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Sensitive detection of NO_2 with cavity enhanced spectroscopy

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We present an experiment with nitrogen dioxide (NO_2) detection with the use of cavity enhanced spectroscopy. The pulsed blue diode laser working at 414 nm as a light source was applied. The cavity was composed of two mirrrors with the reflectivity of $R = 0.99992$. The off-axis adjustment of the resonator was used. The absorbing gas concentration was determined by the measurement of the decay time of the light pulse trapped in the cavity. The detection limit better than 1 ppb was obtained.

Keywords: absorption spectroscopy, optical cavity, gas detector.

1. Introduction

Cavity enhanced absorption spectroscopy (CEAS) was developed by ENGELN *et al*. [1] as a modification of cavity ring down spectroscopy (CRDS) [2]. Both belong to the most sensitive techniques of absorption measurement. In these methods, the laser light is trapped inside the resonator composed of two mirrors characterized by a very high reflectivity coefficient R. When an absorber is present in the cavity, the resonator quality decreases. Therefore, by measuring the resonator quality, determination of the absorption coefficient is possible.

In CRDS experimental setup (presented in Fig. 1), the pulsed laser light usualy passes through the spatial filter in order to excite the single transverse mode in the cavity. The light leaking through one of the mirrors (*i.e*., output mirror) is registered by a photodetector. Due to the transverse mode selection, the exponential decay of the radiation is observed. The resonator quality can be determined by measurement of the radiation decay time constant. The absorption coefficient α can be found

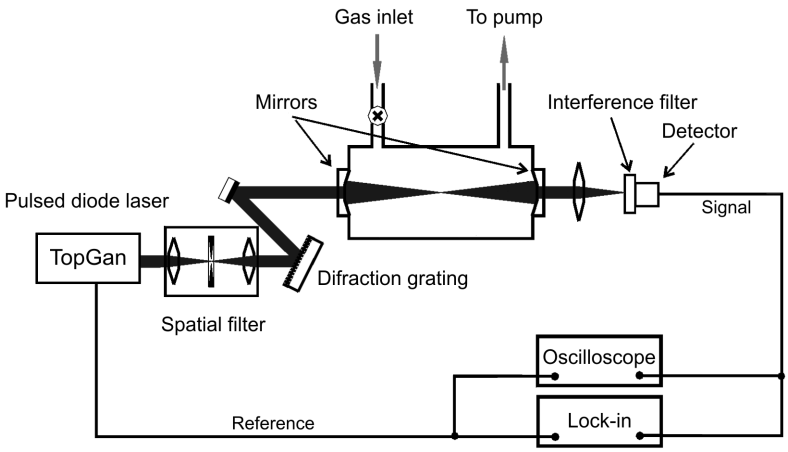

Fig. 1. Experimental setup for CRDS method.

comparing the time constants τ_0 and τ, characterizing the empty resonator and the resonator filled with the absorber, respectively [3]:

$$\alpha = N\sigma = \frac{1}{c}\left(\frac{1}{\tau} - \frac{1}{\tau_0}\right) \tag{1}$$

where N denotes the absorber concentration, c is the velocity of light, and σ is the absorption cross section. For pulsed light sources, when the high reflectivity mirrors are applied, coefficient α as low as 10^{-8} m^{-1} can be measured. In the case of the use of cw amplitude modulated laser light, due to the energy deposition in the cavity, the phase shift ϕ between the output signal and the modulation signal occurs [4]. This phase shift is related to the cavity decay time according to the formula

$$\mathrm{tg}\phi = 4\pi f\tau \tag{2}$$

where f denotes the modulation frequency. This is the alternative way of the resonator quality determination, which allows to register the absorption coefficient lower than 10^{-11} m^{-1} [4].

Thanks to their high sensitivity, the cavity enhanced methods can be applied for the construction of fully optoelectronic trace gas detectors, which could replace numerous currently used chemical sensors. Diode lasers are especially useful for these purposes. Successful implementations were already presented. Using these methods, BAER *et al.* [5] recently investigated the weak absorption of carbon monoxide, acetylene, ammonia, and methane in 1500–1660 nm spectral range. They achieved the detection limit of 36, 0.3, 2 and 1 ppb for CO, C_2H_2, NH_3 and CH_4, respectively. Also CO_2 can be observed within this spectral range [6]. CRDS with cw diode laser working at 410 nm was already used for NO_2 detection by MAZURENKA *et al.* [7]. Then,

KASYUTICH *et al.* [8] achieved the detection limit of 0.7 ppb using the CEAS arrangement.

In the practical realization, the CRDS experiments are connected with a number of serious problems, especially when a precise scanning over an absorption spectrum consisting of narrow lines is required. Efficient storing of light in the resonator occurs only when the frequency of probing laser mode is well matched to a longitudinal cavity mode. Therefore, when single mode lasers are used, a good electronic stabilization and synchronization of the cavity and the laser frequency are necessary. The system requires efficient elimination of mechanical instabilities and the refraction coefficient variations. When spectra of the absorbing species fill the cavity consisting of narrowband resonances, both the laser frequency and the cavity mode must be well matched to the absorption line. When, additionally, a precise scanning over such sharp, narrowband spectrum is required, tuning and stabilization of the system are connected with serious problems. As far as it can be realized in laboratory realization, it is hard to ensure the stable work of such system in portable optoelectronic detectors.

