

Full Length Article

Flame chemistry and stability of ammonia counterflow diffusion flames: Effects of hydrogen addition and oxygen enrichment

Hanna M. Hülsmann^{a,1}, Daniel Kretzler^{a,1}, Florian J. Bauer^b, Peter Habisreuther^a,
 Phillipp A. B. Braeuer^b, Björn Stelzner^a, Stefan Will^b, Dimosthenis Trimis^a,
 Fabian P. Hagen^{a,*}

^a Karlsruhe Institute of Technology (KIT), Engler-Bunte-Institute (EBI), Combustion Technology, Engler-Bunte-Ring 7, Karlsruhe, 76131, Baden-Württemberg, Germany

^b Friedrich-Alexander-Universität Erlangen-Nürnberg (FAU), Lehrstuhl für Technische Thermodynamik (LTT) & Erlangen Graduate School in Advanced Optical Technologies (SAOT), Paul-Gordan-Straße 6, Erlangen, 91052, Bavaria, Germany

HIGHLIGHTS

- Extinction strain rate, temperature and in-flame species profiles to characterize flames.
- $\text{NH}_3\text{-H}_2\text{-Ar}$ flames at constant T_{max} to decouple thermal and kinetic effects.
- Preferential diffusion as driver of secondary reaction zone in $\text{NH}_3\text{-H}_2$ flames.
- Double peaks in excited species exposing limitations of kinetic mechanisms.

ARTICLE INFO

Keywords:

Ammonia combustion
 Counterflow diffusion flames
 Hydrogen co-combustion
 Oxygen enrichment
 Emission spectroscopy
 Flame structure

ABSTRACT

This study investigates ammonia (NH_3) counterflow diffusion flames (CDFs) under various conditions and evaluates contemporary kinetic mechanisms against experiments. First, ammonia CDFs with hydrogen additions and air are examined; second, pure ammonia flames with oxygen-enriched oxidizers are investigated; third, the influence of H_2 addition on ammonia-hydrogen-argon CDFs is studied. Argon dilution maintains identical maximum flame temperatures, thereby achieving decoupling of thermal and kinetic effects. Extinction strain rates (ESR) are used to assess flame stability and kinetic mechanism performance. Flame structure is characterized by temperature and optical diagnostics of key excited species, including OH^* , NH^* , NH_2^* , and NO^* . For selected CDFs, profiles of NH_3 , H_2 , and NO are quantified using a microprobe coupled with gas-phase diagnostics. Experimental results show good agreement with numerical predictions of ESR and temperatures in ammonia-hydrogen flames. However, under oxygen-enriched conditions, all mechanisms underpredict the peak temperatures. The mechanism proposed by Konnov [Combust. Flame 253 (2023) 112789] accurately reproduces NH^* and NH_2^* profiles, whereas deviations remain for NO^* . At higher hydrogen admixtures, the local depletion of NH_3 and H_2 becomes spatially separated due to preferential hydrogen diffusion. The measured chemiluminescence peaks coincide with these depletion zones, forming a double-peak structure that indicates a second reaction zone dominated by H_2 oxidation. Numerical predictions reproduce NH_3 and H_2 depletion, but fail to capture the corresponding chemiluminescence double peaks. For OH^* , the reaction $\text{OH}^* + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O}_2 + \text{H}$ suppresses double-peak formation, whereas the governing pathways for NH^* , NH_2^* , and NO^* remain to be identified.

1. Introduction

Ammonia (NH_3) has emerged as a promising energy carrier in the transition to sustainable energy systems. Beyond its role as a hydrogen (H_2) carrier, its direct combustion is increasingly being explored as a

viable energy conversion pathway [1]. However, ammonia combustion presents several challenges, including low laminar burning velocity and poor flammability, as well as the formation of undesired emissions such as nitrogen oxides (NO_x) and unburned NH_3 . Addressing

* Corresponding author.

Email address: fabian.hagen@kit.edu (F.P. Hagen).

¹ Authors made an equal contribution.

<https://doi.org/10.1016/j.fuel.2026.141356>

Received 30 April 2026; Received in revised form 3 July 2026; Accepted 12 September 2026

Available online 14 October 2026

0016-2361/© 2026 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (<http://creativecommons.org/licenses/by/4.0/>).

Open access funding enabled and organized by Projekt DEAL.

these challenges requires a fundamental understanding of ammonia flame chemistry and combustion behavior to ensure its reliable use in large-scale applications [2].

Despite significant progress in ammonia combustion modeling, current mechanisms still lack sufficient validation under well-controlled, reproducible conditions. While ammonia flames have been studied in counterflow configurations, comprehensive datasets remain scarce, particularly for pure ammonia flames and oxygen-enriched oxidizer conditions.

At the same time, previous studies have begun to map relevant regions of the parameter space and thus provide a valuable foundation for further investigation. Thomas et al. [3] examined ammonia-hydrogen CDFs with hydrogen mole fractions in a range of $x_{H_2} = 0 \dots 15\%$. Choi et al. [4] investigated ammonia-hydrogen CDFs in the range of $x_{H_2} = 1 \dots 11\%$, while Alfazazi et al. [5] explored pure ammonia flames with oxygen (O_2)-enriched air at $x_{O_2} = 30\%$ and 45% , ammonia-hydrogen mixtures with $x_{H_2} = 10 \dots 40\%$, and ammonia mixtures with $C_1 \dots C_3$ hydrocarbons.

In this context, electronically excited species detected by chemiluminescence provide valuable information on flame structure and reaction progress and can serve as indicators of local equivalence ratio and heat release rate in complex combustion systems [6–8]. However, their reliable modeling remains challenging due to the limited understanding of the reaction pathways governing their formation in ammonia flames. Recently, Issayev et al. [9] applied spatially resolved chemiluminescence imaging of NH^* and OH^* in ammonia-hydrogen CDFs over a hydrogen mole fraction range of $x_{H_2} = 10 \dots 90\%$. By comparing their measurements with the mechanism introduced by Konnov [10,11], they proposed modifications to four key reactions of NH^* chemistry within the reported uncertainty limits, resulting in a slight improvement in prediction accuracy. Capriolo et al. [12] measured spatially resolved OH^* intensity in ammonia-hydrogen CDFs for $x_{H_2} = 20 \dots 80\%$, evaluating a tailor-made mechanism based largely on [13]. Zhu et al. [14] performed spectrally resolved emission spectroscopy in premixed ammonia-hydrogen twin flames stabilized in a counterflow burner to derive correlations with equivalence ratio and hydrogen mole fraction. Pugh et al. [15] employed line-of-sight integrated imaging of NH^* , NH_2^* , and OH^* in turbulent diffusion flames, finding that NH_2^* intensity reliably indicates NO consumption in rich NH_3 flames, while the combined chemiluminescence measurements further support detailed analysis of intermediate chemistry.

The present study aims to provide a comprehensive, high-quality dataset of ammonia combustion by (i) systematically investigating ammonia CDFs with oxygen-enriched air as well as ammonia-hydrogen CDFs, (ii) measuring extinction strain rates (ESR), temperature profiles, and spatially resolved excited species profiles to provide a comprehensive characterization of flame behavior, (iii) examining ammonia-hydrogen-argon flames under conditions where the argon mole fraction is adjusted to maintain identical maximum flame temperatures for all investigated mixtures, thereby separating temperature effects resulting from hydrogen addition from its direct kinetic influence, (iv) complementing measurements of excited species with in-flame species measurements, including NH_3 , H_2 , and NO , to further understand reaction kinetics and transport processes, and (v) using ESR measurements as an initial validation step for seven state-of-the-art chemical kinetic mechanisms and employing the complete experimental dataset for a broader assessment of their predictive capabilities. Together, these efforts enable a direct comparison of numerical simulations with experimental observations and provide new insights into the strengths and limitations of current kinetic models, particularly with respect to the prediction of excited species.

2. Experimental and numerical approach

2.1. Counterflow burner setup

All experiments were conducted using a counterflow burner based on the design by Niemann et al. [16]. Fig. 1 shows a schematic of the burner and the experimental setup, along with three representative CDFs, while Fig. 2 introduces the terminology and defines the computational domain. The burner consists of two vertically opposed outlets with a diameter of $D = 25$ mm and a separation distance of $L = 20$ mm, supplying oxidizer from the top (outlet 2) and fuel from the bottom (outlet 1). A nitrogen sheath flow, directed through two external concentric outlets, isolates the system from ambient disturbances. The exhaust gas is extracted concentrically on the fuel outlet side and passes through a water-cooled system to prevent the burner from heating up.

To investigate different types of CDFs, three separate cases were considered, with all compositions given as mole fractions:

- ammonia-hydrogen CDFs with $x_{H_2} = 0 \dots 20\%$ and air as oxidizer,
- pure ammonia CDFs with an oxygen content of $x_{O_2} = 21 \dots 35\%$ in the oxidizer, and
- ammonia-hydrogen-argon CDFs with relative hydrogen mole fractions of $x_{H_2,rel} = 25 \dots 95\%$ (based on the NH_3 - H_2 content) and air as oxidizer.

For the ammonia-hydrogen-argon CDFs, the argon fraction in the fuel was adjusted such that all flames in this experimental series exhibited an approximately constant maximum temperature; the detailed flame compositions are provided in Appendix A.

Fine wire meshes with a wire diameter of $50 \mu m$ ensure a plug flow inflow profile, as described in [16]. The global strain rate was determined following Seshadri and Williams [17],

$$a_2 = \frac{2|u_2|}{L} \left(1 + \frac{|u_1|\sqrt{\bar{\rho}_1}}{|u_2|\sqrt{\bar{\rho}_2}} \right), \quad (1)$$

where u_1 and u_2 indicate the outlet velocities of the fuel (1) and oxidizer (2) streams, respectively, and $\bar{\rho}_1$ and $\bar{\rho}_2$ represent the corresponding gas densities at the outlets. The outlet velocity was adjusted to satisfy the momentum balance, yielding a simplified expression for the global strain rate:

$$a_2 = \frac{4|u_2|}{L}. \quad (2)$$

In the setup, gas flow rates were regulated using thermal mass flow controllers (MFCs) with a maximum uncertainty of $< 1\%$. A strain rate of $a_2 = 40 \text{ s}^{-1}$ was maintained for all measurements except for ESR determination, as it ensured stable combustion of pure NH_3 with air.

2.2. Diagnostics

To characterize the CDFs, flame images were captured, and ESR, temperature profiles, in-flame species and emission spectra were measured.

Extinction strain rates serve as an indicator of flame stability. For ESR measurements, the strain rate was incrementally increased, ensuring that at each step the MFCs reached steady-state operation, continuing until flame extinction. Each measurement was repeated at least three times per data point.

