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**by Logan S Marcus, Ellen L Holthoff, John F Schill, and Paul M Pellegrino**

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# Photoacoustic chemical sensing: ultracompact sources and standoff detection

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## ABSTRACT

Photoacoustic spectroscopy (PAS) is a useful monitoring technique that is well suited for trace detection of gaseous and condensed media. We have previously demonstrated favorable PAS gas detection characteristics when the system dimensions are scaled to a micro-system design. This design includes quantum cascade laser (QCL)-based microelectromechanical systems (MEMS)-scale photoacoustic sensors that provide detection limits at parts-per-billion (ppb) levels for chemical targets. Current gas sensing research utilizes an ultra compact QCL, SpriteIR, in combination with a MEMS-scale photoacoustic cell for trace gas detection. At approximately *one tenth* the size of a standard commercially available QCL, SpriteIR is an essential element in the development of an integrated sensor package. We will discuss these results as well as the envisioned sensor prototype. Finally, expanding on our previously reported photoacoustic detection of condensed phase samples, we are investigating standoff photoacoustic chemical detection of these materials and will discuss preliminary results.

**Keywords:** photoacoustic, spectroscopy, laser Doppler vibrometer, standoff

## 1. INTRODUCTION

There will always be a critical need for detection and identification of hazardous materials. The desire to make improvements in sensitivity and safety of those measurements is the impetus for basic research conducted at the United States Army Research Laboratory. Photoacoustic spectroscopy (PAS) is a sensitive and flexible chemical sensing technique. There are several related sensing methodologies that measure different facets of the same physical phenomena under the umbrella of photoacoustic (PA) sensing. Photothermal deflection (PD), photothermal interferometry (PTI), and photothermal lensing (PTL) measure temperature fluctuations with lasers and optical detectors.<sup>1-6</sup> Traditional PA techniques use a microphone to measure the pressure waves correlated to the temperature fluctuations measured by the aforementioned thermal techniques. PAS techniques have been shown to be capable of parts-per-billion (ppb) level detection of gaseous analytes,<sup>7</sup> and molecular discrimination.<sup>8</sup> In the realm of solid spectroscopy, PAS has been used for condensed phase sample interrogation and depth profiling in layered samples.<sup>9</sup> This versatility makes PAS one of the premier chemical sensing technologies.

PAS shares its basic foundation with other electromagnetic spectroscopic techniques. At the most basic level, a PA spectrometer is constructed from three main components, the sample holder, an excitation source, and a detection device. In traditional PAS, for example, the sample chamber is a resonant cavity in which the detection device, a microphone, is located to measure the resulting acoustic signal produced when the sample is exposed to an intensity modulated excitation source, most commonly a laser.<sup>8</sup> Research into improving the size, versatility, or sensitivity of the PA sensor is important for the overall goal of the PA sensing platform.

In PAS, the measurable physical processes that result from the absorption of an intensity-modulated excitation source manifest as two distinct responses when studying condensed phase samples. The first is the periodic expansion and contraction of the surface that is subject to a fluctuating temperature profile induced by absorption of the excitation beam. Second, there is a transfer of heat from the surface of the analyte to the boundary gas layer adjacent to the heated surface. This heat transfer produces a thermal gradient, which in turn produces a periodic pressure fluctuation – the acoustic part of the PA effect. Traditional PAS with a microphone as the sensor measures only the pressure fluctuations; in current work we measure both.

Previous work has been accomplished in miniaturizing the PA cell, microphone, and the excitation source.<sup>7, 10</sup> The work described herein is basic research aimed at increasing the versatility of PAS. We describe a standoff PA sensor, used to

measure the PA response of a condensed matter sample. The sample chamber, found in most PAS applications, is eschewed so that the spectroscopic excitation and detection apparatus can be moved away from the target being investigated; this is done with the safety of the sensor operator in mind. Standoff sensing has obvious utility when dealing with hazardous substances, and the elimination of the traditional PA cell also has the benefit of lessening or eliminating the sample preparation requirements. This allows greater flexibility for the sensing platform on both what it can measure and where the measurement can be taken. This investigation into standoff PAS is designed to form the basis of further research into condensed phase photoacoustics at a distance.

## 2. METHODOLOGY

### 2.1 Experimental Setup

Figure 1 depicts the basic elements required for the standoff PA sensing experimental setup. The experiment is not drawn to scale, and minor components are neglected for clarity. Though there is no sample holder, the rest of the setup resembles the typical electromagnetic spectroscopy setup. The quantum cascade laser (QCL) is the modulated excitation source used to induce the PA effect, and the laser Doppler vibrometer (LDV) is the sensing apparatus that allows for the PA measurement to be completed at distance. The components are discussed in depth later.

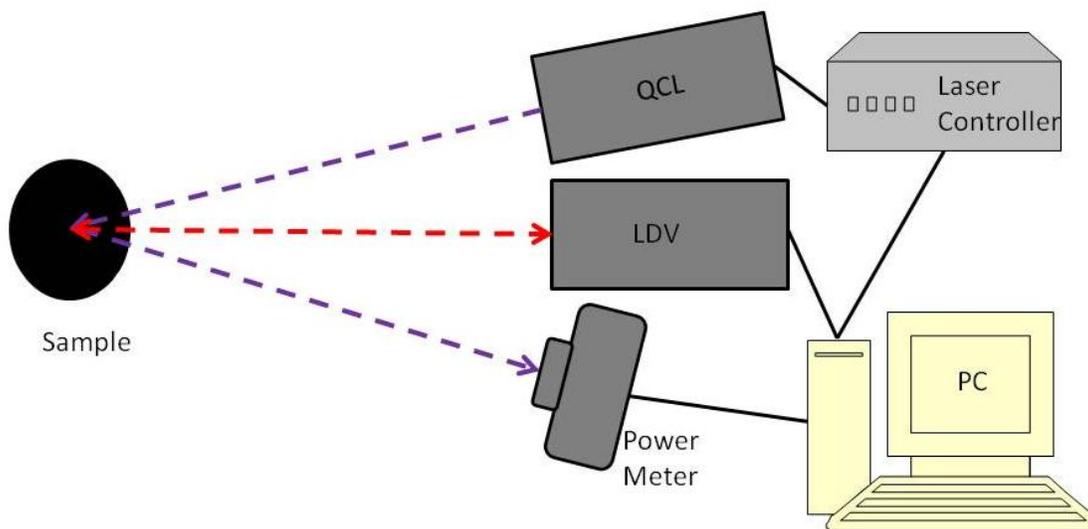


Figure 1. Block diagram of the standoff PA sensing setup.

### 2.2 Excitation Source

The PA effect is initiated by an analyte absorbing periodically modulated electromagnetic radiation. The excitation source for this standoff PAS experiment is a QCL that is both the source of the electromagnetic radiation required for PA excitation and the source of the intensity modulation. The QCL used was a broadly tunable, external cavity, pulsed QCL manufactured by Daylight Solutions (DLS 11088). The continuous wavenumber tuning range of the QCL was between  $1015\text{ cm}^{-1}$  to  $1240\text{ cm}^{-1}$ . No external cooling was required to run the laser at a pulse rate of 18.4 kHz; the pulse width was  $1\text{ }\mu\text{s}$  with a current of 1600 mA and a duty cycle of 1.8%. The QCL is used to excite a solid target, and the remaining reflected radiation is captured by a power meter (Ophir Optronics Nova II).

Concurrent research is ongoing into improving the excitation source for PAS. SpriteIR is a prototype laser developed during an Army Small Business Innovation Research (SBIR) Phase II Development program.<sup>10</sup> This source offers performance, in a smaller package (a 2 in. cube), that is associated with larger lasers. The laser prototype contains a voice coil motor-based tuning mechanism that utilizes both sweeping and stepping motions for rapid wavelength

tunability. The SpriteIR is tunable from  $1000\text{ cm}^{-1}$  to  $1205\text{ cm}^{-1}$  ( $10.0\text{ }\mu\text{m}$ – $8.3\text{ }\mu\text{m}$ ) and has a spectral resolution of  $1\text{ cm}^{-1}$ . This initial research uses a commercial QCL as the excitation source, and future SpriteIR use in LDV PAS is planned.

### **2.3 Laser Doppler Vibrometer (LDV)**

A standard microphone, though well suited for traditional cell-based PAS, is not the appropriate measurement tool for ranged measurements of the PA effect. Instead, we use an LDV manufactured by Polytec (CLV-2534) to measure the periodic system changes that arise from PA excitation. The LDV and QCL beams are carefully aligned to intersect at the same point on the surface of the target. The LDV, a sophisticated Michelson interferometer, measures the PA system response by measuring the total change in optical path length of a probe HeNe laser beam reflected off of the expanding surface and travelling twice through the heated boundary layer adjacent to the heated surface. The measurement is made by examining the interference of the recombined probe and reference beams.

The LDV measurement cannot discriminate between path length changes produced by the expansion and contraction of the analyte surface and path length changes arising from index of refraction variations brought about by the induced temperature and pressure fluctuations in the heated boundary layer. We assume that the signals are in phase and constructively contribute to the total PA signal measured by the LDV. A commercial interferometer was selected to take advantage of the engineering work already expended by the manufacturer. Hardware and software for computer control and data collection came from Polytec, and eliminated the need for time consuming development in those areas.

### **2.4 Data Acquisition**

The LDV measures the time rate of change of the interference signal between a single split laser beam recombined at a photodiode. That signal is digitized as a voltage and recorded as a function of time by the digital signal analyzer built into the included software from Polytec (VibSoft-1000). The voltage signal is then Fourier transformed to obtain the frequency spectrum of the signal. The PA signal is highly frequency specific because it is produced by a periodically modulated phenomenon. The frequency spectrum of the PA signal measured by the LDV is overwhelmingly concentrated at the modulation frequency of the QCL. The signal is averaged fifty times to reduce signal fluctuations due to background noise when recording experimental spectra.

The LDV is wholly dependent on the reflection from the sample surface for signal generation. That light must be collected in sufficient quantity to recombine with the reference beam to perform any sort of measurements. This requirement puts limits on how the optical components can be placed and even the analytes that can be studied. There is a downward progression that is seen in the signal to noise ratio (SNR) of the LDV measurement as the reflected light quality is decreased. The goal of this work is to serve as a test system examining the basics of standoff pulsed PAS as it pertains to chemical sensing.

## **3. RESULTS AND DISCUSSION**

The focus of the experimental work described in this paper is the reproduction of an absorption spectrum of a basic analyte at a distance. This work will form the basis for future work developing a standoff sensor platform for hazardous chemicals. The chosen analyte is polytetrafluoroethylene (PTFE), a polymer commonly known under the DuPont brand Teflon<sup>®</sup>. PTFE was chosen because it has absorption features in the wavelength range of the tunable QCL and because it is stable at room temperature.

Additionally, PTFE has been used previously in traditional cell-based PA experiments and the results of those experiments are the reference spectra to which the standoff LDV PA spectra are compared. Comparison of data from two different collection methodologies is made easier by keeping the experimental parameters as close together as possible. The sample material was cut from the same sheet of PTFE, the samples were of similar size, and the QCL used to excite the PA effect in both methods was the same. Not all of the experimental parameters were able to be replicated between experiments.

For the standoff measurements, a 2.54 cm diameter circular piece of 0.75 mm thick PTFE was placed into an adjustable optical mount. The optical mount does not mimic the function of the traditional PA cell, merely it is used to complete alignment between the surface and the normally incident LDV beam. The PTFE sample and the LDV were set apart at a distance of 0.9 meters to investigate the standoff capability of the sensing method; this measurement tests the ability of both the LDV and the QCL to operate at standoff distances.

There are differences between the two experimental setups beyond distance and measurement tools. The reference data was collected using a resonant PA cell where the resonant modes of the cell were used to amplify the acoustic signal to improve SNR.<sup>9</sup> The standoff data was collected without the benefit of cell based signal amplification at a modulation frequency higher than that of the cell based data. Spectral resolution of the standoff PA data is  $2\text{ cm}^{-1}$ , and the cell based PA data has twice the resolution at  $1\text{ cm}^{-1}$ . The wavenumber spectra were compiled over most of the tuning range of the QCL, from  $1050\text{ cm}^{-1}$  to  $1238\text{ cm}^{-1}$  ( $9.52\text{ }\mu\text{m}$  –  $8.07\text{ }\mu\text{m}$ ). Figure 2 below compares the measured LDV PA spectrum (blue) to the microphone PA cell based spectrum (red) both of which have been normalized for comparison purposes.

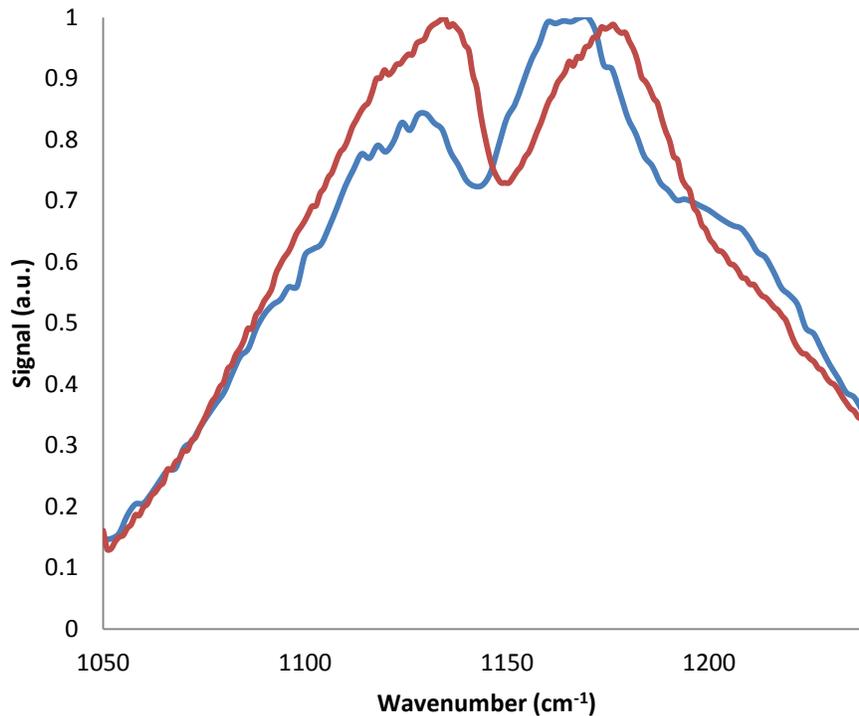


Figure 2. Normalized photoacoustic spectra for PTFE.

There is clear, but not perfect, agreement between the standoff and cell-based PTFE spectra. The two peaks of the spectrum are clear in both data sets, and the relative position of both peaks is constant as well. There is a slight translation towards the low wavenumber end of the spectrum for the local minimum located at around  $1140\text{ cm}^{-1}$ . This translation remains constant when comparing the higher wavenumber peak in the two spectra. The differences in some of the experimental parameters contribute to the slight shift of the higher wavenumber peak. Additionally it is unknown how much of a difference the measurement methods make on the recorded spectra. Both the LDV and the microphone measure the acoustic disturbance created by the photoacoustic effect, but the LDV also measures the temperature fluctuations and surface motion without discriminating between signal sourcing. This major difference point is a possible contributor to the shifted spectrum. If the phases of the signal generating mechanisms are not synchronized, the different excitation frequencies of the methods could generate the observed spectral deviation.

The standoff PTFE spectrum is accurate enough to warrant further investigation into the technique. Changing the size and shape of the PTFE target is one such avenue, and it might help to isolate the vibrational modes of the thin excited

sample from measured signal. PTFE is not the end goal analyte, and it will be enlightening to see if the slight shift in spectral features is related to the choice of PTFE as the analyte. There are several avenues of planned research to investigate standoff spectroscopy. Areas of focus include investigation of new analytes, analyte/substrate interaction, and analyte deposition methods. The work on standoff PAS will build a knowledge base for LDV spectroscopy that can be used as a foundation for the development of a standoff chemical detection and identification device.

#### 4. CONCLUSION

We have successfully demonstrated the use of a commercial LDV for standoff sensing of the photoacoustic effect for spectroscopy. This sensing paradigm is a step towards the development of safer chemical identification and detection methods, and the use of commercially available components increases the versatility. Planned future work will investigate the limitations of the system and build a library of analytes of interest. Parallel work completed on the evaluation of new excitation sources will be combined with the LDV sensor research to facilitate the development of a smaller sensing system.

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#### 6. REFERENCES

1. W. Jackson and N. M. Amer, *Piezoelectric photoacoustic detection: theory and experiment*, J. Appl. Phys **51** (6), 3343-3353 (1980).
2. M. A. Olmstead, N. M. Amer and S. Kohn, *Photothermal displacement spectroscopy: an optical probe for solids and surfaces*, Applied Physics A **32**, 141-154 (1983).
3. J. Opsal, A. Rosencwaig and D. L. Willenborg, *Thermal-wave detection and thin-film thickness measurement with laser beam deflection*, Applied Optics **22** (20), 3169-3176 (1983).
4. V. Aranchuk, L. S. Marcus, J. Sabatier and R. Raspert, *Application of laser Doppler vibrometer for standoff photoacoustic detection of solid chemicals*, Proceedings of the Military Sensing Symposia (2010).
5. L. C. M. Miranda, *Photodisplacement spectroscopy of solids: theory*, Applied Optics **22** (18), 2882-2886 (1983).
6. J. C. Murphy and L. C. Aamodt, *Photothermal spectroscopy using optical beam probing: mirage effect*, J. Appl. Phys **51** (9), 4580-4588 (1980).
7. E. L. Holthoff and P. M. Pellegrino, *Development of a MEMS-scale photoacoustic chemical sensor for trace vapor detection*, SPIE Proceedings **7304** (2009).
8. E. Holthoff, J. Bender, P. Pellegrino and A. Fisher, *Quantum Cascade Laser-Based Photoacoustic Spectroscopy for Trace Vapor Detection and Molecular Discrimination*, Sensors **10**, 1986-2002 (2010).
9. E. L. Holthoff, L. S. Marcus and P. M. Pellegrino, *Quantum cascade laser based photoacoustic spectroscopy for depth profiling investigations of condensed-phase materials*, Applied Spectroscopy **66** (9), 987-992 (2012).
10. E. L. Holthoff, L. S. Marcus and P. M. Pellegrino, *Towards the Realization of a MEMS-based Photoacoustic Chemical Sensor Using Ultracompact EC-QCL (SpriteIR)*, Proceedings of the IEEE Sensors Conference, 1-4 (2013).

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