Standoff photoacoustic spectroscopy

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Here, we demonstrate a variation of photoacoustic spectroscopy that can be used for obtaining spectroscopic information of surface adsorbed chemicals in a standoff fashion. Pulsed light scattered from a target excites an acoustic resonator and the variation of the resonance amplitude as a function of illumination wavelength yields a representation of the absorption spectrum of the target. We report sensitive and selective detection of surface adsorbed compounds such as tributyl phosphate and residues of explosives such as trinitrotoluene at standoff distances ranging from $0.5-20$ m, with a detection limit on the order of 100 ng/cm^2. © *2008 American Institute of Physics*.
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Photoacoustic spectroscopy (PAS) is a useful technique for probing the optical properties of a variety of materials. Demonstrated by Alexander Graham Bell in the late 1880s,[1] PAS has been increasingly used for selective identification of materials using their optical absorption characteristics. The PAS signal originates from the nonradiative de-excitation of the energy absorbed by the material in optical transitions. Therefore, the PAS spectrum can be correlated with optical absorption spectra of the sample. PAS is mostly applied to samples in vapor phase where the vapor is kept in a chamber with optical windows. The enclosed sample is then sequentially exposed to pulses of light at different wavelengths. Molecular absorption of the light creates thermomechanical expansion and contraction of the vapor at the air/surface interface which may be regarded as a vibratory piston.[2] Since the optical excitation is oscillatory, the expansion and contraction generates acoustic waves of extremely small amplitude. However, being in a sealed chamber constrains the gas, increasing the overall pressure.[3] The acoustic waves are then measured using a microphone. The PAS technique has also been used to investigate nongaseous samples such as solids, granular materials, and biosamples.[1] PAS has many advantages over optical spectroscopy such as direct measurement of nonradiative transitions, high signal-to-noise ratio, and its ability to work with samples in any physical form or different optical properties, for example, transparent or opaque.

Despite its many advantages, carrying out PAS on samples in open air poses many challenges. Without a sealed chamber, the resulting acoustic waves spread, stretching their already feeble energy below the detection limits of acoustic detectors. Attempts to overcome these challenges include using stronger light sources and more efficient sound wave collection methods, such as the use of parabolic focusing mirrors. A more powerful light source will increase the amplitude of the acoustic waves while the parabolic mirror captures and refocuses the sound back onto the microphone.[4] Although these techniques do help, the resulting signal amplitude is still much smaller than when using a closed chamber method, and is difficult to extract from typical ambient background noise levels. This ultimately results in reduced range and detection sensitivity of the technique.

Standoff detection of chemical signatures is gaining attention due to its immediate relevance in security and commercial applications. Here, the term standoff detection refers to a paradigm where the source, detector, and the operator remain at a safe distance from the target sample as opposed to remote detection, where the detector is in close proximity of the sample while the operator remains at a safe distance.[5] Demonstrations of open air PAS are quite unreliable. Previous attempts to use PAS as a standoff technique involved direct microphone detection of sound created by light at a distance.[3,4] However, this approach fails due to the influence of wind effects on the light-induced expansion of air above the sample. Although the generated sound waves are affected by atmospheric conditions, the reflected or scattered light is not. Therefore, we exploit this reflected light for indirect generation of sound.

In this letter, we report a variation of PAS which involves illuminating the target sample with a pulsed light source and allowing the scattered light to be detected by a quartz crystal tuning fork (QCTF). The pulse frequency of the illuminating light is matched with the mechanical resonant frequency of the QCTF, generating acoustic waves at the tuning fork's air/surface interface. This produces oscillating localized pressures which drive the tuning fork into resonance. The amplitude of this vibration is proportional to the intensity of the scattered or reflected light beam falling on the QCTF. Due to the material nature of quartz, a piezoelectric voltage is produced as the QCTF vibrates.

Recently, QCTF resonators have been used in PAS as a highly sensitive replacement for the microphone in the PAS gas cell, where pulsed laser induced vibrations in the gas produced detectable vibrations of the QCTF.[6–10] QCTF resonators have many key advantages over other optical detectors. For example, the quality factor for our tuning forks in vacuum is around 85 000 (manufacturer specs). In air, this quality factor is lowered to approximately 10 000 due to the damping effect of the air, yet maintaining frequency sensitivity on the order of 0.1 Hz. When applying the QCTF as an acoustic detector, the large quality factor allows them to maintain high sensitivity while making them immune to environmental noise. Other advantages of quartz tuning fork resonators include compact size, low cost, commercial availability, no saturation limits, and the ability to operate in harsh environments.

