Experimental study of canonical flames for new insight on ammonia combustion

NETL Ammonia Combustion Seminars

Presenter: Gaetano Magnotti

Acknowledgement

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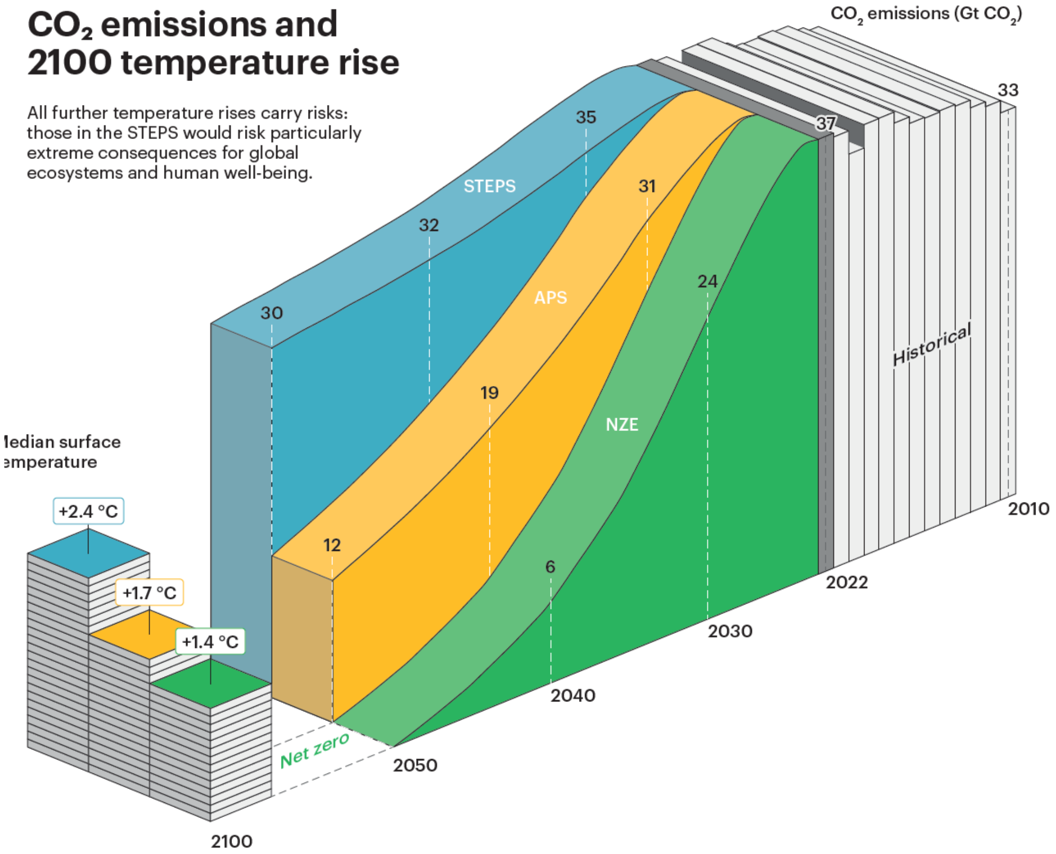
The need for the green energy transition

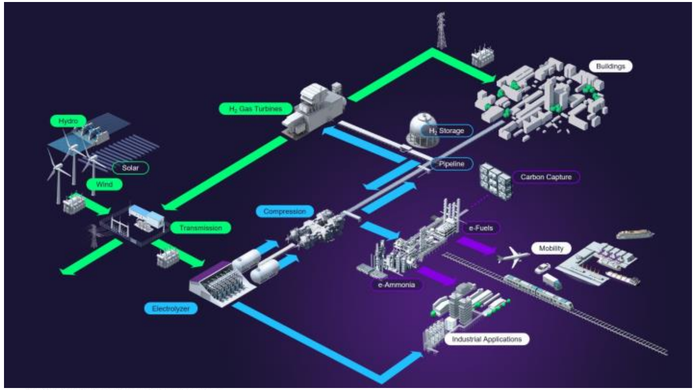
- Combustion has enabled society as we know it
  - Industrial and agricultural revolution possible thanks to energy from fossil fuel
  - Massive anthropogenic release of CO2 in the atmosphere
- Epochal shift needed to limit global warming
- Stated Policy Scenario (STEPS) will lead to an unacceptable 2.4℃ by 2100
- Announced Pledges Scenario will limit increase to 1.7℃
- Net Zero scenario is what we truly need, but no policies are currently in place to achieve it.

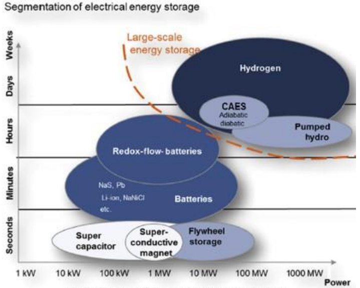


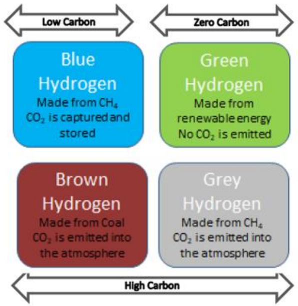
Renewable sources for “carbon-free” energy

- Share of renewable sources in the energy mix will increase in the next decades
- Renewable sources are intermittent
  - Curtailment or storage needed if sized for peak demand

The hydrogen economy

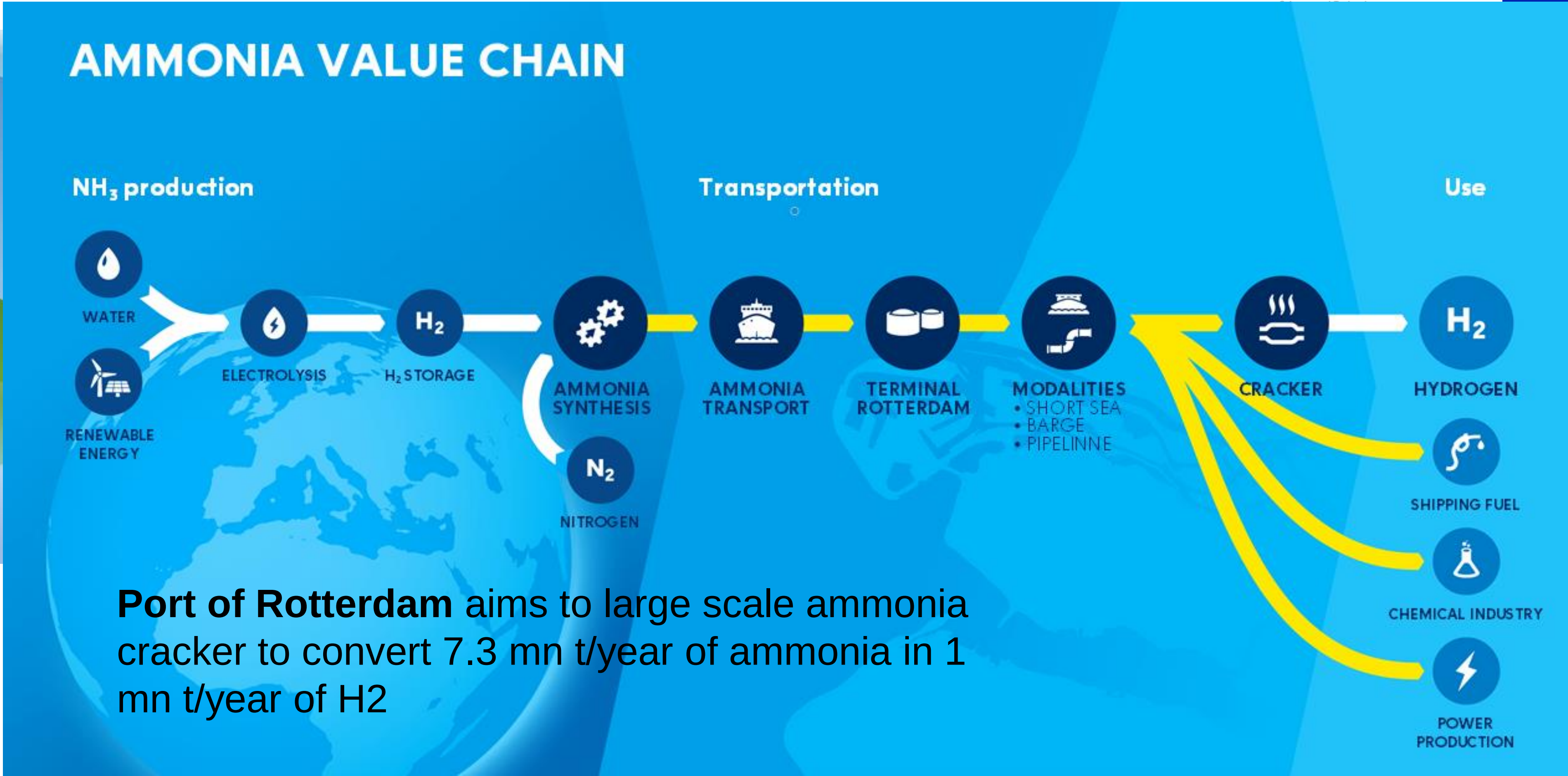






- Battery suitable for daily fluctuations
- Storage in chemical bonds (e-fuels) provides greater flexibility
  - Excess energy as a commodity to exchange on the global market
  - Hydrogen and ammonia as energy carriers
- Route to decarbonize heavy duty transportation (road, locomotive and marine), industrial machinery, industrial sector, and aviation

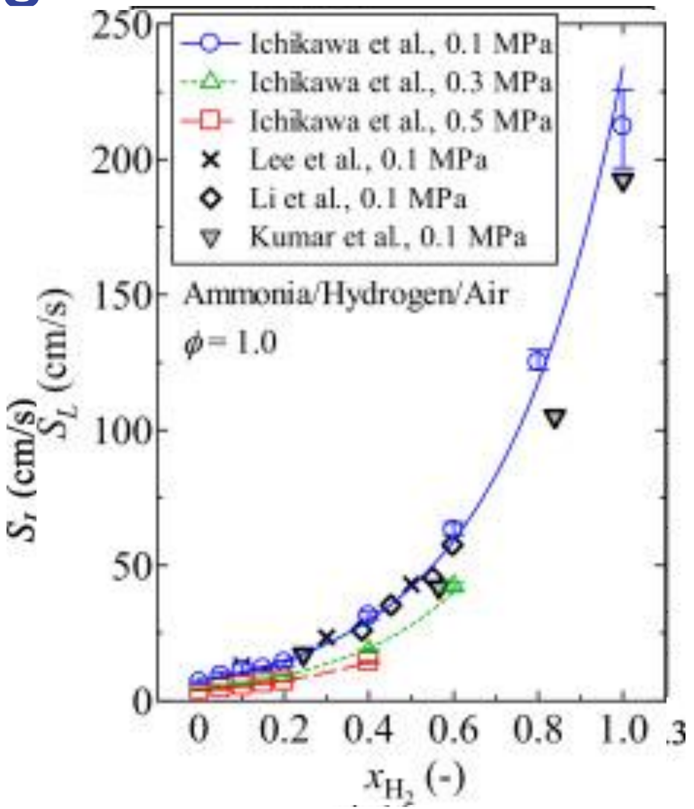
Ammonia as energy carrier



Port of Rotterdam aims to large scale ammonia cracker to convert 7.3 mn t/year of ammonia in 1 mn t/year of H2

Ammonia combustion challenges

- Very low-flame speed, hard to ignite and sustain
- Strong turbulence-chemistry interaction
- Chemistry not fully understood
- NOX at engine relevant conditions
- H_2 introduce by partial cracking leads to strong preferential diffusion effects



Hayakawa et al. Fuel, Vol. 159, November 2015

Ammonia research activities at KAUST

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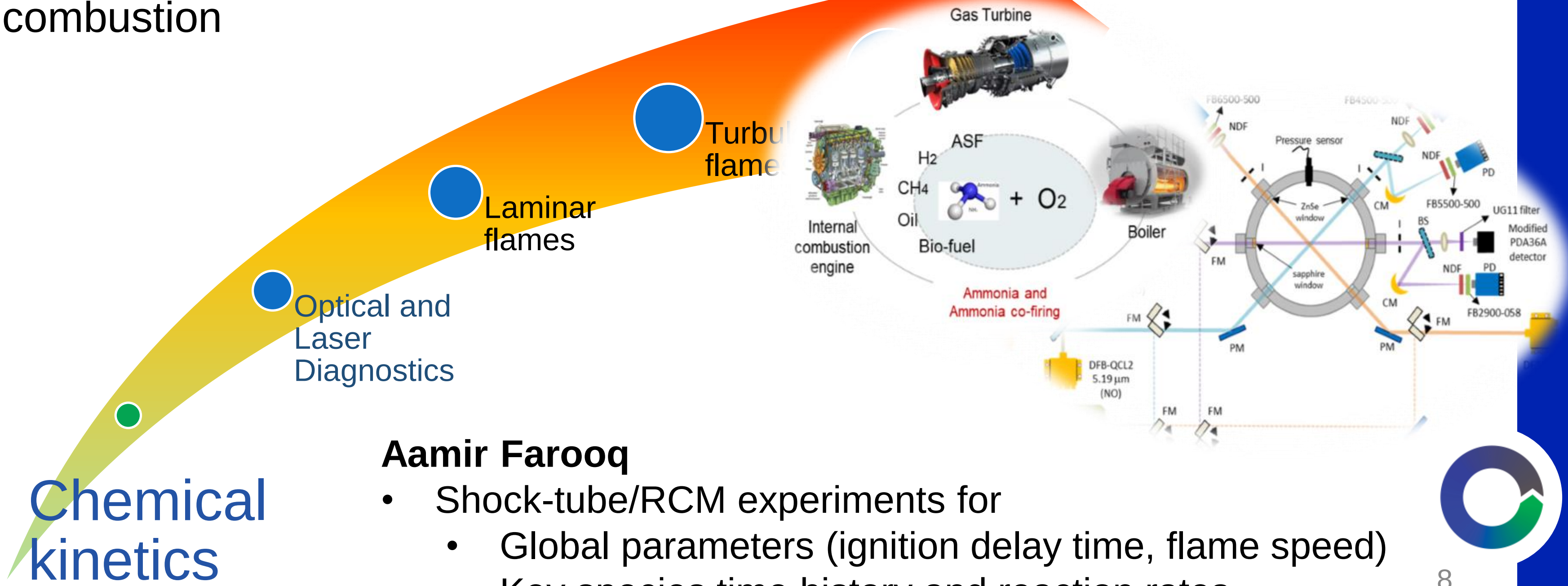
Mani Sarathy

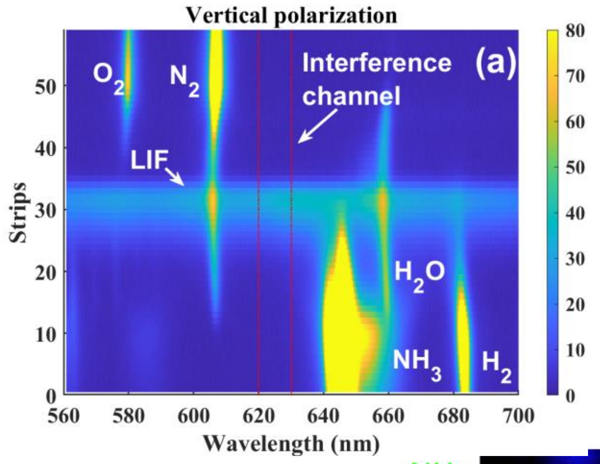
- Comprehensive chemical kinetic model development
- Computational chemistry for ammonia/hydrocarbon combustion

