

NO and N₂O Detection with CEAS Method

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Abstract— The article describes an application of cavity enhanced absorption spectroscopy in nitric oxide and nitrous oxide sensors. For detection of both gases the vibronic molecular transitions were used. The wavelength ranges of these transitions are situated in mid-infrared spectra spectrum of radiation. To achieve optimal sensitivity and selectivity interferences by absorption lines from other gases commonly present in atmosphere (like H₂O or CO₂) should be minimised. The best results were obtained in the spectral regions of 5.23 μm –5.29 μm for NO and of 4.46 μm –4.54 μm for N₂O. A setup of the sensors consists of pulsed laser sources, optical cavities and photodetectors. As a radiation sources single mode quantum cascade lasers (QCL) were applied. Their narrow emission lines were precisely tuned to the wavelengths of interest. The optical cavities were built with spherical mirrors of high reflectance. The optical signal from the cavities outputs were registered with specially developed low noise detection modules. Thanks to this, the detection limits of single ppb were obtained.

1. INTRODUCTION

Nitric oxide (NO) and nitrous oxide (N₂O) are important compounds of the air. According to HITRAN database, in the standard atmosphere their concentrations are as follows: NO — 0.3 ppbv, N₂O — 320 ppbv [1]. However, in real ambient air the concentrations differ strongly due to influence of various emission sources (anthropogenic and natural). Both NO and N₂O are important greenhouse gases that have a large influence on environment, living organisms and human health. Acid rains occur due to reactions of these compounds with H₂O contained in the air. Moreover, NO and N₂O are produced during a decomposition process of specific explosive materials so these gases can be used as markers [2, 3]. Therefore these gases monitoring is of great importance for various applications: from routine air monitoring in industrial area and regions of intensive traffic, detection of explosives in airports, finally in medicine investigation, for health care, etc.

There are many techniques for NO and N₂O detection. For example, in the case of gas chromatography (GC) and mass spectrometry (MS), a detection limit of a few dozen ppb is reported [4, 5]. Detection methods using the photoacoustic phenomenon provide a sensitivity of about 20 ppb [6]. In gas detection applications, a special role is played by optoelectronic methods. They are characterized by both high selectivity and high sensitivity (low limit detection). In practice, cavity enhanced absorption spectroscopy (CEAS) belongs to the most sensitive sensors. In this technique, off-axis direction of laser beam to the optical cavity is applied (Figure 1). Inside the cavity the light is repeatedly reflected by the mirrors. In comparison to cavity ring-down spectroscopy (CRDS), the light spots on the mirrors surfaces are spatially separated and weak mode structure is occurred. It causes that the entire system is much less sensitive to instability in the cavity and to instability in laser frequencies. Additionally, due to off-axis illumination of the front mirror, the source interference by the optical feedback from the cavity is eliminated. The CEAS sensors can obtain a detection limit of about 10^{-9} cm^{-1} [7]. Therefore, this method makes the best opportunity to develop a portable optoelectronic sensor of nitrogen oxides.

In this technique determination of the concentration of the examined gas can be carried out during two-step process. In the frame of the first step, measurement of the signal decay time

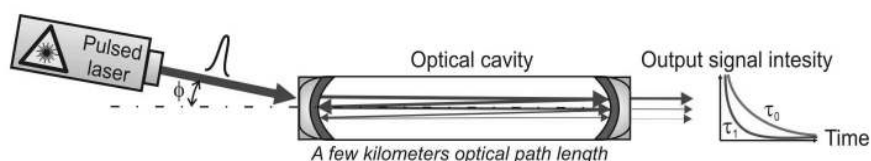


Figure 1: CEAS idea.

(τ_0) in the optical cavity not containing the absorber (tested gas) is performed. In the same way the signal decay time τ_1 in the cavity filled with the tested gas is also determined. Knowing the absorption cross section (σ) of the examined gas, its concentration can be calculated from the formula

$$C = \frac{1}{Nc\sigma} \left(\frac{1}{\tau_1} - \frac{1}{\tau_0} \right), \quad (1)$$

where N denotes the *Loschmidt's number*, c — the light speed, and

$$\tau_0 = \frac{L}{c(1-R)}. \quad (2)$$

2. SENSITIVITY ANALYSIS

The lowest concentration (concentration limit) of analyzed gas molecules (C_L), which causes a measurable change of the output signal, can be determined from the formula

$$C_L = \frac{1}{c\sigma\tau_0} \delta\tau = \frac{1-R}{\sigma \cdot L} \delta\tau, \quad (3)$$

where $\delta\tau$ is the relative measurement precision of the decay time (uncertainty). The relationship between uncertainty $\delta\tau$ and τ_0 can be described as

$$\delta\tau = \frac{\tau_0 - \tau_L}{\tau_0} \cdot 100\%, \quad (4)$$

where τ_L denotes a decay time for the minimal absorber concentration.

In the other hand, C_L can be treated as the detection limit of the sensor. It is a function of two variables: the decay time for the empty cavity (τ_0) and measurement uncertainty ($\delta\tau$). Furthermore, the decay time τ_0 , according to the formula (2), depends on the length of the resonator and the mirrors reflectivity. The increase in this time points growth of effective path of absorption. As results, the greater the sensitivity of the sensor and the lower concentrations of the absorber can be measured.

