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Nitrogen Oxides Optoelectronic Sensors Operating in Infrared Range of Wavelengths

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Investigation of nitric oxide and nitrous oxide optoelectronic sensors is described. The detection of both components was done by measurement of absorption that occurs due to transition between vibronic molecular transitions. The improvement of the sensitivity was achieved due to application of cavity enhanced absorption spectroscopy. Two optical cavities (each one for each gas) built of high reflectance spherical mirrors were used. While the spectra of observed transitions are situated in mid-infrared range, two single mode quantum cascade lasers were applied. Their narrow emission lines were precisely tuned to the absorption lines of both investigated gases. The measurement of different mixtures of Ar–NO and Ar–N_2O within the range from 100 ppb to 10 ppm was performed. The relative uncertainty of the results did not exceed the level of 13%.

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1. Introduction

Detection of nitrogen oxides (NO_x) is of great importance because these compounds play a significant role in many different fields. For instance, NO_x are important greenhouse gases, and their reactions with H_2O lead to acid rains [1]. However in ambient air their concentrations vary strongly due to dependence of localization of emission sources (anthropogenic, natural) and of meteorological conditions [2]. In medicine nitrous oxide (N_2O) is used as an anaesthetic, especially in dentistry and minor surgery. Its excess in air lead to mild hysteria and a laughter [3]. Thus it is also known as "laughing gas". For instance, by analyzing of nitric oxide (NO) in the human breath the asthma or chronic lung inflammation can be detected [4]. Furthermore, the compounds of nitrogen and oxygen are the characteristic products that occur during the decomposition of specific explosives [5–10]. Therefore there is a large importance to construct novel, compact and sensitive sensors of these gases.

In this paper, we present optoelectronic sensors of nitric oxide and nitrous oxide. Laser spectroscopy methods are applied for determination of properties of the gas sample by the measurement of light absorption [11–16]. Good results are achieved in mid-infrared spectral range. The corresponding spectra occur due to transitions between rotational-vibrational levels of the molecules. The set of such absorption lines becomes a fingerprint of the compounds due to specific scheme of the energy levels [17]. High absorption cross-section and a good selectivity, provide opportunity of trace detection of specific gases. Very sensitive measurement of the concentration is possible when special methods like cavity enhanced spectroscopy (CEAS) are applied [18–21].

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CEAS has been known for decades, but its successful application for trace gas detection has only been possible since few years [22–29]. The dynamic development of this method is caused by novel achievements in semiconductor lasers and photodetectors technologies. Wide and precise tunability of modern semiconductor lasers (quantum cascade lasers — QCL) operating in mid-infrared range as well as their narrowband generation, provide new opportunities in construction of optoelectronic apparatus.

2. Experimental setup

Our experimental setup is presented in Fig. 1. Both NO and N_2O sensors were integrated into common detection system. Each of the sensors consists of an optical system, laser control system, sample module and a signal processing system.

Two-channel optical system provides opportunity for simultaneous detection of both gases. Optical cavity was the main part of each channel. It was built of two mirrors of high reflectance ($R > 0.995$). One of the cavities was designed for N_2O detection, while the other one for NO measurement. It should be noticed that in CEAS technique gas absorption coefficient is determined by investigation of the respective cavity Q-factor. Thus each cavity was monitored by respective pulsed QCL and detection module (VIGO System S.A.). The lasers were tightly tuned to the absorption lines of detected compounds, i.e. to 4.530 μm for N_2O and to 5.260 μm for NO. Selection of these absorption lines enabled avoiding of interferences by other gases (H_2O or CO_2) that are present in the atmosphere [3, 11, 30]. Precise laser current drivers and temperature controllers (in laser control system) guaranteed achievement of high stability of generated wavelengths.

The main elements of the detection modules are MCT photodetectors and low-noise transimpedance preamplifiers [31]. Two-stage thermoelectric coolers were applied to temperature stabilization of the photodetectors

[32, 33]. The output signals from the detection modules were digitized using an A/D converter. While the Q-factor is proportional to the time τ of radiation decay in the cavity ($Q = \omega\tau$ where ω denotes light frequency) the data were transferred via USB interface to a portable computer where the value of radiation decay in the cavity τ was determined.

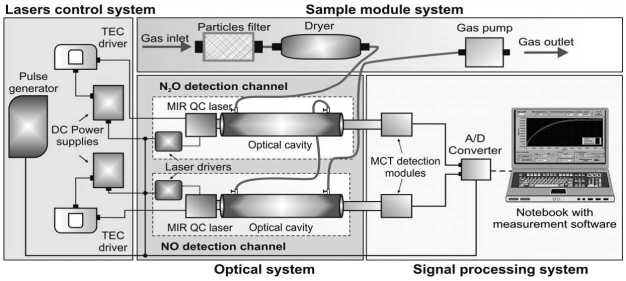

Fig. 1. Block diagram of the experimental setup.

