

REPORT

**Final Report to The
British Council**

Measurement of Stratospheric Ozone Depletion and Air Pollution using Tunable Diode Lasers

N A Martin, N R W Swann,
N T Driskell, T P Allott,
P A Noyes, W Bell,
C Paton-Walsh and P T Woods

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ABSTRACT

This report describes the contribution made by NPL to the development of a ground-based tunable diode laser heterodyne spectrometer (TDLHS) operating in the mid-infrared. Details are also given regarding the deployment of the instrument to make heterodyne measurements of the important stratospheric trace species-chlorine nitrate, nitric acid and ozone.

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Approved on behalf of the Managing Director, NPL,
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I INTRODUCTION

This Report describes the results obtained from a joint Anglo-German collaboration between the National Physical Laboratory (NPL) and the Institute of Physical Measurement Techniques (IPM), Freiburg. The work reviewed here is the NPL contribution to the development of a ground-based tunable diode-laser heterodyne spectrometer (TDLHS) that operates in the mid-infrared region. The major NPL project milestones are each discussed, in turn, and details are given of further work which has been carried out at NPL to deliver a final working instrument. The main components developed are discussed - including the detection electronics, data acquisition system and an optical breadboard instrument. There is also a thorough assessment of the long wavelength (12.8 μm and 11.5 μm) tunable diode lasers available for use as local oscillators. Finally heterodyne measurements are presented of the target stratospheric species-chlorine nitrate and nitric acid, together with ozone.

II PROJECT BACKGROUND

Heterodyne spectroscopy is a technique that can be used to make high resolution measurements of important trace gases that are involved in the chemistry of the atmosphere. The method operates by coherently mixing on a photodetector incoming radiation from the sun with that of a narrow bandwidth local oscillator (LO) source present in the instrument. The atmospheric absorption spectrum is obtained from the heterodyne difference frequency which, in this particular case, is in the radiofrequency region. The solar signal passes through the atmosphere so that some of the light is absorbed at characteristic wavelengths due to the species present. The wavelength of the tunable mid-infrared diode LO is then selected to coincide with regions where stratospheric molecules of interest absorb. By accurately quantifying the amount of absorption the concentration of each molecule in the stratosphere can be determined from ground level.

The target species to be measured in this project are ClONO_2 and HNO_3 which are important reservoir molecules that are involved in the issue of stratospheric ozone depletion. A major aim of this work is to improve the present monitoring capability by making use of the increased theoretical heterodyne efficiency at long wavelengths.

The final contributions made by the two collaborating institutions are defined below.

The main NPL milestones for the project were:

- Design and construct the detection electronics and data acquisition system.
- Characterisation of the tunable diode lasers.
- Incorporation and testing of electronics package into spectrometer.
- Deployment of final compact instrument to make atmospheric measurements.

The IPM role was:

- The development and supply of liquid nitrogen cooled lasers at specified target wavelengths.
- Integration of diodes and dewar into a small robust package for each species to be measured.
- Incorporation of external resonator into the dewar package for narrowing of laser linewidth.
- Construction of control unit with low rf noise characteristics for wavelength tuning.

The following sections describe the progress made in the work programme.

III MAIN RESULTS OBTAINED

1 TDLHS DETECTION ELECTRONICS AND DATA ACQUISITION SYSTEM

1.1 INTRODUCTION

The TDLHS control electronics which have been developed for this project by NPL consist of three main elements. These are the filter bank, TDLHS electronic data acquisition system, and computer with the associated software. A schematic diagram of the completed electronics is given in Figure 1. For each of the important components a brief description of the mode of operation now follows.

1.2 FILTERBANK

The amplified chopper modulated heterodyne signal received at the photomixer-preamplifier combination is passed into the radiofrequency (rf) filterbank unit. The photomixer (photodetector) employed is manufactured by SAT and has a bandwidth of 310 MHz. This is coupled to a matched preamplifier developed at NPL which has a bandwidth of 150 MHz.

The heterodyne signal is split by a power divider into four separate channels in the filterbank. Each channel has its own programmable attenuator to adjust the output signal level emerging from the wideband amplifier. Since all the amplifiers have a fixed gain of 45 db, each attenuator is set individually so that the emerging signals are approximately equal. This ensures that all signals that reach the rf detectors are in the square law regime.

The amplified outputs are each fed into four nine-pole Butterworth rf bandpass filters. Each channel has a filter of different intermediate frequency (IF) bandwidth (5-56 MHz, 2-20 MHz, 0.95-10 MHz and 0.27-4.9 MHz). This enables heterodyne spectra to be acquired simultaneously at different double-side-band resolutions. The bandwidths have been selected to enable high resolution Doppler limited spectra to be recorded provided that the laser has a narrow linewidth. An additional modification occasionally uses a 2 MHz high pass filter between the preamplifier and filterbank. This removes low frequency local oscillator noise and increases the signal to noise ratio in the narrow band channels.

The signals from the rf filters in each channel are then passed to four high frequency detector diodes. These have a bandwidth of 100 kHz to 2 GHz and demodulate the incoming heterodyne signal at the chopper frequency. The square wave produced in each case is then fed into the electronic data acquisition system.

1.3 ELECTRONIC DATA ACQUISITION SYSTEM

The four autobias integration circuits are used to centralise and amplify the four square wave signals about the zero voltage axis. This is followed by phase sensitive detection at the chopper frequency of 128 Hz. Each of the analogue output signals is then integrated over 63 chopper cycles which is equivalent to a true time constant of 0.5 second. The values of the four integrated signals are then digitised and passed to an IBM compatible personal computer via a 12 bit analogue to digital converter. The computer controls the tunable diode laser (TDL) local oscillator fine current and commands the analogue integration sequence. The acquisition system has four additional diagnostic channels available. One is used to record the photocurrent giving a measure of the TDL power. Two other channels are reserved for monitoring the TDL current and temperature servo error.

The final channel is available to simultaneously record homodyne spectra with atmospheric heterodyne spectra. This option is only used when the atmospheric spectra obtained do not have conveniently located absorption lines for wavelength calibration.

1.4 COMPUTER AND ASSOCIATED SOFTWARE

The computer software package developed to control the TDLHS is written in C. It enables the heterodyne and diagnostic channels described earlier to be displayed in real time as a function of laser current. The user may select the start point of the TDL injection current and the current increment. The number of points in each scan can then be selected up to a maximum of 4096.

There is also a software facility for assessing the heterodyne performance of the TDLHS in terms of the signal-to-noise ratio (SNR). It is most convenient to do this

by determining the precision with which a blackbody source can be measured at a constant laser current. In this case the analogue output of the control electronics is disconnected from the TDL current controller external input. The laser wavelength is thus held constant at a selected value which is near to an atmospheric spectral absorption feature of interest. After the data has been recorded the software calculates and displays the value of the SNR, signal level and standard deviation for all the four heterodyne channels.

2 CHARACTERISATION OF LASERS

2.1 INTRODUCTION

This part of the project has been carried out in two phases. In Phase I tests were performed to assess the performance of the laser dewar package and new TDLs with emission from both faces. Phase II was concerned with testing lasers in conventional mounts at the target wavelengths for measuring atmospheric species.

2.2 TESTING OF LASERS IN LIQUID NITROGEN DEWAR PACKAGE (PHASE I)

The dewar package was designed to enable single mode diode lasers to operate at liquid nitrogen temperatures. The technique of optical feedback was also tested to reduce the laser spectral linewidth.

A $^{12}\text{C}^{18}\text{O}_2$ laser emitting at 1067.4 cm^{-1} (9P(22) transition) with a linewidth of less than 1 MHz was heterodyned with the output of a liquid nitrogen cooled single mode laser at the same frequency. The width of the heterodyne beat between the TDL and CO_2 laser gave a measure of the TDL linewidth. Three diodes were available for this test. It was necessary to temperature cycle the lasers in order to obtain the correct wavenumber coverage. Only laser #1438-2-27 was found to have a single mode coincident with the CO_2 laser output. The TDL power was adequate for this experiment but was too low for recording atmospheric heterodyne spectra with the required sensitivity.

The emission from one face of the TDL was used to provide optical feedback when coupled to an external resonator. The resonator consisted of a diffraction grating with a fine piezo electric adjustment together with an off axis parabola. Without external feedback the TDL linewidth was found to be 50 MHz (FWHM). This was reduced to 20 MHz when coupled to the resonator and demonstrates for the first time that line narrowing is possible at $9.4\text{ }\mu\text{m}$. It may be feasible to reduce this further by minimizing étalon effects and antireflection coating one of the faces of the laser. Figure 2 shows an example of the line narrowing results in the region of the 9P(22) transition of $^{12}\text{C}^{18}\text{O}_2$.

The present resonator package has been found to be difficult to adjust and is very sensitive to vibrations. A practical method for tuning the external resonator to provide a typical 1.5 cm^{-1} scan is to be implemented by the IPM in the near future.

2.3 TESTING OF SEMICONDUCTOR LASERS DESIGNED TO MAKE ATMOSPHERIC MEASUREMENTS (PHASE II)

2.3.1 Introduction

Due to the technical complexity of the fabrication process the yield of suitable TDLs in the target spectral regions of 12.8 μm and 11.5 μm that operate above 77K is low. For this reason the project efforts have focussed on developing TDLs that can be used to measure ClONO_2 . These have been mounted in a conventional laser housing and can therefore not be used with the external resonator.

2.3.2 Batch 1 Lasers

The first batch of lasers were delivered in March 1995 for testing. The TDLs were mounted in a helium closed-cycle cooler fitted with a Modion pump to allow for operation, if necessary, at just above liquid nitrogen temperatures. The wavenumber of the TDL was regulated using a Laser Photonics temperature and current controller.

The radiation from each laser was passed in turn through a low pressure calibration gas cell and the emerging beam focussed onto a HgCdTe detector. To obtain gas absorption spectra the TDL was used in the current modulation mode so that the output of the detector could be displayed on an oscilloscope. A Polaroid camera was used to record hard copies of the spectra.

The gases available for accurate absolute wavenumber calibration of each diode were acetylene, ammonia and carbonyl sulphide. Line positions for C_2H_2 were derived from high resolution Fourier Transform Infrared (FTIR) spectra and the HITRAN 1992 database. In the case of NH_3 and OCS the lines were identified from the Handbook of Infrared Standards (Guelachvilli and Rao, 1986) and Wavenumber Calibration Tables from Heterodyne Frequency Measurements (Maki and Wells, 1991). Relative wavenumber calibration was achieved by substituting the gas cell in the laser beam with a one inch long solid long germanium étalon. The free spectral range of the étalon was 0.048 cm^{-1} .

Only one of the three IPM diodes supplied in conventional mounts covered the Q-branch region of ClONO_2 at 780 cm^{-1} in a single mode. The TDL operating temperature was 79K which is suitable for use in the NPL coldhead with the adaption described earlier. Nevertheless this temperature would be too low for the laser to be used in the IPM dewar without pumping of the liquid nitrogen reservoir. Experiments in Phase I have shown that the IPM dewar configuration will operate at a base temperature of 82.8K. This could be reduced to 73.2K when connected to a complex reservoir pumping system.

Figure 3 shows an example of the calibration spectra that were obtained using laser #L-287-5a-5. It can be seen that the C_2H_2 features in the diode laser absorption spectrum match the FTIR spectrum in the 780 cm^{-1} region at the optimum operating temperature of 79.3 K. The fringes in the étalon trace also confirm the near single mode performance of the TDL. A small change in the diode temperature, however, did give rise to multimode behaviour and mode-hopping. The current tuning rate was also found to be non-linear at the target wavenumber.

It was necessary to operate the TDL near to the threshold current. As a result, to achieve the required conditions, there was a significant change in the laser emission power when the current was scanned. Nevertheless this laser was incorporated into

a heterodyne spectrometer developed by NPL to make a set of atmospheric measurements during the Second European Stratospheric and Mid-latitude Experiment (SESAME). This is discussed in Section 4.

2.3.3 Batch 2 Lasers

The final batch of five IPM lasers operated at much lower temperatures than those in Batch 1. It was hoped that this would increase the probability of meeting the target wavelengths, and would deliver extra output power. The above TDLs were characterised during January 1996.

