Open-path trace gas detection of ammonia based on cavity-enhanced absorption spectroscopy

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Abstract. A compact open-path optical ammonia detector is developed. A tunable external-cavity diode laser operating at 1.5 µm is used to probe absorptions of ammonia via the cavity-enhanced absorption (CEA) technique. The detector is tested in a climate chamber. The sensitivity and linearity of this system are studied for ammonia and water at atmospheric pressure. A cluster of closely spaced rovibrational overtone and combination band transitions, observed as one broad absorption feature, is used for the detection of ammonia. On these molecular transitions a detection limit of 100 ppb (1 s) is determined. The ammonia measurements are calibrated independently with a chemiluminescence monitor. Compared to other optical open-path detection methods in the 1–2 µm region, the present result shows an improved sensitivity for contactless ammonia detection by over one order of magnitude. Using the same set-up, a detection limit of 100 ppm (1 s) is determined for the detection of water at atmospheric pressure.

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Industrial emissions and intensive livestock breeding are dominant contributors to the total amount of ammonia in the atmosphere. The ambient concentration and the time-integrated deposition of ammonia are important parameters in acidification and eutrophication processes. These processes can result in environmental damaging effects and in public health hazards. It is therefore necessary to map out and control the ammonia emissions and depositions. Hence, fast (> 1 Hz), sensitive (sub-ppb) and non-intrusive ammonia detectors capable of measuring ammonia in ambient air are indispensable.

Most of the commercially available ammonia monitors use chemical, thermochemical, or optochemical detection schemes and require the collection of atmospheric samples. Their sensitivity ranges from 1 ppt (chemical, thermochemical) [1] to 1 ppm (optochemical) but their response time, however, is usually long and, above all, their intrusive properties are unwanted for several applications. The sampling of air prohibits contactless measurements and, due to the adhesive properties of ammonia, long-term memory effects can introduce measurement errors.

These drawbacks can be circumvented by using the optical properties of the ammonia molecule. A measurement of the molecular absorption spectrum provides information about the ammonia concentration in the probed volume. Over the years various optical detection schemes have been developed and used with the aim to construct a highly sensitive ammonia monitor. High detection sensitivities have been achieved using opto-acoustical techniques with detection limits in the low ppb range [2–6]. Nevertheless, these methods still require the sampling of gas and thus are not suitable for open-path monitoring of ammonia.

The use of diode lasers for trace-gas detection offers various advantages, among which are their narrow laser bandwidth with the associated high frequency and species selectivity. Moreover, they are very compact, easy to use, and affordable. These qualities make them well suited for the implementation in laser-based trace-gas detection systems. Diode lasers are commercially available throughout the 0.7–2.0 µm region, where many trace-gas species of interest have rovibrational transitions. The rovibrational line strengths in these combination and overtone bands are weak compared to the line strengths in the fundamental bands, and highly sensitive detection schemes are therefore needed.

For ammonia many vibrational bands have been reported in the 1–2 µm region [7–10]. On the basis of motives such as the line strength of the absorptions and the avoidance of interference with other atmospheric gases, different combination and overtone bands of ammonia have been chosen for the construction of an open-path ammonia sensor. This resulted in best detection limits of 2 ppm under atmospheric conditions in the 1.5-µm band [11–14] and of 55 ppm at a total pressure of 76 Torr in the 1.65-µm region [15]. Recently, new diode lasers operating in the 2.0-µm region have been used for the detection of ammonia and a detection limit
of 1 ppm has been demonstrated \[16, 17\]. These sensitivities have been achieved by using a diode laser system in combination with advanced measurement schemes such as (two-tone) frequency modulation.

Recently, we have reported on the cavity-enhanced absorption (CEA) technique, a versatile and sensitive tool for spectroscopic studies \[10, 18\]. With this technique, rotational transitions of the $b^1Σ_g^+(ν = 2) ← X^1Σ_g^− (ν = 0)$ band of molecular oxygen have been measured around 628 nm \[18\]. Additionally, a sensitivity of $10^{-9}$ mbar for the detection of ammonia under reduced background pressure was demonstrated in the 1.5-μm band. The CEA technique has been successfully combined with magnetic rotation spectroscopy to obtain cavity-enhanced magnetic rotation spectra of the $^3P_1 (1)$ transition of the aforementioned, magnetic-dipole-allowed, band of molecular oxygen. Absorption features narrower than 270 MHz can be recorded, as was shown by measuring the $^3P_1 (1)$ transition of the $b^1Σ_g^+(ν = 0) ← X^1Σ_g^− (ν = 0)$ band of molecular oxygen in an optical cavity positioned around a slit-jet expansion \[18\]. With the same set-up, we have recorded absorption spectra of rotationally cold ammonia molecules in the 6400–6630 cm$^{-1}$ region, enabling us to assign all of the lower rotational transitions of the $v_1 + v_3$ band and of the $|l| = 2$ component of the $v_1 + 2v_3$ band of ammonia \[10\].

