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Standoff Spectroscopy of Surface Adsorbed Chemicals

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Despite its immediate applications, selective detection of trace quantities of surface adsorbed chemicals, such as explosives, without physically collecting the sample molecules is a challenging task. Standoff spectroscopic techniques offer an ideal method of detecting chemicals without using a sample collection step. Though standoff spectroscopic techniques are capable of providing high selectivity, their demonstrated sensitivities are poor. Here we describe standoff detection of trace quantities of surface adsorbed chemicals using two quantum cascade lasers operated simultaneously, with tunable wavelength windows that match with absorption peaks of the analytes. This standoff method is a variation of photoacoustic spectroscopy, where scattered light from the sample surface is used for exciting acoustic resonance of the detector. We demonstrate a sensitivity of 100 ng/cm² and a standoff detection distance of 20 m for surface adsorbed analytes such as explosives and tributyl phosphate.

Selective and sensitive detection of surface adsorbed chemicals such as explosive traces in a standoff fashion is of great interest, with application ranging from homeland security to environmental monitoring.^{1–4} For example, the very low vapor pressures of military explosives make their detection using point-contact sensors extremely challenging. Point-contact sensors are sensors that require collection and delivery of the analyte molecules to the sensor or sensor surface for analysis. This sample collection process is very difficult because low vapor pressure chemicals such as explosives tend to stick to surfaces, including sample collection and delivery lines. Elimination of analyte condensation in the delivery lines requires heating the lines to high temperatures. Although heating of the system does not interfere with sensors such as ion mobility spectrometers (IMS), it can result in poor performance for sensors that require the adsorption of analyte molecules on a detector element.

Standoff detection, defined as where equipment and operator stay away from the sample,⁵ is mostly based on optical spectroscopic techniques such as infrared (IR) spectroscopy, laser-induced breakdown spectroscopy, laser-induced fluorescence, LIDAR, Raman, and so forth⁶ because spectroscopic techniques offer very high selectivity. Since standoff techniques do not require collecting and bringing the sample to the sensor surface for detection, they are ideal for detection of low vapor pressure analytes, such as explosives. In addition, standoff methods give a non-contact analysis of the sample which may also be non-contaminating and non-destructive for techniques with low illumination levels. Achieving chemical selectivity using optical spectroscopic signals is highly reliable (low false positives) compared to techniques based on the chemical interaction between immobilized selective interfaces and the analyte molecules, such as those often employed in point-contact sensors. This is mainly due to the limited number of reversible chemical interactions that can serve as a basis for analyte-interface interactions. With laser based standoff spectroscopies, the detection distance can be tens of meters. Because of the inverse square dependence of light intensity, larger distances require high power light sources such as lasers. For homeland security applications such as detection of suicide bombers or improvised explosive devices, a distance of 50–100 m is generally sufficient.

Here we demonstrate standoff detection of trace quantities of explosives and tributyl phosphate (TBP) using a variation of photoacoustic spectroscopy⁷ using two external cavity quantum cascade lasers (QCL). The external cavity allows the QCL wavelength to be tuned within a window of 5% on either side of the center wavelength. The tuning windows of QCL wavelengths were selected in such a way that major identifying peaks of the selected analytes fall within these windows. Two QCLs, pulsed at different rates, were used for illuminating the sample surface. The reflected/scattered light was collected and focused using a mirror and detected acoustically using tuning forks whose frequencies match the pulse rates of the individual lasers. Plots of the amplitudes of the mechanical resonance frequencies of the tuning forks as a function of illuminating wavelength show excellent agreement with the traditional infrared spectroscopic absorption peaks of the analytes.

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(1) Colton, R. J.; Russell, J. N. *Science* **2003**, *299*, 1324.

(2) Hollowell, S. F. *Talanta* **2001**, *54*, 447.

(3) *Counterterrorist Detection Techniques of Explosives*; Yinon, Y., Ed.; Elsevier: Amsterdam, 2007.

(4) *Trace Chemical Sensing of Explosives*; Woodfin, R. L., Ed.; John Wiley & Sons: Hoboken, NJ, 2007.

(5) Parmeter, J. E. *Proceedings of the 38th Annual 2004 International Carnahan Conference on Security Technology*; 355 IEEE: New York, 2004.