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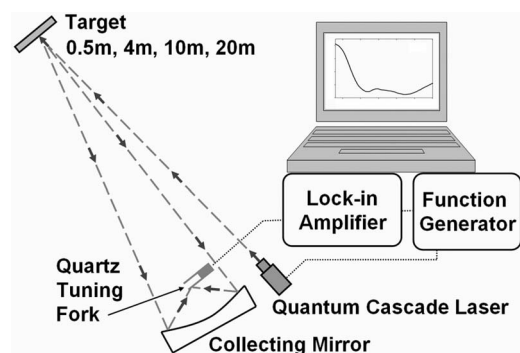
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FIG. 1. Diagram of experimental setup. Pulsed IR light is reflected off the target and focused onto the quartz tuning fork sensor. The vibration signal amplitude from the photoacoustic stimulated tuning fork is recorded as a function of illumination wavelength.

A schematic diagram of the experimental setup is shown in Fig. 1. The light source and the acoustic detector are situated away from the target sample. We have used a quantum cascade laser (QCL) as our optical source for illuminating the target surface located 0.5–20 m away (available from Daylight Solutions, Inc., Poway, CA). The QCL can be tuned in a wavelength range from 9.25798 to 9.80407 μm in 0.01 nm increments. The power of the QCL was 100 mW with a duty cycle of 5%. The QCL beam spot size is approximately 6 mm at the laser and expands to about 25 mm at 20 m. The light reflected/scattered off the target is collected near the source using a spherical mirror (with a radius of 10 cm) and focused onto the QCTF (Citizen CFS308, frequency=32.768 kHz). A function generator was used to control the pulse frequency of the QCL and a lock-in amplifier was used to extract the amplitude and phase information from the tuning fork signal. As the wavelength of light emitted from the QCL changes, the target will either absorb or scatter the light. Increased absorption by the sample will decrease the reflected light intensity reaching the tuning fork, resulting in a decrease in the vibrational amplitude of the tuning fork.

In the experiments, a background spectrum of the clean stainless steel target surface was taken initially. The target surface was then coated with varying amounts of chemical residue prior to illumination by the QCL. The target chemicals chosen were tributyl phosphate (TBP) and three explosives: cyclotrimethylenetrinitromine (RDX), trinitrotoluene (TNT), and pentaerythritol tetranitrate (PETN). The explosive sample solutions were prepared in acetonitrile (1 mg/ml) and uniformly deposited on a target surface and allowed to dry. The acetonitrile evaporates completely and does not add to the photoabsorption spectra. The surface concentrations of explosives were calculated from the known solution concentration, the volume used, and the area of solution coverage, and range from 100 ng/cm^2 to 4 μg/cm^2 in these experiments. The desorption rates of these chemicals are extremely low at room temperature and measurements taken several hours after sample application gave reproducible results.

