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CAVITY RING-DOWN SPECTROSCOPY FOR TRACE GAS ANALYSIS*

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Cavity Ring-Down Spectroscopy (CRDS) is a novel technique of measurement of the absorption coefficient based on determination of the Q-factor of an optical resonator which contains the investigated absorber. We present a modified CRDS method (so called CRD-Spectrography) in which the signal is simultaneously analysed within a broad spectral range. This technique was used for monitoring of trace gases (nitrogen oxides) in the atmosphere. Another modification of CRDS technique allows to determine the transient absorption coefficient. This method was applied for studies of kinetics of CH radical produced by pulsed electric discharge in methane.

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1. Introduction

Cavity Ring-Down Spectroscopy (CRDS) is an optical technique developed in early 1980s. The method is based on the phenomenon of light trapping in an optical resonator of a high Q-factor. Initially Herbelin [1] used it for investigations of mirrors of high reflectivity. Then O'Keefe and Deacon in 1988 [2] applied it for measurements of absorption spectra of a gas filling the cavity.

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The decrease of light intensity $I(t)$ in a resonator is caused by losses on mirrors and by extinction occurring in the matter filling the cavity. Generally, the intensity evolution can be described by the equation [1]:

$$\frac{dI(t)}{dt} = -I(t)\left(\frac{1}{\tau_0} + c\alpha\right) , \tag{1}$$

where τ_0 denotes a time constant of the radiation decay in the case of empty cavity, α is the extinction coefficient, and c is the speed of light. Under the assumption of sufficiently short light pulse entering the cavity, the solution of the above equation can formally be given by:

$$I = I_0 \exp\left[-\int dt \frac{1 + c\tau_0\alpha}{\tau_0}\right] , \tag{2}$$

where I_0 is the initial intensity of the light pulse. In the case of the stationary absorption in the cell the light intensity decreases exponentially:

$$I = I_0 \exp\left(-\frac{t}{\tau}\right) . \tag{3}$$

Then the absorption coefficient can be expressed by two decay time constants. One of them (τ_0) is measured when the cavity is empty, and the other one (τ) when the cavity is filled with the investigated absorber:

$$\alpha = \frac{1}{c}\left[\frac{1}{\tau} - \frac{1}{\tau_0}\right] . \tag{4}$$

The result does not depend neither of the light source intensity fluctuations nor of the spectral sensitivity of the detector. When high reflectivity ($R > 0.9999$) mirrors are applied the absorption coefficients as low as $10^{-8}\mathrm{m}^{-1}$ can be measured [3]. For this reason the CRDS has found many applications, for example in monitoring of atmospheric impurities, detection of trace gases, *etc.*

2. Typical CRDS system

Typical experimental setup for CRDS is shown in Fig. 1. It consists of the pulsed tunable laser, optical cavity, light detector and transient digitiser (digital oscilloscope). In our experiments the light pulses were generated either in an optical parametric oscillator or in a dye laser, both pumped by the third harmonic of a pulsed Nd:YAG laser. Duration time of the laser pulse was about 7 ns, while the repetition rate was about 10 Hz. The laser light was directed to the cavity composed of two mirrors. Their radius of curvature was 1 m and the reflection coefficient in the spectral range of 415–440 nm was higher than 0.997. The mirrors were 0.8 m apart. In order to excite mostly the TEM_{00} mode, and thereby to reduce the contribution of higher modes in the CRDS signal, the laser beam passed through a spatial filter made of two lenses of 5 cm focal length and through an iris diaphragm. As a light detector the photomultiplier or intensified CCD camera equipped with a spectral filter was used.

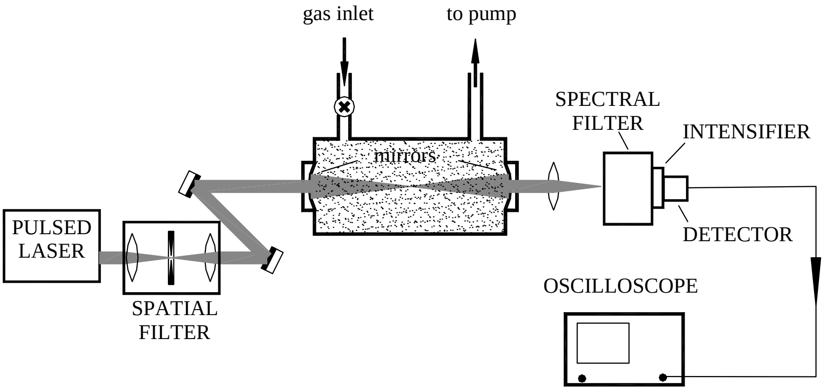

Fig. 1. Typical experimental setup for CRDS

This system was applied for detection of NO_2. Results are shown in Fig. 2. The upper curve presents the absorption spectrum achieved by means of CRDS method. The reference absorption spectrum of NO_2 achieved using a classical spectrophotometer at high densities is shown as the bottom curve.

