High Sensitivity Laser Absorption Measurements of Broad Band Absorbers in the Near-Infrared Spectral Region

Kevin L. McNesby[Ψ] Richard T. Wainner, Andrzej W. Miziolek, W.M. Jackson[Ω], and Ian A. McLaren[*]

U.S. Army Research Laboratory

Aberdeen Proving Ground, MD 21005-5066

[Ω]*Dept. of Chemistry, University of California-Davis, Davis CA 95616*

[*] *McLaren Research, Mountain View, CA 94043*

[Ψ] author to whom correspondence should be addressed

Abstract

The development and characterization of a diode laser-based sensor to measure the vapor from broad band absorbers in the near-infrared spectral region is described. Data is presented for the detection and measurement of vapor from pyridine, C_5H_5N, using a novel technique based on laser mixing. The discussion focuses upon experimental determination of whether a compound may be classified as a "broad band absorber" and methods used for laser selection, phase sensitive detection, and for data reduction.

Introduction

This paper describes efforts towards the development of a tunable diode laser-based sensor for quantitative measurements of vapor of broadband absorbers in the near-infrared spectral region.

The development of such a sensor is driven by the need for rapid, quantitative measurements of middle distillate fuel vapors (e.g., diesel fuel, JP-8) for detection of fire hazards on board military vehicles. The specific application reported here is for detection of vapor from pyridine (C_5H_5N), but the method is readily applicable to measurement of vapor of any molecule that possesses a spectral envelope which does not show well-resolved rovibrational absorption lines and which has an absorption spectral width greater than the tuning range of available near-infrared tunable diode lasers.

The method of detection employed here uses a laser mixing technique that relies upon absorption of radiation of one of the lasers (near the wavelength of 1.65 micrometers) by pyridine vapor. The near-infrared spectral region is used because of the commercial availability of room temperature lasers and detectors (the wavelength region near 1.65 micrometers is widely used for 2f detection of methane gas) and because laser radiation in this spectral range may be easily transported at low loss using inexpensive optical fibers.

Background

Most gas phase concentration measurements using line-of-sight near-infrared tunable diode laser absorption spectroscopy use wavelength modulation spectroscopy (WMS) techniques [3,4] or balanced ratiometric detection (BRD) [5,6]. Wavelength modulation spectroscopy (WMS) typically employs distributed feedback (DFB) tunable diode lasers. High sensitivity is achieved by phase sensitive detection at frequencies (KHz to MHz) where noise contributions to signal are minimized. Detection is made at twice the modulation frequency, and absorption features have a second derivative lineshape. Measurements are made using a single probe laser beam. Balanced ratiometric detection (BRD) uses a balanced photoreceiver to cancel laser intensity noise. To use this technique, a signal and reference beam are generated by splitting the output beam from a single laser source. It is necessary to balance the DC photocurrent from signal and reference lasers, in the absence of any absorption, prior to making a measurement. This

technique has the advantage of reporting the true absorption lineshape, and may be employed with widely tuneable lasers such as external cavity tunable diode lasers, which are not suitable for use with phase sensitive detection at high modulation frequencies.

Broad Band Absorbers

Both WMS and BRD techniques give good results for gas phase concentration measurements of small molecules with well resolved ro-vibrational absorption lines, such as hydrogen fluoride, methane, carbon monoxide, water, etc [7]. However, large and/or heavy molecules might not posses well resolved ro-vibrational absorption bands because of overlap between fundamental, combination, and/or overtone vibrations, and because of rotational constants which may be less than typical gas phase linewidths [8]. Figure 1 shows the near-infrared gas phase absorption spectrum of pyridine (C_5H_5N) and of methane (CH_4) near a wavelength of 1.65 micrometers measured using a Fourier transform spectrometer. Shown in the inset of Figure 1 is the absorption spectrum of a mixture of pyridine and methane gases (total pressure 13.5 torr, $P_{pyridine}$ = 3 torr, $P_{methane}$ = 10.5 torr, path length = 400 cm-1) measured using wavelength modulation spectroscopy employing 2f detection. Low pressure was used to minimize absorption linewidths. Figure 1 shows attenuation of near infrared radiation by both pyridine and methane near a wavelength of 1.65 micrometers at this pressure. However, the inset to Figure 1 shows that when using wavelength modulation spectroscopy employing 2f detection, only the absorption by methane is detected, even though pyridine and methane have similar gas phase absorption coefficients near a wavelength of 1.65 micrometers (see Table 1). This means that there is minimal change in the absorption of the laser radiation by pyridine vapor during the wavelength scan used to detect and measure methane gas. Relative to the wavelength tuning range used for 2f methane detection, this result demonstrates the criteria that we use to determine if a molecule is a "broad band absorber".

