

TDLAS Spectrometer for the Quantification of Ammonia under Elevated Temperature and Pressure

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1 Introduction

Given today's urgent target of global carbon reduction, carbon-free NH_3 is considered a promising energy carrier and supplier of hydrogen for thermal energy conversion systems. NH_3 has a comparable energy density (22.5 MJ/kg) to that of fossil fuels and it can be liquefied at $-33\text{ }^\circ\text{C}$ under atmospheric pressure or ~ 8 bar at an atmospheric temperature, making it convenient and cost-effective for storage and transportation [1]. However, the widespread use of NH_3 is bound to bring emission and deposition problems that cannot be neglected. It has detrimental effects on human health and contributes to the eutrophication and acidification of land and freshwater, leading to a reduction in soil and water quality, a loss of biodiversity, and changes to the ecosystem. Hence, accurate quantification and monitoring of NH_3 in different application scenarios, such as environmental gas analysis or in the automotive, chemical and medical industries are vital.

Optical gas sensors have the advantage of contactless sensing and can operate in harsh and corrosive environments over a wide temperature and pressure range. They are therefore preferred for more sensitive and selective detection conditions, especially where trace NH_3 is involved. Among the optical gas sensors, tunable diode laser absorption spectroscopy (TDLAS) is well-established and developed for the detection of different gases, chlorides, and hydroxides [2-4]. The knowledge of spectroscopic parameters such as line strength, pressure broadening coefficients and cross-section data is essential for TDLAS-based spectrometers in the perspective of accurately quantifying the absolute mole fraction of trace species. For certain conditions and spectral ranges, the line-by-line parameters are neither possible nor feasible, so the cross-section data often serves to quantify the NH_3 mole fraction at elevated temperatures and pressures, especially in reactive systems, e.g., combustion reactors. Weng et al. [5] measured the ultraviolet absorption cross-section of NH_3 in the temperature range of 295-590 K, and the cross-section data was applied to quantify NH_3 in the post-flame zone of premixed flames. Alturaifi et al. [6] measured the cross-section of NH_3 in Ar near 961 cm^{-1} in the temperature range of 2000-3000 K and pressure range of 0.89-1.28 bar in a shock tube using a fixed-wavelength method. This data was used to quantify the NH_3 mole fraction during the pyrolysis process. Similarly, He et al. [7] measured the NH_3 cross-section in Ar near 1122 cm^{-1} at 1000-2200 K and 0.8-3.9 bar in a shock tube and used the results to determine the NH_3 mole fraction during the oxidation process.

In this work, we give an overview of the development and application of our new NH_3 spectrometer, the details of the work have been submitted to the journal [15]. In this abstract, we firstly introduce the

methodology and experimental setup, including the optical gas cell and shock tube experiments coupled with a newly developed NH₃-TDLAS spectrometer, which can run in three modes. The NH₃-Ar pressure broadening experiments were performed in a gas cell, and the measured NH₃-Ar pressure broadening coefficients were used to determine the NH₃ mole fraction. The cross-section experiments were performed with a 1%NH₃/99%Ar gas mixture in a shock tube at elevated temperatures and pressures. The cross-section data was utilized to quantify the NH₃ mole fraction in the shock tube during the NH₃ oxidation process.

2 Methodology and experimental setup

To quantify the foreign pressure broadening coefficients of six NH₃ transition lines near 1084.6 cm⁻¹, a Mid-IR TDLAS spectrometer has been developed. The intensity of a monochromatic continuously tunable laser source transmitted through a gaseous sample is given by the Beer-Lambert law:

$$I(\nu) = E(t) + I_0(\nu) \cdot T(t) \cdot \exp \left[-\frac{S(T) \cdot p \cdot L \cdot g(\nu - \nu_0) \cdot x}{k_B \cdot T} \right] \quad (1)$$

