High sensitivity stand-off detection and quantification of chemical mixtures using an Active Coherent Laser Spectrometer (ACLaS)

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ABSTRACT

High sensitivity detection, identification and quantification of chemicals in a stand-off configuration is a highly sought after capability across the security and defense sector. Specific applications include assessing the presence of explosive related materials, poisonous or toxic chemical agents, and narcotics.

Real world field deployment of an operational stand-off system is challenging due to stringent requirements: high detection sensitivity, stand-off ranges from centimeters to hundreds of meters, eye-safe invisible light, near real-time response and a wide chemical versatility encompassing both vapor and condensed phase chemicals. Additionally, field deployment requires a compact, rugged, power efficient, and cost-effective design.

To address these demanding requirements, we have developed the concept of Active Coherent Laser Spectrometer (ACLaS), which can be also described as a middle infrared hyperspectral coherent lidar. Combined with robust spectral unmixing algorithms, inherited from retrievals of information from high-resolution spectral data generated by satellite-based spectrometers, ACLaS has been demonstrated to fulfil the above-mentioned needs.

ACLaS prototypes have been so far developed using quantum cascade lasers (QCL) and interband cascade lasers (ICL) to exploit the fast frequency tuning capability of these solid state sources. Using distributed feedback (DFB) QCL, demonstration and performance analysis were carried out on narrow-band absorbing chemicals (N₂O, H₂O, H₂O₂, CH₄, C_2H_2 and C_2H_6) at stand-off distances up to 50 m using realistic non cooperative targets such as wood, painted metal, and bricks. Using more widely tunable external cavity QCL, ACLaS has also been demonstrated on broadband absorbing chemicals (dichloroethane, HFC134a, ethylene glycol dinitrate and 4-nitroacetanilide solid) and on complex samples mixing narrow-band and broadband absorbers together in a realistic atmospheric background.

Keywords: stand-off detection, infrared, quantum cascade lasers, explosives, threat chemicals, heterodyne.

1. INTRODUCTION

1.1 Threat chemical stand-off detection requirements

Stand-off detection of threat chemicals, in both vapor and condensed phases is a highly sought after capability encompassing a range of applications relevant to the detection of explosive materials, poisonous or toxic substances, and illicit drugs. However, any operational system needs to deliver far more than simple "detection" of a molecule isolated from any deployment scenario. Realistically, the key requirements include:

1) multi-species detection, identification, and quantification: a versatile stand-off system ought to be able to respond to multiple threats involving different chemicals. Even in cases where only one threat chemical is in scope, background molecules will be present in the surrounding environment and effective threat identification within a complex chemical background is needed. Following detection and identification, the final step consists of gathering information on the level of threat, studying temporal evolution, and ultimately selecting possible actions based on quantification thresholds.

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Chemical, Biological, Radiological, Nuclear, and Explosives (CBRNE) Sensing XVII, edited by Augustus Way Fountain III, Proc. of SPIE Vol. 9824, 98240B · © 2016 SPIE · CCC code: 0277-786X/16/\$18 · doi: 10.1117/12.2223045 2) High detection sensitivity and dynamic range: vapor pressures of threat chemicals under ambient conditions span a range of values from parts per billion (ppb) up to parts per thousand. In addition, concealed or packaged chemicals will show a local vapor pressure that can be orders of magnitude lower than the equilibrium value. A versatile instrument needs to have extremely low detection sensitivity (ppb range) combined with a wide dynamic range for the detection of multiple species under varying conditions.

3) Detection range: the specific requirements can vary greatly depending on the actual application. A fully versatile instrument should have the flexibility to work at short (< 1 m) and far stand-off distances (> 1000 m).

4) Rapid temporal response: rapid update times (seconds to minutes) are needed to allow high screening throughput, fast spatial information gathering, and real-time identification and reaction to threats.

5) Eye-safe operation: operational laser spectrometers deployed in public open areas should meet laser emission limits for a class 1 laser and must pose no risk of harm to the public.

6) Compact and portable design: weight, power requirements and physical size are key aspects to enhance the deployment capability of a stand-off detection system. Ultimately, a portable or hand-held device would be extremely desirable.

7) Cost effectiveness.

These combined requirements present a formidable challenge and are currently not fully addressed.

1.2 Current instrumentation

Parts per billion limits of detection in a genuine stand-off operational mode are beyond the capabilities of passive systems relying on thermal contrast. Laser spectroscopy is a far more promising tool to fulfill the requirements previously mentioned¹. Recently developed instruments for active stand-off detection include resonance Raman scattering in the UV region² and absorption in the infrared region (1-12 μ m) using a variety of laser sources including parametric oscillators³, ultrafast laser frequency combs⁴ and semiconductor lasers⁵. The common underlying architecture is the active transmission of light towards a distant target (cooperative or topographic), the collection and detection of the backscattered or reflected radiation and its analysis to provide chemical identification and quantification. Instruments can be operated in a "point and shoot" mode using a single pixel detector or in an imaging configuration using a detector array. This second mode has been successfully applied to the detection of solid and liquid contaminants on surfaces^{6,7,8}.

These developments have shown the potential for stand-off detection using laser spectroscopy and a number of the instruments do meet some of the requirements specified in section 1.1. Widely tunable laser sources in the infrared, in particular, provide a multi-species detection capability with eye-safe operation in a relatively compact and portable design. However, the major limiting factors of the current generation of stand-off instruments are the detection sensitivity and temporal response which are currently not up to the standards required for detection of threat chemicals. In addition, the use of cooperative targets such as retro-reflectors are not within the scope of a genuine stand-off detection configuration and as such miss out on a key requirement.

For vapor phase sensing, a useful metric for comparison between different instruments is the minimum detectable concentration (in parts per million) normalized to a 1 m wide gas plume, and a 1 s total acquisition time (units, ppm.m.Hz^{-1/2}). For stand-off detection of vapor phase chemicals, published detection limits vary greatly depending on the detection scenario and the absorption cross-section of the chemical of interest^{3,5,9,10,11,12,13}. In general, the larger absorption cross-sections found in the shortwave- and longwave-infrared regions (3-5 μ m, SWIR and 8-12 μ m, LWIR) provide higher sensitivity than the near-infrared (1-2 μ m). In addition, the use of an open-path configuration with a cooperative target (e.g. corner-cube retro-reflector) provides higher sensitivity than scenarios using diffusely scattering topographic targets, although this is not true stand-off sensing and is therefore no longer considered here. The majority of studies have utilized direct detection methods where detector noise is the major limit on detection sensitivity. This provides detection limits in the range 1-100 ppm.m.Hz^{-1/2} which are 2-3 orders of magnitude worse than found for *in-situ* measurements on the same species. To put these numbers into the context of detection of threat chemicals, the explosive TNT provides a good example. TNT has an equilibrium vapor pressure (at 25°C) of ~ 10⁻⁵ Torr¹⁴, which corresponds to a concentration of ~ 0.013 ppm at ambient pressure (760 Torr). For the best detection limits measured by the current generation of instruments (1 ppm.m.Hz^{-1/2}), a 1 m wide gas plume of TNT would give rise to a considerably smaller vapor

pressure, which would require acquisition times of days. Clearly there currently exists a capability gap for the detection of low concentrations of threat chemicals.

