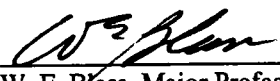


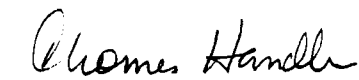
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INFRARED SPECTRAL LINE INTENSITIES  
OF ETHYLENE

A Thesis  
Presented for the  
Master of Science  
Degree  
The University of Tennessee, Knoxville

Alan C. Ewing

December 1993

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## ABSTRACT

Spectra of the  $\nu_7$  band of ethylene were recorded using a tunable diode laser spectrometer and their linewidths were measured. Spectra acquired at pressures between 10 and 50 milliTorr and in a 45 cm cell are analyzed. Temperature is also accurately recorded. Line intensities are retrieved from the observed line widths. A broad band spectrum acquired at the Kitt Peak National Observatory on a Fourier transform spectrometer was also studied. TDL line intensities are used to calibrate the FTS data, and  $\text{CO}_2$  lines present in the FTS spectrum are used to calibrate line positions. A corrected pressure is determined and a series of line strengths from the Fourier transform spectra is reported.

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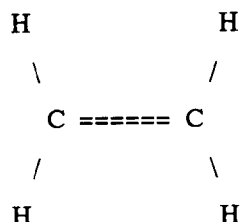
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# Chapter 1

## Justification of Research

### Introduction

Ethylene,  $C_2H_4$ , belongs to the alkene family of hydrocarbon molecules. Its structure is well known as a planar, asymmetric-top molecule. Inter-nuclear distances and H-C-H angles have been determined via many different methods including electron diffraction [1], infrared analysis [2] and Raman analysis [3]. Recent work has refined these values and increased their accuracy [4]. A structural representation of the molecule is:



The following equation is used to determine the number of normal modes of a non-linear molecule :

$$N.M. = 3N - 6 \quad (1.1)$$

where N is the number of nuclei in the molecule. Since there are six nuclei present there are twelve normal modes. While rotational bands can not be directly observed due to the lack of a permanent electric dipole moment, infrared and Raman spectroscopic investigations can be used to study the vibrational bands.

By use of group theory we can predict how each of these normal modes will interact with radiation. The structure of the molecule allows for assignment to the  $D_{2h}$  symmetry species and from this we derive the results shown in Table 1.1 [5, 6, 7, 8, 9]. This table contains a list of these normal modes, their symmetry species, vibrational mode type and fundamental frequency.

This study is concerned with the  $\nu_7$  vibrational-rotational infra-red band whose transitions are centered about  $942\text{ cm}^{-1}$ . The bending mode responsible for this band, shown in figure 1.1, corresponds to a

Table 1.1  
Normal modes of ethylene

| Symmetry Species | Band            | Bending Mode              | Frequency (cm <sup>-1</sup> ) | Observation Technique |
|------------------|-----------------|---------------------------|-------------------------------|-----------------------|
| a <sub>g</sub>   | ν <sub>1</sub>  | CH <sub>2</sub> s-stretch | 3002.03(5) [5]                | Raman                 |
| a <sub>g</sub>   | ν <sub>2</sub>  | CC stretch                | 1625.4 [6]                    | Raman                 |
| a <sub>g</sub>   | ν <sub>3</sub>  | CH <sub>2</sub> scissor   | 1343.54(5) [5]                | Raman                 |
| a <sub>u</sub>   | ν <sub>4</sub>  | CH <sub>2</sub> twist     | 1025.5897(2) [7]              | Inactive              |
| b <sub>1g</sub>  | ν <sub>5</sub>  | CH <sub>2</sub> a-stretch | 3083.36(5) [5]                | Raman                 |
| b <sub>1g</sub>  | ν <sub>6</sub>  | CH <sub>2</sub> rock      | 1217 [8]                      | Raman                 |
| b <sub>1u</sub>  | ν <sub>7</sub>  | CH <sub>2</sub> wag       | 948.770952(6) [7]             | Infrared              |
| b <sub>2g</sub>  | ν <sub>8</sub>  | CH <sub>2</sub> wag       | 940.1 +/- .6 [9]              | Raman                 |
| b <sub>2u</sub>  | ν <sub>9</sub>  | CH <sub>2</sub> a-stretch | 3104.941(15) [8]              | Infrared              |
| b <sub>2u</sub>  | ν <sub>10</sub> | CH <sub>2</sub> rock      | 825.92668(16) [7]             | Infrared              |
| b <sub>3u</sub>  | ν <sub>11</sub> | CH <sub>2</sub> s-stretch | 2988.653(8) [8]               | Infrared              |
| b <sub>3u</sub>  | ν <sub>12</sub> | CH <sub>2</sub> scissor   | 1442.4750 [7]                 | Infrared              |

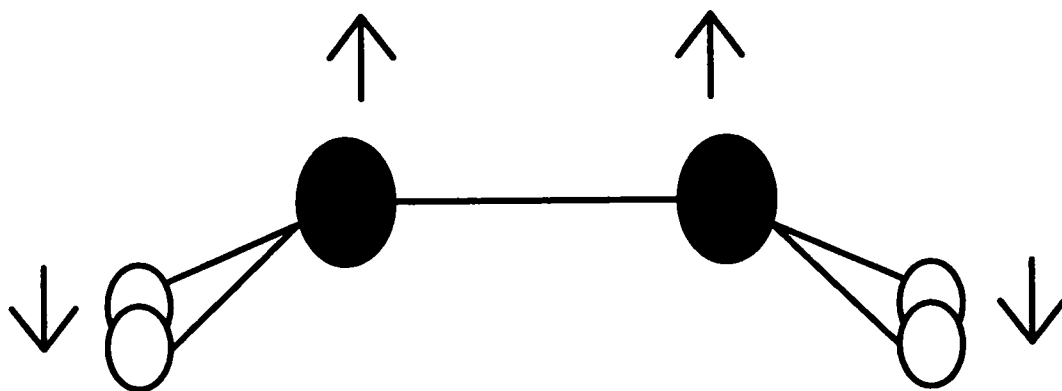


Figure 1.1  
Representation of the  $\nu_7$  bending mode of ethylene

displacement of the two carbon nuclei above and the four hydrogen nuclei below the plane of the molecule. A low resolution spectrum,  $\Delta\nu \approx .8 \text{ cm}^{-1}$ , of the transitions due to  $\nu_7$  is shown in figure 1.2 [10]. This figure also contains the transitions due to the  $\nu_{10}$  vibrational-rotational band.

The data for this work was acquired from two sources. The first is the University of Tennessee Molecular Spectroscopy Laboratory (UTMSL). A Tunable Diode Laser (TDL) system at the UTMSL was used to record data in the  $940 \text{ cm}^{-1}$  to the  $960 \text{ cm}^{-1}$  infrared region. The second source is the McMath Solar Telescope Fourier Transform Spectrometer located at the National Solar Observatory at Kitt Peak. Fourier transform data was made available to UTMSL by members of the Laboratory for Extraterrestrial Physics at Goddard Space Flight Center. This data includes the region from  $800$  to  $1100 \text{ cm}^{-1}$ .

The importance of the results from the analysis of high resolution laboratory spectra cannot be overstated. Line position studies refine the ability to "fingerprint" the presence of ethylene in planetary atmospheres and interstellar gas clouds. Intensity studies offer a probe of the partial pressures, temperatures and overall abundance of the gas. Therefore, analysis of laboratory spectra aids in the study of ethylene as it occurs in the earth's atmosphere, the solar system and elsewhere in the galaxy.

## Ethylene in the Earth's Atmosphere

The presence of ethylene in the Earth's atmosphere is due to both natural and human initiated processes. The primary man-made source of the ethylene is the automobile. Several studies of urban regions have shown that ethylene is present in concentrations of 2 to 50 parts per billion [11]. The natural sources of ethylene include large scale forest fires, volcanoes and plant life. In the case of natural emission, forest fires are responsible for the greatest contribution to the global ethylene budget [12], while volcanoes produce only trace amounts during an eruption [13]. Plant life produces about 20,000 metric tons per year of ethylene as a part of their respiratory processes [12].

After entering the earth's atmosphere, ethylene reacts with oxygen ( $\text{O}_2$ ), hydroxyl ( $\text{OH}$ ) and ozone ( $\text{O}_3$ ) in the presence of light from the sun to form many different compounds. The main compounds resulting from these reactions are formaldehyde ( $\text{H}_2\text{CO}$ ) and nitrous oxide ( $\text{NO}_2$ ). These, however, are not the only compounds formed in the complex photochemical sequence. Formic acid ( $\text{CHCOOH}$ ) is another product, but the quantity of this substance is very small in comparison with formaldehyde [14]. The reactions with ozone, a molecule of current interest, are not as well known but do include carbon monoxide ( $\text{CO}$ ), water ( $\text{H}_2\text{O}$ ) and formaldehyde [14].

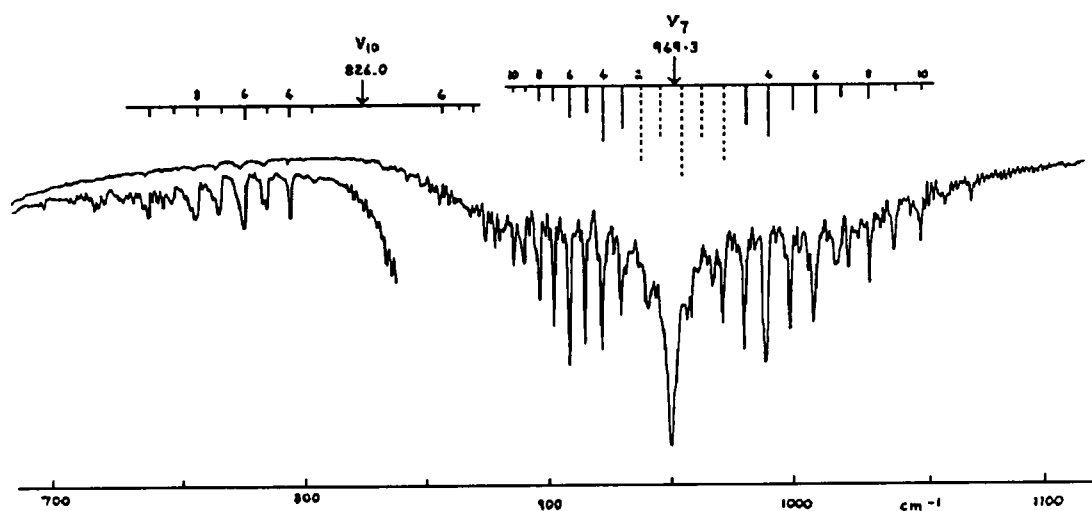


Figure 1.2  
Low resolution spectra of the  $\nu_7$  region of  $\text{C}_2\text{H}_4$  [10]

## Ethylene in the Atmospheres of Other Planets

It is commonly accepted that the spectroscopic parameters which are vital for atmospheric modeling include individual line intensities [15]. The line intensities determined in this work can be used to improve the models currently used for simulation of planetary atmospheres. To date, the presence of ethylene has only been confirmed spectroscopically in the atmosphere of Saturn's largest satellite Titan[16], and Jupiter[44] but should be present in small amounts in Saturn and Neptune .

The presence of ethylene is expected in the atmosphere of any body which has a large concentration of methane gas, since it is a product of methane photolysis [16]. Spectra taken of Titan at Kitt Peak using the 2.1 and 4 meter telescopes before the Voyager fly-by missions yielded interesting results. Spectral features around  $940\text{ cm}^{-1}$  were assigned to the  $\nu_7$  Q-branch [17, 18]. Estimates of the abundance of ethylene are determined directly from intensity measurements, and in the case of Gillet's work refer to laboratory measurements made in 1947 by Thondike *et al.* [19]. Higher resolution intensity measurements would make abundance estimates much more accurate.

Observing ethylene in the atmosphere of Jupiter is somewhat more of a challenge. This is due to relative abundance of ammonia in its atmosphere which makes observing the  $\nu_7$  band of ethylene difficult. The difficulty is due to the fact that ammonia transitions tend to obscure the ethylene transitions at lower resolution. In the initial analysis of low resolution spectra, observed features were attributed to ethylene [20]. More recent results from higher resolution observations [44] indicate that the gas is present, albeit in low concentrations. Of the few individual line intensity measurements available only three lines have been measured to within five percent error [45]. In the case of Kostiuk's work [44] several of the line intensities reported are known only within a 30 percent error.

The determination of ethylene concentrations inferred from laboratory spectra aids in specific modeling cases on Jupiter. One such case is the Great Red Spot. Its presence can be attributed to a photochemical reaction in which ethylene plays a significant part [21]. This, of course, is just one example. Ethylene, while in low concentrations, still plays a significant role in the overall atmospheric chemistry of the planet.

## Ethylene observable in the Galaxy

One of the most intriguing discoveries of ethylene is in the circumstellar cloud surrounding IRC +10216. The work of A. L. Betz [22] at Kitt Peak's McMath Solar Telescope indicate that lines from the  $\nu_7$  band

are detectable. Betz's analysis of the data indicates the circumstellar shell is expanding at a rate of  $14 \text{ km s}^{-1}$ , the temperature is at least 400 K and the radial column density is approximately  $10^{16} \text{ cm}^{-2}$ . Later investigations by Goldhaber, et. al., indicate that the column density is about  $4 \times 10^{15} \text{ cm}^{-2}$  [23]. The temperature and radial column density were determined by use of intensity data. If the intensity of these spectral lines were better known then a more reliable probe of pressure and temperature would become available.

## Overview

Intensity measurements from high resolution spectra enable astrophysicists and atmospheric scientists to generate more accurate models of earth's atmosphere, planetary atmospheres and other astrophysical objects. The use of the information presented in this work may prove to be invaluable for improving these models.

This work is broken into five chapters containing information about theoretical and experimental considerations. Chapter 2 describes some of the general and specific theoretical structure needed for understanding intensity measurements of molecule's spectral transitions. Chapter 3 is a description of the experimental set-up of the Kitt Peak Fourier transform spectrometer and the University of Tennessee Molecular Spectroscopy Laboratory tunable diode laser system. Chapter 4 discusses the data and its reduction and draws comparisons between the data from the UTMSL TDL and the Kitt Peak FTS. Chapter 5 discusses error and recommendations for future work.

## Chapter 2

### Intensities of Molecular Transitions

#### Introduction

Molecules interact with radiation in a number of ways. Changes in the energy state of molecules are quantized, and these transitions have energies in many parts of the electromagnetic spectrum. There are electronic transitions, just as in the case of individual atoms, whose energies are in and near the visible region. There are also transitions which are due to changes in the rotational state of a molecule. These typically have energies in the microwave region of the electromagnetic spectrum. The type of transitions that are studied in this work are molecular vibrational-rotational transitions, whose energies reside in the mid-infrared region of the spectrum (3-20  $\mu\text{m}$ ).

In generating a theoretical framework in which to describe the behavior of the molecule one must take symmetry into consideration. In general, the more symmetric a molecule, the fewer non-degenerate energy levels exist. Symmetry also helps determine which transitions between energy levels are possible. Just because a photon with precisely the energy required to span two energy levels comes along, does not mean that a transition will occur [24].

One of the most powerful theoretical tools for predicting and understanding the behavior of molecules is quantum mechanics. Quantum mechanics utilizes the quantum nature of physical models, such as the rigid rotator and harmonic oscillator, and their perturbations to generate Hamiltonians which describe the molecular system. From these Hamiltonians energy level maps and the probability of the transitions from one state to another can be calculated.

In generating a Hamiltonian which describes the molecule's behavior, all the different interactions must be taken into consideration. These include the zero order model which contains the rigid rotator, harmonic oscillator and electron interactions. Higher order terms which contain all perturbations must also be considered, and this leads to a very complex expression. Fortunately, however, the Born-Oppenheimer approximation allows the separation of the terms associated with those interactions due to the electron cloud [25], since the nuclei are much more massive than the electrons, and will, therefore, move much more slowly. The expression that is, therefore, employed deals only with the nuclei and their interactions.

## Molecular Quantum Mechanics

In general the starting point for all treatments of the quantum mechanics of rigid molecules is the Hamiltonian for the rigid rotator [26]. This can be most generally stated as:

$$\hat{H}_{rot} = \frac{1}{\hbar^2} \left( \frac{1}{I} \right) \hat{J}^2 \quad (2.1)$$

where  $I$  is the moment of inertia for the rotator and  $\hat{J}$  is the angular momentum operator. When the Hamiltonian is reduced from the non-rigorous statement in equation (2.1) to a three dimensional statement the result is:

$$\hat{H}_{rot} = \frac{1}{\hbar^2} \left( \frac{1}{I_x} \hat{J}_x^2 + \frac{1}{I_y} \hat{J}_y^2 + \frac{1}{I_z} \hat{J}_z^2 \right) \quad (2.2)$$

Here  $I_x$ ,  $I_y$  and  $I_z$  are the moments of inertia along the principal axes of rotation. Angular momentum operators are also defined corresponding to the principle axes. The assignments of the x, y and z axes to the moments of inertia axes can be made in six different ways. In place of the inverse of  $I_x$ ,  $I_y$  and  $I_z$  the symbols A, B and C are used. These are always ordered so that  $A > B > C$ . Each of the six different ways of mapping x, y and z into A, B and C is known as a representation, and the representations are shown below in table 2.1 [27]:

Table 2.1  
Moment of Inertia Representations

|   | I <sup>r</sup> | I <sup>l</sup> | II <sup>r</sup> | II <sup>l</sup> | III <sup>r</sup> | I <sup>l</sup> |
|---|----------------|----------------|-----------------|-----------------|------------------|----------------|
| x | B              | C              | C               | A               | A                | B              |
| y | C              | B              | A               | C               | B                | A              |
| z | A              | A              | B               | B               | C                | C              |

The representation that will be used in this work is the I<sup>r</sup>. Therefore the assignments of the values of the moments will be ordered as z, x and y from smallest to largest respectfully, and the rigid rotator Hamiltonian becomes:

$$\hat{H}_{rot} = \frac{1}{\hbar^2} (A \hat{J}_x^2 + B \hat{J}_y^2 + C \hat{J}_z^2) \quad (2.3)$$

Calculating the matrix elements for the Hamiltonian is now possible. After the matrix elements are determined then the matrix can be diagonalized and energy levels can be determined. The matrix elements are represented by  $\langle j, k | \hat{H} | j, k \rangle$ .

So now the problem is to reduce the Hamiltonian to a form in which all non-zero matrix elements can be determined. The following expressions will be useful in this task:

$$\langle j, k | J^2 | j, k \rangle = j(j+1)\hbar^2 \quad (2.4)$$

$$\langle j, k | J_z^2 | j, k \rangle = k^2\hbar^2 \quad (2.5)$$

$$\langle j, k | J_+^2 | j, k+2 \rangle = \{ [j(j+1) - (k-1)(k-2)] [j(j+1) - k(k-1)] \}^{\frac{1}{2}} \hbar^2 \quad (2.6)$$

$$\langle j, k | J_-^2 | j, k-2 \rangle = \{ [j(j+1) - (k+1)(k+2)] [j(j+1) - k(k+1)] \}^{\frac{1}{2}} \hbar^2 \quad (2.7)$$

The matrix elements for  $(k-1)$  and  $(k+1)$  are zero. To put equation (2.2) into a form that will allow the use of equations (2.4) through (2.7) the angular momentum operators  $J_x$  and  $J_y$  need to be defined in other terms. The most common redefinition is done in terms of raising and lowering operators as shown below:

$$J_x = \frac{1}{2} (J_+ + J_-) \quad (2.8)$$

$$J_y = \frac{1}{2i} (J_+ - J_-) \quad (2.9)$$

Squaring these expressions yields:

$$J_x^2 = \frac{1}{4} (J_+^2 + J_+ J_- + J_- J_+ + J_-^2) \quad (2.10)$$

$$J_y^2 = -\frac{1}{4} (J_+^2 - J_+ J_- - J_- J_+ + J_-^2) \quad (2.11)$$

Now, all terms for which the matrix elements are not defined can be rewritten with two exceptions. These exceptions are the presence of the  $J_+ J_-$  and the  $J_- J_+$  terms. The following relations will rectify this problem [28]:

$$J_+ J_- = J^2 - J_z^2 + \hbar J_z \quad (2.12)$$

$$J_- J_+ = J^2 - J_z^2 - \hbar J_z \quad (2.13)$$

When equations (2.12) and (2.13) are placed into equations (2.10) and (2.11):

$$J_x^2 = \frac{1}{4}(J_+^2 + 2J^2 - 2J_z^2 + J_-^2) \quad (2.14)$$

$$J_y^2 = -\frac{1}{4}(J_+^2 - 2J^2 + 2J_z^2 + J_-^2) \quad (2.15)$$

Now the relations (2.14) and (2.15) can be substituted into the original expression (2.3). This generates an expression which contains only values for which the matrix element expressions are defined in equations (2.4) through (2.7).

$$\hat{H}_{rot} = \frac{1}{\hbar} \left[ \left( \frac{B+C}{2} \right) J^2 + \left( A - \left( \frac{B+C}{2} \right) \right) J_z^2 + \left( \frac{B-C}{4} \right) (J_+^2 + J_-^2) \right] \quad (2.16)$$

Using equations (2.4) through (2.7) the following expressions are arrived at that will generate all non-zero matrix elements for the rigid rotor Hamiltonian.

$$\langle j, k | \hat{H} | j, k \rangle = \frac{B+C}{2} [j(j+1)] + \left[ A - \left( \frac{B+C}{2} \right) \right] k^2 \quad (2.17)$$

$$\langle j, k | \hat{H} | j, k+2 \rangle = \frac{B-C}{4} [(j-k)(j+k+1)(j-k-1)(j+k+2)]^{1/2} \quad (2.18)$$

$$\langle j, k | \hat{H} | j, k-2 \rangle = \frac{B-C}{4} [(j+k)(j-k+1)(j+k-1)(j-k+2)]^{1/2} \quad (2.19)$$

With these expressions and those reflecting the vibrational energies the Hamiltonian matrix may be calculated for the ground and each upper state energy levels. After diagonalization the resulting eigenvalues represent the energy levels and the eigenvectors can be used to model the probability of transition and, therefore, the line strength.

## Measurement of Line Intensities

A typical infrared absorption line is not one which is infinitely sharp, but instead it has a finite width which is measurable [29]. While the width of the line is due to a number of factors, there are two major

influences which have effect. These two influences are due to the instrument the spectra was recorded on and the absorbing gas itself. Instrument functions are highly individualized, and each spectrometer introduces effects due to its design. The instrument function present in TDL studies can be cautiously ignored only when it's much narrower than the line shape [30]. Effects which can never be ignored, however, are those due environmental conditions under which the gas is studied.

