Measurement of nitric oxide with an antimonide diode laser

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An antimonide diode laser operating near 2.65 μm was used to measure absorption lines of NO gas in the first overtone band. A blended line pair of NO that is sufficiently free of interference from H_2O to permit the selective detection of NO under reduced pressure conditions was identified. With wavelength-modulation spectroscopy, a rms noise level equivalent to an absorbance of 3.2×10^{-5} was achieved at a measurement integration time (for a single spectral data point) of 0.1 s. The corresponding detection sensitivity (signal-to-noise ratio of 2) for NO in air at reduced pressure was ~15 ppm m (ppm is parts in 10^6). Antimonide diode lasers show substantial promise for gas-sensing applications because they can gain access to relatively strong absorption lines of several gases of environmental interest at operating wavelengths at which cryogenic cooling is not required.

Key words: Diode laser, antimonide, nitric oxide, gas sensing, absorption spectroscopy.

1. Introduction

Semiconductor diode lasers, including lead salt lasers operating at wavelengths beyond 3 μm and InGaAlP, GaAlAs, or InGaAsP lasers operating at wavelengths less than 2 μm, have been used extensively for the measurement of trace gases by optical absorption.[1–5] The inherently narrow linewidths of these light sources, combined with high-sensitivity detection techniques such as wavelength-modulation spectroscopy[6–8] (WMS) or frequency-modulation spectroscopy,[9–11] provide a capability for the highly selective and sensitive measurement of a wide range of species important in atmospheric and combustion research, environmental monitoring, and process monitoring. The lead salt lasers generally permit the highest detection sensitivity because they have access to the fundamental absorption bands of most molecular species. However, the development of commercial diode-laser-based instrumentation for environmental or industrial applications has focused on the use of the short-wavelength devices because of their characteristics of room-temperature operation and compatibility with silica optical fibers. In addition, device structures that constrain the laser to single longitudinal-mode operation are often available at the short wavelengths because of the extensive development of these lasers for communications applications. In contrast, commercial lead salt diode lasers are typically multimode, which reduces their utility for gas-sensing applications.

Several research groups have been pursuing the development of semiconductor lasers with operating wavelengths in the 2–4-μm range based on III–V antimonide materials systems.[12–18] Devices that exhibit room-temperature cw operation have been demonstrated at the short-wavelength end of this range, and recent results suggest that at least thermoelectrically cooled operation should be possible at wavelengths beyond 3 μm.[16,17] For detection of several species of environmental interest (e.g., CO, NO, H_2S, and CH_4), such lasers offer the promise of access to much stronger absorption bands than can be measured with shorter-wavelength communication lasers while retaining the practical advantages of room-temperature or thermoelectrically cooled operation. For example, the first overtone band of CO near 2.3 μm that is accessible with antimonide lasers is a factor of 160 times stronger than the third overtone band near 1.57 μm.[19] Although the potential of antimonide lasers for gas-sensing applications is usually cited as a principal motivation for their development,[12–18] examples of such applications are not evident in the literature. Recently the measurement of a H_2O absorption line near 2.65 μm with an antimonide laser was briefly described.[18]

In this paper we report the laboratory measure-

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ment of nitric oxide gas (NO) with an antimonide laser operating in the 2.65-μm region. When high-frequency WMS with second-harmonic detection was used, a detection sensitivity for NO of 15 ppm m (ppm is parts in 10^6) was achieved. Spectral interferences from H_2O, which absorbs strongly in this wavelength region, can be avoided by carefully selecting the NO analysis line and by sampling the gas to be analyzed into a reduced pressure cell.

