Broadband standoff detection of large molecules by mid-infrared active coherent laser spectrometry

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Abstract: A widely tunable active coherent laser spectrometer (ACLaS) has been demonstrated for standoff detection of broadband absorbers in the 1280 to 1318 cm⁻¹ spectral region using an external cavity quantum cascade laser as a mid-infrared source. The broad tuning range allows detection and quantification of vapor phase molecules, such as dichloroethane, ethylene glycol dinitrate, and tetrafluoroethane. The level of confidence in molecular mixing ratios retrieved from interfering spectral measurements is assessed in a quantitative manner. A first qualitative demonstration of condensed phase chemical detection on nitroacetanilide has also been conducted. Detection performances of the broadband ACLaS have been placed in the context of explosive detection and compared to that obtained using

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distributed feedback quantum cascade lasers.

OCIS codes: (280.3420) Laser sensors; (300.6310) Spectroscopy, heterodyne; (140.5965) Semiconductor lasers, quantum cascade; (280.1545) Chemical analysis.

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1. Introduction

In the context of security and defense applications, the reliable detection, identification, and quantification of explosive traces in a remote configuration represents a major technical challenge. The stringent requirements placed upon the sensing system include high sensitivity for trace detection of low-volatility chemicals, response times of the order of seconds, operational distances extending up to several hundred meters, and wavelength agility to confidently quantify and identify potentially complex mixtures [1]. In addition, when a "true" standoff operating mode is required, as it would be for a fully uncooperative sensing configuration, the difficulty increases even further [2]. Active sensing techniques based on laser spectroscopy are believed to provide the best means of addressing the challenge [1] as they advantageously combine remote operation, speed, sensitivity, and selectivity.

Mid-infrared (MIR) spectroscopy provides valuable information on the chemical composition of both gas-phase and condensed-phase compounds due to the fundamental rovibrational absorption bands in this spectral region. These bands are significantly more intense than analogous bands found in the near-infrared or visible regions of the spectrum. In addition, atmospheric transmission windows in the MIR (3-5 and 8-12 μ m) allow remote sensing at long distances (>100 m) with limited water vapor interference. The unambiguous spectral signatures of chemicals in the MIR can be exploited for definitive molecular identification and to obtain reliable quantitative mixing ratio information, even in the presence of complex chemical backgrounds [2]. Finally, operating at MIR wavelengths offers significant practical advantages for "real world" applications, including invisibility of the illumination to human eyes, relaxed constraints in terms of eye safety, and greater immunity to weather conditions than shorter wavelengths.

Recently, the concept of the Active Coherent Laser Spectrometer (ACLaS) has been proposed and demonstrated [3] for standoff molecular vapor detection in the MIR. At the core of this approach lies a continuously tunable MIR laser source which provides active illumination of distant topographic obstacles, as well as the local oscillator field used for heterodyne detection of the light backscattered by the scene. This approach inherits all the advantages of passive laser heterodyne spectro-radiometers which rely on thermal contrast [4, 5], with an additional sensitivity boost from the active illumination. ACLaS offers high

detection sensitivity, extremely efficient background noise rejection (due to the ultra-high spectral resolving power, $> 10^7$), and hyperspectral information through continuous tuning of the laser frequency. The demonstration was carried out using distributed feedback quantum cascade lasers (DFB-QCL), which were demonstrated to be highly relevant for standoff detection of narrow band absorbers (FWHM < 0.5 cm⁻¹). Standoff detection of a variety of chemical species, including hydrogen peroxide, nitrous oxide, methane, water and acetylene, was demonstrated with topographic targets at distances of up to 30 m.

However, to realize the full benefits of the ACLaS, particularly for standoff detection of threat chemicals, the ability to detect the broadband absorption features characteristic of large molecules is highly sought after and would allow the detection of both vapor and condensed phase chemicals. This is achieved by employing a widely tunable, continuous wave (CW) MIR laser source as the core of the ACLaS.

The intrinsically broad gain curve of QCL, further broadened by ad hoc structures [6], can be exploited in an external cavity (EC) configuration to significantly increase the frequency coverage accessible with CW MIR laser sources [7]. EC-QCL devices with tuning ranges larger than 100 cm⁻¹ have been employed in a variety of configurations to detect the broadband spectral signatures of surface contaminants [8–10].

In this framework, the work reported here extends the ACLaS standoff detection method to broadband molecular signatures. To explore and demonstrate the technique's capabilities, a commercial EC-QC has been used as the spectroscopic source. The first section gives insights on a theoretical model for the ACLaS, including signal, noise, and spectral processing. This is followed by a description of the experimental implementation of the system. Subsequently, results from a measurement campaign are presented, starting with narrow band absorbers used to benchmark the broadband version of the system against earlier results obtained with DFB-QCL. Measurements on broadband absorbers in both the vapor and condensed phases follow. Lastly, in a concluding section, a summary of the study's outcomes is provided along with a discussion on the performances achieved to date with the ACLaS.

2. Standoff heterodyne detection modelling

The ACLaS can be described as a MIR hyperspectral CW coherent lidar, which measures molecular absorption integrated over its line of sight, between the instrument and a non-cooperative rough target. The basic architecture has already been reported [3]. The approach involves illuminating a topographic target with, in the present case, radiation from an EC-QCL. A small fraction (~1 per mil) of the illumination field is diverted to become the local oscillator (LO) of an optical heterodyne receiver. A frequency offset between the LO and the transmitted field is produced by an acousto-optical frequency shifter (AOS). In this arrangement, coherent detection of the backscattered field is performed at the intermediate frequency set by the AOS. As the continuously tunable laser source is frequency swept, the received signal contains spectral information from molecules interacting with the field over the standoff distance. A comprehensive model to describe the instrument has been developed. It includes a) backscattering from aerosols and topographic targets within the coherent field of view of the heterodyne receiver, b) noise terms associated with the coherent process and speckle effects, and c) the absorption of light by molecular species and aerosols along the illumination path.