Two mechanisms which generate the most noticeable effects are Doppler and collisional broadening [31]. Doppler broadening occurs when the individual molecules being studied move with random direction and speed. The Doppler halfwidth of a particular spectral line may be calculated from:

$$b_d = \left( \frac{v_0}{c} \right) \left[ \left( \frac{2kN_A T (\ln 2)}{M} \right) \right]^{1/2} \quad (2.20)$$

where  $k$  is the Boltzmann constant,  $N_A$  is Avogadro's number,  $T$  is the temperature of the gas in degrees Kelvin,  $c$  the speed of light and  $M$  the molecular weight of the molecule in a.m.u. Collisional broadening only occurs when the pressure of the gas reaches a point at which significant amounts of energy are transferred when the molecules collide and exchange energy. The pressure at which collisional broadening becomes a factor is highly dependent upon the molecule under study. Generally, however, the larger the dipole moment the lower the pressure required to observe this effect.

The usual starting point for the discussion of intensities is the Beer-Lambert law. This law describes the transmission of radiation through a gas sample. The Beer-Lambert law is expressed as [32]:

$$I(\nu) = I_0 e^{-k(\nu)x} \quad (2.21)$$

The relationship between  $I_0$  and  $I(\nu)$  can be expressed in terms of absorbance or transmittance is shown in figure 2.1 [33]. The value of  $I(\nu)$  is the absorption between the half maximum of the line and complete absorption. The  $I_0$  is the value between the complete absorption and complete transmission. The other quantities in equation (2.21) are the optical density or pressure path length,  $x$ , of the gas being studied.  $k(\nu)$  is known as the absorption coefficient and is defined as:

$$k(\nu) = S \cdot f(\nu - \nu_0) \quad (2.22)$$

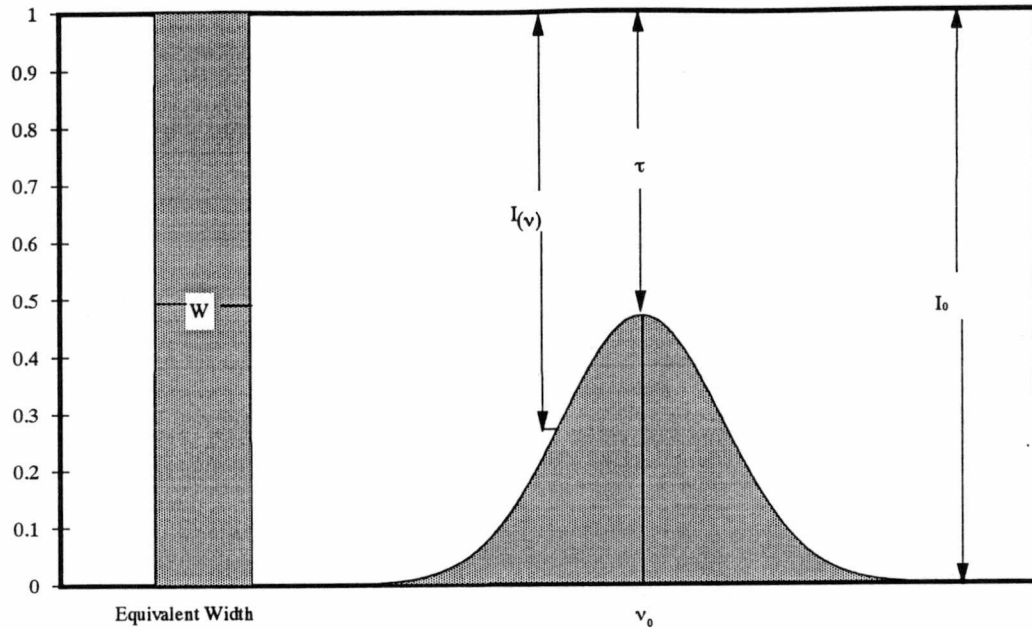


Figure 2.1  
Definition of  $I(v)$ ,  $I_0$  and equivalent width

where  $f(v-v_0)$  is the function which describes the shape of line and is normalized in wavenumber space and  $S$  is the line strength, as yet undefined. It is unfortunate that the term strength is often interchanged with intensity and even integrated absorption coefficient.

Since the spectra that is analyzed in this work is not measurably pressure broadened, the only line shape function that is important is the Doppler profile. This is defined by equation (2.23).

$$f(v - v_0) = \left( \frac{1}{b_d} \right) \left[ \left( \frac{\ln 2}{\pi} \right) \right]^{\frac{1}{2}} \exp \left[ -(\ln 2) \left( \frac{(v - v_0)}{b_d} \right)^2 \right] \quad (2.23)$$

In this equation  $b_d$  is the Doppler halfwidth at half maximum as defined earlier, and  $v_0$  is the line center.

In an ideal world, where spectrometers would have infinite resolving power the line strength could be determined by the combination of equations (2.21) and (2.22). The result would be [34]:

$$(2.24)$$

$$S = \int_0^{\infty} \left( \frac{1}{x} \right) \ln \left( \frac{I_0}{I(\nu)} \right) d\nu$$

But since the instruments in use do have a limited resolving power, another means must be discovered to determine the line strength from observed spectra. This can be accomplished through the use of two different methods. The first is the equivalent width method. The equivalent width for a particular line is graphically represented in figure 2.1. The equivalent width is simply the width of the rectangle in absorbance space which has area equal to that under the absorption curve. The area of this rectangle is measured in terms of wavenumbers since the height dimension is normalized and unitless.

Measurement is actually quite simple once the type of line profile is determined. The equivalent width may be calculated directly from equation (2.25):

$$E.W. = \int_{-\infty}^{+\infty} (1 - e^{-k(\nu)x}) d\nu \quad (2.25)$$

Once the equivalent width of the line is known the value of the strength can be determined through the use of the tables of Jansson and Korb [37]. These tables contain a representative list of equivalent widths, temperature, and pressure path lengths and a corresponding strength. A computer program written by Mark Weber extrapolates between the table values to determine experimental values is employed in this work and is discussed in the experimental section.

The second method for the determination of line strengths from observed spectra is known as the direct method. This method employs the value of  $\tau$  shown in figure 2.1, which is the amount of transmitted energy in the normalized absorption window. The line strength can then be calculated from [38]:

$$S = - \left( \frac{2\pi kT}{mc^2} \right)^{1/2} \left( \frac{\nu_0}{PL} \right) \ln \tau_0 \quad (2.26)$$

$$S = -(0.5794) \left( \frac{\nu_0}{PL} \right) \left( \frac{T}{M} \right)^{1/2} \ln \tau_0 \quad (2.27)$$

Where  $\nu_0$  is the line center in wavenumbers, P is the pressure in milliTorr, L is the absorption pathlength in cm and M is the molar mass in grams. This method offers simplicity as its chief attribute. From a measurement of the transmittance of a line, the value of its strength can be calculated. In this method

there is only one major drawback. This is the requirement that the line under study be only approximately 30% absorbed or less. As long as this rule of thumb is adhered to the method is sound.

To connect this discussion to the quantum mechanics that was presented in the earlier section of this chapter requires the following equation [36]:

$$S_{A \rightarrow B} = \left( \frac{8\pi^3}{3hc} \right) \left( \frac{n_A}{g_A} \right) \nu_{AB} \left[ 1 - \exp\left( -\frac{hc\nu_{AB}}{kT} \right) \right] \left| \langle A | \mu | B \rangle \right|^2 \quad (2.28)$$

Where  $S_{A \rightarrow B}$  is the strength of a particular transition from state A to state B. The term which contains a statistical expression of the number of molecules in the upper state ( $n_A/g_A$ ) can be expressed in terms of the Boltzmann distribution to make the result more useful. The matrix element  $\langle A | \mu | B \rangle$ , however, is that connection that we wish to make. The A state is the upper vibrational energy state and B is the lower. The  $\mu$  is the dipole moment of the molecule.

## Chapter 3

### Experimental Setup

#### Kitt Peak Fourier Transform Spectrometer

The Kitt Peak Fourier Transform Spectrometer has been discussed in the literature, and a relatively complete account has been given by B. A. Palmer [39]. The Fourier Transform Spectrometer is a Michelson interferometer with modifications which make it very useful in the study of high resolution infrared spectroscopy. The classical interferometer is comprised of a light source, a beam splitter, one moveable and one stationary mirror and a detection point where the interference pattern can be observed. The light beam passes through the beamsplitter where it is directed to the two mirrors. Each beam is then reflected back to the beamsplitter where they are recombined and a series of circular fringes is observed. When the movable mirror is translated the observer sees the interference fringes change. The intensity versus the path difference is known as an interferogram. To create an interferogram the intensity of the central fringe is recorded for a series of path differences. The interferogram is then Fourier transformed to produce a spectrum. The optical arrangement of the classical interferometer is shown in figure 3.1.

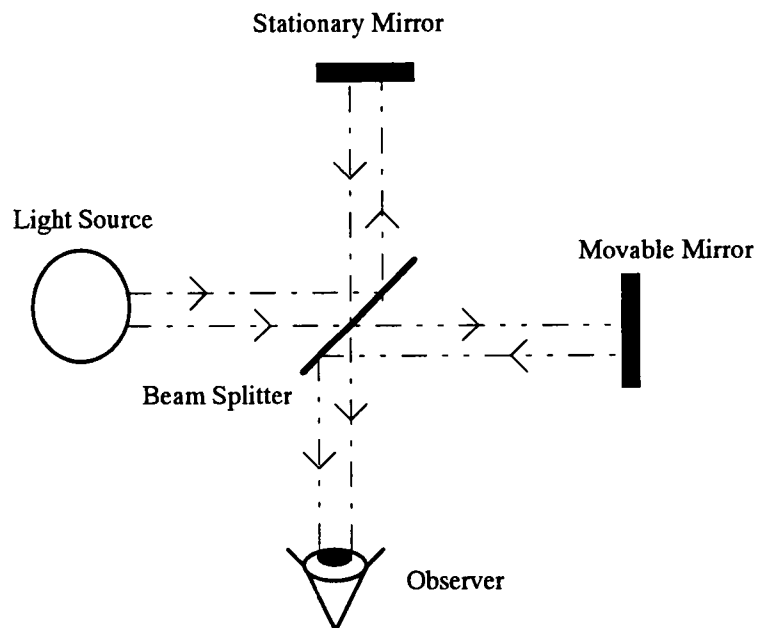


Figure 3.1  
Classical Michelson interferometer

The type and quality of the spectra is determined by two factors. The first is the size of the step the movable mirror makes between data points. Step size determines what frequency range or free spectral range (FSR). FSR can be calculated as  $(.5)(s)^{-1}$ , where  $s$  is the step size. The second factor is the maximum optical path difference the light travels. The greater the path difference the higher the resolution of the resulting spectra. The resolution can be calculated as  $(.5)(L)^{-1}$ , where  $L$  is the total difference length.

The major difference between the classical interferometer and the Kitt Peak FTS, is that on the FTS both mirrors are moveable, beamsplitters and detectors are optimized for frequency range and step size is controlled to an accuracy of 3 angstroms. The mirrors, while not a design requirement, are movable cat's eye type. The step size control is accomplished through the use of highly sensitive motion control servo systems using a He-Ne laser which is frequency stabilized by Zeeman splitting. By the comparison of two Zeeman components after they have passed through the optical system, the position of the mirrors can be obtained and a constant travel speed can be maintained. A schematic of the configuration is shown in figure 3.2.

To eliminate vibration that may be transferred to it, the instrument rests upon a 14 inch thick granite slab. The entire system is run under vacuum which prevents slight changes in the composition and condition of the surrounding atmosphere to effect the quality of the spectra.

The total path length of the Kitt Peak FTS is 2.5 meters which gives it a resolution of  $.010\text{ cm}^{-1}$  when using double sided interferograms and  $.005\text{ cm}^{-1}$  in single sided mode. Double sided interferograms are obtained using information from both sides of zero path difference. To increase the effective resolution of the instrument it is often set up in a double pass configuration. This means that flat mirrors are placed in front of the cat's eye reflectors in such a way that the optical path length is doubled (shown in figure 3.3). The only way that this effects the spectrometer in a negative fashion is by converting from a dual- to a single-output configuration. The loss of dual-output is, in most cases, acceptable when the signal to noise ratio is relatively large since resolution is greatly improved [40]. When using this mode with single sided interferograms an effective resolution of  $0.0025\text{ cm}^{-1}$  is achieved.

Data is processed using a 22-bit analog to digital converter which is comprised of seven 16-bit A/D converter stages. The converter is able to digitize data at a rate of 50 KHz and is calibrated with a 18-bit D/A converter. The D/A converter generates correction coefficients for the different offsets, gains and nonlinearities of each converter stage. Digital filtering techniques are used to process the data before it

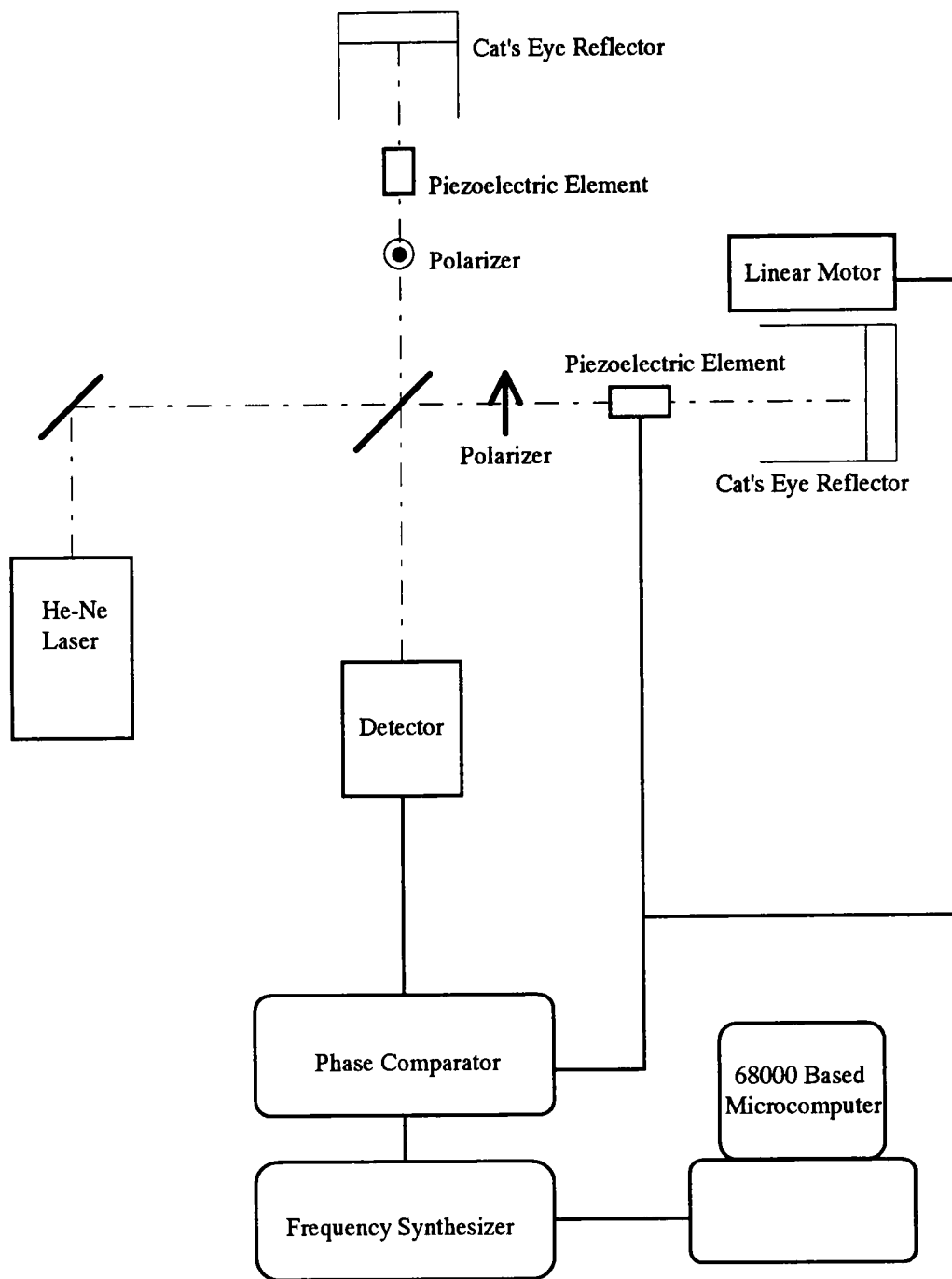


Figure 3.2  
Kitt Peak Fourier Transform Spectrometer servo control system

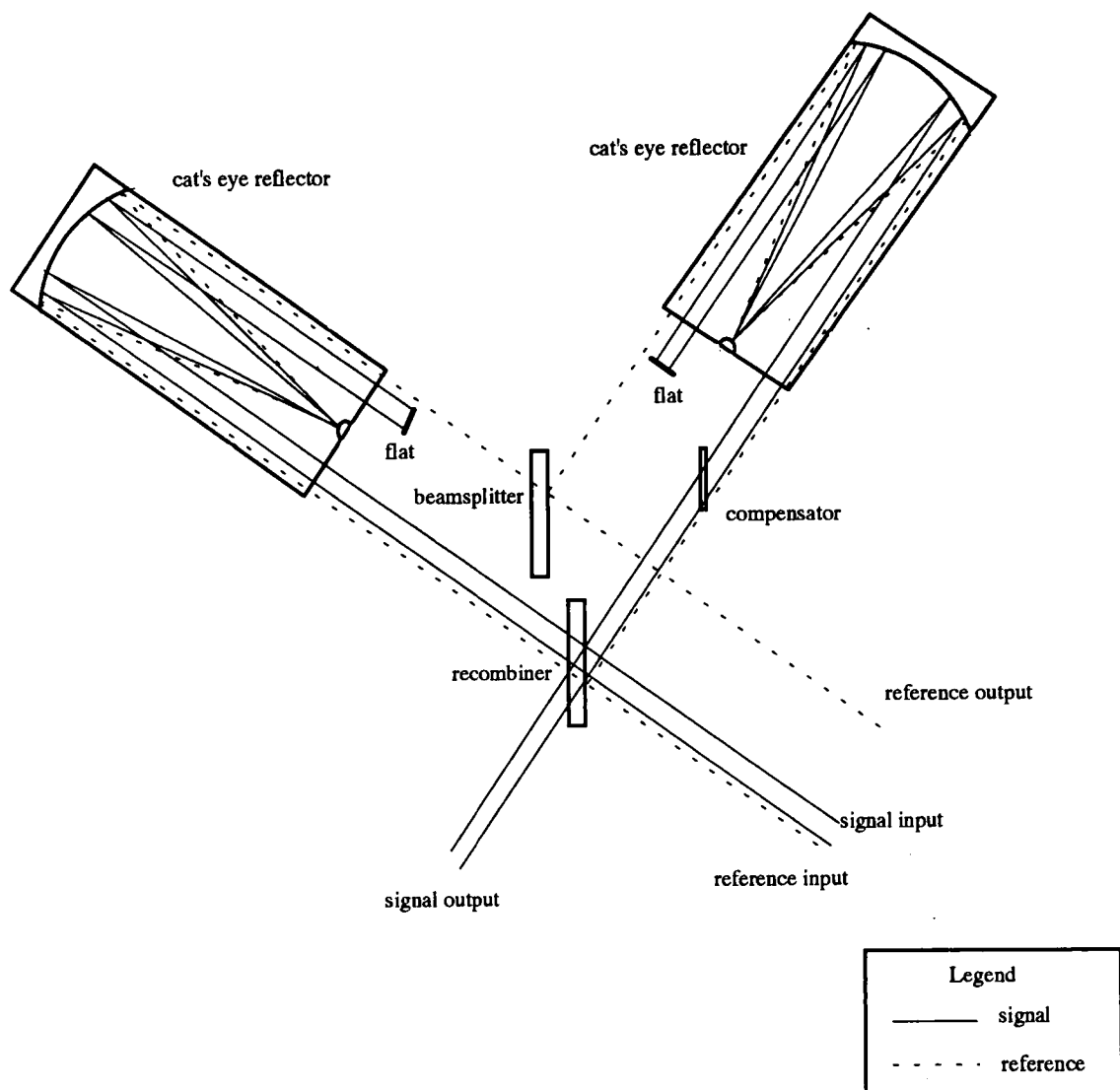


Figure 3.3  
Kitt Peak FTS in double pass configuration

is recorded, and after it is recorded the 68000 based microcomputer which controls the system can co-add scans to improve signal to noise ratio.

The data used in this work was taken at Kitt Peak National Solar Observatory on April 24, 1983 by the members of the Laboratory for Extraterrestrial Physics located at Goddard Space Flight Center. The data set contains spectra from 800 to 1100  $\text{cm}^{-1}$  and the interferogram was co-added 30 times. The pressure of the 30 cm sample cell was reported to be 93 milliTorr. Carbon Dioxide ( $\text{CO}_2$ ) was added in another cell in the beam path for the purposes of frequency calibration.  $\text{CO}_2$  calibration lines were from the difference band responsible for the well known 10  $\mu\text{m}$   $\text{CO}_2$  laser transitions [41].

A series of programs, produced by Dr. Mark Weber formerly of the UTMSL, was used to reduce and analyze the Kitt Peak data [46]. The first analysis program is known as F (version 3.2). Program F allows the user to select a narrow region of spectra, normalize this region, and prepare the data for a least squares fitting procedure. The second program in the series is known as LSQ (version 7.2.1). LSQ fits the normalized spectra prepared by F. Several parameters may be fit for in a particular session. The most common parameters varied are the center frequency of the line, the cell length and the strength of the line. At the conclusion of a successful fitting session the strengths for the fit lines is reported along with error values. The final program in this series is called PLOT (version is 7.9) by Larry Jennings of the UTMSL. PLOT allows the user to graphically see the quality of the fit that LSQ prepared.

## **UTMSL Tunable Diode Laser Spectrometer**

Data acquisition performed at UTMSL was made possible using a tunable diode laser spectrometer (TDL). There are many advantages to using a TDL in spectroscopic investigations [42]. These include:

1. Narrow line widths of the laser emission
2. High signal to noise ratio
3. High spectral power
4. Continuous tuning over a wavelength range.

The heart of the TDL system is the Pb-Sn-Te salt crystal compounds which make up the diode laser itself [43]. These diodes are cryogenically cooled and typically operate over a 100  $\text{cm}^{-1}$  range when an excitation current is placed through them. The wavenumber region in which the diode operates is determined by its composition. The diode used in this work was supplied by Laser Photonics of Bedford, Massachusetts and its operational parameters are:

|                      |                                                                                  |
|----------------------|----------------------------------------------------------------------------------|
| Operating Conditions | 947 $\text{cm}^{-1}$ at 187 mA and 52 K                                          |
| Power                | 1.10 mW at 315 mA and 52 K                                                       |
| Operating Range      | Threshold at 837 $\text{cm}^{-1}$ at 1 mA and 20 K<br>Maximum at 500 mA and 80 K |

In the setup at UTMSL up to four diodes are placed in a sealed, evacuated chamber. A cold finger which is attached to a closed cycle helium refrigeration unit cools the diodes to a temperature of approximately 12 K.

