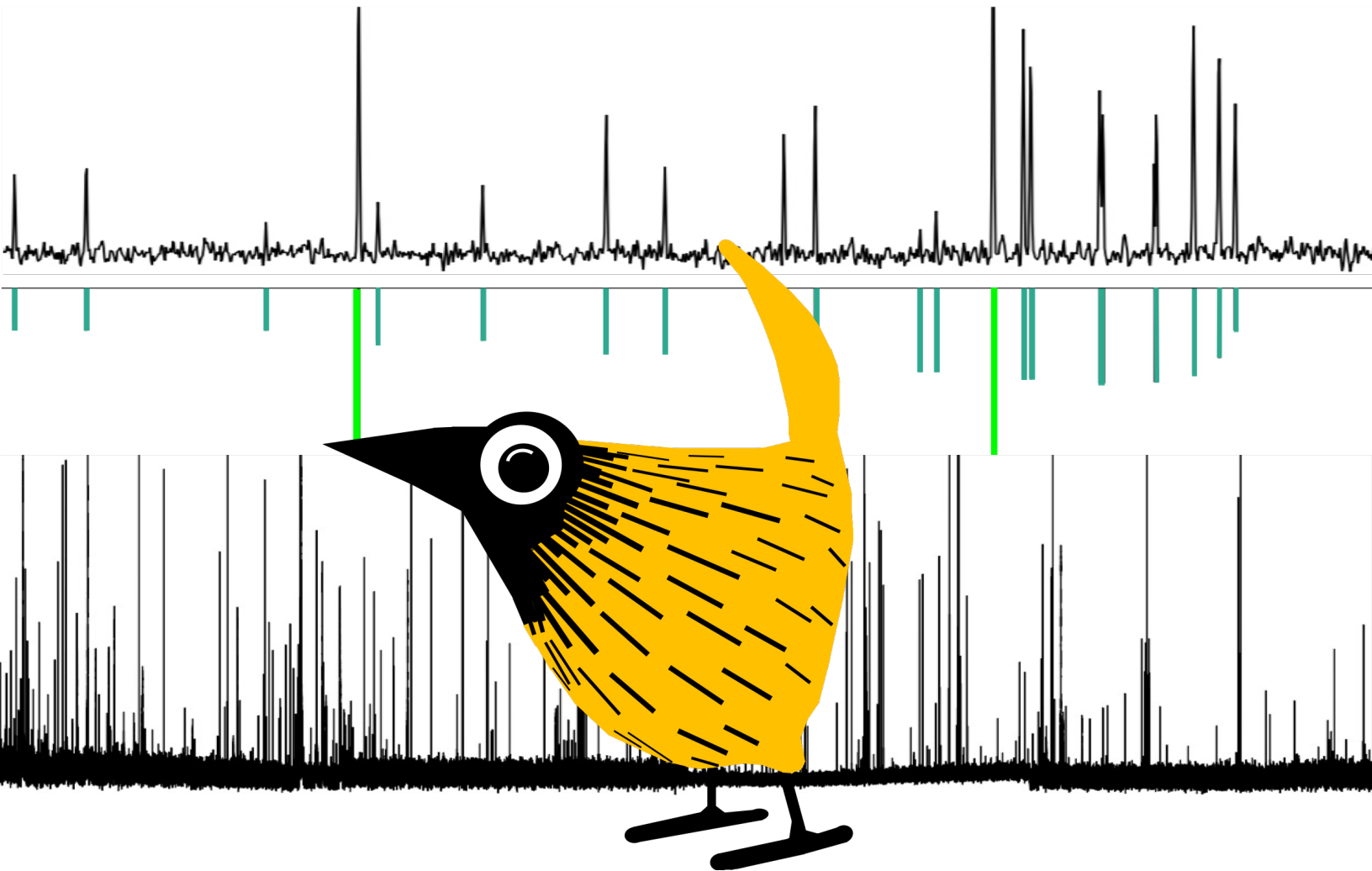


# DAPPERS DOCUMENTATION

2019 Version 1.0

Program Designer: Nathan Love



University of Minnesota  
Ken Leopold Lab

# TABLE OF CONTENTS

<b>PROGRAM OVERVIEW .....</b>	<b>4</b>
A SUMMARY OF DAPPERS.....	4
LIMITATIONS .....	4
<b>GENERAL OPERATING INSTRUCTIONS .....</b>	<b>5</b>
OVERVIEW .....	5
INSTRUCTIONS .....	5
<b>GRAPHICAL PEAK FINDER.....</b>	<b>7</b>
OVERVIEW .....	7
SPECTRAL DATA FORMATTING REQUIREMENTS .....	8
KEYBOARD CONTROLS .....	8
METHODS.....	9
<i>Global Intensity Threshold</i> .....	9
<i>Local Average Intensity Threshold</i> .....	9
FIND PEAKS.....	10
SAVE, VIEW, USE LIST, AND INVERTED PEAKS .....	10
SET DEFAULT .....	10
DISPLAY SETTINGS .....	11
<b>UPLOADING A PEAK LIST.....</b>	<b>12</b>
OVERVIEW: .....	12
WHAT MAKES A GOOD PEAK LIST? .....	12
PEAK LIST FORMATTING REQUIREMENTS.....	12
<b>CAT FILE GENERATOR.....</b>	<b>13</b>
OVERVIEW .....	13
VAR FILE SETUP .....	13
VAR FILE MORE SETTINGS.....	14
INT FILE SETUP.....	14
INT FILE MORE SETTINGS .....	15
GENERATING CAT FILES: .....	15
<b>QUANTUM FILTERS.....</b>	<b>16</b>
OVERVIEW .....	16
WHY QUANTUM FILTERS ARE IMPORTANT IN DAPPERS FITTING .....	16
HOW TO SELECT QUANTUM FILTERS.....	17
RECOMMENDED QUANTUM FILTERS .....	18
<i>a-type Quantum Filter Guide</i> .....	18
<i>b-type Quantum Filter Guide</i> .....	19
<i>c-type Quantum Filter Guide</i> .....	20
USING MULTIPLE QUANTUM FILTERS .....	21
FREQUENCY LIMITS, VIEW, AND J SPAN .....	21

<b>SEARCH FOR FITS .....</b>	<b>22</b>
OVERVIEW .....	22
SEARCH WINDOW RECOMMENDATIONS .....	22
UNDERSTANDING THE ALGORITHM .....	23
INTERPRETING THE ALGORITHM RESULTS .....	24
ADVANCED SETTINGS .....	25
WHAT AFFECTS THE ALGORITHM'S ACCURACY?.....	25
<b>PAR FILE SETUP.....</b>	<b>26</b>
OVERVIEW .....	26
INPUTTING ROTATIONAL CONSTANTS .....	26
INPUTTING DISTORTION CONSTANTS .....	27
MORE SETTINGS .....	27
VIEW .....	27
<b>RUN FITS.....</b>	<b>28</b>
OVERVIEW .....	28
RUNNING FITS WITH SPFIT .....	28
INTERPRETING THE RUN FITS DISPLAY.....	29
<b>FIT BANK.....</b>	<b>30</b>
OVERVIEW .....	30
INTERPRETING THE FIT BANK DISPLAY.....	30
COMPILING FITS FROM THE FIT BANK .....	31
RUNNING COMPILED FITS .....	31
SAVING COMPILED FITS .....	32
<b>FIT POLISH .....</b>	<b>33</b>
OVERVIEW .....	33
UPLOADING CAT FILES AND PEAK LISTS.....	33
APPLYING FILTERS AND SEARCHING FOR MATCHES.....	34
RUNNING AND SAVING POLISHED FITS.....	34
<b>SPECTRAL SCRUBBER .....</b>	<b>35</b>
OVERVIEW .....	35
UPLOADING SPECTRAL FILES .....	35
LOCAL AVERAGES .....	36
SCRUBBING .....	36
SCRUBBING MODES .....	36
SPECTRAL NAVIGATION .....	37
SAVING SCRUBBED FILES.....	37
FITTING WITH SCRUBBED SPECTRA.....	37
<b>ADDITIONAL OPTIONS .....</b>	<b>38</b>
SET DEFAULT .....	38
FULL RESET .....	38

SET PATH.....	38
QUIT.....	38
SPECTRAL SCRUBBER.....	38
<b>REFERENCES.....</b>	<b>39</b>
<b>APPENDIX.....</b>	<b>40</b>
QUANTUM FILTER TABLES.....	40
ALGORITHM EXAMPLE.....	47
ALGORITHM ACCURACY PLOTS FOR J1J TRANSITIONS.....	53

# **PROGRAM OVERVIEW**

## **A SUMMARY OF DAPPERS**

DAPPERS stands for Data Analysis Package for Productive and Enthusiastic Rotational Spectroscopists. DAPPERS is designed to be an all-in-one tool for rotational spectroscopy that simplifies and expedites the processing and fitting of microwave spectra. The program features a graphical peak finder, a sophisticated fit searching algorithm based on spectral progressions, and the ability to quickly and easily run Pickett's SPCAT and SPFIT programs.<sup>1</sup> Additionally, DAPPERS is organized in a user-friendly format with informative help menus designed to instruct the user how to properly operate every component of the program.

While the fit searching algorithm and certain processing components in DAPPERS are unique, some of its features are not new to the field. The process of automatically assigning rotational spectra through programmatically wrapping Pickett's SPFIT has previously been explored with the Autofit program from the Pate group.<sup>2</sup> The idea of organizing spectra into progressions of transitions has been eloquently described by Cooke<sup>3</sup>. The spectral displays that are featured in DAPPERS are modelled directly after Kisiel's SVIEW\_L program.<sup>4</sup>

## **LIMITATIONS**

DAPPERS' fitting algorithm is best suited for relatively dense microwave spectra that feature transitions from at least four consecutive J-levels in most cases. The current version of the program is not designed to fit hyperfine structure but has been shown to work very well in fitting spectra that have unresolved hyperfine structure. Additionally, the current version of DAPPERS does not support fitting spectra with spectral effects from internal rotation or large amplitude motion. Lastly, DAPPERS acts as a wrapper for both Pickett's SPCAT and SPFIT and, thus, is subject to these programs' limitations.

# GENERAL OPERATING INSTRUCTIONS

## OVERVIEW

While DAPPERS features many tools that can be helpful in dealing with rotational spectra, the primary focus of the program is fitting dense asymmetric-top rotational spectra. Accordingly, the following instructions are designed to guide the user through fitting an asymmetric rotational spectrum starting with predicted rotational constants and an experimental spectrum. For the sake of keeping the general operating instructions brief, some of DAPPERS' more complex features will be skimmed over here. When this occurs, the user should navigate to that component's section of the documentation for further instruction and help.



## INSTRUCTIONS

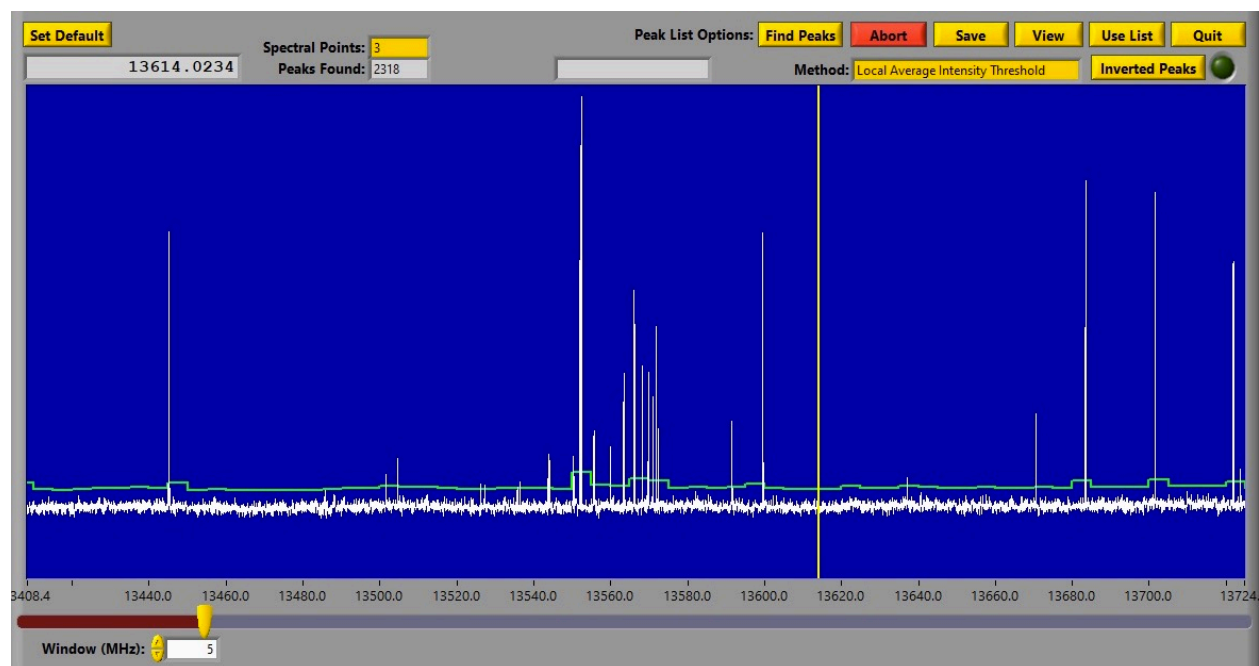
- 1) Input a peak list by either:
  - a. using the Graphical Peak Finder to directly measure a peak frequency list from an experimental spectrum that follows DAPPERS' formatting requirements
  - b. uploading a peak frequency list that follows DAPPERS' formatting requirements
- 2) Input a .cat file by either:
  - a. using the Cat File Generator to generate a .cat file based on predicted dipole moments and rotational/distortion constants
  - b. uploading an existing prediction .cat file

- 3) Select an appropriate Quantum Filter to apply to the .cat file
- 4) Adjust the Frequency Limits to the desired frequency values
- 5) Press “View” to view the Quantum Filtered and Frequency Limited list of predicted frequencies that have been chosen for DAPPERS fitting algorithm
- 6) Set the starter, ratio test, and derivative ratio test windows to desired values
- 7) Press “Find Fits” to run the fit searching algorithm
- 8) Press “View Results” to view the results of the algorithm and refine (optional)
- 9) Press “Run Fits” to run the set of assignments that have been found by DAPPERS algorithm with SPFIT and move good fits to the Fit Bank
- 10) Select a new Quantum Filter and return to step 4
- 11) Press “Fit Bank” to compile different Quantum Filtered fits together, run them with SPFIT, and save the results
- 12) Press “Fit Polish” to automatically add experimental frequencies that are within a user-specified window to improve an existing fit and save the results

# GRAPHICAL PEAK FINDER

## OVERVIEW

The Graphical Peak Finder allows the user to quickly and easily measure thousands of peak frequencies in a matter of seconds. The user interface features an interactive spectral display that allows the user to see exactly which peaks will be measured as peak finding thresholds are adjusted. The spectral display was modelled after the program SVIEW\_L from Kisiel's AABS package for the ease of those who already use that program.<sup>4</sup> Once a peak list is generated, the program allows the user to save, view, and use the peak list for fitting with DAPPERS. If the user does not want to use the Graphical Peak Finder to generate a peak list for DAPPERS, they are able to upload their own peak list by pressing the "Load Peak List" button on the main window of DAPPERS. This section of the documentation is designed to outline how to use the Graphical Peak Finder and the peak finding methods in order to quickly determine the frequencies of peaks present in the user-inputted spectrum.





