BULLETIN OF THE POLISH ACADEMY OF SCIENCES
TECHNICAL SCIENCES, Vol. 59, No. 4, 2011
DOI: 10.2478/v10175-011-0050-x

Applying CEAS method to UV, VIS, and IR spectroscopy sensors

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Abstract. In the paper, several applications of Cavity Enhanced Absorption Spectroscopy (CEAS) for trace mater detection are described. NO_2 sensor was constructed using this technique with blue-violet lasers (395–440 nm). The sensor sensitivity reaches the level of single ppb and it was applied in security portal. For detection of two gases at the same time, two-channel sensor was constructed. Used method allows a significant reduction in the cost of optoelectronic CEAS sensor designed to measure of concentrations of many gases simultaneously. Successful monitoring of N_2O and NO in the air requires high precision mid-infrared spectroscopy. The constructed sensors are able to measure concentration at ppb level. These sensors might be used for monitoring of atmospheric purity as well as for detection of explosives.

Key words: CEAS, N_2O, NO, NO_2 detection, optoelectronic sensor.

1. Introduction

Spectroscopic measurements based on light absorption belong to 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 limited to the range of 10^{-4}–10^{-5} cm^{-1}. The range is determined by detection thresholds of small light intensity changes, the instabilities in light source intensity, and the fluctuation of detector detectivity. The both instabilities and fluctuations provide noises and interferences of absorption signal [1]. To improve the sensitivity, a longer absorption path length should be used. For this reason, a multipass spectroscopy is applied (in White or Herriott cells). Also the absorption spectroscopy with a modulation technique could be used. O'Keefe and Deacon proposed a novel measuring technique called cavity ring-down spectroscopy [2]. It provides 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 optical cavity (resonator) consisting of two spherical and high-reflective mirrors. Radiation is multiply 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, which is often referred to as the decay time or ring-down time. The decay of light intensity $I(t)$ can be described as

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

where I_0 denotes the initial optical radiation intensity, and t denotes time.

When intrinsic cavity losses can be disregarded, the decay time constant depends on mirror reflectivity R, resonator length L, and extinction factor α (absorption and scattering of light in cavity) [3, 4]

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

where c denotes speed of light in the medium.

In this way determination of the absorption coefficient is possible by the measuring of decay time. Firstly, it is measured for the case without absorption ($\alpha = 0$), when the decay time τ_0 depends only on mirrors reflectivity and the cavity length. Secondly, decay time is measured in the case of cavity filled with the analyzed gas. By comparison of these two situations, the absorber concentration C can be determined by

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

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 provides measurable change of the output signal. The concentration limit of absorbing molecules can be described with the formula

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

where δ_τ is the relative precision of 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 measured decay time of the optical cavity for minimal absorber concentration.

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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. The instabilities can degrade cavity Q-factor and provide fluctuations of the output signal [5]. Such disadvantage was minimized in CEAS method – cavity enhanced absorption spectroscopy [6].

CEAS is based on off-axis arrangement of the cavity. The radiation beam is injected under a very small angle in respect to the cavity axis. As usually the beam is repeatedly reflected by the mirrors, however, the reflection points are spatially separated. As the result a dense structure of weak modes is obtained or the modes do not occur due to overlapping. The system is much less sensitive for mechanical instabilities. CEAS sensors attain the detection limit of about 10^{-9} cm^{-1} [7, 8]. Another advantage is that due to off-axis illumination of the front mirror the interference of the light source by the optical feedback from the cavity is eliminated.

At the Institute of Optoelectronics MUT, three models of CEAS sensors for detection of N_2O, NO, and NO_2 were constructed.