The axial **temperature profiles** of the investigated CDFs were measured using an S-type thermocouple probe as introduced in [18]. A spring mechanism prevents deformation of the thin thermowires $100 \mu m$ in diameter, which are fixed under tension parallel to the reaction zone. To eliminate catalytic effects, the wires were coated with ZrO_2 . The measured temperatures were corrected for radiation losses as described in

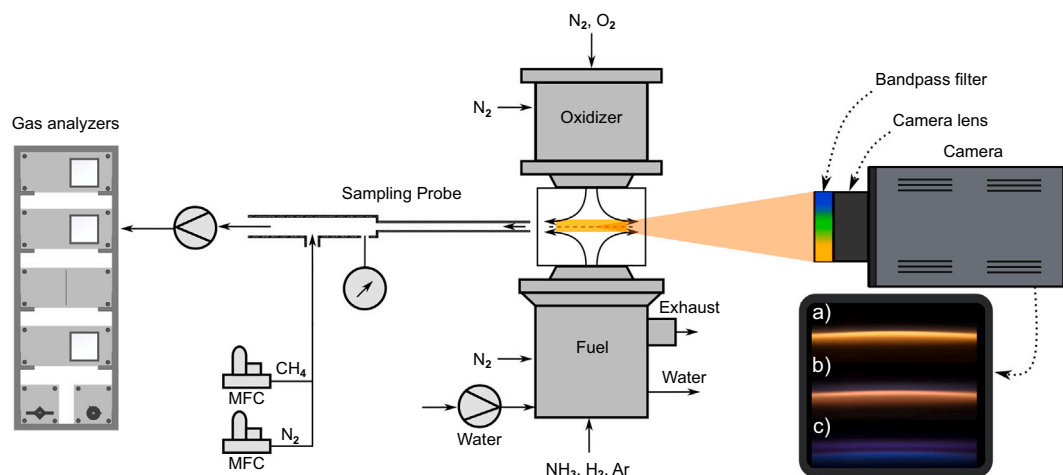


Fig. 1. Schematic of the counterflow burner configuration including oxidizer and fuel outlets, the microprobe connected to the gas analyzing system, and the optical setup for spectrally integrated 2D chemiluminescence imaging using a UV camera lens and bandpass filters. Representative RGB flame images are shown for a) NH_3/air CDFs with $x_{\text{NH}_3} = 100\%$, and $\text{NH}_3\text{-H}_2\text{-Ar}/\text{air}$ CDFs with b) $x_{\text{H}_2,\text{rel}} = 80\%$ and c) $x_{\text{H}_2,\text{rel}} = 95\%$.

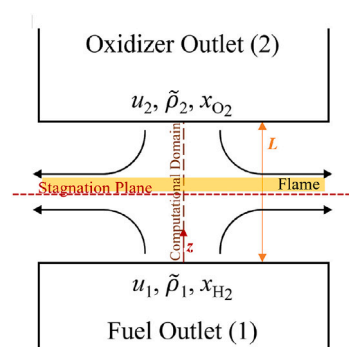


Fig. 2. Schematic of counterflow burner, terminology, and computational domain.

[18]. To cross-validate the intrusive measurements, they were compared against non-intrusive, *in situ* temperature measurements obtained in a hydrogen CDF using a temperature sensor based on the detection of near-infrared thermal radiation from water vapor, as described in [19]. The results showed good agreement within the experimental uncertainty. Additional details are provided in Appendix B.

To visualize the flame structure, **broadband flame imaging** was performed using an RGB CMOS camera (Blue Fox 3-2071aC, Matrix Vision) operated at a constant exposure time of 4 ms.

To probe electronically excited species, spectrally resolved UV measurements were first performed using a grating spectrograph (2400 lines mm^{-1} ; Kymera 193i, Andor) coupled to an sCMOS camera (Dhyana 95 V2, Tucsen) with calibrated wavelength and intensity responses. The focusing optics, similar to those described in Schmidt et al. [19], provided a measurement volume of approx. 105 μm in diameter and 2.0 mm FWHM in length. The recorded spectra, covering the emission regions of NO^* , OH^* , and NH^* , are shown in Fig. 3. By integrating species-specific wavelength intervals within the spectrally resolved measurements, 1D intensity profiles were extracted, as presented in Fig. 4. Based on these spectrally resolved reference measurements, 2D chemiluminescence imaging was subsequently carried out using an intensified CCD (ICCD) camera system (PI-MAX 4: 1024f, Teledyne Princeton Instruments) equipped with a UV camera lens ($f = 100$ mm, $f/2$). Bandpass filters centered at 250 nm (FWHM 10 nm, OD 6) and at 310 nm and 337 nm (both FWHM 10 nm, OD 4) were selected to capture the characteristic emission bands listed in Table 1. Spacer rings

were used to achieve an effective focal length of 200 mm, corresponding to a spatial pixel resolution of 19.5 $\mu\text{m px}^{-1}$ over a field of view (FOV) of 20 mm. Excellent agreement was obtained between the 1D profiles extracted from the spectrally resolved measurements and the corresponding 2D chemiluminescence signals obtained through the bandpass filters (Fig. 4).

To quantify **in-flame species**, a microprobe similar to those used in Vlavakis et al. [20], Carbone et al. [21], and Bufferand et al. [22] was employed. The chemically inert ceramic probe (Degussit AL23) has an inner diameter of 300 μm , an outer diameter of 600 μm , a length of 45 mm, and is schematically shown in Fig. 1. The probe was positioned horizontally at the burner centerline and connected to a transfer line. Both the probe connections and the transfer line were heated to 175 $^\circ\text{C}$ to prevent condensation in the sampling path. Vertical scanning was performed by moving the burner with a traverse system using a minimum step size of 200 μm .

Due to the low sampling flow imposed by the microprobe geometry and the high species concentrations exceeding the analyzer range, the extracted gas stream was diluted prior to analysis using a nitrogen carrier flow containing CH_4 as a tracer. The transfer line therefore included an injection point for the tracer-containing nitrogen flow as well as a connection to a differential pressure sensor to monitor the pressure drop across the probe tip, which reached values of up to 100 mbar. The corresponding pressure signal was measured with an accuracy of 0.5 mbar. Gaseous species were quantified using the measurement setup described by Kretzler et al. [23], with NH_3 and NO measured in the wet gas phase and H_2 in the dry gas phase. The setup was complemented by an additional gas analyzer (ABB Uras26) for CH_4 measurements in the dry gas phase over a range of 0...3000 ppmv. The N_2 carrier flow was set to 60 L h^{-1} and contained 2444 ppmv of CH_4 .

The measured diluted wet and dry species concentrations were converted to the corresponding undiluted sampled concentrations using the tracer-based correction described in Appendix C (Eq. C.3). All reported microprobe-derived concentrations are given as dry gas mole fractions. For NH_3 and NO , which were measured in the wet gas phase, conversion to dry-gas mole fractions introduces an additional uncertainty of less than 3%, based on the upper-bound estimate described in Appendix C (Table C.3). The overall measurement uncertainty was estimated to be approximately 20%. A detailed assessment of (i) potential microprobe-induced conversion during sampling and (ii) the systematic uncertainty associated with the tracer-based reconstruction and dry gas correction is provided in Appendix C.

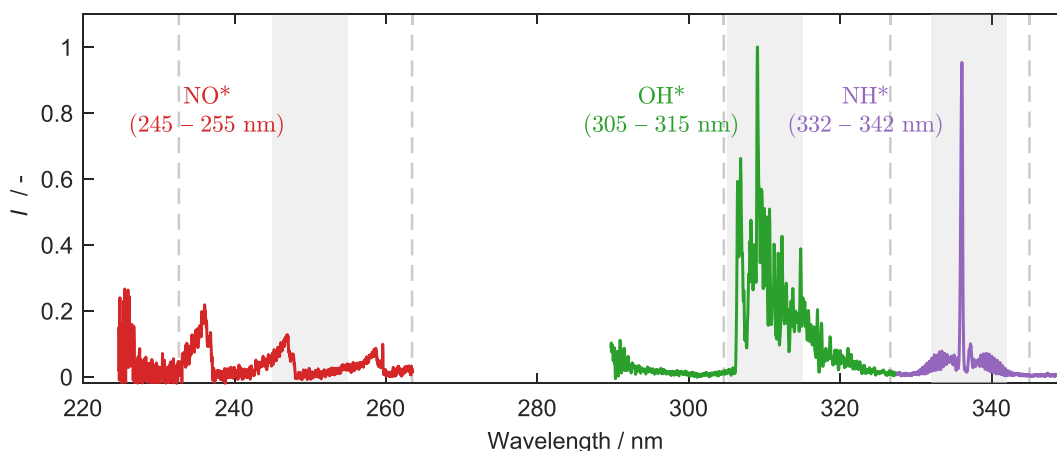


Fig. 3. Calibrated and normalized UV chemiluminescence spectrum of the NH_3/air CDF. Shaded regions indicate the UV bandpass filter windows used for spectrally integrated 2D chemiluminescence imaging, while dashed vertical lines mark the wavelength intervals used for integration of the spectrally resolved measurements corresponding to the NO^* , OH^* , and NH^* emissions.

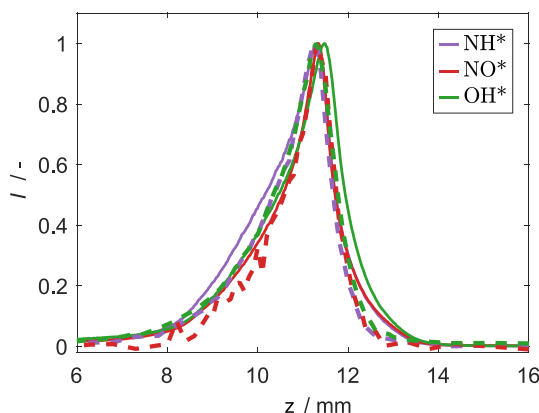


Fig. 4. Comparison of normalized NH^* , NO^* , and OH^* intensity profiles obtained from spectrally integrated 2D chemiluminescence imaging (solid lines) and from integration of the spectrally resolved measurements (dashed lines) as a function of the axial coordinate z for the NH_3/air CDF.

Table 1

Characteristic wavelengths of the investigated radicals and their electronic transitions.

Species	λ (nm)	Transition	Ref.
NO^*	247	$A^2\Sigma^+ \rightarrow X^2\Pi$ (0–2)	[24]
OH^*	309	$A^2\Sigma^+ \rightarrow X^2\Pi$	[10]
NH^*	336	$A^3\Pi \rightarrow X^3\Sigma^-$	[10]
NH_2^*	630	$A^2A_1 \rightarrow X^2B_1$	[15]

2.3. Numerical setup

To evaluate state-of-the-art numerical mechanisms against the obtained experimental data, simulations were performed using *Chemkin* and the *Opposed Flow Flame Model*, which is stationary and one-dimensional. Multicomponent transport and the Soret effect were accounted for, while thermal radiation was neglected due to its minor influence on the results [3].

To calculate the ESR, the inlet velocity was progressively increased until extinction occurred and subsequently refined by weighted interpolation between the last stable and first extinguished solution; convergence was assumed when the relative change in inlet velocity between two consecutive iterations fell below 2×10^{-3} .

The simulations were configured to replicate experimental conditions, ensuring momentum balance at the outlets. Measured boundary

temperatures were used as outlet temperatures: at higher strain rates, temperatures stabilized at 306 ± 1.2 K at the fuel outlet and 311 ± 6.2 K at the oxidizer outlet. At a strain rate of $a_2 = 40 \text{ s}^{-1}$, the cooled fuel outlet (1) maintained a constant temperature of 315 ± 5.8 K. In contrast, the uncooled oxidizer outlet (2) exhibited a dependency of outlet temperature on fuel and oxidizer composition. To account for this, linear correlations were established: $T = (1.3145 \cdot x_{\text{H}_2}(\text{mol}\%) + 323) \text{ K}$ for ammonia-hydrogen CDFs, and $T = (1.7622 \cdot x_{\text{O}_2}(\text{mol}\%) + 275) \text{ K}$ for ammonia CDFs with varying oxidizer compositions. For the experimental series conducted at constant maximum temperature, an identical temperature at the oxidizer outlet of 335 K was determined.

