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Cavity Enhanced Absorption Spectroscopy in Air Pollution Monitoring

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Abstract: The paper presents some practical aspects of cavity enhanced absorption spectroscopy application in detection of nitrogen dioxide (NO_2), nitrous oxide (N_2O), nitric oxide (NO) and carbon monoxide (CO). These gases are very important for monitoring of environment. There are shown results of lab-setups for N_2O, NO, CO detection and portable sensor of NO_2. The portable instrument operates in the UV spectral range and reaches a level of single ppb. The lab–devices use high precision mid-infrared spectroscopy and they was demonstrated during testing the laboratory air. These sensors are able to measure concentration at the ppb level using quantum cascade lasers, high quality optical cavities and modern MCT detection modules. It makes it possible to apply such sensors in monitoring the atmosphere quality. *Copyright © 2015 IFSA Publishing, S. L.*

Keywords: Laser absorption spectroscopy, Cavity enhanced spectroscopy, CEAS, Gas sensors, QCL.

1. Introduction

Detection of various gases and measurement of their concentration are very important for monitoring of industrial processes and investigation of their environmental impact. Nitrous oxide is so-called greenhouse gas emitted from agriculture, transportation, fossil fuel combustion, wastewater management, and industrial processes agriculture. This gas is naturally present in the atmosphere and has a variety of natural sources e.g. plants, animals, and microorganisms. Nitrous oxide is removed from the atmosphere by absorption of some bacteria or by ultraviolet radiation destruction or by chemical reactions. However, N_2O can stay in the atmosphere for an average of 114 years before being “natural” removed. In practice, it is observed ca. 300 times stronger impact of N_2O on warming the atmosphere in comparison with carbon dioxide [1].

Carbon monoxide and oxides of nitrogen are ones of the most important air pollutants from petrol, diesel, and alternative-fuel engines. The concentration of these pollutants is regulated by the Euro emissions standards. Modern cars are not significant problem for air quality but their large quantity. Carbon monoxide and oxides of nitrogen are generally invisible, and in comparison to CO_2 their concentrations are less dependent on fuel consumption. Carbon monoxide reduces the blood’s oxygen-carrying capacity and it can be fatal in the case of extreme levels of exposure. At lower concentrations CO may increase a health risk, particularly to those suffering from heart disease.

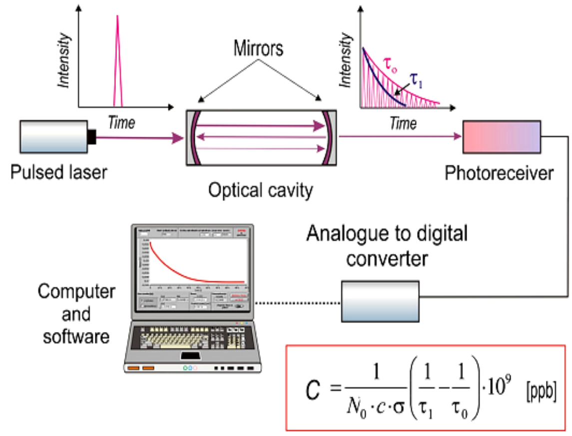
Nitrogen oxide NO reacts in the atmosphere to form nitrogen dioxide which can have adverse effects on people health with respiratory illness. The gas concentration have been linked with increased hospital admissions due to respiratory problems and the exposure time may affect lung function and increase the response to allergens in sensitive people.

Within the last decades, many methods were developed for detection of volatile substances. There is a few classifications of gas sensors. For example, they can be classified into semiconductor-type, solid electrolyte-type, electrochemical-type and catalytic combustion-type, capacitor and a simple NDIR type. A separate group of gas sensors are gas analyzers. In this group, the main roles play mass spectrometry and gas chromatography. Their main inconveniences are size, cost of the apparatus and the maintenance, complicated exploitation. But the designing process of sensitive pollution air sensors is very dynamic. It is shown, that optoelectronic sensors employing laser absorption spectroscopy are very useful in the effort to minimize the level of the environment contamination [2]. They use the phenomenon of optical radiation interaction with specific compounds to detect and to 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 precisely tuned to the spectral range characterized by strong absorption of the tested molecules. Such sensors are more sensitive and selective than many others [2].

2. Cavity Enhanced Absorption Spectroscopy in Atmosphere Monitoring

Cavity enhanced absorption spectroscopy (CEAS) was proposed by R. Engeln in 1998. The principle of its operation is very similar to cavity ring down spectroscopy (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]. A pulse of optical radiation is injected into the cavity through one of the mirrors. Then inside the cavity multiple reflections are 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.

The main difference between CEAS and CRDS relates to the laser beam and the optical cavity alignment. In CEAS the light is injected at a very small angle in respect to the cavity axis (Fig. 1). As a result, dense structure of weak radiation modes is obtained or they overlap. Sometimes, a piezoelectric-driven mount that modulates the cavity length (position of the output mirror) is used in order to prevent the establishment of a constant mode structure within the cavity [3].



N_0 - Loschmidt number, τ_1 - decay time with absorber, τ_0 - decay time without absorber, c - light speed, σ - gas absorption cross section.

Fig. 1. The scheme of CEAS setup.

The 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} [5]. Therefore, this method creates the best opportunity to develop a portable optoelectronic sensor of nitrogen oxides.

