Appendix C

Spectral Assignment

C.1 The CALPGM Suite

The CALPGM suite, developed by Pickett et al. (1998) at JPL, was designed to fit spectral information to quantum mechanical models to both obtain information about the structure of the molecule and to enable predictions in other spectral regions. Detailed information for the files associated with the CALPGM programs is available at `http://spec.jpl.nasa.gov`. The programs included in this suite can process the ground state and up to 99 vibrationally excited states, and can be used in conjunction with the Submillimeter Analysis Program (SMAP, described below) to assign spectral data.

The SPCAT program performs spectral predictions from a set of user-defined parameters that are defined in two input files, namely the .var file and the .int file. These parameters include molecule-specific information such as the dipole moment, rotational constants, distortion constants, and partition function. Other parameters include temperature, frequency range, and quantum number range as well as the type of reduction to be used for the Hamiltonian. Line positions and strengths are then calculated based on these user-defined parameters. Initial predictions are written to a .cat file.

The .cat file can be merged with spectral assignments with the CALMRG program.

This program produces a .mrg file that is formatted similarly to the .cat file, but markers distinguish between transitions that have been assigned and those that are predictions.

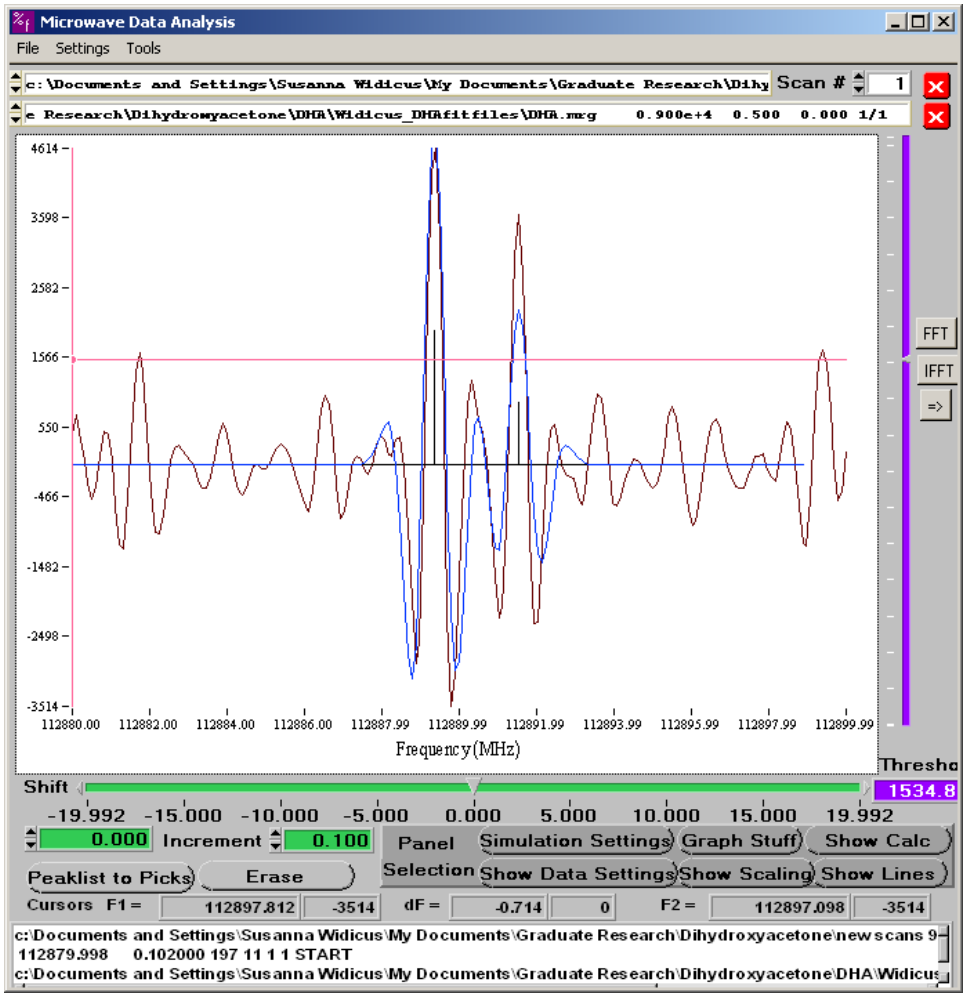
The SPFIT program utilizes files containing the frequency, intensity, and quantum numbers (J, K_a, K_c, ν) assigned for transitions to fit such spectroscopic information by a least squares analysis using a user-defined reduction of the Hamiltonian to a user-defined set of rotational and centrifugal distortion constants. The output of the SMAP program is formatted appropriately for a .lin file, which is the input file for SPFIT and contains the quantum numbers and frequencies for each of the assigned spectral lines. The initial spectral parameters are read from a .par file, which is identical to the .var file used by SPCAT. Both of these files are overwritten with the new spectral parameters each time the SPFIT program is run.

