

Middle infrared active coherent laser spectrometer for standoff detection of chemicals

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Using a quantum cascade laser emitting at 7.85 μm , a middle infrared active coherent laser spectrometer has been developed for the standoff detection of vapor phase chemicals. The first prototype has been tested using diffuse target backscattering at ranges up to ~ 30 m. Exploiting the continuous frequency tuning of the laser source, spectra of water vapor, methane, nitrous oxide, and hydrogen peroxide were recorded. A forward model of the instrument was used to perform spectral unmixing and retrieve line-of-sight integrated concentrations and their one-sigma uncertainties. Performance was found to be limited by speckle noise originating from topographic targets. For absorbers with large absorption cross sections such as nitrous oxide ($>10^{-19}$ $\text{cm}^2 \cdot \text{molecule}^{-1}$), normalized detection sensitivities range between 14 and 0.3 $\text{ppm} \cdot \text{m} \cdot \text{Hz}^{-1/2}$, depending on the efficiency of the speckle reduction scheme implemented. © 2013 Optical Society of America

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Sensitive standoff detection and identification of trace chemicals is a highly sought-after capability for applications related to security and defense, environmental sensing, and industrial monitoring. In the field of security and defense, remote detection and identification of threat chemicals requires systems that fulfill stringent requirements [1], including high sensitivity for detection of low-volatility chemicals, rapid response times of less than a few minutes, operational distances greater than a few tens of meters and wavelength agility to confidently quantify and identify potentially complex mixtures. In addition, any laser-based system must be eye safe for unrestricted deployment options. A variety of optical methods have been developed to detect both surface contaminants [2,3] and vapor phase species [4,5]. However, none of these have proven capable of simultaneously addressing all the requirements for standoff detection of vapor phase threat chemicals.

Mid-infrared hyperspectral coherent (or heterodyne) detection systems offer the potential to meet the aforementioned criteria. A coherent spectrometer yields three simultaneous advantages for standoff detection: ideally shot noise limited detection, ultrahigh spectral resolving power ($>10^7$), and an inherently narrow field of view that allows high spatial resolution [6,7]. Thermal infrared passive laser heterodyne spectroradiometry based on quantum cascade lasers (QCL) has been developed and demonstrated for atmospheric remote sensing applications [6]. However, passive methods are not sufficiently sensitive for terrestrial standoff detection of trace chemical plumes over distances of tens to hundreds of meters. Here we report what we believe is the first prototype of a mid-infrared active coherent laser spectrometer (ACLaS), which relies on active illumination and topographic backscattering from a distant target to generate spectrally resolved absorption signals occurring within the instrument's line of sight.

The light source for the thermal-infrared ACLaS prototype is a continuous wave distributed feedback (DFB)

QCL operating between 1274 and 1281 cm^{-1} and delivering up to 50 mW of optical power. While the tuning range of this DFB QCL is insufficient to resolve wide broadband spectral features, it offers a cost-effective way to establish the performance of the ACLaS instrument using narrowband absorbers. The laser wavelength range has been specifically chosen to target hydrogen peroxide (H_2O_2), a common precursor and decomposition product of improvised explosives. Additionally, other light molecules are accessible within the QCL spectral window, including methane (CH_4), water vapor (H_2O), and nitrous oxide (N_2O).

Figure 1 shows the simplified optical layout of the ACLaS. The QCL radiation is collimated using an aspheric lens and directed to a R90/T10 beam splitter (BS1). The transmitted portion of the optical power is used as the heterodyne local oscillator (LO). The reflected part of the beam passes through a germanium acousto-optical frequency shifter driven at 76 MHz. The unshifted zeroth-order output is used for relative frequency calibration of the laser via transmission through a 76.1 mm long germanium etalon. The first-order diffracted beam from the shifter, containing a maximum of ~ 30 mW of power, is transmitted toward a solid, diffusely reflective target several meters away. The transmission optics are adjusted to form a beam waist at the target plane. The intensity of the coherent illumination is

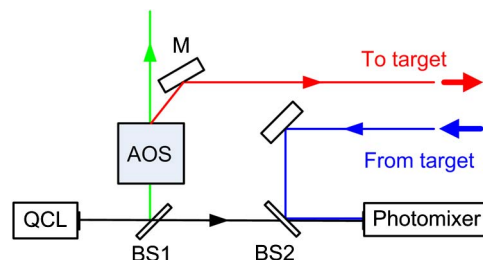


Fig. 1. Optical schematic of the ACLaS. M, mirror; BS, beam splitter; AOS, acousto-optical shifter.

well within eye-safety laser exposure limits. A small fraction of the radiation backscattered by the target is collected by the ACLaS receiver mirror, and conditioned to be superimposed with the LO field on a ~ 200 MHz bandwidth liquid-nitrogen-cooled mercury cadmium telluride photodiode.

