DiVA – Digitala Vetenskapliga Arkivet <http://umu.diva-portal.org>

This is an author produced version of a paper published in **Applied Optics**

This paper has been peer-reviewed but does not include the final publisher proof-corrections or journal pagination.

Citation for the published paper:

Jie Shao; Lemthong Lathdavong; Jonas Westberg; Pawel Kluczynski; Stefan Lundqvist; Ove Axner

“Faraday modulation spectrometry of nitric oxide addressing its electronic $X^2\Pi - A^2\Sigma^+$ band: II. Experiment”

Applied Optics, 2010, Vol. 49, Issue 29, pp. 5614-5625

URL: 10.1364/AO.49.005614

Access to the published version may require subscription. Published with permission from:

OSA - The Optical Society

Faraday Modulation Spectrometry of Nitric Oxide

Addressing its Electronic $X^2\Pi - A^2\Sigma^+$ Band: II. Experiment

Jie Shao,¹ Lemthong Lathdavong,² Jonas Westberg,² Pawel Kluczynski,³

Stefan Lundqvist,³ and Ove Axner^{2,*}

¹*Institute of Information Optics of Zhejiang Normal University, Jinhua, 321004, China*

²*Department of Physics, Umeå University, SE-901 87 Umeå, Sweden*

³*Siemens AB, IIA SLA R&D, Box 14153, SE-400 20 Göteborg, Sweden*

**Corresponding author: ove.axner@physics.umu.se*

A first demonstration of Faraday Modulation Spectrometry (FAMOS) of nitric oxide (NO) addressing its strong electronic $X^2\Pi(\nu''=0) - A^2\Sigma^+(\nu'=0)$ band is presented. The instrumentation was constructed around a fully-diode-laser-based laser system producing mW powers of ultraviolet light targeting the overlapping $Q_{22}(21/2)$ and $Q_{12}(21/2)$ transitions at ~ 226.6 nm. The work verifies a new two-transition model of FAMOS addressing the electronic transitions in NO given in an accompanying work. Although the experimental instrumentation could not address all the parameter space of the theory, the lineshapes and the pressure dependence could be verified under low-field conditions. NO could be detected down to a partial pressure of 13 μ Torr, which demonstrates the feasibility of FAMOS for sensitive detection of NO addressing its strong electronic band. 2010 Optical Society of America

OCIS codes: 010.0280, 020.0020, 020.7490, 120.0280, 300.6540, 300.6260, 300.6390.

1. Introduction

Nitric oxide (NO) is an environmentally hazardous, reactive and strongly toxic pollutant that contributes to ground-level ozone, causes smog and acid rain, and gives rise to direct health effects [1-3]. It is mainly anthropogenically produced by, for example, vehicle engines, power and incineration plants, and cigarette smoke [4-5]. On the other hand, NO is also an important intermediate in the chemical industry and an essential signaling molecule that participate in many physiological and pathological processes within the mammalian body [3, 6-11]. All this makes it of importance to monitor and assess the presence of NO under various conditions. This requires first of all access to a detection technique with sufficient sensitivity. In addition, since gas samples from industrial processes as well as from biological sources, e.g. combustive emissions and exhaled human breath, usually contain large amounts of water and carbon dioxide that often interfere with the detection of other constituents, also a good species selectivity is needed. This calls for a technique that allows for on-line detection of NO with a detectability in the low (or preferably also sub-) ppb-m range in the presence of significantly higher concentrations (often percentages) of concomitant species.

The most common non-extractive technique for on-line detection of molecular species in gas phase is based upon diode laser Absorption Spectrometry (AS) and referred to as Tunable Diode Laser Absorption Spectrometry (TDLAS) [12-15]. For robust implementation, it often uses Distributed Feedback Lasers (DFB) to address various overtone bands and incorporates Wavelength Modulation Spectrometry (WMS) for reduction of noise [16-20]. Although this technique is versatile and regularly used for detection of a number of species under various conditions [12-15, 21-27], its detectability is not yet sufficient for in-situ detection of NO [28-34], primarily caused by a combination of low transition probabilities of the overtone bands in

the infrared (IR) region and a lack of reliable diode lasers producing light in the wavelength regions of these bands. In addition, the overtone bands are susceptible to spectroscopic interferences from concomitant species, which can hamper quantitative assessments. It is therefore of interest to develop alternative methodologies for detection of NO, with respect to both increased sensitivity and selectivity.

Since transitions in the fundamental vibrational band in the mid-IR (MID) region in general have two or three orders of magnitude larger linestrengths than those in the overtone bands, an attractive way to improve on the sensitivity of conventional TDLAS techniques is to address such transitions. Although this was technically complicated and non-trivial until some years ago, primarily due to the lack of reliable laser sources at these wavelengths, the recent development of Quantum Cascade (QC) lasers has opened up for new possibilities. Detection of NO in ppb and sub-ppb concentrations (in single and multi-pass pass configurations respectively, utilizing an appropriate modulation technique), has been demonstrated during the last years using QC lasers addressing the fundamental vibrational band at $\sim 5.3 \mu\text{m}$ [35-56].

On the other hand, the linestrengths for electronic transitions in many types of molecules are significantly larger than those of the fundamental vibration (by around two orders of magnitude for NO [57]). Such transitions give therefore rise to even stronger absorption signals whenever they can be addressed [57-58]. An alternative approach for efficient detection of NO, which has the potential to provide even higher sensitivities, is therefore to address its electronic transitions. It was recently shown by Shao *et al.* that NO could be detected in low ppb·m concentrations by direct absorption spectrometry (DAS) in a single pass configuration utilizing a fully diode-laser-based (DLB) laser system producing mW power of light in the UV region by addressing the electronic $X^2\Pi(v''=0) - A^2\Sigma^+(v'=0)$ band [57]. In addition, electronic

transitions appear in wavelength regions less affected by spectral interferences than vibrational transitions. All this makes the electronic transitions an interesting alternative for sensitive detection of NO.

However, since the electronic transitions in the NO molecule are in the UV region (predominantly around 226 and 227 nm), and diode lasers produce light preferably in the visible or the IR region, frequency conversion (most often frequency doubling) in one or several stages has to be used to achieve the appropriate wavelengths. Since frequency conversion processes yield a higher level of noise, the previous detection of NO by DLB-AS in the UV region (DLB-UV-AS) was limited by laser excess noise [57]. It is therefore expected that an improvement of the detectability of NO can be obtained if DLB-UV-AS can be combined with a modulation technique.

Unfortunately, it is non-trivial to combine DLB-UV-AS with the most common modulation technique, WMS, since it normally utilizes a modulation of the wavelength of the light in the kHz (of tens of kHz) ranges. The reason is that frequency doubling of continuous-wave light needs to be performed in frequency-locked resonant cavities to be efficient. Modulation of a frequency-doubled laser over a Doppler or pressure-broadened absorption profile in the UV region (which often has a width of a couple of GHz) puts large strain on the locking and gives therefore rise to significant amount of intensity noise. In a similar way, frequency modulation (FM), which is an alternative modulation technique, and which often incorporate the use of an external electro-optical modulator (EOM), is difficult to achieve because of the lack of EOM material in the UV range. Hence, none of the most common modulation techniques is suitable for DLB-UV-AS.

An alternative modulation technique, capable of enhancing the sensitivity of laser techniques for detection of paramagnetic molecules in general, and NO in particular, is Faraday Modulation Spectroscopy (FAMOS) [59-73]. This technique takes advantage of the fact that a transition in a paramagnetic molecule can alter the polarization state of incident linearly polarized light in the presence of a magnetic field. The field breaks the magnetic degeneracy of the states, which gives rise to a splitting of the levels as well as the transition. As the frequency of the light is scanned across the transition, right-handed and left-handed circularly polarized light (RHCP and LHCP, respectively) experience dissimilar refractive indices (referred to as circular birefringence), which in turn leads to dissimilar phase shifts and a rotation of the polarization plane of a linearly polarized beam (often referred to as the Faraday effect). By placing the sample between nearly crossed polarizers, the rotation is detected as an alteration of the power. By employing a modulated magnetic field and detecting the signal at the modulation frequency, laser amplitude noise and background signals from spectrally interfering diamagnetic compounds or etalons can be largely suppressed; the detectability of FAMOS can supersede that of ordinary DAS by 2–3 orders of magnitude [59-60, 62-64, 70]. The technique has proven to be very useful for detection of NO on its fundamental vibrational band, where one particular transition, $Q_{3/2}(3/2)$, has been identified as the most sensitive [59, 63]. Even transportable systems with low or even sub-ppbv detectabilities have been developed [70]. All this suggests that also FAMOS addressing the strong transitions in the electronic $X^2\Pi(v''=0) - A^2\Sigma^+(v'=0)$ band should be an attractive method for detection of NO.

