Title: Spectroscopic Study of Atmospheric Trace Gases

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Abstract: Molecular spectroscopy offers the tools and instrumentation needed to unveil the structure and characteristics of molecules that are found within planetary atmospheres. In order to do this we examine the frequencies of light that these molecules either absorb or emit. It is the fine structure of these absorption or emission features that give us information about their physical state.. In our lab we use a near-infrared source to probe various molecules and examine absorption features and their dependency on both temperature and pressure. In this study we plan to retrieve the N2-broadened widths, pressure-induces N2-shifts and N2-broadened line mixing coefficients for twenty two transitions in the P branch of the Î½1+Î½3 band of acetylene mixed with nitrogen. The gas mixture has been selected to be 10% acetylene and 90 % nitrogen. We will record spectra using a 3 channel tuneable diode laser spectrometer. The system contains a temperature controlled single pass absorption gas cell of fixed length, a room temperature cell filled with pure acetylene gas used to create a reference spectra and a third background cell. The system is controlled by LabVIEW software which will be discussed.Simulations have been performed on the v1+v3 band using data obtained from the HITRAN database and will be presented. . From the simulations we determined that we can measure twenty two lines in the P-branch of this band. These lines are all within the interval of P(1)-P(31). For each line we will record spectra at pressures of 100, 250, 400 and 500 torr and for each pressure we plan on measuring 7 different temperatures ranging from -60 to 60C. From these recorded spectra we hope to obtain line parameters using a nonlinear least squares fitting routine. The routine will allow for use of several different line shape models. This study will be the first one over a range of temperatures.

Outline

- System Overview
- Simulation
- Creating transmission files from recorded spectra
- Line parameters for 22 acetylene transitions in the $\nu 1+\nu 3$ band
- Summary

What is molecular spectroscopy?

- Molecular spectroscopy offers the tools and instruments needed to reveal the structure and characteristics of molecules of practical importance to the environment, astronomy and fundamental science.
- In order to do this we examine the molecular spectra.
- Molecular spectra result from either the absorption or the emission of electromagnetic radiation as molecules undergo changes from one quantized energy state to another.

How to measure molecular spectra

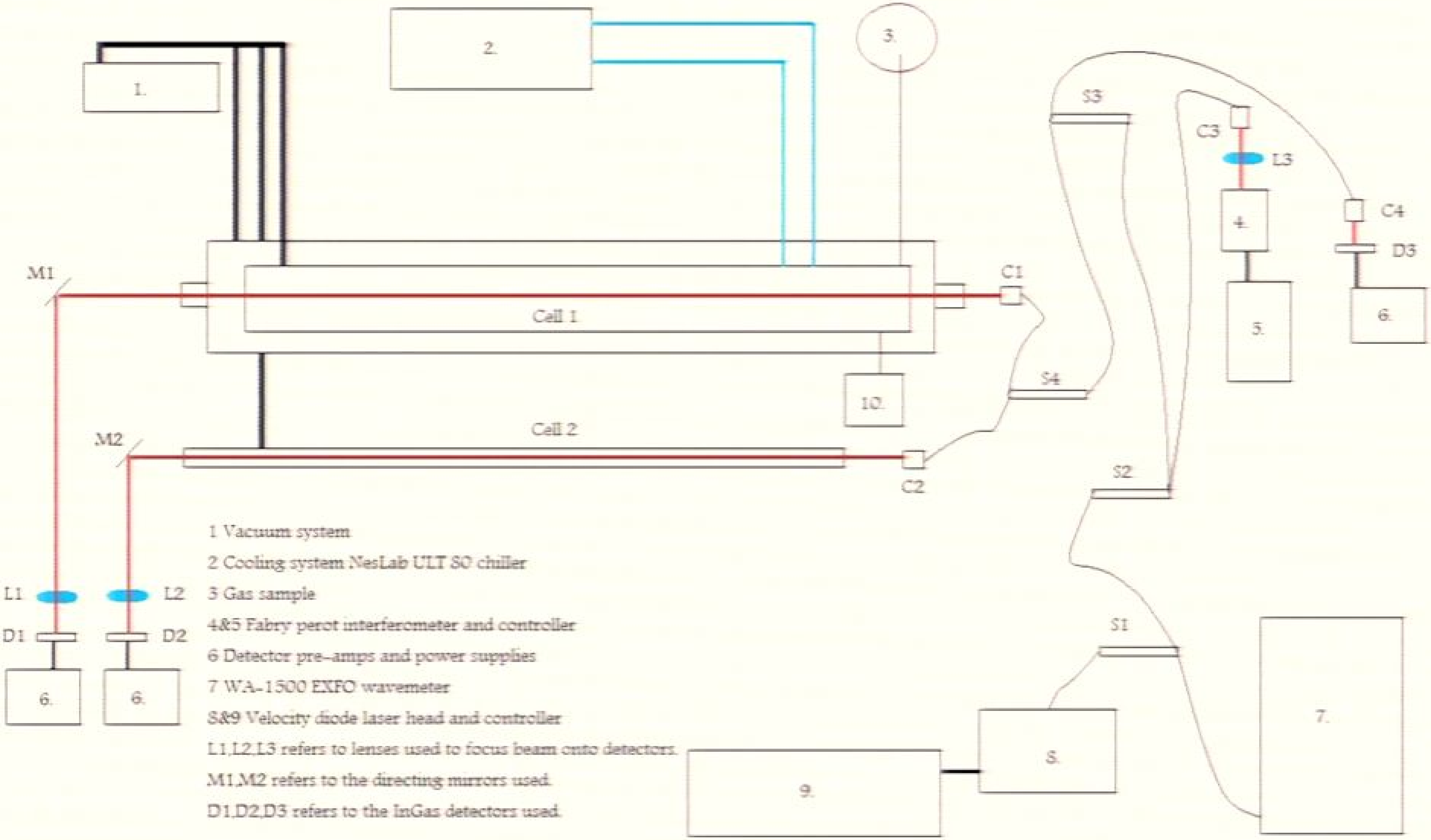
Three fundamental components are needed to measure molecular spectra:

- Source : light can be used to interact with sample
- Sample : a chamber filed with gas
- Detector : measure absorption of light passing through the chamber

Research constituent

- Retrieve the N_2 -broadened widths, pressure-induced N_2 –shifts and line mixing coefficients for twenty two transitions in the P branch of the $\nu1+\nu3$ band of acetylene mixed with nitrogen using Voigt and Hard collision profile.
- The gas mixture has been selected to be 10% acetylene and 90 % nitrogen.