For the simulations, well-established reaction mechanisms from the literature were employed, and selected based on their validation under conditions relevant to this study. The mechanisms considered include those by Glarborg et al. [25], Zhang et al. [26] (KAUST2023), Stagni et al. [27] (POLIMI2020) and its subsequent refinement by Stagni et al. [28] (POLIMI2023), as well as the mechanism by Otomo et al. [29]. Additionally, the mechanism developed by Konnov [10,11] was included, as it is currently the only mechanism that considers all investigated excited species. Lastly, the mechanism proposed by Thomas et al. [3], building upon the work of Shrestha et al. [30], provides significant improvements for ammonia-hydrogen CDFs and was therefore included in this study.

For clarity, the mechanisms are referred to throughout this work by the surname of the first author or by a name commonly used in literature for the mechanism, along with the year of publication.

3. Results and discussion

ESR is first used to evaluate flame stability and validate the reaction mechanisms. Temperature profiles are presented, with maximum values compared to model predictions. To further investigate flame chemistry, axial intensity profiles of selected electronically excited species are compared with predictions obtained using the Konnov2023 mechanism. To support the interpretation of these results, in-flame species, i.e., NH_3 , H_2 , and NO , are additionally measured for selected flames using the microprobe.

3.1. Extinction strain rates

ESR was measured for fuel compositions in the range of $x_{\text{H}_2} = 0 \dots 10\%$ and oxidizer compositions between $x_{\text{O}_2} = 21 \dots 27\%$. The results are presented in Figs. 5 and 6. In both the experiments and the numerical simulations, increasing the oxygen content in the oxidizer

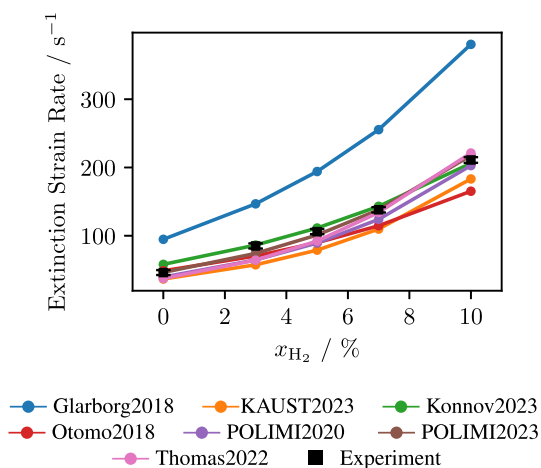


Fig. 5. Experimentally determined ESR for ammonia-hydrogen CDFs with air over molar hydrogen content in the fuel, compared with numerical predictions from different reaction mechanisms.

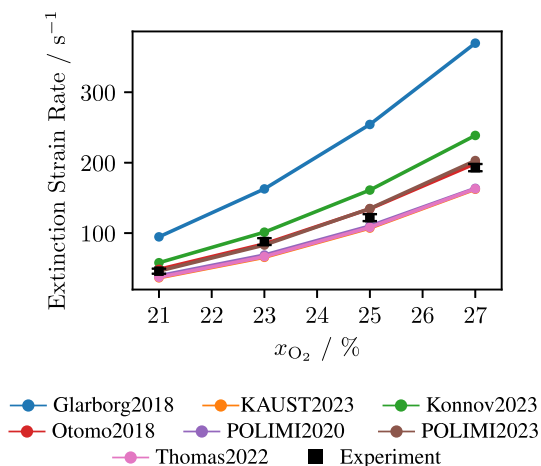


Fig. 6. Experimentally determined ESR for ammonia CDFs over molar oxygen content in the oxidizer, compared with numerical predictions from different reaction mechanisms.

or the hydrogen content in the fuel results in higher ESR, thereby improving flame stability. These overall trends are consistent with the available findings from [3–5]. Notably, Thomas et al. [3] also reported ESR measurements for the H₂ series, showing good agreement with the present results within the experimental uncertainty and thereby further validating the burner.

With the exception of the Glarborg2018 mechanism, which significantly overestimates ESR, all reaction mechanisms show good agreement with the experimental data. According to [3], this discrepancy observed for the Glarborg2018 mechanism, which was developed as a general mechanism for nitrogen chemistry rather than specifically for ammonia as the primary fuel, may be related to an overestimation of H and OH concentrations, whose high diffusivity and reactivity could significantly influence the ESR.

For ammonia-hydrogen CDFs (Fig. 5), the Konnov2023 mechanism shows the best agreement with the experimental data, yielding an overall standard deviation of 3.5 s⁻¹. For ammonia CDFs with varying oxygen concentrations (Fig. 6), most mechanisms exhibit comparable or higher standard deviations, with the exception of the Otomo2018 mechanism, which provides the closest agreement with a standard deviation of 3.8 s⁻¹. When considering both datasets jointly, the POLIMI2023

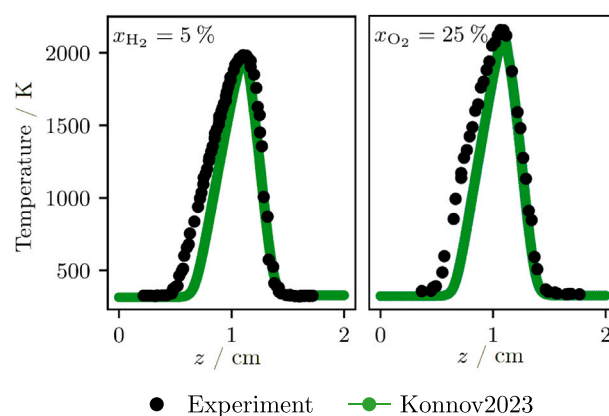


Fig. 7. Measured and predicted temperature profiles for $x_{H_2} = 5\%$ (left) and $x_{O_2} = 25\%$ (right).

mechanism provides the best overall agreement, with standard deviations of 4.1 s⁻¹ and 4.9 s⁻¹, respectively.

3.2. Temperature profiles

Two representative temperature profiles are shown in Fig. 7, along with predicted temperatures using the Konnov2023 mechanism. On the left, the profile for an ammonia-hydrogen CDF with $x_{H_2} = 5\%$ is shown, while on the right a pure ammonia CDF with $x_{O_2} = 25\%$ is presented.

For both CDFs, the numerical results closely match the experimental data, particularly toward the oxidizer outlet. However, on the fuel side ($z = 0 \dots 10$ mm), the experimental profile is consistently about 1.6 mm broader than predicted across all measured flames.

A comparison of maximum temperatures reveals that at $x_{O_2} = 25\%$, the temperature is about 190 K higher than that at $x_{H_2} = 5\%$. This suggests that increasing the oxygen content in the oxidizer has a greater impact on the maximum flame temperature than hydrogen addition to the fuel, likely due to the simultaneous reduction of inert gas fraction in the oxidizer. This observation is further supported by maximum temperatures shown in Figs. 8 and 9 for various ammonia and ammonia-hydrogen CDFs.

In Fig. 8, the maximum measured temperatures of ammonia-hydrogen CDFs are compared with numerically predicted values. The numerical results of all mechanisms closely match the experimental data, remaining within the unavoidable experimental uncertainty of approx. ± 100 K [18] due to radiation corrections. Fig. 9 presents the maximum temperatures for ammonia CDFs with varying oxidizer compositions. For lower oxygen fractions, the numerical simulations agree with the experimental data within the measurement uncertainty. However, the temperature increase with rising oxygen fraction is underestimated, such that at $x_{O_2} = 27\%$ only some mechanisms remain within the experimental uncertainty, and at $x_{O_2} = 30\%$ all mechanisms significantly underpredict the temperature. This systematic deviation may be related to the limited validation of the mechanisms considered in this study for oxygen-enriched ammonia (diffusion) flames. It also emphasizes the need for dedicated experimental data in this regime to support the validation and further development of kinetic models.

3.3. In-flame and chemiluminescent species

Fig. 10 presents spatially resolved profiles of NH*, NO*, OH*, and visible (Vis) emission for selected ammonia-hydrogen CDFs with hydrogen mole fractions up to $x_{H_2} = 20\%$, compared with predictions from the Konnov2023 mechanism. The visible emission is recorded over the accessible spectral range of the ICCD camera without optical filtering and without correcting for the wavelength-dependent sensitivity of the photocathode, i.e., its quantum efficiency, and is compared to NH₂*

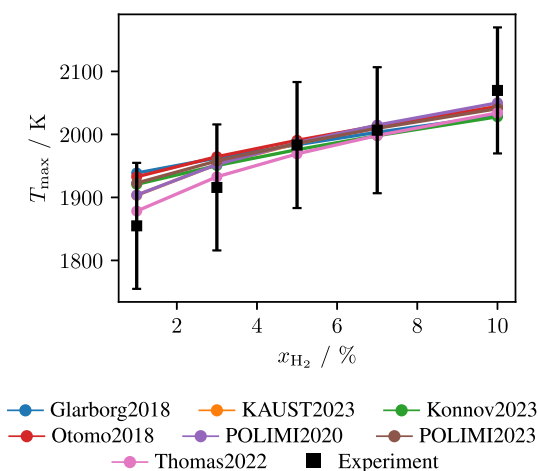


Fig. 8. Comparison of experimental and numerically determined maximum temperatures for various ammonia-hydrogen CDFs.

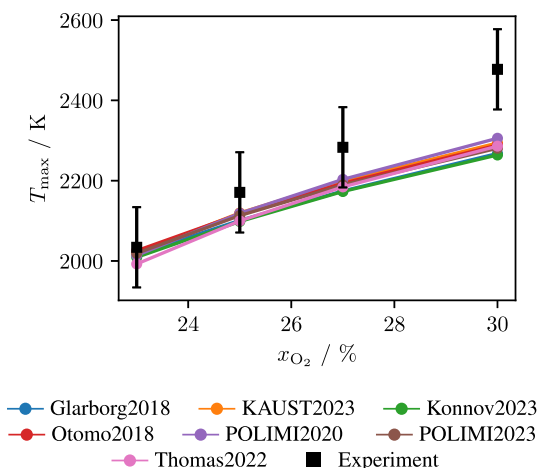


Fig. 9. Comparison of experimental and numerically determined maximum temperatures for ammonia CDFs with various oxidizer compositions.

which dominates the radiation in the visible spectral range in the reaction zone, with additional contributions from species such as NO_2^* [6]. The predicted profiles were temperature-corrected following [10] to enable comparison with the measured intensity profiles. Since spectrally integrated 2D measurements, converted into 1D profiles, do not provide absolute intensity values, all profiles were normalized to their respective maxima.

For all species except NO^* , both experimental and numerical results indicate an increase in the maximum intensity with increasing hydrogen content, although the experimental profiles are spatially broader than predicted by the Konnov2023 mechanism. Notably, good agreement between experiments and simulations is observed for the maximum intensities of NH^* and Vis emissions, with the peaks exhibiting similar relative magnitudes. For the Vis emission, the peaks also occur at nearly identical spatial locations. However, the mechanism does not reproduce the experimentally observed shift of the NH^* peak toward the oxidizer outlet with increasing hydrogen addition. For OH^* , the simulations correctly capture the increase in signal intensity with hydrogen content and the predicted peak positions agree very well with the measurements. Nevertheless, the experimentally observed peak intensities span a narrower range in amplitude than predicted by the simulations. Additionally, the experiments show a broadening of the OH^* profile shape toward the oxidizer outlet with increasing hydrogen content,

which is not reproduced by the simulations. Significant discrepancies are observed for NO^* . While the simulations predict a maximum NO^* intensity at a hydrogen admixture of $x_{\text{H}_2} = 10\%$, the experimental results show a continuous increase with increasing hydrogen content, although the differences diminish at higher hydrogen mole fractions.