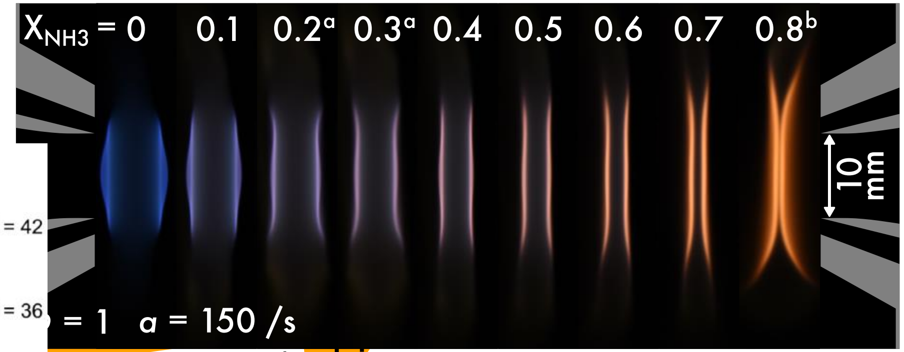


Aamir Farooq

- Shock-tube/RCM experiments for
  - Global parameters (ignition delay time, flame speed)
  - Key species time history and reaction rates

Ammonia research activities at KAUST





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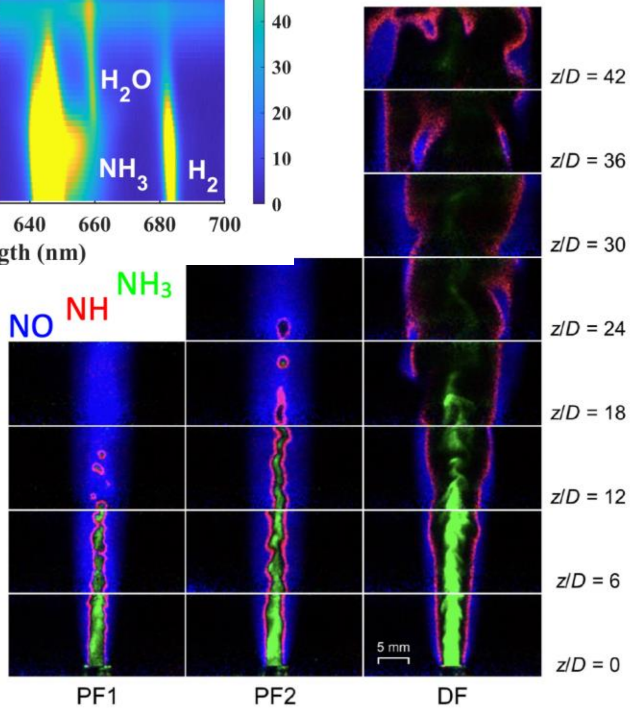
turbines



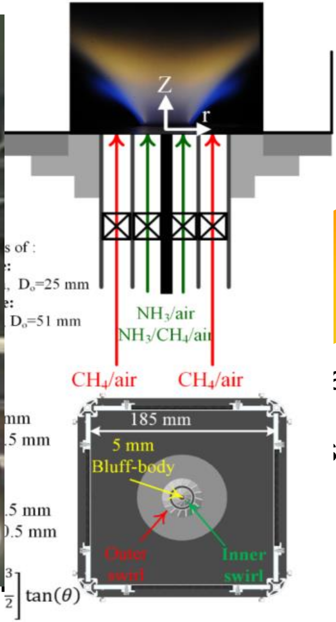
Chemic
kinetics

Magnotti

- Raman,Rayleigh, LIF

Ammonia research activities at KAUST

Magnotti, Guiberti, Lacoste , Dally, Roberts, Lacoste, Im



Laminar flames

Turbulent flames

ICE an
turbine

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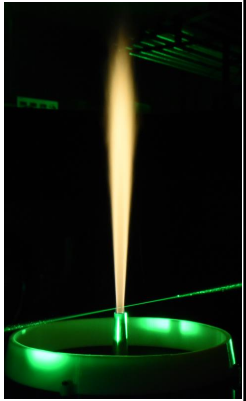
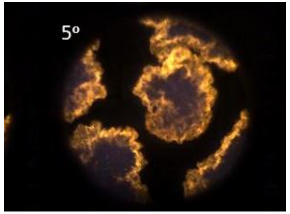
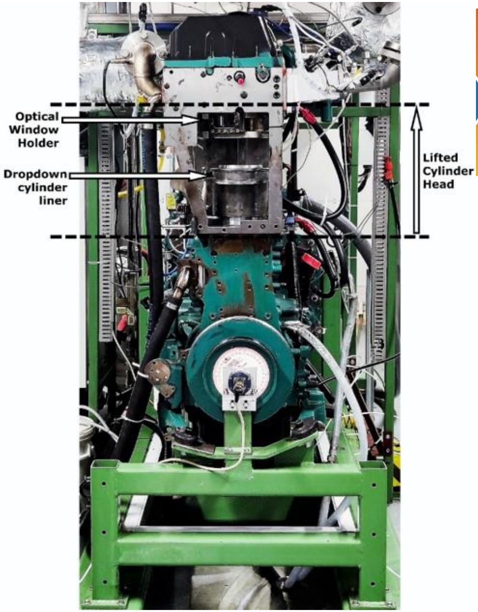


Ammonia research activities at KAUST

Turner, Magnotti
- Ammonia combustion in heavy duty ICE
- Pre-chamber assisted combustion





Turbulent flames

ICE and gas turbines

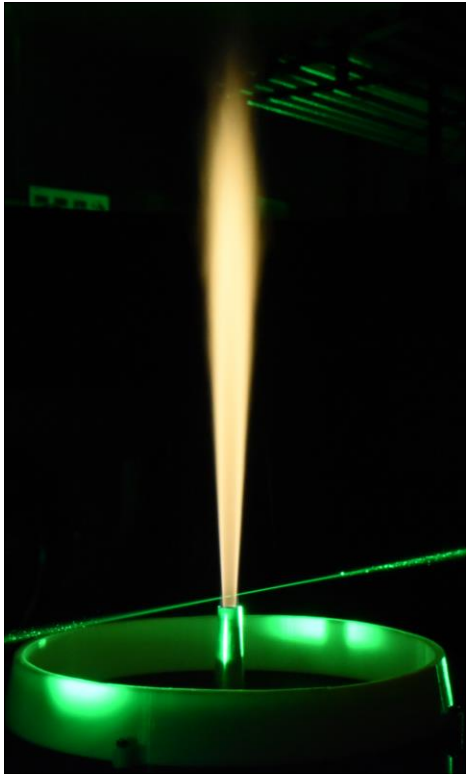
Chemical kinetics

Guiberti, Roberts
- Conversion of micro-gas turbines

Ansaldo AE-T100 NG
(Up to 100 kWe)

Canonical flames

- Simple configuration
- Relevant to practical applications
- Designed with validation of numerical models as target
- Well defined boundary conditions
- Coupled to state-of-the-art laser diagnostics
  - Raman/Rayleigh scattering for Temperature and major species
  - Quantitative LIF for minor species
  - Velocity and boundary conditions
  - High-quality dataset providing insight in the physics and validation to numerical models



Ammonia combustion challenges

Key phenomena to be investigated

- Stabilization, ***local extinction***, blowout
- ***NO_x formation and emissions***
- ***Differential diffusion effects***
- Pressure effects

Selection of turbulent target cases

- Computationally accessible geometries with well-defined bc's and inflows
- Large variety of burners already available that can be operated with ammonia
- Collaboration on experimental design, common burners, comparison with simulations

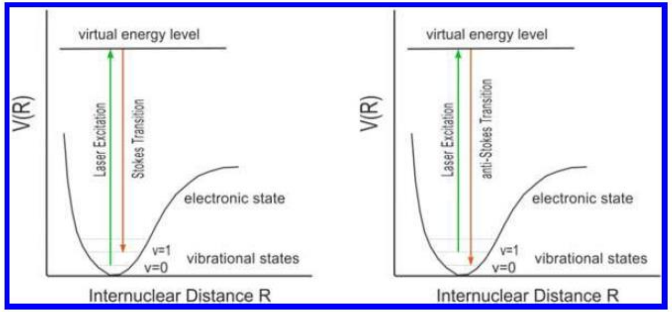
Measurement needs and diagnostic challenges

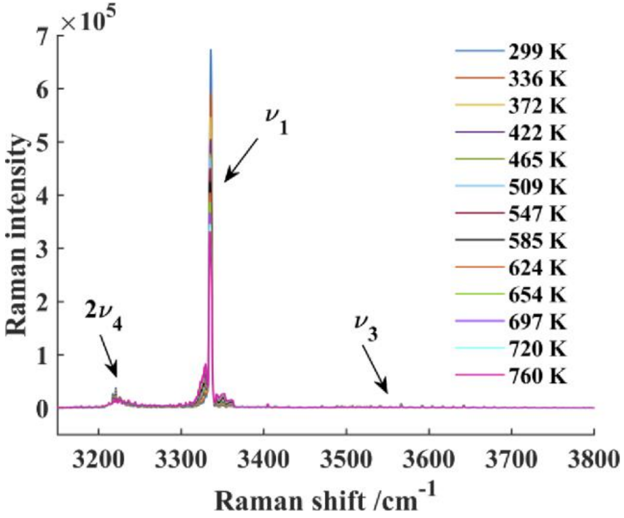
- ***Extend Raman methods to ammonia/hydrogen flames***
- Combine with quantitative measurements of NO, OH, NH, NH_2

Raman and NH_2 LIF for ammonia flames

Why Raman/Rayleigh scattering for reacting flows

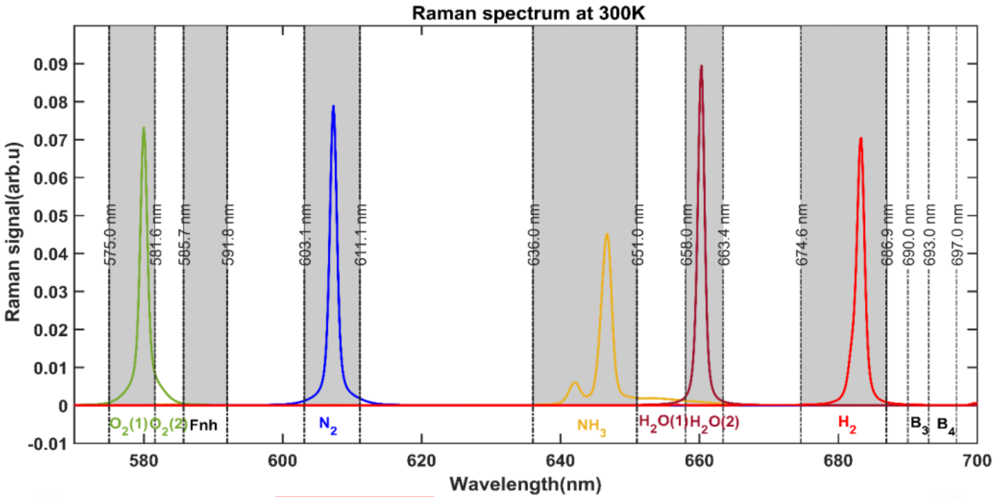
- Raman/Rayleigh scattering is an essential tool in the study of turbulent reacting flows
  - Non intrusive
  - Spatially (<100 μm) and temporally (< 500 ns) resolved
  - Non-resonant (no need to tune to a specific wavelength)
  - All species excited simultaneously with a single laser beam
  - Mixture fraction, atom ratios, scalar dissipation
- Coupled with LIF for quantitative measurements of minor species
  - Temperature and bath-gas composition





Yang et al. Optics Express Vol. 29, Issue 21, pp. 33234-33244 (2021)

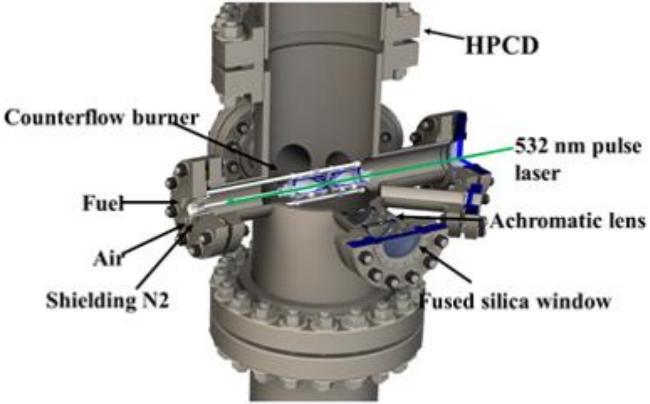
Matrix inversion for ammonia flames

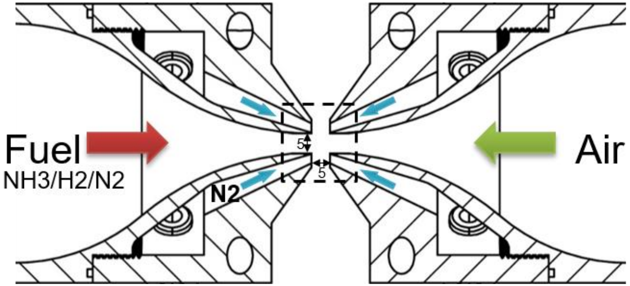


$$\begin{matrix} S_{O_2} \\ S_{N_2} \\ S_{NH_3} \\ S_{H_2O} \\ S_{H_2} \\ S_{F_{nh}} \end{matrix} = \begin{bmatrix} C_{O_2} & 0 & \boldsymbol{c_{O_2 \ll NH_3}} & 0 & c_{O_2 \ll H_2} & \boldsymbol{c_{O_2 \ll F_{nh}}} \\ 0 & c_{N_2} & \boldsymbol{c_{N_2 \ll NH_3}} & 0 & 0 & \boldsymbol{c_{N_2 \ll F_{nh}}} \\ 0 & 0 & \boldsymbol{c_{NH_3}} & \boldsymbol{c_{NH_3 \ll H_2O}} & \boldsymbol{c_{NH_3 \ll H_2}} & \boldsymbol{c_{NH_3 \ll F_{nh}}} \\ 0 & 0 & \boldsymbol{c_{H_2O \ll NH_3}} & c_{H_2O} & c_{H_2O \ll H_2} & \boldsymbol{c_{H_2O \ll F_{nh}}} \\ 0 & 0 & \boldsymbol{c_{H_2 \ll NH_3}} & 0 & c_{H_2} & \boldsymbol{c_{H_2 \ll F_{nh}}} \\ 0 & 0 & \boldsymbol{c_{F_{nh} \ll NH_3}} & 0 & c_{F_{nh} \ll H_2} & \boldsymbol{c_{F_{nh}}} \end{bmatrix} \begin{bmatrix} N_{O_2} \\ N_{N_2} \\ N_{NH_3} \\ N_{H_2O} \\ N_{H_2} \\ N_{F_{nh}} \end{bmatrix}$$

- NH_3 has a very rich spectrum
- The matrix inversion approach requires only knowledge of the elements of the C-matrix
- No detailed knowledge of the spectra needed
- Response curves of ammonia on all other channels determined empirically
- Additional column to remove effects of fluorescence interference

