Geophysical Research Abstracts,
Vol. 11, EGU2009-12890, 2009
EGU General Assembly 2009

Cavity enhanced absorption spectroscopy using room temperature quantum cascade lasers

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Achieving the high sensitivity necessary for trace gas detection generally requires long absorption path lengths. An alternative approach to conventional linear absorption spectroscopy employing multiple pass cells is to use a high finesse cavity. With the help of such cavities the effective path length of the laser beam in the absorbing medium can essentially be increased to more than the 200 m limit usually available from conventional optical multi-pass cells while keeping the sample and pumped volume small. Optical cavity based techniques, Cavity Ring Down Spectroscopy (CRDS) and Cavity Enhanced Absorption Spectroscopy (CEAS) among them, have been successfully applied as a highly sensitive absorption technique for several years. The majority of cavity based methods have used sources of radiation in the ultraviolet and visible regions. For many years the mid-infrared (MIR) molecular fingerprint region could not be employed either for CRDS or for the CEAS techniques, because of the lack of suitable radiation sources with the required power and tunability and small scale dimensions. Experiments were carried out with optical parametric oscillators, Raman cells or shifters or CO and CO_2 lasers. In all these cases sophisticated optical geometries were developed which were more suitable for the research laboratory than for field applications. Attempts to use lead salt lasers clearly suffered from low laser intensity. In addition, for wider application, especially for field measurements, compact and cryogen free spectrometers are definitely preferable. Recent advances in semiconductor laser technology, in particular the advent of quantum cascade lasers (QCL) provides new possibilities for highly sensitive and selective trace gas detection using MIR absorption spectroscopy.

Thermoelectrically (TE) cooled pulsed and cw QCLs have therefore been combined with resonant optical cavities. While pulsed QCLs working at room temperature have been commercially available for several years, room-temperature cw QCLs have only recently been introduced. Distributed feedback QCLs combine single-frequency operation with tunability over several wavenumbers, and average powers over a mW. Pulsed lasers seemed to be suitable for CRDS since the QCL needs to be interrupted periodically. However the inherent chirp of the laser pulse with a typical rate of 0.005 cm^{-1}/ns (150 MHz/ns) hampers an sufficient intensity build-up on the cavity modes. Furthermore the spectral coverage of the laser pulse excites too many cavity modes simultaneously. The results achieved by this method do not show significant improvement compared to long path cells and the combination of CRDS with pulsed QCLs has only a limited number of useful applications.

In contrast, CEAS employing continuous wave (cw) QCL emitting at 7.66 μm and a TE cooled detector yielded path lengths of 1080 m with a $\sim$ 0.5 m long cavity of 0.3 l. The cavity length was not actively changed or dithered nor was the cavity locked to the illuminating light source. With a noise equivalent absorption of 2×10^{-7} $cm^{-1}Hz^{-1/2}$ the detection limit with a 20 s integration time was found to be 6×10^8 molecules/cm^3 for N_2O and 2×10^9 molecules/cm^3 for CH_4 which is good enough for the selective measurement of trace atmospheric constituents at 2.2 mbar. The main limiting factor for achieving even higher sensitivity, such as that found for larger volume multi pass cell spectrometers, is the incomplete averaging over cavity resonances, i.e. the residual mode structure of the cavity. With a 1.3 m long cavity and an optimised averaging over the cavity modes due to a small dither on the QCL current the required integration time and the noise equivalent absorption could be reduced down to the 10^{-9} $cm^{-1}Hz^{-1/2}$ range. The advantage of CEAS combined with cw QCLs over CRDS with pulsed QCLs is that the spectral resolution is no longer limited by bandwidth effects of the light source. This enables measurements at low pressure to increase the selectivity in complex gas mixtures or plasma diagnostics at

low pressure plasmas.