## SPECTRAL DATA FORMATTING REQUIREMENTS

Spectral data must be formatted into two tab-delimited columns: frequency and intensity. The numerical values can be in either a standard number or scientific notation format. All headers and comments present in the document must be removed in order for the program to read the inputted spectrum correctly. If, when uploading a spectrum, the user encounters an error or the spectrum does not display, the spectral data file must be reformatted. It is recommended to use a program such as Microsoft Excel to easily reformat data by importing the data, removing comments or headers, and saving the data as a tab delimited .txt document.

## KEYBOARD CONTROLS

The spectral display was modelled according to Kisiel's SVIEW\_L spectral viewing program.<sup>4</sup> The spectral navigation commands that are featured in the Graphical Peak Finder are outlined in the table below and are the same as those in SVIEW\_L. These commands are also used in the Spectral Scrubber, which is described in detail in the Spectral Scrubber section of the documentation.

Key	Command
A	Shift Left
S	Shift Right
Q	Zoom Left
E	Zoom Right
W	Zoom In
Z	Zoom Out
2	Shift Down
3	Shift Up
K	Cursor Left
L	Cursor Right
Shift	Accelerator

## **METHODS**

Two peak finding methods are featured in this program and are described below. While peak measurement is the same for both methods, this section focuses on how the program determines what is a peak and what is not. See the next section (“Find Peaks”) for details on how peaks are measured.

### **GLOBAL INTENSITY THRESHOLD**

The Global Intensity Threshold method allows the user to find the center frequency of any peak that has at least one data point with an intensity greater than that of the user-selected threshold. When this method is selected, a draggable horizontal cursor will appear as a green dashed line on the spectral display. When the “Find Peaks” button is pressed, the center frequency of all peaks with at least one data point above this global threshold will be measured. If the inverted peaks option is selected, all peaks below the threshold will be measured.

### **LOCAL AVERAGE INTENSITY THRESHOLD**

This option is particularly useful for spectra with a drifting or fluctuating baseline. The Local Average Intensity Threshold method allows the user to find the center frequency of any peak that has at least one data point with an intensity greater than that of a user-controlled local threshold. (Local Average refers to the locally averaged baseline level). When this method is selected, a window control and a slider will appear below the spectral display, and a piecewise green threshold will appear on the display. The window control allows the user to adjust the width of the local averages in MHz with a minimum value of 1 MHz. Adjusting the slider will raise and lower the local average threshold. The multiplier option adjusts the maximum intensity of the slider. When the “Find Peaks” button is pressed, all peaks with at least one data point above this threshold will be measured. If the inverted peaks option is selected, the local average threshold will be mirrored below the spectrum and all peaks below the threshold will be measured. Note that using smaller windows will potentially slow down the speed at which the display works for larger data sets, but not the speed at which peaks are measured.

## **FIND PEAKS**

Pressing the “Find Peaks” button allows the user to quickly measure peaks with at least one data point above (or below if inverted peaks is selected) the current threshold. Peaks are measured using the linear least square fit of a second order polynomial of N data points in the vicinity of the extremum, where N is an odd number selected by the user by using the “Spectral Points” numeric control. The center of the resulting parabola is calculated and used as the center frequency. Note that if a far too low threshold is selected, or the user has accidentally selected (or forgot to select) the inverted peaks option, the program will take several minutes to calculate the peak list. The user can press the “ABORT” button to resume normal program function.

## **SAVE, VIEW, USE LIST, AND INVERTED PEAKS**

Pressing the “Save” button allows the user to save their generated peak list as a .txt file in a user-specified location. The filename cannot contain the character “.” and no file extensions are allowed. The program will overwrite any files with the same name in the same location. This peak list will automatically follow correct DAPPERS peak list formatting requirements. Pressing the “View” button allows the user to quickly look at the frequencies that were measured by pulling up a window with the list.

Pressing the “Use List” button exits the Graphical Peak Finder and sends the measured peak list to the main DAPPERS window. If the user has not saved their peak list, it will not be saved anywhere once the Graphical Peak Finder has been closed. Once DAPPERS has been closed, the program will forget the peak list.

The “Inverted Peaks” option allows the user to toggle between measuring peaks with center frequencies at maximum and minimum intensities. If the green LED is on, pressing find peaks will measure peaks below the current intensity threshold; if the green LED is off, pressing find peaks will measure peaks above the intensity threshold.

## **SET DEFAULT**

Pressing the “Set Default” button will save the current settings as default. Defaultable settings in the Graphical Peak Finder include the peak finding method, non-inverted or inverted peaks, number of spectral points for peak fitting, and the Local Average Intensity Threshold’s window size.

## **DISPLAY SETTINGS**

The user can press the display button to access a settings window that allows the user to enable/disable decimation. If enabled, the user can select the number of data points per pixel (PPP). A smaller PPP will result in a faster dynamic display response, but the displayed data may not appear accurate when zoomed out (this is not an issue when zooming in on spectra). Appropriate values of PPP depend on spectral file size. Additionally, the user can save these settings as default values.

## UPLOADING A PEAK LIST

### OVERVIEW:

The user is able to upload their own peak list to use in DAPPERS by pressing the “Load Peak List” button on the main DAPPERS window. Once pressed, a standard file input menu will pop up so that the user can navigate to the peak list file location.



### WHAT MAKES A GOOD PEAK LIST?

DAPPERS is fully capable of fitting very dense spectra with thousands of peaks. However, the fitting algorithm will work much more efficiently with shorter and more refined peak lists. For example, the user can fit the most prominent species of a spectrum, remove the peaks that correspond to the most prominent species from the peak list, and then run the fitting algorithm again with the newly refined peak list to find fits for any remaining chemical species in the spectrum. This is particularly useful for identifying isotopologues in natural abundance after the parent has been assigned. Alternatively, the user can use relatively high (or low if inverted) intensity thresholds to consider only the most intense peaks in fitting the most prominent species in a spectrum before lowering the threshold and further refining the peak list.

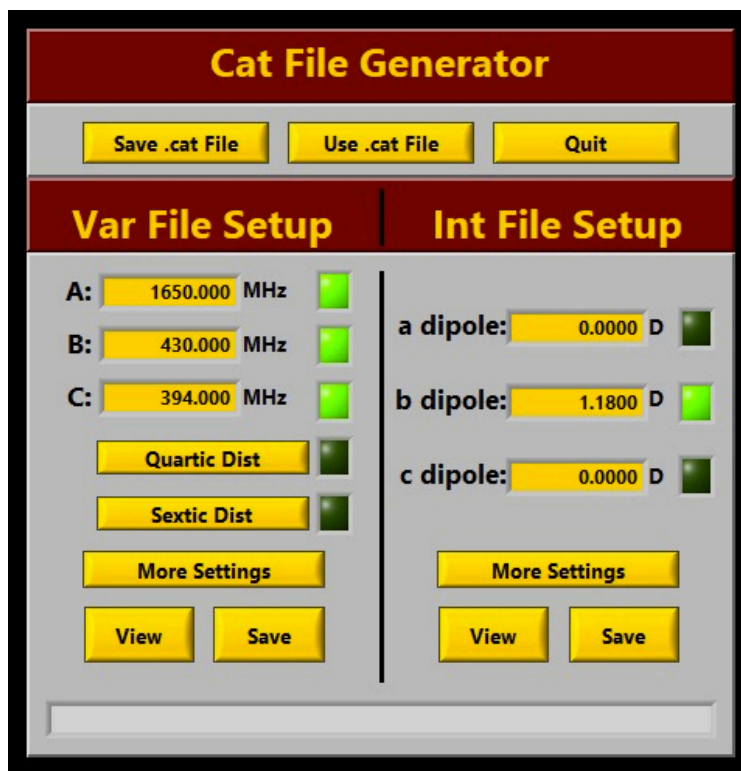
### PEAK LIST FORMATTING REQUIREMENTS

- No headers allowed
- The file must be a .txt file type
- Frequencies only, no intensities needed
- Frequencies are in a column format (leftmost)
- Frequencies may be represented in numeric or scientific (XXX.XXXE+00X) format
- Comments can be entered in rows that already have a frequency
  - No comment character is necessary other than at least one space
- A frequency equal to exactly zero is not allowed

# CAT FILE GENERATOR

## OVERVIEW

The purpose of the Cat File Generator is to allow the user to easily generate files to run with Pickett's SPCAT program (.var, .int, and .cat). This window allows the user to generate these files types for use inside or outside of DAPPERS by inputting predicted or experimental constants, including up to sextic distortion constants. If the user does not want to use this program to generate .cat files, they are able to upload their own .cat file by pressing the "Load Cat File" button on the main DAPPERS window. This section of the documentation is designed to outline how to format and generate .cat files quickly and easily with the Cat File Generator interface.



## VAR FILE SETUP

The Var File Setup section allows the user to input rotational constants A, B, and C in MHz into the gold entry boxes on the main Cat File Generator window. These values are defaulted to 1.000 MHz when the program is opened. When the user enters rotational constant values greater than 1.000 MHz, the green square LED directly to the right of each gold entry box will turn on. The user will not be able to generate .cat files unless  $A > B > C > 1.000$  MHz.

Pressing either the quartic or sextic distortion buttons pulls up small windows that allow the user to input distortion constants in kHz and Hz respectively. The labels next to each gold entry box in these distortion windows correspond to whether the user has selected the Watson-A or the Watson-S option as described in the Var File More Settings section of the documentation.

-DeltaJ	4.235000	kHz
-DeltaJK	0.000000	kHz
-DeltaK	-2.002300	kHz
-deltaJ	0.023500	kHz
-deltaK	0.000000	kHz

Enter

Lastly, the user can view the automatically formatted .var file by pressing the “View” button. A window will open showing the .var file as it would be displayed in a text editor. It is formatted based on the user-inputted constants and the current .var file settings that are further described in the Var File More Settings section of the documentation. The user can also press the “Save” button to save only the .var file to a location of their choosing.

## VAR FILE MORE SETTINGS

The user can access the Var File Settings window by pressing the “More Settings” button under the Var File Setup section of the main Cat File Generator window. Doing so will open up a window with gold entry boxes representing all of the .var file settings that the user can change in DAPPERS. The default values are those used by the Leopold lab. Additionally, the user can save the currently entered settings as default by pressing the “Save as Default Settings” button at the bottom of the window. Saving these settings to default is highly recommended if the user has an experimental setup different than the Leopold lab setup. If the user is unfamiliar with these parameters, it is recommended that they refer to the [SPFIT and SPCAT Documentation](#).

Okay

Title:	
CHR:	Watson-A
SPIND:	1
NVIB:	1
KNMIN:	0
KNMAX:	40
IXX:	0
IAX:	1
WTP:	1
WTMN:	1
VSYM:	0
EWT:	0

Save as Default Settings

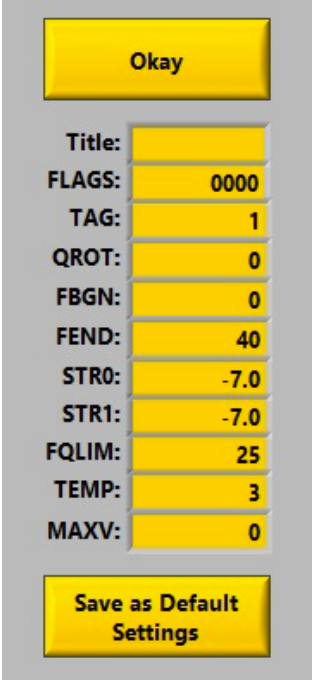
## INT FILE SETUP

The Int File Setup section allows the user to easily input a, b, and c, dipole moments. These dipole moments are defaulted to 0.0000 D. When the user inputs a nonzero dipole value, the green square LED next to the corresponding dipole moment entry box will turn on. At least one dipole moment must be nonzero to generate a .cat file. Additionally, the user can view the automatically formatted .int file by pressing the “View” button in the Int File Setup section. A window will open showing the .int file as it would be displayed in a text editor. It is formatted based on the user-inputted constants and the current .int file settings that are further described in the Int File More Settings

section of the documentation. The user can also press the “Save” button to save only the .int file to a location of their choosing.

## INT FILE MORE SETTINGS

The user can access the Int File Settings window by pressing the “More Settings” button under the Int File Setup section of the main Cat File Generator window. Doing so will open up a window with gold entry boxes representing all of the .int file settings that the user can change in DAPPERS. The default values are those used by the Leopold lab. Additionally, the user can save the currently entered settings as default by pressing the “Save as Default Settings” button at the bottom of the window. Saving these settings to default is highly recommended if the user has an experimental setup different than the Leopold lab setup. If the user is unfamiliar with these parameters, it is recommended that they refer to the [SPFIT and SPCAT Documentation](#).



Okay	
Title:	
FLAGS:	0000
TAG:	1
QROT:	0
FBGN:	0
FEND:	40
STR0:	-7.0
STR1:	-7.0
FQLIM:	25
TEMP:	3
MAXV:	0
Save as Default Settings	

## GENERATING CAT FILES:

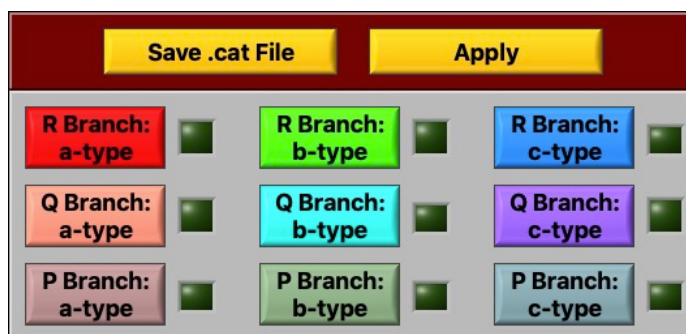
Once the constants, dipole moments, and settings have been entered for both the Var and Int File Setup sections, the user has two options to generate .cat files. By pressing “Save Cat File”, the user is able to generate and save a .cat file to a save location of the user’s choice. By pressing “Use Cat File”, a .cat file is generated and saved internally to DAPPERS memory. It should be noted that the latter option does not permanently save .cat files. When working on a project, it is recommended that the user takes advantage of both the “Save Cat File” and “Use Cat File” options so that no .cat files are overwritten or forgotten.