The majority of current instruments for stand-off detection rely on direct detection of the light scattered by the distant target. Heterodyne detection provides a potential means for increasing detection sensitivity to the shot noise limit^{15,16,17,18,19}. Coherent detection was first applied to stand-off detection in the 1970's using fixed frequency gas lasers for atmospheric sensing. More recently, it has found use as a stand-off wind velocity sensor by exploiting the Doppler shift of the transmitted radiation following scattering by atmospheric particles²⁰. The concept of an active heterodyne stand-off spectrometer (ACLaS) combined with a broadly tunable mid-infrared laser source has been developed^{18,19} over the last few years into a compact instrument demonstrated on various vapor chemicals. ACLaS was shown to outperform other approaches to stand-off detection, in light of the above-mentioned requirements.

2. THE ACLaS DETECTION CONCEPT

2.1 Heritage

The Active Coherent Laser Spectrometer (ACLaS) concept is inherited from our program of work in the field of middle infrared laser heterodyne spectro-radiometers for atmospheric remote sounding¹⁶. These systems deliver very high spectral resolution (up to a resolving power of >1 million), high detection sensitivity (ideally shot noise limited), high spatial resolution (spatially coherent), and, by virtue of a continuously tunable local oscillator such as a quantum cascade laser, frequency agility²¹. However, passive laser heterodyne spectro-radiometry derives its sensitivity from the background brightness temperature when used in transmission mode, which limits its ability to deliver ppb limits of detection in any realistic stand-off detection configuration. In contrast, the ACLaS adopts an active approach, which eliminates the SNR limitations of passive systems while maintaining all the advantages of mid infrared heterodyne systems.

2.2 Concept and advantages

The ACLaS can be viewed as a mid-infrared heterodyne hyperspectral lidar system. A schematic of the optical layout is shown in Figure 1. In generic terms, a tunable mid infrared laser source (SWIR or LWIR), represented by a quantum cascade laser (QCL) in Figure 1, emits most of its optical power towards a distant topographic target (walls, ground, motor vehicles, aerosols, ...). A small fraction of the laser optical power (~ a few hundred microwatts) is sampled by beamsplitter BS1 and shifted in frequency by, in this case, an acousto-optical crystal, while retaining coherence with the field emitted towards the target. This produces the local oscillator (LO) field required for heterodyne detection. Finally, the diffusely backscattered radiation from the distant target falling into the instrument heterodyne field of view (FOV) is superimposed with the LO field via BS2, imaged onto a photomixer and down-converted into the radio-frequency domain (~100 MHz).



Figure 1: Left, optical schematic of the Active Coherent Laser Spectrometer (ACLaS). QCL is a quantum cascade laser, BS are beamsplitters, AOS is an acousto-optical frequency shifter, OAPM are off-axis parabolic mirrors and PD is a fast photodiode. Middle, ACLaS prototype assembled on a portable 0.75 by 0.75 m square optical workstation. Right, ACLaS installed in a 50 m long tunnel facility with a stationary wooden target positioned at a distance of 30 m.

This configuration offers a number of advantages. Firstly, the heterodyne receiver can be set to a very high spectral resolution. Typically, we use a $\sim 3 \times 10^{-5}$ cm⁻¹ (1 MHz) spectral resolution (resolving power of $\sim 3.3 \times 10^{7}$ at 1000 cm⁻¹)

such that the receiver spectral width corresponds to that of the laser light used for illumination of the scene. By doing so, any potential parasitic background radiation remains insignificant even against the brightest background. In addition, the high spectral resolution combined with the frequency tuning of the LO provides full spectral information and allows chemical selectivity. Absorption profiles are fully recorded and can be used to carry out spectral unmixing to efficiently recover concentration information of even the most complex chemical mixtures. Spectral "clutter" can be efficiently discriminated against the useful information. Secondly, a single laser configuration ensures permanent full coherence between the received signal and the LO. In this way, any phase noise originating from the laser source can be fully cancelled, as long as the phase fluctuations are small compared to the width of the heterodyne receiver. Thirdly, the high detection sensitivity of the heterodyne detection process is maintained and allows an extremely small amount of returned power (< pW) to be detected. Finally, the inherently narrow coherent FOV provides high spatial resolution for the monitoring of highly localized chemical distributions. By incorporating a scanning mechanism, ACLaS would also allow for high spatial resolution imaging.

2.3 Implementation

ACLaS has been demonstrated using a variety of laser sources including DFB-QCL, DFB-ICL and broadly tunable external cavity (EC) QCL targeting both the SWIR and LWIR spectral regions^{18,19}. The middle panel of Figure 1 shows the ACLaS prototype assembled on a portable 0.75 by 0.75 m square optical workstation. Stand-off distances up to 12 m have been used within the laboratory environment while longer range measurements (40 m) have been made in an underground tunnel facility on the RAL site. The right hand panel of Figure 1 shows the ACLaS prototype installed at one end of the tunnel with a wooden target positioned downstream at a distance of 30 m.

Initial characterization measurements were made using a spinning target as a simple and straightforward way to test speckle reduction²². Target materials included roughened aluminum, paper/cardboard and various grit sizes of silicon carbide abrasive paper. For stand-off detection at longer range a variety of stationary targets (house brick, bare and painted wood and cardboard boxes) were used to simulate conditions for realistic sensing. Transmitted laser intensities were found to be well within the limit for eye-safe operation in the infrared (< 100 mW/cm²). Experimental results are presented starting from section 4. For the sake of clarity, before stepping into experimental results, the approach to spectral unmixing and data processing is presented in the next section.

3. SPECTRAL UNMIXING AND QUANTIFICATION

3.1 Generic approach

In general terms, the sensitivity of the instrument will be primarily determined by the signal to noise ratio (SNR) with which the instrument collects hyperspectral data. However, this relationship is not straightforward since the raw data and the underlying concentrations are related by a complex retrieval process in which many other physical parameters can intervene. A robust approach to concentration retrieval from spectral information is needed to confidently analyse ACLaS measurements. This should include full error propagation of the instrument SNR to determine the concentration detection limit, analysis of cross-talk between variables, information content and bias analysis. The end result is a concentration measurement accompanied by robust metrics describing the level of confidence that can be placed in the measurement. The approach we retain is based on optimal estimation (OE) used in atmospheric data retrieval from space-borne spectrometers²¹. It has been mathematically formalized in a comprehensive and consistent way by C. Rogers²³.

The OE provides a method for inverting measurements, such as lidar backscattered power measurements, to provide an indirect determination of a desired quantity of interest, such as molecular concentration or other variables of the physical model describing the measured quantities. The problem can be described by Equation 1 where y is the measurement vector (here, the backscattered power spectrum), F(x,b) is a forward model describing the physics of the problem for an unknown state of the quantities of interest (here, molecular concentrations, x) which are to be retrieved.

$$y = F(x, b) + \varepsilon \tag{1}$$

The vector of parameters b comprises the quantities which influence the measurement but are assumed to be well known and are not to be retrieved (here for example, the pressure or the target distance), and ε represents the measurement noise. A retrieval problem consists of finding the reciprocal function of F, giving x with y, b being known. Therefore, the OE method returns the optimal values of x for a particular measurement vector y, known with a certain level of confidence quantified by ε . However, the problem is often under determined, meaning that the information contained in the measurement vector is insufficient for a unique solution of x to be returned. To further constrain the problem, *a*-*priori* information about the state vector x provides an initial estimate of the state vector based on past observations, or physical arguments. In any case, the level of confidence one has on this prior information needs to be factored into the forward model. A key assumption underpinning the OE is that all uncertainties are truly random with a Gaussian distribution. This assumption is usually true in reality as the central limit theorem applies for complex measurements, and providing the physical model is accurate enough not to introduce non-random sources of bias.

