N$_2$O detection with the CEAS method

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Abstract

Nitrous oxide (N$_2$O) plays a significant role in many different fields therefore its monitoring is an important task. In this paper the opportunity of application of cavity enhanced absorption spectroscopy for N$_2$O detection is presented. This method is a modification of cavity ring down spectroscopy. The laser radiation tuned to absorption line of N$_2$O is injected into an optical cavity under a very small angle in respect to its axis. In the case of lack of the absorption, the result is determined by the mirrors reflectivity coefficient, diffraction losses and length of the cavity. When the absorber is present in the cavity, the result additionally depends on absorption and scattering of light in cavity. The method provides the determination of a very weak absorption coefficient as well as the concentration of the absorbing gas.

Our N$_2$O sensor consisted of a pulsed radiation source, optical cavity, detection module and a digital oscilloscope. As the light source anoptical parametric generator was applied. It enabled the wavelength tuning in a broad spectral range with resolution of 1 nm. The optical cavity was composed of two high-reflective spherical mirrors. Optical signal registration was done with detection module equipped with HgCdTe photodetector.

The spectral range of 4.52–4.53 μm is the best for N$_2$O detection. Operation at these wavelengths provides opportunity avoiding of interferences with other atmosphere gases, like CO$_2$ and H$_2$O. Assuming 2% uncertainty of measurements and the effective value of the absorption cross section of about $6 \cdot 10^{-19}$ cm^2 the detection limit of 10 ppb was achieved.

Keywords: CEAS, N$_2$O detection, optoelectronic sensor.

1   Introduction

Nitrous oxide (N_2O) is a colorless gas with a slightly sweet odor. N_2O is an important greenhouse gas and the major natural source of NO. In consequence, it initiates the catalytic NO_x ozone destruction cycles in the stratosphere. The gas is used as an anesthetic, especially in dentistry and minor surgery. It produces mild hysteria and laughter preceding the anesthetic effect. Thus it is also known as 'laughing gas'. Excessive exposure may cause headache, nausea, fatigue and irritability. Simultaneously, N_2O is a strong oxidizer above 300°C and it self-explodes at higher temperatures. Nitrous oxide is also a characteristic compound emitted by majority of explosive materials. Therefore, measuring and monitoring of N_2O concentration is very important [1, 2].

   N_2O can be analyzed by gas chromatography (GC) on a molecular sieve column using a thermal conductivity detector (TCD). For this method detection limit of 4 ppm is achieved [3]. In the case of the electron capture detector (ECD) application, detection limit is about 50 ppb [4]. Nitrous oxide may be identified by GC/MS basing on its mass spectra as well. For solid phase microextraction GC/MS the sensitivity of 72 ppb for N_2O is reported [5]. Other nitrous oxide detection system with detection limit of 50 ppb is described by Hellebrand [6]. It consists of Fourier transform infrared spectrometer (FT-IR), heated measuring cell with an optical path length of 20 m and HgCdTe-detector (MCT).

   During the last several years some spectroscopic methods for gas detection were alsosignificantly developed. In the paper the opportunity of application of cavity enhanced absorption spectroscopy (CEAS) for N_2O detection is presented. This method is a modification of cavity ring down spectroscopy (CRDS).

2   Cavity enhanced measurements analyses

Spectroscopic measurements based on light absorption are the most popular methods of matter investigation. Absorption spectroscopy is a simple, non-invasive, in situ technique for obtaining information about different species. However, the sensitivity of traditional spectroscopic methods is approximately limited to values of 10^{-4}–10^{-5} cm^{-1}. It is mainly caused by detection limits of small differences of light intensities between input and output of the measuring system. Others reasons are the instabilities in light source intensity and the fluctuation of photodetector detectivity, which provide noises and interferences of absorption signals [7]. To improve the sensitivity, a longer absorption path length should be used. Such solution is used in multipass spectroscopy, e.g. in White or Herriott cells. Also the absorption spectroscopy with a modulation technique could be applied. O'Keefe and Deacon proposed novel measuring technique called cavity ring-down spectroscopy [8]. It allows to increase the sensitivity of about 3–5 orders of magnitude or even higher. CRDS system requires high–finesse stable optical cavity.