with the background emission $E(t)$ at time t , initial laser intensity $I_0(\nu)$, and the spectrally broadband transmission losses $T(t)$, which are synchronously derived from the individual raw signals and absorption profiles. The exponential term embraces the absorption line strength $S(T)$ at gas temperature T , the area normalized (integrated area=1) line shape function $g(\nu - \nu_0)$ (centered at the wavenumber ν_0), the Boltzmann constant k_B , the total pressure p , the NH₃ mole fraction x , and the optical path length L . The absorbance spectrum can be computed using the following equation:

$$\alpha(\nu) = -\ln \left(\frac{I(\lambda) - E(t)}{I_0(\lambda) \cdot T(t)} \right) = \frac{S(T) \cdot p \cdot L \cdot g(\nu - \nu_0) \cdot x}{k_B \cdot T} \quad (2)$$

The Voigt function can be used to model the line shape of the absorbance spectrum in Equation (2), which considers the combined effects of Doppler and collisional broadening on the spectral line. These effects are characterized by the Doppler-broadening full width at half maximum (FWHM), $\Delta\nu_D$, and the collisional-broadening FWHM, $\Delta\nu_L$, given by

$$\Delta\nu_D = \nu_0 \sqrt{\frac{8k_B \cdot T \cdot \ln 2}{M \cdot c^2}} \quad (3)$$

$$\Delta\nu_L = 2 \cdot p \cdot \gamma_s \cdot x + 2 \cdot p \cdot \gamma_f \cdot (1 - x) \quad (4)$$

where M is the molecular mass of the absorbing species, c is the speed of light, and the coefficients γ_s and γ_f are the self and foreign broadening coefficients, which are dependent, among other things, on the gas temperature T . Normally, Doppler broadening is calculated directly using Equation (3) and thus does not have to be fitted since the gas temperature is measured in the experiment. Note that the broadening coefficients (γ_s , γ_f) calculated from the measurements using Equation (4) are the corresponding values at an experimental temperature T and have not been converted to the reference temperature 296 K, which is used in HITRAN [8]. The absorption cross-section, k_ν (cm²/molecule), is defined as:

$$k_\nu = \alpha(\nu) \cdot Z \cdot \frac{k_B \cdot T}{x \cdot p \cdot L} \quad (5)$$

where $\alpha(\nu)$ is the absorbance at wavenumber ν under pressure p and temperature T , and Z is the compression factor. For an ideal gas, the density is assumed to be linearly dependent on the pressure. In this study, the pressure is in the 1-4 bar range, so we consider $Z=1$.

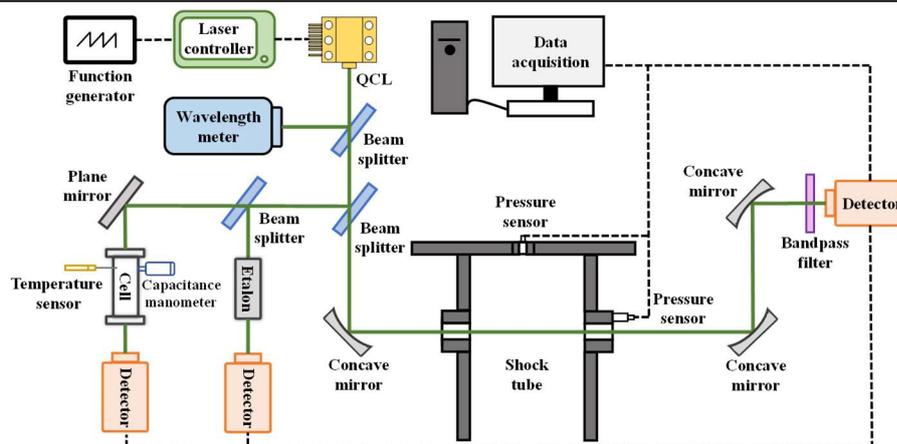
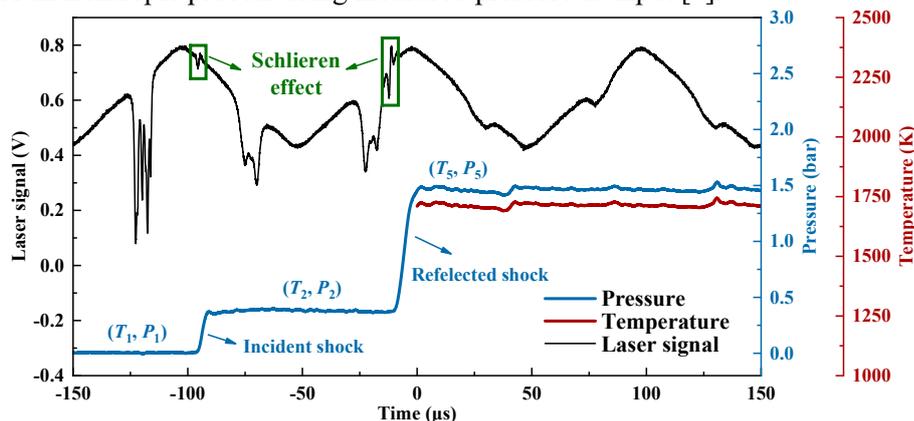


