

## Sensors for Advanced Combustion Systems

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The **advanced sensors** task has had activities in each of the five proposed milestone areas. These activities are discussed in the sections below. Absorption spectroscopy has long been an important tool for combustion diagnostics measurements and the work on this project strives to develop absorption diagnostics into robust, real-time sensors to aid the combustion engineer in designing fuel-efficient, clean-burning, combustors of the future. Our long-term goal will be to combine these sensors into control systems for early identification of combustion instabilities and eventually sensors with sufficient reliability for closed-loop active combustion control. We envision that advanced combustion systems with such active control will lead to substantial improvements in fuel efficiency and air quality.

### 1. Tunable Diode Laser Sensors for Combustion Temperature

Tunable diode lasers in the near-infrared have recently been developed for the telecommunications industry and are available at wavelengths overlapping the water vapor absorption bands near 1400 and 1800 nm. These devices offer the opportunity for robust real-time gas temperature monitors. Temperature is determined from the ratio of absorbance on transitions originating from different ground ro-vibrational states of H<sub>2</sub>O. In combustion systems the population in these quantum states is determined by a thermal Boltzmann distribution. Thus, the absorption strength from each lower state has different temperature dependence, and temperature can be determined by ratios of absorbance.

We have demonstrated two different strategies for gas temperature measurements in laboratory flames: 1) scanned-wavelength of a single diode laser over multiple absorption transitions, and 2) multiplexed-wavelength sensors which combine several diode lasers for simultaneously probing multiple absorption transitions. Each of these strategies offers unique advantages and disadvantages, and can be further improved, as diode laser technology advances and provides increased wavelength scan ranges.

During this first year we have surveyed the water vapor spectrum using the HITRAN/HITEMP simulation tool. We identified ten potential pairs of transitions within the scanning range of a single DFB diode laser whose absorbance ratio provides a sensitive measure of combustion temperature.

With support from a related project, we acquired a laser near 1800 nm which can scan one of these line-pairs at a scan-rate of 1 kHz. Fig. 1 shows sample absorption spectra of water vapor in a cell near 1040 and 1340 K; notice the ratio of absorption between the two lines changes by nearly a factor of two from this 300K change in temperature. We have recently demonstrated this

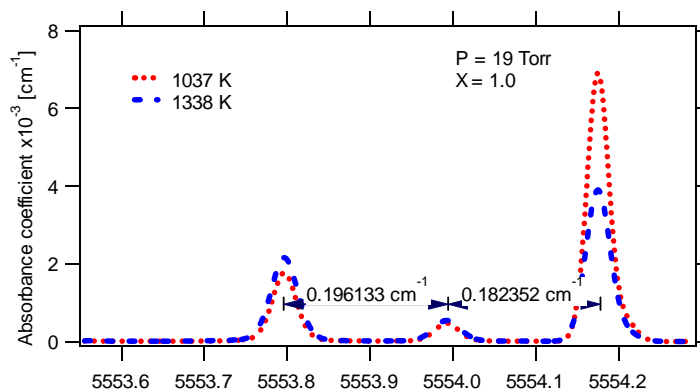


Fig. 1. Illustration of scanned-wavelength measurement of multiple absorption features in water vapor in a heated cell ~1040K and ~1340K. Note the 300K temperature change produces a factor of 2 change in the absorbance ratio for line 1 and 2.

