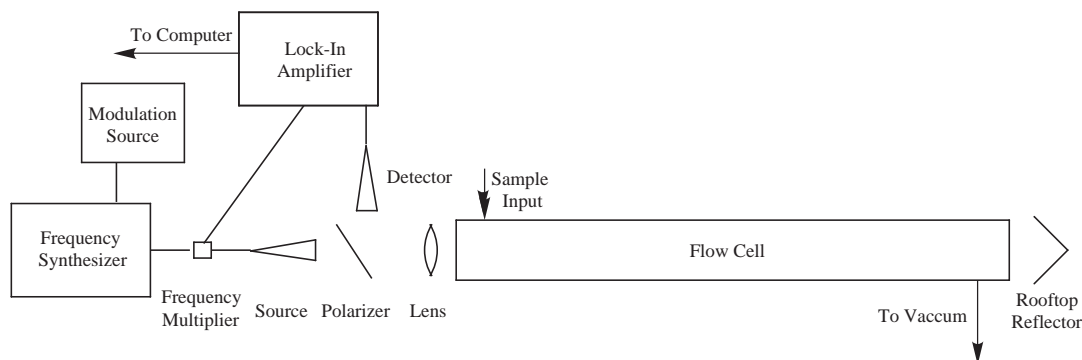


Appendix B

Flow Cell Operation

B.1 Instrumentation

The Caltech Direct Absorption Flow Cell Spectrometer is controlled by the Submillimeter Spectroscopy Scanning Program software developed by the Microwave, Millimeter, and Submillimeter Spectroscopy Laboratory at JPL. A general schematic diagram of the experimental setup and detailed information on the instrumentation are shown below:



B.2 Spectrometer Startup Procedure

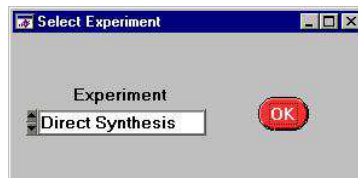
1. Turn on the frequency synthesizer and the lock-in amplifier.
2. Confirm that none of the power supply connections are connected to the multiplier chain

Table B.1: Caltech Direct Absorption Flow Cell Spectrometer Instrumentation

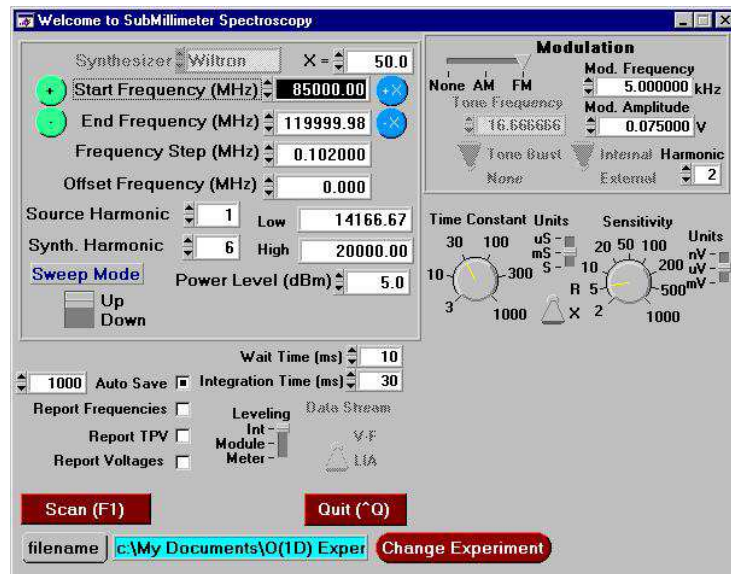
Equipment	Specifications
Frequency Synthesizer	Wiltron 6747A-20 Swept Frequency Synthesizer
Modulation Source	lock-in amplifier internal modulation source
Lock-In Amplifier	Stanford Research Systems SR830 DSP Lock-In Amplifier
Multiplier Chain	Miteq MAX2M2040 Active Frequency Doubler Miteq JP2-26004000-110-20SP Power Amplifier Virginia Diodes WR-9.3x3 Frequency Tripler Spacek SPW-18-14 Power Amplifier Virginia Diodes WR-3.4x3 Frequency Tripler (1 mm)
Power Supplies	Harrison dual power supply (± 8 V for Miteq Amplifier) HP dual output power supply (± 15 V for Miteq Doubler; ± 12 V for Spacek Amplifier)
Source	waveguide horn matched to multiplier chain output flange
Polarizer	wire grid
Lens	teflon
Cell	d = 0.05 m, l = 2.44 m (3 mm) d = 0.035 m, l = 2.56 m (1 mm)
Rooftop Reflector	gold coating
Detector	Pacific Millimeter WD GaAs Schottky diode (3 mm) 4 K InSb hot electron bolometer (1 mm)
Computer	930 MHz Pentium III; National Instruments GPIB card