The DC component of the detector photocurrent is used to drive a PID feedback loop that maintains the LO power constant at the optimum heterodyne efficiency level of $150 \mu\text{W}$ during the laser frequency sweep. The AC output is amplified and filtered by a bandpass filter centered at 76 MHz with a 3 dB bandwidth of 0.76 MHz chosen to match the typical free-running linewidth of DFB QCLs [8]. Contributions from background radiation are well suppressed with a receiver that has a spectral resolving power greater than 5×10^7 . In addition, the coherence between the LO and the received field ensures the returned radiation remains centered relative to the receiver spectral band and cancels any contribution that can arise 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 (100 ms integration time unless otherwise stated) whose reference is synchronized to the amplitude modulation of the transmitted beam at ~ 2 kHz. A DAQ card acquires in-phase and quadrature output signals from the lock-in amplifier. The QCL is temperature and current controlled and an external sawtooth current modulation produces the laser frequency sweeps (100 s duration unless otherwise stated).

An ideal coherent receiver is limited only by the shot noise arising from LO detection. The receiver part of the prototype ACLaS has been experimentally tested, using thermal incoherent radiation as a source. Indeed, the background noise and Johnson noise are negligible, while detection at 76 MHz within an extremely narrow band renders the laser excess noise insignificant. However, in the context of coherent illumination of an optically rough surface, speckle induced by the diffuse reflectivity of the target will produce scintillation and phase fluctuations of the received field at the detector plane, manifesting as an additional noise source.

The signal-to-noise ratio (SNR) of the ACLaS can be expressed by Eq. (1), where $\langle i_{\text{Het}}^2 \rangle$ indicates the time-averaged heterodyne signal, $\langle i_{\text{SN}}^2 \rangle$ and $\langle i_{\text{Sp}}^2 \rangle$ represent the shot noise and speckle noise contributions, respectively. Using the speckle diversity parameter M , as defined by Goodman [9], and considering that the speckle noise is several orders of magnitude larger than the LO shot noise, the SNR is given by $\sqrt{M}$:

$$\text{SNR} = \frac{\langle i_{\text{Het}}^2 \rangle}{\langle i_{\text{SN}}^2 \rangle + \langle i_{\text{Sp}}^2 \rangle} = \frac{\langle i_{\text{Het}}^2 \rangle}{\langle i_{\text{SN}}^2 \rangle + \frac{\langle i_{\text{Het}}^2 \rangle}{\sqrt{M}}}. \quad (1)$$

Assuming the instrument receives a fully developed and unchanging speckle pattern from the target, M will be equal to 1 and speckle noise will dominate, giving a SNR of $\sqrt{M} = 1$. Figure 2 illustrates this situation. The left-hand side shows the speckle pattern recorded using an infrared camera situated 10 cm from the target (roughened aluminum foil) while the right-hand side shows a plot of the statistical distribution of the measured

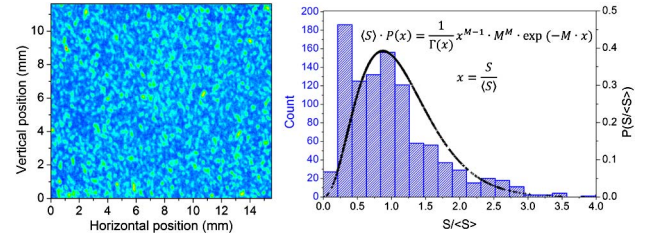


Fig. 2. Speckle image (left panel) and statistical distribution of the heterodyne signal (right panel) for a roughened aluminum target at a distance of 12 m from the instrument. The solid line is the expected distribution for an M parameter of 2.3.

heterodyne signal for a standoff range of 12 m with the QCL set at a fixed wavelength. For illustrative purposes, the theoretical distribution derived from Goodman's formula [9, Chap. 3, Eq. (54)], using $M = 2.3$, is overlaid as a solid line.