Phase Sensitive Detection

The method used here for detection of pyridine vapor, and vapors of other molecules which may be classified as broad band absorbers, as well as other detection methods based upon phase sensitive detection, takes advantage of the following relations:

$$\int_0^{\pi} m(\sin at)n(\sin bt)\, dt = 0 \qquad a \neq b \tag{1}$$

$$2C \int_0^{\pi} m(\sin at)n(\sin bt)\, dt = Cmn\pi \qquad a=b \tag{2}$$

For the discussion to follow, a and b are laser amplitude modulation frequencies, t is time, m and n are amplitudes, and C represents the number of periods over which the integration is carried out.

If the signal of interest is sinusoidal at frequency a (in equation 1), upon multiplication of this periodic signal by a reference sinusoid at frequency b, the resulting integral will be non-zero only when a=b. If the measurement is made at a frequency at which the Fourier component of the broadband noise in the signal is small, the integral of the product of the signal and the reference will exclude broadband signal noise, and only include the signal noise component at the reference frequency. Furthermore, the result of the integration in (2) yields a value directly proportional to the amplitude of the signal of interest.

Experimental Design

The method used here takes advantage of the power modulation which occurrs when a DFB diode laser is driven by a time varying injection current. For the experiments described here, two

different DFB lasers are driven using a sinusoidally varying injection current. Each laser is modulated at the same frequency but out of phase by 180 degrees [9]. These two lasers are combined to produce the probe beam used for the line-of-sight measurement. When the power output amplitudes of each laser are the same, the combined output of the two lasers will have an amplitude that is (ideally) invariant with time. The key to the method is selection of one laser wavelength coincident with a wavelength absorbed by the gas of interest, and selection of the second laser wavelength in a region where no absorption is anticipated. When the mixed, modulated probe beam is passed through a gas which preferentially absorbs the laser radiation from only one of the lasers, the signal at the detector is modulated at the injection current modulation frequency and, for small absorptions, has an amplitude proportional to the concentration of absorbing gas.

Modulation Design

A time (t) dependent sinusoidal wave, S(a,n,t), at frequency a with amplitude n may be expressed as:

$$S(a,n,t) = n\sin(at) \tag{3}$$

The signal at the detector, in the absence of any absorption, from two combined sinusoidally amplitude modulated lasers differing in phase by 180 degrees is:

$$S1(a,n,t)+S2(a,m,t) = n\sin(at) + m\sin(at+\pi) \tag{4}$$

Using the relationship $-\sin(ax) = \sin(ax + \pi)$, multiplying by a reference sine wave (frequency locked to the laser modulation) and integrating gives:

$$2C \int_0^{\pi} (S1(a,n,t) + S2(a,m,t))p\sin(at)\, dt = Cp\pi(n-m) \tag{5}$$

Here, p is the amplitude of the reference sine wave and C is the number of periods over which the integration is carried out. Equation 5 shows that for a probe beam composed of modulated lasers with equal amplitude, the signal at the detector is zero in the absence of any absorption. When the amplitudes of the modulated lasers differ, then the zero absorption signal must be corrected for offset. When the output radiation of laser two is preferentially absorbed by an analyte gas in the path of the probe beam, equation 5 becomes:

$$2C \int_0^{\pi} (S1(a,n,t) + S2(a,m,t))\,(\exp{-\alpha cl})\,p\sin(at)\,dt = Cp\pi(n-m(\exp(-\alpha cl))) \quad , \qquad (6)$$

Where α is the absorption coefficient of the analyte gas (cm^2/molecule), c is analyte gas concentration (molecules/cm^3), and l is the probe beam path length through the analyte gas (cm). When the product $\alpha cl << 1$, exp($-\alpha cl$) may be rewritten as1-A, (where A is absorbance = (αcl)) so equation 6 may be rewritten:

$$2C \int_0^{\pi} (S1(a,n,t) + S2(a,m,t))\,(\exp{-\alpha cl})\,p\sin(at)\,dt = Cp\pi(n-m + mA) \qquad (7)$$

