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 halocarbon emissions?
- 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.

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 CO₂, CH₄, and N₂O 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:
  \[ I(t) = I₀ \exp\left(-\gamma_c t - \frac{t}{\tau_c}\right) \]

(d: decay time for the empty cavity, \( \gamma_c \): absorption coefficient)

Problem:

- \( \gamma_c \) Needs to be measured separately.
- Temporal and spectral variation of \( \gamma_c \).

Solution: Sat-CRDS

- At high laser power, non-linear absorption can occur due to the saturation phenomena.
  \[ \alpha(v) = \frac{\alpha(0)}{\sqrt{1 + S}} \]

Setup and First Data Example

- Laboratory 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 overtones absorption).

Radiocarbon-CO₂ Detection [2,3]

- The actual minimum detectable concentration of ^14C/CO₂ is 43 ppq.
- ^14C/CO₂ 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.

Evanescent-wave CRDS

- A novel cw-IR laser source (PPLN OPOs)

Sat-CRDS

- The mode spacing between two longitudinal modes
  \[ \Delta \nu = \frac{c}{\lambda} \]
  of ringdown resonator shown on the left.

Literature