Spectroscopic Diagnostics for Assessing and Improving Ammonia Combustion Chemistry Models

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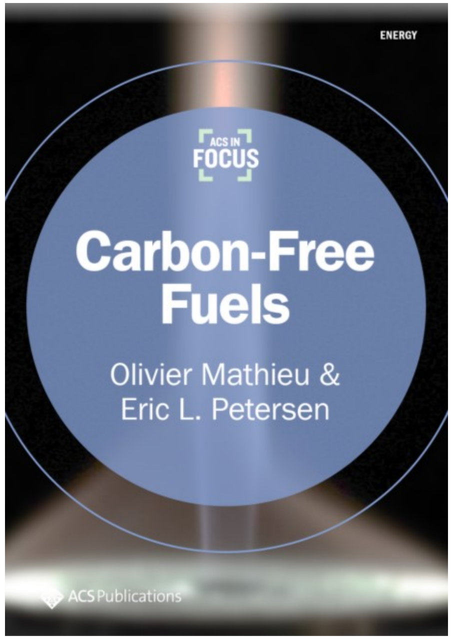
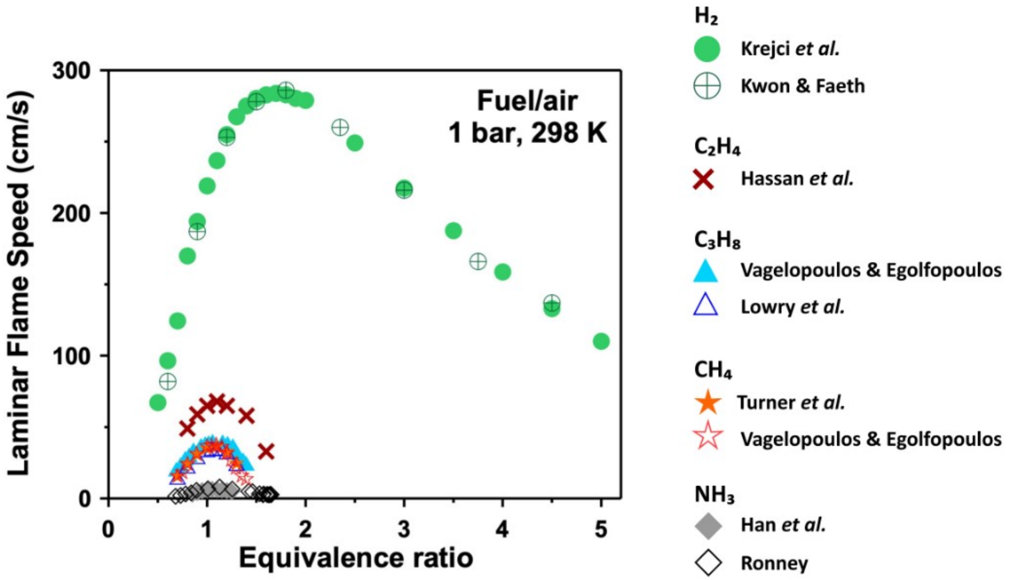
Introduction

Ammonia good candidate for carbon-free energy and energy storage



- Can be produced from renewable energy, air (N_2), and H_2O
- Easy to store and transport
- Industrial scale infrastructure already in place

- But **poor** burning properties
  - Probably have to be mixed with other fuels
  - H_2 good candidate (from NH_3 cracking)



