Appendix A

Flygare Operation

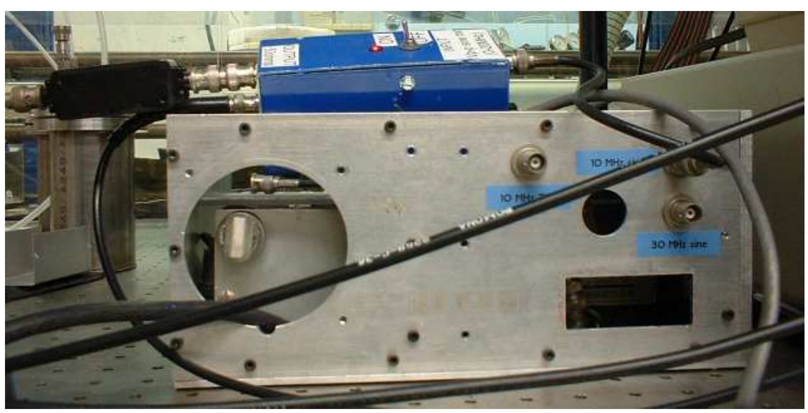
A.1 Instrumentation

The original FTMW instrument was moved to the Blake labs at Caltech in September 2000. Most of the instrumentation is that from the most recent upgrade of the spectrometer, which was performed by Dr. Tryggvi Emilsson and colleagues at the University of Illinois [21]. While much of the original instrumentation is still in use, some components have been upgraded, and more upgrades are planned for the near future. While many previous publications have described the specific instrumentation used with this instrument, none have presented the general operating procedures. This appendix is therefore a detailed outline for general use of this specific instrument and assumes a general knowledge of FTMW principles. Reference [21] should be consulted for more detailed information on the instrumentation, and the general FTMW principles are outlined in reference [20].

An FTMW instrument involves a pulsed molecular source and a pulsed microwave source. When an experiment begins, a valve is triggered, expanding a pulse of gas into the cavity. This expansion can occur either transversely or coaxially to the incident radiation (there are gate valves that act as pulsed valve feedthroughs at both the top and side of the instrument). A train of 16 microwave pulses is fired for each gas shot. The sample resides in the cavity for a finite amount of time, and the length of and spacing between the microwave pulses determines the extent to which each sample pulse is probed. The switch to the detector is closed when a microwave pulse is fired, and this switch remains closed until the majority of the radiation in the cavity has rung down. The molecules are excited by the radiation pulse, and the molecules de-excite to the ground state and emit radiation at their resonant frequencies. This emission occurs after the cavity has rung down, and the free induction decay is monitored by the detector.

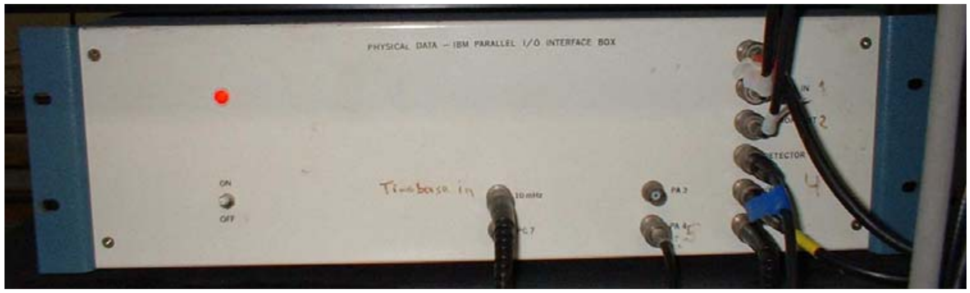
A.1.1 Instrument Control System

A very precise time base is required for control of each of the experimental aspects. This time base is provided by a rubidium clock that is housed in the metal box shown in the bottom of the picture below. This clock produces a 10 MHz sine wave signal that is then converted to two output signals by the blue filter box that is located on the top of the rubidium clock housing. The signals produced are a 30 MHz sine wave and a 10 MHz TTL pulse.



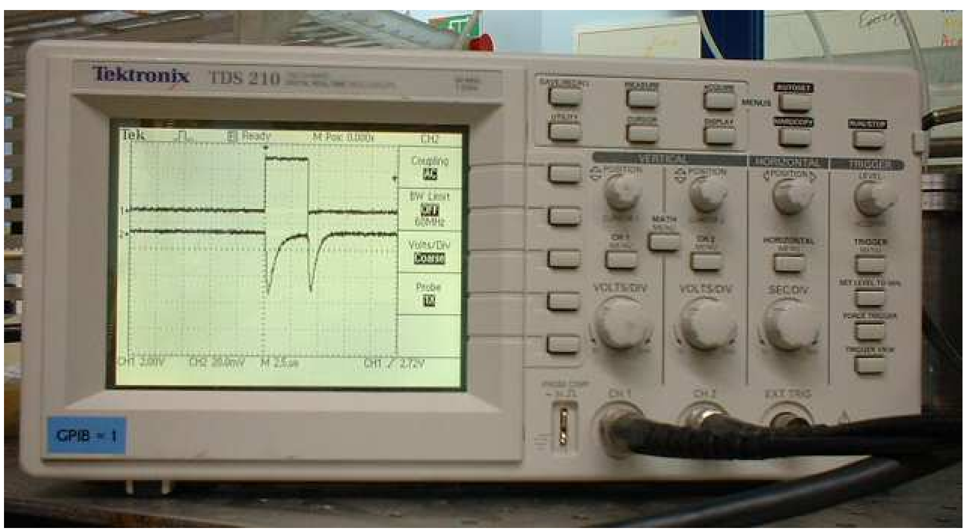
The 10 MHz TTL pulse is the timing signal for the instrument. This signal is the input to the "Physical Data–IBM Parallel I/O Interface Box," which communicates with

the computer and issues all of the control signals for the valve, mirrors, and microwave switches:



The 'detector' and 'μwave' output signals from the interface box control the switches for the detector and the microwave input into the cavity, respectively.