Fig. 11 shows spatially resolved profiles of NH^* , NO^* , OH^* , and Vis emission for ammonia CDFs with varying oxidizer compositions up to $x_{\text{O}_2} = 35\%$, compared with predictions from the Konnov2023 mechanism. Similar to the hydrogen variation, the numerically predicted profiles remain axially narrower than the experimentally measured ones. Furthermore, increasing the oxygen content in the oxidizer leads to higher maximum intensities for all species. In contrast to the $\text{NH}_3\text{-H}_2$ measurement series, the peak maxima shift toward the fuel outlet with increasing oxygen addition rather than toward the oxidizer outlet. This behavior results from shifts in the stoichiometric mixture fraction (Z_{st} , defined according to [31]). Hydrogen addition moves the stoichiometric surface toward the oxidizer outlet, decreasing the stoichiometric mixture fraction from $Z_{\text{st}} = 0.142$ for pure ammonia to $Z_{\text{st}} = 0.127$ at $x_{\text{H}_2} = 20\%$, thereby stabilizing the flame closer to the oxidizer outlet. In contrast, oxygen enrichment shifts the stoichiometric surface toward the fuel outlet, as reflected by an increase in the stoichiometric mixture fraction from $Z_{\text{st}} = 0.142$ in air to $Z_{\text{st}} = 0.213$ at $x_{\text{O}_2} = 35\%$.

The predicted and measured peak intensities of NH^* and Vis emission agree well, whereas the experimental NH^* peak positions are consistently shifted toward the oxidizer outlet compared to the simulations. The simulations reproduce the general increase of OH^* intensity with increasing oxygen enrichment; however, the experimental OH^* peak magnitudes are further apart than predicted by Konnov2023. The numerical results further indicate a broadening of the OH^* profiles toward the fuel outlet, which is qualitatively reflected in the experimental data. In contrast, substantial discrepancies are observed for NO^* as neither peak intensity nor peak position are accurately captured. While the simulations predict a maximum NO^* intensity at $x_{\text{O}_2} = 30\%$, the experimental results show a continuous increase in NO^* intensity with increasing O_2 concentration. NO^* exhibits the largest deviations between simulations and measurements in both datasets. Predicting NO^* is particularly challenging in $\text{NH}_3\text{-H}_2$ flames because the reduction in fuel-bound nitrogen associated with increasing hydrogen content counteracts the enhanced NO formation promoted by the higher flame reactivity and temperatures [32]. It should also be emphasized that the Konnov2023 mechanism is the first chemiluminescence mechanism specifically developed for ammonia combustion and has not been validated for detailed species profiles or non-premixed flames. Considering these limitations, its overall agreement with the experimental data is noteworthy. The remaining discrepancies in NO^* predictions therefore underline the need for continued development of reaction mechanisms for electronically excited species.

Returning to Fig. 10, the observed increase in the maximum emission intensities of the excited species with increasing hydrogen content in the fuel may originate from a thermal effect associated with the higher peak flame temperatures (see Fig. 8) and/or from hydrogen-induced changes in the underlying chemical kinetics.

To isolate the influence of hydrogen on the reaction kinetics from the thermal effect, a third measurement series was conducted. In this series, argon was added to the fuel mixture in order to maintain the same maximum flame temperature across all flames. This approach allows the chemical effect of hydrogen to be investigated over a broad range while largely ruling out temperature-induced contributions. The resulting flames covered a hydrogen fraction range from $x_{\text{H}_2,\text{rel}} = 25\% \dots 95\%$, where $x_{\text{H}_2,\text{rel}}$ excludes the argon fraction in the fuel mixture. Further details on the procedure are provided in Appendix A.

Fig. 12 presents spatially resolved profiles of NH^* , NO^* , OH^* , and Vis chemiluminescence for these ammonia-hydrogen-argon CDFs. In contrast to the previously observed trends, the intensities of NH^* , NO^* , and Vis decrease with increasing H_2 fraction, while only OH^* intensity increases. This behavior is primarily attributed to the significantly

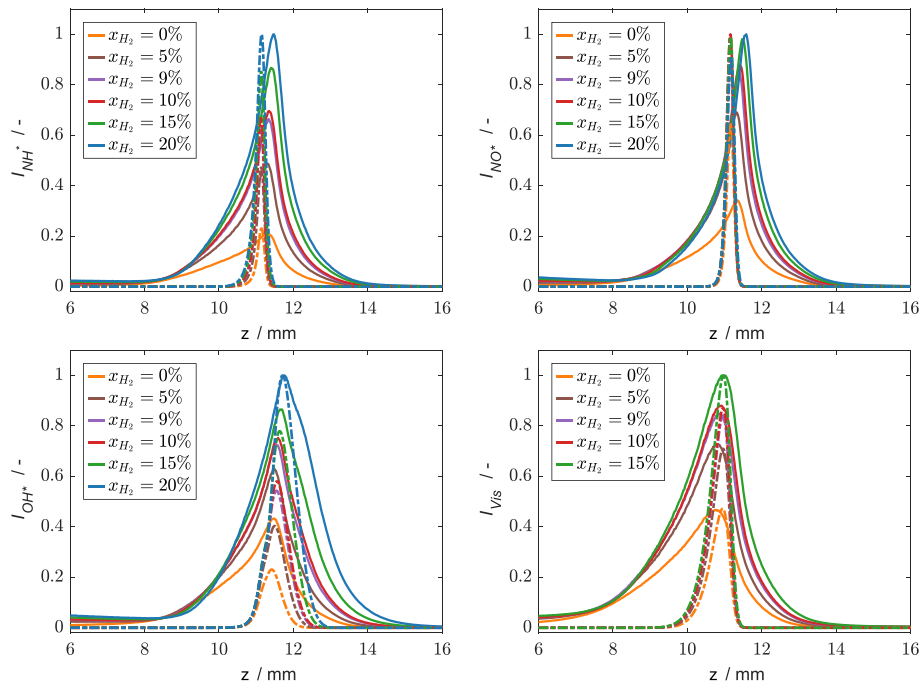


Fig. 10. Comparison of measured and simulated normalized intensity profiles of NH^* , NO^* , OH^* , and visible emission in $\text{NH}_3\text{-H}_2/\text{air}$ CDFs with varying hydrogen fraction. Measurements from spectrally integrated 2D chemiluminescence imaging are shown as solid lines, and numerical predictions based on the Konnov2023 mechanism as dashed lines. Profiles are shown along the axial coordinate z ; colors indicate the hydrogen fractions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

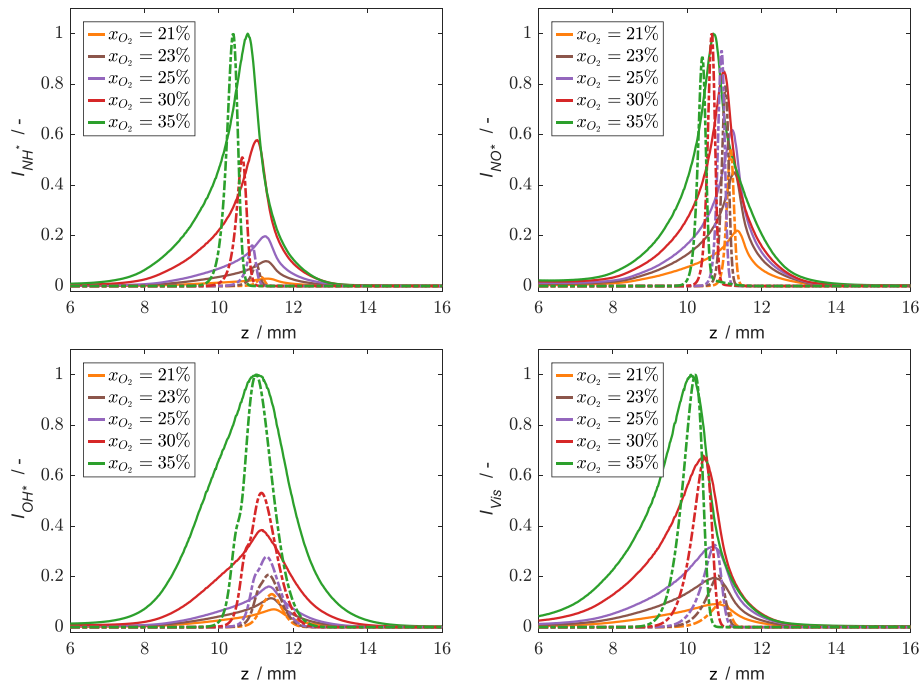


Fig. 11. Comparison of measured and simulated normalized intensity profiles of NH^* , NO^* , OH^* , and visible emission in NH_3/air CDFs with varying oxygen fraction. Measurements from spectrally integrated 2D chemiluminescence imaging are shown as solid lines, and numerical predictions based on the Konnov2023 mechanism as dashed lines. Profiles are shown along the axial coordinate z ; colors indicate the oxygen fractions. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

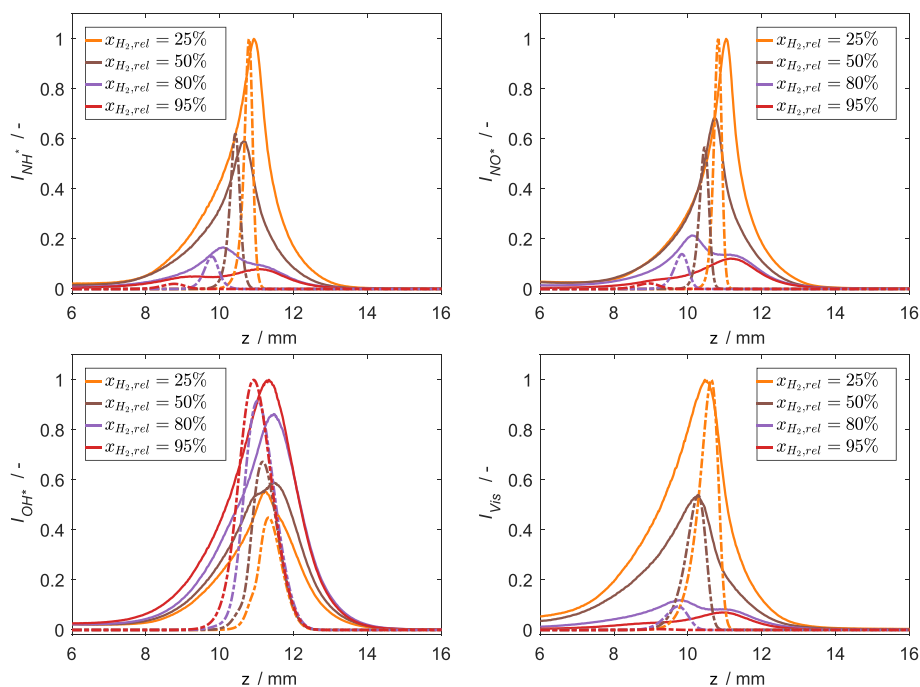


Fig. 12. Comparison of measured and simulated normalized intensity profiles of NH^* , NO^* , OH^* , and visible emission in $\text{NH}_3\text{-H}_2\text{-Ar/air}$ CDFs at constant peak temperature and varying relative hydrogen fraction, $x_{\text{H}_2,\text{rel}}$, in the $\text{NH}_3\text{-H}_2$ fuel blend. Measurements from spectrally integrated 2D chemiluminescence imaging are shown as solid lines, and numerical predictions based on the Konnov2023 mechanism as dashed lines. Profiles are shown along the axial coordinate z ; colors indicate $x_{\text{H}_2,\text{rel}}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