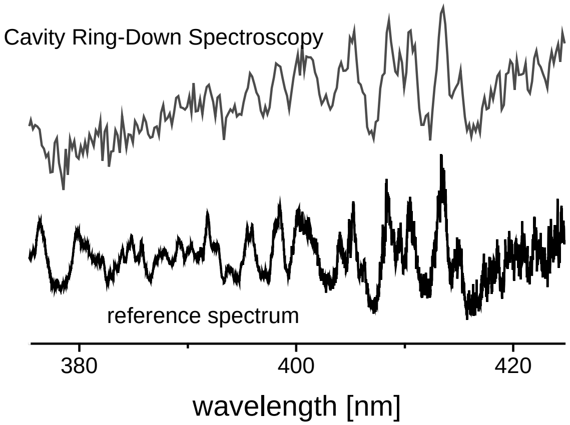

Fig. 2. Absorption spectrum of the air with 10 ppb NO_2 registered with CRDS method compared to the reference spectrum.

It is worth to point out that this spectrum was recorded for the mixing ratio as small as 10 ppb, *i.e.* corresponding to a typical NO_2 concentration in the atmosphere. A good coincidence between both spectra is easily seen. The experiment shows that the CRDS technique can be successfully applied for monitoring the NO_2 in the atmosphere. One can evaluate that when the mirrors of reflectivity coefficient as high as 0.9999 are used the lower limit of the NO_2 detection reaches about 0.1 ppb, which is better than sensitivity obtained by means of commonly used chemical detectors.

In practice the experimental difficulties can disorder application of this method for the useful trace gases detectors. The scanning of the absorption spectrum becomes time consuming. The consecutive tuning of the laser to the selected wavelength, the signal averaging over many laser pulses (in order to get a proper signal to noise ratio) is laborious and takes quite a long-time, even when the experimental system is fully automated. In some cases, at long lasting measurements, the problem of the sample stability can occur, especially in the case of environmental monitoring applications.

3. Cavity Ring-Down Spectrography

We found that many of the problems mentioned above can be solved by modification of the conventional setup. In our modified system we used spectrally broadband light source. Here the dye laser consisting of single dye cell (with Stilbene 3) without tuning elements as well as without the output mirror was applied. The FWHM of the laser spectrum as large as 15 nm was achieved. Then the output signal was analysed with a spectrograph and a CCD camera equipped with gated image intensifier (PCO, DICAM-3). It was used to register the time-dependent spectrum of the light leaving the cavity. The gate width as low as 50 ns was applied.

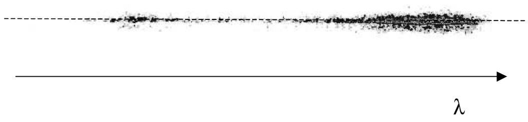

Fig. 3. Spectrogram of the CRDS signal observed on TV monitor at the gate delay 50 ns.

An example of the picture observed on the monitor connected to the ICCD camera, within 50 ns just after the laser pulse, is shown in Fig. 3. Since the horizontal axis corresponds to the wavelength, the light spectrum can be registered by measuring the signal intensity along a single TV line by means the oscilloscope operating with the TV-trigger modus. The TV line (in Fig. 3 shown by dashed markers) corresponding to the most intense part of the spectrum picture was selected for analysis. The gate was consecutively delayed with respect to the triggering laser pulse and at each step the spectrum was registered. Then, using this data set, the decay time constant for each wavelength was determined.

An example of the time dependent CRDS spectrum is shown in the Fig. 4. The spectrum consists of two maxima. The maximum localised at longer wavelengths (441 nm) corresponds to the wing of the laser line. Due to relatively high transmission coefficient of the mirrors at this spectral range the cavity Q-factor was lower, so at these wavelengths the decay time of the light trapped in the cavity was equal to about 250 ns only. The second peak localised at 426 nm corresponds to the maximum of the dye laser generation. Here the reflection coefficient of the cavity mirrors is much higher, so this peak is strongly depressed. However in this spectral range Q-factor of the cavity is good enough to register the decay time τ of the signal as long as 1.5 μs.