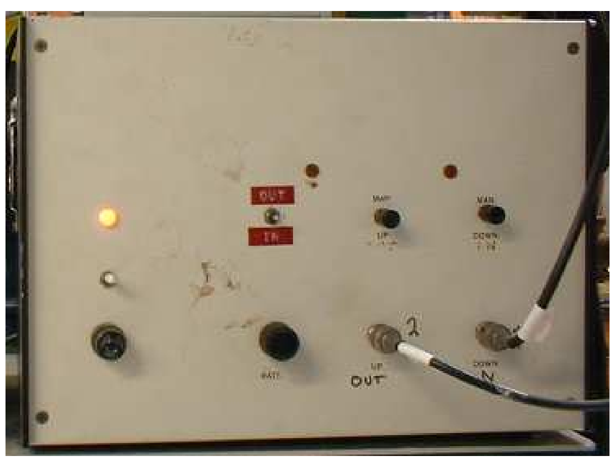
The 'scope' output signal from the interface box is identical to the microwave output signal and is the trigger used by the oscilloscope to monitor the cavity tuning. There are two channels displayed on this oscilloscope, the top signal being the trigger, and the bottom signal being the signal from the cavity:



The signal shape shown here is that observed when the cavity is properly tuned to the MO frequency. The first peak is due to the radiation that is backscattered from the waveguide and the mirror, while the second peak is due to the cavity ringdown. This wide microwave pulse is not one of the segments of the microwave pulse train, but rather is a signal produced by the spectrometer for the purposes of tuning. The train of microwave pulses can be observed on the oscilloscope if the scaling is changed appropriately.

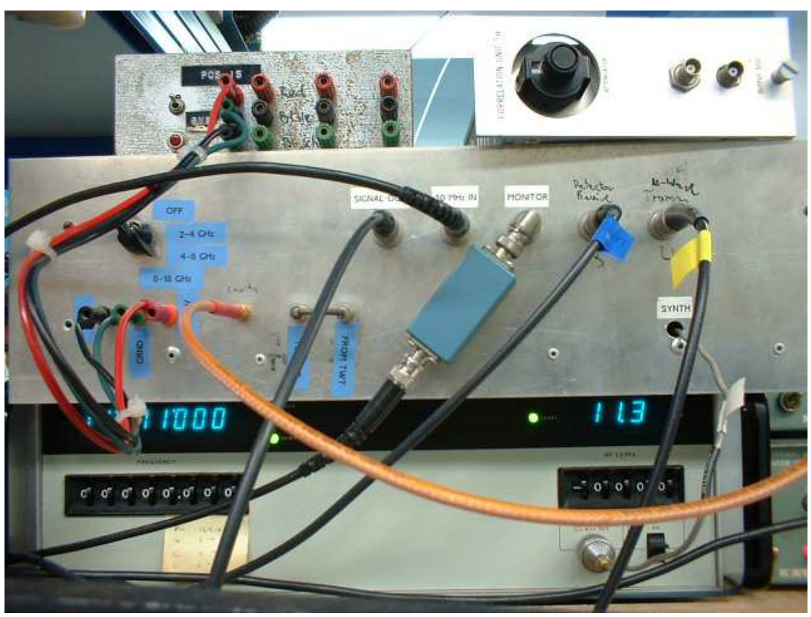
The 'valve' output signal from the interface box drives the voltage supply for the valve. The rep rate of the valve can be controlled by varying the voltage and capacitance:

The 'mirror in' and 'mirror out' output signals from the interface box drive the control for the step motor. One of the mirrors can be moved such that the cavity is tuned to the MO frequency. The step motor can also be controlled manually by the switches on the front of this control box:



Amplifiers are used to amplify the 30 MHz sine wave output of the timing circuit and the output signal from the cavity:

The MO signal is produced by the frequency synthesizer, which is the bottom instrument in the picture below. The metal box located on top of the frequency synthesizer contains the switches, detectors, and other microwave components. The power supply for this microwave box is the small box at the top of the equipment rack:



The output signal from the detectors is then routed to the "Quadruture Box," which is the metal box located at the top of the interface box equipment rack. The quadruture box downconverts the detected signal and sends it to the computer:

A.1.2 Gas Handling and Sample Delivery

The gas handling system is based on the design developed in Illinois [21]. A picture of the mixing manifold is shown below, and a schematic diagram is shown in Figure A.1:

This system involves four mass flow controllers, two of which are high-throughput for carrier gas delivery. The low-throughput flow meters can be used for gas samples or to