For component lasers of equal amplitude, equation 7 becomes:

$$2C \int_0^{\pi} (S1(a,n,t) + S2(a,m,t))\,(\exp{-\alpha cl})\,p\sin(at)\,dt = Cp\pi mA \qquad (8)$$

The value of the integral in Equation 8 is directly proportional to the absorbance, A, and hence to the concentration of the analyte gas. Additionally, the value of the integral is directly proportional to the amplitude of the reference sine wave, to the base amplitude of the detector laser signal, and to the number of periods over which the integration is carried out. Figure 2 shows the value of the integral in Equation 8 (calculated signal) for a moderately strong absorbing gas as a function of Absorbance, (A = αcl). The measured signal using the mixed laser method described here is predicted to vary linearly with pressure.

Experimental Apparatus

A diagram of the experimental apparatus is shown in Figure 3. The two DFB laser diodes (Sensors Unlimited) used to produce the mixed wavelength probe beam have nominal wavelengths of 1.307 micrometers and 1.653 micrometers. The laser diodes are driven using an ILX LDC-3900 laser diode controller. The variable phase sinusoidal injection currents are supplied by two SRS Model DS345 function generators operating on a common timebase. The fiber coupled, sinusoidally modulated (100 KHz) laser diode radiation is launched into free space using GRIN-lens tipped single mode fibers (Sentech Corp.). The grin lens-tipped fibers are arranged in a quasi-co-linear, "stop-light" configuration. The near co-linear output beams are directed into a variable pathlength gas cell (Laser Photonics L5210). Radiation exiting the variable path length cell is detected using a New Focus Model 2034 InGaAs large element photodetector. The detector signal is demodulated at the laser injection current modulation frequency using a lock-in amplifier (SRS 844), displayed on an oscilloscope (LeCroy 7200), and recorded on a laptop computer (Dell Latitude) running LabView software (National Instruments). Pyridine (99%) and methane (UHP) were supplied by EM Science and Matheson, respectively, and were used without any further purification. Near infrared survey spectra were recorded using a Bomem DA-8 spectrometer using a liquid nitrogen-cooled InSb detector.

Results

Figure 4 shows the vapor phase absorption spectrum of pyridine between wavelength values of 1.3 and 1.75 micrometers. Also shown in Figure 4 are the spectral positions of the two lasers used to make the mixed wavelength probe beam. The absorption coefficient for pyridine vapor at a wavelength of 1.653 micrometers was measured for this work. Table 1 shows that the absorption coefficient for pyridine vapor at this wavelength is similar in magnitude to that for

methane. As shown in Figure 4, the laser used for pyridine detection emits radiation that is not in the most intense region of the pyridine absorption band.

Figure 5 shows the demodulated mixed laser signal for pyridine vapor versus pressure, measured using a 400 cm path length. Each data point represents the average of 100 measurements of output from the lock-in amplifier, using a time constant of 10 milliseconds, laser modulation at 100 KHz. The measured signal is seen to be approximately linear with respect to changes in pressure, as predicted by Equation 8. For the sensor system described here, we estimate the limit of detection for pyridine vapor in air, measured at a wavelength of 1.653 micrometers, to be approximately 200 ppm-meter. For measurements in which the on-resonance laser wavelength was coincident with the center of the pyridine absorption band, the sensitivity would be increased.

Discussion

The main purpose of these experiments was to demonstrate the feasibility of the mixed laser technique for concentration measurements of vapor phase molecules which cannot be measured using conventional wavelength modulation spectroscopy. During the course of the design and implementation of the method, criteria were developed to maximize sensitivity, and several improvements were considered for future experiments using the technique.

For the mixed laser technique, the most important element for high sensitivity is the minimization of the amplitude of the unattenuated mixed laser probe beam. We discovered during the course of these experiments that our laser amplitudes did not vary directly with injection current, so a Fourier analysis of the signal at the detector for each individual laser contained components at frequencies other than the frequency of the variation of the injection current. These other frequency components made it impossible for us to get an unattenuated mixed laser power signal that was devoid of any AC component. Minimization of this unwanted AC component of the unattenuated mixed laser power signal is an important factor affecting sensitivity.

