Detection of chemical clouds using widely tunable quantum cascade lasers

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ABSTRACT

Widely tunable quantum cascade lasers (QCLs) spanning the long-wave infrared (LWIR) atmospheric transmission window and an HgCdTe detector were incorporated into a transceiver having a 50-mm-diameter transmit/receive aperture. The transceiver was used in combination with a 50-mm-diameter hollow retro-reflector for the open-path detection of chemical clouds. Two rapidly tunable external-cavity QCLs spanned the wavelength range of 7.5 to 12.8 µm. Open-path transmission measurements were made over round-trip path-lengths of up to 562 meters. Freon-132a and other gases were sprayed into the beam path and the concentration-length (CL) product was measured as a function of time. The system exhibited a noise-equivalent concentration (NEC) of 3 ppb for Freon-132a given a round-trip path of 310 meters. Algorithms based on correlation methods were used to both identify the gases and determine their CL-products as a function of time.

Keywords: atmospheric sensing, open-path spectroscopy, gas detection, vibrational spectroscopy, infrared spectroscopy, quantum cascade lasers, chemical detection

1. INTRODUCTION

Open-path atmospheric spectroscopy is used to measure the gas concentration along an optical path. There are many such systems and they operate within one or more of the atmospheric transmission bands that exist between the ultraviolet (UV) and mid-infrared (MIR) portions of the optical spectrum [1-4]. The MIR spans roughly $\lambda \approx 2.5$ to 14 µm (in wavenumbers, $\bar{\nu} = c/\lambda \approx$ 4000 to 700 cm^{-1}) and is of particular interest for a variety of commercial and military applications because many chemical threats have strong and unique absorption features in this range enabling high sensitivity and high-specificity detection.

Block Engineering has been developing MIR spectroscopy products for decades. In fact, Block Engineering originated the rapid-scan Fourier-Transform Infrared (FTIR) spectrometer and introduced the first commercially available FTIR spectrometer in 1969 through its subsidiary Digilab. Recently, Block has developed a miniature external-cavity quantum cascade laser (EC-QCL) called the Mini-QCL™ that can rapidly scan in wavelength across a large portion of the MIR [5, 6]. These sources have numerous applications and are ideally suited for certain classes of open-path spectroscopic sensing. Block's atmospheric sensing system is called LaserWarn™.

2. OPEN-PATH ATMOSPHERIC SENSING

Figure 1 shows a typical configuration for open-path atmospheric sensing. The transceiver includes both a wavelength-tunable laser transmitter and a receiver. The laser beam is aimed at a distant retro-reflector and a fraction of the optical power is returned to the system. The return signal is measured by the receiver as a function of wavelength to generate a transmission spectrum. The system operates by first measuring a reference spectrum under an initial set of conditions and then the relative change in transmittance is monitored over time. The changes in transmittance can be correlated to large-scale changes in the atmospheric gas concentrations (e.g., humidity) and the presence of localized chemical clouds. A detection algorithm coupled with a spectral library converts the transmission spectra into gas concentrations versus time in terms of a concentration-length (CL) product along the path of the laser beam.

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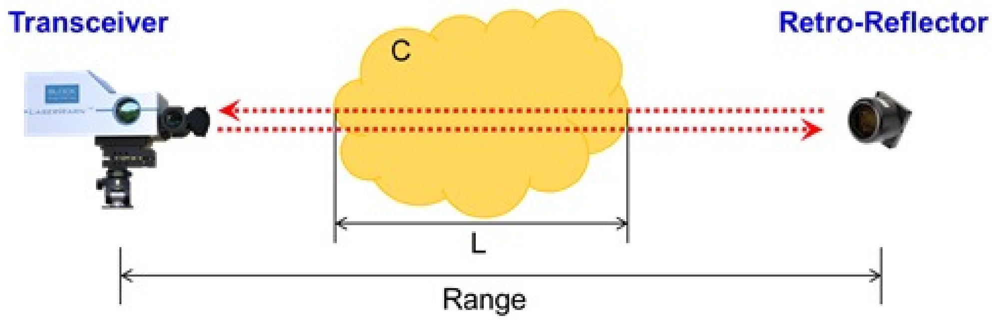

Figure 1: Schematic drawing of open-path atmospheric sensing system that is formed between the laser transceiver and a retro-reflector. Chemical clouds that intercept the laser beam, and that have absorption features within the laser's tuning range, are identified and quantified in terms of their concentration-length (CL) product.