The tuning of an individual diode laser is done in two ways. The first is by changing the excitation current. This is accomplished by use of a highly stable current supply, manufactured by Laser Analytics, which is capable of providing up to 2 amperes. The second is by modifying the temperature of the diode. This is can be done through the use of a thermostatically controlled heating unit which is attached to the cold finger. The heating unit, also supplied by Laser Analytics, can be set to maintain a specific temperature between 12 and 70 K.

The electronics associated with the TDL system make the recording of high resolution spectra possible. The electronic configuration is shown in figure 3.4. This configuration may be broken down into four major sections. The first section includes all equipment which is physically on the TDL optical bench. Two stepper motors supplied by Superior Electric are used to control the position of the defraction grating and to rotate the optical shutter at 100 Hz. The TDL containment vessel and the cold head used to maintain cryogenic temperatures are physically attached to one another. The HgCdTe detector, also cryogenically cooled with liquid nitrogen, is the final electronic element to reside on the table.

The second section includes the devices used to control the Superior Electric stepper motors, model M061-FD02, located on the optical bench. Two different types of control systems are employed. The first is the SC-149 Smart Stepper Motor Controller produced by Alpha Products. The SC-149 is controls the grating position motor. The controller is attached to the computer and uses a simplified set of commands to move the motor. A PD-123 power driver card, also manufactured by Alpha Products, is inserted between the SC-149 and the motor. This is due to the fact that the motor requires more current than the controller card is capable of producing. In fact, modifications to the PD-123 itself were required to enable it to operate reliably. These modifications are contained in Appendix A. The other type of controller employed is the Superior Electric Slo-Syn Translator. This controller is attached to the motor which rotates the optical shutter. The trigger signal to the translator is supplied by the Kron-Hite Wave Form Generator.

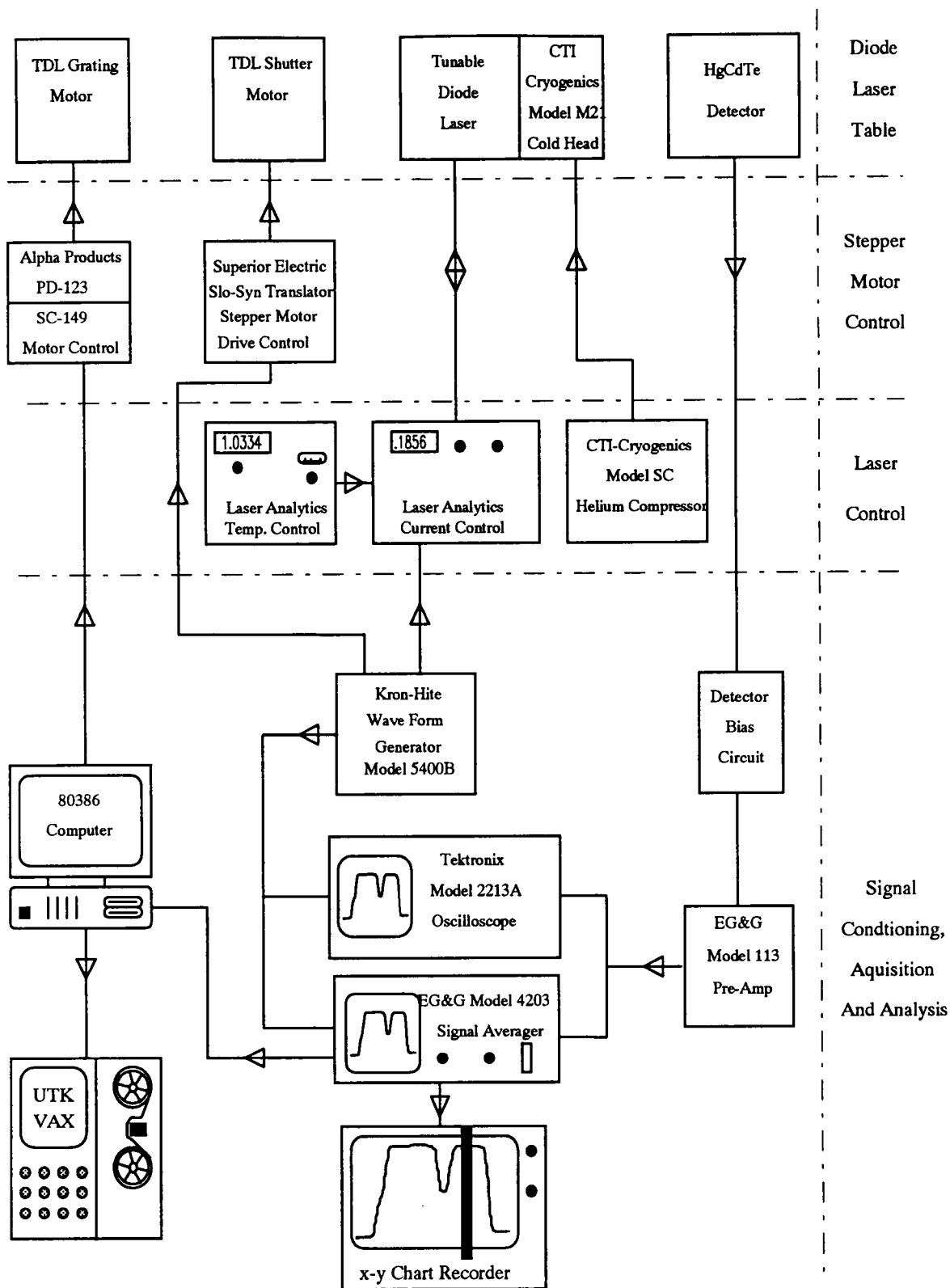


Figure 3.4  
UTMSL tunable diode laser electronic configuration

The third section includes the equipment which controls the laser diode. The importance of the controlling hardware has been previously discussed. The helium compressor, manufactured by CTI-Cryogenics, supplies the cold head with power as well as the refrigerated gaseous helium necessary to cool the laser.

The final section includes all equipment used to help generate and acquire the laser signal. It is important at this point to understand how a narrow wavelength region is scanned by the TDL. To generate spectra the laser must be able to sweep over and record a limited wavelength region. Two scanning modes are available for use in the UTMSL TDL system. The first is known as slow scan mode. In this case the current supply itself alters the amount of current delivered to the diode. The detector then receives the information and a small wavelength range can be scanned. An advantage to this method is that only a single scan is required to generate spectra which has a very good signal to noise ratio. The second method is known as fast scan mode. In this mode an external signal is sent to the current supply. The current supply uses the signal to slightly alter the amount of current the diode receives and thus perform a scan. Typically a 100 Hz ramp type signal is supplied, but saw-tooth and sine waveforms are also available. The scans are averaged together to generate high signal to noise ratio spectra. The fast scan method was used in this work and is currently employed as the standard in the UTMSL. The advantages to this method include the ability to determine a reference between 100% absorption and 100% transmission through the use of the chopper. The reference window is what makes the measurement of intensities possible.

In the fast scan method the instrument which is most important is the Kron-Hite signal generator. It generates the wave form used by the TDL current control needed to scan a wavelength region. It also supplies the oscilloscope and signal averager with their trigger signals. The signal generator supplies the shutter motor with its control signal. The oscilloscope, Tektronix model 2213A, is used to observe data in real time. The signal averager, EG&G model 4203, is used to average from 2 to 999,999 scans, typically between 2 and 500 scans were used in this work. The number of scans is determined by the user. The signal from the detector is conditioned by a battery bias circuit and a pre-amp, EG&G model 113. After the signal averager records the spectra it can be directly dumped to a chart recorder for manual measurement or to the controlling 80386 based computer. The computer, which also controls the position of the grating motor, can process the data using analysis programs or store the data on diskettes. After the data is stored it can be sent via ethernet to other computers in the UTMSL or the University of Tennessee VAX cluster for further analysis.

The electronics are all required to generate, control and observe the infrared energy required for the study of molecular spectra. After the energy is generated it must be directed through a series of optics. Energy produced by the diode laser is directed through several optical elements before being directed to the detector and the electronics described above. Figure 3.5 shows how this is accomplished.

The energy leaves the diode and is collimated by a 26.7 cm focal length mirror. It then is then directed through a series of 3 flat mirrors before a 121.9 cm focal length mirror sends the energy through the gas sample cell and the 100 Hz chopper. The beam is then recollimated by a 63.5 cm focal length mirror. The germanium etalon may be placed between this mirror and the next flat when fringes are required to calibrate the wavelength scale. The next flat directs the beam to a 63.5 cm focal length mirror. The focal point of this mirror is located at the entrance slit of the monochromator in the system.

A 40.6 cm focal length mirror collimates the beam before reaching the grating. The grating diffracts the beam and the desired wavelengths from that order are directed to another 40.6 cm focal length mirror which focuses the light on the exit slit of the monochromator. A 63.5 cm focal length mirror collimates the beam and it is directed through two flats before being focused on the detector by a 63.5 cm mirror.

The alignment of these mirrors is accomplished by use of a Helium-Neon (He-Ne) laser. The main advantage to using the He-Ne laser is that it produces a visible beam where the tunable diode laser produces an invisible infrared beam. To accomplish the alignment of the laser the combination of pellicle and glass beamsplitters are used to direct the He-Ne beam two different directions. A schematic of the alignment beam path is shown in figure 3.6. The major differences between the alignment and the operational configuration of the optical table are that the grating is replaced with a flat mirror and the detector is moved from the beam path. The grating is replaced to maximize the He-Ne energy. Alignment is not hindered by this procedure because the grating acts as a mirror at zero order. It should be noted that where no direction is indicated the beam is traveling in both directions.

After the alignment process has been completed, the He-Ne laser has yet another function. When the alignment is complete the grating is reinstalled at zero order. Zero order can be determined by using a white light source at the entrance slit of the monochromator section of the optical setup. The light is dispersed into its spectral components on all but the zero order. The zero order component is then aligned with the exit slit. The pellicle and glass beamsplitters are placed in the beam path. When the He-Ne beam strikes the grating it is dispersed into various orders. The frequency of each of the orders can be calculated with the following equation:

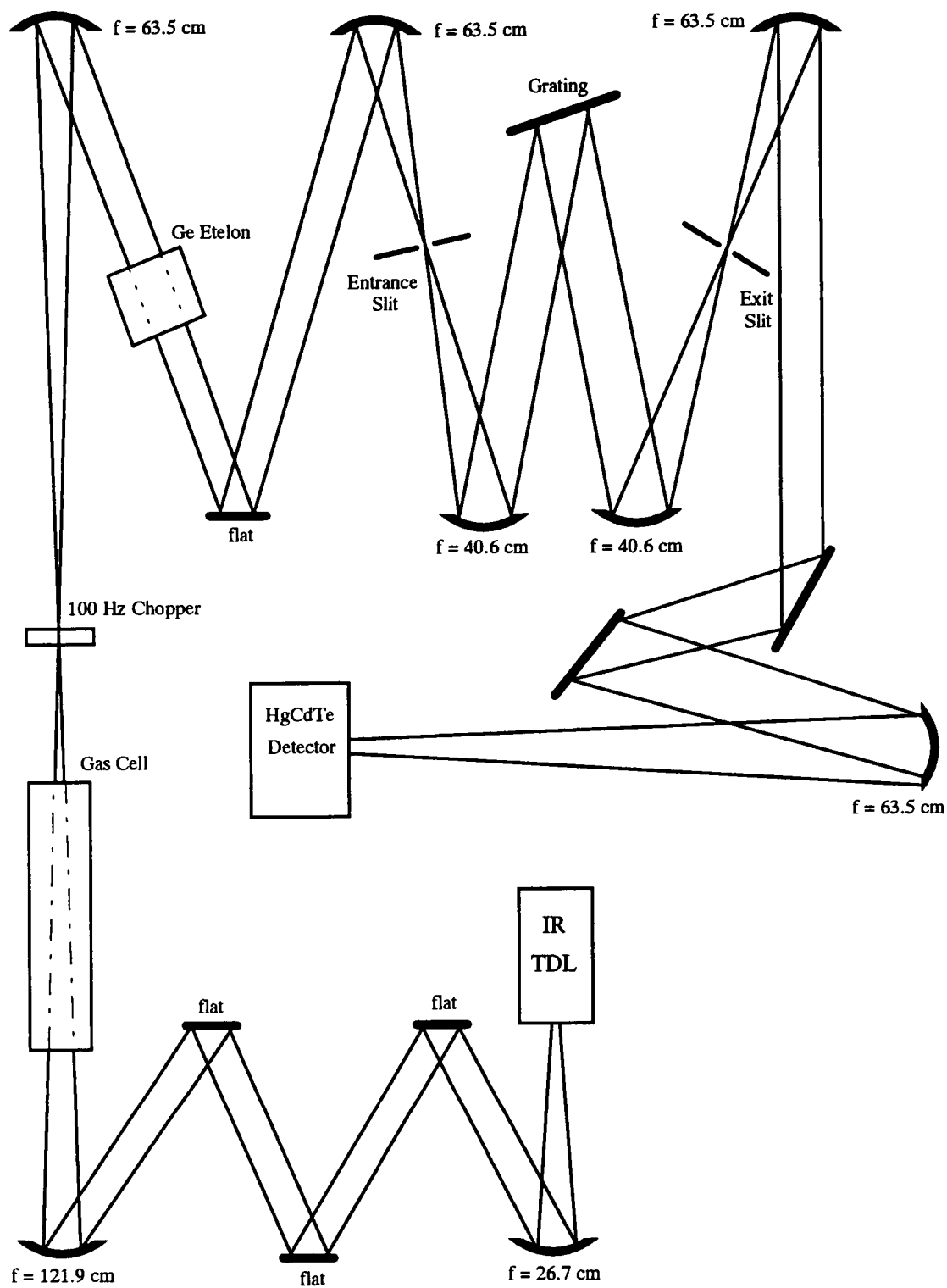


Figure 3.5  
Schematic diagram of infrared beam path of the UTMSL TDL system

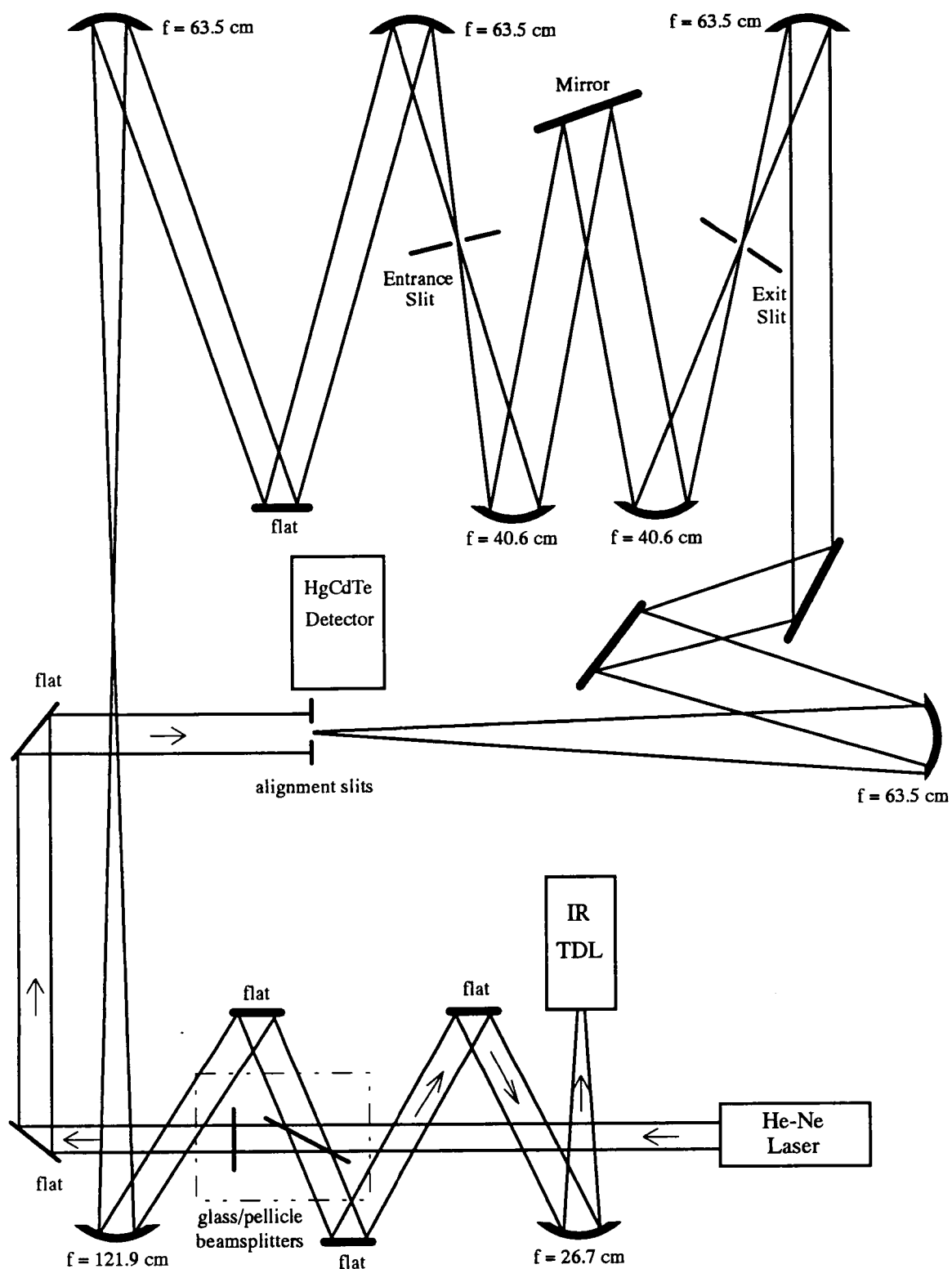


Figure 3.6  
Alignment beam path of the UTMSL TDL system

$$v_n = \frac{1}{\lambda n} \left( \frac{10^8 \text{ Å}}{\text{cm}} \right) \quad (3.1)$$

In this equation  $n$  is the order number and  $\lambda$  is the wavelength of the He-Ne laser (6328 Å). From this a calibration curve for the stepper motor position versus wavelength can be determined. The grating is moved from step position zero at zero order to each of the orders in sequence and a table of wavenumber versus step number is recorded. In the software which controls the laser system, which is known as DIODE, the calibration is accessed using two cubic splines which interpolate between calibration data points. The reason that two cubic splines are used is so that a frequency can be determined from a given step number or a step number from a frequency. DIODE was written in the Visual BASIC for Windows programming language by the author of this work as well as Larry Jennings and Stewart Hager of the UTMSL. This replaced the original FORTRAN based software written by W. E. Blass [47]. The programs are virtually the same in the sense that they use the same algorithms to access the calibration, move the grating and take data. The major difference is in the ease of taking data and moving it to any Windows application for analysis and display.

While the calibration of the line position is accomplished in the manner described above, the calibration of the linewidths is obtained using a germanium etalon. The refractive index of the etalon,  $n=4$ , yields a small free spectral range. This determines the spacing of the fringes in terms of wavelength. The spacing can be determined from the following where  $l$  is the cavity length,  $n$  is the index of refraction and  $\lambda$  is the wavelength of the incident energy.

$$\Delta v = \left[ \frac{1}{2nl} \left( 1 - \frac{\lambda}{n} \frac{\partial n}{\partial \lambda} \right) \right] \quad (3.2)$$

After each spectral line is recorded with the TDL the etalon is inserted into the beam path and the fringe pattern is recorded in the same manner as a spectrum. This gives a calibration for the spacing in the spectral region being observed. To ensure that the value of the line spacing is correct, an independent scan of a region of spectra containing several known lines is taken. A corresponding etalon scan is also recorded. A comparison of fringe spacings from equation 3.2 and a calibration using line positions from the Kitt Peak data is made. This allows for verification of the actual fringe spacing. An example of a spectra and associated etalon fringes is shown in figure 3.7.