(6) Committee on the Review of Existing and Potential Standoff Explosives Detection Techniques, *Existing and Potential Standoff Explosives Detection Techniques*; The National Academies Press: Washington, DC, 2004.

(7) Van Neste, C. W.; Senesac, L. R.; Thundat, T. *Appl. Phys. Lett.* **2008**, *92*, 234102.

SURFACE CONCENTRATION OF ANALYTES

In general most surfaces can act as preconcentrators for analytes. For surfaces with high surface energies, such as metals, oxides, and nitrides, the concentrations on the surface, measured in g/cm^2 , may be orders of magnitude higher than that in the air. This preconcentrating ability of most surfaces is very advantageous for trace standoff detection techniques.

If the rate at which the analyte molecules impinging on a surface is N (# of molecules/second), and if n is the rate at which the adsorbed molecules are leaving the surface, then the rate of adsorption is

$$\frac{dQ}{dt} = aN - n$$

where Q is the surface concentration of the adsorbed molecules and a is the condensation coefficient. At equilibrium, adsorption and desorption are equal. The desorption rate can be calculated as

$$n = \nu_0 e^{-q/kT}$$

where q is the heat of adsorption, k is Boltzmann's constant, T is the surface temperature, and ν_0 is the molecular vibration frequency of the adsorbed analyte. The average residence time is proportional to Q , but exponentially depends on adsorption energy and temperature and is given by

$$\tau = \frac{Q}{n} = \frac{Q}{\nu_0} e^{q/kT}$$

Our earlier experiments⁸ have shown that explosives such as RDX and PETN desorb very slowly and stay on a surface for days.

It should be noted, however, that most surfaces encountered in field conditions have contaminants adsorbed on them making the surfaces inhomogeneous. Therefore, some of the adsorbed analytes may be weakly adsorbed on a "real surface" (a real surface is defined as a surface that is not a clean surface such as those prepared in clean vacuum conditions). In addition, "real surfaces" may also be contaminated with analytes because of handling, such as fingerprint residues.

STANDOFF PHOTOACOUSTIC SPECTROSCOPY

Unique molecular fingerprints for many analytes exist in the mid infrared region of the optical spectrum. These mid-IR spectra, which are related to the vibrational modes of the different groups in the molecules, are highly selective indicators for identifying molecules. One of the infrared spectroscopic techniques that can work with samples in any physical form or with different optical properties (transparent or opaque) is photoacoustic spectroscopy (PAS).^{9–12} In conventional PAS, absorption of pulses of light by the sample confined in a closed chamber results in the creation

of acoustic waves due to the pulsed expansion of air around the sample. The frequency of sound matches the pulse rate of the illumination light beam. PAS may be practiced in vapor phase where the vapor is kept in a chamber with optical windows. The sample, when exposed to pulses of light of different wavelengths, creates sound due to the light absorption-induced mechanical expansion and contraction of the vapor. When the sample absorbs light, that light is converted into heat due to relaxation mechanisms. Therefore, the intensity of the sound varies with the extent of absorption of light by the sample. The more the sample absorbs a particular wavelength, the higher the intensity of sound. A plot of intensity of the observed sound as a function of illumination wavelength is the PAS spectrum. Since these sound waves are extremely small in amplitude, a sealed chamber is essential for measuring the sound, and therefore, cannot be practiced in a standoff fashion because of interference from ambient noise. The PAS technique may also be used to investigate nongaseous samples such as solids, granular materials, and bio samples confined in chambers.

Recently, quartz crystal tuning fork (QCTF) resonators have been used in PAS as highly sensitive replacements for the microphones in PAS gas cells.^{13–17} In our standoff method, instead of using the QCTF to detect the sound created on the sample surface, the scattered light returning from the sample surface is focused onto a QCTF to produce an acoustic wave on the sensor surface. When the sample is absorbing a particular wavelength, the intensity of scattered light returning from the sample is less than when the sample is not absorbing. The pulse rate of the light is adjusted such that it matches the resonance frequency of the tuning fork. The returning light from the sample creates an acoustic wave on the tuning fork surface due to the photoacoustic effect, driving the QCTF into resonance. The quality factor (Q-factor) for these tuning forks in vacuum is around 90,000, but in air the Q-factor is lowered to approximately 5,000 because of damping. However, this Q-factor is still much higher than can be obtained with other devices. This large Q-factor achieves high sensitivity with high signal-to-noise ratios. It also allows the use of multiple QCLs where each QCL is pulsed at a different frequency that matches the resonant frequency of a single QCTF in a tuning fork array.