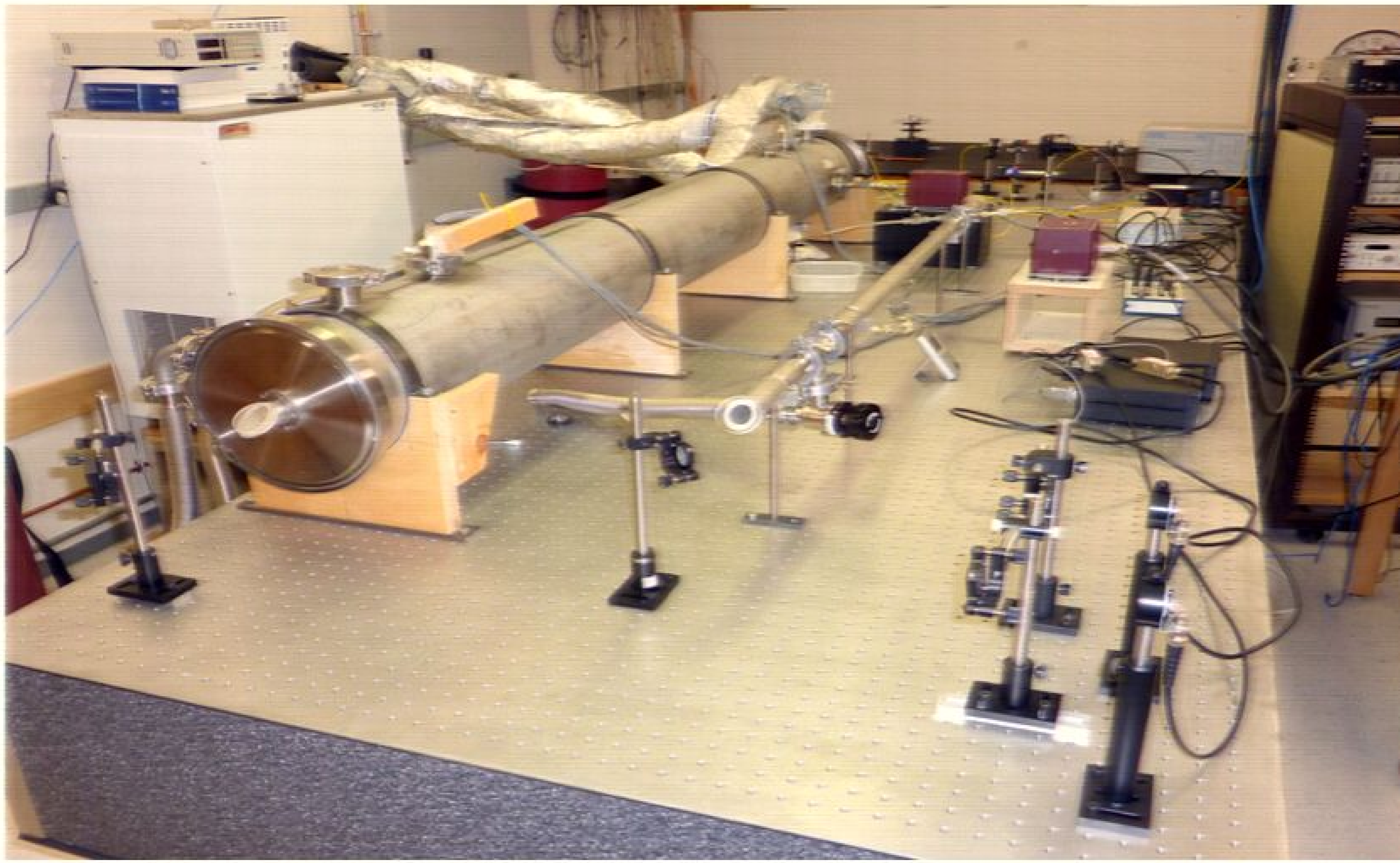
System Overview



1 Vacuum system
2 Cooling system NesLab ULT 80 chiller
3 Gas sample
4&5 Fabry perot interferometer and controller
6 Detector pre-amps and power supplies
7 WA-1500 EXFO wavemeter
8&9 Velocity diode laser head and controller
L1,L2,L3 refers to lenses used to focus beam onto detectors.
M1,M2 refers to the directing mirrors used.
D1,D2,D3 refers to the InGas detectors used.

C1,C2,C3,C4 refers to the collimators used to couple the fiber laser to free optics.
S1,S2,S3,S4 refers to the fiber splitters used to send signal to the various channels.
Cell 2 is the reference cell.
Cell 1 is the temperature/pressure control cells.
Vacuum lines are shown in thick dark black lines. Coolant lines are shown in blues lines. The laser path is depicted with red lines, and the curved lines represent the fibers used.

Laser Spectrometer Facility



Detection of Optical Signals

Optical signals detected using 3 InGaAs detectors.

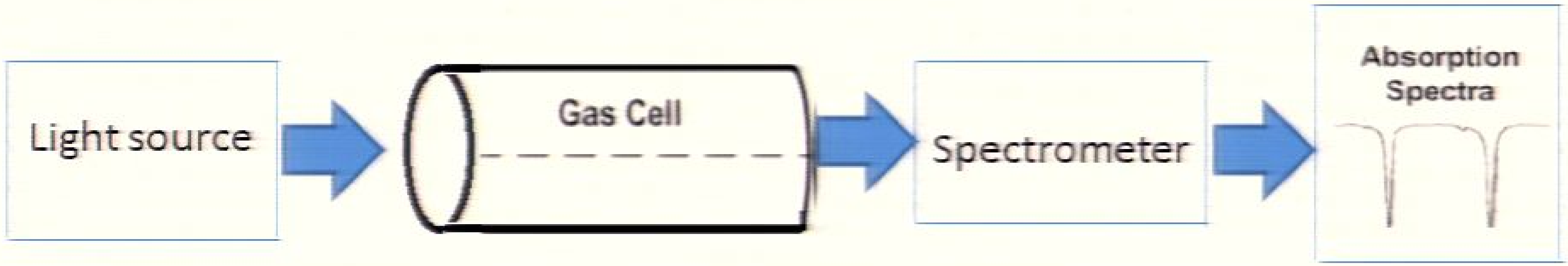
- Detector 1 : measures the incoming light from the control cell
- Detector 2 : measures the incoming light from the reference cell
- Detector 3 : measures the background power of the laser and is used to calculate spectral transmission

Control and Reference Cells

The are two sample chambers:

- Channel 1 allows control of both pressure and temperature. This control cell has been designed for temperatures in the range of -80^{0}C to $+80^{0}$ C.
- The other cell is used as a reference cell for measurements of pressure shifts for the gas of interest.

Spectroscopic Measurements



The relationship between the intensity of light before and after travelling path length L through a target gas which given by Beer-Lambert law.

$$I\,(L) = I(0)\, e^{-\alpha C}$$

Where : I(0) and I(L) are the light intensity before and after traveling distance L through the gas

C: gas concentration

α : gas absorption coefficient (depend on wavelength).

