE ADDED):
  2mne
#------------------------------------------------------------------------------
#------------------------------------------------------------------------------
# ASSIGNMENT FILENAME:
  2mne.asn
#------------------------------------------------------------------------------
#------------------------------------------------------------------------------
# J & K MAXIMUM OF ASSIGNED LINES TO FIT:
  -1            -1
#------------------------------------------------------------------------------
#------------------------------------------------------------------------------
# MAXIMUM J TO CALCULATE:
  30
#------------------------------------------------------------------------------
#------------------------------------------------------------------------------
# GROUND STATE A, B AND C ROTATIONAL CONSTANTS:
  2.80370062e+03   8.22797124e+02   6.38859058e+02
#------------------------------------------------------------------------------
# GROUND STATE PHI, THETA AND CHI EULER ANGLES (UHU-1 CCW+):
  0.000000       0.000000       0.000000
#------------------------------------------------------------------------------
# GROUND STATE FIT INDICATORS: 0|1=OFF|ON
  1        1        1
#------------------------------------------------------------------------------
#------------------------------------------------------------------------------
# GROUND STATE STATUS OF CONSTANTS:
  1        0        1
#------------------------------------------------------------------------------
# GROUND STATE <PX>(B), <PY>(C) & <PZ>(A) CONSTANTS:
  8.00039176e+00   0.00000000e+00   6.91689529e+01
#------------------------------------------------------------------------------
# GROUND STATE FIT INDICATORS: 0|1=OFF|ON
  1        0        1
#------------------------------------------------------------------------------
#------------------------------------------------------------------------------
# GROUND STATE STATUS OF CONSTANTS:
  0        0        0
#------------------------------------------------------------------------------
# GROUND STATE <PXPY + PYPX>, <PXPZ + PZPX> & <PYPZ + PZPX> CONSTANTS:
  0.00000000e+00   0.00000000e+00   0.00000000e+00
#------------------------------------------------------------------------------
```

GROUND STATE FIT INDICATORS: 0|1=OFF|ON
  0   0   0
#---
#---
GROUND STATE STATUS OF CONSTANTS:
  0   0   1
#---
GROUND STATE <DK>, <DJK> & <DJ> WATSON D DISTORTION CONSTANTS:
  0.00000000e+00   0.00000000e+00   1.43369769e-05
#---
GROUND STATE FIT INDICATORS: 0|1=OFF|ON
  0   0   1
#---
#---
GROUND STATE STATUS OF CONSTANTS:
  0   0   1
#---
GROUND STATE <dK> & <dJ> WATSON D DISTORTION & <PZ**3> CONSTANTS:
  0.00000000e+00   0.00000000e+00   4.27435378e-03
#---
GROUND STATE FIT INDICATORS: 0|1=OFF|ON
  0   0   1
#---
#---
EXCITED STATE A, B AND C ROTATIONAL CONSTANTS:
  2.72978104e+03   8.14588554e+02   6.30288152e+02
#---
EXCITED STATE PHI, THETA AND CHI EULER ANGLES (UHU-1 CCW+):
  0.000000   0.000000   0.000000
#---
EXCITED STATE FIT INDICATORS: 0|1=OFF|ON
  1   1   1
#---
#---
EXCITED STATE STATUS OF CONSTANTS:
  1   0   1
#---
EXCITED STATE <PX>(B), <PY>(C) & <PZ>(A) CONSTANTS:
  4.56960401e+01   0.00000000e+00   4.07424568e+02
#---
EXCITED STATE FIT INDICATORS: 0|1=OFF|ON
  1   0   1
#---
#---
EXCITED STATE STATUS OF CONSTANTS:
  0   0   0
#---
EXCITED STATE <PXPY + PYPX>, <PXPZ + PZPX> & <PYPZ + PZPX> CONSTANTS:
  0.00000000e+00   0.00000000e+00   0.00000000e+00
#---
EXCITED STATE FIT INDICATORS: 0|1=OFF|ON
  0   0   0
#---
#---

EXCITED STATE STATUS OF CONSTANTS:
```
   0          0          1
```
#---
EXCITED STATE <DK>, <DJK> & <DJ> WATSON D DISTORTION CONSTANTS:
```
  0.00000000e+00   0.00000000e+00   2.89808193e-05
```
#---
EXCITED STATE FIT INDICATORS: 0|1=OFF|ON
```
   0          0          1
```
#---
#---
EXCITED STATE STATUS OF CONSTANTS:
```
   0          0          1
```
#---
EXCITED STATE <dK> & <dJ> WATSON D DISTORTION & <PZ**3> CONSTANTS:
```
  0.00000000e+00   0.00000000e+00   -5.21773343e-02
```
#---
EXCITED STATE FIT INDICATORS: 0|1=OFF|ON
```
   0          0          1
```
#---
#---
ORIGIN FREQUENCY AND FIT INDICATOR: 0|1=FIXED|FIT
```
   3.34473572e+05
   1
```
#---
#---
TRANSITION MOMENT METHOD & REFERENCE FRAME: 0|1=ANG|%INT & 0|1=GND|EXE FRAME
```
   0          0
```
#---
TRANSITION MOMENT (CCW+): TM MAG/THETA/CHI FROM A | %INT ON A(Z) & B(X) & C(Y)
```
   1.000000       50.000000        0.000000
```
#---
#---
DELTA K ORDER & AMPLITUDE STATUS: 1|3|5=ORDER & 0|1=AMP STATUS OFF|ON
```
   3          0
```
#---
#---
TEMPERATURE IN KELVIN (TO MHZ) & INTENSITY CUTOFF: 3.0 & 0.01
```
   9.000000        0.050000
```
#---
#---
OUTPUT FORMAT INDICATOR & ERG & ITN SCALARS & FSR: 0|1=JB FORMAT OFF|ON
```
   1          0.01         1.00          599.504000
```
#---
#---
PARITY STAT & GND & EXE KaKc PARITY PRODUCTS: Y|N=OFF|ON & E|O & E|O
```
   N          E          O
```
#---
#---
LS FIT EXACT CYCLES & APPROX & REJ LEVEL: 0(-1)|1=OFF|ON & 1|.. & 1|..