# QUANTUM FILTERS

## OVERVIEW

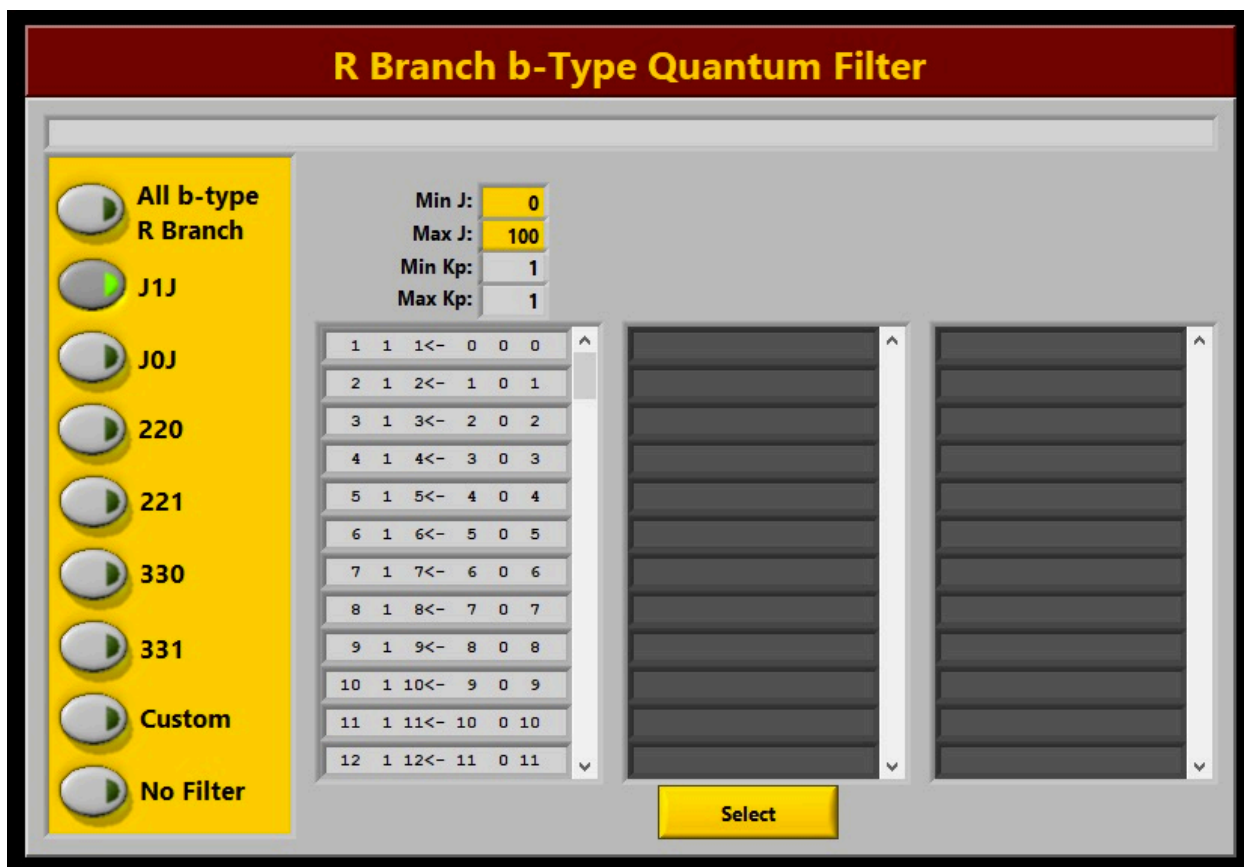
Quantum Filters are one of several features that defines DAPPERS as an intelligent fitting program. Quantum Filter application is the process of isolating spectral progressions for the purposes of fitting just one piece of an experimental spectrum. DAPPERS defines these progressions according to the K prolate values, branch (P, Q, or R), and transition type, as further differentiated by the  $(\Delta K_p, \Delta K_o)$  ordered pair. This ordered pair is referred to as the “ $\Delta K$  pair.” Selecting appropriate Quantum Filters is one of the most important factors for successfully fitting spectra with DAPPERS’ fitting algorithm. This section of the documentation will focus on why Quantum Filters are important in DAPPERS, which Quantum Filters to select, and how other variables affect success in fitting with DAPPERS. Additionally, it should be noted that transitions are designated according to their **upper state quantum numbers**.



## WHY QUANTUM FILTERS ARE IMPORTANT IN DAPPERS FITTING

DAPPERS’ fitting algorithm uses the frequencies and spacings of predicted transitions to estimate experimental frequencies. DAPPERS takes advantage of the fact that, while absolute transition frequencies may be very different from those obtained from predicted rotational constants, the relationship between members of a progression involving successive values of J is often more tightly defined. This approach to assigning spectra has been noted by Cooke and Ohring.<sup>3</sup> Accordingly, the DAPPERS fitting algorithm requires the user to choose one of these progressions of similar transitions in order to begin fitting a spectrum.

## HOW TO SELECT QUANTUM FILTERS



The user may start by selecting R branch Quantum Filters that correspond to the largest predicted dipole moment of the species they are analyzing. As a general note, the Max J of the upper energy state is defaulted to J=100, but the user can increase the value up to J=358 for any of the default options. Furthermore, when the user presses the “Custom” button, they can specify upper and lower limits for both the J and K prolate of the upper energy state of the transition. The 3 fields on this screen allow for displays corresponding to different  $\Delta K$  ordered pairs. The user can always see which transitions have been selected in the display(s) that are shown in each branch/type window. The number of displays is determined by the number of general expressions that are used to model that type/branch of spectra. All of these expressions for all types/branches of spectra can be found in the Quantum Filter Tables section of the Appendix of this documentation. A brief guide for selecting Quantum Filters is shown below according to the dominant spectral type/branch.

## RECOMMENDED QUANTUM FILTERS

The purpose of this section is to outline typical Quantum Filters that can be used to quickly find fits for a, b, and c-type spectra. This section is designed to help spectroscopists, who are already familiar with fitting rotational spectra, use Quantum Filters to select transitions they are familiar with; it is not meant to be an all-encompassing guide to fitting rotational spectra. The following guides focus on different Quantum Filtered progressions that are likely to result in predictive fits for each type of spectrum. Each guide will begin by recommending R-branch progressions. As a general note, the user should consider using one quartic distortion constant (Delta J for Watson-A or DJ for Watson-S) if fitting more than 4 transitions for one Quantum Filtered progression.

### A-TYPE QUANTUM FILTER GUIDE

- For fitting all of the following R branch progressions, consider constraining A when running fits in the Run Fits window

- Begin with the default button:  $K_p=0$ . Here are some examples of transitions from this progression:

$$1_{0,1} \leftarrow 0_{0,0}$$

$$2_{0,2} \leftarrow 1_{0,1}$$

$$3_{0,3} \leftarrow 2_{0,2}$$

$$4_{0,4} \leftarrow 3_{0,3}$$

- Next, select the default button:  $K_p=1-$ . The “-“ refers to the lower of the two  $K_p=1$  transitions. Here are some examples of transitions from this progression:

$$2_{1,2} \leftarrow 1_{1,1}$$

$$3_{1,3} \leftarrow 2_{1,2}$$

$$4_{1,4} \leftarrow 3_{1,3}$$

$$5_{1,5} \leftarrow 4_{1,4}$$

- Next, select the default button:  $K_p=1+$ . The “+“ refers to the upper of the two  $K_p=1$  transitions Here are some examples of transitions from this progression:

$$2_{1,1} \leftarrow 1_{1,0}$$

$$3_{1,2} \leftarrow 2_{1,1}$$

$$4_{1,3} \leftarrow 3_{1,2}$$

$$5_{1,4} \leftarrow 4_{1,3}$$

- Next, select the default button:  $K_p=2-$ . Here are some examples of transitions from this progression:

$$3_{2,2} \leftarrow 2_{2,1}$$

$$4_{2,3} \leftarrow 3_{2,2}$$

$$5_{2,4} \leftarrow 4_{2,3}$$

$$6_{2,5} \leftarrow 5_{2,4}$$

- Next, select the default button:  $K_p=2+$ . Here are some examples of transitions from this progression:

$$3_{2,1} \leftarrow 2_{2,0}$$

$$4_{2,2} \leftarrow 3_{2,1}$$

$$5_{2,3} \leftarrow 4_{2,2}$$

$$6_{2,4} \leftarrow 5_{2,3}$$

- These five progressions will likely be sufficient to produce a relatively predictive fit, but the user can select the custom option to select progressions with higher  $K$  prolate values if desired.

### **B-TYPE QUANTUM FILTER GUIDE**

- Begin with the default button: J1J. Here are some examples of transitions from this progression:

$$1_{1,1} \leftarrow 0_{0,0}$$

$$2_{1,2} \leftarrow 1_{0,1}$$

$$3_{1,3} \leftarrow 2_{0,2}$$

$$4_{1,4} \leftarrow 3_{0,3}$$

- Next, select the default button: JOJ. Here are some examples of transitions from this progression:

$$2_{0,2} \leftarrow 1_{1,1}$$

$$3_{0,3} \leftarrow 2_{1,2}$$

$$4_{0,4} \leftarrow 3_{1,3}$$

$$5_{0,5} \leftarrow 4_{1,4}$$

- Next, select a JJ0 progression that is predicted to feature intense transitions. The JJ0 is the designation for the first transition of a series, not each transition of the series. Here are some examples of transitions from the  $K_p=2$ , JJ0 progression:

$$2_{2,0} \leftarrow 1_{1,1}$$

$$3_{2,1} \leftarrow 2_{1,2}$$

$$4_{2,2} \leftarrow 3_{1,3}$$

$$5_{2,3} \leftarrow 4_{1,4}$$

- Next, select a JJ1 progression that is predicted to feature intense transitions. The JJ1 is the designation for the first transition of a series, not each transition of the series. Here are some examples of transitions from the  $K_p=3$ , JJ1 progression:

$$3_{3,1} \leftarrow 2_{2,0}$$

$$4_{3,2} \leftarrow 3_{2,1}$$

$$5_{3,3} \leftarrow 4_{2,2}$$

$$6_{3,4} \leftarrow 5_{2,3}$$

- Note that the JJ1 and JJ0 transitions are a doublet series of each other and may not be resolvable depending on the J and Kp value.
- 2-3 of these progressions will likely be sufficient to produce a relatively predictive fit, but the user can select the custom option to select other progressions if desired.

### C-TYPE QUANTUM FILTER GUIDE

- Next, select the default button: JOJ. Here are some examples of transitions from this progression:

$$\begin{aligned} 2_{0,2} &\leftarrow 1_{1,0} \\ 3_{0,3} &\leftarrow 2_{1,1} \\ 4_{0,4} &\leftarrow 3_{1,2} \\ 5_{0,5} &\leftarrow 4_{1,3} \end{aligned}$$

- Next, select a JJ0 progression that is predicted to feature intense transitions. The JJ0 is the designation for the first transition of a series, not each transition of the series. Here are some examples of transitions from the K<sub>p</sub>=2, JJ0 progression:

$$\begin{aligned} 2_{2,0} &\leftarrow 1_{1,0} \\ 3_{2,1} &\leftarrow 2_{1,1} \\ 4_{2,2} &\leftarrow 3_{1,2} \\ 5_{2,3} &\leftarrow 4_{1,3} \end{aligned}$$

- Next, select a JJ1 progression that is predicted to feature intense transitions. The JJ1 is the designation for the first transition of a series, not each transition of the series. Here are some examples of transitions from the K<sub>p</sub>=3, JJ1 progression:

$$\begin{aligned} 3_{3,1} &\leftarrow 2_{2,1} \\ 4_{3,2} &\leftarrow 3_{2,2} \\ 5_{3,3} &\leftarrow 4_{2,3} \\ 6_{3,4} &\leftarrow 5_{2,4} \end{aligned}$$

- Note that the JJ1 and JJ0 transitions are a doublet series of each other and may not be resolvable depending on the J and Kp value.
- 2-3 of these progressions will likely be sufficient to produce a relatively predictive fit, but the user can select the custom option to select other progressions if desired.

## **USING MULTIPLE QUANTUM FILTERS**

While DAPPERS does not restrict the user from selecting multiple Quantum Filters at once when searching for initial fits, doing so in the early stages of a fitting project is highly inadvisable. However, using multiple Quantum Filters in DAPPERS' Fit Polish feature (see p. 33) can be an extremely useful tool to finalizing the fit of a species.

## **FREQUENCY LIMITS, VIEW, AND J SPAN**

The user is able to fine-tune which Quantum Filtered transitions are being analyzed by adjusting the frequency limits. For large molecules, it is often wise to start with only four transitions in a Quantum Filtered progression to determine minimum window values for the starter, ratio test, and derivative ratio test window (see the algorithm's documentation for more information on these windows and tests).

The user can view exactly which transitions have been selected by the Quantum Filter and Frequency Limits by pressing the "View" button in the Quantum Filter section of the main DAPPERS window. The view window shows the predicted frequencies alongside their transitions in Pickett's .lin file format. Additionally, a variable called "J Span" is located to the left of the "View" button. J Span indicates the total number of possible transitions in any given progression that have been specified by the user through Quantum Filters and Frequency Limits.

# SEARCH FOR FITS

## OVERVIEW

DAPPERS prominently features an intelligent fitting algorithm for identifying and assigning members of a particular Quantum Filtered progression. The algorithm is able to estimate experimental frequencies based on an inputted predicted spectrum with relatively high accuracy, though it is worth noting that the accuracy of the algorithm is dependent on the accuracy of the predicted spectrum. This section of the documentation will generally outline the fit searching algorithm, guide the user in how to effectively use search windows, and explain how to analyze the accuracy of the algorithm results for real and theoretical data.



## SEARCH WINDOW RECOMMENDATIONS

DAPPERS algorithm uses three user-controlled search windows to intelligently assign spectra: the Starter Window, the Ratio Test Window, and the Derivative Ratio Test Window. Assuming the correct experimental frequencies are present in the user-inputted peak list, DAPPERS' algorithm can correctly assign any combination of Quantum Filtered transitions with large enough windows. However, windows that are too broad will result in hundreds or thousands of potential fits. The true power of DAPPERS lies within its ability to correctly estimate transition frequencies to a few MHz or less. In order to do this, the user must select reasonable window values to begin and then refine these window sizes based on the results.

The starter window will almost always be the largest window. This window represents the maximum error the user believes the first predicted Quantum Filtered and frequency limited transition is from its experimental value. Depending on a number of factors including molecule size, prediction accuracy, experimental frequency range, reasonable starter window values can range from 10 to 10,000 MHz. Luckily, larger starter window values do not drastically affect the efficiency of DAPPERS algorithm (within reason).

The ratio test will almost always be the second largest window. This window represents the maximum error the user believes the DAPPERS guess frequency of the second predicted Quantum Filtered and frequency limited transition is from its experimental value. The equation DAPPERS uses to calculate this frequency can be found in the Understanding the Algorithm section of the documentation. Depending on a number of factors, reasonable ratio test window values can be as high as ~50 MHz, though they tend to be closer to 2-5 MHz.

The derivative ratio test will almost always be the smallest window. This window represents the maximum error the user believes the DAPPERS guess frequency of the third or higher predicted Quantum Filtered and frequency limited transition is from its experimental value. The equation DAPPERS uses to calculate this frequency can be found in the Understanding the Algorithm section of the documentation. Depending on a number of factors reasonable derivative ratio test values tend to be less than 2 MHz, though they tend to be smaller.

An example of how to use all three of these windows worked out with the algorithm can be found in the appendix. This example will bring the user step-by-step through the fitting algorithm, showing the results that it finds at each step of the algorithm.