components. Turn on the power supplies and then connect the leads to the appropriate multiplier chain components, attaching the negative leads first, followed by the positive leads. Care should be taken, as connecting the leads in the opposite order could short the multipliers and amplifiers.

3. Double click on the “JPL Scanning Program” icon on the desktop to start the Submillimeter Spectroscopy Scanning Program. Click ‘ok’ to select a Direct Synthesis experiment:



The next window is the main control window for the scanning program. The experimental parameters for the spectrometer are entered here:



4. One of the lock-in amplifier settings must be changed before beginning an experiment so as to establish communication between the computer and the lock-in.

B.3 Spectrometer Parameters

- The frequency range to be covered by the experiment is set with the start and end frequency options by either typing the desired frequencies in the boxes, or by clicking on the blue '+X' and '-X' buttons to change the start and end frequencies, respectively, by the increment entered in the 'X=' box.
- The frequency step can be changed to the desired experimental resolution.
- The source harmonic setting should always remain as 1, while the synthesizer harmonic should be changed to the harmonic of the multiplier chain in use (in this example, the 3

mm multiplier chain is in use, so the output frequency is the 6th harmonic of the synthesizer frequency; for the 1 mm multiplier chain, the synthesizer harmonic should be set to 18).

- The power level option controls the output power level of the frequency synthesizer and should be optimized experimentally such that the multiplier chain is driven with the optimum input power.
- The scanning program will save the spectrum in a temporary file if the ‘Auto Save’ option is selected. The number of points to be taken between each auto save should be entered in the box next to this option.
- The wait time is the amount of time that the program waits after the frequency is stepped before beginning to integrate the lock-in signal. The integration time is the amount of time over which the program integrates the lock-in signal before stepping the frequency.
- The modulation settings control the internal modulation of the lock-in amplifier. These parameters should be optimized to give the best signal-to-noise ratio without significantly broadening the linewidths. AM modulation and a harmonic setting of ‘1’ should be used when monitoring the power, while FM modulation and a harmonic setting of ‘2’ should be used when recording spectral data.
- The lock-in amplifier phase setting should be set manually on the front panel of the instrument. This parameter is not included in the control software so that it can be changed during an experiment without stopping the scan.
- The time constant and sensitivity settings for the lock-in can also be controlled from the main window. The optimum time constant for all flow cell experiments is 30 ms. The

sensitivity should be set to the dynamic range of the spectrometer, which is often governed by the strength of the observed lines. The lock-in signal is set to either ‘R’ (for power scans) or ‘X’ (for spectral scans).

