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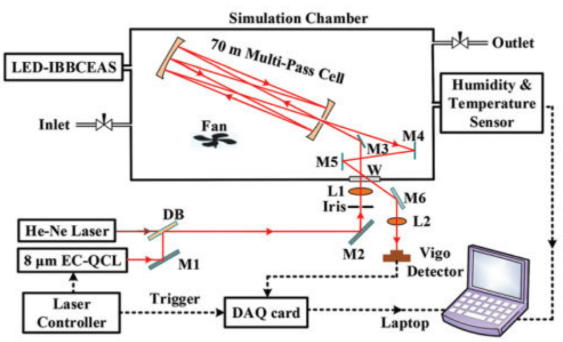
High-accuracy and high-sensitivity optical tracing of dinitrogen pentoxide (N2O5) involved in a nocturnal tropospheric chemical reaction process in smog chamber using quantum cascade laser

Dinitrogen pentoxide (N_2O_5) is an important reactive intermediate in the atmospheric chemistry of nitrogen oxides and nitrate aerosol, especially during night-time. It is also an important reservoir of NO_3 radical that can react with various volatile organic compounds (VOCs) including alkenes and dimethyl sulphide (DMS). The heterogeneous removal of N_2O_5 through the reactions of NO_3 (and N_2O_5) with aerosol particles may lead to a global O_3 reduction, thus directly and indirectly impacting on climate. Despite its importance and several decades of research, there are still many open questions about the role of N_2O_5 in tropospheric chemistry due to the lack of suitable measurement methods for precise quantification of N_2O_5 concentration.

Tunable laser absorption spectroscopy in the infrared involving fundamental ro-vibrational molecular transitions could provide a useful tool for high-sensitivity and high temporal resolution measurements of N_2O_5. However, the N_2O_5 absorption in the infrared exhibits a broad band absorption feature (over ~40 cm^{-1}) and the usually used distributed feedback lasers with a tuning range of ~5 cm^{-1} were unable to scan a whole N_2O_5 absorption feature for accurate quantification. Widely-tunable external-cavity quantum cascade laser (EC-QCL) is mostly suitable for such application. However, the prominent drawback of the commercially available broadband EC-QCL is the unavoidable etalon fringes resulting from its external cavity design structure. These etalon fringes limit the ultimate detection sensitivity and measurement accuracy.



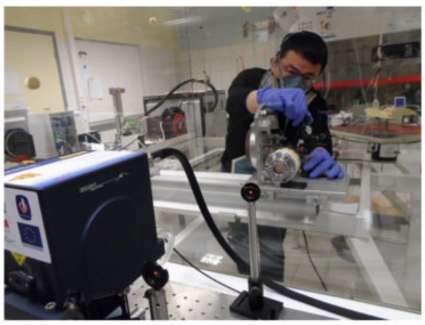


Fig. 1. left: Schematic of the EC-QCL-MPC apparatus used for quantitative measurements of N_2O_5 in an ASC. A He–Ne laser (λ =632.8 nm) overlapped with the mid-IR EC-QCL beam by means of a dichroic beamsplitter DB (ISP Optics, model BSP-DI-25-3) was used for optical alignment. L: focusing lens; M: reflective mirror; W: CaF2 window; LED-IBBCEAS: Light emitted diode based incoherent broadband absorption spectrometer for NO_2 and NO_3 measurement; right: Picture of the ASC involved in the present work.

We report recently on the development of an EC-QCL based spectroscopic instrument for N_2O_5 measurement by direct long path absorption spectroscopy near 8 μm. The experimental set-up is schematically depicted in Fig. 1. A water-cooled continuous-wave EC-QCL (Daylight Solutions, Model CW-MHF 41000), mode-hop free tunable in the infrared spectral region from 1223 to 1263 cm^{-1}, was used to probe broadband absorption of N_2O_5 of the ν_{12} band near 8 μm. The EC-QCL beam was collimated and injected into a home-made multipass cell (MPC) installed inside the atmospheric simulation chamber (ASC) in open-path configuration. MPC was formed with two spherical mirrors separated by about 1 m resulting in an effective optical pathlength of L_{eff} = 70 m. The laser beam emerging from the MPC was focused onto a VIGO detector (PVI-4TE-4). The direct absorption signal of N_2O_5 from the VIGO detector was digitalized with a data acquisition card (NI-6036E) and processed with a Labview-based program associated with a laptop computer. The developed EC-QCL-based N_2O_5 sensing platform was evaluated by real-time tracking N_2O_5 concentration in its most important nocturnal tropospheric chemical reaction of $NO_3 + NO_2 \leftrightarrow N_2O_5$ (*Eq.1*) in an ASC operating at atmospheric pressure and room temperature (293.2 ± 0.5 K) under dry conditions (RH < 1%).