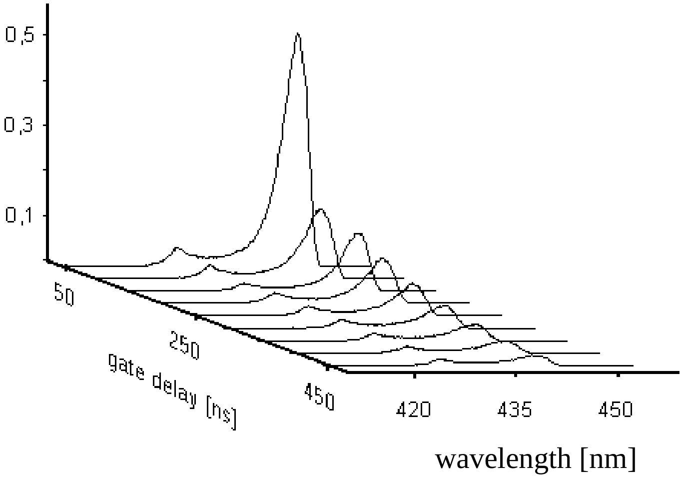

Fig. 4. Time dependent spectrum of CRDS signal.

Cavity Ring-Down Spectrography was check for the absorption of NO_2 at pressure of 0.01 Torr, which corresponded to the mixing ratio of about 10 ppm of NO_2. The results are presented in Fig. 5. The absorption was investigated within the spectral range between 410 and 435 nm. Due to high amplification of the image intensifier the investigations could be performed even at far wings of the laser line. The spectrum is compared with the spectrum of NO_2 achieved by means of conventional absorption technique. One can notice a good agreement between both methods; some discrepancies can be explained by low purity of our NO_2 sample which in this case was produced directly through the reaction between copper and nitric acid. We evaluate that the relative uncertainty in determination of the absorption coefficient was about 5% within 50 ns just after the laser pulse.

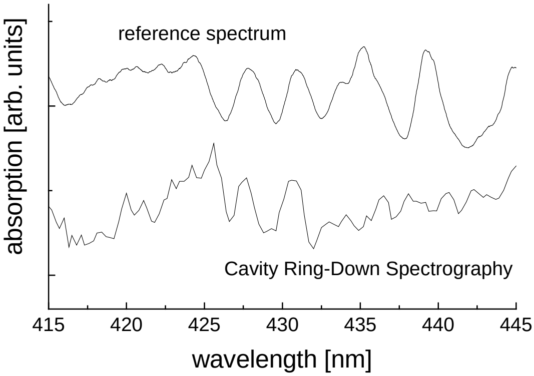

Fig. 5. Absorption spectrum of NO_2 registered with the Cavity Ring-Down Spectrography.

This method offers new advantages in investigations of the absorption spectra. Due to simultaneous registration of the signal on all wavelengths it is much faster than a commonly used CRDS technique. Using the spectrographic method at sufficiently strong signals the complete absorption spectrum can be found even with two laser shots. At the first pulse the cavity output spectrum should be registered just after the laser shot. At the second laser pulse the spectrum should be registered with a delay which is sufficient to calculate the cavity decay constant. Allying the speed of this method with the advantages of conventional Cavity Ring-Down Spectroscopy we found that this technique provides opportunity to study dynamic changes of the absorption coefficients even at their low values. The temporal resolution of these studies is limited by repetition rate of the pulsed lasers, which at nowadays can reach even tens of kilohertz. This new spectroscopic method may lead to very promising and useful applications like time-dependent environmental monitoring, as well as the observation of kinetics of chemical reactions in long time scale.

4. Measurements of transient absorption

Recently Brown *et al.* [4, 5] have shown that observing the time dependent cavity loss the CRDS method can be also applied for kinetic studies in microsecond time scale. This method, called by the authors Simultaneous Kinetics and Ring-down (SKaR), was applied for investigation of the evolution of NO_3 and OH molecules produced by flash photolysis. In this work we present the application of SKaR for kinetic studies of the decay process of CH radicals formed during a pulse discharge in methane.

For non-stationary conditions, *i.e.* when the absorption coefficient depends on time ($\alpha = \alpha(t)$), transforming the equation (2) one obtains:

$$\alpha(t) = -\frac{1}{c}\left[\frac{1}{\tau_0} + \frac{d\ln(I(t))}{dt}\right]. \tag{5}$$

Substituting in the above equation the light intensity $I(t)$ registered during the experiment one can get information about kinetics of the absorber changes.

