



Towards absolute laser spectroscopic CO₂ isotope ratio measurements

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Knowledge of isotope composition of carbon dioxide (CO₂) in the atmosphere is necessary to identify sources and sinks of this key greenhouse gas. In the last years, laser spectroscopic techniques such as cavity ring-down spectroscopy (CRDS) and tunable diode laser absorption spectroscopy (TDLAS) have been shown to perform accurate isotope ratio measurements for CO₂ and other gases like water vapour (H₂O) [1,2]. Typically, isotope ratios are reported in literature referring to reference materials provided by e.g. the International Atomic Energy Agency (IAEA). However, there could be some benefit if field deployable absolute isotope ratio measurement methods were developed to address issues such as exhausted reference material like the Pee Dee Belemnite (PDB) standard. Absolute isotope ratio measurements would be particularly important for situations where reference materials do not even exist.

Here, we present CRDS and TDLAS-based absolute isotope ratios (¹³C/¹²C) in atmospheric CO₂. We demonstrate the capabilities of the used methods by measuring CO₂ isotope ratios in gas standards. We compare our results to values reported for the isotope certified gas standards. Guide to the expression of uncertainty in measurement (GUM) compliant uncertainty budgets on the CRDS and TDLAS absolute isotope ratio measurements are presented, and traceability is addressed. We outline the current impediments in realizing high accuracy absolute isotope ratio measurements using laser spectroscopic methods, propose solutions and the way forward.

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References

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