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Three mirror off axis integrated cavity output spectroscopy for the detection of ethylene using a quantum cascade laser

R. Centeno*, J. Mandon, S.M. Cristescu, F.J.M. Harren

Life Science Trace Gas Facility, Institute of Molecules and Materials, Radboud University, P.O. Box 9010, NL-6500 GL, Nijmegen, The Netherlands

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ABSTRACT

We demonstrate the performance of a compact and robust gas sensor based on a pulsed distributed feedback quantum cascade laser (QCL, laser pulses 30 ns, repetition rate 1 MHz) in combination with off-axis integrated cavity output spectroscopy (OA-ICOS) in an improved 3 mirror configuration. The room temperature laser (wavelength 915 cm^{-1}) was wavelength tuned over ~0.25 cm^{-1} with a 4 kHz repetition frequency. A detection limit of 10 ppbv (part-per-billion volume) for regular OA-ICOS is demonstrated for ethylene in 2 min averaging time, which is equal to a noise equivalent absorption sensitivity (NEAS) of 1×10^{-8} cm^{-1} $Hz^{-1/2}$. An improved three mirror configuration OA-ICOS scheme showed a four times increase in sensitivity as compared to standard OA-ICOS, resulting in a NEAS of 2.5×10^{-9} cm^{-1} $Hz^{-1/2}$. The sensor was used for ethylene detection from apples, stored under controlled atmosphere conditions.

1. Introduction

Ethylene is a gaseous hormone that plays an important role in many aspects of plant growth and development; it is revealing stress responses in plants, induces wilting in flowers and causes fruit ripening [1,2]. As such, there is a strong demand for a compact and easy to operate ethylene detector to monitor and control its emission in growth chambers, greenhouses and fruit storage facilities. The concentration levels at which ethylene is active range from the single ppbv level to ppmv levels, for flowers (carnations, orchids) and ripening fruit, respectively [1,2]. The current standard of preventing ethylene levels from increasing in fruit storage facilities is the use of controlled atmosphere (CA); such that the storage life can be extended. CA storage uses an atmosphere that differs substantially from normal air in respect to CO_2 and O_2 levels. Several methods for measuring ethylene levels have been implemented in agricultural research and fruit storage facilities [3]. Gas Chromatography (GC) is currently the standard technique where ethylene concentrations down to a few ppbv can be measured [4]. Disadvantages are the slow response time and the use of consumables such as chromatography columns and carrier gases, which make GC's maintenance intensive and costly in manpower. Other ways to detect ethylene are *via* non-dispersive infrared detection [5], amperometric [6] or electrochemical [7] methods or they rely on changes in luminescence properties [8,9]. However in general, these methods are not sensitive and selective enough to detect ethylene at low ppbv concentration levels.

Nowadays laser-based detection of atmospheric trace gases can reach sub-ppbv levels on-line and at second timescale [10–12]. Such highly advanced laser systems can be costly and mostly operate under laboratory conditions. One approach is the detection of ethylene with tunable diode lasers in the near-infrared wavelength region [13]. As the absorption strength of ethylene in this region is weak, only high concentrations can be measured and long optical path lengths are needed to improve the sensitivity. Therefore, it is more favorable to measure ethylene in the mid-infrared wavelength region, where it presents its strongest optical absorption spectra. Here, we present a sensor for the detection of ethylene that is compact, robust and cost effective and has a low maintenance level.

In the past, high power CO_2 lasers were used in combination with photoacoustic spectroscopy to reach sub-ppbv levels [14]. The main advantages of the photoacoustic detection over other laser-based techniques are its high sensitivity and background free detection. Their disadvantage is that atmospheric CO_2 gas absorbs at the laser lines [15,16]. Although this can be solved by using chemical scrubbers, this limit its use of CO_2 laser based ethylene detectors in fruit storage facilities of greenhouses, due to its consumables, manpower and operational costs.

Since two decades room temperature Quantum Cascade Lasers (QCLs), operating in the mid-infrared wavelength region, became available [17]. Due to their low laser power, other spectroscopic

* Corresponding author. Tel.: +31 24 365 23 80; fax: +31 24 365 33 11.
E-mail address: R.Centeno@science.ru.nl (R. Centeno).

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techniques besides photoacoustic spectroscopy became preferable such as Cavity Ring-Down Spectroscopy (CRDS) [18,19] and Off-Axis Integrated Cavity Output Spectroscopy (OA-ICOS) [20,21]. These techniques make use of optical cavities that enhance the optical path length largely, thereby increasing its sensitivity for trace gas detection. In CRDS the lifetime of a photon inside a high finesse cavity is measured, the latter directly connected to the absorption strength of a gas [18,19]. Within OA-ICOS the total transmitted power through a high-finesse cavity is measured [20–23].

Several groups have reported on the detection of ethylene using QCL's [24–26]. Manne et al. showed a detection limit of 5 ppbv in 10 s with an astigmatic Herriot cell with 150 m path length [24] and have reported later on 20 ppbv in 5 s using a high-finesse cavity with an optical path length of 76 m [25]. Weidmann et al. obtained a detection limit of 30 ppbv in 80 s with path length of 100 m using a Herriot cell [26]. All these results were achieved in the mid infrared with a thermoelectrically cooled pulsed QCLs and liquid nitrogen cooled detectors. Despite these results, laser-based OA-ICOS sensors are not yet in use for monitoring ethylene from plants and fruits.

Here, we use a pulsed DFB (Distributed FeedBack)-QCL at room temperature in combination with an OA-ICOS cell for the detection of ethylene. The radiation from the QCL is coupled into a high finesse cavity and the spectroscopic information is extracted from a measurement of the time integrated light intensity that leaks out of the cavity. We discuss the optimization of the signal-to-noise ratio based on cavity and laser parameters and report on the implementation of an optical enhancement scheme using a third mirror to couple the rejected light back into the high finesse cavity. The suitability of such system is demonstrated for apple storage under several conditions.

