Enhanced CRDS Methods for Trace Gas Detection and Surface Analysis

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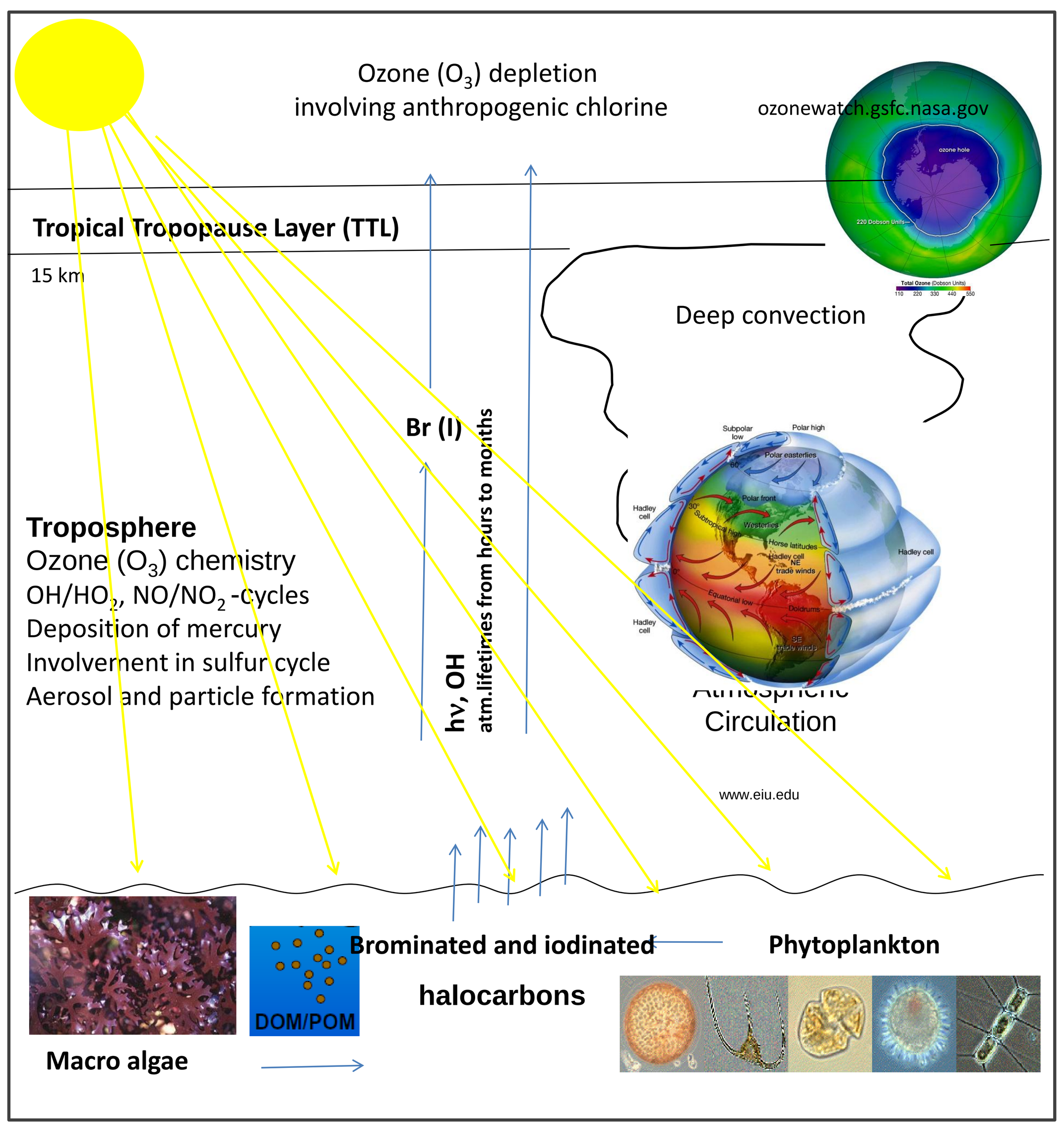
Organohalogen Detection

- Halocarbons play an important role in atmospheric chemistry, *e.g.* for ozone depletion.
- What is the role of the ocean for halocarbon emissions?
- What are the sources of halocarbons?
- How large is the **variability** of halocarbons emission?
- What controls the distribution of Halocarbons?