In order to develop an iterative approach to finding a solution to Equation 1, a "cost" function is built whose minimum defines the optimum solution. In simple routines for example, the sum of the squared differences between a model and an observation is often used. For a more complex situation such as that of active heterodyne measurements, it is desirable to include more parameters into the cost function. Based on prior work in satellite measurements retrieval, the cost function to be minimized is given by Equation 2 where S_{ε} is the measurement covariance matrix, S_a is the *a-priori* covariance matrix, x_a is the *a-priori* estimate of x and ()^T indicates the transpose of a matrix.

$$\chi^{2} = (y - F(x_{n}, b))S_{\varepsilon}^{-1}(y - F(x_{n}, b))^{T} + (x_{a} - x_{n})S_{a}^{-1}(x_{a} - x_{n})^{T}$$
(2)

Minimising χ^2 is therefore equivalent to minimizing the weighted differences between the measurement vector and what is expected from the forward model given the current state vector, and between the current state vector and the *a-priori*, with weighting introduced by covariance matrices describing the uncertainty in both the *a-priori* and the measurement vector. In other words, the cost function takes into account not only the measurements and their accuracy, but also the knowledge one has of the stand-off detection scheme. A good retrieval will increase our knowledge of x. A retrieval algorithm will always return a result; however, in some situations this result may add no additional information to our prior knowledge.

In general, the relationship in Equation 1 is nonlinear and is solved using local linearization using the well-known iterative Levenberg-Marquardt approach described in Equation 3 where K is the Jacobian or weighting function matrix which is a measure of the sensitivity of the forward model to the state vector.

$$x_{i+1} = x_i + \left[(1+\lambda)S_a^{-1} + K_i^T S_{\varepsilon}^{-1} K_i \right]^{-1} \left[K_i^T S_{\varepsilon}^{-1} \left(y - F(x_i, b) \right) + S_a^{-1} (x_a - x_i) \right]$$
(3)

When the problem is well conditioned, the iterative minimisation of the cost function should converge towards a solution. In addition to providing a solution, the OE also allows full error propagation analysis. The level of confidence in the solution found can be estimated, as well as its physical meaning through a set of diagnostic analysis tools. This allows a robust and reliable means of estimating detection sensitivities based on the noise characteristics of the instrument.

Following the definition given in Equation 1, the measured spectrum y is related to the concentrations to be retrieved x and to the fixed parameters of the detection scenario b by Equation 4. This is similar to Equation 1 with the difference that here the function f is assumed to be ideal and describes the full physics of the problem, unlike F which was the actual forward model we have knowledge about.

$$y = f(x, b) + \varepsilon \tag{4}$$

Reciprocally, a retrieved state x can be expressed as a function R of the measurement vector y, as well as the vector of

best estimate of the model parameters \hat{b} , the *a*-priori x_a and any other parameters affecting the retrieval but independent of the forward model, grouped into a vector *c* (the convergence criteria for instance). This can be written in Equation 5.

$$\hat{x} = R(y, \hat{b}, x_a, c). \tag{5}$$

Substituting Equation 4 into Equation 5, the retrieved state appears as a function of the true one as expressed in Equation 6.

$$\hat{x} = R(f(x,b), \hat{b}, x_a, c). \tag{6}$$

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Understanding the properties of the transfer function relating x to x is fundamental to understanding the sensitivity of the retrieval to all sources of error in the retrieval function and for characterising the sensitivity of the retrieval to the true state. The remainder of this section presents the methodology for characterising such sensitivities.

In the forward model, the true physics of the measurement described by the function f is approximated by the actual numerical model F, as given by Equation 7 where Δf is a function accounting for the difference between the forward model and the true forward function (i.e. the difference between the true physics and the physics of the model).

$$\hat{x} = R[F(x,b) + \Delta f(x,b,b') + \varepsilon, \hat{b}, x_a, c]$$
(7)

The vector b' represents those forward function parameters, which may be ignored in an incomplete construction of the forward model. Local linearization in the vicinity of a retrieved state of Equation 7 and subsequent rearrangement gives the expression shown in Equation 8 for the error in the true state x which forms the basis of the error analysis.

$$\hat{x} - x = (A - I_n)(x - x_a) + G_y K_b (b - \hat{b}) + G_y \Delta f(x, b, b') + G_y \varepsilon$$

$$\tag{8}$$

Here, x - x is the difference between the retrieved and the true value of the state vector and defines the error in x. The expression on the right hand side is composed of four summed terms, which individually contribute towards the retrieval error. The first term is the smoothing error, the second the model parameter error, the third the forward model error, and the fourth is the retrieval noise.

The smoothing error is defined by the first term appearing in Equation 8. A is the averaging kernel and gives the sensitivity of the retrieval \vec{x} to changes in the true state x:

$$A = G_y K_x = \frac{\partial \hat{x}}{\partial x} \tag{9}$$

The averaging kernel matrix is the product of the weighting function or Jacobian matrix K_x and the gain matrix G_y , which are defined in Equations 10 and 11, respectively. It is instructive to investigate these matrices before considering the averaging kernel matrix. The Jacobian matrix defines the sensitivity of the forward model to the state vector and therefore the contribution of the measurement vector channels to the retrieval, while the gain matrix reflects the sensitivity of the retrieved quantities to the measurement vector. Calculation of the Jacobian matrix is straightforward; the derivatives can be calculated algebraically or numerically via perturbation of the forward model.

$$K_x = \frac{\partial F}{\partial x} \tag{10}$$

$$G_y = \frac{\partial R}{\partial y} = (K_x^T S_\varepsilon^{-1} K_x + S_a^{-1})^{-1} K^T S_\varepsilon^{-1}$$
(11)

The averaging kernel A gives the response of the retrieval to perturbation of each corresponding component of the state vector. In the ideal case, the response of the retrieval should be one (full response) for the perturbed quantity and zero elsewhere. Deviations from the perfect identity matrix I_n indicates cross-talk between the components of the state vector. In addition, when the sum of the responses for one component is less than 1, this indicates that the *a-priori* information contaminates the retrieved results. Therefore, the averaging kernel matrix is a powerful analysis tool, which should always be examined in order to validate the results of the inversion algorithm by providing information on cross-talk and the true information content of the measurement.

The second term of Equation 8 is the model parameter error, which allows the propagation of errors introduced by the constant parameters b of the forward model. In practice, the errors in the fixed parameters can be due to either bias or random errors. As a result, these will propagate through the forward model to produce either a bias on the retrieved concentration of interest, or a reduction in the limit of detection. In a similar way to the Jacobian matrix defined in Equation 10, the sensitivity matrix K_b is defined as the sensitivity of the forward model to the "known" parameters.

The third term of Equation 8 defines the error in the forward model, F(x,b), relative to the true physics described by $\Delta f(x, b, b')$, where b' defines all of the physical parameters which are not included in the forward model. Modelling error is hard to evaluate, as it requires a full and correct description of the physics of the problem under evaluation. Analysing this error analytically is difficult and an iterative method to make it negligible is usually retained. As a starting point, the initial forward model $F_1(x,b)$ is daringly assumed to capture the full physics of the problem well. Following a retrieval,

the residuals between the experimental trace and the model trace y- $F_1(x, b)$ are examined. If this residual does not exhibit random statistics, this may indicate underlying issues with the model and new physics needs to be added to generate an improved forward model $F_2(x, b, b_1)$ which may include, for example line mixing effects or a new absorption profile model, or standing wave effects, etc. A new retrieval using $F_2(x, b, b_1)$ is run, the updated residuals are analysed and further updates to the model $F_n(x, b, b_1)$ can be implemented. If the model cannot be further improved, the error introduced by an incomplete forward model can be estimated from $G_y[y - F(x, b)]$.