The experiment was performed with a conventional set up (Fig. 2). The light pulses were generated by a tunable dye laser working on Stilbene 3. The laser light was directed to a cavity. The cavity mirrors were attached to a quartz tube with the inner diameter and the length of about 2 cm and 20 cm, respectively. The electric discharge took place between two electrodes placed in the tube near both mirrors. The current pulse with FWHM duration time of about 300 ns was switched by a thyratron discharging a capacitance of 15 nF charged to 17 kV. The methane flow through the tube was induced by a pumping system, and was adjusted to activate each pulse in a fresh gas portion. The pressure of methane was about 4 Torr.

The ring-down signal which leaked out of the cavity mirror was recorded with a photomultiplier and the digital oscilloscope (HP 54522A). The signal was averaged over 256 laser shots. As the optical filter we used a double glass prism monochromator (tuned to the laser line) which allowed to mitigate a strong luminescence light emitted by the plasma. In order to obtain the pure ring-down signal, we used a differential technique, *i.e.* the noise related to the discharge (both electrical and luminescence) was recorded without coupling laser pulse to the cavity, and then it was subtracted from the measured signal.

The electronic transition $A^2\Delta$–$X^2\Pi$ (431.4 nm) was chosen for monitoring the presence of CH radical. The measurements were performed within R(0–0) branch around the wavelength 426 nm using transitions from the rotational levels with $K'' = (9 \rightarrow 10)$.

The representative signals recorded in our experiment are shown in Fig. 6. The upper curve (dashed line) represents the exponential decay of the radiation in the cell filled with methane when the electric discharge was not applied. In such a case the decrease of the radiation intensity is characterised by the decay time constant equal to τ_0=0.92 μs, which corresponds to the mirror losses, since methane practically does not absorb radiation from our dye laser. Similar signal was observed with the presence of the electric discharge when the laser was tuned out of the CH absorption line.

The lower curve shows the evolution of the radiation intensity when the laser wavelength corresponded to the selected CH transition and the electric discharge was ignited. The discharge started approximately 400 ns after the laser shot. At this moment an evident strong decrease of the cavity Q-factor could be observed, as manifested by a drop of the output signal. Obviously, the CH radicals that are generated in methane by the discharge caused this effect [6–11]. The process of the CH formation is too fast to be time resolved in this experiment.

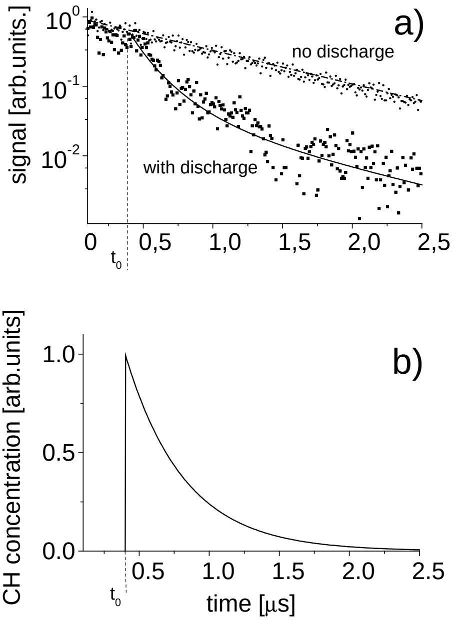

Fig. 6. CRDS signals registered in methane in presence of the discharge (a), and retrieved changes of CH radical concentration (b). The laser pulse starts at zero on the time scale.

From the slopes of the tangent (solid curve) at the moment of the discharge initiation ($t_0 = 0.4$ μs), using equation (4), one can determine the absorption coefficients α_0. Few microseconds after the initiation of the discharge the CH concentration becomes so low that the decay rate of the light intensity is nearly as fast as the decay rate characteristic for the empty cavity. As a consequence both curves in Fig. 6(a) become parallel.

It has already been established that, under similar conditions, only 20% of methane undergo to decomposition [7]. In our case the decomposition degree can even be lower because of the lower energy density. Therefore, we assume that the main process responsible for CH scavenging after the pulse discharge is the pseudo-first order reaction with methane:

$$\mathrm{CH} + \mathrm{CH}_4 \to \mathrm{C}_2\mathrm{H}_4 + \mathrm{H}\,. \tag{6}$$