Introduction

Accurate kinetics model required to successfully implement NH_3 as a fuel

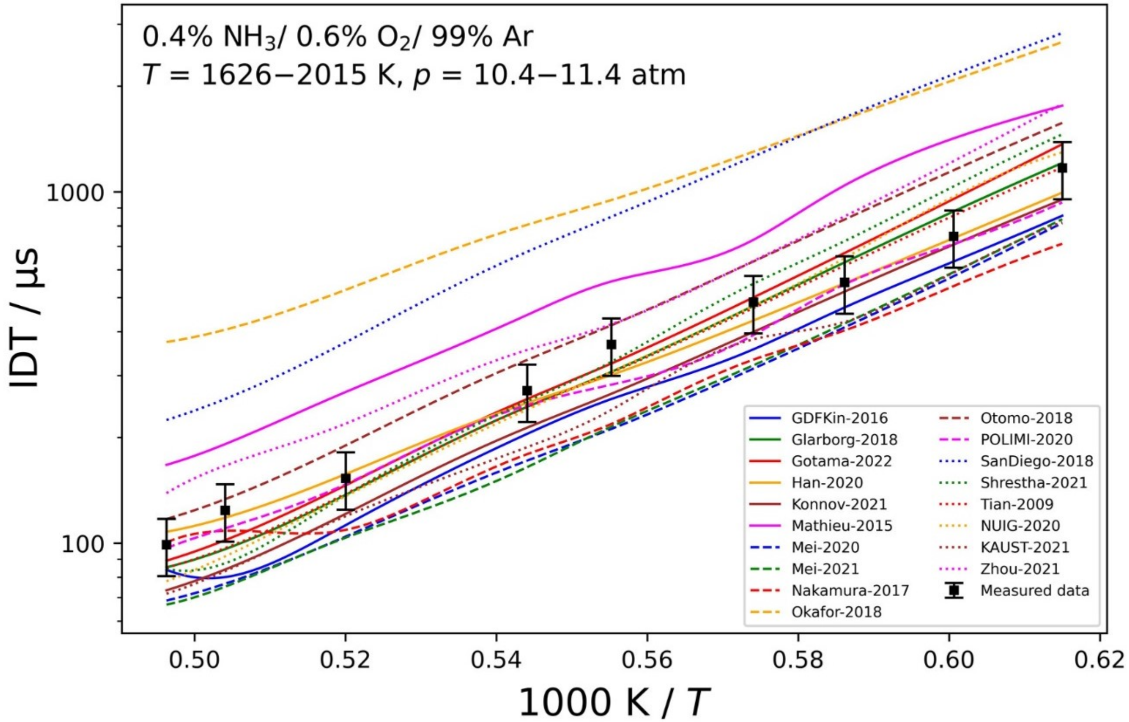
- Turbines and ICEs need to be designed around the fuel they use
- Global kinetics data (Ignition delay time, laminar flame speed)
  - Relate to key combustion properties in real-world applications
  - Useful for design and to set the dimensions
- Detailed chemistry needed for pollutants (NH_3, NO, NO_2) and GHG (N_2O) emissions
- Numerous NH_3 models available in the literature
  - Which ones are the best?
  - How good are the models?
    - Several model reviews recently published
  - **How to make better models?**

Limitations of global kinetics data for model validation

Global kinetics data relate to real properties in real-world applications but…

$\Rightarrow$ **Models w/ different reaction schemes can achieve the same (good) predictions**

- **Global kinetics data (IDT)**
  - Measurement based on physical parameter (P increase)
  - Qualitative measurement of chemical species (OH*)

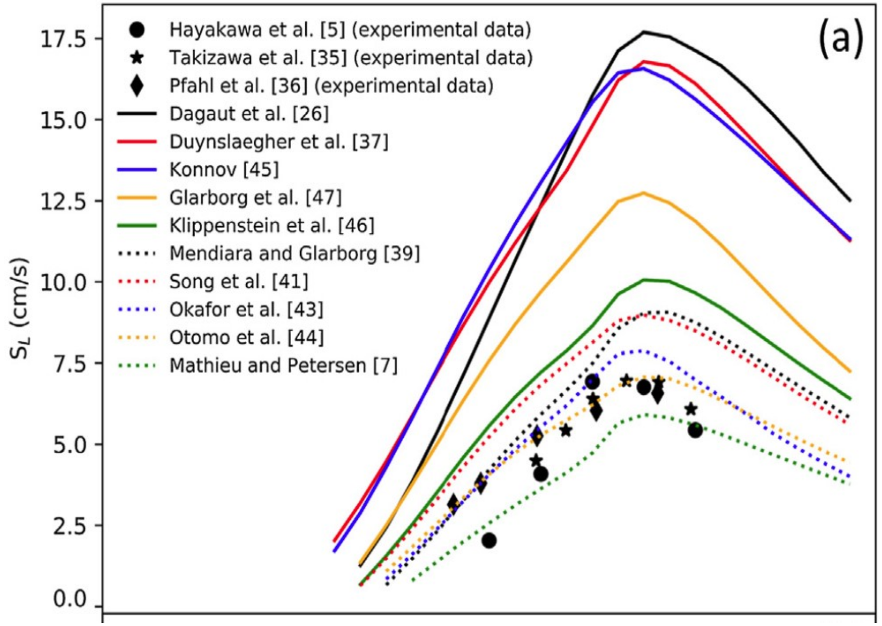


Szanthoffer, Turyani et al., Appl. En. Comb. Sci. 14 (2023) 100127.

