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Quantum cascade laser absorption spectrometer with a low temperature multipass cell for precision clumped $^{12}C^{18}O_2$ measurement

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High precision measurement of multiply substituted ("clumped") isotopologues of CO_2 is a topic of significant interest in the fields of isotope geochemistry and paleoclimate research [1, 2]. The temperature-dependent behavior of ^{13}C and ^{18}O isotopes in gaseous carbon dioxide is widely used as a temperature proxy for paleoclimate reconstruction. The basis for it lies in the temperature dependence of the equilibrium constant, K(T), of the isotope exchange reactions $^{12}C^{18}O_2 + {}^{12}C^{16}O_2 \rightleftharpoons 2{}^{12}C^{16}O^{18}O$ and $^{13}C^{16}O^{18}O + {}^{12}C^{16}O_2 \rightleftharpoons {}^{13}C^{16}O_2 + {}^{12}C^{16}O^{18}O$ [3, 4] as these reactions have a slight tendency to move towards the right at higher temperatures. Currently, the established method to perform clumped isotope thermometry is Isotope Ratio Mass Spectrometry (IRMS) [5]. However, IRMS measurements, in particular for rare isotopologues, typically require several hours of analysis time and extensive sample preparation to properly separate isobaric interferences. In contrast to IRMS, optical absorption spectroscopic techniques allow the realisation of isotopologue specific, non-destructive, and compact spectrometers with short analysis time and high-precision capabilities. Recently, Wang et al. [6], Prokhorov et al. [3], and Nataraj et al. [4] have demonstrated the great promise of laser absorption spectroscopy for measurements of clumped isotopes of carbon dioxide.

The major challenge for clumped isotope thermometry using $^{12}C^{18}O_2$ resides in its very low natural relative abundance (4.1 ppm) and the spectral interference from the major ($^{12}C^{16}O_2$) and singly substituted isotopologues. These factors seriously limit the achievable analytical performance of spectroscopic measurements and thus the applicability of this technique. However, the interference caused by the hot-band transitions of the abundant species can be suppressed by reducing the gas temperature. Moreover, working at low pressure (5 mbar) narrows the absorption lines and reduces the overlap between neighbouring transitions.

Here, we present a novel quantum cascade laser absorption spectrometer (QCLAS) employing a low-volume segmented circular multipass cell (SC-MPC) [7] operated at cryogenic temperatures (153 K) and low pressure (5 mbar). For the first time, we optically measure the abundances of all three isotopologues involved in the reaction $^{12}C^{18}O_2 + {}^{12}C^{16}O_2 \rightleftharpoons 2{}^{12}C^{16}O^{18}O$ simultaneously. We report a precision of 0.05 ‰ in the isotope ratios [$^{12}C^{18}O_2/{}^{12}C^{16}O_2$] and [$^{12}C^{16}O^{18}O/{}^{12}C^{16}O_2$] with 25

s integration time. In addition, we determine and resolve the tiny variation in the equilibrium constant, K(T), of the above exchange reaction for carbon-dioxide samples equilibrated at 300 K and 1273 K, respectively. This versatile system can be extended to other chemical species where spectroscopic measurements are impacted by the hot-band transitions of abundant isotopologues — (e.g., methane and its deuterated isotopologues, CH_3D and CH_2D_2, or propane and the two isotopomers, $^{12}CH_3{}^{13}CH_2{}^{12}CH_3$ and $^{13}CH_3{}^{12}CH_2{}^{12}CH_3$) — thereby opening up new perspectives in environmental sciences and fundamental research.

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