Problem:

- Organohalogen detection is mainly based on gas chromatography techniques that require considerable calibration effort and is limited to low sampling frequencies.

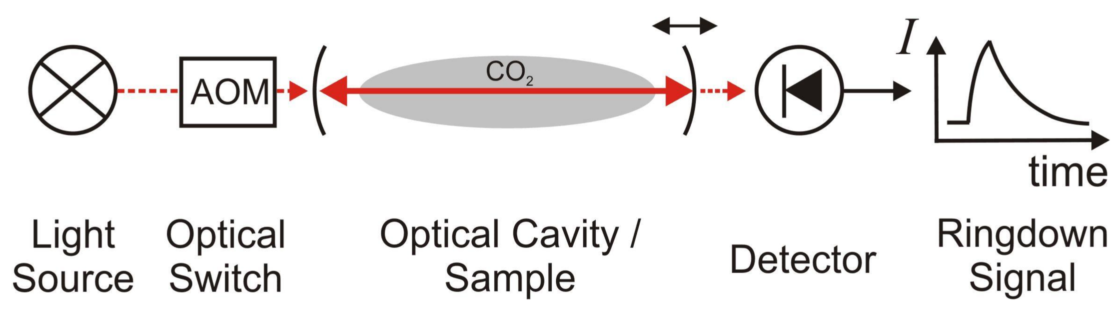


(adopted from Quack et al.)

Solution:

- Use of optical detection techniques such as cavity-ringdown spectroscopy.
- Unfortunately, most of the commercially available and field-deployable CRDS instruments are limited to the most abundant trace gases such as, CO_2, CH_4, and N_2O and operated in the near infrared (NIR) spectral range (where absorption cross sections are low).
- The project will be concerned with the fundamental spectroscopic and experimental work needed to range the potential of cavity ringdown spectroscopy (CRDS) for environmental monitoring of various halogenated hydrocarbons including bromoform and methyl iodide.

Basic principle of CRDS



- For **linear** absorption:

$$I(t) = I_0 \exp\left(-c\,\alpha\,t - \frac{t}{\tau_0}\right)$$

(τ_0: decay time for the empty cavity, α: absorption coefficient)

Problem:

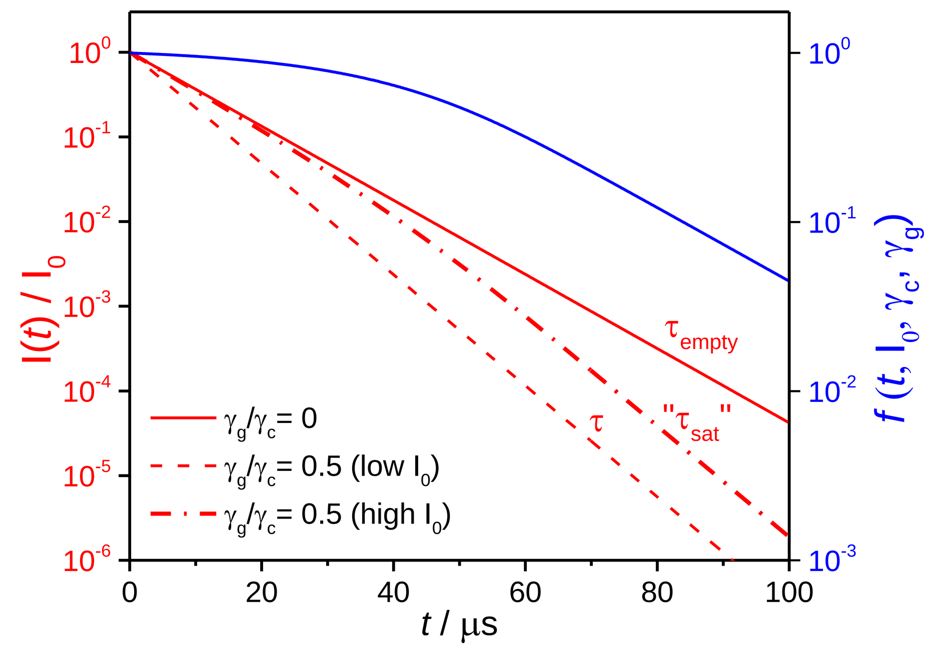
- τ_0 Needs to be measured separately.
- Temporal and spectral variation of τ_0.