Figures 4 and 5 show the results obtained with the best diodes #120-61-12 and #210-7-1. Diode #120-61-12 was operated at 51.8 K where there was a very short 0.5 cm^{-1} mode covering much of the Q-branch region of ClONO_2 . Figure 4 shows the acetylene spectrum together with the étalon trace. Again since this diode was used near its threshold current the power varied between $4.5 \text{ }\mu\text{W}$ at the start of the scan to $10 \text{ }\mu\text{W}$ at the end.

Heterodyne tests were performed later with black body and solar signals. This is described more fully in Section 3.

Figure 5 shows the single mode coverage of laser #210-7-1 at 52.8 K. This laser did not cover the ClONO_2 region but emitted near 869.5 cm^{-1} where HNO_3 has a P-branch manifold. Although the OCS calibration spectrum and étalon trace are satisfactory the power emitted by this laser was only $1 \text{ }\mu\text{W}$. This power is too low to be useful in the heterodyne mode.

Diodes #932-13-65 and #81-8-33 were also too low in power and did not have single mode coverage at the target wavelengths. Diode #1603-1-3 was characterised by high multimode power, with very short wavelength modes. The typical mode pattern is given in Figure 6 at an operating temperature of 78.7K and 486.1 mA.

It is planned to return the diodes to the IPM for antireflection coating. Preliminary studies have shown that enhancements in power by up to a factor of three can be achieved by this method.

3 INCORPORATION AND TESTING OF NPL ELECTRONICS PACKAGE INTO SPECTROMETER

3.1 INTRODUCTION

An optical breadboard and active solar tracker have also had to be developed at NPL in order to have a complete spectrometer available to test the electronics package. The essential components of both modules are briefly described below in Sections 3.2 and 3.3.

3.2 OPTICAL MODULE OF NPL HETERODYNE SPECTROMETER

A schematic diagram of the TDLHS is given in Figure 7. Solar radiation is acquired by an active tracker which directs the beam into the optical section of the spectrometer. The solar radiation is passed through a monochromator which is fitted

with a wide bandpass optical filter at the entrance. This combination removes unwanted wavelength components that only contribute electronic noise to the rf detection system. The emerging beam is then amplitude modulated by a mechanical chopper at 128 Hz. After this, it is combined with the collimated output of a single mode laser onto a 2° wedged 50% transmitting, 50% reflective ZnSe beamsplitter. The TDL and solar beams are then focussed onto the HgCdTe fast photomixer. To minimize the adverse effects of optical feedback the photomixer is tilted slightly with respect to the incident beam direction and, where possible, reflective optics are employed.

A second optical channel is available to record spectra in the direct detection mode for the calibration of heterodyne spectra. This scheme makes use of the portion of the TDL beam transmitted through the beamsplitter. The TDL radiation is passed through a calibration gas cell and is chopped at 168 Hz. It is then focussed onto a HgCdTe detector. The amplified output of the detector is connected to a commercial phase sensitive detector (PSD) referenced to the second chopper frequency. The PSD output is fed to the data acquisition system as detailed in Section 1.3.

During poor weather conditions when no sun is available, a collimated blackbody source at 1600K is used to record laboratory heterodyne spectra. This is accessed by placing a mirror with a kinematic mount in the solar path (see Figure 7).

3.3 NPL SOLAR TRACKING TELESCOPE

The system that has been developed provides accurate positioning of the sun's image into the heterodyne spectrometer to enable atmospheric spectra to be recorded. The optical layout of the tracking telescope is shown in Figure 8. The sun's rays are directed by an input steering mirror with automatic control in both the directions of azimuth and elevation. The reflected beam is focused onto a temperature controlled quadrant silicon cell with an optical filter system centred at 840 nm forming the eye assembly. This detector provides information to the control electronics as to the exact orientation of the input mirror.

Error signals are produced in both planes to drive the two-directional motors attached to the input mirror. The system is aligned such that when a balance condition is achieved the solar beam is directed exactly through the base of the tracker and onto the input optics of the TDLHS.

During operation the tracking telescope uses two modes. The SEARCH mode is used to perform a raster scan of the sky with both azimuth and elevating motors driving at a pre-selected rate. The optimum position is reached when the optics are pointing with the sun falling into a set field of view. The control electronics will automatically stop the scan and switch to a high sensitivity POINTING mode. This mode is then maintained while accurately following the sun's movement across the sky.

If the sun signal is lost, then the system can go back to the search mode centred at its last registered solar position.

3.4 TESTING OF ELECTRONICS

Section 1.4 provided a brief introduction regarding the measurement of the TDLHS

signal-to-noise ratio (SNR). For the SNR results quoted here, and in later Sections of this report, it should be noted that all tests were based on single scans of short duration. The increase in SNR obtained by substituting a solar source over the blackbody source is also briefly discussed. For the atmospheric measurements presented of ClONO_2 , HNO_3 and O_3 it should be emphasised that the SNR can of course be increased by the coaddition of a number of short scans, n , since the SNR is proportional to $(n)^{1/2}$.

Blackbody heterodyne scans were performed with the TDL maintained at a constant current to test the electronics module. Laser #L-287-5a-5 was centred at the Q-branch wavenumber of ClONO_2 . The blackbody and local oscillator beams were each blocked in turn to ensure that the heterodyne signal went to zero. The photomixer was in addition blocked to confirm that there were no electrical offsets present due to earth loops.

The signal to noise ratio of the four heterodyne channels was measured in each case. In addition the noise levels were monitored when the detector, blackbody and TDL beam were each blocked in turn. A pinhole was available to vignette the diode laser beam. This reduces the radiofrequency excess noise of the laser but also reduces the power falling on the photomixer. For diode #L-287-5a-5 the optimum SNR of 46 was achieved by cutting the intensity level by approximately one half to 13 μW . Under these conditions the SNR of the heterodyne system was dominated by laser noise over electronic noise by approximately a factor of two.

Similar tests were performed on the other IPM diode that covered the ClONO_2 region. TDL #120-61-12 was very weak with only 7 μW of power being available. This gave a heterodyne signal with a SNR of 26. It was not practical to vignette the TDL beam in this case to increase the SNR. Experiments showed that with such low laser power the electronics were the dominant source of noise.

For completeness, however, TDL #120-61-12 was scanned in current using the ramp supplied by the electronics. An acetylene cell was placed in the blackbody path in order to record a laboratory heterodyne spectrum. Figure 9(a) shows a current scan recorded through the 2-20 MHz filter. The laser power can be seen to vary from 4 μW to 10 μW as the current is ramped from 0.3677A to 0.4066A. The C_2H_2 lines match the direct detection spectrum in Figure 3 and regions of large noise clearly show the laser mode hops.

Although atmospheric solar spectra were recorded on 17th January 1996 with laser #120-61-12 (See Figure 9(b)) the SNR was too low for the results to be analysed. Figure 9(c) shows the noise levels in an atmospheric heterodyne scan as various beams were blocked. Over a period of a few days this low power laser (#120-61-12) changed its output characteristics slightly, requiring the temperature to be modified by about 3K. As a consequence the 780 cm^{-1} region could only be accessed at lower power since it was operating nearer the threshold current. It may be that this laser is unstable over the long term.

Figure 10 shows a typical example of a high resolution atmospheric heterodyne scan recorded with laser #L-287-5a-5 as the local oscillator. The Q-branch maximum of the 4_0^1 band of ClONO_2 is at 780.22 cm^{-1} together with nearby spectral transitions due to

O₃ and CO₂. At mid-latitudes the SNR is just adequate at low solar elevations to quantify the normal ambient levels of ClONO₂ with a single scan. In contrast it is much easier to measure ozone which is more abundant in the stratosphere and has strongly absorbing features in this region. Laser #L-287-5a-5 was the best candidate of the IPM diodes to make atmospheric measurements.

4 DEPLOYMENT OF FINAL COMPACT INSTRUMENT TO MAKE ATMOSPHERIC MEASUREMENTS

4.1 INTRODUCTION

Results are reported here for stratospheric measurements taken during March 1995. These were carried out partly to complement the measurements of the Rutherford Appleton Laboratory (RAL) which were unable to detect ClONO₂ during the Second European Stratospheric and Mid-latitude Experiment (SESAME) and partly to demonstrate the instrument measurement capability. During this period the new solar tracker developed by NPL was integrated into the TDLHS.

4.2 ANALYSIS OF HETERODYNE SPECTRA

The atmospheric heterodyne spectra recorded during SESAME were analysed using a set of simulation programs written in C. These programs are designed to deliver total vertical column amounts of ClONO₂ and O₃. The package is based on Windows and employs Matlab. It enables raw spectral data to be calibrated in wavenumber and then prepares it in a format that is compatible with a column retrieval routine. This consists of the non-linear least squares program package called SFIT which is the widely accepted standard for the analysis of Fourier-transform infrared spectra.

The program package calculates the solar path through the atmosphere and takes into account refraction and atmospheric curvature. Pressure and temperature data were employed from representative sites which were also making measurements during SESAME.

In the fitting procedure an initial trial concentration profile was selected from the World Meteorological Organisation Report 1966. This was scaled at all altitudes to simulate the 780 to 780.6 cm⁻¹ spectral region taking into account absorptions from O₃ and CO₂. Line parameters were selected from the 1986 HITRAN database. The residuals near 780.22 cm⁻¹ were used to calculate the ClONO₂ columns. Absorption cross sections for ClONO₂ at the relevant stratospheric temperatures were obtained from a linear interpolation of published laboratory measurements carried out at 213K and 296K.

4.3 DISCUSSION OF RESULTS

Figure 11 gives a time series of O₃ and ClONO₂ total column amounts from March 1994. For comparison, columns derived from FTIR spectra recorded in Aberdeen Scotland are also included. During this period both sites were outside the Arctic polar vortex as defined by the dynamic tracer potential vorticity at the 475K level. In addition, temperatures were too high for Type I polar stratospheric clouds to be formed.

The ClONO_2 columns are above the typical mid-latitude value of 1.55×10^{15} molec cm^{-2} reported for the International Scientific Station of the Jungfraujoch in Switzerland. However, substantial burdens of ClONO_2 are expected to be detected during late winter at or near the edge of the polar vortex. At these locations there is sufficient NO_2 present from nitric acid photolysis to react with the available active species of chlorine to form ClONO_2 .

The ozone columns derived from the heterodyne spectra show a typical mid-latitude value of 1.01×10^{19} molec cm^{-2} on the 20th March with a steep reduction to 0.67×10^{19} molec cm^{-2} on 22nd March. The end of the measurement period shows partial recovery to the expected typical ozone column value. There is good agreement in the trends between data from both sites where NPL instruments were deployed.

IV ADDITIONAL NPL WORK TO SUPPLEMENT MILESTONES

In order to maximise the chance of obtaining suitable TDLs for measuring ClONO_2 , and HNO_3 other sources of lasers were also investigated. This required additional resources from internal NPL funding. Three lasers were purchased from Laser Photonics (Analytics Division) Inc. These were supplied on a long lead time due to technical difficulties in the production process. Their characteristics are discussed below.

Laser #5104-01

Laser #5104-01 had output energy at 780.2 cm^{-1} using an operating temperature of 88.3 K and an injection current of 0.4892 A. This was therefore housed in a Laser Photonics liquid nitrogen dewar which could reach a base temperature of 83 K without pumping of the liquid nitrogen reservoir. Under the optimum conditions laser #5104-01 gave 130 μW of power. However, analysis of the radiation passed through a 1 cm^{-1} resolution monochromator revealed five contributing laser modes. These modes are illustrated in Figure 12.

By removing the helium closed-cycle coldhead from the heterodyne spectrometer it was possible to incorporate the dewar system onto the NPL optical breadboard. Blackbody-TDL heterodyne lasers confirmed that mode competition noise made diode #5104-01 unsuitable for atmospheric measurements. This was despite the fact that the target wavelength could be reached at liquid nitrogen temperatures.

Laser #3354-01

Laser #3354-01 was found to have single mode emission 780.2 cm^{-1} at a temperature of 82.2 K. The current scan range for the ClONO_2 region was from 0.2808A to 0.2966A. Figure 13 gives the C_2H_2 calibration spectrum together with the étalon trace to confirm single mode behaviour. This diode was operated in the helium closed-cycle cooler.