   In this technique, the laser pulses are injected into an optical cavity (resonator) consisting of two spherical high-reflective mirrors. The optical radiation is multiplied by reflected inside the resonator. After each reflection, a

small part of laser radiation leaves the optical cavity due to residual transmission of mirrors. The transmitted light is registered with a photodetector. The signal from the photodetector can be measured e.g. with digital oscilloscope. The amplitude of single–mode radiation trapped within the cavity decays exponentially over time with a time constant τ. The time constant is often referred to as the decay time or ring–down time. The decay of light intensity $I(t)$ can be described as

$$I(t) = I_0 \cdot e^{-\frac{t}{\tau}}. \tag{1}$$

The value of decay time constant depends on mirror reflectivity R, resonator length L, and extinction factor α (absorption and scattering of light in cavity) [9]

$$\tau = \frac{L}{c \cdot [(1-R)+\alpha L]}. \tag{2}$$

In this way determination of the absorption coefficient is possible by the decay time measurement. Firstly, it is measured for the case without absorption (α=0), when the decay time τ_0 depends only on mirrors reflectivity and the cavity length. Secondly for cavity filled the analyzed gas. By comparison of these two times, the absorber concentration C can be achieved from

$$C = \frac{\alpha}{\sigma} = \frac{1}{\sigma \cdot c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right), \tag{3}$$

where σ denotes the absorption cross section.

The sensitivity of this spectroscopic method is determined with the lowest detectable concentration of analyzed gas molecules C_L, which causes measurable change of the output signal. The concentration limit of absorbing molecules can be described with the formula

$$C_L = \frac{1}{c \cdot \sigma \cdot \tau_0} \cdot \delta_\tau = \frac{(1-R)}{\sigma \cdot L} \cdot \delta_\tau, \tag{4}$$

where δ_τ is the relative precision of the decay time measurement. The relationship between uncertainty δ_τ and τ_0 can be described as

$$\delta_\tau = \frac{\tau_0 - \tau_L}{\tau_0} \cdot 100\%, \tag{5}$$

where τ_L denotes a decay time of the optical cavity for minimal absorber concentration. The analysis presented in Figs. 1 and 2 show that sensitivity of the N_2O experimental setup better than 10 ppb can be obtained.

Effective storage of light in the resonator is ensured only when laser frequency is well-matched to a cavity mode. Then the best sensitivity can be achieved. However the major disadvantage of this method is a strong dependence of cavity modes frequency on mechanical instabilities. They damage cavity Q-factor and provide fluctuations of the output signal [10].

Such disadvantage is eliminated in cavity enhanced absorption spectroscopy. This modification of CRDS technique was described in 1998 by Engel et al. [11].
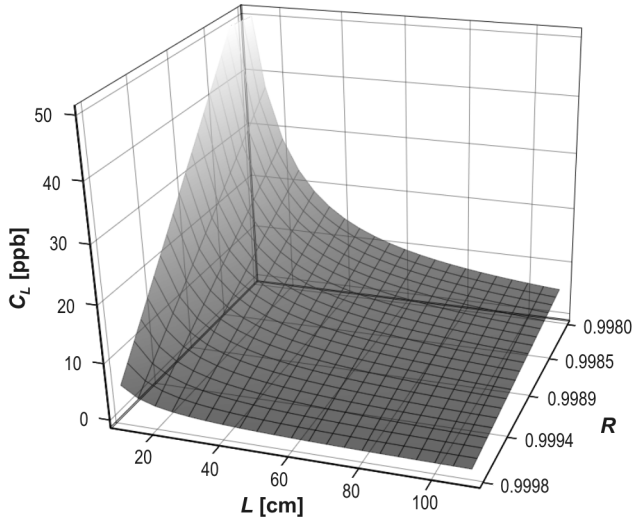
Figure 1: Dependence of the concentration limit C_L on the cavity length L and the reflectivity of mirrors R (calculations were performed for $\delta_\tau = 2.5\%$ and $\sigma = 4 \cdot 10^{-18}$ cm^2).
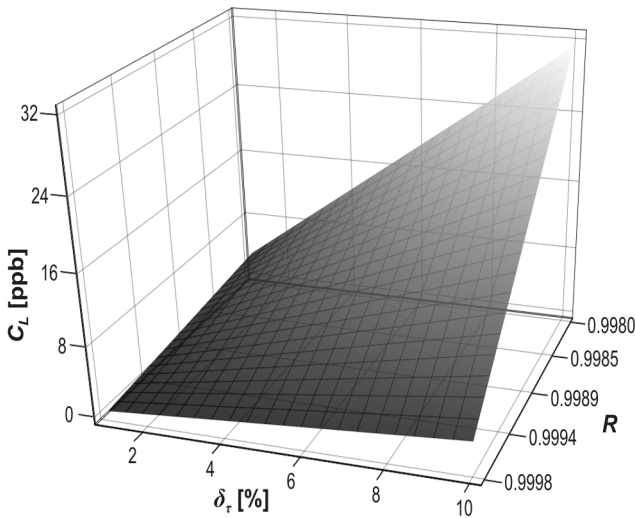