Solution: Sat-CRDS

- At high laser power, **non-linear** absorption can occur due to the saturation phenomena.

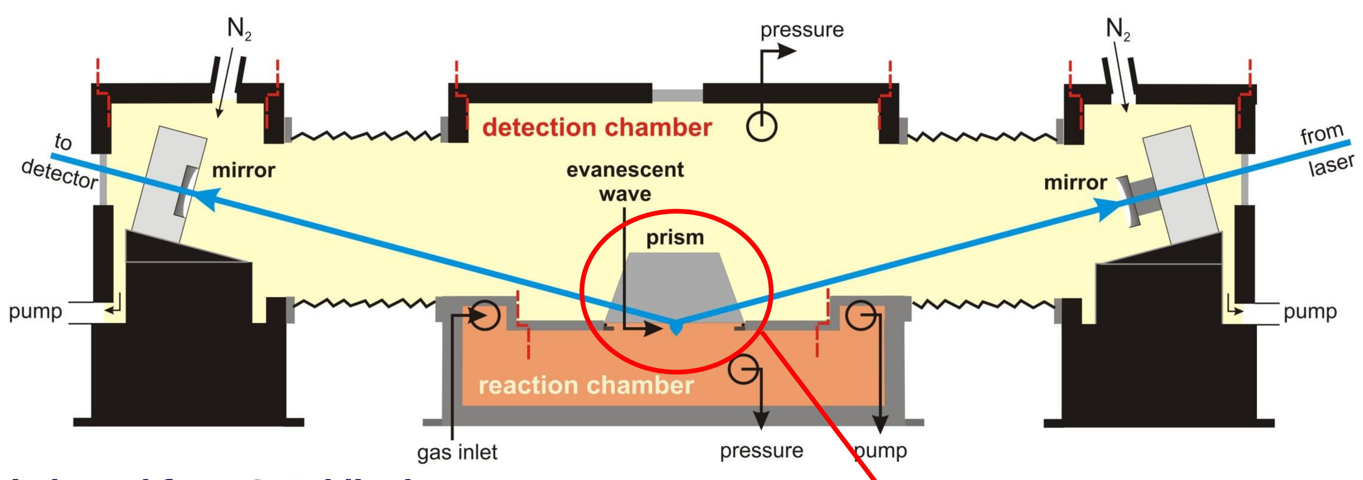
$$\alpha(\nu, I) = \alpha(\nu, 0) / \sqrt{(1+S)}$$

(S: the saturation parameter)

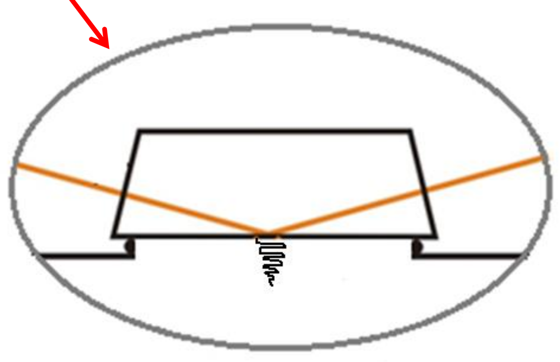


- The decay curves can be described by: $I(t) = I_0 \times \exp(-\frac{t}{\tau_0}) \times f(t, \tau_0, I_0, \alpha)$
- By using saturation CRDS, as illustrated, the empty cavity decay rate and the gas absorption are decoupled and can be retrieved from a single ringdown event.