MOLECULAR MOTIONS AND THEIR ENERGIES

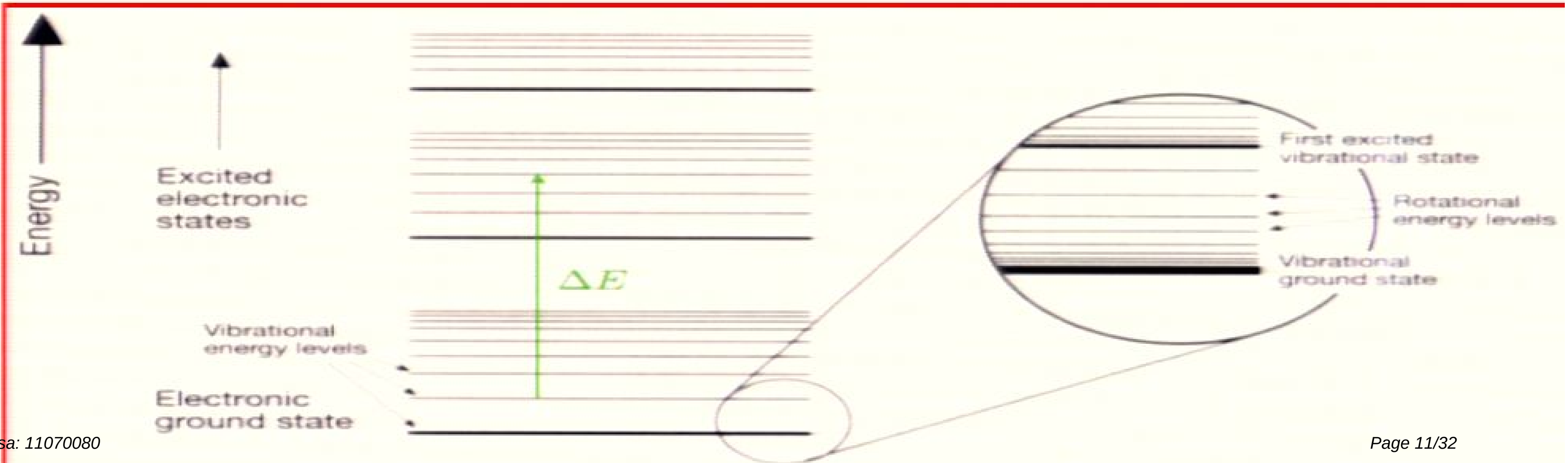
- *Molecule = ensemble of interacting electrons and nuclei*

Quantized energies: $E \approx E_{elec} + E_{vib} + E_{rot}$

Motion of the electrons

Motion of the nuclei

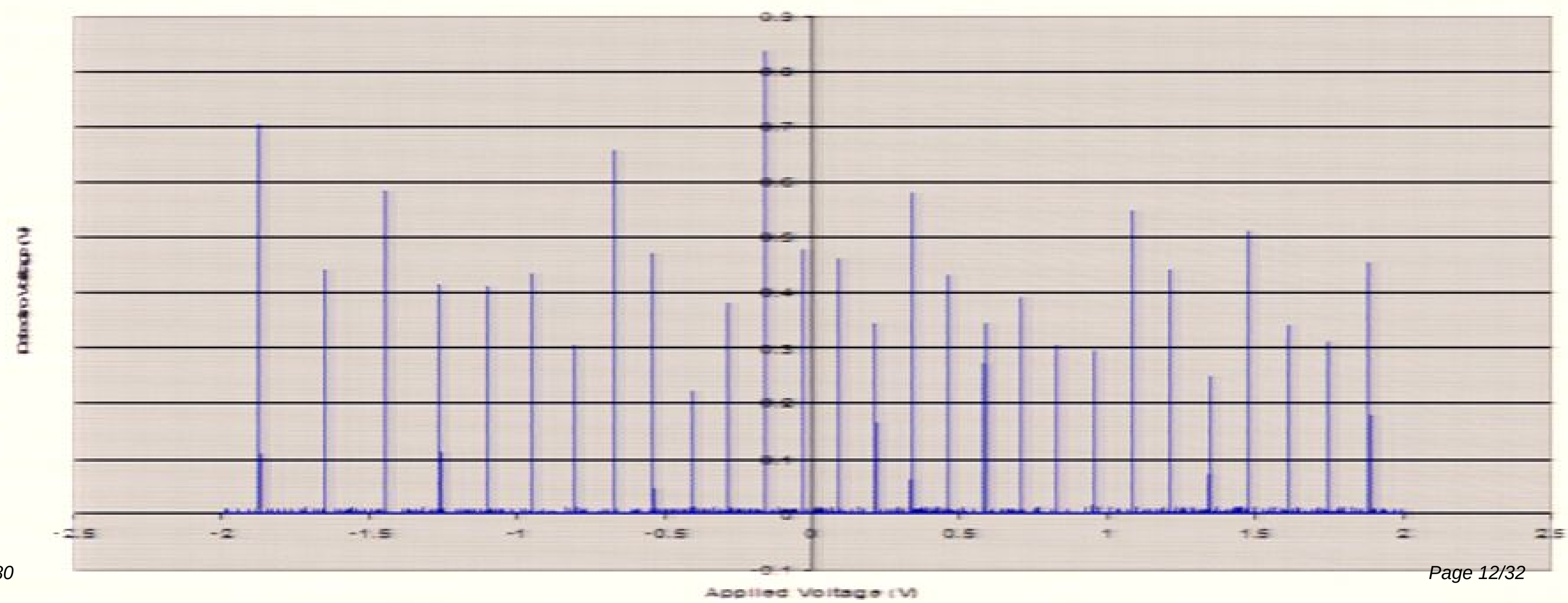
$\Psi = \Psi_{elec}\,\Psi_{vib}\,\Psi_{rot}$