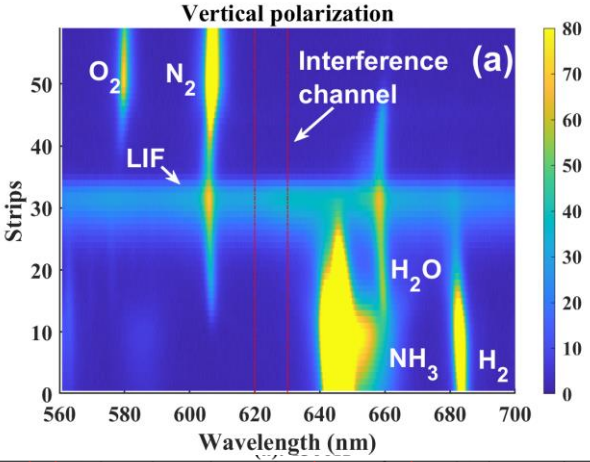
Empirical approach to ammonia response curves

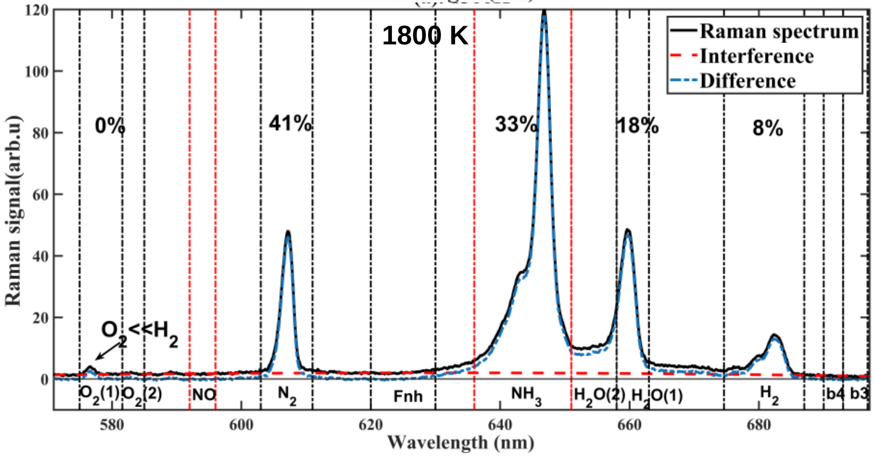


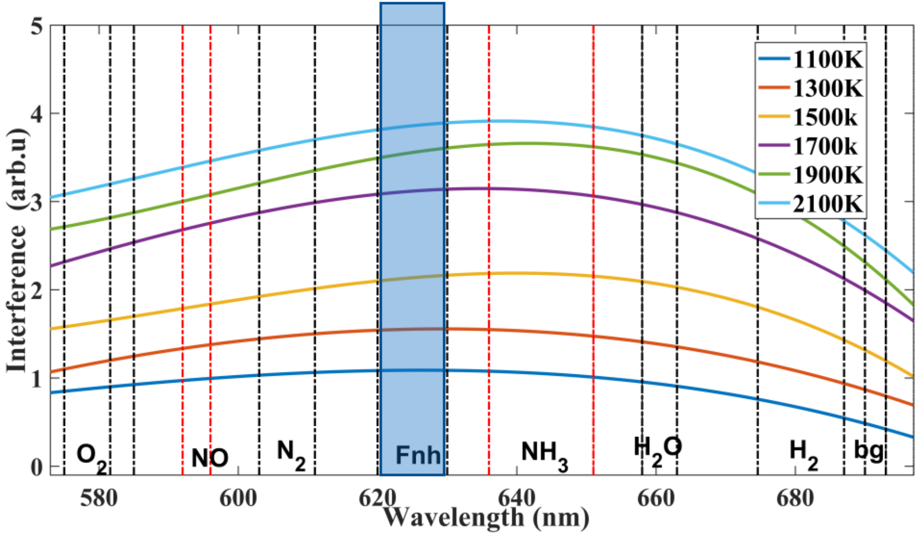


- Counterflow burner accessible along centerline
- Entire thermochemical structure captured on a single shot basis
- Installed in KAUST HPCD and operated at 5 bar
- Platform to calibrate and characterize laser diagnostics at elevated pressure and temperatures
- Several counterflow flames tested varying composition and strain rates
- Chemkin 1D simulations to calibrate/validate experiments

Fluorescence interference correction







$$S_{Xi} = SRam - C_{Xi \ll Fnh} * S_{Fnh}$$

Validation and accuracy/precision estimates

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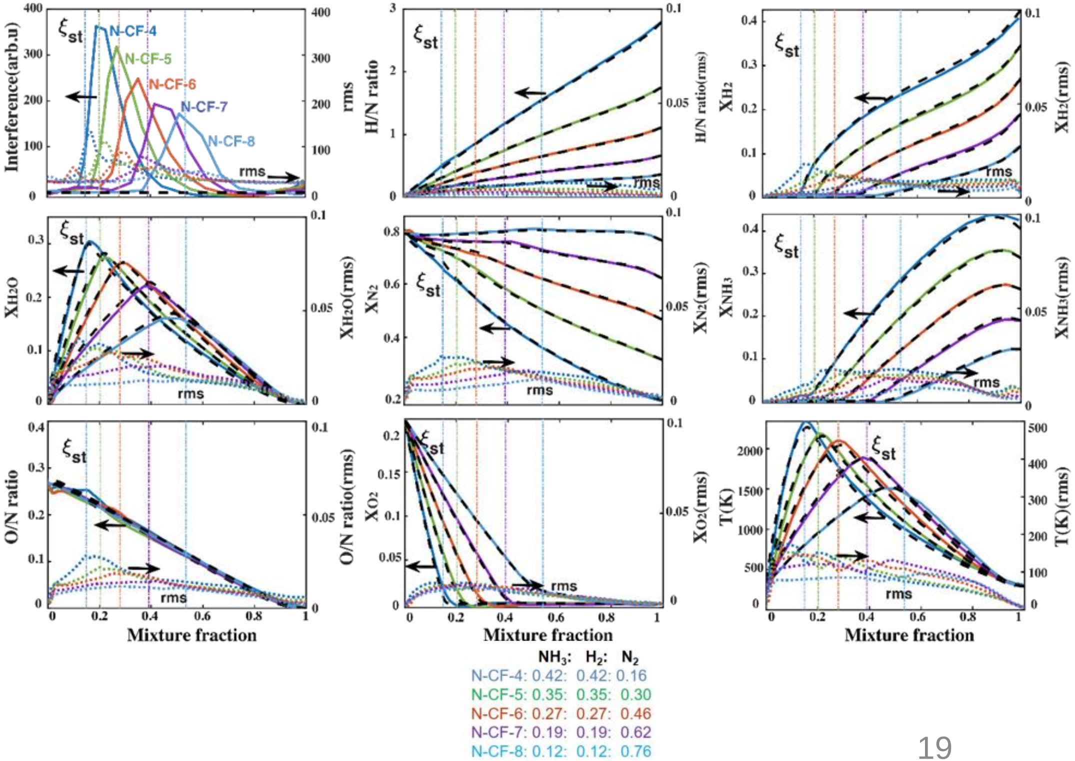
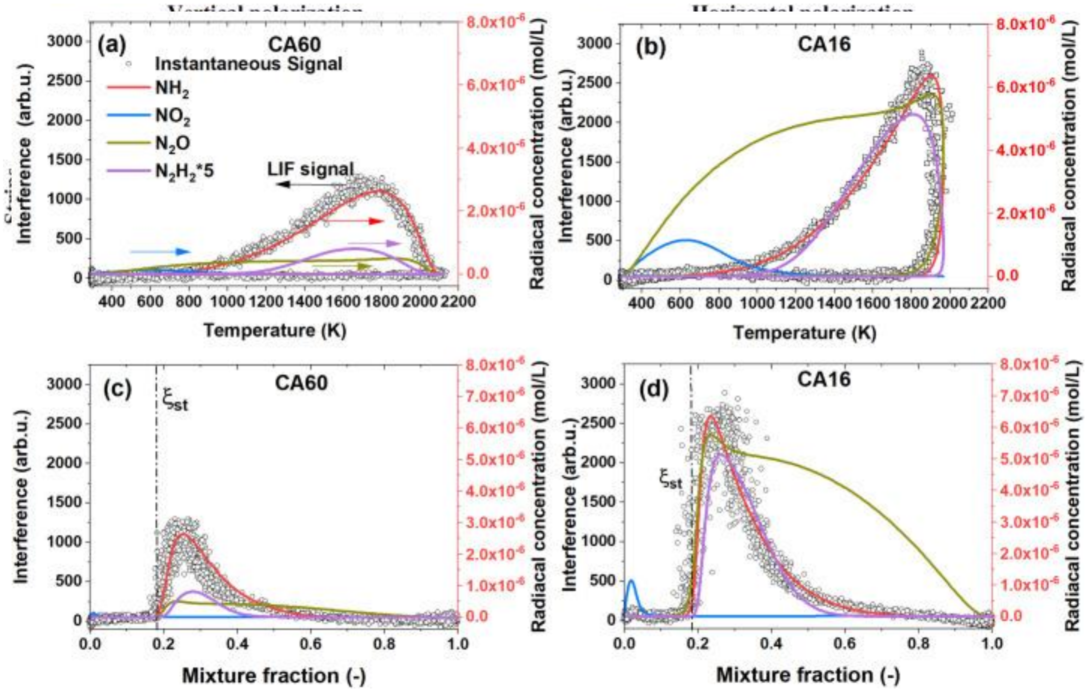
- Calibrated using 2 counterflow flames
- Validated over additional 13 flames without any tuning of the parameters
- Mole fractions within 0.01
- Temperature within 40 K
- Coefficient of variation ranging from 0.3% to 3%
- Higher standard deviation near peak fluorescence interference

Tang et al. Combustion and Flame Volume 237, March 2022, 111840



Source of fluorescence interference

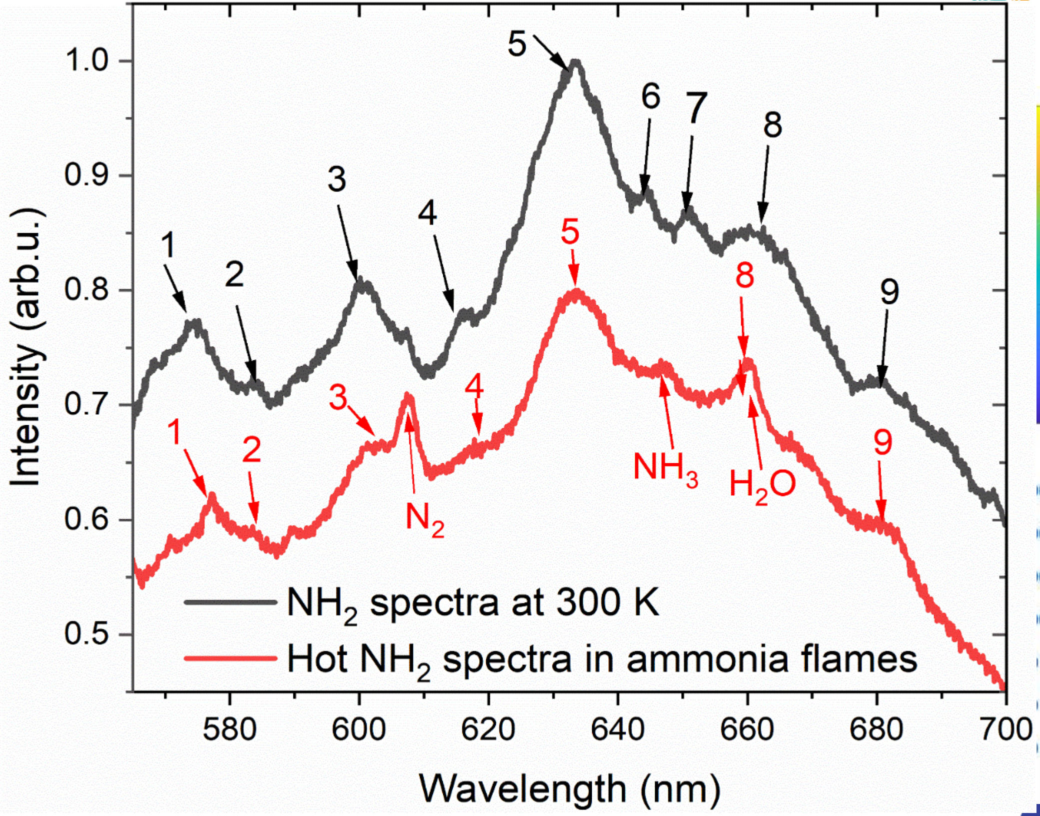
- A single, temperature dependent response curve can correctly remove the fluorescence over a wide range of conditions
- Possibly a single species gives the most significant contribution
- NH_2 shows surprisingly good agreement
- Other possible contributions may come from NO_2 and N_2O



Tang et al. Combustion and Flame, Vol. 250, April 2023, 112639

Source of fluorescence interference

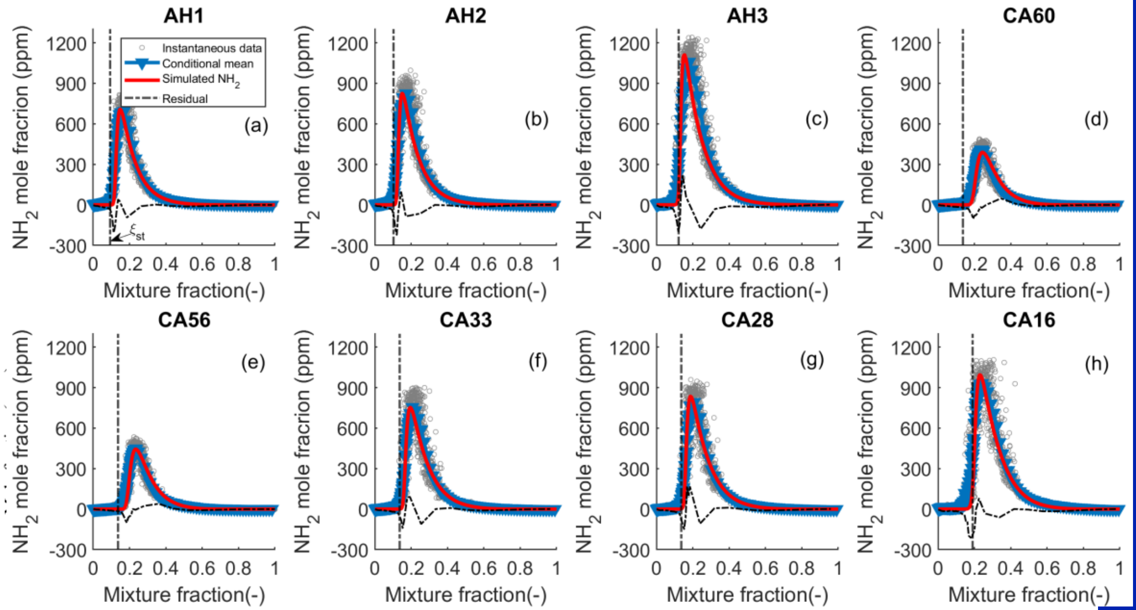
- Experiments in flows seeded with NO, and N_2O, show negligible contribution from these species
- NO_2 has a 10 times weaker contribution, and only appears at low temperature
- Experiments in NH_2 created from photolysis of NH_3, shows a striking similarity with the recorded spectrum



Tang et al. Combustion and Flame, Vol. 250, April 2023, 112639

Source of fluorescence interference

- Linear with number density.
- Calibrated by matching the peak NH_2 concentration from 1-counterflow flame using the Otomo mechanism
- Accuracy < 10% over 23 flames tested, across all range
- ~ 100 ppm standard deviation at peak temperature, ~ 50 ppm elsewhere
- Small crosstalk from NO_2 (<50 ppm)
- Absolute, independent measurements needed (TDLAS?)
- Useful for turbulent-chemistry interaction studies



