Research Group FRIEDRICHS – Physical Chemistry

Ocean Surface Chemistry & Reaction Kinetics

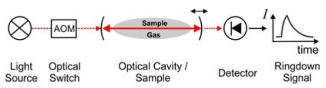
Objectives

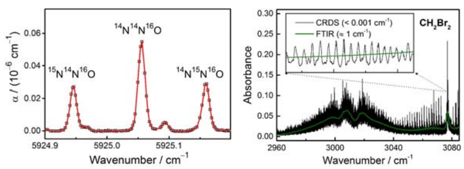
- Identifying and studying heterogeneous chemical processes at environmental interfaces – in particular the water/air interface – by using sensitive laser spectroscopic methods.
- Providing modern and quantitative optical detection techniques for use in environmental research applications such as trace gas detection and biofilm monitoring.
- Making available kinetic data to model pollutant formation, in particular in combustion processes, based on sensitive time-resolved absorption (and MS) techniques.
- Modeling of molecular structures at the water/air interface and prediction of chemical reaction rates.

The interdisciplinary working group „Ocean Surface Chemistry & Reaction Kinetics“ aims to link expertise from physical chemistry with marine sciences and combustion chemistry in order to gain a molecular level understanding of processes of environmental interest.

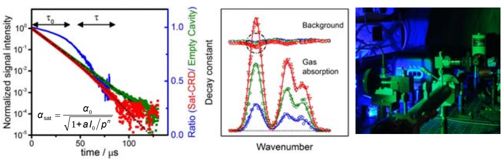
CRDS: Ultrasensitive Optical Trace Gas Detection

- High resolution, quantitative detection of trace gases by continuous wave near-infrared and infrared cavity-ringdown spectroscopy (cwCRDS).





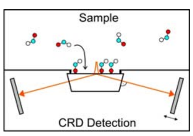
- Saturated Absorption CRDS for enhanced sensitivity



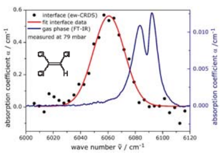
Simultaneous measurement of empty cavity (background, τ_0) and absorption signal (τ).

IR-CRDS: 2175 - 4000 cm^{-1}
$\Delta\nu$ < 60 kHz, P > 1.0 W.

- Evanescent wave CRDS for interface studies.



Principle of ew-CRDS.



TCE (≈12 layers) adsorbed on quartz.

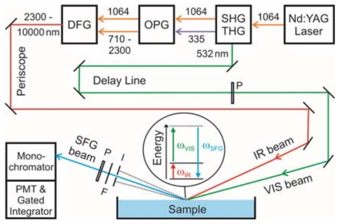
Contributing Group Members

Current: Alexandra Dabrowski & Florian Lange (Organic Monolayer Reactivity & Photochemistry), Nancy Faßheber & Sebastian Hesse (High Temperature NO_x Chemistry), Inga Piller Nancy & Ibrahim Sadiek (innovative CRDS schemes), Saira Riaz (Functionalized Surfaces).

Former: Meike Becker, Johannes Dammeier, Carsten Fehling, Matthias Fischer, Joscha Kleber, Kristian Laß.

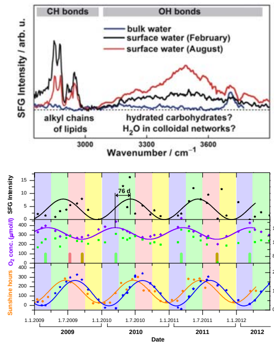
Sum Frequency Generation Spectroscopy: Studying Organic Monolayer Films on Water

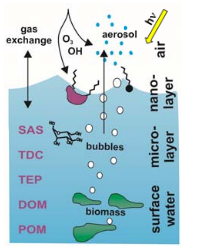
- **SFG Spectroscopy**



SFG spectroscopy is intrinsically surface specific (due to selection rules), species selective (IR spectra are measured), and orientation sensitive (polarization dependence of signal).