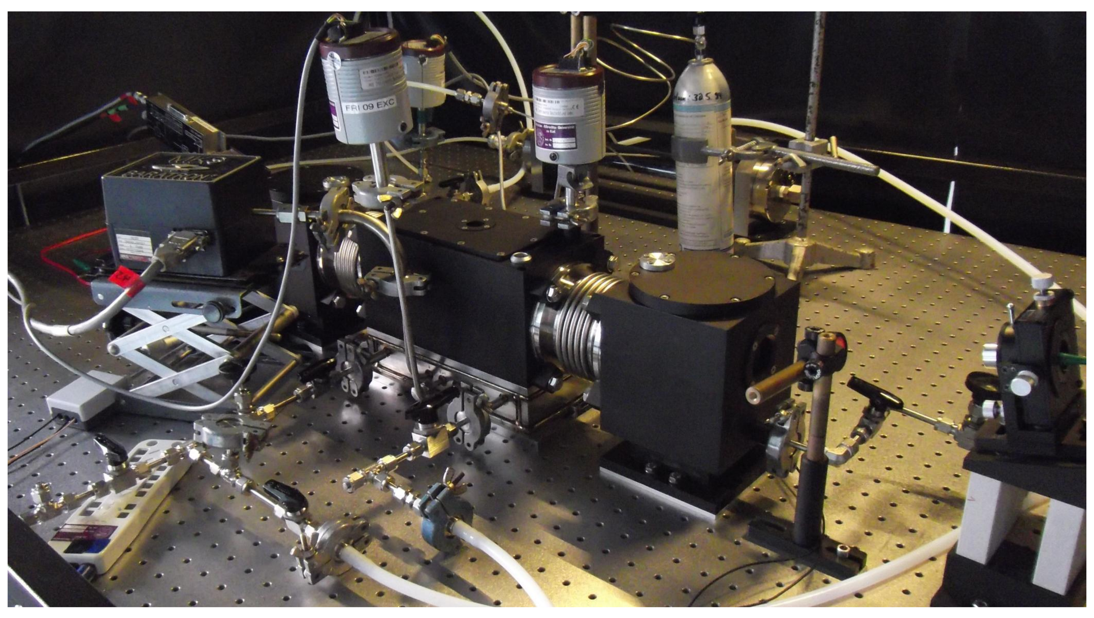
Evanescent-wave CRDS



(adopted from C. Fehling)



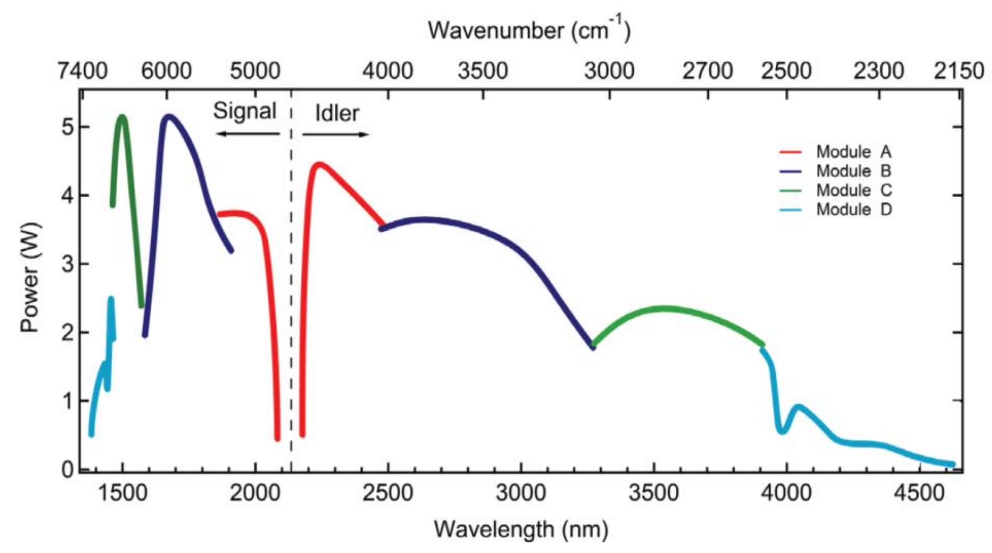
- Laborarory studies of atmospheric and marine reactions at quartz-air and quartz-water interfaces.
- TIR surface at the base side of the prism mounted in the middle of the cavity induces an exponential decaying evanescent-wave in the space below.
- Chemical compounds can adhere at the base side of the prism, absorb energy of the evanescent wave and thus decrease the ringdown time.
- NIR-laser source provides radiation in the 1620-1690 nm spectral range (e.g., CH overtone absorption).

