

Cool mid-IR Absorption Spectroscopy of cold Molecules

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Abstract: We present a QCL based absorption spectroscopy setup with a Stirling cooled circular multipass absorption cell at 150 K. We report the first high-precision measurements of clumped $^{12}\text{C}^{18}\text{O}_2$ and $^{12}\text{C}^{17}\text{O}^{18}\text{O}$, and of site-specific propane isotopomers. © 2022 The Author(s)

1. Introduction

High-precision measurements of multiply substituted (clumped) isotopes or site-specific isotopomers are topics of great interest, e.g. in the field of isotope geochemistry. Examples include the temperature-dependent abundance of clumped CO_2 ($^{12}\text{C}^{18}\text{O}^{18}\text{O}$) or the intramolecular distribution of ^{13}C in propane, i.e. the relative abundance of central ($2\text{-}^{13}\text{C}$) and terminal ($1\text{-}^{13}\text{C}$) isotopomers. In both examples, the information on isotopic composition helps to constrain source attribution, mechanisms of formation and destruction, and temperature histories of the respective molecules.

The established method to perform both clumped isotope thermometry and position-specific isotope analysis is Isotope Ratio Mass Spectrometry (IRMS) [1,2]. However, IRMS measurements, in particular for rare isotopologues, typically require very demanding instruments, several hours of analysis time and extensive sample preparation to separate isobaric interferences.

The main experimental challenge to optically measure $^{12}\text{C}^{18}\text{O}_2$ (natural abundance 3.95×10^{-6}) is the large spectral interference caused by the most abundant $^{12}\text{C}^{16}\text{O}_2$ isotopologue. This can be largely overcome by measuring CO_2 at low temperature, i.e. close to its sublimation point. Thereby, the strength of the hot band transitions of the main isotopologue are substantially reduced. This strategy is also useful for propane, because it accentuates the fine-structure of the absorption features and reduces the strong, broadband background signal, which is due to unresolved absorption by hot-band transition.

2. Experimental setup

The experimental setup is based on a thermoelectrically cooled, distributed feedback (DFB) quantum cascade laser emitting either at 2305 cm^{-1} or at 1384 cm^{-1} . The laser is operated in intermittent continuous wave (iCW) mode [3] with a repetition rate of 6.5 kHz. Its beam passes through a compact circular multipass cell (MPC) [4] with an optical path length of 6 m, cooled with a Stirling-type cryo-cooler, kept in a vacuum chamber that is maintained at $5 \cdot 10^{-5}$ mbar [Fig.1].

3. Carbon dioxide, including clumped $^{12}\text{C}^{18}\text{O}_2$

The sample is cooled to 153 K, i.e. close to the sublimation point at 10 mbar. This enables efficient suppression of interfering hot-band transitions of the more abundant isotopic species and thereby enhances analytical precision. This is illustrated by measuring the amount fractions of all three CO_2 isotopologues involved in the kinetic isotope exchange reaction of $^{12}\text{C}^{16}\text{O}_2 + ^{12}\text{C}^{18}\text{O}_2 \rightleftharpoons 2 \cdot ^{12}\text{C}^{16}\text{O}^{18}\text{O}$. The precision in the ratios $[^{12}\text{C}^{18}\text{O}_2]/[^{12}\text{C}^{16}\text{O}_2]$ and $[^{12}\text{C}^{16}\text{O}^{18}\text{O}]/[^{12}\text{C}^{16}\text{O}_2]$ is 0.05 ‰ with 25 s integration time. The accuracy is confirmed by agreement with literature values of the equilibrium constant, K , of the above exchange reaction for carbon-dioxide samples equilibrated at 300 K and 1273 K. An example of the repeatability of $\delta^{12}\text{C}^{18}\text{O}^{18}\text{O}$ and $\delta^{12}\text{C}^{16}\text{O}^{18}\text{O}$ measurements is given in Fig [1].

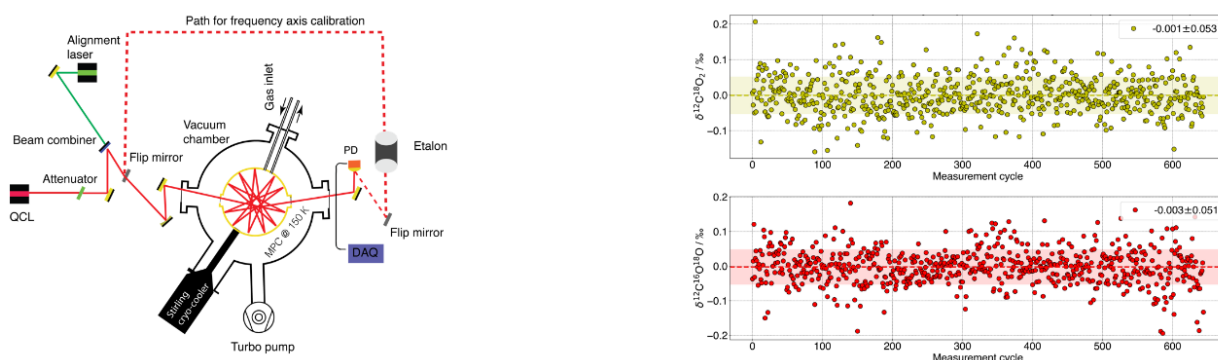


Fig.1. Left: Schematic of the setup. Right: Repeatability of $\delta^{12}\text{C}^{18}\text{O}^{18}\text{O}$ and $\delta^{12}\text{C}^{16}\text{O}^{18}\text{O}$.

4. Central and terminal propane

We further demonstrate the capability of the setup by acquiring the first high-resolution spectra of propane and its site-specific isotopomers ($1\text{-}^{13}\text{C}$ and $2\text{-}^{13}\text{C}$). In mixtures containing ^{12}C , $1\text{-}^{13}\text{C}$ and $2\text{-}^{13}\text{C}$ propane, we distinguish their individual contributions to the overall absorption spectrum [Fig. 2]. We demonstrate a precision better than 0.1 ‰ for both isotopocule ratios ($2\text{-}^{13}\text{C}/^{12}\text{C}$ and $(1\text{-}^{13}\text{C})/^{12}\text{C}$).

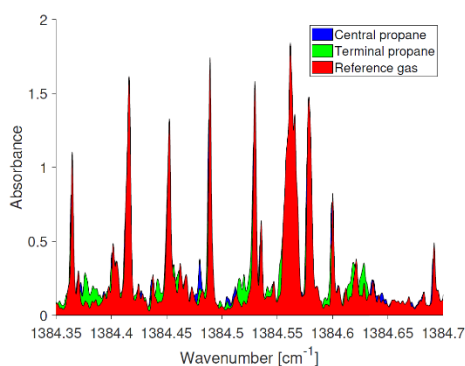


Fig. 2. Measured propane spectra of reference (red), spiked central only (blue) and spiked terminal only (green). Pure propane is spiked by both 2.5 % $1\text{-}^{13}\text{C}$ -propane and $2\text{-}^{13}\text{C}$ -propane.

5. References

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