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This is an accepted version of a paper published in *Applied physics. B, Lasers and optics (Print)*. This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the published paper:

Kluczynski, P., Lundqvist, S., Westberg, J., Axner, O. (2011)

"Faraday rotation spectrometer with sub-second response time for detection of nitric oxide using a cw DFB quantum cascade laser at 5.33 μm "

Applied physics. B, Lasers and optics (Print), 103(2): 451-459

URL: <http://dx.doi.org/10.1007/s00340-010-4336-8>

Access to the published version may require subscription.

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Faraday rotation spectrometer with sub-second response time for detection of nitric oxide using a cw DFB quantum cascade laser at 5.33 μm

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Abstract

A Faraday modulation spectrometer for sensitive and fast detection of nitric oxide at 5.33 μm utilizing a room temperature continuous wave distributed feedback quantum cascade laser and a Peltier cooled MCT detector is presented. The magnetic field was modulated at 7.4 kHz whereas the laser wavelength was scanned at 20 Hz across the most favorable rotational-vibrational transition for FAMOS, $Q_{3/2}(3/2)$, at 5.33 μm . Using a 15 cm optical path and lineshape fitting, the spectrometer provides a detection limit of 4.5 ppb for a response time of 1 s. An Allan variance analysis demonstrates that the system has an excellent stability, up to several hours of operation.

OCIS codes: 140.5965, 230.2240, 300.1030, 300.6340, 300.6380.

1 Introduction

Faraday Modulation Spectroscopy (FAMOS) is a spectroscopic detection technique for detection of paramagnetic molecules in general, and nitric oxide (NO) in particular [1-5]. The technique utilizes the fact that, in the presence of a magnetic field, a transition in a paramagnetic molecule can rotate the polarization plane of linearly polarized light. By placing the sample between nearly crossed polarizers, the rotation is monitored as an alteration of the detected optical power. Modulation of the magnetic field and detection of the signal at the modulation frequency largely suppress background signals originating from optical interference effects and possible spectral interferences from diamagnetic constituents.

Primarily due to the rapid development of quantum cascade lasers during recent years, the FAMOS technique has lately been repeatedly used for detection of NO addressing the strong fundamental rotational-vibrational transitions, where one particular transition, $Q_{3/2}(3/2)$, at 5.33 μm , has been identified as the most sensitive [1-4]. Using an external cavity quantum cascade laser (QCL), a high performance, transportable FAMOS spectrometer, capable of detecting 4.7 ppb of NO with a 1 second response time, has recently been realized by Lewicki *et al.* [4]. However, since that system is based upon an external cavity laser it requires stable running conditions to obtain the optimum detectability, which restricts its use in industrial applications. In addition, it utilizes a laser source with a moderate output power (3 mW) that is modulated through a mechanical actuator.

Here, we present a Faraday modulation spectrometer for sensitive detection of NO that is based upon a distributed feedback (DFB) QCL with an output power of 60 mW and a Peltier cooled mercury-cadmium-telluride (MCT) detector. A DFB laser provides more output power than an external cavity laser, which increases the sensitivity of the spectrometer. It is also more

compact and it is solely scanned through the injection current of the laser, which makes it less susceptible to drifts (as no mechanical parts are involved in scanning the laser wavelength). Furthermore, application of a rapid magnetic field modulation (in the kHz regime) and a fast wavelength scan allow for further enhancement of the signal-to-noise ratio and at the same time yields a sub-second response time of the spectrometer. In addition, the concentration of NO is extracted via curve fitting, which is an advantage when high accuracy assessments are to be made since it reduces the risk for contributions from structured or drifting background signals. All these features make the presented spectrometer suitable for industrial and field applications.

An Allan variance analysis demonstrates that the system has an excellent stability, i.e. a white noise behavior, for up to several hours of operation, with a detection limit of 4.5 ppb for a response time of 1 s.