Although there has been numerous investigations of the Zeeman effect of both the $X^2\Pi(v''=0)$ and the $A^2\Sigma^+(v'=0)$ state of NO, often investigated by ordinary absorption or fluorescence spectrometry [74-77], to the authors' knowledge, there are no prior FAMOS studies

in which the electronic band of NO has been addressed. On the other hand, there has been a few studies encompassing static Magnetic Rotation Spectroscopy (MRS) addressing the electronic $X^2\Pi(\nu''=0) - A^2\Sigma^+(\nu'=0)$ band. For example, an early but thorough investigation of MRS was that by Robinson using a 5 m vacuum spectrograph in high order and photographic techniques [78-79]. The present work provides thereby the first demonstration of FAMOS addressing an electronic transition in the $X^2\Pi(\nu''=0) - A^2\Sigma^+(\nu'=0)$ band of NO.

In order to perform an efficient development of a novel detection methodology, it is of importance to have access to a theoretical description that can predict the general properties of the technique and assess the experimental conditions for an efficient detection. As is discussed in some detail in an accompanying work [80], although a consistent and user-friendly theoretical description of conventional FAMOS [i.e. FAMOS addressing pure rotational-vibrational (ro-vib) transitions within the ground electronic state] has been worked out in some detail during the years [60-64, 67, 70], this description is not applicable to FAMOS addressing the $X^2\Pi - A^2\Sigma^+$ band in NO. The reason is that the excited $A^2\Sigma^+$ state of NO responds differently to a magnetic field than the $X^2\Pi$ ground state; it does not split according to the M_J quantum number, i.e. into $2J+1$ components, as a rotational state in the electronic ground state of NO does, it splits with respect to the M_S quantum number, which for NO with a single valence electron implies that it splits solely into only two components, separated by $2\mu_B B$. This implies that the conventional description of FAMOS, which addresses pure rotational-vibrational transitions of NO, cannot be used to describe the signal shape or strength. In fact, no theoretical description of FAMOS addressing the $X^2\Pi - A^2\Sigma^+$ band had until recently been developed.

A full description of FAMOS addressing electronic transitions in the $X^2\Pi - A^2\Sigma^+$ band, in particular regarding the signal strength or when low-rotational quantum states are addressed, is fairly complicated and requires more attention than the conventional realization of the technique addressing pure ro-vib transitions. On the other hand, the structure of the magnetically split upper level suggests some simplifications, allowing for a simplified description. Such a description, which can model the lineshape shape and a number of general properties of FAMOS addressing transitions in the $X^2\Pi - A^2\Sigma^+$ band of NO (e.g. its magnetic field and pressure dependence) from all but the lowest rotational states reasonably well, without requiring any detailed knowledge about the various sub-state-specific processes involved, has recently been developed and is presented in an accompanying work [80]. The present work constitutes thereby not only the first demonstration of FAMOS addressing the electronic transitions of NO but also a first experimental verification of the theoretical description of the FAMOS technique given in that work. Moreover, since the instrumentation encompasses a fully DLB laser system, it also demonstrates the feasibility of DLB-FAMOS addressing electronic transitions in NO.

However, the construction of the instrumentation was initiated before the general conditions for FAMOS addressing the electronic transitions of NO had been fully assessed. The instrumentation for the magnetic modulation was therefore constructed in a manner similar to that for conventional FAMOS addressing the ro-vib transitions, which, among other things, comprise a magnetic field amplitude of ~ 100 G. Since the predicted optimum conditions for FAMOS addressing electronic transitions comprise ~ 1500 G [80], this implies that the instrumentation used in this first assessment of DLB-FAMOS addressing electronic transitions in NO could not address all the parameter space of interest for the technique (measurements could

only be performed for magnetic field amplitudes up to ~ 150 G [63, 70]). Despite this, it could verify the predicted lineshapes and the magnetic field and pressure dependence under low-field conditions. The work also finally demonstrates that FAMOS addressing electronic transitions truly has the potential of detecting NO at (sub- or low) ppb-m concentrations.

2. Theory

As has been discussed in some detail in the accompanying work [80], FAMOS addressing the electronic transitions in NO has some general features in common with, and some different from, FAMOS addressing ro-vib Q-transitions. The differences are all related to the fact that the upper electronic state is a Σ^+ state. Since such a state lacks orbital angular momentum (it has $\Lambda = 0$), the electronic spin is only loosely coupled to the molecular axis and thereby to the rotation of the nuclei, whereby it follows Hund's coupling case (b) [81]. This has some important consequences for FAMOS, both regarding the energy level structure in the absence of magnetic field (and thereby the number of accessible branches) and the splitting of the levels, which affect the generation of the FAMOS signal from a given transition.

A. The energy level structure of NO: The $X^2\Pi(v''=0) - A^2\Sigma^+(v'=0)$ band contains 12 types of branches, not three

The energy level diagram pertinent to the electronic transitions in the $X^2\Pi(v''=0) - A^2\Sigma^+(v'=0)$ band of NO is schematically illustrated in Fig. 1. The lower Π -state is split into two by spin-splitting, giving rise to a $^2\Pi_{1/2}$ and a $^2\Pi_{3/2}$ state (where the subscript refers to the total electronic angular momentum, Ω). Each such state is then split into various rotational states according to its total angular momentum, J [82]. Within the upper

electronic state the energy of the various rotational states is not given by the total angular momentum, J , but predominantly by the quantum number associated with the rotation of the nuclei, N [83]. However, although the energy of a rotational state in a Σ -state is predominantly given by the rotation of the nuclei, there can be a weak coupling between this rotation and the electronic spin, i.e. between N and S . This implies that each state with a given N quantum number splits (by a splitting that sometimes is referred to as a ρ -type doubling in the literature) into two, referred to as F'_1 and F'_2 , for which $J' = N' + 1/2$ and $J' = N' - 1/2$, respectively, that in general have slightly dissimilar energies [81]. All this implies that there are more than three branches of transitions that can be addressed; not only P , Q , and R (as is the case for pure ro-vib transitions), but also satellite branches, for which $\Delta N \neq \Delta J$ [84]. Since the two $^2\Pi_{1/2}(J'')$ and $^2\Pi_{3/2}(J'')$ states in the lower level have dissimilar N quantum numbers, given by $N'' = J'' - 1/2$ and $N'' = J'' + 1/2$, respectively, there are, in general, 6 different types of branches from each spin-split state, i.e. in total 12 [81, 84-85]. On the other hand, since the ρ -type doubling is small for NO, the branches with the same ΔN but dissimilar ΔJ overlap. This implies in practice that the 12 branches appear frequency-wise as 8 [84].

Figure 1 here.

As is schematically illustrated in Fig. 1, the particular branches addressed in this work, $Q_{22}(J'')$ and $Q_{R12}(J'')$, (for which $\Delta N = \Delta J = 0$ for the former and $\Delta N = 0$ and $\Delta J = +1$ for the latter) originate from common lower states of type $^2\Pi_{3/2}(J'')$ (for which $N'' = J'' + 1/2$) to two more or less degenerate types of upper states, $^2\Sigma(F'_1, N' = N'')$ and $^2\Sigma(F'_2, N' = N'')$. Due to the small ρ -type doubling, these two branches overlap strongly. Hence, excitation of a transition

in the $Q_{22}(J'')$ branch implies inevitably that two transitions, both a $Q_{22}(J'')$ and a $Q_{R_{12}}(J'')$ transition, to two upper states with the same N but dissimilar J , are simultaneously induced [74, 76]. In this particular case, the $Q_{22}(21/2)$ and the $Q_{R_{12}}(21/2)$ transitions, appearing at around 226.58 nm, were simultaneously targeted.

