Application of Cavity Enhanced Absorption Spectroscopy in Detection of Selected Gas Pollutants

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***Abstract*— The paper presents applications of cavity enhanced absorption spectroscopy in detection of nitrogen dioxide (NO_2), nitrous oxide (N_2O), nitric oxide (NO) and carbon monoxide (CO). In the constructed portable sensor of nitrogen dioxide, blue-violet laser was used. The sensor sensitivity reaches a level of single ppb. Additionally, successful monitoring of N_2O, NO and CO was demonstrated in the laboratory air. These sensors required high precision mid-infrared spectroscopy. All of the developed sensors are able to measure concentration at the ppb level using quantum cascade lasers. It makes it possible to apply these instruments in monitoring the atmosphere quality.**

Keywords-laser absorption spectroscopy; cavity enhanced spectroscopy; CEAS; gas sensors; QCL.

I. INTRODUCTION

Detection of various gases and measurement of their concentration are very important for monitoring of industrial processes and investigation of their environmental impact. Within the last decades, many methods were developed for stand-off and in-situ detection of volatile substances. They are dominated by mass spectrometry, gas chromatography, chemiluminescence, semiconductor gas sensors or electrochemical devices. Their main inconveniences are size and cost of the apparatus, complicated maintenance, drifts and cross-response issues, e.g., high-sensitive to humidity, poor detection limit and limited lifetimes.

Optoelectronic sensors employing cavity enhanced absorption spectroscopy (CEAS) are very useful in the effort to minimize the level of the environment contamination [1]. These sensors use the phenomenon of optical radiation absorption to detect and measure the concentrations of the molecules, provide achieving low detection limits and high selectivity. For this purpose, it is necessary to apply radiation, the wavelength of which is matched to the spectral range characterized by strong absorption of the tested molecules. Such sensors are more sensitive and selective than many other detection techniques [2]. The rest of this paper is organized as follows. Section II describes CEAS in atmosphere monitoring. Section III describes experiments results. The acknowledgement and conclusions close the article.

II. CAVITY ENHANCED ABSORPTION SPECTROSCOPY IN ATMOSPHERE MONITORING

In practice, nitrogen oxides together with sulfur dioxide are the main gas air pollution. They cause strong acidification of precipitation, the formation of photochemical smog and highly toxic secondary pollutants (ozone, aromatic hydrocarbons). They also rapidly accelerate corrosion of stone buildings and metal structures, threaten human health, irritate the respiratory system and general weaken the body's resistance to infectious diseases. That is why, the preliminary research was focused on the development of nitrogen oxides sensors providing the detection limit as low as possible. Detection limits at the ppb-level and short measurements time (< 3 s) were demonstrated.

CEAS was proposed by R. Engeln in 1998. The principle of its operation is very similar to cavity ring down spectroscopy one (CRDS). In both setups there is applied an optical cavity with a high quality factor that is made up of two concave mirrors with very high reflectivity *R*. This results in a long optical path, even up to several kilometers [5]. The idea of the CRDS method is shown in Figure 1.

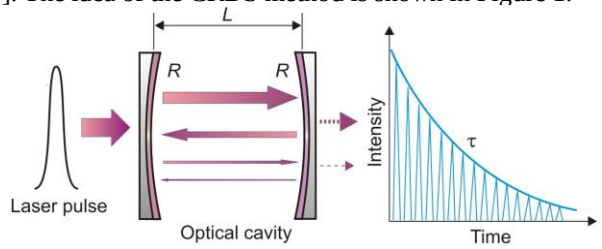

Figure 1. Cavity ring down spectroscopy idea

A pulse of optical radiation is injected into the cavity through one of the mirrors. Then inside the cavity multiple reflections is observed. After each reflection, part of the radiation exiting from the cavity is registered with a photodetector. The output signal from the photodetector determines the intensity of radiation propagated inside the optical cavity. If the laser wavelength is matched to the absorption spectra of gas filling the cavity, the cavity quality decreases. Thus, parameters of the photodetector signal are changed. Thanks to this, the absorption coefficient and concentration of gas can be determined. These calculations will be discussed in a subsequent section.