In this paper, we report on the design and performance characteristics of our compact and open-path ammonia sensor based on CEA spectroscopy. An external-cavity diode laser (ECDL) is used to probe ammonia absorptions in the 1.5-μm region. The ammonia sensor is tested and calibrated in a climate chamber \[19\]. A test-gas generator is used to mix predetermined concentrations of ammonia with air in a well-controlled and reproducible way. The ammonia concentration is calibrated independently using a chemiluminescence monitor. It is shown that with a simple set-up involving CEA a sub-ppm detection limit for ammonia is readily achieved.

1 Theory

The CEA technique is already described elsewhere \[18\], and only the main principles of the technique will be given here. Light of a scanning laser is coupled into a high-finesse optical cavity when the frequency of the light is in resonance with one of the cavity modes. In this experiment the laser is continuously scanned over the same spectral region (typically 1 cm$^{-1}$), and at the same time the length of the optical cavity is periodically changed with a piezo-element that scans the mode spectrum over one free spectral range (FSR). As a result, different laser frequencies can be coupled into the cavity each subsequent single scan (‘interleaved sampling’). By summing over several single scans, each frequency will be sampled with an equal probability and spectral features narrower than the FSR of the cavity can be studied.

The intensity of the light coupled into the optical cavity is determined by the spectral overlap between the laser frequency and the frequency of the matching cavity mode, and depends on the finesse of the cavity, the spectral profile of the laser, the scanning rate of the laser frequency, and the scanning rate of the cavity length by the piezo on the end-mirror. The scanning rates must be set in such a way that the laser frequency stays in resonance with the cavity mode sufficiently long, resulting in a maximum intensity that is proportional to the exponential decay time \(τ(ν)\),

\[
τ(ν) = \frac{d}{c(1-R+κ(ν)d)},
\]

where \(d\) is the cavity length, \(c\) is the speed of light, \(R\) the mirror reflectivity, and \(κ(ν)\) the absorption coefficient of an absorbing species inside the cavity. This restriction sets the upper limit for the scanning rate of the laser frequency. In addition there also is a restriction to the lower limit of the scanning rate of the laser. Apart from the periodic change of the cavity length controlled by the piezo-element, there will also be an additional jittering of the cavity modes due to the mechanical instability of the cavity. In order to minimise the intensity fluctuations inside the cavity, all laser frequencies must be in resonance with a cavity mode equally long and the scanning rate of the laser must therefore be significantly higher than the rate at which the cavity modes are jittering. When both of these restrictions are fulfilled, the intensity coupled into the cavity is linearly dependent on \(τ(ν)\). Furthermore, when the laser is tuned out of resonance with the cavity mode, the intensity inside the cavity shows an exponential decay in time, also proportional to \(τ(ν)\). In a CEA experiment, the time-integrated intensity of the light exiting the cavity is measured. This signal is proportional to the exponential decay time \(τ(ν)\), and thus contains information on the absorption coefficient \(κ(ν)\), which is the product of the concentration and the absorption cross-section of the absorbing species in the cavity. By plotting the inverse of the time-integrated detector signal versus the frequency of the laser, an absorption spectrum over the full scanning range of the laser is obtained.

2 Experiment

A scheme of the CEA experiment is depicted in Fig. 1. A continuous-wave ECDL (New Focus, model 6262), operating in the 1512–1590 nm region with a 5-mW maximum power and a laser bandwidth narrower than 5 MHz, is used as a light source. Temperature, current, and frequency of the laser are regulated with an external controller. The frequency region of interest can be attained by adjusting the end-mirror of the laser cavity with a pico-motor. During the measurement, the laser is scanned mode-hop free, and linearly in time, over 1 cm$^{-1}$ frequency intervals. It is important that the full spectral range is covered rather fast, in this particular case at a rate of 32 Hz. This is done by applying a voltage ramp to the piezo-electric transducer that is connected to the end-mirror of the laser cavity.

The light of the laser is coupled into a high-finesse optical cavity formed by two plano-concave mirrors with a specified reflectivity \(R\) of 0.9997, a diameter of 25 mm, and a radius of curvature \(r\) equal to –1 m. Optical feedback from the cavity back to the laser is minimized by a Faraday isolator placed in the beam directly behind the laser aperture. The mirrors are mounted in two mirror-holders that can be aligned independently. The distance \(d\) between the two mirrors is 65 cm. The exact cavity length is continuously varied by a piezo-element fixed to the end-mirror in such a way that the cavity mirror will travel one wavelength in one full piezo-scan (scan rate typically 0.5 Hz). This is equivalent to an ‘active destabilization’ of the detection cavity, and enhances the efficiency with