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# Open-path remote sensing for multi-species gas detection using a broadband optical parametric oscillator

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## ABSTRACT

We demonstrate path-integrated simultaneous concentration measurements of water, methane and ethane, measuring spectra across the 3.1–3.5- $\mu\text{m}$  range using 0.05  $\text{cm}^{-1}$  resolution Fourier-transform spectroscopy in-line with an ultrafast optical parametric oscillator and a simple, non-compliant target. Illumination spectra were extracted from a fitting procedure which simultaneously minimized the rms error between the experimental spectrum and a synthetic spectrum calculated from the envelope and a fitted mixture of PNNL or HITRAN absorbance data for water, methane and ethane. Simultaneous methane, ethane and water measurement at 30-m range were initially performed. Indoor measurements launched light from the OPO through a 20-cm-long gas cell containing a 1.5 $\pm$ 0.15% ethane-in-air mixture. Light was reflected from a rough Al-foil target. Best-fit concentrations were determined to be 1.15% (water), 1860 ppb (methane) and 1.37 % (ethane). The methane background value is consistent with reported ambient levels. Respective water and ethane values were consistent with the ambient relative humidity. The second experiment demonstrated real-time methane emission measurement at 70-m range. A 2% methane:air mix was released for 100 seconds at a rate of 103  $\mu\text{g s}^{-1}$  at a distance of 65 m from the OPO. The signal was recorded from a simple target of rough aluminum foil situated 70 m from the OPO, with the beam passing near the emission point. This work demonstrates our ability to extract concentration data from a single spectrum with no need for averaging, which provides a real-time and quantitative monitoring capability.

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**Keywords:** FTIR Spectroscopy, Open Path Spectroscopy, Optical Parametric Oscillator, Broadband, Remote Sensing, Multi-Species

## 1. INTRODUCTION

With fugitive hydrocarbon emissions accounting for 12% of greenhouse gas emissions they jeopardize safety and public health. These emissions are also costing the energy sector \$5B per year.

The most advanced technique for remote emission measurement and detection is via differential absorption lidar (DIAL), where intense infrared (IR) pulses originating from a narrow-line source such as an optical parametric oscillator (OPO) [1,2] are directed into the atmosphere and returned to a ground-based detector via weak scattering from airborne particles.

DIAL, with its range-gating capability [3] has been developed into several different forms [4–6], and recently extending to multi-species measurements [7,8]. One of the draw backs for this technique is the need for multi-mJ lasers light sources, which can be large and inconvenient to operate and maintain.

An alternative to DIAL is Fourier transform infrared (FTIR) spectroscopy which is naturally broadband and offers far wider coverage to DIAL. Furthermore, in an open-path embodiment FTIR can detect hundreds of atmospheric gases with a small system footprint but normally without a range-gating capability. Indeed, active open-path mid-IR Fourier-transform spectroscopy using thermal sources [9–11] is already used for quantitative hydrocarbon emissions monitoring in and around landfill sites, in agricultural contexts and at petrochemical sites, with resolutions around 0.5  $\text{cm}^{-1}$  [12].

This is adequate for species identification but presents difficulties when absorption lines of multiple species are spectrally overlapped.

With laser-based active FTIR spectroscopy it is possible to deliver higher resolution, thus providing the capability to distinguish similar gases such as methane and ethane which, as an example, makes it possible to separate petrochemical methane contributions—typically accompanied by a weak ethane signature—from biogenic sources (cattle, landfill, compost) which produce only methane.

The first quantitative high resolution open-path gas sensing was achieved using an Er: fiber dual-comb system in the near-IR, which provided 100-MHz resolution spectroscopy of CO<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>O, HDO and <sup>13</sup>CO<sub>2</sub> across a 2 km path [13]. This was followed by a demonstration in the mid-infrared at 3.25 μm using a single Yb:laser-pumped OPO to measure atmospheric water and methane over a 26-m path at 700-MHz resolution with a virtually imaged phase array spectrometer [14].

Here we present an eye-safe active FTIR spectroscopy system making use of a broadband ultrafast OPO operating in the 3.1–3.5-μm wavelength range and capable of acquiring sub-0.1-cm<sup>-1</sup> resolution gas absorption spectra from a simple target at ranges exceeding 70 meters. In contrast to previous work which employed optical quality targets (plane mirrors or retroreflectors) to return the beam, the combination of sufficient laser power, collection aperture, and detector sensitivity allows us to measure high quality spectroscopy from simple scattering targets such as aluminum foil, paper or concrete. Simultaneous quantitative measurement of atmospheric background levels of water and methane is also demonstrated, even in the presence of strong absorption from a control cell of 1.5±0.15% ethane gas. The system is also shown to be capable of real-time measurement of a localized 2% methane emission at a range of 65 m.