The first improvement to the apparatus for the next set of experiments will be to fiber mix the lasers prior to launch into the gas cell. Because our two lasers were not truly co-linear, we noticed some beam walk problems when going through the long pass cell. These beam walk problems necessitated the use of the large element photodetector. Further experiments are planned using the next iteration of the technique for detection of middle distillate fuel vapors.

This work was supported by the Next Generation Fire Suppression Technology Program (NGP), administered by the Strategic Environmental Research and Development Program (SERDP). The authors would like to thank Lawrence Ash of the Naval Air Systems Command for his assistance in development of the sensor apparatus.

Bibliography

[I] Linnerud, P. Kaspersen, and T. Jaeger, "Gas monitoring in the process industry using diode laser spectroscopy", Applied Physics B, Vol. 67, pp. 297-305, (1998).

[2] L.S. Rothman, R.R. Gamache, R.H. Tipping, C.P. Rinsland, M.A.H. Smith, D. Chris, V. Benner, M. Devi, J.-M Flaud, C. Camy-Peyret, A. Perrin, A. Goldman, S.T. Massie, L.R. Brown, R.A. Toth, "The Hitran Molecular Database: Editions of 1991 and 1992", J. Quant. Spectrosc. Radiat. Transfer, Vol. 48, p. 469, (1992).

[3] J. Reid and D. Labrie, "Second-Harmonic Detection with Tunable Diode Lasers - Comparison of Experiment and Theory", Appl. Physics, B 26, pp. 203-210, (1981).

[4] J.A. Silver, Appl. Opt., Vol. 31, p. 707, (1992).

[5] D.M. Sonnenfroh, W.J. Kessler, J.C. Magill, B.L. Upschulte, M.G. Allen, J.D.W. Barrick, "In-situ sensing of tropospheric water vapor using an airborne near-IR diode laser hygrometer", Appl. Phys. B, Vol. 67, pp. 275-282, (1998).

[6] P.C.D. Hobbs, Proc. SPIE 1376, Laser Noise, p. 216, (1991).

[7] McNesby, K.L., Skaggs, R.R, Miziolek, A.W., Clay, M., Hoke, S.H, and Miser, C.S., "Diode Laser-Based Measurements Of Hydrogen Fluoride Gas During Chemical Suppression Of Fires", Applied Physics B, Vol. 67, p443, 1998.

[8] G. Hertzberg, Infrared and Raman Spectra, Van Nostrand Rheinhold Co., New York, 1945.

[9] personal communication, Mark Allen, Physical Sciences, Inc.