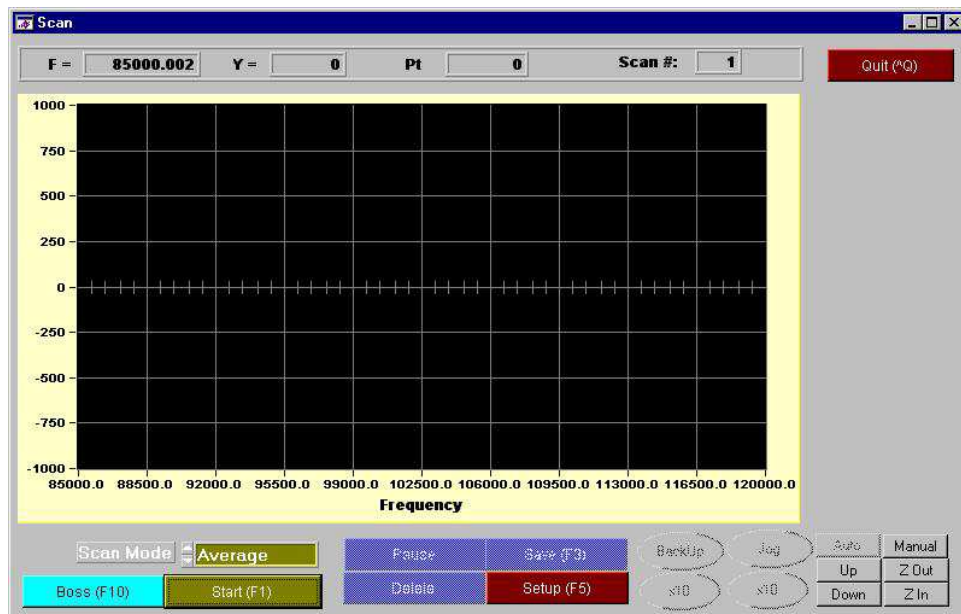
- The file in which the spectral data is recorded is set by clicking on the ‘filename’ button and choosing the desired directory and filename.

B.4 Spectrometer Alignment Procedure

1. Set the start frequency to the frequency in the middle of your desired scanning range.
2. Switch to AM modulation and decrease the harmonic number to 1. Switch to R (rather than X) for the lock-in setting. Generally the sensitivity should be set to 1000 mV, but this setting should be adjusted to the appropriate value to give a fluctuating lock-in signal (i.e., such that the spectrometer is sensitive to noise). An attenuator may be required if the power is overloading the lock-in when it is on the least sensitive setting.
3. Note the modulation setting (in volts). Unhook the BNC cable that connects the lock-in to the ‘Ext FM’ input on the synthesizer. Attach the BNC cable from the ‘Ext. AM’ input on the synthesizer to the lock-in. Press the ‘return to local’ button on the Wiltron. Then press the ‘measure FM from dev/ measure AM depth’ button on the synthesizer until ‘measure AM depth’ is selected. Set the modulation setting to 0.775 V (or an appropriate voltage resulting in a ‘modulation time’ readout on the Wiltron close to 99%).
4. Place all optical components in the appropriate positions and roughly align them. At this point some signal should be registering on the ‘Channel One’ readout on the lock-in. Adjust

the x, y, and z positions of each component to maximize the power by either adjusting the positions of the mounts or by adjusting the micrometers on the translation stages. It is best to begin with the lens and polarizer, followed by the source and detector. Iteratively align each component until all are optimized. If the rooftop is in use, monitor the output of ‘Channel One’ on the lock-in with a voltmeter and carefully align the rooftop (the tilt stage is the most important adjustment here). The voltmeter will also be required if it is a 1 mm experiment, as only single-pass experiments are possible when the InSb bolometer detector is in use, and so the detector will be on the opposite end of the cell from the instrumentation.

5. Set the scanning increment to a large value (generally between 10 and 50 MHz). Change the filename to the appropriate file. Change the range to the desired frequency range. Click on the ‘scan’ button to go to the scanning window:



Click the ‘start’ button to begin a scan. Click the ‘Auto’ button to auto scale the window. After one scan across the full range, click ‘Save,’ enter any comments, and click ‘save’ again.

Note the regions in which there was sufficient power. Click ‘Setup’ to return to the main screen.

B.5 Spectral Acquisition Procedure

1. Change the sensitivity to $5\ \mu\text{V}$, the lock-in setting to X (rather than R), the modulation to FM, the harmonic number to 2, and the frequency step to 0.1 MHz. Set the frequency range to that which had sufficient power. Reconnect the FM BNC cable to the frequency synthesizer. Press the “return to local” button on the synthesizer and then change the option to ‘measure FM from DEV.’ Adjust the modulation amplitude to the previous setting. Regulate the sample pressure (see below).
2. Press ‘scan.’ Press ‘start’ on the scanning window to begin the scan. Once the scan reaches the upper frequency limit, the scanning direction will reverse and the scan will continue back to the start frequency. The forward and reverse scans will be averaged. This averaging will continue until the scan is saved or stopped. The current scan is displayed in yellow or magenta, depending on whether the scaling is changed after the scan begins. The averaged scan is offset above the current scan and is displayed in white. Clicking on the ‘Boss’ option loads the most recently saved scan onto the screen; this scan is displayed in green. There is a ‘save and continue’ option that allows the current state of the scan to be saved without stopping the scan.
3. Spectral lines are typically ~ 1 MHz FWHM and should have the characteristic second derivative shape. They should be well above noise level and should retrace on the reverse scan. Wide frequency coverage is often required before a line is observed, especially for

molecules with weak spectra. Once a line is observed, return to the main screen after saving the scan.