One other sub-system of the TDL system must be discussed before the actual procedure of taking data can be explained. This system is the sample gas handling system. Figure 3.8 shows the manifold used to

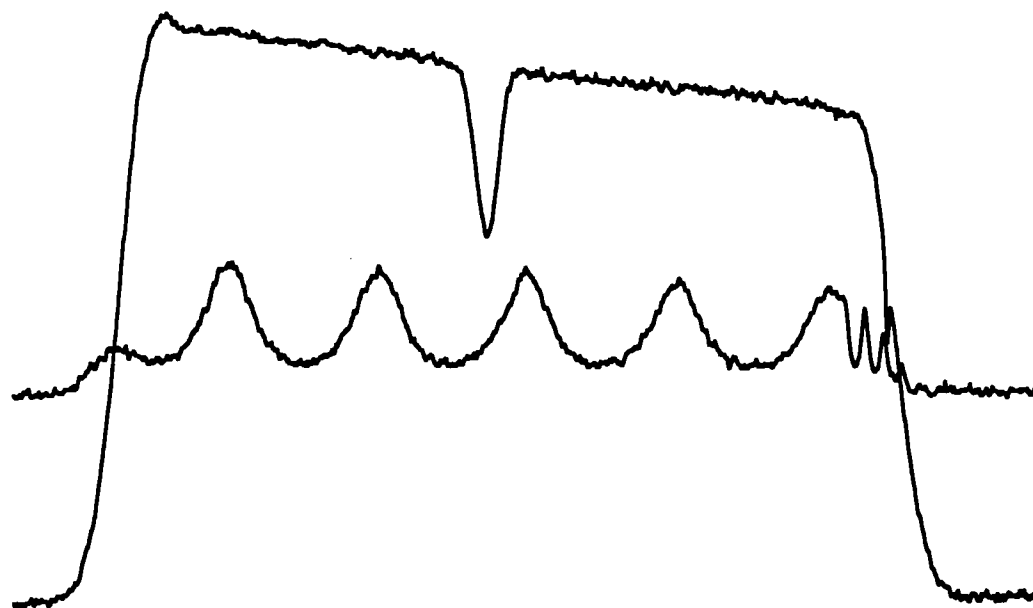
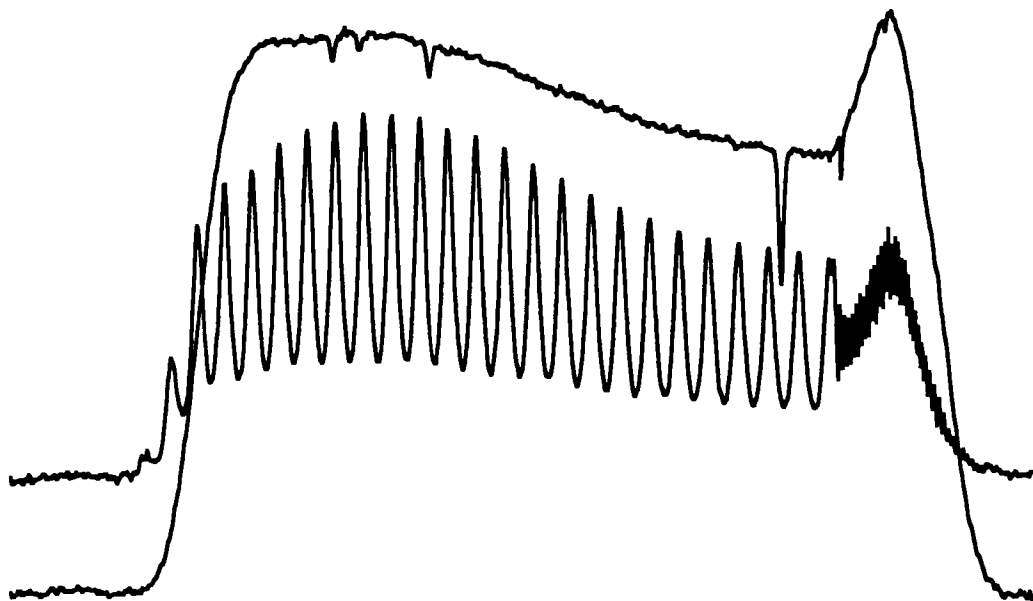


Figure 3.7  
TDL spectra and associated etalon fringes

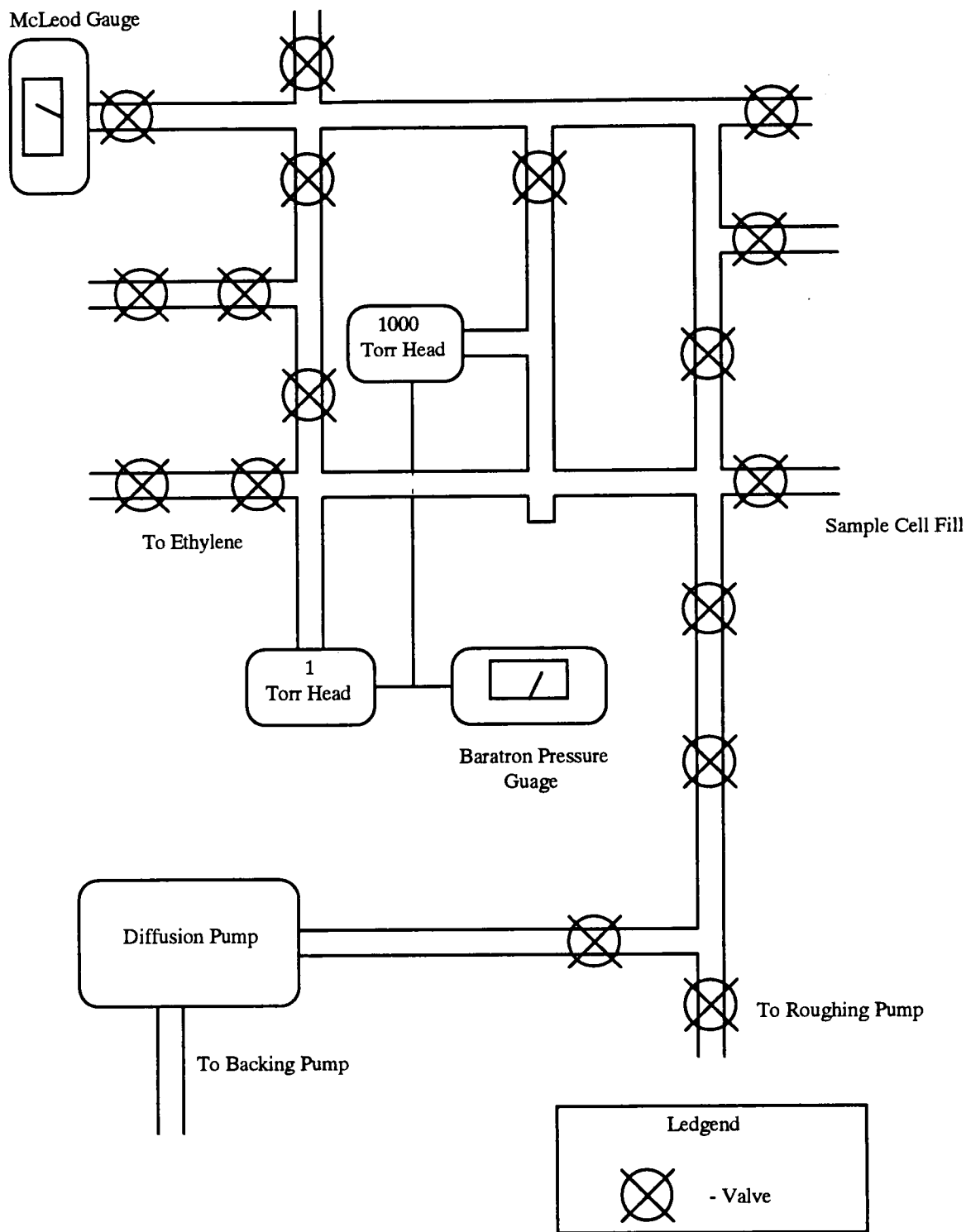


Figure 3.8  
Sample gas manifold vacuum system of the UTMSL TDL

control the sample gas whose spectra is being measured. The principle parts of this sub-system are the Baratron pressure gauge. This gauge is used to determine the pressure that is ambient in the manifold when spectra is being taken. Two different sensor heads can be attached to the gauge. The sensor used most for the measurements contained in this work is the 1 Torr head. This head allows for the measurement of pressures from 0 to 1 Torr. Occasionally higher pressures are required, usually for broadening studies, and in this case the 1000 Torr head can be used. The unconnected portions of the manifold can be used to include various gases when broadening studies are undertaken, or other sample cells that are being prepared for use. A McLeod type gauge is used to independently measure the pressure in the gas manifold. The McLeod is an absolute pressure gauge and can be used to calibrate the electronic gauges.

The gas handling system is used to maintain the sample cells with the proper pressure for spectroscopic studies. This study employed a 45 cm long cell. It is connected utilizing an UltraTorr fitting for ease of removal. The cells were filled in a manner to reduce the pressure fluctuation which would be due to the absorption and outgassing of the cell walls. This effect is most noticeable in the first thirty minutes after filling the cell. After experimentation the following procedure was arrived at. First, the cells were determined to be leak free by monitoring the pressure over extended periods of time. Second, the cells were maintained at a pressure higher than any used in the experimental procedure when not in use. Third, when the cells were about to be used in experimental work they would be evacuated and then refilled with the desired pressure. At the conclusion of data recording the cells would then be returned to their "overfilled" state until their next use.

The only other parameter that needed to be determined before line strengths may be calculated was the temperature at the time of measurement. This is done by use of an Omega Engineering DP41-TC High Performance Temperature Indicator and a Iron-Constantan thermocouple. The thermocouple is directly attached to the cell wall through the use of an adhesive tape. The usual reference temperature for the thermocouple gauge was supplied internally by the DP41-TC and temperature, accurate to .1 degree Kelvin, is indicated on the digital display.

### **Data Acquisition Procedure on the UTMSL TDL System**

All the systems described in the above sections are required to work together to make the acquisition of spectra possible. Typically, the procedure for recording of data follows the following pattern:

1. Check all vacuum readings in system: detector dewer, sample cell and laser cold head. Make sure that cold head and helium compressor are functioning properly.
2. Fill detector dewer with liquid nitrogen if necessary. Turn on Laser Analytics temperature control unit. Allow temperature to stabilize for approximately 30 minutes.
3. Turn on oscilloscope, signal averager, signal generator, and pre-amp. Check that the chopper is rotating smoothly.
4. Determine if signal from detector is reaching oscilloscope. This can be accomplished by waving a warm object, such as one's hand, in front of the detector window. If no noticeable signal is present the usual difficulty is the batteries on the detector bias circuit. Replace batteries if necessary.
5. Remove cover from TDL window and turn on Laser Analytics current supply. Make sure that laser current is less than diode rating.
6. After moving grating to desired position check to see if signal from diode laser is reaching detector by observing the oscilloscope and signal averager. Slight alterations in the alignment of the optical system can be performed to optimize the signal.
7. Select sample cell and fill with desired pressure of ethylene by method discussed above. Isolate a region of spectra by making small changes in the laser current, laser temperature and the amplitude of the waveform supplied by the signal generator.
8. Record spectra by setting the signal averager in normal averaging mode and starting the sweep counter. Typically between 50 and 500 scans are recorded for a particular region.
9. Dump data to the computer by use of the DIODE program or any data terminal package.
10. Analyze data using the N17 program provided by Mark Weber. See the appendix for a complete listing.
11. Isolate new region of spectra and repeat steps 8 through 10.

12. Shut down system by shutting down all electronics, and pumping down sample cell and returning to "overfilled" state.

## Chapter 4

### Experimental Results

#### FTS Data Reduction

Reduction of FTS data was accomplished using software available in the UTMSL. This software as described earlier in this work was prepared by Mark Weber, formerly of the UTMSL. There are two stages to data reduction. The first stage is to modify the data files that are generated at Kitt Peak into a form usable by the F and LSQ. Programs which reduce the data set into smaller, more manageable blocks were used. There are several versions of this software available, but REDUCE and BLKKPD were employed in this work.

The second stage is to bring these smaller data blocks into the F and LSQ programs. F prepares the data by allowing the user to select a narrow region of spectra and normalize it. LSQ then fits the data and returns an equivalent width and intensity.

#### Results of FTS Data Analysis

F and LSQ generates data for both textual and graphical interpretation of the data. Sample plots of fit data are shown in figures 4.1 and 4.2. The plots are useful for observing the quality of the fit. The solid line on the plots is the actual observed data. The dashed line is the fit to the observed data. The lines at the bottom of each plot are the residual for the fit. While the error value that is reported by the program in numerical sense could be very good, the only true test of the quality of the fit is to observe the residual data. The FTS data also has a sine cardinal function convolved with the line shape. This leads to the characteristic effect observed in the strongly absorbing lines which was dubbed "sincing". Since useful information is contained within the sincing, the Weber programs are able to recover equivalent width information from the sinc convolution.

The results from the reduction of the data from the FTS spectra are shown in table 4.1. This includes the quantum numbers of the upper and lower state of the transition, the line position and intensity as calculated by the Mark Weber spectral decomposition programs. Statistical sum squared error values from the fits are also included.

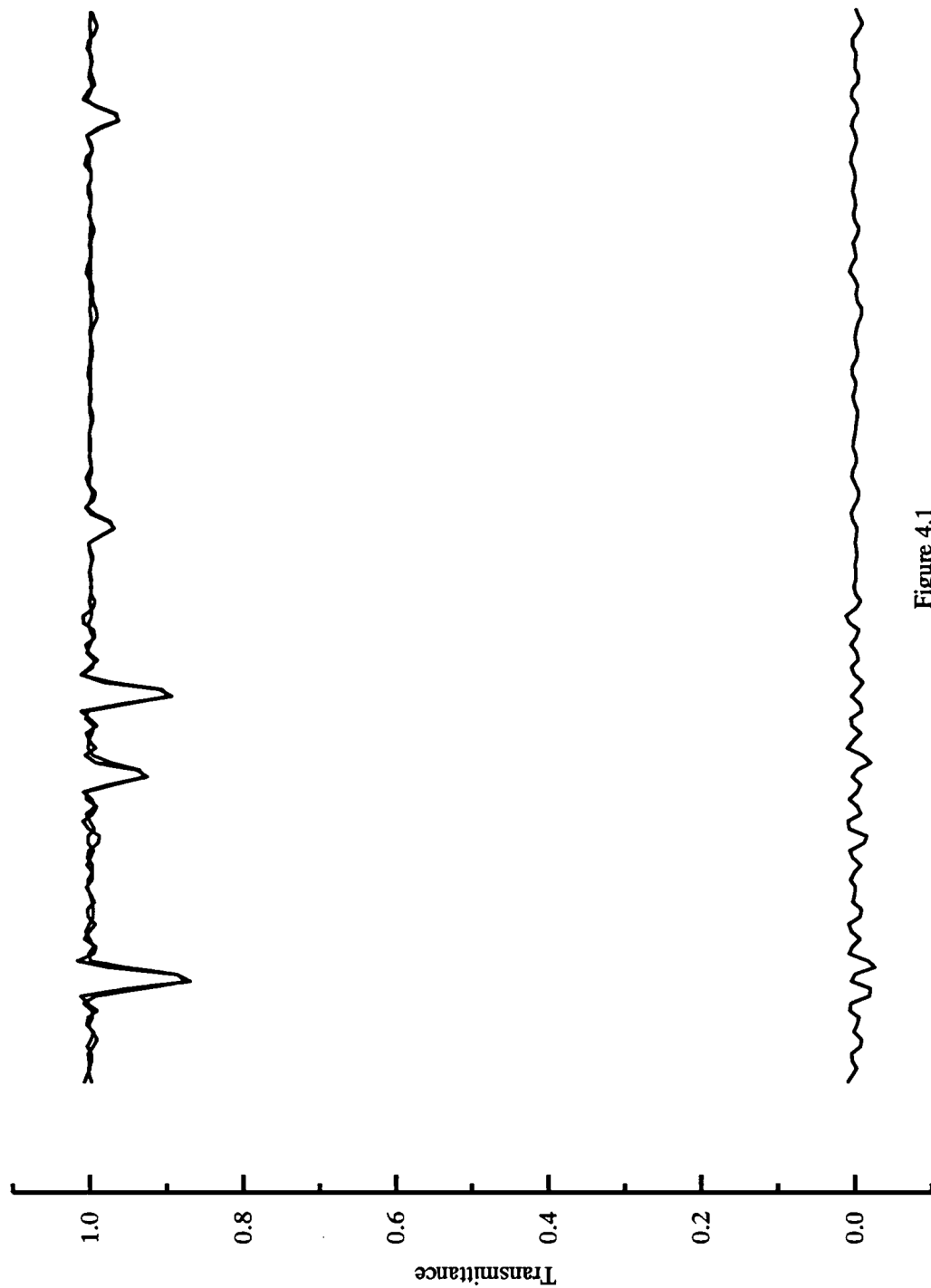


Figure 4.1

The ethylene FTS spectrum from 942.0 to 942.25 wavenumbers and the fitted model spectrum are shown in the top two traces.

The bottom trace shows the residuals for the fit

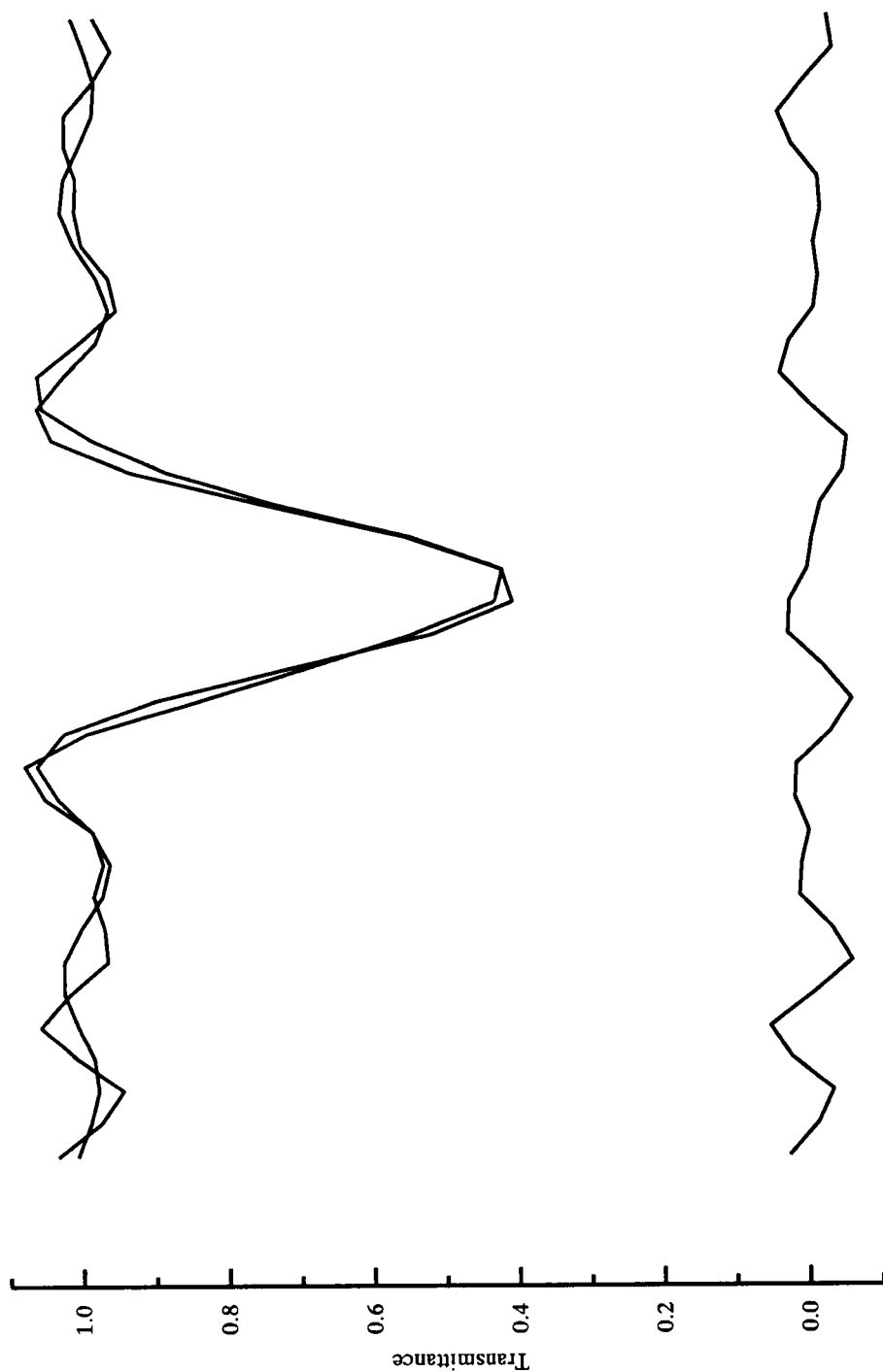


Figure 4.2

The ethylene FTS spectrum for the  $13_{1,12} \leftarrow 13_{2,12}$  transition and the model spectrum are shown in the top trace.

The bottom trace shows the residuals for the fit.

Table 4.1  
Preliminary data reduction results from  
Kitt Peak FTS data (uncalibrated line positions, uncorrected strengths)

| J' | K <sub>a</sub> ' | K <sub>c</sub> ' | J'' | K <sub>a</sub> '' | K <sub>c</sub> '' | $\nu_o(\text{obs})$ | S    | Error    |
|----|------------------|------------------|-----|-------------------|-------------------|---------------------|------|----------|
| 9  | 2                | 7                | 10  | 1                 | 9                 | 940.07461           | .119 | 5.03E-03 |
| 9  | 1                | 8                | 10  | 0                 | 10                | 940.15526           | .195 | 5.51E-03 |
| 9  | 1                | 8                | 9   | 2                 | 8                 | 940.4339            | .633 | 7.49E-03 |
| 1  | 0                | 1                | 2   | 1                 | 1                 | 940.89723           | .105 | 4.08E-03 |
| 21 | 2                | 19               | 21  | 3                 | 19                | 940.98645           | .108 | 4.10E-03 |
| 10 | 1                | 9                | 10  | 2                 | 9                 | 941.12162           | .293 | 7.48E-03 |
| 7  | 1                | 6                | 8   | 0                 | 8                 | 941.41146           | .251 | 2.96E-03 |
| 19 | 4                | 16               | 20  | 3                 | 18                | 942.042245          | .122 | 4.49E-03 |
| 6  | 1                | 5                | 7   | 0                 | 7                 | 942.33129           | .104 | 3.67E-03 |
| 11 | 3                | 9                | 10  | 4                 | 7                 | 942.52972           | .129 | 5.48E-03 |
| 12 | 1                | 11               | 12  | 2                 | 11                | 942.59452           | .313 | 5.74E-03 |
| 11 | 3                | 8                | 10  | 4                 | 6                 | 942.79391           | .109 | 4.35E-03 |
| 13 | 1                | 12               | 13  | 2                 | 12                | 943.35138           | .772 | 1.27E-02 |
| 5  | 1                | 4                | 6   | 0                 | 6                 | 943.43372           | .255 | 7.27E-03 |
| 12 | 3                | 10               | 11  | 4                 | 8                 | 944.31531           | .103 | 3.96E-03 |
| 11 | 3                | 8                | 12  | 2                 | 10                | 944.66737           | .154 | 6.00E-03 |
| 14 | 3                | 12               | 15  | 2                 | 14                | 944.79594           | .119 | 1.09E-02 |
| 1  | 0                | 1                | 1   | 1                 | 1                 | 944.90151           | .107 | 2.77E-03 |
| 2  | 0                | 2                | 2   | 1                 | 2                 | 945.06059           | .182 | 4.43E-03 |
| 16 | 1                | 15               | 16  | 2                 | 15                | 945.50489           | .313 | 7.50E-03 |
| 4  | 0                | 4                | 4   | 1                 | 4                 | 945.58018           | .324 | 7.59E-03 |
| 5  | 0                | 5                | 5   | 1                 | 5                 | 945.91591           | .408 | 1.06E-02 |
| 3  | 1                | 2                | 4   | 0                 | 4                 | 946.11649           | .205 | 3.97E-03 |
| 17 | 1                | 16               | 17  | 2                 | 16                | 946.13291           | .733 | 7.17E-03 |
| 6  | 1                | 6                | 5   | 2                 | 4                 | 946.17431           | .108 | 3.54E-03 |
| 6  | 0                | 6                | 6   | 1                 | 6                 | 946.28093           | .490 | 7.20E-03 |
| 7  | 0                | 7                | 7   | 1                 | 7                 | 946.6576            | .537 | 1.31E-02 |
| 18 | 1                | 17               | 18  | 2                 | 17                | 946.69826           | .303 | 5.32E-03 |
| 13 | 3                | 10               | 12  | 4                 | 8                 | 946.75965           | .124 | 8.10E-03 |
| 19 | 1                | 18               | 19  | 2                 | 18                | 947.19698           | .652 | 7.24E-03 |
| 5  | 1                | 4                | 4   | 2                 | 2                 | 947.28478           | .105 | 5.53E-03 |
| 9  | 0                | 9                | 9   | 1                 | 9                 | 947.37911           | .650 | 1.03E-02 |
| 12 | 3                | 10               | 13  | 2                 | 12                | 947.45192           | .141 | 5.77E-03 |
| 20 | 1                | 19               | 20  | 2                 | 19                | 947.62944           | .256 | 8.02E-03 |
| 10 | 0                | 10               | 10  | 1                 | 10                | 947.69847           | .677 | 1.61E-02 |
| 14 | 3                | 12               | 13  | 4                 | 10                | 947.8328            | .120 | 4.78E-03 |
| 11 | 0                | 11               | 11  | 1                 | 11                | 947.98123           | .742 | 1.56E-02 |
| 21 | 1                | 20               | 21  | 2                 | 20                | 948.00042           | .561 | 1.28E-02 |
| 12 | 0                | 12               | 12  | 1                 | 12                | 948.2261            | .760 | 3.01E-02 |
| 22 | 1                | 21               | 22  | 2                 | 21                | 948.31641           | .203 | 4.54E-03 |
| 13 | 0                | 13               | 13  | 1                 | 13                | 948.43473           | .708 | 2.88E-02 |
| 23 | 1                | 22               | 23  | 2                 | 22                | 948.58496           | .431 | 6.97E-03 |
| 14 | 0                | 14               | 14  | 1                 | 14                | 948.61142           | .701 | 9.38E-03 |
| 15 | 0                | 15               | 15  | 1                 | 15                | 948.76194           | .684 | 1.72E-02 |
| 24 | 1                | 23               | 24  | 2                 | 23                | 948.81496           | .198 | 3.55E-03 |

