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Standoff reflection–absorption spectra of surface adsorbed explosives measured with pulsed quantum cascade lasers

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ABSTRACT

We demonstrate a standoff detection scheme of surface adsorbed explosives based on the broadband quantum cascade laser (QCL) infrared reflection–absorption spectroscopy and ultraviolet laser photodecomposition. We utilized a sub-second rapid-scan data acquisition scheme to record continuously scanned spectra which revealed the broad-band absorption features of surface adsorbed explosive molecules such as cyclotrimethylene trinitramine (RDX) and trinitrotoluene with a surface concentration of 1 μg/cm^2. The standoff QCL spectra perfectly reproduce the reflectance spectra obtained with a conventional Fourier transform infrared spectroscopy instrument. The conformation conversion of RDX molecules is also observed and studied.

1. Introduction

The standoff detection of trace explosives is currently of great interest due to its immediate relevance in defense and homeland security. Standoff detection requires the operator and the "vital assets" of detection to be physically separated from the explosive device by a certain safe distance. For a pedestrian suicide bomber, the standoff distance is considered to be 10 m, while for a vehicle borne suicide bomber the distance could be 100 m [1]. A standoff detection technique with adequate sensitivity has a wide variety of potential applications in forensics, environment, public health, and homeland security. This type of technique requires the modulation of the suspected object in order to produce a reliable and reproducible signal to propagate in the open space between the target and the detector. Laser spectroscopy, which investigates interactions between molecules and laser light, meets these requirements.

A laser beam can effortlessly propagate through the air for interrogation. All explosives have characteristic spectroscopic features which can be detected for the purpose of identification [2]. The absorption feature in the ultraviolet–Visible (UV–Vis) spectral region of explosives is usually broad, resulting in a relatively poor selectivity for detection schemes such as UV cavity ring-down spectroscopy (CRDS) [3] or double pulse laser-induced breakdown spectroscopy [4]. In contrast to the UV–Vis region, all explosive molecules exhibit strong characteristic absorbance peaks in the mid-infrared (IR) spectral range or the so called "molecular fingerprint" region, where the difference in the masses of nuclei and the strength of chemical bonds results in characteristic vibrational modes which are unique for different isotopologues and conformation of different molecules [5]. Traditionally, such vibrational features are measured by a Fourier transform infrared (FTIR) spectrometer, which requires sample preparation in the FTIR instrument [6,7]. For standoff detection of surface adsorbed explosives, the vibrational spectra of explosives are usually measured using Raman Spectroscopy [8], surface-enhanced Raman spectroscopy [9], or vibrational sum-frequency spectroscopy [10], with high power visible lasers which are usually not eye-safe. Direct tunable IR laser absorption spectroscopy of explosives is usually performed on these molecules in the vapor phase, where gas phase molecules exhibit sharp absorption features. Since laser beam reflection on any surface is between the two extremes of diffuse reflection from an ideal matte surface and specular reflection from a smooth surface, the vibrational spectroscopy of the molecules adsorbed on a smooth surface can also be measured by the single reflection mode IR reflection–absorption spectroscopy (IRAS) [11]. A main stimulus for the application of mid-IR reflection–absorption spectroscopy for standoff detection of surface adsorbed explosives is the recent advances in the development of the high

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power quantum cascade laser (QCL). The QCL is a new type of mid-IR tunable semiconductor laser based on inter-subband transitions in a multiple-quantum-well heterostructure, designed by means of band-structure engineering grown by molecular beam epitaxy. Recently, the QCL has attracted much attention due to its superior output power and mode quality as compared to that of lead salt diode lasers. Many vapor phase chemical sensors based on QCL have been demonstrated [12]. Parts-per-billion (ppb) concentration levels of explosive vapor were readily detected using mid-IR CRDS [13] or photoacoustic spectroscopy [14]. The broadly tunable QCL based on external cavity is ideal for measuring broadband laser spectroscopy of condensed phase materials, which have stronger interactions between molecules which lead to homogeneously broadening of the absorption peaks. Condensed phase explosives have been investigated by photoacoustic spectroscopy, which requires the deposition of the explosive films on a photoacoustic cell [15]. In standoff detection, the temperature increase caused by the molecular absorption of IR light can be monitored by a mercury cadmium telluride (MCT) IR detector [16] or by a probing laser deflection [17] and a hyperspectral image can be obtained to identify the explosives against the background [18,19].

Recently, we utilized piezoelectric quartz crystal tuning forks as detectors in the standoff QCL IR spectroscopy of surface adsorbed explosive residues [20–22] as a variation of the quartz enhanced photoacoustic spectroscopy [23]. The decrease in the reflected or scattered IR laser power from the target due to molecular excitation is obtained by taking the difference between the spectra of remote target surface with and without the chemical residue. This requires an alternative clean target surface [20,21] or UV decomposition of surface adsorbed molecules to serve as a reference spectrum for acquiring the differential spectrum for molecular identification [22]. In this study, we used a long range UV laser to achieve photodecomposition of the explosives from the standoff distance. The pulsed QCL acting as the IR light source has the advantage of room temperature operation, however it also suffers from a pulse-to-pulse intensity fluctuation. Furthermore, the previously employed slow step-scan scheme produced scan-to-scan fluctuations on the QCL baseline spectrum with many sharp absorption peaks from aerial water. Here we demonstrate a continuous rapid-scan scheme which makes use of an MCT IR detector and a 1 MHz quartz crystal oscillator which enable fast data acquisition during a rapid-scan time frame. A drawback of the low frequency oscillator is that a function generator is needed to match the laser pulsing frequency to the harmonic frequency of the oscillator and consequently a lock-in amplifier is needed to obtain the signal amplitude. The 1 MHz oscillator allows the implementation of a high speed data acquisition card to perform analog to digital conversions so that the bulky instruments such as a function generator and a lock-in amplifier are no longer needed.

