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Direct and wavelength modulation spectroscopy using a cw external cavity quantum cascade laser

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A continuous wave external cavity quantum cascade laser (EC-QCL) operating between 1872 and 1958 cm^{-1} has been used to make rotationally resolved measurements in the fundamental band of nitric oxide at 140 mTorr, and the ν_2 band of water at atmospheric pressure. These measurements demonstrate the advantages of wide tunability and high resolution of the EC-QCL system. From direct absorption spectroscopy on nitric oxide a laser bandwidth of 20 MHz has been deduced and a sensitivity of $8.4\times10^{-4}\ \text{cm}^{-1}\ \text{Hz}^{-1/2}$ was achieved. Wavelength modulation spectroscopy using current modulation enhances the sensitivity by a factor of 23 to $3.7\times10^{-5}\ \text{cm}^{-1}\ \text{Hz}^{-1/2}$. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3141521]

Continuous wave (cw) quantum cascade lasers (QCLs) are becoming increasingly popular sources for high resolution molecular spectroscopy owing to their increasingly high output powers, near room temperature operation, and intrinsic narrow linewidth. Furthermore such cw devices are attractive sources for cavity enhanced spectroscopy techniques because unlike pulsed QCLs, they do not suffer from the fast frequency chirping, which has so far prohibited the use of pulsed QCLs in combination with optical cavities.[1] The frequency chirping also limits the resolution of direct absorption spectroscopy studies with pulsed external cavity (EC)-QCLs, but an advantage is that their application with long path cells such as Herriott cells is not hampered by fringing effects.[2–6] True cw sources are generally limited however, in terms of both the wavelengths commercially available (~4–10 μm), and their tuning range (of the order of a few cm^{-1}). There is therefore great interest in the development of cw EC-QCLs with wide tunability that will allow detection of either multiple species within a reasonable spectral range, or continuous spectra of large gaseous and condensed phase species.[7–18] In this letter, we detail the performance of such a commercially available EC-QCL system operating around 5 μm and demonstrate its application for high resolution spectroscopy employing direct and wavelength modulation spectroscopy (WMS) throughout its entire tuning range.

The water-cooled EC-QCL was purchased from Daylight Solutions (model 21052-MHF) and has a specified tuning range of 1872–1958 cm^{-1} at a chip temperature of 15 °C, with output powers in excess of 60 mW over this range. The laser can be scanned over the entire wavenumber range using the laser controller with 6 different preset tuning rates for the grating inside the laser head in time periods of between 5.5 and 25 s. To show its performance over the whole tuning range, the emitted radiation was allowed to propagate a distance of two meters through the ambient air before being directed onto a thermoelectrically cooled mercury cadmium telluride (MCT) detector (VIGO PVI-2TE-6) connected to a 2 Gsample/s, 350 MHz bandwidth digital oscilloscope (LeCroy Wavesurfer 434). Figure 1(a) shows the intensity output of the laser over the whole tuning range scanned at a rate of 3.4 cm^{-1}/s; on average there are ~40 mode hops over this range, largely localized in the longer wavelength region. These mode hops are due to manufacturing issues with the antireflective coating on the laser chip. Several absorption lines due to aerial water (~1% water in the labora-

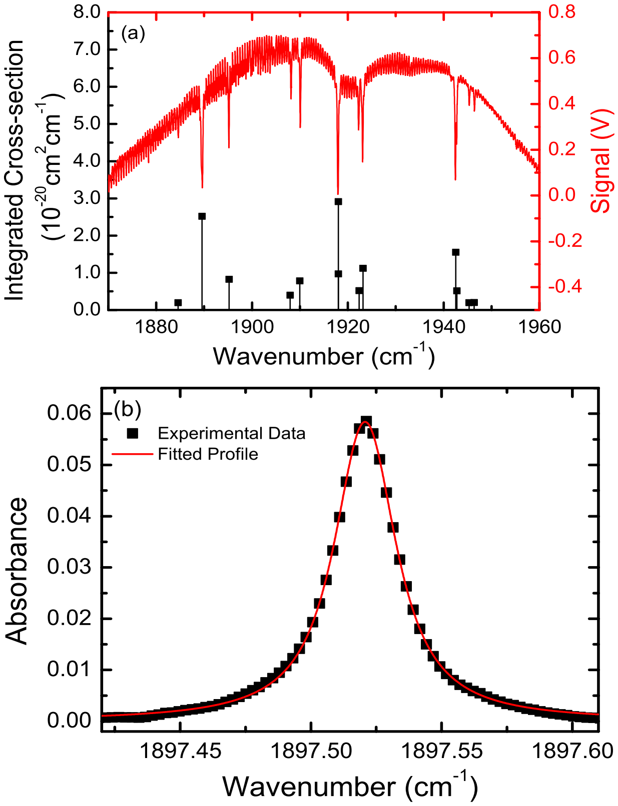

FIG. 1. (Color online) (a) Transmitted intensity after a path length of 2 m in laboratory air (~1% water in the laboratory air) showing a spectrum of the ν_2 band of water between 1872 and 1958 cm^{-1} obtained by scanning with the laser controller. The line positions and intensities from the HITRAN 2004 spectral database are plotted as a stick spectrum in the lower part of the figure. (b) A typical spectrum of the $(14,2,13)\leftarrow(13,1,12)$ transition of water recorded by scanning the PZT.

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tory air) are clearly observable and their positions and intensities are in good general agreement with the assignments from the HITRAN 2004 spectral database[19] plotted as a stick spectrum in the lower part of Fig. 1(a). The dip observed in the center of the spectrum is likely due to the imperfect antireflective coating on the laser chip.

In order to fine tune the laser radiation over a rotationally resolved absorption line the grating tuning is controlled using a piezoelectric transducer (PZT) attached to the grating of the EC system. The laser frequency was scanned over $\sim 1\ \mathrm{cm}^{-1}$ by applying a sinusoidal voltage ramp of 70 V peak-to-peak at a frequency of 10 Hz to the PZT. A typical spectrum of aerial water (~1% water in the laboratory air) measured over a path length of 2 m through the ambient air is shown in Fig. 1(b), where the absorbance is defined as $-\ln(I/I_0)$ with I and I_0, the signals with and without absorber present, together with a Voigt fit for the $(14,2,13) \leftarrow (13,1,12)$ transition within the ν_2 band of water. Frequency calibration was achieved by passing the radiation through a germanium etalon placed in the beam line, the free spectral range of which is 500 MHz. The measured transition full width at half maximum linewidth is 850 MHz and is consistent with an air-broadening parameter of $0.51\ \mathrm{MHz\ Torr}^{-1}$ as reported in the HITRAN 2004 database.[19]

Doppler limited studies were conducted by passing the radiation through a 10 cm long glass cell containing 140 mTorr of NO—set at an angle from the incoming beam in order to minimize optical feedback to the laser and then onto the MCT detector. Figure 2(a) shows an example of the absorption spectrum of NO, probing the R(8.5) rovibrational transition centered at $1906.145\ \mathrm{cm}^{-1}$. The data correspond to 100 averages taken while applying a 10 Hz sine wave with 900 mV amplitude. The two lines shown correspond to excitation from both the e/f Λ-doublets, and their splitting, ~320 MHz, provided an independent check on the frequency calibration. The spectral fitting routine allowed for hyperfine splitting caused by ^{14}N and treated each of the components independently, fitting 10 Voigt functions with their integrated area determined by the line strengths reported in the HITRAN 2004 database and returning both the Gaussian and Lorentzian components separately. The measured Doppler width is 135 MHz and is in good agreement with the calculated value of 130 MHz for a thermal sample, while the Lorentzian component allows us to estimate the laser bandwidth to be 20 MHz over ~10 s. However, this value varies within the tuning range of the laser and is on average around 50 MHz. This is in reasonable agreement with other previously reported values for the linewidth of a free running cw EC-QCL.[9,10,16,18] Typical direct absorption spectra such as Fig. 2(a) display a sensitivity of $8.4 \times 10^{-4}\ \mathrm{cm}^{-1}\ \mathrm{Hz}^{-1/2}$. This sensitivity is less than expected from analogous diode laser studies and this is caused by the intensity fluctuations of the emitted laser light. Measurements conducted at both ends of the laser tuning range returned similar values for the spectral resolution, but with sensitivities reduced by a factor of 5 due to lower powers, and intensity fluctuations and etalon effects associated with the poorer quality of the antireflective coating at lower wavelengths.

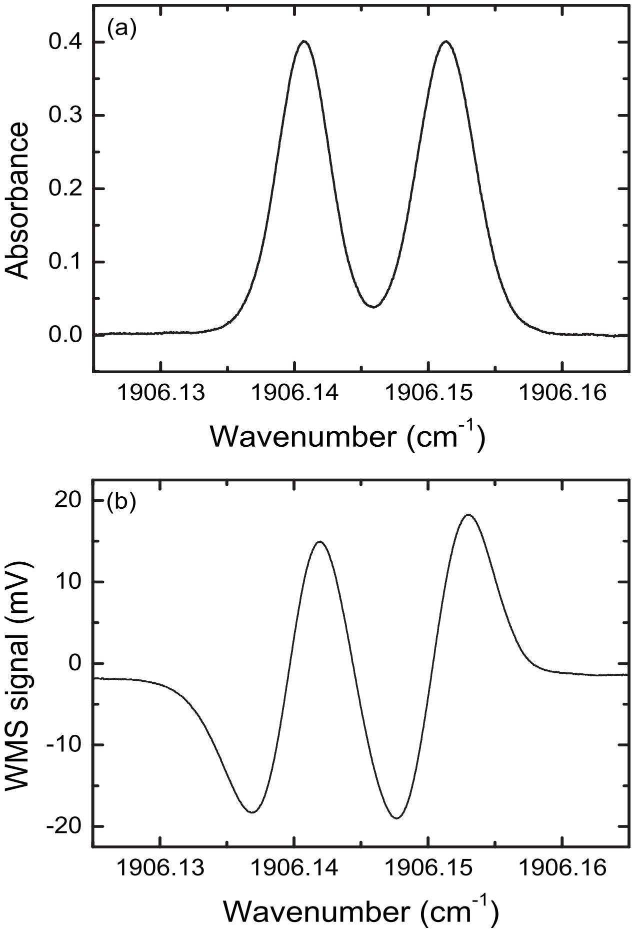

FIG. 2. (a) Spectrum of 140 mTorr of NO for the R(8.5) rovibrational transition centered at $1906.145\ \mathrm{cm}^{-1}$. (b) The corresponding $1f$ WMS spectrum.

It is well know that the sensitivity of absorption measurements can be enhanced by using modulation techniques to transpose the absorption signal into a frequency regime where noise sources are less likely to interfere with the signal. To this end, we performed WMS by directly modulating the injection current of the laser with a rapid sinusoidal modulation;[20] WMS at a modulation frequency of 130 Hz using the PZT inside the EC-QCL was demonstrated recently by Karpf and Rao.[18] WMS was conducted at 15 kHz with modulation amplitudes in the range of 1.5 mV–1.5 V to the injection current while slowly scanning the laser frequency with the PZT. The corresponding absorption spectra were obtained by demodulating the detected signal at the desired harmonic using a lock-in-amplifier (Stanford Research Systems, SR830 DSP) with the time constant set to 100 μs, before being displayed on the oscilloscope, 100 averages were taken for each spectrum. Figure 2(b) shows the same transition being probed under the same sample conditions as in Fig. 2(a) but with $1f$ WMS at 1.5 mV modulation. The sensitivity of a WMS measurement can generally be increased by taking measurements far from the derivative limit.[21] The magnitude of the WMS line shape, and thus the signal to noise ratio (S/N), will initially increase with the modulation amplitude, but as we move further from the derivative limit, there is also an associated increase in the linewidth, eventually leading to a decrease in signal. This is shown in Fig. 3(a) for the line consisting of the combined transitions Q(2.5) and Q(4.5) at $1875.724\ \mathrm{cm}^{-1}$, where as the modulation voltage increases, the peak both widens and its amplitude increases. In Fig. 3(b), the measured amplitude

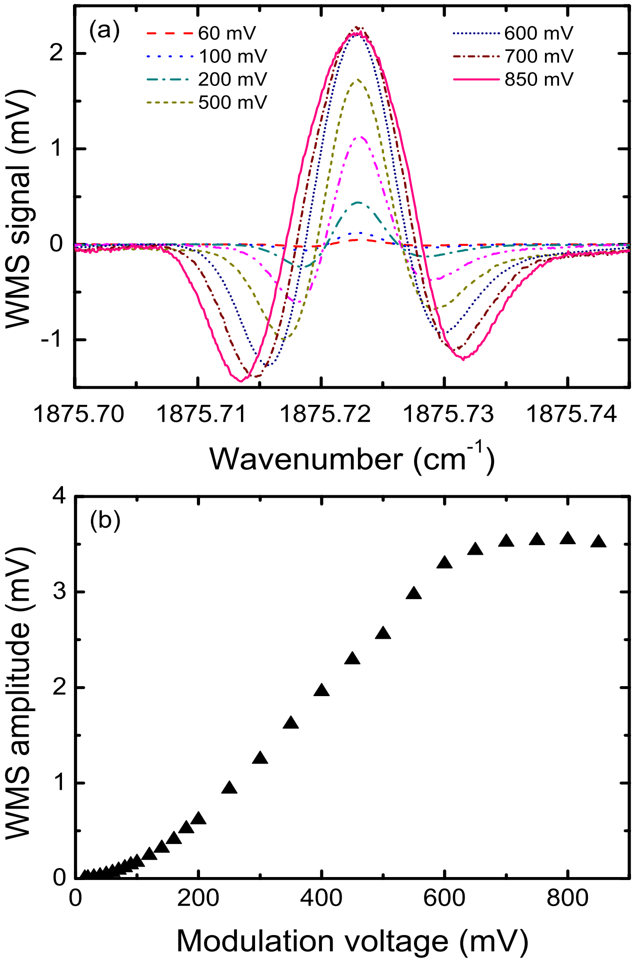

FIG. 3. (Color online) (a) $2f$ WMS spectra of 140 mTorr of NO for the Q(2.5) rovibrational transition centered at 1875.724 cm^{-1} as a function of modulation amplitude. (b) The amplitude of the second harmonic WMS signal as a function of the applied modulation voltage.

of the $2f$-harmonic signal is plotted as a function of modulation voltage and a maximum signal occurs at an amplitude of 700 mV for a modulation index of 2.2 (defined as the ratio of the modulation amplitude to the half-width half maximum of the transition),[22] corresponding to an modulation depth of 142 MHz. Under these conditions, a sensitivity of 3.7×10^{-5} cm^{-1} $\text{Hz}^{-1/2}$ was achieved, a factor of 23 better than direct absorption. Coupling this radiation source with a long path absorption cell (say 100 m) such as a Herriot or White cell should result in a minimum detectable NO concentration of <1 ppb (part per 10^9), which is at the detection limit required for concentration monitoring of NO levels in exhaled breath for medical diagnostics.[23]

Initial high resolution measurements with a cw EC-QCL have been presented. WMS at 15 kHz has been achieved by direct modulation of the injection current, and the sensitivities for direct absorption spectroscopy and WMS have been determined to be 8.4×10^{-4} and 3.7×10^{-5} cm^{-1} $\text{Hz}^{-1/2}$, respectively. These detection levels for WMS indicate that such high power, widely tunable radiation sources will find broad application in sensing measurements, and in modulation, and photoacoustic spectroscopies.

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