4. Set the start frequency to the exact center frequency of the line. Adjust the phase option on the lock-in until the signal in the ‘Channel One’ readout is maximized. Once the maximum is found, pressing the +/- 90 degrees buttons should reduce the signal to the noise level. Changing the phase by 180 degrees should result in the negative of the optimized signal.
5. Narrow the scanning range to a 5–10 MHz range around the line. Record a spectrum of the line at these instrument settings, and then adjust the modulation amplitude, modulation frequency, power level, and sample pressure, monitoring the change in the line intensity after each adjustment. Optimized values for the 3 mm and 1 mm experimental setups are shown in Table B.2. Once optimum parameters are found for a given experiment, return to the main screen and begin a large scan.

Table B.2: Optimized parameters for flow cell experiments.

Parameter	3 mm	1 mm
Phase	80 degrees	-80 degrees
Mod. Amplitude (V)	0.05 V	0.05 V
Mod. Frequency (kHz)	6 kHz	4 kHz
Power level	12 dBm	5 dBm

B.6 Sample Pressure and Temperature Regulation

The sample cell pressure should be optimized to give maximum signal strength without significant line broadening. Pressures on the order of ~ 30 mtorr are typical for such

experiments. The cell pressure is regulated by adjusting the valve between the cell and the pump. A needle valve can also be placed at the sample input port to further regulate the pressure. Gas sample lines should be directly attached to the input of the cell.

Liquid samples should be placed in either a ball flask (high vapor pressure) or a sparger (low vapor pressure). A ball flask can be attached directly to the cell input through use of an UltraTorr fitting, and direct pumping on the sample will set up ample pressure in the cell. For lower vapor pressure samples, however, a carrier gas should be bubbled through the sample to increase the amount of sample vapor in the cell. A sparger is used for this purpose. The carrier gas line should be attached to the sparger input, and the sparger output should be connected to the cell.

Solid samples should be placed directly in the cell by removing the endcap near the source (be cautious of the polarizer while doing this). Use of a sample boat often significantly reduces the transmitted power, and so aluminum foil should be used as a sample holder, as it can be formed to the shape of the cell. Be VERY cautious when first evacuating or venting the cell, as powdered samples are likely to scatter. If this does occur, the “flow cell squeegee” that is located in the lab (next to the vacuum cleaner) can be used to clean the sample from the cell walls.

Reduction of the cell temperature is often used to depopulate higher energy states for molecules with large partition functions. Baking out the cell is also sometimes necessary to remove adsorbed contaminants from the cell walls. The cell used in the 1 mm studies has a jacket around the inner cell that can be filled with liquid and appropriately cooled or heated. Water is most often used for this purpose, and a water recirculator is located under the cell, beneath the optics table. Fill the water reservoir before using the recirculator. Turn on the recirculator and monitor the water level, refilling when necessary until the

level does not change. Adjust the temperature to desired value. The heating system will run automatically, but the cooling system must be turned on separately if the desired temperature is below room temperature.

B.7 Spectral File Format

The spectral information saved during scanning is saved in the file designated in the filename box in the main control window. The file extension should be set to the ‘.lwa’ option. The file is a simple ASCII text file, with a format as follows:

```
DATE MM-DD-YYYY TIME hh:mm:ss
comment
start frequency  step frequency  number of points  1 1 1 START
Y1   Y2   Y3   Y4   ...   Yn
```

The header information is that which is recorded from the scanning program, and the Y_n 's are the signal intensities read from the lock-in amplifier at each frequency step. The information for each scan is appended to the end of a given file upon saving until the filename is changed in the scanning program.