## 2. SPECTROSCOPY SETUP

The light source was an ultrafast OPO (Chromacity-OPO, Chromacity Ltd. [15]). This system is capable of delivering broad bandwidth light across the 1.45 μm – 4 μm. Up to 850 mW can be generated across the signal wavelengths (1.4–1.8 μm) and up to 350 mW across the idler wavelengths (2.4 μm – 4 μm), at a pulse repetition rate of 100 MHz. A fan-out MgO:PPLN crystal design was used to provided tunability from 2800–3900 nm. The broad spectra generated across these wavelengths are shown in Fig. 1. To access the strongest absorptions in methane and ethane we selected a grating position that provided instantaneous coverage from 3.1–3.5 μm, with an average power >300 mW and a 1-cm-diameter beam with a measured M<sup>2</sup> value of 1.05.

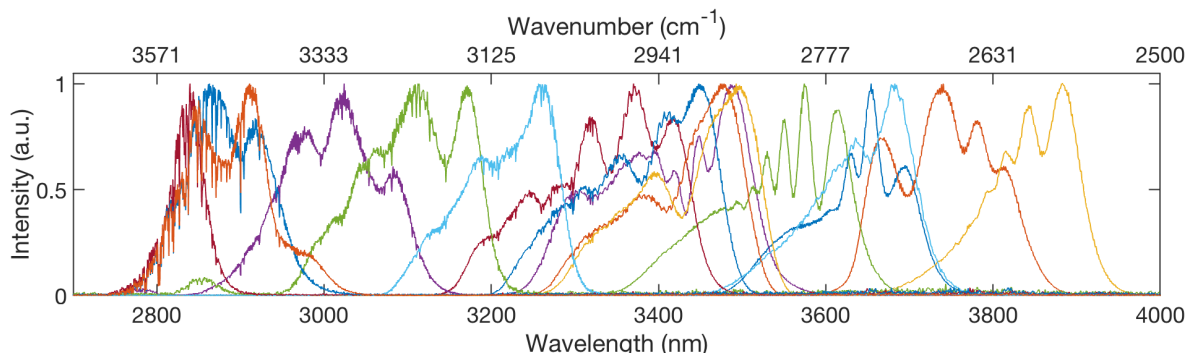


Figure 1. Measured idler spectra produced by fan-out-grating tuning of the Chromacity OPO. The spectral shapes are determined by the phasematching characteristics of the MgO:PPLN crystal and by the OPO pump-laser spectrum. Water absorption lines are visible at shorter wavelengths.

The spectrometer is shown in Figure 2 and was based on a design described in [16]. In this arrangement the OPO light was first coupled into a scanning Michelson interferometer before being launched into free-space. The light that was returned from the remote target was collected by a 6-inch f/4 Newtonian telescope. To detect this returned light an InSb liquid-nitrogen-cooled photodiode was situated at the telescope focus. Light from the OPO was launched along an optical axis co-aligned with the telescope's field of view using a small 45° steering mirror situated directly before the

secondary mirror of the telescope. The scanning interferometer operated at 1 Hz and achieved a typical resolution of  $0.05 \text{ cm}^{-1}$ . This is sufficient to resolve the narrow and complex absorption-line structure of light molecules like water, methane and ethane.

