



Simultaneous detection of ambient methane, nitrous oxide, and water vapor using an external-cavity quantum cascade laser



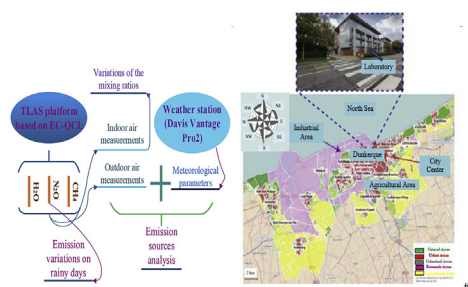
Xiaojuan Cui^{a,b}, Fengzhong Dong^{a,b,*}, Zhirong Zhang^{a,b}, Pengshuai Sun^a, Hua Xia^{a,b}, Eric Fertein^c, Weidong Chen^{c,**}

^a Anhui Provincial Key Laboratory of Photonic Devices and Materials, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, 230031, Hefei, China

^b Key Laboratory of Environmental Optics and Technology, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, 230031, Hefei, China

^c Laboratoire de Physicochimie de l'Atmosphère, Université du Littoral Côte d'Opale, 59140 Dunkerque, France

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:

Methane emission
Nitrous oxide emission
Water vapor
Mid-infrared
EC-QCL

ABSTRACT

A compact laser-based absorption sensor system associated with a 152-m path length absorption cell for simultaneous second harmonic (2f) detection of atmospheric nitrous oxide (N₂O), methane (CH₄), and water vapor (H₂O) is presented. An 8 μm external cavity quantum cascade laser (EC-QCL) was used as an excitation source to simultaneously target three neighboring absorption lines, N₂O at 1255.424 cm⁻¹, CH₄ at 1255.000 cm⁻¹, and H₂O at 1254.732 cm⁻¹. Minimum detection limits (1σ) of 0.9 ppb for N₂O, 4.8 ppb for CH₄ and 31 ppm for H₂O were achieved with a 1-s integration time at an optimum pressure of 50 Torr. Both laboratory and atmospheric environmental mixing ratios of these three gases associated with basic meteorological parameters were recorded and the corresponding emission sources were analyzed. In particular, the N₂O emission was studied during extended time periods including rainy intervals.

1. Introduction

Methane (CH₄), nitrous oxide (N₂O), and water vapor (H₂O) are three major atmospheric greenhouse gases and sensitive indicators for climate change and temperature variability (Liu et al., 2012; MacDonald et al., 2006; Loulergue et al., 2008; Montzka et al., 2011;

Höhne et al., 2011). CH₄ is the second most important greenhouse gas after carbon dioxide (CO₂), contributes to the increase in global warming with a lifetime of about 9 years and an atmospheric mixing ratio of ~1.8 ppm (Prather et al., 2012). It is emitted into the atmosphere by natural sources as well as anthropogenic activities (Walter et al., 2006; Wang et al., 2015). N₂O has a longer atmospheric lifetime

* Corresponding author. Anhui Provincial Key Laboratory of Photonic Devices and Materials, Anhui Institute of Optics and Fine Mechanics, Chinese Academy of Sciences, 230031, Hefei, China.

** Corresponding author.

E-mail addresses: fzdong@aiofm.ac.cn (F. Dong), chen@univ-littoral.fr (W. Chen).

<https://doi.org/10.1016/j.atmosenv.2018.07.001>

Received 23 August 2017; Received in revised form 25 June 2018; Accepted 1 July 2018

Available online 04 July 2018

1352-2310/ © 2018 Elsevier Ltd. All rights reserved.