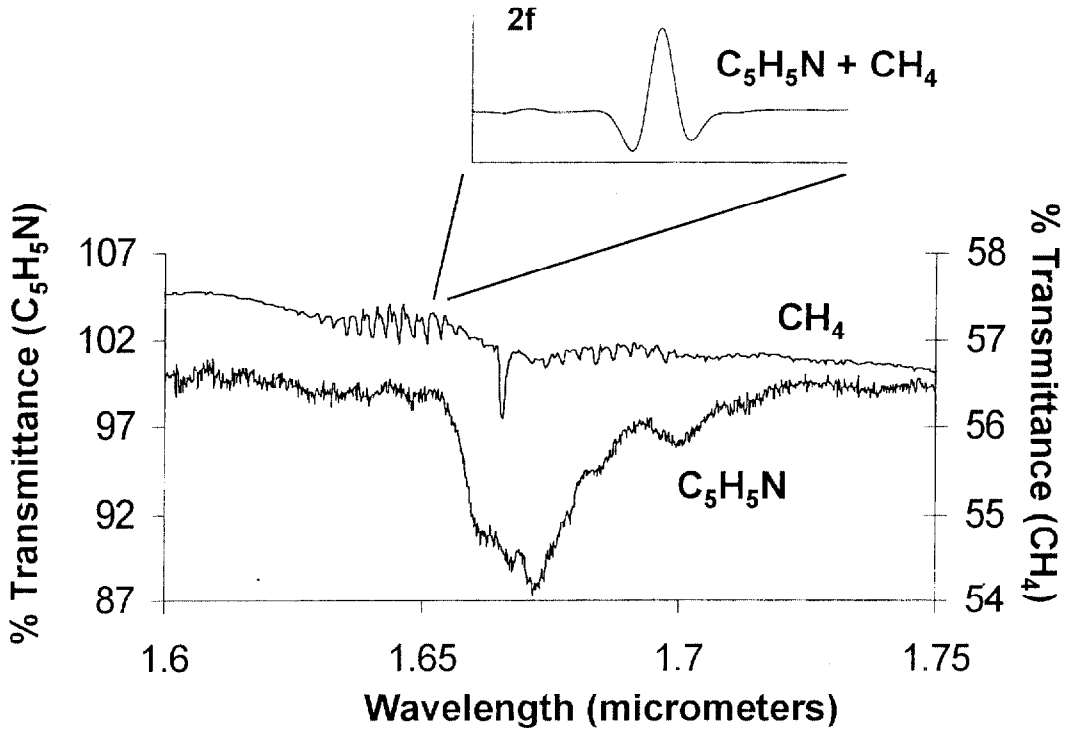

Figure 1: The % Transmittance spectrum of pyridine (C_5H_5N, P_T= 4 torr, 225 cm path length) is shown, together with the % Transmittance spectrum of methane (CH_4, P_T= 10.5 torr, 15 cm path length). The inset shows the wavelength modulation spectrum of a mixture of pyridine and methane (P_T=16 torr, pathlength=400 cm) measured at 2f near a wavelength of 1.653 micrometers. The breadth of the 2f scan is approximately 0.4 cm^{-1}. The absorption coefficient of pyridine at a wavelength of 1.653 micrometers was found to be 3.6 X 10^{-22} cm^2/molecule .

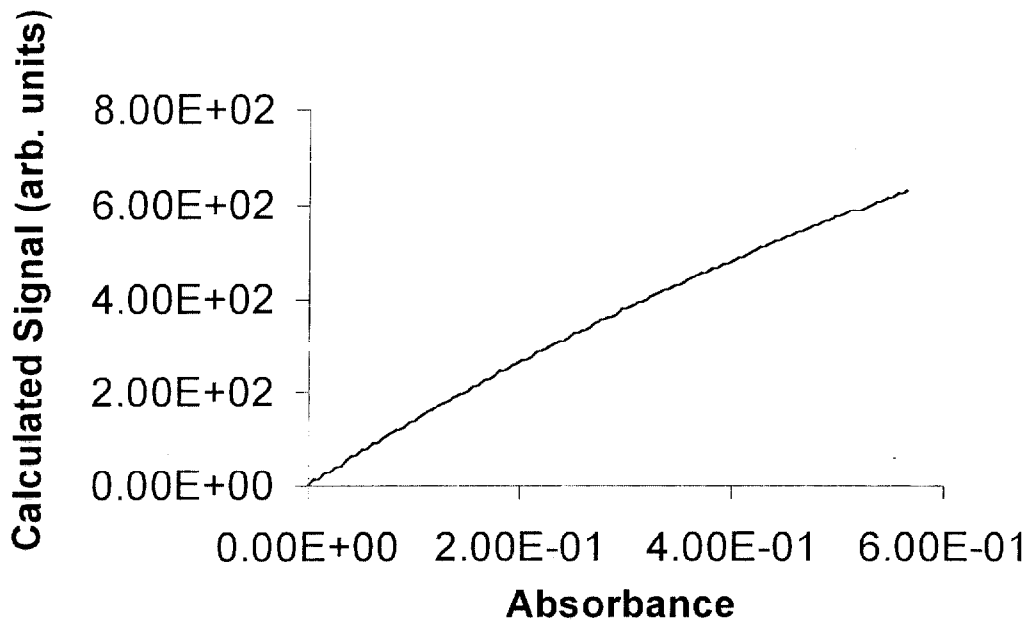

Figure 2: The value of the integral in Equation 8 (calculated signal) is shown for a moderately strong absorbing gas as a function of Absorbance, ($A = \alpha cl$).