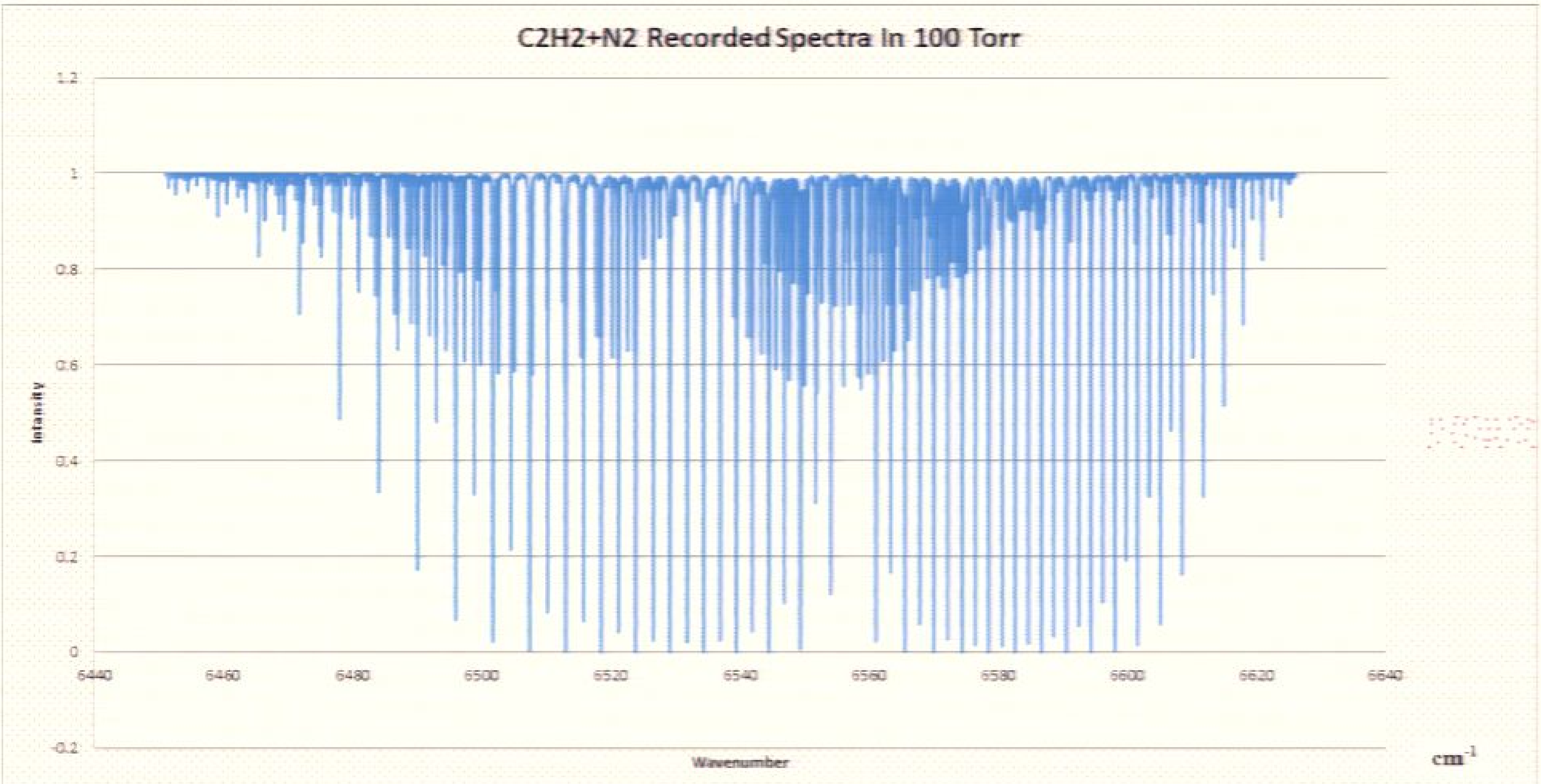
Wavelength Measurement

- The wavelength of light measured using a combination of a Febry Perot cavity and a WA-1500 Wavemeter

Fringe Pattern of Fabry Perot With the Diode Laser set to 1520nm



Simulation Using HITRAN



Selected Lines

- 22 Lines in the P branch were measured in 100, 250, 400 and 500 torr at 296K within the wavenumber 6471.756300 to 6554.111700 cm^{-1}:

- P(1)
- P(2)
- P(4)
- P(6)
- P(8)
- P(10)

P(12)
P(14)
P(16)
P(18)
P(20)
P(21)

P(22)
P(23)
P(24)
P(25)
P(26)
P(27)

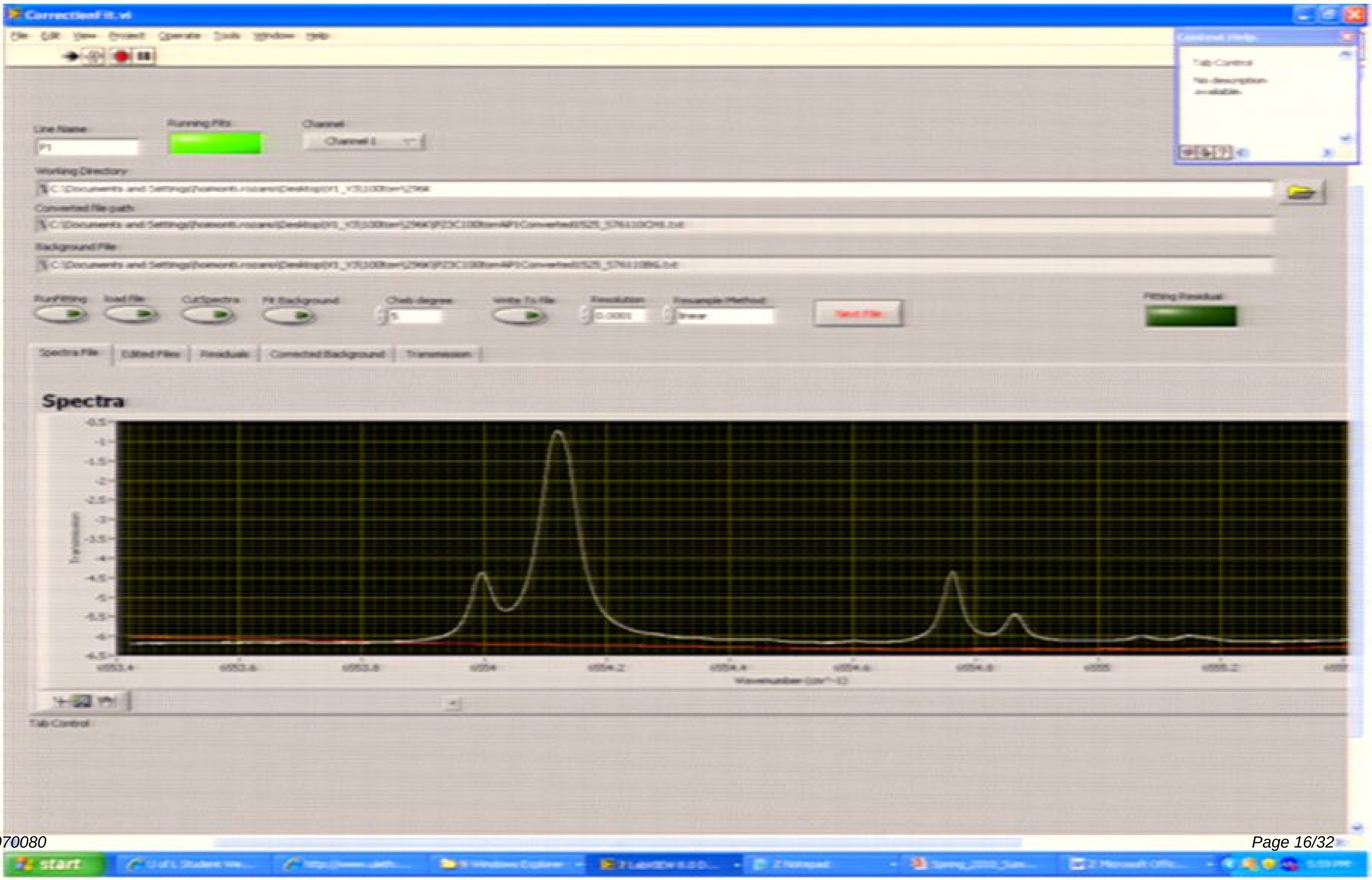
P(28)
P(29)
P(30)
P(31)

LabVIEW:

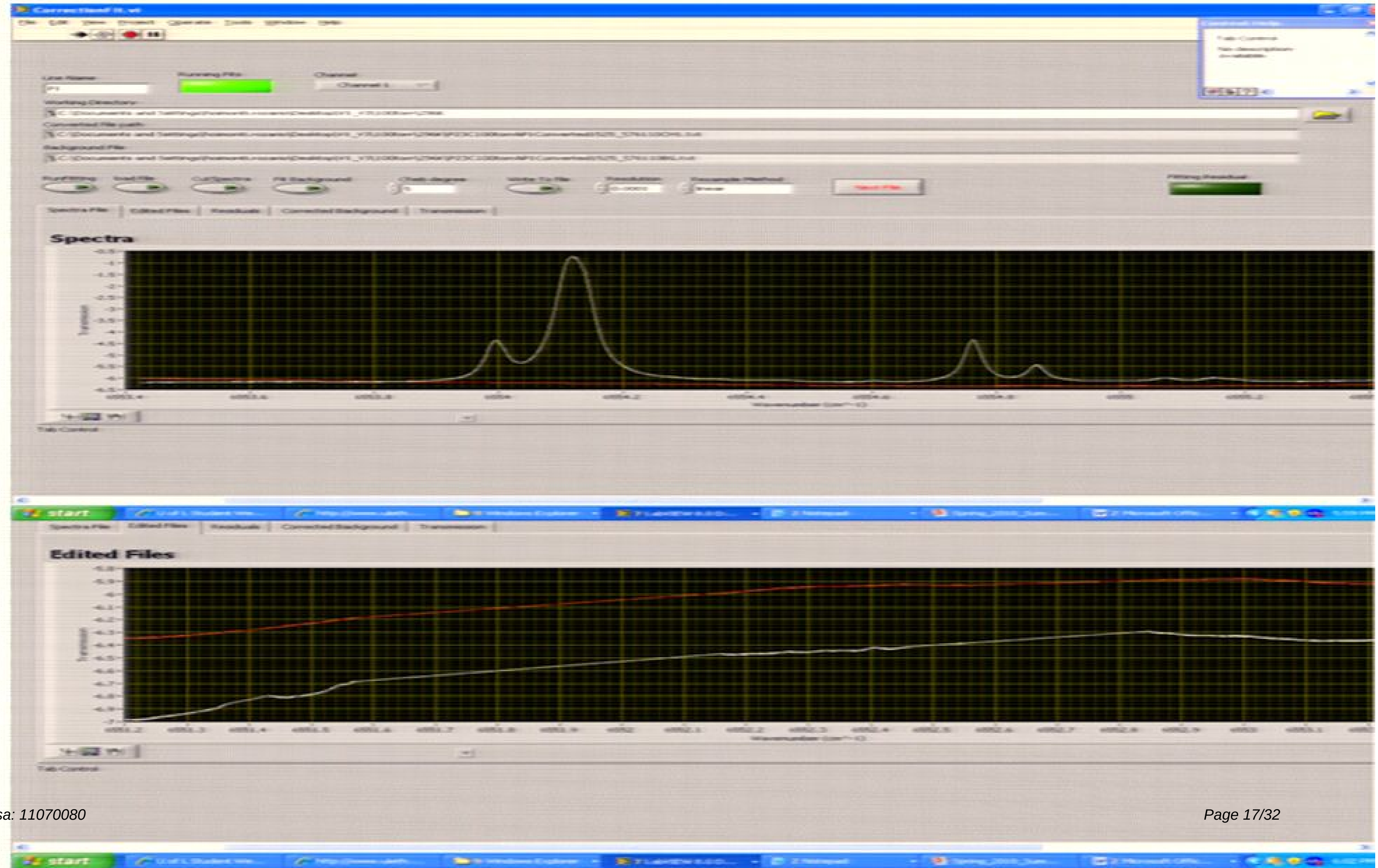
We have used labVIEW software to create transmission file from recorded spectra. Creating transmission files from the recorded spectra has been performed in the following steps:

- We cut the spectral feature out of the raw file
- We calculate a difference between the background spectra and the measured spectra.
- After that we fit the difference using the Chebyshev Polynomial
- Finally the signal file is divided by the corrected background to create the transmitted file

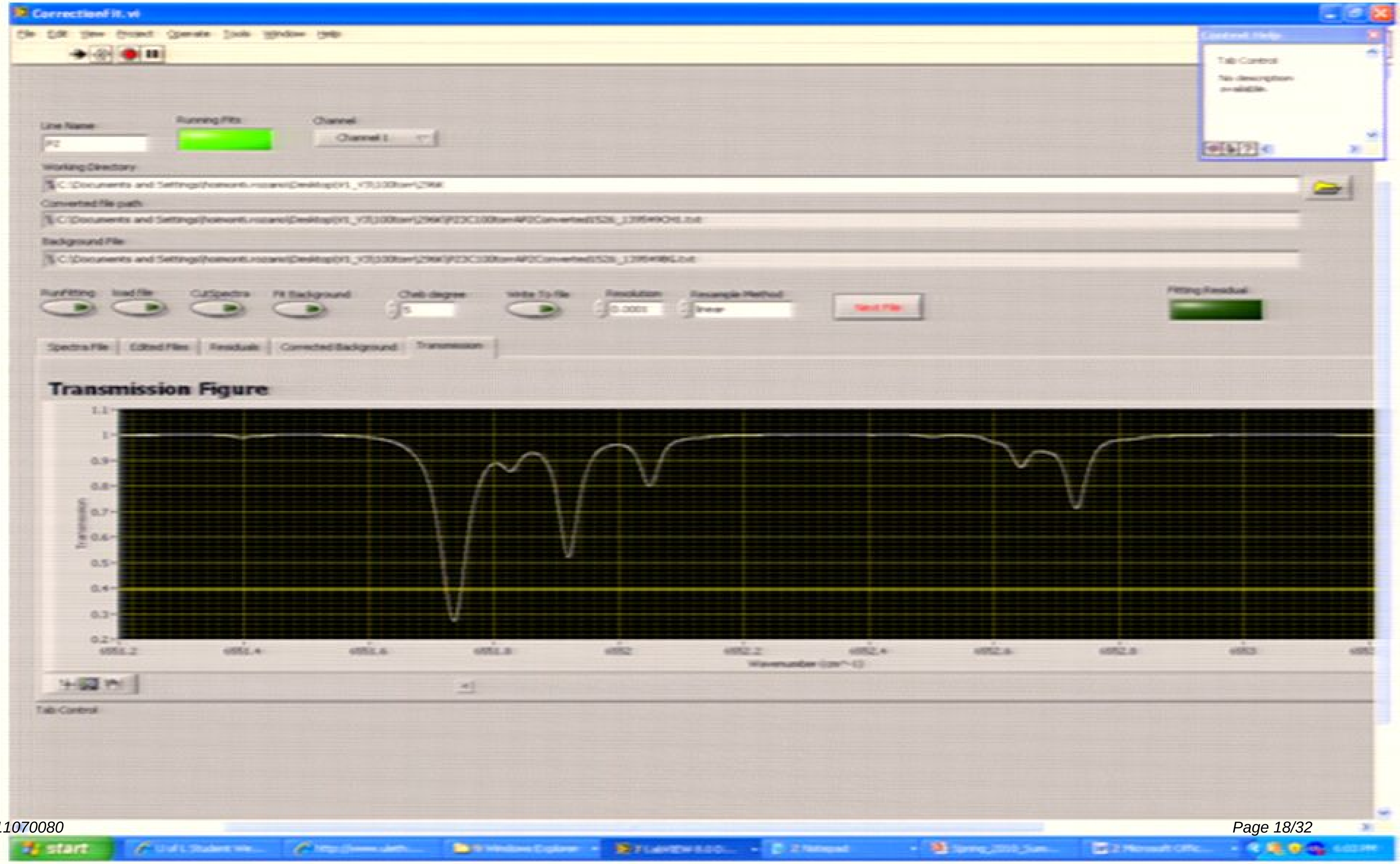
Recorded Spectra



Spectral features are cut from the raw file



Transmission file



Pressure Broadening and Shift Equations

- $\gamma^0 = \gamma/p$
- $\gamma^0(296K) = \gamma^0(T)\,[T/296]^n$
- $\gamma(p,T) = p[\gamma^0(N_2)(p_o,T_o)(1\text{-}x)(T_o/T)^n + \gamma^0(\text{self})(p_o,T_o)x(T_o/T)^n]$
- $\delta^0(T) = \delta^0(T_o) + \delta'\,(T\text{-}T_o)$
- $\nu = \nu_o + p\delta^0$