(131 years) and exceeds the global warming potential of CO₂ by 310 times (Prather et al., 2012; Stocker et al., 2013). Atmospheric N₂O is currently around a level of 330 ppb, its emissions are poorly understood in space and time, despite its important contribution to global climate change and ozone depletion. Water vapor in the upper troposphere is the most important greenhouse gas and represents a key specie for Earth climate. The line intensity data of water vapor are of primary scientific significance for radiative transfer issues in atmospheric and astrophysical applications (Höhne et al., 2011; Joly et al., 2006). Accordingly, for a better understanding of global warming, climate change and variability, and also the clear emission sources of these gases, there is an urgent need for developing instruments that can simultaneously detect N₂O, CH₄ and H₂O, and resolving the spatial and temporal variances in emissions, especially through field measurements.

Several optical techniques have been developed to detect these three gases in the atmosphere (Nelson et al., 2004; Wojtas et al., 2013; Vardag et al., 2014; Scherer et al., 2013; Lima et al., 2006; Ma et al., 2013). Cavity enhanced spectroscopy (CEAS) or cavity ring-down spectroscopy (CRDS) have been demonstrated to enable measurements of NO and N₂O gas concentrations in the range from 100 ppb to 10 ppm with a relative uncertainty smaller than 13% (Wojtas et al., 2013; Vardag et al., 2014). However, these two technologies require critical optical alignment and regular cleaning of mirrors of the external cavity which affects continuous measurements of atmospheric species in the field. In another study a mid-infrared difference frequency generation (DFG) laser system combined with a 5-m absorption path length was used for ambient CH₄, CO, and N₂O monitoring. An averaging time of 10 s was required to achieve sub-ppb level detection (Scherer et al., 2013). Nevertheless, such a DFG system is complex due to the laser configuration which requires two diode lasers and fiber amplifiers. Photoacoustic detection of N₂O and CH₄ was also reported (Lima et al., 2006; Bjorneberg et al., 2009a). A methane (CH₄) and nitrous oxide (N₂O) sensor based on a quartz enhanced photoacoustic spectroscopy (QEPAS) technique was developed for environmental and biomedical measurements. Minimum detection limits (MDLs) (1 σ) of 13 ppb and 6 ppb were achieved for the targeted CH₄ and N₂O absorption lines at 7.83 μ m with a 1-s data acquisition time, respectively (Wojtas et al., 2013). But the high modulation frequencies used in QEPAS may represent a problem for multi-component gas mixtures containing varying amounts of water vapor such as ambient air, due to the strong influence of water vapor on the molecular vibrational-translational (V-T) relaxation times. Other spectroscopic methods such as open path Fourier transform infrared spectrometry (FTIR) have been reported for atmospheric molecules detection (Bjorneberg et al., 2009a), however, the MDLs of FTIR usually exceed the requirements for high sensitivity measurements of the atmospheric species.

The most widely used method for detection of atmospheric CH₄, N₂O and H₂O is tunable laser absorption spectroscopy (TLAS) especially in the mid-infrared region involving continuous-wave quantum cascade lasers (cw-QCLs) combined with a multipass absorption cell (MPAC) (Nelson et al., 2004; Tao et al., 2012; Mappé et al., 2013; Wysocki et al., 2008; Cao et al., 2015; Sajid et al., 2015; Grossel et al., 2008). Particularly, the cw broadly tunable external cavity QCL (EC-QCL) enables simultaneous measurement of multiple atmospheric species (Craig et al., 2013; Suter et al., 2012; Cui et al., 2016). Beyond that, in combination with wavelength modulation second harmonic (WM-2f) detection, sensitivities are expected to be further improved by up to two orders of magnitude compared to direct absorption measurements (Chao et al., 2012; Hancock et al., 2009; Zhao et al., 2007). Recently, a 7.73- μ m cw-QCL based absorption sensor system was demonstrated and developed for simultaneous detection of these three gases. MDLs of 6.5 ppb for N₂O, 23 ppb for CH₄, and 62 ppm for H₂O were achieved with a 1-s integration time for simultaneous detection of three gases (Cao et al., 2015).

