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# Set-up of a Near-Infrared Cavity Ringdown Spectrometer for Quantitative Surface Coverage Measurements on Quartz Glass

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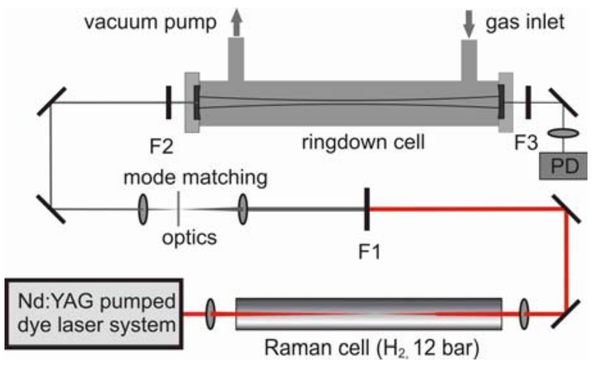
## Introduction

Whereas cavity ringdown spectroscopy is well established for gas phase measurements, its application for the quantitative determination of surface coverage is still developing [1]. In recent years, several approaches have been reported including both Fabry-Perot cavity designs with a planar substrate placed directly inside the cavity (transmission configuration) and evanescent wave cavity designs utilizing the total internal reflection of the detection light at an internal surface (reflection configuration, monolithic design).

A new pulsed near-infrared (NIR) CRD spectrometer operating at wavelengths around 1600 nm has been set-up and characterized. Since the bandwidth of the ringdown probe laser exceeded the absorption line width of the detected species, a pronounced laser bandwidth effect was observed causing multi-exponential ringdown decays. Nevertheless, based on an iterative forward fitting procedure of the observed CRD spectra, it was possible to perform sensitive and quantitative concentration measurements.

A Brewster's angle transmission configuration was tested by placing a thin quartz glass substrate inside the cavity. Although a rather high additional intensity loss component mainly caused by surface scattering occurred, the sensitivity of the spectrometer was still sufficient to detect trace gases in ambient air. After silylation of the surface with phenyltrimethoxysilane, broad absorption bands were observed which could be tentatively attributed to first overtone CH-stretching vibrations of the phenyl moieties.

## Experimental Setup




**NIR laser source:**

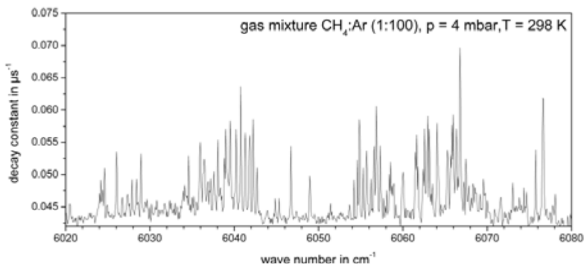
The output power of a Nd:YAG laser pumped tunable dye laser system was significantly increased using an additional separately pumped amplification stage (E = 65 mJ/Puls). Frequency conversion to near infrared was achieved by using the second Stokes of a single pass hydrogen filled Raman cell (λ = 1450-1900 nm, E = 1 mJ/Puls). For the separation of the NIR radiation, several filters (F1-F3) have been used.

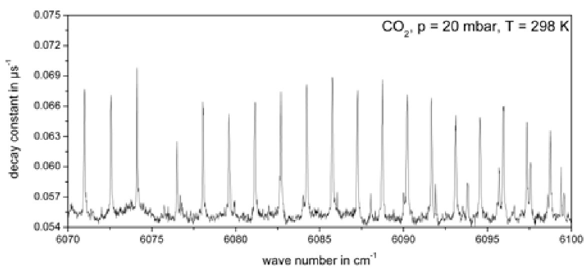
**Rindown cell:**

A high finesse cavity consisting of two high reflection mirrors (R = 99.999 %) in a distance of 1 m was used. In the case of thin film measurement, the flow reactor was replaced by an optical mount holding the quartz substrate.

