Geophysical Research Abstracts,
Vol. 10, EGU2008-A-07472, 2008
SRef-ID: 1607-7962/gra/EGU2008-A-07472
EGU General Assembly 2008

Nitrous oxide isotopomer determination with a quantum cascade laser based spectrometer

H. Waechter (1), J. Mohn (2), B. Tuzson (2), L. Emmenegger (2) and M.W. Sigrist (1)

(1) ETH Zurich, Institute for Quantum Electronics, Zurich, Switzerland, (2) Laboratory for Air Pollution & Environmental Technology, Empa, Switzerland (joachim.mohn@empa.ch / Fax: +41 44 821 62 44 / Phone: +41 44 823 46 87; sigrist@iqe.phys.ethz.ch)

The main sources of atmospheric nitrous oxide (N_2O) are bacterial nitrification and denitrification processes in soils and aquatic systems. Because isotopic fractionation is substantially different for nitrification and denitrification, determination of the intramolecular distribution of ^{15}N in N_2O can be used to probe their relative flux strengths [1]. Furthermore, N_2O isotopomer analysis can help to elucidate stratospheric transport and chemistry as the photolytic N_2O decomposition is isotope selective [2]. Having the same mass the isotopomers $^{14}N^{15}N^{16}O$ and $^{15}N^{14}N^{16}O$ cannot be distinguished directly using standard isotope-ratio mass-spectrometry (IRMS).

Laser spectroscopy in the mid-infrared region is a valuable alternative to IRMS because the N_2O isotopomers can be differentiated due to their highly characteristic rotational-vibrational bands [3]. Additionally, the technique is suited for compact, mobile instruments that can be used for field studies with a good time resolution.

We present a laser spectrometer consisting of a thermoelectrically (TE) cooled , pulsed quantum cascade laser (QCL) at 4.6 μm, a multipass cell with a path length of 56 m and a TE cooled IR detector, allowing continuous, liquid nitrogen-free operation. The isotope mixing ratios of $^{15}N^{14}N^{16}O$ (α), $^{14}N^{15}N^{16}O$ (β) and $^{14}N_2^{16}O$ were analyzed simultaneously at 1 Hz time resolution at concentrations down to 9 ppm. The instrument performance was tested using the Allan variance technique. At a N_2O concentration of 90 ppm, the short term noise (1 Hz) is $6.1^o/_{oo}$ for $^{\alpha}\delta^{15}N$ and $4.2^o/_{oo}$ for $^{\beta}\delta^{15}N$, while the minimum is $0.46^o/_{oo}$ for $^{\alpha}\delta^{15}N$ and $0.76^o/_{oo}$ for $^{\beta}\delta^{15}N$ with an

averaging time of 300 s. At a concentration of 9 ppm the system is very stable yielding a maximum precision of $1.1^{o}/_{oo}$ ($^{\alpha}\delta^{15}$N and $^{\beta}\delta^{15}$N) with 3700 s averaging time. The spectrometer performance was extensively characterized based on gravimetrically prepared calibration gases with different isotopic composition.

[1] R.L. Sutka, N.E. Ostrom, P.H. Ostrom, J.A. Breznak, H. Gandhi, A.J. Pitt, and F. Li; Appl. Environ. Microbiol. 72 (1), 638-644 (2006)

[2] T. Röckmann, J. Kaiser, C.A.M. Brenninkmeijer, J.N. Crowley, R. Borchers, W.A. Brand and P.J. Crutzen; J. Geophys. Res. 106, 10403-10410 (2001)

[3] H. Waechter and M.W. Sigrist; Appl. Phys. B 87, 539-546 (2007)