



Proceedings Photoacoustic Detection of Short-Chained Hydrocarbon Isotopologues *

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Abstract: We report, to our knowledge, the first optical detection of the main isotopologues of short-chained hydrocarbons. The sensor system is based on photoacoustic (also known as optoacoustic) spectroscopy (PAS, OAS). This technique takes advantage of the fact that absorbed electromagnetic radiation is partially transferred into kinetic energy via inelastic molecular collisions. This is equivalent to a temperature increase of the irradiated volume. If the radiation is modulated, a pressure wave with an amplitude proportional to the concentration of the absorbing molecules is generated, the so called PA (OA) signal. Two continuous wave (cw), thermoelectrically cooled (TEC), distributed feedback interband cascade lasers (DFB-ICLs) with emission wavelengths around 3.33 and 3.38 μ m, respectively, serve as light sources. The PA signal is detected with a microphone and phase-sensitively amplified. The new sensor is applied for the stable carbon isotope-selective analyses of methane (CH4), ethane (C2H6) and propane (C3H8). We report first measurements of 1^2 C2H6, 1^3 C1²CH6 and 1^3 C2H6 as well as of 1^2 C3H8 and 1^3 C1²C2H8, all at approximate room temperature and atmospheric pressure. The listed isotopologues were selected because of their importance for numerous applications from atmospheric and planetary research to natural gas exploration.

Keywords: photoacoustic; spectroscopy; PAS; ethane; propane; carbon isotope; interband cascade laser; ICL; mid-infrared; MIR

1. Introduction

The measurement of hydrocarbon concentrations is essential to many applications from medical diagnostics and environmental research to natural gas exploration and planetary research [1–3]. In many cases, even the isotopic composition of a certain hydrocarbon has to be known to acquire certain information. The measurement of the methane isotope ratio (¹³CH₄ : ¹²CH₄), for instance, is critical to understanding the earth's carbon cycle [4].

Anthropogenic fossil fuel consumption generates approximately 8 gigatons of atmospheric carbon per year (GtC/year). The arctic permafrost reservoir, however, is estimated to enclose at least 600 GtC while the earth's oceans contain more than 11,000 GtC. A release of only a small fraction of the oceanic or permafrost reservoirs due to a temperature increase of the polar troposphere would lead to serious climate effects. Evidence for previous outflow of hydrocarbons from these sources is provided. Their isotope ratio allows tracing the outflows back to their various ecological or anthropogenic sources [4]. The mixing ratios of ethane and other non-methane hydrocarbons (NMHC) are useful indicators of atmospheric oxidation and transport processes on regional up to

global scales. Although the number of NMHC isotopologue studies is still quite limited, the stable carbon isotope ratio measurements can provide additional insight into its sources, sinks and distribution in the atmosphere and allows estimating the photochemical age of each hydrocarbon. Altogether this information can help verify and constrain atmospheric models [5–7].

For the past 30 years, the gold standard for the detection of carbon isotopes has been the isotope-ratio mass spectrometry (IRMS). This technique is extraordinarily precise but expensive and quite complex and, therefore, usually carried out at an off-site facility, which makes real-time and in-situ measurements impossible. Furthermore, the hydrocarbon must be converted into CO₂ by burning prior to analysis which destroys the sample and makes the method an indirect one [8].

A further development of the isotope ratio measurement techniques is, therefore, highly desirable. In a previous study, infrared absorption cross sections of the ethane and propane isotopologues were measured in the mid-infrared (MIR) range using an FTIR spectrometer [9]. The aim of this project is to develop an optical sensor that allows direct isotope-selective measurement of short-chained hydrocarbon.

2. Materials and Methods

The new analyzer applies distributed feedback interband cascade lasers (DFB-ICLs). These recently introduced emission sources enable continuous wave radiation in the MIR between 3 μ m and 6 μ m at room temperature operation [10]. This spectral region coincides with the strongest absorption of hydrocarbons. The lasers are compact and easy to use and their intrinsic DFB structure allows continuous and mode-hop free wavelength tuning with a spectral linewidth below 10 MHz. Due to its advantageous properties, photoacoustic spectroscopy (PAS) is applied [11]. This technique is based on the absorption of modulated radiation and its transformation into a sound wave [12,13]. As an offset-free technique, it enables extremely high detection sensitivity. Figure 1 shows the experimental setup as block diagram.