## UNDERSTANDING THE ALGORITHM

DAPPERS' fit searching algorithm reads a list of predicted frequencies that have been specified by the user through the application of Quantum Filters and frequency limits, and searches for similar frequency patterns in the user-inputted experimental frequency list. Rather than taking a brute force approach, the algorithm reads user-controlled search windows to selectively calculate which experimental frequencies are likely candidates for assignment. DAPPERS predicts the next frequency of a transition in a Quantum Filtered Progression based on the predicted relationship determined from a .cat file. This can be roughly thought of as an asymmetric rotor version of looking for a 2B, 4B, 6B... sequence on a symmetric top. Depending on how many transitions have been assigned the algorithm determines a guess frequency,  $\nu_N^{guess}$ , through the application of one of the three tests outlined in the table below. For each of the three types of tests in the following table, if an experimental frequency is within +/- the value specified in the user-controlled window, then the frequency is assigned and added to a line list for a potential fit. If there are N experimental frequencies within that window, N new potential fits are generated. If there are no frequencies within that window and there are still other potential fits, the fit is forgotten.

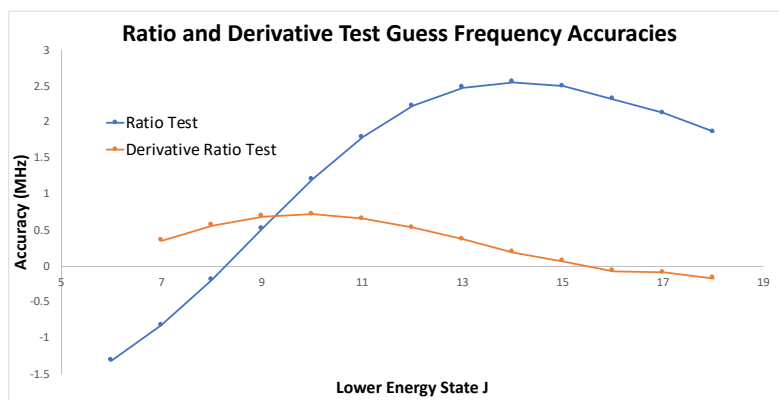


Test	When is it applied?	Equation
Starter Test	When searching for the first transition in a fit.	$v_1^{guess} = v_1^{pred}$
Ratio Test	When searching for the second transition in a fit.	$v_2^{guess} = v_1^{Obs} \left[ \frac{v_2^{Pred}}{v_1^{Pred}} \right]$
Derivative Ratio Test	When searching for the third or higher transition in a fit.	$v_N^{guess} = (v_{N-1}^{Obs} - v_{N-2}^{Obs}) \left[ \frac{v_N^{Pred} - v_{N-1}^{Pred}}{v_{N-1}^{Pred} - v_{N-2}^{Pred}} \right] + v_{N-1}^{Obs}$

## INTERPRETING THE ALGORITHM RESULTS

The user has the option to view, analyze, and refine the potential fits that were found by DAPPERS' algorithm by pressing the "View Results" button in the Search for Fits section of DAPPERS' main window. This window displays the results of the algorithm in 6 columns: experimental frequencies, predicted frequencies, transition quantum numbers, ratio test accuracies, derivative ratio test accuracies, and residual correction accuracies. The final three of these columns can be used to determine which fits are more likely to feature correctly assigned transitions.

The ratio test column shows the difference between the guess frequency and the experimental frequency in MHz. This column can be used to judge whether or not the fit is likely a correct assignment based on whether these values fluctuate randomly or change slightly in an ordered manner from transition to transition. For example, if one were to plot the ratio test accuracy of predicting the next member of a Quantum Filtered series as a function of the lower energy state J value, the resulting plot would be a relatively smooth looking curve similar to that shown in the figure below, which represents real data from the trifluoroacetic anhydride J1J progression. For example, the ratio test predicted the  $J'' = 11$  member of this progression within  $\sim 1.7$  MHz. Correspondingly, a similarly smooth plot can be derived from plotting the derivative ratio test accuracies as function of the lower energy state J value. For the trifluoroacetic anhydride spectrum, the derivative ratio test predicted the  $J'' = 11$  member of this progression within  $\sim 0.7$  MHz.



The final column is the residual correction accuracy. This column takes the error of the derivative ratio test used to calculate the guess frequency of the previous transition and adds it to the guess frequency of the current transition to generate a new guess frequency. The error between this new guess frequency and the experimental frequency is displayed as the residual correction accuracy. A correctly assigned set of transitions will tend to have residual correction values with lower magnitudes.

## ADVANCED SETTINGS

Future versions of DAPPERS will feature more options in the advanced settings, but the one option currently available is Max Skip. Max Skip tells the algorithm how many transitions in the predicted Quantum Filtered and frequency limited list it can skip if no peaks are found using either the ratio or derivative ratio tests. For example, if the algorithm is looking for a progression with lower energy state J's spanning 1 to 6 and there are experimental peaks for every J except for J=4, setting the Max Skip to 1 will allow the algorithm to assign J=1-3 and 5-6 in one fit.

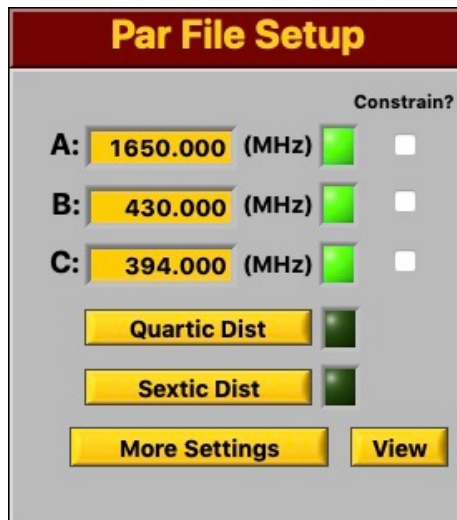
## WHAT AFFECTS THE ALGORITHM'S ACCURACY?

DAPPERS requires the user to input predicted rotational constants (and predicted distortion constants if applicable) or a .cat file that has been based on these predicted constants. As a general rule, the more accurate the predicted rotational constants, the easier it is for DAPPERS to fit the experimental spectrum. While the accuracy of the values of the predicted rotational constants is important, the accuracy of the predicted asymmetry parameter is significantly more important. Luckily, DAPPERS' algorithm is compatible with any asymmetry parameter value. To illustrate this compatibility, a series of plots comparing the accuracy of both the ratio and derivative ratio tests with varying asymmetry parameters can be found in the Appendix.

# PAR FILE SETUP

## OVERVIEW

Two files are required to run fits using SPFIT: .par files and .lin files (which are described elsewhere). Unfortunately, setting up .par files by hand according to the many formatting requirements of SPFIT can be a somewhat tedious process. DAPPERS' Par File Setup feature is designed to greatly simplify .par file formatting and generation, all while retaining the ability to customize .par files. As you fit spectra, you will often encounter this Par File Setup section shown at the right. This section of the documentation is designed to outline and explain the Par File Setup sections that can be found in the Run Fits, Fit Bank, and Fit Polish windows.



## INPUTTING ROTATIONAL CONSTANTS

The user is able to enter rotational constants A, B, and C in MHz into the corresponding gold entry box. These box values are defaulted to 1.000 MHz. If an entered rotational constant is greater than 1.000 MHz, the square LED to the right of the corresponding entry box will light up. DAPPERS will not let the user run fits with SPFIT if the following conditions are not met:

$$A > B > C > 1.000 \text{ MHz}$$

Additionally, DAPPERS will not run any fits in which the number of fitting parameters is greater than or equal to the number of lines. For example, the user cannot try to fit three transitions to A, B, and C. However, DAPPERS does allow the user to constrain A, B, or C by pressing the checkbox located to the right of the corresponding constant entry box. In this case, the user can fit three transitions to A, B, and C if one or more of the constants are constrained.

## INPUTTING DISTORTION CONSTANTS

The user is able to select quartic and sextic distortion constants by pressing either of the buttons labelled “Quartic Dist” and “Sextic Dist”. The respective distortion window will open with distortion constants whose labels depend of whether Watson-A or Watson-S has been selected (Watson-A is the factory default). The user can press the button labeled “Select” to the right of each gold entry box to quickly input -1.000 kHz and 1.000 Hz for quartic and sextic distortion constants respectively as they would normally be entered in Pickett. Alternatively, the user can input their own value directly into each gold entry box. Pressing clear will set all distortion constants in the active window to zero. If the user has entered at least one nonzero distortion constant, the green square LED next to the corresponding distortion button will turn on.

## MORE SETTINGS

Pressing the “More Settings” button will open a window full of gold entry boxes that control the many settings available in SPFIT .par files. These boxes are labeled according to the labels detailed in the SPFIT/SPCAT documentation [SPFIT and SPCAT Documentation](#) where the user can familiarize themselves with these settings if unfamiliar. Labels that are split into “Value” and “Power” sublabels are expressed in scientific notation, where “Value” is the decimal coefficient and “Power” is the integer exponent. The setting labelled “(.lin file) ERR” corresponds to the experimental error associated with each line in the .lin file and is the only setting not used in generating a .par file.

Additionally, the user can set values that correspond to their experimental parameters in the various settings and save them as default settings. The user will likely only need to change these settings the first time they are using DAPPERS if they save them as default. The factory default settings are those used by the Leopold lab. As described in the Additional Options section, performing a “Full Reset” will restore the factory default settings.

## VIEW

The user can press the “View” button to view and edit the .par file they are generating. Any edits made to the .par file in this window will be overwritten if any changes are made to the rotational constants, distortion constants, or settings. Editing .par files is not recommended if the user is not familiar with the .par file formatting requirements. The editing feature is not available in the Run Fits window.

# RUN FITS

## OVERVIEW

The Run Fits window allows the user to run the Quantum Filtered progressions that were found using DAPPERS' algorithm with SPFIT. Once the fits have been run, the user can determine which fits are reasonable and move those fits to the Fit Bank for further compilation. This section of the documentation is designed to describe how to use the Run Fits window and how to interpret the Run Fits display.

The screenshot shows the 'Par File Setup' window. On the left, there are input fields for rotational constants A (1650.000 MHz), B (430.000 MHz), and C (394.000 MHz), each with a 'Constrain?' checkbox. Below these are buttons for 'Quartic Dist', 'Sextic Dist', 'More Settings', and 'View'. The main area is a table with columns: SPFIT RMS (MHz), A (MHz), B (MHz), C (MHz), QF Code, Kp', and Fit #. The table contains 10 rows of fit data. To the right of the table are two columns of buttons: 'View .fit File' and 'Move to Fit Bank'. At the bottom right are 'Run Fits' and 'Exit' buttons. A scroll bar is visible at the top right.

SPFIT RMS (MHz)	A (MHz)	B (MHz)	C (MHz)	QF Code	Kp'	Fit #		
0.004968	1643.503	426.630	392.366	b.R 1, 1	1	4	View .fit File	Move to Fit Bank
0.030826	1643.533	426.608	392.357	b.R 1, 1	1	5	View .fit File	Move to Fit Bank
0.044584	1643.460	426.662	392.378	b.R 1, 1	1	2	View .fit File	Move to Fit Bank
0.054140	1643.556	426.591	392.350	b.R 1, 1	1	1	View .fit File	Move to Fit Bank
0.076893	1643.578	426.574	392.344	b.R 1, 1	1	6	View .fit File	Move to Fit Bank
0.101774	1643.603	426.556	392.336	b.R 1, 1	1	0	View .fit File	Move to Fit Bank
0.114892	1643.391	426.714	392.399	b.R 1, 1	1	3	View .fit File	Move to Fit Bank
							View .fit File	Move to Fit Bank
							View .fit File	Move to Fit Bank

## RUNNING FITS WITH SPFIT

Running fits with SPFIT is made extremely easy in this window assuming the user has already setup their own default settings as described in the Par File Setup section of this documentation. To run fits, the user only needs to enter estimated rotational constants, distortion constants, and press Run Fits in the bottom right hand corner of the window. A small window will then open, telling the user how many fits have been run and how many fits are remaining. This window also gives the user the option to abort this process. Additionally, the user can test which distortion constants are determined by quickly interchanging which distortion constant(s) are active with the quartic and sextic distortion selection windows and then pressing the Run Fits.

## INTERPRETING THE RUN FITS DISPLAY

Once fits have been run, the resulting fits are sorted from low to high RMS. The fitted rotational constants A, B, and C (MHz) are also displayed for each fit. The QF code tells the user the type, branch, and  $\Delta K$  pair of the transitions in the fit. The K prolate value for the upper energy state of each transition in the Quantum Filtered fit is displayed in the column next to the QF code. The fit number displayed in the final column is an arbitrary fitting index. If more than 9 fits were run, the user can scroll through the fits using the scroll control in the upper right-hand corner of the window.

By pressing the “View .fit File” button to the right of each fit, the user can view the final iteration of the resulting .fit file. If the user believes one or more of the fits may have correctly assigned transitions, they can move these fits to the fit bank by pressing the “Move to Fit Bank” button to the right of each fit. Moving a fit to the Fit Bank will remove it from the Run Fits display. However, that fit’s combination of experimental frequencies and transitions is still in DAPPERS memory and will be used again if the user presses the Run Fits button again. Details on what to do with fits that have been moved to the Fit Bank is described in the Fit Bank section of the documentation. Results from multiple Quantum Filtered selections will be compiled into a single Fit Bank fit during a single DAPPERS session.

# FIT BANK

## OVERVIEW

The Fit Bank window allows the user to compile the assigned transitions of the Quantum Filtered fits that have been moved to the Fit Bank from the Run Fits window and run those compiled fits with SPFIT. This window allows the user to easily try fitting different combinations of Quantum Filtered progressions with different combinations of quartic and sextic distortion constants as well. The user can save any compiled fits they are satisfied with to a location of their choosing.

The screenshot shows the 'Par File Setup' window. On the left, there are input fields for parameters A, B, and C, each with a 'Constrain?' checkbox. Below these are checkboxes for 'Quartic Dist' and 'Sextic Dist', and buttons for 'More Settings' and 'View'. The main area is a table with columns: FB #, Quantum Filter, Type, Branch, and Parity, Kp', Min and Max J', SPFIT RMS, and Scroll. The table contains 6 rows of fit data. At the bottom of the table are buttons for 'Compile .lin file' and 'View .lin file', along with a 'Lines Selected' field showing 44. Below the table is a 'Run Fit' button and a row of numerical values for RMS (kHz), A (MHz), B (MHz), and C (MHz). At the very bottom are buttons for 'View', '.cat', 'Save', 'Help', and 'Exit'.