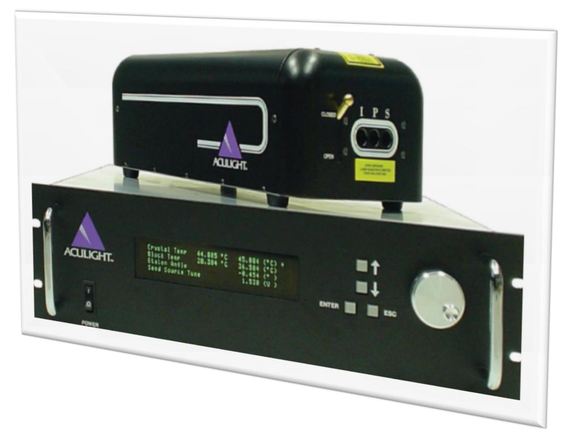


ew-cw-NIR-CRDS experiment

Sat-CRDS

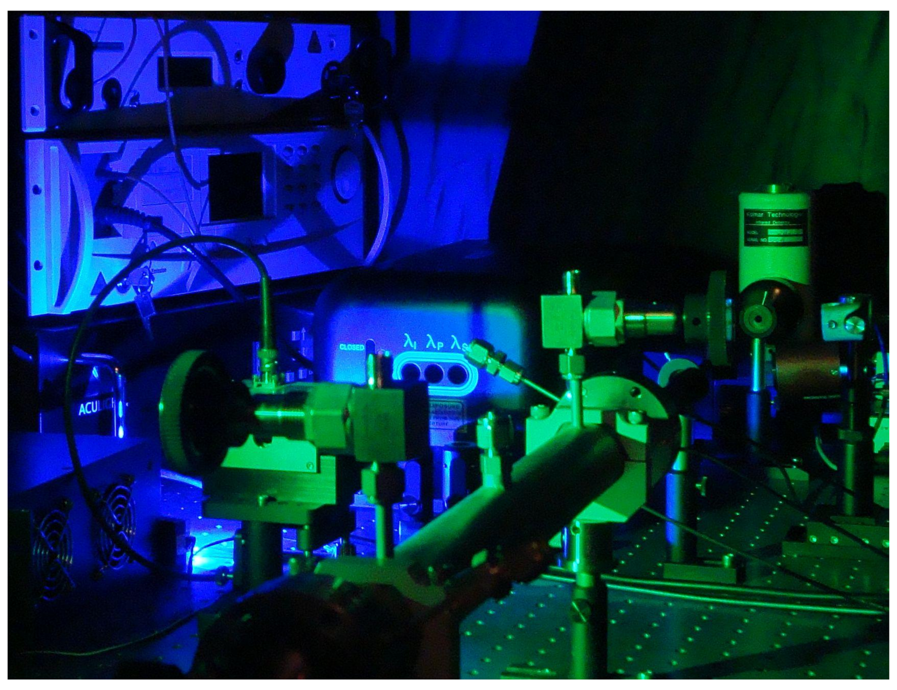
A novel cw-IR laser source (PPLN OPOs)



