Long-path monitoring of NO2 with a 635 nm diode laser using frequency-modulation spectroscopy

Somesfalean, Gabriel; Alnis, J; Gustafsson, U; Edner, Hans; Svanberg, Sune

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Long-path monitoring of NO\textsubscript{2} with a 635 nm diode laser using frequency-modulation spectroscopy

Gabriel Somesfalean, Janis Alnis, Ulf Gustafsson, Hans Edner, and Sune Svanberg

In situ monitoring of traffic-generated nitrogen dioxide (NO\textsubscript{2}) emissions using long-path absorption spectroscopy is reported. High-sensitivity detection of NO\textsubscript{2} is achieved by employing two-tone frequency-modulation spectroscopy at a visible absorption band using a tunable high-power diode laser operated around 635 nm. A real-time absorption spectrometer is accomplished by repetitively applying a rectangular current pulse to the diode-laser operating current, allowing detection of isolated NO\textsubscript{2} absorption lines. A detection limit of 10 \(\mu g/m^3\) for NO\textsubscript{2} at atmospheric pressure using a 160 m absorption path is demonstrated. Continuous monitoring of NO\textsubscript{2} over a road intersection at peak traffic is performed. © 2005 Optical Society of America

1. Introduction

There is a large interest in detection and precise measurement of nitrogen dioxide (NO\textsubscript{2}), which is a combustion-generated atmospheric trace gas acting as an important agent in several chemical cycles in the atmosphere. Optical monitoring applications in the field of air-quality control and traffic-emission monitoring are employing, e.g., differential optical absorption spectroscopy\textsuperscript{1,2} (DOAS) and light detection and ranging\textsuperscript{3,4} (LIDAR) techniques, both methods being suitable to use in conjunction with long absorption path lengths. Very few remote-sensing line-of-sight measurements have been performed employing tunable diode-laser spectrometers for atmospheric NO\textsubscript{2} monitoring.\textsuperscript{5} The majority of diode-laser-based applications for NO\textsubscript{2} detection utilize multiple-pass absorption cells, mostly at reduced pressures in order to minimize line broadening.\textsuperscript{6–11} Such an arrangement has the disadvantage of introducing unwanted optical fringes due to etalon effects,\textsuperscript{6} and of depending on a gas-extraction procedure, which is prone to introduce measurement errors. In the present work, long-path absorption in combination with a retroreflector is used instead, making remote sensing over several hundred meters possible, to be compared with the point-monitoring mode obtained in a multiple-pass absorption cell configuration. Thereby it is possible to obtain the pollutant concentrations in a large volume with less sensitivity to local fluctuations.

Field instruments for air pollution monitoring are preferably operated at ambient pressure, with the disadvantage of increased line broadening and reduced peak absorption, which leads to lower detection sensitivity. The NO\textsubscript{2} spectrum is comparatively dense (\(\sim 10\) lines/cm\textsuperscript{-1}), and lines are partially overlapping at ambient atmospheric pressure due to collisional broadening. Another problem that has to be considered is interference from other molecular species, such as oxygen and water lines. The probing wavelength is therefore carefully selected to overlap a strong isolated absorption line of the gas, which has sufficiently well-resolved features and does not interfere with other species. At wavelengths longer than 350 nm, the absorption spectrum of NO\textsubscript{2} exhibits sharp spectral features,\textsuperscript{10} that extend over the blue region into the visible wavelength region. We use a diode laser emitting at a wavelength around 635 nm in order to probe the red wing of the \(X^2\text{A}_1 \rightarrow A^2\text{B}_2\) visible absorption band of NO\textsubscript{2}.