A specific algorithm was developed for the precise retrieval of N_2O_5 concentration (Fig. 2. *left*), which allowed us to significantly eliminate the unavoidable intrinsic etalon fringes of the EC-QCL and spectral interference lines of H_2O vapor absorption, allowing us to improve detection sensitivity of the EC-QCL instrument by a factor of 10 and to eliminate bias error of ~21% caused by the etalon effects in the retrieved N_2O_5 concentration. Using a L_{eff} = 70 m, a minimum detection limit (DL) of 15 ppbv was achieved with a 25 s integration time (Fig. 2. *right*).

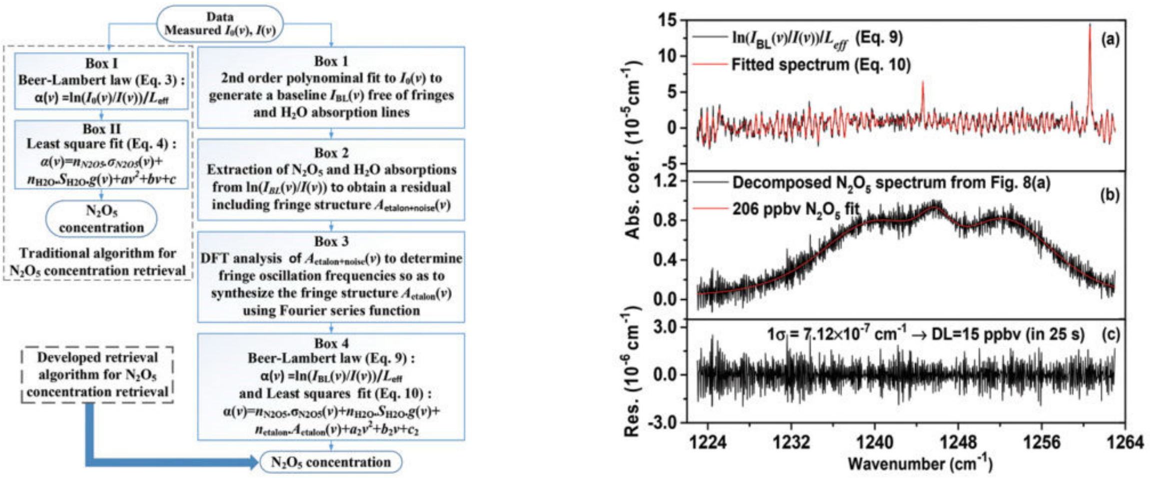


Fig. 2. left: Flow chart illustrating the developed N_2O_5 concentration retrieval algorithm, in comparison with a traditional method. right: Retrieval of N_2O_5 concentration. (a) Measured (black) and fitted (red) N_2O_5 absorption spectra including H_2O vapor, etalon fringe and baseline fluctuation. (b) Decomposed 206 ppb N_2O_5 absorption spectrum (black) and the corresponding fit (red) from (a). (c) Fit residual.

The equilibrium rate constant K_{eq} in *Eq.1* was determined with the help of the direct concentrations measurements using the developed EC-QCL sensing platform. The result agreed well with the theoretical value deduced from a referenced empirical formula under well controlled experimental conditions. This work demonstrates the potential and the unique advantage of using a modern EC-QCL for applications in direct quantitative measurement of broadband absorption of key climate-change related molecular species.

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Publication

High-accuracy and high-sensitivity spectroscopic measurement of dinitrogen pentoxide (N2O5) in an atmospheric simulation chamber using a quantum cascade laser.
Yi H, Wu T, Lauraguais A, Semenov V, Coeur C, Cassez A, Fertein E, Gao X, Chen W
Analyst. 2017 Dec 4