In the applied methods, determination of the gas concentration is performing by measuring the decay time of the photodetector signal [3-4]. 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 measured. The decay time of signal in the cavity (τ) depends on the reflectivity of mirrors, diffraction losses and the extinction coefficient α:

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

where *L* is the length of the resonator, *c* is the 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

$$C = \frac{1}{c\sigma}\left(\frac{1}{\tau_1} - \frac{1}{\tau_0}\right), \qquad (2)$$

where

$$\tau_0 = \frac{L}{c(1-R)} \tag{3}$$

3. Laboratory Experiments

Nitrogen oxides are very important to control in the air because they cause 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 first research was focused on the development of nitrogen oxides sensors providing the detection limit as low as possible. In our experimental setups, visible and mid-IR semiconductor lasers were applied. 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. For detection of NO, N_2O, the mid-IR lasers operating at the wavelength located in the infrared region were applied (Fig. 2) [6].

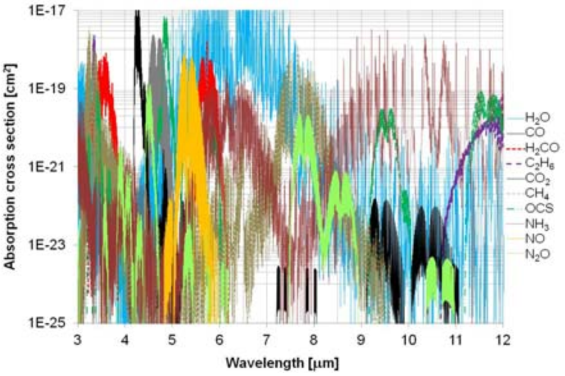
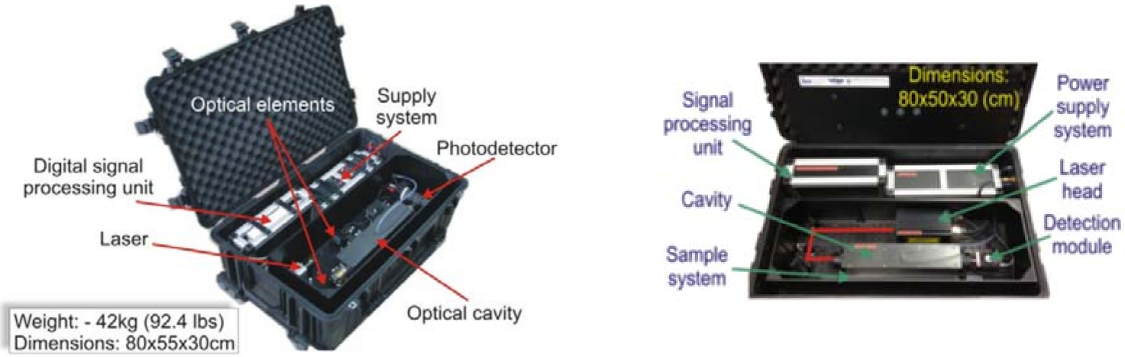


Fig. 2. The results of the calculations of the absorption cross section for selected gases.

There were applied quantum cascade lasers (4.53 µm and 5.27 µm) from Alpes Lasers SA, Switzerland.

In the case of CO, the prototype quantum cascade laser (4.78 µm) from the Institute of Electron Technology, Poland was used.

The views of the constructed NO and NO_2 sensors are presented in Fig. 3.



(a)

(b)

Fig. 3. Photos of NO_2 sensor (a) and prototype NO sensor (b).

During the sensor investigation, concentration measurements of reference gas samples were carried out. Reference samples were prepared using the 491M type gas standards generator from KIN-TEK Laboratories, Inc. (La Marque, TX, USA, Fig. 4).

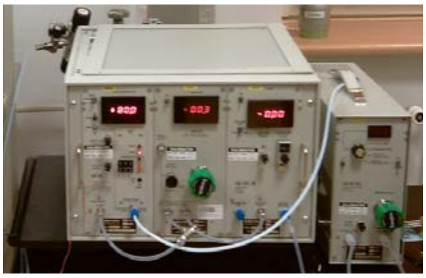


Fig. 4. Photo of 491M type gas standards generator.

The achieved results are summarized in Table 1.

Table 1. Measured detection limit of the designed sensors [7].

Type of sensor	Operation Wavelength	Detection Limit
NO_2	414 nm	1 ppb
N_2O	4.53 µm	45 ppb
NO	5.27 µm	70 ppb
CO	4.78 µm	Approx. 150 ppb

4. Outdoor Tests

The outdoor tests were performed with portable NO_2 sensor. The measurements were made in the neighborhood of the university camp for different kind of environment. The results are listed in Table 2.

Table 2. The measured NO_2 concentration for environments.

Place of measurement	Concentration [ppb]		
	Min.	**Max.**	**Mean**
Wooded area	5	30	14
In the neighborhood of garbage dumps	23	35	30
Intersection	32	55	42
Rondo with high traffic	65	87	75
Overpass the road S8	30	57	44
In the neighborhood of the shooting range	28	51	35

The lowest concentration value was obtained for forest area. This value increases with movement in the more urban area. The highest level is observed for area with large car traffic. That is why, the addition tests were performed for direct diesel car exhaust. The mean value was 980 ppb. These results shown that the NO_2 sensor can be applied in many scenarios of environment monitoring.

5. Conclusions

CEAS sensors are able to measure concentration of atmosphere gases at the ppb level. Their sensitivity is comparable with the sensitivities of other detecting instruments. But in comparison, they offer quick response, no-impact on tested air samples, online operation, high selectivity and ease of use.

It is observed, that detection of NO_2 molecules can be performed using broadband multimode lasers. It is possible because a relatively large mean absorption cross section within the range of several nanometers resulting from analyses of electronic transitions.

However, for other compounds (like N_2O, NO and CO) mid-IR absorption lines are very narrow. That is why, these sensors require to apply precisely defined lasers wavelengths. The presented results shown, that application of mid-IR QCL lasers in such sensors is very promising. Currently, several works related to the development of these sensors is still continuing.

Acknowledgements

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