Heterodyne tests with a blackbody gave a SNR of 79 with 24 μW of laser power. In dry mid-latitude winter conditions the solar heterodyne signal at 780 cm^{-1} was found to be a factor of 2.5 greater than the blackbody signal. Consequently this has yielded an increase in the SNR when recording solar spectra. Diode #3354-01 was therefore the most suitable TDL to date to record atmospheric spectra of ClONO_2 . Figure 14

shows a typical atmospheric spectrum recorded on 27th June 1995 and highlights the suitability of this laser for atmospheric measurements. Coaddition of spectra would be expected to further enhance the SNR obtained.

It should be noted that TDL #3354-01 had the correct single mode output well above its threshold current. This had the advantage that the power level increased by only about 1 μW over the total current scan range required for ClONO_2 measurements. However, the disadvantage is that the high injection current necessary for this Laser Photonics diode could have caused some device failure. This is probably the reason for the laser malfunction which occurred in Summer 1995.

Laser #4013-15

Recently, a laser from Laser Photonics (#4013-15) was found to have single-mode coverage over one of the nitric acid manifolds between 868 and 869 cm^{-1} of the 5_0^1 band (see Figure 15). This device was again originally intended to operate at above liquid nitrogen temperatures, but it was not possible to reach the target wavenumber without further cooling.

TDL #4013-15 was operated in the coldhead with 34 μW of power incident on the photomixer. Under the above conditions a SNR of 99 was achieved in the heterodyne mode at constant laser current using the blackbody.

Figure 16 shows a typical scan in current with a simultaneous blackbody heterodyne spectrum and homodyne OCS calibration spectrum. The power level remained approximately constant throughout the scan range since the start current of 180.6 mA was well above the threshold current. In the 868 cm^{-1} spectral region the solar heterodyne signal was three times greater than that obtained with the blackbody. The SNR performance of laser #4013-15 was, therefore, more than adequate for recording atmospheric spectra of HNO_3 with a single short scan. Figure 17 shows this with a typical atmospheric heterodyne spectrum of HNO_3 together with the simultaneous calibration. The data was recorded on 4th April 1996 and completes the list of target species originally identified for measurement. A larger dataset of stratospheric HNO_3 scans will be acquired in the future if funding is available.

There are also other technical deviations from the original milestones that have been agreed by the consortium partners. These have entailed extra expenditure by NPL to develop a photomixer-preamplifier combination, optical breadboard and solar tracker which are capable of being deployed in the field. Finally the purchase of a low noise temperature and current controller suitable for the control of the lasers has also been required.

V CONCLUSIONS

The main conclusions of this project are summarised below:

- A spectral linewidth reduction has been demonstrated for the first time in a liquid-nitrogen cooled TDL at 9.4 μm using an external feedback cavity.
- The IPM dewar package requires further optimisation before it can be

integrated into a practical and compact field instrument.

- It has proved technically difficult at the IPM to produce lasers at the target wavelengths that operate at above liquid nitrogen temperatures.
- Although it has been possible for the IPM to produce a single mode laser to measure ClONO₂, the power needs to be increased and the rf excess noise needs to be reduced to be applicable to laser heterodyne spectroscopy.
- Any further work on diode laser development should aim to relax the liquid nitrogen temperature diode operation restriction in favour of higher powers, single mode, low rf noise operations.
- NPL has successfully developed a photomixer-preamplifier combination together with the instrument control electronics.
- A solar tracker for field measurements has also been developed and integrated into an NPL TDLHS optical module.
- A portable heterodyne instrument has been developed at NPL which has recorded spectra of stratospheric ClONO₂ and O₃ during SESAME Phase III.
- New software has been developed to convert measured atmospheric heterodyne spectra into total vertical columns.
- Stratospheric measurements recorded during SESAME have revealed a low ozone episode during March 1995.
- Trends in stratospheric ClONO₂ and O₃ column concentrations have been obtained to complement measurements carried out using an FTIR spectrometer.
- A diode has recently been employed to measure stratospheric HNO₃, thereby making it possible to measure all the target species originally proposed.

VI PUBLICATIONS

1. Developments of mid-infrared diode lasers for ground based atmospheric measurements. M Tacke, A Lambrecht, M Simpfendorfer, C Thiebaux, D Courtois, A Dalahaigue, P T Woods, N A Martin. International Conference on tunable diode laser spectroscopy. 9-11 July 1995. Moscow, Russia.
2. Ground-based stratospheric trace gas measurements by tunable diode laser heterodyne spectrometry in the mid-infrared. C Thiebaux, D Courtois, A Delahaigue, M Tacke, A Lambrecht, M Simpfendorfer, N A Martin, P T Woods. Third European Symposium on Stratospheric Ozone Research, 18-22 September 1995, Schliersee, Germany.
3. Ground-based measurements of stratospheric trace gases by tunable diode laser heterodyne spectrometry. N A Martin, T P Allott, P A Noyce, N R W Swann, P T Woods, Third European Symposium on Stratospheric Ozone

Research, 18-22 September 1995, Schliersee, Germany.

VII ACKNOWLEDGEMENTS

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Figure 16: Blackbody Heterodyne Spectrum near P-branch manifold of HNO_3 together with OCS calibration.

Figure 17: Atmospheric Heterodyne Spectrum of HNO_3 using Laser #4013-15.

Figure 1: TDLHS Electronics

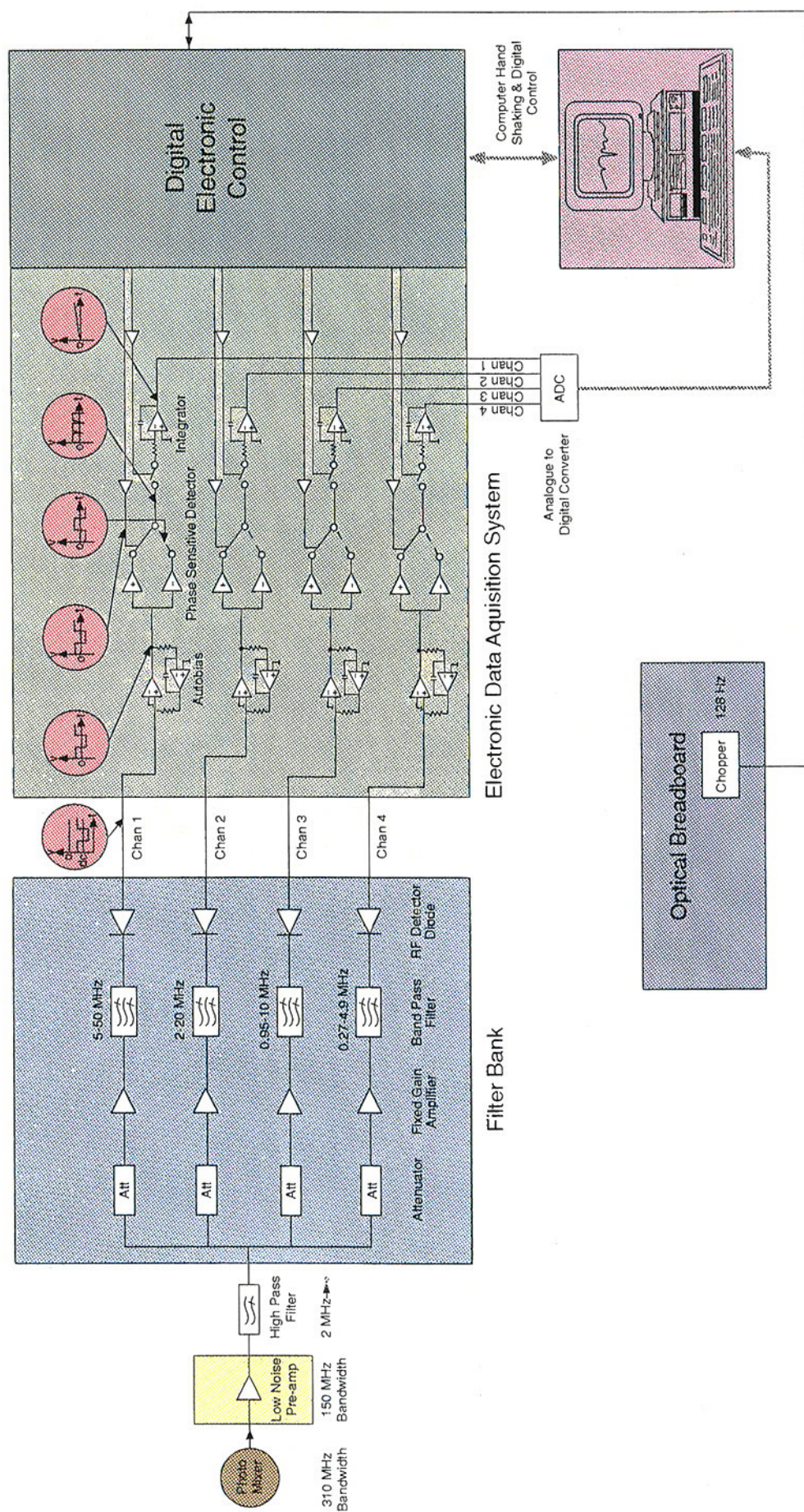


Figure 2: CO₂/TDL Heterodyne linewidth measurement
with and without external feedback.