B. A simple two-transition model

It was shown in the accompanying paper [80] that it is possible to describe the signal generation process for FAMOS addressing a single transition within the electronic $X^2\Pi(v''=0) - A^2\Sigma^+(v'=0)$ band of NO by a three-level/two transition model in which the two transitions, which are shifted by the magnetic field and induced by RHCP and LHCP light (although to dissimilar degrees), have equal net signal strength. An expression for the FAMOS signal addressing a particular transition between a $^2\Pi_i(J'', N'')$ and a $^2\Sigma(F'_i, J', N')$ state, $S_{\Pi, \Sigma}^{F, E}(\Delta \bar{\nu}_{\Pi, \Sigma}^{D, 0})$, can be written as

$$S_{\Pi, \Sigma}^{F, E}(\Delta \bar{\nu}_{\Pi, \Sigma}^{D, 0}) = S_{\Pi, \Sigma}^{F, E, 0, atm} c_{NO} \frac{P_{tot}}{P_0} \bar{\chi}^{F, 2} \left(\Delta \bar{\nu}_{\Pi, \Sigma}^{D, 0}, \bar{\nu}_{\Pi, \Sigma}^{a, D}, \delta \bar{\nu}_L^D \right), \quad (1)$$

where $\Delta \bar{\nu}_{\Pi, \Sigma}^{D, 0}$ is the Doppler-width-normalized detuning of the light from the unmodulated transition, given by $\Delta \tilde{\nu}_{\Pi, \Sigma}^0 \sqrt{\ln 2} / \delta \tilde{\nu}_D$, where $\Delta \tilde{\nu}_{\Pi, \Sigma}^0$ is the detuning of the light given in units of inverse centimeters [86], i.e. given by $\tilde{\nu} - \tilde{\nu}_{\Pi, \Sigma}^0$, where $\tilde{\nu}_{\Pi, \Sigma}^0$ is the center frequency of the transition and $\delta \tilde{\nu}_D$ the half widths half maximum (HWHM) of the Doppler broadening.

$S_{\Pi, \Sigma}^{F, E, 0, atm}$ is an entity referred to as the signal strength of FAMOS addressing an electronic

transition in NO from a sample with pure NO, i.e. with 100% of the analyte, under atmospheric pressure condition (given below), c_{NO} is the concentration (mole fraction, or relative partial pressure) of NO in the gas, p_{tot} the total pressure of the gas, p_0 a reference pressure (760 Torr, corresponding to atmospheric pressure conditions) and $\bar{\chi}^{F,2}(\Delta\bar{\nu}_{\Pi,\Sigma}^{D,0}, \bar{\nu}_{\Pi,\Sigma}^{a,D}, \delta\bar{\nu}_L^D)$ the FAMOS lineshape function for a two transition system (which is valid for both a Q-transition in the ro-vib band and the three-level model used for describing FAMOS addressing electronic transitions in NO [80]), given by

$$\bar{\chi}^{F,2}(\Delta\bar{\nu}_{\Pi,\Sigma}^{D,0}, \bar{\nu}_{\Pi,\Sigma}^{a,D}, \delta\bar{\nu}_L^D) = 2\bar{\chi}_1^{disp,even}(\Delta\bar{\nu}_{\Pi,\Sigma}^{D,0}, \bar{\nu}_{\Pi,M_J,\Sigma,1/2}^{a,D}, \delta\bar{\nu}_L^D) \quad (2)$$

where $\bar{\nu}_{\Pi,\Sigma}^{a,D}$ is given by $g_S\mu_B B_0\sqrt{\ln 2}/\delta\tilde{\nu}_D$, where g_S the g -factor for the upper state (assumed to be equal that of a free electron, i.e. ~ 2), μ_B is the Bohr magneton, and B_0 the amplitude of the magnetic field. $\delta\bar{\nu}_L^D$ 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 HWHM of the homogeneous broadening (i.e. the pressure broadening). The $\bar{\chi}_1^{disp,even}(\Delta\bar{\nu}_{\Pi,\Sigma}^{D,0}, \bar{\nu}_{\Pi,M_J,\Sigma,M_S}^{a,D}, \delta\bar{\nu}_L^D)$ function is the (even component of the) 1st Fourier coefficient of the Doppler-peak-normalized magnetic-field-modulated dispersion lineshape function, given by

$$\begin{aligned} \bar{\chi}_1^{disp,even}(\Delta\bar{\nu}_{\Pi,\Sigma}^{D,0}, \bar{\nu}_{\Pi,M_J,\Sigma,M_S}^{a,D}, \delta\bar{\nu}_L^D) \\ = \frac{2}{\tau} \int_0^\tau \bar{\chi}^{disp}[\Delta\bar{\nu}_{\Pi,M_J,\Sigma,M_S}^D(t), \delta\bar{\nu}_L^D] \cos(\omega t) dt, \end{aligned} \quad (3)$$

where $\bar{v}_{\Pi, M_J, \Sigma, M_S}^{a,D}$ is the normalized modulation amplitude, given by $M_S \bar{v}_{\Pi, \Sigma}^{a,D}$ where M_S is the magnetic quantum number for the upper state, and, in turn, $\bar{\chi}^{disp}[\dots]$ is the dispersion counterpart to the Doppler-peak-normalized Voigt absorption profile and $\Delta \bar{v}_{\Pi, M_J, \Sigma, M_S}^D(t)$ is the time-dependent Doppler-width-normalized detuning of the magnetically induced transition to the M_S -state by one of the circular components of the light, given by

$$\Delta \bar{v}_{\Pi, M_J, \Sigma, M_S}^D(t) = \Delta \bar{v}_{\Pi, \Sigma}^{D,0} - \bar{v}_{\Pi, M_J, \Sigma, M_S}^{a,D} \cos(\omega t), \quad (4)$$

where ω is the angular frequency of the modulation. Finally, $S_{i,j}^{F,E,0,atm}$ is given by

$$S_{\Pi, \Sigma}^{F,E,0,atm} = \eta \frac{S_{\Pi, \Sigma} N_{NO} L \hat{\chi}_0 \Delta \bar{S}_{\Pi, \Sigma}^{net(1/2)}}{8} \sin(2\varphi) I_0 \quad (5)$$

where η is an instrumentation factor (comprising the sensitivity of the detector and the gain of the lock-in amplifier), $S_{\Pi, \Sigma}$ is the integrated linestrength of the transition, given in units of $\text{cm}^{-1}/(\text{molecules cm}^{-2})$, N_{NO} is the number density of molecules that corresponds to the reference pressure, which is given by $2.48 \times 10^{19} (T_0 / T) \text{ cm}^{-3}$, where T_0 is a reference temperature, here taken as 296 K, L is the interaction length (cm), $\hat{\chi}_0$ is the peak value of the area-normalized absorption Gaussian line-shape function (cm), and $\Delta \bar{S}_{\Pi, \Sigma(M_S)}^{net}$ the net relative linestrength of the transition to one of the magnetically split upper states, i.e., defined as $\left| \bar{S}_{\Pi, \Sigma(M_S)}^L - \bar{S}_{\Pi, \Sigma(M_S)}^R \right|$ where $\bar{S}_{\Pi, \Sigma(M_S)}^L$ and $\bar{S}_{\Pi, \Sigma(M_S)}^R$ are the relative linestrengths for RHCP

and LHCP light addressing a given M_S -state. Moreover, φ is related to the angle between the axes of the polarizer and the analyzer, θ , as $\pi/2 - \theta$, and I_0 the power of the radiation after the polarizer entering the sample. ω is the angular modulation frequency.

3. Simulations

Using a previously developed simulation program for absorption of light in the $X^2\Pi(\nu''=0) - A^2\Sigma^+(\nu'=0)$ band of NO [57], which encompasses calculations of transition frequencies, Einstein coefficients, linestrengths, and lineshapes for all transitions in a given wavelength range, an absorption spectrum was simulated in the vicinity of the transitions addressed, i.e. in the 226.55 – 226.60 nm range. Figure 2(a) displays the integrated linestrength for the various transitions in the $X^2\Pi(\nu''=0) - A^2\Sigma^+(\nu'=0)$ band of NO for a temperature of 296 K. The lines chosen as the pilot transitions for the study were the overlapping $Q_{22}(J''=21/2)$ and $Q_{12}(J''=21/2)$ transitions at 226.577 nm (44135.22 cm^{-1}), which are marked with an asterisk in both panels, since they were found to be the strongest lines in a lightly congested part of the spectrum. Figure 2(b), which shows the corresponding Doppler broadened spectrum from 300 ppm NO in N_2 at a total pressure of 0.01 atm and at the reference temperature, illustrates that these two transitions can, to a first order, be considered as a single unsplit transition, with no spectral overlap with any neighboring line.