Limitations of global kinetics data for model validation

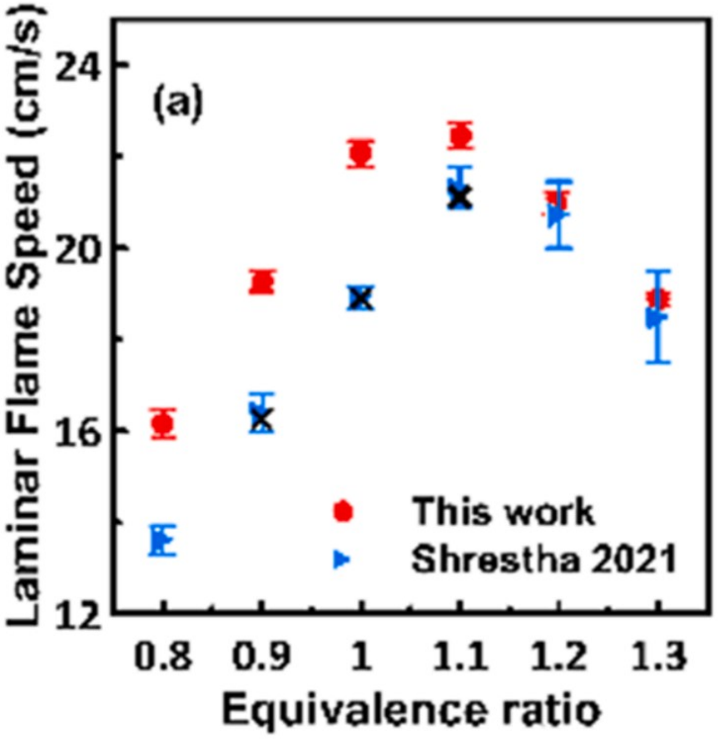
LFS measurements are not consistent

- **Experimental difficulties/limitations**
  - Most experiments in air/low T (where buoyancy is more prevalent)
  - Great importance of the flame radius domain size



(Rocha et al., https://doi.org/10.1016/J.FUEL.2019.02.102)

Vessel size:
- Shrestha: 4.2 L
- Hamadi: 56 L

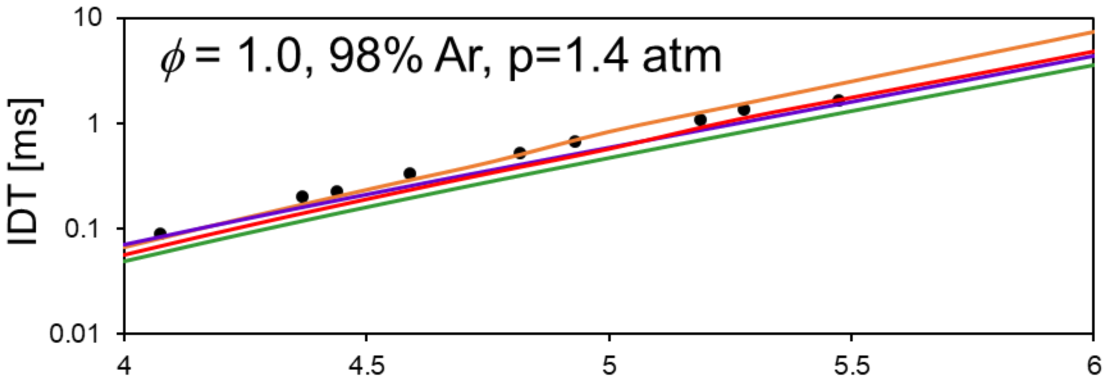


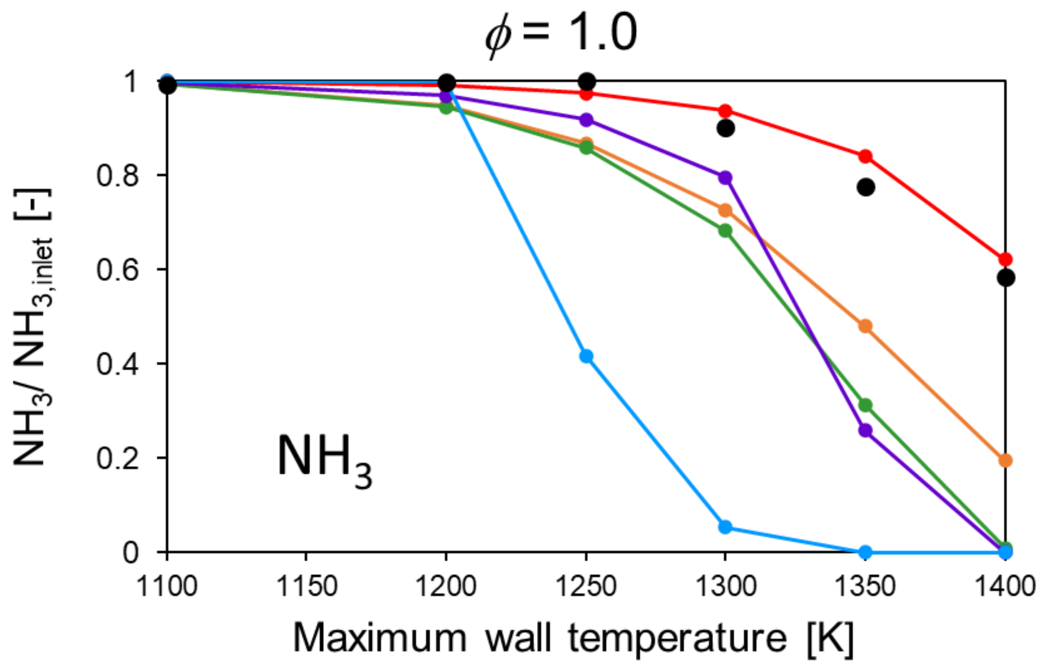
Hamadi, Chaumeix et al., *PROCI* 40 (2024) 105380.