As shown in Figure 2, there are many applications for an atmospheric sensor that covers a wide wavelength range in the MIR. The examples in Figures 2a-b show how a series of mirrors and retro-reflectors can be used to create a "chemical tripwire" that crisscrosses a facility. A chemical cloud that crosses the laser beam at any point will be detected. Outdoor installations can be used to monitor fugitive emissions from facilities or to protect critical infrastructure (e.g., embassies, public arenas) against chemical attack. An indoor system could be used for protection of airports. Figure 2c shows that multi-path scanning is possible by integrating a pointing system with the transceiver. With multi-path scanning, the system sequentially interrogates different beam paths in order to extend the spatial coverage of the system and enable the ability to localize the cloud along particular optical paths. Figure 2d shows an example of an "on-the-fly" configuration that can be used, for example, by first responders. In an emergency situation, the LaserWarn system can be quickly setup on a tripod and retro-reflectors can be thrown into the facility. The retro-reflectors can be optically probed to determine the composition of an intervening chemical cloud. An integrated pointing system will facilitate the locating of multiple retro-reflectors that are dispensed as well as to allow automated multi-path scanning.

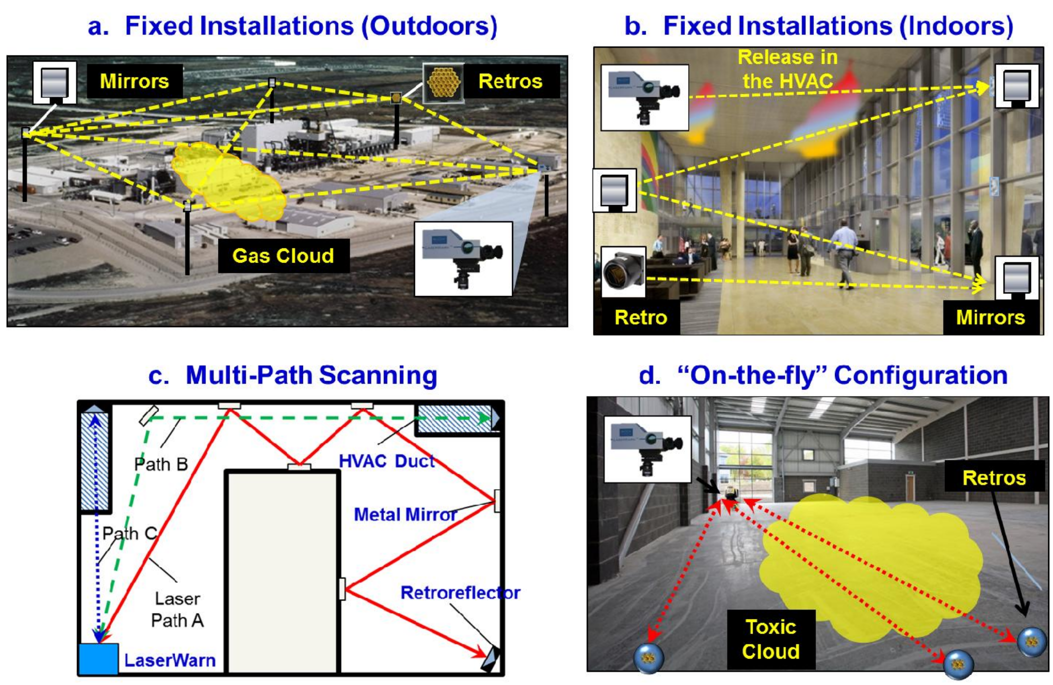

Figure 2: Examples of how a QCL-based atmospheric sensing system can be used in security applications. (a-b) Examples are shown of both indoor and outdoor fixed installations in which LaserWarn creates a "chemical tripwire" to detect the presence of a chemical cloud that crosses the laser beam. (c) By integrating a pointing system with LaserWarn, multi-path scanning can be achieved to monitor multiple beam paths. (d) An "on-the-fly" configuration can be setup quickly and is suitable for use by emergency responders.