The coated target sample was illuminated with the QCL and the vibrational amplitude of the tuning fork was collected as a function of illuminating wavelength. A ratio of the target sample to the measured background was generated, producing a unique photoacoustic spectrum of the sample. Figure 2 shows the resulting spectra for the surface coated
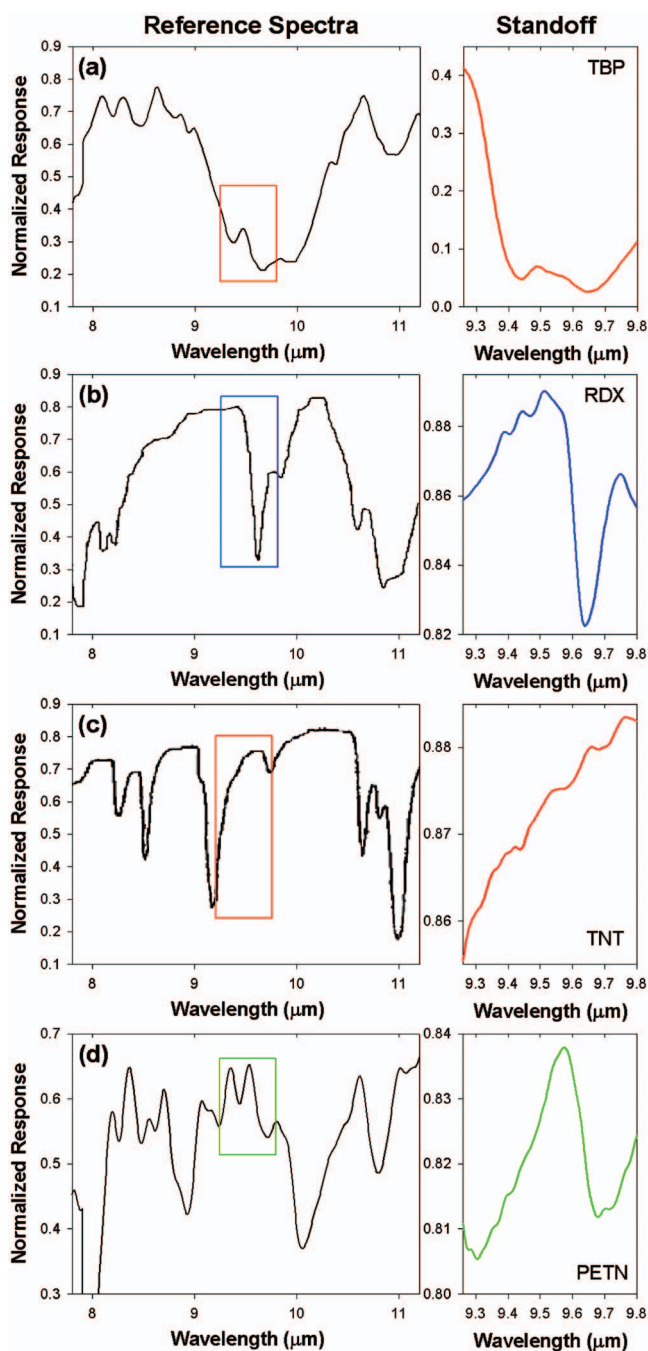

FIG. 2. (Color) Standoff photoacoustic spectra (in color) of (a) TBP at a distance of 4 m, (b) RDX at 20 m, (c) TNT at 0.5 m, and (d) PETN at 4 m. As the target chemicals absorb the IR radiation as a function of wavelength, the energy reflected to the QCTF detector is lowered, resulting in a decrease of photoacoustic stimulation of the QCTF. The inverted absorption peaks in the plots are therefore found at the wavelength corresponding to the peaks in molecular IR absorption of the target species. The black Reference Spectra plotted to the left of each standoff photoacoustic spectrum is the published IR absorption spectrum of the corresponding chemical (Refs. 11 and 12). The colored box in each Reference Spectra indicates the IR wavelength scan range of the QCL for easy comparison with the standoff photoacoustic spectra plotted in the same color to the right.

with TBP, RDX, TNT, and PETN. Also shown in Fig. 2, for comparative reference, are the published absorption spectra for RDX and TNT obtained with traditional infrared (IR) absorption spectroscopy[11] and for PETN and TBP obtained with photothermal spectroscopy.[12] As can be seen, the presented results compare reasonably well with the reference spectra.

The experiments were repeated at standoff distances of 0.5, 4, 10, and 20 m. There was virtually no change in the spectra as the target distance increased. However, for the longer distances (10 and 20 m), the signal from the tuning fork did reduce to a point where amplification was needed (gains ranging from 10 to 10 000). For the experimental distances up to 10 m, the ambient temperature in the laboratory was approximately 22 °C with a relative humidity in the range of 35% to 40%. For the experiments performed at 20 m, the ambient temperature was approximately 27 °C with a relative humidity in the range of 60% to 65%. For the 9.5 μm wavelength region of the QCL, the intensity of the reflected light was reduced much more by an increase in distance than by an increase in humidity. Reproducibly identifiable spectra could be obtained for surface concentrations as low as approximately 100 ng/cm^2.

In conclusion, we have demonstrated a variation of PAS that is suited for the standoff detection of surface adsorbed chemicals. We have shown a detection limit on the order of 100 ng/cm^2 for this technique, and have so far achieved a standoff detection distance of 20 m. This could be further improved by using larger collection mirrors and stronger illumination sources. Development of QCL with wider tuning ranges or using many QCL in tandem will enable obtaining wider optical spectra. Efforts are presently underway to establish the technique with longer distances, higher diffusive targets, wider optical range, and beam sweeping capabilities.

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