2.1 Coherent signal

The total laser power returning to the instrument receiver can be split into three contributions. Firstly, as the laser field travels from the transmitter to the target (if any), laser power is backscattered by atmospheric aerosols characterized by a backscattering coefficient $\beta_b(z, v)$. This coefficient accounts for dependences with laser frequency v and with position along the line of sight z to account for a potentially inhomogeneous atmosphere. For simplicity, an ideal Lambertian scatterer is assumed. The backscattered power contribution reaching the receiver due to aerosols between the transmitter (z = 0) and the topographic target (z = L) is given by

Eq. (1) where A_R represents the receiver area and $P_0(v)$ the transmitted power. Molecular scattering is taken to be negligible at MIR wavelengths.

$$P_{BS}(L,\nu) = \frac{A_R}{2\pi} \cdot P_0(\nu) \cdot \int_0^L \beta_b(z,\nu) \cdot \frac{1}{z^2} \cdot \exp\left(-2\int_0^z \gamma(z',\nu) \cdot dz'\right) \cdot dz$$
(1)

The second (exponential) term in the integral of Eq. (1) accounts for the extinction occurring both on the transmitted and backscattered laser power characterized by an extinction coefficient $\gamma(z, v)$. This extinction is composed of both absorption $\alpha(z, v)$, and scattering terms. For convenience, the scattering has been split into two coefficients (assuming Lambertian scattering), $\beta_b(z, v)$ already mentioned, which is valid for the half space solid angle opposite to the direction of propagation, and $\beta_f(z, v)$, the equivalent forward scattering coefficient. The overall extinction term then becomes the sum of these three.

The second contribution to the received laser power results from the diffuse reflection occurring at the target. The diffuse reflection (again assumed Lambertian) is characterized by the reflectivity coefficient $\rho(v)$. The optical power diffusely reflected by the target that reaches the receiver is given by Eq. (2) where L is the distance between receiver and target.

$$P_{DR}(L,\nu) = \frac{A_R}{2\pi \cdot L^2} \cdot P_0(\nu) \cdot \rho(\nu) \cdot \exp\left(-2\int_0^L \gamma(z,\nu) \cdot dz\right)$$
(2)

Finally, as the diffusely reflected contribution travels back to the receiver aperture, it undergoes extinction and scattering in the same manner as the transmitted radiation. A part of the forward scattering contributes to the power received. The amount of forward scattering reaching the receiver is given by Eq. (3).

$$P_{FS}(L,\nu) = \frac{A_R}{2\pi} \cdot P_0(\nu) \cdot \rho(\nu) \cdot \exp\left(-2\int_0^L \gamma(z,\nu) \cdot dz\right) \cdot \int_0^L \beta_f(z,\nu) \cdot \frac{1}{z^2} \cdot \exp\left(-\int_0^z \gamma(z',\nu) \cdot dz'\right) \cdot dz$$
(3)

From all the contributions, the total optical power reaching the instrument aperture can be calculated. However, to actually determine the amount of power contributing to the ACLaS signal, additional aspects needs to be considered.

The heterodyne detection process, via its sensitivity to wavefront overlap, makes the ACLaS range-sensitive with respect to the backscattered signal, even though CW illumination is provided. This has been detailed in [11] and is illustrated in Fig. 1, where the illumination and the back-propagated LO (BPLO) beams have been assumed perfectly overlapped (blue wavefronts). Figure 1(a) shows wavefronts from backscattering from a single particle (red) located at the exact location where the transmitted beam is focused. In this case, the backscattered signal and the BPLO are fully overlapped. Figure 1(b) shows a converse case where the particle considered backscatters the illuminated field away from the illumination focus. In the latter case the heterodyne efficiency will be close to zero and the contribution to the total ACLaS signal will be negligible. This range-sensitivity of the heterodyne receiver can be taken into account by adding a heterodyne mixing efficiency function of z weighting the contribution from backscattering.

The ACLaS system described in this work has a bistatic configuration with separate transmission and receiver optics. Therefore, in addition to the heterodyne mixing dependence with *z*, an additional overlap function needs to weight the scattering contribution [12].



Fig. 1. Wavefronts of the backscattered (red) and transmitted (blue) fields for a single scattering particle co-located at the focus of the transmitted beam (a) and away from transmitted beam focus (b). The black rectangle (left in both plots) represents transmitter/receiver optics of focal length F.

#228991 - \$15.00 USD (C) 2015 OSA Received 4 Dec 2014; revised 7 Jan 2015; accepted 10 Jan 2015; published 15 Jan 2015 26 Jan 2015 | Vol. 23, No. 2 | DOI:10.1364/OE.23.000912 | OPTICS EXPRESS 915 With the focus and distance dependent weighting added, in the particular scenario considered here, the contribution of scattering to the received signal appears far weaker than that from the target diffuse reflection as shown in Fig. 2. Calculations were made with instrument parameters close to the experimental system described in the next section. The operating wavelength was 8 μ m, and 20 mW of laser power was transmitted. The target reflectivity was set to 0.2, backscattering and forward scattering coefficients were set to 10^{-8} m⁻¹ and 10^{-7} m⁻¹ respectively, to account for a clean atmosphere, and the absorption coefficient was 6×10^{-5} m⁻¹. For simplicity the medium was assumed to be homogenous with no spatial variation of absorption or scattering.

The plot in Fig. 2(a) shows calculated optical power scattered by atmospheric aerosols as a function of the focus location. In the case of the presence of a hard topographic target, the focus and the target are collocated as this ensures an optimized signal to noise ratio. The power contribution from the target diffuse reflection was calculated and is shown in Fig. 2(b) (black squares). Clearly, in the MIR and for a clean atmosphere, in the case of a sensing configuration where a topographic target exists at medium range (up to a few hundred meters), the contribution from aerosol scattering is insignificant (femtoWatts versus nanoWatts). Therefore, in the scope of the work presented here, aerosol backscattering will no longer be considered.



