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Diode-laser-based ultraviolet absorption sensor for nitric oxide

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ABSTRACT An all-solid-state continuous-wave laser system for ultraviolet absorption measurements of the nitric oxide (NO) molecule has been developed and demonstrated. The single-mode, tunable output of a 10-mW, 395-nm external-cavity diode laser (ECDL) is sum-frequency-mixed with the output of a 115-mW, frequency-doubled, diode-pumped Nd:YAG laser in a beta-barium-borate crystal to produce 40 nW of tunable radiation at 226.8 nm. The wavelength of the 395-nm ECDL is then scanned over NO absorption lines to produce fully resolved absorption spectra. Initial results from mixtures of NO in nitrogen in a room-temperature gas cell are discussed. The estimated NO detection limit of the system for a demonstrated absorption sensitivity of 2×10^{-3} is 0.2 ppm per meter of path length for 300 K gas. The estimated accuracy of the measurements is $\pm 10\%$.

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1 Introduction

A new diode-laser-based sensor system for ultraviolet (UV) absorption measurements of the nitric oxide (NO) molecule in the 226-nm region has been developed. UV laser radiation is generated by sum-frequency mixing (SFM) of an external cavity diode laser (ECDL) and a diode-pumped, intracavity frequency-doubled (IFD) Nd:YAG laser. The system offers the potential for very sensitive and accurate measurements of NO because of the strength of the UV $A^2\Sigma^+ - X^2\Pi$ electronic transition and because the frequency line width of the UV laser radiation is so narrow compared with the resonance line widths. Initial absorption measurements were performed in a room-temperature gas cell using mixtures of 100 ppm NO in N_2.

A number of UV absorption measurements for various species have been reported in the literature [1–7]. Oh [1] used SFM of the 830-nm output of a diode laser and a large-frame argon-ion laser to generate UV radiation at 308 nm for detection of OH radicals. Koplow et al. [8] used the frequency-quadrupled output of a pulsed 860-nm diode laser that was amplified in a tapered amplifier for NO absorption measurements. Peterson and Oh [3] used second-harmonic generation (SHG) of the output of a 860-nm diode laser for absorption and laser-induced fluorescence (LIF) measurements of the CH radical. Alnis et al. [4] used SFM of the outputs of a newly developed blue diode laser at 404 nm and a 688-nm diode laser to generate radiation at 254 nm for spectroscopy of the mercury atom. Corner et al. [7] have reported a similar SFM scheme for the detection of OH at 309 nm. Barry et al. [5] reported OH absorption measurements based on SHG of the output of a 618-nm diode laser. Ray et al. [6] generated 266-nm radiation for OH absorption measurements by frequency quadrupling the output of a 1064-nm ECDL. The ECDL output was first amplified in a Nd-doped, double-clad fiber amplifier and then periodically poled lithium niobate and beta-barium-borate (BBO) crystals were used for the frequency doubling and quadrupling steps, respectively. The sensor system that is discussed in this paper takes advantage of a new, compact green Nd:YAG laser system, which produces over 100 mW of single-longitudinal-mode (SLM) laser radiation at 532 nm, and the incorporation of blue diodes in commercial ECDL systems. The simplicity, generality, and relatively low cost of the SFM-based sensor strategy discussed in this paper will enable the development of absorption sensors throughout much of the UV spectrum, opening up a wide range of new possibilities for sensing and control of chemically reacting flow processes.

2 Experimental system and procedures

The laser system is illustrated schematically in Fig. 1. This system is based on sum-frequency mixing of the radiation of a tunable, 395-nm ECDL (Toptica Lasers, 10 mW, beam diameter approximately 1 mm) with a diode-pumped IFD Nd:YAG laser (CrystaLaser, 115 mW, beam diameter 0.3 mm) in a BBO crystal. The wavelengths of both the ECDL and the IFD Nd:YAG system were measured with a Burleigh WA-1000 cw wavemeter. The vacuum