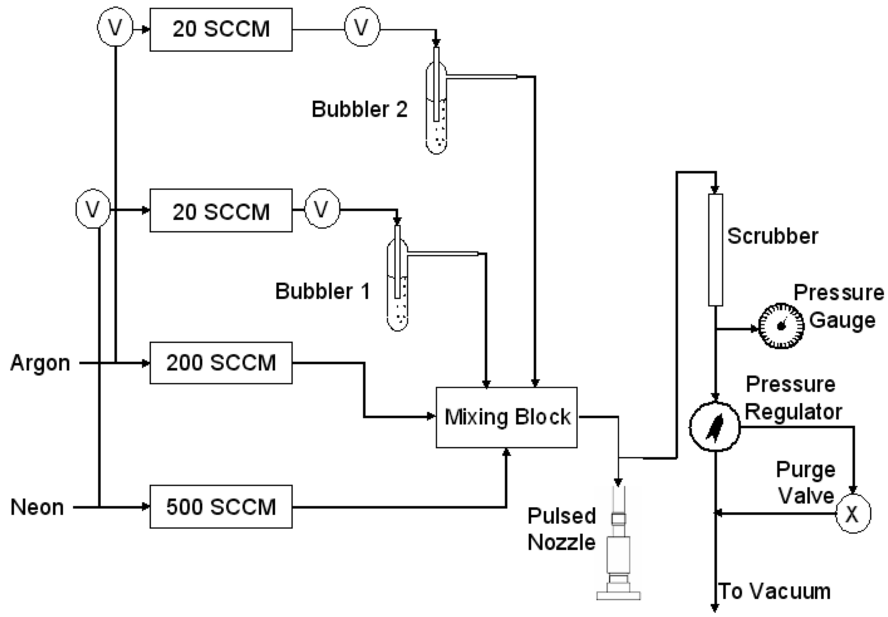


Figure A.1: A schematic diagram of the FTMW mixing manifold.

control the gas delivery to the bubblers for liquid samples. Experiments are typically conducted with flow rates of a few hundred SCCM of carrier gas and less than 10 SCCM of gas through the bubbler. The mass flow meters are controlled by a flow controller:

The valves (V) used in the mixing manifold are Hamilton HV plug valves. The two valves at the input of the flow controllers are four-port flow valves, while the two valves between the flow meters and bubblers are four-port loop valves. Details of the valve design and operation can be found at `http://www.hamiltoncompany.com/product/valve/valves.html`.

Teflon tubing connects the output of the mixing block with the valve. A tee-fitting is connected to the end of the metal valve assembly (described in detail below) with an O-ring fitting. Another O-ring fitting on this tee couples the tubing into the valve assembly. The tubing is inserted such that it is as close to the valve as possible without forming a complete seal. This allows the gas to flow through the tubing and up to the valve. The valve consumes gas when it is running; the excess gas flows around the end of the tubing and back through the valve assembly. The output goes through the scrubber and into the pressure regulator. This regulator is a diaphragm that has a control valve that can be used to adjust the pressure in the line and thus regulate the valve backing pressure. Turning the control valve on the pressure regulator clockwise will increase the backing pressure, turning it counter-clockwise will decrease the pressure, and turning it to a vertical position will hold the backing pressure at the current value. Backing pressures are typically on the order of 1–10 in. Hg above atmospheric pressure (1 in. Hg = 0.0334 atm).

A.1.3 Valve Assemblies

There are currently two valve assemblies that can be used with the instrument, one with six electrical feedthroughs and one with eight electrical feedthroughs. These valve assemblies utilize pulsed General Valves (see `http://www.parker.com/pneutron` for more information). The feedthroughs consist of a 1/4 inch metal tube inside of a 1/2 inch metal tube. Electrical leads for the valve and any accessories run through the space between these two tubes and are held in place with heat shrink. These leads are soldered to electrical feedthroughs that are on a circular metal disk that is welded to the inner tube and sealed to the outer tube by an UltraTorr fitting near the base of the valve. A circular piece of plexiglass with an O-ring groove is connected to the outside of the 1/2 inch tube with an

UltraTorr fitting. This component is free to slide over the length of the tube until the UltraTorr fitting is tightened. A plexiglass tube forms an O-ring seal with the chamber on one end and with this circular component on the other. The valve assembly is placed against this plexiglass tube and positioned at one of the gate valves. This forms a vacuum interlock for insertion and removal of the valve.

A.1.4 Heated Sample Holder

Studies of solid samples often require that the sample be heated such that a sufficient vapor pressure can be maintained. A heated sample holder was developed at Illinois for such studies [21], and a similar sample holder has been constructed at Caltech. A schematic diagram of this sample holder is shown in Figure A.2. This sample holder can be attached to the valve face plate. A carrier gas is pulsed over the sample, and a molecular beam is formed by a Laval nozzle at the exit of the heated compartment. Stainless steel poppets have been constructed for use with this sample holder. A valve face plate press-fit with a Kevlar insert should be used with these poppets. Poppet lifetimes are generally on the order of several weeks with this setup.