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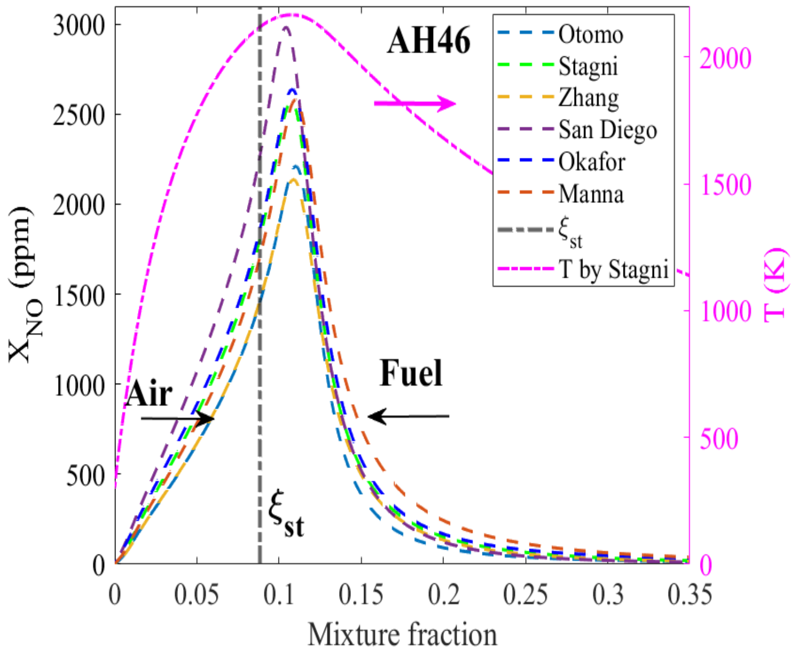
Improving NO predictions

Improving NOX prediction

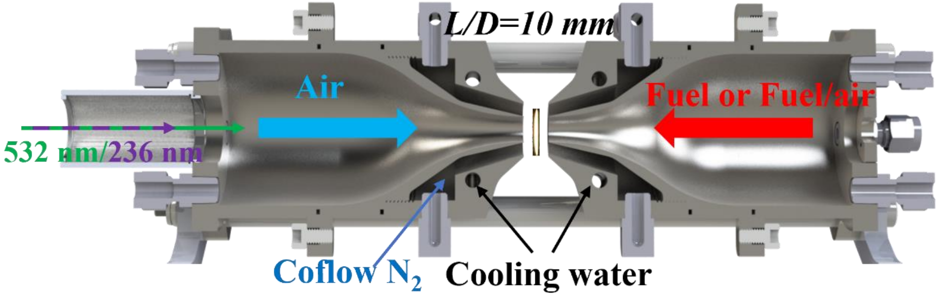
- Ammonia chemical kinetics models are still under development
- Large discrepancy among models on predictions of key radicals
- Models often tuned to match global parameters (ignition delay time, laminar flame speed,…)
- Detailed experimental data needed for mechanism development

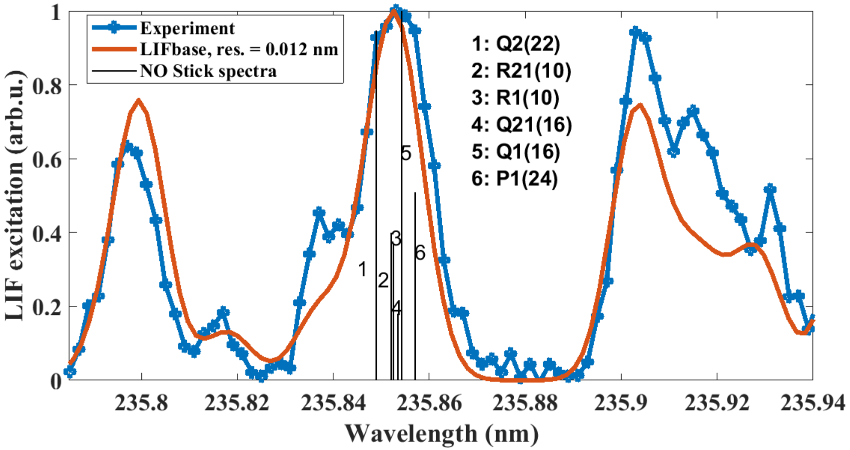


KAUST CF flames

Tang et al. CNF, 267, 113556, 2024

- 1D quantitative Raman/LIF of major species, temperature and NO
- NO excitation at 235.85 nm to avoid NH_3 absorption
- Operated in the saturated regime
- Full thermochemical structure for each laser shot
- Comparison in mixture fraction space to minimize sensitivity to boundary conditions
- Large dataset of 15 counterflow flames made available to modelers.





Calibration

Tang et al. CNF, 267, 113556, 2024

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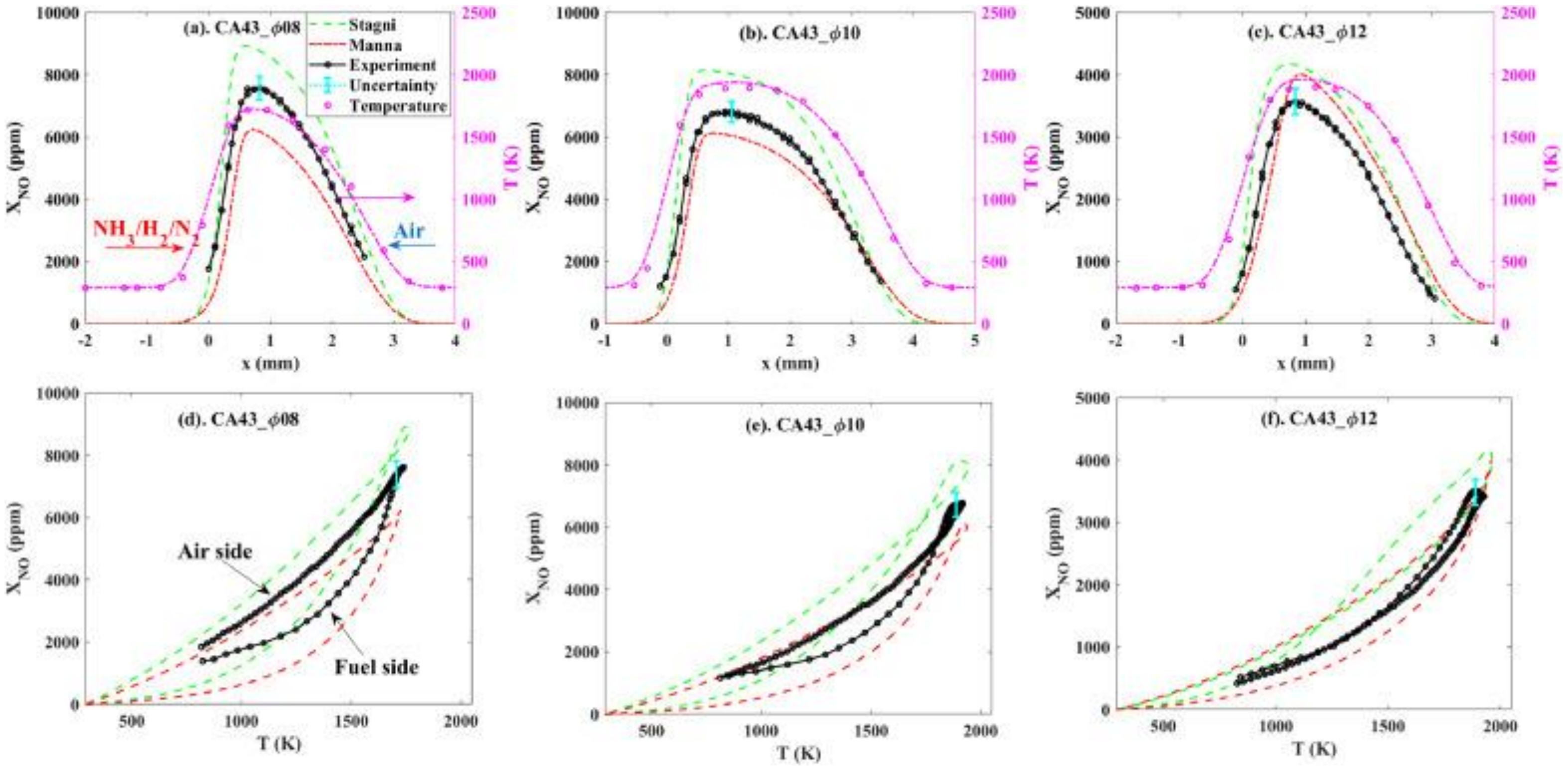
NOX in premixed flames

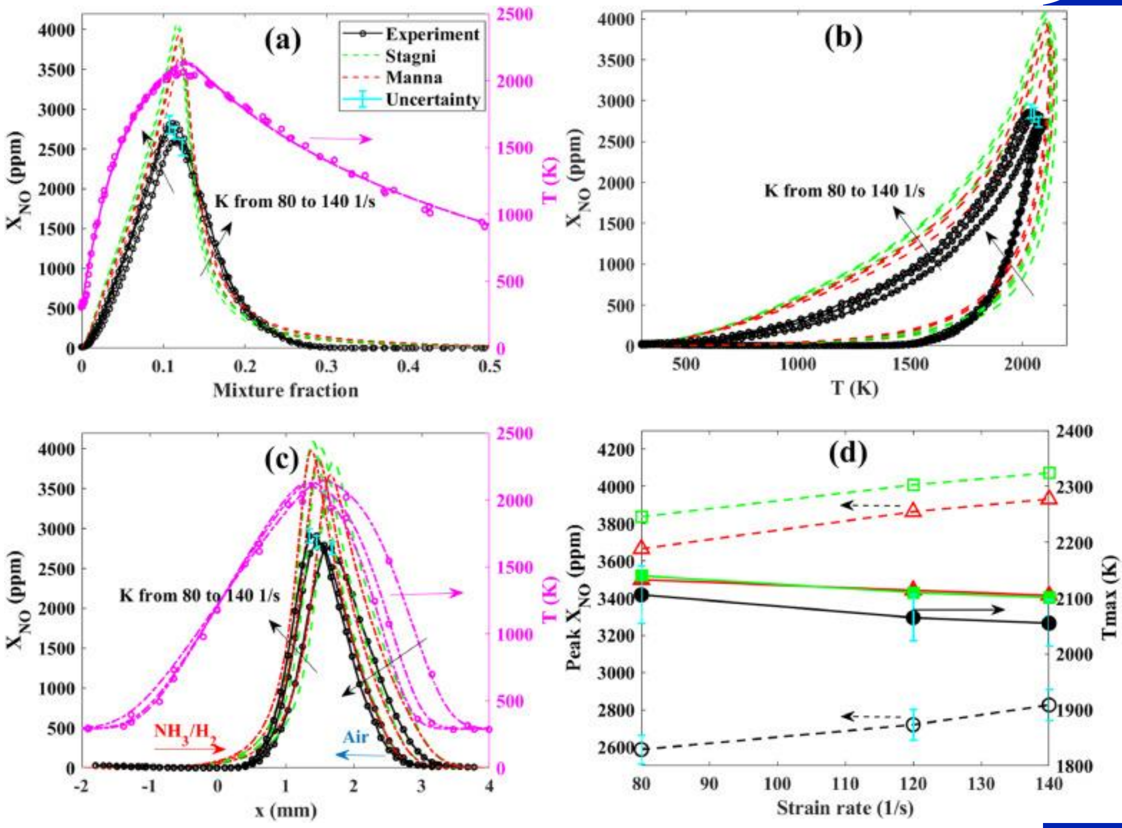
Tang et al. CNF, 267, 113556, 2024



- Experiments show NO concentration in between models for non-premixed flames

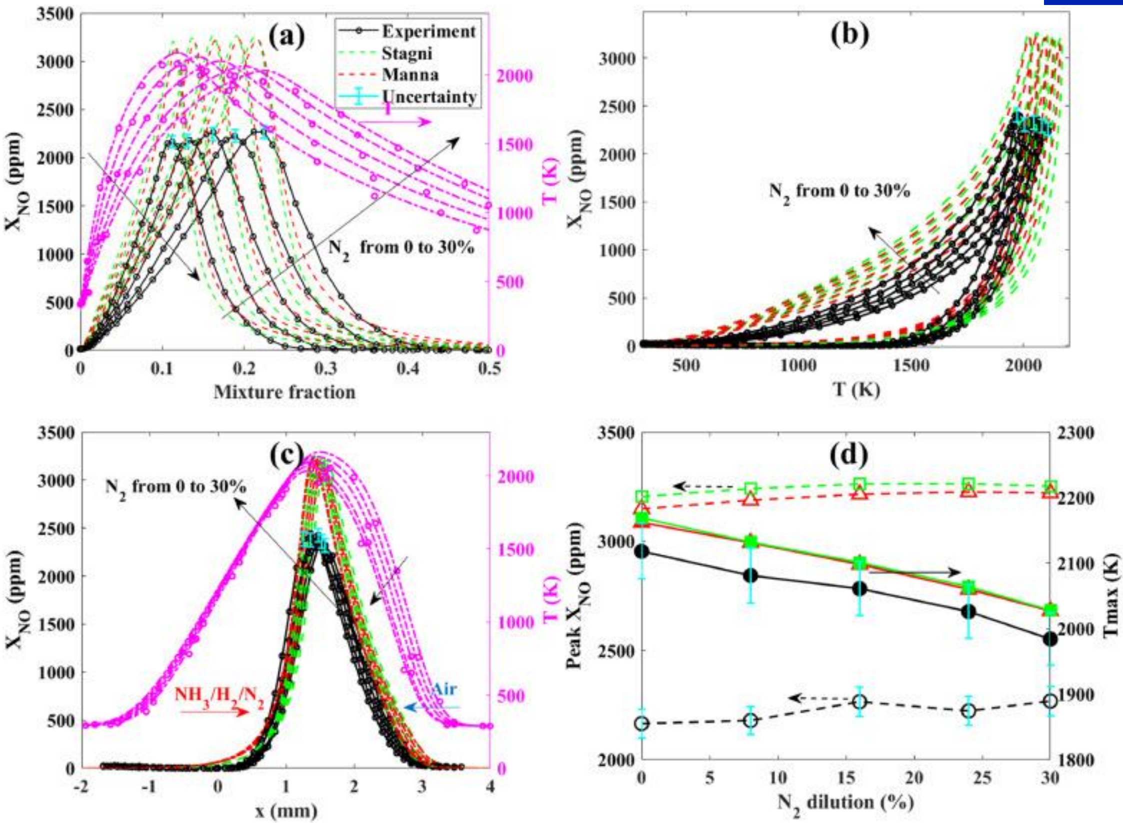
NOX in non-premixed flames: effect of strain

- Small effect of strain
  - ~20 K on Temperature
  - NO increase by 162 ppm (% 6%)
- Models
  - Greatly overestimate (35-40%) the NO peak values
  - Underpredict NO in the rich region
  - Correctly predict the observed trends in T and NO