2 Theory

Theoretical descriptions of the FAMOS signal from Q-transitions in NO have previously been given in the literature [1-4]. It was recently shown by Westberg *et al.* [6] that it is possible to express the FAMOS signal, based upon the Faraday effect, $S_F(\tilde{\nu})$, conveniently in terms of the integrated line strength S , [in units of $\text{cm}^{-1}/(\text{molecules cm}^{-2})$], as well as the even component of the first Fourier coefficient of the Doppler-peak-normalized magnetic-field-modulated dispersion lineshape function for the transition, $\bar{\chi}_1^{disp,even}$, as

$$S_F(\tilde{\nu}) = \eta \frac{SNL\hat{\chi}_0}{4} \sin(2\varphi) I_0 \cdot \bar{\chi}_1^{disp,even} \left(\Delta\bar{\nu}_0, \bar{\nu}_a, \delta\bar{\nu}_L \right), \quad (1)$$

where η is an instrumentation factor (comprising the sensitivity of the detector and the gain of the lock-in amplifier), N is the density of molecules to be detected (cm^{-3}), in this case NO, L is the interaction length (cm), $\hat{\chi}_0$ is the peak value of the area-normalized absorption Gaussian lineshape function ($1/\text{cm}^{-1}$), φ is related to the angle between the axes of the polarizer and the analyzer, θ , as $\varphi = \pi/2 - \theta$, and I_0 is the power of the radiation entering the gas sample, whereas $\bar{\chi}_1^{disp,even}(\Delta\bar{\nu}_0, \bar{\nu}_a, \delta\bar{\nu}_L)$ is given by

$$\bar{\chi}_1^{disp,even}(\Delta\bar{\nu}_0, \bar{\nu}_a, \delta\bar{\nu}_L) = \frac{2}{\tau} \int_0^{\tau} \bar{\chi}^{disp}[\Delta\bar{\nu}(t), \delta\bar{\nu}_L] \cos(\omega t) dt, \quad (2)$$

where $\delta\bar{\nu}_L$ is the Doppler-width-normalized homogeneous broadening (also referred to as the Voigt parameter), given by $\delta\tilde{\nu}_L \sqrt{\ln 2} / \delta\tilde{\nu}_D$, where $\delta\tilde{\nu}_L$ is the half-width half-maximum (HWHM) of the homogeneous broadening (i.e. the pressure broadening) and $\delta\tilde{\nu}_D$ is the HWHM of the Doppler broadening. The tilde sign indicates that the entity is given in units of inverse centimeters whereas the over bar shows that the entity is dimensionless, normalized with respect to $\delta\tilde{\nu}_D / \sqrt{\ln 2}$. Furthermore, $\bar{\chi}^{disp}[\dots]$ is the dispersion counterpart to the Doppler-peak-normalized absorption lineshape function, which for a Voigt profile can be written as

$$\bar{\chi}^{disp}[\Delta\bar{\nu}(t), \delta\bar{\nu}_L] = -\text{Im} \left\{ w \left[\Delta\bar{\nu}(t) + i\delta\bar{\nu}_L \right] \right\}, \quad (3)$$

where $w[\dots]$ is the complex error function and where $\Delta\bar{\nu}(t)$ is the instantaneous Doppler-width-normalized detuning of the laser light from the transition, given by

$$\Delta\bar{\nu}(t) = \Delta\bar{\nu}_0 - \bar{\nu}_a \cos(\omega t), \quad (4)$$

where $\Delta\bar{\nu}_0$ is the detuning in the absence of magnetic field [i.e., given by $(\tilde{\nu} - \tilde{\nu}_0)\sqrt{\ln 2} / \delta\tilde{\nu}_D$, where $\tilde{\nu}$ and $\tilde{\nu}_a$ are the center frequencies of the laser and the transition, respectively, and $\bar{\nu}_a$ the Doppler-width-normalized modulation amplitude, given by $\sqrt{\ln 2} g_J \mu_B B_0 / \delta\tilde{\nu}_D$, where, in turn, g_J is the g -factor for the states addressed, μ_B is the Bohr magneton, and B_0 is the amplitude of the magnetic field.