Previously a sensitivity of 0.2 \(\mu g/m^3\) has been demonstrated using a gas cell at low pressure and monitoring with a cryogenically cooled diode laser operating around 6.2 \(\mu m\).\textsuperscript{6} Measurements using near-infrared\textsuperscript{7} or red diode lasers\textsuperscript{9,10} have been performed achieving sensitivities of a few \(\mu g/m^3\). The
most common methods to enhance measurement sensitivity use balanced detection\textsuperscript{9,10} or frequency-modulation techniques.\textsuperscript{6,12–15} In the present work we reduce the noise bandwidth of the laser by employing a high-frequency modulation technique, namely, two-tone frequency-modulation spectroscopy\textsuperscript{16–18} (TTFMS). TTFMS using visible diode lasers is a convenient technique for sensitive trace-gas detection in that it combines high-speed, high-precision, zero-background, and remote-sensing capabilities, although modulation broadening is introduced at maximum sensitivity. At atmospheric pressure the absorption lines in NO\textsubscript{2} are broadened, and the modulation frequency must be correspondingly high. The modulation amplitude applied to the diode must also be increased compared to low-pressure measurements. The resulting line shapes resemble the second derivative, but are somewhat modified at atmospheric pressure because of overlapping lines.

2. Experimental

A schematic diagram of the experimental setup is shown in Fig. 1, with the long-path absorption arrangement shown in the upper part and the TTFMS electronics in the lower part. The tunable high-power diode laser used was an InGaAsP index-guided device manufactured by Hitachi (HL6320G). It has a nominal wavelength of 635 nm at 25 °C and a typical output power of 10 mW. Wavelength stability is ensured by controlling temperature and current of the laser diode with a precision diode-laser driver (Melles Griot 06DLD103). The temperature of the diode-laser capsule is stabilized to within 0.05 °C over one hour of measurement. An antireflection-coated molded glass aspheric lens (Geltech C240TM-B) collimates the laser output. A small mirror directs the laser beam across a busy intersection about 5 m above the ground level until it hits a retroreflector. The back-reflected light is collected by a telescope with an aperture of 10 cm and is focused onto the detector that contains a p-i-n photodiode (Hamamatsu S-1190) and a homemade transimpedance amplifier. The beam can also be sent through two reference cells containing known concentrations of NO\textsubscript{2} that are used for calibration purposes. The windows of the cells are tilted to the Brewster angle to reduce spurious optical feedback.

Spectral scanning is achieved by applying a rectangular current pulse with a duration of 1–2 ms and a repetition rate of 250 Hz to the diode-laser drive current, which is biased below threshold. Thereby a longer wavelength scan is produced compared to a current ramp, and an almost constant frequency-modulation index during the scan is ensured.\textsuperscript{17} At the same time the sweep becomes highly nonlinear, as can be seen on the signals from a low-finesse glass etalon [Fig. 2(d)] used for frequency calibration of the absorption spectrum. The tuning range produced is approximately 25 GHz, sufficient to capture a single atmospheric pressure-broadened transition of NO\textsubscript{2}. A Burleigh WA-4500 wavemeter is used to measure the laser frequency and to verify single-mode operation of the diode laser.

The two-tone frequency-modulation setup used here is described thoroughly in some previous papers of our group.\textsuperscript{12,13,17–19} We have in this work used diode-laser modulation at 935 and 925 MHz with a signal demodulation at 10 MHz. The demodulated signal is amplified and low-pass filtered in a low-
noise preamplifier (Stanford SR560) that was set to 30 kHz, and subsequently averaged 256 times in a digital oscilloscope (Tektronix TDS520B), resulting in a total sampling time of 6 s. The TTFMS signal has a zero background, which is advantageous when the light intensity at the detector fluctuates due to atmospheric turbulence. The recorded waveforms are finally stored on floppy disks and transferred to a computer for postprocessing and evaluation.

3. Measurements and Results
Initially, measurements were performed to investigate the NO$_2$ absorption lines at different pressures. A reference cell was filled at 50 Torr with a calibration gas containing 0.2% NO$_2$ in high-purity synthetic air. A retroreflector was placed at a few meters distance. Survey spectra in the visible wavelength region around 635 nm were used to identify isolated lines for sensitive measurement. A strong absorption feature was selected by temperature tuning the diode laser, and this wavelength was used for NO$_2$ monitoring. The valve of the cell was then opened, and air was allowed slowly to enter. As the pressure increases, the absorption lines broaden with a corresponding decrease in the peak absorption. The TTFMS signal was maximized by significantly increasing the laser modulation index. At atmospheric pressure, the shape of the modulation signal is quite complex due to close-lying or overlapping absorption lines.

