



Low-temperature mid-IR absorption spectroscopy for isotopomer-specific measurements

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The measurement of singly substituted, stable isotopologues, such as $^{13}\text{CO}_2$, by mid-IR spectroscopy is well established. In addition, there is a great interest to exploit the information carried by more exotic isotopologues, i.e. of low abundance, multiply substituted (clumped) isotopic species or site-specific isotopomers. This information on isotopic composition can be used as proxy to constrain formation pathways, source attribution, temperature histories or dating (radioactive isotopes) of the respective molecules. The established method to perform such isotopic analysis is isotope ratio mass spectrometry (IRMS). This approach, however, in particular for rare isotopologues, typically requires very demanding instruments, several hours of analysis time and extensive sample preparation to separate isobaric interferences.

Here, we demonstrate an alternative analytical method based on optical interrogation of the molecules by directly probing their ro-vibrational frequencies. This makes the method inherently suitable to distinguish between isotopomers (structural isomers). Furthermore, we propose a low temperature approach that substantially reduces the spectral interferences due to hot-band transitions of more abundant isotopologues. The effectiveness and versatility of this strategy are highlighted by three different applications: i) high-precision mid-IR measurements of clumped $^{12}\text{C}^{18}\text{O}_2$, ii) the detection of $^{14}\text{CO}_2$ in enriched CO_2 samples, and iii) a new scheme for determination of the intramolecular distribution (terminal and central positions) of ^{13}C in propane.

We developed a quantum cascade laser (QCL) spectrometer using a Stirling-cooled circular multipass absorption cell. The distributed feedback (DFB) QCL is driven in intermittent continuous wave (iCW) mode [1] with a repetition rate of 6.5 kHz. Its beam passes through a compact segmented circular multipass cell (SC-MPC) [2] with an optical path length of 6 m. The SC-MPC is placed in a vacuum chamber that is maintained at 5×10^{-5} mbar and cooled down to 150 K.

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. Its accuracy is confirmed by agreement with literature values of the equilibrium constant, K , of the exchange reaction for CO_2 samples equilibrated at 300 K and 1273 K [3].

As proof of concept, we adapted the system to allow the detection of the radiocarbon ^{14}C in enriched CO_2 samples. Due to its ultra-low abundance (10^{-12}), the absorption signatures of this isotopic species is completely hidden by the spectral contributions of the other, more abundant,

CO₂ isotopologues. Therefore, it is the perfect candidate for low-temperature spectroscopy. We present first results on ¹⁴CO₂ with a precision of 50 ppt.

And finally, we demonstrate the first high-resolution spectra of propane and its site-specific isotopomers (1-¹³C and 2-¹³C). We distinguish their individual contributions to the overall absorption spectrum and show a precision better than 0.1 ‰ for both isotopomer ratios (2-¹³C)/¹²C and (1-¹³C)/¹²C.

[1] M. Fischer et al., Opt. Express, 22(6), 7014–7027 (2014), doi: 10.1364/OE.22.007014.

[2] M. Graf, L. Emmenegger, and B. Tuzson, Opt. Lett., 43(11), 2434-2437, (2018), doi: 10.1364/OL.43.002434.

[3] A. Nataraj et al. Opt. Express 30, 4631-4641 (2022): doi.org/10.1364/OE.447172.