

User Guide to the *JB95* Spectral Fitting Program

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Abstract

A graphical user interface computer program based on a Windows¹ API platform has been written in the *C* programming language to aid in the rotational analysis of complex molecular spectra. Dialog boxes provide a user interface for the calibration, linearization and manipulation of experimental data and for the generation and optimization of the simulated spectra. Resources are provided for the deconvolution of multiple overlapping rotational bands from different conformations and/or isotopomers of a molecule and for the analysis of molecular spectra when internal rotation, centrifugal distortion, nuclear quadrupole coupling interactions, large amplitude motion and inertial frame reorientation effects are resolved.

¹ Certain commercial equipment, instruments, or materials are identified in this paper to foster understanding. Such identification does not imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

A. Overview

The graphical user interface (GUI) computer program, *jb95.exe*, accepts experimental data in an ASCII format consisting of frequency and intensity pairs. Cubic spline interpolation routines are used to linearize the ASCII data in frequency. After input conversion, three separate binary files are created, each representing a different level of horizontal scale expansion. The compression factor and the method of determining the intensity per unit frequency interval is selected by the user for each level of scale expansion. The top level of view is usually chosen to have a horizontal compression factor so that the entire file will be displayed over a single screen. In this case, the maximum intensity over each frequency interval is typically used since, otherwise, digital averaging would wash out most spectral features. The most expanded level of view provides access to the linearized raw data at full experimental resolution. An intermediate level is also available for reviewing larger spectral regions and for precise positioning during scale expansion of very large data files. Various sections of the spectrum are accessed *via* tool bar buttons that expand and contract the data about the cursor position by rapidly switching between these different levels. Once these files are created, the speed to access any spectral region is nearly instantaneous and independent of the original data record length. Up to nine independent channels may be simultaneously displayed and additional tool bar buttons are provided for scaling and offsetting the data in each channel. All of relevant files are kept in a separate folder including a special working directory file used to record the filenames, display factors and calibration information for that folder.

Theoretical rotational spectra are generated by an independently-executed console-based rotor program, *iar95.exe*. A dialog in *jb95.exe* provides an interface to the rotor program for convenient access to the input parameters. Rotational constants, Watson's centrifugal distortion parameters, and Coriolis and quadratic angular momentum cross terms are easily added or modified to calculate rotational spectra for one-state (microwave) and two-state (vibrational and electronic) systems. Based on these parameters, the rotor program generates a simulated set of transitions (a line set). Each transition is assigned an electric dipole selection rule label (band type label), six asymmetric rotor quantum numbers, and a calculated frequency and intensity for each line. The theoretical stick spectrum is imported into one of nine simulation channels that can be graphically overlaid and compared with the experimental data. The independent channels are useful for the deconvolution of overlapping spectra. Each simulated line may be convoluted with a Lorentzian, Gaussian, or Voigt lineshape function to adequately match the experimental data.

Two fitting strategies are implemented for the refinement of the model parameters: i) spectral pattern matching through step-wise parameter adjustment and ii) linear least-squares regression after quantum-number assignment of experimental frequencies. For the first method, the simulated spectrum is regenerated upon step-wise changes in the model parameters. Each new transition frequency is calculated from the sum over the products of the modified parameters and the Feynman energy derivatives calculated from the eigenvectors of the Hamiltonian. The method is accurate for small changes in the parameters and when the derivatives are slowly

varying functions of the parameters. The line intensities are not altered by this procedure and therefore, are not exact. The primary advantage of using this method is that it allows for the rapid regeneration of the theoretical line set, which permits the user to visually evaluate its parameter dependence for pattern matching purposes. Additional dialog boxes are used as a convenient interface for making step-wise changes in the parameter values. Mouse-controlled track bars provide for smooth variation of individual rotational constants or for changes in the parameter pairs, $B+C$ and $B-C$. The magnitude of the parameter change per unit track bar step is user adjustable. An additional control in the dialog is provided for regeneration of the exact frequencies, intensities and derivatives using the rotor program, when the validity of the approximation may be suspect. When nuclear quadrupole interactions are important, separate control and track bar dialogs are available for quantum-number listings that include experimental assignments and for variation of the coupling constants.

