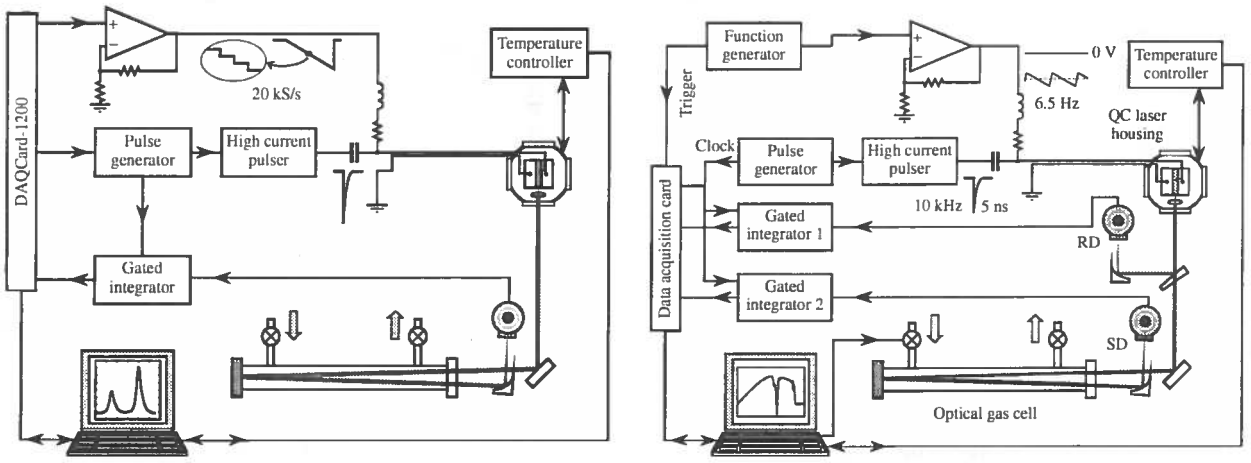

Fig. 1. Schematic of the pulsed QC-DFB based gas sensors. (a) a one-channel configuration used to detect NH_3; (b) a configuration with an added reference channel, was used for atmospheric CO monitoring. SD – signal detector, RD – reference detector.

The laser current was supplied in 5 ns long, 2 to 4 A peak current pulses. The repetition rate of the laser pulses was limited to 20 kHz by the gated integrator (Stanford Research Systems, model SR250) used as an interface between the fast IR detector and data acquisition card. The concentration of the sample was found from the absorption data by finding the best fit as described by the equation

$$y_i = Bf(i - x)$$

where y_i are the acquired fractional absorption data, $f(i)$ is an absorption line envelope as measured for a known high-concentration sample at the same pressure, temperature and laser operation parameters; B is proportional to the species concentration in the test sample, and x is introduced to take into account laser frequency drift.

To detect NH_3, the absorption lines $^aR_1(2)$ at 992.4503 cm^{-1} and $^aR_0(2)$ at 992.6988 cm^{-1} (~10.1 μm) in the ν_2 fundamental absorption band were selected. These lines are strong, well resolved at pressures below 200 Torr and free from interference by water and other air components absorption. The pulsed QC-DFB laser available for this work accessed this wavenumber region when operated at a temperature of –11.7°C. An example of the acquired spectrum is presented in Fig. 2a. This plot shows the averaged data obtained after 400 frequency scans, 256 laser pulses each. A sensitivity of better than 0.3 ppmv was achieved with a 1 m optical pathlength.

For detection of CO the laser frequency was scanned over a 0.41 cm^{-1} region encompassing the R(3) absorption line at 2158.300 cm^{-1}. This transition is free from interferences from atmospheric species such as H_2O. The R(3) line of CO was obtained by the 4.6 μm QC-DFB laser when its substrate temperature was maintained at –23.3°C. The subthreshold current used to scan the laser frequency [3] in these experiments was driven by the external function generator and not by the synchronized D/A converter, as in the ammonia detection experiment. This was made to avoid the limitation of 256 points per scan imposed by the available 12-bit DAQCard-1200 (National Instruments) data acquisition card. A number of laser pulses per frequency scan was increased to 1500. This result in the sensitivity gain, according to the equation [4]

$$\delta A = \sigma \sqrt{\frac{\Delta\nu}{\int g^2(\nu)d\nu}}$$

where δA is a standard deviation of the measured absorption line area, $\Delta\nu$ is the frequency scan resolution (inversely proportional to the number of pulses in the scan) and $g(\nu)$ is the absorption spectrum normalized by the condition $\int g(\nu)d\nu = 1$.

Spectroscopic trace gas detection with pulsed quantum cascade lasers

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Abstract: Pulsed quantum cascade lasers operating at wavelength of 10 and 4.6 microns were used for detection of ammonia and carbon monoxide, respectively. Variations of atmospheric CO concentration were continuously monitored with 12 ppbv precision using a 1 m optical pathlength.

OCIS codes: (280.1120) Air pollution monitoring; (280.3420) Laser sensors

Sensitive, compact devices for the quantification of trace gases are required for a number of applications that include industrial process control, environmental monitoring, and non-invasive medical diagnostics. A well-established technique for detecting molecular species in the gas phase is high-resolution infrared absorption spectroscopy. Fundamental vibrational absorption bands of molecular species are located in mid-IR region (3 to 20 μm). Quantum cascade (QC) lasers are the only kind of semiconductor lasers that enable to reach this region without the use of cryogenic cooling. When the distributed feedback (DFB) structure is embedded into such a device, it operates in a single-frequency mode, which is of particular use for spectroscopic applications [1]. However, most of the available QC-DFB lasers can operate at near-room temperature (that is, with thermoelectric cooling) only in pulsed low-duty cycle mode. This mode of operation leads to a relatively broad (>300 MHz) and asymmetric laser line [2]. These device characteristics require the development of new approaches to measurement procedures, data acquisition and analysis compared to those developed for the diode laser spectroscopy.