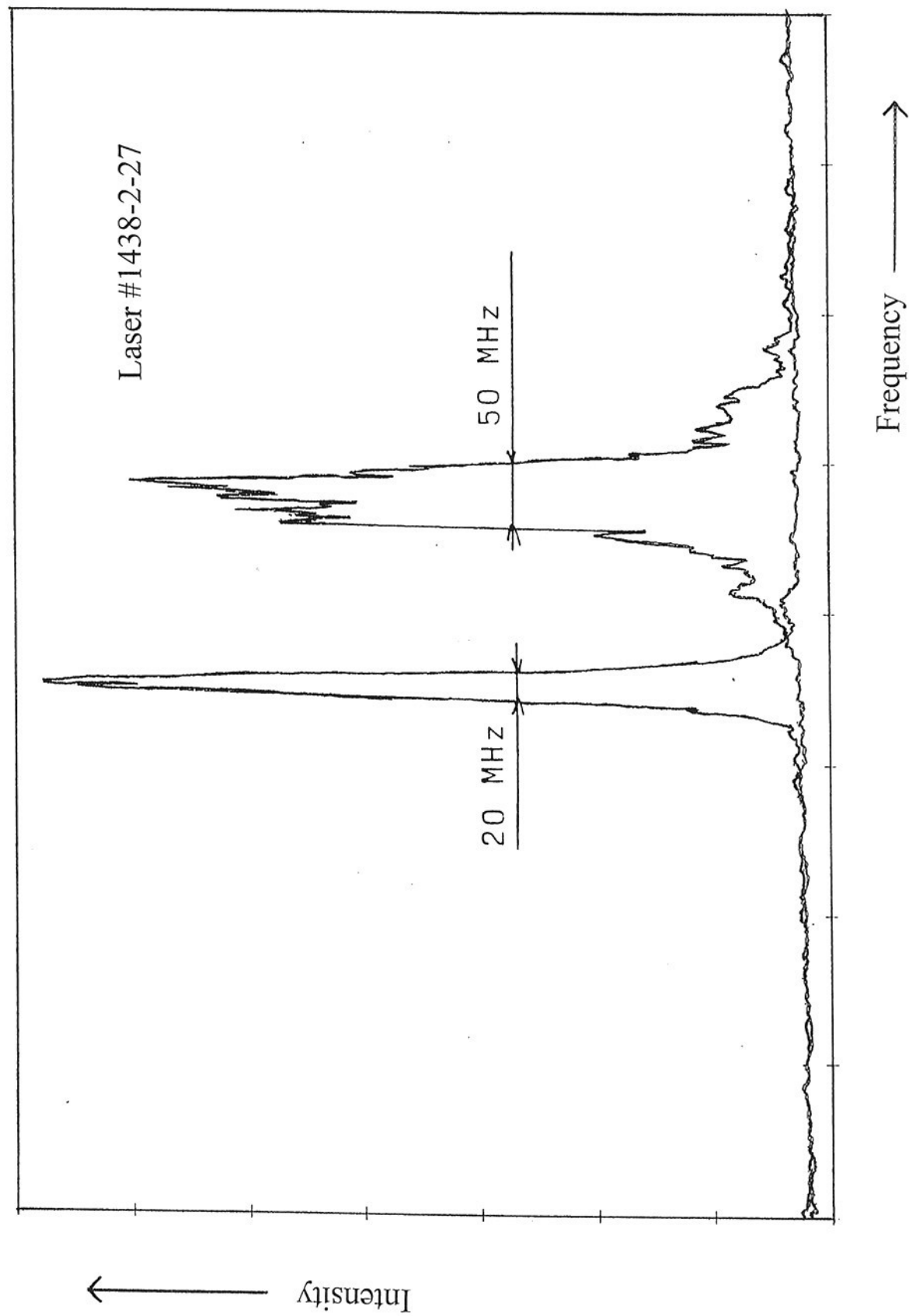
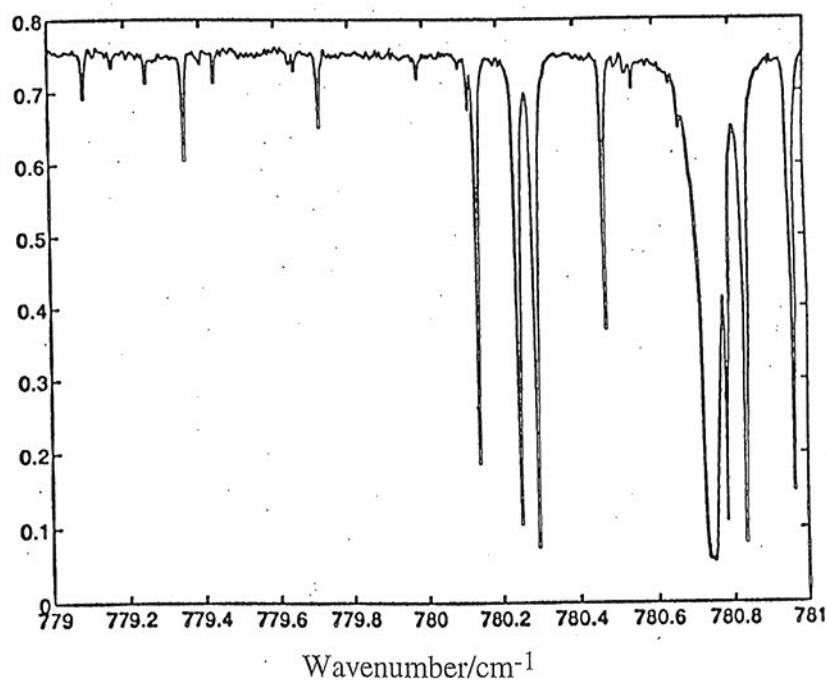
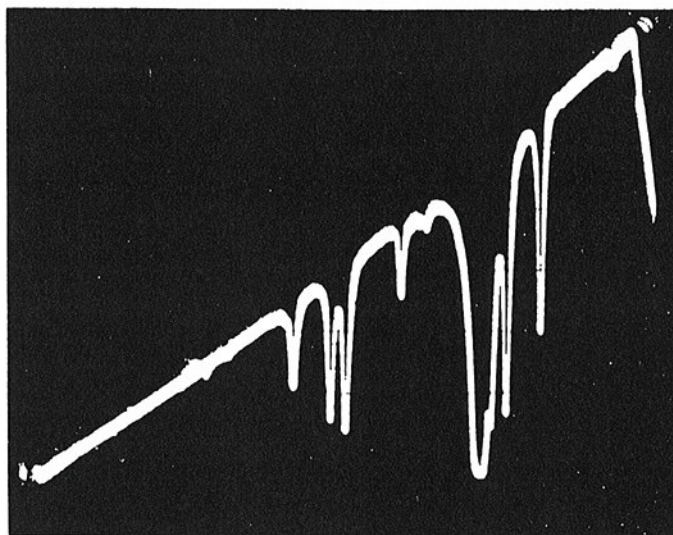


Figure 3: Calibration Results for Laser #L-287-5a-5
FTIR Spectrum of Acetylene



Diode Laser Absorption Spectrum of Acetylene (Direct Detection)

Laser #L-287-5a-5
T=79.3K



One inch Ge étalon calibration trace

f_{sr}=0.048 cm⁻¹

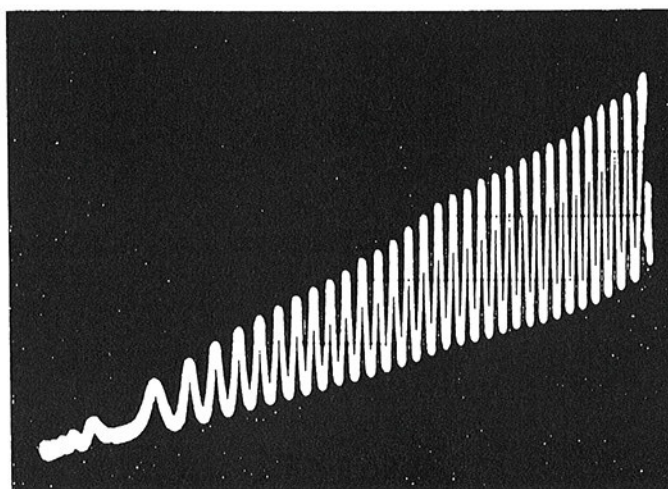
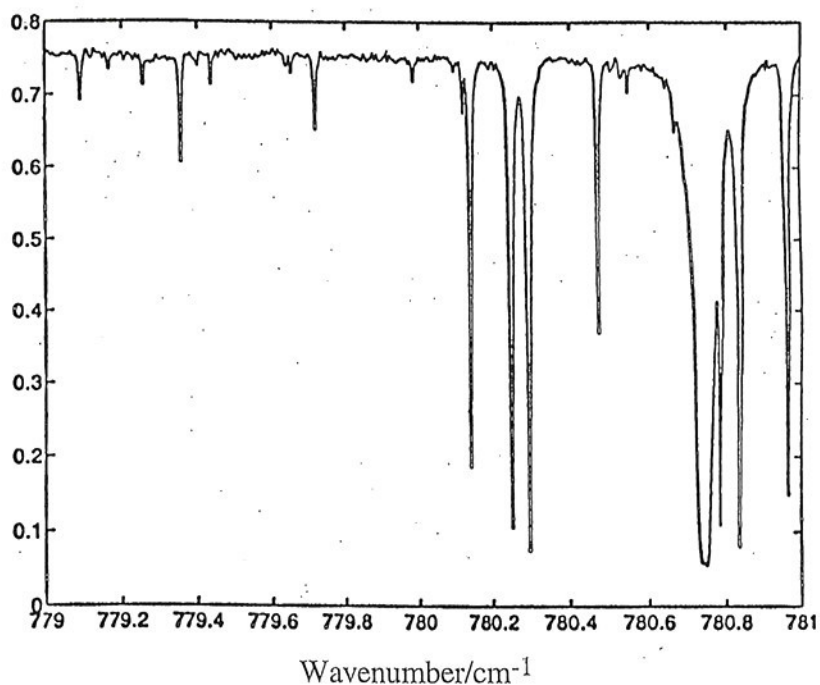


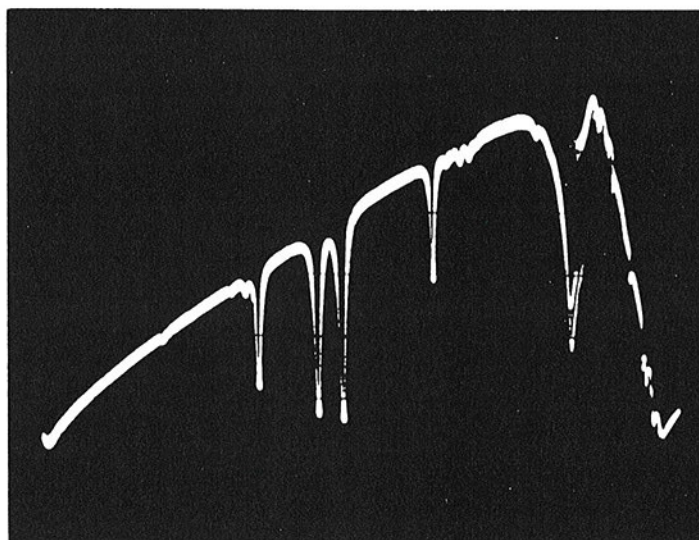
Figure 4: Calibration Results for Laser #120-61-12

FTIR Spectrum of Acetylene



Diode Laser Absorption Spectrum of Acetylene (Direct Detection)

Laser #120-61-12
T=51.75K



One inch Ge étalon calibration trace

f_{sr}=0.048 cm⁻¹

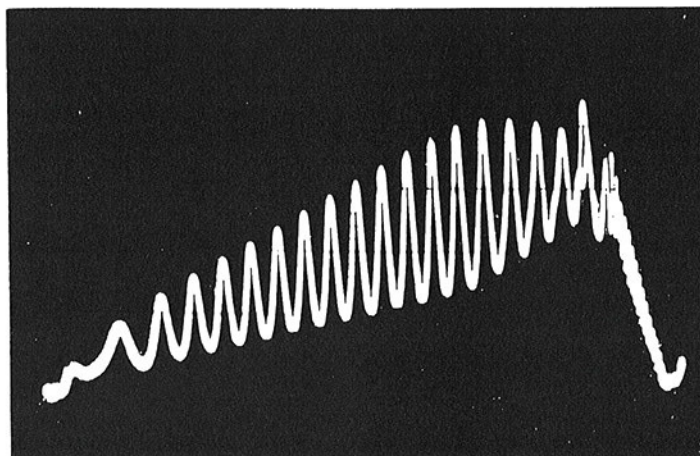
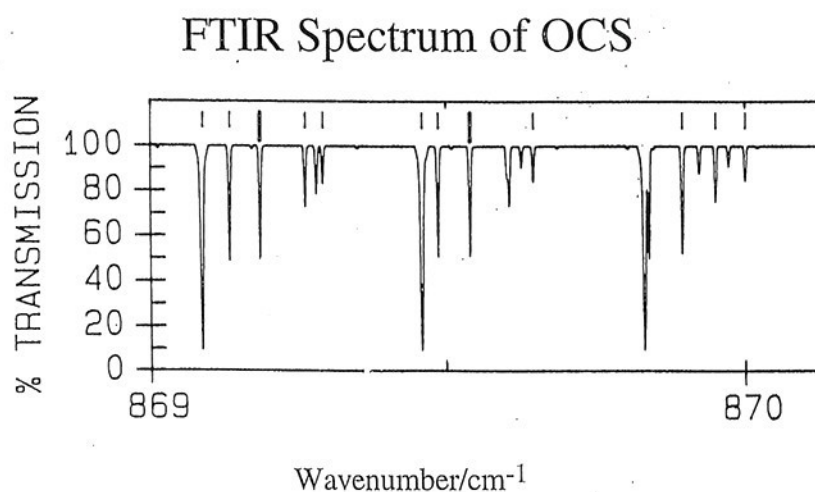
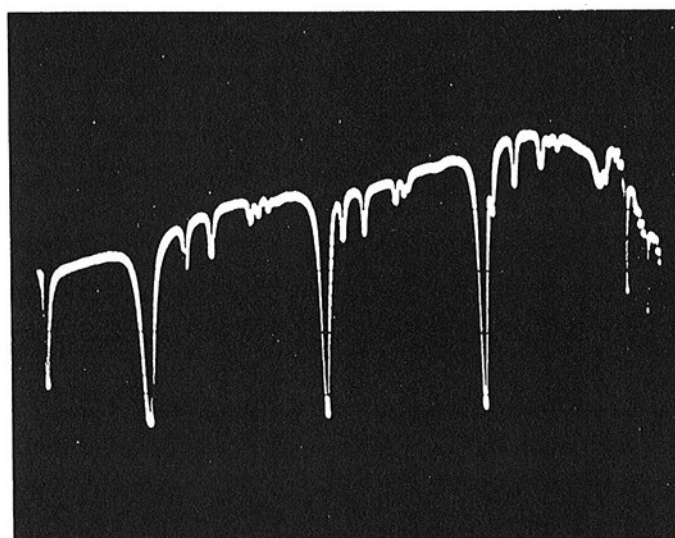