4. Experiment and Process

The experimental set up is schematically illustrated in Fig. 3. The instrumentation is based upon a fully-diode-laser-based UV laser system producing mW powers at ~ 226.6 nm that has been described previously (Toptica, TA-FHG-110) [63]. In short, it consists of an external-cavity

diode laser (ECDL) laser whose output is first amplified in a tapered amplifier before it is frequency doubled in two consecutive resonant frequency doubling systems. The light was sent through two nearly crossed Rochon prism polarizers (CVI Melles Griot, RCHP-5.0-MF) with extinction ratios of about 10^{-5} placed on each side of a 10 cm long fused silica cell with wedged windows into which gas was let by the use of a combined gas and vacuum system. The polarizer behind the cell (also referred to as the analyzer) was offset with respect to the perpendicular direction of the first polarizer by an angle of 12° . The transmitted light was detected by a UV sensitive GaP detector (New Focus, Large Area UV photoreceiver Model 2032).

The magnetic field was generated by a coil (with an inner diameter of 76 mm) made of 530 turns of a copper wire, which was coupled in series with a capacitor (with a capacitance of $0.31 \mu\text{F}$) to create a resonant circuit with a resonance frequency of 2.5 kHz. A lock-in amplifier served two purposes; in addition to demodulating the detector signal, it generated the sinusoidal signal that was used to modulate the magnetic field at the resonance frequency. This modulation signal was fed to a power amplifier (PA, APart, Pubdriver 2000) whose output was driving the resonant circuit. The maximum magnetic field amplitude was ~ 150 G, limited by the power of the PA. Hence, the system had properties similar to those previously used for detection of FAMOS on ro-vib transitions [70]. The output of the lock-in amplifier was sent to a computer equipped with a 16-bits A/D card (National Instruments, DAQmx 6251) and sampled and stored using LabVIEW software. The system also incorporated a wavelength meter (WM, Burleigh, WA-1500M) for wavelength calibration.

Scanning was achieved by supplying the ECDL in the UV-laser-system with a slowly modulated signal from a function generator (FG). For each series of experiment, the center wavelength of the ECDL was first tuned to the vicinity of 906.30 nm by the use of the

wavelength meter to produce UV radiation around the targeted NO transitions at 226.58 nm by the two frequency-doubling stages. The UV light was then tuned back and forth across the selected transitions by modulating the piezo crystal transducer (PZT) in the ECDL laser in either a saw-tooth or a sinusoidal fashion by a function generator at a rate of 1 Hz, where the latter mode of scanning provides less strain on the locking at the turning points but has also the drawback of producing non-linear scanning. The scanning range was typically 38 GHz (1.3 cm^{-1}) in UV, which is slightly more than ten times the Doppler width of the NO transition. Data was acquired at a rate of 6 kHz. NO was available with a concentration of 100 ± 10 ppm in N_2 in a cylinder (AGA, Sweden). Experiments were made with this gas at various total pressures. All experiments were done in room temperature, assumed to be 23 °C (296 K).

5. Results

A number of FAMOS spectra from the overlapping $Q_{22}(21/2)$ and $Q_{12}(21/2)$ lines at around 226.58 nm were taken under various conditions. Figure 4 displays, by the solid curves in the panels (a) – (f), spectra from 4.2, 20, 40, 60, 90, and 150 Torr of 100 ppm NO, thus corresponding to partial pressures of NO between 420 μTorr and 15 mTorr. Each curve represents the average over 10 spectra. The dashed curves represent fits of the two-transition model above, Eq. (1), with $S_{\Pi,\Sigma}^{F,E,0,atm}$, p_{tot} , B_0 , and $\Delta\bar{\nu}_{\Pi,\Sigma}^{D,0}$ as free parameters. Since the simulation given in Fig. 2(b) shows no splitting between the $Q_{22}(21/2)$ and $Q_{12}(21/2)$ transitions, which indicates a small or no ρ -type doubling in the $A^2\Sigma^+$ state, in line with previous observations [76], it was considered sufficient to model the system as a single two-transition system. In addition, although the experimental conditions could not guarantee a homogeneous magnetic field over the interaction region, neither in the axial, nor in the radial

direction, the simulations were made for a single magnetic field amplitude. Moreover, due to the associated intensity modulation of the laser, the fits were based on Eq. (1) assuming a sinusoidal power over the scan, $I_0(t)$. Furthermore, the detected signals also comprised a certain yet unidentified non-specific background. To account for this, the fits included also a modeling of a background assumed to be proportional to the instantaneous power. The lowermost part in each panel displays the residual between the fit and the measured data.

As can be seen from the figure, there is a reasonably good (although not perfect) agreement between the various spectra and the fits. The theoretical model accounts for the major features of the FAMOS signal. The rms of the residual is around 3 % for the lowest pressure but consistently around 1 – 1.5 % for the higher pressures. For the latter ones, the center parts of the residuals are fully reproducible which shows that they have a systematic (and thus not a stochastic) origin, assumed to originate from either a non-complete overlap of the two $Q_{22}(21/2)$ and $Q_{12}(21/2)$ transitions, the description of the FAMOS signal in terms of a two-transition model, or the use of the Voigt function, which neglects Dicke narrowing and velocity-changing collisions that are known to play a role under the prevalent pressure conditions [87-91].

Figure 5(a) displays a set of FAMOS spectra from 100 ppm NO taken under a variety of total pressures for a fixed magnetic field. The various curves represent total pressures ranging from 0.5 to 250 Torr, thus representing partial pressures of NO from 50 μ Torr and 25 mTorr. Figure 5(b) presents simulations of the FAMOS signal according to Eq. (1) for the same set of pressure and for a magnetic field amplitude of 130 G. As can be seen by a comparison of the two panels, the agreement between the two set of curves is adequate.

Figure 6(a) shows, by the individual markers, the peak value of the FAMOS signal as a function of pressure, evaluated from the measurements presented in Fig. 5(a) whereas Fig. 6(b) displays the corresponding peak values from the simulations. Although the two curves differ, however, by their initial slope and curvature (with the experimental one displaying a slower increase with pressure), the general trends of the two curves are the same, with a FAMOS signal that increases with pressure up to a maximum, at around 130 Torr, after which it decreases.

6. Discussion and Conclusions

This work constitutes the first demonstration of detection of nitric oxide (NO) by the FAMOS technique addressing transitions in the strong electronic $X^2\Pi(v''=0) - A^2\Sigma^+(v'=0)$ band. The instrumentation, which encompassed a fully diode-laser-based laser system producing mW power of light in the UV-region, could produce clear and reproducible FAMOS signals from μ Torr and mTorr pressures of NO in N₂. However, since no theoretical description of FAMOS addressing these transitions was available at the initiation of this project, the optimum conditions for the technique were not known. The solenoid was therefore constructed around the conditions for FAMOS addressing most sensitive ro-vib Q-transitions of NO (for which the optimum magnetic field amplitude is ~ 100 G), whereby it allowed for measurements solely up to 150 G. However, as is predicted by an accompanying work [80], the maximum FAMOS signal from the electronic transitions in NO is obtained for a magnetic field that is an order of magnitude larger than that for FAMOS addressing the ro-vib $Q_{3/2}(3/2)$ transition, viz. ~ 1500 G. The instrumentation used in this work could therefore only allow for measurements under undermodulated conditions [the maximum magnetic field amplitude available provided a splitting of the upper level of ~ 0.014 cm⁻¹, which is only 14% of the FWHM of the linewidth of the absorption profile under low pressure conditions (for which the linewidth is given by the

Doppler width, which is 0.099 cm^{-1} FWHM), and only 7% of that for a pressure of 200 Torr (for which the FWHM is 0.20 cm^{-1}) and it could thereby not, in this first demonstration, experimentally verify all of the predictions of the novel two-transition model of FAMOS addressing the electronic transitions in NO [80].