FB #	Quantum Filter	Type, Branch, and Parity	Kp'	Min and Max J'	SPFIT RMS	Scroll
1	J1J	b.R 1, 1	1	7   20	0.005	Delete View
2	J0J	b.R-1, 1	0	9   21	0.005	Delete View
3	JJ0	b.R 1, -1	3	3   13	0.005	Delete View
4	JJ1	b.R 1, 1	3	3   15	0.007	Delete View
5	JJ0	b.R 1, -1	4	4   11	0.005	Delete View
6	JJ0	b.R 1, -1	5	5   8	0.001	Delete View

Run Fit    RMS (kHz): 0.005233    A (MHz): 1643.511    B (MHz): 426.631    C (MHz): 392.365    View    .cat    Save    Help    Exit

## INTERPRETING THE FIT BANK DISPLAY

The Fit Bank display is used to organize Quantum Filtered fits that have been moved to the Fit Bank from the Run Fits window. The first column shows an arbitrary Fit Bank index associated with each fit. The second column shows a brief keyword that indicates which Quantum Filter was used to generate each fit. The third and fourth columns show the Quantum Filter Code and upper energy state K prolate value for the transitions in the fit respectively. The fifth and sixth columns show the minimum and maximum upper energy state J values for each fit. The last column shows the RMS calculated for that fit with SPFIT in the Run Fits window.

Additionally, the user can delete any fit from the Fit Bank by pressing the delete button directly to the right of each fit. The user can view the last iteration of the .fit file that was generated for each fit in the Run Fits window by pressing the view button next to each fit's delete button. If there are more than 7 fits in the fit bank, the user can

use the scroll control in the top right-hand corner to scroll through the fit bank. Lastly, it should be noted that every time DAPPERS is closed, the Quantum Filtered fits in the Fit Bank are deleted.

## **COMPILING FITS FROM THE FIT BANK**

In order to compile multiple Quantum Filtered fits together, the user can press the grey button directly to the left of the desired fits in the Fit Bank display then press the “Compile .lin File” button once all desired fits have been selected. Every time the user chooses different fits to compile, they must press the “Compile .lin File” button. If any of the transitions in the compiled .lin file have two frequencies assigned to the same quantum numbers, the .lin file will still be compiled but the user will be warned of duplicate assignments with an error message.

The user can view, edit, and organize the .lin file by pressing the “View .lin File” button. When pressed, a window will open that allows the user to organize the .lin file by frequency, upper energy state J, upper energy state K, or Quantum Filters. Note that the errors that are inputted into the .lin file are determined by the ERR: setting that can be accessed in the More Settings window in the Par File Setup section. Any edits that are made to the .lin file must be in accordance with the .lin file formatting requirements. Otherwise SPFIT is not guaranteed to work correctly.

## **RUNNING COMPILED FITS**

Running fits with SPFIT is made extremely easy in this window assuming the user has already setup their own default settings as described in the Par File Setup section of this documentation. Once the user has compiled a .lin file, they only need to enter estimated rotational constants, distortion constants, and press Run Fit in the bottom left hand corner of the window to run the compiled fit with SPFIT. When pressed, a small window will open telling the user that the compiled fit is running. Once the fit has completed, the RMS and fitted A, B, and C constants will be displayed at the bottom of the window. The user can view the last iteration of the .fit file by pressing the “View” button located directly to the right of the fitted rotational constants display.



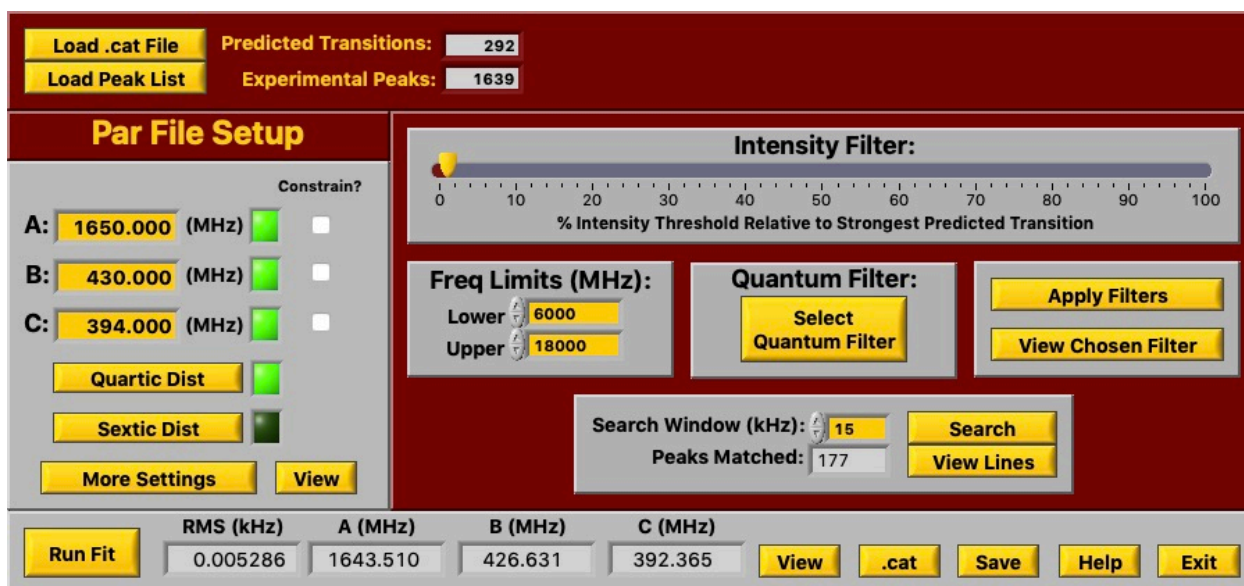
## SAVING COMPILED FITS

At this point, the user can press the “Save” button to save all of the Pickett files associated with the compiled fit to a location of their choosing. If the user presses the “Save” button before they generated a .cat file, all of the Pickett files will be saved except for the .int and .cat files. Generating .cat files before saving is required if the user would like to use the compiled fit’s .cat file with DAPPERS’ final fitting window: Fit Polish. To generate a .cat file from the compiled fit, the user must first press the “.cat” button located directly to the right of the “View” button. Doing so will open up the Int File Setup window, in which the user can input predicted dipole moments. In order to proceed, at least one of the inputted dipole moments must be nonzero. Additionally, the user can adjust Int file settings by pressing the “More Settings” button, which will open a window full of gold entry boxes that control the many settings available in SPCAT .int files. These boxes are labeled according to the labels detailed in the [SPFIT and SPCAT Documentation](#) where the user can familiarize themselves with these settings if unfamiliar. The user can also view the .int file by pressing the “View” button in this window. Once the “Enter” button has been pressed a .cat file will be generated and saved to DAPPERS’ memory.

# FIT POLISH

## OVERVIEW

The Fit Polish window allows the user to quickly add experimental frequencies that are not yet in the compiled fit to a new fit with a high degree of transition selectivity and control. This program allows the user to first upload an experimental peak list and the .cat file of a predictive fit, and then add experimental frequencies that are within a user-controlled frequency window of the .cat file frequency to a new fit through the application of frequency, intensity, and transition filters.



## UPLOADING CAT FILES AND PEAK LISTS

Before the user can use any of the features in the Fit Polish window, they must first upload an experimental peak list and the .cat file of a predictive fit. The formatting requirements for the peak list can be found in the Uploading an Experimental Peak List section of this documentation. This program will not work (at least not very well) with .cat files that are not based on predictive fits. In this case, predictive means transition frequencies are correct within several hundred kHz.

## **APPLYING FILTERS AND SEARCHING FOR MATCHES**

Rather than search the entire .cat file for matching experimental frequencies, the user can apply intensity, frequency, and transition filters. The intensity filter works by including any transitions that have predicted intensities above an intensity threshold that is defined by a percentage of the most intense predicted transition in the entire .cat file. This percentage is controlled by a user-controlled slider and is defaulted to start at 1%. Next, the user can apply a frequency filter to the remaining transitions by controlling the labelled frequency limits. Finally, the user can use Quantum Filters to specify certain progressions, types, or branches of transitions (or any combination of those) to consider matching with experimental frequencies. The decision of which Quantum Filters (if any) to use at this stage is up to the spectroscopist!

Once all of the filter values have been set, the user must press the “Apply Filters” button to implement these filters. Once implemented, the number of predicted transitions (located in the upper left-hand corner) will indicate how many transitions were selected as a result of the applied filters. These transitions can be viewed by pressing the “View Chosen Filter” button.

With the filter applied, the user can now adjust the search window to a value they deem reasonable and press the “Search” button. Once DAPPERS has finished searching, the number of peaks matched display will be updated. Pressing the “View Lines” button will allow the user to view, organize, and edit the .lin file in the same manner described in the Fit Bank section of the documentation.

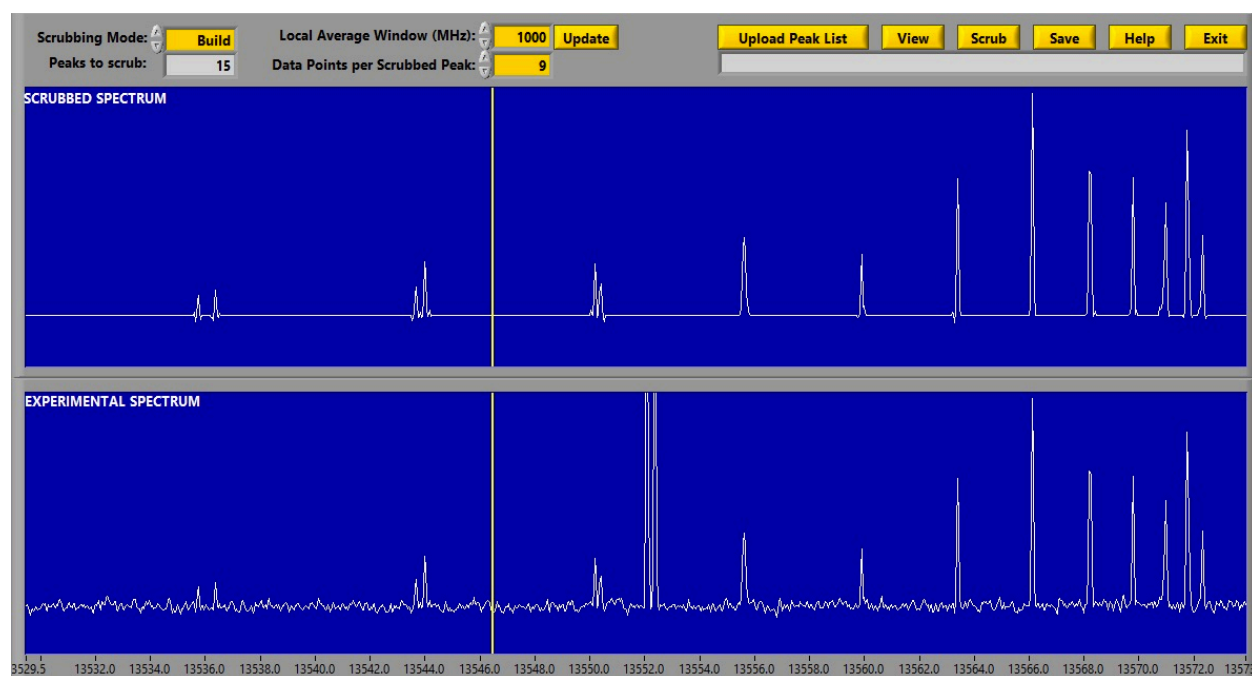
## **RUNNING AND SAVING POLISHED FITS**

Polished fit running and saving is identical to the fit running and saving method outlined in the Fit Bank section of the documentation.

# SPECTRAL SCRUBBER

## OVERVIEW

The spectrum scrubbing program is designed as a spectral processing tool for the purpose of visualization, **not to modify raw experimental spectra**. The program takes an experimental spectrum and generates a scrubbed file according to peaks the user would like to add to an empty spectrum or remove from an experimental spectrum. The resulting spectrum is called a “scrubbed spectrum.” The original file is never replaced or altered in any way. Similar to the Graphical Peak Finder, this program uses local averages to generate both types of scrubbed spectra. The program displays the original experimental spectrum in parallel with the working scrubbed spectrum.



## UPLOADING SPECTRAL FILES

In order to run the scrubbing program, the user must first upload an experimental spectrum that follows DAPPERS experimental spectrum formatting requirements. These requirements can be found in the Graphical Peak Finder section of the documentation.

## **LOCAL AVERAGES**

Once a spectrum has been uploaded, the corresponding local average spectrum is generated with a default window of 1000 MHz (local average refers to the locally averaged baseline level). This spectrum can be replaced with a local average spectrum based on a different window size if the user adjusts the Local Average Window to the desired value and presses the “Update” button. If the window is small and the Local Average calculation is taking too long, the user can abort the process by pressing the “ABORT” button. In any case, the user has two options for the Scrubbing Mode: Build and Remove.

## **SCRUBBING**

In general, scrubbing is the process of taking data from one spectrum and replacing it with the data of another spectrum. To do so, the user builds or uploads a peak list. To upload a peak list, the user presses the “Upload Peak List” button. This peak list can be viewed and edited by pressing the “View” button. Once the peak list is uploaded, the user must press the “Scrub” button to update the scrubbed spectrum with those frequencies. Additionally, the user is able to easily add single peaks to the scrubbed display by pressing the “O” key to automatically add the current frequency of the cursor to the peak list and update the scrubbed spectrum display. The user can control how many data points about each of the frequencies in the peak list are added to the scrubbed spectrum by changing the numeric control labelled “Data Points per Scrubbed Peak.”

## **SCRUBBING MODES**

For the Build mode, the local average spectrum is plotted in the scrubbed spectrum display. The data for scrubbed peaks that are added to this spectrum come from the uploaded experimental spectrum. In doing so, the user can start from an essentially empty spectrum (constructed from the local averages described above) and build a spectrum containing only peaks that have been specified by the user.

For the Remove mode, the uploaded experimental spectrum is plotted in the scrubbed spectrum display. The data for scrubbed peaks that are added to this spectrum come from the local average spectrum. In doing so, the user can start from the raw experimental spectrum and remove unwanted peaks that might come from a previously characterized species or instrument artifacts/known noise.

## SPECTRAL NAVIGATION

The dual spectral displays are linked, and their keyboard commands are the same as those that can be found in the Graphical Peak Finder documentation (p. 8). Additionally, it should be noted that the points per pixel can be adjusted manually on the main scrubbing window. Unlike the Graphical Peak Finder, data decimation is always on.

## SAVING SCRUBBED FILES

The user is able to save the scrubbed spectrum shown in the top display as an .spe file. Because scrubbed spectra are processed, they are always saved as `__SCRUB__userinputtedfilename.spe` so that they are always distinguishable from experimental spectra.

## FITTING WITH SCRUBBED SPECTRA

While the primary focus of scrubbing spectra is helping the user visualize spectra, it is possible to use scrubbed spectra to aid in the fitting process. For example, imagine an extremely dense experimental spectrum that contains two species: Molecule 1 and Molecule 2. Assume that Molecule 1 features both the most intense peaks and the majority of the peaks in the experimental spectrum, and Molecule 2 has less intense peaks and the minority of the peaks in the spectrum. Also assume that Molecule 1 has already been fit. If the user inputs the list of fitted peaks for Molecule 1 into the spectral scrubber (Remove Mode), only the unassigned peaks from Molecule 2 should remain. The user can then feed this scrubbed spectrum back into the Graphical Peak Finder to remeasure only the frequencies for Molecule 2, making the fitting process significantly easier. This can be particularly useful for assigning spectra of rare isotopologues in natural abundance.

