Quantum Cascade Laser Cavity Ring Down Spectroscopy: New Method For the Characterization and Detection of Aerosols

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Abstract

Aerosolized chemical warfare agents (CWAs) and toxic industrial chemicals (TICs) are potential threats for the Warfighter, resulting in the need for aerosol identification and detection for further developments in protection and mitigation. One of the most reliable techniques for the identification of trace gas species is absorption spectroscopy. Cavity ring down spectroscopy (CRDS) is a highly sensitive and selective absorption method with the ability to detect trace levels of chemical species. Its advantage is based on the extremely long effective path length, providing precise detection of the rate of decay of light from a high finesse optical cavity to directly measure the absorption of the trace gas. The mid-wave (MWIR) and long-wave (LWIR) infrared regions are of particular interest due to the characteristic rotovibrational absorption bands exhibited in these regions for identification of a species. Quantum cascade lasers (QCLs) have the capability of emitting both infrared wavelength regions of 3-8 μm and 8-15 μm, respectively.

We have developed a new method for the characterization of aerosols by combining the highly powerful spectroscopic method of CRDS and the ability to detect in the infrared (IR) fingerprint region using QCLs for identification. This novel technique results in in-situ investigations of chemical aerosols. The development of this method and preliminary data on accepted test vapors and simulants, leading up to aerosols of CWAs, are presented.

Objective

To protect the Warfighter against exposure to aerosolized CWAs and TICs through development of better detection methods for a wide range of chemical concentrations in ambient air over real-time. This will be performed by constructing a CRDS within a rotating drum.

What Are Quantum Cascade Lasers?

QCLs are a new class of semiconductor lasers that emit in the mid-to-far IR region of the electromagnetic spectrum. The design takes advantage of quantum tunneling thus allowing one electron to emit a cascade of photons, hence the name "quantum cascade" lasers.

What Is Cavity Ring Down Spectroscopy?

CRDS is a highly sensitive absorption technique which measures the absolute optical extinction of a chemical species.

Combining QCLs with CRDS pairs a powerful laser capability operating in the MWIR and LWIR for unique spectral identification.

For CRDS you need:
(1) An excitation (laser) source
(2) A high finesse optical cavity where the light injected is reflected back and forth between two high reflectance (R> 99.99%+) mirrors
(3) A detector placed behind the cavity to record the light transmitted through the back mirror with each reflection over time

Basic Principles

Intensity of light transmitted (I) with each reflection will decrease as function of time (t):

$$I(t) = I_0 e^{(-t/\tau)}$$

I_0= initial detected light intensity;
τ= the ring-down time for intensity to reach 1/e of I_0

Ring-down time τ is dependent on:

$$\tau = L/[c\,(\ln R)]$$

L= distance between mirrors; R= mirror reflectivity; c= speed of light

When a chemical species (absorber) is present within the cavity, the ring-down time decreases due to the additional decay process of absorption:

$$I(t) = I_0 e^{(-t/\tau - \alpha ct)}$$

α= molecular absorption coefficient

Relationship between an empty cavity and one with the absorber present:

$$1/\tau' = 1/\tau + c\alpha$$

Absorbance of molecular species is determined directly.

Paired QCL and CRDS Capabilities

Once a laser pulse enters the high finesse optical cavity, the light bounces back and forth between the mirrors and with each pass a fraction of light is lost and signal collected by the detector. The result is a CRDS measuring the light absorption (loss of light) vs. excitation laser wavelength as shown in Figure 1.

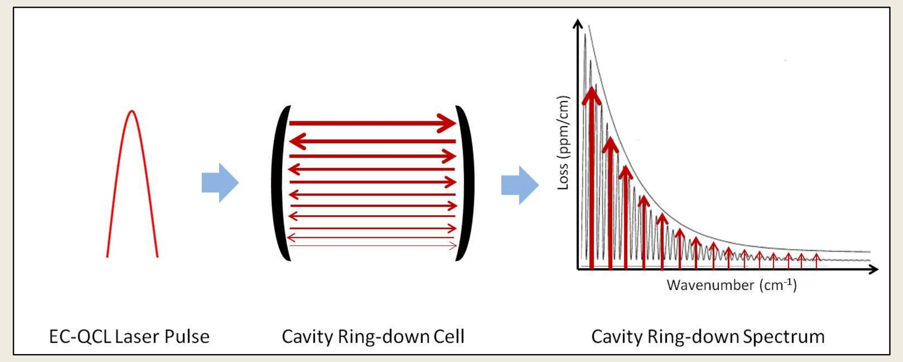

Figure 1. Paired QCL and cavity ring-down process. The schematic representation of a spectrum shown is one of an empty cavity, i.e. a background scan. This spectrum is also characteristic for any IR inactive carrier gas such as nitrogen, N_2.