During the investigation of the detection system, concentration measurements of reference gas samples were carried out. Gas samples were prepared using the gas standards generator 491M type from Kin-Tek. The modular construction of the generator enables production of multicomponent gas mixtures using different mixing techniques. High precision of mixing ratios of the components from a level of part per trillion (ppt) to the initial concentration of 1:1 can be achieved. The generator can also create both dry and moistened standard gas, which can be supplied to the sensor at an adjustable pressure. Beside the optoelectronic NO and N_2O sensors and the gas generator, the setup contains gas containers, and digital oscilloscope, which was used to observe the voltage signals at the output of detector modules.

Special algorithm for determination of each NO_x concentration has been implemented. The measurement was carried out during two-step process. First, the decay time τ of lasers radiation in each optical cavity without an absorber was found. It provided opportunity to determine the Q-factors for clear conditions. Then the cavities were filled with the absorbing mixture and the respective decay times τ_1 were measured. Knowing the absorption cross-section σ of the compounds, their concentration in respective cavities was calculated from the formula

$$N_x = \frac{1}{N_0 c\sigma}\left(\frac{1}{\tau_1} - \frac{1}{\tau_0}\right), \tag{1}$$

where N_0 denotes the *Loschmidt number*, while c is the light speed.

3. Results

The measurement of τ_0 was done for the cavities filled with pure argon. Next, the reference samples were prepared using gas standard generator. The gas mixtures of nitric oxide or nitrous oxide at concentrations from 100 ppb to 10 ppm in argon were used.

Figure 2a presents the results of NO concentration measurements of the reference samples. Maximum uncertainty of nitric oxide determination was not larger

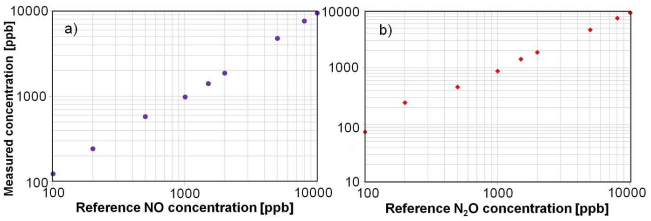

Fig. 2. Results of concentration measurements for NO reference samples (a) and for N_2O reference samples (b).

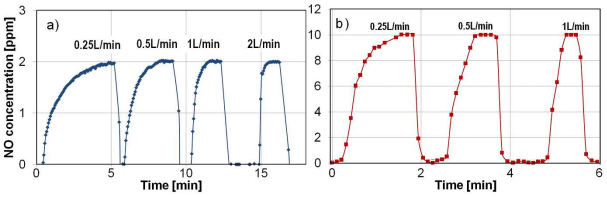

Fig. 3. Time changes of nitric oxide (a) and nitrous oxide (b) measured concentration for different flow rate of reference sample.

than 12%. The same investigation procedures were performed for nitrous oxide detection channel (Fig. 2b). The maximal uncertainty was lower than 13%.

In order to generate the gas of high concentration by Kin-Tek system, a low flow of transfer argon was necessary. Therefore, output NO mixtures were transferred to the sensor with low flow as well. The same influence of sample flow rate on time changes of measured concentration was observed. Thus the investigation of gas flow rate on registered concentration was performed. The mixtures of NO (2 ppm) and of N_2O (10 ppm) were prepared. Temporal evolution of the sensors output signal for various flow rates are shown in Fig. 3.

For NO, five minutes was necessary to reach the appropriate sensor indication (2 ppm) at flow of 0.25 l/min, while the time of 30 s was sufficient for the flow of 2 l/min (Fig. 3a). It was connected with the volume of pneumatic part of the sensor. It can be seen that the N_2O sensor indicated value of 10 ppm within about 1.5 min at 0.25 l/min while at 1 l/min this time was reduced to 25 s only (Fig. 3b). So, it can be concluded that measurement time should be appropriately matched to the flow of examined gas.

Summarizing, the obtained results have shown that correct and fast measurement requires a proper amount of gas volume, while a good filling of the sensor volume is necessary. This amount is about 0.4 l for N_2O channel and 1 l for NO one. Due to serial connection of the cavities, the investigated gas is first directed to N_2O channel and then it fills nitrous oxide sensor (Fig. 1).

4. Conclusions

In the article, the optoelectronic system for detection of nitric oxide and nitrous oxide was presented. These chemical compounds are important greenhouse gases that have a large influence on environment, living organisms, and human health. Therefore, monitoring of these gases

is of great importance to various applications: from routine air monitoring in industrial area and regions of intensive traffic, in detection of explosives at airports, finally in medicine investigation, for health care, etc.

It was shown that for detection of N_2O and NO the most sensitive laser absorption method — cavity enhanced absorption spectroscopy can be applied. Operating at the mid-infrared spectral range, interferences by absorption lines from other trace gases which are commonly present in atmosphere (like H_2O or CO_2) were minimized.

The investigation of the developed system has shown that it enables measurements of NO and N_2O gas concentration in the range from ppb to 10 ppm with the relative uncertainty smaller than 13%. For correct and fast measurements a proper ratio of gas volume to the flow rate should be guaranteed.

Our system can be applied to air quality control or to human breath analysis. Moreover, the detection of vapours of some explosive materials is also possible. Some successful research with nitroglycerine, nitrocellulose, and TNT has been already performed [6, 34].

Acknowledgments

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