Figure 1: Schematic of the experimental setup.

The experimental setup is depicted schematically in Figure 1. The Ar collisional broadening measurements were performed at room temperature and low pressures in a 29 cm long single-pass gas cell made of stainless steel and equipped with wedged CaF₂ windows. The laser current was modulated by a triangle-shaped ramp at 140 Hz supplied by a function generator, capturing the NH₃ transition lines near 1084.6 cm⁻¹. The dynamic laser tuning was determined before starting the measurements using a Germanium etalon. The experiments for measuring the NH₃ cross-section at high temperatures and pressures were carried out in a high-pressure shock tube. A detailed description of the system can be found in [9]. To quantify the NH₃ cross-section, the wavelength-scanned TDLAS was used again but with a much higher scan frequency of 10 kHz to capture enough absorption spectra behind the reflected shock wave. As an example, Figure 2 shows the raw pressure, laser signal and calculated temperature for cross-section experiments. It is worth to note that at higher temperature and pressure (T_5, P_5), the six NH₃ lines are mixed into one ‘absorption peak’ due to the pressure broadening. Note that only the first three absorption spectra immediately behind the reflected shock wave were used and averaged for cross-section determination. During such a short period (less than 200 μs), the temperature and pressure behind the reflected shock wave were considered constant. Here the temperature was calculated based on the assumption of an isentropic process using measured pressure as input [9].

Figure 2: Exemplary raw pressure, laser signal and temperature in the shock tube with the 1% NH₃/99% Ar mixture ($T_1=295$ K, $P_1=0.04$ bar; $T_2=911$ K, $P_2=0.35$ bar; $T_5=1710$ K, $P_5=1.45$ bar).

3 Results and discussion

Figure 3(a) shows the measured line profiles for the NH₃/Ar gas mixture at two different pressures, 3.94 mbar and 10.11 mbar. The measured laser intensity was averaged over 10 scans and fitted with a third-order polynomial for the baseline and six Voigt models using a non-linear Levenberg–Marquart

algorithm for the NH₃ absorption profile. The residual between measured and fitted data shown below in Figure 3(a) is depicted for two pressures. The average residuals were around (1σ) 2.4×10^{-3} and 9.9×10^{-3} optical density. To clearly discriminate the pressure broadening effect, the Gaussian width was calculated in all experiments using the measured temperature in the gas cell according to Equation (3). The line width progression at different pressures was used to extract the pressure broadening coefficient γ_f . All six measured Ar broadening parameters are listed in Table 1.