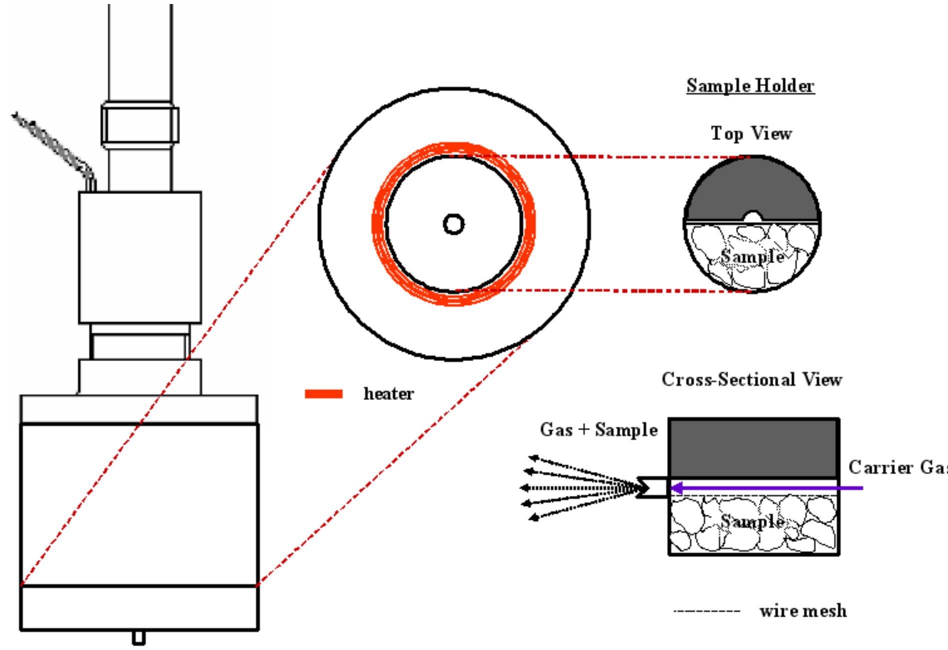


Figure A.2: A schematic diagram of the FTMW heated nozzle.

A.2 Spectrometer Startup Procedure

1. Insert the correct waveguide and tuner assembly. The instrument has two frequency ranges, 2–8 GHz and 8–18 GHz, and an SMA assembly is used for low frequency applications while a waveguide assembly is used for high frequency applications. The high frequency assembly is simply a waveguide that should be bolted to the instrument at the O-ring seal. The low frequency assembly is an SMA throughput that slides through the waveguide and then seals to the outside of the waveguide at the same O-ring seal:

For low frequency experiments, insert the SMA until the connector passes through the mirror iris. A dipole antenna can be found in the box labelled "dipole," and this antenna should be connected to the SMA connector in the chamber (remove the gate valve flange at the top of the instrument to do this). The entire SMA assembly should then be pushed back through the iris such that the antenna is positioned against the face of the mirror. The low frequency tuner is connected to the SMA at the input of the assembly and has two rods that slide up and down to adjust the tuning:

At high frequency the tuner is a slide tuner directly attached to the waveguide. This tuner has a coarse and fine adjustment:

Cavity coupling is quite bad at frequencies between 8 and 10.5 GHz, and a teflon dielectric waveguide should be inserted into the mirror iris for this frequency range. This waveguide is also located in the "dipole" box.

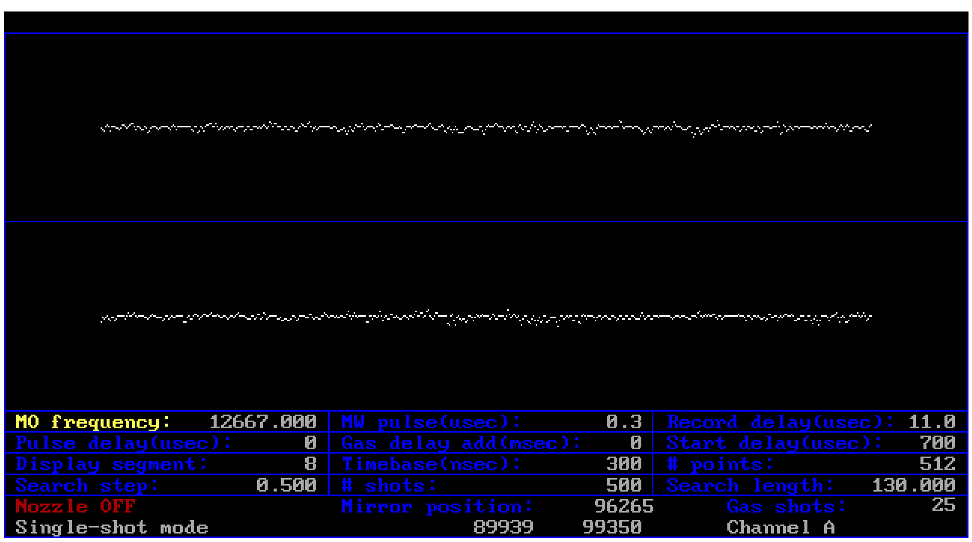
2. Turn on both water recirculators in the pump room. The diffusion pump flow meter readout next to the chamber should be reading a flow rate of ~5 GPM. Close the gate valve

between the cold trap and the pump line and turn on the two mechanical pumps. Slowly open the gate valve and pump down the chamber. Turn on the Roots blower once the line pressure reaches ∼1 Torr. Turn on the diffusion pump once the chamber pressure is <10 mtorr. It will take approximately 30 minutes for the chamber to pump down to $\sim10^{-6}$ Torr. The diffusion pump cooling water output temperature should be ∼70 degrees when the pump is warmed up completely.

