



NIR-cw-(ew)-CRDS: A Tool for Monitoring Isotope Ratios and Heterogeneous Chemistry

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The availability of tunable continuous wave (cw) diode lasers and highly reflective mirrors makes possible sensitive and high resolution absorption measurements in the near-infrared (NIR) spectral range based on cavity ringdown spectroscopy (CRDS). We present the results of several test measurements assessing the potential of NIR-CRDS by using a commercially available carbon dioxide analyzer (Picarro EnviroSense) for field applications and a home-made cw-CRD-spectrometer based on an external cavity diode laser (ECDL) system for laboratory studies.

On the one hand, quantitative isotope ratio measurements of CO₂ in air were measured by continuously scanning over rovibrational absorption lines of ¹²CO₂ and ¹³CO₂ at wavelengths around $\lambda = 1605$ nm. Using reference gas samples, a detection accuracy of $\Delta(\delta^{13}\text{C}) < 0.1\text{‰}$ was achieved, thus comparable to the detection accuracy of isotope ratio mass spectrometry. Moreover, the instrument was successfully operated in combination with a water-air equilibrator showing its potential for simultaneous and continuous field measurements of pCO₂ and $\delta^{13}\text{C}$ in seawater samples. On the other hand, the home-made spectrometer working in the spectral range from 1625 - 1690 nm is especially well suited for trace gas detection and isotope studies in natural environments since several atmospherically relevant gas phase species such as CH₄, N₂O, and - due to CH-overtone vibrations - many halogenated hydrocarbons show strong absorption compared to the inevitable water background. The spectrometer can also be operated in evanescent wave (ew) configuration by placing a specially designed quartz prism within the ringdown cavity. This setup permits a sensitive and selective detection of molecules at the quartz sample surface and thus enables gas-solid interaction studies.