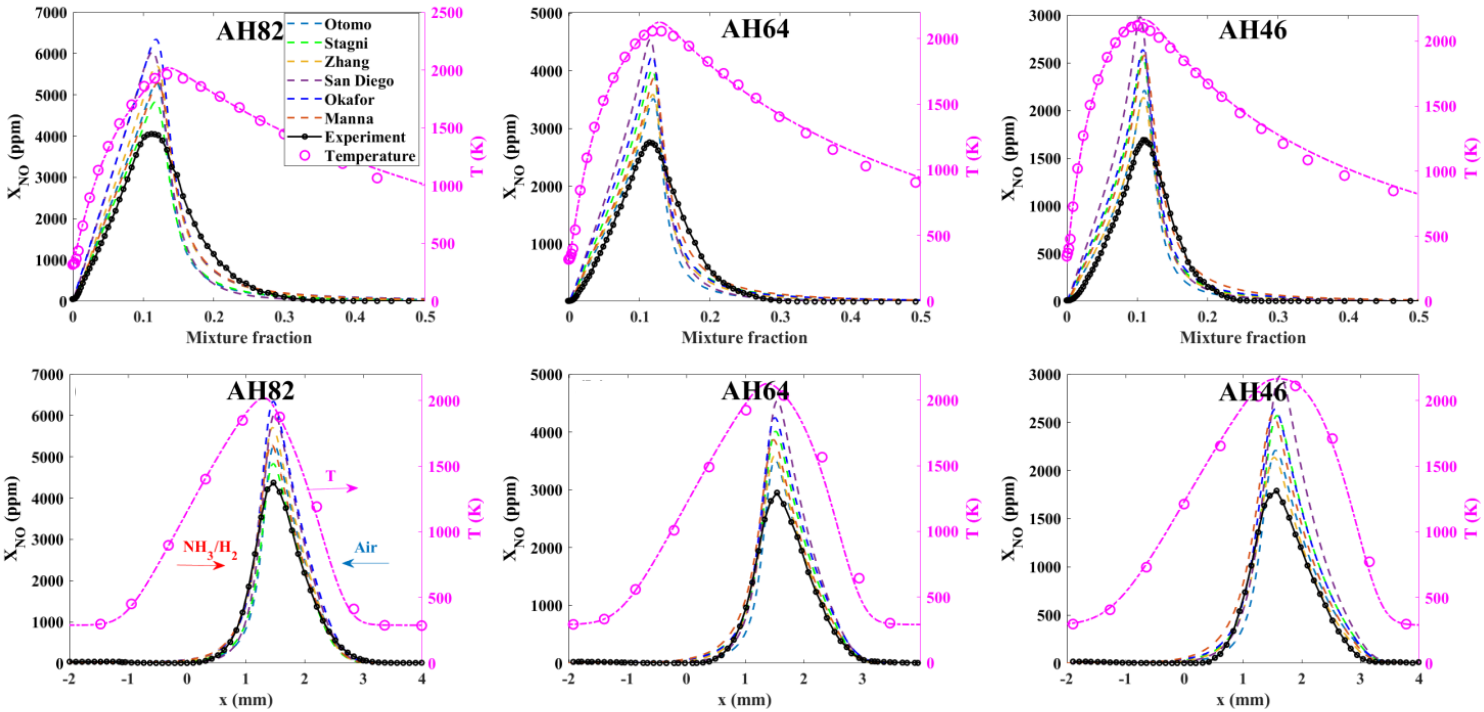


NOX in non-premixed flames: N2 addition

- N2 addition:
  - Temperature drops from 2160 K to 2023 K
  - NO increase by 50 ppm (~2%)
- Models
  - Correctly predict temperature variation
  - Similar trend in NO increase (1.5%-2.5%)
  - Peak NO overestimated by 42%.

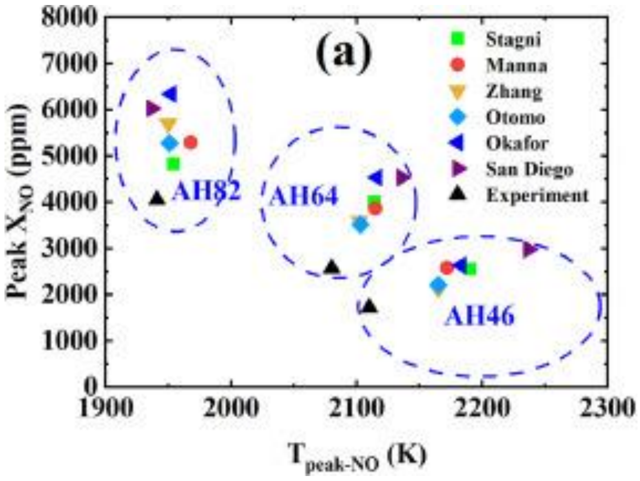


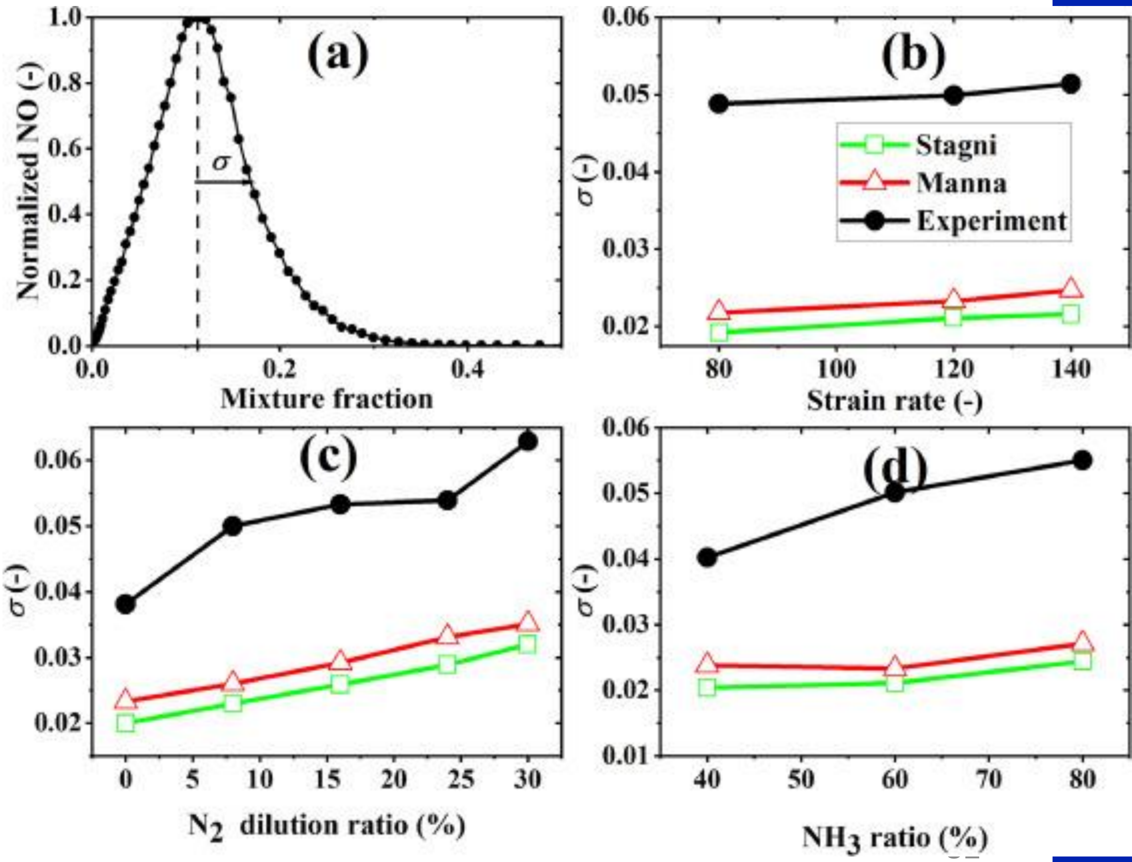
NOX in non-premixed flames: H2 addition



- Qualitative trend captured, with NO decreasing with H_2 addition
- NO peak overestimated by all models
- NO underestimated by all models in the rich region

NOX in non-premixed flames: summary





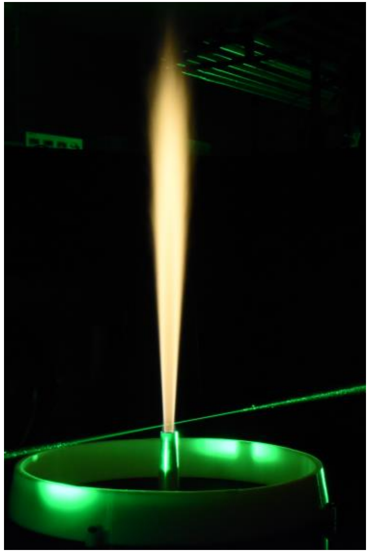
- Models overpredict peak NO
- Models underpredict NO in the rich region
    - Width of the NO profile in mixture fraction is underestimated

Ammonia turbulent jet flames

Ammonia canonical jet flames

Turbulence-chemistry interactions, differential diffusion effects,…

5 bar $NH_3/H_2/N_2$-air flame



Sandia piloted flame operated with partially cracked ammonia

10% NH_3

40% NH_3

Sydney inhomogenous burner with NH_3/H_2 as fuel

Bluff-body stabilized ammonia/hydrogen burner

Laminar and turbulent cracked ammonia/air jet flame at high pressure

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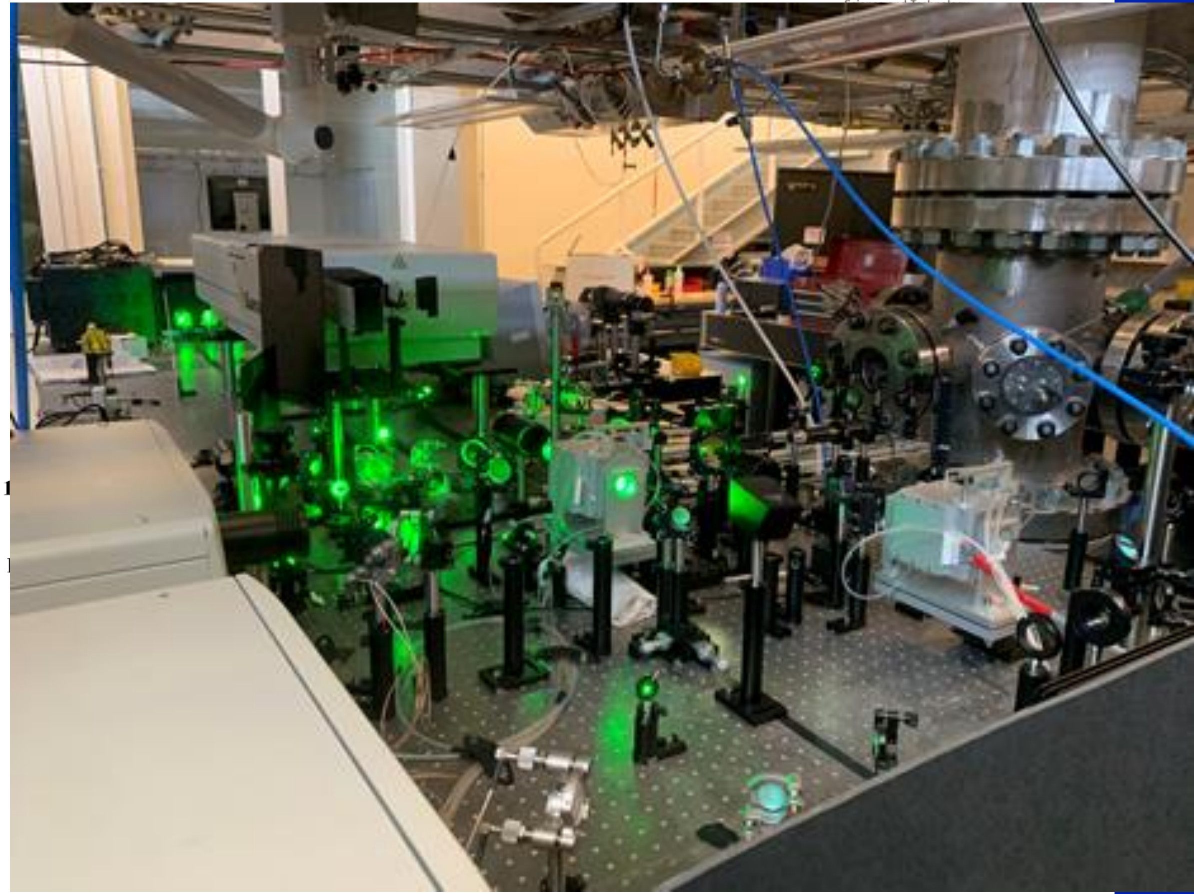
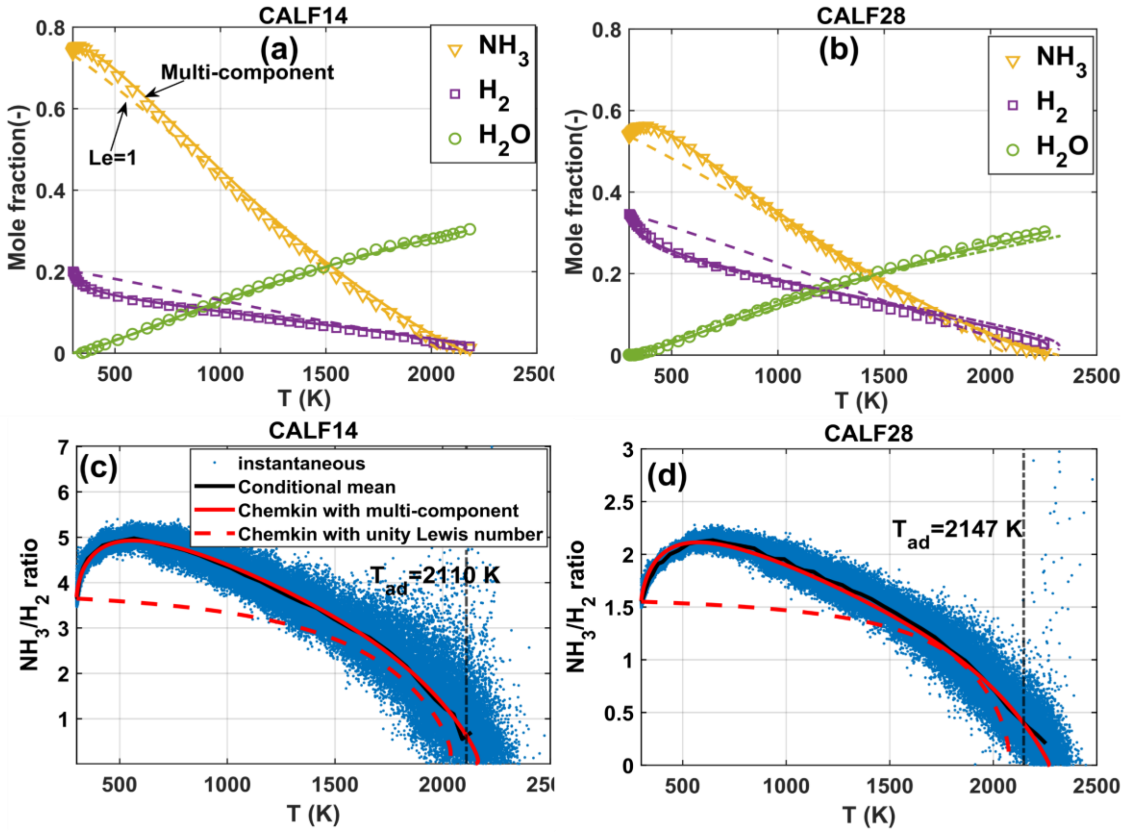
- Simplest canonical flame
  - 4.58 mm inner diameter
  - 150 mm air co-flow
- Two compositions
  - NH_3:H_2:N_2=76:18:6 by Vol.
  - NH_3:H_2:N_2=56:33:11 by Vol.
- Operated at 5 bar in KAUST High-pressure combustion duct
- Reynolds number of 2500 and 11000
  - ***Raman for temperature and major species***
  - ***Quantitative NO-LIF***
  - ***2D velocity field from PIV***