2. NO, N_2O, and NO_2 optoelectronic sensor

In optical spectroscopy sensors, determination of tested gas concentrations basis on measurements of the optical radiation changes, which are caused by light absorption phenomenon. Therefore, both characteristic absorption spectrum of the investigated gas and proper selection of probing radiation source are very important. In the case of NO_2, the maximum of the absorption spectrum is in the wavelength range of $400 \div 450$ nm (Fig. 1a). The absorption cross section (σ) at the range exhibits several minima and maxima varying from about $3.5 \cdot 10^{-19}$ till $6 \cdot 10^{-19}$ cm^2 [9]. Moreover, there are no absorption interferences from other gases or vapors normally existing in the air. Thus, it could be assumed that the intensity changes of registered radiation are caused by changes of nitrogen dioxide concentration. The assumption does not take into consideration an influence of scattering by some aerosols and smokes existing in the air. However, the scattering effect can be minimized using special filters. The developed sensor consists of pulsed laser diode, diffraction grating and mirror, optical cavity, photomultiplier tube (PMT), analogue to digital converter, and computer with special software (Fig. 1b).

In the sensor, there is used 500 mW pulsed diode laser (TopGaN) operating at the wavelength of 416 nm. The laser generates radiation pulses with FWHM duration time of about 50 ns and with repetition rate of about 1 kHz. Due to pulsed emission and broadband spectrum of the laser, there is no problem of coupling with the cavity modes. The laser radiation is directed to the cavity using the diffraction grating and the mirror. The use of the diffraction grating and diaphragm eliminates the broadband fluorescence of the diode, which can affect the output signal. The optical cavity is built of two mirrors, the reflectivities of which reach value of 0.99995 at the wavelength of interest. The distance between the mirrors is 60 cm. The output signal is registered with a photomultiplier tube (R7518, Hamamatsu). Next, the signal is digitized with fast 14-bit analogue-to-digital converter (CS328, Cleverscope). The measurement data are transmitted to the computer through USB interface. There has been developed special software, which provides control of the measuring process and processing measuring data. The control of the measuring process embraces inspecting the data transmission, the arrangement of analogue-to-digital conversion parameters, archiving measuring data, and display measurement results. Investigations of the developed NO_2 sensor showed that its sensitivity reaches the level of 1 ppb and measurement uncertainty of 10%.

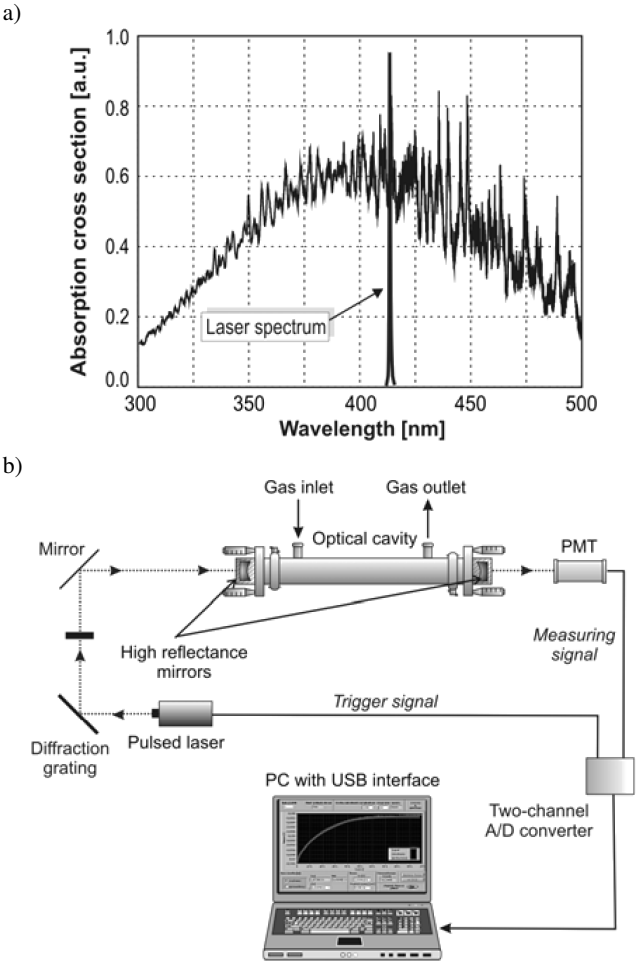

Fig. 1. Absorption cross-section of nitrogen dioxide and matched laser spectrum (a), scheme of nitrogen dioxide sensor (b)