Fig. 2. (a) Power contribution to the heterodyne signal of the back and forward scattering as function of the illumination beam focus distance. (b) Power contribution from the diffuse reflection of a hard topographic target and total power contributing to the heterodyne signal as function of the target range.

Lastly, to work out the received optical power contributing to the heterodyne signal, further additional losses have to be considered. These include phase front misalignment due to the bistatic arrangement (in the range of few per mil and decreasing with target distance), polarization loss of up to 50% due to depolarization of the received field, optical system loss (~15%), and the detector intrinsic heterodyne efficiency (40%). With these included, the actual received power contributing to the heterodyne signal is show in Fig. 2(b) as red dots.

2.2 Noise

An ideal heterodyne receiver is limited only by the shot noise from the LO. In this case the noise equivalent power per unit of bandwidth is given by hv with a further correction from the overall heterodyne efficiency. Detector noise may also contribute if the photodiode detectivity falls below ~10¹⁰ cm.Hz^{1/2}/W, which is not the case in this work as a liquid nitrogen cooled HgCdTe photodiode was used for photomixing.

The initial ACLaS demonstration, using a DFB-QCL as the laser source, clearly established that performance is far from being shot noise limited due to speckle effects [3]. The use of a coherent source for active illumination of an optically rough surface typically leads to the formation of speckle patterns [13]. The speckle induced produces scintillation and phase fluctuations of the received field at the detector plane, manifesting as an additional

noise source. With speckle noise dominating, the ACLaS signal to noise ratio (SNR) is given by the square root of the speckle diversity parameter M [13] which can be interpreted as the number of independent speckle patterns averaged over the measurement time.

Speckle has also implication on the actual ACLaS receiving aperture. The speckle lobe size affects the coherence area onto the receiver [14] and therefore, the received signal also depends on M through A_R .

2.3 Mixing ratio retrieval

Under the assumption of medium range remote sensing in a clean atmosphere, the atmospheric extinction is solely due to molecular absorption occurring over the standoff distance. As the laser is frequency tuned, a full high resolution absorption spectrum is obtained. From the spectral data, molecular mixing ratios of potentially complex chemical mixtures have to be retrieved in a traceable and confident manner.

A spectral processor using an Optimal Estimation Method (OEM) algorithm has been developed [15]. It was originally initiated for vertical profiling of atmospheric constituents using high resolution spectral data delivered by a passive laser heterodyne spectro-radiometer [16]. Subsequently, it was adapted to process raw spectral data from a variety of remote and in situ laser spectroscopy instruments [17–19].

The OEM approach involves an instrument simulator that outputs a synthetized instrumental spectral trace, taking into account a given detection scenario. This forward model, which includes the standoff detection scenario as well as the instrument properties, describes the relation between the directly measured spectral signal, the unknown state vector of molecular mixing ratios, and instrument parameters. In addition to retrieving mixing ratios from spectral information, this approach permits the control and understanding of error and information propagation throughout the measuring system, assuming a normal statistical distribution of the variables involved in the problem. Most importantly, since any retrieval algorithm returns a numerical result, it also allows the use of analytical tools to critically evaluate and assess the quality of the retrieved results.

For this study, a mathematical model of the ACLaS instrument has been built (whose first steps are shown in section 2.1). The absorption coefficient involved in the atmospheric extinction is calculated from a spectral model that includes line by line calculation (using HITRAN data [20]) and broadband absorber calculations (using the PNNL database [21] and/or our own reference cross-section measurements).

3. Experimental description

3.1 Optical system

At the core of the broadly tunable ACLaS is the MIR spectroscopic source. A commercial CW EC-QCL was used (Daylight Solutions Inc, model TLS-21078-MHF). The laser is nominally continuously tunable between 1280 and 1318 cm⁻¹, and delivers up to 115 mW of optical power. The laser operates at a fixed factory-set operating point (T = 18.7°C, I = 930 mA) and laser frequency sweeps are obtained through grating angle tuning. The laser output beam has a diameter of 2.3 mm and a divergence of ~2 mrad (1/e² intensity FWHM).

Figure 3 shows a simplified optical layout of the ACLaS instrument. The EC-QCL radiation is directed to a R90/T10 beam splitter (BS1). The reflected part of the beam passes through a germanium AOS driven at 76 MHz. The unshifted zeroth-order output (not represented in Fig. 3 for clarity) is used for relative frequency calibration of the laser via transmission through a 1 mm long germanium etalon. The first-order diffracted beam from the shifter, containing a maximum of ~40 mW of power, is conditioned and transmitted toward a solid, diffusely reflective target about three meters away. The transmission optics are adjusted so that an illumination beam waist is formed on the target surface.

The portion of the optical field transmitted by BS1 provides the LO for optical heterodyne detection of the received field. The LO field goes through a variable attenuator connected to a PID loop that ensures constant and optimum LO power (~150 μ W), regardless of the laser

power modulation introduced by the optical frequency tuning. The LO field is then imaged onto a 200 MHz bandwidth liquid-nitrogen-cooled mercury cadmium telluride photodiode (PD). A small part of the returned optical field diffusely reflected by the target is captured by the receiver (OAPM4), conditioned, and superimposed onto the LO field by BS2.



Fig. 3. Simplified optical layout of the ACLaS instrument. M: mirror, BS: beamsplitter, OAPM: off-axis parabolic mirror, AOS: acousto-optical shifter, MOD: amplitude modulation. The left hand side illustrates the arrangement of the test gas cell and rough surface three meters away from the instrument.