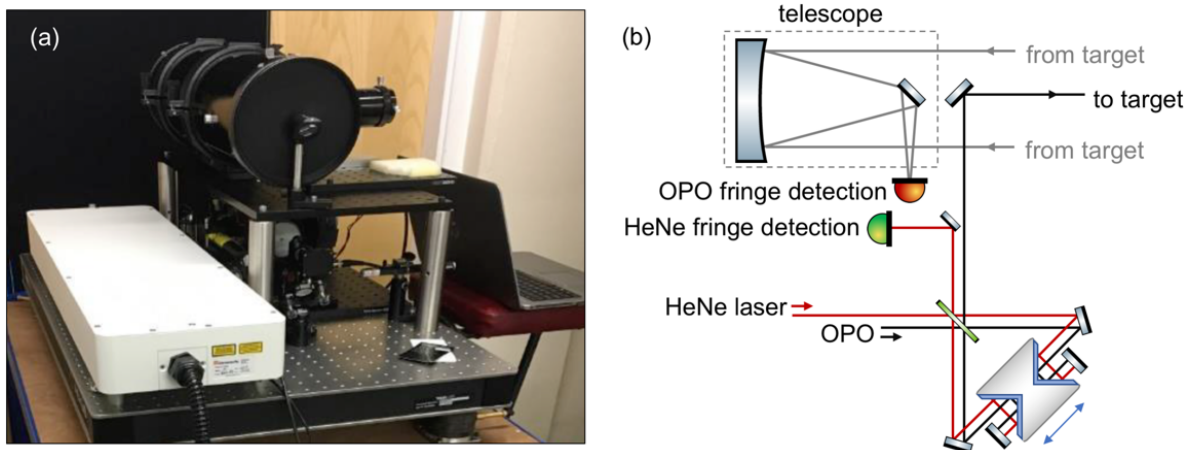


Figure 2. (a) OPO, telescope and scanning Michelson interferometer on a 60 x 90 cm breadboard. (b) Layout of the Fourier-transform spectrometer.

Due to the compact nature of the interferometer and the fact that the Chromacity OPO, with its fully integrated pump, does not require water cooling, the entire system was assembled on a 60 x 90 cm breadboard and mounted on a trolley to allow measurements to be made out with the laboratory environment.

### 3. EXPERIMENTS AND RESULTS

#### 3.1 Simultaneous methane, ethane and water measurement at 30-m range

The first series of experiments looked to establish the ability to measure multiple spectrally-overlapping species simultaneously. Indoor measurements were performed from a rough Al-foil target which was placed 30 meters away from the spectroscopy system. Light launched from the Chromacity OPO entered a 20-cm-long gas cell containing a  $1.5 \pm 0.15\%$  ethane-in-air mixture and was situated directly in front of the secondary mirror of the collection telescope. Figure 3(a) (blue) displays an example of a single measured spectrum (no averaging) exhibiting densely packed absorption lines from water, methane and ethane, as well as continuum absorption from ethane, which suppresses the overall spectral intensity.

For quantitative open-path spectroscopy either a reliable reference spectrum or a method of inferring the original illumination spectrum is required. This problem has been treated in different ways and reported in previously studies [13,14]. The approach used here is described in work by Kara et al.[17]. In essence, we developed an algorithm that obtains a rapid, accurate estimate of instantaneous intensity of the illumination source and the absorbance values from a piecewise fitting of small fragments of the measured spectrum then use these as a robust starting point to refine the values in a full-spectrum fit. This results in the retrieval of an illumination spectrum (Fig. 3(a), dashed line) and represents the OPO output spectrum before undergoing atmospheric absorption.

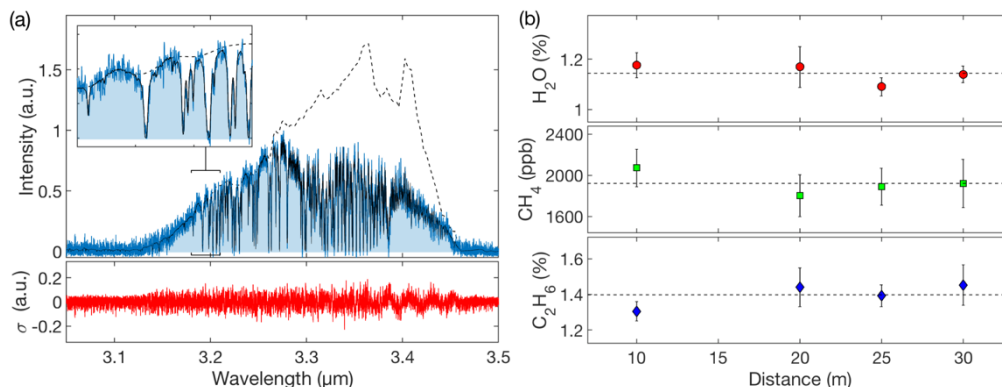


Figure 3. (a) Example spectrum collected at 30-m range from a rough aluminum- foil target. The upper plot shows the envelope of the illumination spectrum extracted from a fitting procedure which simultaneously minimized the rms error between the experimental spectrum (blue) and a synthetic spectrum (black) calculated from the envelope and a fitted mixture of PNNL absorbance data for water, methane and ethane. In this plot, the best-fit concentrations were 1.15% (water), 1860 ppb (methane) and 1.37 % (ethane). The rms fitting residual is shown in the lower plot. (b) Measured concentrations at 10, 20, 25 and 30 m, with data points showing the average values from approximately 45 spectra each. Error bars show the  $\pm 1$  standard deviation range. The methane background value is consistent with reported ambient levels measured at  $1885 \pm 15$  ppb [18]. Respective water and ethane values were consistent with the ambient relative humidity measured in the building and the filling concentration of the ethane cell. The dashed lines show the average of all the measured values.

