Chapter 2

Experimental Laboratory Methods

2.1 Introduction

Prebiotic monomers are expected to have strong torsional transitions in the terahertz (THz) frequency range. Due to experimental limitations in this range, however, rotational spectral lines searches are more straightforward at microwave, millimeter, and submillimeter wavelengths. The OVRO and CSO observatories cover spectral ranges of 88–116 GHz / 210–270 GHz and 200–900 GHz, respectively, and so these frequency ranges were the highest priority target ranges for laboratory studies. Predictions from microwave spectral data are often required before millimeter and submillimeter spectra can be assigned. Microwave spectral information was available in the literature for all species but dihydroxyacetone and dimethyl carbonate. A Fabry-Perot cavity pulsed Fourier-Transform MicroWave (FTMW) spectrometer, also known as a Balle-Flygare instrument, was used for the microwave investigation of these two molecules. The spectral prediction derived from the microwave study of a species then served as the basis for further millimeter and submillimeter studies with the JPL and Caltech Direct Absorption Flow Cell Spectrometers. Overviews of the FTMW and direct absorption techniques are presented below.

2.2 Spectroscopic Techniques

2.2.1 Pulsed Fourier Transform Microwave Spectroscopy

Fourier-Transform microwave spectroscopy, developed by Balle and Flygare in 1971 [20], is an extremely sensitive method for high resolution rotational spectroscopy. This technique utilizes a pulsed molecular nozzle for adiabatic expansion of the species of interest into vacuum, which cools the sample to rotational temperatures of 1–4 K, and a Fabry-Perot cavity for polarization of resonant transitions of the species of interest. A pulse of microwave radiation is introduced into the cavity, exciting the molecules. After the pulse dies away, the molecules emit coherent radiation at their resonant frequencies. A superheterodyne detector is used to collect the time-domain free induction decay (FID), and the Fourier transform of this record gives the frequency-domain spectrum.

A schematic diagram of the current configuration of the original FTMW instrument is presented in Figure 2.1 (adapted from [21]). A signal of frequency ν is generated by the master oscillator (MO). The MO signal is upconverted by 30 MHz in a single sideband (SSB) mixer, and this signal is then coupled into the cavity upon the opening of a PIN diode. The radiation is pulsed into the cavity by the opening and shutting of this PIN diode, which is controlled by the timing control circuit. This timing control circuit also controls the molecular pulse valve. The pulse of radiation passes through the coupling iris of the Fabry-Perot cavity. The molecular nozzle pulses a beam of molecules into the cavity at the same time. The incident radiation excites the molecules, and they emit radiation at a transition frequency offset from the microwave pulse by Δ ($\sim$ 500 kHz). This emission is longer-lived than the incident radiation trapped in the cavity, but much weaker, and sets up a standing wave in the cavity. When the switch is again opened to the cavity, some