3. Turn on the filter box, the interface box, the oscilloscope, the microwave box power supply, the frequency synthesizer, and the amplifiers. Be sure to do this before starting the operating program. (Note: The rubidium clock should remain plugged in at all times.)

4. Select the desired detector with the switch on the front of the microwave box.

5. Turn on the computer. Change to the directory where data should be saved (normally the C:\MWDATA directory). Type “v15” at the command prompt and press enter to load the operating program. The main control screen for the operating program should appear:



6. Confirm that the frequency synthesizer output is equal to the MO frequency minus 30 MHz.

7. The top window in the main control screen displays the signal, while the bottom window displays the noise in single-shot mode and the average of all 16 FIDs in averaging mode. Some noise should appear in both windows. The figure above shows a typical noise level. Check the amplifiers if no noise is observed.

The digitizer board in the computer may also not always work properly. If the signal is completely static, exit the v15 program, change directories to C:\DIGI, type "WAAG2," and press enter. This loads a diagnostic program for the digitizer card. The card should begin working properly again if a command is issued from this program. Exit the program, change directories to C:\MWDATA, and start the v15 program.

8. The experimental parameters are entered in the bottom of the main control window and are defined as follows:

- MO frequency: The experimental frequency
- Pulse delay: The delay in the train of microwave pulses
- Display segment: The segment of the pulse train displayed in the top two windows
- Search step: The increment by which the frequency is changed during an autosearch
- MW pulse: The length of the microwave pulses
- Gas delay add: The delay in the gas pulses
- Timebase: The sampling time (the inverse of the sampling rate)
- # shots: The number of shots to be averaged in averaging mode
- Record delay: The delay before digitization
- Start delay: The delay between the gas pulse and the beginning of the pulse train
- # points: The number of points recorded
- Search length: The amount of frequency to be covered in autosearch mode
- Nozzle: 'ON' or 'OFF' gives the status of the nozzle
- Mirror position: The current position of the mirror, in steps
- Gas shots: A counter for the number of gas shots
- Mode: The mode of data acquisition: 'single-shot,' 'averaging,' or 'autosearch'
- The numbers below the mirror position are the nearest resonant mirror positions.
- Channel: Channel being viewed (B = A + 90°)

Enter the desired experimental settings in the main control screen. The timing settings shown above are those used in standard experiments. The pulse width should be increased to 1 μsec for species with small dipole moments (< 0.5 D).

The commands for the main control screen are as follows:

a: Averaging mode
b: Toggle between Auto Search display and Single-Shot display during Auto Search mode
c: Toggle view of channels
d: Averaging mode (until certain number of shots)
f: new frequency
i: search increment (advance frequency by search step, move mirrors)
k: search decrement (decrease frequency by search step, move mirrors)
m: New mirror position (used to correct mirror calibration)
n: Nozzle on/off
s: Single-shot mode
t: Stop averaging and go to Pre-FFT screen
v: Auto Search mode
x: Exit program and save startup information
z: Averaging mode (reset on overflow)
‘: Turbo mode toggle
F1: Microwave power level decrement
F2: Microwave power level increment
F3: Mirror in continuously slow
Shift-F3: Mirror in continuously fast
F4: Mirror out continuously slow
Shift-F4: Mirror out continuously fast
F5: Mirror in 1 step
F6: Mirror out 1 step
F7: Mirror in 5 steps
F8: Mirror out 5 steps
F9: Mirror in 20 steps
F10: Mirror out 20 steps
Home: Large increment of value highlighted by cursor (if applicable)
End: Large decrement of the value highlighted by the cursor (if applicable)
Page up: Small increment of value highlighted by cursor
Page down: Small decrement of the value highlighted by cursor
Right arrow: Move cursor right
Left arrow: Move cursor left
Up arrow: Move cursor up
Down arrow: Move cursor down

9. Load the sample. Liquid samples should be placed in a bubbler and solid samples should be placed in the heated sample holder. If using the heated sample holder, be sure to secure the lid with the small set screw on the side or the lid could fall off in the chamber. Attach the sample holder to the valve face plate. The sample holder is not C_{2v} symmetric, so confirm that it is aligned appropriately or the valve will not completely insert in the coaxial setup.

10. Optimize the valve, set the tensioning with the set screw, and use electrical tape to secure the leads so that they do not get caught in the chamber.

11. Turn on the carrier gas and set the flow controller rates and the backing pressure.

12. Insert the valve assembly into the chamber by placing it against the plexiglass tube, positioning this tube at one of the gate valves, and opening the gate valve. Warning: Firm O-ring seals should be established before and maintained while the gate valve is open! If the seal is broken, quickly pull the valve assembly out of the chamber and immediately shut the gate valve. Wait at least 10 minutes before reinserting the valve assembly so that the diffusion pump is not overloaded.