Laminar flames results at Z/D=1

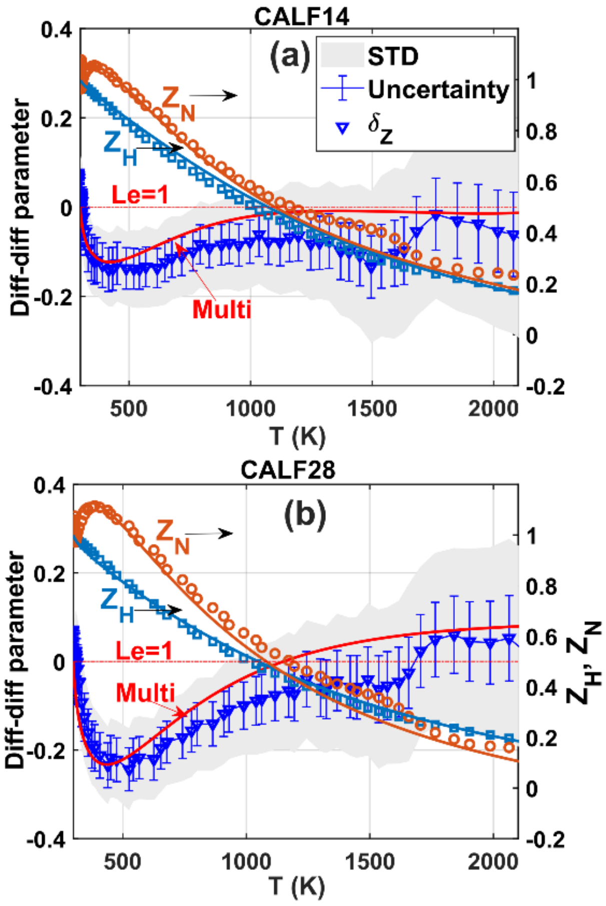
- Major species in good agreement with the full multi-component transport model
- Non-unity Le effects leading to super-adiabatic peak temperature
- H_2 burns ahead of the ammonia leading to a rapid increase in the NH_3/H_2 ratio



Tang et al. Experimental Thermal and Fluid Science Vol. 149, Nov. 2023

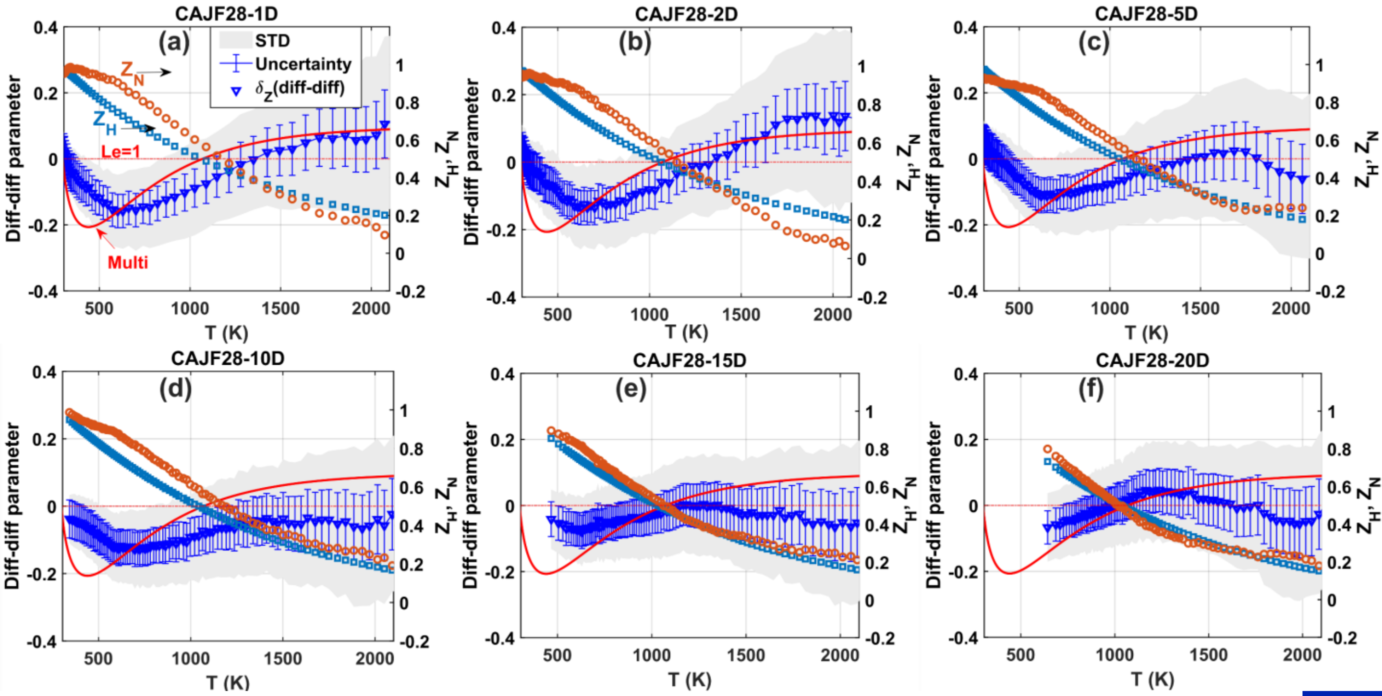
Differential Diffusion parameter

- Diff-Diff parameter based on atom-ratios to better capture diff-diff effects
- *N* replaces *C* in the conventional definition
- $\delta_Z = Z_H - Z_N$
- Z_X is the elemental mixture fraction:
- $Z_H = \frac{Y_H - Y_{H,air}}{Y_{H,fuel} - Y_{H,air}}$
- $Z_N = \frac{Y_N - Y_{N,air}}{Y_{N,fuel} - Y_{N,air}}$
- Correct trend captured in Z_H, some issues in Z_N
- Small denominator in Z_N (0.05) amplifies measurement errors



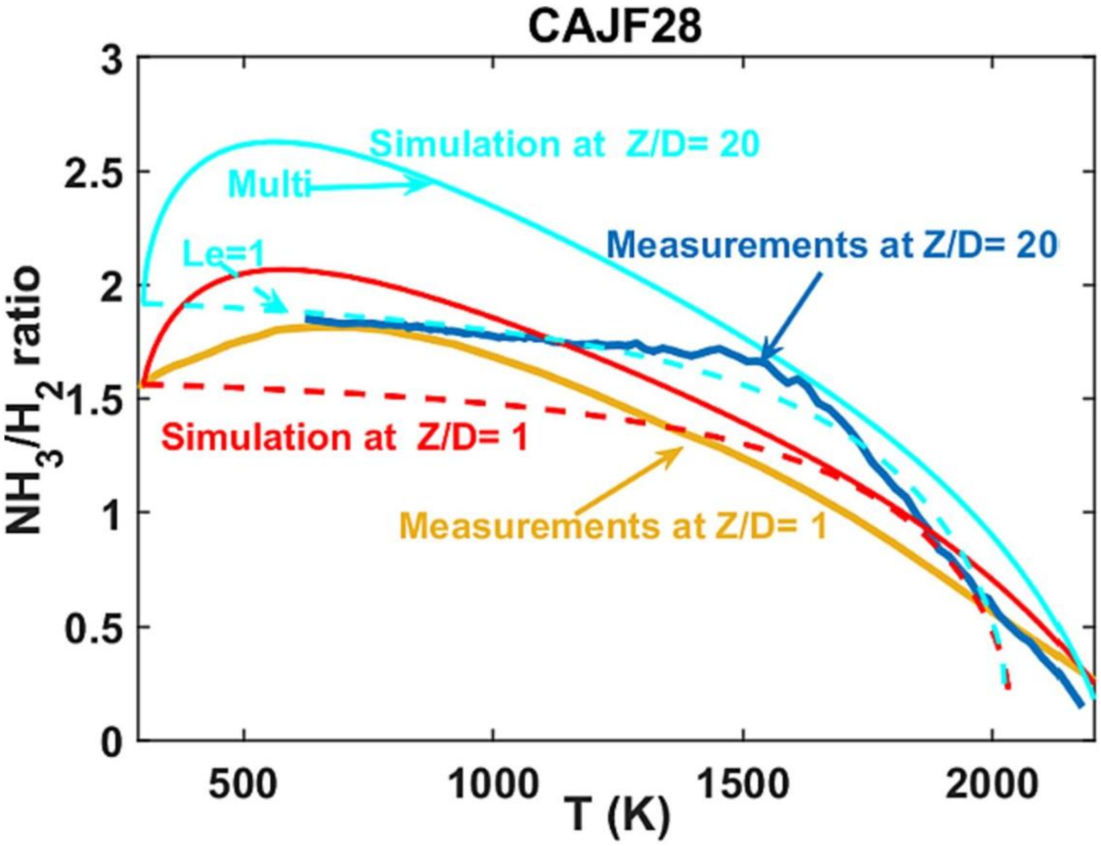
Differential Diffusion parameter in turbulent flames

- Diff-diff parameter indicates that differential diffusion is important up to 15 diameters
- Improvements needed to obtain lower uncertainties



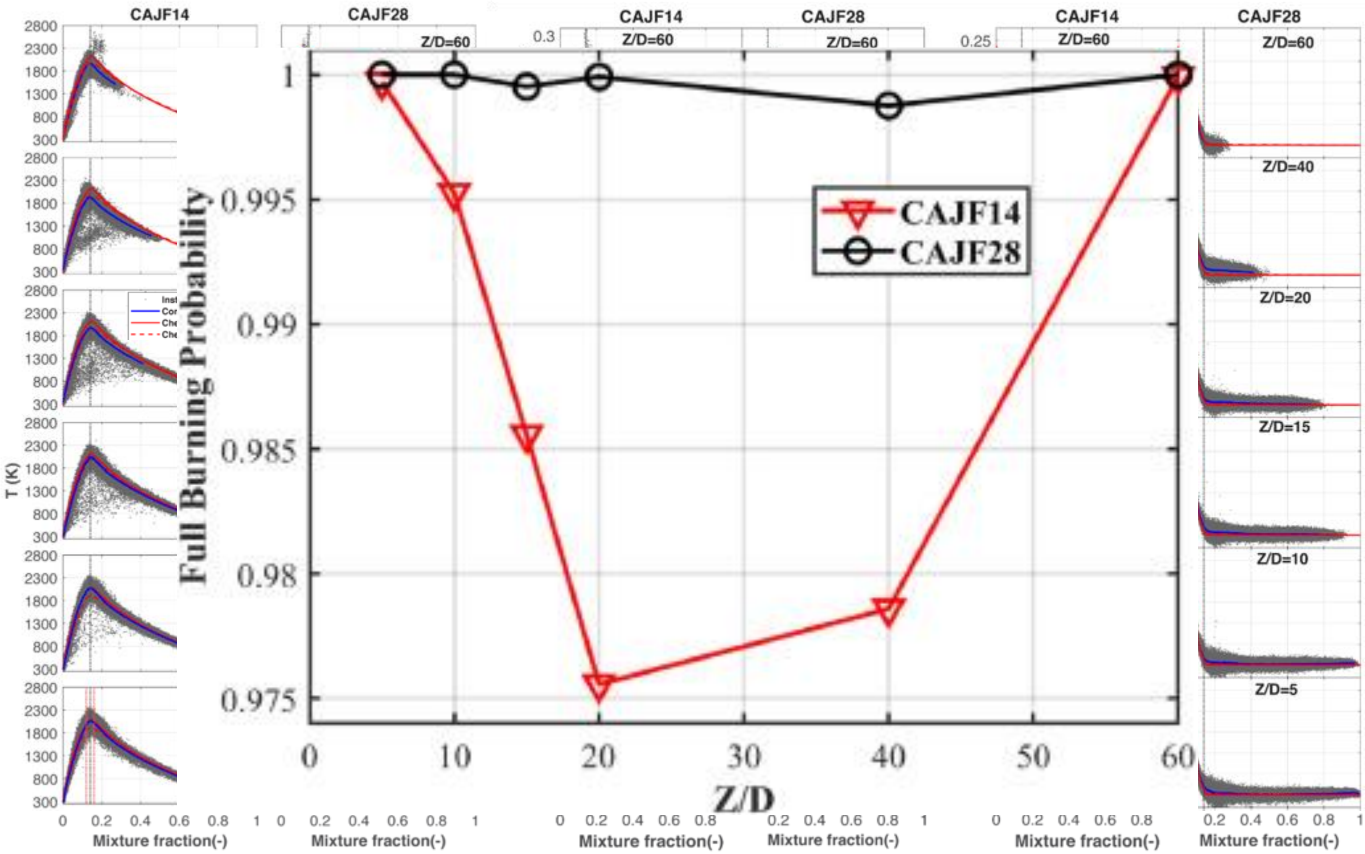
NH_3/H_2 ratio in turbulent flames

- NH_3/H_2 ratio affected by preferential diffusion
- For laminar flames, excellent agreement with the calculations when including multi-component transport
- For turbulent flame
  - Intermediate solution between multi-component and Le=1 at Z/D=1
  - NH_3/H_2 larger than simulations for Z/D=20
  - Good match with Le=1 results when matching the fuel composition
  - Diff-diff effects acting near the nozzle, affect the NH_3/H_2 downstream



Turbulent flames: mixture fraction space

- Temperature profile matches the full multi-diffusion simulation near the exit, and the Le=1 downstream
- Evidence of localized extinction for the CAJF14 flame (40% of blowoff velocity)
- Full burning probability: fraction of samples near stoichiometry ($0.12 < \xi < 0.16$) with T>1500 K
- Different flame series needed to study extinction



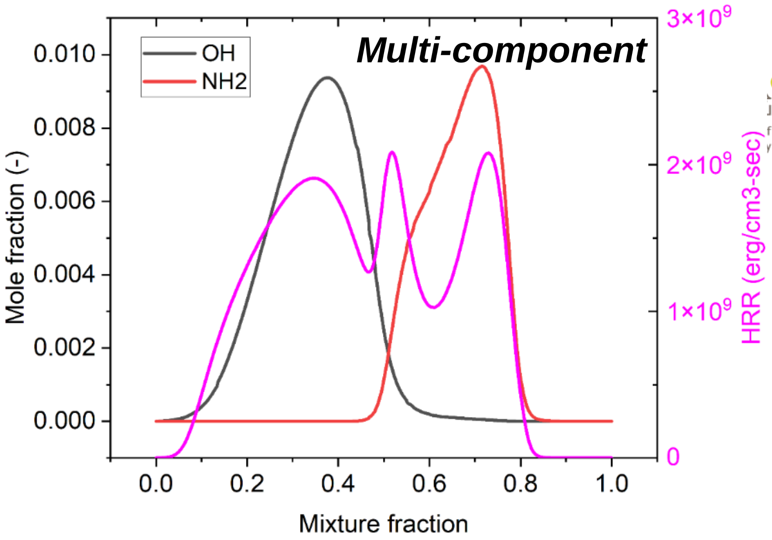
Cracked ammonia piloted flames

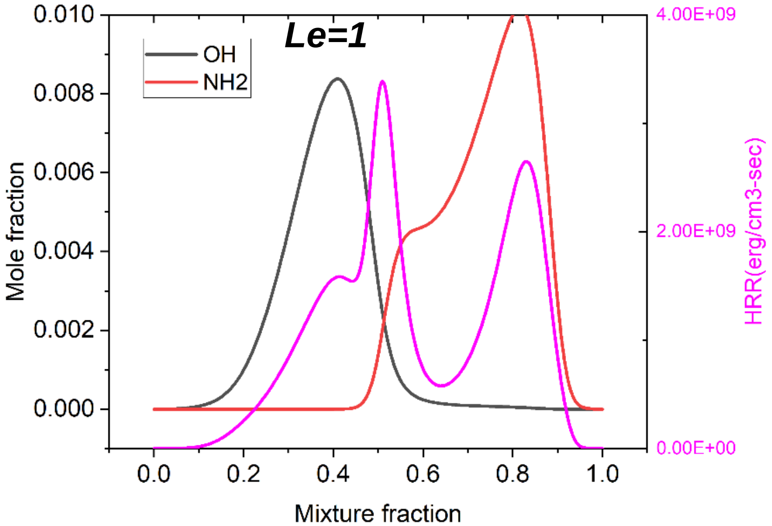
- Three partially premixed piloted jet flames
- Sandia piloted burner
- Raman/Rayleigh+OH LIF
- Fuel: Simulated partially cracked ammonia (43%), and air with $\Phi = 3$
- Pilot jet: Simulated partially cracked ammonia (43%), and air with $\Phi = 0.9$ 520W
- Three Reynolds numbers
  - Flame D Re=24000 (59% Exctintion Re)
  - Fleme E Re=32000 (79% of extinction Re)
  - Flame F Re=36000 (89% of extinction Re)