For the development of nitric oxide and nitrous oxide sensor, there could be applied both the electronic and vibronic transitions. In the case of ultraviolet wavelength range (UV) the gases absorption cross sections reach the value of $6 \times 10^{-18} \text{ cm}^2$ for NO and value of $1.5 \times 10^{-19} \text{ cm}^2$ for N_2O [8, 9]. In comparison with infrared spectrum (IR), these values of about 10^{-18} cm^2 can be observed [1]. However, reflectivity of available UV mirrors does not exceed the value of 90%. Thus, higher sensitivity of the sensor can be obtained using IR absorption lines (Figure 2). Moreover, in the UV range, there are interferences of both investigated gases and oxygen (O_2), normally occurred in the atmosphere.

3. EXPERIMENT

The analysis shown, that application of CEAS method in the IR wavelength range provides possibility to develop NO and N_2O sensor, the sensitivity of which could reach the level of ppb. An

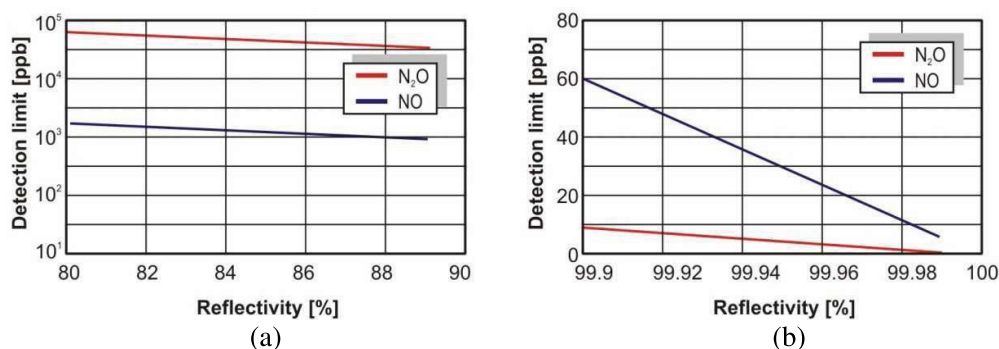


Figure 2: Detectable concentration limit vs. cavity mirrors reflectivity in the wavelength ranges of (a) UV, and of (b) IR.

experimental setup consists of two pulsed lasers with the control electronics, optical system and signal processing system (Figure 3). Two optical cavities were used, for detection of NO and N₂O respectively. Each cavity was built with highly reflective spherical mirrors (99.98%, Los Gatos Research, Inc.) characterized by curvature radius of 1 m. The distance between the mirrors was about 60 cm.

The main task of the laser electronics is to stabilize parameters of QCL's (power, lasing wavelengths). It was guaranteed with high quality power supplies (E3634A, Agilent) and thermoelectric cooling system with control unit TCU151 (Alpes Lasers SA). Laser wavelengths were precisely tuned to the selected absorption lines of NO and NO₂. Figure 4 shows selected tuning ranges of lasers spectrum.

The spectrum tuning was ensured with using temperature and power supply control. The pulsed modulations of the lasers were done using DG645 generator (Stanford Research Systems, Inc.) connected to laser drivers (LDD400, Alpes Lasers). For registrations of the optical signals from the cavity detection modules with HgCdTe (MCT) photodetectors were applied (VIGO System S.A.). Their spectral responsivity related to the selected nitrous and nitric oxides absorption lines are presented in Figure 4. The MCT modules use monolithic optical immersion technology and thermoelectric cooling. These photodetectors offer a high detectivity (about 10^{11} cm $\sqrt{\text{Hz/W}}$) and wide bandwidth (up to 1 GHz). The modules include special transimpedance preamplifiers that match output parameters of the photodetector to measuring circuits [10]. Signals from the detection modules were observed and analyzed using real-time oscilloscope DSA 70404 series (Tektronix, Inc.). Its software provided possibility to implement procedure of gas concentrations determination.

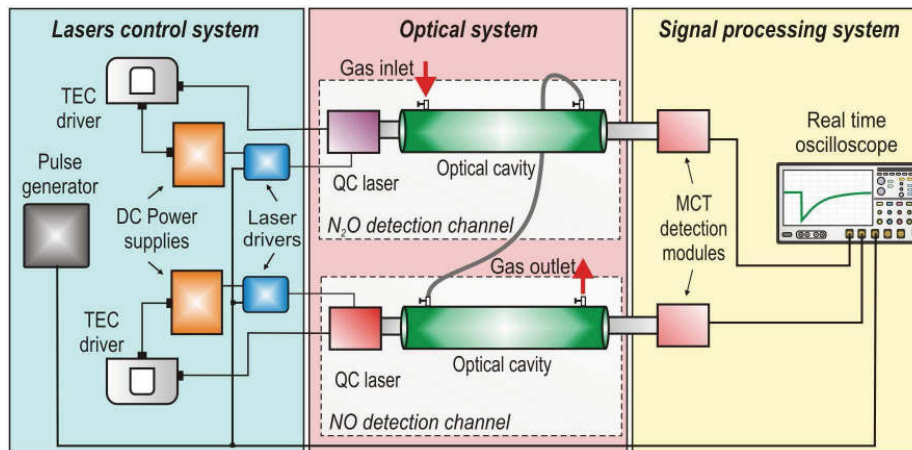


Figure 3: Simplified scheme of the experimental setup.