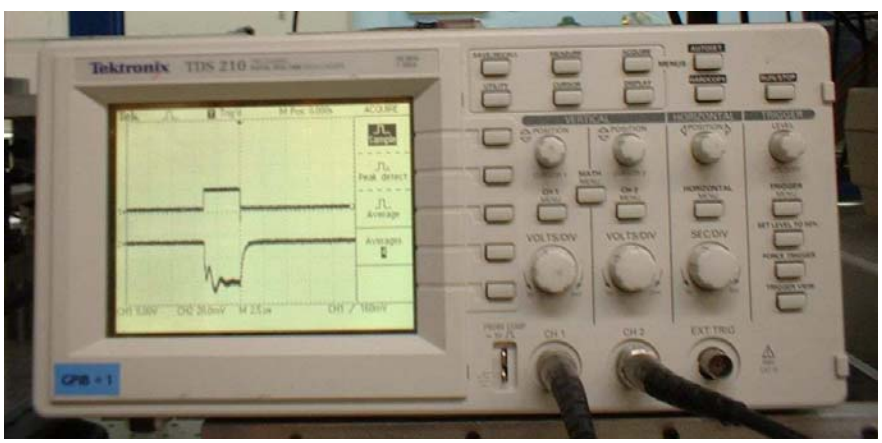
13. Slowly insert the feedthrough until it is at the position marked on the outer tube. The valve should be gently resting against the mirror when using the coaxial setup. Some rotation of the assembly may be required for the last few inches of insertion, as the valve face plate is matched to the size of the chamber to ensure alignment with the mirror iris. Warning: There is a plug in the mirror that can be knocked into the chamber when the valve is inserted coaxially! Be gentle! The UltraTorr fitting should be tightened once the valve is inserted completely. The chamber pressure should quickly decrease to a value only

slightly higher than that observed with the static system. If a drastic change in pressure occurs, there is likely a leak in the valve assembly.

14. Set the MO frequency to the desired value.

15. The cavity now requires tuning. Begin moving the mirror out in the 'mirror out continuously slow' mode. Watch the oscilloscope signal, as the tuning signal will 'wiggle' when close to a cavity mode. Find the mode farthest **out** in mirror position and stop the mirror by pressing any of the mirror control hot keys. Warning: Caution should be taken to ensure that the mirror is not driven too far to either end of its track, as it will become stuck. The current outer limit for the mirror position is ∼110,000. If the mirror does become stuck, loosen the bolts on the step motor and manually move the mirror in the appropriate direction with the step motor control box.

16. Move the mirror (out) just past the cavity mode (where the signal stops wiggling). Move the mirror inward stepwise until it is at the outermost edge of the mode. The signal on the oscilloscope should be similar to that shown below:



17. Iteratively adjust the two settings of the tuner and the mirror position until a tun-

ing signal such as the one shown in Section A.1.1 is achieved. In the low frequency setup the SMA and dipole can also be rotated and adjusted in horizontal position to aid in tuning.

18. It is often the case that, despite the appearance of excellent tuning with the oscilloscope signal, some modes will produce ringing that is observable on the main control screen. This ringing can be mistaken for signal and should be avoided. If slight adjustments in tuning do not eliminate the ringing, move the mirror inward until the next cavity mode is reached and retune.

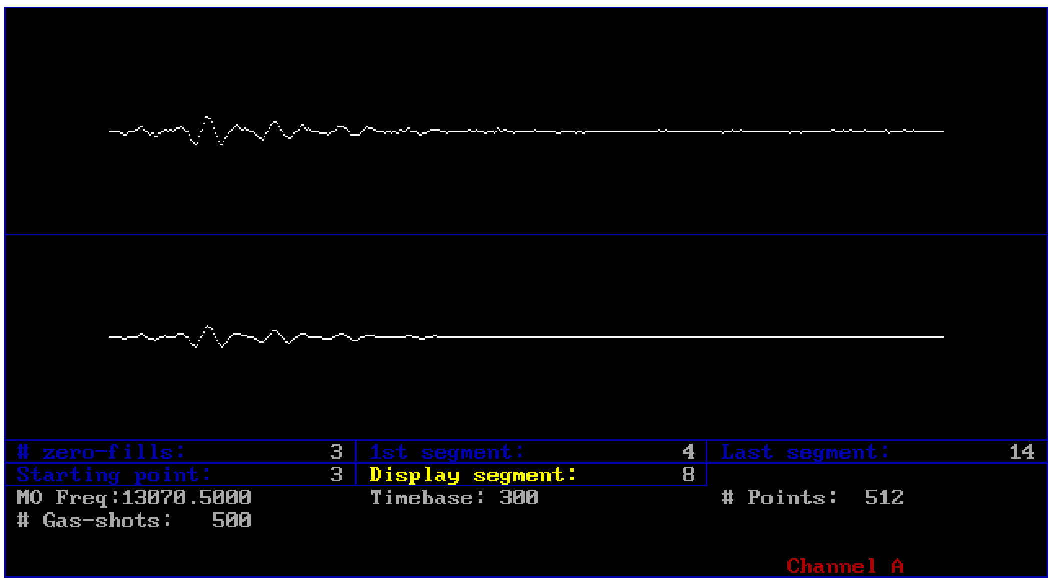
19. Once the cavity is tuned, set the desired experimental parameters. Turn on the nozzle and ensure that the chamber pressure does not rise above 4×10^{-4} Torr.