- γ^0 - the retrieved broadening coefficient (in $cm^{-1}atm^{-1}$)
- γ -the measured broadened half width
- p - pressure in atm
- T - temperature in K
- δ^0- pressure-induced shift coefficients (in $cm^{-1}atm^{-1}$)
- x -line mixing ratio

Parameters of an Absorption Line

$$\alpha(\nu) = \alpha_i^{\mathrm{int}} \times g(\nu - \nu_i)$$

$$\alpha_i^{\mathrm{int}} = \int_{line} \alpha_i(\nu) d\nu$$

Overall surface of the line: Line intensity

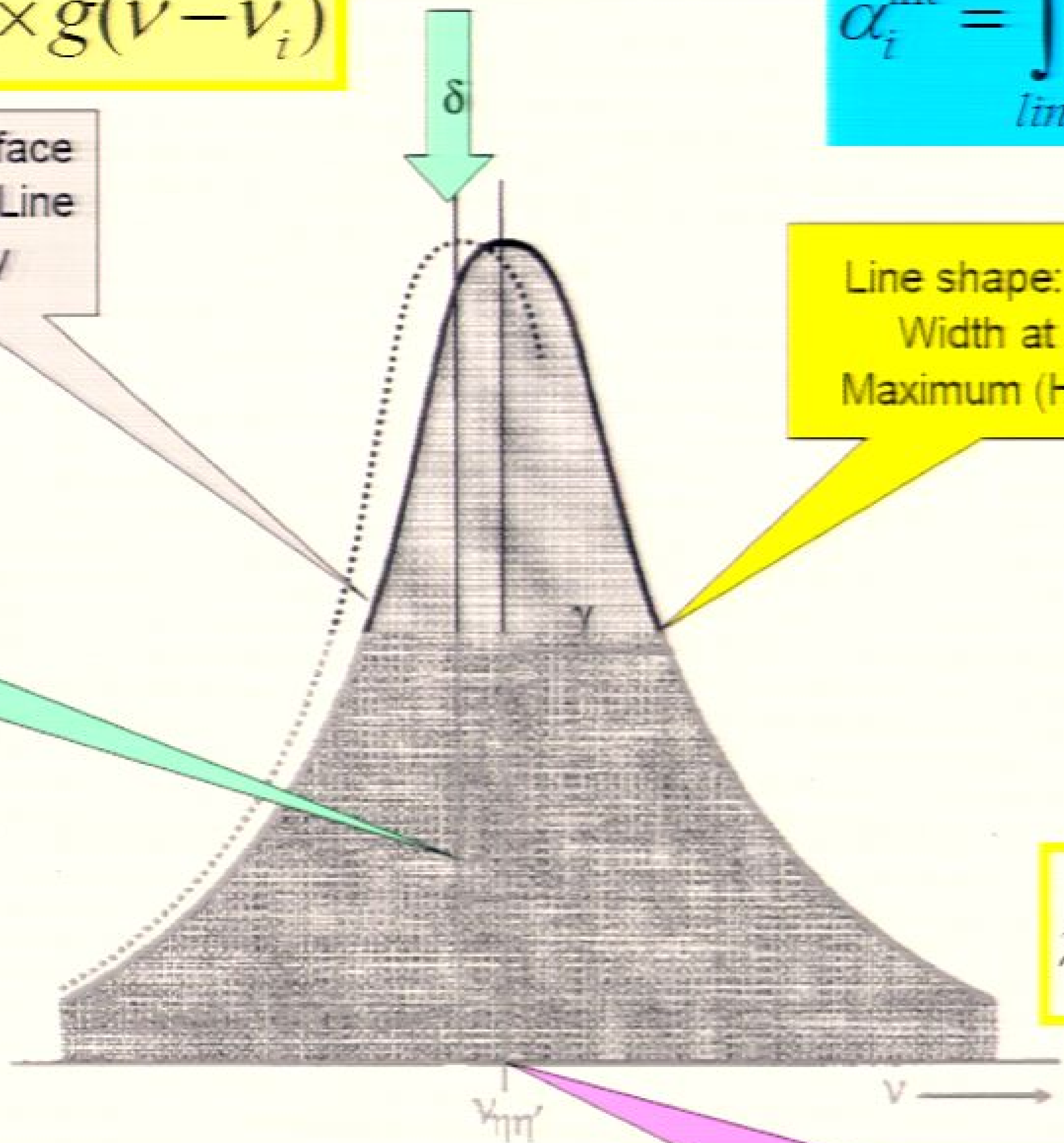
Line shape: γ Half Width at Half Maximum (HWHM)

$$\nu = \nu_0 + p\delta$$

Pressure shift δ

$$\gamma^0 = \frac{\gamma}{p}$$

$$\gamma^0(296K) = \gamma^0(T)\left[\frac{T}{296}\right.$$



Position ν in (cm⁻¹ or MHz)

Traditional Line Profiles

The Voigt Profile combines the effects of both:

$$I_D(\nu) = \frac{2\sqrt{\ln 2}}{\gamma_D\sqrt{\pi}}\exp\left(-4\ln 2\,\frac{(\nu-\nu_0)^2}{\gamma_D^2}\right.$$

1. The **thermal motion** of molecules
   Leading to a *Gaussian (Doppler) Line Shape*
2. The effect of **molecular collisions** leads to a *Lorentzian Line Shape*.

$$I_L(\nu) = \left(\frac{\gamma_L}{2\pi}\right)\frac{1}{(\nu-\nu_0-\delta)^2+\left(\frac{\gamma_L}{2}\right)^2}$$

where

$$\gamma_D = \frac{2\nu_0}{c}\sqrt{\frac{2k_B T\ln 2}{m_E}}$$

is the Doppler Half-Width

- The two effects occur simultaneously and thus **the Voigt profile is a convolution of the two broadening mechanisms** and can be written as:

$$I_v(\nu) = I_L(\nu)\otimes I_D(\nu) = \int_{-\infty}^{\infty} d\nu'\, I_L(\nu-\nu')I_D(\nu')$$