3. WIDELY TUNABLE QCL SOURCE

Passive MIR systems for the detection of gas clouds typically use FTIR spectrometers and are best suited for situations where the chemical cloud is viewed against the background of a clear sky in order to achieve a high thermal contrast. But to detect gases against the background of a cloudy sky, along a horizontal path, or indoors where the thermal contrast is low or non-existent, systems that utilize active illumination are required. Active FTIR-based systems typically use heated filaments as the light source. Since filaments have low radiance, they necessitate the use of large optics, long integration times, and cryogenically cooled detectors. As compared to a heated filament, a laser source has much higher radiance and can overcome all of these limitations. For example, a thermal source at 1100 K has a radiance of 0.3 $W/cm^2/sr$ over the $\lambda = 8 – 14$ μm band while a 1-mW diffraction-limited laser beam at $\lambda = 10$ μm has a radiance of about 10^3 $W/cm^2/sr$. This corresponds to a laser radiance that is roughly 10^4 greater than for the thermal source. The advent of the QCL as a practical source of wavelength-tunable MIR radiation enables long-distance sensing using optics of modest size, short integration times, and the use of thermo-electrically cooled (TEC) detectors.

QCLs are a revolutionary mid-IR laser technology that makes mid-IR spectroscopy practical in configurations that were previously not possible [7, 8]. For gas-sensing applications, QCLs can be classed in terms of their spectral properties. Distributed-feedback (DFB) QCLs emit light at a single frequency having narrow linewidth that can be tuned over a narrow band of a few cm^{-1} [9, 10]. These are most appropriate for targeted, high-resolution detection of one (or a few) simple gases that have narrow absorption features. EC-QCLs, on the other hand, can be tuned over a wide wavelength range for the identification of multiple gases that are present either by themselves or in mixtures. Since most EC-QCLs have linewidths that are relatively broad in comparison with the absorption linewidth of simple gases, they are most suitable for detection of complex molecules that have broad absorption features. It is worth noting that almost all of the chemical threats have broad absorption features and fall into this latter category. Recently, there have been efforts to combine the advantages of wide wavelength coverage with high-resolution spectroscopy by using optical frequency combs (OFCs) [11, 12]. OFC-based spectrometers are an active area of research and have many potential advantages, but current laboratory demonstration systems are complex.

Block Engineering/MEMS is leading the development of miniaturized, widely tunable EC-QCLs. Figure 3a shows a photograph of our mini-QCL™ module [6]. The Mini-QCL is an EC-QCL in which the laser cavity is formed between the front facet of the QCL chip and a diffraction grating. The Mini-QCL is extremely compact, having dimensions (excluding the electrical leads) of only 43 x 23 x 17 mm (L x W x H). Modules are available that operate anywhere within the $\lambda = 5.4 – 13$ μm range. Each module are broadly tunable (typically >250 cm^{-1}) such that only four modules are needed to cover the entire $\lambda = 5.4 – 13$ μm range. Figure 3c shows the normalized spectra for a Mini-QCL over its tuning range. The laser linewidth is <2 cm^{-1} which is suitable for the detection of complex molecular gases. Lasers operate pulsed with peak powers of 100's of mW, pulse lengths from 30 – 500 ns, and a pulse repetition frequency (PRF) as high as 3 MHz. Most modules can operate up to a duty factor of at least 10% with air cooling. Figure 3d shows the average power versus wavelength for two Mini-QCLs when operated with a duty factor of 5%. Beam quality and beam pointing stability are important factors for atmospheric sensing applications since the laser beams are projected over long distances. The beam quality of the Mini-QCL is generally near-diffraction-limited. As an example, Figure 3b shows an image of the far-field at $\lambda = 10$ μm in which the beam profiles very nearly approximate a Gaussian. The beam pointing stability is also excellent having a maximum deviation of ±0.5 mrad which is a small fraction of the beam divergence of 5 mrad $FW1/e^2$. For most of the tuning range, the beam pointing error is less than ±0.2 mrad.

To the best of our knowledge, these modules have the fastest tuning speed of ~25 cm^{-1}/msec of any commercially available widely tunable EC-QCL. This enables a single Mini-QCL to tune over a bandwidth of >250 cm^{-1} at scan rates >100 Hz. Using Block's custom electronics, the laser pulses from multiple Mini-QCLs can be interleaved such that the entire tuning range from $\lambda = 5.4 – 13$ μm can be scanned at >100 Hz. While tuning at high speed, custom electronics can simultaneously measure the optical signal using a mercury cadmium telluride (MCT) detector to perform high-speed, wide-bandwidth spectroscopy.