Figure 2: Dependence of the concentration limit C_L on uncertainty δ_τ and the reflectivity of mirrors R (calculations were performed for $L = 60$cm and $\sigma = 4 \cdot 10^{-18}$ cm^2).

CEAS is based on off-axis arrangement of the cavity and laser beam. The beam is injected under a very small angle in respect to the cavity axis. Usually the beam is repeatedly reflected by the mirrors, however, the reflection points are spatially separated. As a result a dense structure of weak modes is obtained or the modes do not occur due to overlapping. The system is much less sensitive to mechanical instabilities. CEAS sensors attain the detection limit of about 10^{-9} cm^{-1} [12, 13]. Another advantage is that due to off-axis illumination of the front mirror, the source interference by the optical feedback from the cavity is eliminated.

3 Laboratory N_2O sensing setup

Detection of nitrous oxide could be done at both the electronic and vibronic transitions. The electronic transitions correspond to ultraviolet range, below 200 nm, where neither the suitable laser sources nor the high reflectivity mirrors are available. Therefore N_2O detection was performed at vibronic transitions related to infrared range. The spectral region of 4.52–4.53 μm was chosen. In this wavelength range N_2O is characterized by relatively large peak cross section ($4 \cdot 10^{-18}$ cm^2) versus weak interference by the atmospheric compounds like CO_2 or H_2O. Comparison of these spectra based on *US Standard Atmosphere 1976* is presented in Fig. 3. According to this standard usual CO_2 concentration is 330 ppm, N_2O–773 ppm, while N_2O–0.32 ppm (at temperature 300 K and normal pressure).
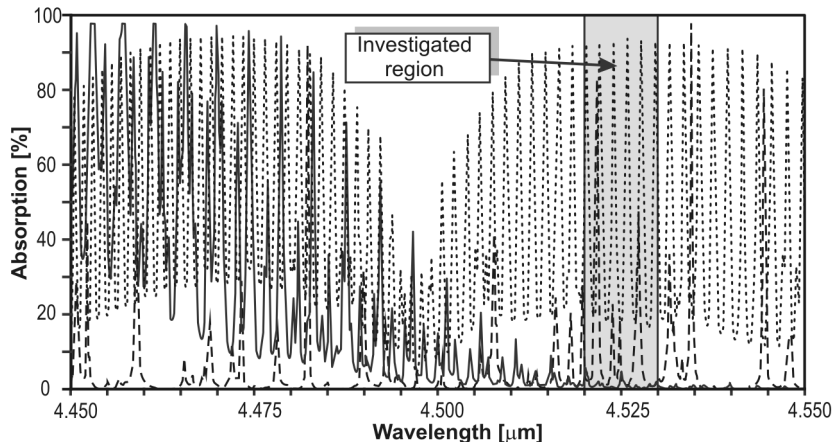

Figure 3: Absorption spectrum for N_2O (dotted line), H_2O (continuous line) and CO_2 (dashed line) (from HITRAN 2008).