Lastly, the fourth term of Equation 8 is the retrieval noise which can be interpreted as the contribution to the uncertainty in the retrieved x vector by the measurement noise ε and it is usually the easiest component to evaluate. For ACLaS, the error term ε includes experimental errors in the measurement vector y from sources such as speckle noise, shot noise and detector noise. It is generally a purely random term that is often uncorrelated between channels and that has a known covariance matrix S_{ε} .

3.2 ACLaS forward modelling

The forward model f we have developed for the retrieval and analysis of ACLaS data has been thoroughly described¹⁹. The steps within the forward model are illustrated by the block diagram shown in Figure 2. In summary, once the parameters of the detection scenario configuration are finalised, the backscattered power received by the instrument can be calculated. The detection scenario module includes the properties of the backscattering target and the effects of atmospheric absorption and scattering. A second module simulates an ideal heterodyne receiver to determine the heterodyne signal produced from the received field. Input parameters include the effective aperture (coherent field of view), overlap between the heterodyne FoV and the transmitted field including beam propagation properties and the impact of atmospheric turbulence. The final module provides a full noise model of the instrument. Sources of noise considered include shot noise, speckle noise, misalignment effects and excess noise from the laser source (including fringing). The outputs of all three modules are combined to produce a full synthetic ACLaS spectrum including noise as would be delivered by the instrument. This synthetic spectral trace provides the input for the OE retrieval of chemical concentrations. In addition, it also offers a means to carry out prior analysis and establish some benchmark performance figures against which to compare real instruments. In the next section is shown an example of such prior analysis done for stand-off detection of gas plumes of the explosive precursor hydrogen peroxide (H₂O₂).





3.3 Prior analysis of H₂O₂

The concepts described in sections 3.1 and 3.2 can be used to carry out a prior analysis for a given stand-off sensing scenario using the ACLaS instrument. The example to be considered is ACLaS deployed in a normal atmosphere, probing towards a hard target 9.7 m away with a gas plume of hydrogen peroxide molecules present within the line of

sight. Table 1 summarizes the state vector parameters and the model parameters used in this example. In this case, atmospheric water concentration also forms part of the state vector and needs to be retrieved alongside H_2O_2 to ensure accurate estimation of the H_2O_2 concentration.

Parameter	Value	Description
State vector		
$[H_2O_2]$	450 ppmv	Concentration of hydrogen peroxide in the plume assumed to be typical
		peroxide vapor pressure at ambient temperatures
[H ₂ O]	9500 ppmv	Natural abundance of water vapor in the atmosphere at ground level
C ₀	1 V	Baseline scaling parameter
Model parameters		
Z_T	9.70 m	Diffuse target location with respect to ACLaS
Z_M	9.60 m	Molecular plume center location
w_M	0.2 m	Molecular plume width
F	9.70 m	Transmitted beam focus location
β_b	10^{-7} m^{-1}	Atmospheric aerosol backscattering parameter
β_{f}	10^{-6} m^{-1}	Atmospheric aerosol forward scattering parameter, defined as 10 x β_b
ρ	0.1	Diffuse target reflectivity
P_{0}	21 mW	Transmitted laser power
P_{LO}	120 μW	Local oscillator power
D_R	50.8 mm	Receiver diameter
η_o	0.825	Optical efficiency
η_q	0.4	Detector quantum efficiency
η_{ol}	1	Overlap efficiency
р	744.9 Torr	Atmospheric pressure
Т	290.0 K	Measurement temperature
[N ₂ O]	0.317 ppmv	Natural abundance of nitrous oxide in the atmosphere at ground level
[CH ₄]	1.864 ppmv	Natural abundance of methane in the atmosphere at ground level

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The left hand side of Figure 3 shows the forward modelling of the expected signal at the output of the ACLaS for a very broad LO spectral scan for each of the main chemical species. As a first step, three narrower spectral windows (greyed areas) are identified as relevant for H_2O_2 stand-off detection where spectral interference from the atmospheric background is minimized. When narrow spectral windows can be used to probe a molecule, the requirements on the LO source are relaxed and narrowly tunable lasers such as DFB QCL can be used.

Using the analytical tools described in the preceding sections, the upper table in the right hand side of Figure 3 shows the averaging kernel matrix. The diagonal elements are close to one (< 0.1 % deviation) indicating the near-perfect sensitivity of the instrument to H_2O_2 concentration change, no cross talk between H_2O_2 and atmospheric H_2O , and retrieved outputs solely derived from the measurement rather than from the *a-priori* information.

The lower table on the right hand side of Figure 3 shows the effects of error propagation analysis of some of the model input parameters down to the retrieved quantities. Considering the measurement of H_2O_2 concentration, an error of 0.1 K on the knowledge of the gas plume temperature will produce an uncertainty contribution of ~0.13% on the measured H_2O_2 concentration. In a similar manner, all other input parameters can be evaluated and a set of requirements on their knowledge can be defined. The criterion we selected is to ensure that the error introduced by input parameters remain smaller than that introduced by the instrument noise. In other word, one wants to be in a position where the most dominant noise contribution relates to the instrument's SNR.



State Vector	[H ₂ O]	[H ₂ O ₂]	C0
[H ₂ O]	0.99987	3.19E-7	-1.07E-6
[H ₂ O ₂]	1.19E-4	0.9992	-0.00106
C0	-4.00E-6	-1.05E-5	0.99998

b	$h - \hat{h}$	Relative uncertainty (%)					
	5 5	$\Delta[H_2O_2]$	$\Delta[H_2O]$	ΔC0			
F	1 m	7.77E-05	1.07E-04	8.06E-3			
Z_T	0.1 m	2.60E-02	8.75E-01	3.47E+00			
Р	0.1 Torr	3.28E-03	6.87E-03	1.61E-03			
Т	0.1 K	1.26E-01	1.19E-01	8.70E-03			
β_b	10^{-6} m^{-1}	9.56E-03	2.4E-04	4.80E+01			
ρ	0.1	2.03E-02	4.39E-04	1.08E+02			

Figure 3: Left, forward modelling of ACLaS signals for the chemical species considered. The top panel shows the total signal whilst the other panels show the individual contributions from the molecules involved in the stand-off detection scenario. Right, top table, calculated averaging kernel matrix values. Right, bottom table, error propagation of some of the model parameters to the uncertainty on the retrieved quantities.

The top-level outcome of the analysis work carried out using the OE framework is given in Table 2. For the three spectral windows identified we were able to establish the limit of detection for hydrogen peroxide for different ACLaS SNR values. The table also shows the expected biases produced by systematic errors in the model input parameters. The figure of merit given in the table has been normalized by the plume length as this truly represents the physical quantity being measured (line of sight integrated concentration). Later in the text, a further normalization taking into account the acquisition time will be introduced to build a versatile and meaningful figure of merit to assess the performances of a stand-off detection system. Table 2 shows that ACLaS has the potential for high sensitivity detection of H_2O_2 vapor.