**Data acquisition:**

Typically, 20 pulses were averaged to determine the decay constant. Despite the significant intensity fluctuations, a good absorption sensitivity of $\alpha_{min}$ = 1,1 x $10^{-8}$ $cm^{-1}$ was achieved. Two typical measured test spectra of gas phase species are shown below.




| λ / nm | ν / cm⁻¹ | $\alpha_{min}$ / cm⁻¹ |
|---|---|---|
| 1450 - 1900 | 5300 – 6900 | 1.1 x $10^{-8}$ |

## Literature

[1] C. Vallance, *New J. Chem.* **29**, 867-874 (2005).
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[6] L. Rothman et al., *J. Quant. Spectrosc. Radiat. Transfer* **96**, 139-204 (2005).
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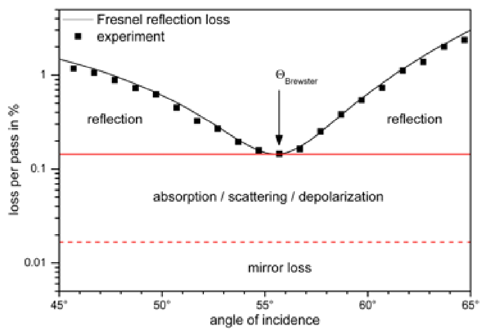
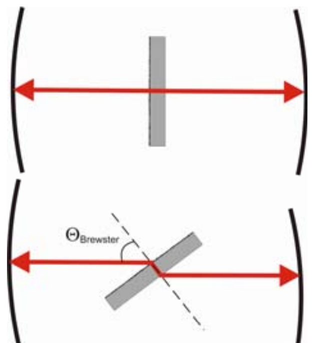
## Organic thin film measurement

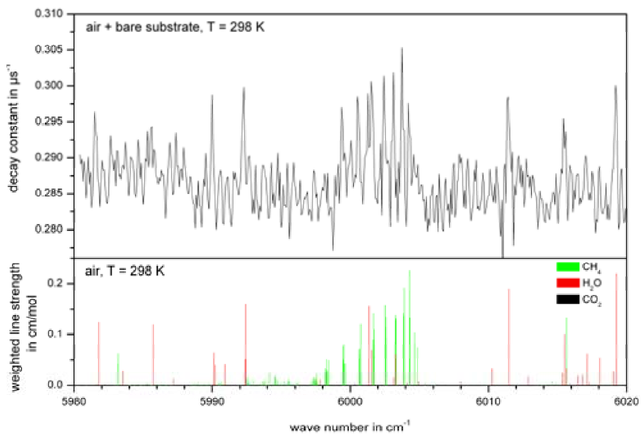
In contrast to nowadays frequently used evanescent wave cavity ring down spectroscopy, several approaches with the substrate placed within the cavity exist. Two different orientations of the substrate are promising to obtain low loss inside the cavity, perpendicular (reflected light stays within the cavity) and in Brewster's angle (no reflection loss) [2,3]. We found both working comparably well.

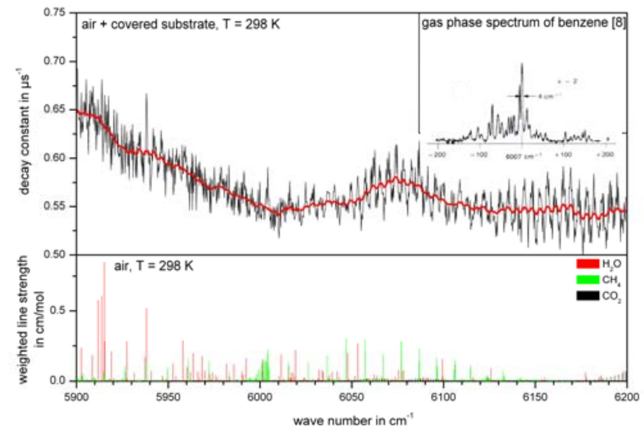



Despite of the high additional loss, several absorption lines of air components like methane, water and carbon dioxide are still visible in a typical CRD-spectrum of the bare substrate aligned in Brewster's angle (τ = 2-5 μs). Based on the measured methane absorption it is possible to estimate the minimum detectable surface coverage to 5 x $10^{15}$ molecules/cm². This is unfortunately still above monolayer sensitivity (≈ 6 x $10^{14}$ molecules/cm²).