Table 4.1 (Continued)

| J' | K <sub>a</sub> ' | K <sub>c</sub> ' | J" | K <sub>a</sub> " | K <sub>c</sub> " | $\nu_0(\text{obs})$ | S    | Error    |
|----|------------------|------------------|----|------------------|------------------|---------------------|------|----------|
| 16 | 0                | 16               | 16 | 1                | 16               | 948.89123           | .639 | 8.78E-03 |
| 17 | 0                | 17               | 17 | 1                | 17               | 949.00449           | .601 | 9.08E-03 |
| 25 | 1                | 24               | 25 | 2                | 24               | 949.0132            | .324 | 6.65E-03 |
| 18 | 0                | 18               | 18 | 1                | 18               | 949.1058            | .549 | 7.43E-03 |
| 26 | 1                | 25               | 26 | 2                | 25               | 949.18743           | .177 | 6.65E-03 |
| 19 | 0                | 19               | 19 | 1                | 19               | 949.19888           | .499 | .161831  |
| 20 | 0                | 20               | 20 | 1                | 20               | 949.28636           | .455 | 7.81E-03 |
| 17 | 1                | 17               | 17 | 0                | 17               | 949.33364           | .596 | 7.51E-02 |
| 16 | 1                | 16               | 16 | 0                | 16               | 949.34033           | 1.62 | .204103  |
| 20 | 1                | 20               | 20 | 0                | 20               | 949.41231           | 1.05 | 2.99E-02 |
| 14 | 1                | 14               | 14 | 0                | 14               | 949.4277            | 1.68 | 5.31E-02 |
| 22 | 0                | 22               | 22 | 1                | 22               | 949.45372           | .348 | 1.05E-02 |
| 23 | 0                | 23               | 23 | 1                | 23               | 949.53642           | .319 | 2.29E-02 |
| 23 | 1                | 23               | 23 | 0                | 23               | 949.59844           | .300 | 1.07E-02 |
| 24 | 1                | 24               | 24 | 0                | 24               | 949.64057           | .619 | 1.57E-02 |
| 12 | 1                | 12               | 12 | 0                | 12               | 949.65144           | 1.71 | 4.39E-02 |
| 9  | 3                | 6                | 10 | 2                | 8                | 949.68057           | .128 | 9.85E-03 |
| 25 | 2                | 24               | 25 | 1                | 24               | 949.71636           | .135 | 3.14E-02 |
| 26 | 0                | 26               | 26 | 1                | 26               | 949.79351           | .195 | 3.70E-02 |
| 26 | 1                | 26               | 26 | 0                | 26               | 949.80499           | .330 | .166924  |
| 27 | 1                | 27               | 27 | 0                | 27               | 949.89037           | .125 | 4.18E-02 |
| 22 | 2                | 21               | 22 | 1                | 21               | 949.95576           | .217 | 5.28E-03 |
| 21 | 2                | 20               | 21 | 1                | 20               | 950.13521           | .261 | 5.66E-03 |
| 30 | 1                | 30               | 30 | 0                | 30               | 950.17496           | .204 | 5.58E-03 |
| 20 | 2                | 19               | 20 | 1                | 19               | 950.37897           | .268 | 1.46E-02 |
| 32 | 1                | 32               | 32 | 0                | 32               | 950.39579           | .124 | 1.25E-02 |
| 10 | 3                | 8                | 11 | 2                | 10               | 950.44991           | .127 | 5.06E-03 |
| 8  | 1                | 8                | 8  | 0                | 8                | 950.64833           | 1.45 | 3.76E-02 |
| 19 | 2                | 18               | 19 | 1                | 18               | 950.69447           | .291 | 1.24E-02 |
| 28 | 3                | 26               | 28 | 2                | 26               | 951.11263           | .105 | 9.63E-03 |
| 16 | 3                | 14               | 15 | 4                | 12               | 951.2284            | .118 | 3.97E-03 |
| 6  | 1                | 6                | 6  | 0                | 6                | 951.37018           | 1.19 | 4.30E-02 |
| 4  | 0                | 4                | 3  | 1                | 2                | 951.502             | .116 | 7.18E-03 |
| 7  | 1                | 6                | 6  | 2                | 4                | 951.57952           | .197 | 5.61E-03 |
| 17 | 2                | 16               | 17 | 1                | 16               | 951.60597           | .322 | 6.58E-03 |
| 26 | 3                | 24               | 26 | 2                | 24               | 951.65109           | .145 | 5.61E-03 |
| 5  | 1                | 5                | 5  | 0                | 5                | 951.73787           | .411 | 2.50E-02 |
| 16 | 2                | 15               | 16 | 1                | 15               | 952.16925           | .354 | 4.94E-03 |
| 3  | 1                | 3                | 3  | 0                | 3                | 952.38445           | .276 | 1.22E-02 |
| 1  | 1                | 1                | 1  | 0                | 1                | 952.79483           | .115 | 1.14E-02 |
| 14 | 1                | 14               | 13 | 2                | 12               | 953.0108            | .118 | 3.48E-03 |
| 14 | 2                | 13               | 14 | 1                | 13               | 953.52908           | .352 | 5.82E-03 |
| 8  | 1                | 7                | 7  | 2                | 5                | 953.66688           | .107 | 6.95E-03 |
| 6  | 0                | 6                | 5  | 1                | 4                | 954.10256           | .117 | 3.10E-03 |
| 13 | 2                | 12               | 13 | 1                | 12               | 954.29169           | .356 | 7.18E-03 |
| 7  | 3                | 4                | 8  | 2                | 6                | 954.34194           | .116 | 5.59E-03 |

Table 4.1 (Continued)

| J' | K <sub>a</sub> ' | K <sub>c</sub> ' | J'' | K <sub>a</sub> '' | K <sub>c</sub> '' | $\nu_0(\text{obs})$ | S    | Error    |
|----|------------------|------------------|-----|-------------------|-------------------|---------------------|------|----------|
| 18 | 3                | 16               | 17  | 4                 | 14                | 954.43639           | .114 | 5.27E-03 |
| 32 | 4                | 29               | 32  | 3                 | 29                | 954.54355           | .627 | 9.60E-03 |
| 1  | 1                | 0                | 0   | 0                 | 0                 | 954.78927           | .191 | 5.86E-03 |
| 12 | 2                | 11               | 12  | 1                 | 11                | 955.08382           | .337 | 4.96E-02 |
| 7  | 0                | 7                | 6   | 1                 | 5                 | 955.16559           | .127 | 1.12E-02 |
| 9  | 1                | 8                | 8   | 2                 | 6                 | 955.6705            | .298 | 7.13E-03 |
| 11 | 2                | 10               | 11  | 1                 | 10                | 955.88453           | .322 | 1.26E-02 |
| 8  | 0                | 8                | 7   | 1                 | 6                 | 956.05043           | .126 | 5.09E-03 |
| 10 | 2                | 9                | 10  | 1                 | 9                 | 956.67406           | .317 | 5.78E-03 |
| 9  | 0                | 9                | 8   | 1                 | 7                 | 956.7498            | .118 | 3.13E-03 |
| 2  | 1                | 1                | 1   | 0                 | 1                 | 956.77471           | .122 | 3.25E-03 |
| 10 | 0                | 10               | 9   | 1                 | 8                 | 957.2621            | .103 | 6.66E-03 |
| 20 | 3                | 18               | 20  | 2                 | 18                | 957.36718           | .319 | 8.06E-03 |
| 14 | 2                | 12               | 13  | 3                 | 10                | 958.57047           | .105 | 2.95E-03 |
| 7  | 2                | 6                | 7   | 1                 | 6                 | 958.81184           | .231 | 1.19E-02 |
| 3  | 1                | 2                | 2   | 0                 | 2                 | 958.84086           | .360 | 1.39E-02 |
| 6  | 2                | 5                | 6   | 1                 | 5                 | 959.40584           | .312 | 9.67E-03 |
| 18 | 3                | 16               | 18  | 2                 | 16                | 959.77795           | .351 | 1.08E-02 |

Table 4.1 requires modifications in order to make the information useful. The first modification required is to calibrate the line positions. While it is true FTS line positions are very accurate in a relative sense, a constant offset is present on the order of a few milli-wavenumbers, which must be corrected. Fortunately, absolute calibration can be easily accomplished by use of CO<sub>2</sub> lines present in the observed spectra. These line positions are well known, since they are part of the laser difference band at 10  $\mu$ m. The Handbook of Infrared Standards by Guelachvili and Rao [41] contains very accurate positions for these lines, and recent studies by Johns and Noël on these lines have improved the precision of the intensities of these lines [48]. Table 4.2 contains a list of these lines, and their standard and FTS recorded line positions.

Fitting this information to generate a calibration is accomplished by means of software written by W. E. Blass. The program known as File5 uses bi-weighted least squares to accurately fit the values and generate a calibration factor[47]. Table 4.3 shows the results of the fitting process. It should be noted that the program reduces the effect of questionable data values from the fit. This is accomplished by modification of the weighting of the data points. Strong, isolated CO<sub>2</sub> transitions have fit weights near 1.0. Transitions which were weak, blended or near other strong spectral lines have fit weights near 0.0. The result of the fit was a calibration equation:

$$y(\text{corrected}) = 1.000001661106 (+/- 0.10026E-07) y(\text{FTS}) \quad (4.1)$$

This equation enables any FTS ethylene line position in the specified FTS data to be properly calibrated.

The second task, which is the central purpose of this work, is to validate the measured strengths from Table 4.1. As shown in Chapter 2 a major factor in properly retrieving the intensity of a spectral transition is a precise value for the pressure of the gas sample. The pressure reported by members of the Goddard Space Flight Center Laboratory for Extraterrestrial Physics was 93 milliTorr. It should be noted that the FTS data was recorded for the purpose of conducting line position studies and attention paid to precise pressure measurements was minimal. After checking the values in Table 4.1 against TDL strength measurements, where pressure and temperature were very carefully monitored, it became obvious that the reported pressure and temperature would require correction.

The discrepancy was checked repeatedly and confirmed. It was then determined that rescaling of the values calculated with the 93 milliTorr pressure would be possible. TDL measurements of several lines for which FTS measurements had been recorded would allow for correction of the pressure.

Table 4.2  
Standard and FTS measured CO<sub>2</sub> line positions

| Line  | Standard (cm <sup>-1</sup> ) [41] | FTS (cm <sup>-1</sup> ) |
|-------|-----------------------------------|-------------------------|
| P(52) | 912.2307011                       | 912.22901               |
| P(50) | 914.4192817                       | 914.4181                |
| P(48) | 916.581769                        | 916.58024               |
| P(46) | 918.7183298                       | 918.71991               |
| P(44) | 920.8291217                       | 920.82885               |
| P(42) | 922.9142932                       | 922.91276               |
| P(40) | 924.9739837                       | 924.97243               |
| P(38) | 927.0083238                       | 927.00681               |
| P(36) | 929.0174356                       | 929.0159                |
| P(34) | 931.0014326                       | 930.9999                |
| P(32) | 932.9604201                       | 932.95885               |
| P(30) | 934.8944952                       | 934.89292               |
| P(28) | 936.8037469                       | 936.80222               |
| P(26) | 938.6882566                       | 938.68693               |
| P(24) | 940.5480976                       | 940.5465                |
| P(22) | 942.3833358                       | 942.38177               |
| P(20) | 944.1940294                       | 944.19249               |
| P(18) | 945.9802291                       | 945.97867               |
| P(16) | 947.7419784                       | 947.74038               |
| P(14) | 949.4793134                       | 949.47772               |
| P(12) | 951.1922631                       | 951.1907                |
| P(10) | 952.8808491                       | 952.87912               |
| P(8)  | 954.5450862                       | 954.54353               |
| P(6)  | 956.1849819                       | 956.18339               |
| P(4)  | 957.8005368                       | 957.79894               |
| P(2)  | 959.3917445                       | 959.39008               |
| R(0)  | 961.7328738                       | 961.73137               |
| R(2)  | 963.2631397                       | 963.26134               |
| R(4)  | 964.7689812                       | 964.76739               |
| R(6)  | 966.2503608                       | 966.24878               |
| R(8)  | 967.7072331                       | 967.70563               |
| R(10) | 969.1395472                       | 969.13795               |
| R(12) | 970.5472441                       | 970.54563               |
| R(14) | 971.9302582                       | 971.92865               |
| R(16) | 973.2885167                       | 973.2869                |
| R(18) | 974.6219395                       | 974.62032               |
| R(20) | 975.9304394                       | 975.92883               |
| R(22) | 977.2139221                       | 977.21244               |
| R(24) | 978.4722856                       | 978.47064               |
| R(26) | 979.7054208                       | 979.70379               |
| R(28) | 980.9132107                       | 980.91154               |
| R(30) | 982.0955309                       | 982.09389               |
| R(32) | 983.2522492                       | 983.25061               |

Table 4.2  
Continued

| Line  | Standard ( $\text{cm}^{-1}$ ) [41] | FTS ( $\text{cm}^{-1}$ ) |
|-------|------------------------------------|--------------------------|
| R(34) | 984.3832255                        | 984.38159                |
| R(36) | 985.4883116                        | 985.48668                |
| R(38) | 986.5673514                        | 986.56585                |
| R(40) | 987.6201804                        | 987.61875                |
| R(42) | 988.6466254                        | 988.64647                |
| R(44) | 989.6465049                        | 989.64464                |
| R(46) | 990.6196287                        | 990.61797                |
| R(48) | 991.5657972                        | 991.56422                |
| R(50) | 992.4848022                        | 992.48307                |

Table 4.3  
CO<sub>2</sub> line position calibration fit results

| FTS Line Position<br>(cm <sup>-1</sup> ) | Standard Line<br>Position (cm <sup>-1</sup> ) | Weight | Calculated<br>Position (cm <sup>-1</sup> ) | Position<br>(Calc-Std) | ΔWeight<br>(Calc-Std) |
|------------------------------------------|-----------------------------------------------|--------|--------------------------------------------|------------------------|-----------------------|
| 912.22901                                | 912.2307011                                   | 0.00   | 912.23052                                  | 0.00018                | 0.00000               |
| 914.4181                                 | 914.4192817                                   | 0.00   | 914.41962                                  | -0.00034               | 0.00000               |
| 916.58024                                | 916.581769                                    | 1.09   | 916.58176                                  | 0.00001                | 0.00001               |
| 918.71991                                | 918.7183298                                   | 0.00   | 918.72143                                  | 0.00310                | 0.00000               |
| 920.82885                                | 920.8291217                                   | 0.00   | 920.83038                                  | -0.00126               | 0.00000               |
| 922.91276                                | 922.9142932                                   | 1.10   | 922.91429                                  | 0.00000                | 0.00000               |
| 924.97243                                | 924.9739837                                   | 1.03   | 924.97396                                  | 0.00002                | 0.00002               |
| 927.00681                                | 927.0083238                                   | 0.95   | 927.00835                                  | -0.00002               | -0.00002              |
| 929.0159                                 | 929.0174356                                   | 1.09   | 929.01744                                  | -0.00001               | -0.00001              |
| 930.9999                                 | 931.0014326                                   | 1.06   | 931.00144                                  | -0.00001               | -0.00001              |
| 932.95885                                | 932.9604201                                   | 1.01   | 932.9604                                   | 0.00002                | 0.00002               |
| 934.89292                                | 934.8944952                                   | 0.99   | 934.89447                                  | 0.00002                | 0.00002               |
| 936.80222                                | 936.8037469                                   | 0.91   | 936.80377                                  | -0.00003               | -0.00003              |
| 938.68693                                | 938.6882566                                   | 0.00   | 938.68849                                  | -0.00023               | 0.00000               |
| 940.5465                                 | 940.5480976                                   | 0.83   | 940.54806                                  | 0.00004                | 0.00003               |
| 942.38177                                | 942.3833358                                   | 1.10   | 942.38333                                  | 0.00000                | 0.00000               |
| 944.19249                                | 944.1940294                                   | 0.91   | 944.19406                                  | -0.00003               | -0.00002              |
| 945.97867                                | 945.9802291                                   | 1.07   | 945.98024                                  | -0.00001               | -0.00001              |
| 947.74038                                | 947.7419784                                   | 0.97   | 947.74195                                  | 0.00003                | 0.00002               |
| 949.47772                                | 949.4793134                                   | 1.04   | 949.4793                                   | 0.00002                | 0.00002               |
| 951.1907                                 | 951.1922631                                   | 1.03   | 951.19228                                  | -0.00002               | -0.00002              |
| 952.87912                                | 952.8808491                                   | 0.00   | 952.8807                                   | 0.00015                | 0.00000               |
| 954.54353                                | 954.5450862                                   | 0.91   | 954.54511                                  | -0.00003               | -0.00003              |
| 956.18339                                | 956.1849819                                   | 1.10   | 956.18498                                  | 0.00001                | 0.00001               |
| 957.79894                                | 957.8005368                                   | 1.09   | 957.80053                                  | 0.00001                | 0.00001               |
| 959.39008                                | 959.3917445                                   | 0.24   | 959.39167                                  | 0.00007                | 0.00002               |
| 961.73137                                | 961.7328738                                   | 0.00   | 961.73297                                  | -0.00009               | 0.00000               |
| 963.26134                                | 963.2631397                                   | 0.00   | 963.26294                                  | 0.00020                | 0.00000               |
| 964.76739                                | 964.7689812                                   | 1.07   | 964.76899                                  | -0.00001               | -0.00001              |
| 966.24878                                | 966.2503608                                   | 0.97   | 966.25038                                  | -0.00002               | -0.00002              |
| 967.70563                                | 967.7072331                                   | 1.10   | 967.70724                                  | 0.00000                | 0.00000               |
| 969.13795                                | 969.1395472                                   | 1.06   | 969.13956                                  | -0.00001               | -0.00001              |
| 970.54563                                | 970.5472441                                   | 1.10   | 970.54724                                  | 0.00000                | 0.00000               |
| 971.92865                                | 971.9302582                                   | 1.09   | 971.93026                                  | 0.00000                | -0.00001              |
| 973.2869                                 | 973.2885167                                   | 1.10   | 973.28852                                  | 0.00000                | 0.00000               |
| 974.62032                                | 974.6219395                                   | 1.10   | 974.62194                                  | 0.00000                | 0.00000               |
| 975.92883                                | 975.9304394                                   | 1.07   | 975.93045                                  | -0.00001               | -0.00001              |
| 977.21244                                | 977.2139221                                   | 0.00   | 977.21406                                  | -0.00014               | 0.00000               |
| 978.47064                                | 978.4722856                                   | 1.01   | 978.47226                                  | 0.00002                | 0.00002               |
| 979.70379                                | 979.7054208                                   | 1.10   | 979.70542                                  | 0.00001                | 0.00001               |
| 980.91154                                | 980.9132107                                   | 0.74   | 980.91317                                  | 0.00004                | 0.00003               |
| 982.09389                                | 982.0955309                                   | 1.08   | 982.09552                                  | 0.00001                | 0.00001               |

Table 4.3  
Continued

| FTS Line Position<br>(cm <sup>-1</sup> ) | Standard Line<br>Position (cm <sup>-1</sup> ) | Weight | Calculated<br>Position (cm <sup>-1</sup> ) | Position<br>(Calc-Std) | ΔWeight<br>(Calc-Std) |
|------------------------------------------|-----------------------------------------------|--------|--------------------------------------------|------------------------|-----------------------|
| 983.25061                                | 983.2522492                                   | 1.09   | 983.25224                                  | 0.00001                | 0.00001               |
| 984.38159                                | 984.3832255                                   | 1.10   | 984.38322                                  | 0.00000                | 0.00000               |
| 985.48668                                | 985.4883116                                   | 1.09   | 985.48832                                  | 0.00000                | 0.00000               |
| 986.56585                                | 986.5673514                                   | 0.00   | 986.56749                                  | -0.00014               | 0.00000               |
| 987.61875                                | 987.6201804                                   | 0.00   | 987.62039                                  | -0.00021               | 0.00000               |
| 988.64647                                | 988.6466254                                   | 0.00   | 988.64811                                  | -0.00149               | 0.00000               |
| 989.64464                                | 989.6465049                                   | 0.00   | 989.64628                                  | 0.00022                | 0.00000               |
| 990.61797                                | 990.6196287                                   | 1.06   | 990.61961                                  | 0.00001                | 0.00002               |
| 991.56422                                | 991.5657972                                   | 0.25   | 991.56587                                  | -0.00007               | -0.00002              |
| 992.48307                                | 992.4848022                                   | 0.07   | 992.48472                                  | 0.00009                | 0.00001               |

## TDL Data Acquisition and Reduction

To maximize the validity of the measurements made on the UTMSL TDL system several precautions were taken to ensure the recording of quality data. Pressure measurements from a Baratron pressure gauge insured accurate values. The pressure stabilization procedure noted in Chapter 3 was employed to reduce the effects of out-gassing/cell absorption. A thermocouple attached to the cell wall recorded sample temperature while data was acquired.

When a spectral transition was identified for measurement the following procedure was employed. First, a spectrum was coadded a various number of times and recorded independently a minimum of six times. The etalon fringes were recorded both before and after this series of spectra. Secondly, a spectrum and its associated etalon fringes were recorded in a wideband mode showing at least two additional transitions in the vicinity to allow calibration of the fringe spacing to the known line spacing with an appropriate polynomial model. There is also a second purpose for this wideband scan. After measuring the strength of the single transition by both the equivalent width and direct method, the results were compared. If they agreed the data was accepted as valid and the strengths of the additional lines in the wideband scans were determined by the direct method. If, however, they did not agree the reliability of the data sets was judged to be poor and discarded.