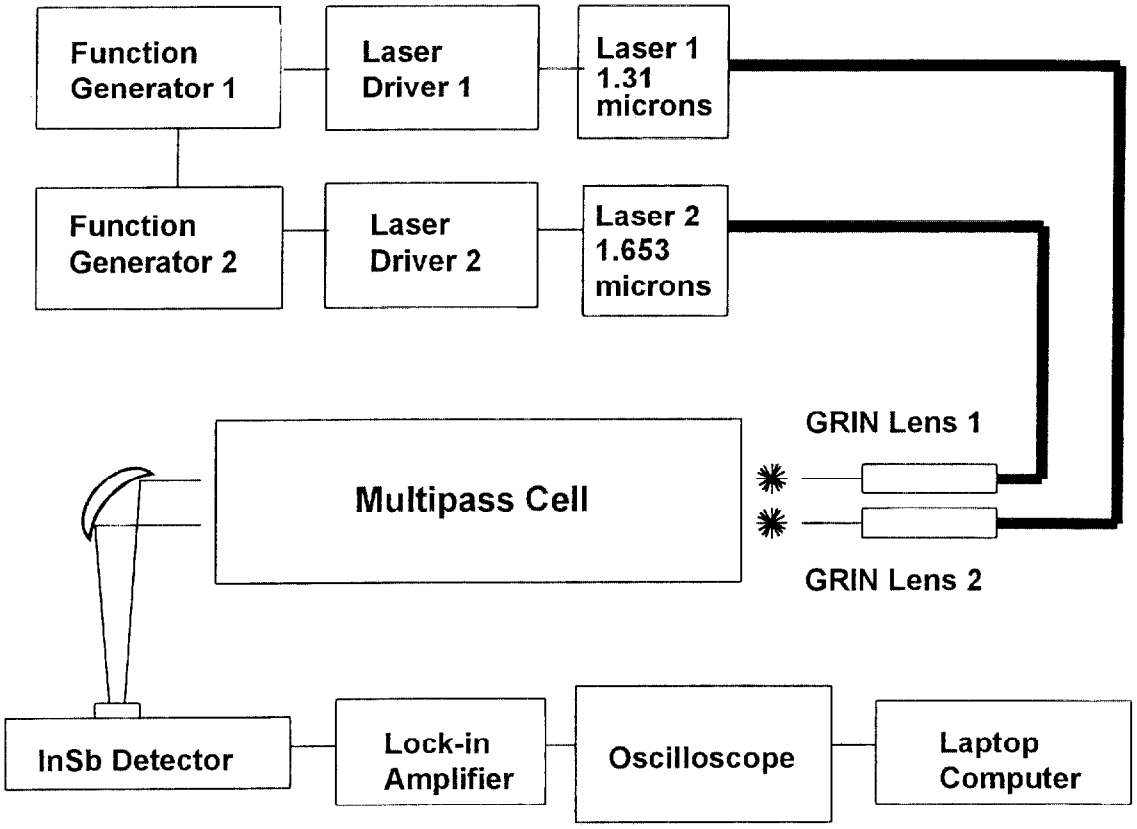

Figure 3: A schematic of the experimental apparatus is shown above.