Cracked ammonia piloted flames

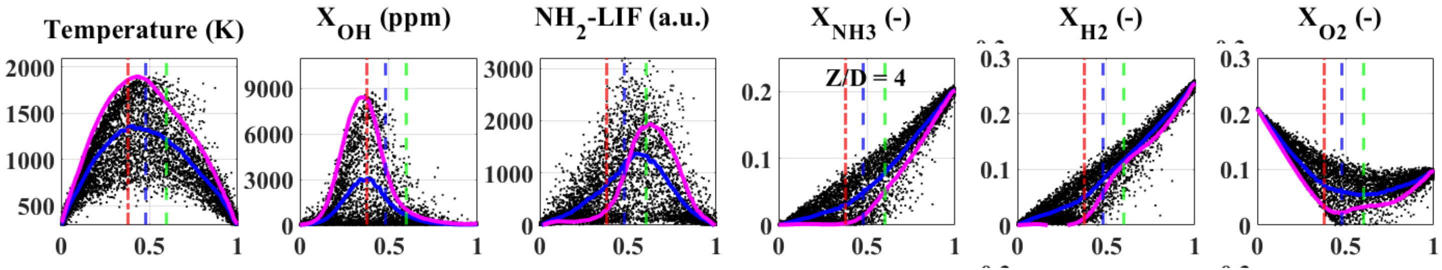
- Laminar flame structure from counterflow flames
- Three peaks of heat release identified
  - A peak near $\zeta = 0.75$ from the premixed, stratified region
  - A peak near $\zeta = 0.5$ corresponding to the peak temperature
  - A peak near the OH peak
- For unity Lewis number
  - Reduced heat release near the peak of OH
  - Increased heat release near stoichiometric mixture fraction

Tang et al. PROCI 2024 in press



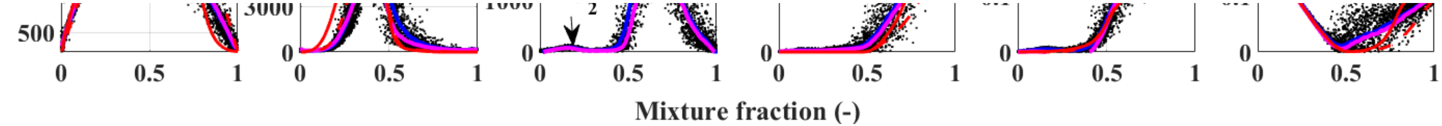


Ammonia piloted flames: near field



Small differences between Flame D and F at z/D=1. Intermediate between unity Le and full multi-component simulation

At z/D=4 extinction propagates to the rich side, as evident by increase in NH_3, and O_2, and drop in NH_2 and T



- At z/D=2 local extinctions starts on lean side. Note drop in OH, and NH_2, and the appearance of NH_3 and H_2 for lean mixture fractions

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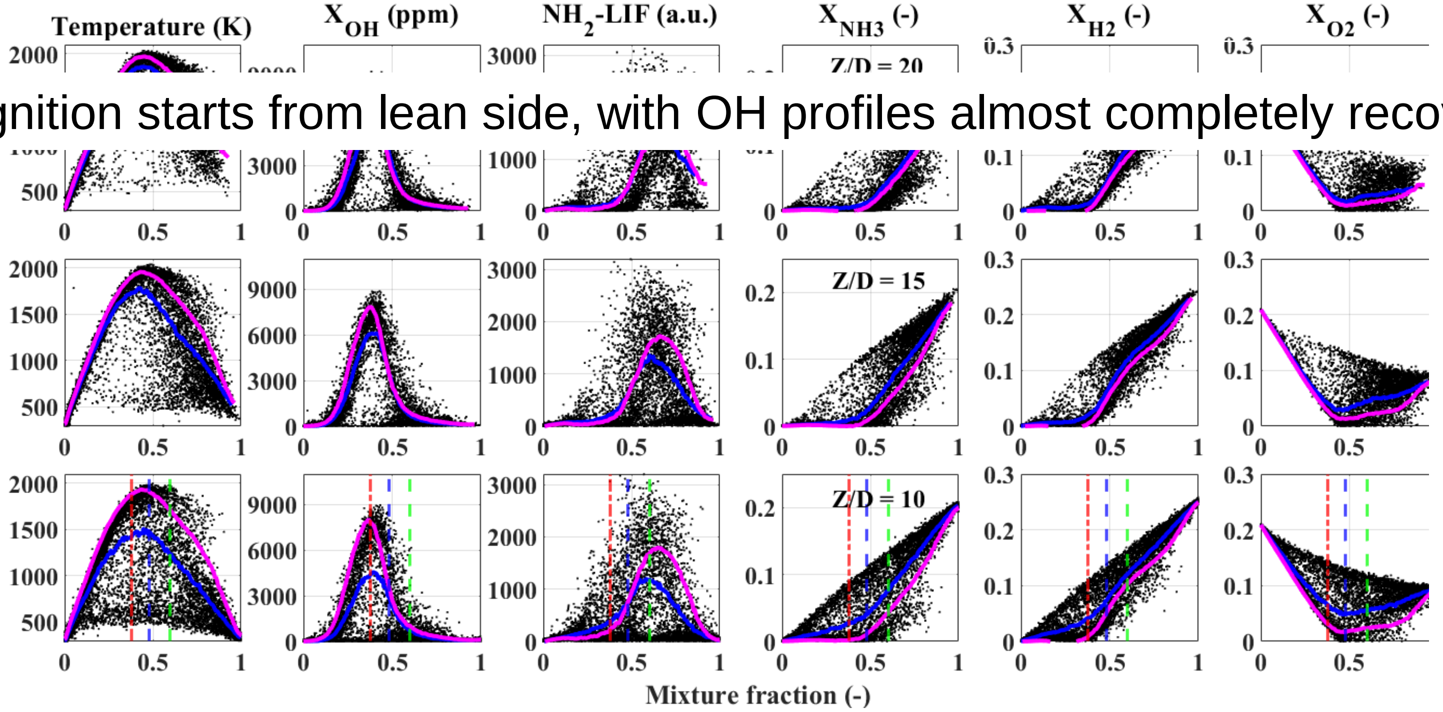
Ammonia piloted flames: far field

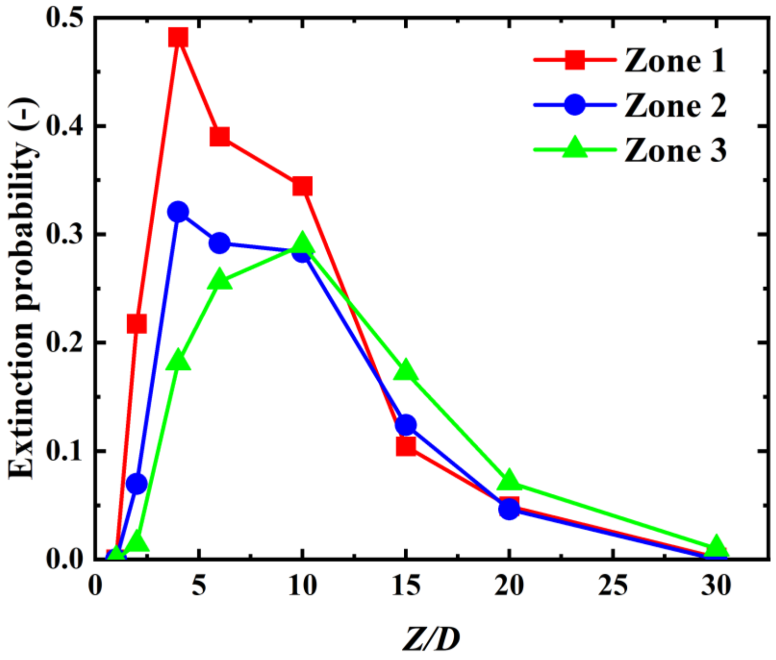


Re-ignition starts from lean side, with OH profiles almost completely recovered

- z/D=10 continues to show extensive localized extinction

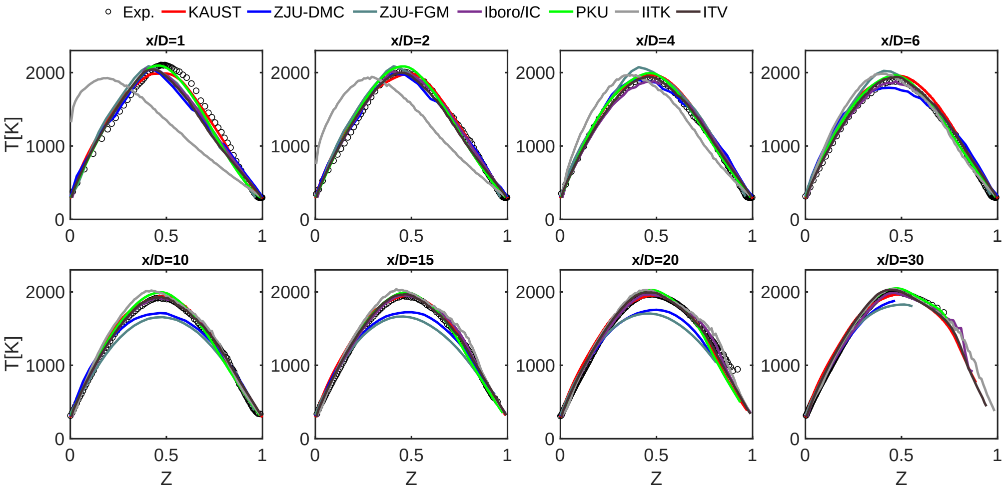
Analysis of local exctinction

- Extinction probability computed based on the mixture fraction corresponding to the OH, T and NH_2 peak
- Zone 1: OH concentrations below 1500 ppm for ξ=0.38
- Zone 2: temperature below 1100 K for ξ=0.48
- Zone 3: NH_2-LIF intensity below 400 counts for ξ=0.60
- Extinction and re-ignition start from the lean size (zone 1) and propagate to the rich side



Comparison with CFD simulations

- TNF Jul1 19-20 2024 Milan
- 7 Contributing groups, 8 datasets
- Flame D and F simulated and compared to experimental results



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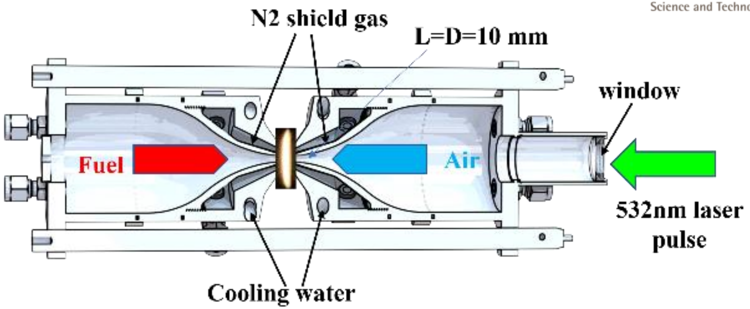
Canonical flames for ammonia combustion

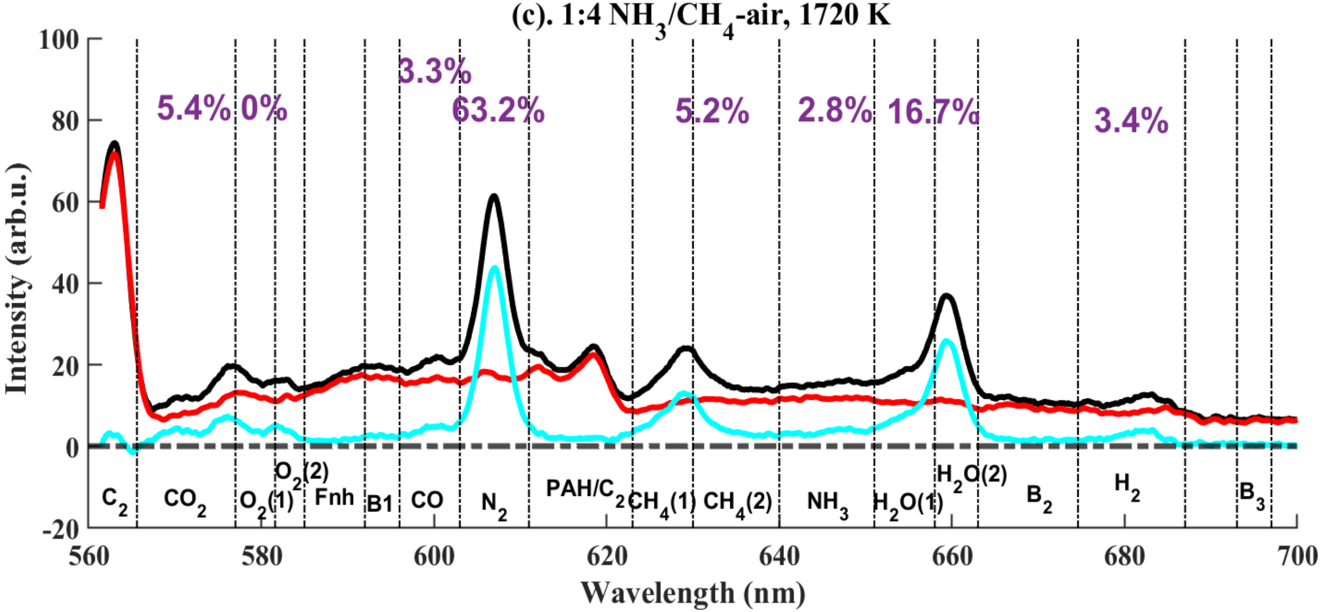
- Novel optical diagnostics for ammonia flames
  - Raman/Rayleigh scattering extended to ammonia flames
  - Semi-quantitative NH_2 measurements with 532 nm excitation
  - Coupling with LIF for quantitative NO and OH
- Detailed measurements in counterflow diffusion flames reveal systematic discrepancy with predictions
- Canonical turbulent flames for model validation
  - High-pressure, turbulent jet flames highlight role of differential diffusion
  - Piloted jet flames to study localized extinction and re-ignition


Questions?