2. Experiments

The diode laser used in this work is an AlGaAsSb/InGaAsSb multiple-quantum-well device fabricated by the David Sarnoff Research Center. The laser has a Fabry–Perot structure so that several different output wavelengths are normally present, corresponding to different longitudinal modes of the laser. As discussed below, the laser exhibited a dominant output mode at operating temperatures at which it was used for NO detection. Single longitudinal-mode antimonide laser devices (distributed Bragg reflector or distributed feedback structures) are under development at several laboratories, and distributed Bragg reflector devices have been demonstrated near 2 μm.[18]

For these initial studies, the laser was mounted on a resistively heated Cu block attached to the cold plate of a liquid-N_2 Dewar, permitting operation from 80 to ~210 K. Over this temperature range, the output wavelength of the laser was tuned from ~2.45 to greater than 2.65 μm. The desired output wavelength (near 2.65 μm) for the measurement of NO was achieved at a laser operating temperature of ~183 K. The maximum cw operating temperature of similar antimonide lasers in this wavelength range that has been achieved to date is 230 K.[18] Multistage thermoelectric (TE) coolers are capable of achieving temperatures of 200 K or lower, so that over at least some range of operating wavelengths, TE cooling of antimonide lasers for use in gas-sensing instrumentation seems quite feasible.

The output of the laser was collimated with an $f/1$ lens and directed through a single-pass evacuable absorption cell with a path length of 50 cm. The transmitted laser beam was detected with a TE-cooled InAs photodiode. A monochromator (1/8-m focal length) could also be inserted into the optical train for coarse measurement of the laser wavelength and characterization of the longitudinal modes of the laser. Only one mode was noted for the laser operating conditions used in our NO experiments, and measurements of NO absorption signals as functions of pressure verified that the laser was operating essentially in a single longitudinal mode, as described below.

For measurements of absorption spectra, the laser temperature was stabilized near 183 K, and the laser wavelength was tuned by repetitive sweeps of the injection current. Direct transmission spectra were recorded by signal averaging of these scans with a 486 computer equipped with a fast analog-to-digital board (Analog Devices). Typically, the laser current

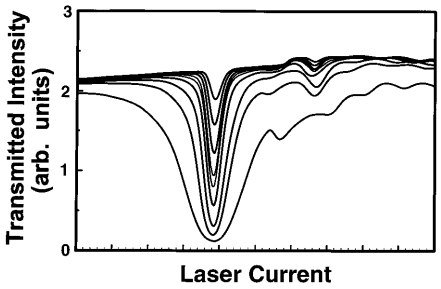

Fig. 1. Absorption feature of NO at different cell pressures, measured near 2.65 μm with an antimonide diode laser. The pressure of pure NO in a 50-cm absorption path length ranges from 2.3 to 140 Torr.

was swept at ~39 Hz, and 256 data points in each sweep were recorded, with a dwell time for each point of 100 μs. Coaveraging 1000 such sweeps results in an effective measurement time per data point of 0.1 s.

Additional data were obtained by WMS with $2f$ detection.[6–8] The advantage of this method is that the absorbance measurement is shifted to high frequency in order to avoid laser excess ($1/f$) noise. A small sinusoidal modulation at 50 kHz was superimposed on the laser current, and the demodulated signal at 100 kHz was processed with an analog lock-in amplifier (Stanford Research). The time constant of this lock-in amplifier was disabled, permitting signal averaging of the lock-in output in the same manner as that used for the direct transmission measurements.

The NO absorption line is shown in Fig. 1 for various NO pressures ranging from 2.3 to 140 Torr. The absorption line broadens very substantially as pressure is increased (collisional self-broadening). At the highest pressure measured (140 Torr), nearly 95% of the laser intensity is absorbed at line center, indicating essentially single longitudinal-mode operation of the laser. From these data, we derive an integrated line strength for this NO absorption feature of $\sim 4.2 \times 10^{-22}$ cm^2 molecule^{-1} cm^{-1}. When the laser wavelength, as measured with the 1/8-m monochromator, is compared with the NO line positions tabulated in the HITRAN compilation (1996 edition) of high resolution molecular spectroscopic parameters,[20] it is found that the most probable identification of this line is a blended line pair at 3772.0066 and 3772.0069 cm^{-1}. Under Doppler-broadened conditions (~0.009 cm^{-1} full line width at half-maximum), this blended line would appear as a single feature. The combined strength of the blended lines as listed by HITRAN is 3.8×10^{-22} cm^2 molecule^{-1} cm^{-1}, in good agreement with our approximate experimental result. These blended lines are identified in the HITRAN compilation as the two (Λ-doublet) components of the $^2\Pi_{3/2}$ $R(16.5)$ transition.