The second computer-assisted method for the systematic refinement of the rotor parameters is by means of a linear least-squares fitting procedure. The process begins with the creation of an assignment file that contains a list of experimental frequencies and the associated quantum-number labels. A dialog control is used to retrieve the quantum labels from simulated lines that are bracketed by an adjustable window positioned using the cursor. Additional dialog controls are used for selecting a specific line in the list and for assigning and deleting the associated experimental frequency also defined by the cursor position. Calculated lines that are selected reveal the experimental frequency with a vertical line on the display. When saved to file, the collection of assigned lines are used by the rotor program to minimize the observed-minus-

calculated (O-C) standard deviation using a least squares procedure based on a singular-value-decomposition algorithm. A dialog control updates an auxiliary parameter set with the best-fit parameters, standard uncertainties, and O-C standard deviation of the assigned line set. Through examination of these values and from comparisons with the original parameters, the quality of the fit may be evaluated prior to updating and displaying the new simulated spectrum. If the changes are acceptable, the process is repeated until all experimental lines are assigned. Once a spectrum is fit, an additional option to create a binary file from the convoluted stick spectrum frees the simulation resource for further analysis of other overlapping subspectra. A separate dialog and console-based program, *quad95.exe*, is available for least-squares refinement of nuclear quadrupole coupling constants for a single nucleus up to second-order in each rotational state.

As a visual aid for the determination and refinement of rotational band types defined by the different K_a and K_c selection rules, an additional dialog is provided for control over the magnitudes of each band type (*a*-, *b*- or *c*-type) by means of three vertical track bars. The simulated intensities of any given band type are rescaled and graphically updated upon adjustment of the track bar position. This procedure is particularly useful if the orientation of the transition dipole moment is unknown. The percentage contribution of each band type to the total band strength is also displayed for accurate determination of the orientation angles.

B. Displaying experimental data.

The folder, *IfnMW*, is the microwave spectrum of 1-fluoronaphthalene taken with at course resolution of 0.5 MHz/point. Start *jb95.exe* and open the working directory file, *IfnMW.wkf*. The experimental spectrum will be displayed starting at 12,000 MHz and ending at 20,000 MHz.

Select the ANALYSIS dialog from the MAIN MENU. The filename *IfnMW_Scan2+1* will appear in channel 1 with display status (DSP STAT) checked. There are three different levels of view: LOW, MED and RAW. The page values for LOW and MED are user adjustable and determine the number of screen pages of data that are viewable upon expanding and contracting (zoom-in and zoom-out) between the different levels of view. TYPE determines whether the data for that view is averaged (AVE) or the maximum value (MAX) is found across each interval. You must click in the TYPE box after scrolling to a new selection to make it active. The page value for the LOW resolution view is usually set at 1.0 so that all of the experimental data is displayed. Following an OK exit from the dialog, two files are created and written having *JBI* and *JBO* extensions. These files correspond to the MED and LOW resolution views, respectively. These files will be read and not created the next time the folder is accessed.

Changing page values (by clicking in the edit box) or clicking in the TYPE box will cause these files to be recreated upon OK exit from the ANALYSIS dialog. The program does not remember the TYPE of averaging done so if *jb95.exe* is restarted and the page values are changed, be sure to reset the desired TYPE parameters. The creation time and date of the *JBI* and *JBO* files are also checked against that of the raw data file. If the *JBI* and/or *JBO* files are older than the raw

data file, they are recreated (so make sure your system clock is set properly). Also when viewing multiple channels, the *JBI* and *JBO* file lengths will be checked against those of the active channel for length consistency. The simultaneous display of channels where large length differences exist is not supported and prevented. The Status Bar of the main window will indicate the actions taken following an OK exit from the ANALYSIS dialog. Expanding the horizontal axis beyond actual size of the file is not possible at this time. This limitation also exists for the LOW and MED resolution views.

For a scalar of 1.0 and offset of 0.0, the full vertical display will range from 0.0 to 10.0. Click the DIG STAT (for digital display) if a one-to-one correspondence is desired (full range from 0 to 1). If the exact scale or offset factor is not known, the RIGHT CLICK MENU from the main window display includes an autoscaling/offsetting option.

The ACTIVE CHANNEL parameter is important if more than one file is displayed. The frequency and intensity information displayed in the Status Bar of the MAIN WINDOW corresponds to that of the active channel. The ANALYSIS dialog also contains parameters to set the initial absolute frequency (INIT ABS FREQ), the free spectral range (FSR) if an etalon is used for relative frequency calibration and the points per FSR (PTS/FSR). The latter two parameters determine the digital resolution at the raw data view. Of course, these parameters are valid only if the experimental data is linearized in frequency (see ASCII INPUT section). If the absolute frequency is known for a particular feature in the experimental data, enter the value in the INIT ABS FREQ and from the main window display, position the cursor cross hair on the

known feature and depress the upper case “hot key” *C*. You will be prompted to recalibrate the INIT ABS FREQ. Be sure to set the correct FSR prior to performing this calibration procedure.