reduced NH_3 concentrations, which limit the formation of NH^* , NH_2^* , and NO^* , as these species are predominantly generated through NH_3 -related reaction pathways. At lower NH_3 fractions the reduced ammonia availability becomes significant, leading to decreased emission intensities, which is also visually reflected by the substantially reduced flame luminosity (Vis intensity), observable in Fig. 1. Considering the mole fraction of NH_3 , which decreases with increasing argon and hydrogen content, it is possible to estimate the expected maxima for the cases $x_{\text{H}_2,\text{rel}} = 50\%$, 80% , and 95% under the assumption that the change in the excited species is solely caused by the reduction in the NH_3 concentration. Under this assumption, the expected peak values would be approximately 0.5 for $x_{\text{H}_2,\text{rel}} = 50\%$, 0.16 for $x_{\text{H}_2,\text{rel}} = 80\%$, and 0.04 for $x_{\text{H}_2,\text{rel}} = 95\%$. When examining the Vis intensity, this scaling appears to be in reasonable agreement with the observations, except for the case $x_{\text{H}_2,\text{rel}} = 95\%$. In this case, the flame hardly exhibits the characteristic orange luminescence, as shown in Fig. 1, which calls into question the suitability of the Vis signal as an indicator for NH_2^* under these conditions, as contributions from other emitting species, such as H_2O^* or NO_2^* , may become comparatively more significant. Within the evaluable range, the observations suggest that the fractional conversion of NH_3 remains largely unchanged.

For the NH^* and NO^* signals, however, the observed peak magnitudes are somewhat higher than would be expected if the decrease in the NH_3 fraction were the only influencing factor. This suggests that the fuel-NO formation pathways originating from ammonia may be slightly enhanced by the addition of H_2 , since thermal NO formation via the Zel'dovich mechanism is expected to contribute similarly in all flames due to the approximately constant maximum temperature. For NH^* this may likewise indicate a mild enhancement of the relevant reaction pathways due to hydrogen addition. In contrast, OH^* is strongly associated with hydrogen oxidation chemistry. The observed increase in OH^* intensity therefore reflects the growing contribution of H_2 oxidation pathways within the flame. This trend is particularly noteworthy given that, with

increasing H_2 (and therefore Ar content) in the fuel mixture, the absolute molar flux of hydrogen atoms decreases.

The relative peak magnitudes of all investigated species are well reproduced by the Konnov2023 reaction mechanism. A compact comparison of the normalized peak values extracted from the measured and simulated species profiles in Figs. 10–12 is provided in the Supplementary Material. However, the peak positions, particularly for OH^* and NO^* , are predicted to be closer to the fuel outlet than observed experimentally.

In addition, at hydrogen fractions $\geq 80\%$ a double-peak structure forms for all investigated species, with the notable exception of OH^* , which exhibits double-peak structures already at $x_{\text{H}_2,\text{rel}} = 25\%$ and $x_{\text{H}_2,\text{rel}} = 50\%$. For NH^* , Vis and NO^* , the dominant peak shifts from the fuel to the oxidizer side between $x_{\text{H}_2,\text{rel}} = 80\%$ and $x_{\text{H}_2,\text{rel}} = 95\%$, consistent with the behavior observed for OH^* , where the dominant peak shifts toward the oxidizer side with increasing hydrogen fraction, until at $x_{\text{H}_2,\text{rel}} = 80\%$ only a single peak near the oxidizer outlet remains. This trend is also visible in the observed RGB flame images shown in Fig. 1. These features suggest the formation of a second reaction zone consistent with preferential diffusion, where hydrogen-dominated combustion occurs in a spatially shifted region.

To further investigate this hypothesis, additional measurements of in-flame species (NH_3 , H_2 , and NO) were conducted using a microprobe sampling system coupled with gas-phase diagnostics, and the resulting concentration profiles were compared with simulations based on the Konnov2023 mechanism. The corresponding results are presented in Figs. 13 and 14. The profiles of the measured chemiluminescent species are also included to enable a direct comparison with the major species.

The simulated in-flame species profiles agree well with the experimental data, indicating that the H_2 mole fraction begins to decrease earlier than that of NH_3 , while NH_3 is fully depleted upstream of H_2 . This behavior is most likely caused by the substantially higher diffusivity of H_2 compared to NH_3 . In addition, the more spatially extended H_2 depletion may be further sustained by local hydrogen formation via

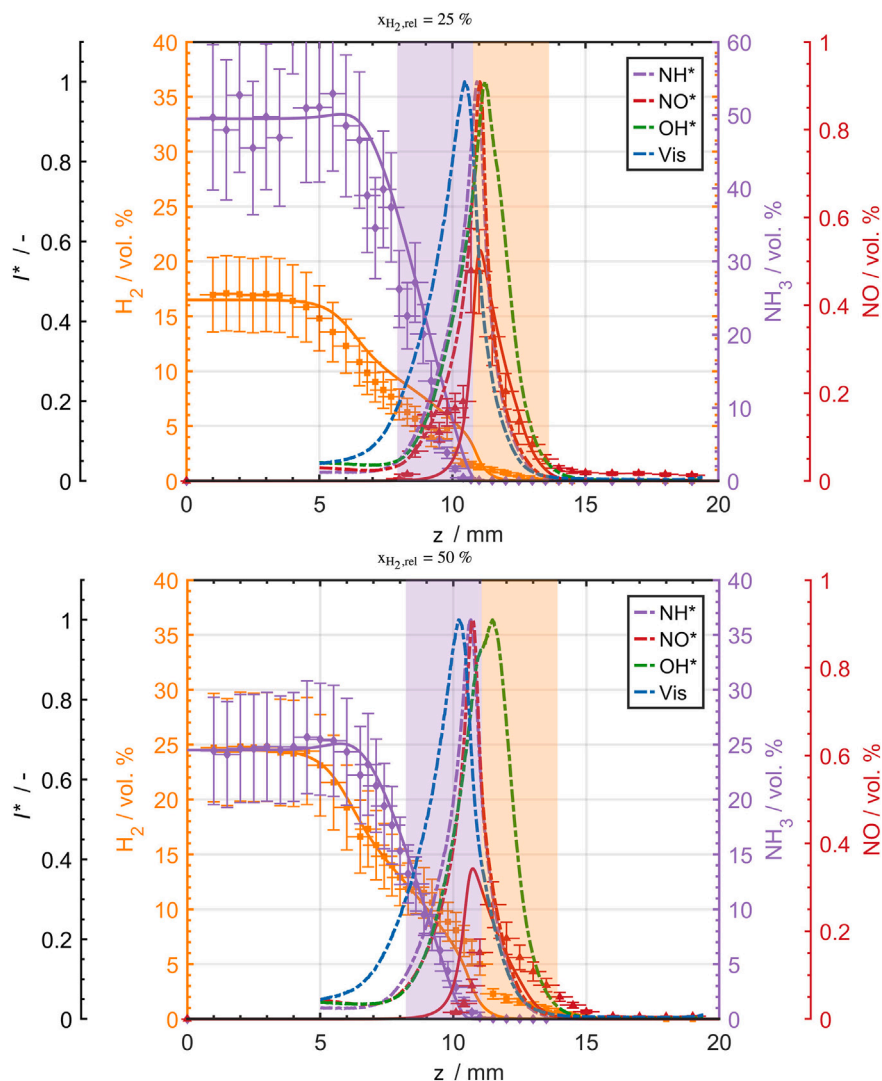


Fig. 13. Measured and simulated in-flame species profiles in $\text{NH}_3\text{-H}_2\text{-Ar/air}$ CDFs at constant peak temperature for the relative hydrogen fractions $x_{\text{H}_2,\text{rel}} = 25\%$ and 50% in the $\text{NH}_3\text{-H}_2$ fuel blend. Measured dry-gas mole fractions of H_2 , NH_3 , and NO obtained with the microprobe sampling system are shown as symbols, while numerical predictions based on the Konnov2023 mechanism are shown as solid lines. Dashed lines indicate measured normalized intensity profiles of NH^* , NO^* , OH^* , and visible emission obtained from spectrally integrated 2D chemiluminescence imaging. Profiles are shown along the axial coordinate z ; colored areas schematically indicate ammonia- and hydrogen depletion zones. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

NH_3 pyrolysis. The peak locations of the chemiluminescent species correlate well with these consumption regions. At high hydrogen fractions, the NH_3 and H_2 depletion zones become clearly spatially separated, together with the corresponding emission maxima. Among the excited species, the OH^* peak is consistently positioned closest to the oxidizer outlet, whereas the Vis signal, used as an indicator of NH_2^* , peaks closest to the fuel outlet. The NH^* and NO^* peak locations nearly coincide.

For $x_{\text{H}_2,\text{rel}} = 80\%$, a secondary peak emerges in the Vis, NH^* , and NO^* profiles at the axial position of the OH^* maximum, approximately coinciding with the location where the H_2 profile reaches near-zero values. At 95% hydrogen, this distribution changes markedly: smaller Vis, NH^* , and NO^* peaks remain near the NH_3 depletion region, whereas the dominant maxima coincide with the OH^* peak and the main H_2 consumption zone. These observations indicate the formation of a second, spatially distinct reaction zone closer to the oxidizer outlet, dominated by H_2 oxidation.

Considering Figs. 13 and 14, the numerical simulations accurately reproduce the differential consumption of the major fuel components,

thereby capturing the demixing behavior between H_2 and NH_3 . However, Fig. 12 shows that the Konnov2023 mechanism fails to reproduce the characteristic double-peak structure observed in the excited species profiles.

Previous studies provide relevant context. Issayev et al. [9] investigated similar ammonia-hydrogen flames without argon dilution and reported the occurrence of a double-peak structure in the NH^* profiles at ammonia mole fractions of $x_{\text{NH}_3} = 0.1$ and 0.2 , as well as a spatial separation between the NH^* and OH^* peak locations. They further observed that the spatial position of the NH^* peak is not accurately predicted by the Konnov2023 mechanism. Based on a sensitivity analysis, four key reactions were identified, and their rate constants were varied within the uncertainty limits specified by Konnov to improve the spatial prediction of the species peak locations.