To assess the performance of the prototype ACLaS, a simple speckle reduction mechanism was first implemented. This mechanism consists of a target mounted on a rotating disc. Within the integration time, the receiver will average over multiple independent speckle patterns to greatly increase M . While this approach is not compatible with a real standoff scenario, it is statistically equivalent to alternate speckle diversity enhancement techniques, remains straightforward to implement, and is representative of the case of an ACLaS instrument mounted on a fast-moving vehicle.

Using the rotating target at 50 turns per second, the M parameter increases to $\sim 15,000$, and the statistical distribution of the heterodyne signal converges toward a Gaussian curve. The equivalence between the square of the SNR and M has been further confirmed by an alternate method, based on calculating the mutual coherence function of the speckle pattern recorded with the infrared camera. Values of M estimated in this way were found to be within the same order of magnitude as those obtained from the ACLaS SNR.

While the roughened aluminum target ensures sufficient diffusely reflected power to allow observation of a speckle pattern on a camera, other less reflective target materials have been tested, including white paper, bricks, wood, cardboard, and silicon carbide sandpaper of various grit sizes (22 – $125 \mu\text{m}$). The SNR of the instrument was found to vary very little ($\pm 15\%$) as the nature of the diffuse target was changed. SNR was more influenced (up to 100% change) by the residual specular reflection component some materials exhibited.

Figure 3 shows a first set of spectral measurements obtained with the ACLaS. From top to bottom, each panel shows the experimental data superimposed with fitted data (solid line), the experimental transmission, and the residual between the data and the fit.

These were taken using a spinning roughened aluminum target located 5.5 or 7.0 m away from the instrument. Laser beam diameters in the target plane were estimated to be ~ 8 mm. A large diameter (75 mm) absorption cell was placed in front of the target to simulate a 19 cm long homogeneous gas plume (only one way passage). The cell was sequentially filled with mixtures of test gases diluted in dry nitrogen: N_2O (~ 1000 ppm), CH_4 (~ 1000 ppm), and H_2O_2 (~ 300 ppm). All samples

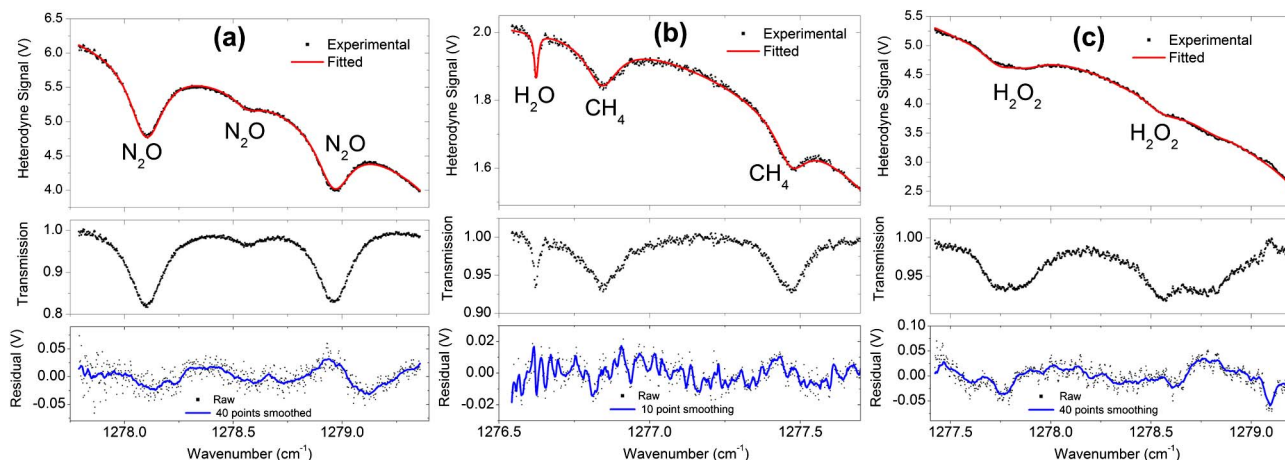


Fig. 3. ACLaS spectra obtained using a spinning roughened aluminum target at distances of (a), (b) 5.5 m and (c) 7.0 m. The upper parts of each panel show measured data (dots) and corresponding forward model fits (lines) while the lower parts show the residuals. The middle panels show the transmission spectra derived from the retrieved baseline parameters.