For the range of parameters that could be addressed it was found that the agreement between the simplified two-transition model presented in the accompanying work and the measured data is reasonably good. As is shown in Figs 4 and 5, the signal shape of FAMOS addressing electronic transitions in NO indicates clearly that the two-transition model is adequate. Although there is a systematic (thus fully reproducible) residual between the two (Fig. 4), the lineshapes agree reasonably well with the data. The discrepancies are assumed to originate from spatial inhomogeneities of the magnetic field in the interaction volume (in the axial as well as radial direction), a non-fully overlap between the two transitions addressed, simplifications in the two-transition model of the signal, or the neglect of Dicke narrowing or velocity-changing collisions. The agreement between the predicted and measured pressure dependence of the peak values of the FAMOS signal, which is displayed in Fig. 6 and shows a signal that increases with pressure up to a maximum, at around 130 Torr, after which the signal starts to decrease, is also adequate (although not perfect). The differences are assumed to have experimental causes, primarily originating from a drifting output power of the frequency quadrupled diode laser over the set of measurements performed, and they are therefore not considered to indicate any inconsistency in the theory. Although not being conclusive, these results support the simplified theoretical model for FAMOS addressing electronic transitions in NO presented in the accompanying work [80], including the predictions of the optimum conditions of the technique. A full assessment of the validity of the theoretical predictions

regarding optimum conditions of the technique, including an investigation of the origin and the properties of the detection-limiting background signal, will be presented in a future work when the experimental facilities addressing the optimum conditions have been reconstructed.

The detectability of the technique, with the instrumentation in its present form, is not yet representative of what is expected from the technique under optimum conditions; it is presently limited by the restricted signal magnitude (originating from undermodulated conditions and the use of transitions with a linestrength that is half of the maximum) and by the noise and drifts of a yet unspecified background signal (possibly originating from circular dichroism), which in turn originates from noise and drifts in the laser power. No further investigation of the detectability of the FAMOS technique addressing electronic transitions in NO, e.g. by an Allan plot, was therefore performed in this work; the present work merely serves the purpose of verifying the theoretical description of the technique, which then can be used for design of a more optimized system. A rough estimate of the detectability was, however, performed in the following way. First a sensitivity of the technique, ξ , given in terms of the signal magnitude per unit of partial pressure of NO, i.e., as $\partial S_F / \partial p_{NO}$, was derived from the Figs 5(a) and 6(a). The standard deviation of the FAMOS signal, σ_N , was evaluated from fits to a number of empty cell measurements (each consisting of the average of 10 consecutive scans). The partial pressure of NO that corresponds to the standard deviation of the FAMOS signal from empty cell measurements was then evaluated. Such a procedure, based on the standard deviation of the FAMOS signal from 17 consecutive empty cell measurements, provided a minimum detectable partial pressure of NO of 13 μ Torr. Recalculating this to a corresponding minimum detectable concentration of NO in an atmospheric pressure sample, and taking into account the fact that the interaction length was 10 cm, provides a detectability of 5 ppb·m NO. Since the conditions for

this first demonstration of FAMOS addressing electronic transitions in NO are far from optimal, it is expected that the detectability of the technique can be substantially improved in the future. A more thorough investigation of the detectability of the technique will be performed when the system has been modified to accommodate for the optimum conditions.

Acknowledgements

This work was supported by SIDA under the contracts 7500728603/605/610 and the Swedish Research Council under the projects 621-2005-4919, 621-2008-3674, and 621-2007-5123. Support from the Kempe foundations and Umeå University Industrial Postgraduate School (*swe. Företagsforskarskolan*) are also acknowledged.

References

1. W. T. Piver, "Global Atmospheric Changes," *Environmental Health Perspectives* **96**, 131-137 (1991).
2. J. H. Seinfeld and S. N. Pandis, *Atmospheric chemistry and physics: from air pollution to climate change* (Wiley-Interscience, New York, 1998), p. 1326.
3. Y. C. Hou, A. Janczuk, and P. G. Wang, "Current trends in the development of nitric oxide donors," *Current Pharmaceutical Design* **5**, 417-441 (1999).
4. M. Radojevic, "Reduction of nitrogen oxides in flue gases," *Environmental Pollution* **102**, 685-689 (1998).
5. P. K. Barton and J. W. Atwater, "Nitrous oxide emissions and the anthropogenic nitrogen in wastewater and solid waste," *Journal of Environmental Engineering-ASCE* **128**, 137-150 (2002).
6. L. J. Ignarro, "Nitric Oxide - A Novel Signal Transduction Mechanism for Transcellular Communication," *Hypertension* **16**, 477-483 (1990).
7. C. Napoli and L. J. Ignarro, "Nitric oxide and atherosclerosis," *Nitric Oxide-Biology and Chemistry* **5**, 88-97 (2001).
8. L. J. Ignarro, C. Napoli, and J. Loscalzo, "Nitric oxide donors and cardiovascular agents modulating the bioactivity of nitric oxide - An overview," *Circulation Research* **90**, 21-28 (2002).
9. B. S. Taylor, Y. M. Kim, Q. Wang, R. A. Shapiro, T. R. Billiar, and D. A. Geller, "Nitric oxide down-regulates hepatocyte-inducible nitric oxide synthase gene expression," *Archives of Surgery* **132**, 1177-1183 (1997).
10. L. C. McKinney, S. J. Galliger, and R. J. Lowy, "Active and inactive influenza virus induction of tumor necrosis factor-alpha and nitric oxide in J774.1 murine macrophages: modulation by interferon-gamma and failure to induce apoptosis," *Virus Research* **97**, 117-126 (2003).
11. C. Napoli and L. J. Ignarro, "Nitric Oxide and Pathogenic Mechanisms Involved in the Development of Vascular Diseases," *Archives of Pharmacal Research* **32**, 1103-1108 (2009).
12. M. G. Allen, "Diode laser absorption sensors for gas-dynamic and combustion flows," *Measurement Science & Technology* **9**, 545-562 (1998).

13. P. Werle, F. Slemr, K. Maurer, R. Kormann, R. Mucke, and B. Janker, "Near- and mid-infrared laser-optical sensors for gas analysis," *Optics and Lasers in Engineering* **37**, 101-114 (2002).
14. A. Fried and D. Richter, "Infrared absorption spectroscopy," in *Analytical Techniques for Atmospheric Measurements*, D. Heard, ed. (Blackwell Publishing, 2006), pp. 72-146.
15. F. K. Tittel, Y. A. Bakhirkin, R. R. Curl, A. A. Kosterev, M. R. McCurdy, S. G. So, and G. Wysocki, "Laser based chemical sensor technology: Recent advances and applications," *Advanced Environmental Monitoring*, 50-63 (2008).
16. D. T. Cassidy and J. Reid, "Atmospheric pressure monitoring of trace gases using tunable diode lasers," *Appl. Opt.* **21**, 1185 - 1190 (1982).
17. D. T. Cassidy and J. Reid, "High-sensitivity detection of trace gases using sweep integration and tunable diode lasers," *Appl. Opt.* **21**, 2527 - 2530 (1982).
18. P. Werle, R. Mucke, and F. Slemr, "The limits of signal averaging in atmospheric trace-gas monitoring by Tunable Diode-Laser Absorption-Spectroscopy (TDLAS)," *Appl. Phys. B* **57**, 131-139 (1993).
19. P. Kluczynski and O. Axner, "Theoretical description based on Fourier analysis of wavelength-modulation spectrometry in terms of analytical and background signals," *Appl. Opt.* **38**, 5803-5815 (1999).
20. P. Kluczynski, J. Gustafsson, Å. M. Lindberg, and O. Axner, "Wavelength modulation absorption spectrometry - an extensive scrutiny of the generation of signals," *Spectrochimica Acta B* **56**, 1277-1354 (2001).
21. A. G. Berezin, O. V. Ershov, and A. I. Nadezhdinskii, "Trace complex-molecule detection using near-IR diode lasers," *Appl. Phys. B* **75**, 203-214 (2002).
22. M. G. Allen and W. J. Kessler, "Simultaneous water vapor concentration and temperature measurements using 1.31- μ m diode lasers," *AIAA Journal* **34**, 483-488 (1996).
23. M. G. Allen, K. L. Carleton, S. J. Davis, and W. J. Kessler, "Ultrasensitive dual-beam absorption and gain spectroscopy: applications for near-infrared and visible diode laser sensors," *Appl. Opt.* **34**, 3240 (1995).
24. K. C. Clemetshaw, "A review of instrumentation and measurement techniques for ground-based and airborne field studies of gas-phase tropospheric chemistry," *Critical Reviews in Environmental Science and Technology* **34**, 1-108 (2004).
25. T. Le Barbu, I. Vinogradov, G. Durry, O. Korablev, E. Chassefiere, and J. L. Bertaux, "TDLAS a laser diode sensor for the in situ monitoring of H₂O, CO₂ and their isotopes in the Martian atmosphere," *Advances in Space Research* **38**, 718-725 (2006).