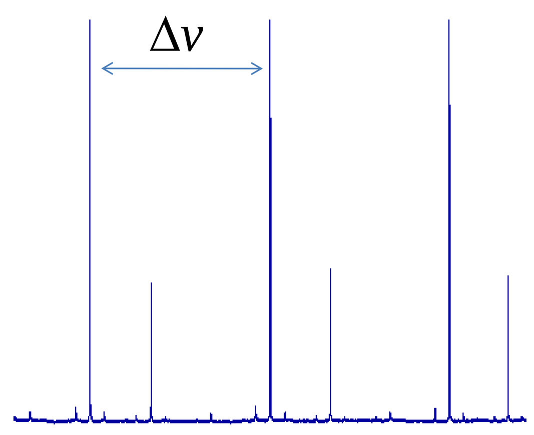


cw-OPO, Aculight Argos™ Model 2400 SF

Setup and First Data Example



New setup for trace gas sensing application.The infrared laser light source (bluish illuminated devices) offers a wide tunability (λ = 1.38 – 1.60 µm & 3.2 – 4.6 µm), a narrow spectral bandwidth (Δν < 60 kHz @ Δt = 500 µs), and high output power (P ≈ 1.0 W).



The mode spacing between two longitudinal modes

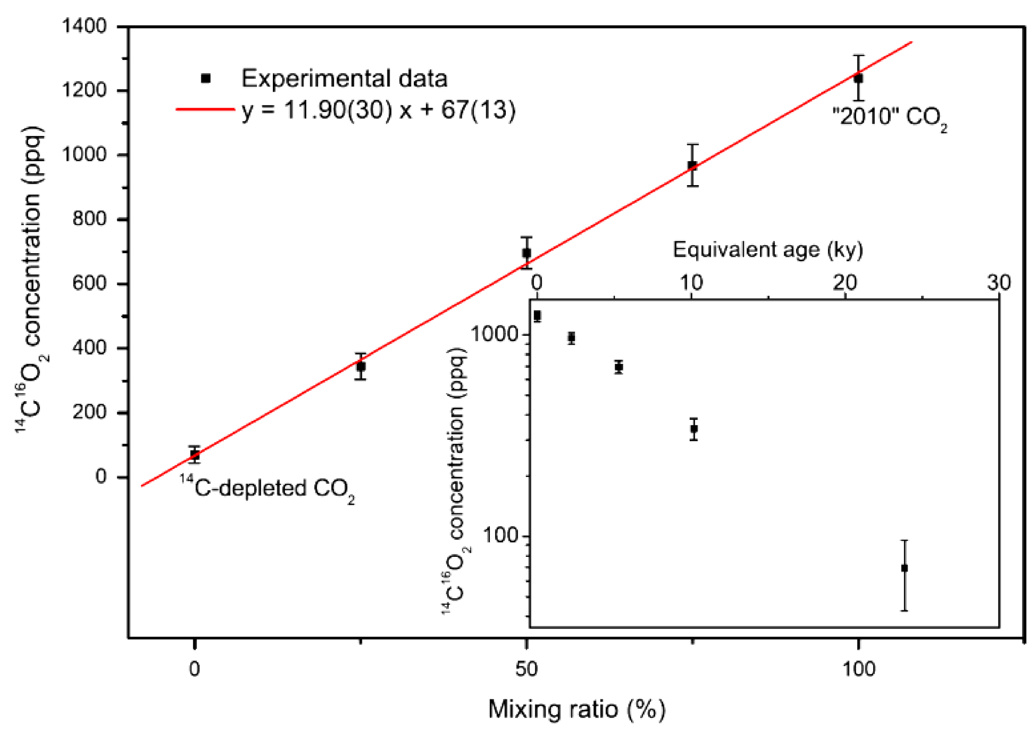
$$\Delta\nu = \frac{c}{2l}$$

of ringdown resonator shown on the left.

Radiocarbon-CO_2 Detection [2,3]

Literature Example of High Sensitivity of Sat-CRDS

- The actual minimum detectable concentration of $^{14}C^{16}O_2$ is 43 ppq.
- $^{14}C/C$ ratios in the present natural abundance samples could be measured with an accuracy of 3.5% in 1 h of averaging. This is merely about 1 order of magnitude worse than the best AMS isotopic ratio uncertainty with the same acquisition time.



Literature

[1] *C. Fehling, G. Friedrichs, Rev. Sci. Instrum. 81, 053109 (**2010**)*
[2] *I. Galli, et al., Phy. Rev. Lett. 104, 110801 (**2010**)*
[3] *I. Galli, et al., Phy. Rev. Lett. 107, 270802 (**2011**)*

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