Additional features in the ANALYSIS DIALOG will permit you to set the background color and the pixel width of the experimental traces. The UNITS control should be set for correct display of units along the X axis of the display. Depressing the hot key *u* from the MAIN WINDOW display will toggle between commonly used units. The HARM (for harmonic) dialog option is useful for easily converting between harmonics using the hot key *U* from the display.

C. Calculating and using simulated spectra.

Select the SIMULATION dialog from the MAIN MENU. The ROTOR CALCULATION OPTIONS DIALOG will be displayed. Depress the READ FILE button in the INPUT FLNM section and click on the file, *lfnMW.in*. This is the input file to the rotor program, *iar95.exe*. See the document, *iar95UserGuide.wpd*, for a more detailed description of this file. Select YES when prompted with the question, COPY PARAMETERS TO CAL/FIT VALUES?. All parameter option fields will be filled in. Descriptions for each of the parameter fields are given in the following paragraphs.

CALC CUTOFF PARAMETERS section:

Enter the maximum J (J MAX) to calculate, the transition intensity cutoff (ITN CUT) and the rotational temperature (TEMP (K)). The rotational temperature specified in Kelvin is converted to frequency (energy) in units of MHz so convert the temperature to agree with the units used to specify the rotational constants.

LINEAR LEAST SQUARES section:

Enter the assignment filename (ASN FLNM), typically having a ASN extension. If this file exists, the number of assignments will appear under the ASN LINES heading. For predicting spectra, set the LSF CYCS to 0. Otherwise, the rotor program will attempt to do a least squares fit of the parameters to the assigned line set if greater than 0. The program will fail, of course, if there are no assigned lines. The rejection level (REJ LEVEL) parameter will be used to remove assigned lines from the fit when the difference in the assigned and calculated frequencies exceed this value. During initial fitting stages when large changes in the parameters are expected, this number should be fairly large. Also note that for least-squares fits, all assigned lines that satisfy the rejection level condition will be included in the fit regardless of band type and/or quantum number.

ROTATIONAL CONSTANT section:

Two sets of values are given for each rotational constant. The first column of parameters with the heading FILE I/O are always the values read from and written to the input file. The values of the asymmetry parameter, κ (KAPPA) and the inertial defect, I (DELTA I) are also calculated using these values. The second column under the heading CALC/FIT contains the initial set of parameters used by the rotor program for predicting or fitting spectra. The check boxes under the heading VAR STAT enable the variation of the parameter when performing linear least-squares fits using the rotor program. The ORIGIN parameter has special meaning when set to exactly zero. In this case, the upper state constants are ignored and derivatives for least squares fits are generated in order to fit pure rotational spectra for the lower state only. Both states are used in the calculation for origin values greater than or equal to 0.000001. (This meaning will change in a future release.)

Selecting the NON-RR PARA button brings up the NON-RIGID ROTOR PERTURBATION OPTIONS DIALOG. This dialog provides access to Coriolis coupling parameters, Watson's centrifugal distortion (A reduction in the I^R representation) and the Euler angles for inertial axis reorientation in each state. See the document, *iar95UserGuide.wpd*, for a complete description of the sign conventions used.

TM/DIPOLE section:

Under the CALC heading, set the percentages of the transition moment components squared (TM) or dipole moment intensity desired along each of the principle axes. The magnitude of the calculated components may be reduced in magnitude by using the TM/DIPOLE ADJUSTMENT DIALOG from the MAIN WINDOW display (*vide infra*).

IAR CALCULATION section:

The rotor program, *iar95.exe*, will be executed upon depressing the RUN button. For a detailed description of the rotor program, see the *iar95UserGuide.wpd*. The path to the executable, *iar95.exe*, is automatically set according to the following upon selecting SIMULATION option from the MAIN WINDOW. If the file, *jb95.dir*, exists in the parent directory of the working folder, the first line of this file is read to set the path. If this file does not exist, the path to the *jb95.exe* executable is used. When the rotor program is run, a generic input file *IAR.in* is written and the rotor program appears in a console mode (DOS) box. After the program finishes (DOS box disappears), depress the READ button to read the generic binary output file (*p*) for the rotational constants, standard uncertainties, number of calculated and assigned lines and the observed-minus-calculated standard deviation of the line set. Checking the SIMS box, brings up SIMULATION CONTROL DIALOG.