were at atmospheric pressure. The QCL was tuned across three spectral windows relevant to the particular molecule to be detected. The spectrum in Fig. 3(a) exhibits absorption from N_2O (cross sections of 4.40×10^{-19} and $3.92 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$) while the spectrum in Fig. 3(b) shows absorption features of both laboratory water vapor ($3.47 \times 10^{-22} \text{ cm}^2 \text{ molecule}^{-1}$) and methane (1.82×10^{-19} and $1.88 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$). The final spectrum in Fig. 3(c) displays absorption features of H_2O_2 (2.81×10^{-19} and $2.00 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$).

Molecular concentrations were retrieved from the experimental traces using a fitting algorithm that includes a detailed forward model of the standoff detection scenario as well as the instrument properties. The fits were carried out by the optimum estimation method (OEM) developed for atmospheric sensing [6,10], to return line-of-sight integrated concentrations of any absorbers whose transitions appear within the QCL wavelength scan. In addition, the model is used for full-error propagation analysis, and yields detection sensitivities. For each molecule under test, the fitted model is shown as a solid line in the spectral plots of Fig. 3. Whenever an experimental spectrum was oversampled, a smoothing also was performed. The smoothing window was chosen as the largest possible that does not degrade spectral information. The residuals obtained from smoothed traces were superimposed to the original ones in the lower panels of Fig. 3.

Table 1 summarizes the speckle diversity parameters and the one-sigma uncertainties in the fitted concentrations. All one-sigma uncertainties have been normalized to a one-meter-long vapor plume, and one second total acquisition time. Concentration uncertainties given in italics correspond to smoothed data. As expected, the detection limits scale with absorption cross sections. The best sensitivity achieved is $280 \text{ ppb} \cdot \text{m} \cdot \text{Hz}^{-1/2}$ for N_2O at 5.5 m. At a given standoff range, and for a given illumination power, the sensitivity relates to the efficiency of the currently implemented speckle reduction scheme.

The spectrum in Fig. 3(b) illustrates the advantage of recording the full spectral profile to provide selectivity and leverage for multispecies concentration retrieval.

Table 1. Speckle Diversity Parameters (M) and One Sigma Detection Sensitivities (ΔC) Corresponding to the Spectra Shown in Figs. 3 and 4^a

Figs.	M	Molec.	Range (m)	ΔC (ppm $\cdot$ m $\cdot$ Hz ^{-1/2})
3(a)	1.5×10^5	N_2O	5.5	1.9 <i>0.28</i>
3(b)	5.8×10^4	H_2O	5.5	15095 <i>751</i>
		CH_4		7.3 <i>1.7</i>
3(c)	1.0×10^5	H_2O_2	7.0	3.4 <i>1.1</i>
4(a)	1.2×10^3	N_2O	30.2	13.7

^aNumbers in italics indicate the detection limits after additional spectral smoothing.

This is a key benefit for the detection of the species of interest in the presence of an absorbing background. For example, in Fig. 3(b), the interfering water line is fully accounted for within the model and does not preclude the measurement of the methane concentration. Its principal effect is on the smoothing window size since the water line is significantly narrower than the methane lines.

Rotation of the target is clearly not practical for any realistic detection scenario in which the instrument is not moving with respect to the topographic target. In a second experimental run, a more realistic standoff detection situation was used. The ACLaS instrument was moved to a longer range test facility. A stationary wooden board painted with white gloss paint was located 30.2 m away from the instrument. The laser beam diameter focused onto the target was ~ 15 mm. A cell containing ~ 4000 ppm of N_2O in dry nitrogen at atmospheric pressure was located in the line of sight toward the target end. The QCL frequency was swept over a N_2O transition over a total time of 1.7 s, while the lock-in integration time was 10 ms. Phase scrambling and dithering of the transmitted beam (at 400 Hz) were used to increase the speckle diversity of the field backscattered by the stationary target. Figure 4(a) shows the spectrum along with the corresponding fit. The lower panel shows the residual trace. Table 1 gives the one-sigma uncertainty obtained from the measurement.