After functionalization of the surface with phenyl moieties an additional loss around 6075 $cm^{-1}$ and below 6000 $cm^{-1}$ can be observed in the CRD-spectrum. A comparison with well known overtone spectra of benzene [8] reveals that these broad bands can tentatively be attributed to the CH-stretching transitions of the phenyl moieties. The reproducible oscillating behaviour of the baseline might be based on an interference effects which has not been further analysed. Confirming these first results and increasing the sensitivity of the spectrometer in order to detect monolayers is part of our ongoing research.



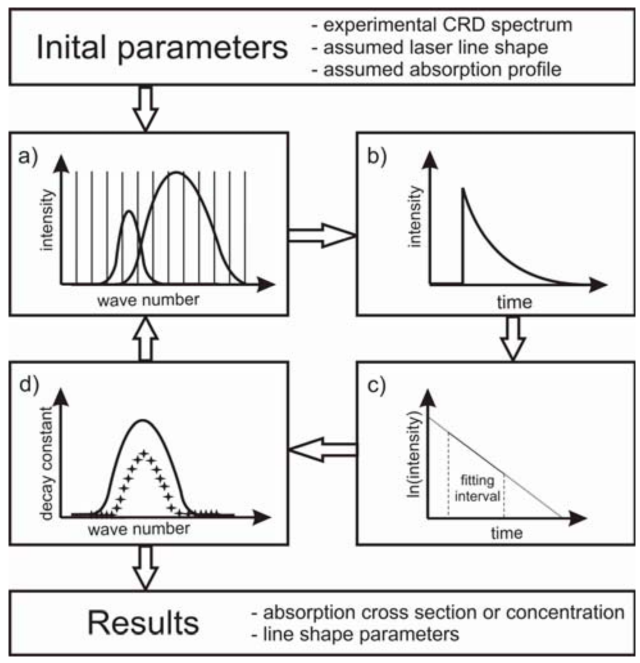



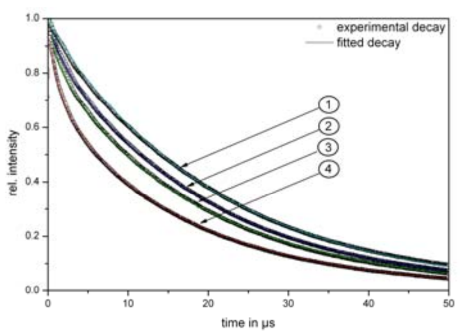

## Quantitative analysis

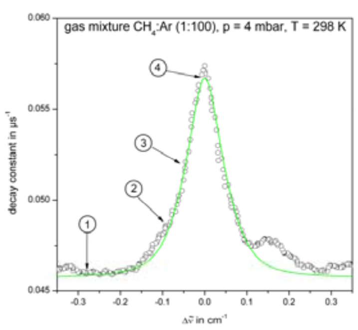
Although multi-exponential decays have been observed, a quantitative treatment should be possible based on an iterative modeling procedure [5]. Following the experimental single exponential analysis an initial guess for the line shape profile of the laser and the absorption line is used to simulate the ringdown decay. After linearization and fitting of this ringdown over the same time interval as it was chosen in the experiment, the associated decay constant is obtained. Scanning the difference between the center frequencies of the profiles gives a simulated spectrum. A least squares fit to the experimental CRD-spectrum yields accurate line shape and line strength data.

Examples for experimental ringdown signals and the corresponding numerical simulations are shown together with the spectrum of the absorption line below. By testing the model with different time intervals for fitting the decay constant, better results have been obtained when choosing longer time periods for the analysis. This is a reasonable result since the correct profile can only be recovered if a fraction of the fast decay as well as a fraction of the slow decay is taken into account.

In order to check the limits of this model, some measurements with comparatively high concentrations have been performed (see Table). Even at concentrations corresponding to a line center single pass absorption of A = 3 x $10^{-3}$ our fitting routine yields a good agreement with HITRAN data. However, it finally fails to fit the more intense line with A = 2.8 x $10^{-2}$.