Nitrous oxide sensing setup consisted of: source of infrared pulses, optical cavity, detection module and an oscilloscope. Nowadays, QCL lasers just elaborated by Alpes Lasers are the best light sources for this application. FWHM duration time of their pulses reaches hundreds of microseconds pulses while the repetition rate might be of some kHz. The emission wavelength can be easily

tuned to the maxima of N_2O cross section, e.g. 4.5239 μm or 4.5297 μm. However, in our preliminary experiments optical parametric generator (OPG) model PG711-DFG produced by Ekspla (Lithuania) was used. It enabled wavelength tuning within a broad spectral range with 1 nm resolution. The OPG was pumped with Nd:YAG pulsed laser. The output energy at the wavelength of 4.5 μm was about of 8.9 μJ. Because of high beam divergence two-lens collimator was applied. The scheme of lab setup for preliminary investigation of CEAS sensor is presented in Fig. 4.
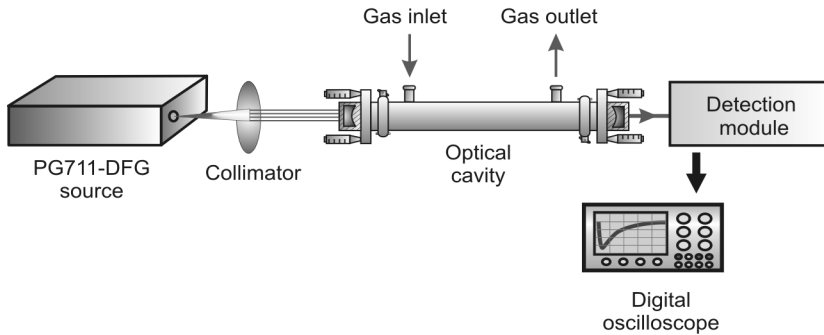

Figure 4:   The scheme of the laboratory CEAS system with PG711-DFG radiation source.

The optical cavity was built of two spherical mirrors, which reflectivity reaches about 0.9998 at the wavelength of interest (Los Gatos Research, Inc., USA).

The radiation leaving the cavity was registered with the low noise detection module PVI-2TE (VIGO System S.A., Poland). In the module, a photodetector (photodiode), cooling system and a preamplifier were integrated in a common housing [14]. Such construction provides opportunity of room temperature operating. Both mechanical and spectral parameters of the module were optimized to the N_2O sensor application. Photodetector maximum responsivity corresponds to the absorption bands of nitrous oxide (Fig. 5).
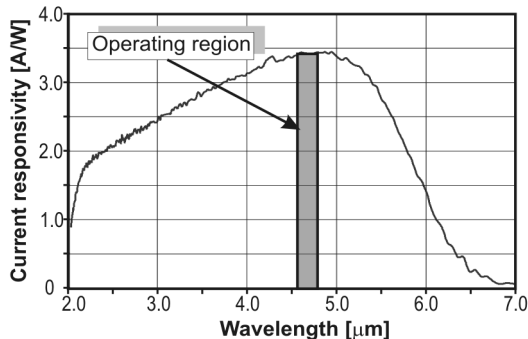

Figure 5:   Spectral characteristics of the HgCdTe photodiode current sensitivity.