The AC output from the PD is amplified and filtered by a bandpass filter centered at 76 MHz with a 3 dB bandwidth of 0.76 MHz. This determines the spectrometer spectral resolution, meaning that the ACLaS provides a spectral resolving power of 5×10^7 at 7.69 µm. Considering that standoff detection of broadband absorbers at atmospheric pressure is to be performed, the rationale for such a high resolving power is not related to ultra-high resolution spectroscopy requirements. Instead, this resolution was chosen to match the spectral linewidth of the illumination laser source. By doing so, the full power from the return signal is captured, whilst MIR background radiation is efficiently suppressed. In addition, even though the radiofrequency filter is very narrow, the full coherence between the LO and the received field ensures that the returned radiation spectrum remains centered relative to the receiver spectral band, hence cancelling any effects from laser frequency noise.

The radiofrequency power at the output of the bandpass filter is detected by a Schottky diode and fed into a lock-in amplifier (50 ms integration time) whose reference is synchronized to the amplitude modulation of the transmitted beam at \sim 2 kHz. A DAQ card acquires in-phase and quadrature output signals from the lock-in amplifier.

Three meters away from the ACLaS, a rough target made of white cardboard is positioned. The illumination beam waist at the target plane is estimated to be \sim 8 mm. A large diameter (75 mm) stainless steel gas-cell, including a liquid sample holder within, was placed in front of the target to simulate a 19 cm long homogeneous gas plume. This arrangement is illustrated in the left hand side of Fig. 3.

Speckle produced by the diffuse reflection of the illuminating laser field on the rough target surface drives the SNR of ACLaS. Therefore, speckle reduction techniques are required to increase detection sensitivity. In previous work, dithering of the illumination beam was found to be efficient at standoff ranges of \sim 30 m [3]. For the demonstration of standoff detection of broadband absorbers, the simple approach of a spinning target was retained. The white cardboard target was mounted on a spinning disk rotating at 3000 rpm. Within the integration time, the receiver will average over multiple independent speckle patterns produced by different surfaces to greatly increase the speckle diversity parameter M. This approach is statistically equivalent to alternative speckle diversity enhancement techniques and it is also representative of an ACLaS instrument mounted on a fast-moving vehicle.

Although a spinning target is not compatible with a real standoff situation, it is straightforward to implement for demonstration purposes.

3.2 Reference absorption cross-sections of explosives

MIR optical standoff detection relies on the prior knowledge of molecular absorption crosssections. Whilst most of the chemicals considered in this work are referenced in spectroscopic databases, threat chemicals, such as explosive materials for instance, are not. As an example relevant to explosives, ethylene glycol dinitrate (EGDN) is considered here.

In order to measure reference spectra of EGDN to be used by the spectral processor, a dedicated facility was set up around a Bruker HR125 Fourier Transform Spectrometer (FTS). A 10 m path length, pressure and temperature controlled, multipass White cell was coupled to the FTS. The cell was insulated and controlled in temperature with a stability better than 0.1 degree as is the tubing that feeds gas into it. The cell is pressure controlled and operates in a flow mode, allowing the analyte to permanently circulate through the cell. This ensures cell passivation, and in most cases, ensures long term equilibrium of the analyte concentration. The input of the gas cell is connected to a gas generator (Owlstone OVG4), which produces a mixture of molecular gas within a high purity nitrogen carrier gas. The concentration of analyte can be controlled via the flow rate of the gas generator (50 ml/min to 500 ml/min). The carrier gas flow circulates through a temperature stabilized oven in which laboratory-built permeation sources are introduced.

The permeation source is made from high purity EGDN. The permeation rate at a fixed oven temperature (30°C) is calibrated from gravimetric measurements of the mass loss of the source as a function of time using a 10 μ g precision analytical balance. The plot in Fig. 4(a) shows the EGDN mass loss versus time. A linear fit gives the permeation rate as 192 ± 11 ng/min. Once installed in the gas generator oven, the mixing ratio of EGDN in the carrier gas is calculated to be 615 ± 42 ppb (resp. 61 ± 4 ppb) with a flow of 50 mL/min (resp. 500 mL/min).

While the known mixture of EGDN in N_2 circulates through the multipass gas cell (set at a pressure of 760 Torr and a temperature of 25°C), the FTS records absorption spectra at a resolution of 0.04 cm⁻¹ from 600 to 5000 cm⁻¹. 200 interferograms from the FTS were averaged and Fourier transformed to produce a spectrum. Typically 20 spectra were averaged to improve the SNR further. Transmission spectra were produced using a reference spectrum collected with a gas flow of pure N_2 . Spectra were recorded over several days for different mixing ratios to confirm consistency. From the data, the absorption cross-section of EGDN was determined with a precision of ~6.9%, dominated by uncertainties in the gravimetric calibration. The cross-section data provide the reference spectra used later for quantitative standoff detection of EGDN.

The plot in Fig. 4(b) shows a transmission spectrum of EGDN in the 600-1800 cm⁻¹ spectral range. Around the intense band (NO₂ asymmetric stretching mode) centered at ~1675cm⁻¹, excess noise can be observed in the transmission spectrum due to residual water vapor permeation into the gas system. For comparison, in red is overlaid the transmission spectrum of liquid EGDN taken from the University of Rhode Island Database of condensed phase explosive materials [22]. The significant differences in band position observed emphasize that confident identification and accurate quantification of vapor phase molecules by optical spectroscopic methods does require the generation of ad hoc reference spectral data rather than reliance on condensed phase data.



Fig. 4. (a) Gravimetric calibration of a pure EGDN permeation source. (b) Transmission spectra used for cross-section calculation, and compared with condensed-phase EGDN.

4. Standoff measurements and results

4.1 Narrow band absorbers

In a previous work, we focused on standoff detection of narrow band absorbers using a DFB-QCL as the spectroscopic source [3]. ACLaS standoff detection of water vapor, methane, hydrogen peroxide, and nitrous oxide was demonstrated. For comparison, the widely tunable EC-QCL-based ACLaS was first tested on narrow band absorbers such as nitrous oxide and, inevitably, water vapor. To do so, the EC-QCL was wavelength scanned over its entire range in 60 s, and 3000 spectral points per scan were recorded.