Cavity enhanced absorption spectroscopy (CEAS), which is based on the off-axis arrangement of the optical cavity, provides an opportunity to overcome the above mentioned difficulties. A typical experimental setup of CEAS technique is presented in Fig. 2. As a light source, pulsed or modulated, the CV laser is usually applied. After transverse mode selection in the spatial filter, the beam is directed to the cavity. The light is repeatedly reflected by the mirrors, like in the multipass cell, where the light spots on the mirror surfaces are spatially separated. Due to that, the free-spectral range of an off-axis cavity can be *n* times less than in the case of the on-axis aligned (where *n* denotes the number of the trips for which a ray returns to its entrance point and interferes with the input beam). Due to that, either the dense mode structure of low finesse occurs or the mode structure is not established at all. In order to better randomize the mode structure, the cavity length might be additionally modulated by a piezoelement. Avoiding the light interference allows to eliminate the sharp

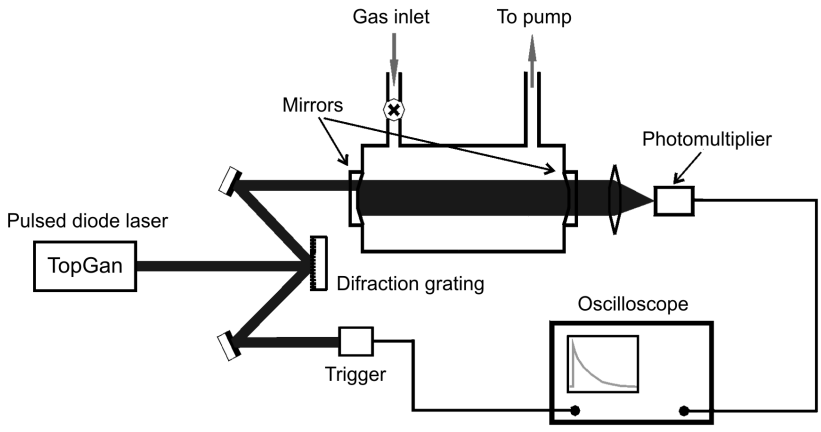

Fig. 2. Experimental setup for off-axis arrangement.

resonances of the cavity, conseqently the problems connected with their coincidence with the laser modes and the sharp absorption lines do not occur. Under these conditions, all wavelengths and phase information of the electric field can be neglected, leading to description of optical intensity only. Therefore, the determination of attenuation of the resonator by an absorber can be easily modeled by measuring the light intensity, leaving the resonator when it is empty

$$I_{\text{out}}^{E} = I_{\text{in}}(1-R)^2\left[2\ln(R)\right]^{-1} \tag{3}$$

and when it is filled with the absorber

$$I_{\text{out}}^{A} = I_{\text{in}}(1-R)^2\exp(-\alpha L)\left[2\ln\left(R\exp(-\alpha L)\right)\right]^{-1} \tag{4}$$

respectively [1].

The absorption coefficient is given by

$$\alpha = \frac{\ln(R)}{L}\frac{I_{\text{out}}^{A} - I_{\text{out}}^{E}}{I_{\text{out}}^{A}} \tag{5}$$

where L denotes the resonator length, and I_{in} – the incoming light intensity. Using the mirrors with the reflectivity $R > 99.99\%$, the absorption detection limit coefficient as low as 10^{-9} m^{-1} can be measured, similarly like for CRDS arrangement.

In comparison with ordinary CDRS, integrating spectroscopy with off-axis cavity adjusting is much less sensitive for the cavity misalignment caused by small mechanical instabilities by the refractive index fluctuations due to turbulences in the absorbing gas. Therefore, it is much more suitable for the construction of portable gas detectors. Moreover, the off-axis design eliminates optical feedback from the cavity to the light source (which is especially destructive for diode lasers stability).

2. Experiment

Our experimental setup was very similar to that presented in Fig. 2. We applied the off-axis arrangement for the detection of trace gases in the atmosphere. A blue diode laser (TopGaN) working at 414 nm was applied as a light source. This wavelength fits well to $^2A_1 \rightarrow {}^2B_1$ and $^2A_1 \rightarrow {}^2B_2$ absorption bands of NO_2 molecule. For nitrogen dioxide, the absorption cross section σ around this wavelength exhibits several minima and maxima varying from about 3.5×10^{-19} to about 6×10^{-19} cm^2 [9]. The diode laser generated the radiation pulses with duration time of about 30 ns and repetition rate about 10 kHz, while their peak power was about 0.5 W. The laser beam was directed to the cavity using the diffraction grating and the mirror. The diffraction grating splited the light beam and eliminated the broadband fluorescence of the diode,