Reduction of the data acquired on the UTMSL TDL system was accomplished using software available in the laboratory. This software was written by Mark Weber and is known as N17. The data is recorded in a machine readable format by the control software and is loaded into N17. The program identifies the zero transmittance and background and then normalizes the data. The normalized line shapes are fit to standard profiles and equivalent width, strength and transmittance are reported. Wing corrections, while important in pressure broadening studies, are not made for the Doppler width lines in this work. A complete description is available in Weber's Ph.D. dissertation [46]. To extract the transmittance for transitions contained in the wideband scans a computer program by California Scientific called Origin was used. Origin allowed for graphical fits of TDL scans and the recovery of transmittances. Calculation of strength by the direct method was done by taking the transmittance and employing equation (2.30).

## Results of TDL Data Analysis

Table 4.4 shows the results of a typical line fitting session for the transition  $951.73937\text{ cm}^{-1}$  which has a Doppler half-width of 1.108 milli-wavenumbers. It should be noted that the two independent methods for calculation of line strengths are employed.

Table 4.4  
Strength measurements for the  $5_{1,5} \leftarrow 5_{0,5}$  transition

| Coadded Scans | HWHM (mK) | EW (mK)  | $S_{\text{enw}}$ | $\tau$   | $S_{\tau}$ |
|---------------|-----------|----------|------------------|----------|------------|
| 135           | 1.178252  | .5077839 | .464660          | .7827570 | .489998    |
| 76            | 1.181254  | .4281633 | .386625          | .7858238 | .482175    |
| 52            | 1.247037  | .6198028 | .578065          | .7815502 | .493085    |
| 63408         | 1.244012  | .5587822 | .515770          | .7951828 | .458490    |
| 66            | 1.195474  | .5057106 | .462609          | .7926252 | .464935    |
| 1             | 1.083398  | .5881072 | .545534          | .76156   | .544919    |

The pressure was 20 milliTorr in the 45 cm path cell. The average temperature of the sample was 298.5 K. The average strength from the equivalent width method is .4815 (+/- .071) and from the direct method .4777 (+/- .015) excluding the data from the single scan. Since the two values do agree within statistical error the values are considered valid.

A compilation of TDL strength values from this work is reported in Table 4.5. This table contains upper and lower state quantum numbers, calibrated line positions, observed strengths and statistical error from lines measured with the equivalent width method and direct method. The data is normalized to a temperature of 296 K.

Table 4.5  
TDL strength measurements for  $\text{C}_2\text{H}_4$

| J' | $K_a'$ | $K_c'$ | J'' | $K_a''$ | $K_c''$ | $\nu_o(\text{calibrated})$ | S (obs) | Error  |
|----|--------|--------|-----|---------|---------|----------------------------|---------|--------|
| 11 | 1      | 10     | 11  | 2       | 10      | 941.84944                  | 0.9680  | 0.0636 |
| 11 | 3      | 9      | 10  | 4       | 7       | 942.53009                  | 0.1409  | 0.007  |
| 12 | 1      | 11     | 12  | 2       | 11      | 942.59618                  | 0.3327  | 0.0672 |
| 9  | 2      | 7      | 8   | 3       | 5       | 947.01212                  | 0.105   | 0.0052 |
| 10 | 2      | 9      | 11  | 1       | 11      | 947.06269                  | 0.0417  | ---    |
| 16 | 4      | 13     | 17  | 3       | 15      | 947.09667                  | 0.0366  | ---    |
| 10 | 2      | 9      | 9   | 3       | 7       | 947.13883                  | 0.0667  | ---    |
| 19 | 1      | 18     | 19  | 2       | 18      | 947.19846                  | 0.8648  | 0.028  |
| 9  | 0      | 9      | 9   | 1       | 9       | 947.38071                  | 0.8317  | 0.015  |
| 12 | 3      | 10     | 13  | 2       | 12      | 947.45336                  | 0.1499  | 0.0074 |
| 11 | 0      | 11     | 11  | 1       | 11      | 947.98445                  | 0.9420  | 0.0153 |
| 21 | 1      | 20     | 21  | 2       | 20      | 948.00356                  | 0.6831  | 0.0166 |
| 6  | 2      | 4      | 7   | 1       | 6       | 951.58101                  | 0.2083  | 0.01   |
| 17 | 1      | 16     | 17  | 2       | 16      | 951.60755                  | 0.3428  | 0.017  |
| 26 | 2      | 24     | 26  | 3       | 24      | 951.65268                  | 0.1581  | 0.0079 |
| 5  | 0      | 5      | 5   | 1       | 5       | 951.73937                  | 0.4815  | 0.071  |

## Compilation of Experimental Results and Recalibration of FTS Data

One of the major goals of this work is to rescale the strength measurements from the Kitt Peak FTS data by using TDL data acquired at the UTMSL. The comparison of the TDL and FTS data and the results of a linear fit are shown in Table 4.6. The calibration of FTS intensities by TDL intensities was accomplished using a linear relationship with a zero intercept as specified in the legend of Figure 4.3.

$$S_{\text{FTS}}(\text{corr}) = (1.26955) [S_{\text{FTS}}(\text{uncorr})] \quad (4.2)$$

The results of the fit make rescaling of the Kitt Peak FTS data possible and in effect correcting the pressure and normalizing the temperature to 296K. A complete list of approximately one-hundred of the strongest lines in the 940 to 960  $\text{cm}^{-1}$  region are listed in table 4.7.

Table 4.6  
Comparison of TDL and FTS strength measurements and results of fitting

| J' | K <sub>a</sub> ' | K <sub>c</sub> ' | J" | K <sub>a</sub> " | K <sub>c</sub> " | v <sub>o</sub> (calib) | S(FTS)<br>uncorr | S(TDL) | S(FTS)<br>corr | S(FTS)-<br>S(TDL) |
|----|------------------|------------------|----|------------------|------------------|------------------------|------------------|--------|----------------|-------------------|
| 11 | 1                | 10               | 11 | 2                | 10               | 941.84944              | .682             | 0.9680 | 0.865833       | -0.10217          |
| 11 | 3                | 9                | 10 | 4                | 7                | 942.53009              | .129             | 0.1409 | 0.163772       | 0.022872          |
| 12 | 1                | 11               | 12 | 2                | 11               | 942.59618              | .313             | 0.3327 | 0.397369       | 0.064669          |
| 9  | 2                | 7                | 8  | 3                | 5                | 947.01212              | .0701            | 0.1050 | 0.088995       | -0.016            |
| 10 | 2                | 9                | 11 | 1                | 11               | 947.06269              | .0583            | 0.0417 | 0.074015       | 0.032315          |
| 16 | 4                | 13               | 17 | 3                | 15               | 947.09667              | .0626            | 0.0366 | 0.079474       | 0.042874          |
| 10 | 2                | 9                | 9  | 3                | 7                | 947.13883              | .0664            | 0.0667 | 0.084298       | 0.017598          |
| 19 | 1                | 18               | 19 | 2                | 18               | 947.19846              | .652             | 0.8648 | 0.827747       | -0.03705          |
| 9  | 0                | 9                | 9  | 1                | 9                | 947.38071              | .650             | 0.8317 | 0.825208       | -0.00649          |
| 12 | 3                | 10               | 13 | 2                | 12               | 947.45336              | .141             | 0.1499 | 0.179007       | 0.029107          |
| 11 | 0                | 11               | 11 | 1                | 11               | 947.98445              | .742             | 0.9420 | 0.942006       | 6.1E-06           |
| 21 | 1                | 20               | 21 | 2                | 20               | 948.00356              | .561             | 0.6831 | 0.712218       | 0.029118          |
| 7  | 1                | 6                | 6  | 2                | 4                | 951.58101              | .197             | 0.2083 | 0.250101       | 0.041801          |
| 17 | 2                | 16               | 17 | 1                | 16               | 951.60755              | .322             | 0.3428 | 0.408795       | 0.065995          |
| 26 | 2                | 24               | 26 | 3                | 24               | 951.65268              | .145             | 0.1581 | 0.184085       | 0.025985          |
| 5  | 0                | 5                | 5  | 1                | 5                | 951.73937              | .411             | 0.4815 | 0.521785       | 0.040285          |

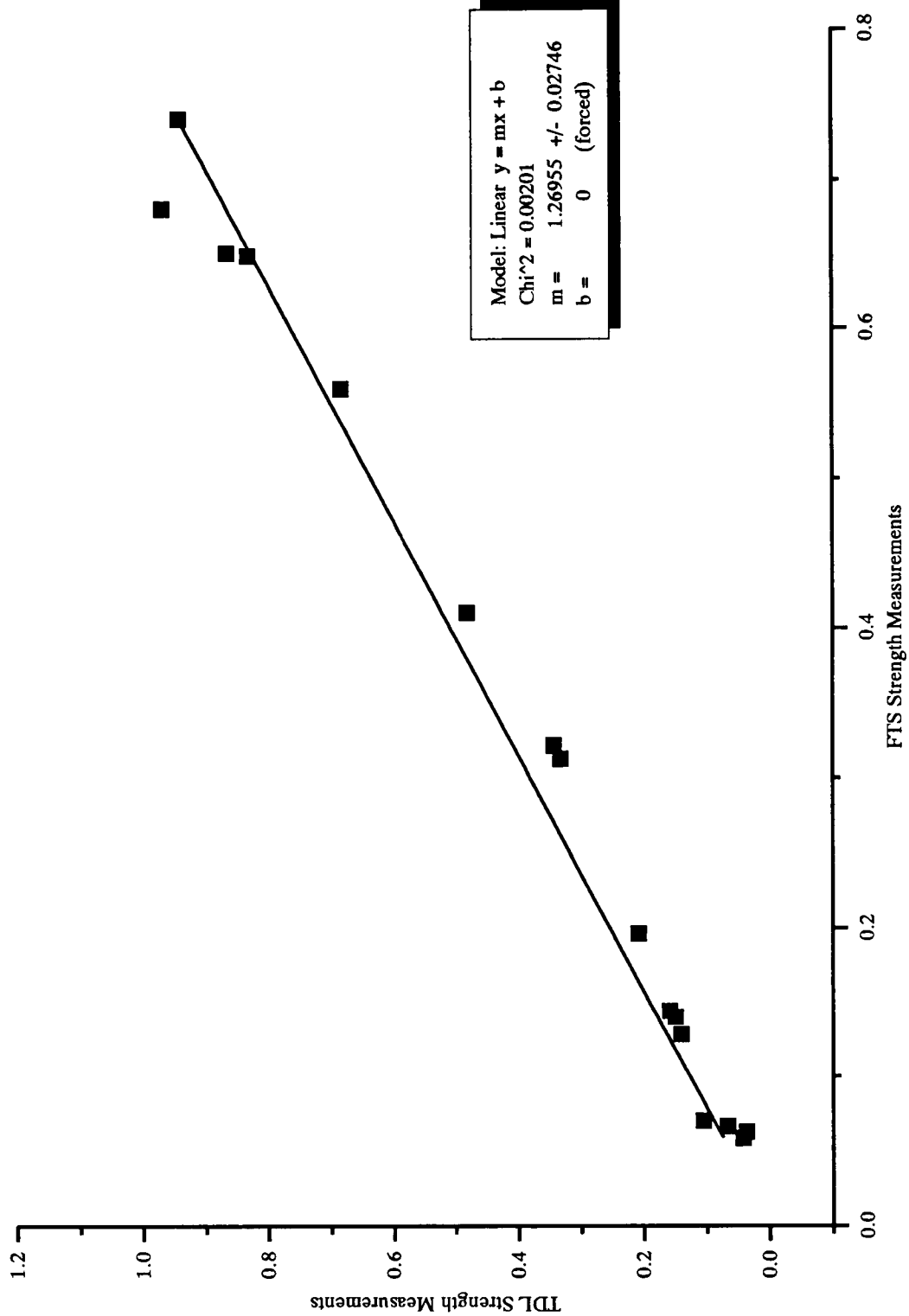


Figure 4.3  
 TDL vs. FTS Strength Measurements

Table 4.7  
Rescaled FTS strengths from 940 to 960 cm<sup>-1</sup>

| J' | K <sub>a</sub> ' | K <sub>c</sub> ' | J'' | K <sub>a</sub> '' | K <sub>c</sub> '' | $\nu_0$<br>calibrated | S(FTS)<br>corrected |
|----|------------------|------------------|-----|-------------------|-------------------|-----------------------|---------------------|
| 9  | 2                | 7                | 10  | 1                 | 9                 | 940.07617             | 0.151               |
| 9  | 1                | 8                | 10  | 0                 | 10                | 940.15682             | 0.248               |
| 9  | 1                | 8                | 9   | 2                 | 8                 | 940.43546             | 0.804               |
| 1  | 0                | 1                | 2   | 1                 | 1                 | 940.89879             | 0.133               |
| 21 | 2                | 19               | 21  | 3                 | 19                | 940.98801             | 0.137               |
| 10 | 1                | 9                | 10  | 2                 | 9                 | 941.12318             | 0.372               |
| 7  | 1                | 6                | 8   | 0                 | 8                 | 941.41302             | 0.319               |
| 19 | 4                | 16               | 20  | 3                 | 18                | 942.04381             | 0.155               |
| 6  | 1                | 5                | 7   | 0                 | 7                 | 942.33286             | 0.132               |
| 11 | 3                | 9                | 10  | 4                 | 7                 | 942.53129             | 0.164               |
| 12 | 1                | 11               | 12  | 2                 | 11                | 942.59609             | 0.397               |
| 11 | 3                | 8                | 10  | 4                 | 6                 | 942.79548             | 0.138               |
| 13 | 1                | 12               | 13  | 2                 | 12                | 943.35295             | 0.980               |
| 5  | 1                | 4                | 6   | 0                 | 6                 | 943.43529             | 0.324               |
| 12 | 3                | 10               | 11  | 4                 | 8                 | 944.31688             | 0.131               |
| 11 | 3                | 8                | 12  | 2                 | 10                | 944.66894             | 0.196               |
| 14 | 3                | 12               | 15  | 2                 | 14                | 944.79751             | 0.151               |
| 1  | 0                | 1                | 1   | 1                 | 1                 | 944.90308             | 0.136               |
| 2  | 0                | 2                | 2   | 1                 | 2                 | 945.06216             | 0.231               |
| 16 | 1                | 15               | 16  | 2                 | 15                | 945.50646             | 0.397               |
| 4  | 0                | 4                | 4   | 1                 | 4                 | 945.58175             | 0.411               |
| 5  | 0                | 5                | 5   | 1                 | 5                 | 945.91748             | 0.518               |
| 3  | 1                | 2                | 4   | 0                 | 4                 | 946.11806             | 0.260               |
| 17 | 1                | 16               | 17  | 2                 | 16                | 946.13448             | 0.931               |
| 6  | 1                | 6                | 5   | 2                 | 4                 | 946.17588             | 0.137               |
| 6  | 0                | 6                | 6   | 1                 | 6                 | 946.28250             | 0.622               |
| 7  | 0                | 7                | 7   | 1                 | 7                 | 946.65917             | 0.682               |
| 18 | 1                | 17               | 18  | 2                 | 17                | 946.69983             | 0.385               |
| 13 | 3                | 10               | 12  | 4                 | 8                 | 946.76122             | 0.157               |
| 19 | 1                | 18               | 19  | 2                 | 18                | 947.19855             | 0.828               |
| 5  | 1                | 4                | 4   | 2                 | 2                 | 947.28635             | 0.133               |
| 9  | 0                | 9                | 9   | 1                 | 9                 | 947.38068             | 0.825               |
| 12 | 3                | 10               | 13  | 2                 | 12                | 947.45349             | 0.179               |
| 20 | 1                | 19               | 20  | 2                 | 19                | 947.63101             | 0.325               |
| 10 | 0                | 10               | 10  | 1                 | 10                | 947.70004             | 0.859               |
| 14 | 3                | 12               | 13  | 4                 | 10                | 947.83437             | 0.152               |
| 11 | 0                | 11               | 11  | 1                 | 11                | 947.98280             | 0.942               |
| 21 | 1                | 20               | 21  | 2                 | 20                | 948.00199             | 0.712               |
| 12 | 0                | 12               | 12  | 1                 | 12                | 948.22768             | 0.965               |
| 22 | 1                | 21               | 22  | 2                 | 21                | 948.31799             | 0.258               |
| 13 | 0                | 13               | 13  | 1                 | 13                | 948.43631             | 0.899               |
| 23 | 1                | 22               | 23  | 2                 | 22                | 948.58654             | 0.547               |
| 14 | 0                | 14               | 14  | 1                 | 14                | 948.61300             | 0.890               |
| 15 | 0                | 15               | 15  | 1                 | 15                | 948.76352             | 0.868               |
| 24 | 1                | 23               | 24  | 2                 | 23                | 948.81654             | 0.251               |

Table 4.7  
Continued

| J' | K <sub>a</sub> ' | K <sub>c</sub> ' | J'' | K <sub>a</sub> '' | K <sub>c</sub> '' | v <sub>o</sub><br>calibrated | S(FTS)<br>corrected |
|----|------------------|------------------|-----|-------------------|-------------------|------------------------------|---------------------|
| 16 | 0                | 16               | 16  | 1                 | 16                | 948.89281                    | 0.811               |
| 17 | 0                | 17               | 17  | 1                 | 17                | 949.00607                    | 0.763               |
| 25 | 1                | 24               | 25  | 2                 | 24                | 949.01478                    | 0.411               |
| 18 | 0                | 18               | 18  | 1                 | 18                | 949.10738                    | 0.697               |
| 26 | 1                | 25               | 26  | 2                 | 25                | 949.18901                    | 0.225               |
| 19 | 0                | 19               | 19  | 1                 | 19                | 949.20046                    | 0.634               |
| 20 | 0                | 20               | 20  | 1                 | 20                | 949.28794                    | 0.578               |
| 17 | 1                | 17               | 17  | 0                 | 17                | 949.33522                    | 0.757               |
| 16 | 1                | 16               | 16  | 0                 | 16                | 949.34191                    | 2.057               |
| 20 | 1                | 20               | 20  | 0                 | 20                | 949.41389                    | 1.333               |
| 14 | 1                | 14               | 14  | 0                 | 14                | 949.42928                    | 2.133               |
| 22 | 0                | 22               | 22  | 1                 | 22                | 949.45530                    | 0.442               |
| 23 | 0                | 23               | 23  | 1                 | 23                | 949.53800                    | 0.405               |
| 23 | 1                | 23               | 23  | 0                 | 23                | 949.60002                    | 0.381               |
| 24 | 1                | 24               | 24  | 0                 | 24                | 949.64215                    | 0.786               |
| 12 | 1                | 12               | 12  | 0                 | 12                | 949.65302                    | 2.171               |
| 9  | 3                | 6                | 10  | 2                 | 8                 | 949.68215                    | 0.163               |
| 25 | 2                | 24               | 25  | 1                 | 24                | 949.71794                    | 0.171               |
| 26 | 0                | 26               | 26  | 1                 | 26                | 949.79509                    | 0.248               |
| 26 | 1                | 26               | 26  | 0                 | 26                | 949.80657                    | 0.419               |
| 27 | 1                | 27               | 27  | 0                 | 27                | 949.89195                    | 0.159               |
| 22 | 2                | 21               | 22  | 1                 | 21                | 949.95734                    | 0.275               |
| 21 | 2                | 20               | 21  | 1                 | 20                | 950.13679                    | 0.331               |
| 30 | 1                | 30               | 30  | 0                 | 30                | 950.17654                    | 0.259               |
| 20 | 2                | 19               | 20  | 1                 | 19                | 950.38055                    | 0.340               |
| 32 | 1                | 32               | 32  | 0                 | 32                | 950.39737                    | 0.157               |
| 10 | 3                | 8                | 11  | 2                 | 10                | 950.45149                    | 0.161               |
| 8  | 1                | 8                | 8   | 0                 | 8                 | 950.64991                    | 1.841               |
| 19 | 2                | 18               | 19  | 1                 | 18                | 950.69605                    | 0.369               |
| 28 | 3                | 26               | 28  | 2                 | 26                | 951.11421                    | 0.133               |
| 16 | 3                | 14               | 15  | 4                 | 12                | 951.22998                    | 0.150               |
| 6  | 1                | 6                | 6   | 0                 | 6                 | 951.37176                    | 1.511               |
| 4  | 0                | 4                | 3   | 1                 | 2                 | 951.50358                    | 0.147               |
| 7  | 1                | 6                | 6   | 2                 | 4                 | 951.58110                    | 0.250               |
| 17 | 2                | 16               | 17  | 1                 | 16                | 951.60755                    | 0.409               |
| 26 | 3                | 24               | 26  | 2                 | 24                | 951.65267                    | 0.184               |
| 5  | 1                | 5                | 5   | 0                 | 5                 | 951.73945                    | 0.522               |
| 16 | 2                | 15               | 16  | 1                 | 15                | 952.17083                    | 0.449               |
| 3  | 1                | 3                | 3   | 0                 | 3                 | 952.38603                    | 0.350               |
| 1  | 1                | 1                | 1   | 0                 | 1                 | 952.79641                    | 0.146               |
| 14 | 1                | 14               | 13  | 2                 | 12                | 953.01238                    | 0.150               |
| 14 | 2                | 13               | 14  | 1                 | 13                | 953.53066                    | 0.447               |
| 8  | 1                | 7                | 7   | 2                 | 5                 | 953.66846                    | 0.136               |
| 6  | 0                | 6                | 5   | 1                 | 4                 | 954.10414                    | 0.149               |
| 13 | 2                | 12               | 13  | 1                 | 12                | 954.29328                    | 0.452               |

Table 4.7  
Continued

| J' | K <sub>a</sub> ' | K <sub>c</sub> ' | J'' | K <sub>a</sub> '' | K <sub>c</sub> '' | $\nu_0$<br>calibrated | S(FTS)<br>corrected |
|----|------------------|------------------|-----|-------------------|-------------------|-----------------------|---------------------|
| 7  | 3                | 4                | 8   | 2                 | 6                 | 954.34353             | 0.147               |
| 18 | 3                | 16               | 17  | 4                 | 14                | 954.43798             | 0.145               |
| 32 | 4                | 29               | 32  | 3                 | 29                | 954.54514             | 0.796               |
| 1  | 1                | 0                | 0   | 0                 | 0                 | 954.79086             | 0.242               |
| 12 | 2                | 11               | 12  | 1                 | 11                | 955.08541             | 0.428               |
| 7  | 0                | 7                | 6   | 1                 | 5                 | 955.16718             | 0.161               |
| 9  | 1                | 8                | 8   | 2                 | 6                 | 955.67209             | 0.378               |
| 11 | 2                | 10               | 11  | 1                 | 10                | 955.88612             | 0.409               |
| 8  | 0                | 8                | 7   | 1                 | 6                 | 956.05202             | 0.160               |
| 10 | 2                | 9                | 10  | 1                 | 9                 | 956.67565             | 0.402               |
| 9  | 0                | 9                | 8   | 1                 | 7                 | 956.75139             | 0.150               |
| 2  | 1                | 1                | 1   | 0                 | 1                 | 956.77630             | 0.155               |
| 10 | 0                | 10               | 9   | 1                 | 8                 | 957.26369             | 0.131               |
| 20 | 3                | 18               | 20  | 2                 | 18                | 957.36877             | 0.405               |
| 14 | 2                | 12               | 13  | 3                 | 10                | 958.57206             | 0.133               |
| 7  | 2                | 6                | 7   | 1                 | 6                 | 958.81343             | 0.293               |
| 3  | 1                | 2                | 2   | 0                 | 2                 | 958.84245             | 0.457               |
| 6  | 2                | 5                | 6   | 1                 | 5                 | 959.40743             | 0.396               |
| 18 | 3                | 16               | 18  | 2                 | 16                | 959.77954             | 0.446               |

## Explanation of Results

Table 4.7 contains the list of lines between 940 and 960  $\text{cm}^{-1}$ . The lines selected for recalibration are ones which were not blended. Only about half of the strong ethylene lines were recalibrated as a result of this work.