Firstly, a spectrum, shown in Fig. 5(a), without any controlled chemical in the line of sight was recorded. The black dots in the upper panel are the experimental points. The narrow absorption features observed were found to be solely due to atmospheric water vapor. The experimental data was fitted using the OEM algorithm (red curve) with a priori information for the different state vector parameters. For all the fittings in this work, a 50% relative uncertainty was chosen for the a priori mixing ratio values, and 100% for the three baseline parameters describing the laser power modulation. The returned H₂O mixing ratio is 4952 \pm 55 ppm. The fit residual shown in the lower panel is not fully random but rather exhibits a spurious standing wave with a free spectral range of 1.7 cm⁻¹. This was consistently observed and most likely originates from residual standing waves within the QCL gain chip or within lenses inside the external cavity. Further nonrandom contributions to the residual stem from model errors in the vicinity of water vapor lines. Indeed, laser chirp rate variations internal to the frequency sweep were observed and are not accounted for in the model. The transmitted power modulation inherent to the frequency scan was accounted for by a quadratic baseline in most cases.

A gas cell, filled with 1 ± 1 Torr of pure N₂O and made up to atmospheric pressure (757 ± 1 Torr) using laboratory air, was subsequently introduced into the line of sight. The corresponding ACLaS spectrum is shown in Fig. 5(b). It covers almost the full R branch and a small portion of the P branch of N₂O. Retrieved mixing ratios from the processing algorithm were 2081 ± 12 ppm for N₂O and 8005 ± 116 ppm for water. The detection sensitivity normalized to the plume length (0.19 m) and to 1 s measurement time is 17.8 ppm.m.Hz^{-1/2} for N₂O.

Estimating the noise of the ACLaS signal as the standard deviation of the residual, the experimental spectrum from Fig. 5(b) exhibits an SNR of ~40. This is considerably less than when the EC-QCL is operated at a fixed frequency (SNR ~300). Clearly, the laser frequency scan produces a large amount of excess noise in the laser source which is detrimental to the detection sensitivity. By comparison, using a DFB-QCL and current tuning, the SNR over a spectrum of N₂O was ~380. This degradation propagates down to the one sigma error in

measuring N₂O, which appears to be ~9 times better when a DFB-QCL is used (1.9 ppm.m.Hz^{-1/2} [3]).



Fig. 5. (a) ACLaS spectral scans of the atmospheric background and (b) with a cell containing N_2O placed within the beam path for a spinning white cardboard target at a distance of 2.89 m. The upper panel shows the experimental trace (black dots) and the fitted trace (red). The bottom panel shows the fit residuals.

4.2 Assessment of mixing ratio retrievals

One of the significant advantages of the OEM processor is the ability to assess the quality of a solution. The notion of the averaging kernel matrix (denoted A) is a powerful diagnostic tool. Given a "true" state vector $\mathbf{x} = (x_1, x_2, ..., x_n)$, and a retrieved solution of this true state \hat{x} , the element (i,j) of the A matrix is given by Eq. (4). For a fully satisfactory solution, the diagonal elements should be equal to one. This means that a change of dx_i in the true value will produce an identical change of $d\hat{x}_i = dx_i$ in the retrieved term. If this is not the case, the estimated solution does not depend solely on the measurements but also includes partial information coming from the a priori values used to constrain the problem.

$$A_{ij} = \frac{\partial \hat{x}_i}{\partial x_i} \tag{4}$$

The off-diagonal elements of A_{ij} contain information on crosstalk between the elements of the retrieved state vector. In the present case the state vector is composite (consisting of mixing ratios and baseline parameters), therefore some form of normalization is needed. The A matrix normalized by the retrieved values as defined in Eq. (5) will be used instead. This provides equivalent information to the A matrix, except that it relates to a relative variation of parameters rather than an absolute one.

$$\widetilde{A}_{ij} = \frac{\widehat{x}_j}{\widehat{x}_i} \cdot \frac{\partial \widehat{x}_i}{\partial x_j}$$
(5)

Using this tool to assess the narrow band absorber mixing ratio retrieval, the confidence on the N₂O mixing ratio retrieval from Fig. 5(b) is found to be excellent. All information comes from the measurement ($\tilde{A}_{22} > 99.98\%$), and cross-talk from other parameters (water vapor mixing ratio and baseline parameters) remains insignificant.

The situation is different for retrieval of water vapor. It appears that the estimated mixing ratio does not depend solely on the measurement ($\tilde{A}_{11} = 78\%$), and significant cross-talk from the quadratic (6.7%) and linear (2.3%) baseline parameters are observed. This is in contrast to the situation shown in Fig. 5(a) in which the water vapor mixing ratio was retrieved with high confidence (> 99.98%). When N₂O is added into the mixture, retrieving accurate information about water vapor becomes more difficult due to the screening effect of the N₂O spectral features and the added laser excess noise already mentioned above.

This analysis will be repeated for all the data presented below. It offers a quantitative framework and provides metrics to assess potential issues in spectral measurements to ultimately work towards reducing false alarm rates in the context of standoff detection of threats. The metric can be adapted to any accuracy requirement. In the present work, a measurement for which the diagonal elements of the \tilde{A} matrix are over 95% is considered as reliable.

4.3 Dichloroethane

The previous section demonstrated the ability of the ACLaS instrument to collect spectral information on narrow band absorbers across a broad spectral range. The spectral signatures of heavier species do not consist of sharp features as observed for N₂O and H₂O but typically have broad ($\sim 10 \text{ cm}^{-1}$) unresolved bands. To demonstrate the ability of the ACLaS instrument to achieve quantitative standoff detection of such species, a number of molecules with absorption features within the EC-QCL spectral tuning range were selected. The volatile liquid 1,2-dichloroethane (DCE), a chlorinated hydrocarbon, was first considered.