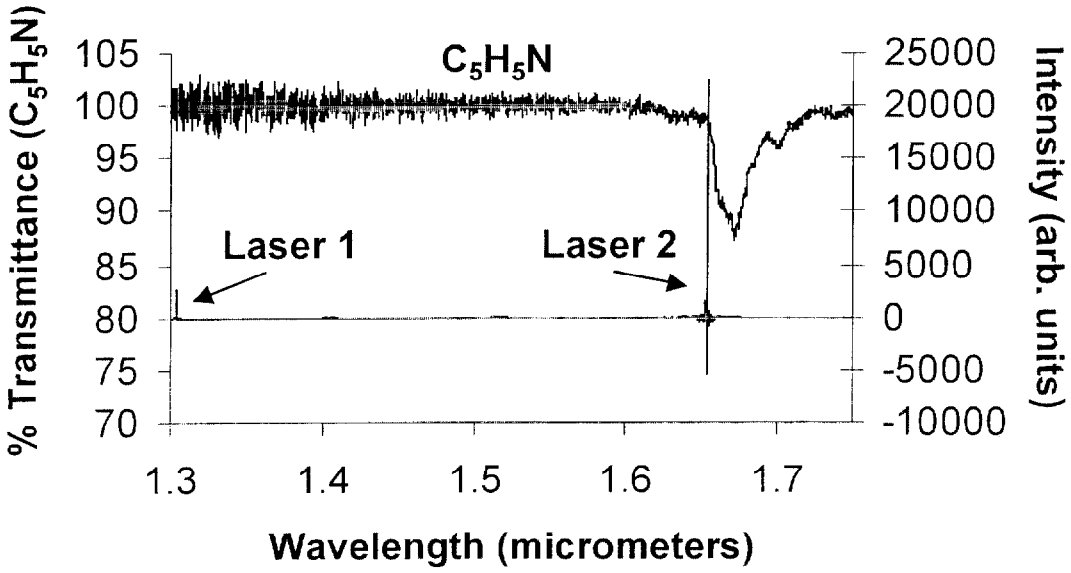

Figure 4: The absorption spectrum of pyridine (C_5H_5N, 225 cm path length, 1 cm^{-1} resolution) is shown superimposed on the spectrum of the mixed laser probe beam (1 cm^{-1} resolution). The decrease in the signal to noise ratio in the %Transmittance spectrum at lower wavelengths is due to decreasing sensitivity of the InSb detector and to increasing scatter in our multipass infrared gas cell.

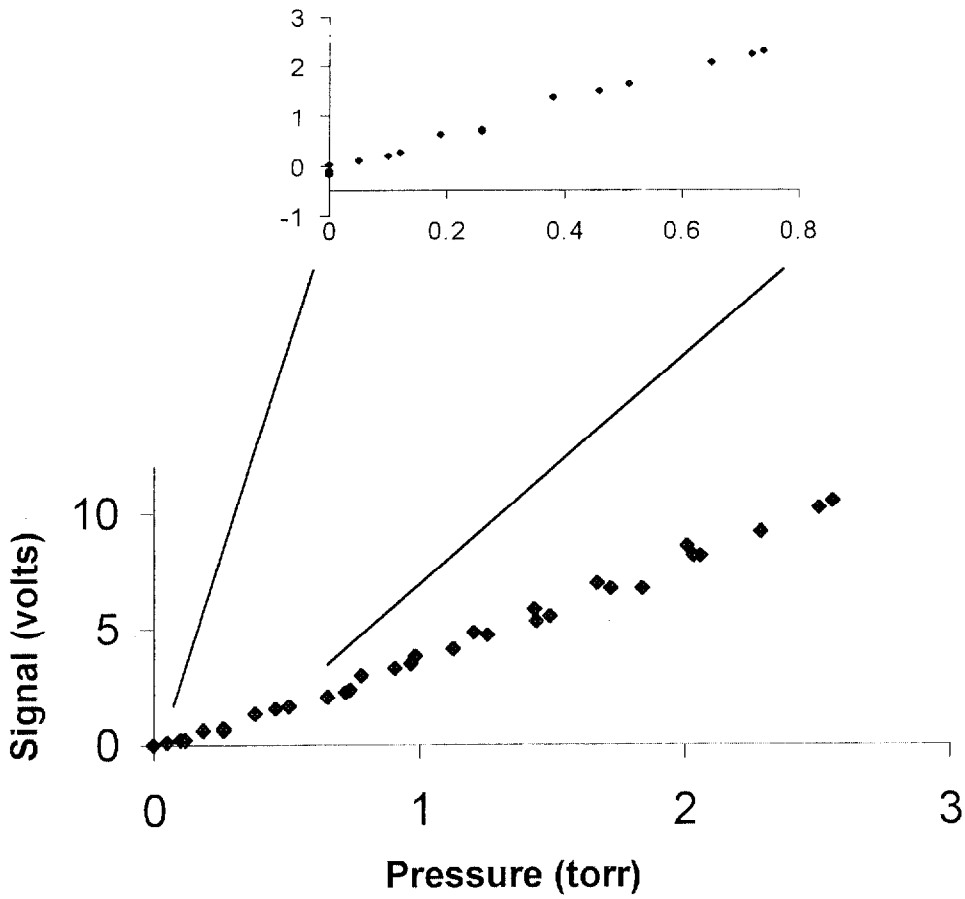

Figure 5: The measured signal for pyridine (C_5H_5N) vapor using the mixed laser technique. The path length used was 400 cm. The inset shows the signal response at the lowest pressures used in these experiments.

Molecule	λ (absorption region, micrometers)	Absorption Coefficient (cm^2/mol)
HF	1.33	1.3×10^{-20}
H_2O	1.393	2.1×10^{-20}
CO	1.567	2.3×10^{-23}
CH_4	1.651	8.7×10^{-22}
C_5H_5N	1.653	$3.6 (\pm 2) \times 10^{-22}$ (this work)

Table 1: Absorption coefficients for pyridine and for selected atmospheric gases.