Limitations of global kinetics data for model validation

Speciation studies provide more constrain but…

- **Speciation studies**
  - Several species => higher level of constrain
  - 1 species = 1 data/condition



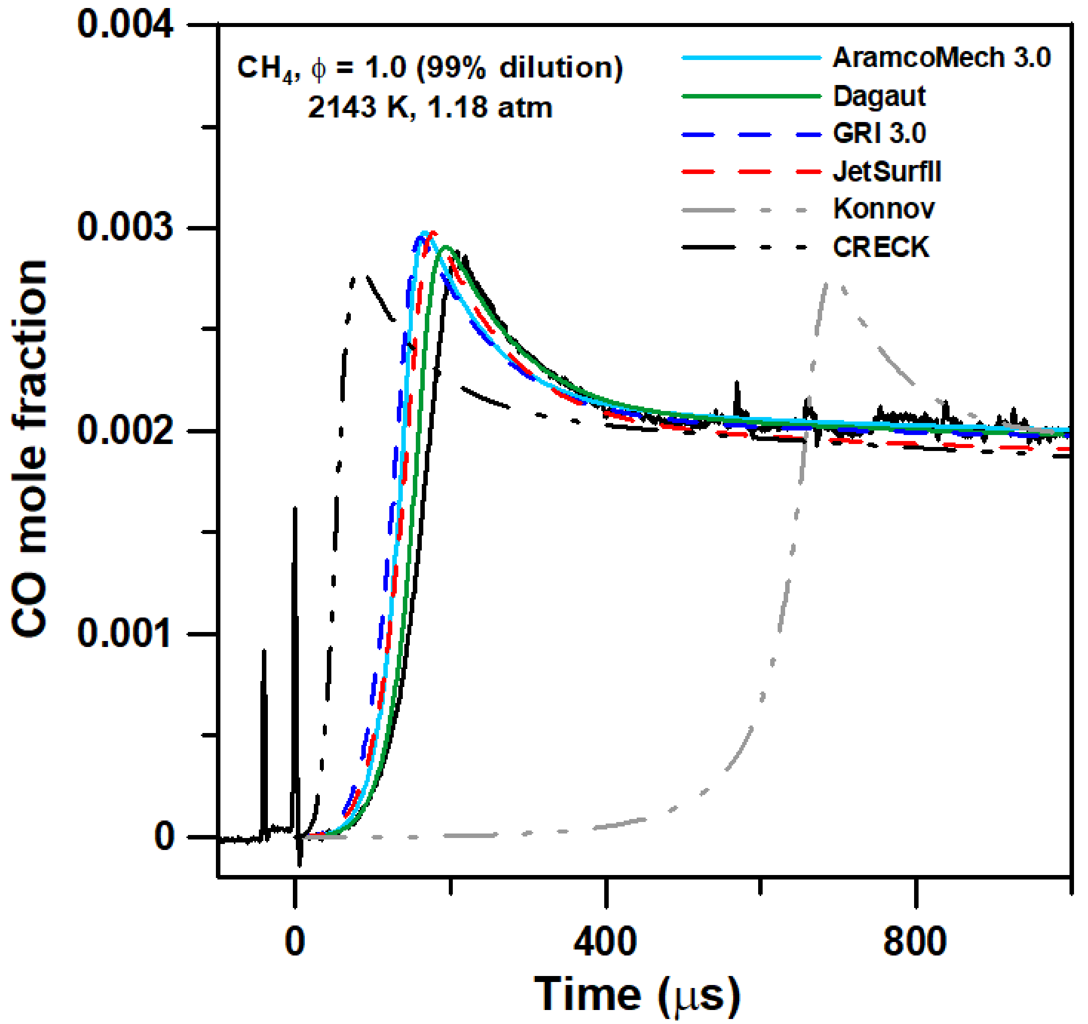


[1] P. Glarborg, J. A. Miller et al., *Prog. Energy Combust. Sci.*, 67 (2018) 31–68. [2] J. Otomo et al., *Int. J. Hydrogen Energy*, 43 (2018) 3004–3014.
[3] X. Zhang et al., *Combust. Flame*, 234 (2021) 111653. [4] A. Stagni et al., *React. Chem. Eng.*, 5 (2020) 696–711.