26. S. Wagner, B. T. Fisher, J. W. Fleming, and V. Ebert, "TDLAS-based in situ measurement of absolute acetylene concentrations in laminar 2D diffusion flames," *Proceedings of the Combustion Institute* **32**, 839-846 (2009).
27. L. Wondraczek, G. Heide, G. H. Frischat, A. Khorsandi, U. Willer, and W. Schade, "Mid-infrared laser absorption spectroscopy for process and emission control in the glass melting industry - Part 1. Potentials," *Glass Science and Technology* **77**, 68-76 (2004).
28. D. M. Sonnenfroh and M. G. Allen, "Absorption measurements of the second overtone band of NO in ambient and combustion gases with a 1.8- μ m room-temperature diode laser," *Appl. Opt.* **36**, 7970-7977 (1997).
29. D. B. Oh and A. C. Stanton, "Measurement of nitric oxide with an antimonide diode laser," *Appl. Opt.* **36**, 3294-3297 (1997).
30. R. M. Mihalcea, D. S. Baer, and R. K. Hanson, "A diode-laser absorption sensor system for combustion emission measurements," *Measurement Science & Technology* **9**, 327-338 (1998).
31. D. D. Nelson, M. S. Zahniser, J. B. McManus, C. E. Kolb, and J. L. Jimenez, "A tunable diode laser system for the remote sensing of on-road vehicle emissions," *Appl. Phys. B* **67**, 433-441 (1998).
32. J. L. Jimenez, M. D. Koplow, D. D. Nelson, M. S. Zahniser, and S. E. Schmidt, "Characterization of on-road vehicle NO emissions by a TILDAS remote sensor," *Journal of the Air & Waste Management Association* **49**, 463-470 (1999).
33. M. Snels, C. Corsi, F. D'Amato, M. De Rosa, and G. Modugno, "Pressure broadening in the second overtone of NO, measured with a near infrared DFB diode laser," *Opt. Comm.* **159**, 80-83 (1999).
34. J. L. Jimenez, G. J. McRae, D. D. Nelson, M. S. Zahniser, and C. E. Kolb, "Remote sensing of NO and NO₂ emissions from heavy-duty diesel trucks using tunable diode lasers," *Environmental Science & Technology* **34**, 2380-2387 (2000).
35. S. W. Sharpe, J. F. Kelly, J. S. Hartman, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, and A. Y. Cho, "High-resolution (Doppler-limited) spectroscopy using quantum-cascade distributed-feedback lasers," *Opt. Lett.* **23**, 1396-1398 (1998).
36. S. W. Sharpe, J. F. Kelly, R. M. Williams, J. S. Hartman, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, and A. Y. Cho, "Rapid scan (Doppler-limited) absorption spectroscopy using mid-infrared quantum cascade lasers," *Application of Tunable Diode and Other Infrared Sources for Atmospheric Studies and Industrial Processing Monitoring II* **3758**, 23-33 (1999).

37. A. A. Kosterev, A. L. Malinovsky, F. K. Tittel, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, and A. Y. Cho, "Cavity ringdown spectroscopic detection of nitric oxide with a continuous-wave quantum-cascade laser," *Appl. Opt.* **40**, 5522-5529 (2001).
38. L. Menzel, A. A. Kosterev, R. F. Curl, F. K. Tittel, C. Gmachl, F. Capasso, D. L. Sivco, J. N. Baillargeon, A. L. Hutchinson, A. Y. Cho, and W. Urban, "Spectroscopic detection of biological NO with a quantum cascade laser," *Appl. Phys. B* **72**, 859-863 (2001).
39. D. D. Nelson, J. H. Shorter, J. B. McManus, and M. S. Zahniser, "Sub-part-per-billion detection of nitric oxide in air using a thermoelectrically cooled mid-infrared quantum cascade laser spectrometer," *Appl. Phys. B* **75**, 343-350 (2002).
40. W. H. Weber, J. T. Remillard, R. E. Chase, J. F. Richert, F. Capasso, C. Gmachl, A. L. Hutchinson, D. L. Sivco, J. N. Baillargeon, and A. Y. Cho, "Using a wavelength-modulated quantum cascade laser to measure NO concentrations in the parts-per-billion range for vehicle emissions certification," *Appl. Spectrosc.* **56**, 706-714 (2002).
41. A. A. Kosterev, C. Roller, and F. K. Tittel, "Applications of pulsed quantum cascade lasers to NO monitoring in industrial exhaust gases," *Proceedings of the IEEE Sensors 2003*, Vols 1 and 2, 673-674 (2003).
42. Q. Shi, D. D. Nelson, J. B. McManus, M. S. Zahniser, M. E. Parrish, R. E. Baren, K. H. Shafer, and C. N. Harward, "Quantum cascade infrared laser spectroscopy for real-time cigarette smoke analysis," *Analytical Chemistry* **75**, 5180-5190 (2003).
43. Y. A. Bakhirkin, A. A. Kosterev, C. Roller, R. F. Curl, and F. K. Tittel, "Mid-infrared quantum cascade laser based off-axis integrated cavity output spectroscopy for biogenic nitric oxide detection," *Appl. Opt.* **43**, 2257-2266 (2004).
44. R. E. Baren, M. E. Parrish, K. H. Shafer, C. N. Harward, S. Quan, D. D. Nelson, J. B. McManus, and M. S. Zahniser, "Quad quantum cascade laser spectrometer with dual gas cells for the simultaneous analysis of mainstream and sidestream cigarette smoke," *Spectrochim. Acta A* **60**, 3437-3447 (2004).
45. C. Mann, Q. K. Yang, F. Fuchs, N. Bronner, K. Kohler, T. Beyer, T. Braun, and A. Lambrecht, "Single-mode InP-based quantum cascade lasers for applications in trace-gas sensing," *Novel in-Plane Semiconductor Lasers III* **5365**, 173-183 (2004).
46. C. Mann, Q. Yang, F. Fuchs, W. Bronner, K. Kohler, and J. Wagner, "Single-mode quantum cascade lasers for applications in trace-gas sensing," *Tm-Technisches Messen* **72**, 356-365 (2005).
47. G. Wysocki, A. A. Kosterev, and F. K. Tittel, "Spectroscopic trace-gas sensor with rapidly scanned wavelengths of a pulsed quantum cascade laser for in situ NO monitoring of industrial exhaust systems," *Appl. Phys. B* **80**, 617-625 (2005).