3 Experiment

The experimental set-up is shown in Figure 1. A room temperature cw QCL DFB laser emitting at 5.33 μm from Maxion Technologies was used as the source. The laser was mounted in a high heat load (HHL) package, which in turn was mounted in the laser head with integrated thermoelectric coolers enabling tuning of the laser temperature in the range between 15°C and 35°C and a temperature stabilization of the laser within 0.1 °C. The laser beam was collimated by a chalcogenide aspheric lens, also referred to as Black Diamond, from Lightpath Technologies with an effective focal length of 1.8 mm and a diameter of 6.5 mm. A small fraction of the laser light was reflected from a CaF_2 wedge, passed through a closed reference cell containing 1000 ppm of NO at 58 mbar, and focused on a Peltier cooled MCT detector (VIGO) by means of a F/2 ZnSe lens with a focal length of 2.54 mm. The active area of the detector was $0.2 \times 0.2 \text{ mm}^2$ whereas its detectivity was $D^* = 5.5 \times 10^9 \text{ cmHz}^{1/2}/\text{W}$. The photocurrent from the reference detector was amplified by a DC-coupled transimpedance amplifier and sent to a DAQ board (NI-USB 6251). The direct absorption signal from the reference cell was used for accurate determination of the laser frequency in the signal processing.

The main part of the beam was transmitted through a CaF_2 wedge and passed two wire grid polarizers stacked in series to clean up and define the plane of polarization from the laser. After the polarizers, the laser beam passed through a 25 cm long absorption cell with an outer diameter of 12 mm. The cell tube was made of borofloat glass whereas the optical windows were made of 2 mm thick CaF_2 plane parallel discs (with a diameter of 12 mm). The cell was connected via a pressure controller to a gas mixing device (HOVAGAS). The cell was inserted in a 15 cm long solenoid with an inner diameter of 12.5 mm. The solenoid, which consisted of 765 turns of 1 mm thick copper wire with 0.3 mm thick isolation, coupled in series with a capacitor stack, was driven by a power audio amplifier. The resonant circuit was tuned to obtain a maximum magnetic field at a frequency of 7.4 kHz. We found this choice of modulation frequency to be a good compromise between the performance of the instrument (detection limit and response time) and the losses inside the solenoid. The solenoid and the resonant circuit electronics were mounted in an aluminum enclosure that shielded the rest of the instrumentation from any stray magnetic field. The dimensions of the shield enclosure were carefully optimized to minimize the leakage of the magnetic field outside the enclosure while still allowing for efficient field generation inside the solenoid. The system was capable of delivering magnetic field amplitudes of 300 Gauss inside the solenoid at 7.4 kHz under continuous operation. The maximum magnetic field amplitude that could be produced was 640 Gauss, although the system could be operated under such conditions only under a short period of time (the maximum magnetic field that could be produced was purely dictated by the excess heat dissipation inside the assembly and not the power available). The cell was equipped with a thermistor to constantly measure the temperature at the surface of the cell inside the solenoid. For calibration and

surveillance purposes, the current through the solenoid was continuously monitored with a custom made current transformer.

After the cell, the beam passed a wire grid polarizer. The maximum extinction ratio after the analyzer was approximately 10^{-5} . We have also tested to exchange the polarizer-analyzer pair with Rochon MgF_2 polarizers (CVI) with a similar extinction ratio. This yielded approximately the same spectrometer performance although the total optical path had to be increased in order to prevent the deflected beam from the second Rochon prism from falling onto the detector. We found that the system with wire-grid polarizers could be made more compact and less sensitive to misalignments.

