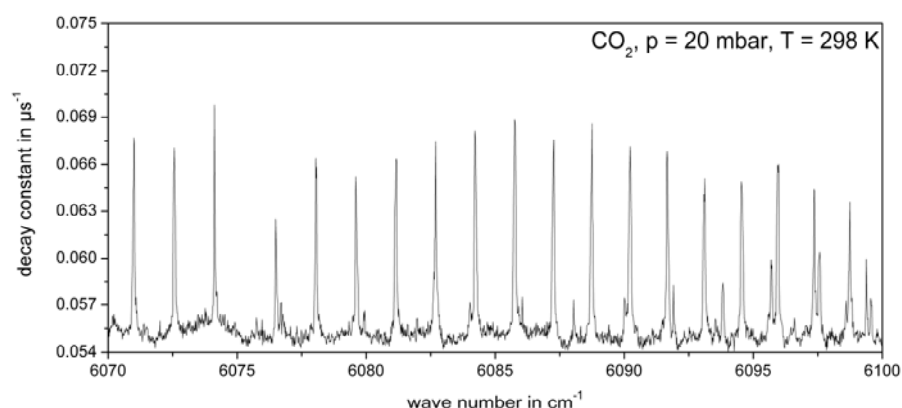


### Introduction and Motivation

Cavity Ringdown Spectroscopy (CRDS) has been proven to be capable of ultra low absorption detection. Several different variants have been developed for gas phase and, more recently, for condensed phase measurements. Despite its high potential, this technique is not used in marine sciences so far. Within the cluster of excellence "The Future Ocean" we are aiming to apply CRDS to study reactions with importance for ocean surface chemistry.

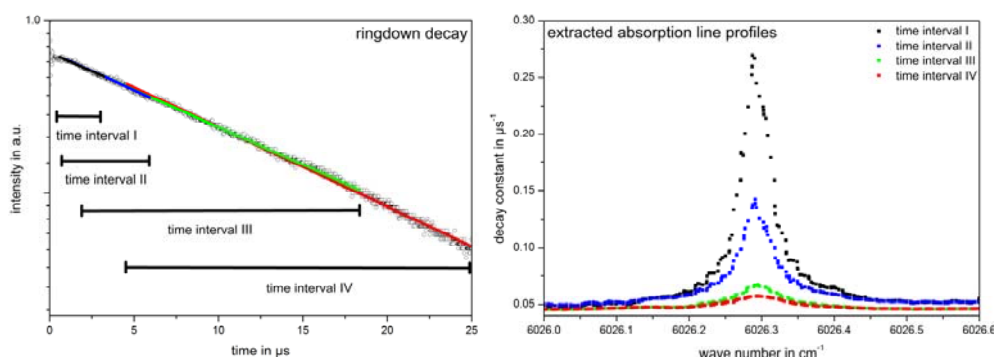


### Quantitative Gas Phase Measurements



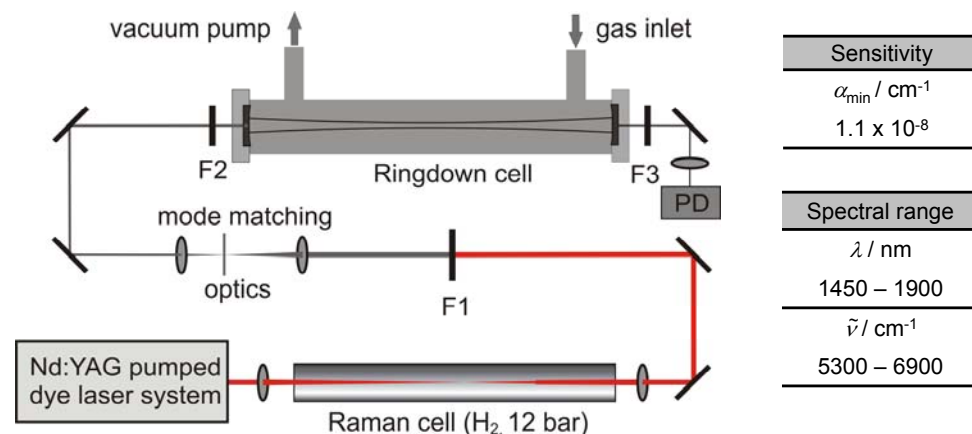
For environmental studies, e.g. the measurement of isotope ratios of CO<sub>2</sub>, CH<sub>4</sub> and other gases, the determination of absolute concentrations from CRD spectra is one of the most desirable features of this technique. In cases where the line width of the detection laser is broad compared to the absorption line width, multi-exponential ringdown decays are observed (bandwidth effect) and, especially in the NIR ( $\Delta\nu_{\text{Laser}}/\Delta\nu_{\text{Abs}} \approx 7$ ), the measured effective absorptions are too small. Simple correction schemes ( $S_{\text{INT}}$ ), e.g. by decreasing the fitting range of the ringdown decay as suggested by Yalin and Zare [1], are often not sufficient to determine the correct integral line strength ( $S$ ).