Figure 5: Calibration Results for Laser #210-7-1



Diode Laser Absorption Spectrum of OCS (Direct Detection)

Laser #210-7-1
T=52.77K



One inch Ge étalon calibration trace

f_{sr}=0.048 cm⁻¹

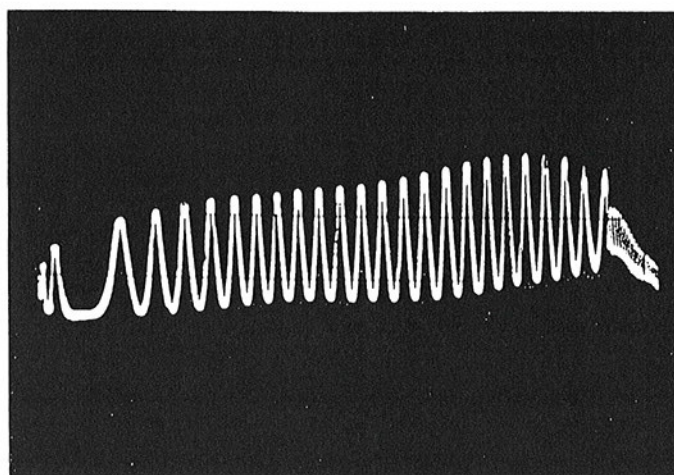
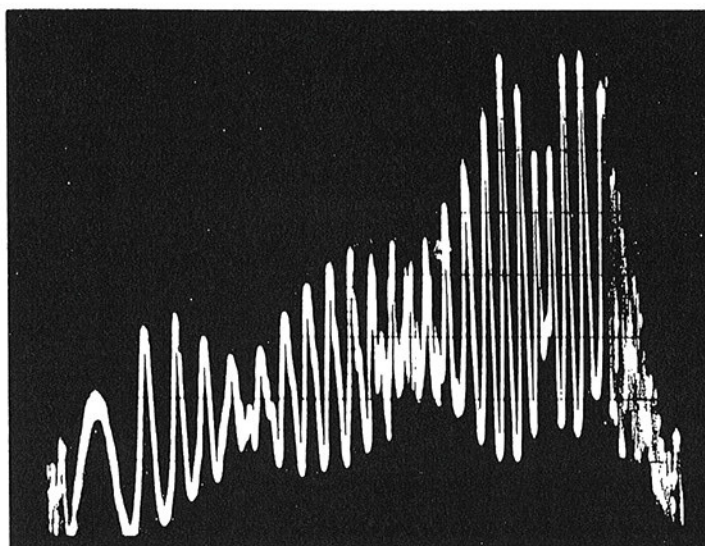


Figure 6: Calibration Results for Laser #1603-1-3

One inch Ge étalon calibration trace



$\text{fsr}=0.048 \text{ cm}^{-1}$
 $T=78.74\text{K}$

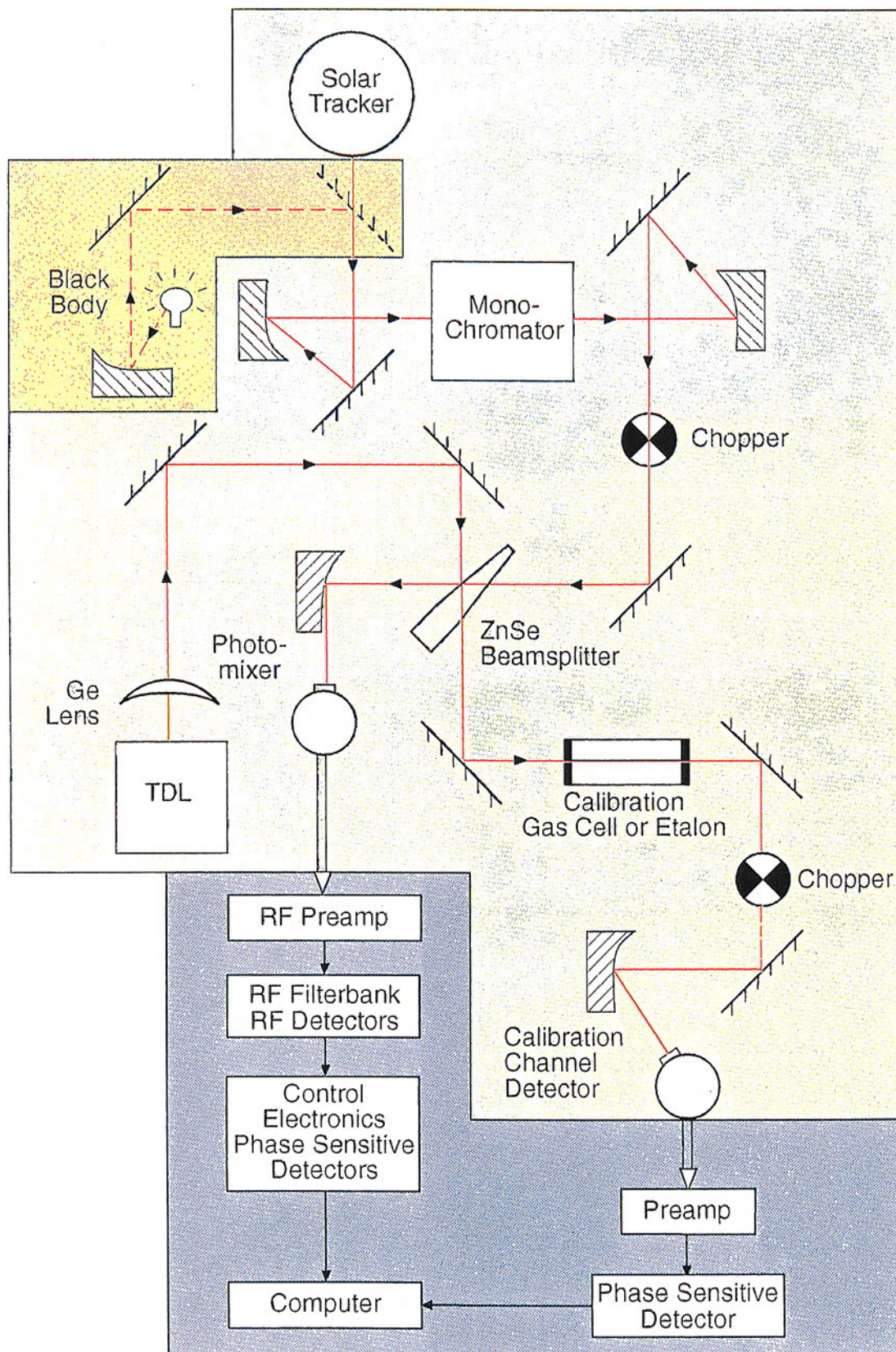


Figure 7: Schematic Diagram Of Tunable Diode Laser Heterodyne Spectrometer

Figure 8: Schematic Diagram of Solar Tracker

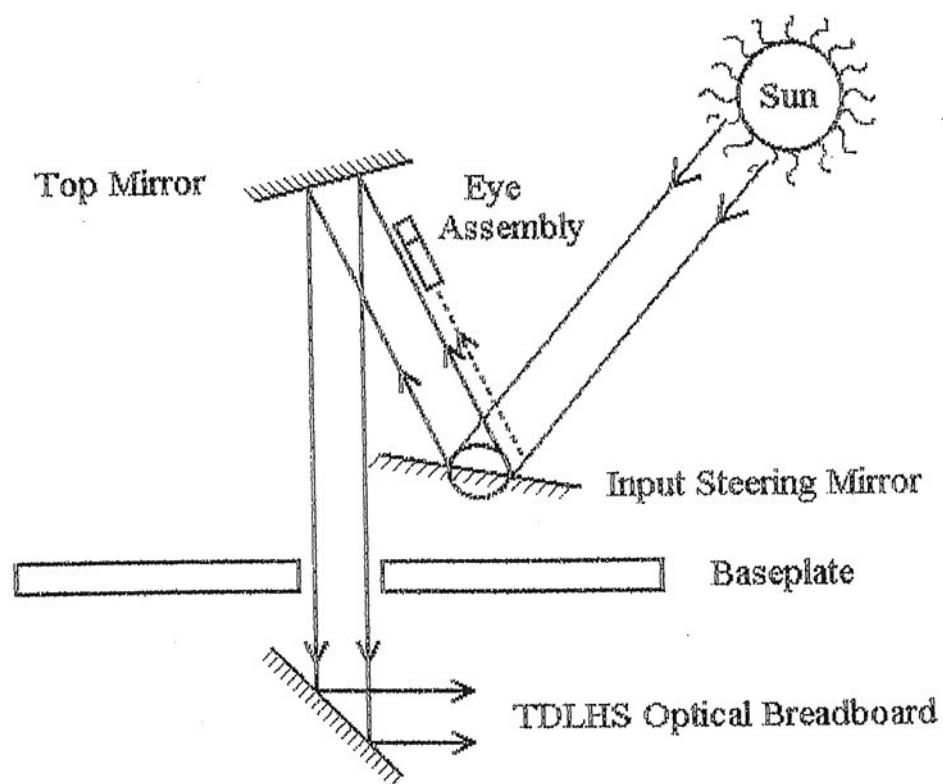


Figure 9(a): Current Heterodyne Scan Of TDL#120-61-12,
C₂H₂ Cell In Black Body Channel

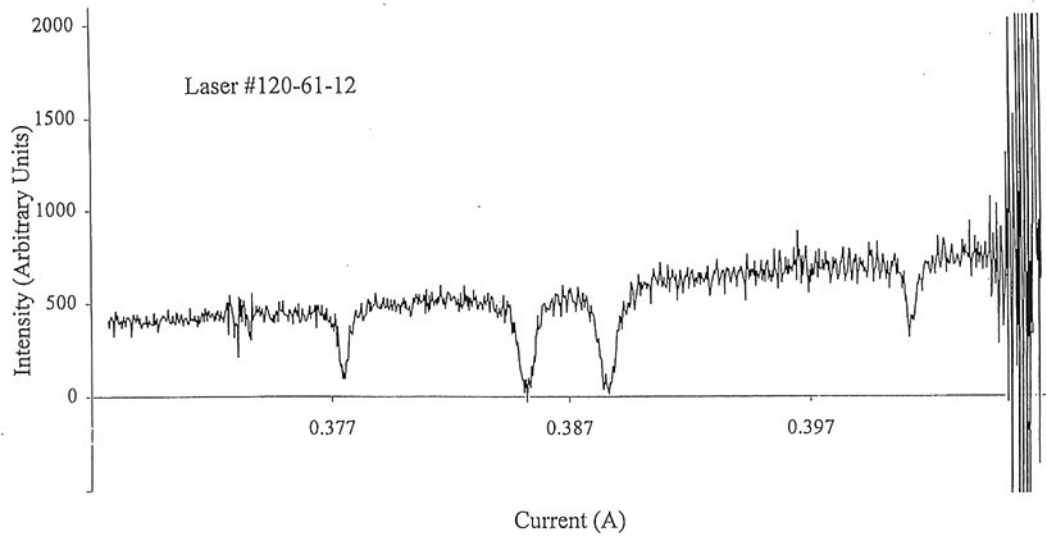


Figure 9(b): Atmospheric Solar Heterodyne Spectrum
Showing ClONO₂ Region

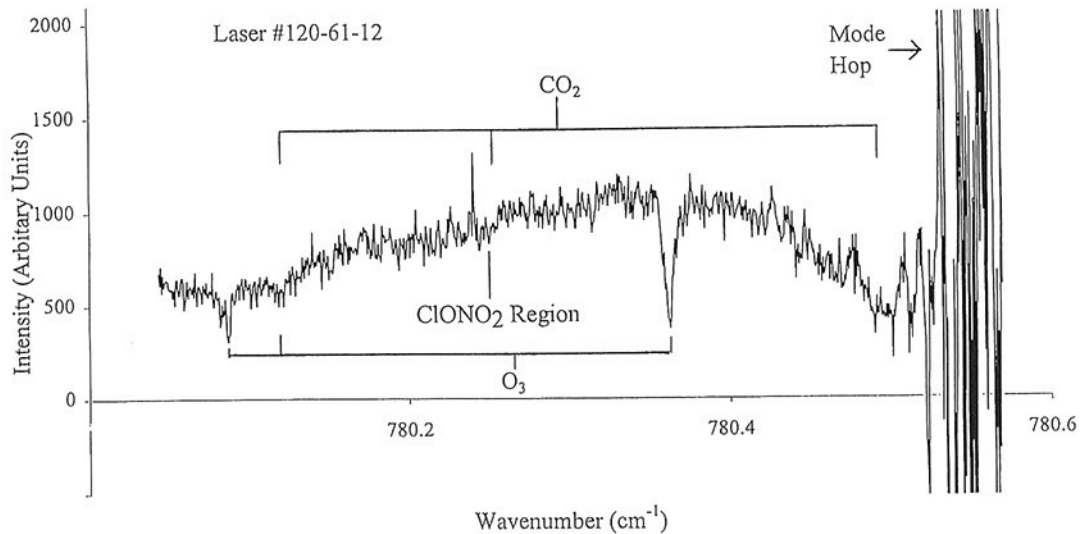


Figure 9(c): Atmospheric Heterodyne Spectrum With Noise
Levels Recorded As Various Beams Are Blocked