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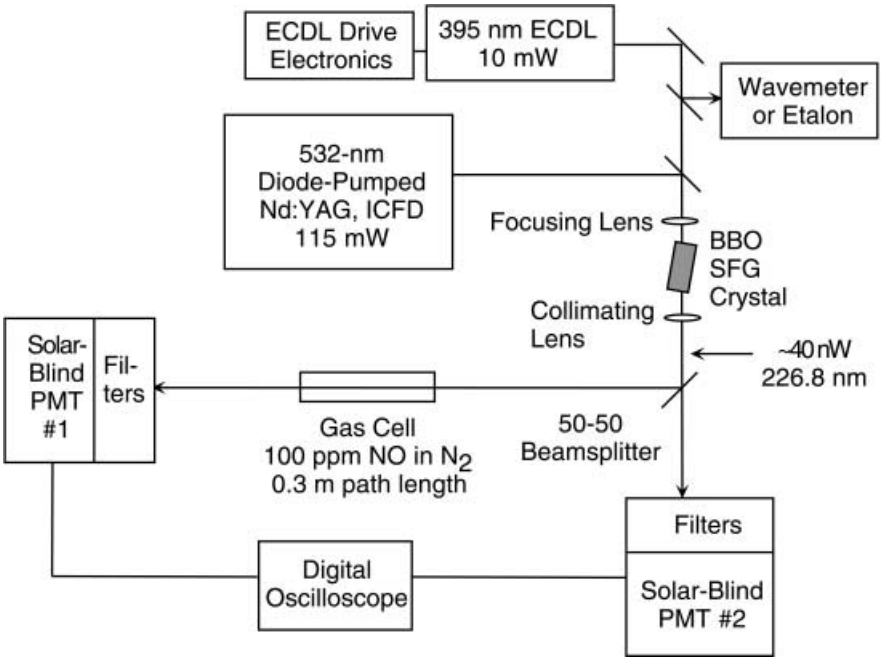

FIGURE 1 Schematic drawing of the diode-laser-based NO sensor

wavelength of the IFD Nd:YAG system was determined to be 532.299 nm. The frequency spectrum of the IFD Nd:YAG system was measured with a spectrum analyzer and it was confirmed that the output was single mode. As required for sensor applications, the physical dimensions of the CrystaLaser Nd:YAG laser head are very compact (3 cm × 3 cm × 12 cm) and it does not require any special cooling. The vacuum wavelength of the ECDL system was tuned to 395.24 nm for the initial measurements, so that the 226.820-nm (vac) SFM output of the sensor system was in resonance with the overlapped $P_2(10)$ and ${}^{P}Q_{12}(10)$ transitions in the ($v' = 0$, $v'' = 0$) band of the $A^2\Sigma^+ - X^2\Pi$ electronic transition [9], as shown in Fig. 2. The frequency spectrum of the ECDL was monitored with a Burleigh SA Plus spectrum analyzer (2 GHz free spectral range) as the ECDL wavelength was tuned over a mode-hop-free tuning range of 25 GHz. The etalon fringes are shown at the bottom of Fig. 2.

The radiation from the ECDL was carefully overlapped with the 532-nm radiation using a dichroic mirror. The transmission of the dichroic mirror for the 395-nm beam was approximately 80%. Both lasers were focused into the BBO crystal at a phase-matching angle of 61.2° (type 1 phase matching) using a bi-convex lens with a focal length of 25 mm. The dimensions of the BBO crystal were 4 mm × 4 mm in cross section and 8-mm long. The 395-nm and 532-nm beams were vertically polarized. To optimize the spatial overlap of the two beams inside the crystal and thus optimize the SFM process, we utilized the following procedure: the crystal was replaced by a 25-μm-diameter pinhole. The transmission of the 532-nm laser beam through the pinhole was optimized by adjusting the position of the focusing lens. A transmission of about 80% of the 532-nm intensity through the pinhole was achieved. The output of the ECDL was then overlapped with the 532-nm beam using mirrors and a telescope for better mode matching. The telescope consisted of a plano-convex lens ($f = 150$ mm) and a plano-concave lens ($f = 100$ mm). Both lenses were anti-reflection-coated for 395 nm. The positions of the lenses were adjusted until optimum transmission of the 395-nm laser beam through the pinhole was achieved. The pinhole was then replaced with the BBO crystal.