The respective equation describing the evolution of the CH concentration is as follows:

$$\frac{dN_{\mathrm{CH}}}{dt} = -N_{\mathrm{CH}}k_{\mathrm{CH,CH_4}}N_{\mathrm{CH_4}}, \tag{7}$$

where N_{CH} and $N_{\mathrm{CH_4}}$ denote the CH radical and the methane concentrations, respectively, while $k_{\mathrm{CH,CH_4}}$ is the rate constant for the reaction process. This reaction was investigated by Braun *et al.* [8]. They found that the rate constant for this process is equal to $2.5{\times}10^{-12}$ cm^{3}s^{-1}. Under the assumption that the CH_4 concentration does not change significantly, the radical's concentration decreases exponentially (Fig. 6(b)):

$$N_{\mathrm{CH}}(t) = N_{\mathrm{CH}}(t_0)\exp[-(t-t_0)k_{\mathrm{CH,CH_4}}N_{\mathrm{CH_4}}], \tag{8}$$

where t_0 denotes the moment of the discharge initiation. The absorbance of the gas column is:

$$\alpha_0 N_{\mathrm{CH}}(t)z = \alpha_0 z N_{\mathrm{CH}}(t_0)\exp[-(t-t_0)k_{\mathrm{CH,CH_4}}N_{\mathrm{CH_4}}], \tag{9}$$

where z is the distance between the electrodes and α_0 is the absorption cross section. Substituting the above formula into equation (5), one obtains the differential equation for changes of the light intensity inside the cavity. Its solution gives the output signal:

$$\ln\left[\frac{I(t)}{I(t_0)}\right] = -\frac{t-t_0}{\tau_0} + \frac{c\alpha_0 z N_{\mathrm{CH}}(t_0)}{k_{\mathrm{CH,CH_4}}N_{\mathrm{CH_4}}}\left\{\exp[-(t-t_0)k_{\mathrm{CH,CH_4}}N_{\mathrm{CH_4}}]-1\right\}, \tag{10}$$

where $I(t_0)$ denotes the signal intensity at the moment of the discharge ignition. This function was fitted to the experimental data (solid curve in Fig. 6(a)). It was found that the decay time of the CH radicals is equal to $\tau_{\mathrm{CH}} = (k_{\mathrm{CH,CH_4}}N_{\mathrm{CH_4}})^{-1} = 0.86\ \mu s$. Since the methane concentration was about $N_{\mathrm{CH_4}} = 7 \times 10^{16}$ cm^{-3}, one can find that the rate constant for the CH radicals destruction was $k_{\mathrm{CH,CH_4}} = 1.7 \times 10^{-11}$ cm^{3}s^{-1}.

The difference between our result for $k_{\mathrm{CH,CH_4}}$ and the data by Braun *et al.* [8] can be explained by contributions of other reactions also possible for the CH destruction. Under the prevailing discharge conditions the amount of hydrogen can reach even 20% of the methane number density [9, 10]. The rate constant destruction of the CH radicals in reaction with hydrogen molecules is about five times larger than $k_{\mathrm{CH,CH_4}}$. Lange [10] and Becker *et al.* [11] have determined the rate constant as equal to $k_{\mathrm{CH,CH_4}} =$

1.2×10^{-11} $\mathrm{cm^3s^{-1}}$ and $k_{\mathrm{CH,CH_4}} = 1.4\times10^{-11}$ $\mathrm{cm^3s^{-1}}$, respectively. Other reactions like acetylene formation due to collisions of two CH radicals (which is also characterised by a large rate constant: $k_{\mathrm{CH,CH_4}} = 2\times10^{-11}$ $\mathrm{cm^3s^{-1}}$ [8]), seem to be negligible because of very low CH concentration. One has to admit that shock waves which usually occur during electric pulse discharges can also significantly accelerate removal of the CH radicals from the tube axis towards the wall where recombination processes is much faster.

5. Conclusion

We presented two modifications of the CRDS method. One of them, Cavity Ring-Down Spectrography, offers new advantages in investigations of the absorption spectra. It is much faster than a commonly used CRDS technique. Using the spectrographic method at sufficiently strong signals the complete absorption spectrum can be found even with two laser shots. At the first pulse the cavity output spectrum should be registered just after the laser shot. At the second laser pulse the spectrum should be registered with a delay that is sufficient to calculate the cavity decay constant $\tau_0(\omega)$. This method unifies high sensitivity of CRDS with speed of registration which is useful for construction of new detectors of trace gases. We found that this technique provides also opportunity to study dynamic changes of the absorption coefficients even at their low values.

We present also another modification of the CRDS method that is useful for investigations of transient processes. Using the mirrors of high reflectivities it provides opportunity to measure weak (10^{-6} $\mathrm{m^{-1}}$) absorption variations with a temporal resolution of 10^{-7} s. The method is useful for investigation of chemical reactions kinetics in millisecond and microsecond time scale.

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