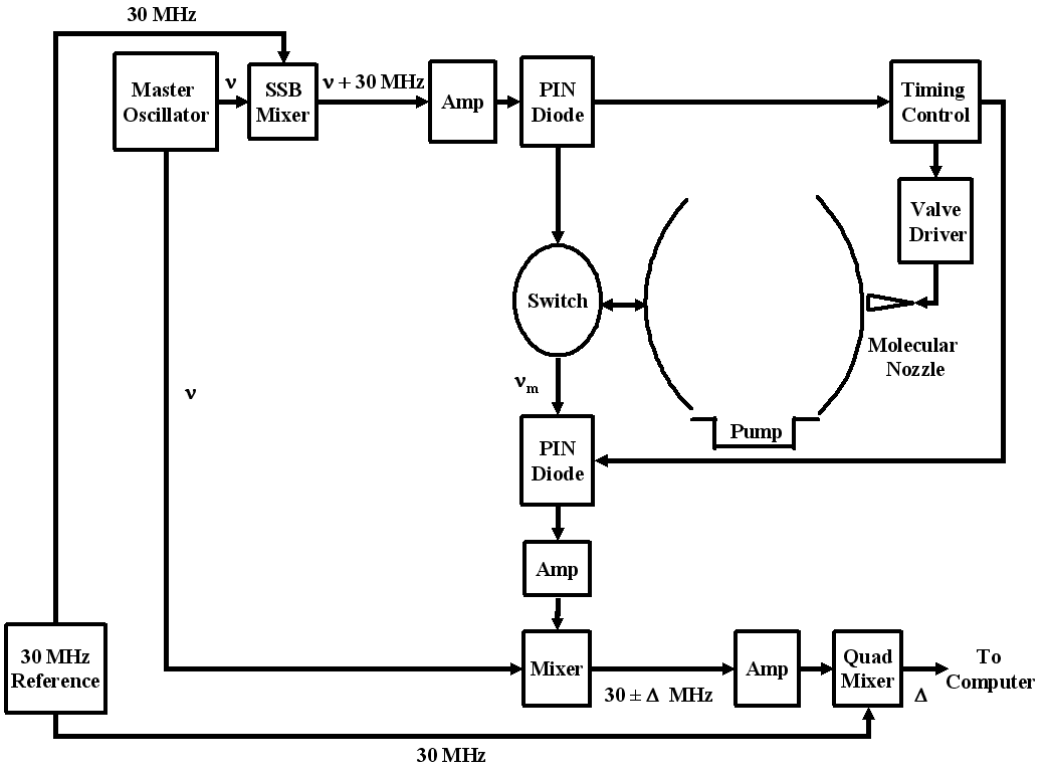

Figure 2.1: Schematic diagram of an FTMW instrument.

of the emitted radiation plus residual incident radiation passes through the same coupling iris, through an isolator, and through a second PIN diode, which is opened only after the majority of the MO radiation pulse has rung down. The radiation, at a frequency ν_m, is amplified and then mixed with the MO signal to yield a frequency $30 \pm \Delta$ MHz. This signal is then mixed with the 30 MHz signal in a quadruture mixer, producing signals near frequency Δ, the widths of which are determined by the finesse of the cavity. The output of this quadruture mixer is two signals, the upper and lower sidebands, which are separated in phase by 90°. These signals are then processed by a computer. The power spectrum is recorded in the time-domain, and the computer then performs the Fourier transform of this spectrum to obtain the final spectrum in the frequency-domain. Cavity pressures on

the order of 10^{-6} torr are maintained with a diffusion pump located below the spectral chamber.

This technique is much more sensitive than standard direct absorption experiments due to the superheterodyne detection and the high finesse of the cavity. The detection scheme lowers the 1/f noise considerably, allowing for detection of much weaker lines than those observable in direct absorption experiments. In addition, pressure broadening effects are eliminated, greatly decreasing the linewidths observed and therefore increasing the resolution. Line widths are limited by Doppler broadening and Doppler splitting due to the angular distribution of the molecules as they pass into the cavity. Although each transition is split into two lines that are sometimes tens of kHz apart, spectral linewidths of 1.4 kHz can be achieved for long-lived species.

The original FTMW instrument has recently been moved to the Blake labs at Caltech. Detailed operating procedures as well as a description of the changes made to the spectrometer since its relocation to Caltech are outlined in Appendix A. This instrument has a frequency range of 2–18 GHz, but Balle and Flygare noted in their original paper that these techniques " ... should also be easily applied to far-infrared and higher frequencies [20]." FTMW instruments based on this original design have been extended up to 40 GHz. Coaxial pulsed-jet instruments have been developed for the millimeter and submillimeter ranges, but these are not FT cavity experiments [22]. FT instruments in the millimeter, submillimeter, and terahertz ranges should have only slightly lower cavity finesse and will have wider cavity modes, enabling wider frequency coverage and therefore much faster data acquisition than traditional FTMW techniques, but no millimeter or far-IR FT instruments have yet been developed. The slow progress is in part due to the fact that, until very recently, very few intense tunable far-IR sources were available. Recent advancements in observational

astronomy have motivated development of new tunable sources in the far-IR, however, and a prototype FT-FIR instrument is currently being developed in the Blake labs.

2.2.2 Direct Absorption Flow Cell Spectroscopy

Direct absorption flow cell spectrometers were developed as a straightforward means of obtaining broadband spectral coverage for molecules with reasonably strong rotational spectra. A schematic diagram of this type of spectrometer is shown in Figure 2.2.