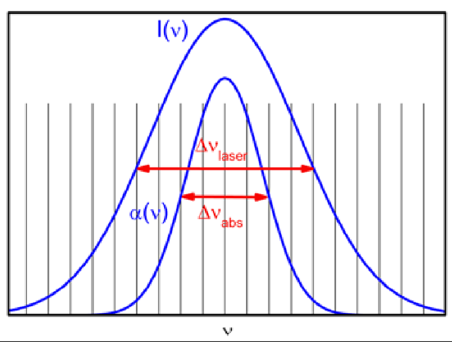



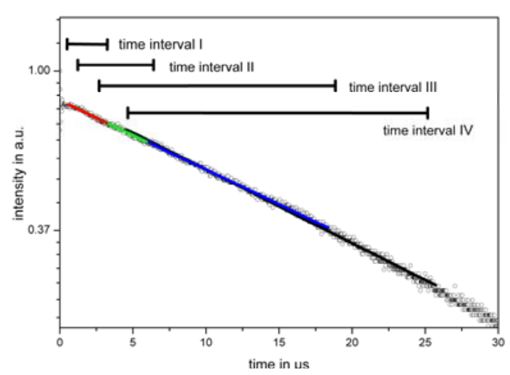



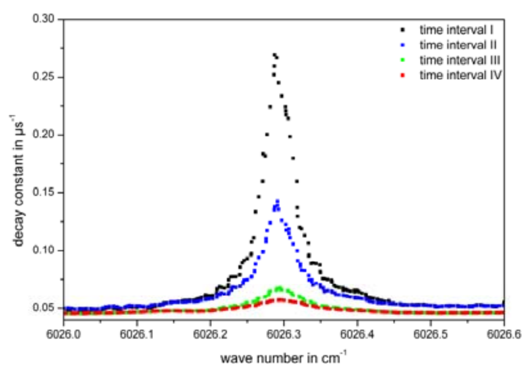

| Molecule | $\nu_c$ / cm⁻¹ | S / (cm/mol) | HITRAN [6] | A = αcl |
|---|---|---|---|---|
| $CH_4$ | 6026.2 | 304.60 | 342.70 | |
| $CO_2$ | 6069.6 | 0.75 | 0.80 | 3.0 x $10^{-3}$ |
| $CO_2$ | 6234.6 | 16.40 | 8.29 | 2.8 x $10^{-2}$ |

## Laser Bandwidth Effect

Using a detection laser source with a spectral bandwidth considerably broader than the line width of the detected species results in the so-called laser bandwidth effect. Different frequency components propagating in the ringdown cavity decay with different time constants causing the resulting ringdown decay to be multi-exponential. Nevertheless, according to Zare et al. [4], appropriate line shape and line strength data can be extracted from the ring down signal if single exponential fitting is limited to short times. However, in this study, because of the unfavorable ratio of laser bandwidth ($\Delta\nu_{laser}$ = 0.087 $cm^{-1}$) and absorption line width ($\Delta\nu_{abs}$ = 0.02 $cm^{-1}$), this procedure fails. The line strength data (see Table) demonstrates a better approximation by using a short time interval but even the shortest is far away from being quantitative.




| Time interval | I | II | III | IV | HITRAN [6] |
|---|---|---|---|---|---|
| S / (cm/mol) | 119.9 | 54.4 | 19.9 | 10.6 | 342.7 |

## Surface Functionalization

Several different options for the preparation of thin films are known from literature. Quartz substrates are advantageous due to the desirable optical properties in the used wavelength range. Furthermore, the free OH-binding sites of quartz offer the opportunity for chemical surface modification.

Silylation is a well known process which is based on slow hydrolysis of an alkyl trimethoxysilane and condensation of a compound with free OH-binding sites at the surface. The presence of water during the synthesis determines which of the processes is dominant such that both monolayer and thick film generation on the surface is possible [7]. Phenyltrimethoxysilane provides absorption lines in the near infrared and a index of refraction that almost match the index of refraction of the substrate. Due to low absorption coefficients in the near infrared, rather thick films were necessary to exceed the detection limit.