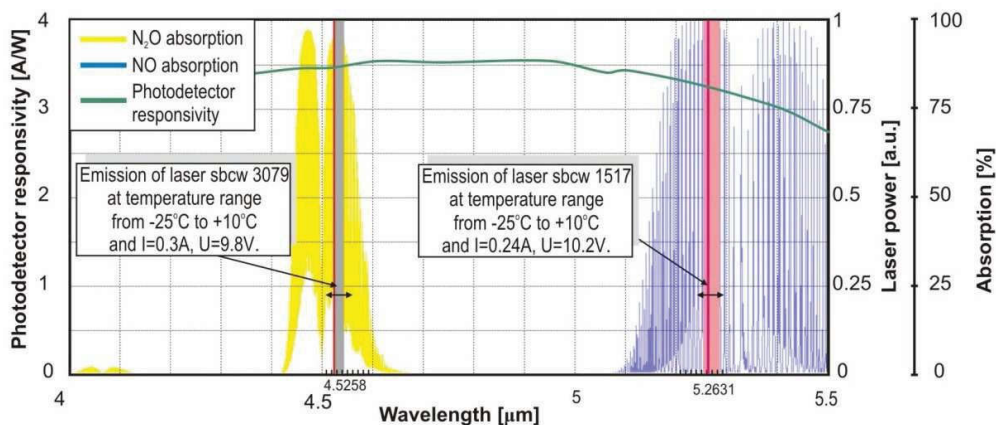


Figure 4: Characteristics of the selected QCL lasers spectra, NO and N₂O absorption lines, and photodetectors responsivity.

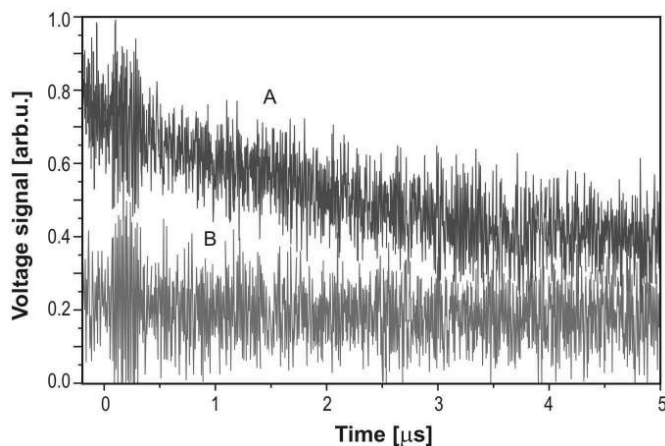


Figure 5: Example of output signals for the cavity filled with pure N_2 (A), and with N_2O (10 ppm) (B).

4. RESULTS AND DISCUSSION

During the measurements pure nitrogen (N_2) and different mixtures of $NO-N_2$ or N_2O-N_2 were used. The gases were let in optical cavities. Next decay times and specified gas concentration were measured at the output appropriate channel (NO or N_2O). Experiments showed that in the case of the cavity filled with nitrogen, so called reference gas, the determined decay time τ_0 was about of $2.2 \mu s$ for the NO channel and $1.6 \mu s$ for the N_2O channel. When the cavities were filled with NO and N_2O mixtures essential decrease in output signals levels was observed (Figure 5).

It should be pointed out that these compounds have no influence on measurement results in the second channel. Moreover, to improve precision of measurements, averaging procedure was applied. Thanks to this a lower uncertainty of decay time determination was obtained (uncertainty value of 0.1%).

Assuming optimal matching wavelengths of lasers radiations to respective nitric oxide and nitrous oxide absorption lines, high cross section factors can be reached: $0.7 \times 10^{-18} \text{ cm}^2$ for NO and $3.9 \times 10^{-18} \text{ cm}^2$ for N_2O . Using the formula (3) it can be noticed that the developed system provides the opportunity to detect N_2O at the level of 225 ppt, while sensitivity of NO channel is about 8 ppb.

5. CONCLUSIONS

The paper presents research of nitric oxide and nitrous oxide detection system based on cavity enhanced absorption spectroscopy. The best sensitivity was obtained at the wavelengths of $5.26 \mu m$ and of $4.53 \mu m$ respectively.

The constructed detection system is able to measure both NO and N_2O concentration at ppb level. Its sensitivity is comparable (or even better) with sensitivities of instruments basing on other methods, e.g., gas chromatography or mass spectrometry. The developed sensor can be applied to control the atmosphere quality. Using the sensor, detection of vapours from some explosive materials is also possible. Some successful research with nitro-glycerine, nitrocellulose, and TNT has been already performed.

ACKNOWLEDGMENT

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