

Frontiers of QC Laser spectroscopy for high precision isotope ratio analysis of greenhouse gases

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An important milestone for laser spectroscopy was achieved when isotope ratios of greenhouse gases were reported at precision levels that allow addressing research questions in environmental sciences. Real-time data with high temporal resolution at moderate cost and instrument size make the optical approach highly attractive, complementary to the well-established isotope-ratio mass-spectrometry (IRMS) method. Especially appealing, in comparison to IRMS, is the inherent specificity to structural isomers having the same molecular mass.

Direct absorption in the MIR in single or dual QCL configuration has proven highly reliable for the stable isotopes of CO₂, N₂O and CH₄. The longest time series of real-time measurements is currently available for $\delta^{13}\text{C}$ and $\delta^{18}\text{O}$ in CO₂ at the high-alpine station Jungfraujoch. At this well-equipped site, QCL based direct absorption spectroscopy (QCLAS) measurements are ongoing since 2008^{1,2}.

Applications of QCLAS for N₂O and CH₄ stable isotopes are considerably more challenging because of the lower atmospheric mixing ratios, especially for the less abundant species, such as N₂¹⁸O and CH₃D. For high precision (<0.1 ‰) measurements in ambient air, QCLAS may be combined with a fully automated preconcentration unit yielding an up to 500 times concentration increase and the capability to separate the target gas from spectral interferants by sequential desorption³.

Here, we review our recent developments on high precision isotope ratio analysis of greenhouse gases, with special focus on the isotopic species of N₂O and CH₄. Furthermore, we show environmental applications illustrating the highly valuable information that isotope ratios of atmospheric trace gases can carry. For example, the intramolecular distribution of ¹⁵N in N₂O gives important information on the geochemical cycle of N₂O⁴⁻⁶, while the analysis of $\delta^{13}\text{C}$ and δD in CH₄ may be applied to disentangle microbial, fossil and landfill sources⁷.

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