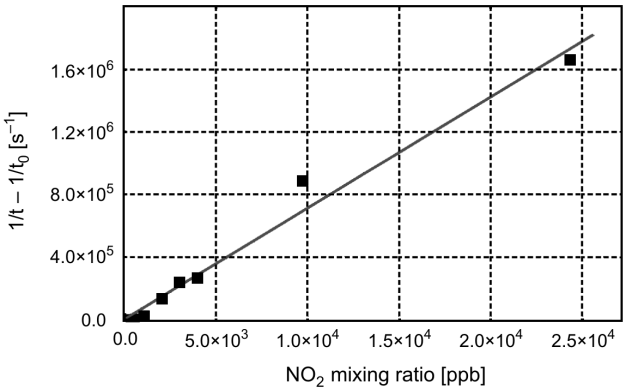

Fig. 3. Calibration of NO_2 detector.

which could affect the output signal. The cavity was constructed of two mirrors (Los Gatos) which reflectivity reached the value higher than 0.9999 at the wavelength of 414 nm. Their radius of curvature was 1 m, while the distance between them was 60 cm. In case of the empty resonator, we observed the decay time $\tau_0 = 25$ μs. The cavity was connected with the gas mixing system supplied from bottle with NO_2-air mixture of 50 ppm mixing ratio. The mixture was additionally diluted with pure nitrogen. The measurement was performed under the steady flow of the gas mixture through the cavity. The output signal was detected by a photomultiplier equipped with the interference filter, the bandpass of which was well matched to the laser line. The signal was recorded with fast 8–bit digital oscilloscope (HP 54520).

In order to eliminate the laser instabilities that may affect the final result when the formula (5) is used, we determined the absorption coefficient by the time constants measurements (1). It eliminates the necessity of knowing the mirror reflectivity R, which can change during the experiment due to the contamination. The Figure 3 shows the dependence of measured concentration of NO_2 *vs*. concentration, which was calculated on the basis of NO_2 and N_2 ratio. The good agreement between experimental data and calculated values was achieved. Slight inaccuracy is either caused by imperfect gas mixing (including poor aerosol filtration) or deposition of nitrogen dioxide on the cavity.

We assume that the relative precision of the CRDS time determination is equal to

$$F = \frac{\tau_0 - \tau}{\tau_0} \tag{7}$$

Thus, following the Eq. (1), detectable concentration limit N_L can be described by the formula:

$$N_L = \frac{F}{c\sigma\tau_0} \tag{8}$$

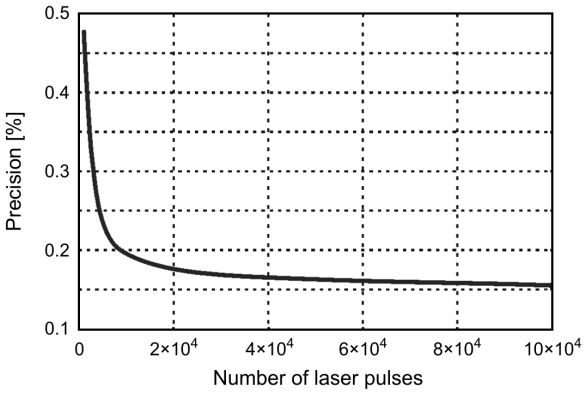

Fig. 4. Precision of the decay time determination as a function of the pulse number.

After averaging of the signal of over 30000 pulses (*i.e*, within the averaging time constant of 3 s), the precision of the decay time determination of about $F \approx 0.13\%$ was achieved (Fig. 4). According to Eq. (7), the detection limit better than 0.5 ppb was obtained for $\sigma = 6\times10^{-19}$ cm^{-3}. We were able to monitor about 13 ppb of NO_2 in the lab air.

In order to achieve high value of τ_0 and high precision of the decay time determination, the proper adjustment of the cavity is necessary. Moreover, the measurement with good detection limit also requires appropriate filtration of the investigated air. This is necessary in order to avoid the light scattering in the aerosol particles as well as the dust deposition on the mirror surfaces. When the concentration of aerosol particles in gas is similar to that in free atmosphere, the extinction of about 10^{-6} m^{-1} occurs. Consequently, at high sensitivity measurements, the losses due to the light scattering can be the same or larger than the absorption losses.

3. Conclusions

In this paper, we demonstrated that CEAS technique can be applied for construction of fully optoelectronic NO_2 detector with the detection limit better than that for commonly used chemical detectors (< 1 ppb). Contrary to the previous solutions [7, 8] we applied the pulsed diode laser, which simplifies the detector construction. The resonator quality was determined by measuring the time of the radiation imprisonment, which is not sensitive for the laser power fluctuation.

Due to limited reflectivity of the mirrors used, the detection limit of the absorption coefficient registered by us reached about 10^{-7} m^{-1}. This value is far from the detection limit observed by other authors, and in our opinion, it can be improved. We also believe that using specialized electronic devices the precision of the time constant measurements can be increased as well. Thus the metod opens promising perspectives for the future development of optoelectronic detectors of trace gases based on cavity enhanced methods.

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