The modified mechanism was subsequently applied to the experimental NH^* dataset corresponding to Fig. 12. As shown in Fig. 15, these modifications do not translate into an improved agreement with the measurements for the present flames. In particular, the relative peak intensities tend to be predicted less accurately, while the peak positions

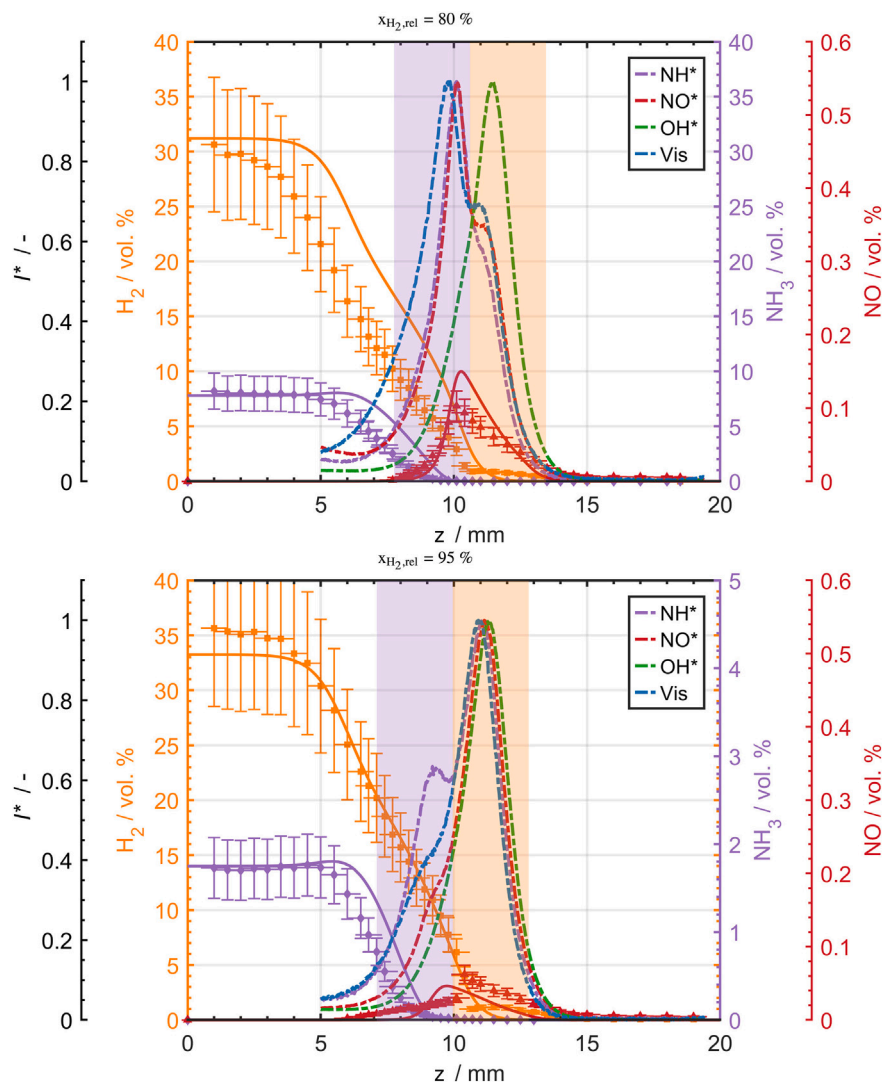


Fig. 14. Measured and simulated in-flame species profiles in $\text{NH}_3\text{-H}_2\text{-Ar/air}$ CDFs at constant peak temperature for the relative hydrogen fractions $x_{\text{H}_2,\text{rel}} = 80\%$ and 95% in the $\text{NH}_3\text{-H}_2$ fuel blend. Measured dry-gas mole fractions of H_2 , NH_3 , and NO obtained with the microprobe sampling system are shown as symbols, while numerical predictions based on the Konnov2023 mechanism are shown as solid lines. Dashed lines indicate measured normalized intensity profiles of NH^* , NO^* , OH^* , and visible emission obtained from spectrally integrated 2D chemiluminescence imaging. Profiles are shown along the axial coordinate z ; colored areas schematically indicate ammonia- and hydrogen depletion zones. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

remain largely unaffected, and discrepancies between simulations and experiments persist.

Capriolo et al. [12] investigated OH^* kinetics in ammonia-hydrogen flames and reported the presence of pronounced double-peak structures, which were successfully reproduced using a dedicated OH^* reaction mechanism. Similar observations were later confirmed by Liu et al. [33]. Reconstructing the OH^* kinetics based on the mechanism description provided by Liu et al. and applying it to the present flame conditions also results in a double-peak structure, as shown in Fig. 16. Although the modified mechanism reproduces the qualitative double-peak behavior, agreement with the experimental data remains limited. Rate of production analysis (see Appendix D) shows that the Konnov2023 mechanism includes the reaction $\text{OH}^* + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O}_2 + \text{H}$, which is not considered in the OH^* mechanism proposed by Capriolo et al. This reaction constitutes a water-quenching pathway that competes with $\text{OH}^* + \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{H}_2\text{O}$. An excessively high rate of the former reaction suppresses the formation of a pronounced double-peak structure. In the Konnov2023 mechanism, equal rate weighting was assumed for these competing

pathways due to the lack of detailed experimental characterization [34]. Therefore, a more comprehensive investigation of OH^* quenching by water is required to improve the predictive capability of OH^* modeling in ammonia-hydrogen flames.

To gain further insight into the formation of the other excited species, namely NH^* , NH_2^* , and NO^* , additional rate-of-production and sensitivity analyses were conducted and are provided in the Supplementary Material. These analyses suggest that the NH_2^* chemistry is primarily influenced by the major species H , NH , and NH_3 , whereas NH^* and NO^* exhibit a pronounced sensitivity to reactions involving N_2^* . The presented suggestions should be regarded as a preliminary step toward a more comprehensive understanding of the occurrence of excited species in NH_3 flames. While the results indicate that existing sub-mechanisms capture certain qualitative trends, significant deviations for all captured species from the experimental data, particularly at elevated H_2 content, highlight the need for dedicated refinements. The development of accurate predictive mechanisms for excited species in $\text{NH}_3\text{-H}_2$ flames remains an open challenge that extends beyond the scope of this work.

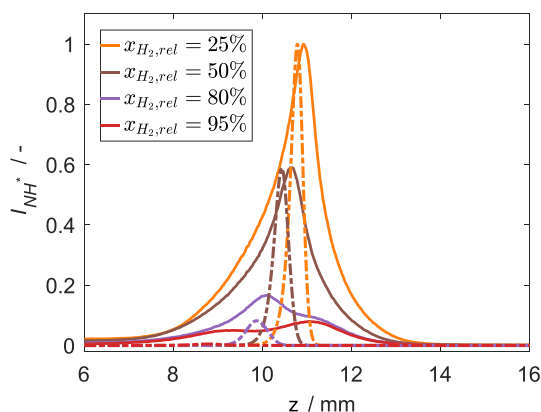


Fig. 15. Comparison of measured and simulated normalized NH^* intensity profiles in $\text{NH}_3\text{-H}_2\text{-Ar}$ /air CDFs at constant peak temperature and varying relative hydrogen fraction, $x_{\text{H}_2,\text{rel}}$, in the $\text{NH}_3\text{-H}_2$ fuel blend. Measured NH^* intensity profiles obtained from spectrally integrated 2D chemiluminescence imaging are shown as solid lines, while numerical predictions based on the Konnov2023 mechanism with the improved NH^* kinetics proposed by Issayev et al. [9] are shown as dashed lines. Profiles are shown along the axial coordinate z ; colors indicate $x_{\text{H}_2,\text{rel}}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

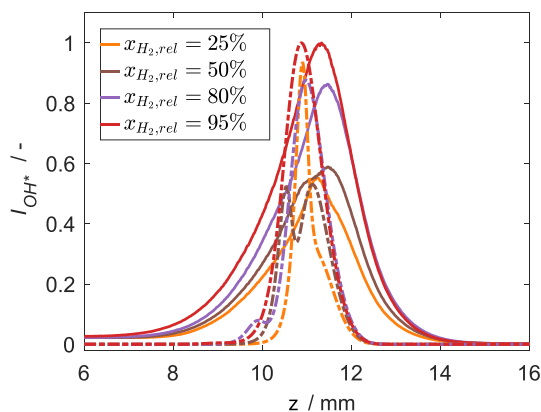


Fig. 16. Comparison of measured and simulated normalized OH^* intensity profiles in $\text{NH}_3\text{-H}_2\text{-Ar}$ /air CDFs at constant peak temperature and varying relative hydrogen fraction, $x_{\text{H}_2,\text{rel}}$, in the $\text{NH}_3\text{-H}_2$ fuel blend. Measured OH^* intensity profiles obtained from spectrally integrated 2D chemiluminescence imaging are shown as solid lines, while numerical predictions based on the combined mechanism adopted by Liu et al. [33], comprising refs. [9,10,12,26], are shown as dashed lines. Profiles are shown along the axial coordinate z ; colors indicate $x_{\text{H}_2,\text{rel}}$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

4. Conclusion

Ammonia CDFs were investigated to provide comprehensive experimental datasets and assess current kinetic mechanisms across hydrogen additions of $x_{\text{H}_2} = 0 \dots 20\%$ and varying oxidizer composition ranging from $x_{\text{O}_2} = 21 \dots 35\%$. Additionally, a third measurement series was conducted in which ammonia-hydrogen-argon CDFs were analyzed, and the argon content was adjusted to achieve the same maximum temperature, while the hydrogen content in the fuel ranged from $x_{\text{H}_2,\text{rel}} = 25 \dots 95\%$. Measurements included ESR, temperature profiles, in-flame species profiles and spatially resolved emission spectra. The key findings are:

- Extinction strain rates (ESR) are well predicted by most state-of-the-art mechanisms. For $\text{NH}_3\text{-H}_2$ flames, the Konnov2023 mechanism shows best agreement, while the POLIMI2023 mechanism

performs best overall across conditions. Measured temperature profiles generally agree well with numerical predictions; however, all mechanisms underestimate the increase in maximum temperature with oxygen enrichment of the oxidizer stream.

- The measured OH^* , NH^* , Vis, and NO^* profiles showed that the Konnov2023 mechanism accurately captures the NH^* and Vis emissions (the latter compared with NH_2^*) under conditions with high ammonia concentrations, whereas pronounced deviations persist for NO^* in both ammonia-hydrogen and pure ammonia flames under oxygen-enriched oxidizer conditions. For OH^* , the overall trends under conditions with high ammonia concentrations are reasonably captured, although discrepancies remain in the relative peak intensities.
- A measurement series with $\text{NH}_3\text{-H}_2\text{-Ar}$ flames was performed, in which argon dilution was used to maintain an approximately constant flame temperature. Experimentally, a double-peak structure was observed for all analyzed excited species, which could not be reproduced using the Konnov2023 mechanism. For OH^* , the reaction $\text{OH}^* + \text{H}_2\text{O} \rightleftharpoons \text{H}_2\text{O}_2 + \text{H}$ was found to suppress the formation of a double-peak structure, whereas for NH^* , NH_2^* , and NO^* further investigation is required to identify the governing reaction pathways.
- To address the formation of double peaks, a microprobe sampling system coupled with gas-phase diagnostics was successfully applied to measure H_2 , NH_3 , and NO concentration profiles. The peak locations were found to coincide with the local depletion of either NH_3 or H_2 , consistent with preferential hydrogen diffusion relative to ammonia. These results further suggest the formation of a second distinct reaction zone dominated by H_2 oxidation.

CRedit authorship contribution statement

Hanna M. Hülsmann: Writing – original draft, Visualization, Software, Methodology, Investigation, Formal analysis. **Daniel Kretzler:** Writing – original draft, Visualization, Methodology, Investigation, Formal analysis. **Florian J. Bauer:** Writing – review & editing, Investigation. **Peter Habisreuther:** Writing – review & editing, Software. **Phillipp A. B. Braeuer:** Writing – review & editing, Investigation. **Björn Stelzner:** Writing – review & editing. **Stefan Will:** Writing – review & editing, Resources. **Dimosthenis Trimis:** Writing – review & editing, Resources. **Fabian P. Hagen:** Writing – review & editing, Supervision, Methodology, Conceptualization.