Table 2: Summary of the fi	ull prior analysis in th	ne ACLaS stand-off detection of H_2O_2 .
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Range (cm ⁻¹)	SNR	Detection Limit (ppm.m)	Biases (ppm.m)
1245 1252	100	0.93	0.13
1243-1232	1000	0.09	0.13
1274-1282	100	1.28	0.13
	1000	0.13	0.13
1208 1206	100	1.08	0.14
1298-1300	1000	0.11	0.13

4. NARROW BAND ABSORBING CHEMICAL VAPORS

4.1 Experimental results

The ACLaS prototype was first demonstrated within a laboratory environment with stand-off detection ranges of up to 12 m on a variety of narrowband absorbing chemical vapors using a spinning metal or paper target. Although this configuration is not applicable to most realistic detection scenarios, it provides identical effects to an internal method for reducing speckle effects, which is the main source of noise²². In the LWIR, the laser source was a DFB-QCL with a

tuning range of $\sim 5 \text{ cm}^{-1}$ centered at 1278 cm⁻¹ (7.82 µm) and was chosen to allow access to the absorption lines of a range of narrowband absorbers detailed below. Illumination power was in the range of $\sim 20 \text{ mW}$ at best. Demonstration experiments on ethane stand-off detection were also made in the SWIR using an ICL operating at 3000 cm⁻¹ (3.33 µm) with a smaller illuminating power ($\sim 5 \text{ mW}$). In the following subsections, each figure follows the same format. The upper panel shows the experimentally measured ACLaS trace (black dots) and the OE retrieved trace (red line). The residuals of the fit are given in the bottom panel to clearly visualize model errors and noise levels. For reference, the middle panel shows a measured transmission spectrum using the retrieved baseline parameters that described the laser power modulation as it is tuned in frequency. The normalized limit of detection figures will be grouped together in Section 6.

Atmospheric species

Experimental results on narrow band atmospheric species are shown for H_2O , CH_4 , and N_2O . Figure 4 shows ACLaS measurements of the atmospheric background within the laboratory for a metal target at a distance of 5.5 m. The tuning range of the laser was chosen to avoid any strong atmospheric absorption but the sensitivity of the instrument (SNR > 200) was sufficient to detect the relatively weak absorption by water (left hand side), CH_4 and N_2O (middle panel) at their natural atmospheric concentrations. The OE retrieval provides concentrations in good agreement with the typical atmospheric values, 0.5-1% (H_2O), ~1.7 ppm (CH_4) and ~0.3 ppm (N_2O). The water concentration was found to vary over a time period of hours due to changes in the relative humidity of the laboratory.



Figure 4: From left to right, experimental and OE retrievals of ACLaS measurements on atmospheric water , atmospheric N_2O and CH_4 , and ethylene. For all plots, the upper panels show the measured trace (black dots) and the OE retrieved trace (red line). Middle panels show the transmission spectrum derived from the measured trace, lower panels show the residual of the fit.

Industrial gases

Industrial gases, primarily in relation to oil and gas applications, were also put under test. The right hand side of Figure 4 shows ACLaS measurements on the industrial gases acetylene (C_2H_2 , left), whilst ethane (C_2H_6) is shown in the left hand side of Figure 5. A metal gas cell containing acetylene or ethane mixed with a standard atmosphere of air was placed immediately in front of the target to simulate a gas plume. The acetylene trace was recorded using a target coated with black metallic car paint to simulate backscattering from a painted metal target. The absorption line chosen within the laser tuning range is partially overlapped with the atmospheric water line shown in Figure 3. The OE diagnostics reveal some cross –talk between the retrieved water and acetylene concentrations due to this near perfect spectral overlap. The left hand side of Figure 5 shows the ACLaS spectrum of ethane recorded using a metallic target at a distance of 1 m.

Explosive precursors

Hydrogen peroxide (H_2O_2) is a readily available chemical that can be used in the production of homemade explosives such as triacetone triperoxide (TATP). The relatively high vapor pressure of H_2O_2 (~ 1 Torr at 25°C) and its position as a decomposition product of the chemically unstable TATP make it an ideal species for explosive detection using a narrowly tunable DFB laser source. A 1:1 solution of H_2O_2 in water was placed in the cold finger of an all-glass absorption cell fitted with BaF₂ windows. The cell was pumped repeatedly and flushed with dry nitrogen in order to produce gas phase H_2O_2 . The cell was placed immediately in front of a spinning metal target at a distance of 7 m from the ACLaS. The middle panel of Figure 5 shows the measured and retrieved data. The measured SNR was ~300 and the retrieved (1-sigma) concentration error was 1.1 ppm.m which is good agreement with the prior analysis shown in section 3.3 (Table 2).



Figure 5: From left to right, experimental and OE retrievals of ACLaS measurements on ethane, hydrogen peroxide, and N₂O. N₂O measurements were carried out at longer distance, 30 m, using a stationary painted wooden target. For all plots, the upper panels show the measured trace (black dots) and the OE retrieved trace (red line). Middle panels show the transmission spectrum derived from the measured trace, lower panels show the residual of the fit.

4.2 Longer range measurements

Following detailed characterization at short range in the laboratory, the prototype ACLaS was deployed to a 50 m long underground tunnel on the RAL site in order to demonstrate longer-range measurements of narrow band absorbers. The right hand panel of Figure 5 shows measured and retrieved ACLaS traces for a metal gas cell containing N₂O placed in front of a stationary wooden board painted with white spray paint. The target was at a distance of 30 m from the spectrometer. Internal speckle reduction was provided by angular dithering of the transmitted field via a mirror mounted on piezoelectric actuators. In this case, the measured SNR was approximately 5 times worse than measured for the spinning metal target at the same distance. However, the higher frequency of the piezoelectric mirror (400 Hz) relative to the spinning target (50 Hz) allows much quicker acquisition times resulting in normalized detection limits of approximately the same (10-15 ppm.m.Hz^{-1/2}). Similar results were found for a variety of "natural" topographic targets including building materials and cardboard boxes. Following a set of repetitive measurements over ~ 7 minutes, Allan variance analysis of the retrieved concentration¹⁸ showed that the concentration error followed white noise statistics, unlike the raw ACLaS signal. This indicates that the OE retrieval is robust enough to compensate for long-term drifts in the ACLaS signal induced by alternate parameters involved in the scenario modelling.

5. BROADBAND ABSORBING CHEMICAL VAPORS

5.1 Test broadband absorbers

Following the demonstration of narrow band absorbers stand-off detection and quantification, ACLaS capabilities were extended by the incorporation of a broadly tunable (1270-1330 cm⁻¹) continuous wave EC-QCL (Daylight Solutions) which allowed a greater frequency agility, and placed broadband absorbing molecules in scope of the ACLaS. Firstly, a set of test broadband absorbers was selected to carry out performance analysis. The left and middle panels in Figure 6 shows measured ACLaS traces using a spinning metal target at a distance of 3 m for the test chemicals HFC-134a (1,1,1,2-tetrafluoroethane) and for DCE (1,2-dichloroethane). The two test chemicals were chosen for their characteristic spectral features matching the broadly tunable laser source, and their high volatility. The volatile liquid DCE was evaporated in a gas cell at ambient pressure while HFC-134a vapor was introduced by firing a compressed air-duster across the instrument field-of-view. In the plots, upper panel shows the measured trace (black dots) and the OE fitted trace (red line). The forward model of the OE includes contributions from both the broadband absorber and from water,

which is the principal contributor to the atmospheric background in this spectral region. The lower panels show the residuals between fit and measured data. The middle panels show the transmission spectrum produced from the raw measured data and the retrieved polynomial baseline.



Figure 6: From left to right, experimental measurement and OE retrievals on HFC-134a, DCE, and EGDN. The upper panels show the measured trace (black dots) and the OE retrieved trace (red line). The lower panels show the residual of the fit. The middle panels show the transmission spectrum derived from the measured trace and the retrieved baseline.