```
   1          1          200.000000
```
#---
#---
LOWER & UPPER EIGENVALUES & EIGENVECTORS LOGGED: 0|.. TO -1|.. & 0|.. TO -1|..
```
   0          -3
```

```
  0             -3
#------------------------------------------------------------------------
#------------------------------------------------------------------------
# DEBUG PRINT STATUS: 0|1=OFF|ON
  0
#------------------------------------------------------------------------
```

The program, *iar95.exe*, is fully three-dimensional for both Hamiltonian rotations in one or two states and for specification of transition moment (*TM*) orientations. The program also includes specification of the Watson *D* distortion parameters which can be fit in rotated frames with the disadvantage that their meaning is obscure. Tests have been done by direct comparison with output from *ASYROT* and *BLZYROT*. The outputs from these three programs are in good agreement as long as the conventions given below are adhered to. The sign conventions used in *BLZYROT* are the same ones used here. See NOTE files in directories *'asy_iar_distortion'* and *'blz_iar_axissw'* for actual test runs and further explanation of output from these programs. Some comments about fitting strategies are included in these notes.

This is an example input file for the program *iar* for **UNIX** or *iar95.exe* for **Windows95**. This file is read by the rotor program in several different ways.

1. *iar95* <RETURN>
    input file ?
You are prompted for the input file name after the program is started. ASCII files like outfile.dat and the outfile.log file are the only survivors. NOTE: a new input file will be created called *'outfile'.in* where *outfile* is the output base filename parameter given as an input parameter below.

2. *iar95* *input file*
Entered as a command line argument. Both ASCII and JB binary files survive.

3. *iar95* *1.0*
    iar95 *1.0 input file*
This entry form is for backward compatibility with old input files used with *iar*. The new input file created is version 2.0 and may then be modified. Note that the new input file format is more informative with comment lines that are ignored by *iar95.exe*. Comment lines always begin with a # sign. However, while parameter entry is still in a free format style, all parameters entries must exist.

A description of the parameters in the above input file are as follows:

2-METHYL NAPHTHALENE - E LINES

A line for comments. Text must be less that 200 characters and must end with a newline character.

2mne

This is the base filename of all output. Files that will be overwritten include:

'outfile'.in   is the new input file format with updated constants from the fit.

'outfile'.log contains a log of the various phases and outputs of the program including the fit phases.

'outfile'.a   gives a listing of the calculated lines in the ASCII format: band type, three upper, three lower state quantum numbers, simulated intensity, observed and calculated frequencies.

'outfile'.dat gives a listing of the calculated lines in the lines.dat format.

'outfile'.f   binary file containing expt. and calc. freq, intensity and band type.

'outfile'.q   binary file containing quantum numbers of calculated lines.

'outfile'.p   binary file containing parameter listing.

'outfile'.m   binary file containing quick reference line positions. (older versions).

2mne.asn

The name of an ASCII file that contains the band type, the three excited, three ground assigned quantum numbers and observed frequency used in the fitting phase. An example follows:

A 10 1 10 9 1 9   13370.8116

//

The end of the assigned line set must have the line //. When simultaneous fits of UV/MW data are desired, the UV lineset ending with // line should be followed by the MW data set ending with // line. The UV and microwave weighting factors are specified after the // line at the end of the file.

-1   -1

These two parameters determine the maximum J and K respectively to use from the assigned line set. -1 signals to use all lines.

30

Maximum value of J to calculate for each state.