The current signal from the photodetector was converted by a low-noise, broadband transimpedance preamplifier. The preamplifier ensured the best possible S/N ratio and matched the signal to the input circuits of the digital oscilloscope (DPO 4104, Tektronix). The experimental setup is presented in Fig. 6.
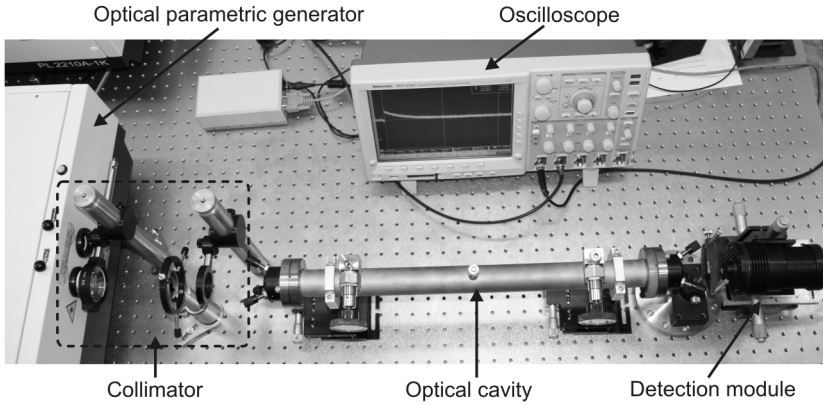
Figure 6: Experimental setup for N_2O detection.

Increase in mirrors reflectivity improves the detection limit. However it also reduces the intensity of the optical signal from the cavity. As a consequence it increases the requirements about detection module parameters. The most important factor describing optical signal detection capability is the signal to noise ratio (S/N). Fig. 7 presents the noise equivalent scheme of the first stage of a detection module using a transimpedance preamplifier.
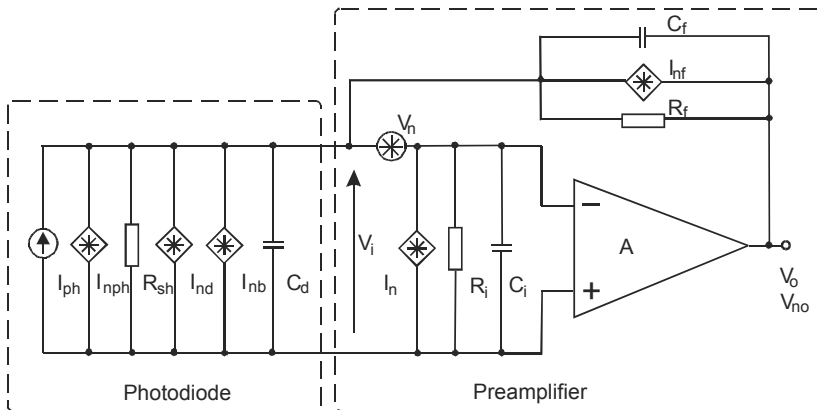
Figure 7: Scheme of the first stage of a detection module [15].

The signal current generator I_{ph} represents the detected signal. Noises in a photodiode are represented by three noise generators: I_{nph} – the shot noise associated with photocurrent, I_{nd} - the shot noise of a dark current, while I_{nb} - the shot noise from a background current. In the scheme, the value of the load resistance of photodetector depends on the feedback resistance R_f and the preamplifier gain A. The resistor R_f affects both the level of preamplifier output signal and its noise. The noise current generator I_{nf} is the thermal noise current and excess noise of the feedback resistance. Since the thermal noise of I_{nf} is inversely related to the square root of the resistance, R_f should be of great value.

In the first stage of detection module the noise is a function of frequency. At very low frequency, the photodiode is the dominant noise source. However preamplifier noise becomes increasingly important at higher frequency. The R_{sh} is the shunt resistance of a photodiode. Preamplifier noise is represented by the voltage source V_n and the current source I_n. From the arrangement in Fig. 7 it can be shown that the equivalent input noise is the square root of the sum of squares of noise components from: the photocurrent I_{ph}, the dark current of a photodiode I_{nd}, the background current I_{nb}, thermal noise of the resistor R_f, the noise sources from a preamplifier: I_n and V_n. Thus, the signal-to-noise ratio can be expressed by

$$\frac{S}{N} = \frac{I_{ph}}{\left[I_{nph}^2 + I_{nd}^2 + I_{nb}^2 + I_n^2 + \frac{4kT\Delta f}{R_f} + \left(\frac{V_n}{R_f} \right)^2 \right]^{1/2}} . \qquad (6)$$