48. M. L. Silva, D. M. Sonnenfroh, D. I. Rosen, M. G. Allen, and A. O'Keefe, "Integrated cavity output spectroscopy measurements of NO levels in breath with a pulsed room-temperature QCL," *Appl. Phys. B* **81**, 705-710 (2005).
49. Y. A. Bakhirkin, A. A. Kosterev, R. F. Curl, F. K. Tittel, D. A. Yarekha, L. Hvozdar, M. Giovannini, and J. Faist, "Sub-ppbv nitric oxide concentration measurements using cw thermoelectrically cooled quantum cascade laser-based integrated cavity output spectroscopy," *Appl. Phys. B* **82**, 149-154 (2006).
50. B. W. M. Moeskops, S. M. Cristescu, and F. J. M. Harren, "Sub-part-per-billion monitoring of nitric oxide by use of wavelength modulation spectroscopy in combination with a thermoelectrically cooled, continuous-wave quantum cascade laser," *Opt. Lett.* **31**, 823-825 (2006).
51. J. B. McManus, D. D. Nelson, S. C. Herndon, J. H. Shorter, M. S. Zahniser, S. Blaser, L. Hvozdar, A. Muller, M. Giovannini, and J. Faist, "Comparison of cw and pulsed operation with a TE-cooled quantum cascade infrared laser for detection of nitric oxide at 1900 cm⁻¹," *Appl. Phys. B* **85**, 235-241 (2006).
52. D. D. Nelson, J. B. McManus, S. C. Herndon, J. H. Shorter, M. S. Zahniser, S. Blaser, L. Hvozdar, A. Muller, M. Giovannini, and J. Faist, "Characterization of a near-room-temperature, continuous-wave quantum cascade laser for long-term, unattended monitoring of nitric oxide in the atmosphere," *Opt. Lett.* **31**, 2012-2014 (2006).
53. M. R. McCurdy, Y. A. Bakhirkin, and F. K. Tittel, "Quantum cascade laser-based integrated cavity output spectroscopy of exhaled nitric oxide," *Appl. Phys. B* **85**, 445-452 (2006).
54. M. R. McCurdy, Y. Bakhirkin, G. Wysocki, and F. K. Tittel, "Performance of an exhaled nitric oxide and carbon dioxide sensor using quantum cascade laser-based integrated cavity output spectroscopy," *Journal of Biomedical Optics* **12**(2007).
55. J. B. McManus, J. H. Shorter, D. D. Nelson, M. S. Zahniser, D. E. Glenn, and R. M. McGovern, "Pulsed quantum cascade laser instrument with compact design for rapid, high sensitivity measurements of trace gases in air," *Appl. Phys. B* **92**, 387-392 (2008).
56. G. Hancock, J. H. van Helden, R. Peverall, G. A. D. Ritchie, and R. J. Walker, "Direct and wavelength modulation spectroscopy using a cw external cavity quantum cascade laser," *Appl. Phys. Lett.* **94**(2009).
57. J. Shao, L. Lathdavong, P. Thavixay, and O. Axner, "Detection of nitric oxide at low ppb center dot m concentrations by differential absorption spectrometry using a fully diode-laser-based ultraviolet laser system," *J. Opt. Soc. Am. B* **24**, 2294-2306 (2007).

58. S. F. Hanna, R. Barron-Jimenez, T. N. Anderson, R. P. Lucht, J. A. Caton, and T. Walther, "Diode-laser-based ultraviolet absorption sensor for nitric oxide," *Appl. Phys. B* **75**, 113-117 (2002).
59. A. Kaldor, A. G. Maki, and W. B. Olson, "Pollution Monitor for Nitric Oxide - Laser Device Based on Zeeman Modulation of Absorption," *Science* **176**, 508-510 (1972).
60. G. Litfin, C. R. Pollock, R. F. Curl, and F. K. Tittel, "Sensitivity Enhancement of Laser-Absorption Spectroscopy by Magnetic Rotation Effect," *J. Chem. Phys.* **72**, 6602-6605 (1980).
61. W. Herrmann, W. Rohrbeck, and W. Urban, "Line-Shape Analysis for Zeeman Modulation Spectroscopy," *Appl. Phys.* **22**, 71-75 (1980).
62. A. Hinz, J. Pfeiffer, W. Bohle, and W. Urban, "Mid-Infrared Laser Magnetic-Resonance Using the Faraday and Voigt Effects for Sensitive Detection," *Mol. Phys.* **45**, 1131-1139 (1982).
63. T. A. Blake, C. Chackerian, and J. R. Podolske, "Prognosis for a mid-infrared magnetic rotation spectrometer for the in situ detection of atmospheric free radicals," *Appl. Opt.* **35**, 973-985 (1996).
64. H. Ganser, W. Urban, and A. M. Brown, "The sensitive detection of NO by Faraday modulation spectroscopy with a quantum cascade laser," *Mol. Phys.* **101**, 545-550 (2003).
65. H. Ganser, M. Horstjann, C. V. Suschek, P. Hering, and M. Murtz, "Online monitoring of biogenic nitric oxide with a QC laser-based Faraday modulation technique," *Appl. Phys. B* **78**, 513-517 (2004).
66. R. Gabler and J. Lehmann, "Sensitive and isotope selective ($^{14}\text{NO}/^{15}\text{NO}$) online detection of nitric oxide by Faraday-laser magnetic resonance spectroscopy," in *Nitric Oxide, Pt E* (2005), pp. 54-60.
67. T. Fritsch, M. Horstjann, D. Halmer, Sabana, P. Hering, and M. Murtz, "Magnetic Faraday modulation spectroscopy of the 1-0 band of ^{14}NO and ^{15}NO ," *Appl. Phys. B* **93**, 713-723 (2008).
68. R. Lewicki, G. Wysocki, J. Doty, R. F. Curl, and F. K. Tittel, "Ultra-sensitive detection of Nitric Oxide at 5.33 μm using an External Cavity QCL based Faraday Rotation Spectroscopic Sensor Platform," 2008 Conference on Lasers and Electro-Optics & Quantum Electronics and Laser Science Conference, Vols 1-9, 514-515 (2008).
69. T. Fritsch, P. Brouzos, K. Heinrich, M. Kelm, T. Rassaf, P. Hering, P. Kleinbongard, and M. Murtz, "NO detection in biological samples: Differentiation of ^{14}NO and ^{15}NO using infrared laser spectroscopy," *Nitric Oxide-Biology and Chemistry* **19**, 50-56 (2008).

70. R. Lewicki, J. H. Doty, R. F. Curl, F. K. Tittel, and G. Wysocki, "Ultrasensitive detection of nitric oxide at 5.33 μm by using external cavity quantum cascade laser-based Faraday rotation spectroscopy," *PNAS* **106**, 12587-12592 (2009).
71. H. Sabana, T. Fritsch, M. B. Onana, O. Bouba, P. Hering, and M. Murtz, "Simultaneous detection of ^{14}NO and ^{15}NO using Faraday modulation spectroscopy," *Appl. Phys. B* **96**, 535-544 (2009).
72. C. V. Suschek, P. Schroeder, O. Aust, H. Sies, C. Mahotka, M. Horstjann, H. Ganser, M. Murtz, P. Hering, O. Schnorr, K. D. Kroncke, and V. Kolb-Bachofen, "The presence of nitrite during UVA irradiation protects from apoptosis," *Faseb Journal* **17**, 2342-2344 (2003).
73. The FAMOS technique has appeared also under a few other names during the years, e.g. Magnetic Rotation Spectroscopy (MRS) [63], Zeeman Modulation Spectroscopy (ZMS) [61, 93], and most lately Faraday Rotation Spectroscopy (FRS) [70]. Originally, however, MRS referred to a technique in which a static field was used to study both magnetic circular birefringence and dichroism [78-79].
74. K. Takazawa and H. Abe, "Electronic spectra of gaseous nitric oxide in magnetic fields up to 10 T," *J. Chem. Phys.* **110**, 9492-9499 (1999).
75. K. Takazawa and H. Abe, "Landau level of gaseous nitric oxide studied by two-color multiphoton ionization spectroscopy," *J. Chem. Phys.* **110**, 11682-11684 (1999).
76. K. Takazawa, H. Abe, and H. Wada, "Zeeman electronic spectra of gaseous NO in very high magnetic fields up to 25 T," *Chem. Phys. Lett.* **329**, 405-411 (2000).
77. K. Takazawa, "Laser-induced fluorescence excitation spectra due to the B-2 $\Pi(v'=0)$ -X-2 $\Pi(v'=0)$ transition of NO in magnetic fields up to 10T," *J. Mol. Spectrosc.* **223**, 120-124 (2004).
78. D. W. Robinson, "Magnetic Rotation Spectrum of the $A^2\Sigma^+ - X^2\Pi_r$ Transition in NO. I," *J. Chem. Phys.* **46**, 4525-4529 (1967).
79. D. W. Robinson, "Magnetic Rotation Spectrum of the $A^2\Sigma^+ - X^2\Pi_r$ Transition in NO. II," *J. Chem. Phys.* **50**, 5018-5026 (1969).
80. L. Lathdavong, J. Westberg, C. M. Dion, J. Shao, P. Kluczynski, S. Lundqvist, and O. Axner, "Faraday modulation spectrometry of nitric oxide addressing its electronic $X^2\Pi - A^2\Sigma^+$ band: I. Theory " In manuscript (2010).
81. G. Herzberg, *Molecular Spectra and Molecular Structure I. Spectra of Diatomic Molecules*, Second Edition ed. (van Nostrand Reinhold Company, New York, 1950).