The black line in Fig. 3(a) is the best-fit absorption spectrum using  $0.1\text{-cm}^{-1}$ -resolution PNNL database data [19] as the fitting reference. The residual (Fig. 3(a), red) shows some deviations of order similar to the rms noise near the spectral lines due to mismatch between the measured line shapes and the PNNL data. The inset in Fig. 3(a) shows the typical correspondence between the measured spectrum and the best-fit data. Figure 3(b) shows the extracted concentration data for water, methane and ethane. This shows that it is possible to obtain environmental concentration values consistent with independent humidity measurements (water), established ambient levels (methane) or known control concentrations (ethane).

### 3.2 Real-time methane emission measurement at 70-m range

By making use of a 78-m indoor corridor we simulated a point emission by releasing a 2% methane:air mix for 100 seconds at a rate of  $103 \mu\text{g s}^{-1}$  at a distance of 65 m from the Chromacity OPO. Again, a simple rough aluminum foil target was used. This target was situated 70 m from the OPO, with the beam passing near the emission point. Spectra were recorded every seven seconds and fitted in the same way as described previously to provide concentrations of water, methane and ethane. Even though the ethane cell had been removed from the experimental setup, ethane concentrations remained as an available fitting parameter, but as expected the resulting fitted concentration for ethane was negligible since it is not naturally present in the atmosphere. Figure 4(a) shows an example of a spectrum recorded without averaging at 70-m range and at a moment close to the peak methane emission. The Q-branch of methane can be clearly seen near  $3.31 \mu\text{m}$ .

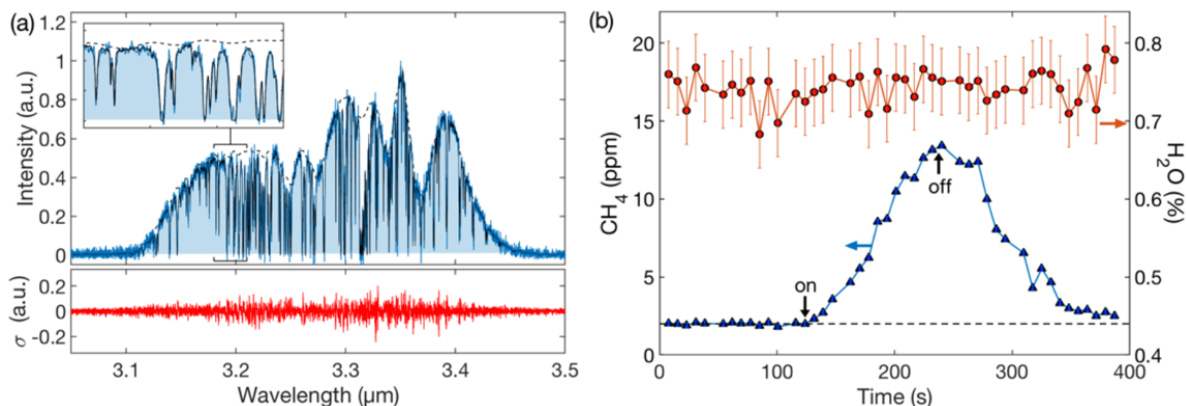


Figure 4. (a) Example spectrum from a set of 51 collected at 70-m range from a rough aluminum- foil target. In this example the best-fit concentrations were 0.77% water, 12650 ppb methane and 0 % ethane. (b) Concentrations of methane (blue) and water (red) measured before, during and after the methane release, showing a recovery to near-background levels after 150 seconds.

The inset of Figure. 4(a) shows the correspondence to the best-fit PNNL database in the 3.18–3.21- $\mu\text{m}$  region. In contrast to ethane, methane and water show very little continuum absorption under these experimental conditions (20°C, 101800 Pa), so the inferred illumination spectrum closely follows the envelope of the measured spectrum. Figure 4(b) shows the measured water and methane concentrations over 400 seconds, showing the methane concentration rising from background levels ( $\sim 1900$  ppb) to a peak of around 13000 ppb before returning to near the original value as the gas disperses. Prior to the methane release, the rms variation of the measured concentration of background methane at this range was  $<100$  ppb. Water showed more variability, which is to be expected due to convection effects and environmental variations within the corridor.