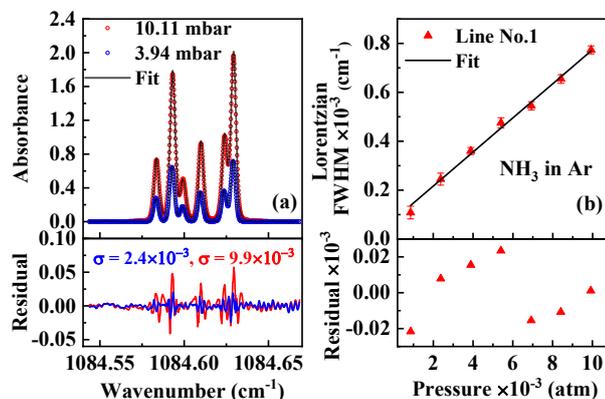


Figure 3: (a) Measured NH₃ absorption spectra (10 scans averaged) in Ar at pressures of 3.94 mbar and 10.11 mbar; (b) Measured Ar-induced pressure broadening of NH₃ absorption Line No. 1 centered at 1084.5836 cm⁻¹ with a linear fitting model.

Table 1: The Ar broadening coefficients of the six measured NH₃ lines

Line No.	Wavenumber (cm ⁻¹)	Ar broadening (cm ⁻¹ /atm)
1	1084.5836	0.0349(24)
2	1084.5931	0.0296(27)
3	1084.5992	0.0538(37)
4	1084.6098	0.0287(25)
5	1084.6237	0.0273(17)
6	1084.6290	0.0225(38)

The obtained Ar-broadening coefficients were further applied to quantify the absolute ammonia mole fraction in the cross-section measurements which were performed in the high-pressure shock tube. Figure 4 (left) shows three representative measured absorbances and converted cross-section using Equation (5) (normalized to 1% NH₃ mole fraction) as a function of wavenumber behind the reflected shock wave at pressures from 1.45 to 1.95 bar and temperatures from 1042 to 1710 K. The absorbance decreased from 1 to 0.12 when the temperature increased from 1042 to 1710 K. With the rise in the temperature, the absorbance drops because the lower state energy of the six NH₃ lines is between 200 and 300 cm⁻¹. Also, the shape and the peak position of the absorption/cross-section profile change slightly.

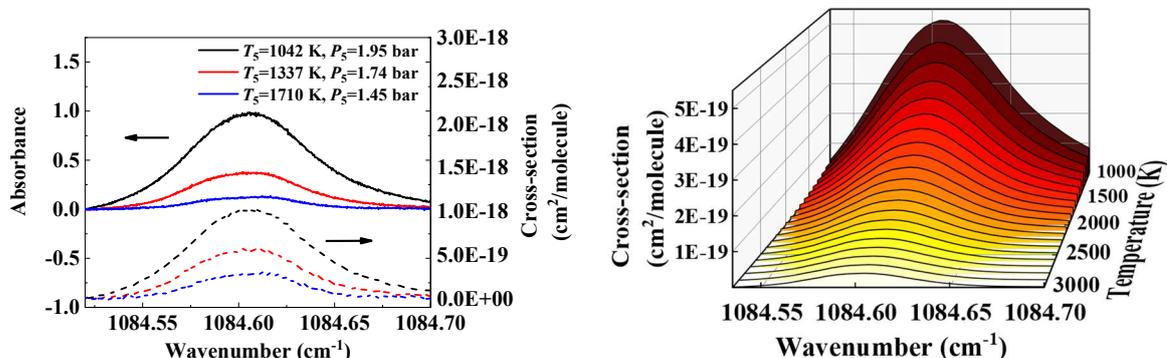


Figure 4: Left: Three representative measured absorbances and corresponding cross-sections as a function of wavenumber behind the reflected shock wave (T_5, P_5) at different temperatures and pressures (1% NH₃/99% Ar mixture); Right: NH₃ cross-section at different wavenumbers and temperatures with the pressure (P_5) in the range of 2.60-3.25 bar.

Figure 4 (right) shows the contouring of the NH₃ cross-sections based on measured values at different wavenumbers and temperatures, with cross-sections over 1800 K calculated by extrapolating exponential equations. Clearly, the cross-section decreases as temperature increases within the measured spectral range. This means that the sensitivity of the spectrometer declines at higher temperatures.

