Measurement of $^{13}CH_4/^{12}CH_4$ ratios in air using diode-pumped 3.3 μm difference-frequency generation in PPLN

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Methane has a significant effect on the radiative balance of the troposphere and stratosphere because it has a strong absorption at 7.66 μm where carbon dioxide and water absorb only weakly. Accurate measurements of the abundance of methane are thus of considerable interest to climatologists.[1] Previously, we demonstrated a spectrometer capable of producing fast, accurate measurements of the methane mixing ratios in natural air samples. This system demonstrated a relative accuracy of less than 10^{-9} mol/mol (1 ppb by volume),[2] which is comparable to what can be achieved using non-spectroscopic methods. This system employed bulk periodically poled lithium niobate pumped by a solitary diode laser at 808 nm and a diode-pumped monolithic ring Nd:YAG laser at 1064 nm, and a multi-pass absorption cell with 18 m path length.

We generated approximately 1 μW of infrared radiation at 3019 cm^{-1} using 21 mW from a grating-tuned extended-cavity diode laser at 806 nm and 382 mW from a diode-laser-pumped Nd:YAG laser at 1064 nm to pump a periodically poled lithium niobate crystal. At this wavelength, a coincidence between the Q(1) line of $^{12}CH_4$ and the R(0) line of $^{13}CH_4$ allows both lines to be observed in a single 10 GHz frequency scan of the difference frequency and avoids significant interference from other lines. The difference frequency output is monitored by a liquid-N_2-cooled InSb detector and sent through a commercial multi-pass cell with an 18 m path length to a second liquid-N_2-cooled InSb detector. The signal from the first detector is used to stabilize the amplitude of the generated light by controlling the power of the Nd:YAG beam with an acousto-optic modulator. Background interference fringes from the multi-pass cell are reduced by vibrating it with an electromagnetic actuator at the frequency of a mechanical resonance in the mirror mounts.

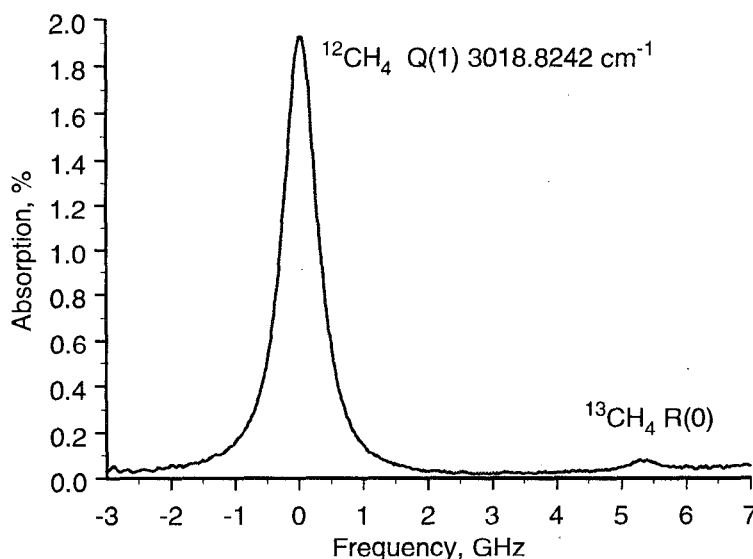A typical spectral trace is shown in Figure 1. The cell contained a sample of natural air at a

Figure 1-Direct absorption spectrum of methane in natural air at 13 kPa (100 Torr) in a multi-pass cell with 18 m path length.

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pressure of 13 kPa (100 Torr). Total measurement time was 60 s, during which 1000 sweeps were averaged resulting in a noise bandwidth of 1.6 Hz. The peak CH_4 absorption amplitudes were determined by a nonlinear least squares fit to Voigt line profiles. The $^{13}CH_4/^{12}CH_4$ ratios were then computed using Hitran catalog values for the line strengths.[3]

The absorptance ratio for the trace shown in Figure 1 is 54 ± 3, which yields a concentration ratio of 95 ± 5. This corresponds to an isotope value relative to the PeeDee belemnite (PDB) standard of -66 ± 44 per mil. The expected isotope value is -47 ± 2 per mil. The accuracy of our measurement is limited by the signal-to-noise ratio (SNR) in the acquired spectra, and the SNR is limited primarily by detector noise.

Once waveguide PPLN crystals become available, it should be simple to generate enough 3 μm power to have shot noise be the dominant limit, even with a longer path length. It should be possible to improve the accuracy of this measurement by an order of magnitude before interference fringes from scattered light in the multi-pass cell become the dominant limit.

Our accuracy for measuring the isotope value relative to PDB of ± 44 per mil is roughly comparable to that achieved by Bergamaschi, Schupp, and Harris using a lead-salt tunable diode-laser absorption spectrometer.[4] They demonstrated an accuracy of ± 0.5 per mil on samples which had 50 ppm CH_4. Our system would have an accuracy of ± 1.4 per mil when analyzing sample of that concentration. Using sample processing and concentration and an isotope ratio mass spectrometer, Stevens and Rust achieved an accuracy of ± 0.06 per mil.[5] We do not envision being able to achieve that kind of accuracy for methane carbon isotope measurements without concentrating the gas sample.

Because this system is compact, uses all solid-state lasers, and could be made transportable, it has potential applications for field measurements where rapid, nondestructive concentration and isotope ratio measurements are needed. Even though it is not competitive with state-of-the-art nonoptical instruments, this system can measure $^{13}CH_4/^{12}CH_4$ ratios at CH_4 concentrations of only $1.6 \cdot 10^{-6}$ mol/mol without gas processing.

References

1. E. J. Dlugokencky, L. P. Steele, P. M. Lang, K. A. Masarie, "The growth rate and distribution of atmospheric methane," J. Geophys. Res. **99**, 17021 (1994).
2. K. P. Petrov, S. Waltman, E. J. Dlugokencky, M. Arbore, M. M. Fejer, F. K. Tittel, and L. W. Hollberg, "Precise measurement of methane in air using diode-pumped 3.4 μm difference-frequency generation in PPLN," Applied Physics B, **64** No. 5 (in press) (1997).
3. L. S. Rothman, et al., "The HITRAN molecular database: editions of 1991 and 1992," J. Quant. Spectrosc. Radiat. Transf. (UK) **48**, 469 (1992).
4. P. Bergamaschi, M. Schupp, G. Harris, "High precision direct measurements of $^{13}CH_4/^{12}CH_4$ and $^{12}CH_3D/^{12}CH_4$ ratios in atmospheric methane sources by means of a long-path tunable diode laser absorption spectrometer," Appl. Opt. **33**, 7704-7716 (1994).
5. C. M. Stevens, F. E. Rust, "The carbon isotopic composition of atmospheric methane," J. Geophys. Res. **87** 4879 (1982).