Fig. 6. (a) ACLaS spectral scans of a cell containing DCE and (b) with a cell containing DCE and N_2O placed within the beam path for a spinning white paper target at a distance of 2.89 m. The upper panel shows the experimental trace (black dots) and the fitted trace (red). The bottom panel shows the fit residuals.

DCE exhibits a broad absorption band consisting of classic P, Q and R branches within the laser tuning range, with a maximum absorption cross-section of 7.773×10^{-20} cm².molecule⁻¹. The sample was prepared as follow: several drops of liquid DCE were pipetted into a sample holder placed inside the cell and allowed to evaporate while the cell is sealed. The vapor pressure of DCE at 25°C is ~80 Torr equivalent to >10⁵ ppm mixing ratio at atmospheric pressure. The liquid DCE evaporated completely within a matter of minutes, indicating that liquid-gas equilibrium was not reached and lower concentrations than equilibrium were to be expected within the cell.

Figure 6(a) shows the ACLaS spectrum of DCE along with the OEM fit. The P, Q and R branch structure of the absorption band of DCE can be clearly seen along with the unavoidable narrow absorption features of atmospheric water vapor. The retrieved mixing ratio values are 9534 ± 92 ppm (H₂O) and 15001 ± 87 ppm (DCE). The averaging kernel matrix indicates that the DCE mixing ratio is retrieved with high confidence, while the water vapor ratio is not fully determined by the measurement (86%) and cross talk is observed with the first and second order coefficient of the baseline (2.1% and 4.5% respectively). The cross talk between water vapor and DCE is below 0.5%. Normalized detection sensitivities are 2605 ppm.m.Hz^{-1/2} (H₂O) and 128 ppm.m.Hz^{-1/2} (DCE).

For further testing of the broadband ACLaS and the spectral processing algorithm, a multi-species mixture was prepared by placing liquid DCE in the cell and adding a small amount of N_2O . The presence of atmospheric water allows the instrument to be tested with three separate absorbers. Figure 6(b) shows the experimental trace and the fit of the three

component mixture. Retrieved mixing ratios of the three species are 3520 ± 186 ppm (H₂O), 2028 ± 23 ppm (N₂O) and 10906 ± 209 ppm (DCE). The mixing ratios of DCE and N₂O are retrieved with a high level of confidence (diagonal elements >99.8% and insignificant cross talk). For water vapor, the addition of N₂O worsens the situation since the sensitivity to the true concentration drops to 43%, and the cross talk with baseline parameter increases (14% for the second order parameter).

In any case, the measurements and the analysis shows that even in the case of intense interference from other species (N_2O and water vapor), the DCE mixing ratio is obtained with a high level of confidence from the broadband ACLaS data. The combination of high resolution hyperspectral information with the unmixing algorithm allows discrimination between the background and the chemical of interest. This is particularly relevant for long path standoff detection, where atmospheric absorption by water vapor will become more important and absorption by trace atmospheric constituents (such as methane and nitrous oxide) will grow significant.

Normalized detection sensitivities from the data are 5239.6 ppm.m.Hz^{-1/2} (H₂O), 33.7 ppm.m.Hz^{-1/2} (N₂O) and 307.1 ppm.m.Hz^{-1/2} (DCE). The three-species scenario produces a reduction on detection sensitivity, from 17.8 to 33.7 ppm.m.Hz^{-1/2} for N₂O and 127.9 to 307.1 ppm.m.Hz^{-1/2} for DCE, reflecting the increase of the magnitude of the residual. The residual appears more structured as well, and the system is more prone to laser frequency noise through the numerous N₂O sharp lines contributing to the spectrum. Intra-scan laser chirp jitter has been observed with the EC-QCL, which is not accounted for in the laser frequency calibration and adds to the excess laser noise.

4.4 Ethylene Glycol Dinitrate

Ethylene glycol dinitrate (EGDN) is an oily liquid with similar chemical and physical properties to the better known explosive nitroglycerin. It is itself an explosive but is also used as a tag or tracer in explosive compositions due to its relatively high vapor pressure (~100 ppm at 25°C). The principal absorption band located in an atmospheric window is centered at 1280 cm⁻¹, with maximum absorption cross-section of 2.76×10^{-18} cm² molecule⁻¹ (see section 3.2). The EC-QCL range nominally starts at 1280 cm⁻¹. However, the tuning range has been found to be temperamental on a day-to-day basis and, on some unpredictable occasions, emission down to 1268 cm⁻¹ could be observed at the expense of an increased laser noise, as can be seen in the spectra of Fig. 7(a). This laser behavior gives a chance to capture a wider part of the EGDN 1280 cm⁻¹ band.

In an attempt to reduce the laser noise, a differential approach was used. ACLaS spectra were taken while the cell temperature was varied between 21°C and 65°C. Those two spectra can be seen in Fig. 7(a) and show a clear absorption feature around 1280 cm⁻¹. The ratio of the spectral traces taken at the two temperatures provides the transmission spectra shown in Fig. 7(b) in which the absorption band can be clearly seen. Excluding the low wavenumber end of the scan in which SNR is very poor (~2), a portion of the excess laser noise could be suppressed and the SNR increases from ~20 for the raw ACLaS trace to ~50 for the transmission spectrum.

The relative transmission spectrum clearly shows the shape of the EGDN absorption band. The spectral processor using the EGDN cross-section reference spectrum measured previously yields a concentration of 73.9 ± 0.5 ppm, and a normalized detection limit of 0.69 ppm.m.Hz^{-1/2}. Although the full band of EGDN is not covered by the laser tuning range, the fit to the reference data is excellent and EGDN can be confidently identified and quantified. The EGDN mixing ratio obtained is smaller than anticipated based on vapor pressure data. This has been traced to our EGDN sample that had already started decomposing, as anticipated for such an unstable chemical.