In this paper, the experimental setup of the rapid-scan scheme is briefly described in Section 2. Significant improvement on the sensitivity and reproducibility is achieved when compared with the previous step-scan scheme. The reflectance spectra of explosives including cyclotrimethylene trinitramine (RDX), trinitrotoluene (TNT), and pentaerythritol tetranitrate (PETN) are measured by a commercially available FTIR microscope and are calculated using *ab initio* theory. The results are presented in Section 3.1, which provides confirmation of the standoff QCL experimental results and a benchmark for the standoff QCL spectroscopy. In Section 3.2, standoff detection of trace amounts of surface adsorbed RDX residues were investigated using a QCL centered at 7 μm, where the aerial water absorption is addressed. In addition, standoff detection of RDX, TNT, and PETN was performed using a QCL centered at 8 μm. A pulsed UV laser was used to perform standoff decomposition of explosives and the amount of time needed to accomplish the photodecomposition of RDX was studied.

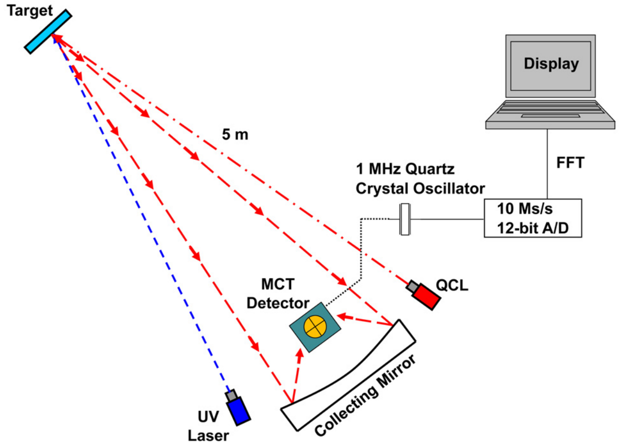

Fig. 1. Schematic illustration of the standoff sensing system. Two pulsed QCLs sequentially illuminate explosive residues on a stainless steel surface 5 m away. IR light reflected from the surface is collected and focused onto an MCT IR detector. Then the surface is exposed to pulsed UV radiation and scanned again with two pulsed QCLs to acquire reference IR spectra. The measured IR signal with the MCT detector is expanded and amplified by a quartz oscillator amplifier. The signal is digitized by a data acquisition card and the amplitude of the signal is obtained by fast Fourier transformation.

2. Material and methods

Fig. 1 presents the schematic illustration of the current standoff sensing setup. The light sources we used are the Über Tuner broad tuning pulsed external cavity QCLs (Daylight Solutions, San Diego, CA). The ÜT-7 and ÜT-8 laser heads were chosen to probe the fingerprint region of the explosives with a tuning range of 1540 cm^{-1} to 1340 cm^{-1} (6.49–7.43 μm in wavelength) and 1410 cm^{-1} to 1145 cm^{-1} (7.10–8.73 μm in wavelength), respectively. The spectral resolution of the pulsed QCL is around 1 cm^{-1}, which is insufficient to accurately measure the sharp absorption peaks of vapor phase chemicals, but ideal for the broad absorption peaks of condensed phase materials on a surface. We used the maximum pulse length of 500 ns at a 100 kHz pulse repetition rate which corresponded to a duty cycle of 5%, providing an average optical power of 4 mW and 20 mW for ÜT-7 and ÜT-8, respectively. The QCL beam was pointed at the stainless steel surface placed 5 m away with patches of explosive residues. The spot size of the laser beam is around 3 mm. The standard RDX, TNT, and PETN samples in a 1:1 methanol:acetonitrile (methanol only for PETN) solution with a concentration of 1 mg/ml were purchased from AccuStandard and used without further purification. Patches of explosive residues were produced simply by the droplet evaporation method to mimic real world sample conditions. The surface concentration of the explosives was estimated using the volume of solution and the area of the droplet. The surface was regenerated by a frequency quadrupled Nd:YAG laser (Big Sky Ultra, MT) which has an energy output of 2 mJ over 6 ns per pulse and a maximum repetition rate of 20 Hz at an optical wavelength of 266 nm. The major part of the reflection light were captured by a gold coated parabolic mirror with 15 cm diameter and focused on a thermoelectrically cooled MCT IR detector. The pulsed laser photon energy is converted into voltage pulses typically with amplitudes of a few hundred mV lasting 500 ns with a repetition rate of 100 kHz. To accurately measure the intensity of these pulses, a quartz crystal oscillator operating at 1 MHz (Citizen Finetech Miyota, Japan) and an operational amplifier were used to transform the sharp pulses into composite sub-harmonic excited waveforms with a fundamental frequency