An ultrasensitive NO$_x$ optoelectronic sensor

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Abstract— The paper presents opportunities of application of the Cavity Enhanced Absorption Spectroscopy (CEAS) technique in nitrogen oxides (NO$_x$) detection. The CEAS technique is a modification of Cavity Ring Down Spectroscopy (CRDS) technique. It is based on the off-axis arrangement of an optical cavity. In this system, an absorbing gas concentration is determined due to the decay time measurement of a light pulse trapped in a optical cavity. Measurements are not sensitive to laser power fluctuation and photodetector sensitivity fluctuation. The setup includes a resonance optical cavity, built with spherical mirrors of high reflectance. As light sources pulsed lasers are used. NO$_x$ detection is carried out in the visible and infrared range. The signal is registered with a specially developed low noise photoreceiver.

The features of a designed sensor show that it is possible to build an optoelectronic trace gases sensor which sensitivity could be comparable with chemical sensors. Such a system has several advantages: relatively low price, small size and weight, and possible detection of other gases and explosives.

Spectroscopic measurements based on light absorption belong to the most common methods of matter investigation. Absorption spectroscopy is a simple, non-invasive, in situ technique for obtaining information about different species. From an absorption spectrum, quantitative absolute concentrations can be retrieved. However, direct absorption spectroscopy is affected by low sensitivity.

Several experimental schemes can improve sensitivity, increasing the absorption path length (multipassing, in White or Herriott cells), and combining direct absorption spectroscopy with a modulation technique. In 1988 O'Keefe and Deacon developed a novel pulsed absorption technique: cavity ring-down spectroscopy – CRDS [1]. Within the recent two decades many various experimental schemes of this spectroscopy have been elaborated.

Recently, Engeln et al. presented a modification of the CRDS technique, called Cavity Enhanced Absorption Spectroscopy (CEAS) [2]. It is based on the off-axis arrangement of an optical cavity. In this configuration, light is repeatedly reflected by mirrors. However, reflection points are spatially separated. There are some advantages of this setup. The off-axis design eliminates

optical feedback from the cavity to the light source, which is especially important when diode lasers are applied. Then in these configurations the light is many times reflected by mirrors and fills the whole volume of the cavity. Moreover, this kind of resonator is characterized by the dense structure of weakly shaped resonances. Therefore its comparison with ordinary CDRS, integrating spectroscopy with off-axis cavity adjusting are? much less sensitive for the cavity misalignment caused, e.g., by refractive index fluctuations due to turbulences or small mechanical instabilities.

In the CEAS method, the pulse of a beam light is injected into an optical cavity (resonator) equipped with spherical and high reflectance mirrors. The pulse yields to multiple reflections in the resonator. After each reflection, part of the laser light leaves the resonator due to residual transmission of mirrors. Light outgoing from the cavity is registered with a photodetector, most frequently by a photomultiplier tube (PMT). The electric signal from the PMT is digitized and analyzed by a computer (Fig. 1).
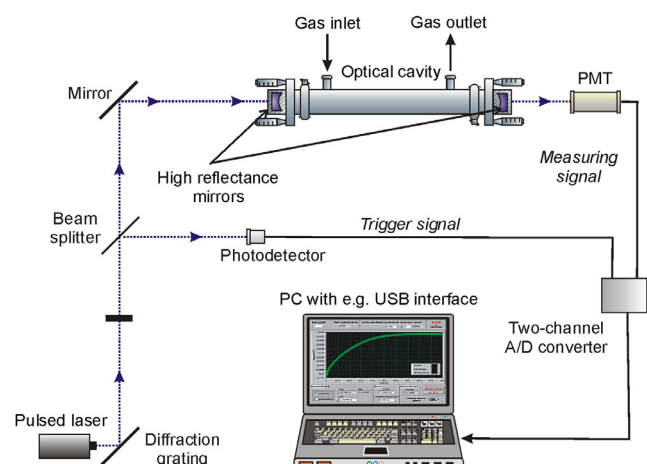

Fig. 1. Typical experimental setup.

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Light intensity inside the resonator decreases exponentially:

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

where I_0 is initial intensity, c - the light speed, α is the absorption coefficient of matter filling the resonator. The decay constant is dependent on mirrors reflectivity coefficient R, resonator length L, diffraction losses, and extinction, that is absorption and scattering of a light in an absorber filled cavity.

Engeln et al. showed that the time-integrated intensity of light leaking the resonator is linearly proportional to the cavity decay time τ. Thus by measuring the radiation decay time constant τ, the determination of an absorption coefficient is possible [3],

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

The decay time τ is measured once, when the cavity is empty ($\alpha = 0$), and next - when the cavity is filled with an absorber ($\alpha > 0$). By comparison of decay times for these two cases, the value of absorber concentration N can be found

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

where σ denotes the absorption cross section, while τ_0 and τ are the time constants corresponding to the empty resonator and the resonator filled with the absorber, respectively.