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Fig. 7. (a) ACLaS spectral scans of a cell containing EGDN at 2 different temperatures for a spinning white paper target at a distance of 2.89 m. (b) EGDN transmission spectrum obtained from the two experimental traces at different temperatures. The upper panels show the experimental traces (black or blue dots) and the fitted traces (red). The bottom panels show the fit residuals.

Unsurprisingly, since spectral interferences are efficiently suppressed when the ratio of the two traces is taken, the EGDN mixing ratio is robustly retrieved (99.1% sensitivity to true value). A small cross talk with the first order coefficient of the baseline has nevertheless been observed (-2.8%) which may be due to the incomplete coverage of the EGDN absorption band by the laser.

4.5 Tetrafluoroethane

During routine operation of the ACLaS instrument, unexpected broadband signatures were observed in the spectral traces. This was traced to a compressed gas air duster being used elsewhere in the laboratory. Using the PNNL database, the signature was identified to be from the propellant gas commonly used in commercial dusters which is HFC-134a (1,1,1,2-tetrafluoroethane, CF_3 - CH_2F). This offered an ideal opportunity to demonstrate the ability of the ACLaS system to monitor the temporal evolution of chemical plumes passing through the instrument line of sight.

Gas releases were organized as follow: gas from the can was squirted about one meter above the instrument's line of sight. The heavier than air HFC-134a then dropped into the instrument field of view before dispersing throughout the laboratory.

During the gas release, ACLaS was producing one full spectral trace every 30 s. Figure 8(a) shows a series of spectra measured during the experiment as well as their corresponding OEM fits. For example, the spectrum taken at a time of 1560 s gives a mixing ratio of 33.3 ± 0.4 ppm, corresponding to a normalized detection sensitivity of 10.5 ppm.m.Hz^{-1/2} assuming that the plume length corresponds to the full standoff distance. The averaging kernel matrix confirmed the highly robust nature of the HFC-134a mixing ratio retrieval. To generate the temporal evolution of the HFC-134a mixing ratio shown in Fig. 8(b), the six measurements from the spectra appearing in Fig. 8(a) were used to directly calibrate the ACLaS signal coinciding with the peak absorption of HFC-134a (absorption cross-section of 2.149×10^{-18} cm².molecule⁻¹) as indicated by a black arrow in Fig. 8(a). During the experiment three consecutive gas releases were made at ~70 s, ~500 s and ~1400 s after the data logging started.

Within one spectral scan (approximately 30 s after release) the gas plume has diffused down into the line of sight of the instrument with maximum absorption occurring after an additional delay (\sim 100 s). The HFC-134a gas then disperses further into the laboratory and establishes a long term background which is slowly removed by the laboratory airconditioning over the course of several hours. Repeated scans on the following day showed no remaining trace of the gas.



Fig. 8. (a) ACLaS spectral scans during release of HFC-134a with associated OEM fitting. (b) Temporal evolution of HFC-134a during three consecutive releases. The blue dots correspond to the spectra shown in Fig. 8(a).

4.6 Condensed phase

The broadband ACLaS, shown to be suitable for the standoff detection of vapors, should also be relevant to detection of condensed phase compounds deposited onto surfaces. As a first qualitative demonstration, 4-nitroacetanilide (4NA) was identified to be an ideal test molecule. It comes in a powder form, is solid and non-volatile and has a number of absorption bands within the laser tuning range.

The experimental conditions were identical to those described in section 3.1. Two white cardboard targets were produced: the first was left bare while the second had 4NA painted onto it as a paste in acetone solvent. The solvent rapidly evaporated leaving a yellowish layer of chemical on the surface. The targets were alternatively illuminated by the ACLaS instrument located three meters away. Spectral traces of the bare and coated targets are shown in Fig. 9(a).

The ACLaS spectra of both targets show spectral signatures from the background including the ubiquitous water vapor lines and the broadband absorption of HFC-134a which was still present in the laboratory atmosphere. However, clear differences are perceptible between the reference (bare) target and the one coated with 4NA. Two broad absorption bands located at 1274 cm⁻¹ and 1307 cm⁻¹ can be recognized. These appear more clearly once the 4NA spectrum is divided by the reference in order to calculate the transmission, indicated in the lower panel of Fig. 9(a).

To further confirm the genuine observation of 4NA signatures, a reference spectrum of 4NA powder was recorded using an FTS (Bruker Model VERTEX 80v) operating in the attenuated total reflectance (ATR) mode. The corresponding spectrum (magenta trace) is shown in the lower panel of Fig. 9(a). The match with the ACLaS trace is qualitatively acceptable. At this stage, inferring quantitative information would be premature. In contrast to vapor phase chemical measurements for which a full forward model exists, a model for condensed phase residues deposited on surfaces remains to be developed. This is a daunting task, as a number of poorly understood factors are involved including the chemical deposition process and the reflectance properties of the target which depends on the standoff sensing configuration [23].



Fig. 9. (a) ACLaS spectral scans of a bare paper target (reference) and a one coated with 4NA (upper panel). The lower panel shows the corresponding transmission overlaid with one measured from 4NA powder on a Fourier transform spectrometer. (b) One-sigma detection sensitivities (normalized to a 1 m wide gas plume and a 1 s acquisition time) as a function of absorption cross-section for the molecules studied. Data from this work obtained using a EC-QCL (stars) and from [3] (squares) using a DFB QCL are included.

5. Summary, conclusion and future outlook

The Active Coherent Laser Spectrometer (ACLaS) has been clearly demonstrated as a versatile and powerful approach for the standoff detection of vapor and condensed phase chemicals. The chemical range of the instrument has been extended from narrow band absorbers such as nitrous oxide to a range of broadband absorbers including chemical solvents (DCE), volatile explosives (EGDN), and industrial fluorocarbons (HFC-134a). Initial trials have also showed the potential for detection of condensed phase surface contaminants. The combination of a broadly tunable mid-infrared laser source with coherent detection has allowed the potential of ACLaS to be exploited fully to provide an instrument that has the capability of meeting the stringent practical requirements for remote sensing of threat chemicals.