### 3.3 Future plans - real-world measurements beyond 70 meters

Due to the compactness of the Chromacity OPO, interferometer and detector system it has been possible to transport the whole system out of the laboratory environment into a more real world environment. The latest series of measurements are being conducted outdoors. Using the aluminum tailgate on the back of a Luton box van as a target, it has been possible to detect the backscattered signal at more than 200 m from the Chromacity OPO and detection system.

## 4. SUMMARY AND CONCLUSIONS

The FTIR spectroscopy system that has been described here offers several advantages to previously reported open-path sensing of atmospheric species.

The measurements conducted here were carried out with very simple, alignment-free targets, typically a coarsely positioned sheet of aluminum foil at a range of up to 70 m, but also with returns from  $> 30$  m available from paper, laminate or similar targets. Indeed, the range limit in our initial experiments was imposed by the dimensions of the building available and, based on the signal:noise performance which we obtained, we have been able to move outdoors to begin conducting experiments at a range of 150–200 m without having to modify the equipment. These results can be compared with the performance of alternative laser technologies [20-23].

In-the-field FTIR spectroscopy that makes use of thermal sources always requires high-quality retroreflecting targets to generate enough return signal. The ability to use a simple topographic target increases the practicality of the system described here, since it both relaxes the beam pointing accuracy and in some cases eliminates the need for a remote target. One particular highlight of this FTIR system is its ability to extract concentration data from a single spectrum with no need for averaging, which can therefore provide a real-time and quantitative monitoring capability and, makes the system suitable for detecting weak, localized emissions.

Although this technique does not achieve the resolution that is possible from dual-comb spectroscopy [13], the resolution of  $\sim 0.05 \text{ cm}^{-1}$  has been shown to be sufficient for extracting concentration measurements from complex, spectrally overlapping multiple species. We also note that open path sensing requires an eye-safe capability. With the current beam parameter, ranges of  $>10 \text{ m}$  from the OPO aperture are eye- safe for prolonged exposure, (irradiance of  $<0.1 \text{ W cm}^{-1}$  in this wavelength band [24]).