In this work, a sensor system based on the WM-2f technique employing an EC-QCL and a commercially available MPAC with an

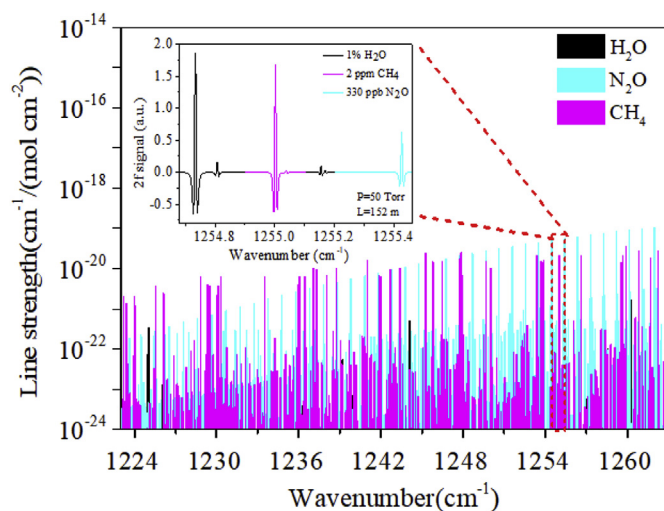


Fig. 1. Absorption lines of N₂O, CH₄ and H₂O in the spectral range of 1223–1263 cm⁻¹. Inset: simulation of 2f signals of 330 ppb N₂O, 2 ppm CH₄ and 1% H₂O based on the HITRAN 2008 database in a relatively narrow spectral range of 0.8 cm⁻¹ for a path length of 152 m at a pressure of 50 Torr. (Modulation broadening effects are not taken into account). N₂O, CH₄ and H₂O absorption lines are shown in blue, purple and black, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

effective path length of 152 m for simultaneous measurements of atmospheric N₂O, CH₄, and H₂O was reported. MDLs of 0.9 ppb for N₂O, 4.8 ppb for CH₄ and 31 ppm for H₂O were achieved with a 1-s integration time at an optimum pressure of 50 Torr. Both laboratory and atmospheric environmental data of these three gases mixing ratios were presented and their emission sources were analyzed. Corresponding meteorological parameters and variations of N₂O emission on rainy days were also reported and discussed.

2. Absorption line selection

The mid-infrared spectral range is the most suitable for qualitative and quantitative analysis of the infrared spectrum for most atmospheric gas species whose strong fundamental absorption bands lie in this spectral range (Fischer and Sigrist, 2003). Fig. 1 shows the absorption lines of N₂O, CH₄ and H₂O on the basis of the HITRAN 2008 database (Rothman et al., 2009) in the accessible spectral range (1223–1263 cm⁻¹) of the EC-QCL employed in this work. There are relatively strong absorption lines near 1255 cm⁻¹ for all three gas molecules, which enables simultaneous sensitive measurement with a single EC-QCL, thereby simplifying the sensor system and reducing its size and cost.

A simulated WM-2f absorption spectrum based on the HITRAN 2008 database of these three gases for specific mixing ratios at a total pressure of 50 Torr in a 152-m absorption path length is depicted in the inset of Fig. 1. Three neighboring absorption lines, a H₂O absorption line at 1254.732 cm⁻¹, a CH₄ absorption line at 1255.000 cm⁻¹, and a N₂O absorption line at 1255.424 cm⁻¹, are well separated from each other within a relatively small spectral range of 0.8 cm⁻¹. It is worth mentioning that the combination of these three absorption lines is not the only choice for simultaneous detection of N₂O, CH₄ and H₂O, but it is based on the wavelength of the available EC-QCL within a minimum tuning range of 0.8 cm⁻¹. Different wavelength ranges have been employed in other studies (Cao et al., 2015).

Download English Version:

<https://daneshyari.com/en/article/8863533>

Download Persian Version:

<https://daneshyari.com/article/8863533>

[Daneshyari.com](https://daneshyari.com)