After the analyzer, the laser radiation was focused on a Peltier cooled MCT detector with an immersion lens by the use of an off-axis parabolic mirror. The detector had an effective active area of $1 \times 1 \text{ mm}^2$ and a $D^* = 7.2 \times 10^{10} \text{ cmHz}^{1/2}/\text{W}$. The photocurrent from the measurement channel detector was amplified by a high-gain transimpedance amplifier incorporating a background current subtraction loop making it effectively AC-coupled. The transimpedance amplifier design was optimized using a SPICE simulator to obtain the desired pass band. After the current-to-voltage conversion, the signal was sent to a lock-in amplifier, configured for detection at 1f. The demodulated 1f signal was then sent to a NI-DAQ board. The lock-in bandwidth, sampling and buffering times varied depending on the mode of operation and are therefore given below in the Results section.

The laser characteristics are shown in Figure 2. Panel A displays the voltage-to-current and the power-to-current responses at 25 °C and 35 °C (upper curve and left axis, and lower curves and right axis, respectively). Panel B illustrates the corresponding spectral power density at 35 °C for 750 and 800 mA of driving current (rightmost and leftmost curves, respectively). To

reach the desired wavelength of 5331 nm (1875.8 cm^{-1}), corresponding to the $Q_{3/2}(3/2)$ transition, the laser was operated at a temperature of 32 °C and with a bias current of 780 mA. At this temperature the threshold current was 460 mA and the side mode suppression ratio was better than 25 dB. The emitted optical power of the collimated beam at the pertinent bias current was 60 mW.

4 Results

Figure 3A shows a Faraday rotation spectrum of 1 ppm NO at a pressure of 67 mbar. The magnetic field amplitude was set to 220 Gauss (156 Gauss rms). The spectrum represents an average of 200 scans, taken with a scan rate of 20 Hz, a lock-in time constant of 100 μs , and a data acquisition rate of 40 kHz. The measurement data comprising the curve in Fig. 3A was thus acquired with a total acquisition time of 10 seconds with an efficient measurement time constant of 20 ms. In order to calibrate the laser frequency sweep, a 2.54 cm Germanium Fabry-Perot etalon with a free spectral range of 1.46 GHz was temporarily inserted behind the cell. The resulting frequency-vs.-injection current characteristic is presented in 3B. As can be seen from the figure, the laser tunes almost linearly with current, which is a manifestation of the fact that the current change over the sweep (25 mA) is small compared to the bias current (780 mA). The observed laser linewidth was estimated to be between 150 and 200 MHz (assessed from a separate experiment utilizing a convolution of the line with low pressure nitric oxide spectra), mainly caused by the noise in the driving electronics (we believe that the linewidth of the laser in reality is much smaller than this). The average FM-index of the laser at the scan frequency, calculated from the etalon trace, was found to be 0.55 GHz/mA.

Figure 4A shows the corresponding frequency-linearized FAMOS spectrum, obtained by using the frequency vs. current dependence shown in Fig. 3B. Figure 4B displays a simulated

FAMOS spectrum based on data from the HITRAN 2008 data base and a magnetic field amplitude (B_0) of 220 Gauss (corresponding to a rms field of 156 Gauss). The simulated spectrum includes the 200MHz broadening of the laser line caused by noise from the laser driver. As can be seen, a good agreement between the two spectra is obtained, not only regarding the line positions but also concerning the line amplitudes and widths. This indicates that the actual magnetic field inside the cell was homogeneous and its amplitude was equal to the predicted value (i.e. no losses due to the shield were observed). However, as compared to the simulated spectrum, the experimental spectrum shows a slight asymmetry, assumed to be caused by circular dichroism originating mainly from imperfect polarizers [7], which is an effect that has not been included in the theoretical description.