Blendings occurred for several reasons. The first, most obvious cause, is accidental degeneracies between states. This is where ethylene lines overlap one another in the spectra. There are also overlaps with lines due to isotopic species. These blendings, however, are only the beginning. The presence of  $\text{CO}_2$ , ammonia and its isotopic species accounted for the rest of the blended ethylene lines. From Table 4.2 it is shown that there are twelve  $\text{CO}_2$  lines present from 940 to 960  $\text{cm}^{-1}$ . The ammonia lines are not identified in this work, but their positions and intensities are well known from other sources.

One of the results that would be beneficial for other researchers in the fields of molecular spectroscopy and infrared astronomy would be a band strength calculated from the results of this work. This would be done by integrating the strengths of the individual lines in the 940 to 960  $\text{cm}^{-1}$  region, determining what portion of the total band intensity was due to this central portion  $\nu_7$  and from this calculating a total band intensity. Due to the unfortunate presence of the blended lines this procedure can not be followed from the information in Table 4.7.

If, however, the line intensities for the blended lines can be determined from the FTS spectra then an integrated band intensity could be calculated. This is hindered by the fact that the  $\text{CO}_2$  lines present in the observed FTS spectra resulted from gas contained in a separate sample cell at a different pressure. Work has been begun by Larry Jennings of the UTMSL on the  $\text{CO}_2$  present in the spectra which should make this procedure feasible. After this work is completed an integrated band intensity can be calculated and reported.

Another benefit of this work is that all lines in the observed FTS ethylene spectrum could eventually be recalibrated to their proper values. When this is accomplished a complete spectral atlas will become available.

A plot of the observed spectrum of the 940 to 960  $\text{cm}^{-1}$  region is shown in Appendix C of this thesis. This includes all lines reported in Table 4.7 as well as the  $\text{CO}_2$  and ammonia lines mentioned above. Each page contains five plot traces of the spectrum in one wavenumber increments. The frequency scale is

generated from the uncalibrated data and should be treated accordingly. The intensity scale located at the left of each trace is a relative scale.

## Chapter 5

### Future Work and Comparison to Recent Results

#### Future Direction of Research on Ethylene

The measurements included in this work make up only a small percentage of the data required to model the vibrational-rotational energy state transitions of ethylene. The rescaled values for the temperature and pressure of the Kitt Peak data will make this task easier. More measurements using TDL systems should be completed for further comparison to the transitions measured in the Kitt Peak data. The extension of measurements into other bands is also necessary before a complete understanding of the various perturbations can be made available.

Other work that should also be completed includes the measurement of broadening parameters for the molecule. Principally the values for self, nitrogen hydrogen and helium broadening and their temperature dependencies would be very useful in the analysis of data pertaining to the observed atmosphere on Titan.

The data that has been extracted to this point can be used to extract atmospheric modeling parameters for the earth, Jupiter and Titan. It would also be useful in modeling the atmospheres of any other solar system bodies that are found to discover ethylene. The usefulness is not limited to solar system data, however. The presence of the gas in bodies throughout the galaxy, as discussed in Chapter 1, will only increase the value of these measurements. Future modeling work on IRC+10216 will require accurate values of intensity of ethylene lines.

#### Comparison to Recent Results

Results made available in an article pre-print Dr. Dennis Reuter of GSFC are the only independently measured comparison values currently available [45]. Dr. Reuter compiled strength measurements for five transitions in the 940 to 960  $\text{cm}^{-1}$  region. These measurements along with the results from this work are shown in table 5.1. The comparison is in good agreement in both lines measured with the UTMSL TDL system and rescaled FTS lines.

Table 5.1  
Comparison of Results

| J' | K <sub>a</sub> ' | K <sub>c</sub> ' | J" | K <sub>a</sub> " | K <sub>c</sub> " | $\nu_0$   | S (this work)      | S (Reuter) |
|----|------------------|------------------|----|------------------|------------------|-----------|--------------------|------------|
| 18 | 1                | 18               | 18 | 0                | 18               | 949.10735 | 0.697 *            | 0.699(10)  |
| 11 | 2                | 10               | 11 | 1                | 10               | 941.84780 | $0.9680 \pm .0636$ | 0.960(15)  |
| 5  | 0                | 5                | 5  | 1                | 5                | 951.73938 | $0.4889 \pm .0306$ | 0.484(20)  |
| 12 | 1                | 12               | 12 | 0                | 12               | 948.22754 | 0.965 *            | 0.99       |

\* line strength reported is from rescaled FTS data

## Conclusion

The goal of this work was to measure ethylene line strengths in the  $\nu_7$  vibrational-rotational band. This was accomplished by two means. The first was direct measurement employing the University of Tennessee Molecular Spectroscopy Laboratory's Tunable Diode Laser System. The second was by measuring spectra recorded at the Kitt Peak McMath Solar Telescope Fourier Transform Spectrometer.

Line strengths measured at Kitt Peak, however, required calibration of both line position and intensity. This was accomplished by using CO<sub>2</sub> line position standards and TDL line strengths from the UTMSL. The line intensity calibration enables the rescaling not only lines measured by the TDL, but the entire FTS spectrum. This will enable the extraction of thousands of line intensities from the data.

As shown in Table 5.1 the lines measured directly and by rescaling FTS data are in good agreement with recent independent measurements. This indicates that the method has good reliability and should generate very useful results.

## LIST OF REFERENCES

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## APPENDICES

## APPENDIX A

### Stepper Controller Modifications

## Notes on Modifications

The resistors R5 and R6 were removed and the +5V lead was soldered in place. LED CR1, CR2, CR3 and CR4 were removed and remotely located by means of and extension wire. All grounds are common. The remaining connections are according to the instructions provided by Alpha Products. A general motor connection scheme is included in the table A.1:

Table A.1  
Stepper Motor Wiring Chart

| Motor Wire  | PD-123 Card |
|-------------|-------------|
| green       | 1           |
| green-white | 2           |
| red         | 3           |
| red-white   | 4           |
| white       | 5           |
| black       | 6           |

The overall wiring diagram is shown in figure A.1.

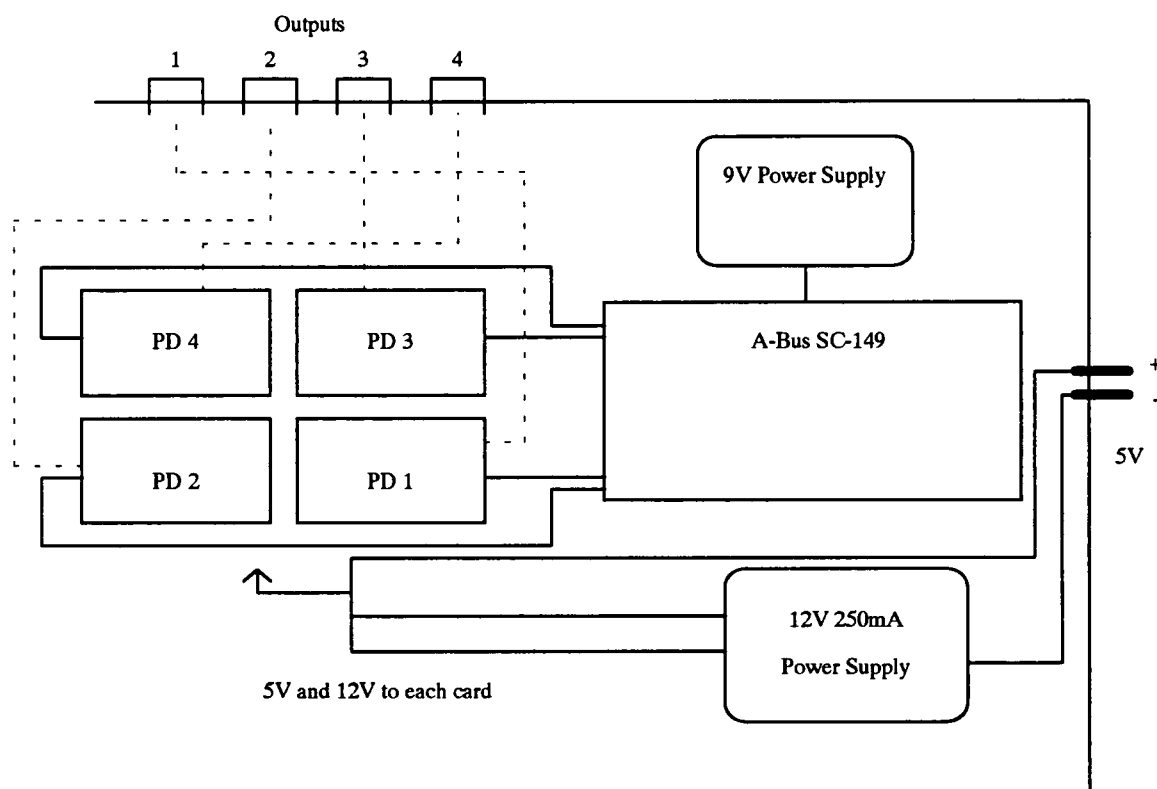


Figure A.1  
Modifications to the Alpha Products SC-149 and PD-123

## APPENDIX B

### Data Summary Sheets

This appendix contains the actual data recorded from the experiment described in this thesis. The first sheet in the appendix is a sample of data which was rejected due to the fact that the pressure was too high and as a result the lines observed were over-absorbed. The decision to reject the data was made on the basis of the discrepancy between strengths calculated from the equivalent width and direct method. The substantive agreement of the equivalent width and direct method intensity retrievals is the criteria on which the data in general was judged.

The other sheets contain data actually used in this work. In each case the strengths calculated from the direct and equivalent width methods were within statistical error then the data was considered valid. The third and subsequent data sheets contain lines which were calculated from the direct method only. This was done from wideband scans in which the intensity of one line had been validated as discussed above. The wideband scan was taken immediately after the validation scan with all parameters (pressure, path length, electronic parameters, etc.) the same as in the validation scan. The temperature is the cell temperature at scan time.

Transition: 11<sub>1,10</sub> ← 11<sub>2,10</sub> @ 941.84944 cm<sup>-1</sup> Operator: Alan Ewing

Date: May 7, 1993

Lab Temp: 294.7 K

Cell: 45 cm

Pressure: 50 mT

| Filename   | Comment     | Scans | Sensor Voltage (V) | Laser Current (A) | Sample Temp (K) | HWHM (mcm <sup>-1</sup> ) | Equivalent Width (mcm <sup>-1</sup> ) | S <sub>ew</sub> | Tau      | S <sub>r</sub> |
|------------|-------------|-------|--------------------|-------------------|-----------------|---------------------------|---------------------------------------|-----------------|----------|----------------|
| WID001.DTA | Wideband    | 500   | 1.0385             | .1788             | 294.9           | n/a                       | n/a                                   | n/a             | n/a      | n/a            |
| WIDE.ETA   | Wide Etalon | 500   | 1.0385             | .1788             | n/a             | n/a                       | n/a                                   | n/a             | n/a      | n/a            |
| DAT001.DTA | Strong Abs  | 500   | 1.0385             | .1529             | 294.9           | 1.254091                  | 1.79377                               | .857674         | .4342322 | over abs       |
| DAT002.DTA | "           | 500   | 1.0385             | .1529             | 294.5           | 1.256455                  | 1.821143                              | .876879         | .4322569 | over abs       |
| DAT003.DTA | "           | 500   | 1.0385             | .1529             | 294.5           | 1.23527                   | 1.802747                              | .863976         | .4247031 | over abs       |
| DAT004.DTA | "           | 500   | 1.0385             | .1529             | 294.4           | 1.258584                  | 1.830232                              | .883330         | .4284777 | over abs       |
| DAT005.DTA | "           | 500   | 1.0385             | .1529             | 294.4           | 1.286614                  | 1.846029                              | .894583         | .4428767 | over abs       |
| ETA001.DTA | Etalon Scan | 500   | 1.0385             | .1529             | n/a             | n/a                       | n/a                                   | n/a             | n/a      | n/a            |

Lines over absorbed, try lower pressure

Transition: 11<sub>1,10</sub> ← 11<sub>2,10</sub> @ 941.84944 cm<sup>-1</sup> Operator: Alan Ewing

Date: May 7, 1993

Cell: 45 cm

Lab Temp: 294.7 K

Pressure: 36 mT

| Filename   | Comment     | Scans  | Sensor Voltage (V) | Laser Current (A) | Sample Temp (K) | HWHM (cm <sup>-1</sup> ) | Equivalent Width (cm <sup>-1</sup> ) | S <sub>ew</sub> | Tau      | S <sub>r</sub> |
|------------|-------------|--------|--------------------|-------------------|-----------------|--------------------------|--------------------------------------|-----------------|----------|----------------|
| DAT001.DTA | Wide Scan   | 1000   | 1.0382             | .1667             | 297.6           | n/a                      | n/a                                  | n/a             | n/a      | n/a            |
| ETA001.DTA | Wide Etalon | 1000   | 1.0382             | .1667             | n/a             | n/a                      | n/a                                  | n/a             | n/a      | n/a            |
| DAT002.DTA | Data Scan   | 1      | 1.0383             | .1547             | 297.6           | 1.187985                 | 1.538312                             | .958717         | .4345664 | .915247        |
| DAT003.DTA | Data Scan   | 1      | 1.0383             | .1547             | 297.6           | 1.235357                 | 1.626453                             | 1.03465         | .4341508 | .916298        |
| DAT004.DTA | Data Scan   | 1      | 1.0383             | .1547             | 297.6           | 1.136963                 | 1.521614                             | .944683         | .4107973 | .97702         |
| DAT005.DTA | Data Scan   | 1      | 1.0383             | .1547             | 297.6           | 1.069294                 | 1.422993                             | .864139         | .4154248 | .964718        |
| DAT006.DTA | Data Scan   | 1      | 1.0383             | .1547             | 297.6           | 1.086297                 | 1.673561                             | 1.07660         | .3933195 | 1.02476        |
| ETA002.DTA | Etalon Scan | 1      | 1.0383             | .1547             | n/a             | n/a                      | n/a                                  | n/a             | n/a      | n/a            |
| ETA003.DTA | Etalon Scan | 500    | 1.0383             | .1541             | 297.6           | 1.312728                 | 1.606423                             | 1.01716         | .4944849 | not calc       |
| DAT007.DTA | Data Scan   | 500    | 1.0382             | .1541             | 297.6           | 1.307718                 | 1.633025                             | not calc        | .4909037 | not clac       |
| DAT008.DTA | Data Scan   | 500    | 1.0382             | .1541             | 297.6           | 1.329322                 | 1.609603                             | 1.01988         | .4972481 | not clac       |
| DAT009.DTA | Data Scan   | 500    | 1.0382             | .1541             | 297.6           | 1.316094                 | 1.595166                             | 1.00732         | .4973936 | not calc       |
| DAT010.DTA | Data Scan   | 500    | 1.0382             | .1541             | 297.6           | 1.295548                 | 1.59711                              | 1.00899         | .4887273 | not calc       |
| DAT011.DTA | Data Scan   | 500    | 1.0382             | .1541             | 297.6           | 1.312958                 | 1.571369                             | .986787         | .4947565 | not calc       |
| ETA004.DTA | Etalon Scan | 500    | 1.0382             | .1541             | n/a             | n/a                      | n/a                                  | n/a             | n/a      | n/a            |
| DAT012.DTA | Data Scan   | 10,000 | 1.0382             | .1542             | 297.7           | 1.296658                 | 1.530811                             | not calc        | .4972379 | not clac       |
| DAT013.DTA | Data Scan   | 10,000 | 1.0382             | .1542             | 297.5           | 1.244796                 | 1.511532                             | not calc        | .4790633 | not clac       |
| DAT014.DTA | Data Scan   | 10,000 | 1.0382             | .1542             | 297.5           | 1.25163                  | 1.60667                              | not calc        | .4750111 | not clac       |
| DAT015.DTA | Data Scan   | 10,000 | 1.0382             | .1542             | 297.3           | 1.259672                 | 1.531439                             | not calc        | .4820329 | not clac       |
| DAT016.DTA | Data Scan   | 10,000 | 1.0382             | .1542             | 297.2           | 1.24019                  | 1.516461                             | not calc        | .4734683 | not clac       |
| ETA005.DTA | Etalon Scan | 10,000 | 1.0382             | .1542             | 297.3           | n/a                      | n/a                                  | n/a             | n/a      | n/a            |

Strength = .968 +/- .0636

Transition: 5<sub>1,5</sub> ← 5<sub>0,5</sub> @ 951.73937 cm<sup>-1</sup>

Operator: Alan Ewing

Date: May 22, 1993

Lab Temp: 297.0 K

Cell: 45 cm

Pressure: 20 mT

| Filename     | Comment   | Scans | Sensor Voltage (V) | Laser Current (A) | Sample Temp (K) | HWHM (mcm <sup>-1</sup> ) | Equivalent Width (mcm <sup>-1</sup> ) | S <sub>av</sub> | Tau      | S <sub>r</sub> |
|--------------|-----------|-------|--------------------|-------------------|-----------------|---------------------------|---------------------------------------|-----------------|----------|----------------|
| WIDE2.DAT    | Wide Scan | 558   | 1.0308             | .1694             | 298.0           | n/a                       | n/a                                   | n/a             | n/a      | n/a            |
| WIDEETA2.DAT | Wide ETA  | 299   | 1.0308             | .1694             | n/a             | n/a                       | n/a                                   | n/a             | n/a      | n/a            |
| DAT007.DAT   | Data Scan | 135   | 1.0307             | .1930             | 298.5           | 1.178252                  | .5077839                              | .464660         | .782757  | .4899981       |
| DAT008.DAT   | Data Scan | 76    | 1.0308             | .1930             | 298.5           | 1.181254                  | .4281633                              | .386625         | .7858238 | .4821754       |
| DAT009.DAT   | Data Scan | 52    | 1.0308             | .1930             | 298.5           | 1.247037                  | .6198028                              | .578065         | .7815502 | .4930843       |
| DAT010.DAT   | Data Scan | 63408 | 1.0308             | .1930             | 298.2           | 1.244012                  | .5587822                              | .515770         | .7926252 | .458490        |
| DAT011.DAT   | Data Scan | 66    | 1.0308             | .1930             | 298.2           | 1.195474                  | .5057106                              | .462609         | .7926252 | .464935        |
| DAT012.DAT   | Data Scan | 1     | 1.0307             | .1930             | 298.1           | 1.083398                  | .5881072                              | .545534         | .76156   | .544919        |

Results Excluding DAT012.DAT

$$S_{eq} = .4815 \pm .0709$$

$$S_{tau} = .4777 \pm .0153$$

Adjacent lines from WIDE2.DAT calculated from direct method:

$$\begin{array}{lcl} 26_{3,24} & \leftarrow 26_{2,24} & = .15811(4697) \\ 17_{2,16} & \leftarrow 17_{1,16} & = .3428(795) \\ 7_{1,6} & \leftarrow 6_{2,4} & = .2083(43998) \end{array}$$

Transition: 12<sub>1,11</sub> ← 12<sub>2,11</sub> @ 942.59618 cm<sup>-1</sup> Operator: Alan Ewing

Date: July 28, 1993

Cell: 45 cm

Lab Temp: 300.0 K

Pressure: 50 mT

| Filename   | Comment     | Scans | Sensor Voltage (V) | Laser Current (A) | Sample Temp (K) | HWHM (mcm <sup>-1</sup> ) | Equivalent Width (mcm <sup>-1</sup> ) | S <sub>ew</sub> | Tau      | S <sub>r</sub> |
|------------|-------------|-------|--------------------|-------------------|-----------------|---------------------------|---------------------------------------|-----------------|----------|----------------|
| ETA001.DAT | Wide Etalon | 435   | 1.0375             | .1639             | n/a             | n/a                       | n/a                                   | n/a             | n/a      | n/a            |
| DAT001.DAT | Wide Scan   | 2     | 1.0375             | .1639             | 300             | n/a                       | n/a                                   | n/a             | n/a      | n/a            |
| DAT002.DAT | Wide Scan   | 10    | 1.0375             | .1639             | 300             | n/a                       | n/a                                   | n/a             | n/a      | n/a            |
| DAT003.DAT | Data Scan   | 2     | 1.0375             | .1631             | 300             | 1.163813                  | .5085609                              | -----           | .6638069 | .3117107       |
| DAT004.DAT | Data Scan   | 3     | 1.0375             | .1643             | 300             | 1.282251                  | .8289271                              | .307596         | .6667113 | .3083896       |
| DAT005.DAT | Data Scan   | 3     | 1.0375             | .1643             | 300             | 1.143649                  | 1.036297                              | .399935         | .6457239 | .3327209       |
| DAT006.DAT | Data Scan   | 3     | 1.0375             | .1643             | 299.5           | 1.192778                  | .9860557                              | .376864         | .6529093 | .324302        |
| DAT007.DAT | Data Scan   | 3     | 1.0375             | .1643             | 299.5           | 1.205742                  | .9257036                              | .349784         | .6589935 | .3172468       |
| ETA002.DAT | Etalon Scan | 3     | 1.0375             | .1643             | n/a             | n/a                       | n/a                                   | n/a             | n/a      | n/a            |