EXPERIMENTAL SETUP AND TECHNIQUE

A schematic diagram of the experimental setup is shown in Figure 1. Two external cavity quantum cascade lasers (QCLs) (available from Daylight Solutions, Inc., Poway, CA) are used for simultaneously illuminating the target surface located between 0.5 to 20 m away. One QCL exhibits a tunable wavelength between 9.25 to 9.80 μm (1081.08 cm^{-1} to 1020.41 cm^{-1}). The other QCL has a tuning range from 7.38 to 8.0 μm (1355.01 cm^{-1} to 1250 cm^{-1}). Each QCL can be tuned in increments of 0.01 nm. The

- (8) Pinnaduwaige, L. A.; Thundat, T.; Gehl, A.; Wilson, S. D.; Hedden, D. L.; Lareau, R. T. *Ultramicroscopy* **2004**, *100*, 211.
- (9) Rosencwaig, A. *Photoacoustics and Photoacoustic Spectroscopy*; John Wiley & Sons: New York, 1980.
- (10) Rosencwaig, A.; Gersho, A. J. *Appl. Phys.* **1976**, *47*, 64.
- (11) Miklós, A.; Pei, S.-C.; Kung, A. H. *Appl. Opt.* **2006**, *45*, 2529.
- (12) Perrett, B.; Harris, M.; Pearson, G. N.; Willetts, D. V.; Pitter, M. C. *Appl. Opt.* **2003**, *42*, 4901.

- (13) Kosterev, A. A.; Bakhrin, Yu. A.; Curl, R. F.; Tittel, F. K. *Opt. Lett.* **2002**, *27*, 1902.
- (14) Kosterev, A. A.; Tittel, F. K.; Serebryakov, D. V.; Malinovsky, A. L.; Morozov, I. V. *Rev. Sci. Instrum.* **2005**, *76*, 043105.
- (15) Wojcik, M. D.; Phillips, M. C.; Cannon, B. D.; Taubman, M. S. *Appl. Phys. B: Laser Opt.* **2006**, *85*, 307.
- (16) Phillips, M. C.; Myers, T. L.; Wojcik, M. D.; Cannon, B. D. *Opt. Lett.* **2007**, *32*, 1107.
- (17) Kosterev, A.; Wysocki, G.; Bakhrin, Y.; So, S.; Lewicki, R.; Fraser, M.; Tittel, F.; Curl, R. F. *Appl. Phys. B: Laser Opt.* **2008**, *90*, 165.

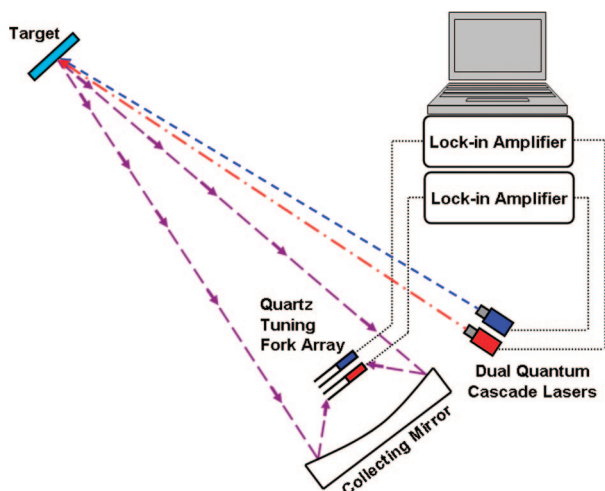


Figure 1. Diagram of the experimental setup. Pulsed IR light from the two QCLs is reflected off the target surface and focused onto the quartz tuning fork sensors. The vibration signal amplitudes from the photoacoustic stimulated tuning forks are recorded as a function of illumination wavelength.

