Appling CEAS method to investigation of NO and N2O absorption lines in infrared spectra

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1. Introduction

Nitric oxide (NO) and Nitrous Oxide (N_2O) are compounds that play a significant role in many different fields. They are an important greenhouse gases and they are also characteristic compound which is emitted by most explosive materials. In the air the nitrogen oxides occur mainly as a mixture of stable NO_2, N_2O and NO molecules. Their reactions with H_2O lead to acid rains. Atmospheric photochemistry induces a complicated conversion mechanism of between nitrogen oxides.

NO and N_2O are also the main products of thermal decomposition of vapors of specific explosives. Most explosives are nitro compounds (i.e. containing a nitro group NO_2), which emit (chemically or biochemically) trace amounts of nitrogen oxides (including NO and N_2O).

There are many methods using for NO and N_2O detection. For example, in the case of gas chromatography (GC) and mass spectrometry (MS), detection limit of a few dozen of ppb is reported [1, 2]. These gases can be also detected using photoacoustic methods with Helmholtz resonator. Such sensors provide sensitivity of about 20ppb [3]. In the gas detection applications, special role is played by optoelectronic methods. One of the most sensitive is Cavity Enhanced Absorption Spectroscopy (CEAS). This is modification of CRDS (Cavity Ring-Down Spectroscopy) technique. In CEAS method pulse of optical radiation is injected into an optical cavity under a very small angle related to its axis [4]. The wavelength of laser radiation is tuned to specified absorption line of investigated gas. The cavity is built of two spherical mirrors with very high reflectivity. Light pulse introduced into the cavity through one of the mirrors yields multiple reflections. Thanks to this optical path up to several kilometres can be obtained. Due to the fact that the reflectivity of the mirrors is less than 100%, some part of the optical radiation leaves the cavity after each reflection. The outgoing radiation is registered with a photodetector. Amplitude of signal from the photodetector exponentially decreases. In the case of lack of the absorption, the decay time τ_0 is determined by the mirrors reflectivity, diffraction losses and length of the cavity. When the absorber is present in the cavity the value of the decay time τ depends on absorption and scattering phenomena.

2. Sensor sensitivity analysis

The dependence of laser radiation intensity on both the tested gas absorption coefficient (α), and some optical cavity parameters can be described using Lambert-Beer-Burger law

$$I(t) = I_0 \cdot e^{-\frac{[(1-R)+\alpha L]c}{L} \cdot t}, \qquad (1)$$

where I_0 denotes the initial optical radiation intensity, R is the resonator mirrors reflectivity, c is the light speed, L – optical path, t - time. The cavity losses are inversely proportional to the decay time of exponential decreasing radiation in the cavity. The maximum value of radiation intensity in the cavity is directly proportional to τ. It is shown that the time-integrated intensity of light leaked out the resonator is linearly proportional to the decay time τ. Thus by measuring the radiation decay time τ, the determination of an absorption coefficient is possible [5, 6],

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

By measurements of two decay times, in the case of lack of tested gas (τ_0), and when the cavity is filled with tested gas (τ), the absorption coefficient, α, can be determined from the formula

$$\alpha = \frac{1}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right). \tag{3}$$

For 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 $6 \cdot 10^{-18} cm^2$ for NO and value of $1.5 \cdot 10^{-19} cm^2$ for N_2O [7, 8]. In comparison with infrared spectrum (IR), these coefficients values of $10^{-18} cm^2$ can be observed [9]. However, reflectivities of available UV mirrors do not exceed value of 90%. Thus, higher sensitivity of the sensor can be obtained using IR absorption lines (Fig. 1.). Moreover, in the UV range, there are interferences of both investigated gases and oxygen (O_2), normally occurred in the atmosphere.