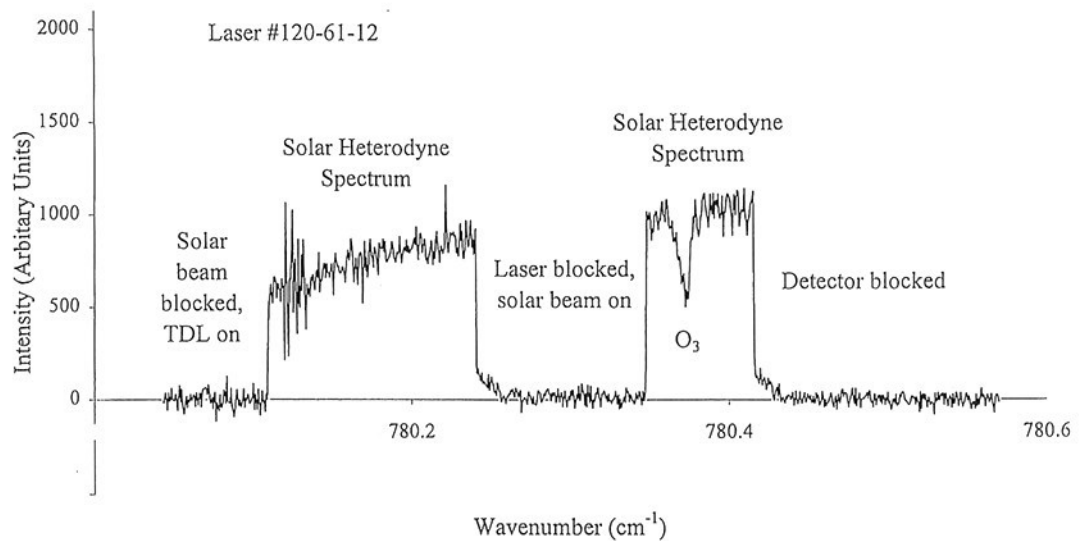
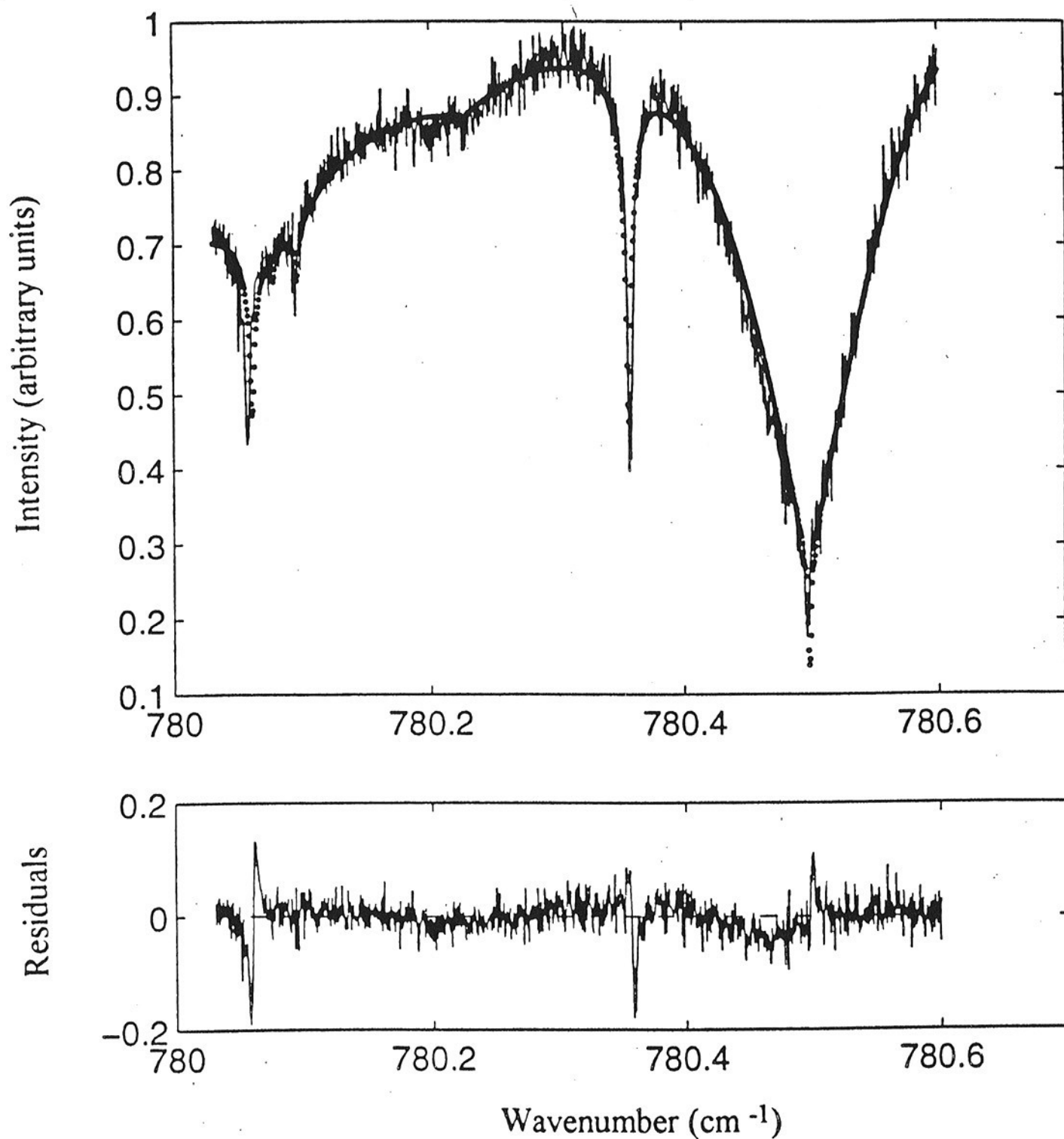


Figure 10: TDLHS Atmospheric Spectrum In The Region Of The Q-Branch Of Chlorine Nitrate At 780.2cm^{-1} (TDL Operating Temperature Of 79K)

Laser #L-287-5a-5



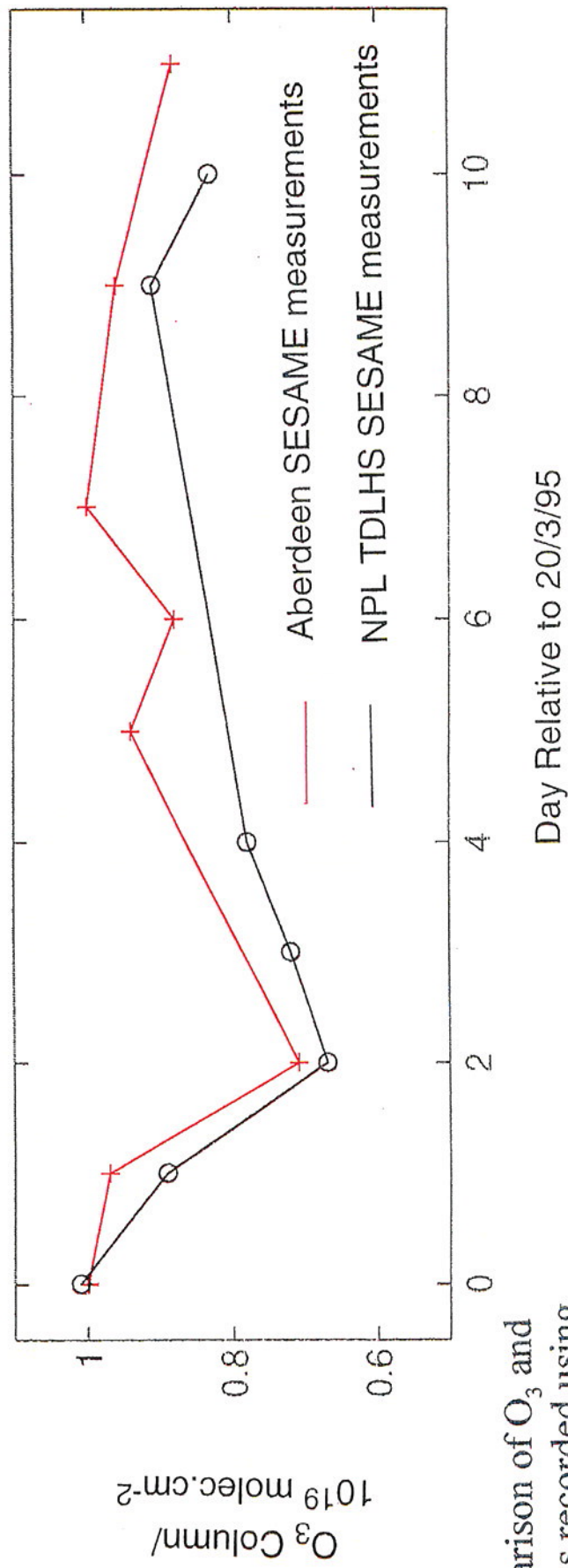
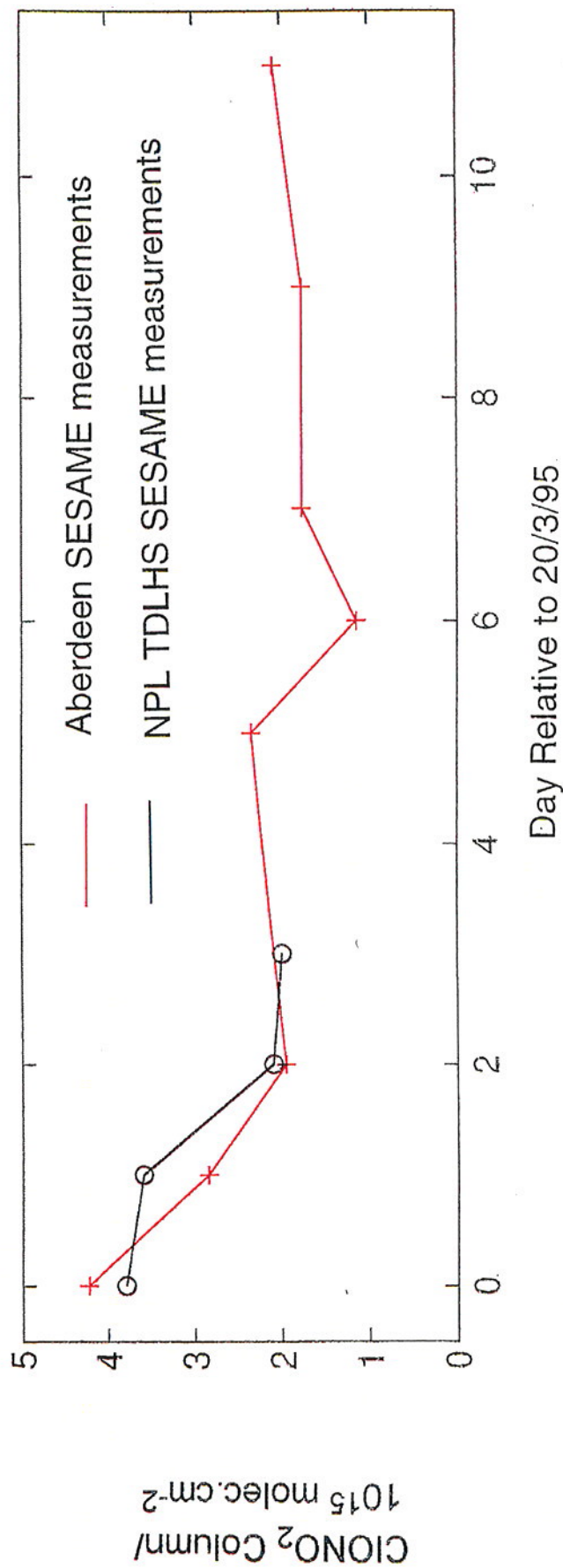
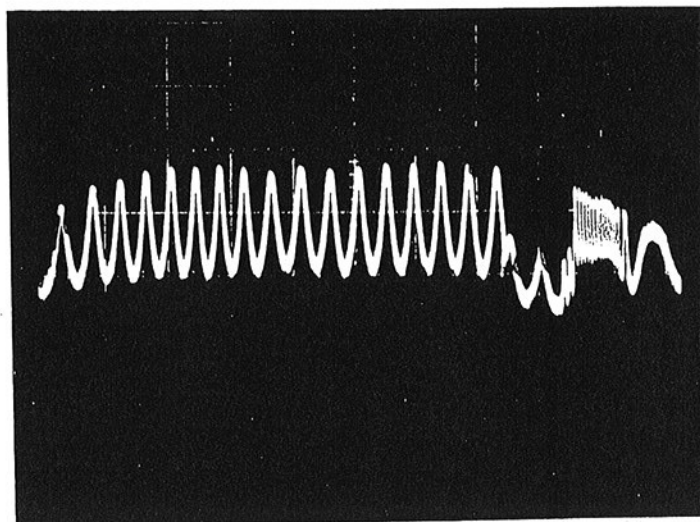
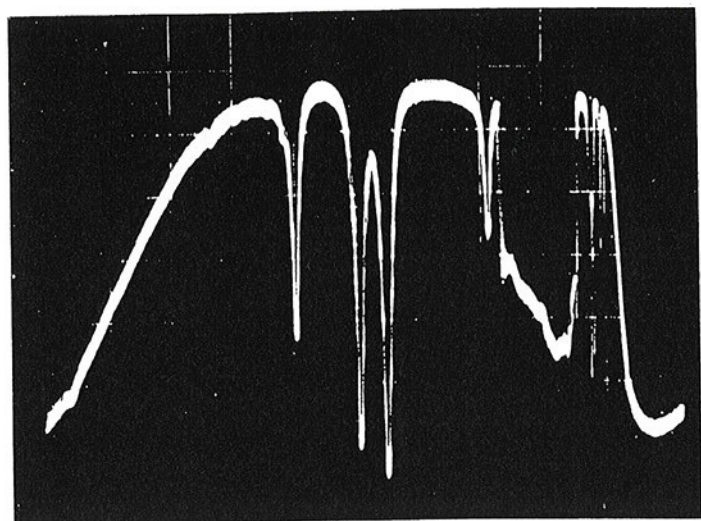