When a chemical species (absorber) is present a spectrum much different from the background is recorded. Peaks characteristic of vibrational modes pertaining to the chemical species of interest are observed, yielding a unique fingerprint identification for the material present.

LGR Infrared Spectrometers and Results

Mid-Infrared Volatile Organic (MIRVOC) Analyzers by Los Gatos Research (LGR)

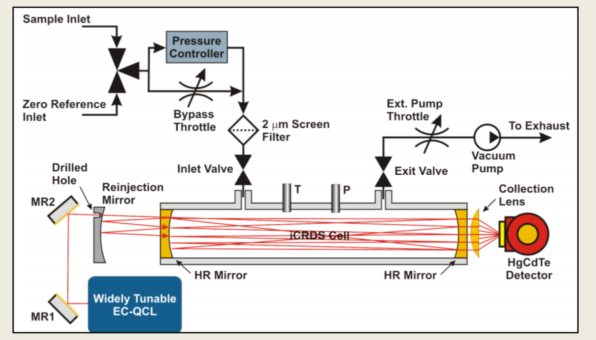

Figure 2. Schematic diagram of our instruments, the MIRVOC-1 and MIRVOC-2, with QCLs operating in ranges of 8.19-10.16 and 9.9-12.4 μm, respectively.*

Patented off-axis and re-injection mirror technology, boosts the circulating laser power and therefore increases sensitivity of measurements (Figure 2).

High reflectivity mirrors of R ≥ 99.99%, a cavity cell of approximately 1 meter length simulates a path length on the order of 10 kilometers. The sensitivity of the system is directly related to the path length and is illustrated by several spectra obtained for TICs and simulants in Figure 3. For this reason, CRDS has superior sensitivity compared to other absorption techniques.

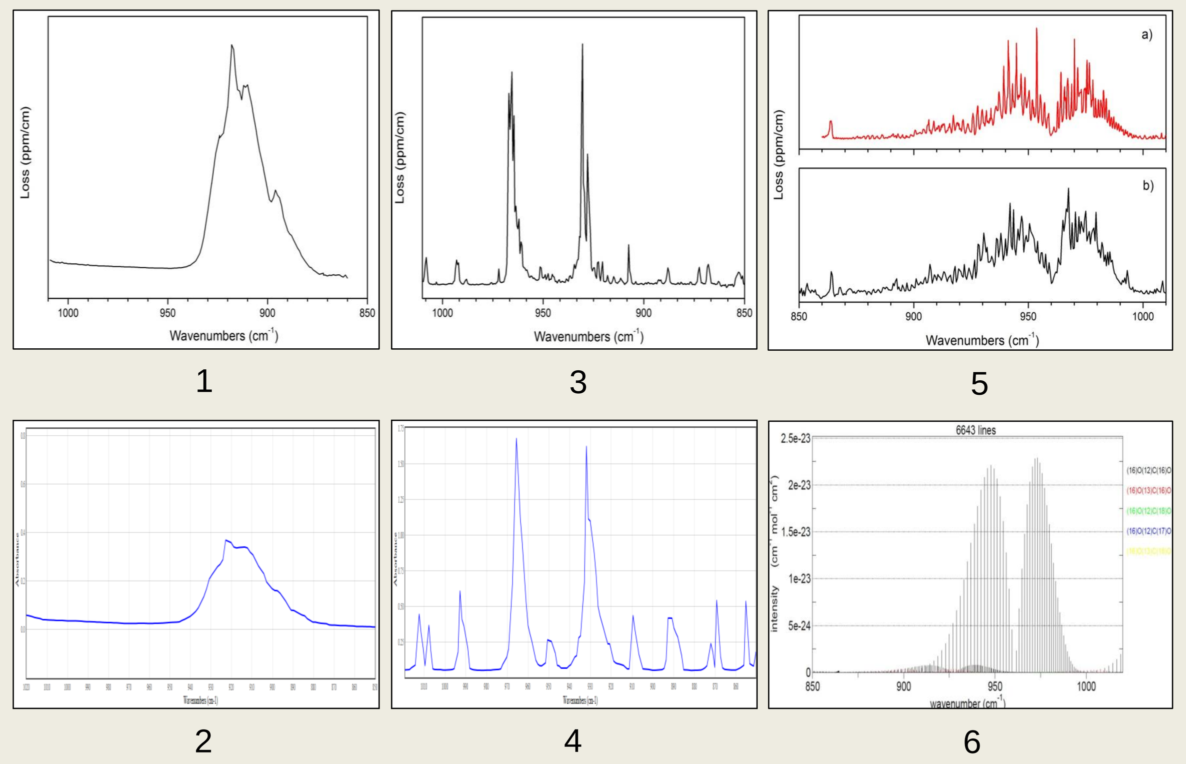

*Figure 3. 1) DMMP IR spectrum collected by our QCL-CRDS 2) DMMP IR spectrum from NIST** 3) NH_3 IR spectrum collected by our QCL-CRDS 4) NH_3 IR spectrum from NIST** 5a) CO_2 IR spectrum by LGR 5b) CO_2 spectrum collected by our QCL-CRDS 6) HITRAN model for CO_2 calculated using www.SpectralCalc.com*