SIMULATION CONTROL DIALOG:

In order to view the simulated line set generated using *iar95.exe*, the generic set of files (containing the *IAR* prefix) must be moved into one of the nine simulation channels given in the SIMULATION CONTROL DIALOG. Access to this dialog is provided by using either the hot key *c* or the RIGHT CLICK menu option from the MAIN WINDOW display. Both options actually toggle on/off the display status of this dialog. Also notice that this dialog is *modeless* and therefore, may remain active while performing other functions from the MAIN WINDOW display or from other *modal* dialogs.

SIMULATIONS section:

Select one of the nine simulation channels using the horizontal scroll list control. Enter a filename (*1fnMW* in this example) in the FILE NAME field. Depress the RD IAR button to rename the generic files to this base filename with appropriate extensions added. If the files already exist, you will be prompted to overwrite them. The calculated spectrum should appear in the MAIN WINDOW display upon checking the DSP STAT box. To add together intensities from more than one simulation channel, first display the simulations and then check the SUM boxes for those channels. The waveform of the co-added simulations will appear in the lowest lettered simulation channel. The WRITE and CLEAR buttons apply to experimentally assigned frequencies and are explained below.

SCALING section:

Enter -1 in the associated channel (CHN) field. If set to a value between 0 and 8, the simulation will scale and offset with the experiment data in this channel. Use the SCALAR and OFFSET factors accordingly. Lorentzian and/or Gaussian line shapes will be convoluted with each calculated line upon entering non-zero value(s) for the full widths in the edit fields. The WIDTHS field corresponds to the number of full widths to extend the lineshape function.

DIALOGS section:

Access to the quantum numbers is provided by checking the JKK(M) QN box. To retrieve the quantum numbers for a simulated line shown on the display, move the mouse cursor and click near a line so that the horizontal cross hair extends over the line of interest. Depress the CALL button from the JKK QN DIALOG or use the hot key, *j*, from the MAIN WINDOW display. The band type, quantum numbers and simulated intensities and frequencies are displayed in a sequential list for all lines under the horizontal cross hair. If more than five lines are found, the list may be scrolled using the up/down scroll list controls or the hot key, *space bar*, from the MAIN WINDOW display. Select a line from the displayed list by clicking its associated radio button. Reposition the cursor cross at the desired experimental frequency and depress the ASSIGN button or use the hot key, *k*, from the MAIN WINDOW display. The experimental frequency field is filled in and a vertical line is displayed showing the location of this frequency.

The lower-case band-type letter above the simulated line changes to an upper-case letter indicating the simulated line has been assigned. To remove (zero) experimental assigned lines, select the line from the list as above and depress the CLEAR button or use the hot key, *K*, from the MAIN WINDOW display.

The experimental assigned frequencies exist in random access memory (RAM) memory only. To save the assignments to disk for use by the rotor program, depress the WRITE button in the SIMULATIONS section. Upon entering a filename and selecting SAVE from the SAVE AS dialog, all assigned lines for that simulation are written to an ASCII assignment file. This new file name will also appear in the LINEAR LEAST SQUARE section of ROTOR CALCULATION OPTIONS dialog. The file can be viewed or edited using WORDPAD but must always be terminated with // for the rotor program to read it properly. The assigned lines in this file are used by the rotor program to refine the parameters if LSF CYCS is greater than 0. However, regardless of the value of LSF CYCS, transitions in the assignment file will always appear in the new simulated line set when the rotor program is run and the generic files renamed. The original assignments from a simulated line set on disk will be restored in RAM memory upon using either the OPEN, RD IAR buttons or by modifying the simulation file name field. If new assignments have been made, first save them using the WRITE button or all new information stored in RAM memory will be lost. To start from 'scratch', first clear all experimental assignments using the CLEAR button.

Another feature that is useful when making assignments in congested spectra is quantum number filtering. The JKK FILTER check box activates this dialog. Scrolled lists are provided to select between the specific quantum numbers, $J' K_a' K_c'$ (for upper state) $J'' K_a'' K_c''$ (for lower state) and/or P , Q or R branch types. The filtered simulation line set is updated on the display when selection is made in either scrolled list or the numeric value is changed. Filtering is disabled when the dialog is unchecked.