The newly measured cross-section data set can be used to quantify the NH₃ mole fraction in different kinds of application scenarios. For example, when considering green NH₃ as a promising fuel, an accurate chemical kinetic mechanism must be utilized in the design of thermal energy conversion systems. As a case study, NH₃ oxidation experiments in the shock tube were performed, and the NH₃ mole fraction was quantified using the cross-section data set and compared with predictions from different mechanisms. Here fixed-wavelength centered at 1084.61 cm⁻¹ was employed for a higher temporal resolution of 0.05 μ s (20 MS/s sample rate). The total uncertainty of the NH₃ mole fraction is 10.5%. Figure 5 shows the dynamic pressure and NH₃ mole fractions during ammonia oxidation using a fixed-wavelength TDLAS ($T_1=295$ K, $P_1=0.07$ bar; $T_2=959$ K, $P_2=0.67$ bar; $T_5=1821$ K, $P_5=2.79$ bar). It can be seen that after a certain induction time (~ 500 μ s), the NH₃ mole fraction starts to decrease due to the consumption of NH₃. We compared the predictions derived from five recent NH₃-related mechanisms [10-14] with the experimental results. Most mechanisms over-predict or under-predict the conversion rate of NH₃ to a varying degree. Among the five mechanisms, that of Alturaifi et al. [14] shows the best prediction accuracy. The plateau at the late phase (from 1500 μ s) is mainly caused by unconsumed NH₃ and partially due to the interference of high temperature water absorption.

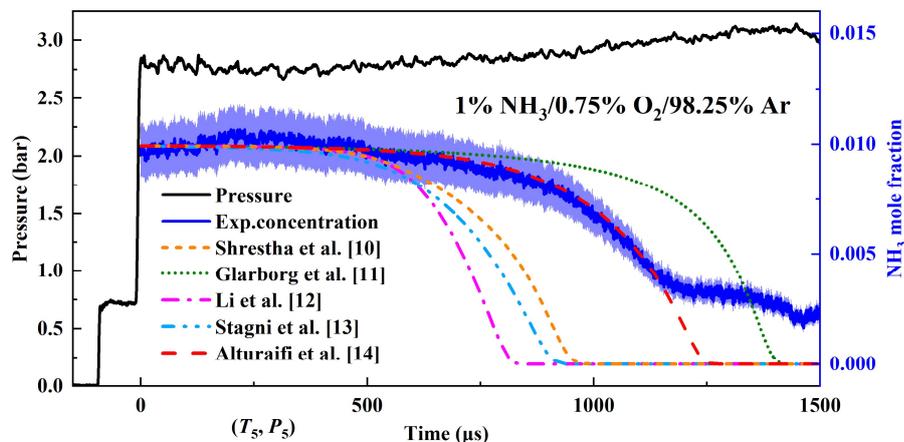


Figure 5: Dynamic pressure and NH₃ mole fraction during ammonia oxidation using a fixed-wavelength method ($T_1=295$ K, $P_1=0.07$ bar; $T_2=959$ K, $P_2=0.67$ bar; $T_5=1821$ K, $P_5=2.79$ bar)

4 Conclusions

For this work, a Mid-IR QCL-based TDLAS spectrometer for NH₃ measurements was developed. With the low-frequency scan mode, Ar collisional broadening experiments of six NH₃ transition lines near 1084.6 cm⁻¹ were performed in an optical gas cell at low pressure and at room temperature. Using the 10 kHz high-frequency scan mode, cross-section measurements were performed in a shock tube in the two pressure ranges of 1.46-1.84 bar and 2.60-3.25 bar over a temperature range of 1000-1800 K. The NH₃ in Ar cross-section data set within the spectral window from 1084.53-1084.70 cm⁻¹, and temperatures from 1000 to 3000 K was reported for a pressure range of 2.60-3.25 bar. Furthermore, as an example of an application scenario, the newly measured cross-section data set was used to quantify the absolute NH₃ mole fraction during the dynamic NH₃ oxidation process in the shock tube with the

spectrometer in time-resolved fixed-wavelength mode. The quantified dynamic NH₃ mole fraction was compared to predictions generated by five chemical kinetic mechanisms and demonstrated its utility in validating these mechanisms.

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