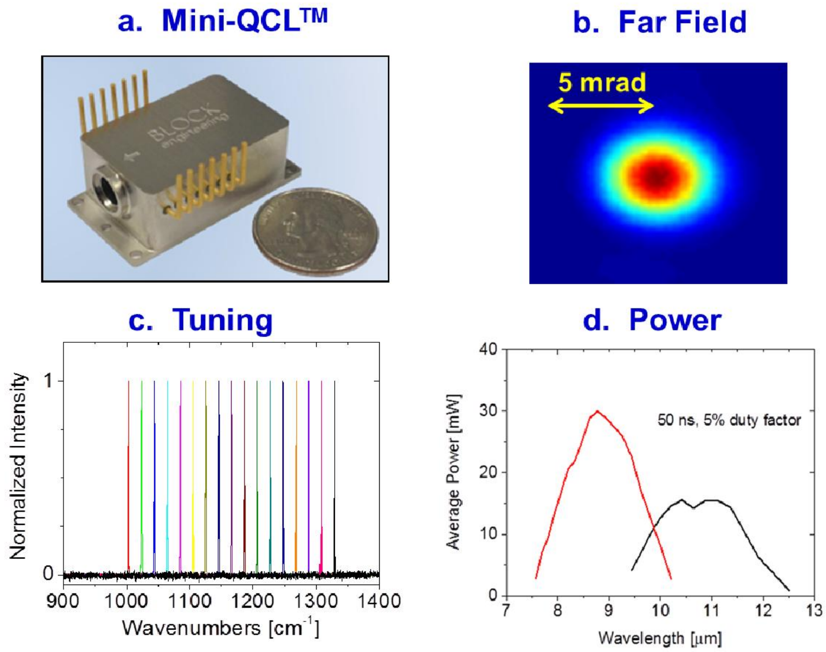

Figure 3: (a) Photograph of a Mini-QCL which is the smallest widely tunable EC-QCL to the best of our knowledge. (b) Image of the far-field beam at $\lambda = 10\ \mu m$. (c) Normalized spectra for a Mini-QCL as it is tuned in wavelength. (d) Average power for two different Mini-QCL modules at a duty factor of 5%.

4. OPEN-PATH SPECTROSCOPY SYSTEM

Figure 4 shows a photograph of the open-path atmospheric sensing system called LaserWarn™ that was developed. Also plotted is the long-wave infrared (LWIR) atmospheric transmission window at two humidity levels. The LaserWarn system spans most of the LWIR window as indicated in the figure.

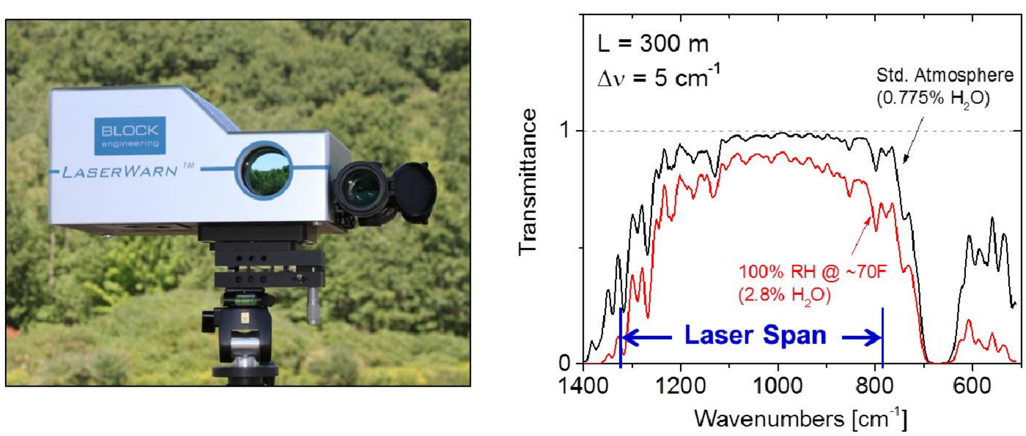

Figure 4: (left) Photograph of the open-path atmospheric sensing system called LaserWarn. (right) LWIR atmospheric transmission window at two humidity levels. Also shown is the spectral range covered by the 2 Mini-QCLs within LaserWarn.