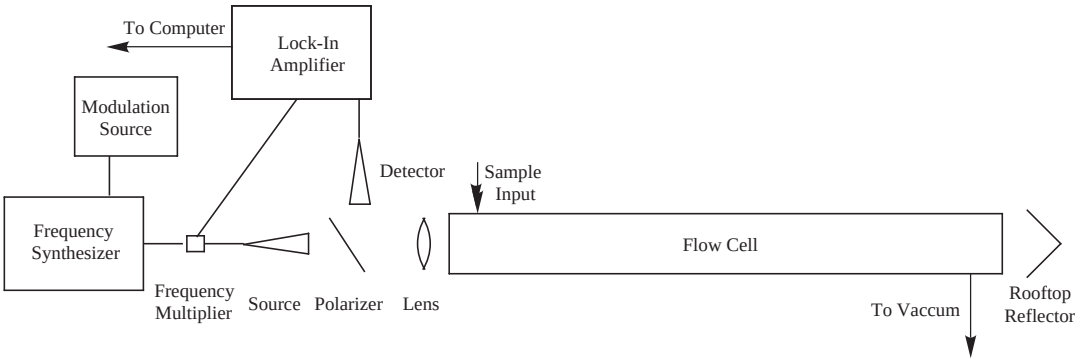

Figure 2.2: Schematic diagram of the Caltech Direct Absorption Flow Cell Spectrometer.

The general flow design involves a long quartz cell with a sample inlet on one end and a vacuum line on the opposite end. The pump is used to maintain a constant flow of gas phase species. Microwaves are generated by a frequency synthesizer that is controlled by a computer and swept through a given frequency range at a designated frequency interval. This radiation is then frequency modulated and multiplied to the desired frequency range by an active multiplier chain. It is emitted from a waveguide horn and passed through a polarizer and teflon lens to focus the coherent radiation into the flow cell. The cell acts as a dielectric waveguide, propagating the waves to the opposite end of the cell where they reflect off of a rooftop reflector. The rooftop changes the polarization by 90 degrees and

transmits the radiation back through the flow cell. The molecules present in the flow cell absorb this radiation as it passes through the cell, and the double-pass nature of the setup increases the amount of absorption and therefore the signal-to-noise ratio. After passing back through the cell, the radiation is then deflected off of the input polarizer and detected by either a Schottky diode detector or an InSb hot electron bolometer at 90 degrees to the source. A lock-in amplifier is used to narrow the detection bandwidth and amplify and rectify the 2f (second-derivative) signal. The resultant DC signal is then sent to a computer that is equipped with a GPIB card for analog to digital conversion. The signal is processed and recorded as a function of frequency.

Two of such spectrometers were used in these studies, one in the Laboratory for Microwave, Millimeter, and Submillimeter Spectroscopy at the Jet Propulsion Laboratory (JPL) and one in the Blake labs at Caltech. The details of the JPL spectrometer are outlined in reference [23]. The Caltech Direct Absorption Flow Cell Spectrometer is comprised of two cells, two detectors, and various combinations of multiplier chain components such that complete spectral coverage is achieved in the 80–120 GHz (3 mm) and 225–360 GHz (1 mm) spectral regions. The specific instrumentation used with this spectrometer as well as detailed operating procedures are outlined in Appendix B.

Two aspects of this design enable extensive spectroscopic studies of the species of interest. First, while most spectra are obtained at room temperature, both low and high temperature experiments are possible with the JPL spectrometer and the 1 mm setup at Caltech due to cooling jackets around the outsides of the cells. This allows for temperature variations, which are quite useful for molecules with large vibrational partition functions when only ground state vibrational spectra are desired or for molecules with very low vapor pressure. Secondly, this apparatus has very wide spectral range capabilities. Broadband,

fixed-tuned coverage of >100 GHz is easily achievable with current multiplier chain sources. Addition of frequency multipliers to the existing setup is limited only by the availability of appropriate power amplifiers in the frequency ranges desired.

Despite the straightforward nature of this experiment, it does have some disadvantages for extended spectroscopic studies. Although the signal to noise ratio for highly populated states is good for this setup, low abundance isotopologues and less populated states are not easily observed. Also, difficulties arise in resolution due to the Doppler and pressure broadening of the signal. Typical linewidths are on the order of 0.5–1 MHz. Such spectral features as hyperfine splittings often remain unresolved in the resultant spectra from this type of apparatus. Also, an extended amount of time is required to obtain a spectrum over a wide frequency range, making static cell experiments difficult, and so large quantities of sample are required to maintain a constant flow of a species for study over wide spectral ranges. While this method is straightforward in nature and allows extended spectral coverage, other spectroscopic techniques can be utilized that require fewer chemicals and less time or that have higher sensitivity.