2.80370062e+03   8.22797124e+02   6.38859058e+02

Values of rotational constants for the lower state: *A(Z)*, *B(X)*, *C(Y)*

0.000000   0.000000   0.000000
Values of Euler angles used to rotate the Hamiltonian operator prior to diagonalization. The angles are   , , and   in degrees. Positive angles refer to counterclockwise rotation of the Hamiltonian or EQUIVALENTLY, CLOCKWISE rotation of the coordinate system (axis system). For example, to rotate the Hamiltonian axis counterclockwise in the *ab* plane (about *c*) by 1.2 degrees, this line would be
0.000000   1.2000000   0.000000

to rotate the Hamiltonian counterclockwise in the *bc* plane (about *a*) by 1.2 degrees, this line would be
1.200000   0.000000   0.000000

to rotate the Hamiltonian counterclockwise in the *ac* plane (about *b*) by 1.2 degrees, this line would be
90.000000   1.2000000   -90.000000

AXIS SWITCHING CASE - To model axis switching effects, the Euler angle(s) for only one state should be non-zero. A positive angle of rotation in the upper state will cause a counterclockwise rotation of the Hamiltonian or equivalently, a CLOCKWISE rotation of the upper inertial axes into the lower state principal axis system about the axis specified. Positive angles for counterclockwise rotation is the convention used to specify both *TM* moment orientations and axis switching angles in reference to the COORDINATE SYSTEM. Therefore, switching angles will have the opposite sign to that specified above. See below for a description of the reference frame for the *TM* angle.

INTERNAL AXIS ROTATION - In general, this program can be used to rotate the Hamiltonians in both states. If the same angles are used, for example, in order to simplify treatments of perturbations, the Euler angle(s) for both states should be the same or axis switching effects will be present.

1   1   1
Least squares analysis variation indicators. Parameters are held fixed when set to zero.

----
1   0   1
Indicates that the perturbation term below is non-zero.

8.00039176e+00   0.00000000e+00   6.91689529e+01

Values of perturbation constants D used to treat Coriolis interactions making use of the linear operators D_bP_b (D_xP_x), D_cP_c (D_yP_y) and D_aP_a (D_zP_z), respectively. Note that the term $P_c(P_y)$ is imaginary and increases the memory required and lengthens the time of the calculation.

1   0   1

Least squares analysis variation indicators. Parameters are held fixed when set to zero.

----

0   0   0

Indicates that the perturbation term below is non-zero.

0.000000   0.000000   0.000000

Values of perturbation constants E used for the product operators P_iP_j where i not equal j: $E_{bc}P_bP_c$ $(E_{xy}P_xP_y)$, $E_{ca}P_cP_a$ $(E_{yz}P_yP_z)$ and $E_{ba}P_bP_a$ $(E_{xz}P_xP_z)$, respectively. Note that terms with $Pc(Py)$ are imaginary and increases the memory required and lengthens the time of the calculation.

0   0   0

Least squares analysis variation indicators. Parameters are held fixed when set to zero.

----

0   0   1

Indicates that the perturbation term below is non-zero.

0.00000000e+00   0.00000000e+00   1.43369769e-05

Values of Watson's centrifugal distortion constants $_K$, $_{JK}$ and $_J$ $(_J[J(J+1)]^2)$

0   0   1

Least squares analysis variation indicators. Parameters are held fixed when set to zero.

----

0   0   1

Indicates that the perturbation term below is non-zero.

0.00000000e+00   0.00000000e+00   4.27435378e-03

Values of the Watson's centrifugal distortion (A REDUCTION) constants $_K$ and $_J$ and the internal rotation FP_a^3 (FP_z^3) terms.

0   0   1

Least squares analysis variation indicators. Parameters are held fixed when set to zero.

2.72978104e+03   8.14588554e+02   6.30288152e+02

0.000000   0.000000   0.000000

1   1   1

1   0   1

4.56960401e+01   0.00000000e+00   4.07424568e+02

1   0   1

0   0   0

0.000000   0.000000   0.000000

0   0   0

0   0   1

0.00000000e+00   0.00000000e+00   2.89808193e-05

0   0   1

0   0   1

0.00000000e+00   0.00000000e+00   -5.21773343e-02

0   0   1

Values of the corresponding parameters for the upper state. When band origin is set to exactly zero, pure rotational (microwave) transitions are assumed and these upper state values are ignored except when doing simultaneous UV/MW fits.

3.34473572e+05

Value of the band origin. Since double precision is now used, all digits can be retained e.g. 950334472.353405 may be used as the origin frequency in MHz. When set to zero, pure rotational (microwave) transitions are assumed and the upper state parameters are ignored.

1

Least squares analysis variation indicator. Parameter is held fixed when set to zero.