Atmospheric NO$_2$ measurements were performed using a round-trip path of 160 m. Interference from sparse oxygen and water lines in the probed spectral region was avoided by use of the HITRAN database. This was also experimentally verified by inserting a cell filled with NO$_2$ into the beam in front of the detector, as shown in Fig. 1, and detecting an equivalent increase of the absorption feature that necessarily pertains to NO$_2$. Vanishing frequency-modulation signals were recorded at times with low traffic intensity. The minimum detectable concentration is estimated using the reference cell containing NO$_2$ at atmospheric pressure. The peak-to-peak value of the recorded TTFMS signal [Figs. 2(b), 2(c)] is related to the absorption and also scales linearly with the power at the detector [Fig. 2(a)]. The detection limit for the system corresponding to a signal-to-noise ratio $S/N = 1$ is found to be about 10 $\mu$g/m$^3$ in a 160 m path and with a 256 times averaging. The main noise sources under monitoring conditions were the light-intensity fluctuations, the detector noise, and the residual optical interference. Using a long-path configuration for ambient NO$_2$ detection, we have not observed significant etalon fringes, which usually limit the minimum detectable absorption when short optical paths or multipass cells are employed.

Figure 3 shows a data set of the measured NO$_2$ concentration in air along the 160 m round-trip path. The data points were acquired sequentially every minute. The wind strength and direction constitute important parameters because the measurements are performed 5 m above the pollution sources, i.e., the exhaust pipes of the passing cars. At the time of the measurement there were calm wind conditions. Two reference cells of the type discussed above, 30 and 5.6 cm long, respectively, were inserted into the beam for calibration (standard addition method). They contained 0.013% NO$_2$ at atmospheric pressure corresponding to an equivalent of 470 $\mu$g/m$^3$ and 87 $\mu$g/m$^3$ of NO$_2$, respectively, inserted into the beam for calibration purposes.

4. Discussion
It can be seen from the graph in Fig. 3 that the span between the long-path concentrations measured directly and the values that can be derived from the almost simultaneous calibrations is changing somewhat from calibration to calibration. This variation can be explained by residual etalon fringes generated by the windows of the reference cells when these are introduced into the beam at calibration. It adds a random contribution to the detected gas signal and limits the accuracy of the calibration. By antireflection coating the cell windows, the effect is expected to decrease.

Comparison of the measured NO$_2$ sensitivity to other works shows that the detection limit is good, although the sensitivity at atmospheric pressure is reduced due to smaller peak absorption. In the equivalent remote-sensing measurements presented in Ref. 5 the estimated noise level was 0.5 ppm-m over an 88 m path, corresponding to an average concentration of 11 $\mu$g/m$^3$ for $S/N = 1$. The relatively high NO$_2$ concentrations obtained in this study are explained by the intense traffic during the measurements, averaging 70 vehicles in 5 minutes. Light-
intensity variations in the time range of several minutes appear to be caused mainly by thermal drifts in the optical alignment, because the optical power could be recovered by realignment. Longer absorption paths would be possible by using a better telescope in order to collect more light, thereby lowering the detection limit. Higher diode-laser output powers are available at a wavelength of 670 m. An additional advantage for operating at wavelengths near 670 nm is that interference with water absorption lines can be completely avoided. Additionally, NO₂ presents larger absorption lines in the blue region, and it is likely that the sensitivity could be further increased using blue diode lasers in remote absorption measurements. Unfortunately, presently available blue diode lasers typically operate on several modes and need to be assembled in external-cavity arrangements that reduce the available output power considerably.

5. Conclusions

We have demonstrated the possibility to use diode-laser-based spectroscopic detection for long-path NO₂ concentration measurements in urban air. The performance is comparable to that of a differential optical absorption spectroscopy system, where the wavelength region around 450 nm is scanned over tens of nanometers, thereby revealing larger absorption structures. In our case the TTFMS technique is used to increase the sensitivity for measurements of small absorption levels. The achieved detection sensitivity of 10 µg/m³ in a 160 m path at atmospheric pressure is lower than for low pressure NO₂ due to the decrease of peak absorption at atmospheric pressure.

In the present work the sensor is operated as a semiportable device. Further development of this diode-laser-based trace-gas detector into a compact, fully portable field instrument should find many applications in pollution monitoring measurements.

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