That all being said, there are alternatives to this process that may be more reliable (e.g. issues could arrive when there are overlapping lines between Molecules 1 and 2). For example, the user could just manually remove the fitted Molecule 1 peaks from the original experimental peak list and use that for DAPPERS fitting since the “Remove Mode” scrubbing process could risk removing peaks that overlap between Molecule 1 and 2.

## **ADDITIONAL OPTIONS**

### **SET DEFAULT**

Pressing the “Set Default” button will save the currently entered frequency limits, max length, starter window, ratio test window, and derivative ratio test window as default. Once settings have been saved, a confirmation window will open to the user.



### **FULL RESET**

Performing a full reset will restore all of DAPPERS’ factory defaults. Any default settings that have been previously saved will be overwritten and forgotten.

### **SET PATH**

Pressing the “Set Path” button allows the user to select a default starting file path every time the user needs to save or open a file. The default starting path is the directory in which the DAPPERS program is saved. When working on a project, setting the start path to a folder devoted to the project can save the user time in navigating through folders for saving and opening files.

### **QUIT**

Pressing the “Quit” button is relatively straightforward. Note that anything in DAPPERS’ memory such as peak lists, algorithm fits, and Fit Bank fits will be forgotten. The user should make sure to save any progress before quitting DAPPERS.

### **SPECTRAL SCRUBBER**

A detailed description of the Spectral Scrubber program can be found in the Spectral Scrubber section of the documentation.

## **REFERENCES**

- (1) Pickett, M. The Fitting and Prediction of Vibration-Rotation Spectra with Spin Interactions. **1991**, 377, 371–377.
- (2) Seifert, N. A.; Finneran, I. A.; Perez, C.; Zaleski, D. P.; Neill, J. L.; Steber, A. L.; Suenram, R. D.; Lesarri, A.; Shipman, S. T.; Pate, B. H. AUTOFIT , an Automated Fitting Tool for Broadband Rotational Spectra , and Applications to 1-Hexanal. *J. Mol. Spectrosc.* **2015**, 312, 13–21.
- (3) Cooke, S. A.; Ohring, P. Decoding Pure Rotational Molecular Spectra for Asymmetric Molecules. *J. Spectrosc.* **2013**, 2013.
- (4) Medvedev, I. R.; Winnewisser, M.; Kisiel, Z.; Pszczo, L.; Lucia, F. C. De; Herbst, E. Rotational Spectrum of Trans – Trans Diethyl Ether in the Ground and Three Excited Vibrational States. **2005**, 233, 231–243.
- (5) Love, N.; Smith, C. J.; Huff, A. K.; Leopold, K. R. A Microwave and Computational Study of Trifluoroacetic Anhydride. *J. Mol. Spectrosc.* **2019**, 365, 111210.



# APPENDIX

## QUANTUM FILTER TABLES

These are the progressions allowed in DAPPERS. Others can be searched for in the Fit Polish if no Quantum Filters are active.

Quantum Filters: Expressions for R branch a-type Transitions				
Transition Type	Limits	$\Delta K_p, \Delta K_o$	Example Transitions	
$J'_{K'_p, J'-K'_p} \leftarrow J''_{K''_p, J''-K''_p}$	$J'' \geq 0$ $J'' = J' - 1$ $J'' \geq K''_p$ $K''_p \geq 0$ $K''_p = K'_p$	$K''_p: 0$ $K''_o: +1$	$1_{0,1} \leftarrow 0_{0,0}$ $2_{0,2} \leftarrow 1_{0,1}$ $3_{0,3} \leftarrow 2_{0,2}$ $4_{0,4} \leftarrow 3_{0,3}$ $\vdots$ $3_{2,1} \leftarrow 2_{2,0}$ $4_{2,2} \leftarrow 3_{2,1}$ $5_{2,3} \leftarrow 4_{2,2}$ $6_{2,4} \leftarrow 5_{2,3}$ $\vdots$	$2_{1,1} \leftarrow 1_{1,0}$ $3_{1,2} \leftarrow 2_{1,1}$ $4_{1,3} \leftarrow 3_{1,2}$ $5_{1,4} \leftarrow 4_{1,3}$ $\vdots$ $4_{3,1} \leftarrow 3_{3,0}$ $5_{3,2} \leftarrow 4_{3,1}$ $6_{3,3} \leftarrow 5_{3,2}$ $7_{3,4} \leftarrow 6_{3,3}$ $\vdots$
$J'_{K'_p, J'-K'_p+1} \leftarrow J''_{K''_p, J''-K''_p+1}$	$J'' \geq 1$ $J'' = J' - 1$ $J'' \geq K''_p$ $K''_p \geq 1$ $K''_p = K'_p$	$K''_p: 0$ $K''_o: +1$	$2_{1,2} \leftarrow 1_{1,1}$ $3_{1,3} \leftarrow 2_{1,2}$ $4_{1,4} \leftarrow 3_{1,3}$ $5_{1,5} \leftarrow 4_{1,4}$ $\vdots$ $4_{3,2} \leftarrow 3_{3,1}$ $5_{3,3} \leftarrow 4_{3,2}$ $6_{3,4} \leftarrow 5_{3,3}$ $7_{3,5} \leftarrow 6_{3,4}$ $\vdots$	$3_{2,2} \leftarrow 2_{2,1}$ $4_{2,3} \leftarrow 3_{2,2}$ $5_{2,4} \leftarrow 4_{2,3}$ $6_{2,5} \leftarrow 5_{2,4}$ $\vdots$ $5_{4,2} \leftarrow 4_{4,1}$ $6_{4,3} \leftarrow 5_{4,2}$ $7_{4,4} \leftarrow 6_{4,3}$ $8_{4,5} \leftarrow 7_{4,4}$ $\vdots$

**Quantum Filters: Expressions for R branch b-type Transitions**

Transition Type	Limits	$\Delta K_p, \Delta K_o$	Example Transitions	
$J'_{K'_p, J'-K'_p+1} \leftarrow J''_{K''_p, J''-K''_p}$	$J'' \geq 0$ $J'' = J' - 1$ $J'' \geq K''_p$ $K''_p \geq 0$ $K''_p = K'_p - 1$	$K''_p: +1$ $K''_o: +1$	$1_{1,1} \leftarrow 0_{0,0}$ $2_{1,2} \leftarrow 1_{0,1}$ $3_{1,3} \leftarrow 2_{0,2}$ $4_{1,4} \leftarrow 3_{0,3}$ $\vdots$ $3_{3,1} \leftarrow 2_{2,0}$ $4_{3,2} \leftarrow 3_{2,1}$ $5_{3,3} \leftarrow 4_{2,2}$ $6_{3,4} \leftarrow 5_{2,3}$ $\vdots$	$2_{2,1} \leftarrow 1_{1,0}$ $3_{2,2} \leftarrow 2_{1,1}$ $4_{2,3} \leftarrow 3_{1,2}$ $5_{2,4} \leftarrow 4_{1,3}$ $\vdots$ $4_{4,1} \leftarrow 3_{3,0}$ $5_{4,2} \leftarrow 4_{3,1}$ $6_{4,3} \leftarrow 5_{3,2}$ $7_{4,4} \leftarrow 6_{3,3}$ $\vdots$
$J'_{K'_p, J'-K'_p} \leftarrow J''_{K''_p, J''-K''_p+1}$	$J'' \geq 1$ $J'' = J' - 1$ $J'' \geq K''_p$ $K''_p \geq 1$ $K''_p = K'_p - 1$	$K''_p: +1$ $K''_o: -1$	$2_{2,0} \leftarrow 1_{1,1}$ $3_{2,1} \leftarrow 2_{1,2}$ $4_{2,2} \leftarrow 3_{1,3}$ $5_{2,3} \leftarrow 4_{1,4}$ $\vdots$ $4_{4,0} \leftarrow 3_{3,1}$ $5_{4,1} \leftarrow 4_{3,2}$ $6_{4,2} \leftarrow 5_{3,3}$ $7_{4,3} \leftarrow 6_{3,4}$ $\vdots$	$3_{3,0} \leftarrow 2_{2,1}$ $4_{3,1} \leftarrow 3_{2,2}$ $5_{3,2} \leftarrow 4_{2,3}$ $6_{3,3} \leftarrow 5_{2,4}$ $\vdots$ $5_{5,0} \leftarrow 4_{4,1}$ $6_{5,1} \leftarrow 5_{4,2}$ $7_{5,2} \leftarrow 6_{4,3}$ $8_{5,3} \leftarrow 7_{4,4}$ $\vdots$
$J'_{K'_p, J'-K'_p} \leftarrow J''_{K''_p, J''-K''_p+1}$	$J'' \geq 1$ $J'' = J' - 1$ $J'' \geq K''_p$ $K''_p \geq 1$ $K''_p = K'_p + 1$	$K''_p: -1$ $K''_o: +1$	$2_{0,2} \leftarrow 1_{1,1}$ $3_{0,3} \leftarrow 2_{1,2}$ $4_{0,4} \leftarrow 3_{1,3}$ $5_{0,5} \leftarrow 4_{1,4}$ $\vdots$ $4_{2,2} \leftarrow 3_{3,1}$ $5_{2,3} \leftarrow 4_{3,2}$ $6_{2,4} \leftarrow 5_{3,3}$ $7_{2,5} \leftarrow 6_{3,4}$ $\vdots$	$3_{1,2} \leftarrow 2_{2,1}$ $4_{1,3} \leftarrow 3_{2,2}$ $5_{1,4} \leftarrow 4_{2,3}$ $6_{1,5} \leftarrow 5_{2,4}$ $\vdots$ $5_{3,2} \leftarrow 4_{4,1}$ $6_{3,3} \leftarrow 5_{4,2}$ $7_{3,4} \leftarrow 6_{4,3}$ $8_{3,5} \leftarrow 7_{4,4}$ $\vdots$

Quantum Filters: Expressions for R branch c-type Transitions				
Transition Type	Limits	$\Delta K_p, \Delta K_o$	Example Transitions	
$J'_{K'_p, J'-K'_p} \leftarrow J''_{K''_p, J''-K''_p}$	$J'' \geq 0$ $J'' = J' - 1$ $J'' \geq K''_p$ $K''_p \geq 0$ $K''_p = K'_p - 1$	$K''_p: +1$ $K''_o: 0$	$1_{1,0} \leftarrow 0_{0,0}$ $2_{1,1} \leftarrow 1_{0,1}$ $3_{1,2} \leftarrow 2_{0,2}$ $4_{1,3} \leftarrow 3_{0,3}$ $\vdots$ $3_{3,0} \leftarrow 2_{2,0}$ $4_{3,1} \leftarrow 3_{2,1}$ $5_{3,2} \leftarrow 4_{2,2}$ $6_{3,3} \leftarrow 5_{2,3}$ $\vdots$	$2_{2,0} \leftarrow 1_{1,0}$ $3_{2,1} \leftarrow 2_{1,1}$ $4_{2,2} \leftarrow 3_{1,2}$ $5_{2,3} \leftarrow 4_{1,3}$ $\vdots$ $4_{4,0} \leftarrow 3_{3,0}$ $5_{4,1} \leftarrow 4_{3,1}$ $6_{4,2} \leftarrow 5_{3,2}$ $7_{4,3} \leftarrow 6_{3,3}$ $\vdots$
$J'_{K'_p, J'-K'_p+1} \leftarrow J''_{K''_p, J''-K''_p+1}$	$J'' \geq 1$ $J'' = J' - 1$ $J'' \geq K''_p$ $K''_p \geq 1$ $K''_p = K'_p - 1$	$K''_p: +1$ $K''_o: 0$	$2_{2,1} \leftarrow 1_{1,1}$ $3_{2,2} \leftarrow 2_{1,2}$ $4_{2,3} \leftarrow 3_{1,3}$ $5_{2,4} \leftarrow 4_{1,4}$ $\vdots$ $4_{4,1} \leftarrow 3_{3,1}$ $5_{4,2} \leftarrow 4_{3,2}$ $6_{4,3} \leftarrow 5_{3,3}$ $7_{4,4} \leftarrow 6_{3,4}$ $\vdots$	$3_{3,1} \leftarrow 2_{2,1}$ $4_{3,2} \leftarrow 3_{2,2}$ $5_{3,3} \leftarrow 4_{2,3}$ $6_{3,4} \leftarrow 5_{2,4}$ $\vdots$ $5_{5,1} \leftarrow 4_{4,1}$ $6_{5,2} \leftarrow 5_{4,2}$ $7_{5,3} \leftarrow 6_{4,3}$ $8_{5,4} \leftarrow 7_{4,4}$ $\vdots$
$J'_{K'_p, J'-K'_p} \leftarrow J''_{K''_p, J''-K''_p}$	$J'' \geq 1$ $J'' = J' - 1$ $J'' \geq K''_p$ $K''_p \geq 1$ $K''_p = K'_p + 1$	$K''_p: -1$ $K''_o: +2$	$2_{0,2} \leftarrow 1_{1,0}$ $3_{0,3} \leftarrow 2_{1,1}$ $4_{0,4} \leftarrow 3_{1,2}$ $5_{0,5} \leftarrow 4_{1,3}$ $\vdots$ $4_{2,2} \leftarrow 3_{3,0}$ $5_{2,3} \leftarrow 4_{3,1}$ $6_{2,4} \leftarrow 5_{3,2}$ $7_{2,5} \leftarrow 6_{3,3}$ $\vdots$	$3_{1,2} \leftarrow 2_{2,0}$ $4_{1,3} \leftarrow 3_{2,1}$ $5_{1,4} \leftarrow 4_{2,2}$ $6_{1,5} \leftarrow 5_{2,3}$ $\vdots$ $5_{3,2} \leftarrow 4_{4,0}$ $6_{3,3} \leftarrow 5_{4,1}$ $7_{3,4} \leftarrow 6_{4,2}$ $8_{3,5} \leftarrow 7_{4,3}$ $\vdots$

**Quantum Filters: Expressions for Q branch a-type Transitions**

Transition Type	Limits	$\Delta K_p, \Delta K_o$	Example Transitions	
$J'_{K'_p, J'-K'_p} \leftarrow J'_{K''_p, J'-K''_p+1}$	$J' \geq 3$ $J' \geq K'_p$ $K'_p \geq 3$ $K''_p = K'_p - 2$	$K''_p: +2$ $K''_o: -3$	$3_{3,0} \leftarrow 3_{1,3}$ $4_{3,1} \leftarrow 4_{1,4}$ $5_{3,2} \leftarrow 5_{1,5}$ $6_{3,3} \leftarrow 6_{1,6}$ $\vdots$	$4_{4,0} \leftarrow 4_{2,3}$ $5_{4,1} \leftarrow 5_{2,4}$ $6_{4,2} \leftarrow 6_{2,5}$ $7_{4,3} \leftarrow 7_{2,6}$ $\vdots$
$J'_{K'_p, J'-K'_p+1} \leftarrow J'_{K''_p, J'-K''_p}$	$J' \geq 2$ $J' \geq K'_p$ $K'_p \geq 2$ $K''_p = K'_p - 2$	$K''_p: +2$ $K''_o: -1$	$2_{2,1} \leftarrow 2_{0,2}$ $3_{2,2} \leftarrow 3_{0,3}$ $4_{2,3} \leftarrow 4_{0,4}$ $5_{2,4} \leftarrow 5_{0,5}$ $\vdots$	$3_{3,1} \leftarrow 3_{1,2}$ $4_{3,2} \leftarrow 4_{1,3}$ $5_{3,3} \leftarrow 5_{1,4}$ $6_{3,4} \leftarrow 6_{1,5}$ $\vdots$
$J'_{K'_p, J'-K'_p} \leftarrow J'_{K'_p, J'-K'_p+1}$	$J' \geq 1$ $J' \geq K'_p$ $K'_p \geq 1$	$K''_p: 0$ $K''_o: -1$	$1_{1,0} \leftarrow 1_{1,1}$ $2_{1,1} \leftarrow 2_{1,2}$ $3_{1,1} \leftarrow 3_{1,3}$ $4_{1,4} \leftarrow 4_{1,4}$ $\vdots$	$2_{2,0} \leftarrow 2_{2,1}$ $3_{2,1} \leftarrow 3_{2,2}$ $4_{2,2} \leftarrow 4_{2,3}$ $5_{2,3} \leftarrow 5_{2,4}$ $\vdots$

