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Sensitive Multi-Species Emissions Monitoring: Infrared Laser-Based Detection of Trace-Level Contaminants

Jeffrey D. Steill, Haifeng Huang, Alexandra A. Hoops, Brian D. Patterson, Salvatore R. Birtola, Mark Jaska, Kevin E. Strecker, David W. Chandler and Scott Bisson

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Abstract

This report summarizes our development of spectroscopic chemical analysis techniques and spectral modeling for trace-gas measurements of highly-regulated low-concentration species present in flue gas emissions from utility coal boilers such as HCl under conditions of high humidity. Detailed spectral modeling of the spectroscopy of HCl and other important combustion and atmospheric species such as H_2O, CO_2, N_2O, NO_2, SO_2, and CH_4 demonstrates that IR-laser spectroscopy is a sensitive multi-component analysis strategy. Experimental measurements from techniques based on IR laser spectroscopy are presented that demonstrate sub-ppm sensitivity levels to these species. Photoacoustic infrared spectroscopy is used to detect and quantify HCl at ppm levels with extremely high signal-to-noise even under conditions of high relative humidity. Additionally, cavity ring-down IR spectroscopy is used to achieve an extremely high sensitivity to combustion trace gases in this spectral region; ppm level CH_4 is one demonstrated example. The importance of spectral resolution in the sensitivity of a trace-gas measurement is examined by spectral modeling in the mid- and near-IR, and efforts to improve measurement resolution through novel instrument development are described. While previous project reports focused on benefits and complexities of the dual-etalon cavity ring-down infrared spectrometer, here details on steps taken to implement this unique and potentially revolutionary instrument are described. This report also illustrates and critiques the general strategy of IR-laser photodetection of trace gases leading to the conclusion that mid-IR laser spectroscopy techniques provide a promising basis for further instrument development and implementation that will enable cost-effective sensitive detection of multiple key contaminant species simultaneously.

ACKNOWLEDGMENTS

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NOMENCLATURE

DOE	Department Of Energy
SNL	Sandia National Laboratories
EM	Electromagnetic radiation
IR	Infrared Radiation
RF	Radio-Frequency radiation
MHz	Megahertz (*i.e.* 10^6 s^{-1})
FWHM	Full-Width Half Maxiumum
CRDS	Cavity Ring-Down Spectroscopy
PAS	Photo-Acoustic Spectroscopy
DEFCOM	Dual-Etalon Frequency COMb
FSR	Free-Spectral Range
FFT	Fast Fourier-Transform
ppm	part-per-million (typically by volume, *i.e.* ppmv)
ppb	part-per-billion (typically by volume, *i.e.* ppbv)

1. INTRODUCTION

1.1. Motivation and Approach

A major challenge of combustion process control is to measure multi-component mixtures rapidly and accurately over a wide dynamic range of concentrations, particularly for sub-ppm trace-gas concentrations in high relative humidity. This challenge requires a sensitive detection strategy that is applicable to a range of species simultaneously and ideally can be performed *in-situ*. In addition to providing a means for improved process control capabilities, the accurate and sensitive measurement of these species is essential because even at low concentrations they pose significant health hazards and are thus highly regulated.

The low concentrations of these regulated species make effective measurement non-trivial, but the primary challenge arises from the necessity of measuring these species simultaneously with other gases present in the exhaust stream. While commercially available instrumentation exists for highly sensitive measurement of individual species, these devices typically require significant pre-processing of the sample, and are effective for only one particular component. These limitations generate considerable expense for monitoring multiple regulated emission species. Based on these fundamental limitations with the current technology and the necessity of developing sensitive, rapid, and cost-effective analysis strategies, we have undertaken the effort towards developing inherently multi-component analysis techniques.

Our approach is to use the many advantages of infrared spectroscopy such as its high selectivity, inherent multiplexed analysis capability and the fact that it is directly quantitative. Within this framework, we leverage the high-intensity characteristics of laser-excitation to drastically improve measurement sensitivity through techniques such as photoacoustic spectroscopy and cavity ring-down spectroscopy. We have focused our specific efforts on the detection of sub-ppm level HCl, and have developed techniques and strategies that are generally applicable without pre-processing of a sample containing significant quantities of other species. We demonstrate that our approach is useful for simultaneous quantification of sub-ppm level HCl under conditions of high-humidity, as well as for important emissions gases such as CO_2, NO_2, SO_2 and CH_4.

There are fundamental and specific challenges that must be negotiated with development and implementation of a spectroscopic technique. While the basic principles and components of optical spectroscopy are relatively straightforward, the increased sensitivity of a spectroscopic measurement technique is often directly related to increased complexity and cost. A major factor of the effectiveness of a spectroscopic measurement is the frequency resolution, as improved resolution invariably provides a more sensitive and accurate measurement. However, the measurement resolution is usually inversely related to the cost of the measurement in terms of both equipment and time. Thus, we explore the balance between sensitivity and resolution, and explore means to improve the measurement resolution in novel and cost-effective ways. With the relationship between cost and complexity in mind we have constrained our efforts to first provide reasonably effective low-cost solutions that can then be significantly improved upon by advanced instrument development.

Our efforts are outlined as follows:

- We explore the contours of the chemical analysis problem though spectral modeling that dictates the basic requirements of an effective measurement system.
- We demonstrate the implementation of a fundamentally simple yet nonetheless highly effective approach: photoacoustic spectroscopy.
- We demonstrate the applicability of well-known highly-sensitive analysis technique for trace-gas measurement: cavity ring-down spectroscopy.
- We explore the crucial role that instrument resolution plays in the fundamental effectiveness of a spectroscopic analysis through modeling.
- We detail our efforts towards the development of the new and potentially revolutionary spectroscopic technique of infrared dual-etalon frequency comb spectroscopy that can achieve extremely high multicomponent measurement sensitivity due to improved spectral resolution, but with relatively low additional instrument cost over traditional cavity ring-down spectroscopy.

In our account of these efforts we outline multiple possibilities for effective measurement strategies, and demonstrate the fundamental applicability of our overall strategy to important chemical analysis problems in industrial coal combustion.

1.2 Technical Background

1.2.1 Relevant Details of IR-Laser Spectroscopy

There are some very particular advantages of infrared spectroscopy as a means to measure trace-gases. These advantages include molecular specificity, quantitative accuracy, measurement rapidity, multi-component capability and the possibility of *in-situ* configurations. In addition, while direct absorption spectroscopy can be very effective for trace-gas measurement over very long path-lengths, the use of IR-laser sources can provide extremely high measurement sensitivity for even very small sample volumes. The specificity of the technique stems from the fact that the exact frequency of light absorption by a molecule is a very precise quantity and thus provides a definitive measurement; therefore the molecule identification is unambiguous. The method is directly quantitative because the spectral response of a given molecule is directly related to the concentration, and is essentially a linear response over a wide dynamic range. The method provides an inherently multicomponent measurement because there are many spectral regions in the infrared where multiple process gases show overlapping/nearby absorption features, as is explored in detail below. A final highly-relevant advantage to the method for the current application is that the gas-phase measurement can be performed quickly and non-disruptively (and even potentially non-extractively) and thus is well-suited to process control.

Low sample concentrations require high sensitivity. The absorption of photons by a sample can be detected with excellent sensitivity if a high-intensity light source is used, i.e. through laser-excitation. The technology is well-developed for IR spectroscopy methods to achieve high sensitivity. Simultaneous multi-component detection is affected by measurement resolution, and thus the spectral bandwidth of the laser source will influence the measurement capability. While effective multi-component analysis is possible at low-resolution, a spectral measurement with resolution that is limited only by the physics of the molecule (e.g. pressure broadening) will provide more information and improved analysis. We focus our initial efforts on the use of a broad-band IR laser source, and show the advantages and limitations that arise from this relatively low-resolution laser source. Improved resolution can be achieved by the use of a different narrow-bandwidth laser source, or by development of a fundamentally new infrared spectrometer for use with a broad-band laser source. The latter approach is explored in detail.

1.2.2 Spectral Modeling: HCl with Other Species

In order to explore the inherent constraints on the approach, we employ a spectral modeling approach to investigate the relevant parameters of a typical spectroscopic measurement. As a representative sample, we consider a gas mixture consisting of trace amounts of HCl in 100% humidity and high CO_2 concentration, with additional combustion products and atmospheric components such as N_2O, NO_2, SO_2, and CH_4. The concentrations of the gases are shown in table 1, below. These components are selected because they share overlapping spectral features with HCl and because they are also important emission chemicals. The HCl volume ratio is set at 1ppm, and the water concentration is at 3%, which corresponds to approximately 100% humidity at room temperature. The CO_2 concentration is high and the oxygen concentration low, both at 10%, to roughly simulate combustion exhaust, and the array of possible interferents is set at 10ppm. These molecules that contribute to the infrared activity are shown in bold in Table 1, below. The other components (including CO due to the lack of any overlapping spectral features) are left at their atmospheric abundance proportions.

The basic spectroscopy of HCl defines the possible spectral regions of interest. Since HCl is a closed shell diatomic molecule, the infrared spectrum is relatively simple and very well-characterized. There are essentially only three possible spectral regions in the mid- and near-IR. The fundamental vibrational mode of the molecule is a highly infrared-active transition in the mid-IR that spans the spectral region of ~3.2 to 3.8 μm. With a sensitive absorption measurement it is possible to also observe overtones of the vibrational modes, despite their much-weaker absorption cross-sections. These transitions are in the near-IR, with the first overtone (from the $v=0 \rightarrow v=2$ transition) at 1.7 to 1.9 μm, and the second overtone ($v=0 \rightarrow v=3$) at 1.18 to 1.25 μm. The infrared spectrum is examined at these three wavelength regions to assess their overall suitability and identify useful and complicating spectral overlap with the other chemicals listed in Table 1.

gas	**ppm**
HCl	**1**
H_2O	**30000**
CO_2	**100000**
CH_4	**10**
NO_2	**10**
SO_2	**10**
N_2O	**10**
NO	10
O_3	0.05
CO	0.10
O_2	100000
N_2	760824
Ar	9101
Ne	18
He	5
Kr	1
Xe	0.08
H_2	0.49
total	1000000

Table 1. Concentrations of gases used for modeling HCl in flue exhaust.

The modeling of the infrared spectra of this representative gas mixture is performed using the HITRAN [1] spectral database as the source of spectroscopy information for the gases. A custom-written MATLAB code was used to simulate the spectra from the database using a temperature of 20 °C and a pressure of 1 atmosphere. Because our initial intent is to demonstrate the applicability of the analysis method with a relatively broad-band laser source we model the spectra with a low-resolution (~4cm^{-1} FWHM), and show the effect of high resolution in a later section of this report. The model is quantitatively accurate for an absorbance measurement; to simulate a highly sensitive laser-spectroscopy measurement an effective path length of 100 meters is used to calculate the spectral absorbance. The results of these modeled spectra are shown in Figure 1 for each of the three spectral regions of interest.

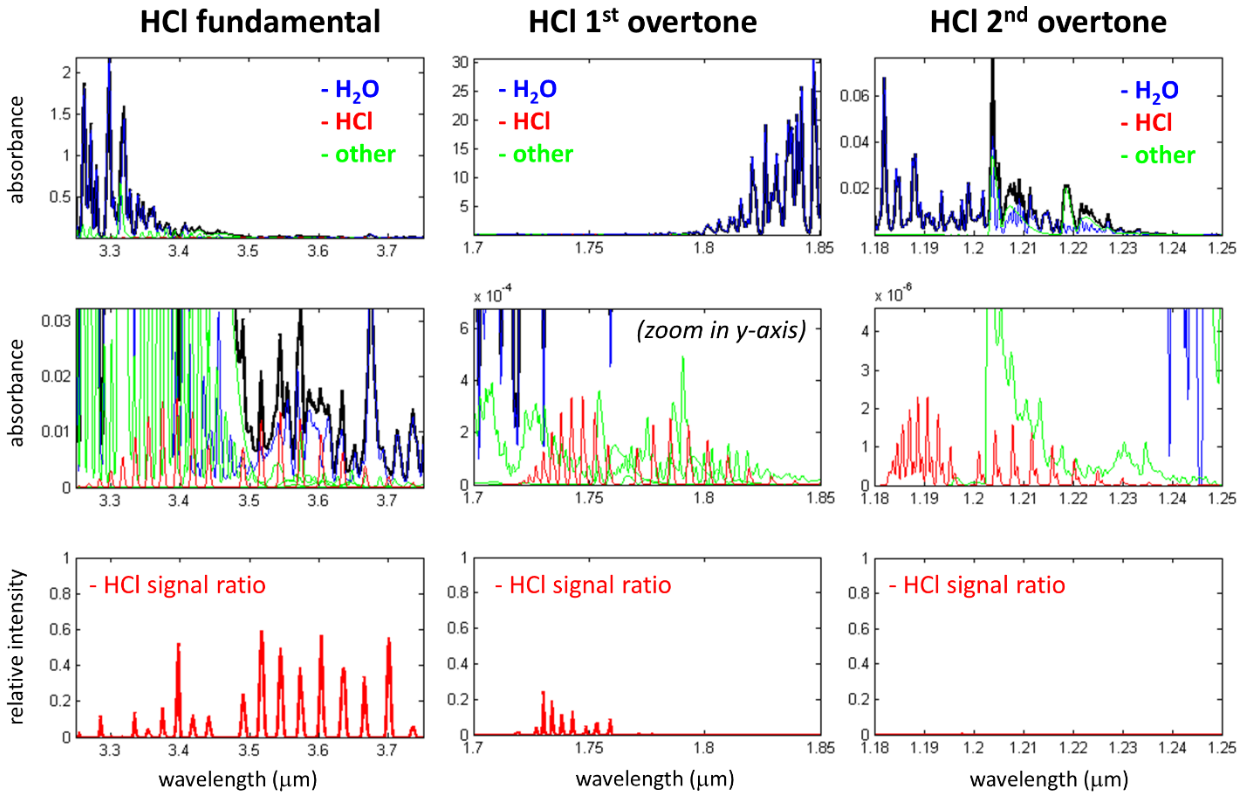


Figure 1. Illustration of possible spectral regions for detection of HCl molecule. The upper panels show the full spectrum, the middle panels show a zoom-in of the HCl contribution, and the lower panels show the proportion of the overall signal due to only the HCl spectral response.

The simulated spectra in Figure 1 show that at the concentration listed in Table 1, the spectra are clearly dominated by water vapor absorption. The spectral contributions of the individual components are shown in color and the summed spectrum is shown as the thick black trace. The HCl is shown in red and the H_2O in blue, the other components are all shown in green. The upper panels of Figure 1 show the full spectral region and intensity, the middle panels are a zoomed-in region of the y-axis to show the relative proportion of the HCl to the spectrum. An effective way to visualize the feasibility of spectroscopic detection of a species in a mixture is illustrated by the ratio shown in the lower panels of Fig. 1. These panels represent the proportion of the spectral response at a given wavelength that is due exclusively to the HCl contribution. Examination of these figures reveals a clear insight: at this spectral resolution, the HCl signal in the overtones is largely swamped by the interference with water vapor. However, as shown in the lower left panel, the proportion of the signal from HCl at 1ppm is greater than 50% in multiple spectral regions of the fundamental band, and thus experimental spectra acquired in this region would only be expected to be properly quantified by including the HCl spectral signature. This spectral region therefore makes a suitable domain for measurement.

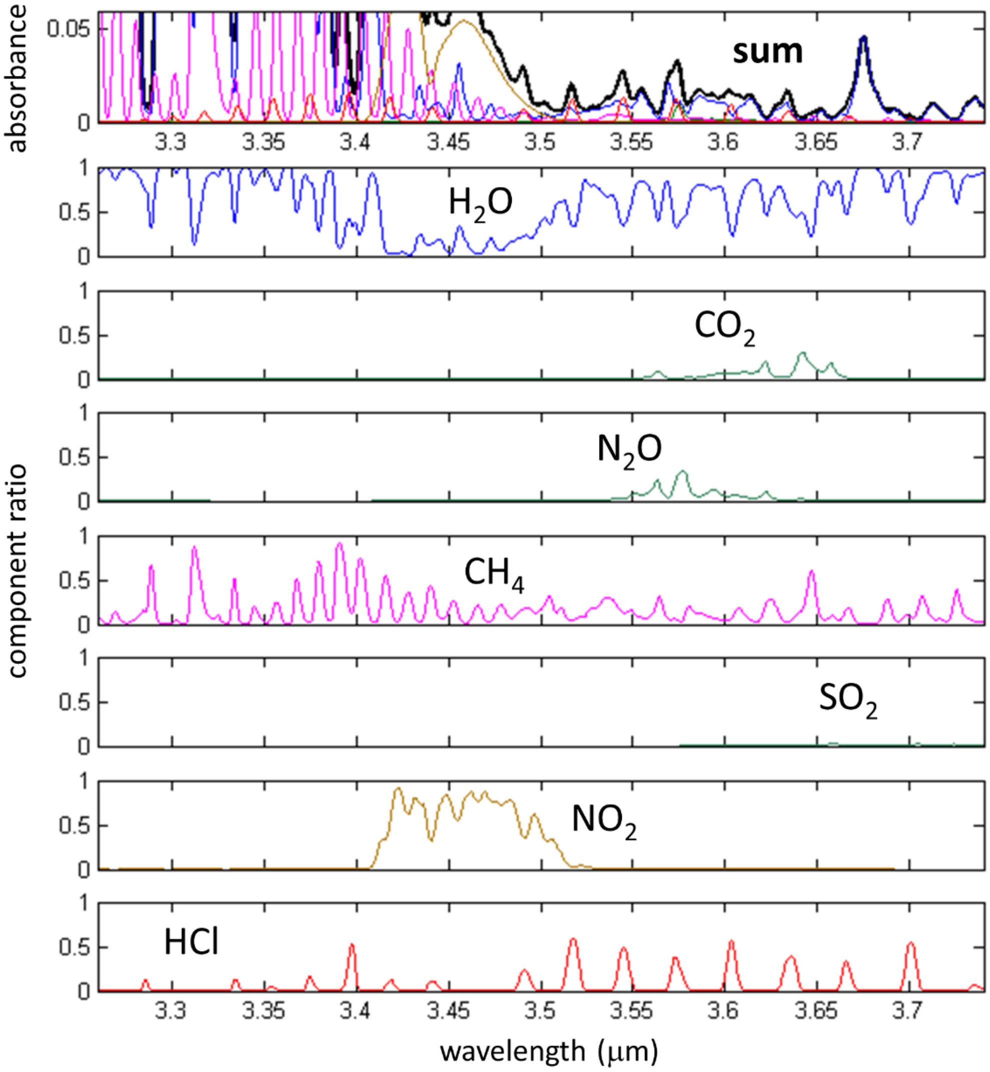


Figure 2. Component proportional contributions to the total spectral response. Focus is on the HCl fundamental band spectral region and the component concentrations are shown in Table 1. Note the variety of useful target species not obscured by H_2O.

There is an additional reason this spectral region in the range of 3.2-3.8 µm is of interest, which is key importance. As seen in the upper panels of Fig. 1, the overlap of HCl with an spectroscopic interfering species can be a hindrance to observation, but as shown in Fig. 2, this overlap can also provide an enormous opportunity. The spectral response over the HCl fundamental band is shown in Fig. 2 for each of the key absorbing species. The upper panel shows the individual absolute contributions (for the concentrations given in Table 1) and the lower panels show the proportional contributions of the individual species. A very promising result is that even at 100% humidity and low measurement resolution, simultaneous ppm-level quantification is feasible for a multiplicity of additional key combustion species, including CO_2, NO_2, and CH_4. Indeed, for an effective measurement of sub-ppm level HCl, the quantification of these other species, like H_2O, is actually required. Thus, this spectral region provides a very rich opportunity for implementation of an inherently multi-component analysis method.

With the target 3μm spectral region defined by the measurement constraints and opportunities it provides, we undertake experimental approaches that will maximize our measurement sensitivity while minimizing investment in equipment cost, instrument complexity, and sample preparation. Because we intend to use small sample volumes and concentrations, we employ laser-based spectroscopy techniques that provide enhanced sensitivity. The method of photoacoustic spectroscopy provides a very low-cost and highly sensitive option, and the extreme sensitivity and relative simplicity of cavity ring-down spectroscopy provides a natural solution for this type of analysis. We describe the results from our implementation of these analysis techniques in the following section.

2. EXPERIMENTAL OVERVIEW AND RESULTS

2.1. IR OPO-OPA Laser

The experiments described below were performed using an intense OPO-OPA IR laser from LaserVision that is pumped by a ns pulse-length 10 Hz Nd:YAG pulsed laser. The OPO-OPA system produces IR laser output at ~10mJ/pulse over the range of 2.8 to 3.8 μm. The laser was operated at full power for the photoacoustic spectroscopy experiments, and for the cavity ring-down experiments we use less than 2mJ pulse energy in order to avoid damaging the high reflectivity coating on the mirrors of the two etalons. The output band-width of the laser is approximately 3 cm^{-1} FWHM when unseeded, which is commensurate with the simulated spectra of Figs. 1 and 2. For spectral acquisition, the spectral scan rate was ~0.4 nm/second.

2.2. Photoacoustic Spectroscopy

The technique of photoacoustic spectroscopy has been in use for many decades [2] and provides an excellent example of the usefulness of "action spectroscopy" techniques where the phenomenon that is monitored is not the loss of input light intensity but rather a response of the sample to the light absorption process. In the case of photoacoustic spectroscopy, absorption of photons by the sample results in rapid heating and localized gas expansion, producing a pressure wave that is detected by microphone. This extremely simple principle of operation results in a simple experimental configuration, as illustrated by the schematic in Fig. 3. The basic components include a laser source, an optical cell, a microphone and an oscilloscope/computer, and little else. Despite the simplicity, the technique provides enormous measurement sensitivity, with examples ranging down to sub-ppb level.

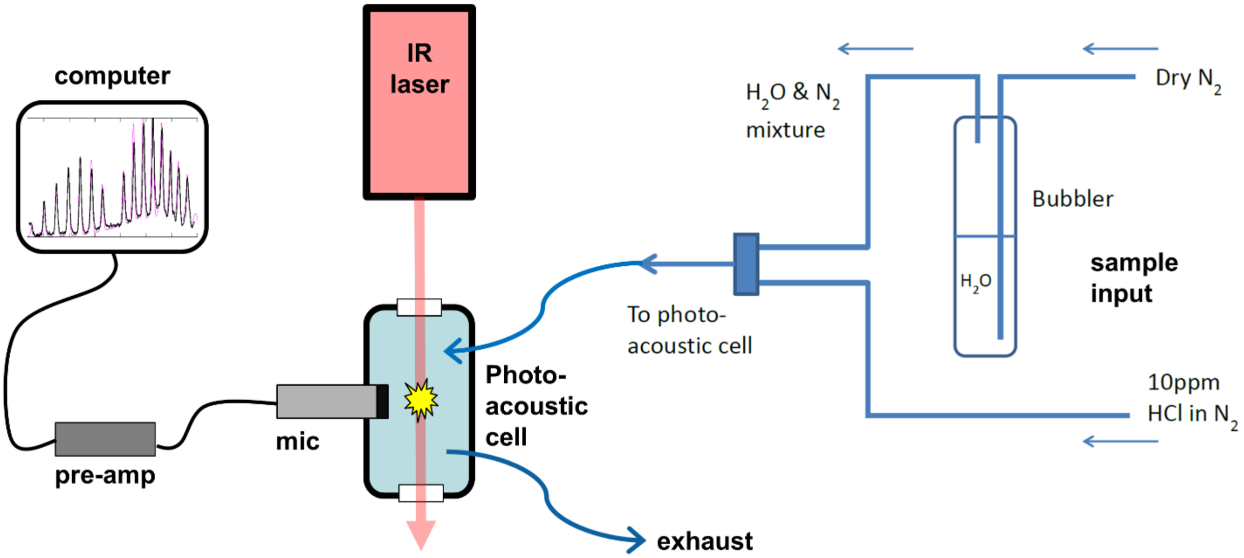


Figure 3. The photoacoustic spectroscopy experimental schematic.

For acquisition of experimental spectra from the photoacoustic cell, the laser was input to the cell through salt windows, the cell was at room temperature and atmospheric pressure, and the sample was set for continuous flow through the cell. For the measurement of HCl gas at ppm levels in a dry atmosphere, the cell was purged with dry N_2 for many hours before introduction of sample through a flow of 10 ppm HCl in balance N_2 at a rate of 100sccm. Due to the loss of HCl to adsorption to tubing and cell walls, the concentration of HCl was diluted to 2ppmv. The spectrum of the HCl was acquired by scanning the laser wavelength while monitoring the microphone signal through a boxcar integrator averaging 30 laser shots per spectral point. The data from this scan is shown as the thick black trace in the upper portion of panel group (a) in Figure 4. Shown in the panel immediately below are the modeled results from each of the components. It is clear that the sample was indeed very dry, with low water content and largely isolated contribution from HCl gas. There is evidence of a small contribution of a contaminant species (green trace), probably a hydrocarbon due to breadth of spectral feature. The summation of the components (magenta trace) is fit to the experimental data and shows an excellent agreement. The very high signal to noise ratio of the 2ppm sample measurement makes it abundantly clear that the limit of detection for this technique is in the sub-ppm range, certainly below 0.1ppm.

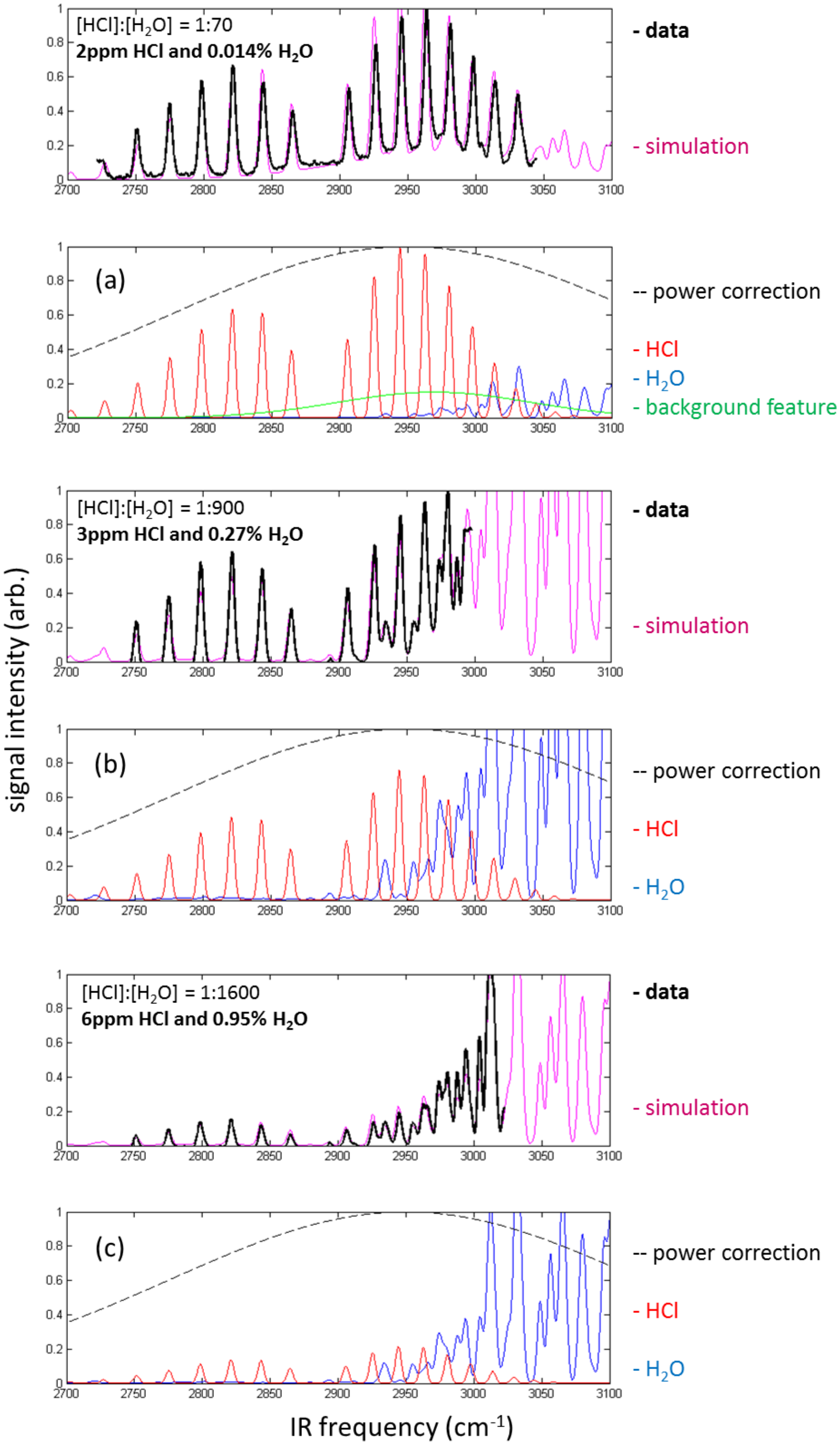


Figure 4. Data from photoacoustic cell quantified by fit to simulation.

The effectiveness of the photoacoustic spectroscopic method provides an excellent opportunity to examine the feasibility of multi-component analysis. Because the primary interfering species in this region is water, HCl spectra at ppm level were acquired with relatively high water concentration. A water vapor bubbler was used to control the water vapor concentration quantitatively, and the H_2O/N_2 mixture was diluted with the HCl/N_2 mixture. For the spectrum shown in upper panel of the set of panels (b) in Fig 4, the flow rate of 10 ppm HCl in nitrogen was 100 sccm and the nitrogen flow rate through the bubbler was 9 sccm, resulting in a water vapor relative concentration of 0.27%. The simulated spectra of panel (b) clearly shows the increased contribution of water vapor to the observed spectrum, and the excellent fit to the data yields an accurate quantitative determination of 3ppm HCl in the presence of significant H_2O. As shown in panel (c) of Fig. 4, increasing the water concentration to nearly 1% (e.g. ~40% humidity) does not hinder the HCl quantification, and the accurate fit of the simulated spectrum to the experimental data yields a HCl level of 6ppm. Based upon the high signal to noise of this spectrum, it is reasonable to expect sub-ppm HCl detection is possible even at 100% humidity, and it is clear that further development of this technique would prove very fruitful.

2.3. Cavity Ring-Down Spectroscopy

Cavity ring-down spectroscopy (CRDS) is a somewhat new experimental technique that was developed in the 1990's and has seen increasing use due to its relative simplicity and extremely high sensitivity [3]. We have constructed and utilized an infrared CRDS system at Sandia National Laboratories for trace-gas measurement, and the principles and results of operation are described below. The three essential components of a CRDS system are an intense collimated light source, a pair of highly-reflective mirrors and a photodetector. The basic principle is that the intense light source is directed into a cavity where the mirrors form a stable resonator, and the light "leaks" out of the cavity (*i.e.* etalon) and is measured by a photodetector. The more reflective the mirrors are at the input optical frequencies, the more passes the light makes through the cavity and the longer the measured signal decay time is. If an absorbing species is in the cavity, the light decays at a faster rate due to the species photoabsorption. The extraordinarily high sensitive of the technique is due to the many passes the light takes through the cavity. These phenomena are elucidated in Fig. 5 below, which shows the experimental ring-down results from the constructed CRDS system.

The ring-down of the cell without an absorbing medium inside is used to determine the basic characteristics of the system. The left panel (a) of Fig. 5 shows the temporal IR light intensity from a single pulse of the OPO IR laser through the cavity without an absorbing gas (i.e. purged with dry N_2) as measured by an InSb photodetector. The laser pulse duration is on the order nanoseconds, so the long decay time of the light pulse (on the order of microseconds) is due to many internal reflections off the highly-reflective mirrors. Based on the relationship between the decay time constant, cavity length and mirror reflectivity, the mirror reflectivity is determined to be 99.8% at the wavelengths employed for the current study. With the addition of a trace gas that absorbs photons at the input laser frequency, the decay constant decreases proportional to the concentration, as shown in panel (b) of Fig 5. The results in Fig. 5 (b) show a very large change in decay time constant due to a significant concentration of the photoabsorbing species, methane. However, because the light decay can be measured accurately, a small change in decay can be quantified and the theoretical sensitivity of this spectrometer to CH_4 and HCl in this spectral region is calculated to be extremely high, on the order of 10 ppbv.

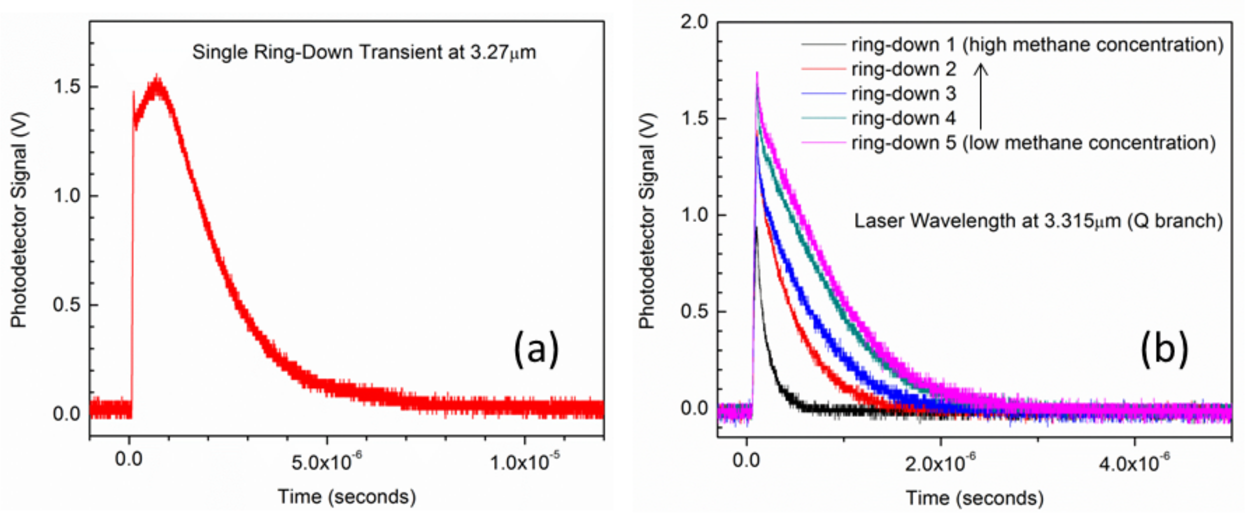


Figure 5. Cavity ring down signals from CRDS cavity without absorbing medium (panel (a)) and with a strong absorber inside (i.e. CH_4 in panel(b)). Note the decrease in ring-down time with an increasing concentration of methane gas in panel (b).

The best signal-to-noise and measurement sensitivity comes from fitting the entire transient signal to a decay time constant; however, a fast measurement can be performed by comparing the signal at a short decay time to a long decay time. A decrease in this ratio is proportional to the absorbance of the light in the cavity. This approach is illustrated in Fig. 6, for the acquisition of an infrared spectrum of ppm-level methane. The upper panel (a) of Fig 6 shows a screen-shot of the oscilloscope where the signal from the ring-down transient (yellow trace) is measured over two windows, one at early time early (blue trace) and the other later in the decay (magenta trace). The input laser wavelength is scanned and these signals are ratioed to produce the spectrum shown in panel (b) of Fig 5. The thick black trace shows the experimental methane spectrum, and the simulated spectrum from HITRAN is shown as a thin red line. The methane concentration is on the order of tens of ppm, and it is clear from both the complete saturation of the signal at the center of the intense CH_4 IR band as well as the very high S/N ratio, that the sensitivity of this instrument is well into the ppb range for this species.

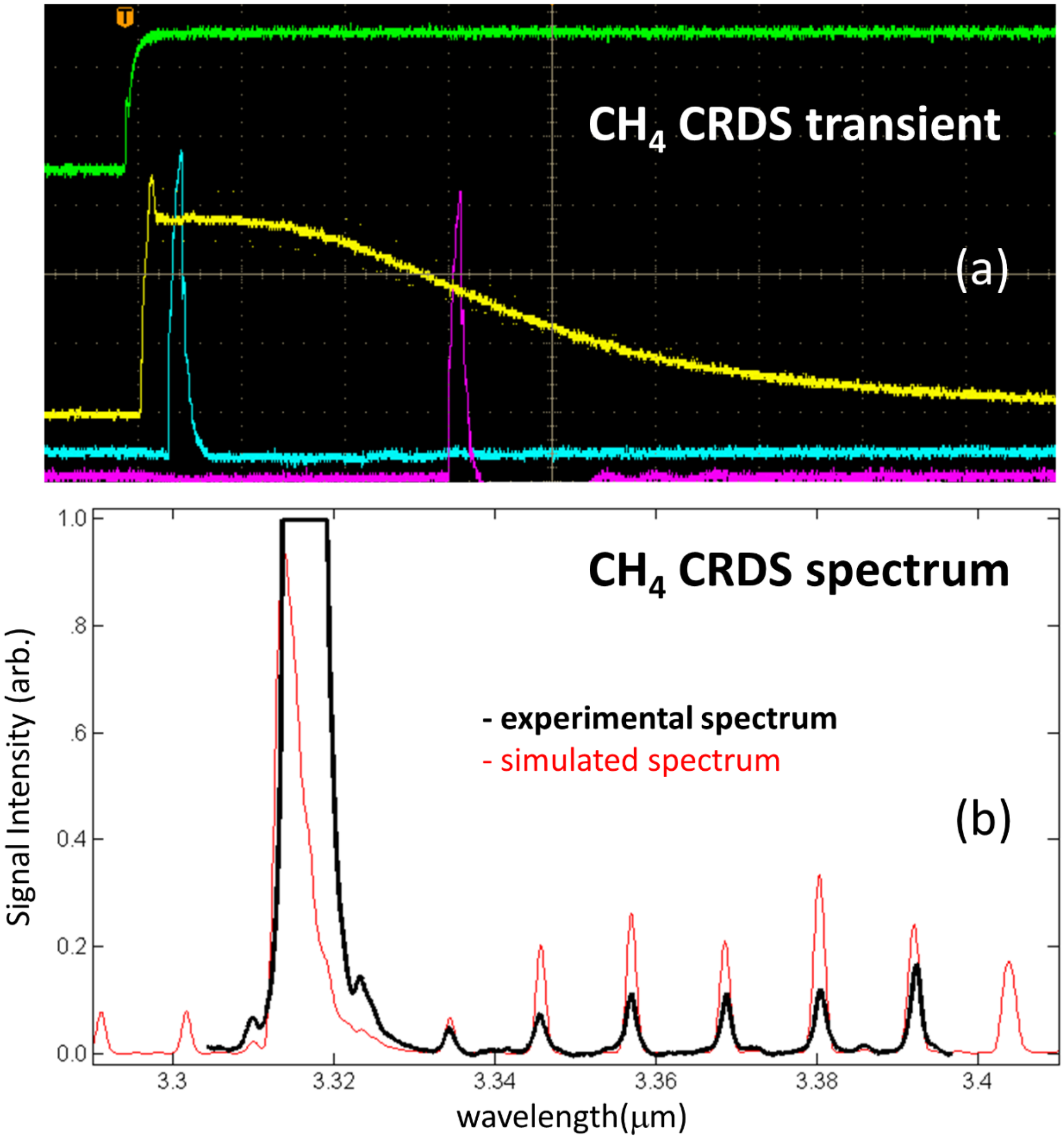


Figure 6. Cavity ring down spectrum of CH$_4$. Panel (a) shows the time trace from the oscilloscope and the selected signal time windows. The ratio of the signal in these windows as a function of laser wavelength is plotted as the thick black line in panel (b), along with the simulated spectrum from the HITRAN database.

3. DISCUSSION

3.1. Importance of Spectroscopic Resolution

The high-sensitivity laser-spectroscopy methods described, photoacoustic spectroscopy and cavity ring-down spectroscopy, both show promise for application due to their high sensitivity and simple experimental configuration. While each has its advantages and are complementary, they both are limited by the resolution of the source laser, which in this case is somewhat broad. It is possible to employ narrow bandwidth lasers for both of these measurements, and that would improve the sensitivity of the measurement systems. Due to the high impact the laser resolution has on the measurement sensitivity, the spectral response of the species investigated is examined by detailed spectral modeling at a higher resolution to demonstrate the advantages available by improvement in this parameter. The spectral modeling approach employed previously for the low-resolution laser source is repeated with the same general conditions. However, as shown in Fig. 7, a change in the resolution of the measurement and a lowering of the HCl concentration to 0.1 ppm demonstrates the extreme effect this parameter makes on the measurement sensitivity.

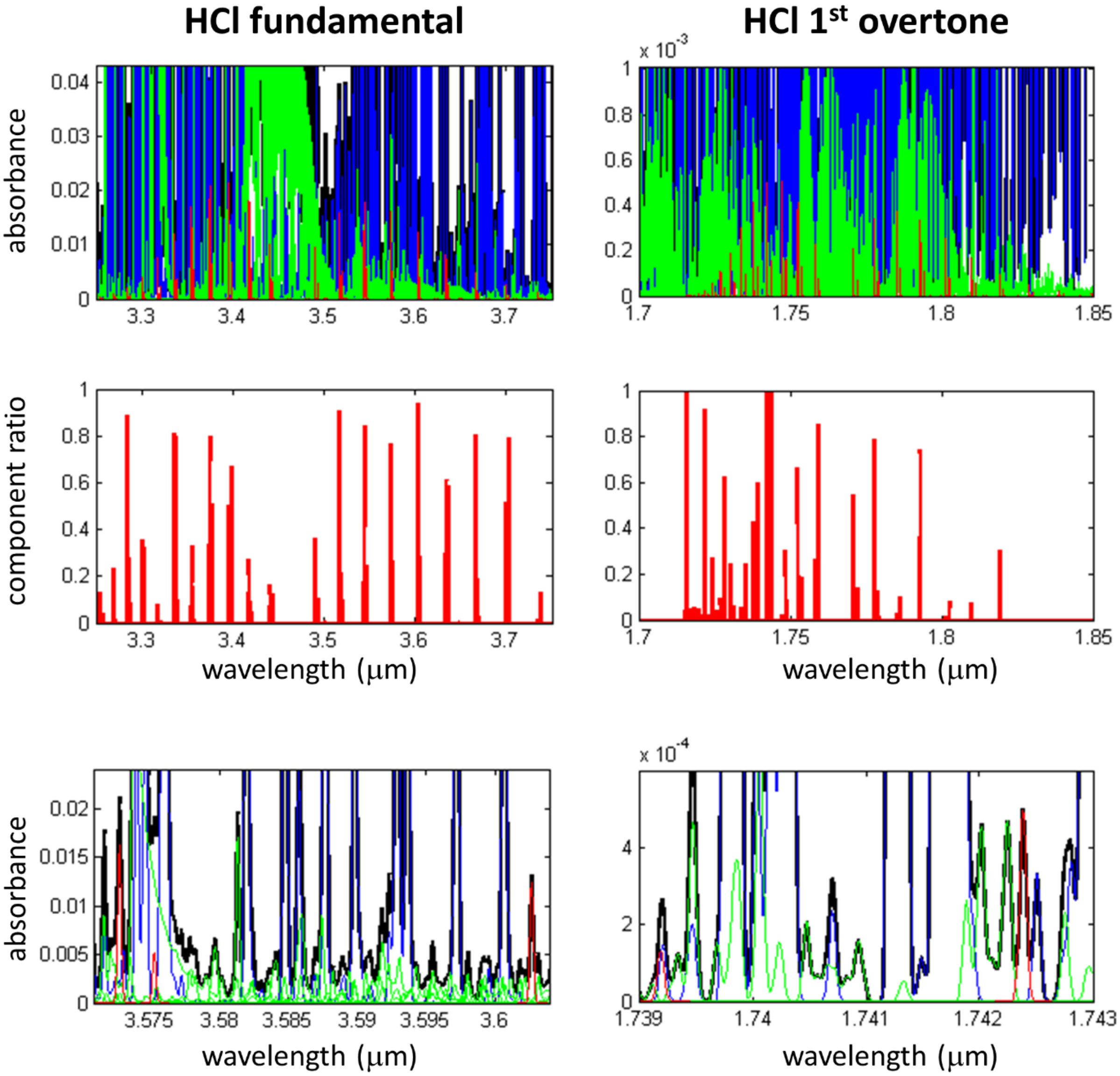


Figure 7. Modeled high-resolution spectra of HCl fundamental and overtone spectral region. The concentration of HCl is lowered to 0.1 ppm and the spectral line-width is 0.1 cm^{-1}. All other parameters are the same as Figure 1. The upper panels show the component and summed spectra (HCl is in red, H_2O is in blue, and sum is in black), the middle panels show the proportion of the HCl to the summed spectrum, and the lower panels are a zoom-in region of the wavelength region to show individually resolved spectral lines.

The spectral resolution of the previous experiments and the modeling simulation of Fig 1 is dictated by the laser bandwidth, about 3 cm^{-1}. The spectral line width at atmospheric pressure is dictated by pressure broadening effects and is typically on the order of 0.1cm^{-1}. Thus, an instrument with measurement resolution in this range will measure much narrower lines than those previously shown in this report. The pressure-broadening limited modeled spectra are shown in Fig 7. For the HCl fundamental and first overtone spectral regions the concentrations were used as listed in Table 1, but with the HCl concentration lowered a full order of magnitude down to 0.1 ppm. A comparison of Fig. 7 to Fig. 1 reveals the extreme improvement in sensitivity that results from the higher resolution. The middle panels of Fig. 7 show the proportion of the total spectral response that is due to the HCl signal. Note that there are many bands that constitute nearly the entirety of the spectral response, even at 0.1 ppm concentration. This is quite different from the low-resolution spectrum in Fig 1, because the width of the nearby lines "buried" the HCl signal. The lower panel is a zoomed-in region of the x-axis that shows how this manifests; the isolated lines that are due only to the HCl (the red trace) stand alone at certain wavelengths. The improvement from resolution not only results in a lower detectable concentration of HCl (and other species) at the fundamental region, but also extends the viable spectral range of the approach. As shown by the left panels of Fig. 7, the 1st overtone also has many isolated HCl lines, which was not the case for the low-resolution overtone spectrum of Fig 1. This improvement could provide a key advantage in the measurement of this species because the current technology for materials for use in the near-IR is somewhat better developed than for the mid-IR. This is the basis by which some currently available commercial instrumentation for HCl detection is designed.

Based on the dramatic potential improvement seen from increased measurement resolution, we explore a means to improve the resolution of our experimental approach. The possibility exists for using narrow-bandwidth lasers, but an advantage of the current broad-band laser source is wide tunability and therefore wide applicability to a number of possible emissions gas detections. With that in mind, we undertake development of an instrument that can improve the resolution of any arbitrary IR-laser source while also providing the high sensitivity of a cavity ring-down measurement, the dual etalon frequency-comb infrared spectrometer.

3.2. Advanced Techniques: Infrared Dual-Etalon Frequency-Comb Cavity Ring-Down Spectrometer

3.2.1. DEFCOM Background

As described in a recent publication [4], the first dual-etalon frequency comb spectrometer (or DEFCOM spectrometer) was constructed and implemented at Sandia National Laboratories for operation in the visible region of the EM spectrum. The system is based upon the simultaneous excitation of two cavity ring-down spectrometers, and basic principle of the instrument function is based upon the way that a single cavity (*i.e.* etalon) imprints an intensity profile on the decay time when a particular spatial mode of the cavity is excited. As shown in panel (a) Fig. 8, a single etalon imprints a "comb" of intensity maxima, the resolution of which (denoted finesse) is set by the quality of the mirrors and the spacing of which (denoted by free spectral range, or

FSR) is set by length of the cavity. This intensity pattern can be combined from two etalons excited by the same laser pulse, as shown in panel (b). If the length of the cavities (*i.e.* FSR) is slightly different, then the combination of the two intensity patterns on the photodetector will produce interference, (*i.e.* beat notes), as shown in panel (c) of Fig. 8.

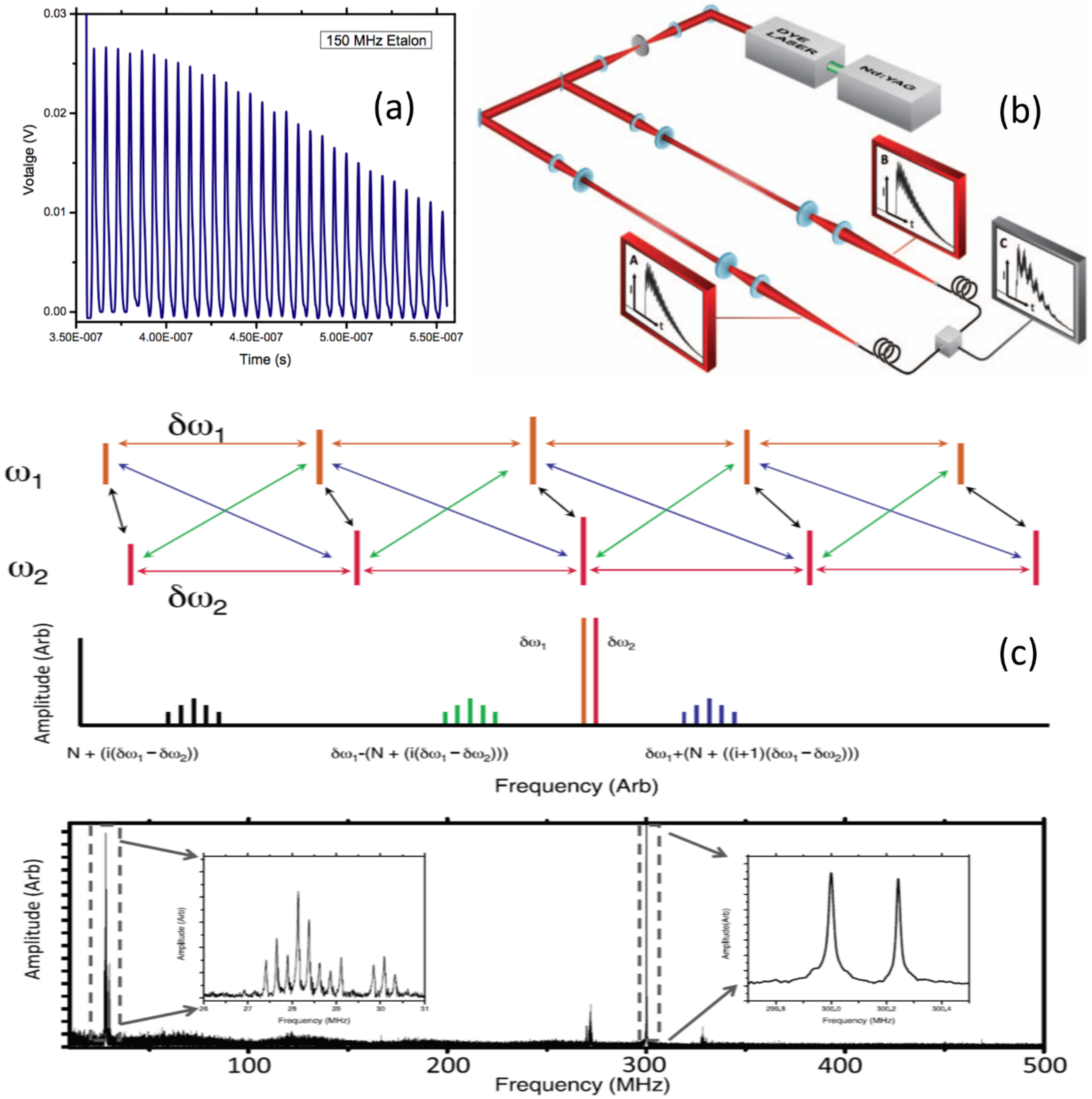


Figure 8. Illustration of principles underlying the dual-etalon spectrometer operation. Panel (a) shows the temporal intensity profile from a single etalon, panel (b) shows the instrument schematic, and panel (c) shows the heterodyne operation of the cavities in frequency space. Images reprinted from Ref. [4].

This interference is a very useful phenomenon because it moves the spectral information in the optical region of the spectrum to lower frequencies in the RF region of the EM spectrum that can be detected by standard electronics and photodetectors. It also records the light intensity with a resolution equal to the free spectral range of the cavity, which can be quite high. The principle of the spectroscopic function of the instrument is illustrated in Fig. 9. The intensity profile of the light from the optical absorption is modulated by one etalon (Comb 1), and the interference of this output with the second "readout" etalon (Comb 2) results in RF frequency beat notes with an intensity modulated by the original absorption feature and a measurement resolution equal to the FSR (f_1) of Comb 1. The fundamental advantage of the instrument is clear from examination of the spectral resolution of Fig. 9: note that it is entirely independent of the laser source bandwidth.

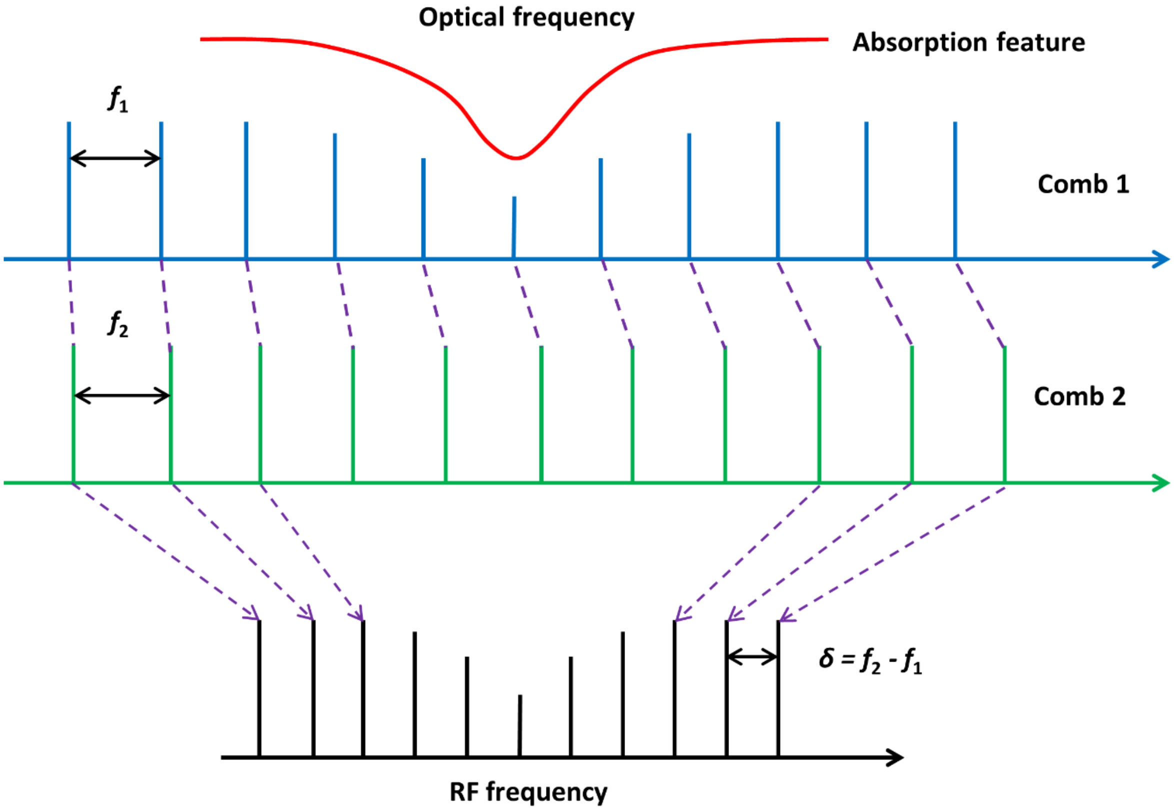


Figure 9. Schematic of high-resolution dual-etalon frequency comb absorption spectroscopy. The optical spectral information is shifted to the lower-frequency RF region through heterodyne interference between the two etalons.

The initial implementation of this new instrument was performed in the visible portion of the spectrum, and due to the facile operation with the relevant components such as photodetectors, optical fibers, highly-reflective mirrors and laser sources, our intial proof-of-principle experiments were also performed in this spectral region. A trial dual-etalon system was constructed to characterize performance parameters and develop data analysis routines. Experimental results from this apparatus are shown in Figure 10.

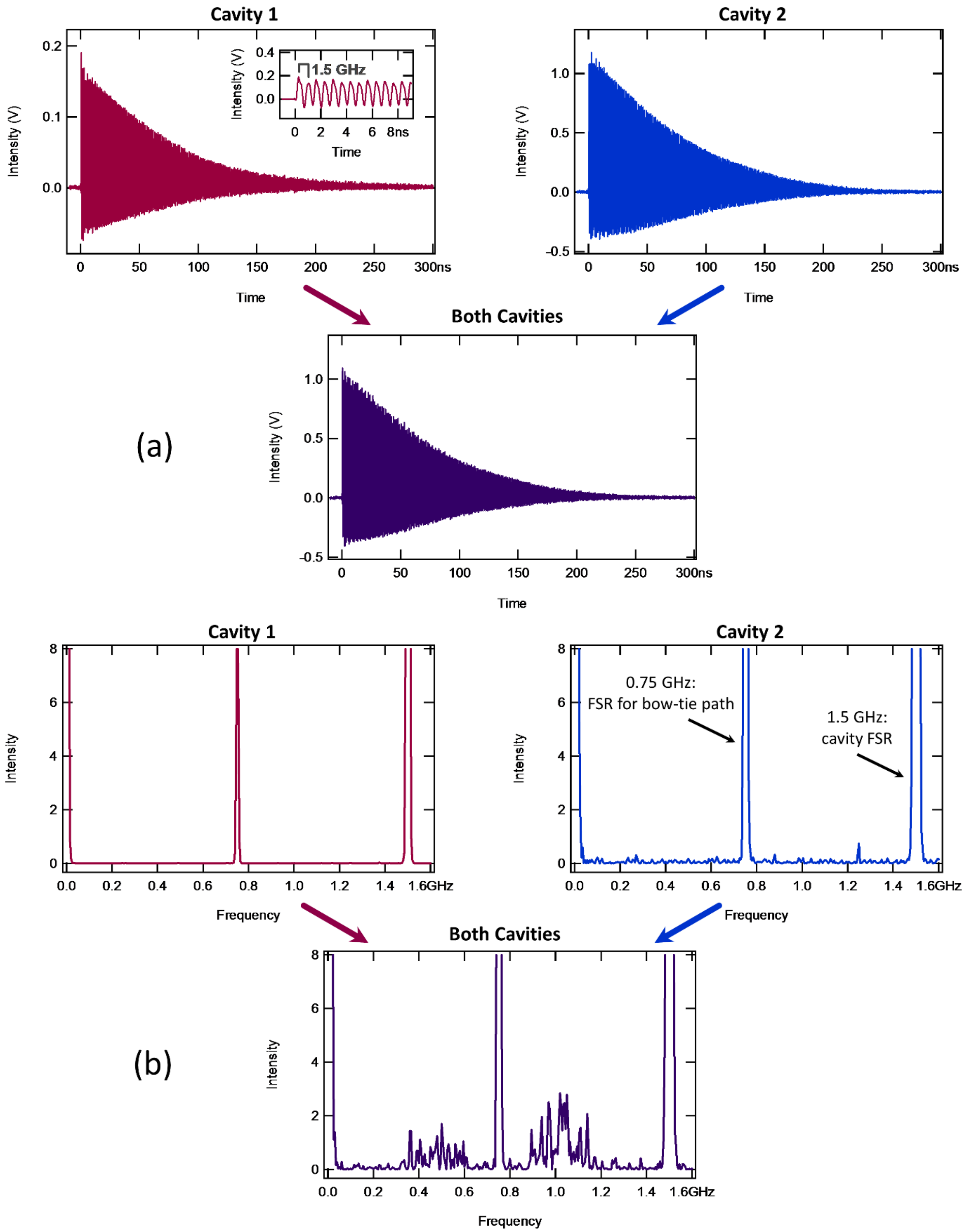
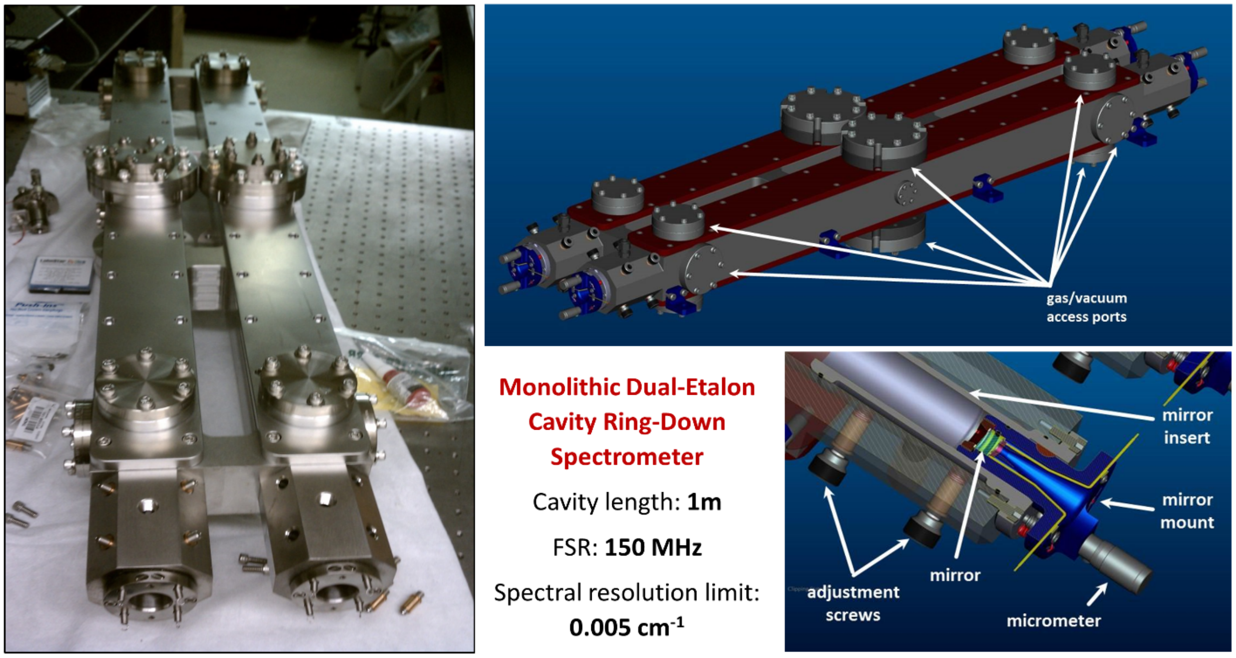


Figure 10. Experimental implementation of proof-of-principle spectrometer operating in visible spectral region. Panel (a) shows the individual and combined time traces, and panel (b) shows the Fourier transform of these traces. Note the complex frequency response due to the heterodyne activity between the cavities.

The images in panel (a) of Figure 10 show the individual etalon decay traces and the result from the combination of the two signals. The Fourier transform of the time traces from the two individual etalons in the upper portion panel (b) shows the frequency response of the individual etalons, which are each clearly dominated by the fundamental and overtone spatial modes. The Fourier transform of the combined time trace in the lower portion of panel (b) reveals the expected interference pattern that carries the spectral information of the input laser source.

3.2.2. Construction and Characterization of IR-DEFCOM Instrument

The above initial experiments demonstrate the principles and advantages of the DEFCOM instrument and significant challenges were identified from these efforts. One particular issue identified was the need to maintain the stability in the difference between the FSR (*i.e.* lengths) of the two cavities. A shift in the ΔFSR will not affect the single-shot measurement, but it will hinder shot-to-shot signal averaging. Thermal and mechanical fluctuations in cavity lengths were identified as key concerns in the proof-of-principle experiments, and thus an apparatus was designed and constructed to minimize these fluctuations. The design and actualization of the monolithic dual-etalon apparatus is shown in the images of Figure 11.



Monolithic Dual-Etalon Cavity Ring-Down Spectrometer

Cavity length: **1m**

FSR: **150 MHz**

Spectral resolution limit: **0.005 cm^{-1}**

Figure 11. Monolithic dual-etalon cavity ring-down spectrometer.

As shown by the spectral modeling and previous experimental results, the operation of the instrument in the infrared spectral region would provide enormous measurement capability. This ambition also poses a significant technical challenge, largely due to the fact that components have been well characterized for performance in the visible region of the spectrum, but the instrument has not yet been implemented in the IR region. The IR-laser source, highly-reflective IR mirrors, IR photodetector intensity response and single-cavity alignment procedures were effectively characterized and implemented to yield the single-cavity ring-down results shown in

Fig. 6, above. There are still technical challenges remaining, however, for implementation of the spectrometer in the IR region. These include the IR photodetector time response, IR beam-combining optics, and dual-cavity length stabilization. The first issue is characterized in detail below, and the latter two are under investigation. The time response of the IR detector is crucial because it dictates whether the detector is sensitive to the fundamental modes and beat notes of the dual-cavity heterodyne. These RF-range frequencies require a fast (i.e. high bandwidth) photodetector, and thus a detector which lacks sufficient high frequency (i.e short rise time) response will not be able to perform the heterodyne spectroscopy. Thus, the bandwidth of the InSb IR detector is examined in detail, as shown by Fig. 12.

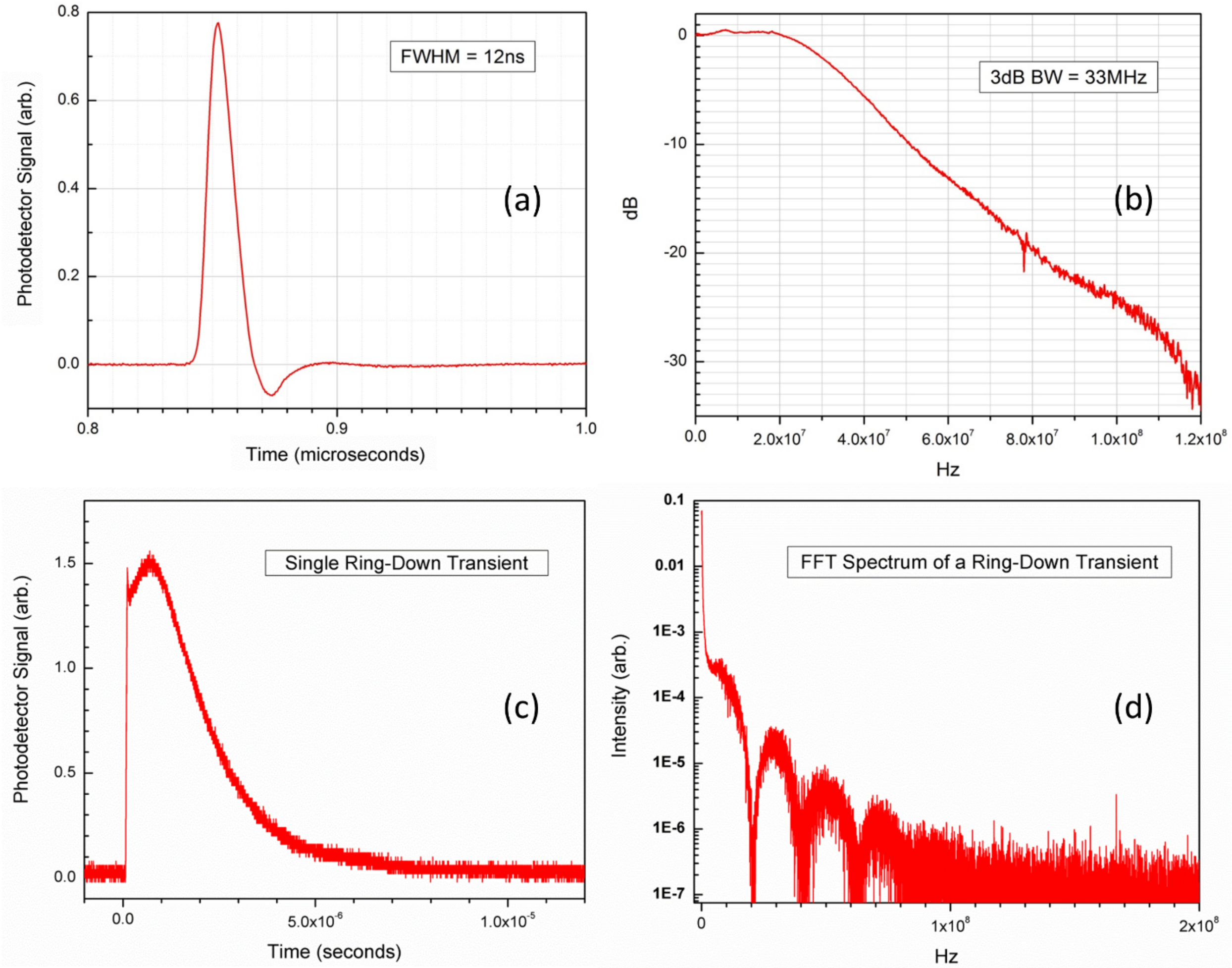


Figure 12. Characterization of IR photodetector response. The panels (a) and (c) show the time response of the detector to a single laser pulse, with and without the cavity. The FFT of these pulses show the detector bandwidth response, which is essentially limited to less that 40MHz.

The time response of the current IR detector is revealed to be somewhat slow to be effective in the IR-DEFCOM system. The rise-time of the IR detector response is too slow, (as shown in panel (a)) and thus the bandwidth too narrow (as shown in panel (b)), to measure the expected etalon fundamental frequencies at 150MHz. As shown in panel (d), the FFT of the ring-down in panel (c) reveals no evidence of the longitudinal mode in the cavity expected at 150MHz. This is a significant technical hurdle to implementation of this IR detector in the system. Effort is currently underway to improve the time response of this detector.

There are other technical hurdles to be surmounted in this instrument development effort, primary among which is the issue of optical coupling to and from the etalons. Effort is underway to determine suitable optical fiber coupling strategies, and the issue of mode-matching to the fundamental longitudinal mode of the cavity was examined in detail in our previous annual report. It is expected that successfully overcoming these issues will provide an opportunity to achieve stable dual-cavity heterodyne interference and thus an instrument with an extraordinary measurement resolution and sensitivity.

5. CONCLUSIONS

Modeling and experiments show that it is feasible to perform multi-species detection at sub-ppm levels with a low-resolution broad-band infrared laser. Target measurement species include CO_2, CH, N_2O, NO_2, SO_2, and HCl, among others, simultaneously, and without process treatment or dehumidification of the exhaust sample. Both the photoacoustic spectroscopy and cavity ring-down methods show promise in this regard. The photoacoustic spectroscopy method in particular is surprisingly sensitive despite its extremely simple configuration, and has the potential to offer an extraordinarily cost-effective platform for multi-component trace-gas measurements at the sub-ppm level. Due to the dramatic improvement in the measurement sensitivity expected from an increase in the resolution, development of a novel infrared spectrometer has been undertaken. Significant progress towards development of the first infrared dual-etalon cavity ring-down spectrometer has been achieved, and future work holds the potential to develop revolutionary capabilities in measurement sensitivity for multi-component systems with this instrument.

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