In order to maximize the signal-to-noise ratio (SNR), both the uncrossing angle, φ , and the amplitude of the modulated magnetic field, B_0 , have to be optimized. The measured FAMOS signal-to-noise ratio (SNR) as a function of φ is shown by the individual markers in Fig. 5A. The solid line represents a fit of the type $a\varphi / (1 + b\varphi + c\varphi^2)$, which is based upon an assumption that the signal has a linear dependence on the uncrossing angle, φ , whereas the noise has a square dependence. The data unveils an optimum uncrossing angle for this instrumentation of 0.6° . Figure 5B displays the peak value of the FAMOS signal from the $Q_{3/2}(3/2)$ transition as a function of magnetic field. For low magnetic fields the signal increases linearly with the field strength. As the field is increased, the slope decreases and the peak value of the FAMOS signal reaches a maximum for an optimum magnetic field of 156 Gauss (rms), after which it starts to decrease due to over modulation, in agreement with earlier predictions [1-2].

In order to assess the NO concentration from a measurement with a fast response time and good accuracy, the system was run in scan mode together with lineshape fitting. The

spectrometer was scanned across the $Q_{3/2}(3/2)$ transition with a sweep amplitude of 3 GHz (0.1 cm^{-1}) at a rate of 20 Hz. The lock-in time constant was set to 1 ms whereas the sampling rate of the DAQ board was lowered to 300 samples/sec resulting in 15 samples over the line. This choice of parameters provided a good compromise between the detection limit, response time and the computational capacity of the computer used. Typical data from such a scan are shown by the individual markers in Figure 6.

Since no analytical expression of Eq. (2) yet has been derived, and to allow for a fast response, the NO concentration was extracted from the measured data by means of a least square fit procedure using a lineshape function stored in a look-up table (LUT) as a trial function. The system was calibrated by scanning the laser over the $Q_{3/2}(3/2)$ transition using a gas with an NO concentration of 1 ppm at a pressure of 67 mbar, prepared by dilution of a 90 ppm NO gas from a certified bottle with N_2 using a HOVAGAS gas mixer. To ensure accuracy, calibration gas was flushed several times into the cell before the calibration procedure was performed. The assessment of the NO concentration from fits using a LUT proved to be fast since the only free parameters in the fitting routine were an offset with a slope (representing the background) and a signal amplitude and a line position (representing the signal). The quality of the fits was in general good, which vouches for a good accuracy. An example of a fit is given by the solid curve in Figure 6.

Since the width of the profile depends on the pressure, the concentration assessments had to be performed at the same pressure as for which the LUT was taken. When an analytical expression of Eq. (2) has been derived, the LUT table can be exchanged to an analytical expression, in a similar manner as is done in a wavelength modulation system [8], whereby there is no more requirement to know the pressure in the curve fit procedure as the line width can be

treated as a free parameter. This implies that immunity to foreign gas broadening would be achieved with this measurement method (although the pressure information still would be needed for the calculation of the gas concentration).

In order to estimate the performance of the instrument (primarily the system stability) a 16 hours long measurement was performed. From that data, an Allan plot was created, from which the detection limit for a given integration time can be estimated. The result is shown in Figure 7. As can be seen from the figure the system stability is excellent, showing a white noise limited performance up to a few thousands seconds. Using the aforementioned curve fit routine in scan mode, it was found that the detection limit (1σ) at 1 second integration time was 4.5 ppb.

For comparison with previous results [4], we have estimated, based on the experimental data taken in the scan mode, what the performance of the system would be if it was configured for locked-line mode operation, i.e. by constantly measuring on the peak of the line with the laser frequency locked to the center of the line. Assuming no drift of the laser frequency and no influence from offset fluctuations, it was found that the corresponding detection limit would be 1.8 ppb (still using a 1 second integration time). However, the locked-line mode of operation is in reality not as robust as the scan mode due to difficulties to compensate for the laser frequency drifts and due to influence of background offsets on the measured signal. As was shown in [4] it was in practice not possible to achieve the theoretical performance using of the locked-line mode of detection, and the SNR was degraded by a factor of 2. As mentioned above, in addition to compensating for frequency drifts and background effects, it is worth to note that application of a curve fit algorithm allows one to reach better detection limits than what is possible by application of a simple line amplitude measurement due to the fact that several points of the scan simultaneously contribute to the calculation of the concentration value.