Detailed analysis using the formalism described in Section 3, indicates that the combination of high resolution hyperspectral data with broad spectral coverage offered by the ACLaS, allows broadband chemicals to be confidently quantified even in complex mixtures¹⁹. Actually, with the full physics forward modelling approach, the spectral "clutter" is no longer disregarded but instead retrieved to enhance the confidence on the target molecule quantification. In addition, the broadband spectral traces could also be observed¹⁹ in the presence of overlapping narrowband absorbers (e.g. N₂O). Limits of detection were found to be 5 to10 times higher when using an EC-QCL rather than a DFB-QCL, owing to the additional excess noise introduced by the EC-QCL system (residual cavity fringing). This can be clearly seen in the residuals of the DCE spectral traces between 1280 cm⁻¹ and 1290 cm⁻¹.

The normalized detection limit for the broadband absorbers was 2.4 ppm.m.Hz^{-1/2} (HFC-134a) and 87.9 ppm.m.Hz^{-1/2} (DCE). The relatively high limit for DCE is due to the smaller absorption cross-section in this spectral region (7.773 x 10^{-20} cm².mol⁻¹ vs 2.149 x 10^{-18} cm².mol⁻¹ for HFC-134a).

5.2 Explosive vapors

In the context of security and defense, volatile molecules exhibiting broadly absorbing spectral features are the prime target for the ACLaS. As a demonstration, a measurement campaign on Ethyl Glycol Dinitrate (EGDN) was carried out. A small amount of EGDN was vaporized into a gas cell, which was placed immediately in front of the target to simulate a gas plume. The temperature of the gas cell could be adjusted to control the vapor pressure and concentration of EGDN The metal target was located 3 m away from the transmission optics. Experimental results and OE analysis are shown in the right hand side plot of Figure 6. The top panel of the plot shows the measured ACLaS trace (black dots) and the OE retrieval trace (red line) of the raw data. The EGDN absorption band lies towards the low wavenumber edge of the laser tuning range and is not fully captured. The middle panel shows a measured transmission spectrum of EGDN. This was produced by lowering the temperature of the gas cell to produce a reference background spectrum. The transmission spectrum (black dots) has a flat baseline with interferences from the atmospheric background and optical fringing greatly reduced. The red line shows the OE fit to the transmission spectrum with the fit residuals shown in the lower panel.

The retrieved concentration error for EGDN was 0.650 ppm.m.Hz^{-1/2} for the transmission spectrum which had an acquisition time of 120 s and a SNR of 80. The acquisition time was chosen to allow the atmospheric background lines to be fully resolved. It is clear from Figure 6 that the absorption band of EGDN is heavily oversampled and that the acquisition time could be reduced by up to a factor of 6 given the specifications of the EC-QCL. The vapor pressure of EGDN at 25C gives a concentration of ~ 132 ppm under ambient conditions which is well within the detection limit of the instrument.

5.3 Reference absorption cross-sections of threat chemicals

The accurate quantification of threat chemicals using the ACLaS together with the OE analysis is strongly reliant on the availability of high quality reference spectral data of threat chemical absorption cross-sections in the SWIR and the LWIR. For instance, the EGDN demonstration described in the preceding section was only possible because we generated reference spectra of EGDN that were used as input data to the OE algorithm. Any inaccurate or low quality reference data used will propagate to produce unreliable and potentially misleading concentration results. In addition, condensed phase spectral data cannot be used as a substitute for vapor spectra since significant differences in band position and shape exist, especially given the high spectral resolution capability of the ACLaS. High-quality gas-phase spectral reference data of explosive materials are generally not readily available in the SWIR and LWIR atmospheric windows. As part of the development of the ACLaS and the processing algorithm, we have developed an experimental protocol for measuring these reference cross-section data, which we briefly describe below.

The experimental system consists of a gas-generator (Owlstone OVG-4) connected to a multi-pass absorption cell which is integrated within a high-resolution Fourier Transform Spectrometer (Bruker IFS-125). Pure samples of explosive (~ 50-100 mg, purity > 99%) are placed within a PTFE permeation tube and held in the oven of the gas generator at a fixed temperature ($\Delta T < 0.1$ K). A constant flow of pure nitrogen carrier gas over the tube produces a flowing mixture in which the concentration of explosive is expressed by Equation 12. The concentration *c* is in ppm, Δm is the mass loss of the analyte (permeation rate) in ng/minute, V_{molar} is the molar volume (in liters), *f* is the flow rate (in ml/minute) and *MW* is the molecular weight (in g/mole) of the analyte.

$$c = \frac{\Delta m}{f} \cdot \frac{v_{molar}}{(MW)} \tag{12}$$

The mass loss of the permeation source is measured gravimetrically over time using a high accuracy balance (Sartorius, 10 μ g accuracy). The left hand panel of Figure 7 shows gravimetric measurements of triacetone-triperoxide (TATP) over a week long period. The black crosses show the measured mass of the tube. The permeation rate is found from the gradient of a linear fit to the measurements (red line) with an accuracy of ~ 1%. For TATP, the permeation rate (208.1 ng/minute) allows concentrations of 0.05 to 0.5 ppm to be generated with an accuracy of less than 5 %, limited by the uncertainty on the flow rate.

The constant flow output from the gas generator is connected to the input of a temperature stabilized multi-pass White cell with a total path length adjustable from 1 to 10 m. The cell is maintained at constant pressure using a high precision pressure controller. Spectral measurements over several months showed the reliability and reproducibility of the system in generating quantifiable concentrations of explosives.



Figure 7: Left, mass loss data as a function of time for a permeation tube containing the home made explosive triacetone triperoxide (TATP). Right, measured transmission spectrum of TATP.

As an example of recorded transmission spectrum, the right hand panel of Figure 7 shows the case of TATP in the LWIR spectral region. Typically, spectra were recorded at relatively high resolution (0.04 cm⁻¹) and 200 interferograms were averaged prior to Fourier transformation to produce a spectrum. The spectra shown in Figure 7 is the average of 20 such

spectra recorded over the course of a single day. Transmission spectra were determined using reference spectra generated from a flow of pure nitrogen through the empty gas generator oven. Absorption cross-sections were measured for a number of explosives including TATP, its decomposition product diacetone diperoxide (DADP), nitroglycerine (NG) and ethylene glycol dinitrate (EGDN) with propagated errors of 5%. The principal sources of errors are the gravimetric determination of the permeation rate (up to 5%, dependent on the measurement duration) and the accuracy of the flow rate of the nitrogen buffer gas (1-2%).

5.4 Towards application to condensed phase deposits

The wide tuning range of the EC-QCL allows spectra of condensed phase species to be measured. The condensed phase absorption band of EGDN was found to lie outside the specified tuning range of the laser and a substitute molecule (4-nitroacetanilide, 4NA) was used for a first demonstration. The solid 4NA was painted onto a white paper target as a paste in a volatile solvent. After evaporation of the solvent, a solid yellowish residue was visible throughout the target surface. Measurements were taken using the ACLaS at a stand-off distance of 3 m. These are shown in the left hand panel of Figure 8. Alternatively, coated and uncoated targets were used to calculate the transmission spectra of the residues, which is shown in the middle panel of the plot. The absorption features of 4NA at 1275 cm⁻¹ and 1310 cm⁻¹ can be clearly seen. The raw AClaS spectra exhibit a complex spectral background that includes atmospheric water and the broadband absorption (centered at 1300 cm⁻¹) of HFC-134a which was still present in the laboratory. For comparison, an absorption spectrum of 4NA was collected using the attenuated total reflectance (ATR) tool of an FTIR (Bruker Vertex 80v). The FTIR spectrum is shown in blue in the bottom panel. The match between the two spectra is good in a qualitative way. However, these measurements cannot lead to qualitative high confidence data on 4NA deposited on the surface. In order to achieve this, far more work is needed to develop a robust forward model. The physics of spectrally resolved backscattering from rough surface deposits is far more complex than that of chemical vapor absorptions. This requires the development of detailed models and specific work for their validation.