The QC-DFB laser based gas sensor architecture is defined by the required sensitivity to a particular gas species. We shall report two versions of the sensor. A one-channel configuration was used to detect ammonia by its absorption in the ν_2 vibrational band ($\lambda \approx 10$ μm). The sensitivity of this sensor was ultimately limited by pulse-to-pulse fluctuations of the QC-DFB laser energy. A two-channel configuration removed this limitation and was used to monitor CO concentrations in ambient air at $\lambda \approx 4.6$ μm.

Configurations of the two sensors are shown in Fig. 1. The same laser housing and a 50 cm long optical gas cell were used in both experiments. The QC-DFB laser was mounted on top of a three-stage thermo-electric cooling element (Melcor 3CP) inside a vacuum-tight housing with overall dimensions of 100×160×180 mm^3 (depicted in Fig. 2) assembled from commercially available vacuum and opto-mechanical components. To remove the heat generated by the operation of the Peltier cooler, the bottom of the thermo-electric assembly was soldered to a water-cooled housing base plate. A temperature controller (Wavelength Electronics LFI-3751 TE) was used to set and monitor the laser temperature. With this arrangement, the operating QC-DFB laser could be cooled to -55°C.

The laser emission was collimated using an aspheric AR coated ZnSe lens with a focal length of 3 mm and a diameter of 6 mm mounted inside the housing. The lens position could be adjusted externally. The collimated laser light emerged from the housing through a 30' wedged AR coated ZnSe window for 10 μm radiation or uncoated CaF_2 window for 4.6 μm radiation and was directed into 0.5 m long optical gas cell. This cell consisted of a glass tube fitted with Teflon valves and stainless steel window holders based on commercial 1⅓" vacuum flanges. One of the cell ends was equipped with a window, and the other one with a SiO protected flat Al mirror (both ∅25.4 mm). This resulted in a two-pass configuration with a total optical pathlength of 1 m.

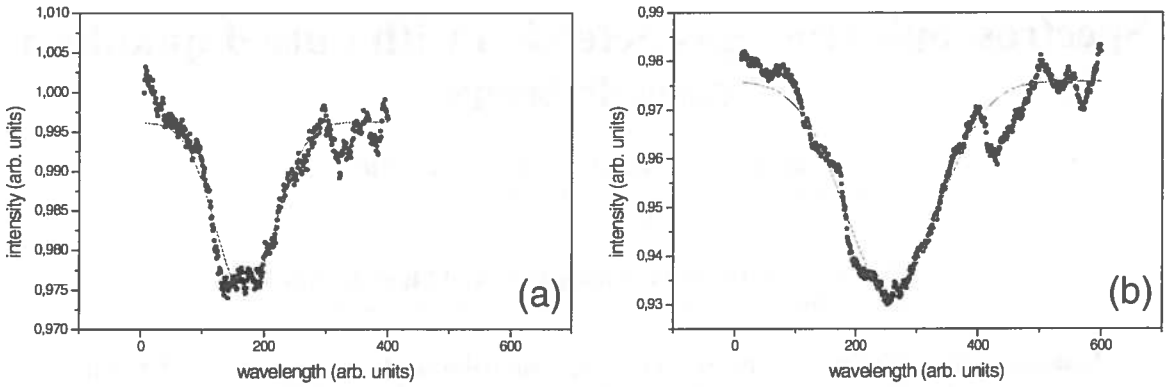

Figure 2: Laboratory evanescent-field spectra for H_2S at 1.57 µm. (a) 100 mbar H_2S pressure. (b) 400 mbar H_2S pressure.

However, the measured signal is mainly dominated by the line at 1571.304 nm because of its strong line strength. The upper trace corresponds to a scan under exactly the same experimental conditions but now the sensor is located beside the volcano fumerole. Then the H_2S concentration is much lower or even close to zero because of dilution effects and no absorption signal is detected by the evanescent-field laser sensor. Therefore these measurements can be used as a reference.

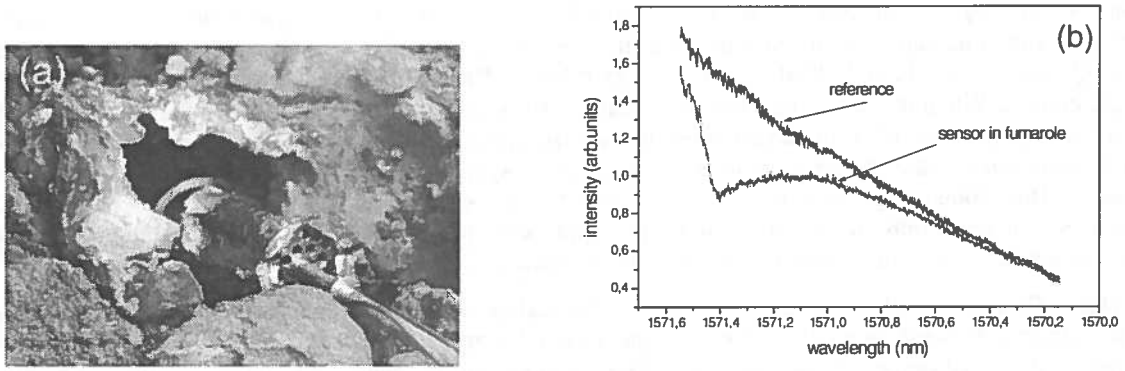

Figure 3: (a) In-situ application of the evanescent-field laser sensor at the volcano site "Solfatara" (Italy). (b) Wavelength scan for the detection of H_2S directly in the volcano fumerole.

4. References

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