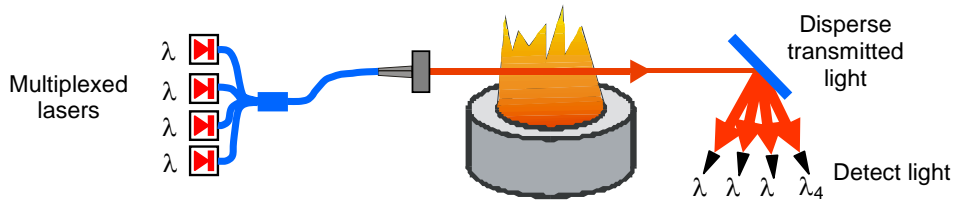


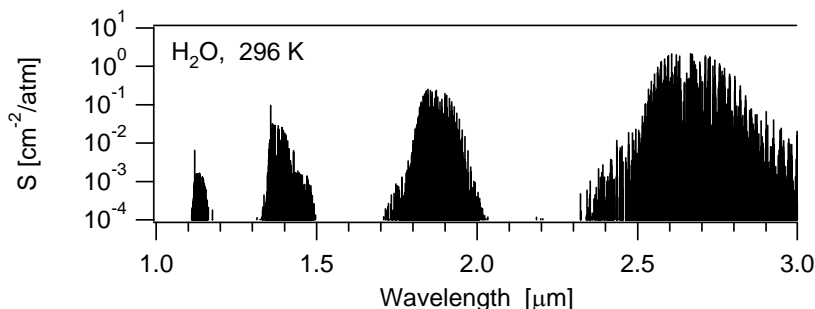
Fig. 2. Multiplexed-wavelength flame sensor concept showing four different diode lasers combined into a single fiber, pitched across the flame, dispersed on a grating and individually detected.

sensor in a laboratory-scale (Hencken burner) flame.

We have also continued our development of wavelength-multiplexed absorption, and our concept is illustrated in Fig. 2. At the cost of increased complexity, this concept offers the potential for extension to many more than two transitions. This can significantly increase the sensor performance. First, multiple transitions provide a significantly increased temperature range, as low, mid-range, and high temperature spectral features can be targeted. Second, multiple transitions can be analyzed to infer the temperature of the high-temperature core independently of cold boundary layers near walls. Third, redundant temperature information enables improved reliability against component failure. Fourth, additional colors can be multiplexed to measure other flame species simultaneously with the water vapor and gas temperature. Work during this year has concentrated on identification and characterization of isolated, strong features in the high-temperature water vapor spectrum.

## 2. Mid-IR Sensors for Combustion Emissions

Fundamental vibrational transitions in several combustion molecules occur in the mid-infrared from 3-10  $\mu\text{m}$ . These fundamental transitions have significantly stronger absorption than the overtone vibrational transitions in the near-IR. As illustrated in Fig 3 for water vapor, the absorption strength decreases approximately an order of magnitude for each overtone order for stretching vibrations involving hydrogen with an oxygen atom. For important non-hydride species such as CO or NO, the absorption strength declines roughly two orders of magnitude for each overtone order. Thus, mid-IR absorption sensors are attractive for sensitive detection of minority combustion species such as the pollutants NO and CO. Unfortunately the laser technology in the mid-IR is not yet as well developed as in the near-IR where the region 1280-1650 nm has seen very intensive development for the telecommunications industry. However, new laser sources based on quantum cascade architecture are emerging that provide laser light in the mid-IR from compact, room-temperature, diode sources.



During this first year, we have acquired mid-IR quantum cascade lasers near 5.2  $\mu\text{m}$  to develop an NO sensor. These QC lasers are distributed feed-back designs and thus have single mode output suitable for spectroscopic sensors.

Fig. 3. Absorption strength is illustrated for fundamental, overtone, and combination bands of H<sub>2</sub>O.

However, the lasers have high threshold currents of several amps and must be pulsed to handle the resulting heat load. Such high-current sources with short ns pulse lengths and MHz repetition rates are not standard commercially available power supplies. In addition, the pulsed power transmission lines for short pulses of high current are technologically challenging. In a NASA-funded collaborative project with Physical Sciences Inc., we acquired the necessary electronics and conducted initial NO measurements in the exhaust duct from a laboratory flame. NO measurements were performed in an insulated, 1 m long, exhaust duct from a C<sub>2</sub>H<sub>4</sub>-air flame at temperatures of ~600 K. Detection sensitivity of 0.36 ppm-m was demonstrated near 5.26  $\mu\text{m}$  on the R(6.5) transition of the fundamental vibrational band. These successful initial measurements position us to develop a sensitive optical sensor for NO emissions.