4.1 System design

The LaserWarn system incorporates 2 Mini-QCLs that together cover the spectral range of 780 – 1330 cm^{-1} (λ = 7.5 – 12.8 μm). The beams from the two lasers are spatially overlapped. As shown in Figure 5, the combined beam is expanded using a telescope such that the transmitted beam diameter is ~20 mm. The final 50-mm-diameter lens also serves as the receive aperture and a beam splitter is used to divert the returned light to a high-speed MCT detector. Figure 5 shows a calculation of the optical efficiency as a function of range when using a 50-mm-diameter retro-reflector. Optical efficiency refers to the fraction of the transmitted optical power that is received by the system assuming losses are only due to diffraction (neglecting any losses due to atmospheric attenuation, etc.). For the current optical design, the efficiency drops to about 1% at a range of 300 m which corresponds to a round-trip (RT) distance of 600 m. This level of optical efficiency is sufficient for system operation. The maximum range of the system can be easily increased by making minor modifications to the system optics or by using larger retro-reflectors.

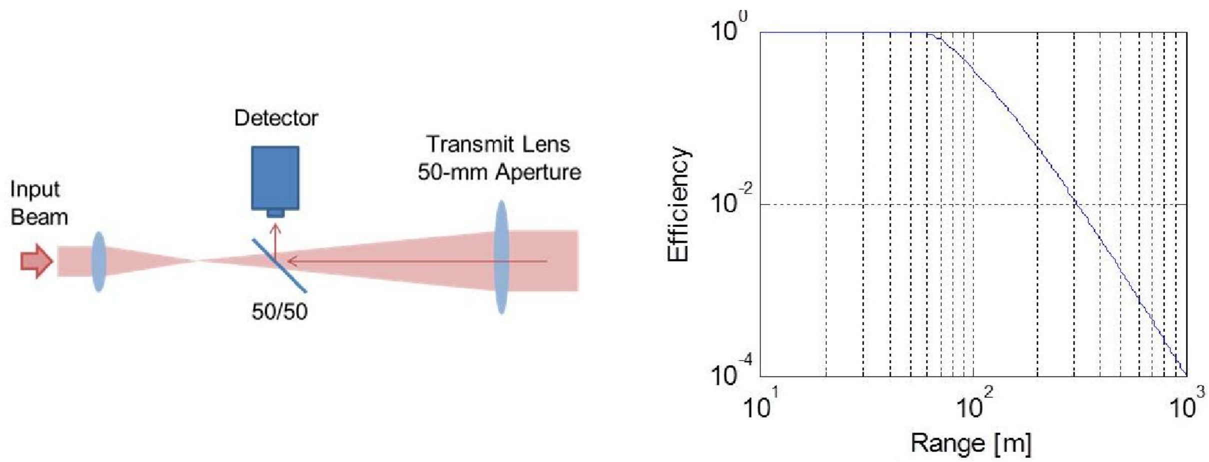

Figure 5: (left) Schematic diagram of the optical design. (right) Optical efficiency versus range when using a 50-mm-diameter retro-reflector.

4.2 Demonstrations

The LaserWarn system was mounted on a tripod and used with a 50-mm-diameter retro-reflector in the parking lot at Block's facility. The system setup is very straightforward and takes only about 15 minutes. Although car-battery power was used for these tests, the system can run for several hours using compact rechargeable batteries. As shown in Figure 6a, two different beam paths were used having round-trip beam path-lengths of 310 m and 562 m.

To account for of the time-of-flight of the transmitted laser pulses, the system was typically configured for pulses to be transmitted with a period of 3 μs and spectral measurements were made at a reduced rate of 20 Hz. Multiple spectra were averaged for between 0.5 – 5 s depending on the desired signal-to-noise ratio (SNR). First a reference measurement is made of the return signal versus wavelength. This reference measurement is used to normalize subsequent measurements to obtain the relative transmittance spectra versus time. A graphical user interface was developed to control the instrument and a detection algorithm was developed that compares the measured transmittance with the entries in a spectral library [13-15].