The TM/DIPOLE TB (track bar) dialog is used to scale the hybrid band intensities for any or all of the different band types using three vertical track bars. The square of the dipole components are given in terms of a percentage along each of the principal axes. Notice that the track bars are operative only for TM/DIPOLE components that have been calculated and always scale relative to these values. These scale factors apply even after the dialog display status box is unchecked.

The ABC RIGID TB activates a horizontal track bar dialog used to make small step-wise changes in the rotational constants. The initial values are the exact values used to generate the simulated line set. These initial values are restored in the track bar dialogs each time the simulated line set is reread. The relative changes per unit track bar step is adjustable in the percent field. The new transition frequencies are calculated based on the derivative approximation and therefore, the modified spectrum is only approximate. The CALC button control is used to generate an exact line set based on the track bar values using the rotor program. These values are automatically copied into the CALC/FIT parameter fields of the ROTOR CALCULATION OPTIONS DIALOG. Other important parameters used in the calculation such as J MAX, TEMP and/or TM

DIPOLE components should be set prior to using this option. Separate track bars are provided for A, B and C in each state and the band origin. By checking the box, B+C/B-C, the B and C track bars are redefined in terms of B+C (+) and B-C (-), respectively. For two-state problems, the DELTA check box redefines the upper state constants in terms of differences relative to the ground state. Similar track bar dialogs are available for the Coriolis coupling parameters and Watson's D centrifugal distortion parameters (A reduction in I^R representation). The COPY S->I control will copy all modified or unmodified values into the CALC/FIT parameter fields of the

ROTOR CALCULATION OPTIONS DIALOG.

An additional dialog is provided to view residuals (difference between simulated and the active experimental traces). If the simulated sum option is activated, the residuals are displayed only for the lowest lettered simulation.

EXTRAS section:

The WRITE SIM control is used to create binary files (4-byte floating precision) from simulated line sets. If the simulated sum option is activated, the binary file will be created using all summed simulations. If viewed from an experimental channel (ANALYSIS OPTIONS DIALOG), the binary file will be an exact duplicate of the simulation if the scalar is 1.0 and offset is -(SIM OFFSET). The READ ASCII control is used to read simulated line sets in ASCII form generated using other programs and is explained in more detail in Section F below.

D. Generating simulated data when no experimental data exists.

From the ANALYSIS OPTIONS DIALOG, uncheck the DSP STAT for all experimental data channels. From the ROTOR CALCULATIONS OPTIONS DIALOG, run *iar95.exe* and read the output files into any simulation channel. Depress the WRITE SIM option in the SIMULATION CONTROL DIALOG to save the simulation as a binary file. Upon entering a filename, the program will prompt you with the question: NO EXPERIMENTAL DATA - CREATE FULL SIMULATION? If answered YES, a binary file will be created based on the full simulated line set and imported into experimental channel 0. Note that this procedure will change the calibration parameters, INIT ABS FREQ and FSR, in the ANALYSIS OPTIONS DIALOG to accommodate the full simulated spectrum. Save the working file after (and perhaps before) using this option. Also note that the size of this file will depend on the frequency range covered by the simulation and the digital resolution determined from the ratio $FSR/(PTS/FSR)$ (free spectral range and points/FSR) in the ANALYSIS OPTIONS DIALOG. To decrease the size of the binary file created, decrease the digital resolution by decreasing the PTS/FSR.

E. Importing experimental ASCII data.

The ASCII input section of the program is designed to read ASCII files having the general format: $x,y1,y2,y3$. The input fields in each row must be separated by at least one space, comma, *etc.* The x data should be sorted according to increasing or decreasing frequency and consecutive x,y pairs should be defined on roughly equally spaced frequency intervals. When this latter

condition is not satisfied, there is also a method to import stick spectra having discontinuous x,y pairs (see below). The x,y ASCII data is first linearized in frequency and the y data is converted to (4-byte float precision) binary format. The procedure makes use of a cubic spline interpolation routine to calculate the best representation of the intensities at even frequency intervals on the output file. It is also designed for patching together sections of spectra covering various spectral regions that are not necessarily contiguous. The undefined data regions are padded with zeros. The procedures for converting these types of files are described in more detail below.