2. Material and methods

2.1. OA-ICOS

We briefly highlight the most relevant aspects of OA-ICOS since it has been extensively reviewed in the literature [20–23]. OA-ICOS is a laser-based spectroscopic method developed from cavity ring down spectroscopy. The laser light is injected into a closed optical cavity formed by a pair of high-reflectivity mirrors, meanwhile tuning over a molecular gas absorption feature of interest. The absorption strength of the gas is extracted from the time-integrated light intensity that leaks out at the backside of the cavity onto the detector. If light enters the cavity on-axis it is only transmitted at specific wavelengths determined by Free Spectral Range (FSR) of the cavity. If laser light is injected off-axis into a cavity, the effective FSR of the cavity becomes smaller, determined by the number of internal reflections before the laser light is back on its initial position. This will result in a dense spectral mode structure of the optical cavity and with a typical laser line width of a few MHz, the laser light is transmitted through the cavity without any strong power fluctuations as it would be with the on-axis configuration [21,22]. As such, OA-ICOS takes advantage of long path absorption spectroscopy without the need of active locking to a single longitudinal cavity mode. In addition, it is also free from spectral interference problems, such as can be observed in multipass-cells. OA-ICOS reduces the complexity of the setup and improves its alignment robustness [23]; it is easy to implement, offers great versatility and selectivity, and does not require fast time-resolved measurements (CRDS) or high laser pulse energies, making it technically less demanding and more cost effective than other laser-based methods. However, there are also disadvantages of this approach: reminiscent light source intensity fluctuations can decrease the signal-to noise ratio, and the intensity at the detector is substantially reduced due to the low throughput by the high finesse cavity. Additionally, in the wavelength region around 10 μm, Peltier cooled infrared detectors have a limited detectivity (typical $D^* \approx 10^9$ cm Hz$^{1/2}$ W^{-1}). Due to this low detectivity and the low power of QCLs, the optical cavity cannot use mirrors with very high reflectivity (>99.98%) but only 99.8%, which reduces the optical path length considerably (effective optical path length 150 m). As a result the overall sensitivity of the system is reduced.

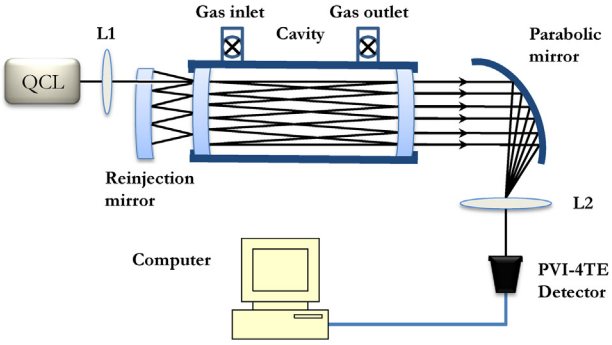

Fig. 1. Schematic of the experimental setup. QCL: pulsed quantum cascade laser; L1, L2: focusing and collimating lens, respectively; PVI-4TE detector: four stages thermoelectrically cooled detector.

By placing an additional highly-reflective mirror with a small entrance hole in front of the cavity, the light reflected from the entrance mirror of the cavity is re-injected by the third mirror into the cavity. This is particularly desirable in the case of a broad laser linewidth, or a small cell diameter. In the first case, only a small portion of the light can be coupled inside a cavity mode, in the latter the off-axis parameter and thus the noise reduction are limited. The absorption signal and the performance of the system can be enhanced significantly depending on various parameters of the re-injection mirror, most importantly the entrance position and angle and its distance to the cavity. In addition, the optical power throughput of the complete system is improved, thereby counteracting the low detectivity of the detector.

2.2. Experimental setup

The experimental setup is shown in Fig. 1. A pulsed DFB-QCL was used, with a center frequency at 915 cm^{-1} (Alpes Laser). The room temperature laser emitted 30 ns pulses at a repetition rate of 1 MHz with a power of 3 mW. To scan the laser over ~0.25 cm^{-1} we applied a bias current ramp of 4 kHz to the laser at sub-threshold level while maintaining the pulse height. With the help of a focusing lens (ZnSe, AR coated, diameter 25.4 mm, f = 30 cm) the laser light was injected into the high finesse cavity formed by two spherical mirrors (diameter 50.8 mm, radius of curvature 1 m) with a reflectivity of R = 99.8% at 10.9 μm (II–VI Infrared). The cavity consisted of a vacuum-tight aluminum tube of 30 cm length (cell volume 0.6 l, free spectral range of 500 MHz), which was mounted on two micrometer XY-translation stages to allow precise alignment. Inlet and outlet gas ports allowed a continuous gas exchange through the cell. Since OA-ICOS does not require an on-axis alignment, it eliminates the need for adjustable mirror mounts at both ends of the cell for parallel alignment. The optical alignment of the configuration was supported by a He-Ne laser, which was co-aligned with the QCL beam *via* a flip mirror. Initially, the high finesse cell was aligned in its on-axis configuration and after that optimized for its off-axis position, using the He-Ne laser. A parabolic mirror behind the cell (f = 10 cm) collected the light and a collimating lens (ZnSe, AR coated) with f = 5 cm focused the light onto the thermoelectrically cooled detector (VIGO PVI-4TE-10.6, 100 MHz bandwidth, τ = 6 ns, $D^* = 7.3 \times 10^9$ cm Hz$^{1/2}$ W^{-1}) with a built-in preamplifier.