*Diagram courtesy of J. Brian Leen, Los Gatos Research, Inc.
**P.J. Linstrom and W.G. Mallard, Eds.,NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, http://webbook.nist.gov

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Rotating Drum Modeling and Design

In aerosol sciences, the study of particles that are suspended over an extended period of time (~ 1 day) are essential for better characterization of the gas-particle or liquid-particle dynamics. However, gravitational settling is inevitably encountered in attempts to maintain suspension. Figure 4 illustrates our design of a rotating drum for elongating particle lifetimes for characterization of long-term properties. This is achieved through slow rotation of a horizontal cylindrical chamber about its axis and will ultimately allow for detection and characterization of CWAs of various particle sizes over a period of time.

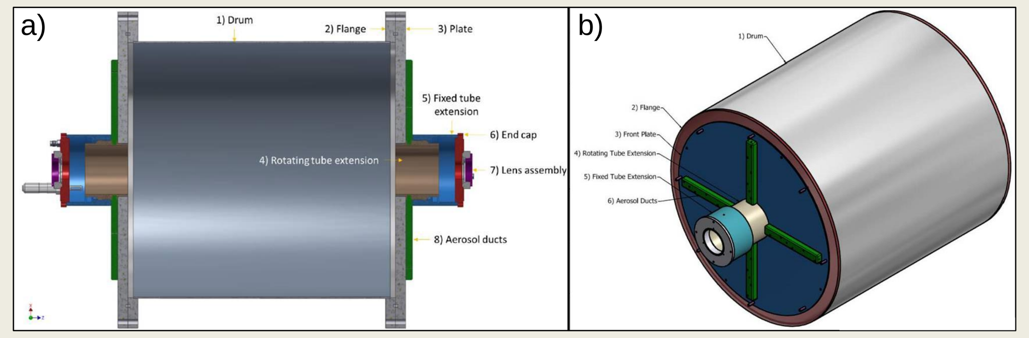

Figure 4. a) side view and b) end flange views of the stainless steel rotating drum for aerosol suspension. This drum is 24" x 24" (not including extension tubes) and weighs approximately 300 lbs.

This final design was based on the predicted particle flow modeling shown in Figure 5. Particle flow modeling is needed to predict the radial and axial velocities that will affect the distribution of particles in the drum. Hence, the drum includes tube extensions to isolate these flow fields from penetrating into the main chamber.

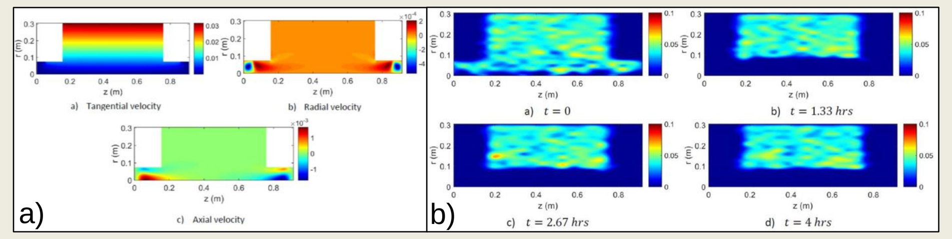

Figure 5. a) velocity contours and b) particle concentration distribution contours for the final design.

To accommodate the CRDS within the rotating drum, the tube extensions include space for the high reflectivity mirrors. Particle flow modeling predicts the centerline will be evacuated, as illustrated from Figure 6b for the optical path of the CRD spectrometer for vapor characterization.

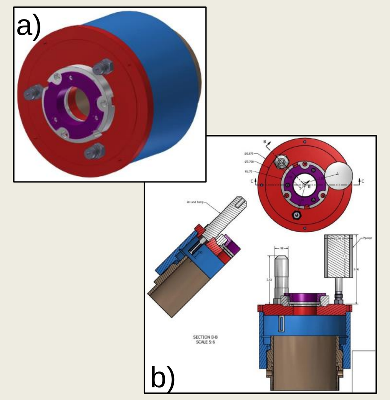

Figure 6. Optical assembly and accessories for a) aerosol introduction end and b) aerosol evacuation end. At the introduction end are 3 VCR ports for reaction gas, mixing gas, and relative humidity (RH) introduction. At evacuation end are ports for an RH and temperature sensor, pressure gauge, and VCR fitting to evacuate the chamber for cleaning.