1. Importing an ASCII x,y file.

To follow the example given, restart *jb95.exe* and open the working directory file, *1fnMW_Scan1.wkf*. From the MAIN WINDOW, select the FILE MENU/ASCII INPUT option. The ASCII DATA INPUT CONVERSION DIALOG will appear. Use the OPEN button to locate the ASCII file, *1fnMW_Scan1.asc*. After opening this file, the fields in the INPUT section of this dialog will be filled in. If the file contains a header line or tailer line (none in this example), select valid regions of the file using either the vertical scroll bars or enter the line numbers directly. The number of accepted lines, 14470 in this example, will be indicated. Also note the input resolution (INPUT RES) field represents the average frequency spacing over all ASCII data points. If frequency gaps exist in the ASCII file that are larger than the MAX FREQ STEP (10 MHz in this example), these regions will be zeroed. The GAPS ZEROED field indicates the number of such regions found. Likewise, the ASCII data is checked against the MIN FREQ STEP (0.025 MHz in this example) to prevent the cubic spline routine from becoming unstable.

In the OUTPUT section of the dialog, click the radio button to the right of Y1 under FILE COLUMN 2. This will associate the intensity data in the second column of the ASCII file with the binary file given in the edit field under the heading BINARY FLNM. Enter a binary filename, *lfnMW_Scan1*. If the file exists (has non-zero length), the OUTPUT BINARY FREQ RANGE will be set to include both the ranges covered by the ASCII data and the existing binary data. The output resolution (OUTPUT RES) will be automatically set to that of the existing binary data. In this example, the input and output ranges and resolutions will be identical. If the binary file does not exist, the INPUT ASCII FREQ RANGE and the OUTPUT BINARY FREQ RANGE should have the same values. In this case, be sure to enter the desired output resolution. In most cases, simply copy (*cntl c*) the INPUT RESOLUTION and paste it (*cntl v*) in the OUTPUT RES edit box. You may also edit the output (final) frequency range to cover a region that is greater than the input range. Entering zero in either field will reset it to the ASCII frequency value. To convert the ASCII file over a smaller output frequency range, change the input frequency range using the scroll bars as described above.

Depress the CONVERT button. If the binary file already exists, you will be prompted with a question to add to it or alternatively, to overwrite it. If you want to overwrite a subset of the existing binary file with the new ASCII intensity data, answer YES to ADD TO OUTPUT FILE question (see below). If you want to create a new binary file containing only the ASCII data, answer NO. If you want to abort, select CANCEL. The progress of the conversion is shown in the MAIN WINDOW STATUS BAR. The message ASCII FILE CONVERTED is displayed and the binary file length is updated when the conversion is complete. In this example, since the

binary file existed prior to conversion, the file length of 14,470 lines will not change. Select OK to exit the dialog. The new data should be displayed in the MAIN WINDOW. The binary data will be automatically scaled and offset to fill the full vertical dimension. Following linearization, the frequency calibration information (the initial absolute frequency and FSR parameters) given in the ANALYSIS OPTIONS DIALOG are modified. Use the floppy-disk tool-bar option to save this calibration information to a working file having a *WKF* extension after each conversion.

As a final note, if the binary file exists and you wish to overwrite it, modify the output frequency range and resolution after selecting and editing the binary file name field. Otherwise, the range and resolution fields will be automatically set after clicking in the binary filename field.

2. Patching an ASCII x,y file into an existing binary file.

Continuing with the example given above, from the MAIN WINDOW, select the FILE MENU/ASCII INPUT option again. Use the OPEN button to locate the ASCII file, *1fnMW_Scan2.asc*. After opening, 1,532 lines should be accepted. If the radio button for Y1 column 2 is still selected, the output frequency range will automatically be updated to include the frequency range of the new ASCII data. Typically, these preset values should be used when patching files together. Depress CONVERT and answer YES to the ADD TO OUTPUT FILE question. Select OK to exit the dialog to view the new data. In this example, the binary file *1fnMW_Scan1* will now have 16,000 lines and cover a range from 12,000 to 20,000 MHz. Always save the new calibration information to a working file after ASCII file conversions.

3. Importing ASCII over a marked region within an existing binary file.

It is sometimes convenient to visually mark from within the MAIN WINDOW the upper and lower file positions over which to substitute the ASCII data. Of course, part or all of the input frequency range must lie within this marked interval or nothing will change. To mark a region within the main window, position the cursor and click the tool-bar button M-> to mark the lower position and <-M to mark the upper position. In the ASCII DATA INPUT CONVERSION DIALOG, check the box marked DATA SUBSTITUTION STATUS. Convert the ASCII file as before. Data outside of the marked region will remain unaltered.