QCLs can be scanned through their full wavelength range in about 0.8 s, or program controlled to any longer interval.

The light reflected/scattered off the target was collected near the source using a spherical mirror (with a radius of 10 cm) and focused onto two quartz crystal tuning forks (QCTFs) (Citizen CFS308, Frequency = 32.768 kHz). A gap of approximately 0.5 mm separated each tuning fork from the other. It was experimentally found that the resonant frequency difference between each tuning fork in air must be at least 10 Hz, otherwise cross talk between QCTFs would develop and the pulses from the two QCLs would generate beat frequencies. However, QCTF with a 10 Hz difference in their resonance frequencies can be easily obtained. Tuning forks exposed to the air typically display a frequency variance of nearly 50 Hz or more. In these experiments, the resonant frequency difference between the two QCTFs was 143 Hz.

For the experiments a baseline spectrum of the target is taken initially. The target is then coated with varying amounts of chemical residues prior to illumination with the QCLs. It should be noted that most of these chemicals adsorb on surfaces in patches, and therefore, a differential measurement can be carried out moving the beam from one location to another. The analyte chemicals chosen were tributyl phosphate (TBP), cyclotrimethylenetrinitromine (RDX), pentaerythritol tetranitrate (PETN), and trinitrotoluene (TNT). 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 photo absorption spectra. We used a quartz crystal microbalance (QCM) as the target surface. This allowed us to quantitatively measure the amount of deposited material. The quantity of explosive adsorbed on the QCM was calculated from the QCM resonance frequency variation. TBP residues were prepared by allowing the liquid to dry on the target surface. The surface concentrations of all residues were calculated from the initial mass (measured by the QCM), area of coverage, and desorption rate of the analytes at room temperature. In these experiments, the concentrations ranged from approximately 100 ng/cm² to 4 μg/cm². The desorption rates of these chemicals

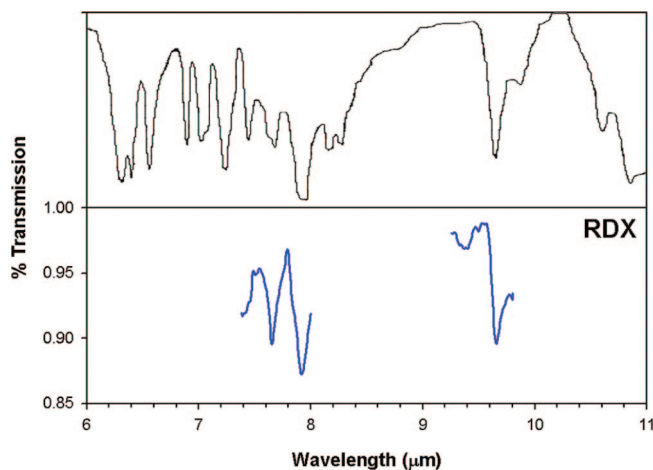


Figure 2. RDX spectra. The bottom portion of the frame shows the transmittance of the RDX residue on the target as taken simultaneously at two different QCL wavelength windows. As the target chemicals absorb the IR radiation as a function of wavelength, the energy reflected to the QCTF detectors is lowered resulting in a decrease of photoacoustic stimulation of the QCTFs. The inverted absorption peaks in the plots are therefore found at the wavelengths corresponding to the peaks in molecular IR absorption of the target species. The top portion of the frame shows an IR transmission spectrum of bulk RDX taken using a conventional IR spectrometer.¹⁸

are extremely low at room temperature, and measurements taken several hours after sample application gave comparable values.

The production of the final spectrum is a ratiometric process required to remove the absorption effects not produced by the target material. The target scan spectrum is always ratioed with a baseline spectrum. If the target of analysis is a surface of one material, the baseline of the system response is used. This system baseline is a scan taken off of a mirror surface and the resulting spectrum is a combination of laser profile (output power varies as a function of wavelength), atmospheric absorption (H₂O, CO₂, etc.), and the absorption response characteristics of the detector. The target of analysis is then scanned by the system to produce a target scan spectrum which is a combination of the baseline absorption plus the target absorption. Dividing this target scan spectrum by the baseline spectrum removes the baseline absorption contribution and leaves the spectrum of the target. This ratio of the target scan spectrum and the baseline spectrum produces the transmission spectrum commonly used in many traditional spectroscopic techniques.