An iterative fitting routine, which takes an appropriate laser line shape model into account and which is based on simulation of the whole ringdown decay [2], is more accurate ( $S_{\text{FIT}}$ ).



molecule	$\tilde{\nu}_c / \text{cm}^{-1}$	$A = \sigma c l$	$S_{\text{INT}} / (\text{cm/mol})$	$S_{\text{FIT}} / (\text{cm/mol})$	$S_{\text{HITRAN}} / (\text{cm/mol})$ [3]
CH <sub>4</sub>	6026.2	$4.3 \times 10^{-5}$	119.9	304.60	342.70
CO <sub>2</sub>	6069.6	$3.0 \times 10^{-3}$	0.09	0.75	0.80
CO <sub>2</sub>	6234.6	$2.8 \times 10^{-2}$	0.32	16.40	8.29

### Experimental



#### NIR Laser Source:

- Nd:YAG laser pumped tunable dye laser system ( $E = 65 \text{ mJ/pulse}$ ).
- Second Stokes of a single pass hydrogen filled Raman cell ( $E = 1 \text{ mJ/pulse}$ ).
- Separation of the NIR radiation was achieved using a suitable filter system (F1 - F3).

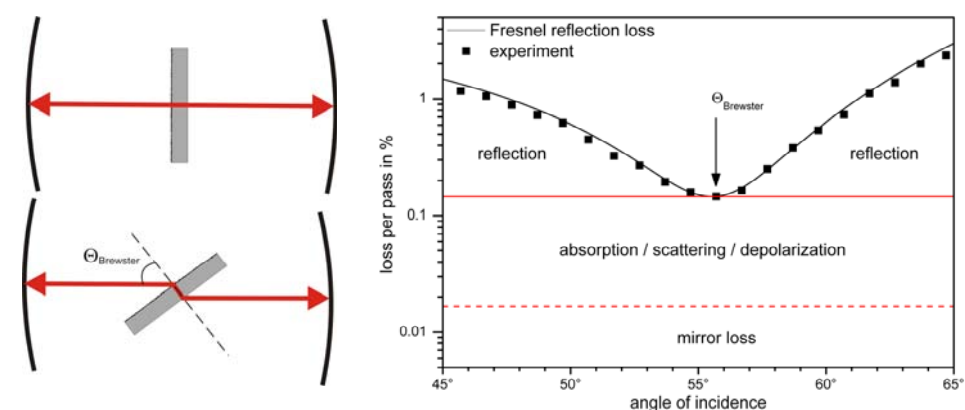
#### High finesse optical cavity:

- Two high reflection mirrors ( $R = 99.99 \%$ , 1610 nm) in a distance of 1 m ( $\tau_0 \approx 25 \mu\text{s}$ ).
- For thin film measurements, the flow reactor was replaced by an optical mount.

#### Detection unit:

- InGaAs photodiode (PD, 150 MHz bandwidth).