Figure 11: Comparison of O₃ and ClONO₂ columns recorded using TDLHS and FT spectrometer over late March 1995

Figure 12: Calibration Results for Laser #5104-01
Diode Laser Absorption Spectrum of Acetylene (Direct Detection) And
One Inch Ge Étalon Calibration Trace



Laser #5104-01

T=88.29K

fsr=0.048 cm⁻¹

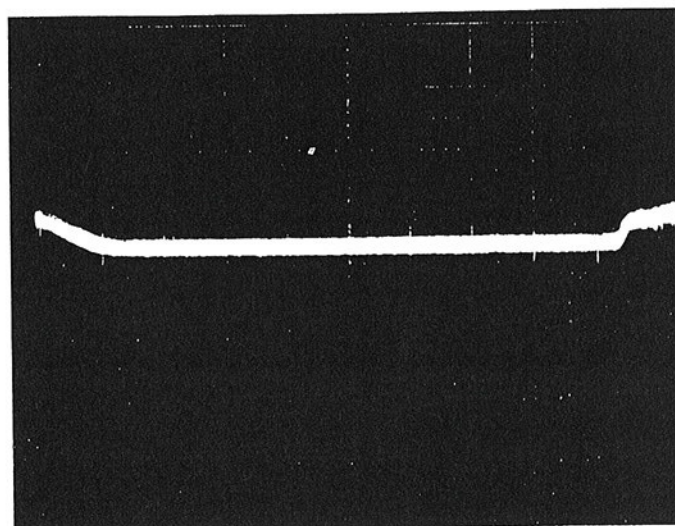
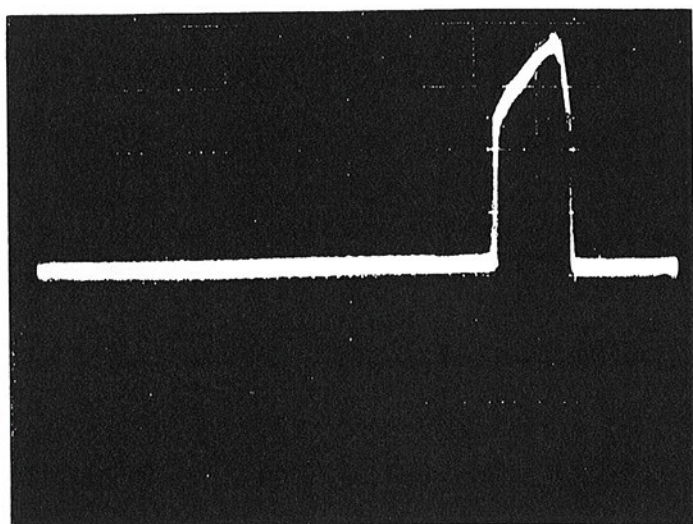
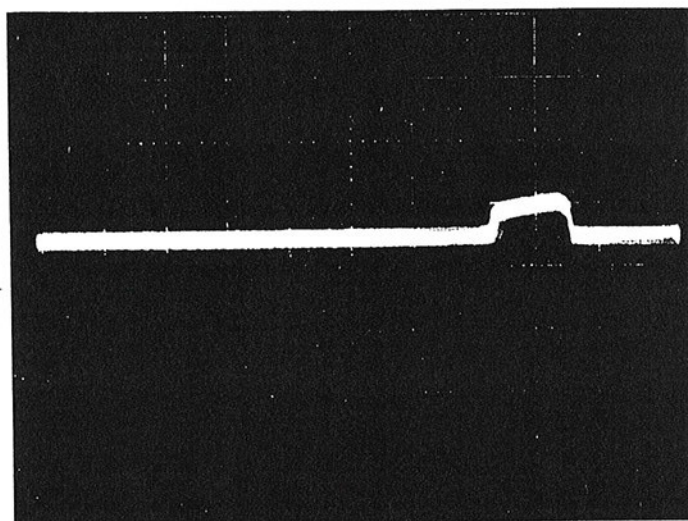
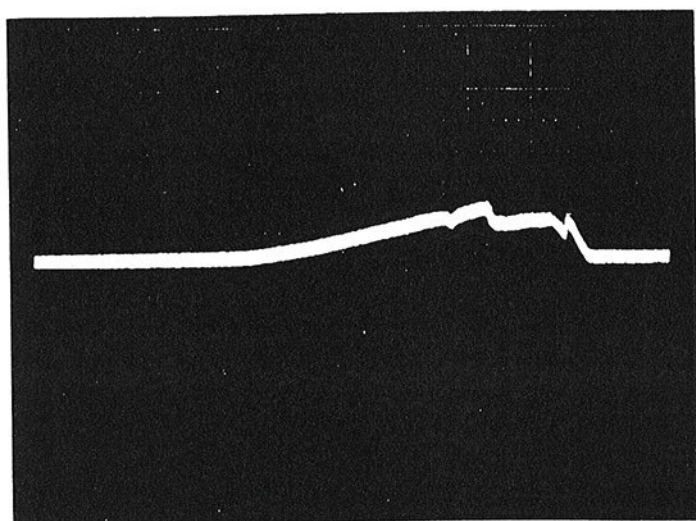
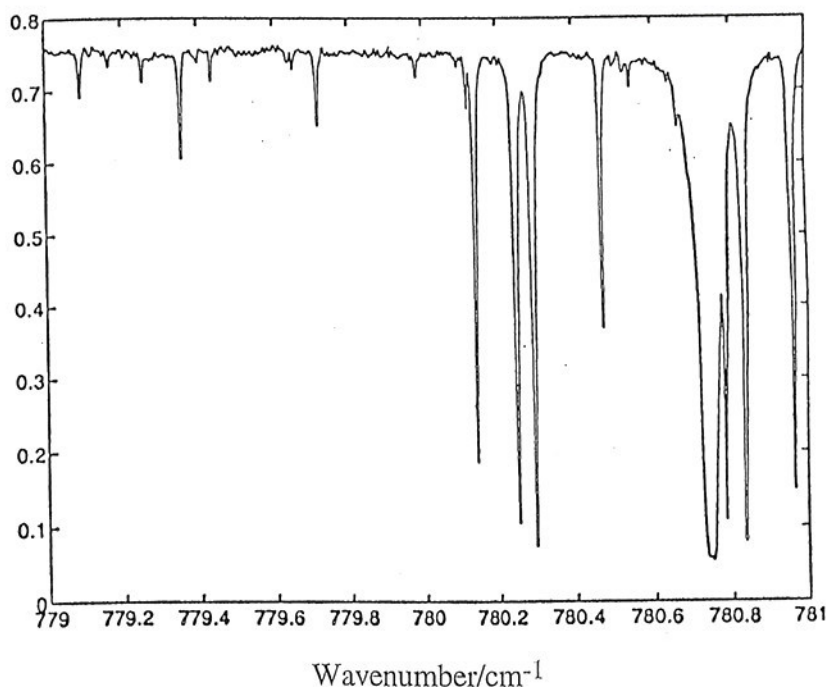


Figure 13: Calibration Results for Laser #3354-01
FTIR Spectrum of Acetylene



Diode Laser Absorption Spectrum of Acetylene (Direct Detection)