Declaration of generative AI and AI-assisted technologies in the manuscript preparation process

During the preparation of this work the authors used DeepL and Claude in order to improve the readability of the manuscript. After using these tools, the authors reviewed and edited the content as needed and take full responsibility for the content of the published article.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors acknowledge financial support from the [German Research Foundation](#) (DFG) within PP2419 HyCAM (Project No. 523876164), and the [European Union](#) (Project: ACCEPT; Grant agreement ID: 101192557). Additionally, this research contributes to the Helmholtz Association's MTET program, Resource and Energy Efficiency, Anthropogenic Carbon Cycle (38.05.01).

Appendix A. Composition of ammonia-hydrogen-argon CDFs

To decouple chemical from thermal effects, an experimental series of ammonia-hydrogen-argon CDFs was conducted in which argon served as a diluent to maintain a nearly constant maximum temperature across varying $\text{NH}_3\text{-H}_2$ ratios. The required fuel compositions were determined through numerical pre-studies using the Konnov2023 mechanism. Subsequent experimental measurements confirmed that the maximum temperatures remained similar within the respective experimental uncertainties. The fuel compositions at the outlet are summarized in Table A.2. Air served as the oxidizer for all flames studied and the strain rate was fixed at $a_2 = 40 \text{ s}^{-1}$, consistent with the ammonia-rich CDFs. Flames are designated by their fuel compositions ($x_{\text{H}_2,\text{rel}}$), excluding the argon content.

Table A.2

Fuel outlet compositions of the ammonia-hydrogen-argon CDFs.

$x_{\text{H}_2,\text{rel}}$ (%)	95	80	50	25
x_{NH_3} at fuel outlet (%)	1.75	7.8	24.5	49.5
x_{H_2} at fuel outlet (%)	33.25	31.2	24.5	16.5
x_{Ar} at fuel outlet (%)	65	61	51	34

Appendix B. Comparison of intrusive and non-intrusive temperature measurements

A hydrogen CDF diluted with 50 mol% nitrogen and opposed by air at a strain rate of $a_2 = 40 \text{ s}^{-1}$ was selected to validate the intrusive thermocouple temperature measurements against the non-intrusive approach introduced by Schmidt et al. [19]. In addition, the flame was simulated using the hydrogen-specific reaction mechanism proposed by Konnov [35], providing an independent numerical reference.

Compared to the simulated maximum temperature value of 2185 K, the temperature determined using the thermocouple, $2238 \pm 100 \text{ K}$, is slightly higher, whereas the maximum temperature of 2152 K obtained from near-infrared H_2O radiation thermometry is marginally lower than the simulated result. Overall, both techniques agree well with the simulation within the experimental uncertainty, supporting the validity of the intrusive temperature measurements.

Appendix C. Evaluation of the intrusive gas-phase species profile measurements

C.1. Evaluation of systematic sampling errors

Intrusive sampling in reactive ammonia flows introduces systematic measurement errors if chemical reactions continue inside the probe due to elevated wall temperatures and finite residence times. To quantify the maximum possible magnitude of this effect, a conservative worst-case bounding analysis of probe-induced conversion was performed. The in-flame species compositions for flame $x_{\text{H}_2,\text{rel}} = 95\%$ predicted with the Konnov2023 mechanism were used as inlet boundary conditions for a simulation of gas transport through an idealized heated probe section. All assumptions were intentionally selected to maximize chemical conversion inside the probe and therefore define an upper bound of the possible sampling-induced error. First, the probe temperature was set equal to the local gas temperature and kept constant. This assumption deliberately neglects radiative heat losses from the probe, as described in [18], and thus provides a conservative upper estimate of continued reaction progress inside the probe. Second, the effective heated probe length was generously assumed to be 30 mm at constant gas or flame temperature, thereby neglecting axial temperature gradients that would reduce reaction rates in practice. Third, the smallest experimentally observed volumetric flow rate of 2 L h^{-1} (at 298 K) at each sampling position was applied, yielding the longest possible residence times of

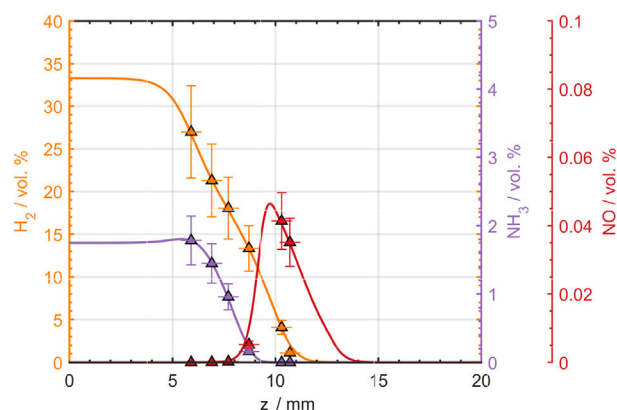


Fig. C.17. Predicted in-flame species concentrations of H_2 , NH_3 , and NO (solid lines) along the sampling height and predicted post-probe concentrations (markers) after accounting for possible reactions within the microprobe during the sampling process at worst-case conditions ($T_{\text{probe}} = T_{\text{gas}}$) at $x_{\text{H}_2,\text{rel}} = 95\%$.

0.52 ms within the probe at flame temperature. These worst-case calculations were performed for representative operating conditions covering the relevant measurement points with relative decreases in concentrations of 80% NH_3 , 80% H_2 , 50% $\text{NH}_3\text{-H}_2$, 10% NH_3 , 10% H_2 , and the maximum temperature case (2018.8 K). As shown in Fig. C.17, the deviations between inlet and outlet compositions remain limited across the investigated parameter range. To ensure a conservative interpretation of the experimental data, a uniform relative uncertainty of 20% is assigned to the measured species concentrations. This uncertainty range exceeds the deviations predicted by the worst-case simulations and includes further measurement uncertainties (see following Section C.2).

C.2. Evaluation of the systematic tracer-related errors

An additional source of systematic uncertainty arises from reconstructing the undiluted sampled-gas composition using the tracer method according to

$$x_{i,\text{sample,dry}} = x_{i,\text{mixture}} \frac{x_{\text{CH}_4,\text{tracer}}}{x_{\text{CH}_4,\text{tracer}} - x_{\text{CH}_4,\text{mixture,dry}}} \quad (\text{C.3})$$

In this procedure, the diluted and wet-measured species concentrations (NH_3 and NO_x) are back-calculated to the original undiluted sample concentrations based on the diluted dry-measured CH_4 tracer fraction. This evaluation accounts for dilution by the injected tracer gas and for the removal of water due to condensation in the measurement device. Table C.3 summarizes the tracer-gas composition, the wet and dry sampled-gas compositions, as well as the resulting mixture compositions after dilution. The reconstructed dry sampled-gas composition obtained

Table C.3

Example compositions of the tracer gas, sampled gas, and resulting diluted (wet and dry) mixtures, together with the reconstructed dry sampled-gas composition used to evaluate the systematic uncertainty of the tracer-based back-calculation (Eq. C.3) arising from differences in water content during CH_4 -based correction of NH_3 and NO with the worst-case assumption of $V_{\text{sample}} = 6 \text{ L h}^{-1}$ and $x_{\text{H}_2\text{O}} = 0.3$.

x_i / %	CH_4	N_2	H_2O	NH_3	Ar	H_2
Tracer	0.244	99.756	—	—	—	—
Sample, wet	—	—	30.000	17.150	35.700	17.150
Sample, dry	—	—	—	24.500	51.000	24.500
Mixture, wet	0.222	90.707	2.721	1.556	3.238	1.599
Mixture, dry	0.228	93.244	—	1.599	3.329	1.599
x_i , Eq. (C.3)	—	—	—	23.833	—	24.500

from Eq. (C.3) is also reported. Assuming a worst-case wet sampling flow rate of 6 L h^{-1} with $x_{\text{H}_2\text{O}} = 30 \text{ vol\%}$, the relative error associated with reporting dry-gas concentrations is below 3%. Therefore, all concentrations obtained via the microprobe and presented in this work are reported on a dry basis.

Appendix D. Analysis of OH*

Fig. D.18 presents rate-of-production (ROP) analysis of OH* for an ammonia-hydrogen-argon CDF with $x_{\text{H}_2, \text{rel}} = 50\%$, showing the ten most influential reactions for the Konnov2023 mechanism (top) and for the mechanism employed by Liu et al. [33] (bottom). While Konnov2023 fails to reproduce the experimentally observed double-peak structure, the mechanism used by Liu et al. successfully captures this feature. A

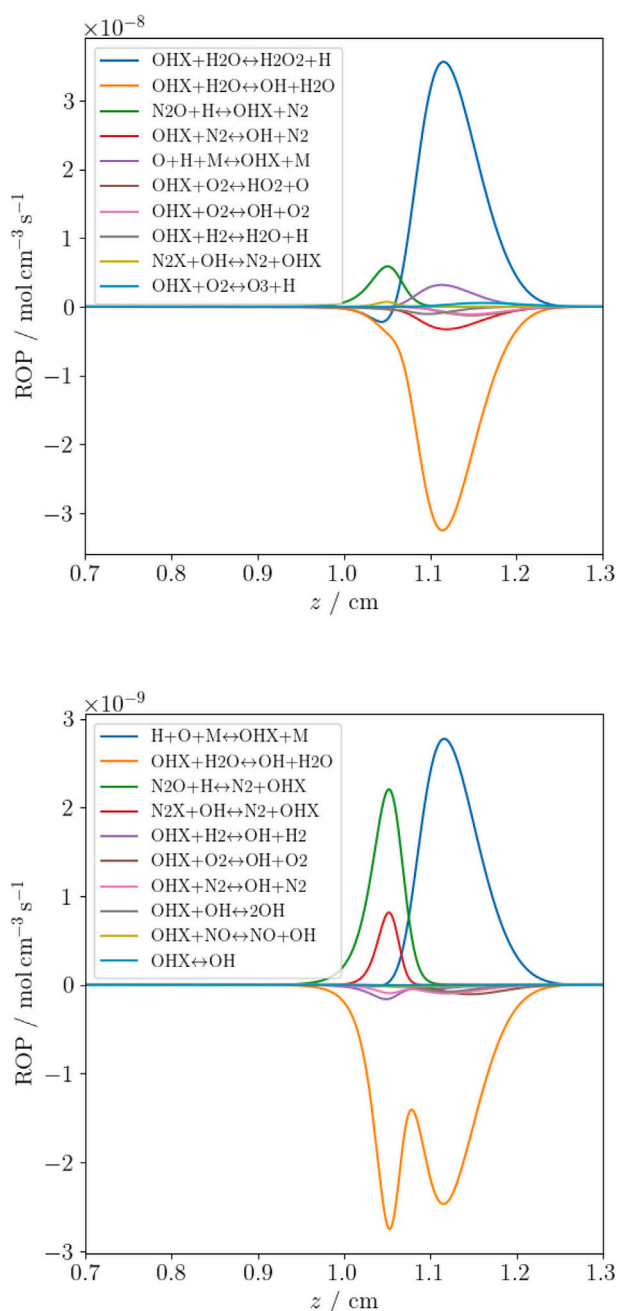


Fig. D.18. Rate-of-production analysis of OH* for Konnov2023 mechanism (top) and the mechanism used by Liu et al. [33] (bottom) which is a combination of [9,10,12,26].