82. As a consequence of a weak coupling between the rotation of the nuclei and the orbital angular momentum of the electron, each lower state is additionally split into two states with opposite symmetry (+ and -, respectively) by a so called Λ -doubling. Since this splitting is smaller than the spin-splitting as well as the separation between consecutive rotational levels, and transitions only are allowed between states of dissimilar symmetry, this splitting does not give rise to any additional transitions; it can therefore be seen as a perturbation that only shifts the transitions slightly in frequency.
83. N is the quantum number that corresponds to the rotational energy of a state that lacks orbital angular momentum (i.e. $\Lambda = 0$) and adheres to Hund's case (b), given by $BN(N+1)$ and associated with the operator $(\mathbf{J}-\mathbf{S})^2$ where $\mathbf{J}$ and $\mathbf{S}$ are the operators for the total angular momentum and the electronic spin, respectively. Although not formally correct, N can for convenience be associated with the rotation of the nuclei.
84. J. R. Reisel, C. D. Carter, and N. M. Laurendeau, "Einstein Coefficients for Rotational Lines of the (0, 0) Band of the NO $A^2\Sigma^+-X^2\Pi$ System," J. Quant. Spectrosc. Radiat. Transfer **47**, 43-54 (1992).
85. The 6 branches from the $^2\Pi_{1/2}$ state are $P_{11}(J'')$, $Q_{11}(J'')$, $R_{11}(J'')$ (for which $\Delta N = \Delta J$), and $Q_{21}(J'')$, $R_{21}(J'')$, and $S_{21}(J'')$ (for which $\Delta N = \Delta J + 1$), whereas those from the $^2\Pi_{3/2}$ state are $P_{22}(J'')$, $Q_{22}(J'')$, $R_{22}(J'')$ (for which $\Delta N = \Delta J$), and $O_{12}(J'')$, $P_{12}(J'')$, and $Q_{12}(J'')$ (for which $\Delta N = \Delta J - 1$).
86. We have here utilized the same nomenclature as in Ref. [92], i.e. a tilde sign indicates that the entity is given in units of inverse centimeters whereas an over bar shows that the entity is dimensionless. The superscript D indicates that it is normalized with respect to $\delta\tilde{\nu}_D / \sqrt{\ln 2}$.
87. R. H. Dicke, "The Effect of Collisions Upon the Doppler Width of Spectral Lines," Physical Review **89**, 472-473 (1953).
88. L. Galatry, "Simultaneous Effect of Doppler and Foreign Gas Broadening on Spectral Lines," Physical Review **122**, 1218-1223 (1961).
89. S. G. Rautian and I. I. Sobelman, "Effect of Collisions on Doppler Broadening of Spectral Lines," Sov Phys Uspekhi **9**, 701-716 (1967).
90. A. Henry, D. Hurtmans, M. Margottin-Maclou, and A. Valentin, "Confinement narrowing and absorber speed dependent broadening effects on CO lines in the fundamental band perturbed by Xe, Ar, Ne, He and N-2," J. Quant. Spectrosc. Radiat. Transfer **56**, 647-671 (1996).

91. G. Casa, R. Wehr, A. Castrillo, E. Fasci, and L. Gianfrani, "The line shape problem in the near-infrared spectrum of self-colliding CO₂ molecules: Experimental investigation and test of semiclassical models," *J. Chem. Phys.* **130**, 184306 (2009).
92. J. Westberg, L. Lathdavong, C. M. Dion, J. Shao, P. Kluczynski, S. Lundqvist, and O. Axner, "Quantitative description of Faraday modulation spectrometry in terms of the integrated linestrength and 1st Fourier coefficients of the modulated lineshape function," In manuscript (2010).
93. W. Urban and W. Herrmann, "Zeeman Modulation Spectroscopy with Spin-Flip Raman Laser," *Appl. Phys.* **17**, 325-330 (1978).

Figure Captions

Fig. 1. Schematic illustration the energy level structure of two specific vibrational states of the electronic $X^2\Pi$ and $A^2\Sigma^+$ states of NO. The $^2\Pi$ ground state is first split into two states because of spin splitting (denoted by $^2\Pi_{1/2}$ and $^2\Pi_{3/2}$). Each such state is then split into various rotational states according to its total angular momentum, J . Each rotational state is subsequently split into two with opposite parity because of A -doubling. The upper $^2\Sigma$ state is first split in various rotational states according to the quantum number N (which for simplicity can be associated with the rotation of the nuclei). Each rotational state is then split into two (denoted by F'_1 and F'_2) because of a coupling between the rotation of the nuclei and the electronic spin, sometimes referred to as ρ -type doubling. A $Q_{22}(J'')$ and a $Q_{R12}(J'')$ transition, which correspond to the types of transitions induced in this work, are specifically marked. The two types of lines correspond to transitions for which $\Delta N = \Delta J = 0$ (for the former) and $\Delta N = 0$ and $\Delta J = +1$ (for the latter), respectively. They originate from a common $^2\Pi_{3/2}(J'')$ state (for which $N'' = J'' + 1/2$), but they couple to dissimilar excited states, $^2\Sigma(F'_2, N' = N'')$ (for which $J' = N' - 1/2 = N'' - 1/2 = J''$), and $^2\Sigma(F'_1, N' = N'')$ (for which $J' = N' + 1/2 = N'' + 1/2 = J'' + 1$), respectively. Since NO has a very small (or no) ρ -type doubling, these two transitions are strongly (often considered fully) overlapping.

Fig. 2. Panel (a): Integrated linestrength for the various transitions in the $X^2\Pi(v''=0) - A^2\Sigma^+(v'=0)$ band of NO. Panel (b): Calculated Doppler broadened absorption spectrum in the 226.55 – 226.61 nm range from 0.01 atm of a gas mixture with 300 ppm NO in N_2 . The temperature was assumed to be 296 K whereas the

(FWHM) Doppler broadening was assumed to be 0.099 cm^{-1} (which corresponds to 3.0 GHz). The targeted lines are those at 226.577 nm marked with an asterisk.

Fig. 3. Schematic illustration of the FAMOS instrumentation: ECDL, external cavity diode laser; OI1 and OI2, optical isolators; BS, beam splitters; M, mirrors; TA, tapered amplifier; L, lenses; FDC1 and FDC2, frequency doubling cavities; D1 – D5, photo detectors; PZT1 and PZT2, piezoelectric transducers; KNbO_3 , potassium niobate (frequency-doubling crystal); BBO, β -barium borate (frequency-doubling crystal); LIA, lock-in amplifier; PA, power amplifier; FG, function generator; WM, wavelength meter.

Fig. 4. (Color online) The upper parts of the six panels, (a) – (f), display, by the solid curves, measured FAMOS spectra from 4.2, 20, 40, 60, 90 and 150 Torr of the 100 ppm NO, respectively. The dashed curves represents fits of Eq. (1). The lower parts of each panel display the corresponding residual.

Fig. 5. (Color online) Panel (a): Measured FAMOS spectra of a gas mixture of 100 ppm NO in N_2 for a set of pressures. The various curves represent total pressures of 0, 0.5, 1, 2, 4.2, 8, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 118, 128, 150, 200, and 250 Torr, respectively. Each spectrum corresponds to an average of ten measurements, which have been corrected for their background. Panel (b): Simulations of the FAMOS signal from Eq. (1) for a magnetic field of 130 G and the same set of pressures as in panel (a). The x-axes: detuning measured from the unshifted center frequency of the transition (i.e. under Doppler limited conditions). The y-axes: arbitrary scale.

Fig. 6. Peak values of the FAMOS signal as a function of total pressure from a gas mixture of 100 ppm NO in N₂. Panel (a): experimental data. Panel (b): simulations. Data taken from Fig. 5, thus corresponding to a magnetic field amplitude of 130 G.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.