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

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## Abstract

The development of a gas sensor to measure concentrations of binary mixtures of oxygen and several volatile organic compounds is described. The sensor is diode laser-based and all signal processing is performed digitally.

## Introduction

This paper describes efforts towards the development of a high measurement speed binary gas sensor for simultaneous quantitative measurements of fuel and oxygen concentrations. The method of detection relies upon absorption of radiation near a wavelength of 760 nanometers by oxygen, and absorption of radiation near a wavelength of 1700 nanometers by hydrocarbon based fuels [1]. These spectral regions were selected because of the commercial availability of room temperature lasers and detectors operating in this spectral range and because laser radiation in this spectral range may be easily transported at low loss using inexpensive optical fibers. The sensor development consists of two concurrent parts. Part one consists of development of the method of measurement for gases with and without well resolved ro-vibrational transitions, and the design and construction of the light source and fiber optics necessary for remote measurement. Part two consists of the design and implementation of the instrument control electronics, and the interface to allow instrument control and data acquisition using a laptop computer. These efforts are described in what follows.

## Background

Large and/or heavy molecules may not posses well resolved ro-vibrational absorption bands because of overlap between fundamental, combination, and overtone vibrations, and because of rotational constants which may be less than typical gas phase linewidths [2]. Figure 1 shows the near-infrared vapor phase absorption spectrum of the hydrocarbon-based turbine fuel JP-8 near a wavelength of 1700 nanometers (measured using a Fourier transform spectrometer), and the calculated absorption spectrum of oxygen near a wavelength of 760 nanometers [1]. For JP-8 vapor, the absorption spectrum near a wavelength of 1700 nanometers is essentially a continuous hump.

## Detection

The proposed method for detection of JP-8 vapor, and all other detection methods based upon phase sensitive detection, takes advantage of the following relations:

$${}_0{}^{\pi}\!\int m(\sin at)n(\sin bt)\,dt = 0 \qquad a\neq b \qquad (1)$$

$$2C\;{}_0{}^{\pi}\!\int m(\sin at)n(\sin bt)\,dt = Cmn\pi \qquad a=b \qquad (2)$$

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, if the signal amplitude is proportional to the desired quantity being measured, the result of the integration in (2) yields a value directly proportional to the quantity of interest.

### Experimental Design

The proposed method uses two fixed frequency amplitude modulated lasers, each modulated at the same frequency but out of phase by 180 degrees [3]. These two lasers are combined to produce the probe beam. Ideally, the combined output of the two lasers will have an amplitude that is invariant with time (in the absence of absorption of either laser output intensity).

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 laser one, the signal at the detector is modulated at the laser modulation frequency and, for small absorptions, has an amplitude proportional to the concentration of absorbing gas.

### Modulation Design

A time (t) dependent square wave, $S(a,n,t)$ at frequency a with amplitude n may be expressed as a sum of sine waves:

$$S(a,n,t) = 0.636n\sin(at) + 0.212n\sin(3at) + 0.1273n\sin(5at) + \dots \qquad (3)$$

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

$$S1(a,n,t)+S2(a,m,t) = (0.636n\sin(at) + 0.212n\sin(3at) + 0.1273n\sin(5at) + \dots) + (0.636m\sin(at+\pi) + 0.212m\sin(3at+\pi) + 0.1273m\sin(5at+\pi) + \dots \qquad (4)$$

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

$$2C \int_0^{\pi} (S1(a,n,t) + S2(a,m,t))p\sin(at)\,dt = Cp\pi(.636n-.636m) \qquad (5)$$

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:

$$2C \int_0^{\pi} (S1(a,n,t) + S2(a,m,t))(\exp{-\alpha cl})p\sin(bt)\,dt = Cp\pi(.636n-.636m(\exp(-\alpha cl))) \;, \qquad (6)$$

Where $\alpha$ 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 $\alpha cl \ll 1$, $\exp(-\alpha cl)$ may be rewritten as$1-A$, (where A is absorbance = $(\alpha cl)$) so equation 6 may be rewritten:

$$2C\ {}_0^{\pi}\!\int (S1(a,n,t) + S2(a,m,t))\ (\exp{-\alpha cl})p\sin(bt)\ dt = Cp\pi(.636n-.636m + .636mA) \tag{7}$$

For component lasers of equal amplitude, equation 7 becomes:

$$2C\ {}_0^{\pi}\!\int (S1(a,n,t) + S2(a,m,t))\ (\exp{-\alpha cl})p\sin(bt)\ dt = .636Cp\pi mA \tag{8}$$

Equation 8 shows that the summation of the amplitudes of the two out of phase lasers is directly proportional to the absorbance, A, and hence to the concentration of the analyte gas. Additionally, the signal 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. Using sine wave modulation of the component lasers instead of square wave modulation changes equation 8 to:

$$2C\ {}_0^{\pi}\!\int (S1(a,n,t) + S2(a,m,t))\ (\exp{-\alpha cl})p\sin(bt)\ dt = Cp\pi mA \tag{9}$$

Equation 9 may be considered the working equation for using this simple method of analysis. It is interesting to note that changing from square wave to sinusoidal amplitude modulation results in almost a 40% increase in signal intensity.

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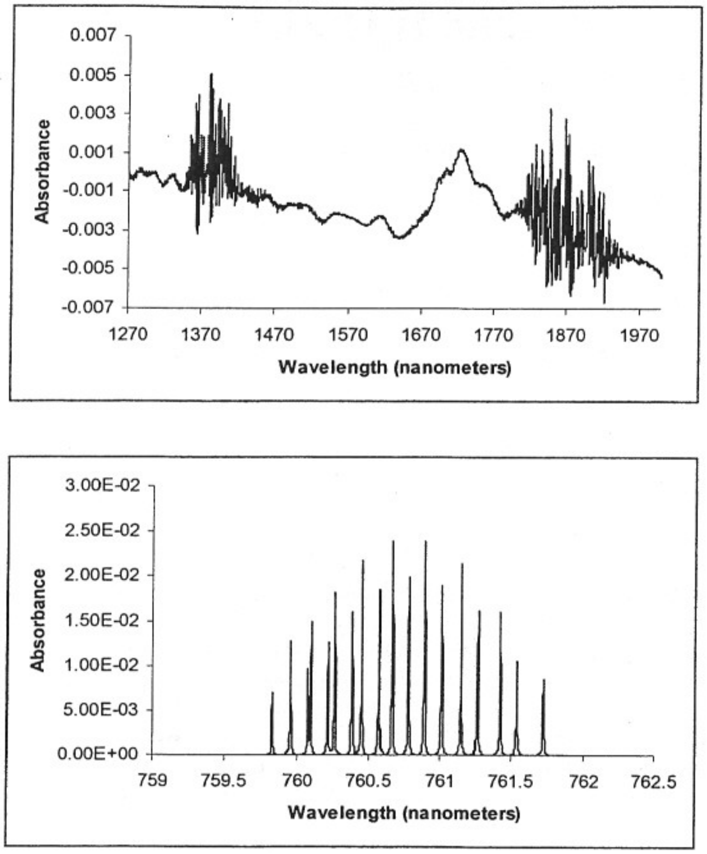

JP-8 vapor, 10 cm path length
355K, 4cm$^{-1}$ resolution,
256 scans.

$O_2$, 1 m path length,
296K, calculated using
HITRAN database.

**Figure 1:** The measured near-infrared absorbance spectrum in the wavelength region near 1700 nanometers of JP-8 vapor at 355K, and the calculated absorbance spectrum in the wavelength region near 760 nanometers of $O_2$.