

Quantum Cascade Laser based Instrument for Fast Simultaneous Measurements of HONO and CH₄ at 8 μm

Xiaojuan Cui^{1,2}, Wenqing Liu², Eric Fertein¹, Cécile Coeur¹, Dorothee Dewaele³, Fabrice Cazier³, Yujun Zhang², Fengzhong Dong², Weidong Chen^{1,*}

¹Laboratory of Atmospheric Physical Chemistry, University of the Littoral Opal Coast
189 Av. Maurice Schumann, 59140 Dunkerque, France

²Anhui Institute of Optics & Fine Mechanics, Chinese Academy of Sciences, Hefei, 230031, China

³Joint Center for Measurement, University of the Littoral Opal Coast, 145, Av. Maurice Schumann, 59140 Dunkerque, France

BIOGRAPHY

Weidong CHEN is full Professor of Physics at the Université du Littoral Côte d'Opale (ULCO) in France. He received his PhD degree in 1991 from the Université des Sciences et Technologies de Lille (USTL) in France. Prior to joining the ULCO in 1993, he was an assistant professor at the USTL where he conducted research focusing on the development of laser sideband-based heterodyne THz spectrometer and its application to molecular rotation spectroscopy. His current research interests include developments and applications of photonic instrumentation (based on QCL, LED or optical parametric source) for spectroscopic detection of trace gas molecules. He published more than 90 refereed technical papers and has co-authored over 120 presentations in the international conferences.



TECHNICAL ABSTRACT

Introduction Gaseous nitrous acid (HONO) is a highly reactive short-lived species playing a significant role in the atmosphere. Despite the research efforts carried out to date, the sources of atmospheric HONO are not well identified^[1]. Apart from its role in tropospheric chemistry, HONO is a toxic in-door pollutant and suspected to be a precursor of carcinogens (nitrosamines) under atmospheric conditions. Sensitive and selective instrument for high precision, high spatial and temporal resolution *in situ* measurements of atmospheric HONO is highly requested for application to identification of missing sources of HONO as well as to air quality monitoring^[1-3]. Contrary to monitoring of long-lived species such as greenhouse gases, accurate and precise direct concentration measurements of reactive short-lived species represent a real challenge^[2] because of their very short lifetime (1 to 100 s) and very low concentration in the atmosphere (down to 10⁶ molecules/cm³, corresponding to 0.1 pptv at standard temperature and pressure). In this paper, we report on the development of a continue-wave (CW) quantum cascade laser (QCL) based instrument operating in the mid-infrared at 8 μm for fast simultaneous quantitative assessment of HONO and CH₄.

Experimental detail The used laser source was a CW, room temperature operation, distributed feedback (DFB) quantum cascade laser (DQ7-M776H, Maxion Technologies, Inc.). It emitted single mode powers of up to 35 mW near 8 μm (~1254 cm⁻¹) with a total wavelength tuning of ~5 cm⁻¹ by ramping the injection current or varying the temperature of the laser. The pre-collimated laser beam from the QCL was first divided into two parts via a beam splitter with 90% transmission and 10% reflection. The main transmitted laser beam was directed to a multi-pass cell with an effective optical path length of 125 m. The spectral absorption signal emerging from the multi-pass cell was focused onto a thermoelectrically cooled (TEC) photovoltaic detector (VIGO PVI-4TE-10.6) by a lens of 5 cm focal length. The 10% reflected beam was coupled to a Fabry-Perot etalon with a free spectral range of 0.03 cm⁻¹. Optical fringe signal resulted from the etalon was monitored by another TEC detector (VIGO PVMI-10.6) and used for laser frequency metrology. The absorption line positions of CH₄ (from the HITRAN database^[4]) and HONO^[5] served as absolute frequency reference. The pressure in the multi-pass cell was measured with a calibrated pressure transducer (Pfeiffer Vacuum, CMR 361, 1100 mbar).

The *trans*-HONO absorption spectrum near 1255 cm⁻¹ from [5] was used for spectral identification and spectroscopic determination of HONO concentration. Our experimental investigation showed that interference-free detection of atmospheric CH₄ and HONO could be performed at ~1254.73 cm⁻¹.

One of the particularities for reactive trace species detection is no certified reference gases available for instrumental validation and concentration measurements calibration. In the present work, gas-phase samples of HONO were prepared by slowly dripping diluted NaNO₂ solution into dilute H₂SO₄ solution^[6]. By controlling the solution concentration of NaNO₂ and H₂SO₄, some tens of ppm HONO could be produced. Although this synthesis does not produce only HONO, but also NO, NO₂ and H₂O by self-reactions, these secondary products don't affect the HONO concentration measurements since there is no any spectral interference of such components^[4] with the HONO absorption lines selected in the present work. Denuder technique was implemented in the present work in association with a conventional NO_x analyzer to determine the concentration of the synthesized HONO samples. The used denuder was similar to that reported in Ref. [7]. The generated gaseous sample (including HONO, NO₂, etc) flows were directed to the NO_x analyzer by passing through sampling lines alternatively with and without carbonate denuder. The HONO concentration was thus obtained as the difference in the NO_x signals.

HONO losses in a closed absorption cell made of borosilicate glass were experimentally studied. The decay time for the HONO concentration losses was found to be 318 s. In order to avoid any "sampling" loss induced inaccuracy in HONO concentration measurements, high frequency scan at a rate of 2.5 kHz was employed in the present work.

Simultaneous monitoring of HONO and CH₄ Performance of the developed QCL instrument was evaluated using the synthesized gaseous HONO sample. The instrument was then employed for simultaneous measurements of HONO and CH₄ in ambient air. By direct absorption spectroscopy in a 125-m long multi-pass cell, 1 σ detection limits (1 σ) of 0.4 ppb and 6 ppb were experimentally achieved for HONO and CH₄, respectively. The detection limit could be further improved by using a longer integration time in combination with implementation of a longer absorption cell^[3], which would make the instrument very suitable for field measurements of atmospheric HONO for photochemistry study.

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