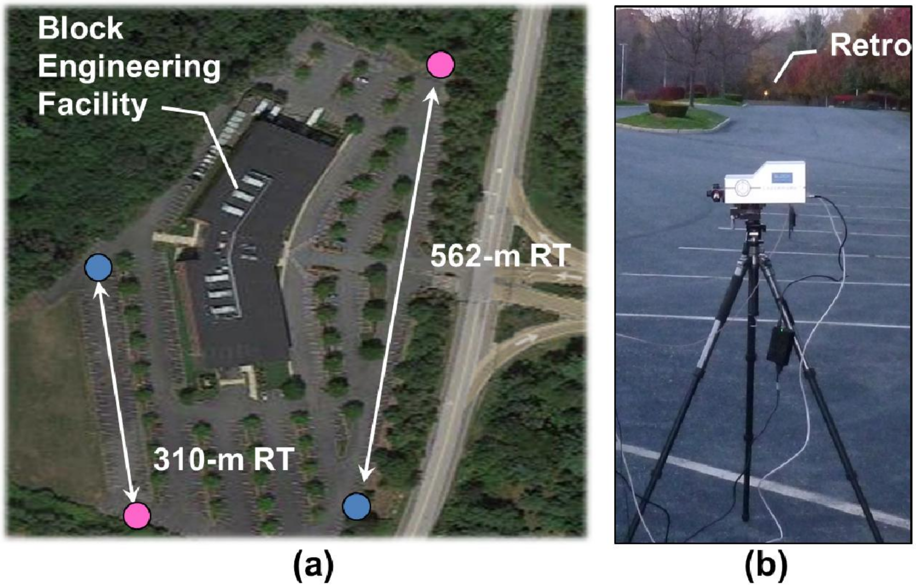

Figure 6: (a) Aerial view of Block's facilities showing the 2 optical paths for testing. (b) Photograph of the tripod-mounted LaserWarn system during the testing. Note the distant retro-reflector which can be seen because a flash was used to take the photograph.

Figure 7a shows the library spectra for some of the gases that were tested [15]. Freon was chosen because it similar to the chemical agents such as Sarin in terms of the strength and spectral width of the absorption features. In this sense, Freon-134a is a suitable simulant for the nerve agents. Figure 7b shows the transmission spectrum measured for a path length of 310-m-RT when Freon-134a was sprayed into the beam path. The relative strengths of the various absorption peaks do not perfectly match the library spectra because the gas concentration was changing in time during the measurement. Nevertheless, the Freon-134a concentration is calculated to be approximately 200 ppb when averaged over the entire path. Since the gas cloud is actually localized along the laser beam path within a few meters, the local concentration within the cloud is, of course, much higher. Under these measurement conditions of 5-s integration time and spectral resolution of 4 cm^{-1}, the SNR is about 400. From this result, the noise equivalent concentration (NEC) is calculated to be 3 ppb.

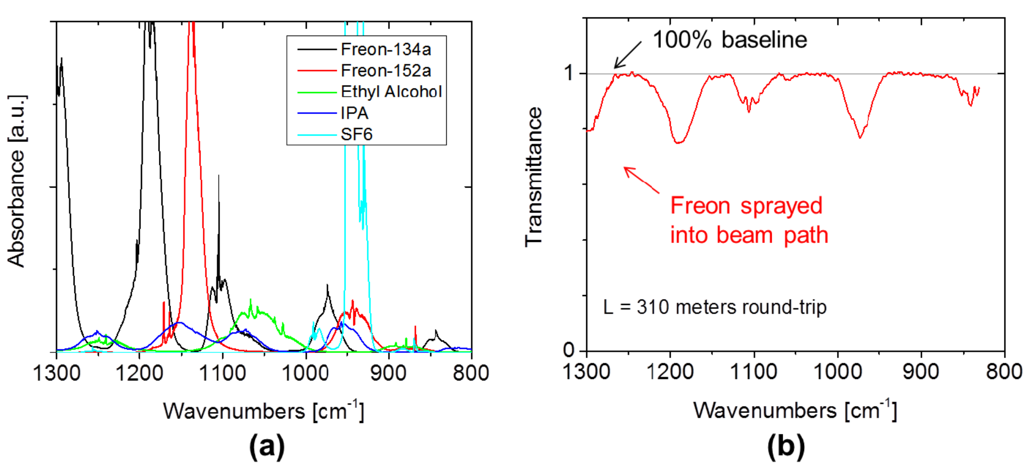

Figure 7: (a) Absorption spectra for various gases that were tested. (b) Transmission spectra when Freon-134a was sprayed into the beam path. The system operated over a 310-m RT path.