For a standoff detection system, the detection sensitivity is of prime interest. A plot summarizing all the experimental normalized sensitivities as a function of the molecular absorption cross-sections obtained with the ACLaS to-date is shown in Fig. 9(b). The sensitivity figures are normalized to a 1 m plume length and a 1 s spectral acquisition time to allow easy comparison with alternative techniques. In all cases, the maximum absorption cross section lying within the laser scan range has been used as abscissa. The data from this work, obtained with an EC-QCL source (stars) and from previous work with a DFB-QCL [3] (squares) are represented. The grey solid line in the plot represents a linear fit obtained on all the DFB-QCL data. These have been retained as reference since no significant laser excess noise beyond the speckle induced one, was observed using DFB-QCL sources.

A systematic sensitivity drop of about one order of magnitude characterizes the use of the EC-QCL source. This originates from significant excess laser noise including residual intracavity fringing, scan to scan instabilities, and intra-sweep chirp variations. Further evidence of this is given by the EGDN detection limit, which is far closer to that expected from the DFB-QCL results. This is due to the partial cancellation of excess noise during the normalization of the spectrum with a reference trace. Technical noise from the laser is therefore a limiting factor in the sensitivity of the broadband ACLaS. Alternative broadly tunable laser sources in the mid-infrared are beginning to reach commercial maturity; CW optical parametric oscillators (OPO) are now available in the 3-5 μ m atmospheric window and have been used for high resolution spectroscopy [24]. For the longer wave atmospheric window (8-12 μ m), the development of CW OPO is an active research area but current systems are only capable of operating in pulsed mode [25]. Investigating the performance of ACLaS using such broadly tunable sources is certainly within the scope of future activities as is the possibility of improved and better-stabilized EC-QCL.

To relate the ACLaS performance to a tangible metric for explosive detection, Table 1 collects the ambient vapor pressure, mixing ratio, absorption cross section and ACLaS detection sensitivity for a number of explosives and related molecules including EGDN, H₂O₂, nitromethane (NM), nitroglycerine (NG), triacetone triperoxide (TATP) and diacetone diperoxide (DADP). The two first species have already been measured with ACLaS while the remaining list is extrapolated using the solid reference line in Fig. 9(b). A potential metric for assessing the ACLaS performance can be constructed from the ratio of the chemical vapor pressure (VP) expressed in mixing ratio (MXR) to the ACLaS normalized detection sensitivity (NDS). A value greater than 1 indicates that the chemical can be detected by the current instrument in one second, considering a 1 m plume. For the chemicals listed in the table, the ratio is always greater than one; in the majority of cases there is always more than two orders of magnitude reserve beyond the vapor pressure mixing ratio. This reserve can account for some level of mixing ratio reduction through dispersion and/or concealment. The exception is nitroglycerin (NG) which has a much lower vapor pressure at ambient temperatures and is representative of a range of less volatile explosive materials (e.g. trinitrotoluene (TNT)). However, even in this worst case, NG is within the range of ACLaS. Longer acquisition times would provide an additional reserve for detection.

Table 1. Summary of measured (underlined) and extrapolated performance of the ACLaS instrument for detection of explosive related molecules.

Molecule	VP @ 25°C ^a Torr	MXR @ 25°C ppm	Cross section cm ² .molecule ⁻¹	ACLaS NDS ppm.m.Hz ^{-0.5}	Ratio MXR/NDS
EGDN	0.0763	100	52.4	0.69	<u>145</u>
H_2O_2	2.13	2802	2.8	<u>1.10^b</u>	2547
NM	36.5	48,000.	9.8	1.13	42,400
NG	4.8 10 ⁻⁴	0.63	89.9	0.09	7
TATP	0.046	61	4.0	0.23	266
DADP	0.133	175	2.8	0.34	590

^a from Ref [26].

^b from Ref [3].

The NDS values given in Table 1 refer to the currently observed performance of ACLaS. From Fig. 9(b), it is clear that there is still approximately four orders of magnitude sensitivity reserve compared to the ultimate shot noise limit of heterodyne detection. The current limiting factor is noise associated with phase and scintillation fluctuations of the coherent signal due to speckle. Improvements in independent speckle patterns averaging present a clear route to enhanced sensitivity. Speckle reduction mechanisms are currently being studied.

In addition to detection sensitivity, reliable chemical detection, identification and quantification is highly sought after to reduce the false alarm rate of a standoff system for detection of threat chemicals. In that respect, the ACLaS spectral processor has demonstrated the ability to confidently extract mixing ratios even in the presence of complex chemical backgrounds. The spectral resolution and broad wavelength tuning ability of the ACLaS, combined with the spectral processor, enables clear discrimination between sharp and/or broad spectral features and yields efficient spectral unmixing. In addition, a set of quantitative diagnostic parameters has been used to assess the confidence in the processor outputs.

The spectral range of the ACLaS has also allowed a first qualitative measurement on condensed phase chemicals deposited onto a surface. This demonstrates the relevance of ACLaS to chemical deposition and the detection of explosive residues, though more work is needed to interpret spectra in a quantitative manner.

The ACLaS approach promises a high level of performance in detection, quantification, and operation for standoff chemical analysis of a wide variety of species, including atmospheric constituents, explosives and other threat chemicals, and industrial gases.

Integration of a widely tunable mid infrared source at the core of the instrument has greatly extended the chemical versatility without compromising the benefits found in the original prototype.

Acknowledgments

Financial support from the Scottish Enterprise Explosive Detection Platform, from the UK Ministry of Defence, and from the Small Business Research Initiative is acknowledged. The authors would like to thank Dr Robert McPheat and Mr Gary Williams of the Molecular Spectroscopy Facility of the RAL Space department for their help with the Fourier transform spectroscopy experiments and Dr Alex Contini from the Centre for Defence Chemistry at Cranfield University for synthesizing the EGDN samples used in this study.