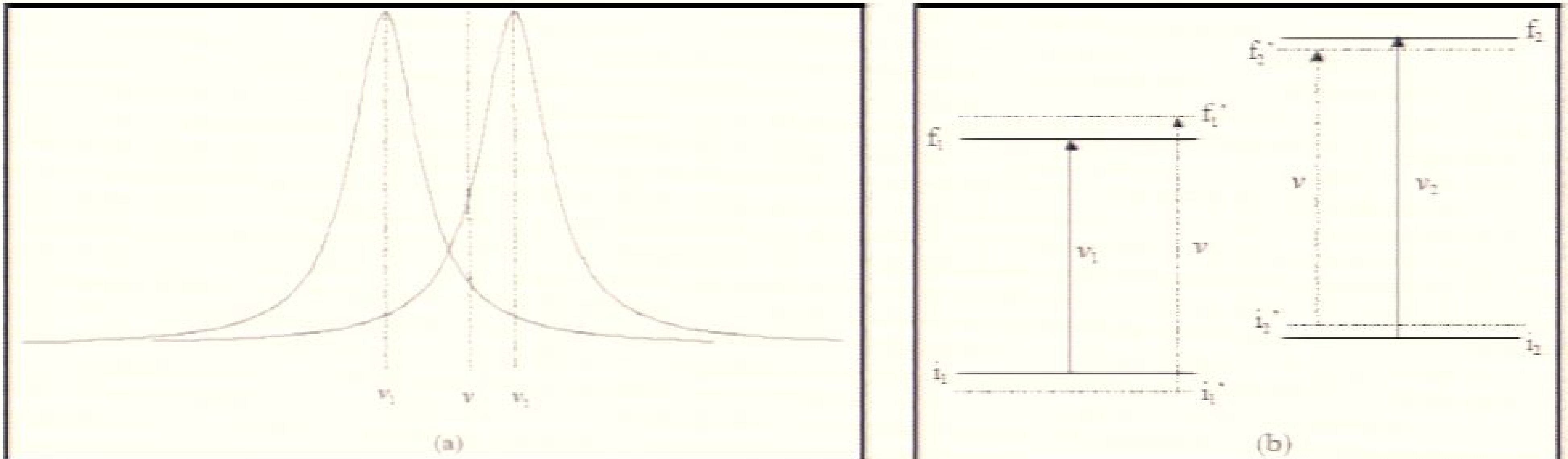
Pressure

Doppler effect only | both effects | collisions only

Gaussian (γ_D) | Voigt profile (γ_v) | Lorentzian (γ_L

Line Mixing

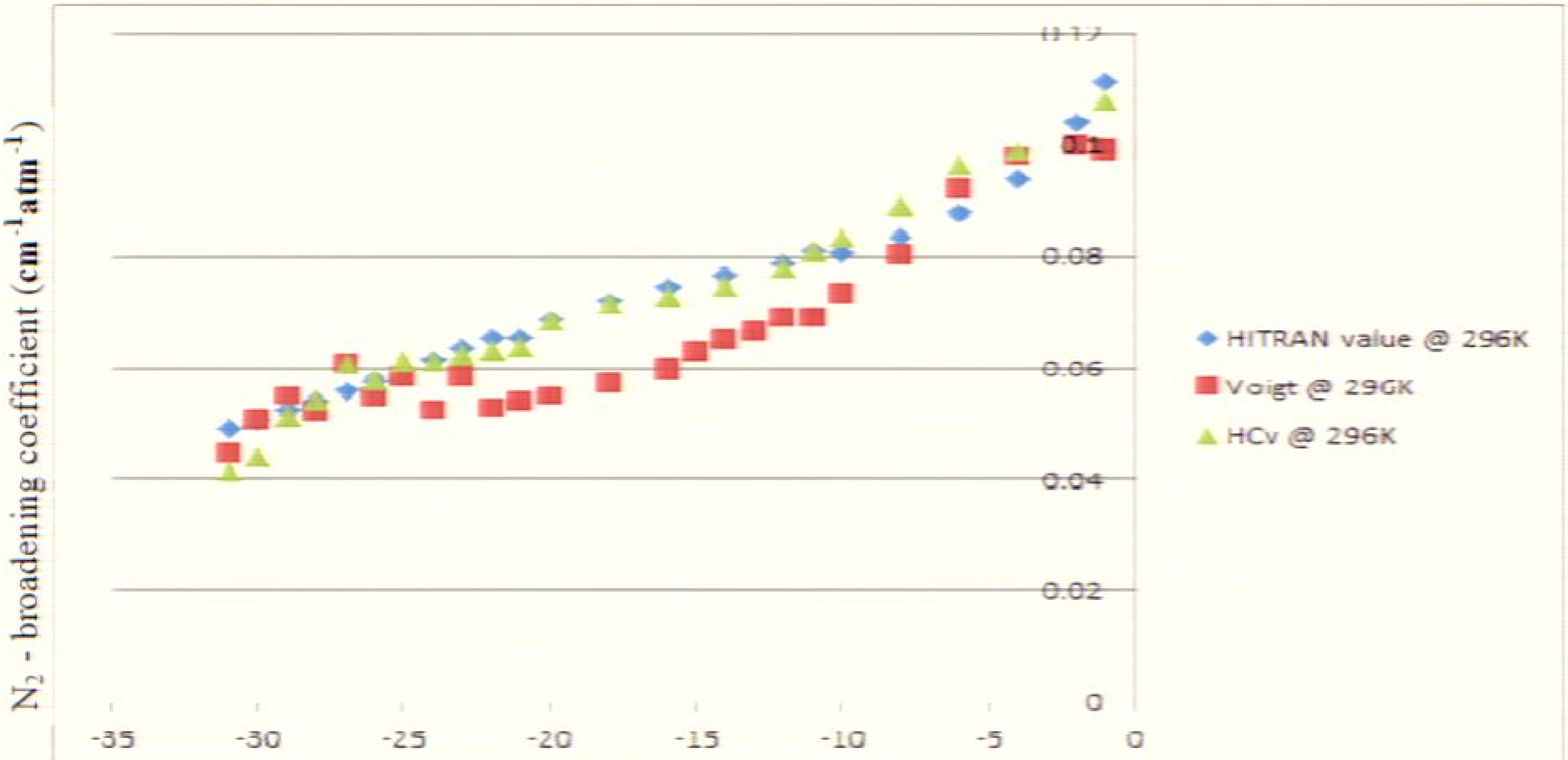
- Consider two adjacent spectral lines that have the same initial and final ***vibrational*** states and whose profiles overlap. Through inelastic collisions, both the initial and final ***rotational*** states of these transitions are perturbed:
  - $i_1 \rightarrow i_1', i_2 \rightarrow i_2', f_1 \rightarrow f_1', f_2 \rightarrow f_2'$
- Because of this, any transition of frequency ν can follow any of the two coincidental paths (vertical dashed lines in the Figure b): $i_1' \rightarrow f_1'$ **or** $i_2' \rightarrow f_2'$