Figure 2 shows experimental CEAS setup with two optical channels, single optical cavity and photoreceiver. The setup makes it possible to detect a trace concentration of two gases with different absorption spectra at the same time. Another possibility is applying one of the channels to optical elements alignment controlling. Therefore, to register optical signal from two channels special photoreceiver was developed. There was applied special registration technique, well-known as time division multiplexing. Each of the lasers is assigned

to the suitable measurement channel – the strictly determined temporary window. In this window, the signal from the optical cavity is registered. In the cavity without absorber the decay time τ_0 is related to the light speed, the optical cavity length, and the mirrors reflectivity.

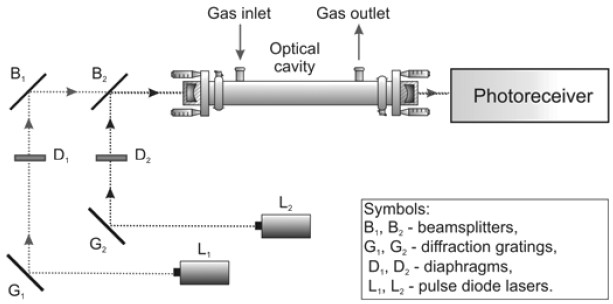

Fig. 2. Scheme of two-spectral CEAS sensor

In the case of the cavity filled with the absorber the decay time τ has additionally dependent on absorption index. The following dependence $\tau_0 > \tau$ is observe. Thereby, the decay time τ_0 is a main parameter determined duration of the measuring window (Fig. 3).

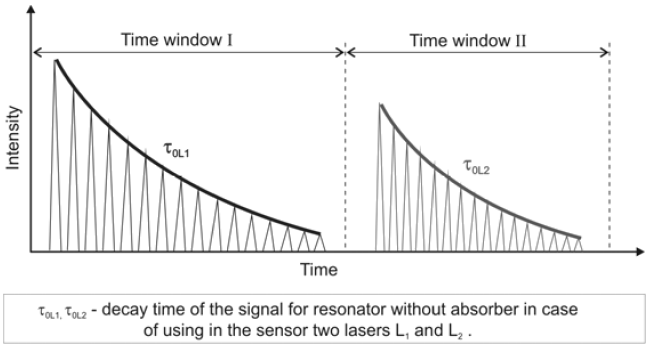

Fig. 3. Example of the cavity output signals

As a radiation sources two laser diodes were applied. The lasers are designed to cw mode operating at the room temperatures. In the first channel, 635 nm wavelength AlGaInP laser diode was used (type DL-5038-031, Sanyo). The second channel is equipped with violet (410 nm) laser diode (type GH04125A2A, Sharp). Next, the laser beams were formed with diffraction gratings and diaphragms. Next they were directed with beam splitters (CVI Melles Griot) into the optical cavity. The optical cavity was built of two spherical mirrors with reflectivity of about 0.999 at the wavelength of interest. The distance between the mirrors was 50 cm. Idea of both detection procedure and signal processing algorithm are similar to previously described NO_2 sensor. The signal-to-noise ratio (*SNR*) was improved by the use of coherent averaging

$$SNR_{AD} = SNR \cdot \sqrt{N_p}, \tag{6}$$

where SNR_{AD} – signal-to-noise ratio on the output A/D converter, N_p – number of the averaging samples.

Thus, the signal-to-noise ratio is directly proportional to a root of the number of the averaging samples. Thanks to averaging the signal of over 2048 pulses, the precision of the decay time determination at the value of 2% was obtained. In the case of NO_2 concentration measurements, 100 ppb sensitivity was achieved.

The CEAS detection system has been also used in the IR wavelength range. The system provides possibility to NO and N_2O detection. At the wavelength ranges of 5.23–5.29 μm and 4.5–4.6 μm, the values of absorption cross section are about 3.9×10^{-18} cm^2 for N_2O and value of 0.7×10^{-18} cm^2 for NO. Additionally, there are no interferences 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.