The MOIAM and IAMCALC programs can be used to generate spectral parameters for molecules with internal rotation groups. The Z-Matrix for the molecule and an initial estimate of the barrier to internal rotation are entered into a .inp file. An internal rotation group has n equivalent structures, and the MOIAM program generates coordinates for each of the atoms in the molecule for each structure. This information is then used to generate a set of parameters for an internal axis system Hamiltonian with the IAMCALC program. These parameters are written to a .par file, and these parameters can be used as the input to SPCAT in a .var file.

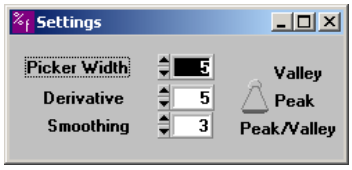
An iterative process is used to analyze spectral data. Literature or *ab initio* information is used to generate a predicted spectrum with the SPCAT program. The SMAP program is then used to compare the experimental spectrum to this prediction and to assign lines accordingly. The SPFIT program is then used to calculate a new set of parameters after spectral assignments are made.

C.2 The Submillimeter Analysis Program

The graphical interface used for spectral analysis is the Submillimeter Analysis Program (SMAP) developed by Brian Drouin from the Microwave, Millimeter, and Submillimeter Spectroscopy Laboratory at JPL. The .lwa files saved during scanning can be loaded into this program, which plots the xy data as either a line or a stick spectrum. Line spectra are most commonly used for line assignment purposes. The buttons in the main window for the SMAP program can be selected to bring up popup control windows for different aspects of the program:

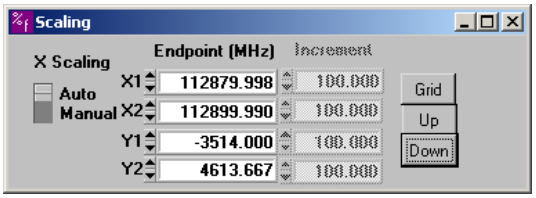


Spectral data files and spectral prediction catalog files can be loaded with the 'Open Data File' and 'Open Catalog' commands at the top of the screen. In the example shown above, the experimental spectrum is shown in black while the prediction is shown in blue. Each saved scan in a given file can be loaded by selecting the appropriate scan number at the top of the screen. The spectral data settings can be selected in the 'Show Data Settings' popup window:



The fifth derivative of the spectrum with a boxcar smoothing of n=3 is commonly used to remove the sinusoidal background from the spectral data. The 'FFT' and 'IFFT' options to the side of the spectral display window can also be used for this purpose.

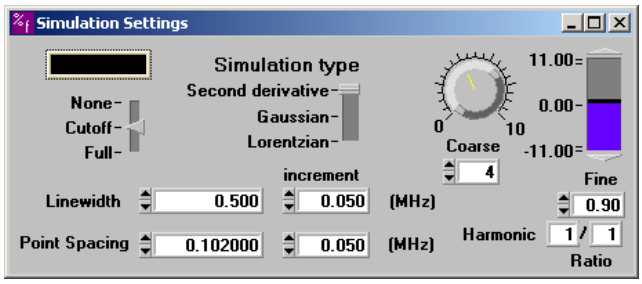
The xy scaling for the displayed spectrum can be adjusted in the 'Show Scaling' popup window:



The 'Up' and 'Down' buttons will shift to a new frequency window by an increment equal to the width of the current view. One can therefore scroll through the spectrum one window at a time, which is quite useful for line assignment. In addition, left-clicking in the spectral display window and dragging the mouse creates a selection box that can be used for changing the spectral scale. Right-clicking will zoom in on the boxed area of the spectrum once the

desired spectral window is selected. Double-clicking will then set the scaling back to the previous setting.