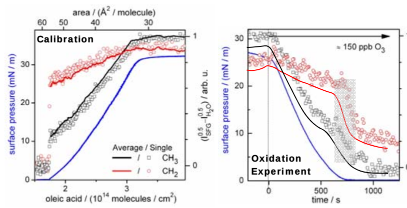
- **Marine Nanolayer: Composition & Abundance**



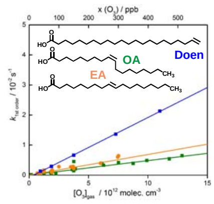


Upper left: typical spectrum of the natural organic nanolayer. **Lower left**: seasonal abundance trend at Boknis Eck Time Series Station.

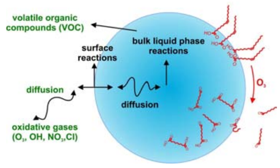
- **Organic Monolayer Reactivity**



Ozonolysis of an oleic acid monolayer.

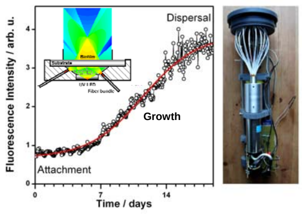


Structure-reactivity trends.

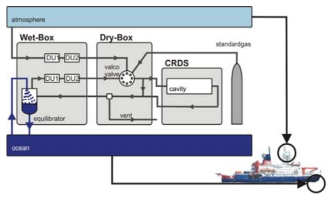


Aqueous Aerosol Ageing.

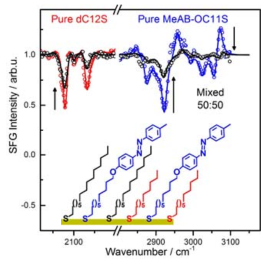
More Interfaces – From Field Studies to Functionalized Surfaces



Fluorescence sensor for monitoring biofilm formation dynamics (with M. Wahl, Benthosecology).



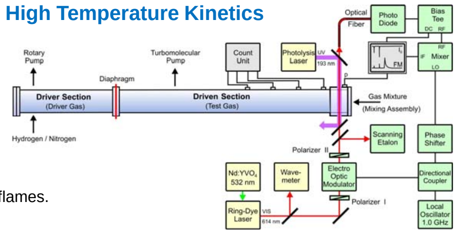
Isotopic CRDS field measurements of $\delta^{13}C(CO_2)$ (with A. Körtzinger, Marine Chemistry).

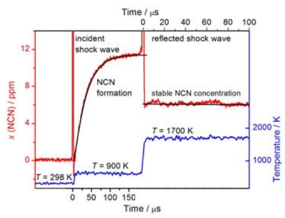


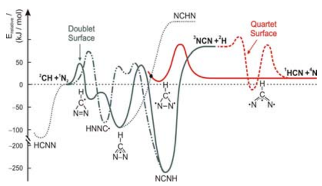
SFG study of the morphology and the switching efficiency of functionalized surfaces (SFB 677).

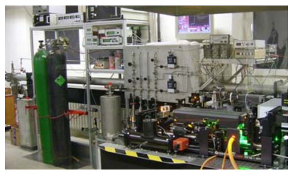
Pollutant Formation in Combustion Processes: High Temperature Kinetics

- Shock tube studies of gas phase reactions.
- Accurate rate constant data are determined from concentration-time profiles of small radicals measured behind shock waves by means of sensitive time-resolved absorption methods (e.g., frequency modulation spectroscopy).
- Current work is concerned with NCN radical chemistry, which has been identified as a key intermediate for NO_x formation in flames.

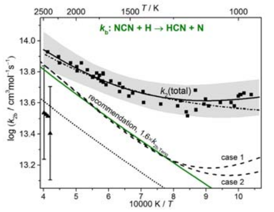


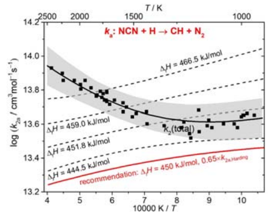






Upper left: Quantitative NCN Radical Source: $NCN_3 \rightarrow N_2 + NCN(^1\Delta) \rightarrow N_2 + NCN(^3\Sigma)$.
Upper middle: Potential energy diagram of the NCN forming reaction CH + $^1N_2$ (revised ‚Fenimore' initiation).
Upper right: Frequency modulation spectrometer & Kiel shock tube apparatus (scheme and photo).
Lower right plots: Branching ratios of the overall rate constant of the reaction NCN + H.





the future ocean

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