The SFM process produced approximately 40 nW of 226.8-nm radiation. The UV laser radiation generated by the SFM process was divided into a reference beam and a signal beam using a 50–50 beam splitter. The simultaneous detection of the reference and signal beams allows the subtraction of common-mode noise and etalon effects at the crystal surfaces and significantly enhances the detection efficiency. The reference beam was directed to a solar-blind photomultiplier tube (PMT). The signal beam was transmitted through a room-temperature gas cell filled with a mixture of 100 ppm NO (nominal concentration) in N_2. Band-pass filters centered at 226 nm with peak transmissions of 12% and 20% and bandwidths of 10 nm were placed in front of the PMTs. The beams were also attenuated by a factor of 20 using neutral-density filters to maintain PMT linearity. Two absorption traces are shown in Fig. 2. One of these was acquired while the ECDL frequency was tuned up, and the other while the frequency was tuned down. The data shown were averaged over 32 traces on the digital oscilloscope. The ECDL was tuned over the mode-hop-free tuning range at a frequency of approximately 5 Hz, and the spec-

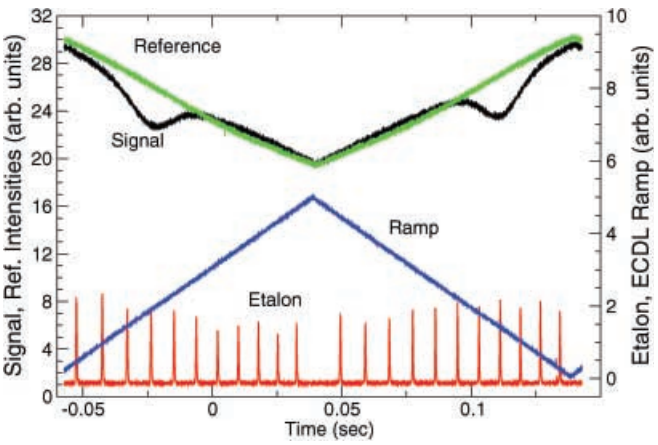

FIGURE 2 NO absorption spectrum of the $P_2(10)$ and ${}^{P}Q_{12}(10)$ overlapped absorption lines. The raw signal, reference, ramp, and etalon traces are plotted

trum shown was acquired in approximately 6 s. Attempts to tune the ECDL at higher rates resulted in drastic decreases in the mode-hop-free tuning range.

After recording the traces shown in Fig. 2, the gas cell was evacuated and filled with 1 bar of pure air. The signal and reference PMT traces were then recorded. The ratio of the signal to reference PMT outputs from Fig. 2 was then divided by the ratio of the signal to reference PMT outputs for the cell filled with pure air. This entire process took a couple of minutes in these demonstration experiments. The result of this operation is shown as the transmission curve in Fig. 3. This procedure was found to reduce structure in the transmission baseline due to the slightly different shapes of the signal and reference traces, to reduce drift in the baseline level due to long-term drifts in laser power or optical alignment, and to account for possible etalon effects. The Tektronix oscilloscope has 10 000 channels, and most of the noise evident in the transmission curve shown in Fig. 3 is read noise that did not decrease substantially with further signal averaging. Fifty channels were binned in software to reduce the noise, and it was verified that this did not affect the spectral line shapes even for very low cell pressures.

3 Experimental results

Our initial set of measurements was performed using a gas mixture of 100 ppm NO in nitrogen. A computer code for the analysis of the absorption spectra is under development and has been used to analyze this initial set of data. The theoretical spectrum shown in Fig. 4 is calculated assuming a Voigt profile with a Doppler width (FWHM) of $\Delta\nu_d = 2.97$ GHz. The collisional width (FWHM) that gives the best fit for the various NO lines that we have analyzed is 0.172 GHz/kPa, with most of the broadening presumably due to the nitrogen molecule. This is in excellent agreement with broadening parameters measured by Chang et al. [10] and Danehy et al. [11] for collisions of NO with N_2. The spectrum in Fig. 4 was recorded at a pressure of 13.1 kPa, and the collisional width of the theoretical line is $\Delta\nu_c = 2.32$ GHz. As evident from Fig. 4, the theoretical spectral line shape is in excellent agreement with the experimental line shape. The NO concentration is also a parameter in the theoretical calculation, and the concentration that gives the best fit to the experimental spectrum is 94 ± 10 ppm. The 10 ppm uncertainty in the experimental measurements is indicative of the range of concentration values that we obtain from measurements on different days and from different spectral regions. The uncertainty is partly due to transmission baseline drifts and may also result from uncertainties in the spectral model. This experimental value is, however, in good agreement with the quoted value of 100 ± 10 ppm for the NO-N_2 gas mixture.