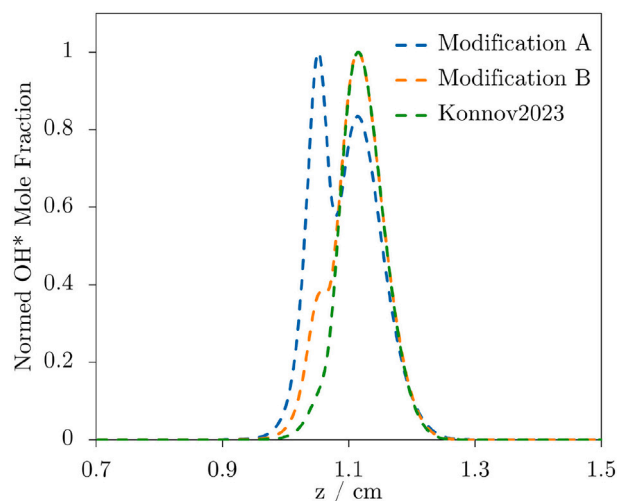
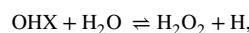


Fig. D.19. Comparison of the Konnov2023 mechanism (branching ratio 1:1) with two modified H₂O quenching branching ratios. Modification A corresponds to a 1:0 ratio, exclusively favoring the reaction $\text{OH}^* + \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{H}_2\text{O}$, whereas modification B assumes a 9:1 branching toward $\text{OH}^* + \text{H}_2\text{O} \rightleftharpoons \text{OH} + \text{H}_2\text{O}$.

notable difference between the mechanisms is the reaction



which exhibits a pronounced positive contribution to OH* production (denoted OHX) in Konnov2023, whereas it is entirely absent in the OH* sub-mechanism used in Liu et al. [33], which is based on Capriolo et al. [12]. Although the production reactions that can be identified by Liu et al. as responsible for the double-peak structure ($\text{N}_2\text{O} + \text{H} \rightleftharpoons \text{N}_2 + \text{OHX}$ and $\text{H} + \text{O} + \text{M} \rightleftharpoons \text{OHX} + \text{M}$) also occur in spatially separated regions in the Konnov2023 case, their contribution is largely masked by the much higher net production rate of the above-mentioned water reaction. This leads to an overall OH* production predicted by the Konnov2023 mechanism that is approximately one order of magnitude higher.

This discrepancy suggests that the presence and parameterization of this water reaction may play a critical role in the formation of the double-peak structure, which is further corroborated by the sensitivity analyses presented in the Supplementary Material.

The reaction is part of the two H₂O quenching pathways described in [34], for which an arbitrary branching ratio of 1:1 was originally assumed. By varying this ratio, the intensity of the double-peak structure can be systematically adjusted, indicating a strong sensitivity of the OH* profile to the relative contributions of these quenching channels. Fig. D.19 shows OH* profiles for an NH₃-H₂-Ar CDF, obtained using the Konnov2023 mechanism with exclusively modified H₂O quenching branching ratios. The results clearly demonstrate that adjusting the branching ratio significantly affects the emergence and shape of the double-peak structure. However, these manipulations also strongly influence the absolute OH* concentration; therefore, the profiles are presented in normalized form. Since no quantitative OH* measurements were performed in this study, the accuracy of the predicted absolute levels cannot be assessed. Nevertheless, the pronounced sensitivity indicates that the corresponding quenching reactions require more detailed investigation and improved parameterization.

Appendix E. Supplementary data

Supplementary data to this article can be found online at doi: 10.1016/j.fuel.2026.141356.

Data availability

The dataset to this article can be found online at doi: 10.35097/bnpe6n1ppv92y4.

References

- [1] Valera-Medina A, Xiao H, Owen-Jones M, David W, Bowen P. Ammonia for power. *Prog Energy Combust Sci* 2018;69:63–102.
- [2] Kobayashi H, Hayakawa A, Somaratne KKA, Okafor EC. Science and technology of ammonia combustion. *Proc Combust Inst* 2019;37:109–33.
- [3] Thomas DE, Shrestha KP, Mauss F, Northrop WF. Extinction and NO formation of ammonia-hydrogen and air non-premixed counterflow flames. *Proc Combust Inst* 2023;39:1803–12.
- [4] Choi S, Lee S, Kwon OC. Extinction limits and structure of counterflow non-premixed hydrogen-doped ammonia/air flames at elevated temperatures. *Energy* 2015;85:503–10.
- [5] Alfazazi A, Es-Sebbar E, Zhang X, Dally B, Abdullah M, Younes M, Sarathy SM. Counterflow flame extinction of ammonia and its blends with hydrogen and C₁-C₃ hydrocarbons. *Appl Energy Combust Sci* 2022;12:100099.
- [6] Weng W, Aldén M, Li Z. Visible chemiluminescence of ammonia premixed flames and its application for flame diagnostics. *Proc Combust Inst* 2023;39(4):4327–34.
- [7] Karan A, Dayma G, Chauveau C, Halter F. Insight into the inner structure of stretched premixed ammonia-air flames. *Proc Combust Inst* 2023;39(2):1743–52.
- [8] Karan A, Dayma G, Khan-Ghauri M, Mathieu O, Petersen EL, Chauveau C, Halter F. Investigating the role of NH₂* as an indicator of preferential diffusion effects in premixed NH₃/air flames. *Fuel* 2025;395:135139.
- [9] Issayev G, Zhu X, Capriolo G, Guiberti TF. Spatially resolved NH* and OH* profiles in ammonia-hydrogen-air counterflow diffusion flames. *Proc Combust Inst* 2024;40:105427.
- [10] Konnov AA. An exploratory modelling study of chemiluminescence in ammonia-fuelled flames. Part 1, Combust. *Flame* 2023;253:112788.
- [11] Konnov AA. An exploratory modelling study of chemiluminescence in ammonia-fuelled flames. Part 2, combust. *Flame* 2023;253:112789.
- [12] Capriolo G, Issayev G, Zhu X, Vargas J, Guiberti TF. An experimental and kinetic study of OH(²Σ⁺) formation and quenching in ammonia-hydrogen-air flames. *Combust Flame* 2024;260:113258.
- [13] Kathrotia T, Fikri M, Bozkurt M, Hartmann M, Riedel U, Schulz C. Study of the H + O + M reaction forming OH*: kinetics of OH* chemiluminescence in hydrogen combustion systems. *Combust Flame* 2010;157(7):1261–73.
- [14] Zhu X, Roberts WL, Guiberti TF. UV-visible chemiluminescence signature of laminar ammonia-hydrogen-air flames. *Proc Combust Inst* 2023;39:4227–35.
- [15] Pugh D, Runyon J, Bowen P, Giles A, Valera-Medina A, Marsh R, Goktepe B, Hewlett S. An investigation of ammonia primary flame combustor concepts for emissions reduction with OH*, NH₂* and NH* chemiluminescence at elevated conditions. *Proc Combust Inst* 2021;38:6451–9.
- [16] Niemann U, Seshadri K, Williams FA. Accuracies of laminar counterflow flame experiments. *Combust Flame* 2015;162:1540–9.
- [17] Seshadri K, Williams F. Laminar flow between parallel plates with injection of a reactant at high reynolds number. *Int J Heat Mass Transf* 1978;21:251–3.
- [18] Khare R, Vlavlakis P, Langenthal TV, Loukou A, Khosravi M, Kramer U, Trimis D. Experimental investigation of the effect of hydrogen addition on the soot-limit and structure of methane/air laminar counterflow diffusion flames. *Fuel* 2022;324:124506.
- [19] Schmidt N, Braeuer PA, Pereira MM, Grauer SJ, Bauer FJ, Will S. Development of a high-speed temperature sensor based on ratiometric nir water emission for hydrogen and methane flames. *Appl Energy Combust Sci* 2025;23:100336.
- [20] Vlavlakis P, Hagen FP, Loukou A, Trimis D. Soot formation in ISO-octane counterflow diffusion flames. *Combust Flame* 2025;282:114513.
- [21] Carbone F, Gomez A. The structure of toluene-doped counterflow gaseous diffusion flames. *Combust Flame* 2012;159(10):3040–55.
- [22] Bufferand H, Tosatto L, Mantia BL, Smooke M, Gomez A. Experimental and computational study of methane counterflow diffusion flames perturbed by trace amounts of either jet fuel or a 6-component surrogate under non-sooting conditions. *Combust Flame* 2009;156(8):1594–603.
- [23] Kretzler D, Puri R, Stelzner B, Zirwes T, Hagen FP, Stein OT, Trimis D. Experimental and numerical investigation of non-premixed ammonia flames stabilized on a heated slot burner. *Proc Combust Inst* 2025;41:105854.
- [24] Danielak J, Domin U, Ke R, Rytel M, Zachwieja M. Reinvestigation of the emission γ band system (A²Σ⁺ – X²Π) of the NO molecule. *J. Mol. Spectrosc.* 1997;181:394–402.
- [25] Glarborg P, Miller JA, Ruscic B, Klippenstein SJ. Modeling nitrogen chemistry in combustion. *Prog Energy Combust Sci* 2018;67:31–68.
- [26] Zhang X, Yalamanchi KK, Sarathy SM. Combustion chemistry of ammonia/C1 fuels: a comprehensive kinetic modeling study. *Fuel* 2023;341:127676.
- [27] Stagni A, Cavallotti C, Arunthanayothin S, Song Y, Herbinet O, Battin-Leclerc F, Faravelli T. An experimental, theoretical and kinetic-modeling study of the gas-phase oxidation of ammonia. *React Chem Eng* 2020;5:696–711.
- [28] Stagni A, Arunthanayothin S, Dehue M, Herbinet O, Battin-Leclerc F, Bréquigny P, Mounaim-Rousselle C, Faravelli T. Low- and intermediate-temperature ammonia/hydrogen oxidation in a flow reactor: experiments and a wide-range kinetic modeling. *Chem Eng J* 2023;471:144577.
- [29] Otomo J, Koshi M, Mitsumori T, Iwasaki H, Yamada K. Chemical kinetic modeling of ammonia oxidation with improved reaction mechanism for ammonia/air and ammonia/hydrogen/air combustion. *Int J Hydrog Energy* 2018;43:3004–14.
- [30] Shrestha KP, Lhuillier C, Barbosa AA, Brequigny P, Contino F, Mounaim-Rousselle C, Seidel L, Mauss F. An experimental and modeling study of ammonia with enriched oxygen content and ammonia/hydrogen laminar flame speed at elevated pressure and temperature. *Proc Combust Inst* 2021;38:2163–74.
- [31] Peters N. *Turbulent combustion*, Cambridge monographs on mechanics. Cambridge University Press; 2000.
- [32] Wei Z, Zhang X, Wang L, Song P, Chen L, Zhang M, Zhen H. Transport and reactivity effects of H₂ additive on NO formation of NH₃-H₂ counterflow diffusion flames. *Fuel* 2024;375:132543.
- [33] Liu S, Wang S, Li Z. Numerical study on chemiluminescence characteristics in ammonia-hydrogen-air counterflow diffusion flames. *Combust Sci Technol* 2025;1–18.
- [34] Konnov AA. On the role of excited species in hydrogen combustion. *Combust Flame* 2015;162(10):3755–72.
- [35] Konnov AA. Yet another kinetic mechanism for hydrogen combustion. *Combust Flame* 2019;203:14–22.