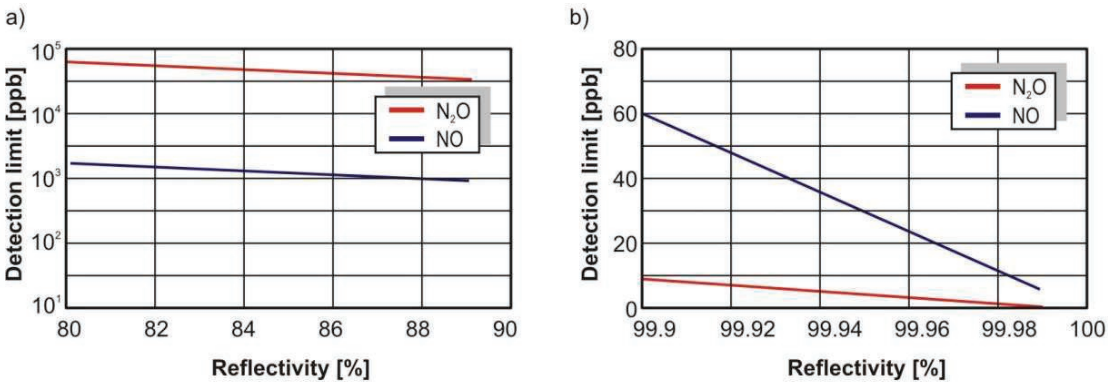

Fig. 1. Detectable concentration limit versus cavity mirrors reflectivity in UV (a), and in IR (b) wavelength ranges

3. Project of the NO and N_2O sensor

The analysis shown, that application of CEAS method in the IR wavelength range provide possibility to develop NO and N_2O sensor, the sensitivity of which could reach the ppb level. At the wavelength ranges of 5.23 μm – 5.29 μm and 4.5 μm – 4.6 μm, the values of absorption cross section is about 3.9×10^{-18} cm^2 for N_2O and 0.7 $\times 10^{-18}$ cm^2 for NO. Additionally, there is no interference of absorption lines of the other atmosphere gases (e.g. CO, O_2). There could be observed only low interference of H_2O, which can be minimized with use of special particles filter or dryer. Both NO and N_2O absorption spectrum are presented in Fig. 2 and in Fig. 3 respectively.