# Results

Sew = .3327 +/- .0672

St = .3182 +/- .0089

Adjacent Line: 11<sub>3,9</sub> ← 10<sub>4,7</sub> = .1410

Transition: 9<sub>0,9</sub> ← 9<sub>1,9</sub> @ 947.38071 cm<sup>-1</sup>

Operator: Alan Ewing

Date: July 29, 1993

Lab Temp: 297.0 K

Cell: 45 cm

Pressure: 30 mT

| Filename   | Comment     | Scans | Sensor Voltage (V) | Laser Current (A) | Sample Temp (K) | HWHM (mcm <sup>-1</sup> ) | Equivalent Width (mcm <sup>-1</sup> ) | S <sub>ew</sub> | Tau      | S <sub>r</sub> |
|------------|-------------|-------|--------------------|-------------------|-----------------|---------------------------|---------------------------------------|-----------------|----------|----------------|
| ETA001.DAT | Wide Scan   | 3     | 1.0349             | .1904             | n/a             | n/a                       | n/a                                   | n/a             | n/a      | n/a            |
| DAT001.DAT | Wide Scan   | 3     | 1.0349             | .1904             | 296.7           | n/a                       | n/a                                   | n/a             | n/a      | n/a            |
| DAT002.DAT | Wide Scan   | 3     | 1.0349             | .1904             | 296.6           | n/a                       | n/a                                   | n/a             | n/a      | n/a            |
| DAT003.DAT | Poor Scan   | 3     | 1.0349             | .1866             | 296.0           | ----                      | ----                                  | ----            | ----     | ----           |
| DAT004.DAT | Data Scan   | 3     | 1.0350             | .1866             | 296.4           | 1.1698                    | 1.2384                                | .866330         | .57493   | no calc        |
| DAT005.DAT | Data Scan   | 3     | 1.0350             | .1866             | 296.3           | 1.11284                   | 1.1594                                | .798130         | .5839    | no calc        |
| DAT006.DAT | Data Scan   | 3     | 1.0350             | .1866             | 296.3           | 1.1106                    | 1.2038                                | .836145         | .57019   | no calc        |
| DAT007.DAT | Change Slp  | 100   | 1.0349             | .1866             | 296.3           | 1.329573                  | 1.19204                               | .826042         | .6201697 | no calc        |
| ETA002.DAT | Etalon Scan | 100   | 1.0349             | .1866             | n/a             | n/a                       | n/a                                   | n/a             | n/a      | n/a            |

$$S_{eq} = .8317 \pm .0282$$

Result

$$\text{Adjacent Line } 12_{3,10} \leftarrow 13_{2,12} = .1499$$

Transition: 19<sub>1,18</sub> ← 19<sub>2,18</sub> @ 947.19846 cm<sup>-1</sup> Operator: Alan Ewing

Date: July 29, 1993

Cell: 45 cm

Lab Temp: 297.0 K

Pressure: 30 mT

| Filename   | Comment     | Scans | Sensor Voltage (V) | Laser Current (A) | Sample Temp (K) | HWHM (mcm <sup>-1</sup> ) | Equivalent Width (mcm <sup>-1</sup> ) | S <sub>ew</sub> | Tau      | S <sub>r</sub> |
|------------|-------------|-------|--------------------|-------------------|-----------------|---------------------------|---------------------------------------|-----------------|----------|----------------|
| DAT008.DAT | Data Scan   | 3     | 1.0349             | .1761             | 296.2           | 1.11675                   | 1.1980                                | .831186         | .56291   | not clac       |
| DAT009.DAT | Data Scan   | 3     | 1.0349             | .1761             | 296.2           | 1.242366                  | 1.274197                              | .898110         | .5684253 | not calc       |
| DAT010.DAT | Poor Scan   | 3     | 1.0349             | .1761             | 296.5           | 1.305959                  | 1.227599                              | .856946         | .575027  | not calc       |
| DAT011.DAT | Data Scan   | 3     | 1.0349             | .1761             | 296.5           | 1.200816                  | 1.072708                              | not calc        | .5427774 | not calc       |
| DAT012.DAT | Data Scan   | 3     | 1.0349             | .1761             | 296.4           | 1.05635                   | 1.2457                                | .872856         | .53039   | not calc       |
| DAT013.DAT | Wide Scan   | 3     | 1.0349             | .1742             | 296.4           | n/a                       | n/a                                   | na/             | n/a      | n/a            |
| ETA003.DAT | Etalon Scan | 3     | 1.0349             | .1761             | n/a             | n/a                       | n/a                                   | n/a             | n/a      | n/a            |

$$S_{eq} = .8648 \pm .0281$$

#### Results

#### Adjacent Lines

$$\begin{array}{lcl}
 9_{2,7} \leftarrow 8_{3,5} & & = .1050 \\
 10_{2,9} \leftarrow 9_{3,7} & & = .0667 \\
 16_{4,13} \leftarrow 17_{3,15} & & = .0366 \\
 10_{2,9} \leftarrow 11_{1,11} & & = .0417
 \end{array}$$

Transition: 21 1,20 ← 21 2,20 @ 948.00356 cm<sup>-1</sup> Operator: Alan Ewing

Date: August 3, 1993

Cell: 45 cm

Lab Temp: 296.0 K

Pressure: 20 mT

| Filename   | Comment     | Scans | Sensor Voltage (V) | Laser Current (A) | Sample Temp (K) | HWHM (mcm <sup>-1</sup> ) | Equivalent Width (mcm <sup>-1</sup> ) | S <sub>FW</sub> | Tau      | S <sub>r</sub> |
|------------|-------------|-------|--------------------|-------------------|-----------------|---------------------------|---------------------------------------|-----------------|----------|----------------|
| DAT001.DAT | Data Scan   | 3     | 1.0428             | .4020             | 296.0           | 1.1317                    | .7218                                 | .6860           | .7397    | not calc       |
| DAT002.DAT | Data Scan   | 3     | 1.0428             | .4020             | 296.0           | 1.50                      | .7384                                 | .7039           | .8168    | not calc       |
| DAT003.DAT | Data Scan   | 3     | 1.0428             | .4020             | 296.0           | 1.1268                    | .7146                                 | .6783           | .72521   | not calc       |
| DAT004.DAT | Poor Scan   | 3     | 1.0428             | .4020             | 296.0           | not calc                  | not calc                              | not calc        | not calc | not calc       |
| DAT005.DAT | Data Scan   | 3     | 1.0428             | .4020             | 296.0           | 1.2581                    | .7012                                 | .6640           | .7794    | not calc       |
| ETA001.DAT | Etalon Scan | 3     | 1.0428             | .4020             | n/a             | n/a                       | n/a                                   | n/a             | n/a      | n/a            |

Results:

$$S_{eq} = .6831 \pm .0166$$

Transition: 11 0,11 ← 11 1,11 @ 947.98445 cm<sup>-1</sup>  
Same conditions as above

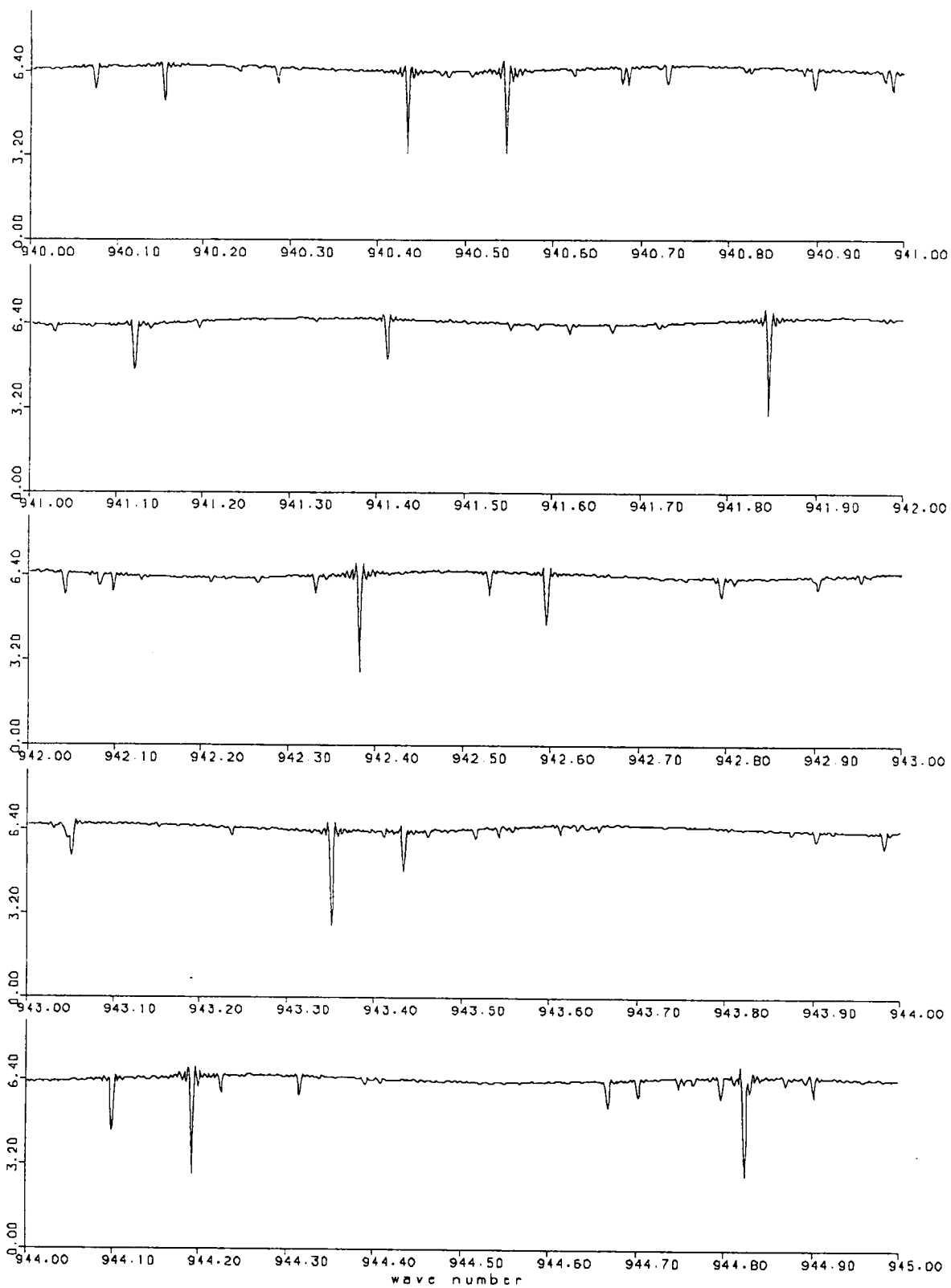
| Filename   | Comment   | Scans | Sensor Voltage (V) | Laser Current (A) | Sample Temp (K) | HWHM (mcm <sup>-1</sup> ) | Equivalent Width (mcm <sup>-1</sup> ) | S <sub>FW</sub> | Tau      | S <sub>r</sub> |
|------------|-----------|-------|--------------------|-------------------|-----------------|---------------------------|---------------------------------------|-----------------|----------|----------------|
| DAT001.DAT | See Above | *     | *                  | *                 | *               | 1.17525                   | .9465                                 | .9377           | .67629   | not calc       |
| DAT002.DAT | See Above | *     | *                  | *                 | *               | 1.3266                    | .9693                                 | .9645           | .7216    | not calc       |
| DAT003.DAT | See Above | *     | *                  | *                 | *               | 1.22095                   | .9445                                 | .9353           | .6637    | not calc       |
| DAT004.DAT | See Above | *     | *                  | *                 | *               | not calc                  | not calc                              | not calc        | not calc | not calc       |
| DAT005.DAT | See Above | *     | *                  | *                 | *               | 1.20715                   | .9403                                 | .9304           | .6971    | not calc       |

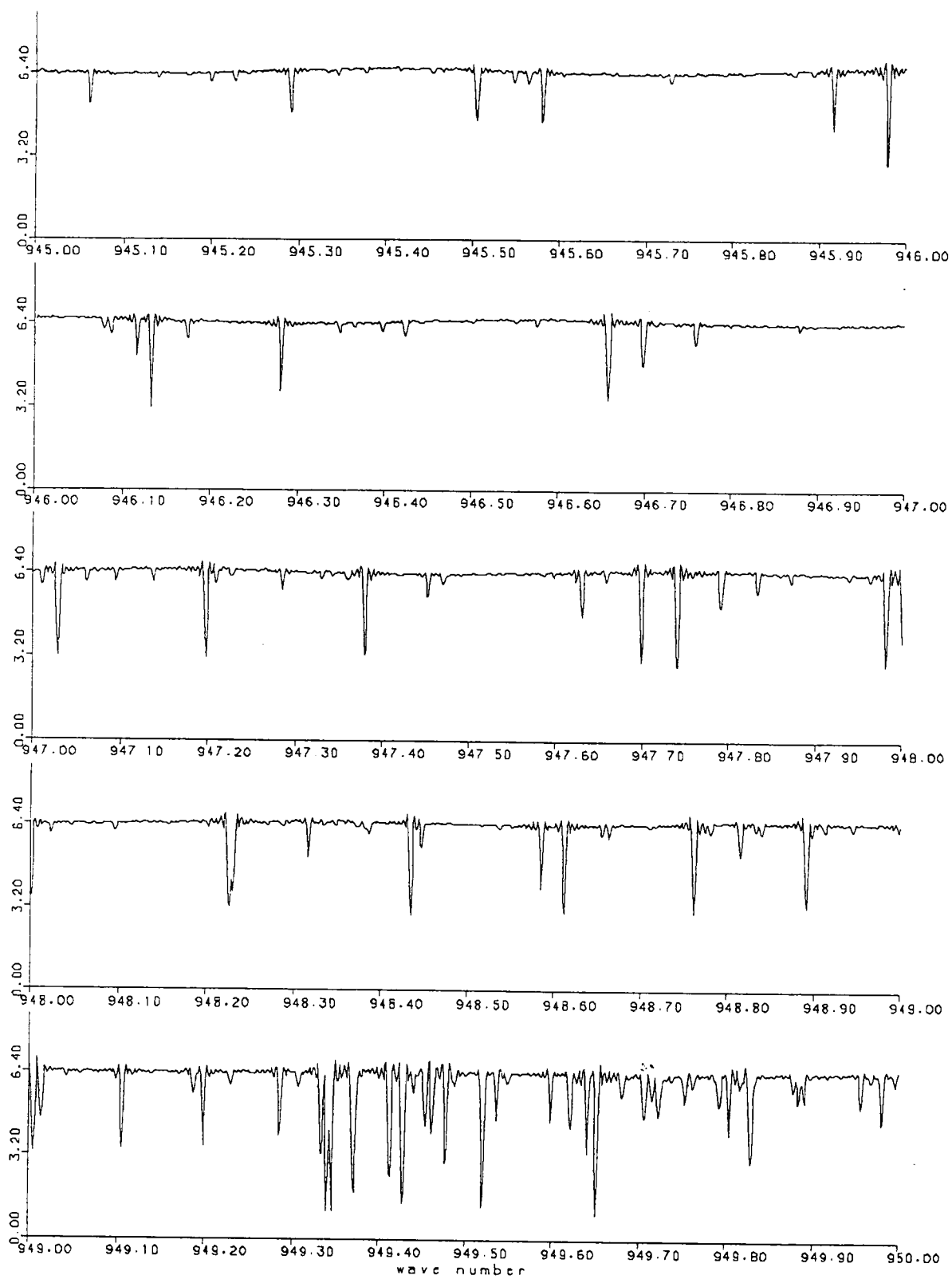
Results:

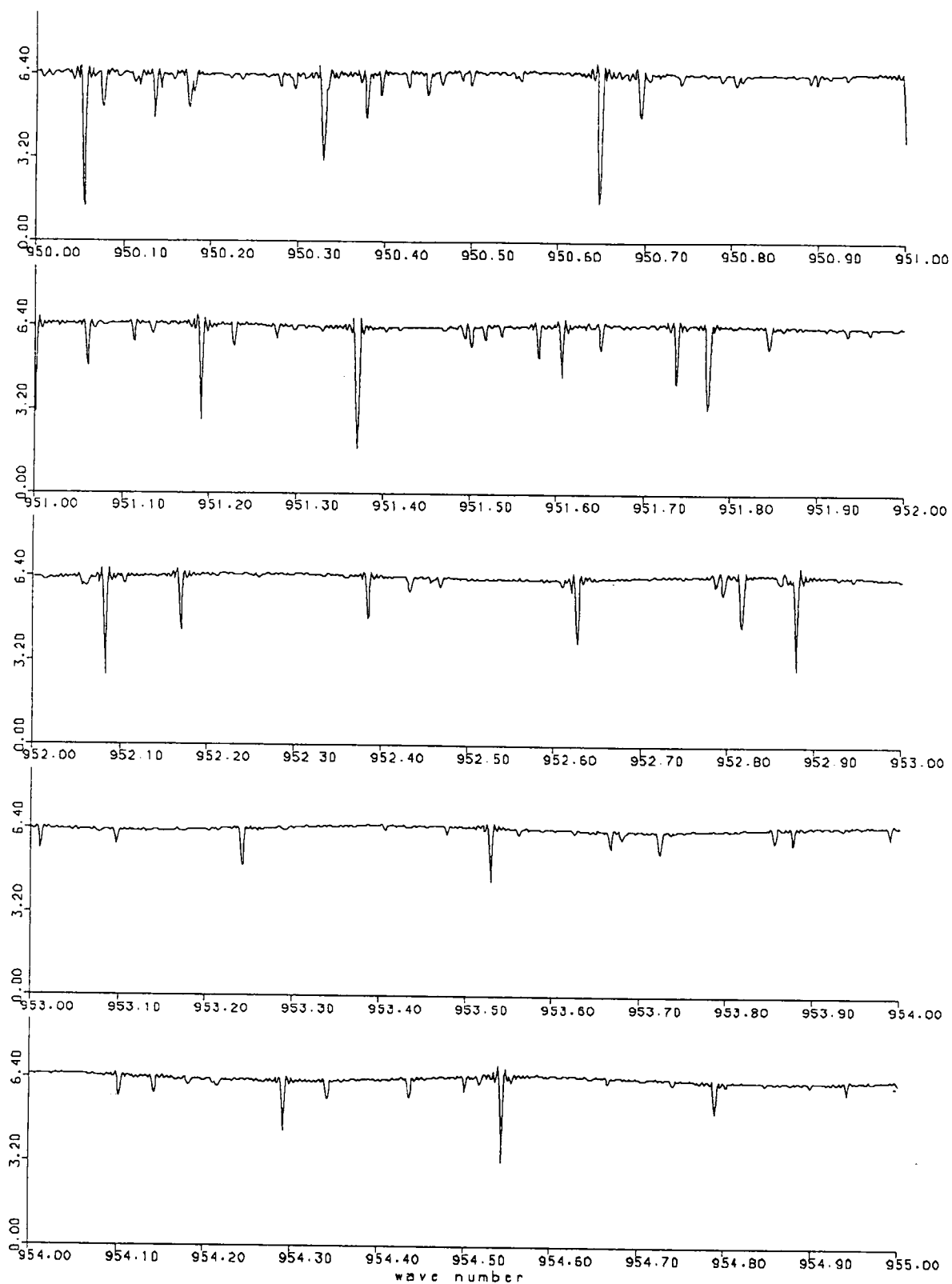
$$S_{eq} = .9420 \pm .0153$$

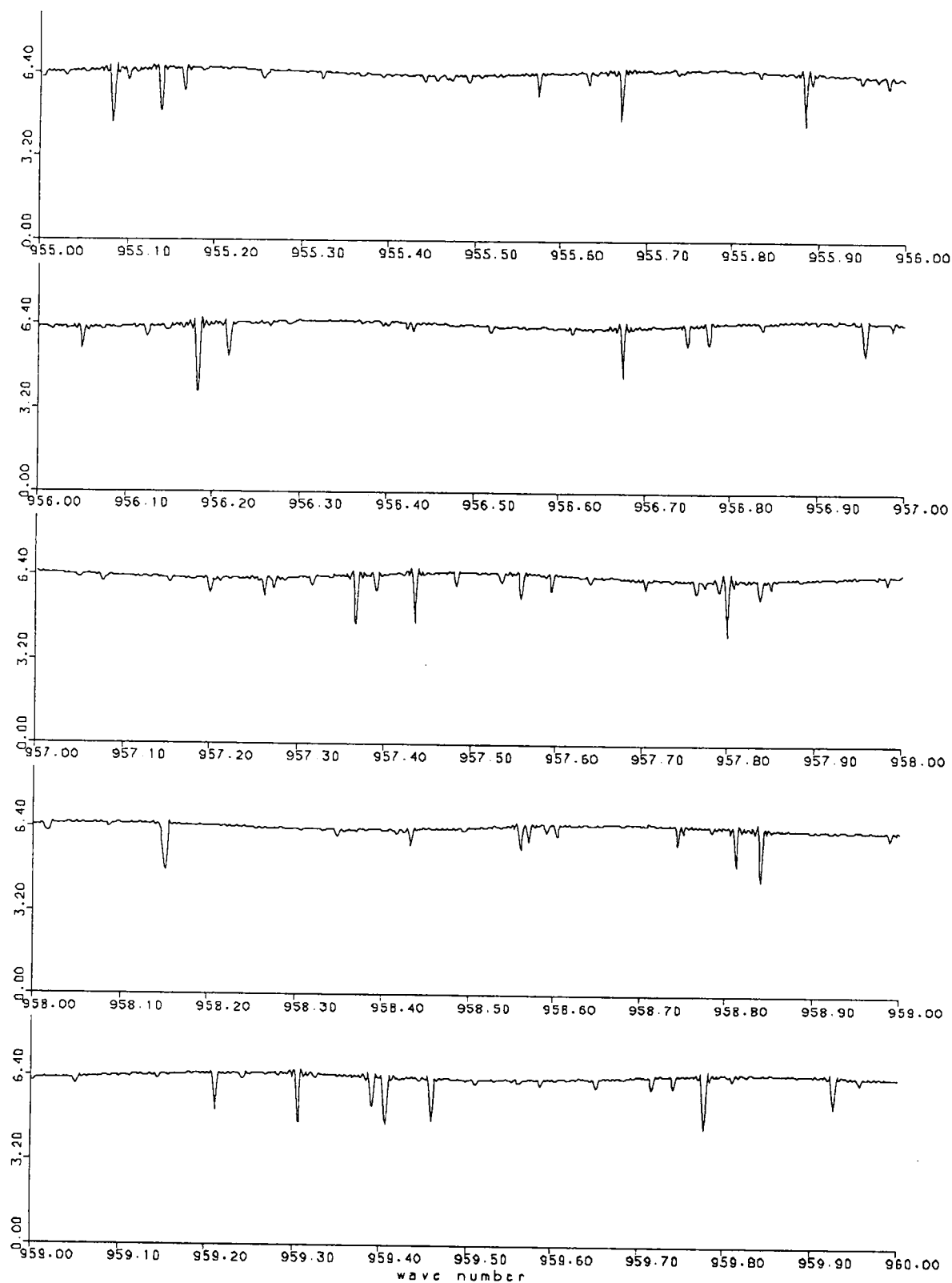
## APPENDIX C

FTS Ethylene Spectra from 940 to 960  $\text{cm}^{-1}$









## VITA

Alan Carroll Ewing was born in Covington, Kentucky on March 23, 1966. He attended public school in Florence, Kentucky and graduated from Boone County High School in May of 1984. The following fall he entered Eastern Kentucky University and completed his B.S. degree in Physics in May of 1989. He was accepted to the Science Allience Summer Fellowship program at the University of Tennessee from May 1989 to August 1989 where then began graduate study with a teaching assistantship. He completed his Master's of Science degree in December of 1993. He is a member of the Coblentz Society and Sigma Pi Sigma.