Extending to atmospheric pressure flames

- Measurements in counterflow diffusion flames to assess accuracy and precision
- In methane flames fluorescence from C2 and PAH
- Single interference channel cannot describe the entire flame

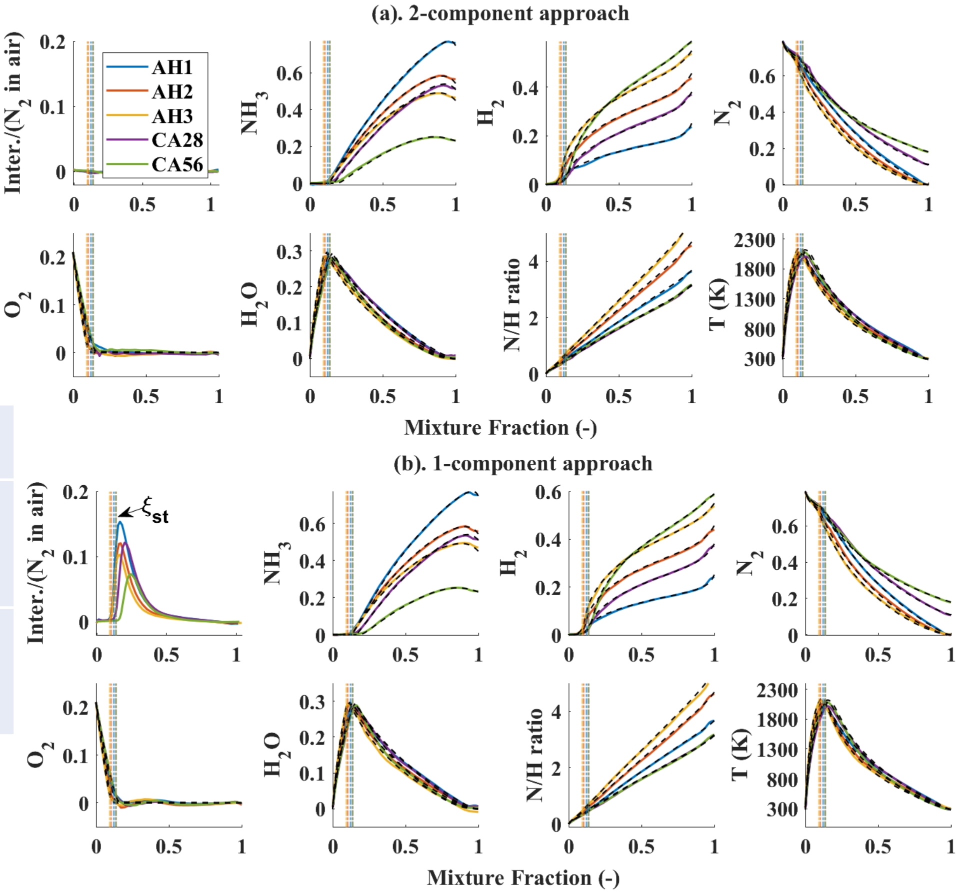




1-component vs Polarization-separation: ammonia

- Wavelet adaptive thresholding and reconstruction algorithm for improved precision
- For ammonia flames both 1-component and polarizaration-separation approach lead to accurate results

	NH_3(%)	H_2(%)	H_2O(%)	O_2(%)	N_2(%)	T (K)
2-com	1 (2.3)	1.3 (1.8)	1.2 (2.1)	0.5 (2.5)	1.2 (4.5)	70 (80)
1-com	1.1 (2.2)	1.4 (1.5)	1.4 (2.0)	0.7 (2.0)	1.2 (3.9)	60 (74)



1-component vs Polarization-separation: CH4/NH3

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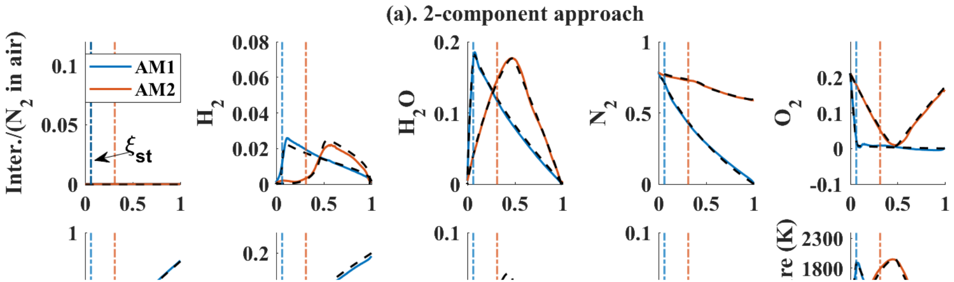
- Large inaccuracies for the 1-component approach
- Improved precision in 2-component approach



Accuracy	O_2	N_2	H_2O	H_2	CH_4	CO_2	CO	NH3	T(K)
NP, 2-com	1.1	0.5	0.6	0.4	0.5	0.4	0.9	0.6	42
NP, 1-com	2.9	7.0	1.6	4.5	0.6	3.0	1.5	0.5	160
Φ =3, 2-com	0.3	0.5	0.2	0.4	0.3	0.6	0.5	0.4	40
Φ =3, 1-com	2.0	3.7	0.5	2.1	0.5	2.4	2.8	0.4	150

Precision	O_2	N_2	H_2O	H_2	CH_4	CO_2	CO	NH3	T(K)
NP, 2-com	1.4	2.2	1.0	0.5	0.8	0.6	1.1	0.3	38
NP, 1-com	1.5	2.5	1.1	0.4	0.8	0.8	0.8	0.3	74
Φ =3, 2-com	2.0	1.5	1.5	0.3	0.8	0.7	1.0	0.3	37
Φ =3, 1-com	1.7	3.0	2.6	1.5	1.5	1.2	1.2	0.4	60

NO experiment and simulations

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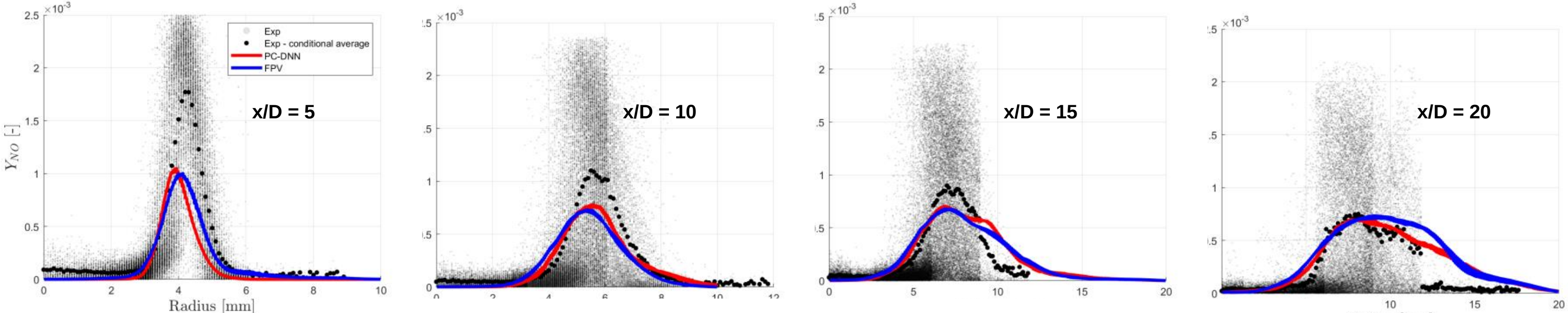
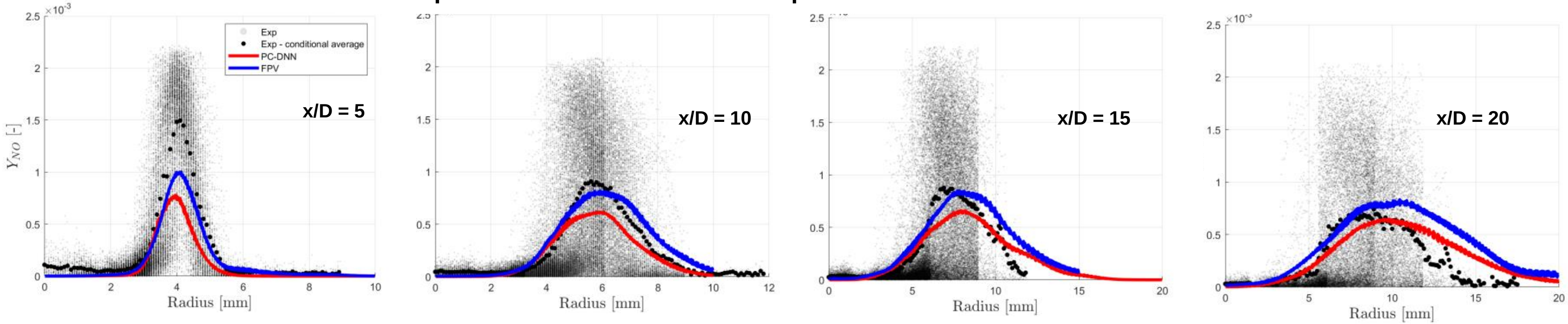


- Qualitatively good agreement, but room for improvement in both experiment and simulations

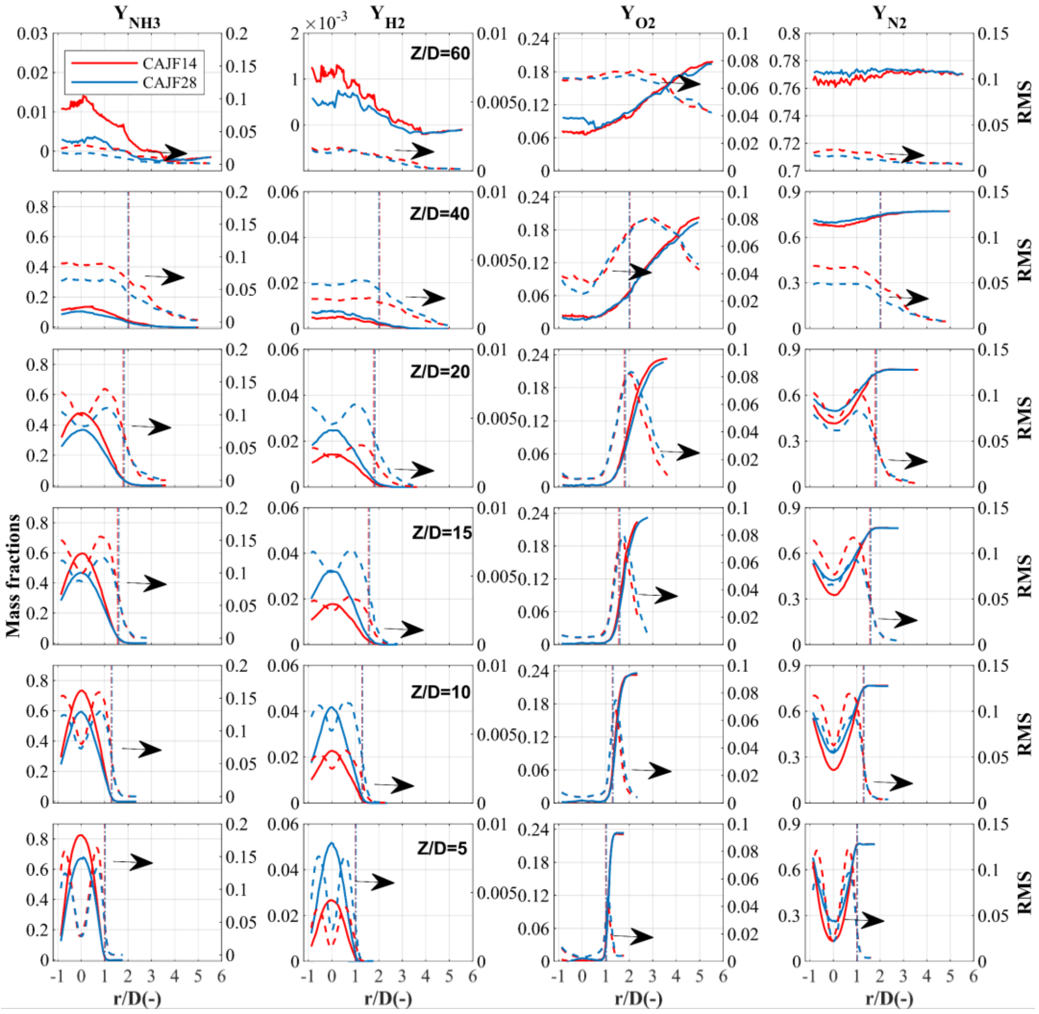


Wang et al PROCI 39 (1), 1465-1474 (2022)

Turbulent flames: radial profiles

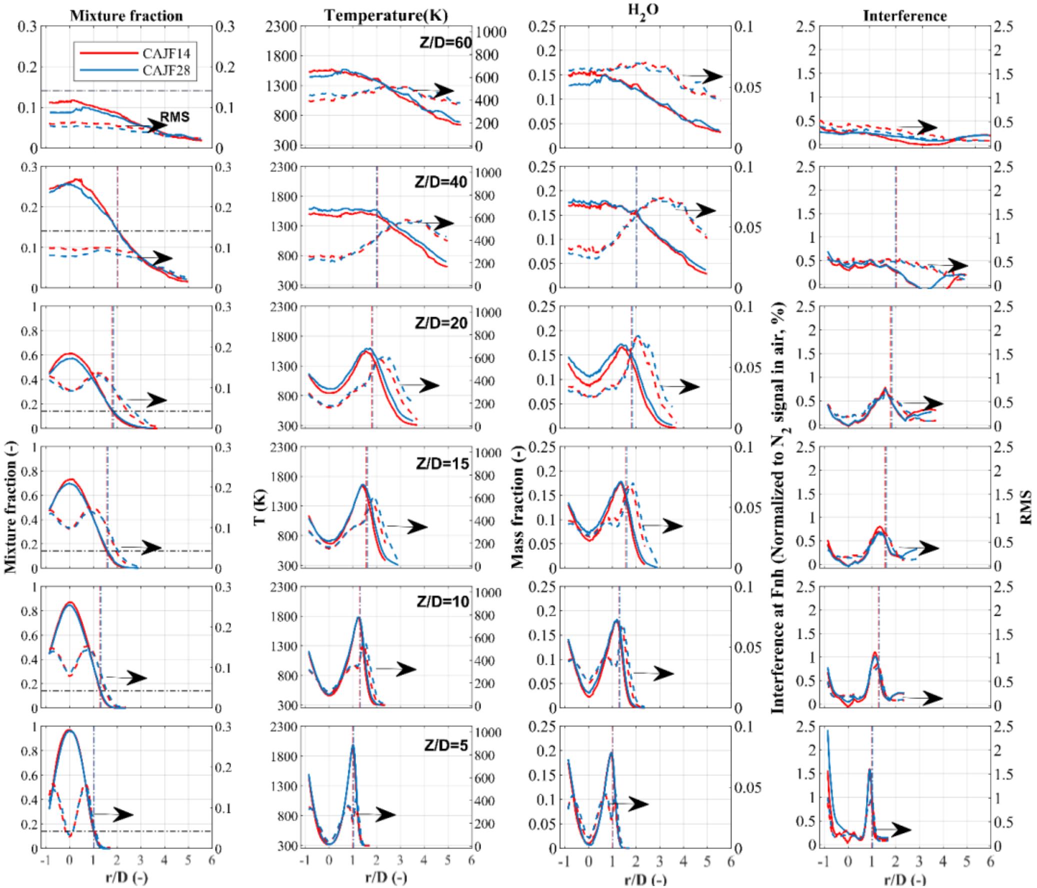
- Mean and RMS data available for Z/D ranging from 1 to 60
- Differences in N_2, H_2 and NH_3 from the different fuel composition
- Slightly enhanced O_2 decay for the higher cracking ratio

Tang et al. CNF 2022



Turbulent flames: radial profiles

- Slightly higher mean temperature and water concentration for the flame with higher hydrogen content
- More insight from analysis in mixture fraction space



Turbulent flames: diff-diff effects

- Ammonia and hydrogen profiles plotted vs temperature
- Profiles intermediate between unity Le and the full multi-component diffusion
- H2 mole fraction drops below both solutions moving downstream
- Diff-diff effect although stronger near exit is cumulative
- NH3/H2 ratios increases with distance from the exit