Since the spectrum of every surface material is different, the identification of residues on the surface requires the removal of the surface spectrum from the data. To identify a small amount of target material (such as a residue) on a surface, the baseline spectrum must be obtained of the surface without the target material. For the residues used in this work, the residue was always in small patches on the surface but not covering the entire surface. This makes it possible to scan the surface and ratio the scans so that any difference shows up as the spectrum of the target residue.

RESULTS AND DISCUSSION

Figure 2 shows the spectra of RDX residue taken simultaneously at two different QCL wavelength windows at a target

distance of about 4 m. Each QCL was tuned simultaneously from starting wavelength to ending wavelength in a total time of about 1 min while the signals from the two QCTFs were recorded. The top plot in Figure 2 shows an IR absorption spectrum of bulk RDX taken using a conventional IR spectrometer.¹⁸ As can be seen, the standoff spectrum agrees very well with the traditional infrared technique. The peak observed near 7.6 μm is caused by the symmetric stretching vibration of the NO_2 (nitro) group bond. In RDX the nitro groups are bounded nitrogen (N- NO_2). This bond has a symmetric stretching vibration at 7.63 μm (1310 cm^{-1}).^{19,20} (All the absorption peaks are discussed in the refs 19 and 20.)

Figure 3 a, b, and c shows spectra of trace quantities of TBP, PETN, and TNT adsorbed on surfaces at a distance of 10 m for TBP and 2 m for PETN and TNT. The top plot in each figure corresponds to conventional, bulk IR absorption spectrum of respective analytes.^{18,21} (Discussion of the peaks may be found in the reference material.) Again the spectral peaks observed with the QCL standoff method agree very well with the traditional IR absorption spectra of the analytes. By using an analyte adsorbed quartz crystal microbalance (QCM) as a substrate for standoff detection, we have measured a limit of detection (LOD) of 100 ng/cm^2 for the present setup. The amount of adsorbate was calculated using changes in resonance frequency of the QCM.

All these experiments were conducted in ambient humidity and in the presence of ambient light, sound, and vibration. To determine the effects of solvents, a small container of acetone was placed near the target. The acetone vapor was allowed to escape from the container and leak into the surrounding air. Figure 4 shows the spectrum of RDX mixed with the acetone vapor. Also plotted in Figure 4 are the individual spectra for RDX and acetone taken separately. The dashed line in Figure 4 is the expected mixture spectrum which was calculated as a superposition of the RDX absorbance and the acetone absorbance (absorbance = 1 – transmittance). It is clear that the spectrum of the mixture is a superposition of their respective spectra.

We have demonstrated detection of surface adsorbed analytes for distances ranging from 0.5 to 20 m. We estimate that this standoff technique is capable of detecting trace quantities of analytes at a standoff distance of 100 m by optimizing the light collection mirror area, power of the source, and readout electronics.

As demonstrated, it is possible to use multiple lasers to cover any desired portion of the mid-IR fingerprint region needed for the identification of selected analytes. Each of these lasers can be pulsed at different frequencies and can be detected with frequency matching tuning forks. Since the Q-factors of the tuning forks are very high, they can be made to have very little cross talk and achieve large signal-to-noise ratios.

It is interesting to note that the location of spectral peaks did not vary on surfaces due to surface effects. It is expected that the spectral peaks of surface adsorbed species will be shifted with respect to bulk peaks due to surface effects. The electric field gradients on a clean surface can change the force constants of