In the N_2O detection system, the shot noise from a background current I_{nb} can be negligible, then, equation (6) becomes

$$\frac{S}{N} = \frac{I_{ph}}{\left[I_{nph}^2 + I_{nd}^2 + I_n^2 + \frac{4kT\Delta f}{R_f} + \left(\frac{V_n}{R_f} \right)^2 \right]^{1/2}} . \qquad (7)$$

In the case of high frequency, the last term of the denominator should contain additional combination of impedances across the input of the preamplifier, i.e. $(\omega \cdot C_d)^{-1}$ and $(\omega \cdot C_i)^{-1}$. Assuming that V_{nd} is the voltage noise of the serial resistance of the photodiode and the preamplifier capacitance C_i is conveniently grouped with photodiode capacitance C_d, the noise equivalent signal current, $I_{n\ total}$, is given by

$$I_{ntotal}^2 = \left[I_{nph}^2 + I_{nd}^2 + I_n^2 + \frac{4kT\Delta f}{R_f} \right] + \omega^2 \left[V_{nd}^2 C_d^2 + V_n^2 (C_d + C_i)^2 \right]. \quad (8)$$

There are two terms: a 'white' noise term in the first square brackets, and a second term which gives frequency proportional increase in a noise current. Although a capacitor does not add noise, the photodetector noise voltage (V_{nd}), and preamplifier noise voltage (V_n) is increased by the C_d and the $C_d + C_i$

respectively. Analyzing equation (8), we see that for matching a preamplifier to a photodetector, it is important to minimize the sum of $I_n + V_n^2 \omega^2 \left(C_d + C_i \right)^2$.

Thus, in order to ensure registration of low-level signals and accurate measurements of decay time, special preamplifier was developed. Moreover, further increase in S/N can be improved by the use of one of the advanced methods of signal detection, i.e. coherent averaging. This technique can be implemented in software for digital processing circuit. Thanks to this increase in S/N is directly proportional to a root of a number of the averaging samples n_{smpl},

$$\left(\frac{S}{N} \right)' = S \left(\frac{N}{\sqrt{n_{smpl}}} \right)^{-1}. \tag{9}$$

4   Experimental results

The main task of experiments was to check the opportunities of N_2O detection by constructed CEAS system. The research was performed for wavelengths range from 4.519 μm to 4.536 μm. Measurement procedure began from setting the appropriate wavelength of interest. Then τ_0 (3) was determined for the cavity filled with pure N_2. Subsequently the flow of N_2O-N_2 mixture was set to the cavity and the corresponding decay time τ was registered. The comparison of both signals is presented in Fig. 8.
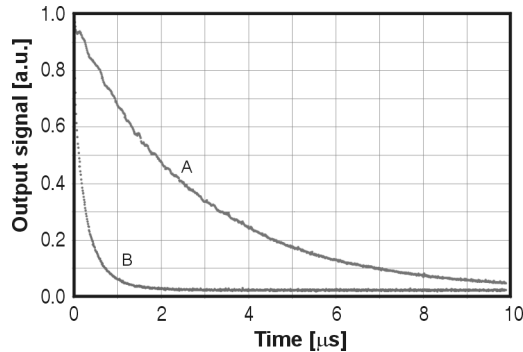

Figure 8:   The exemplary output signals from the cavity filled with reference gasN_2 (τ_0) (line A), and from the cavity filled with 10 ppm $N_2O(\tau)$ (line B).