Measurement of the same absorption line at a pressure of 3.4 Torr by WMS is shown in Fig. 2. Analysis of the rms baseline noise indicates a noise-equivalent absorbance level of 3.2×10^{-5} at a measurement integration time of 0.1 s. Further improvement in the signal-to-noise ratio should be possible by optimi-

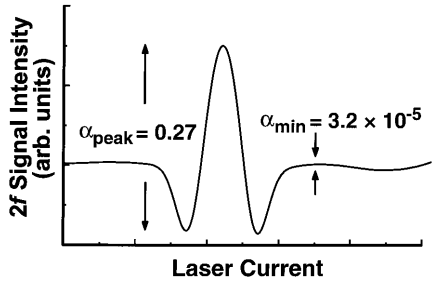

Fig. 2. NO absorption feature of Fig. 1 measured by WMS with 2*f* detection at 100 kHz. The sample pressure for this scan is 3.4 Torr. The rms noise in the baseline, recorded with an effective measurement time per data point of 0.1 s, is equivalent to an absorbance of 3.2×10^{-5}.

zation of the laser modulation and detection frequencies to minimize the effects of laser noise and possibly by use of a longer measurement averaging time.

This result can be translated to an estimate of the concentration sensitivity for NO detection. If the measurement of NO in air is performed at reduced pressure such that the absorption line is essentially Doppler broadened, then the minimum detectable NO partial pressure in a 50-cm path length (corresponding to 6.4×10^{-5} absorbance or a signal-to-noise ratio of 2) is ~0.8 mTorr. From the broadening coefficients tabulated in the HITRAN database, the air-broadened width of the NO lines equals the Doppler width at approximately 58 Torr. Under conditions of equal Doppler and pressure broadening, the line center cross section is reduced by a factor of 0.47 from the purely Doppler-broadened condition. Thus, for performance equivalent to that achieved in the present study, we would expect to be able to detect 1.7 mTorr of NO in 58 Torr of air over a path length of 0.5 m. This sensitivity, expressed as the product of concentration and path length, is ~15 ppm m.

For spectroscopic detection of trace species in the 2.65-μm region, a particular concern is the possibility of interference from H_2O or CO_2, both of which have strong absorption bands in the region and both of which are present in large concentrations in combustion exhaust and in the atmosphere. In the immediate region of the NO absorption feature studied here, CO_2 lines are weak and sparsely distributed, and we were unable to detect any CO_2 absorption features in the vicinity of the NO line.

The immediate vicinity of the NO absorption feature studied here also contains only exceptionally weak H_2O lines. No interfering signals that were due to H_2O were detected in the low-pressure cell, even when the cell was filled with H_2O under room-temperature saturated conditions and WMS was used. However, in these experiments the external atmospheric paths in the optical setup were less than 0.25 m. We experimented with other optical setups in which we had much longer external atmospheric paths of several meters. In these designs, the absorption by the wings of more distant, strong H_2O lines was sufficient to degrade the optical transmission at the wavelength of the NO line. Thus the use of this approach for measurement of trace NO requires a design in which external optical paths are minimized and the gas to be analyzed is sampled into a reduced pressure cell.

3. Conclusions

An antimonide diode laser operating near 2.65 μm was used to measure absorption lines of NO in the first overtone band. An absorption feature that is sufficiently free of interference from H_2O to permit the selective detection of NO under reduced pressure conditions was identified. With WMS, a rms noise level equivalent to an absorbance of 3.2×10^{-5} was achieved at a measurement integration time of 0.1 s. The corresponding detection sensitivity for NO in air at reduced pressure is ~15 ppm m at a signal-to-noise ratio of 2. Further improvement in sensitivity should be possible if the effects of laser noise are minimized, e.g., by use of higher modulation and detection frequencies or by use of a dual-beam noise-cancellation approach.[21–23] This level of sensitivity makes antimonide laser-based sensing of NO potentially attractive for continuous emissions monitoring. More generally, antimonide diode lasers show substantial promise for gas-sensing applications because they can gain access to relatively strong absorption lines of several gases of environmental or process monitoring interest at operating wavelengths at which cryogenic cooling is not required.

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