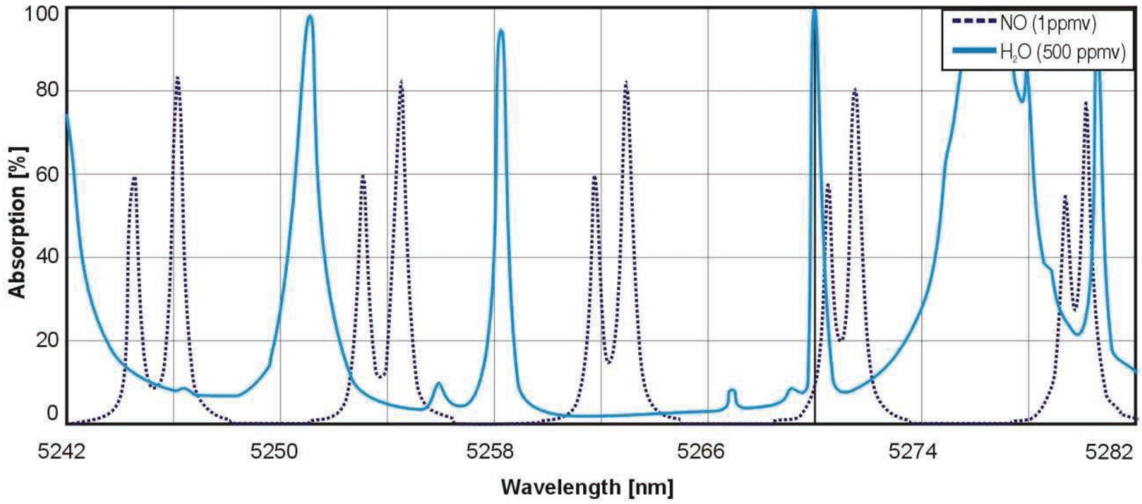

Fig. 2. NO absorption spectrum

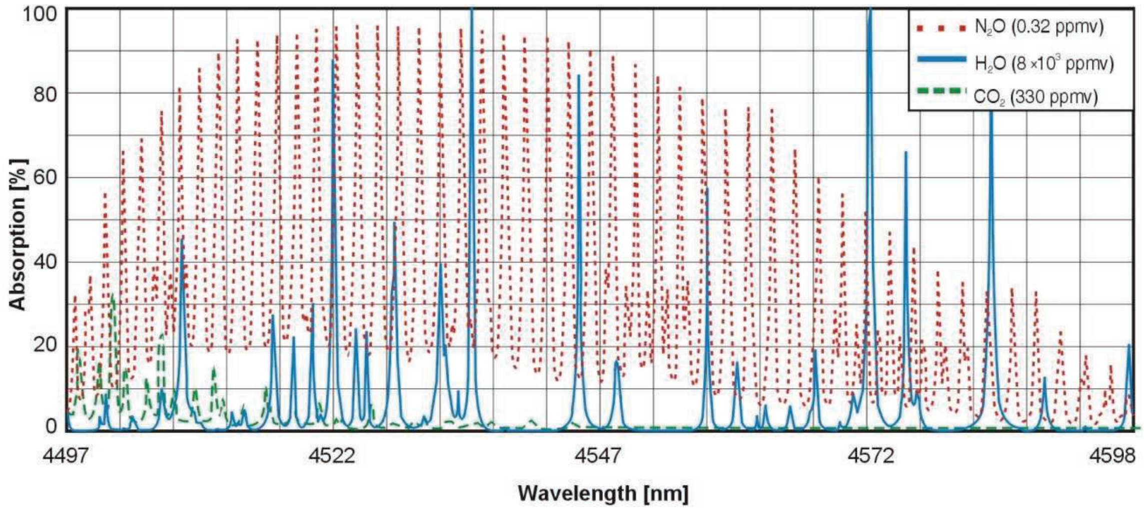

Fig. 3. N_2O absorption spectrum

The project of the NO and N_2O sensor is presented in Fig. 4. It is built of laser control system, optical system, sample module and signal processing unit. The main task of the laser control system is to stabilize parameters of applied optical radiation. In the sensor, two quantum cascade lasers (QCL) were applied. Their emission lines are very narrow and also are characterised by both high power and good spectral stability. The laser spectra could be tuned with temperature or current changes. Thus, it is necessary to precise control of their operation conditions (voltage, current, temperature). It should be noticed that the QCL laser are very sensitive to electrical surges and instabilities. That is why in the system, high quality power supply was applied (E3634A, Agilent). For pulsed mode of the lasers operations, pulse generator (DG645 type, Stanford Research Systems, Inc.) connected to laser drivers (LDD400, Alpes Lasers) was used.

The designed optical system consists of two optical channel equipped with QCL lasers and two optical cavities. To assure high sensitivity of the sensor, wavelengths of the QCL lasers radiation are matched to the selected absorption lines of the tested gases: 5.2629µm (for NO) and 4.5258µm (for N_2O). In each channel, the laser beam are directly injected into optical cavity under a very small angle in respect to its axis. In the cavities two pairs of high-reflective mirrors (Los Gatos Research, Inc.) were applied. Their reflectivities reach the value of about 99.98% at the wavelengths of interest. The distance between them was about 60 cm.