Figure 8: Left, ACLaS spectra of condensed phase 4NA. The upper panel shows the spectra for a coated (red trace) and uncoated target (black trace). The middle panel is a transmission spectrum using the uncoated trace as the reference. The lower panel compares the measured ACLaS transmission spectrum (black trace) to a reference spectrum of 4NA measured using attenuated total reflection spectroscopy on a FTIR spectrometer (blue trace). Right, summary of normalized detection limits (in ppm.m.Hz^{-1/2}) of ACLaS stand-off detection measurements using DFB lasers (squares) and EC-QCL (stars). The dotted arrows show the known absorption cross-sections for the chemical warfare agent Sarin (GB) and the explosive TATP.

6. DISCUSSION

6.1 Summary of demonstrated limit of detection

To summarize all the results obtained in stand-off detection of narrow and broad band absorbing vapor molecules, one sigma detection limits were all normalized to a 1 m plume and a 1 s integration time. Once normalized, individual molecular absorption cross-section remains the only parameter influencing the limit of detection. For this reason, the plot

shown in the right hand side of Figure 8 gives the summary as a function of the absorption cross-section (peak value within the spectral scan). The plot shows two clear groupings related to the laser sources used, and linear guidelines have been superimposed to emphasize the two trends. The excess noise from the EC-QCL degrades the sensitivity by almost one order of magnitude. The EGDN point seems to be consistent with the DFB QCL trend only because this measurement was made using background subtraction to compensate for the EC-QCL excess noise.

The ACLaS developments are still very recent and we believe that significant improvements in the sensitivity limits can be obtained. The current limitation is due to the speckle noise generated by diffuse reflection on a rough surface. Using the forward model, the ultimate sensitivity, solely limited by the shot noise, would be \sim 4 orders of magnitude better than the best of our results obtained so far. This implies that there is a significant reserve for improvement, and the implementation of optimized speckle reduction mechanisms is one way forward to lower further the limit of detection.

6.2 Extrapolation to further threat chemicals

The excellent match found between the measured ACLaS results and the forward model/OE validated the physical model. Therefore, the algorithm can confidently be used to extrapolate ACLaS performance data to a wider range of threat molecules, providing reference absorption cross-section data are available. Table 3 shows calculated performance data for some selected chemicals, including the explosives nitroglycerine (NG), TATP and DADP¹⁴ and the chemical warfare agents, Sarin (GB), Soman (GD) and Tabun (GA)^{24,25,26}, using the experimentally demonstrated instrument SNR. Absorption cross-sections for TATP and Sarin are also indicated with black arrows on the right hand side of Figure 8 and are approximately 1 order of magnitude greater than those of narrow band absorbers such as N₂O or CH₄.

The data in Table 3 includes the peak absorption cross-section within the LWIR window, the measured vapor pressure at 25°C expressed in Torr, the mixing ratio in ppm under ambient conditions, the extrapolated ACLaS limit of detection assuming a 1 m long gas plume and a 1 s acquisition time, and finally the ratio of the mixing ratio to the extrapolated LoD. A value greater than 1 in this column indicates that the current ACLaS instrument has the potential sensitivity to detect the threat chemical. All the molecules listed in Table 3 should be detectable at ambient concentrations by ACLaS, although in the case of the explosive nitroglycerine (NG), the detection would be marginal.

Threat Chemical	Cross-section / cm ² .molecule ⁻¹ (v)	Vapor Pressure (25°C) / Torr	Mixing Ratio (25°C) / ppm	ACLaS LOD / ppm.m.√Hz	Ratio Mixing/LOD
NG	$3.68 \times 10^{-18} \\ (1277 \text{ cm}^{-1})$	4.8 x 10 ⁻⁴	0.63	0.25	3
DADP	$\begin{array}{c} 2.79 \text{ x } 10^{-18} \\ (1207 \text{ cm}^{-1}) \end{array}$	0.133	175	0.345	515
ТАТР	$3.98 \times 10^{-18} \\ (1194 \text{ cm}^{-1})$	0.046	61	0.23	265
Sarin (GB)	$\begin{array}{c} 3.00 \text{ x } 10^{-18} \\ (1020 \text{ cm}^{-1}) \end{array}$	2.74	3605	0.317	11360
Soman (GD)	$\begin{array}{c} 3.25 \text{ x } 10^{-18} \\ (1010 \text{ cm}^{-1}) \end{array}$	0.4	526	0.29	1817
Tabun (GA)	$\frac{1.86 \text{ x } 10^{-18}}{(1020 \text{ cm}^{-1})}$	0.07	92	0.55	168

Table 3.	Extrapolation	of ACLaS	limits of	detection	for a range	of threat	chemicals
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6.3 Conclusion and forward look

The series of experimental results presented in this paper have established the ACLaS concept performance. Using continuously tunable laser sources, the combination of broad spectral coverage with high spectral resolution was found

to be highly effective in detecting and quantifying complex chemical mixtures combining narrow band and broadband absorbers. The heterodyne detection approach of ACLaS makes it very sensitive, and stand-off detection at ranges of a few 10's of meters was demonstrated using only up to 20 mW of illuminating power. The combination of the dense hyperspectral data with the full physics of the OE algorithm was found to deliver chemical quantification as well as robust metrics for assessing the quality of the algorithm output. Even though currently limited by speckle noise, the system has demonstrated limits of detection well suited to the genuine stand-off detection of some volatile threat chemicals, fulfilling the key requirements mentioned in Section 1.

Taking a forward look, the current ACLaS SNR is known to be four orders of magnitude above the absolute ideal shot noise limit allowed by heterodyne detection. Currently, work on efficient speckle reduction mechanisms is under way with the target goal of improving sensitivity by two orders of magnitude. In addition, the demonstration work presented here used a relatively low illumination power and in the SWIR/LWIR this could be increased by a factor of 10 whilst maintaining the eye safety criteria. Higher sensitivity and longer range operations are therefore well within the capabilities of the system and will be subject to further developments.

The spectral agility of the source is a prime requirement to enable chemical versatility. To that end, an external cavity QCL have been used and demonstrated as a relevant ACLaS source but appears to show limitations both in terms of spectral coverage (\sim 50 cm⁻¹ in the LWIR) and noise performance (excess noise due to residual intracavity fringing). The use of continuous wave optical parametric oscillators (OPO) covering the entire SWIR and/or LWIR bands would dramatically enhance the capability of the ACLaS and will be explored in the near future.

The full physics modelling coupled with the optimum estimation algorithm was found to be highly efficient in the context of vapor sensing. Extending ACLaS capability to the quantification of liquids or solids deposited onto surfaces would be highly desirable. However, the quantification in this case is far more challenging and requires a more complex full physics modelling and a higher level of detection scenario parametrization. Moving into the development and the validation of models is another future direction for operational ACLaS developments.

Whilst the current demonstrator exploits the narrow coherent field of view through extremely localized probing ($\sim 1 \text{ cm}$ diameter probing zone at 40 m distance), the advantage could be further levered into high resolution imaging using a raster scanning mechanism. This would allow the processing and delivering of concentration images for threat localization. This demonstration as well as the associated processing algorithm is also in scope for further works.