The main difference relates to the laser beam and the optical cavity alignment. In this technique the light is injected at a very small angle in respect to the cavity axis (Figure 2). As a result, dense structure of weak radiation modes is obtained or modes do not occur due to overlapping. Sometimes, a piezoelectric-driven mount that modulates the cavity length (position of the output mirror) is used in order

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to prevent the establishment of a constant mode structure within the cavity [3].

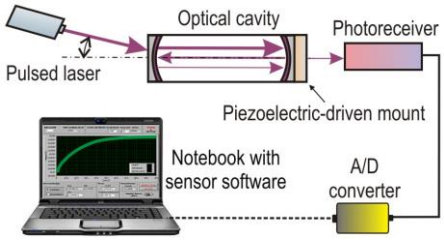

Figure 2. The scheme of CEAS setup

The weak mode structure 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. CEAS sensors attain the detection limit of about 10^{-9} cm^{-1} [4]. Therefore, this method creates the best opportunity to develop a portable optoelectronic sensor of nitrogen oxides.

III. EXPERIMENTS

In the applied methods, determination of the gas concentration is performing by measuring the decay time of the photodetector signal [2][3]. If the laser pulse duration is negligibly short and only the main transverse mode of the cavity is excited, then exponential decay of radiation intensity can be observed. The decay time of signal in the cavity (τ) depends on the reflectivity of mirrors, diffraction losses and the extinction coefficient α:

$$\tau = \frac{L}{c(1-R+\alpha L)}. \quad (1)$$

where L is the length of the resonator, c - speed of light. Determination of the examined gas concentration is a two-step process. First, measurement of the decay time (τ_0) of radiation in the optical cavity without tested gas is performed. During next step, the same measurements is made (decay time τ) for the cavity filled with the gas. Knowing the absorption cross section (σ) of the examined gas, its concentration can be calculated from the formula

$$C = \frac{1}{c\sigma}\left(\frac{1}{\tau}-\frac{1}{\tau_0}\right), \text{ where } \tau_0 = \frac{L}{c(1-R)}. \quad (2)$$

In our experimental setups, we applied visible and mid-IR semiconductor lasers. The first one was constructed using a blue-violet semiconductor laser (414 nm) developed at the Institute of High Pressure of the Polish Academy of Sciences. It was applied in outdoor tests consisting in determination its applicability for measuring NO_2 concentrations in the atmosphere. During the test, the developed sensor demonstrated a low detection limit (1 ppb) and a short measurement time (~ 3 s).

The mid-IR lasers were applied to investigate gases, the absorptions lines of which are located in the infrared region of spectrum [5]. There were applied quantum cascade lasers (4.53 μm and 5.27 μm) from Alpes Lasers SA, Switzerland and the prototype quantum cascade laser (4.78 μm) from the Institute of Electron Technology, Poland. The achieved results using the constructed CEAS systems in some gas pollutants detection are summarized in Table 1. The developed setups were enabling laboratory research a few gases: nitric oxide, nitric dioxide and carbon monoxide.

TABLE I. THE TEST RESULTS OF OUR SENSORS

Type of sensor	*Operation Wavelength*	*Detection Limit*	*Measurement Uncertainty*	*Comments*
NO_2	414 nm	1 ppb	5%	Outdoor tests
N_2O	4.53 μm	45 ppb	13%	Laboratory tests
NO	5.27 μm	70 ppb	12%	Laboratory tests
CO	4.78 μm	Approx. 150 ppb	-	Under laboratory tests

IV. CONCLUSIONS

CEAS sensors are able to measure concentration of atmosphere gases at ppb level. Their sensitivity is comparable with the sensitivities of instruments based on other methods, e.g., gas chromatography or mass spectrometry. Observation of NO_2 molecules can be done at electronic transitions which are characterized by a broad absorption spectra providing a relatively large mean absorption cross section within the range of several nanometers. Therefore, using broadband multimode lasers it is possible to detect this gas. However, for other compounds (like N_2O, NO and CO) mid-IR absorption lines are also very promises.

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