Quantum Filters: Expressions for Q branch b-type Transitions				
Transition Type	Limits	$\Delta K_p, \Delta K_o$	Example Transitions	
$J'_{K'_p, J'-K'_p} \leftarrow J'_{K''_p, J'-K''_p}$	$J' \geq 2$ $J' \geq K'_p$ $K'_p \geq 2$ $K''_p = K'_p - 1$	$K''_p: +1$ $K''_o: -1$	$2_{2,0} \leftarrow 2_{1,1}$ $3_{2,1} \leftarrow 3_{1,2}$ $4_{2,2} \leftarrow 4_{1,3}$ $5_{2,3} \leftarrow 5_{1,4}$ $\vdots$	$3_{3,0} \leftarrow 3_{2,1}$ $4_{3,1} \leftarrow 4_{2,2}$ $5_{3,2} \leftarrow 5_{2,3}$ $6_{3,3} \leftarrow 6_{2,4}$ $\vdots$
$J'_{K'_p, J'-K'_p+1} \leftarrow J'_{K''_p, J'-K''_p+1}$	$J' \geq 2$ $J' \geq K'_p$ $K'_p \geq 2$ $K''_p = K'_p - 1$	$K''_p: +1$ $K''_o: -1$	$2_{2,1} \leftarrow 2_{1,2}$ $3_{2,2} \leftarrow 3_{1,3}$ $4_{2,3} \leftarrow 4_{1,4}$ $5_{2,4} \leftarrow 5_{1,5}$ $\vdots$	$3_{3,1} \leftarrow 3_{2,2}$ $4_{3,2} \leftarrow 4_{2,3}$ $5_{3,3} \leftarrow 5_{2,4}$ $6_{3,4} \leftarrow 6_{2,5}$ $\vdots$

Quantum Filters: Expressions for Q branch c-type Transitions				
Transition Type	Limits	$\Delta K_p, \Delta K_o$	Example Transitions	
$J'_{K'_p, J'-K'_p} \leftarrow J'_{K''_p, J'-K''_p+1}$	$J' \geq 2$ $J' \geq K'_p$ $K'_p \geq 2$ $K''_p = K'_p - 1$	$K''_p: +1$ $K''_o: -2$	$2_{2,0} \leftarrow 2_{1,2}$ $3_{2,1} \leftarrow 3_{1,3}$ $4_{2,2} \leftarrow 4_{1,4}$ $5_{2,3} \leftarrow 5_{1,5}$ $\vdots$	$3_{3,0} \leftarrow 3_{2,2}$ $4_{3,1} \leftarrow 4_{2,3}$ $5_{3,2} \leftarrow 5_{2,4}$ $6_{3,3} \leftarrow 6_{2,5}$ $\vdots$
$J'_{K'_p, J'-K'_p+1} \leftarrow J'_{K''_p, J'-K''_p}$	$J' \geq 2$ $J' \geq K'_p$ $K'_p \geq 2$ $K''_p = K'_p - 1$	$K''_p: +1$ $K''_o: 0$	$2_{2,1} \leftarrow 2_{1,1}$ $3_{2,2} \leftarrow 3_{1,2}$ $4_{2,3} \leftarrow 4_{1,3}$ $5_{2,4} \leftarrow 5_{1,4}$ $\vdots$	$3_{3,1} \leftarrow 3_{2,1}$ $4_{3,2} \leftarrow 4_{2,2}$ $5_{3,3} \leftarrow 5_{2,3}$ $6_{3,4} \leftarrow 6_{2,4}$ $\vdots$

Quantum Filters: Expressions for P branch a-type Transitions				
Transition Type	Limits	$\Delta K_p, \Delta K_o$	Example Transitions	
$J'_{K'_p, J'-K'_p} \leftarrow J''_{K''_p, J''-K''_p}$	$J'' \geq 3$ $J'' = J' + 1$ $J'' > K''_p + 2$ $K''_p \geq 0$ $K''_p = K'_p - 2$	$K''_p: +2$ $K''_o: -3$	$2_{2,0} \leftarrow 3_{0,3}$ $3_{2,1} \leftarrow 4_{0,4}$ $4_{2,2} \leftarrow 5_{0,5}$ $5_{2,3} \leftarrow 6_{0,6}$ $\vdots$	$3_{3,0} \leftarrow 4_{1,3}$ $4_{3,1} \leftarrow 5_{1,4}$ $5_{3,2} \leftarrow 6_{1,5}$ $6_{3,3} \leftarrow 7_{1,6}$ $\vdots$
$J'_{K'_p, J'-K'_p+1} \leftarrow J''_{K''_p, J''-K''_p+1}$	$J'' \geq 4$ $J'' = J' + 1$ $J'' > K''_p + 2$ $K''_p \geq 1$ $K''_p = K'_p - 2$	$K''_p: +2$ $K''_o: -3$	$3_{3,1} \leftarrow 4_{1,4}$ $4_{3,2} \leftarrow 5_{1,5}$ $5_{3,3} \leftarrow 6_{1,6}$ $6_{3,4} \leftarrow 7_{1,7}$ $\vdots$	$4_{4,1} \leftarrow 5_{2,4}$ $5_{4,2} \leftarrow 6_{2,5}$ $6_{4,3} \leftarrow 7_{2,6}$ $7_{4,4} \leftarrow 8_{2,7}$ $\vdots$

Quantum Filters: Expressions for P branch b-type Transitions				
Transition Type	Limits	$\Delta K_p, \Delta K_o$	Example Transitions	
$J'_{K'_p, J'-K'_p} \leftarrow J''_{K''_p, J''-K''_p+1}$	$J'' \geq 3$ $J'' = J' + 1$ $J'' > K''_p + 1$ $K''_p \geq 1$ $K''_p = K'_p - 1$	$K''_p: +1$ $K''_o: -3$	$2_{2,0} \leftarrow 3_{1,3}$ $3_{2,1} \leftarrow 4_{1,4}$ $4_{2,2} \leftarrow 5_{1,5}$ $5_{2,3} \leftarrow 6_{1,6}$ $\vdots$	$3_{3,0} \leftarrow 4_{2,3}$ $4_{3,1} \leftarrow 5_{2,4}$ $5_{3,2} \leftarrow 6_{2,5}$ $6_{3,3} \leftarrow 7_{2,6}$ $\vdots$
$J'_{K'_p, J'-K'_p+1} \leftarrow J''_{K''_p, J''-K''_p}$	$J'' \geq 3$ $J'' = J' + 1$ $J'' > K''_p + 1$ $K''_p \geq 1$ $K''_p = K'_p - 1$	$K''_p: +1$ $K''_o: -1$	$2_{2,1} \leftarrow 3_{1,2}$ $3_{2,2} \leftarrow 4_{1,3}$ $4_{2,3} \leftarrow 5_{1,4}$ $5_{2,4} \leftarrow 6_{1,5}$ $\vdots$	$3_{3,1} \leftarrow 4_{2,2}$ $4_{3,2} \leftarrow 5_{2,3}$ $5_{3,3} \leftarrow 6_{2,4}$ $6_{3,4} \leftarrow 7_{2,5}$ $\vdots$

**Quantum Filters: Expressions for P branch c-type Transitions**

Transition Type	Limits	$\Delta K_p, \Delta K_o$	Example Transitions	
$J'_{K'_p, J'-K'_p} \leftarrow J''_{K''_p, J'-K''_p}$	$J'' \geq 3$ $J'' = J' + 1$ $J'' > K''_p + 1$ $K''_p \geq 1$ $K''_p = K'_p - 1$	$K''_p: +1$ $K''_o: -2$	$2_{2,0} \leftarrow 3_{1,2}$ $3_{2,1} \leftarrow 4_{1,3}$ $4_{2,2} \leftarrow 5_{1,4}$ $5_{2,3} \leftarrow 6_{1,5}$ $\vdots$	$3_{3,0} \leftarrow 4_{2,2}$ $4_{3,1} \leftarrow 5_{2,3}$ $5_{3,2} \leftarrow 6_{2,4}$ $6_{3,3} \leftarrow 7_{2,5}$ $\vdots$
$J'_{K'_p, J'-K'_p+1} \leftarrow J''_{K''_p, J'-K''_p+1}$	$J'' \geq 3$ $J'' = J' + 1$ $J'' > K''_p + 1$ $K''_p \geq 1$ $K''_p = K'_p - 1$	$K''_p: +1$ $K''_o: -2$	$2_{2,1} \leftarrow 3_{1,3}$ $3_{2,2} \leftarrow 4_{1,4}$ $4_{2,3} \leftarrow 5_{1,5}$ $5_{2,4} \leftarrow 6_{1,6}$ $\vdots$	$3_{3,1} \leftarrow 4_{2,3}$ $4_{3,2} \leftarrow 5_{2,4}$ $5_{3,3} \leftarrow 6_{2,5}$ $6_{3,4} \leftarrow 7_{2,6}$ $\vdots$

## ALGORITHM EXAMPLE

The following example works through the automated fit searching algorithm that is employed in DAPPERS. This example is structured such that the reader can reproduce the same calculations on their own while following along. This example highlights fitting real data from the microwave chirped-pulse spectrum of trifluoroacetic anhydride<sup>5</sup> by taking the user step-by-step through the algorithm. In accordance with the fact that DAPPERS fit searching algorithm is optimized for Quantum Filtered progressions (as previously defined), this example fits the J1J Quantum Filtered progression between 6.0 and 9.5 GHz. It should be noted that DAPPERS is capable of performing the same calculation outlined in this example in several milliseconds.

### STEP 0):

Step 0 is the only manual step of the fit searching process. In this step, the user specifies which transitions to search for. An example of the predicted transitions that a user might have selected from the .cat file through the application of both a Quantum Filter and frequency limits is shown below. These transitions will thus forth be referred to as the “predicted transitions”.

$\nu_{pred}$ (MHz)	Transition
6535.431	$7_{1,7} \leftarrow 6_{0,6}$
7243.822	$8_{1,8} \leftarrow 7_{0,7}$
7948.544	$9_{1,9} \leftarrow 8_{0,8}$
8652.944	$10_{1,10} \leftarrow 9_{0,9}$
9360.067	$11_{1,11} \leftarrow 10_{0,10}$

Additionally, the user must manually set the starter, ratio test, and derivative ratio test windows before searching for fits. These three windows are defined in detail in the “Search for Fits” section of this documentation. In this example, values of 20 MHz, 3.0 MHz, and 0.8 MHz will be used for the starter, ratio test, and derivative ratio test windows respectively.



**STEP 1):**

Once the predicted frequencies have been selected, the user will press the “Find Fits” button in the “Search for Fits” section of the main DAPPERS window to initiate the fit searching algorithm. For the first predicted transition ( $7_{1,7} \leftarrow 6_{0,6}$ ), the algorithm will apply the starter test by adding and subtracting 20 MHz (the starter window) from the guess frequency. Because this is the first transition the algorithm is searching for, the guess frequency is set to the first predicted transition (6535.431 MHz). If there are any experimental peaks within the range of  $6535.431 \pm 20$  MHz, they are assigned to  $7_{1,7} \leftarrow 6_{0,6}$  as the first frequency in separate, respective potential fits as shown in the table below. For this example, three experimental peaks met this criterion (6517.642, 6536.638, and 6550.997 MHz) and are assigned accordingly. The table below also shows the predicted frequency, the guess frequency, and the difference between the experimental and guess frequencies. Throughout this example, rows that are highlighted in green will indicate that a new experimental frequency has been added to the corresponding fit.

<b>Fit</b>	<b><math>\nu_{exp}</math> (MHz)</b>	<b><math>\nu_{pred}</math> (MHz)</b>	<b><math>\nu_{guess}</math> (MHz)</b>	<b><math>\nu_{exp} - \nu_{guess}</math> (MHz)</b>	<b>Transition</b>
1	6517.642	6535.431	6535.431	-17.789	$7_{1,7} \leftarrow 6_{0,6}$
2	6536.638	6535.431	6535.431	-1.207	$7_{1,7} \leftarrow 6_{0,6}$
3	6550.997	6535.431	6535.431	15.566	$7_{1,7} \leftarrow 6_{0,6}$

**Step 2)**

The algorithm will now apply the ratio test to each of the potential fits generated in step 1. First, a guess frequency will be calculated for each of these three potential fits using the below equation:

$$v_2^{guess} = v_1^{Obs} \left[ \frac{v_2^{Pred}}{v_1^{Pred}} \right]$$

where  $v_1^{Pred}$  is the first predicted transition's frequency (6535.431 MHz),  $v_2^{Pred}$  is the second predicted transition's frequency (7243.822 MHz), and  $v_1^{Obs}$  is the experimental peak found in step 1. If there are any experimental peaks within the range of  $v_2^{guess} \pm 3.0$  MHz (ratio test window), they are each assigned as the second frequency in each potential fit respectively as shown in the table below. If there are no experimental frequencies within this range for any of the fits found in step one, the potential fit will be removed and forgotten assuming the advanced setting, "Max Skip", is set to zero (as it is by default).

The table below shows the results of the ratio test for this example. Throughout this example, rows highlighted in red indicate that a new experimental frequency was not found and that the corresponding potential fit will be removed from consideration.