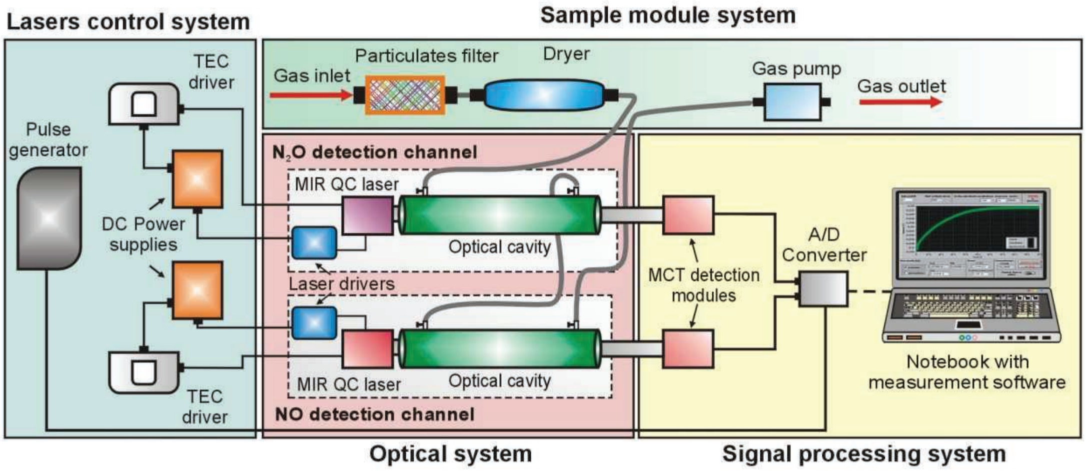

Fig. 4. Block diagram of NO and N_2O sensor

Signal from the cavities were registered with two optimized detection modules - PVI-2TE (VIGO System S.A.). The main elements of the modules are HgCdTe (MCT) photodetectors and low-noise transimpedance preamplifiers [10, 11]. For temperature control of the photodetectors, two-stages thermoelectric coolers were applied. Next, signal from the preamplifiers were digitized using A/D converter. The measurements data were transferred via USB interface to the portable computer equipped with special sensor software. The software automatically provides determination of gas concentrations.

In Fig. 5, there is shown both selected ranges of QCL lasers spectrum tuning for two lasers (sbcw3079 and sbcw1517) and photodetectors responsivity related to selected nitrous and nitric oxides absorption lines.

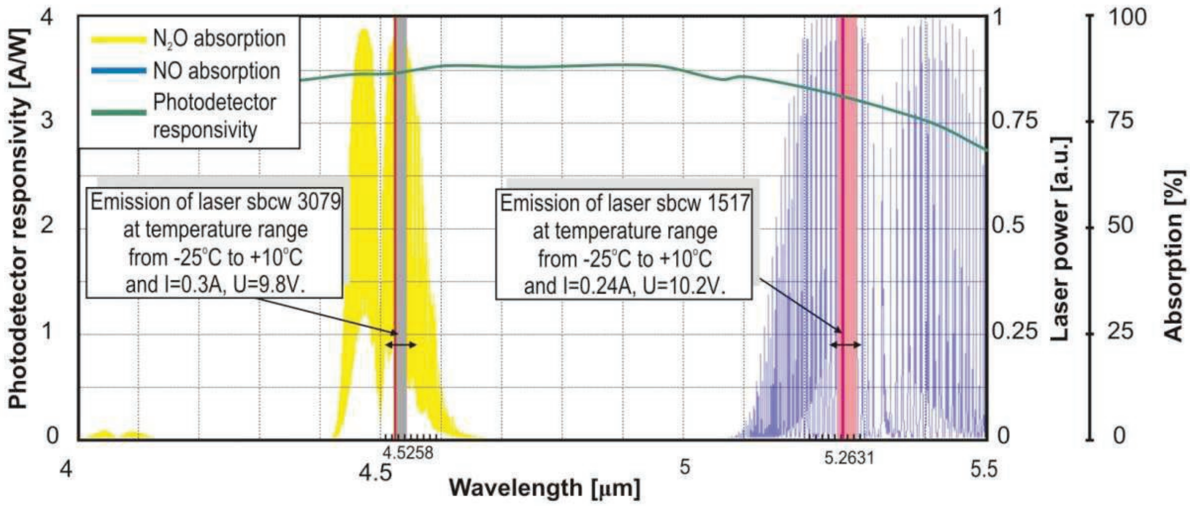

Fig. 5. Characteristics of the selected QCL lasers spectra, N_2O and NO absorption lines, and photodetector responsivity.

4. Summary

In the paper the cavity enhanced absorption spectroscopy technique applied to nitric oxide and nitrous oxide sensor was presented. The constructed detection system is able to measure NO and N_2O concentration at ppb level. Its sensitivity is comparable with sensitivities of instruments basing on other methods, e.g. gas chromatography or mass spectrometry. The developed sensor can be applied to monitoring of atmosphere quality. Using the sensor, detection of vapours from some explosive materials is also possible. Applying CEAS technique, some successful researches of explosive materials detection at the visible wavelength range were performed.

5. Acknowledgements

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6. References

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