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Real-time multiplexed digital cavity-enhanced spectroscopy

TOBY K. BOYSON,¹ PAUL J. DAGDIGIAN,² KARL D. PAVEY,³ NICHOLAS J. FITZGERALD,³ THOMAS G. SPENCE,⁴ DAVID S. MOORE,⁵ AND CHARLES C. HARB^{1,*}

¹School of Engineering and Information Technology, UNSW Australia, Canberra, ACT 2600, Australia

²Department of Chemistry, Johns Hopkins University, Baltimore, Maryland 21218, USA

³Defence Science and Technology Organization, Fishermans Bend, Melbourne, Victoria 3207, Australia

⁴College of Science and Mathematics, Belmont University, Nashville, Tennessee 37212, USA

⁵Shock and Detonation Physics Group, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA

*Corresponding author: c.harb@adfa.edu.au

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Cavity-enhanced spectroscopy is a sensitive optical absorption technique but one where the practical applications have been limited to studying small wavelength ranges. This Letter shows that wideband operation can be achieved by combining techniques usually reserved for the communications community with that of cavity-enhanced spectroscopy, producing a multiplexed real-time cavity-enhanced spectrometer. We use multiple collinear laser sources operating asynchronously and simultaneously while being detected on a single photodetector. This is synonymous with radio frequency (RF) cellular systems in which signals are detected on a single antenna but decoded uniquely. Here, we demonstrate results with spectra of methyl salicylate and show parts-per-billion per root hertz sensitivity measured in real-time. © 2015 Optical Society of America

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Traditional cavity ringdown spectroscopy (CRDS) is a cavity-enhanced direct-absorption spectroscopic technique that, rather than measuring relative attenuation after a light source passes through a sample, measures the temporal decay of a light field contained within an optical cavity [1,2]. CRDS is a highly sensitive technique: the cavity provides a long effective path-length (potentially kilometers), and the measurement of a decay constant, τ , rather than relative intensity, decouples the measurement from laser intensity noise. However, the precedent (both commercially and in the literature) for instruments based on this technology is to scan across a single molecular absorption line, generally an overtone in the near infrared (IR). While useful for quantifying the concentration of simple molecules, this is not effective for the detection and identification of large, complicated molecules with broad and rotationally unresolved

spectral features, nor for analysis in the presence of interfering absorbances. There are many applications where a sensitive, direct-absorption spectroscopic technique with a broad tuning range and a rapid analysis time would extend the use of CRDS and potentially replace more complicated techniques (e.g., for the detection and analysis of explosives and chemical-warfare agents).

In order to capture spectral signatures from multiple species simultaneously and in real-time [3,4], an instrument needs to have a wide spectral bandwidth and real-time signal processing. Attempts at wideband cavity-enhanced spectroscopy have been previously demonstrated [5–8], but the implementations were complicated.

We have previously demonstrated a signal-processing method that allows data from a cavity-enhanced spectrometer to be accurately, precisely, and rapidly analyzed. With our method, the ringdown time is extracted by measuring the relative attenuation of frequency components of a modulated laser beam after it passes through an optical cavity [3,4]. Here, we show that our technique can be extended to multiplex laser sources, such that simultaneous extraction of the ringdown time from separate lasers that are co-aligned, co-resonant in the cavity, and detected on a single photodetector can be obtained. This allows us to increase the spectral coverage of the instrument without adding any extra analysis time. With this approach, we show that the only added experimental components are the second laser and an additional channel in the digital signal processing (DSP).

The multiplexing is achieved by operating the two lasers at different pulse rates, producing orthogonality in the frequency domain, shown in Fig. 1. A picture of the apparatus is presented in Fig. 2. This means that we are able to use our signal-processing technique to extract the ringdown time from both lasers simultaneously, even though, in the time-domain, the individual ringdowns often overlap. The power of working in the frequency domain is demonstrated by comparison of the scans in Fig. 3. The low time-domain signal-to-noise and the

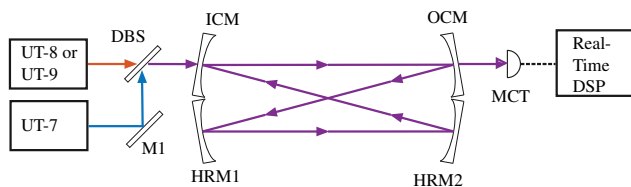


Fig. 1. Experimental schematic. The lasers (operated two at a time), labeled UT-7 and UT-8 or UT-9, are co-aligned through the use of turning mirror M1 and a dichroic beam splitter DBS. The resulting beam is aligned into the cavity, through the input coupler mirror ICM, the two high-reflecting mirrors HRM1 and HRM2, and the output coupler mirror OCM. The signal is detected by a single MCT photodetector and passed to a real-time digital signal-processing system for analysis. (The lasers are known as *Über* tuners and are commercially available from Daylight Solutions, Inc., San Diego, California, USA.)

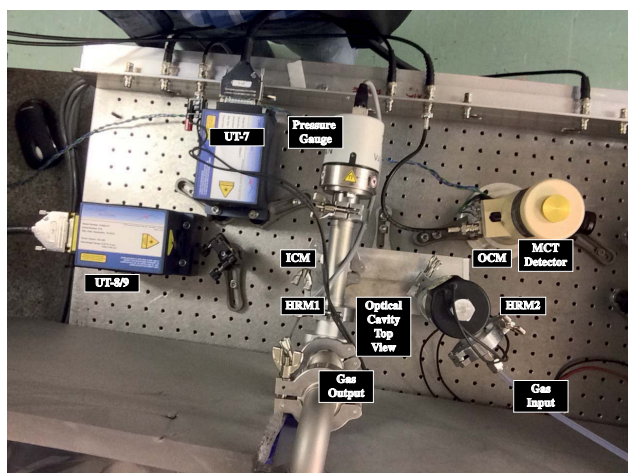


Fig. 2. Picture of the system illustrated in Fig. 1.

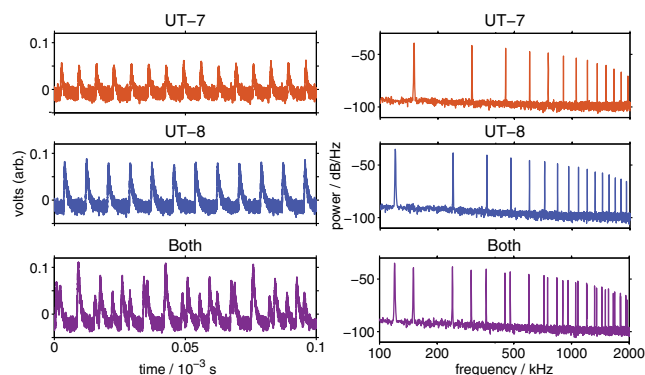


Fig. 3. Left-hand panels: time-domain signals as seen by the photodetector; right-hand panels: power spectral density of the photodetector traces. The individual laser traces (taken with one of the lasers shuttered) are shown in red and blue, while the combined traces, with the lasers running simultaneously, are shown in purple.

fact that the ringdowns from each laser regularly occur at the same time would make it very difficult to analyze the combined time trace using traditional fitting techniques (such as non-linear least squares). In the frequency domain, however, the frequency components of each laser are clearly resolvable; moreover, there is more than 60 dB of signal-to-noise at each of the four frequencies (the fundamental and second harmonic of each modulated beam) that we have chosen to analyze. We note that this analysis technique is not limited to two lasers; the number of lasers may be arbitrarily scaled, given enough demodulation channels.

Techniques to increase the bandwidth and throughput of cavity-enhanced spectroscopies increasingly use frequency combs (e.g., [5,6]). While the results from such experiments are impressive, they are complicated and expensive to setup and maintain. In contrast to frequency-comb-based experiments, our method requires no active stabilization of any of the elements of the spectrometer; the lasers are allowed to scan freely (for this work, they are not even synchronized to each other), and the cavity is totally unsterilized. This significantly reduces the experimental complexity and results in a simple, robust instrument that is well-suited to field deployment. By using pulsed lasers, we eliminate the need for a separate switching device (such as an acousto-optic modulator), again reducing the experimental complexity and increasing the robustness of the instrument.

The experimental schematic, shown in Fig. 1, has the rapidly pulsed quantum cascade lasers co-aligned into a four-mirror cavity through an input coupler mirror and exiting through an identical output coupler mirror. Although any optical configuration could be used, this setup minimizes the back-reflections to the lasers while maximizing the single-pass pathlength. With this setup, the effective optical pathlength is greater than 300 m. The optical fields exiting the cavity are measured on a mercury-cadmium-telluride (MCT) detector. This combined signal is sent to a real-time DSP system and passed to MATLAB for analysis. To take a spectrum, the headspace of a sample of interest is drawn into the cavity by evacuating the cavity first and then drawing the sample in through a vacuum valve. The lasers are set to scan freely and a single forward scan of each laser is captured. The raw information is converted in real time to the ringdown lifetime. The absorbance spectrum is calculated by comparing this ringdown time to that acquired from a scan when the cavity is empty [9].

In order to demonstrate the utility of our multiplexing technique, we have taken spectra of methyl salicylate, a chemical often used in both sports rubs (for short-term local analgesia) and as a chemical-warfare simulant [10] (due to its physical properties that are similar to the chemical warfare agent sulfur mustard). The spectra shown in the top two panels of Fig. 4 were taken by drawing a sample from the headspace of a small vial containing ≈ 5 mL of methyl salicylate into the spectrometer. These spectra were recorded using different pairs of the quantum cascade lasers, scanned asynchronously. The cavity was first pumped down to below 10^{-4} mbar and then allowed to fill to atmospheric pressure with the headspace vapor. We note that the sample will also draw in room air, resulting in additional peaks from water absorbances along with any other contaminants in the room at the time. All spectra were taken as a single wavelength scan, taking less than 5 s to acquire data from both lasers. The scan time is limited by the scan rates

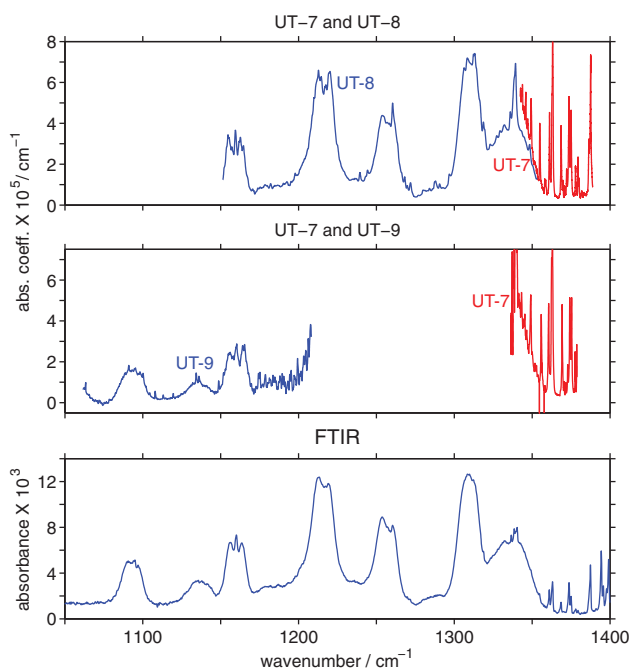


Fig. 4. Methyl salicylate processed spectra generated by (top) UT-7 and UT-8 running simultaneously and asynchronously and (middle) UT-7 and UT-9 running simultaneously and asynchronously. The additional peaks in the UT-7 part of the spectrum are from water absorbances. Both spectra are from a single scan; there is no averaging applied. The bottom trace shows a reference spectrum taken with an FTIR spectrometer for comparison.

of the lasers rather than the data analysis time. The combined system covers the wavenumber range 1065 to 1390 cm^{-1} or a scan width of 325 cm^{-1} , which corresponds to a wavelength span of ≈ 2200 nm.

The bottom trace of Fig. 4 shows the spectrum of methyl-salicylate vapor recorded with a commercial Fourier transform IR (FTIR) spectrometer (Nicolet IS-5), for comparison with our recorded spectra. The spectra from our instrument are very similar to that from the FTIR and display clearly the vibrational bands of methyl salicylate; these bands are broad and not rotationally resolved. All three scans in Fig. 4 display sharp lines due to the water vapor in the room air. It should be noted that the wavelength scan rate of the quantum cascade lasers is not constant, which introduces some nonlinearity in the recorded spectra. The spectra displayed in the top two panels of Fig. 4 were linearized by using the water vapor lines and the sharp features (band heads) in the methyl-salicylate spectrum. This scanning nonlinearity is not important for the applications for which we intend to use this instrument because we will be comparing spectra to an internal library. By analyzing the noise present on a background trace, and by noting the absorption cross sections for methyl salicylate in this wavelength range, we are

able to report a noise-equivalent absorption of approximately 1 ppb/ $\sqrt{\text{Hz}}$.

We have shown here that our signal-processing technique can be extended to the use of multiple lasers without significant increases in experimental complexity and without any additional processing time. While we have used mid-IR lasers here, the technique is applicable to any wavelength range. We believe that this technique has great promise to extend the use of CRDS and to potentially supplant existing gas-detection techniques.

A number of improvements can be made to our present experimental apparatus to decrease the signal acquisition time and/or to increase the covered spectral range. For the purpose of identifying bands of unknown species, the wavenumber scan can be linearized with the inclusion of an auxiliary etalon marker channel in the apparatus. Developments of quantum cascade lasers will undoubtedly increase their wavelength range to cover a complete mirror reflectivity range, but if the scan rate is the same, then signal collection time will increase. Faster scanning lasers (e.g., distributed feedback [DFB] lasers) could be employed as laser sources. It is also possible to employ more than two lasers to cover the mirror reflectivity range; this approach would be limited only by the availability of suitable dichroic mirrors for combining the laser beams.

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