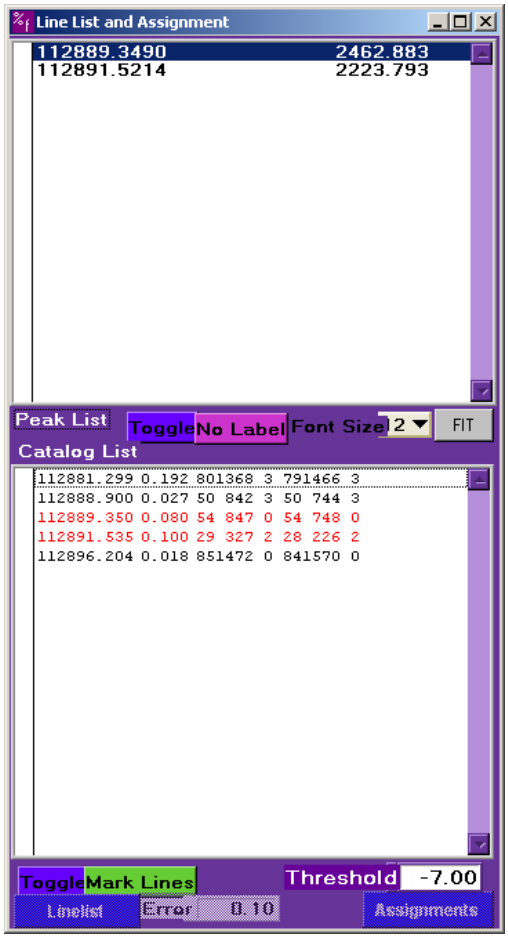
A total of eight different catalogs can be loaded with the current version of the program. The parameters of the predicted spectrum are controlled by the 'Simulation Settings' popup window:



Changes implemented in this window only change the settings for the catalog that is selected at that time, and so different settings can be used for different catalogs. The course and fine adjustments can be used to scale the intensity of the prediction relative to the spectral data. The simulation type can be chosen to match the spectral data line shape (flow cell spectra are second derivative spectra). The linewidth and point spacing can also be adjusted to match the spectral data. The prediction appears as a stick spectrum until the toggle is changed from 'None' to either 'Cutoff' or 'Full.' The cutoff option loads only the predicted spectral features in the window displayed on the screen, while the full option loads the entire prediction. The harmonic option can be used to select a different harmonic of the observed frequency, which is particularly useful when tunable frequency sources are used.

Spectral assignment is performed by comparing the simulated spectrum to the laboratory spectral data. The simulation can be shifted in frequency by using the green control boxes in the lower left corner of the main window. Once the simulation is shifted to match the observed spectral lines, the threshold option to the right of the display window should be

adjusted such that the desired spectral line is selected by the peak picker. The 'Show Lines' popup window shows the selected lines from the experimental data in the top window, and the predicted lines and their respective quantum numbers in the bottom window:



Clicking the 'Toggle' button in the bottom window will select all of the lines from the simulation, making them eligible for assignment. Clicking the 'Mark Lines' button will select the experimental lines that match these predictions to within the error value set at the bottom of the window (this value is usually set to the experimental resolution, 0.1 MHz). Clicking the 'Assignments' button at this point will write the quantum numbers from the prediction and the frequency of the observed line to the selected .lin file. The threshold

option in the lower right corner of this window can be used to set a minimum intensity threshold for assigned lines. No lines weaker than this threshold value will be included in the written assignments.

While the initial prediction is a .cat file, subsequent predictions are loaded in .mrg files. The lines that have been experimentally assigned are displayed in red font in the 'Show Lines' popup window and are not eligible for assignment. This ensures that the same set of quantum numbers is not assigned to multiple frequencies in a given spectral line file.

The SMAP program also includes a calculator option that can be accessed in the 'Show Calc' popup window. Mathematical manipulation of spectral data (i.e., the current scan, other scans, simulations, etc.) can be performed, and the results can be loaded over the displayed spectral data: