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Photoacoustic Spectroscopy for Chemical Detection

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Photoacoustic Spectroscopy for Chemical Detection

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ABSTRACT

The Global War on Terror has made rapid detection and identification of chemical and biological agents a priority for Military and Homeland Defense applications. Reliable real-time detection of these threats is complicated by our enemy's use of a diverse range of materials. Therefore, an adaptable platform is necessary. Photoacoustic spectroscopy (PAS) is a useful monitoring technique that is well suited for trace detection of gaseous media. This method routinely exhibits detection limits at the parts-per-billion (ppb) or sub-ppb range. The versatility of PAS also allows for the investigation of solid and liquid analytes. Current research utilizes quantum cascade lasers (QCLs) in combination with an air-coupled solid-phase photoacoustic cell design for the detection of condensed phase material films deposited on a surface. Furthermore, variation of the QCL pulse repetition rate allows for identification and molecular discrimination of analytes based solely on photoacoustic spectra collected at different film depths.

Keywords: Photoacoustic spectroscopy, quantum cascade laser, solid-phase, depth profiling

1. INTRODUCTION

The rapid detection and identification of hazardous materials (i.e., chemical, biological, energetic) deposited on surfaces is of great importance for military and homeland defense applications. A non-destructive method for determining the composition of unknown materials deposited on a surface, as well as discrimination between the material and the surface, is an attractive analysis tool. Photoacoustic spectroscopy (PAS) offers unique capabilities for investigating condensed phase samples due to its simplicity and resistance to scattering effects, which is often an issue associated with other common techniques such as infrared (IR) reflectance spectroscopy.^{1, 2} Additionally, PAS, as well as other photothermal techniques, have proven advantageous for depth profiling, as they offer a frequency dependent, and therefore adjustable, probe depth.

Photothermal spectroscopy encompasses a group of highly sensitive methods that can be used to detect trace levels of optical absorption and subsequent thermal perturbations of the sample in gas, liquid or solid phases. The underlying principle that connects these various spectroscopic methods is the measurement of physical changes (i.e., temperature, density, or pressure) as a result of a photo-induced change in the thermal state of the sample. Examples of photothermal techniques include photothermal interferometry (PTI), photothermal lensing (PTL), photothermal deflection (PTD), and PAS. All photothermal processes consist of several linked steps that result in a change of the state of the sample. In comparison to other photothermal techniques, which measure the refractive index using combinations of probe sources and detectors, PAS measures the pressure wave produced by sample heating.³ Successful applications of PAS in gases and condensed matter have made this a notable technique.

Investigating solid samples using the photoacoustic technique is advantageous as it allows optical absorption measurements to be made for optically opaque samples and is insensitive to scattered light. This unique capability of photoacoustic spectroscopy for the investigation of condensed phase samples is attractive,⁴⁻⁷ especially in comparison to commonly used passive IR reflectance techniques. Reflectance data can depend strongly on the refractive index of the sample, the particle size and size distribution, packing density, and sample homogeneity.² The surface on which the sample is deposited may also interfere with the collection of a quality reflectance spectrum. In contrast, PAS allows for discrimination between the sample and surface or different sample layers. PAS of condensed phase samples is also often applied to depth profiling of layered samples and two- and three-dimensional tomographic imaging for biomedical applications.⁸⁻¹⁰ Although there have been several reports discussing the use of tunable infrared sources, such as quantum cascade lasers (QCLs) and CO₂ lasers, to obtain photoacoustic spectra of gases,¹¹⁻¹⁸ the application of these sources in photoacoustic experiments on condensed phase samples are minimal.^{7, 19, 20} In this current work, we report on the use of a continuously tunable pulsed QCL, in combination with a photoacoustic cell designed for solid and liquid

Quantum Cascade Laser. A broadly tunable, external cavity pulsed QCL (Daylight Solutions 11088) was employed as the excitation source for the sensing system. The laser was powered by an external controller (Daylight Solutions TLC 1001). The QCL was continuously tunable from 1015 cm^{-1} to 1240 cm^{-1} ($9.85\text{ }\mu\text{m}$ – $8.06\text{ }\mu\text{m}$) and had a spectral resolution of 1 cm^{-1} . The pulsed source operated at room temperature with convective cooling. Current pulses of 1600 mA with a $1\text{ }\mu\text{s}$ duration and pulse rate ranging from 10.0 kHz to 40.0 kHz corresponded to duty cycles of 1.0% to 4.0% and provided average optical powers of 1.60 mW to 6.50 mW, respectively.

Photoacoustic Cell. An aluminum cylindrical photoacoustic cell was fabricated in-house to meet our design specifications (0.001 in. tolerance) using standard machining techniques. The cell consisted of a 4 mm long resonator with a diameter of 16 mm. The closed cell had a zinc selenide window (Edmund Optics, model: NT63-210) on one side of the resonator and the sample substrate material on the other. The cell was equipped with a microphone (Knowles, model: FG-23629), which was wired to a power supply (AA battery) and a lock-in amplifier (via a BNC cable). Figure 2 provides a simplistic illustration and a photograph of the photoacoustic cell.

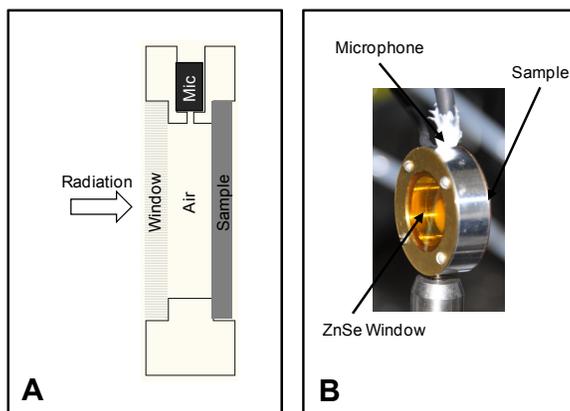


Figure 2. (A) Basic photoacoustic cell components and orientation, (B) photograph of the photoacoustic cell used when collecting data.

Data Acquisition. The signal detected by the microphone was extracted using the voltage input on a lock-in amplifier (Stanford Research Systems SR530) with a time constant of 3 s operating at the pulse frequency of the laser. LabVIEW (National Instruments, version 2009) was used to create a virtual instrument (VI) to read and record the voltage outputs from the lock-in amplifier under various conditions directly to a personal computer (PC). The VI was programmed to collect the X (in-phase), Y (quadrature), R (amplitude) and θ (phase angle) components of the photoacoustic signal. Frequency spectra were obtained by holding the laser wavelength constant while scanning the specified laser pulse frequency range. This allowed for the determination of the resonance frequencies for the photoacoustic cell. 50 measurements were made at each increment, and a mean value was calculated and recorded for the subsequent construction of a frequency spectrum. Photoacoustic spectra were obtained by holding the laser pulse frequency constant while scanning the laser wavelength range. 50 measurements were made at each increment, and a mean value was calculated and recorded for the subsequent construction of a photoacoustic spectrum. For each analyte, the photoacoustic spectrum revealed a constant background signal, attributed to the absorbance of laser radiation by the cell windows and walls.

All photoacoustic data was collected at room temperature (average $21\text{ }^{\circ}\text{C}$) and an average relative humidity of 25%.

3.3 Instrumentation

All Fourier transform infrared (FTIR) absorbance spectra were collected using a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a potassium bromide (KBr) beamsplitter and a mercury cadmium telluride (MCT)-A (narrow band– 650 cm^{-1} cutoff) detector. A GladiATRTM (Pike Technologies) accessory was used to collect infrared spectra of solid samples using attenuated total reflectance (ATR). Each spectrum was acquired at a resolution of 2.0 cm^{-1} averaging 100 scans.

3.4 Sample Preparation

Precision micro-pipettes were used to deposit known volumes of urea and TNT solutions onto ZnSe windows. The solvent was allowed to evaporate under a fume hood, leaving solid material on the surface for spectroscopic investigations.

Photoresist was deposited onto silicon substrates using an EV Group 120 Resist Processing Cluster Tool. The pre-resist coating process included hexamethyldisilazane (HMDS) vapor wafer priming. 5 mL of the photoresist was spun cast onto the primed wafers at 2,000 rpm for 40 s. The coated wafer substrates were baked at 110 °C for 75 s. The substrates were then diced using a diamond scribing tool into 0.75 in. x 0.75 in. (1.9 cm x 1.9 cm) pieces for use in the photoacoustic cell.

A solution of 0.25% glycerol in H₂O was prepared. Volumes in increments of 100 μL were deposited using a micropipette onto a single photoresist-coated substrate. The substrate was oriented to allow complete coverage by the glycerol/water solution. Following each deposition, the sample was stored overnight on a flat surface in the dark. Glycerol film thicknesses were calculated based on deposited material volume, average relative humidity, and substrate area.

4. RESULTS AND DISCUSSION

A frequency spectrum was collected experimentally for the photoacoustic cell. This spectrum is provided in Figure 3. The spectrum was collected as the laser frequency was continuously tuned from 10 kHz to 40 kHz, in 0.1 kHz increments. The photoacoustic cell was designed to have resonance features in this frequency range, which was limited by the operational range of the microphone. Experimental resonance frequencies of 12.5 kHz, 20.9 kHz, 26.0 kHz, and 36.3 kHz were observed for the cell. These results are in agreement with the predicted theoretical radial resonance frequencies for a cylindrical cavity resonator.^{26, 27}

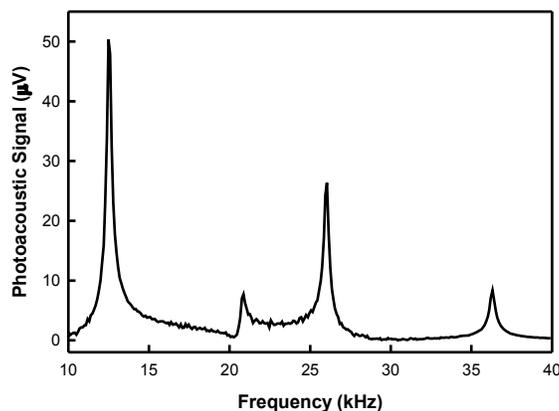


Figure 3. Measured frequency response of photoacoustic cell.

4.1 Spectroscopic Data for Energetic Samples

Laser photoacoustic spectra were collected for urea and TNT at 26.0 kHz. This frequency was chosen based on the experimental frequency data collected for the photoacoustic cell (Fig. 3) and the average laser power at this laser pulse repetition rate. The intensity-normalized spectra are provided in Figure 4. All spectra were collected as the laser continuously tuned from 1,020 cm⁻¹ to 1,240 cm⁻¹ (9.80 μm – 8.06 μm), in 1 cm⁻¹ increments. These analytes have known absorption features in this region, assigned to primary amine (NH₂) rocking vibrations in the urea molecules,² and carbon—hydrogen (ring) in-plane bending, carbon—nitrogen and carbon—methyl (CH₃) stretching vibrations, and ring breathing found in the TNT molecules.²⁸ For both urea and TNT, there is good peak agreement between the photoacoustic and FTIR spectra. Small differences in peak frequency and bandshape between the spectra are due to refractive index effects that are often a result of ATR measurements.² The TNT spectrum collected using the FTIR exhibits a spectral feature at ~1030 cm⁻¹. This absorption band is not present in the photoacoustic spectrum collected for

TNT. This spectral disagreement may be due to a poor signal-to-noise ratio at the edge of the laser tuning range for this particular analyte. Furthermore, the sharp absorption feature observed at $\sim 1029\text{ cm}^{-1}$ in the photoacoustic spectrum collected for urea is also present in the spectral data found in the NIST spectral database of urea taken in Nujol.²⁹

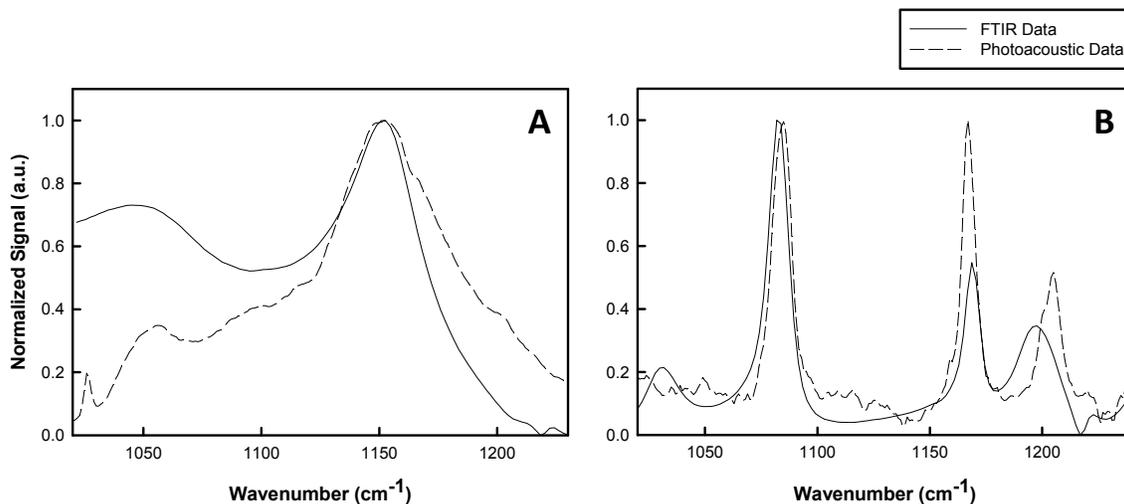


Figure 4. Measured laser photoacoustic spectrum of (A) urea; and (B) TNT compared to FTIR reference spectrum. All spectra have been intensity normalized.

4.2 Depth Profiling Investigations of Glycerol Thin Films

Laser photoacoustic spectra were collected for glycerol and photoresist. The spectra are provided in Figure 5. All spectra were collected as the laser was continuously tuned from $1,025\text{ cm}^{-1}$ to $1,240\text{ cm}^{-1}$ ($9.76\text{ }\mu\text{m} - 8.06\text{ }\mu\text{m}$), in 1 cm^{-1} increments. As illustrated in Figure 5, this spectral region is appealing as it contains absorption features representative of vibrational modes present in the selected molecules, specifically, carbon—oxygen stretching vibrations.² Spectral differences among glycerol and photoresist make it possible to distinguish these compounds.

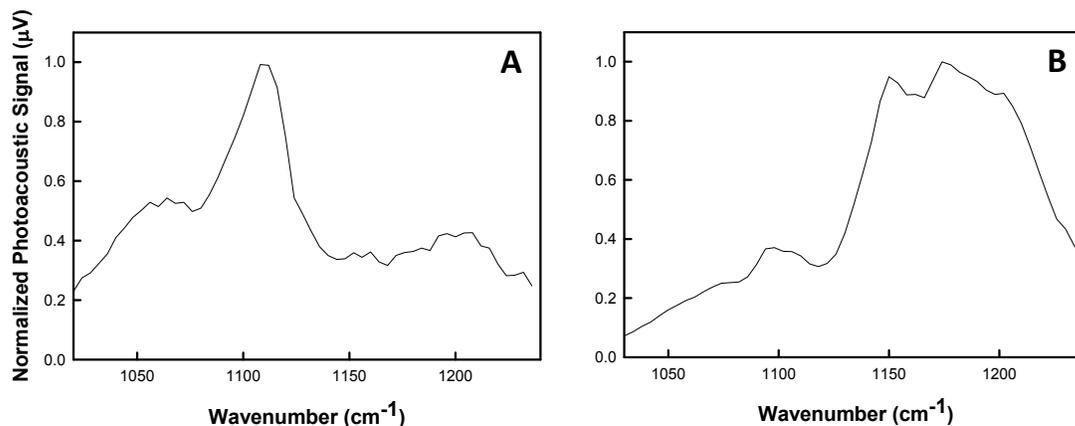


Figure 5. Measured laser photoacoustic spectrum of (A) glycerol; and (B) photoresist. The spectra have been intensity normalized.

Photoacoustic spectra collected for varying thicknesses of glycerol films on a photoresist-coated silicon substrate are shown in Figure 6. For each film thickness, spectra were 12.5 kHz . This frequency was chosen based on the experimental frequency data collected for the photoacoustic cell (Fig. 3). Using (1), the diffusion length for glycerol could be calculated at this frequency. The thermal diffusivity of glycerol can be found in the literature.³⁰ At

12.5 kHz, the calculated diffusion length from the glycerol-gas interface is 1.5 μm . Based on this value, glycerol films having a thickness $<1.5 \mu\text{m}$ will result in thermal diffusion lengths that are greater than the sample thickness and therefore allow for heat generated in the photoresist layer (in phase with the excitation light) via optical absorption to interact with the gas interface. In such cases in which the glycerol film is both optically and thermally thin, the observed photoacoustic spectra will exhibit absorption features characteristic of glycerol and photoresist. This effect can be seen in Figure 6 for the photoacoustic spectra collected for glycerol film thicknesses of 0.5 μm and 1.0 μm . Glycerol films having a thickness $>1.5 \mu\text{m}$ will result in thermal diffusion lengths that are less than the sample thickness and therefore allow for only heat generated in the glycerol film via optical absorption to interact with the gas interface. In such cases in which the glycerol film is both optically and thermally thick, the collected photoacoustic spectra will exhibit absorption features characteristic of glycerol only. This effect can be seen in Figure 6 for the photoacoustic spectra collected for a 2.5 μm glycerol film.

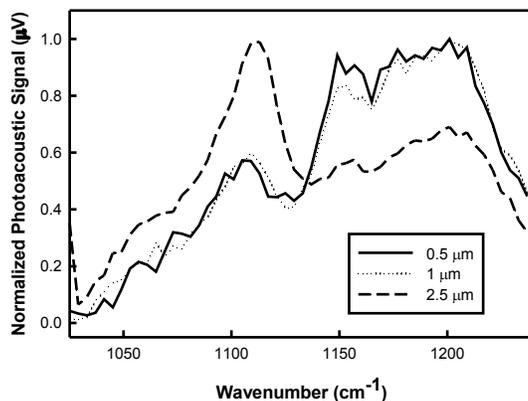


Figure 6. Laser photoacoustic spectral absorption features for varying thicknesses of glycerol films on a photoresist-coated silicon substrate collected at 12.5 kHz.

As the glycerol film thickness was increased, the magnitude of the absorption feature at $\sim 1100 \text{ cm}^{-1}$ (associated with the glycerol molecules) also increased. The opposite observation can be made for the broad absorption feature centered at $\sim 1175 \text{ cm}^{-1}$ (associated with the photoresist molecules). For thinner glycerol films, the magnitude and appearance of this broad feature were significant; however, as the glycerol film thickness increased, the magnitude of this absorption feature decreased. These results were due to the film thickness approaching the maximum diffusion length at 12.5 kHz.

A more comprehensive set of pulse repetition rates and precisely controlled sample thicknesses may result in improved analyte spectral differentiation. Nonetheless, the results for glycerol demonstrate the ability of this photoacoustic platform to accurately discriminate between species deposited on a surface.

5. CONCLUSION

We have successfully demonstrated a QCL-based PAS platform for the detection of condensed phase materials. Our results illustrate that this method can be used to collect quality infrared spectra of energetic analytes of interest, including urea and TNT, and for depth profiling analyses to distinguish among glycerol films deposited on photoresist-coated silicon wafers based on their laser photoacoustic spectra. The availability of continuously tunable QCLs having a broad wavelength and pulse or modulation frequency tuning range makes this an attractive approach for a variety of military and homeland defense applications.

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