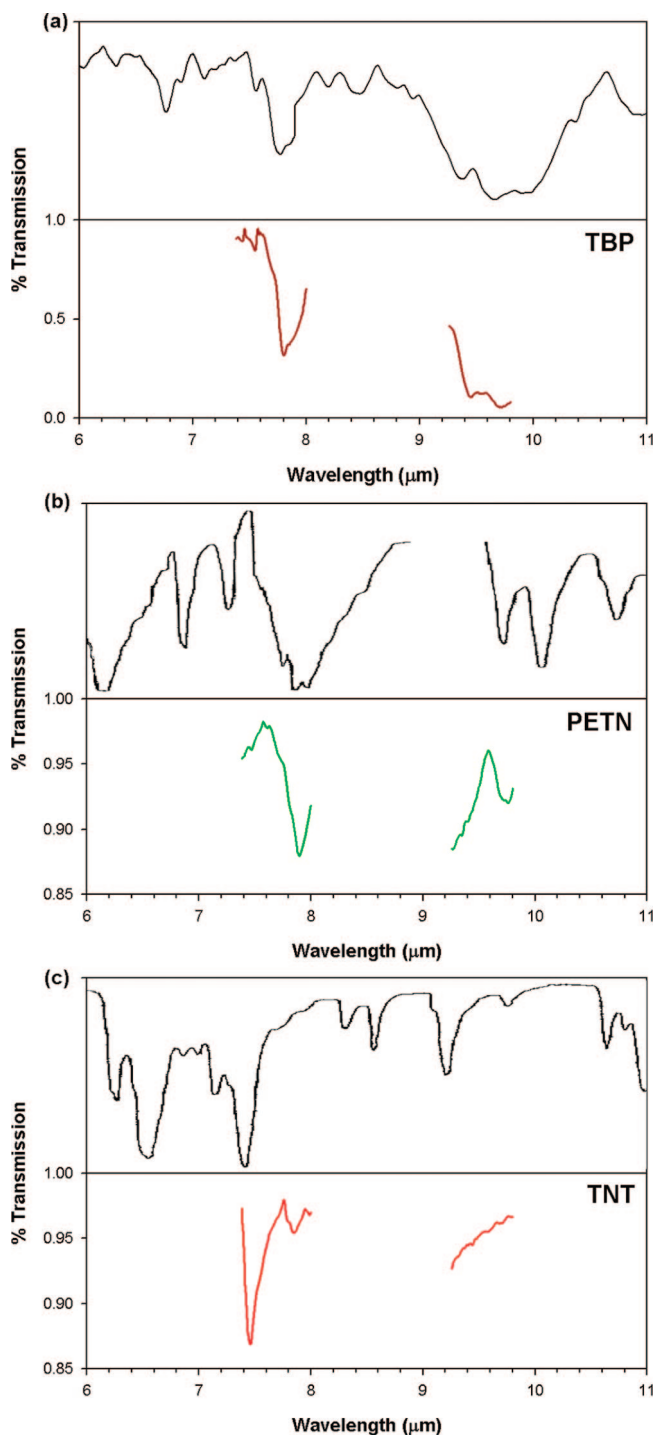


Figure 3. Spectra of (a) TBP, (b) PETN, and (c) TNT. In each, the lower portion of the frame shows the transmittance of the target residue taken with the two different QCLs. The top portion of the frames for PETN and TNT show the IR transmission spectra of the bulk explosives taken using a conventional IR spectrometer.¹⁸ The top portion of the frame for TBP shows an IR transmission spectrum of trace TBP residue taken using a point sensor photothermal spectroscopic technique.²¹

molecular vibrations. Since we did not observe any peak shifts for trace samples on surfaces, the surface fields may not be playing a significant role on “real surfaces” (surfaces exposed to ambient conditions).

Since the optical spectra of the analytes are a linear superposition of individual spectra, it is possible to identify mixtures of

(18) Pristera, F.; Halik, M.; Castelli, A.; Fredericks, W. *Anal. Chem.* **1960**, *32*, 495.

(19) Lewis, I. R., Jr.; Griffiths, P. R. *Appl. Spectrosc.* **1997**, *51*, 1854.

(20) Krause, A. R.; Van Neste, C. W.; Senesac, L. R.; Thundat, T.; Finot, E. *J. Appl. Phys.* **2008**, *103*, 094906.

(21) Van Neste, C. W.; Senesac, L. R.; Yi, D.; Thundat, T. *Appl. Phys. Lett.* **2008**, *92*, 134102.