Assuming that the relative precision of τ determination is equal to

$$F = \frac{\tau_0 - \tau}{\tau_0}, \qquad (4)$$

detectable concentration limit N_L can be described by the formula

$$N_L = \frac{F}{c\sigma\tau_0} . \qquad (5)$$

In our investigation we used the experimental scheme presented in Fig. 1. The resonator consisted of two mirrors (Los Gatos) which reflectivities R reached the value better than 0.99992 at the wavelength of interest. The distance between the mirrors was 60 cm. A 200 mW pulsed diode laser (TopGaN) working at 414 nm, and dye a laser with Rhodamine B as a lasing medium were used . The diode generated pulses of radiation which FWHM duration time was about 50 ns at the repetition rate of 1 kHz. The duration time of dye laser pulses was about 6 ns while their repetition rate was 10 Hz. Laser radiation was directed to the cavity using diffraction grating and a mirror. The use of diffraction grating eliminated the broadband fluorescence of a diode, which affected the output signal. The cavity was applied to the gas mixing system (two mass flow controllers: β-ERG) supplied from a bottle with a calibrated NO_x mixture and source of pure nitrogen. Intensity leaking of the resonator through the rear mirror was measured with a photomultiplier applied to a computer with an A/C transient digitizer and USB interface. After averaging the signal over 100 000 pulses, the precision of decay time determination about F = 0.1% was achieved (Fig. 2). It corresponds with the NO_2 detection limit of few hundreds of ppt.
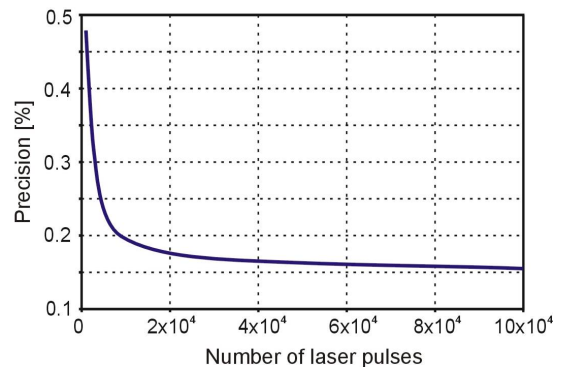

Fig. 2. Precision of decay time determination as a function of a pulses number.

In the case of nitrogen dioxide detection a pulsed blue diode laser (414 nm) was applied. This wavelength is well matched to the NO_2 absorption spectrum (Fig. 3). The value of the absorption cross section σ at this wavelength exhibits several minima and maxima, but varies around the value of 6×10^{-19} cm^2 [4].

The measurement with a good detection limit requires also good filtration of the investigated air, which is necessary to avoid light scattering in aerosol particles as well as dust deposition on the mirror surfaces. After averaging the signal of over 2048 pulses, about F = 1% precision of decay time determination was obtained, and after averaging the signal of over 10 000 laser pulses, precision about F = 0.2% [6]. Due to such optimization of an optical system and due to signal processing we achieved the detection limit better than 0.5 ppb (for σ = 6×10^{-19} cm^{-2}) [5].
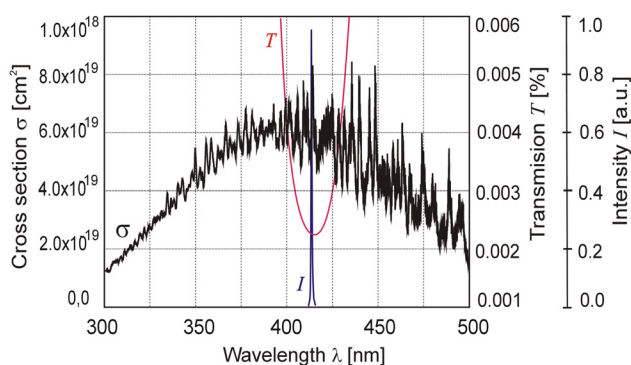

Fig. 3. Dependence NO$_2$ absorption cross section σ, mirrors transmission T, and laser intensity I on wavelength λ.

Our sensor was also used to demonstrate nitrate (NO$_3$) absorption spectrum measurements. In this case a dye laser working in the 629 nm - 676 nm range was applied. We achieved the results which are comparable with a NO$_3$ reference spectrum (Fig.4) [7].
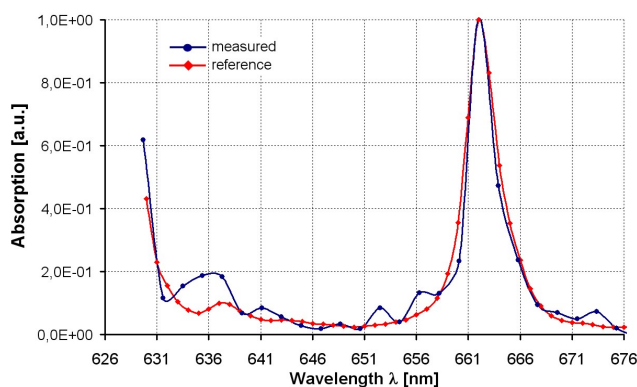

Fig. 4. Measured and reference NO$_3$ absorption spectrum.

In the next stage of our research the sensor will be applied to nitric oxide (NO) and nitrous oxide (N$_2$O)

detection. There will be used QCL lasers (e.g. Alpes lasers, #sb1770DN and #sb1840) and photoreceivers with detectors optimized for wavelength of interest (ca. 5.25 μm and 4.46 μm). The detectors working at room temperature are available from Vigo Systems (e.g. PVI-2TE-5 type). They are produced using mercury cadmium telluride (MCT) epitaxial techniques [8].

The paper presents the spectroscopic technique, CEAS, which was applied to construct an optoelectronic NO$_x$ detection system. The resonator quality was determined by measuring the time of radiation imprisonment. Therefore the result is not sensitive to fluctuation of both the laser power and photodetector sensitivity. The features of a constructed detection system show that it is possible to build an optoelectronic trace nitrogen oxide sensor, which sensitivity could be comparable with that of chemical sensors. Such a kind of system has several advantages, for example: a relatively low price, small size and weight. It might be applied to explosive materials detection and identification.

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