The values of decay times were used to calculate the concentration of N_2O accordingly to the relationship (3). However the line width of optical parametric generator was about 0.001 μm. Thus it overlapped several absorption peaks of N_2O (Fig. 9). Therefore, in order to determine the absorber concentration the effective absorption cross section was taken into account. In the vicinity of the investigated lines the mean value of this parameter reached about $6 \cdot 10^{-19}$ cm^2.
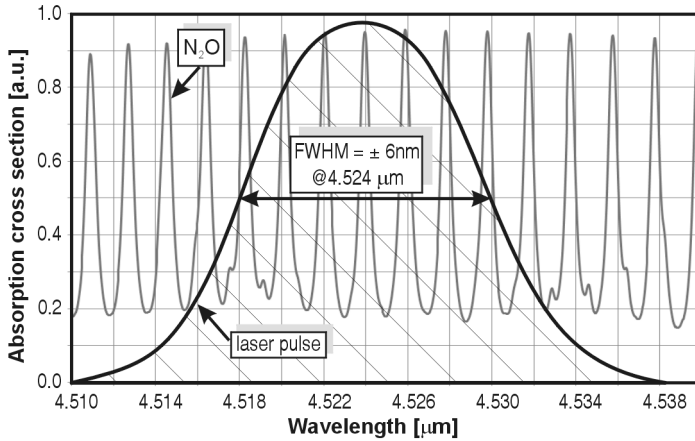
Figure 9: The spectral characteristics of N_2O absorption cross section and the laser radiation.

During the experiments the gas samples containing about 10 ppm N_2O were investigated. Concetration measurements were carried out at the different wavelengths. A good agreement between various results was achieved (Fig. 10). The differences are caused by uncertainity of gas sample preparations (~10% precision). Furthemore, 2% uncertainty of the decay time determination was obtained. In accordance with equation (4) the value of concentration limit of detection C_L of 10 ppb was achieved.
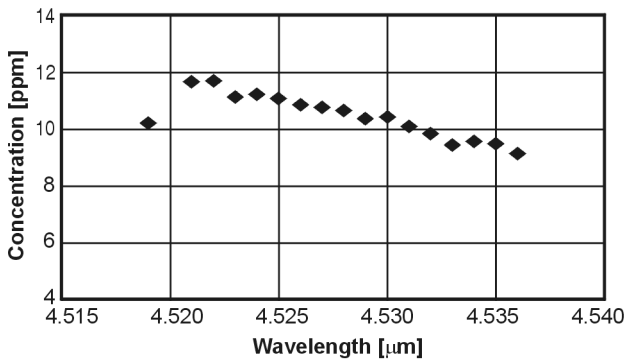

Figure 10: Measured N_2O concentration at the different wavelength.

5 Summary and conclusion

The paper presents the preliminary research of a nitrous oxide detection system based on cavity enhanced absorption spectroscopy. The best sensitivity was obtained in the wavelength range of 4.52 μm–4.53 μm. During experiments with

a broadband parametric oscillator the sensitivity of 10 ppb was achieved. One can expect that with a specialized narrowband light source (like QCL laser), with a wavelength well matched to the peak of the absorption spectrum the sensitivity might be increased about one order of magnitude.

Our N_2O sensor will be applied for detection of vapours from explosive materials. Some successful research with nitrogen dioxide sensor to detect nitroglycerine and nitrocellulose has been already performed. CEAS technique with blue violet laser diodes was applied [9, 16, 17]. We expect that an additional channel, i.e. the nitrous oxide sensor, would enable detection of other types of explosives. In Fig. 11 block diagram of two-channel CEAS sensor is presented.
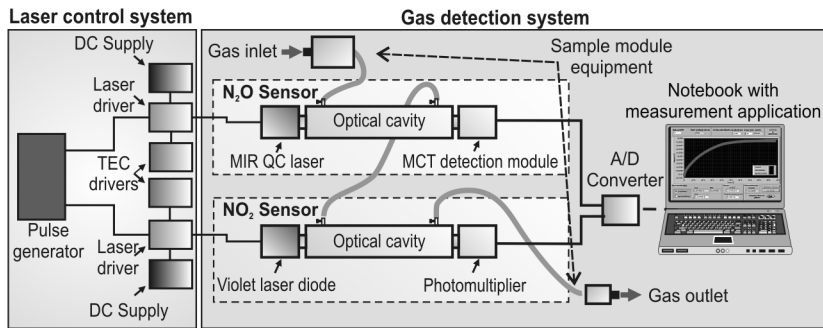

Figure 11:   Block diagram of NO_2 and N_2O optoelectronic sensor.

Acknowledgement

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