4. Importing ASCII stick spectra.

The cubic spline routine for interpolating intensities will fail horribly when large discontinuities exist along the x frequency axis. This might be the case when, for instance, the ASCII file is a stick spectrum containing discrete x,y pairs only for points having non-zero intensities. In this case, check the STICK SPECTRUM STATUS box before converting. The cubic spline routine will be bypassed and the program will simply add the intensities into a zeroed array. Be sure to set the output resolution to a reasonable value.

F. Importing simulated line sets generated using other programs.

It is possible to import simulated stick spectra generated from other programs to access quantum numbers, make assignments and compare convoluted spectra with experiment data. In the SIMULATIONS CONTROL DIALOG, select a simulation channel and enter a new FILE NAME. Depress the READ ASCII button to locate and open the ASCII line set file. You are then prompted with a series of questions beginning with:

FORMAT WITH FREQUENCY + INTENSITY ONLY?
FORMAT WITH 8 QUANTUM NUMBERS?
FORMAT WITH 6 QUANTUM NUMBERS?
FORMAT FOR ASYROT?

Answering NO brings up the next question. Answering YES will convert the ASCII file according to the format selected and generate a new binary simulation. The ASCII file must conform to one of the following formats with each field separated by a least one space, comma, etc.

FORMAT WITH FREQUENCY + INTENSITY ONLY:

<i>calc. freq.</i>	<i>calc. intensity.</i>
10618.01	0.1022

FORMAT WITH 8 QUANTUM NUMBERS:

<i>band type</i>	J'	K_a'	K_c'	M'	J''	K_a''	K_c''	M''	<i>calc. intensity</i>	<i>expt. freq.</i>	<i>calc. freq.</i>
B	14	9	6	6.5	13	8	5	5.5	0.020	0.0000	42858.892

FORMAT WITH 6 QUANTUM NUMBERS:

<i>band type</i>	J'	K_a'	K_c'	J''	K_a''	K_c''	<i>calc. intensity</i>	<i>expt. freq.</i>	<i>calc. freq.</i>
B	14	9	6	13	8	5	0.020	0.0000	42858.892

FORMAT FOR ASYROT: for backward compatibility only.

G. Calibration, normalization and linearization procedures.

Most spectroscopic data will need to be normalized and calibrated (linearized) prior to any detailed analysis. The calibration is usually based on a relative frequency reference and performed by simultaneously recording the marker fringes from, for instance, a Fabry-Perot cavity. A procedure is described to generate a normalized and linearized data file under these conditions. In this procedure, it is assumed that the signal file is named *PmtF*, that of the reference cavity marker file is *MarkersF*, and that of the laser power is *PwdF*.

1. Calibration

- Select the MANIPULATION/CALNORMLINEAR dialog.
- Run the peak-finding (PEAK FIND) procedure on the *MarkersF* file.
- Display the *MarkersF* channel and depress the *t* key from the MAIN WINDOW to display the file positions found. The file positions are only shown in the MED and RAW data views.
- Correct problems using *P* to erase or add marker positions.

2. Normalization

- Toggle the display status off for the *MarkersF* channel and the display status on for the *PwdF* channel. Make sure *PwdF* is the active channel.

- Shrink the view and position the cursor cross hair over a region representative of the average power across the scan.
- Depress the *h* key to determine average voltage value. This factor is used as the normalizing factor.
- Reposition the cursor in a region where laser was blocked to determine the voltage for power zero. Depress the *l* key to determine the average voltage value for zero power. Note that depressing the *W* key will zero both the *h* and *l* values. Display the *PmtF* channel to make sure it is zero when the laser is blocked. If not, use the OFFSET option in the MANIPULATION/ CONVERSION dialog to manually offset this file.
- Select the MANIPULATION/CALNORMLINEAR dialog. If the *h* and *l* values are not displayed in the REFER (*h*) and OFFSET (*l*) fields, enter 0 in either field and they should be updated.
- Edit the filenames fields in the NORMALIZATION section to read

IN FLNM	<i>PmtF</i>
OUT FLNM	<i>PmtFn</i>
NORM FLNM	<i>PwdF</i>
- Normalization of the *PmtF* file will be done using the following formula:

$$PmtFn[n] = PmtFn * V_h / [PwdF[n] - V_l].$$
 Depress the NORM button.
- Note that the %CUT is defined on the power channel as a percentage of the voltage range between the *h* and *l* values. Regions of the spectrum where powers fall below this value will not be normalized and are set to zero.
- Also, in some cases, you may want to smooth the power channel file prior to normalization. Use the FFT SMOOTH option in the MANIPULATION/ CONVERSION dialog prior to normalization.