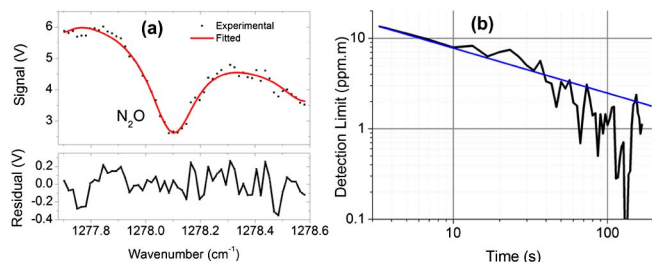


Fig. 4. (a) ACLaS spectrum obtained using a stationary painted wooden target at a distance of 30.2 m. The upper part shows measured data (dots) and corresponding forward model fit (line) while the lower part shows the residual. (b) Allan deviation of the retrieved N_2O concentration over 100 scans.

The temporal stability of the standoff concentration measurements was experimentally assessed by repeating the previously described experiment to record a series of 100 spectra at 3.4 s intervals. The temporal record of N_2O concentration over ~ 6 min was derived from OEM fits to each spectrum, and the Allan variance of the retrieved concentration calculated. Figure 4(b) shows the Allan plot where the path-length-normalized Allan standard deviation has been used as an estimator for the detection limit. The solid line indicates the white noise limit, which is well followed by the experimental data.

From the preliminary results presented here, the ACLaS prototype has been successfully demonstrated and its relevance for sensitive standoff detection of chemicals has been established. Even in the case where the speckle reduction is minimal, as shown in Fig. 4(a), detection limits obtained with ACLaS are similar or better than those demonstrated with mid-infrared systems using distant retroreflectors [5,11,12]. Closer to genuine standoff detection scenarios is the work reported by Hardy *et al.* [13] and Force *et al.* [14], using tunable optical parametric oscillators for direct detection of carbon dioxide (CO_2), and DIAL detection of ammonia using CO_2 gas lasers, respectively. In [13], there is a direct comparison with ACLaS. The range reported was between 10 and 30 m, and hyperspectral data were recorded. The raw sensitivity figures provided are not fully normalized. A quoted concentration limit of 150 ppb of CO_2 over a path length of 30 m with a 15 s acquisition time, yields a normalized detection limit of $17.4 \text{ ppm} \cdot \text{m} \cdot \text{Hz}^{-1/2}$. ACLaS already provides greater sensitivity even though the N_2O absorption cross section targeted with ACLaS is ~ 30 times smaller than the CO_2 one relevant to [13]. In terms of coherent detection, the work by Menzies and Shumate [15] on ozone, using a coherent DIAL system based on a CO_2 gas laser is comparable to ACLaS, without the continuous hyperspectral capability. In [15], the normalized ozone detection limit is between 22 and 27 $\text{ppm} \cdot \text{m} \cdot \text{Hz}^{-1/2}$ (2 ppb over a 1 km path with acquisition times of 2–3 min). The ozone cross section used in [15] is ~ 10 times weaker than that of N_2O used for the ACLaS demonstration, corresponding to an extrapolated sensitivity of $\sim 2.5 \text{ ppm} \cdot \text{m} \cdot \text{Hz}^{-1/2}$, close to the one obtained with ACLaS in the case of Fig. 3(a), without smoothing. A direct side-by-side comparison is

difficult to establish between instruments, as the laser power and ranges were significantly different.

For all the reported results on the ACLaS, instrument noise is dominated by speckle and remains at best four orders of magnitude above the ultimate shot noise limit of coherent detection. This gives confidence that improvements are achievable by increasing the speckle diversity, which is an ongoing work. Further improvements are expected by the availability of higher power laser sources. The maximum laser power used to illuminate the target in the hereby reported ACLaS prototype has been limited to ~ 30 mW. An order of magnitude increase in the illuminating power is still within eye-safety limits. Since the detection sensitivity has been measured to scale linearly with the illumination power, a tenfold improvement in detection sensitivity can be expected simply by switching to a more powerful laser source.

The spectral agility of the ACLaS can also be extended to broadband absorbers by incorporating external cavity QCL and/or optical parametric oscillators. In combination with the spectral unmixing algorithms developed previously [10], widely tunable laser sources will expand the ACLaS capabilities to encompass the standoff detection of broadband absorbers and complex molecular mixtures.

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