Lastly, to favor the practical deployment of ACLaS, we are currently developing highly miniaturized and ruggedized versions using hollow waveguides and hybrid optical integration technology²⁷. Practical deployment could then involve ground based robotic/autonomous systems or airborne deployment for chemical surveillance.

7. ACKNOWLEDGEMENTS

The authors would like to thank Dr. Francisco Molero-Menendez for his contribution to the development of the broadband ACLaS instrument. Technical support from Mr. Gary Williams, Dr. Robert McPheat and Mr. Wayne Robins (RAL Space Science department) is also acknowledged. We also wish to thank Dr. Alex Contini from the Centre for Defence Chemistry at Cranfield University for synthesizing the pure explosive samples. Financial support from the Scottish Enterprise Explosive Detection Platform, from the UK Ministry of Defence, The Defence Science and Technology Laboratory and the Innovate UK SBRI IRC is acknowledged.

8. REFERENCES

[1] Hodgkinson, J. and Tatam, R.P., "Optical gas sensing: a review," Meas.Sci.Technol 24, 012004 (2013).

[2] Gares, K.L., Hufziger, K.T., Bykov, S.V. and Asher, S.A., "Review of explosive detection methodologies and the emergence of stand-off deep UV resonance Raman," J.Raman.Spectrosc 47, 124-141 (2016).

[3] Mitev, V., Babichenko, S., Bennes, J., Borelli, R., Dolfi-Bouteyre, A., Fiorani, L., Hespel, L., Huet, T., Palucci, A., Pistilli, M., Puiu, A., Rebane, O. and Sobolev, I., "Mid-IR DIAL for high-resolution mapping of explosive precursors," Proc. SPIE 8894, 88940S (2013).

[4] Boudreau, S., Levasseur, S., Perilla, C., Roy, S. and Genest, J., "Chemical detection with hyperspectral lidar using dual frequency combs," Opt. Express 21(6), 7411-7418 (2012).

[5] Michel, A.P.M., Liu, P.Q., Yeung, J.K., Corrigan, P., Baeck, M.L., Wang, Z., Day, T., Moshary, F., Gmachl, C.F. and Smith, J.A., "Quantum cascade laser open-path system for remote sensing of trace gases in Beijing, China," Opt. Engineering 49(11), 111125 (2010).

[6] Fuchs, F., Hugger, S., Jarvis, J., Blattmann, V., Kinzer, M., Yang, Q.K., Ostendorf, R., Bronner, W., Driad, R., Aidam, R. and Wagner, J., "Infrared Hyperspectral Standoff Detection of Explosives," Proc. SPIE 8710, 87100I (2013).

[7] Chen, X., Guo, D., Choa, F.S., Wang, C.C., Trivedi, S., Snyder, A.P., Ru, G. and Fan, J., "Standoff photoacoustic detection of explosives using quantum cascade laser and an ultrasensitive microphone," Appl.Optics 52(12), 2626-2632 (2013).

[8] Goyal, A., Myers, T., Wang, C.A., Kelly, M., Tyrrell, B., Gokden, B., Sanchez, A., Turner, G. and Capasso, F., "Active hyperspectral imaging using a quantum cascade laser (QCL) array and digital-pixel focal plane array (DFPA) camera," Opt.Express 22(12), 14392-14401 (2014).

[9] Pal, A., Clark, C.D., Sigman, M. and Killinger, D.K., "Differential absorption CO₂ laser system for remote sensing of TATP related gases," Appl.Optics 48(4), B145-B150 (2009).

[10] Vaicikauskas, V., Kaucikas, M., Svedas, V. and Kuprionis, Z., "Mobile spectroscopic system for trace gas detection using a tunable mid-IR laser," Rev.Sci.Instrum 78, 023106 (2007).

[11] Hardy, B., Raybaut, M., Dherbecourt, J.B., Melkonian, J.M., Godard, A., Mohamed, A.K. and Lefebvre, M., "Vernier frequency sampling: a new tuning approach in spectroscopy-application to multi-wavelength integrated path DIAL," Appl.Phys.B. 107, 643-647 (2012).

[12] Geng, H, Liu, J.G., He, Y., Zhang, Y.J., Xu, Z.Y., Ruan, J., Yao, L. and Kan, R.F., "Research on remote sensing of broadband absorbers by using near-infrared diode lasers," Appl.Optics 53(28), 6399-6408 (2014).

[13] Lambert-Girard, S., Allard, M., Piche, M. and Babin, F., "Differential optical absorption spectroscopy lidar for midinfrared gaseous measurements," Appl.Optics 54(7), 1647-1656 (2015).

[14] Ostmark, H., Wallin, S. and Ang, H.G., "Vapor pressures of explosives: a critical review," Propellants.Explos.Pyrotech 37, 12-23 (2012).

[15] Menzies, R.T. and Tratt, D.M., "Airborne CO₂ coherent lidar for measurements of atmospheric aerosol and cloud backscatter," Appl.Optics 33(24), 5698-5711 (1994).

[16] Weidmann, D., Reburn, W.J. and Smith, K.M., "Ground based prototype quantum cascade laser heterodyne radiometer for atmospheric studies," Rev.Sci.Instrum. 78, 073107 (2007).

[17] Daghestani, N.S., Brownsword, R. and Weidmann, D., "Analysis and demonstration of atmospheric methane monitoring by mid-infrared open-path chirped laser dispersion spectroscopy," Opt.Express 22(S7), A1731-A1743 (2014).

[18] Macleod, N.A., Rose, R. and Weidmann, D., "Middle infrared active coherent laser spectrometer for standoff detection of chemicals," Opt.Letts. 38(19), 3708-3711 (2013).

[19] Macleod, N.A., Molero, F. and Weidmann, D., "Broadband standoff detection of large molecules by mid-infrared active coherent laser spectrometry," Opt.Express. 23(2), 912-928 (2015).

[20] Reitebuch, O., Werner, C., Leike, I., Delville, P., Flamant, P.H., Cress, A. and Engelbart, D., "Experimental validation of wind profiling performed by the airborne 10-μm heterodyne Doppler lidar WIND," J.Atmos.Oceanic Technol. 18, 1331-1344 (2001).

[21] Weidmann, D., Reburn, W.J. and Smith, K.M., "Retrieval of atmospheric ozone profiles from an infrared quantum cascade laser heterodyne radiometer: results and analysis," Appl.Optics 46(29), 7162-7171 (2007).

[22] Goodman, J.W., [Speckle phenomena in optics: theory and applications], Roberts and Company Publishers, Colorado, (2010).

[23] Rodgers, C.D., [Series on atmospheric, oceanic and planetary physics-Volume 2, Inverse methods for atmospheric sounding, theory and practice], World Scientific Publishers, Singapore, (2000).

[24] Sharpe, S.W., Johnson, T.J., Chu, P.M., Kleimeyer, J. and Rowland, B., "Quantitative, infrared spectra of vapor phase chemical agents," Proc.SPIE 5085, 19-27 (2003).

[25] Buchanan, J.H., Sumpter, K.B., Abercrombie, P.L. and Tevault, D.E., "Vapor pressure of GB," US Army Research, Development and Engineering Command, ECBC-TR-686, (2009).

[26] Balboa, A., Buchanan, J.H., Buettner, L.C., Sewell, T. and Tevault, D.E., "Vapor pressure of GD," US Army Research, Development and Engineering Command, ECBC-TR-575, (2007).

[27] Weidmann, D., Perrett, B.J., Macleod, N.A. and Jenkins, R.M., "Hollow waveguide photomixing for quantum cascade laser heterodyne spectro-radiometery," Opt.Express 19(10), 9074-9085 (2011).