### 3. Sensors for Unburned Hydrocarbons

Polyatomic hydrocarbon fuel molecules have very rich ro-vibrational spectra. At atmospheric pressure and above, pressure broadening of the individual transitions broadens the individual transitions and they blend into unresolved features. The overtone spectrum of ethanol near 1.39  $\mu\text{m}$  shown in Fig. 4 is a typical example. The entire feature extends beyond the scan

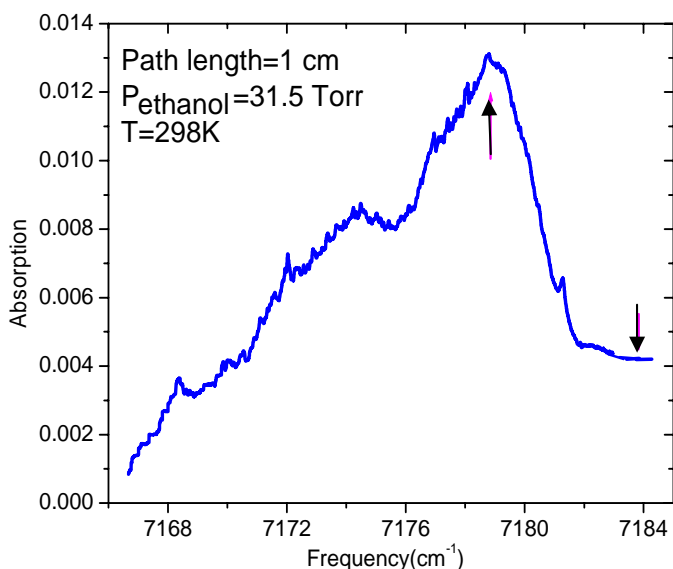


Fig. 4. Absorption feature of ethanol near 1.39  $\mu\text{m}$ ; arrows denote the range identified for differential absorption detection.

range of an individual diode laser; however, the two arrows in Fig. 4 indicate a region suitable for sensitive detection with differential absorption. We envision that differential absorption may develop into a general strategy for sensitive absorption detection of species with broad, unstructured absorption spectra typical of hydrocarbon fuels.

In the past few months, we have begun a series of investigation of differential absorption detection methods. In addition to differential absorption monitored with two lasers, tuned to the peak and valley wavelengths illustrated in Fig. 4, differential absorption can also be measured with a single wide-tuning laser using wavelength modulation methods. We anticipate such wavelength modulation methods will also provide increased detection sensitivity. Real-time analysis is facilitated by wavelength modulation strategies, and thus such methods are attractive for active control sensors.

### 4. Sensors for Combustion Control

Section 1 above discusses our progress on diode laser sensors for combustion temperature using wavelength-scanned and wavelength-multiplexed approaches; both strategies infer temperature from the ratio of direct absorption measurements. However, when the absorptions are less than 1% the analysis of direct absorption data becomes more difficult and time consuming, which limits the time response when used as a control sensor. In addition, the temperature is determined by the ratio of two small signals and thus can have a large uncertainty. We are currently investigating wavelength modulation strategies to ameliorate both of these problems. First, wavelength modulation yields inherently a zero baseline signal; thus, greatly