Figure 1. Experimental setup of the photoacoustic sensor system.

3. Results

Measurements were performed on the main stable carbon isotopologues of methane (CH₄), ethane (C₂H₆) and propane (C₃H₈). Figure 2 shows exemplary photoacoustic spectra of ${}^{12}C_{2}H_{6}$ and ${}^{13}C_{2}H_{6}$, each approximately 1% in N₂, and of a mixture of the two isotopologues (each 1% in N₂). All measurements were recorded at approximate room temperature and atmospheric pressure.



Figure 2. Photoacoustic spectra of ¹²C₂H₆, ¹³C₂H₆ and a mixture of both isotopologues (ca. 20 °C; 1013 hPa).

4. Conclusions

The new optical analyzer is compact and robust and allows the measurement of hydrocarbon isotopologues directly, in real-time and in-situ for various applications. The detection sensitivity is in the parts-per-million range.

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References

- 1. Atkinson, R. Gas-phase tropospheric chemistry of organic compounds: A review. *Atmos. Environ. Part A. General Topics* **1990**, 24, 1–41.
- 2. Faramawy, S.; Zaki, T.; Sakr, A.-E. Natural gas origin, composition and processing: A review. J. Nat. Gas Sci. Eng. 2016, 34, 34–54.
- 3. Villanueva, G. L.; Mumma, M. J.; Magee-Sauer, K. Ethane in planetary and cometary atmospheres: Transmittance and fluorescence models of the v7 band at 3.3 μm. *J. Geophys. Res.* **2011**, *116*, E08012.
- 4. Witinski, M.F.; Sayres, D.S.; Anderson, J.G. High precision methane isotopologue ratio measurements at ambient mixing ratios using integrated cavity output spectroscopy. *Appl. Phys. B* **2011**, *102*, 375–380.
- Saito, T.; Stein, O.; Tsunogai, U.; Kawamura, K.; Nakatsuka, T.; Gamo T. et al. Stable carbon isotope ratios of ethane over the North Pacific: Atmospheric measurements and global chemical transport modeling. *J. Geophys. Res.* 2011, 116, D02308.
- 6. Rudolph, J.; Czuba, E. On the use of isotopic composition measurements of volatile organic compounds to determine the "photochemical age" of an air mass. *Geophys. Res. Lett.* **2000**, *27*, 3865–3868.
- Saito, T.; Kawamura, K.; Tsunogai, U.; Chen, T.-Y.; Matsueda, H.; Nakatsuka T., et al. Photochemical histories of nonmethane hydrocarbons inferred from their stable carbon isotope ratio measurements over east Asia. J. Geophys. Res. 2009, 114, D11303.
- 8. Sessions, A.L. Isotope-ratio detection for gas chromatography. J. Sep. Sci. 2006, 29, 1946–1961.
- Loh, A.; Wolff, M. Absorption cross sections of ¹³C ethane and propane isotopologues in the 3 μm region. JQSRT 2017, 203, 517–521.
- 10. Vurgaftman, I., et al. Interband cascade lasers. J. Phys. D: Appl. Phys. 2015, 48, 123001.

- 11. Wolff, M.; Rhein, S.; Bruhns, H.; Nähle, L.; Fischer, M.; Koeth, J. Photoacoustic methane detection using a novel DFB-type diode laser at 3.3 μm. *Sens. Actuator B: Chem.* **2013**, *187*, 574–577.
- 12. Bell, A.G. On the production and reproduction of sound by light. *AJS* **1880**, *3*, 305–324.
- 13. Michaelian, K.H. *Photoacoustic IR spectroscopy*, Wiley-VCH: Weinheim, Germany; [Chichester, England], 2010.



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