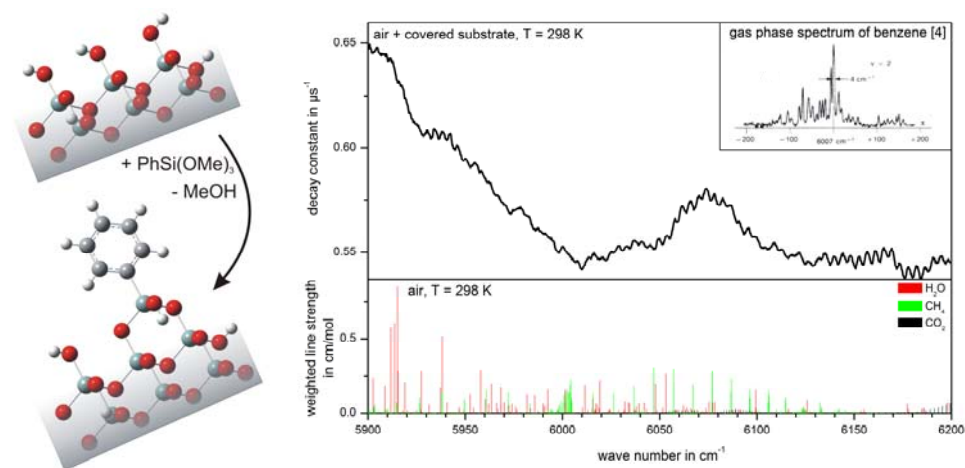
### Thin Film Measurements



The application of CRDS to study heterogeneous reactions is complicated due to additional optical losses arising from surface scattering and absorption of the substrate placed inside the ringdown cavity. The easiest way to investigate a surface within an optical cavity under low loss conditions is a thin film deposited on a transparent medium. Two different orientations of the substrate are promising to obtain low loss inside the cavity:

- perpendicular configuration (reflected light stays within the cavity)
- Brewster's angle configuration (no reflection loss)

As a test for the feasibility of condensed phase measurement, CRD spectra of a quartz substrate before and after functionalization with phenyl moieties were measured. The resulting CRD spectrum is shown in comparison with gas phase spectrum of benzene in the figure below. Most likely, the additional loss of the thin film can be attributed to overtone absorption of the slightly red-shifted CH-stretching vibration of the phenyl moieties. Since detectable absorption was limited to rather thick films, a monolayer sensitivity could not be reached.

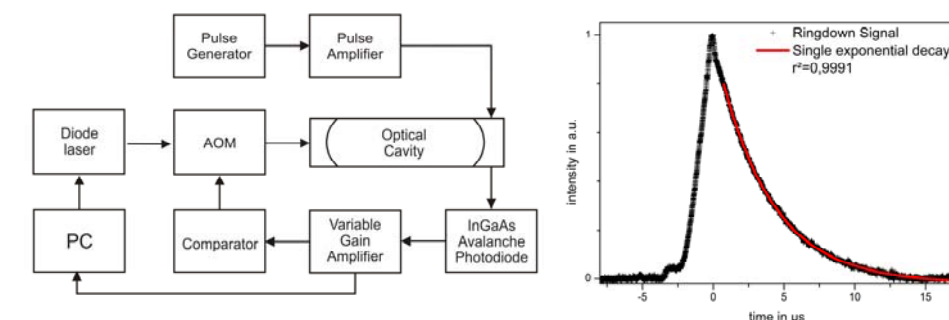


### Current Projects (cw- and ew-CRDS)

#### Enhanced sensitivity: "continuous wave Cavity Ringdown Spectroscopy"

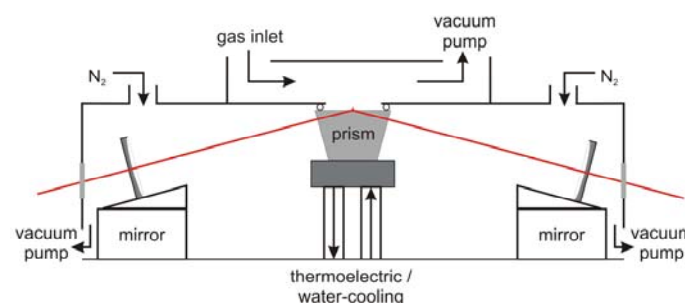
Setup of cw-NIR-CRDS detection system ( $\lambda = 1610 - 1690 \text{ nm}$ )

Ringdown signal obtained by cw-CRDS



#### Interface studies: "evanescent wave Cavity Ringdown Spectroscopy"

Reaction chamber design for ew-CRDS



### Literature

- [1] A. P. Yalin and R. N. Zare, *Laser Phys.* **12**, 1065-1072 (2002).
- [2] G. Friedrichs et al., *J. Phys. Chem. A* **109**, 4785-4795 (2005).
- [3] L. Rothman et al., *J. Quant. Spectrosc. Radiat. Transfer* **96**, 139-204 (2005).
- [4] R. H. Page et al., *Phys. Rev. Lett.* **59**, 1293-1296 (1987).