----

0   0

1.000000   50.000000   0.000000

Transition moment orientation can now be specified in one of two different ways using the factors in the second line depending on value of parameter 1 on the first line. If parameter 1 set to 0, the first value is the magnitude of the *TM* and the last two values

are angles in degrees. The first angle is the amount of rotation in the *ab* plane (like Euler angle) with positive values for counterclockwise rotation as is the convention. The second angle is the angle of rotation about the *a* axis relative to the *b* axis with the same positive angles for CCW rotation convention. Examples:

a	1.0	0.0	0.0
b	1.0	90.0	0.0
c	1.0	90.0	90.0
ab	1.0	TM ANGLE	0.0
ac	1.0	TM ANGLE	90.0
bc	1.0	90.0	TM ANGLE
abc (33.3/33.3/33.3)	1.0	54.73561	45.0

The second method is used if the first parameter on first line is 1. The three values on the second line are the (%)*TM* intensity components on the *a*, *b* and *c* axis, respectively. Note that these are the *TM* components and not the   components. Signs should be included if necessary as with axis switching. These numbers are consistent with ***BLZYROT***.

Note that by increasing the magnitude parameter using method 1 or the percentages using method 2, the intensities of the transitions printed out are scaled by this same amount. The second parameter on line 1 is the reference frame for the *TM*. Usually this is the ground state in which case the parameter value should be zero. If set to 1 the coordinate frame from which the *TM* is measured is that of the excited state.

----

3   0

   K order to calculate and the line intensity indicator =0 (or for amplitudes =1).

9.000000   0.050000

Temperature of band in Kelvin when rotational constants are in MHz. Scale appropriately when different units such as cm^{-1} is used. The second parameter is the intensity cutoff factor.

----

1   0.01   1.00   599.504000

Factors for compatibility with an old unix version (MASSCOMP) of the *jb* program. The first parameter when set to 0 indicates that frequencies and intensities files are written out as normal without modification. The first parameter when set to 1 indicates that the input assigned line set and binary and ascii output files are to be used in conjunction with *jb*. For the binary files, all frequencies will be converted to integers

in the binary files after multiplication by the 1.0e3 and all intensities will be converted to short after multiplication by 1.0e3. For the *lines.dat* formatted output file, all frequencies will be multiplied by the second factor (0.01) and all intensities will be multiplied by the third factor (1.0) before being written out in ascii form. This is to maintain compatibility with the assigned line file and to prevent overflow in JB. The assigned line set must ALREADY have all frequencies multiplied by the second factor (0.01) as is usual for assigned line sets used with *ASYROT*. The fourth factor is the FSR of the reference cavity and is used to create quick reference binary file (.m) also used by *jb*. Also, the ASCII file written out has the same form of a *lines.dat* file produced by *ASYROT* and *BLZYROT*.

N   E   O

Parity selection status indicator. N means ignore parity when calculating transition intensities and the next two labels are meaningless (but necessary). If status is *Y*, then *E* and *O* determine which transitions are kept based on the ground and excited state overall K parities, respectively. If *E(O)* is used then only when K_a+K_c is even (odd) will the transition be printed. This condition must be true in both states, *i.e.* for the *Y E O* combination (*a*-type band), transitions will be saved only when both K_a+K_c ground is even and K_a+K_c excited is odd. Note that Wang transformation of the rotational Hamiltonian is not applied in this program and therefore quantum labels may become switched for degenerate levels. This results in a mislabeling of the eigenvectors and the absence of transitions in the output when option *Y* is used above. *N* should be used in these cases. Mis-labeled transitions will occur only for degenerate levels (of little consequence since the correct label is obvious) or when perturbations become large enough to change the normal ordering of the asymmetric top energy levels. This latter condition can lead to problems during least squares fitting of assigned lines especially in the initial phases where constants change by "large" amounts. BEWARE!

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1   1   200.000000

Factors used in the least squares analysis using SVD algorithms. The first parameter is the number of exact energy cycles to perform. The constants in each iteration are the previous cycle's best fit parameters and are the ones used for rediagonalization of the full Hamiltonians. When set to -1 (or 0), no LSA is done and a simulated line set is printed based on the initial parameters (0 will save additional derivative files which are used by *jb*). The second parameter is the number of approximate cycles performed for each exact cycle. In combination with the rejection level given as the third parameter, assigned lines are accepted/rejected based on calculated energies obtained from the new parameters but old derivatives. The rejection level is in units of the rotational constants used in the least squares analysis.

----

0   -3

0   -3

These parameters are used to print to the log file the eigen energies and eigen vectors between $J = 0$ and $J = -3$ for the ground and excited states, respectively. In this case nothing is printed since J initial is larger than J final.

0

This factor is for debugging purposes. It should always be set to 0 unless you want a great deal of information about every operation in this program. This information is printed to the standard output.

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