## REFERENCES

- [1] T. Henningsen, M. Garbuny, and R. L. Byer, "Remote detection of CO by parametric tunable laser," *Appl. Phys. Lett.* **24**, 242–244 (1974).
- [2] M. Endemann and R. L. Byer, "Simultaneous remote measurements of atmospheric temperature and humidity using a continuously tunable IR lidar," *Appl. Opt.* **20**, 3211–3217 (1981).
- [3] D. J. Brassington, "Differential absorption lidar measurements of atmospheric water vapor using an optical parametric oscillator source," *Appl. Opt.* **21**, 4411–4416 (1982).
- [4] M. J. Milton, T. Gardiner, F. Molero, and J. Galech, "Injection-seeded optical parametric oscillator for range-resolved DIAL measurements of atmospheric methane," *Opt. Commun.* **142**, 153–160 (1997).
- [5] G. Poberaj, A. Fix, A. Assion, M. Wirth, C. Kiemle, and G. Ehret, "Airborne all-solid-state DIAL for water vapour measurements in the tropopause region: system description and assessment of accuracy," *Appl. Phys. B* **75**, 165–172 (2002).
- [6] P. Weibring, H. Edner, and S. Svanberg, "Versatile mobile lidar system for environmental monitoring," *Appl. Opt.* **42**, 3583–3594 (2003).
- [7] G. A. Wagner and D. F. Plusquellic, "Multi-frequency differential absorption LIDAR system for remote sensing of CO<sub>2</sub> and H<sub>2</sub>O near 16  $\mu\text{m}$ ," *Opt. Express* **26**, 19420–19434 (2018).
- [8] E. Cadiou, D. Mammez, J.-B. Dherbecourt, G. Gorju, J. Pelon, J.-M. Melkonian, A. Godard, and M. Raybaut, "Atmospheric boundary layer CO<sub>2</sub> remote sensing with a direct detection LIDAR instrument based on a widely tunable optical parametric source," *Opt. Lett.* **42**, 4044–4047 (2017).
- [9] T. L. Marshall, C. T. Chaffin, R. M. Hammaker, and W. G. Fateley, "An introduction to open-path FT-IR atmospheric monitoring," *Environ. Sci. Technol.* **28**, 224A–232A (1994).
- [10] C. Schütze, S. Lau, N. Reiche, U. Sauer, H. Borsdorf, and P. Dietrich, "Ground-based remote sensing with open-path fourier-transform infrared (OP-FTIR) spectroscopy for large-scale monitoring of greenhouse gases," *Energy Procedia* **37**, 4276–4282 (2013).
- [11] T. E. L. Smith, M. J. Wooster, M. Tattaris, and D. W. T. Griffith, "Absolute accuracy and sensitivity analysis of OP-FTIR retrievals of CO<sub>2</sub>, CH<sub>4</sub> and CO over concentrations representative of 'clean air' and 'polluted plumes,'" *Atmos. Meas. Tech.* **4**, 97–116 (2011).
- [12] K. C. Cossel, E. M. Waxman, I. A. Finneran, G. A. Blake, J. Ye, and N. R. Newbury, "Gas-phase broadband spectroscopy using active sources: progress, status, and applications [Invited]," *J. Opt. Soc. Am. B* **34**, 104–129 (2017).
- [13] G. B. Rieker, F. R. Giorgetta, W. C. Swann, J. Kofler, A. M. Zolot, L. C. Sinclair, E. Baumann, C. Cromer, G. Petron, C. Sweeney, P. P. Tans, I. Coddington, and N. R. Newbury, "Frequency-comb-based remote sensing of greenhouse gases over kilometer air paths," *Optica* **1**, 290–298 (2014).
- [14] L. Nugent-Glandorf, F. R. Giorgetta, and S. A. Diddams, "Open-air, broad-bandwidth trace gas sensing with a mid-infrared optical frequency comb," *Appl. Phys. B* **119**, 327–338 (2015).
- [15] Full laser specifications are available from the manufacturer's website: <http://www.chromacitylasers.com/>
- [16] L. Maidment, Z. Zhang, C. R. Howle, and D. T. Reid, "Stand-off identification of aerosols using mid-infrared backscattering Fourier-transform spectroscopy," *Opt. Lett.* **41**, 2266–2269 (2016).
- [17] E. J. Dlugokencky, A.M. Crotwell, P.M. Lang, J.W. Mund and, M.E. Rhodes (2018), "Atmospheric methane dry air mole fractions from quasi-continuous measurements at Barrow, Alaska and Mauna Loa, Hawaii, 1986–2017," Version: 2018-03-19, Path: [ftp://aftp.cmdl.noaa.gov/data/trace\\_gases/ch4/in-situ/surface/](ftp://aftp.cmdl.noaa.gov/data/trace_gases/ch4/in-situ/surface/).
- [18] O. Kara, F. Sweeney, M. Rutkauskas, C. Farrell, C. G. Leburn and D. T. Reid, "Open-path multi-species remote sensing with a broadband optical parametric oscillator," *Opt. Express* **27**, 21358–21366 (2019).
- [19] S. W. Sharpe, T. J. Johnson, R. L. Sams, P. M. Chu, G. C. Rhoderick, and P. A. Johnson, "Gas-phase databases for quantitative infrared spectroscopy," *Appl. Spectrosc.* **58**, 1452–1461 (2004).

- [20] K. Numata, H. Riris, S. Li, S. Wu, S. R. Kawa, M. Krainak, and J. Abshire, "Ground demonstration of trace gas lidar based on optical parametric amplifier," *J. Appl. Remote Sens.* **6**, 63561–1 (2012).
- [21] J. Barrientos Barria, A. Dobroc, H. Coudert-Alteirac, M. Raybaut, N. Cézard, J.-B. Dherbecourt, T. Schmid, B. Faure, G. Souhaité, J. Pelon, J.-M. Melkonian, A. Godard, and M. Lefebvre, "Simultaneous remote monitoring of atmospheric methane and water vapor using an integrated path DIAL instrument based on a widely tunable optical parametric source," *Appl. Phys. B* **117**, 509–518 (2014).
- [22] N. A. Macleod, R. Rose, and D. Weidmann, "Middle infrared active coherent laser spectrometer for standoff detection of chemicals," *Optics Letters* **38**, 3708-3711 (2013).
- [23] M. C. Phillips and B. E. Brumfield, "Standoff detection of turbulent chemical mixture plumes using a swept external cavity quantum cascade laser," *Opt. Eng.* **57**, 011003 (2017).
- [24] IEC 60825-1:2001, Edition 1.2, *Consolidated Edition; Safety of Laser Products—Part 1: Equipment classification, requirements and user's guide*.