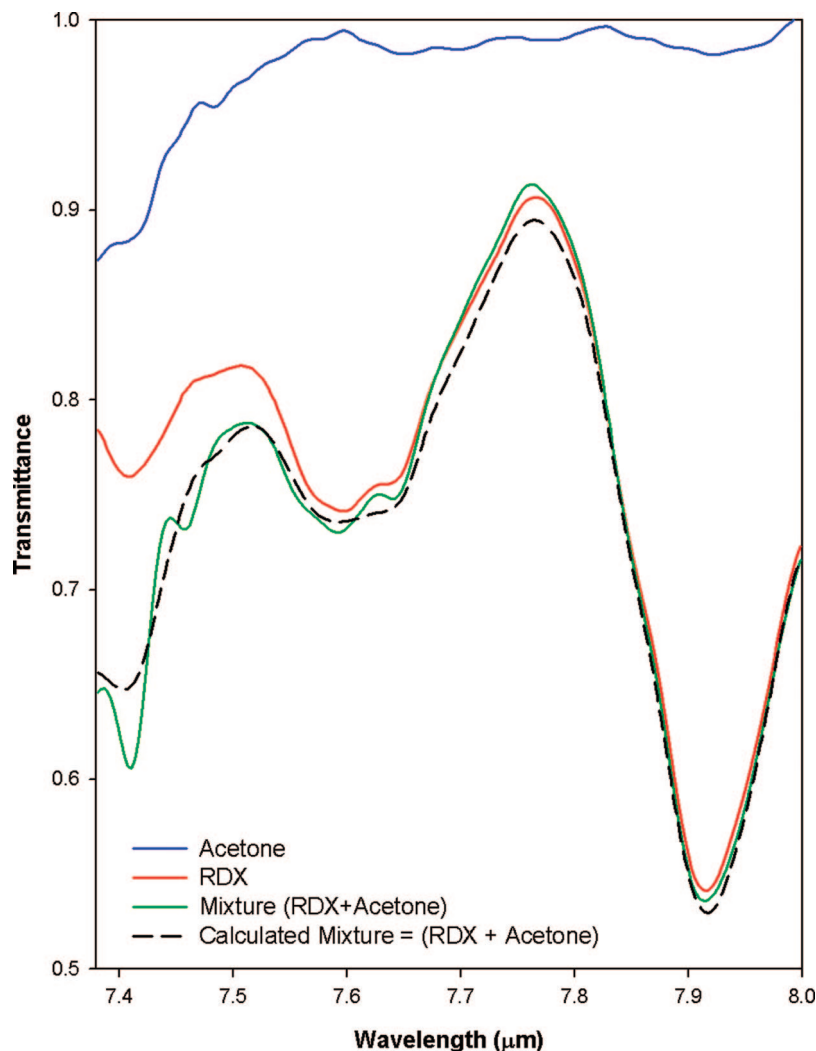


Figure 4. Mixture of RDX and acetone vapor. The spectra data plotted here for RDX, acetone vapor, and a mixture of RDX and acetone vapor were all taken with the same method described in this paper. The dashed line plot is a calculation of the superposition of the individual RDX and acetone vapor absorption data. The calculated spectrum agrees reasonably well with the experimentally measured mixture spectrum.

substances with this technique. By using multiple QCLs and a QCTF array it is possible to scan large spectral windows for molecular identification. The use of multiple lasers that can be simultaneously used for illuminating the surface allows fast operation. Since QCTFs resonances have very high quality factors, the sensitivity of mechanical detection will be very high. Spectroscopy based operation allows high selectivity detection without probe contamination or operator hazards.

CONCLUSIONS

A standoff detection technique that uses multiple, tunable quantum cascade lasers has been demonstrated, where the reflected light from a target surface is detected acoustically using a quartz crystal tuning fork. In this technique, which utilizes the high Q-factor of the quartz tuning fork, the amplitude modulation frequency of the laser beam is matched with the mechanical resonance frequency of the tuning fork for increased sensitivity. The resonance amplitude of the tuning fork as a function of wavelength resembles the infrared absorption characteristics of

the sample. We have demonstrated detection of trace quantities of RDX, PETN, TNT, and TBP adsorbed on surfaces with a limit of detection of 100 ng/cm² and a standoff distance of 20 m. These results show that using this standoff detection method it is possible to detect surface adsorbed analytes with high sensitivity and selectivity.

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