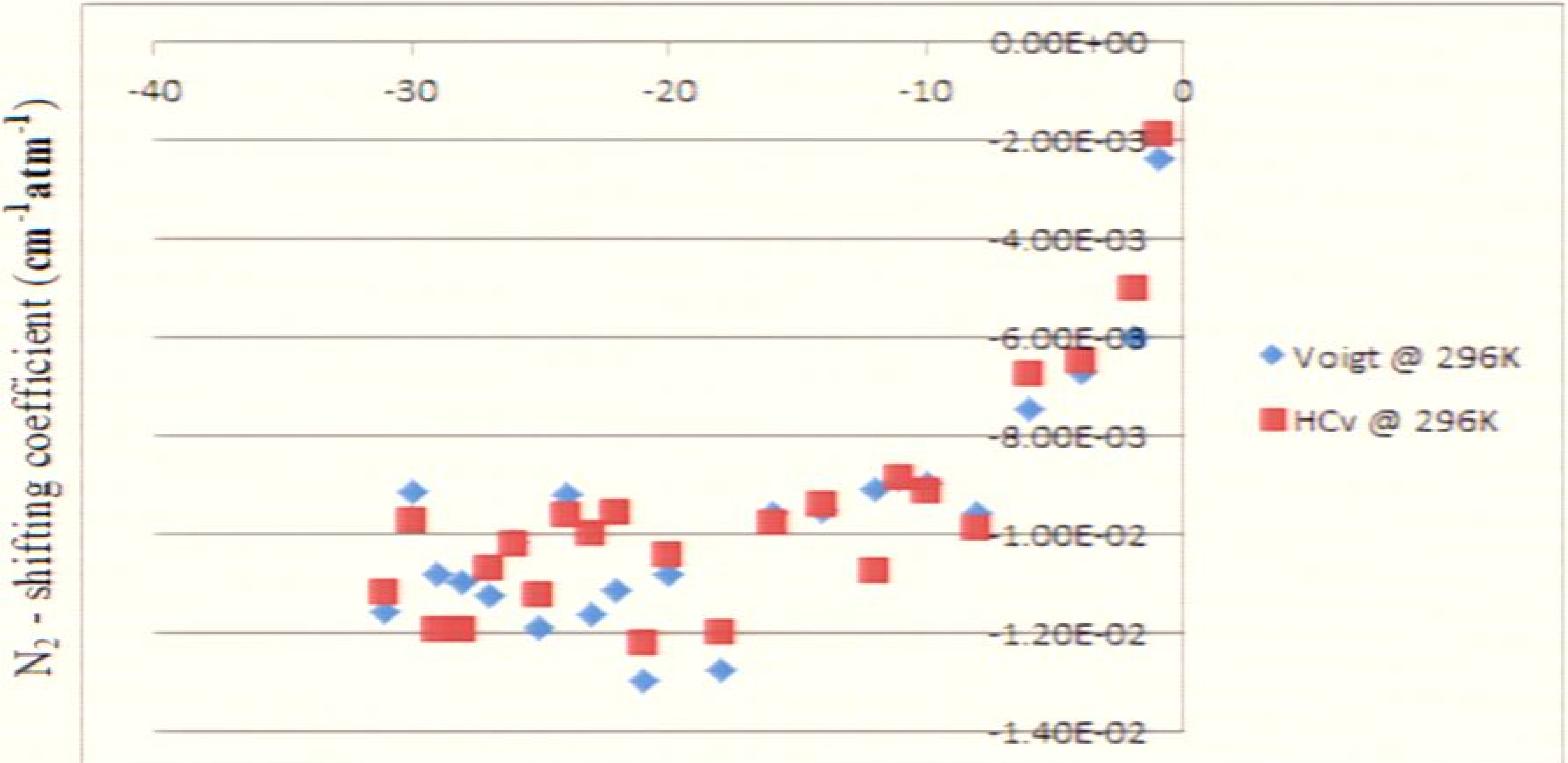
(a) Two adjacent lines overlapping and allowing two probabilities of absorption for a photon *v*

(b) Perturbed energy levels (dashed horizontal lines) leading to line mixing

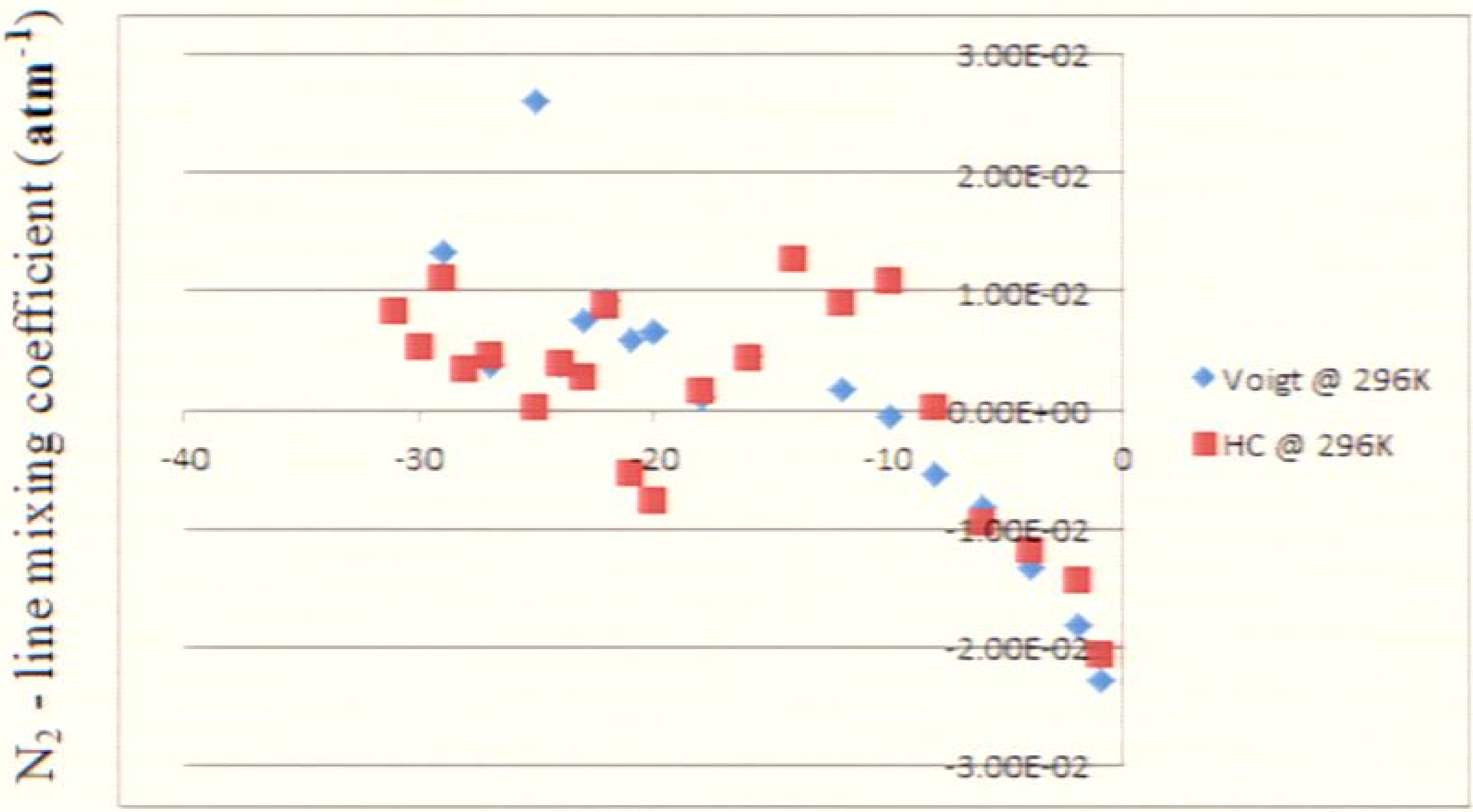
Comparison Between N_2 Broadening Coefficients



Comparison Between N_2 Shifting Coefficients



Comparison Between N_2 Line Mixing Coefficients



Summary

- Simulation has been done to select lines to measure.
- Spectra is recorded at pressures of 100, 250, 400 and 500 torr and for each pressure we have measured 7 different temperatures ranging from -60^0 C to 60^0 C.
- Transmission files with in the interval of P(1) - P(31) of the $\nu 1 + \nu 3$ band is calculated.
- Spectral line parameters : N_2-broadening, N_2-shift and line mixing is retrieved for room temperature 296K.

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- *Chad povey, Adriana Predoi-Cross, Daniel R. Hurtmans. Line shape study of acetylene $v1+v2+v4+v5$ band over a range of tempereatures.*
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THE END

THANK YOU

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