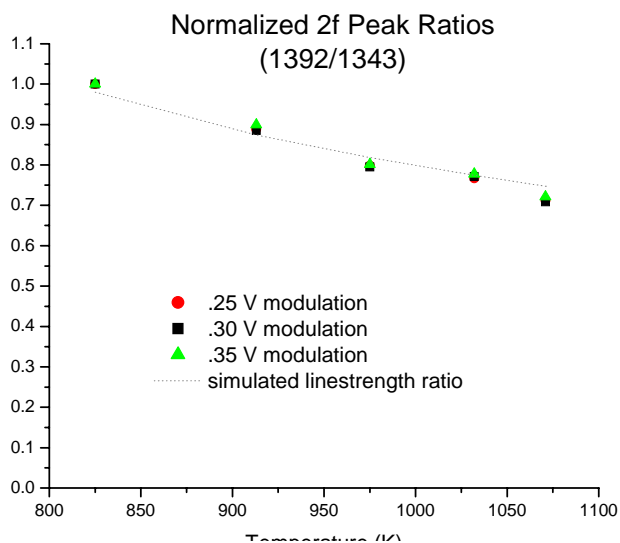


Fig. 5. Ratio of 2f-WMS absorption of water vapor in a heated cell follows the ratio of line strengths and is insensitive to modulation index showing the feasibility of WMS temperature

inferred from the ratio of two wavelength modulated signals.

During the past six months, we developed wavelength modulation software and hardware for a multiplexed diode laser sensor. Multiplexed diode lasers are used to probe second-harmonic (2f) line shapes of two water absorption features, at 1343 nm and 1392 nm, to infer gas temperatures in combustion flows. Wavelength modulation is performed at 170 kHz, and is superimposed on 1 kHz wavelength scans in order to recover full harmonic line shapes. Fig. 5 illustrates that the normalized 2f-WMS signal follows the predicted line strength ratio for water vapor in a heated cell.

## 5. Alternative Energy Conversion – Fuel Cells

We have begun to explore potential applications of laser-based sensing to two facets of fuel cell development: 1) fundamental understanding of chemical kinetics and transport mechanisms and 2) optical sensors for practical monitoring and control of fuel cell power plants.

Potential diagnostics to monitor the relevant surface chemistry and the transport of reactants through the membranes between the electrodes have been evaluated based on a review of surface science literature. Optical diagnostics offer the most potential for *in situ* measurements of fuel cell power generation because the typical spatially resolved surface diagnostics using scattered ion or electron beams require a high vacuum. Thus, these diagnostics are ill-suited for fundamental fuel cell studies where the catalysis must co-exist with feedstock fuel and oxidizer streams as well as membranes that often must remain moist. The potential optical surface diagnostic strategies of sum (difference) frequency generation and infrared absorption have the needed species selectivity, but their spatial resolution is limited by the wavelength of the light. We conclude that a hybrid diagnostic combining optical methods with a tapered fiber probe has the potential to make the *in situ*, species-specific and spatially-resolved measurements on the

reducing the data reduction time and uncertainty. Second, wavelength modulation has long been used for sensitive detection of trace concentrations of species; the typical minimum detectable absorbance for direct absorption is  $10^{-4}$  while optimized limits for wavelength modulation absorption spectroscopy are often reported as low as  $10^{-6}$ . Thus, the precision of the temperature scale can be much improved. However, wavelength modulation strategies require calibration. We are investigating the hypothesis that the calibration requirements can be reduced or eliminated for gas temperature measurements which are

catalyst-doped membrane surface needed for fundamental understanding of fuel cell chemistry/transport.

Advanced sensors have the potential to solve several practical problems for power plant operation, and to get a better understanding of some of these issues for molten carbonate fuel cells, Dr. Jeffries visited Fuel Cell Energy in Torrington, CT. One interesting practical problem identified is the “peak-shaving” practice of adding a combination of air and propane to natural gas during periods of high demand in New England. Although the mixture maintains constant BTU fuel for standard combustion facilities, the air load can be 10-20% and premixing up to 4% oxygen in the fuel stream significantly reduces the efficiency of the MCFC electrical production while increasing the temperature of the fuel cell stack. We believe that diode laser sensors for O<sub>2</sub> may provide an effective means of monitoring the natural gas purity. In addition, sensors discussed above for unburned hydrocarbons could be used for *in situ* leak testing during the burn-in of the stack.

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