We then tuned the wavelength of the ECDL to 395.40 nm so that the SFM radiation would be in resonance with a group of NO lines near 226.87 nm. There are numerous closely spaced transitions in this region. Therefore, the structure of the spectrum is useful for verifying the wavelength of the SFM radiation independently of the wavemeter readings. Absorption spectra at pressures of 13.1 and 1.11 kPa are shown in Fig. 5. The shape of the calculated absorption spectrum is in excellent agreement with the shape of the experimental spectrum, validating our wavemeter readings. The NO concentration that gave the best agreement between theory and experiment was 85 ± 10 ppm, slightly less than the value listed for the spectrum shown in Fig. 4, but still in good agreement with the nominal

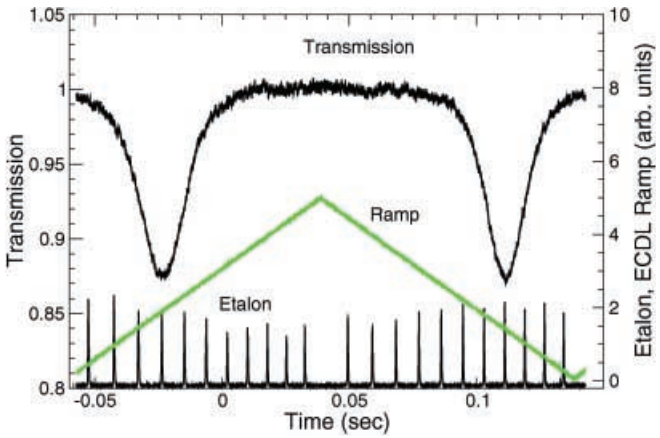

FIGURE 3 NO transmission spectrum for the $P_2(10)$ and $^PQ_{12}$ (10) overlapped absorption lines. The ratio of the signal to reference shown in Fig. 2 for the gas cell at $P = 13.1$ kPa, $x_{NO} = 100$ ppm, was divided by the ratio of the signal to reference in a gas cell at $P = 100$ kPa, $x_{NO} = 0$ ppm, to give the transmission curve shown

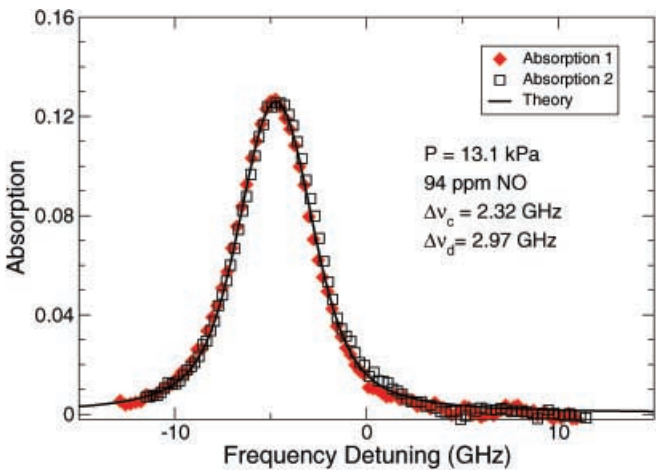

FIGURE 4 Comparison of measured and calculated NO absorption line shapes for the P_2 (10) and $^PQ_{12}$ (10) overlapped absorption lines. The overlapped P_2 (10) and $^PQ_{12}$ (10) transitions have frequencies of 44 087.79 and 44 087.77 cm^{-1}, respectively [9]. $\Delta\nu_c$ and $\Delta\nu_d$ are the collisional and Doppler widths of the Voigt profile

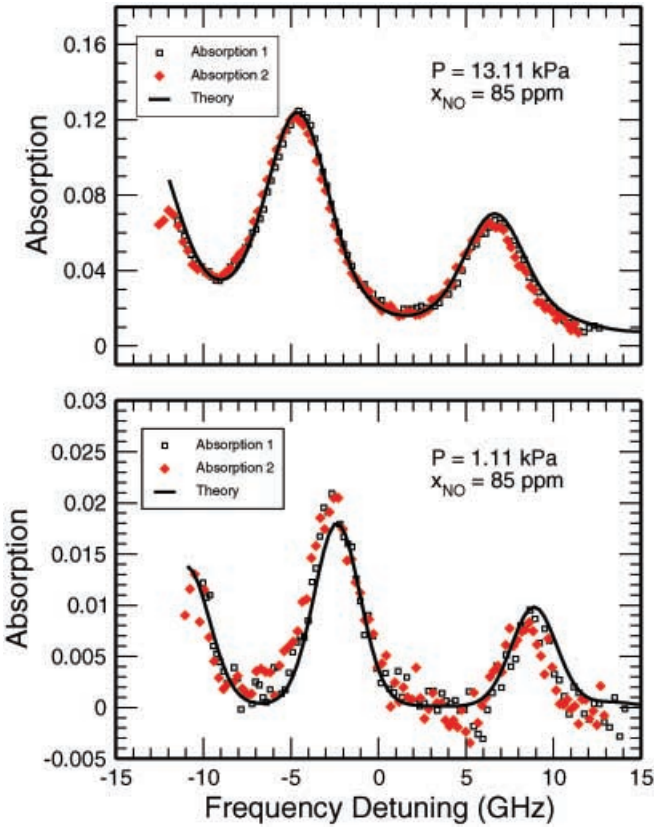

FIGURE 5 Comparison of measured and calculated NO absorption line shapes for the absorption features near overlapped absorption lines. The absorption feature centered at a frequency detuning of approximately 5-GHz is due to the overlapped P_2 (5) and ${}^{P}Q_{12}$ (5) transitions with frequencies of 44 077.71 and 44 077.70 cm^{-1}, respectively [9]. The absorption feature centered at a frequency detuning of approximately +7 GHz is due to the overlapped P_2 (2) and ${}^{P}Q_{12}$ (2) transitions at a frequency of 44 078.08 cm^{-1} [9]

NO concentration of the NO-N_2 gas mixture.

The theoretical power from the SFM process was estimated using the 2D-mix LP module of the program SNLO [12]. Using the parameters of our experimental set-up, the expected power from the SFG process is 270 nW. However, since the ECDL has a non-Gaussian beam profile the experimentally achievable UV power is expected to be much lower. The actual observed power of 40 nW was approximately a factor of 6.5 lower. No special efforts were made to optimize our SFM output power, because the SFM power was such that our dc PMT anode current was close to the maximum level, and PMT saturation was more of a concern, which was the reason for placing the neutral-density filters in front of each PMT.

The sensitivity of the NO sensor system in its present configuration is limited by the noise level in the detection channel. We are limited currently to detecting an absorption level of approximately 0.2%, determined by lowering the pressure in our gas cell to below 0.1 kPa and monitoring the resulting absorption. The baseline noise has an rms standard deviation of 0.17%, which is about a factor of eight higher than the shot-noise limit for the power of our laser. Assuming a S/N ratio of 1 at the detection limit, our estimated sensitivity for the current system is thus approximately 0.2 ppm for a 1-m path length in 300 K gas, or 0.5 ppm for a 1-m path length in 1000 K gas, a temperature that is more typical of combustion exhaust. Sonnenfroh et al. recently reported a detection limit of 0.5 ppm per meter path length at an absorption level of 9×10^{-4} using a mid-infrared quantum cascade laser system [13]. The more favorable detection limit for our system results from the strength of the ultraviolet transitions of NO.

Although this is sufficient sensitivity for monitoring the exhaust of practical combustion devices, that sensitivity can be improved by at least an order of magnitude using wavelength-modulation spectroscopy (WMS). For cw absorption systems, absorption levels of 10^{-5} or lower can be measured by wavelength-modulation techniques and phase-sensitive detection [14]. We can modulate the frequency of our ECDL by modulating the injection current of the 395-nm diode at frequencies f of approximately 1 to 10 kHz and detecting the $2f$ absorption signal using a lock-in amplifier. We have not yet implemented this WMS technique, but Peterson and Oh demonstrated a minimum detectable absorbance of about 2×10^{-5} using a similar detection system and estimated that, with further effort to reduce etalon effects, the minimum detectable absorbance could be lowered to 10^{-6} [3].

4 Summary and future work

A diode-laser-based sensor system for high-resolution, sensitive absorption measurements of the NO radical has been developed. The relatively high power of the diode-pumped IFD Nd:YAG laser results in the production of significant laser intensity at 226.8 nm. Initial direct absorption measurements showed a detection limit in terms of absorption level of 2×10^{-3}, equivalent to an NO detection limit of well under 1 ppm per meter of path length in 300 K gas. The use of WMS techniques to increase the sensitivity of the system will be explored in the near future. The use of different ECDL systems and the diode-pumped Nd:YAG laser to probe different species using UV laser radiation will also be explored. A system to perform absorption measurements of the OH radical at 309 nm incorporating a 745-nm ECDL is under development.

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