20. Select the desired data acquisition mode and begin collecting data. Single-shot mode displays the instantaneous FID. Averaging mode averages the FIDs for all shots. Auto Search can be used with predefined parameters to do fast line searches over a large frequency range. Retuning will be required after each manual change in frequency unless the search increment and decrement options are used. These functions step the frequency by the search step increment and appropriately adjust the mirror position. Slight retuning may be required, but these options do keep the spectrometer very close to optimum tuning.

21. Before selecting Auto Search mode, set the number of shots, search step, and search length to the desired values. Turn on the printer and add paper. Once Auto Search mode begins, the computer will automatically step the frequency, move the mirror, integrate, take a transform internally, and record the information on the printout. Be prepared for on-the-fly tuning while in autosearch mode, as the instrument tends to detune slightly with each frequency step. The program will prompt for a threshold when autosearch mode is selected.

This is the cutoff intensity for saved files, and so if there is a spectral feature with intensity higher than this threshold the data will be saved. A threshold of 10–20 is generally used.

22. The spectrum can be viewed during single-shot mode and general averaging mode by pressing 't,' which loads the Pre-FFT screen. Another version of averaging mode can be used in which the program automatically goes to the Pre-FFT screen after the defined number of shots. The Pre-FFT screen displays the obtained FIDs and allows the user to choose the parameters for the transform:



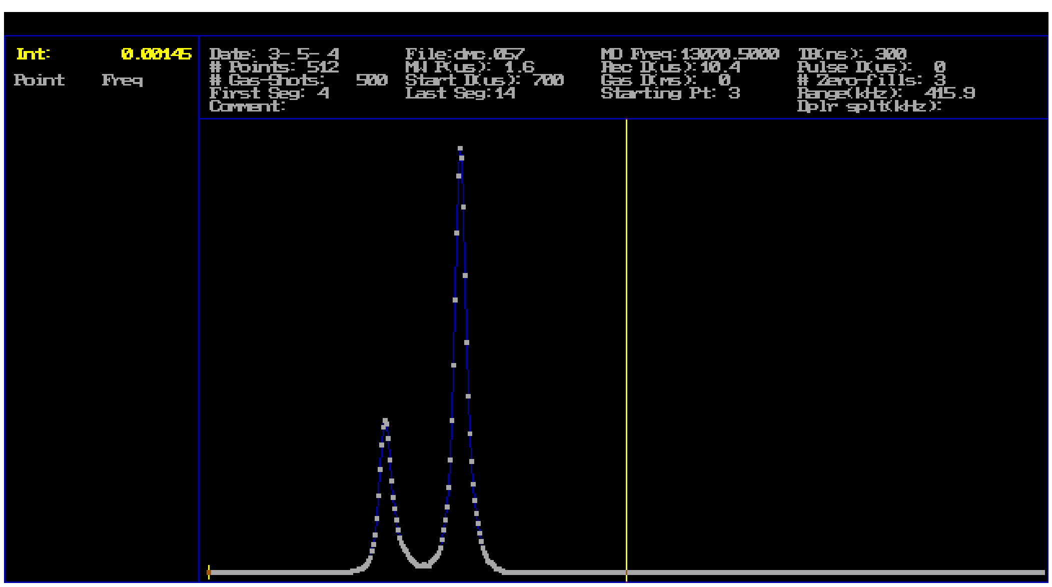
The FID is displayed on this screen in the same manner as it is displayed in the main control screen. The data to be included in the analysis can be selected with the parameters at the bottom of this screen, which are defined as follows:

- # zero fills: The number of times to double the length of the FID by adding zeroes
- 1st segment: The first FID segment to be included in the transform
- Last segment: The last FID segment to be included in the transform
- Starting Point: The first point in the FID that is to be transformed
- Display segment: The screen segment shown above

The commands for the Pre-FFT screen are as follows:

b: FFT of channel B
c: Toggle view of channels
e: Return to main screen without zeroing data array (nondestructive return)
n: Complex FFT (power spectrum)
r: Return to main screen
v: FFT of Channel A
F3: 0 order phased real FFT
Shift-F3: 0 & 1st order phased real FFT
F4: 0 order phased imaginary FFT
Shift-F4: 0 & 1st order phased imaginary FFT
F5: Real FFT
F6: Imaginary FFT
Page up: Small increment of value highlighted by cursor
Page down: Small decrement of the value highlighted by cursor
Right arrow: Move cursor right
Left arrow: Move cursor left

23. The FFT of the FID can now be taken. The real FFT of the FID gives a spectrum with the upper and lower sidebands superimposed, and so the frequencies are ambiguous. The complex FFT, however, gives the power spectrum, and so the sidebands are separated:



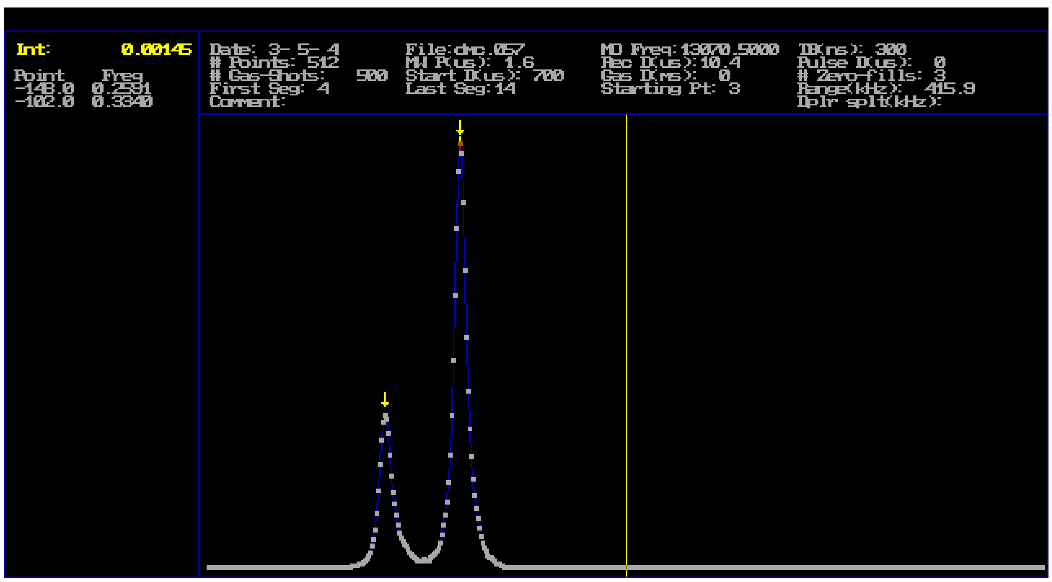
It is common for the program to prompt for a scaling factor when averaging mode is in use. Enter any number and press enter. The screen will then slowly go entirely blue. This is due to a program overload, and although it is irritating, it does not have any bearing on the spectral information. Simply press ‘r’ to enter the complex FFT screen. The position of the MO frequency is indicated in the complex FFT screen by the yellow line.

The commands for the complex FFT screen are as follows:

a: Mark point
A: Pseudo amplitude scale [sqrt(power spectrum)]
b: FFT of channel B
c: Clear marked points
d: Mark point + 1/2
f: New filename
l: Logarithmic scale y $\rightarrow$ log(y)
L: Loglog scale y $\rightarrow$ log(log(y))
m: Input comment
o: Save transform in Auto LISP format for Auto CAD in file called ft.tsp
p: Print transform
r: Return from current level to next valid level
s: Save transform
v: FFT of channel A
F1: auto peak picking
Shift-F1: auto peak picking with user defined threshold
F2: De-dopplerize
Shift-F2: De-Dopplerize with user defined range in pts
F3: 0 order phased real FFT
Shift-F3: 0 & 1st order phased real FFT
F4: 0 order phased imaginary FFT
Shift-F4: 0 & 1st order phased imaginary FFT
F5: Real FFT
F6: Imaginary FFT
Home: Move cursor +8
End: Move cursor -8
Page up: Move cursor +1
Page down: Move cursor -1
Right arrow: Scroll transform right
Left arrow: Scroll transform left
Up arrow: Increase magnification on transform
Down arrow: Decrease magnification on transforms

The spectrum can be saved at this point. The filename should be changed before saving. Three-digit numerical extensions are required. It is advisable to begin a search for a molecule with the extension .001, and any further spectra will automatically be assigned the subsequent numbered filename (i.e., if the first spectrum is saved as dha.001, the next spectrum will automatically be named dha.002).

The peaks can be chosen by either moving the cursor and manually marking the point or by auto peak picking. The frequencies are displayed to the right of the screen, and only the MHz place and decimal places are shown:



Any additional adjustments to the spectrum can be made at this point, but the raw data (before transform) rather than the FFT will be written to the file when saved. Doppler split lines will be observed in the coaxial setup, and the program can perform de-Dopplerization of the data in the FFT screen.

24. The saved files can be viewed at a later time by running the plot15 program. This program can be loaded similarly to the v15 program, by typing ‘plot15’ at the command

prompt in the directory where the files are saved. The program will prompt for “Input filename [path]cccccc.nnn>.” The filename should be entered here (i.e., ‘dha.001’). The program will then prompt “Read file dha.001 to dha.” Enter the appropriate numbered extension for the last file to be viewed (i.e., ‘005’ will allow files dha.001 - dha.005 to be viewed). The Pre-FFT screen for each file will load in sequence. All commands for the Pre-FFT screen and the complex FFT screen are the same as those used in v15. To close the first file and move to the next, press ‘r’ in the Pre-FFT screen. Pressing ‘x’ will close the program.

25. The best way to transfer the data to another computer is by printing a hardcopy of the spectrum and subsequently scanning this hardcopy to obtain a digital version. The other option is saving the transform in Auto LISP format for Auto CAD in a file called ‘ft.tsp.’ It has been found, however, that the intensities are often written incorrectly in this format. This is a major programming flaw that should be corrected.

A screen capture program has also been loaded on this computer. Change to the C:\SCRAP directory, type SCRCAP, and press enter to load the program. Load the image to be captured (a change in directory may be required). Press ‘ALT’ and ‘c’ at the same time to capture the screen image. This saves the file with the name ‘CAP-xxx.SCR’, where xxx is a three-digit number. Transfer the file to the SCRAP directory and then type ‘SCR2GIF’ at the prompt to convert the .SCR file to a .GIF file. The computer’s floppy drive (A:\) can be used to transfer the files to another computer.