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.

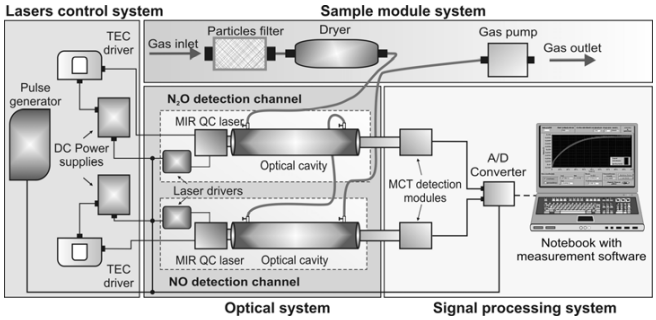

Fig. 4. Block diagram of NO and N_2O sensor

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: 5.2629 μm (for NO) and 4.5258 μm (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.

Signals 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

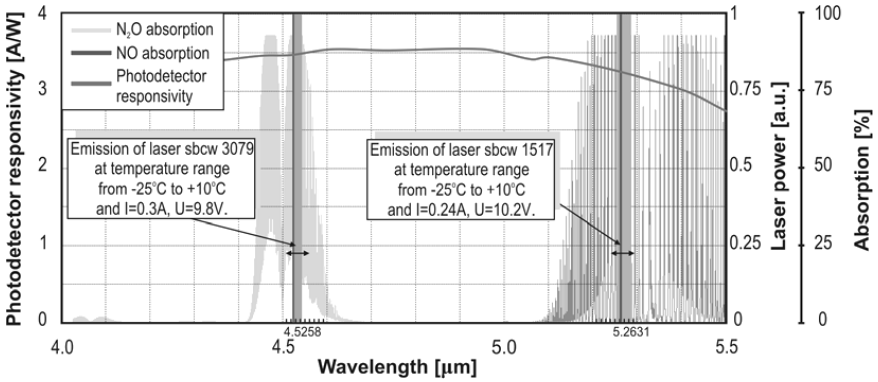

Fig. 5. Characteristics of the selected QCL lasers spectra, N_2O and NO absorption lines, and photodetector responsivity

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 are shown both selected ranges of QCL lasers spectrum tuning for two lasers (sbcw3079 and sbcw1517) and photodetectors responsivity related to the selected nitrous and nitric oxides absorption lines. The constructed detection system is able to measure of NO and N_2O concentration at ppb level.

3. Summary

In the paper, different applications of cavity enhanced absorption spectroscopy were described. Generally, they consist of pulsed laser, beam directing and shaping system (mirrors, diaphragms, and diffraction grating), optical cavity and photoreceiver with signal processing system (e.g. digital oscilloscope in the simplest case). Developed systems are designed to in-situ gas concentrations measurements. Thus, there have been taken into account the appropriate matching cavity parameters and the laser emission wavelength to the test gas absorption spectrum.

For example, in the case of NO_2 optoelectronic sensors sensitivity of 1 ppb is achieved. They provide concentrations measurements with resolution of 0.2 ppb and with uncertainty of 10%. A similar sensor was used in the security portal. The portal enables to detect gas contamination in air flows over a body of the inspected person.

The developed two-channel sensor is able to detect trace concentration of two gases at the same time. For the detection of one gas, an increase in sensor sensitivity can be achieved, because one gas can be investigated at the two different wavelengths of its absorption spectra. In addition, the second channel can be applied to control the sensor optical system alignment.

The constructed sensors for detection of NO and N_2O gases are able to measure concentration at the level of ppb. Its sensitivities are comparable with sensitivities of instruments basing on other methods, e.g. gas chromatography or mass spectrometry.

The presented sensors can be used in environment monitoring, luggage monitoring in ports, at airports, entry points, as well as in strategic objects and rooms also in undertakings connected with the counteraction to terrorist attacks.

Acknowledgements. The presented works were supported by the Polish Ministry of Science and Higher Education in 2009–2011 (No. OR00002807, O N515 115836, and OR00011109).

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