Laser #3354-01
T=82.23K



One inch Ge étalon calibration trace

f_{sr}=0.048 cm⁻¹

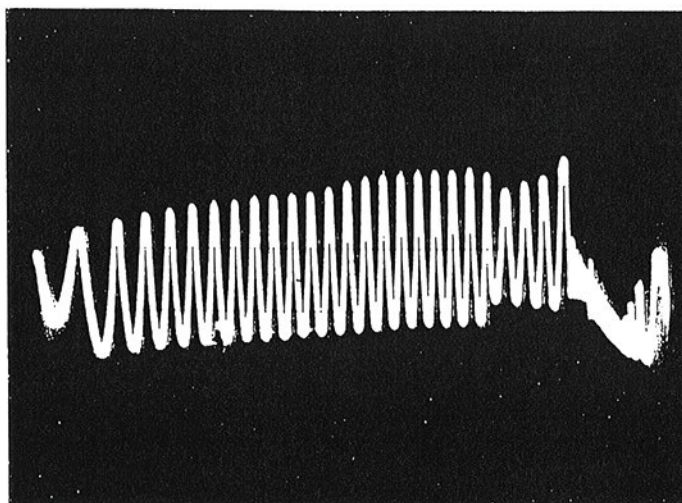


Figure 14: Atmospheric Heterodyne Spectrum
Near Chlorine Nitrate Region

Laser #3354-01

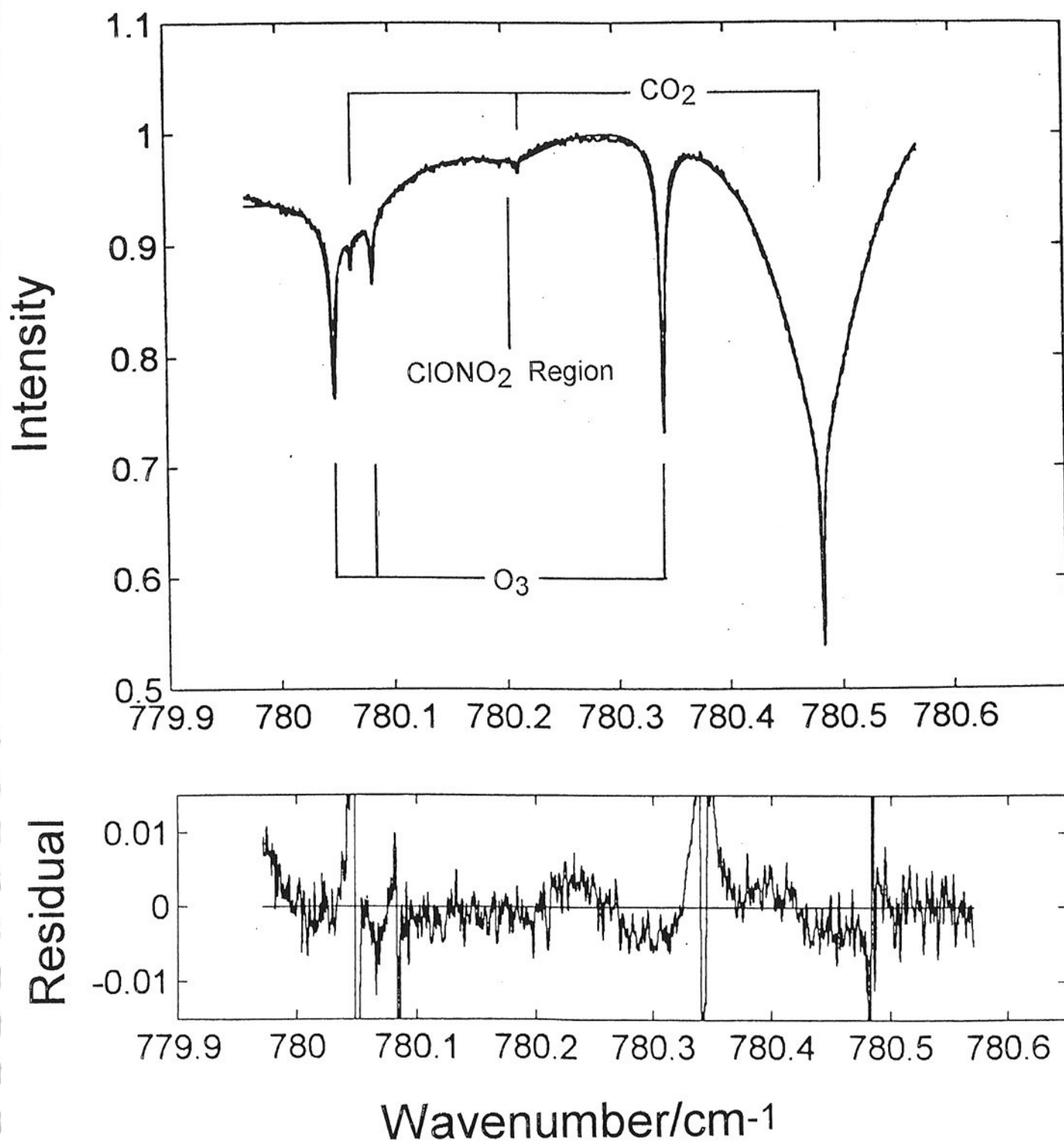
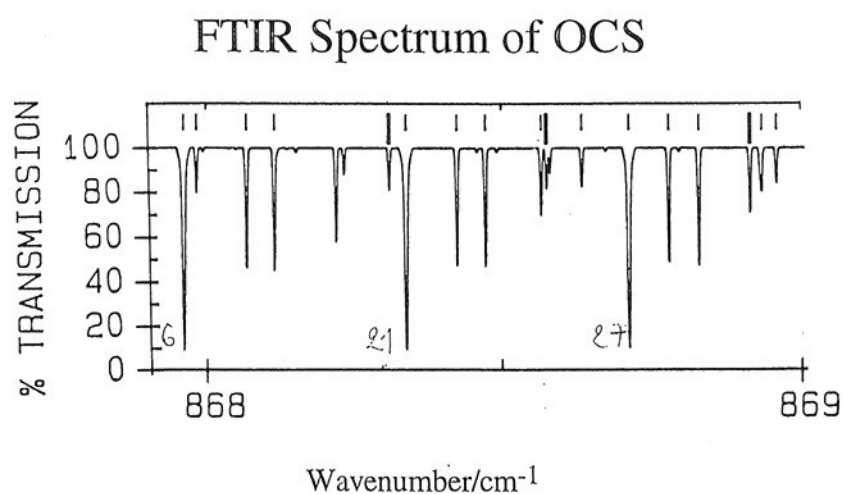
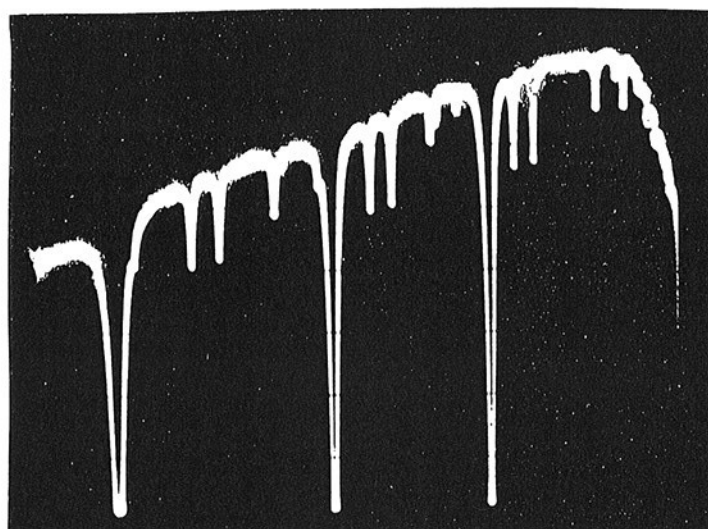


Figure 15: Calibration Results for Laser #4013-15



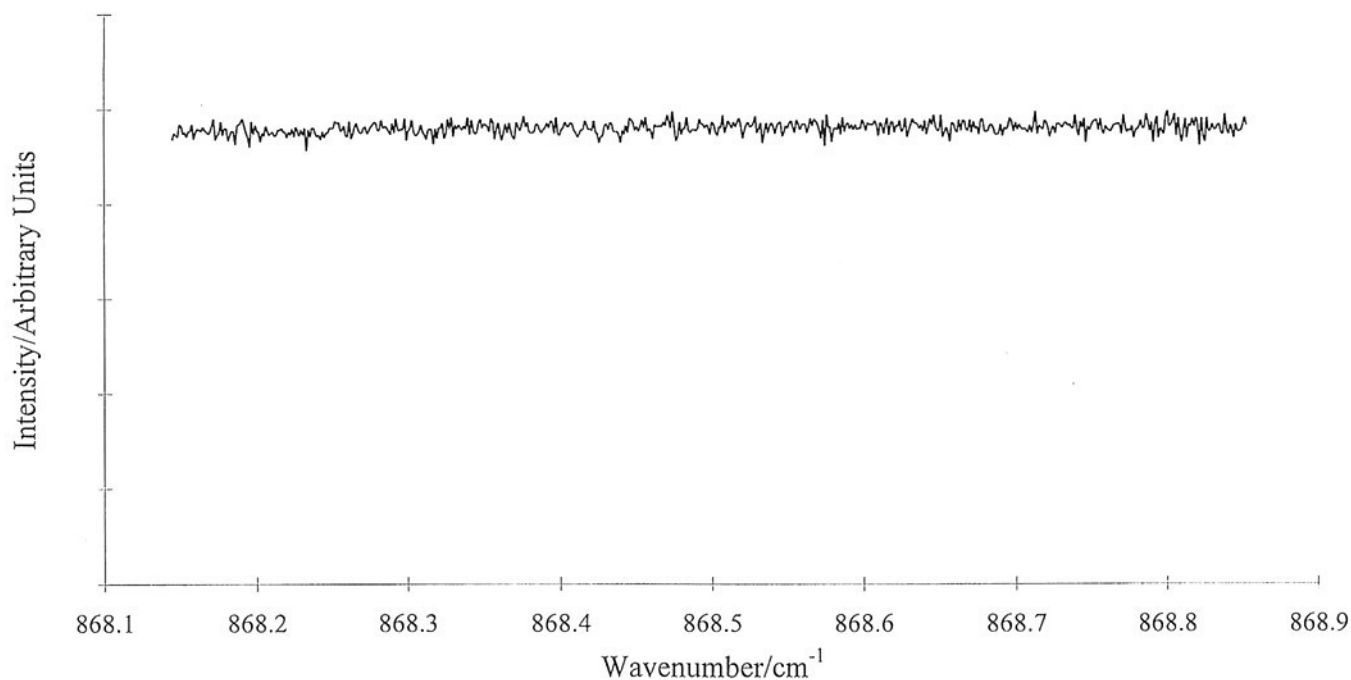
Diode Laser Absorption Spectrum of OCS (Direct Detection)



Laser #4013-15
T=79.5K

Figure 16: Blackbody Heterodyne Spectrum
near P-Branch Manifold of HNO_3 together
with OCS Calibration

Blackbody Heterodyne Spectrum



Simultaneous OCS Calibration Scan

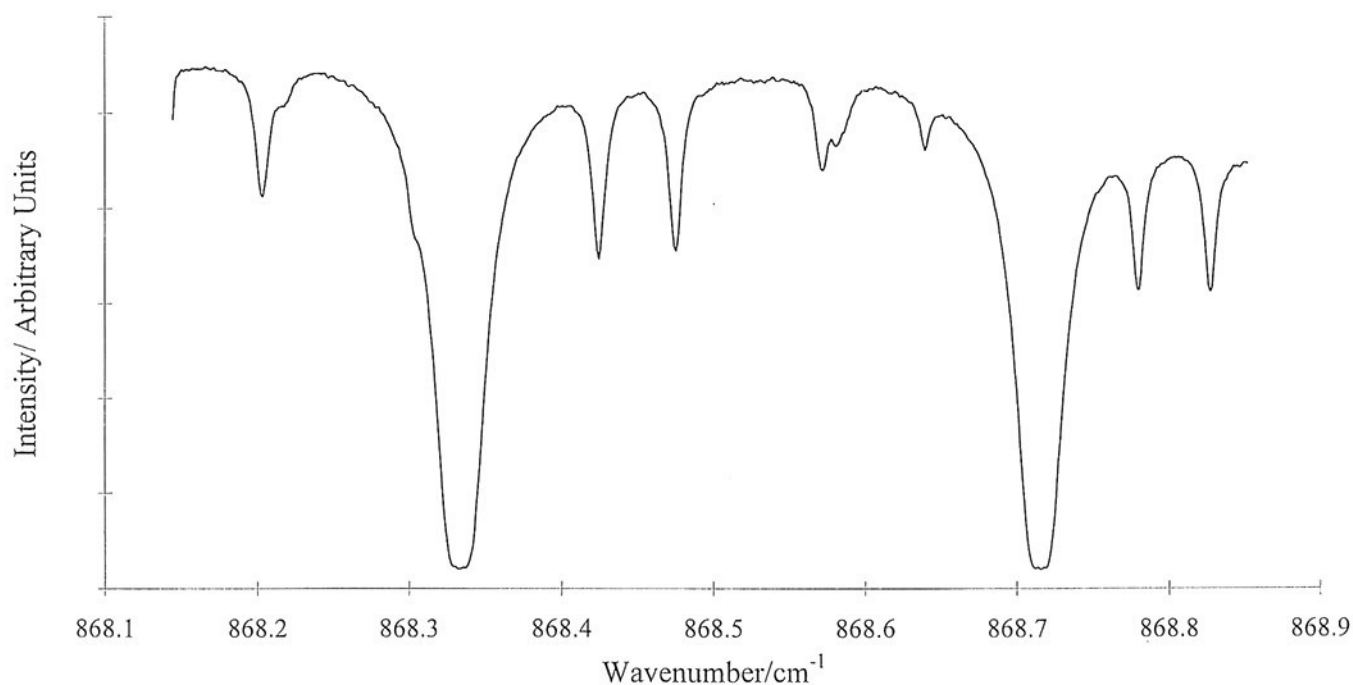


Fig 17: Atmospheric Heterodyne Spectrum
of HNO_3 using Laser #4013-15