Measurements were then made for a round-trip path of 562 m with a measurement time of 2 s and measurement interval of 2.5 s. Again various gases were sprayed into the beam path. For these measurements, the transmittance spectra were converted to absorbance units (log base-10) and then compared with entries in a spectral library. The detection algorithm identifies the gas and determines its concentration. The algorithm can also identify and quantify multiple gases simultaneously (i.e., mixtures). Figure 8a shows the absorbance spectrum at one moment in time when difluoroethane (Freon-152a) and tetrafluoroethane (Freon-134a) were simultaneously into the beam path. Figure 8b shows the concentration for each of these gases versus time as determined by the detection algorithm in units of ppm-m. As can be seen in Figure 8b, difluoroethane (blue curve) is first dispensed. Then, tetrafluroethane (red curve) is dispensed. Finally, both gases are dispensed at the same time. The spectrum in Figure 8a corresponds to the last data point in Figure 8b.

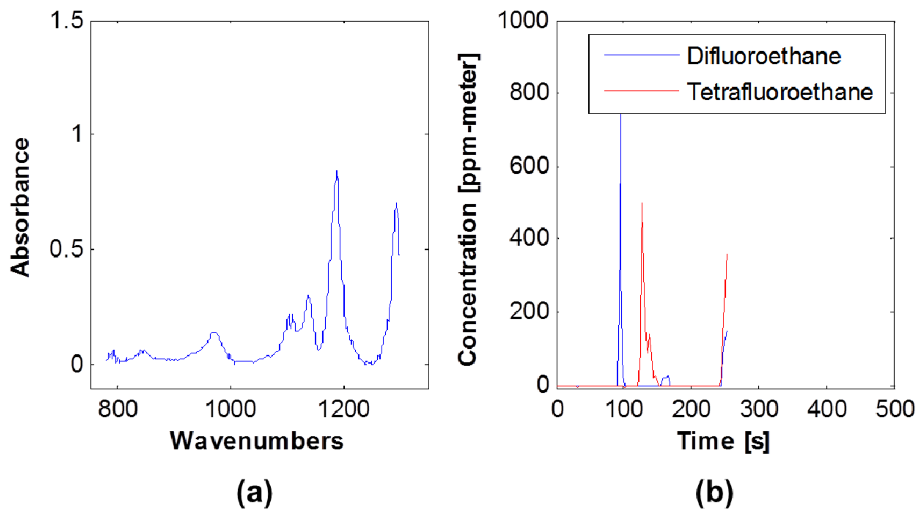

Figure 8: (a) Absorbance spectra at a single moment in time when both difluoroethane and tetrafluoroethane were simultaneously sprayed into the beam path. (b) Gas concentration versus time in units of ppm-meter. The detection algorithm identifies the gas and determines its concentration.

4.3 Calculated detection limits

The table in Figure 9 gives calculated limits of detection (LOD) for various chemical agents using LaserWarn taking a system SNR of 500. These assume a cloud that has an extent of 25 m along the path of the laser beam. Note also that these estimates are simply based on the magnitude of the peak absorbance within the LWIR atmospheric window. They do not take into account the width of the spectral features which is typically much broader than the spectral resolution of the system. As a result, the actual LODs should be significantly lower than the values given in the table for many of the gases.

Type	Agent	Calculated LOD (ppm) 25-m-long cloud
Nerve	Tabun (GA)	0.03
	Sarin (GB)	0.03
	Soman (GD)	0.03
	Cyclosarin (GF)	0.03
	VX	0.03
Blister	Sulfur Mustard (HD)	0.16
	Nitrogen Mustard (HN_3)	0.04
	Lewisite (L)	0.17
Blood/TIC	Hydrogen Cyanide (AC)	2.7
	Cyanogen Chloride (CK)	5.4
	Phosgene (CG)	0.07
TIC	Nitric Acid (HNO_3)	0.15
	Ammonia (NH_3)	0.08
	Sulfur Dioxide (SO_2)	2.4
	Chlorine as HClO	0.26

Figure 9: Calculated limits of detection (LOD) for various chemical agents and toxic industrial chemicals (TICs). This assumes a cloud length of 25 m along the path of the laser beam.

5. SUMMARY

Block's Mini-QCL is a miniature and widely tunable EC-QCL that enables practical open-path atmospheric sensing systems. Using this technology, we have developed the LaserWarn sensor which incorporates 2 Mini-QCLs to rapidly span most of the LWIR atmospheric window. The system can make spectral measurements in less than a second. The system is compact and can be installed at fixed sites or can be configured for portable use by emergency responders. The current design of LaserWarn allows round-trip path-lengths of ~500 m. We have demonstrated the use of LaserWarn to detect and identify various simulant gases over optical paths of up to 562 m. Simple modifications to the optics will allow increasing the path length to multiple kilometers.

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