3. Linearization

- Edit the filenames fields in the LINEARIZATION section to read,

IN FLNM	<i>PmtFn</i>
OUT FLNM	<i>PmtFnI</i>
- Check that the value for PTS/FSR is the same as that for AVE PTS/FSR shown in the CALIBRATION section.

- Check that the FINAL MARKER number is the same as the # MKS in the CALIBRATION section.
- Check the FSR value.
- Depress LINEARIZE.
- Select the ANALYSIS OPTIONS dialog and enter *PmtFnl* in a channel filename. Check the DSP STAT box and set the page values and TYPE fields for each view.

Appendix A. MAIN WINDOW hot key options (short cuts) from the keyboard

Experimental data

- 0-8* Toggles ON/OFF display status of channel. Last channel displayed is active channel.
- o* Condenses (zoom-out) view for lower resolution display of data (toolbar button).
- x* Expands (zoom-in) view for higher resolution display of data (toolbar button).
- F* Toggles data smoothing on/off using an FFT/IFFT algorithm. The smoothing factor is set in the MANIPULATION/CONVERSION dialog FFT WINDOW field.
- C* Set absolute frequency given in the ANALYSIS OPTIONS DIALOG to file location defined by the cursor cross hair. This procedure will recalculate the initial frequency.
- s* Toggles the scaling factor for moving the cursor cross hairs using arrow keys and for scaling and offsetting experimental data from the MAIN WINDOW. The scaling factor changes from 100 to 10 to 1 to 0.1 and then repeats the sequence.
- w* Toggles the status for setting the cursor cross hair window width using up/down arrows keys. The window width determines the quantum number search range and the frequency range to average the y values on the active channel when the l and h hot keys are depressed.
- W* Resets cursor cross hair window width to the default value.
- r* Toggles on/off the relative frequency scale.
- t* Toggles on/off the display of file positions listed in the ASCII marker file, *mks*.

<i>P</i>	Adds a new file position to a <i>mks</i> file on disk. When the position already exists in this file, it is deleted. The ASCII filename written to is given in the MANIPULATION/CALNORMLINEAR dialog under the MK POS FLNM heading.
<i>l</i>	Calculates the average y value over cursor cross hair width for the active channel.
<i>h</i>	Calculates the average y value over cursor cross hair width for the active channel.
<i>m</i>	Marks the lower file position (toolbar button).
<i>M</i>	Marks the upper file position (toolbar button).
<i><shift> left mouse button</i>	Shifts data on page to the left (toolbar button).
<i><shift> right mouse button</i>	Shifts data on page to the right (toolbar button).
<i><cntl> left mouse button</i>	Shifts data down by scale factor on active channel.
<i><cntl> right mouse button</i>	Shifts data up by scale factor on active channel.
<i>right mouse button down/left mouse button</i>	Scales data smaller by factor of two (toolbar button).
<i>left mouse button down/right mouse button</i>	Scales data up by factor of two (toolbar button).

Simulated data.

<i>c</i>	Toggles the display status of the SIMULATION CONTROL DIALOG (right click menu option).
<i>[</i>	Toggles the display status of the A SIMULATION (toolbar option).
<i>]</i>	Toggles the display status of the B SIMULATION (toolbar option).
<i>j</i>	Displays JKK QN DIALOG (toolbar option) and updates the simulated line list in the dialog.

- k* Assigns the experimental frequency of the cursor cross hair location to the selected simulated line.
- space* Scrolls the simulated line selection in the JKK QN DIALOG.
- J* Removes JKK QN DIALOG (toolbar button).
- K* Clears (zeros) the experimental assignment of the selected simulated line.
- R* Toggles frequency tracking of the A SIMULATION with the cursor cross hair location.
- z* Zeros the frequency offset factor of the A SIMULATION.
- Z* Calculates the truncation factors for frequency offsetting both the A and B SIMULATIONS. These factors appear in the NON-RIGID ROTOR PERTURBATION OPTIONS DIALOG.
- +* Toggles the lineshape summing status of the A and B SIMULATIONS (toolbar button).
- l* Toggles on/off the band-type labeling status of unassigned lines in the A and B SIMULATIONS.
- L* Toggles on/off the band-type labeling status of the A and B SIMULATIONS.