5 Conclusion

In this paper we have demonstrated, to our knowledge for the first time, a Faraday modulation spectrometer for sensitive detection of nitric oxide addressing its sensitive $Q_{3/2}(3/2)$ transition around $5.33\text{ }\mu\text{m}$ utilizing a cw DFB QC laser. An Allan variance analysis demonstrates that the system has an excellent stability and white noise behavior up to several hours of operation, with a detection limit of 4.5 ppb for a response time of 1 s. The system was operating in a scanned mode of detection and a curve fit algorithm was applied for extraction of the gas concentration. A comparison with the performance a locked-line mode was also performed. Although the application of a scanned mode of operation that includes a curve fitting procedure provides in general a lower SNR than locked-line assessments, it allows for elimination of problems with background offsets and frequency drifts. It is thereby concluded that the use of scan mode detection and a curve fit algorithm provides the best compromise between detection limit and long term stability for a practical system.

6 Acknowledgements

This work was supported by the Swedish Research Council under the project 621-2007-5123. Umeå University Industrial Postgraduate School (*swe.* Företagsforskarskolan) is also acknowledged. The design of the magnetic coil and enclosure was performed by Tomas Lock of MetriNova AB.

References

1. G. Litfin, C. R. Pollock, R. F. Curl, and F. K. Tittel: J Chem Phys **72**, 6602 (1980)
2. T. A. Blake, C. Chackerian, and J. R. Podolske: Appl. Optics **35**, 973 (1996)

3. T. Fritsch, M. Horstjann, D. Halmer, Sabana, P. Hering, and M. Murtz: Appl. Phys. B-Lasers Opt. **93**, 713 (2008)
4. R. Lewicki, J. H. Doty, R. F. Curl, F. K. Tittel, and G. Wysocki: Proc. Natl. Acad. Sci. U. S. A. **106**, 12587 (2009)
5. H. Ganser, W. Urban, and G. J. Brown: Molecular Physics **101**, 545 (2003)
6. J. Westberg, L. Lathdavong, C.M. Dion, J. Shao, P. Kluczynski, S. Lundqvist, and O. Axner: To appear in JQSRT (2010)
7. R. J. Brecha and L. M. Pedrotti: Opt Express **5**, 101 (1999)
8. P. Kluczynski and O. Axner: Appl. Optics **38**, 5803 (1999)

Figure captions

Figure 1 Experimental setup.

Figure 2 Laser characteristics. Panel A: The voltage-to-current and the power-to-current responses of the DFB laser at 25 °C and 35 °C, displayed by the upper curve and left axis, and the lower curves and right axis, respectively. Panel B: The spectral power density at 35 °C for 750 and 800 mA of driving current (rightmost and leftmost peaks, respectively).

Figure 3 Panel A: A Faraday rotation spectrum of 1 ppm NO at a pressure of 67 mbar as a function of injection current acquired with an effective time constant of 20 ms with a magnetic field (rms) of 156 Gauss. Panel B: The corresponding frequency vs. current dependence of the laser.

Figure 4 Panel A: Linearized Faraday spectra of 1 ppm NO. Panel B: A simulated FAMOS spectra. Panel C: A Transmission spectra (based on Hitran 2008).

Figure 5 Panel A: Individual markers: The FAMOS signal-to-noise ratio (SNR) as a function of polarizer uncrossing angle, φ ; Solid curve: Fit of the type $a\varphi / (1 + b\varphi + c\varphi^2)$. Panel B: Individual markers: The amplitude of the FAMOS signal as a function of magnetic field (rms). Solid curve: Dependence according to theory given.

Figure 6 Individual markers: Measurement data for the $Q_{3/2}(3/2)$ transition. Solid curve: fit of a lineshape function stored in a look-up table.

Figure 7 Upper curve (red on-line): Allan variance for scan mode detection. Lower curve (blue on-line): Estimated Allan variance for locked-line mode detection.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7