

## CRDS with Cavity Mode-Based Frequency Axis for PPM-Level Quantitative Spectroscopy

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When acquiring absorption spectra for quantitative analysis of molecular mole fractions or isotope ratios, it is essential that the spectrometer have a stable, precise frequency axis. This presents a special challenge for the design of compact, field-deployable analyzers for environmental monitoring and similar applications. We describe the operation of a CRDS spectrometer that uses the ring-down cavity as its own optical frequency scale. While it is clear that a high-finesse cavity provides a convenient comb of longitudinal modes, the implementation of a spectrometer that relies on the CRDS cavity itself for its frequency axis has to contend with several practical obstacles: (1) the mode spacing of cavities of convenient length is generally substantial compared to the width of molecular absorption lines at moderate temperature and pressure; (2) the cavity modes are generally not aligned to the molecular features of interest; and (3) long-term stability of the longitudinal mode frequencies is not assured, especially when sampling gases of variable composition and therefore varying index of refraction. These difficulties can be overcome by a combination of measures: least-squares fitting of (relatively sparse) experimental spectra to a high-resolution spectral model; fine tuning of the cavity optical path length (OPL) to align the mode spectrum to the molecular spectrum; and stabilization of the cavity OPL using spectroscopic feedback from the measured spectrum of the analyzed gas sample. The CRDS spectrometer with cavity mode-based frequency axis reports molecular concentrations with very little sensitivity to undesired perturbations in cavity pressure, and improves in precision with averaging for intervals on the order of hours, permitting measurements with relative precision better than  $10^{-5}$ . Examples of precise analyses that have been demonstrated using this method include  $^{17}\text{O}$ -excess in water and molecular oxygen concentration in air.