Fit	$v_{exp}$ (MHz)	$v_{pred}$ (MHz)	$v_{guess}$ (MHz)	$v_{exp} - v_{guess}$ (MHz)	Transition
1	6517.642	6535.431	6535.431	-17.789	$7_{1,7} \leftarrow 6_{0,6}$
	7225.417	7243.822	7224.105	1.312	$8_{1,8} \leftarrow 7_{0,7}$
2	6536.638	6535.431	6535.431	-17.789	$7_{1,7} \leftarrow 6_{0,6}$
	NONE	7243.822	7245.160	NONE	$8_{1,8} \leftarrow 7_{0,7}$
3	6550.997	6535.431	6535.431	15.566	$7_{1,7} \leftarrow 6_{0,6}$
	7261.994	7243.822	7261.075	0.919	$8_{1,8} \leftarrow 7_{0,7}$

### Step 3)

The algorithm will now apply the derivative ratio test to the potential fits generated in step 2. First, a guess frequency will be calculated for both of the remaining potential fits using the below equation:

$$\nu_N^{guess} = (\nu_{N-1}^{Obs} - \nu_{N-2}^{Obs}) \left[ \frac{\nu_N^{Pred} - \nu_{N-1}^{Pred}}{\nu_{N-1}^{Pred} - \nu_{N-2}^{Pred}} \right] + \nu_{N-1}^{Obs}$$

where  $\nu_{N-2}^{Pred}$  is the first predicted transition's frequency (6535.431 MHz),  $\nu_{N-1}^{Pred}$  is the second predicted transition's frequency (7243.822 MHz),  $\nu_N^{Pred}$  is the third predicted transition's frequency (7948.544 MHz),  $\nu_{N-2}^{Obs}$  is the first experimental peak in the potential fit (found in step 1), and  $\nu_{N-1}^{Obs}$  is the second experimental peak in the potential fit (found in step 2). If there are any experimental peaks within the range of  $\nu_N^{guess} \pm 0.8$  MHz (derivative ratio test window), they are each assigned as the third frequency in the potential fit respectively as shown in the table below. If there are no experimental frequencies within the range of  $\nu_2^{guess} \pm 3.0$  MHz for either of the fits found in step two, the potential fit will be removed and forgotten.

Fit	$\nu_{exp}$ (MHz)	$\nu_{pred}$ (MHz)	$\nu_{guess}$ (MHz)	$\nu_{exp} - \nu_{guess}$ (MHz)	Transition
1	6517.642	6535.431	6535.431	-17.789	$7_{1,7} \leftarrow 6_{0,6}$
	7225.417	7243.822	7224.105	1.312	$8_{1,8} \leftarrow 7_{0,7}$
	7929.172	7948.544	7929.526	-0.354	$9_{1,9} \leftarrow 8_{0,8}$
3	6550.997	6535.431	6535.431	15.566	$7_{1,7} \leftarrow 6_{0,6}$
	7261.994	7243.822	7261.075	0.919	$8_{1,8} \leftarrow 7_{0,7}$
	NONE	7948.544	7969.309	NONE	$9_{1,9} \leftarrow 8_{0,8}$

**Step 4)**

For the fourth predicted transition, the algorithm will again apply the derivative ratio test as described in step 3. There are three experimental peaks within the range of the resulting guess frequency for the only fit that remains from step 3 ( $8632.605\text{MHz} \pm 0.8\text{ MHz}$ ), so the single fit splits into 3 new fits as shown in the table below.

<b>Fit</b>	<b><math>\nu_{exp}</math> (MHz)</b>	<b><math>\nu_{pred}</math> (MHz)</b>	<b><math>\nu_{guess}</math> (MHz)</b>	<b><math>\nu_{exp} - \nu_{guess}</math> (MHz)</b>	<b>Transition</b>
1	6517.642	6535.431	6535.431	-17.789	$7_{1,7} \leftarrow 6_{0,6}$
	7225.417	7243.822	7224.105	1.312	$8_{1,8} \leftarrow 7_{0,7}$
	7929.172	7948.544	7929.526	-0.354	$9_{1,9} \leftarrow 8_{0,8}$
	8631.853	8652.944	8632.605	-0.752	$10_{1,10} \leftarrow 9_{0,9}$
4	6517.642	6535.431	6535.431	-17.789	$7_{1,7} \leftarrow 6_{0,6}$
	7225.417	7243.822	7224.105	1.312	$8_{1,8} \leftarrow 7_{0,7}$
	7929.172	7948.544	7929.526	-0.354	$9_{1,9} \leftarrow 8_{0,8}$
	8632.039	8652.944	8632.605	-0.566	$10_{1,10} \leftarrow 9_{0,9}$
5	6517.642	6535.431	6535.431	-17.789	$7_{1,7} \leftarrow 6_{0,6}$
	7225.417	7243.822	7224.105	1.312	$8_{1,8} \leftarrow 7_{0,7}$
	7929.172	7948.544	7929.526	-0.354	$9_{1,9} \leftarrow 8_{0,8}$
	8632.465	8652.944	8632.605	-0.140	$10_{1,10} \leftarrow 9_{0,9}$

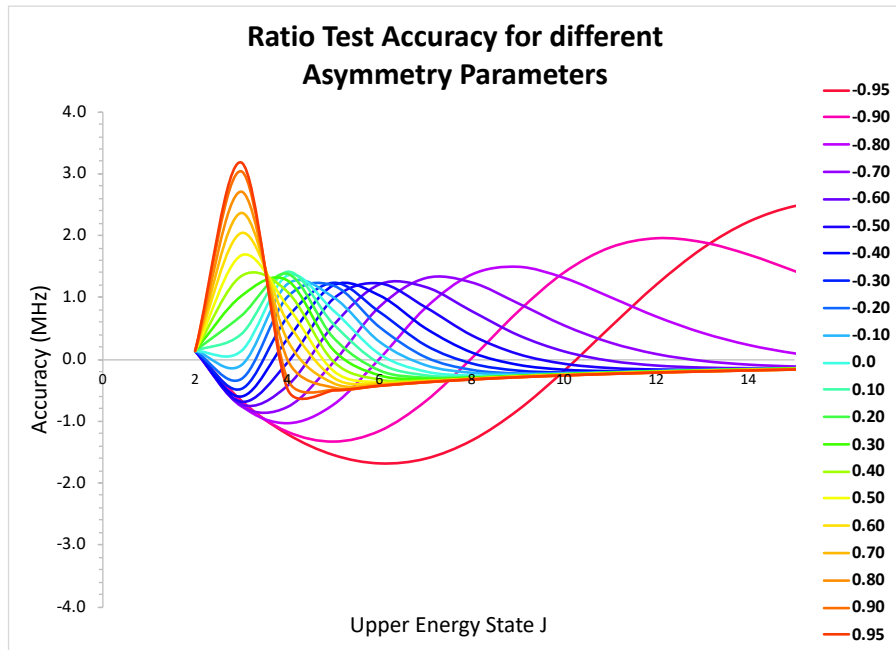
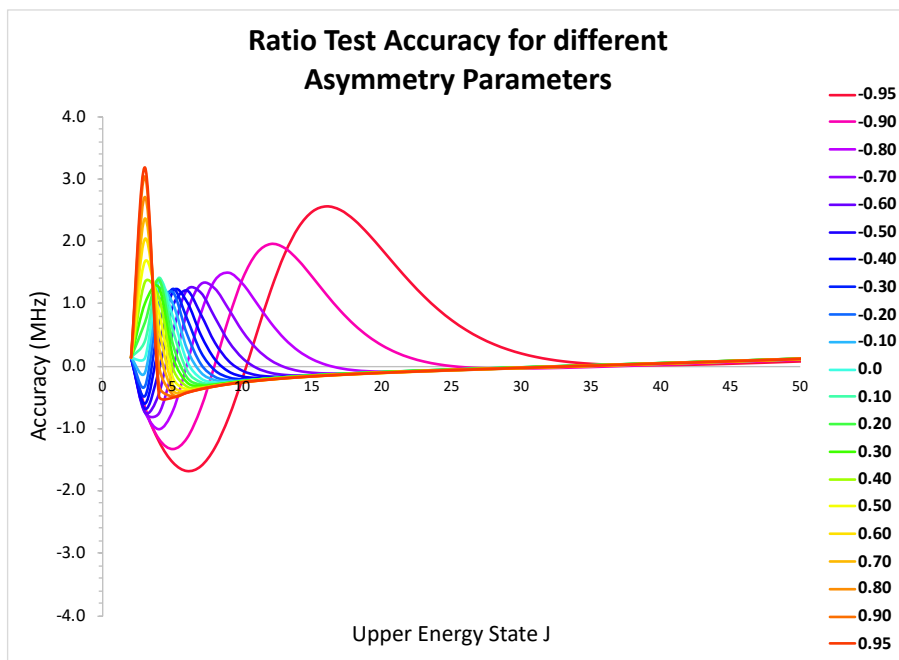
**Step 5)**

For the fifth and final predicted transition, the algorithm will again apply the derivative ratio test as described in step 3. The results are shown in the table below.

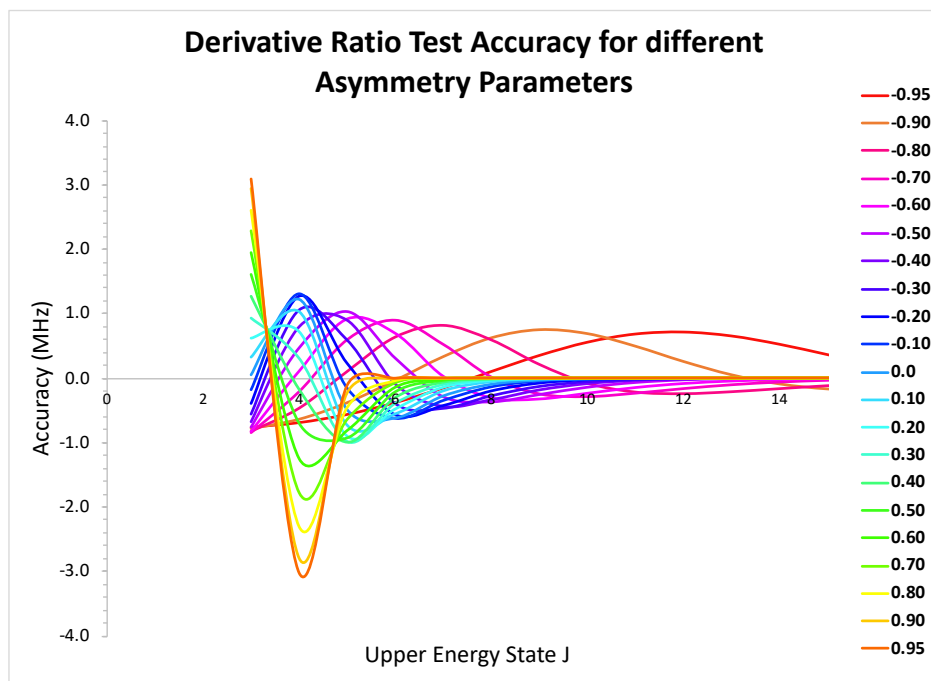
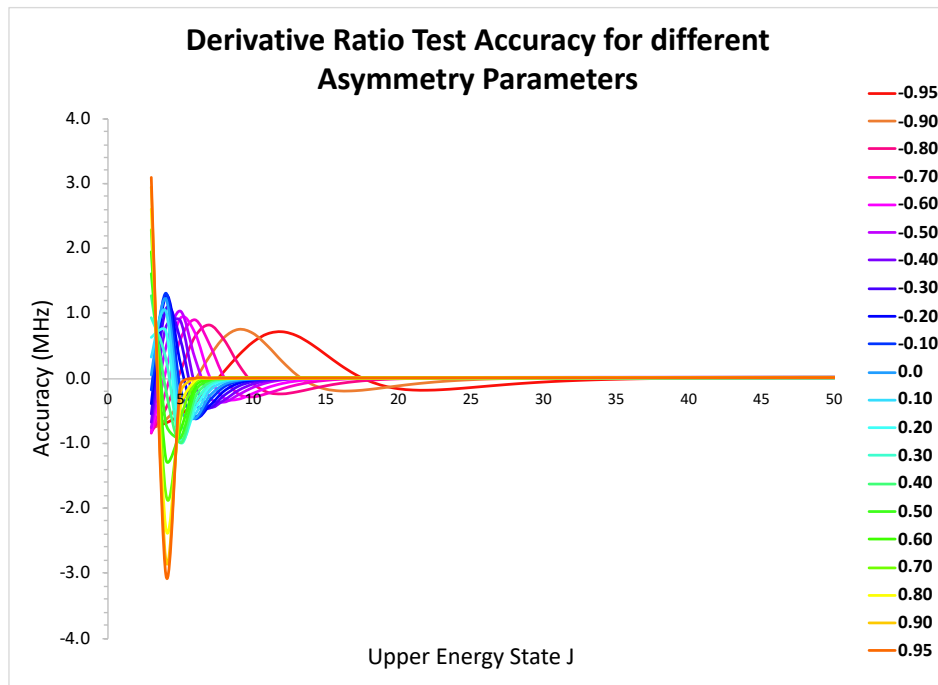
Fit	$\nu_{exp}$ (MHz)	$\nu_{pred}$ (MHz)	$\nu_{guess}$ (MHz)	$\nu_{exp} - \nu_{guess}$ (MHz)	Transition
1	6517.642	6535.431	6535.431	-17.789	$7_{1,7} \leftarrow 6_{0,6}$
	7225.417	7243.822	7224.105	1.312	$8_{1,8} \leftarrow 7_{0,7}$
	7929.172	7948.544	7929.526	-0.354	$9_{1,9} \leftarrow 8_{0,8}$
	8631.853	8652.944	8632.605	-0.752	$10_{1,10} \leftarrow 9_{0,9}$
	9336.933	9360.067	9337.250	-0.317	$11_{1,11} \leftarrow 10_{0,10}$
4	6517.642	6535.431	6535.431	-17.789	$7_{1,7} \leftarrow 6_{0,6}$
	7225.417	7243.822	7224.105	1.312	$8_{1,8} \leftarrow 7_{0,7}$
	7929.172	7948.544	7929.526	-0.354	$9_{1,9} \leftarrow 8_{0,8}$
	8632.039	8652.944	8632.605	-0.566	$10_{1,10} \leftarrow 9_{0,9}$
	9336.933	9360.067	9337.623	-0.690	$11_{1,11} \leftarrow 10_{0,10}$
5	6517.642	6535.431	6535.431	-17.789	$7_{1,7} \leftarrow 6_{0,6}$
	7225.417	7243.822	7224.105	1.312	$8_{1,8} \leftarrow 7_{0,7}$
	7929.172	7948.544	7929.526	-0.354	$9_{1,9} \leftarrow 8_{0,8}$
	8632.465	8652.944	8632.605	-0.140	$10_{1,10} \leftarrow 9_{0,9}$
	NONE	9360.067	9338.477	NONE	$11_{1,11} \leftarrow 10_{0,10}$

At this stage, the fit searching algorithm is done and has found two potential fits that match the user-inputted search window criteria. If the user chooses to run these fits with SPFIT (by pressing “Run Fits”), they will find that the RMS values of fit 1 and 4 are 0.6 and 64.4 kHz respectively when fit to a Watson-a reduced rigid-rotor Hamiltonian. When the algorithm finds one or more potential fits, you can run these fits with SPFIT in the Run Fits window. If the fits look reasonable, move them to the fit bank and select other Quantum Filtered progressions to continue assigning the spectrum.

## ALGORITHM ACCURACY PLOTS FOR J1J TRANSITIONS



The top plot shows the ratio test accuracy for different asymmetry parameters from  $J=2$  to  $J=50$  for J1J transitions. The bottom plot shows the same information, but for J ranging between 2 and 15.



The top plot shows the derivative ratio test accuracy for different asymmetry parameters from  $J=3$  to  $J=50$  for  $J1J$  transitions. The bottom plot shows the same information, but for  $J$  ranging between 3 and 15.