Importance of time-history profiles

Laser diagnostics => great tool for model validation

- **Concentration time history: 1 species = multiple targets per condition**
  - Induction delay time
  - Rate of formation/consumption
  - Final concentration level
  - Specific features
  - Max concentration
  - …
- **Limitations:**
  - Experimental conditions (pressure)
  - Cost/complexity



Mathieu et al., *Fuel* 236 (2019) 1164-1180.

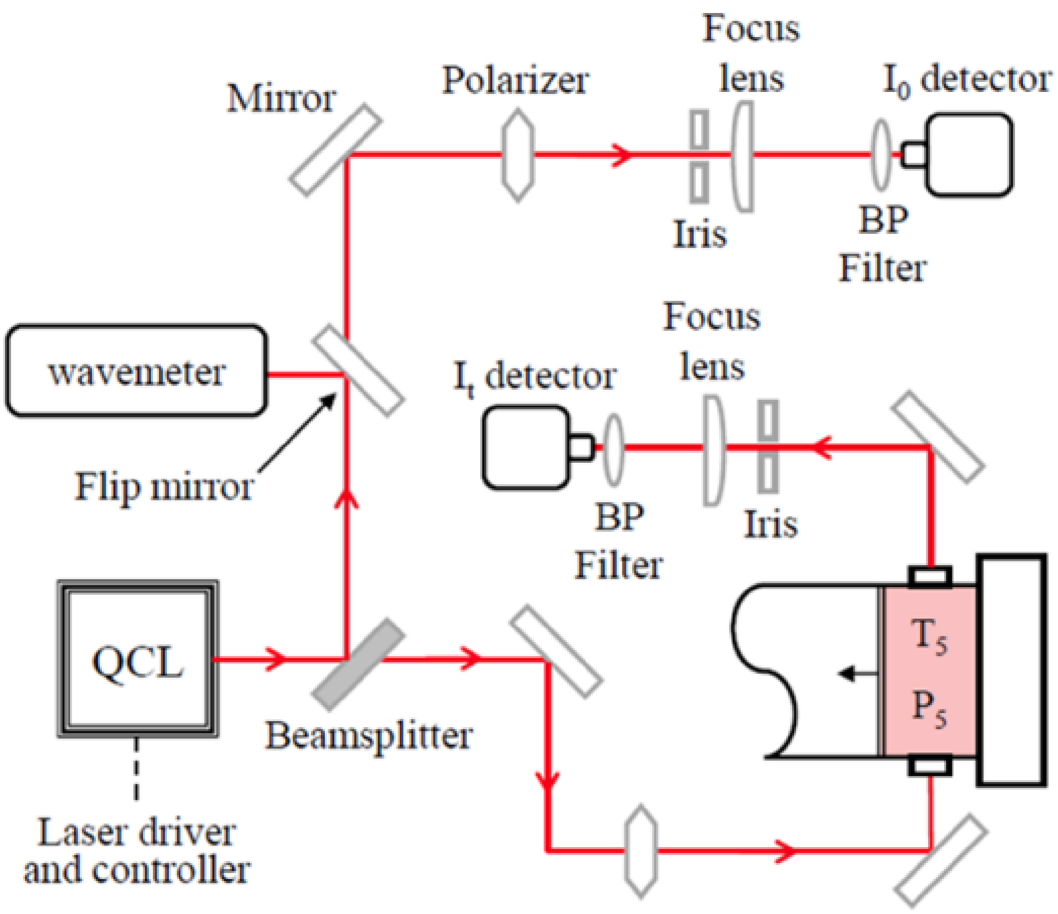
Experimental Method: Species Measurement in a ST

Absorption Laser Diagnostic

- *Laser diagnostics for:*
  - ***NH_3*** *(957.839 cm^{-1})*
  - ***NH_2*** *(16741.3 cm-1)*
  - ***N_2O*** *(2062.026 cm^{-1})*
  - ***H_2O*** *(1348.186 cm^{-1})*

Beer-Lambert relation

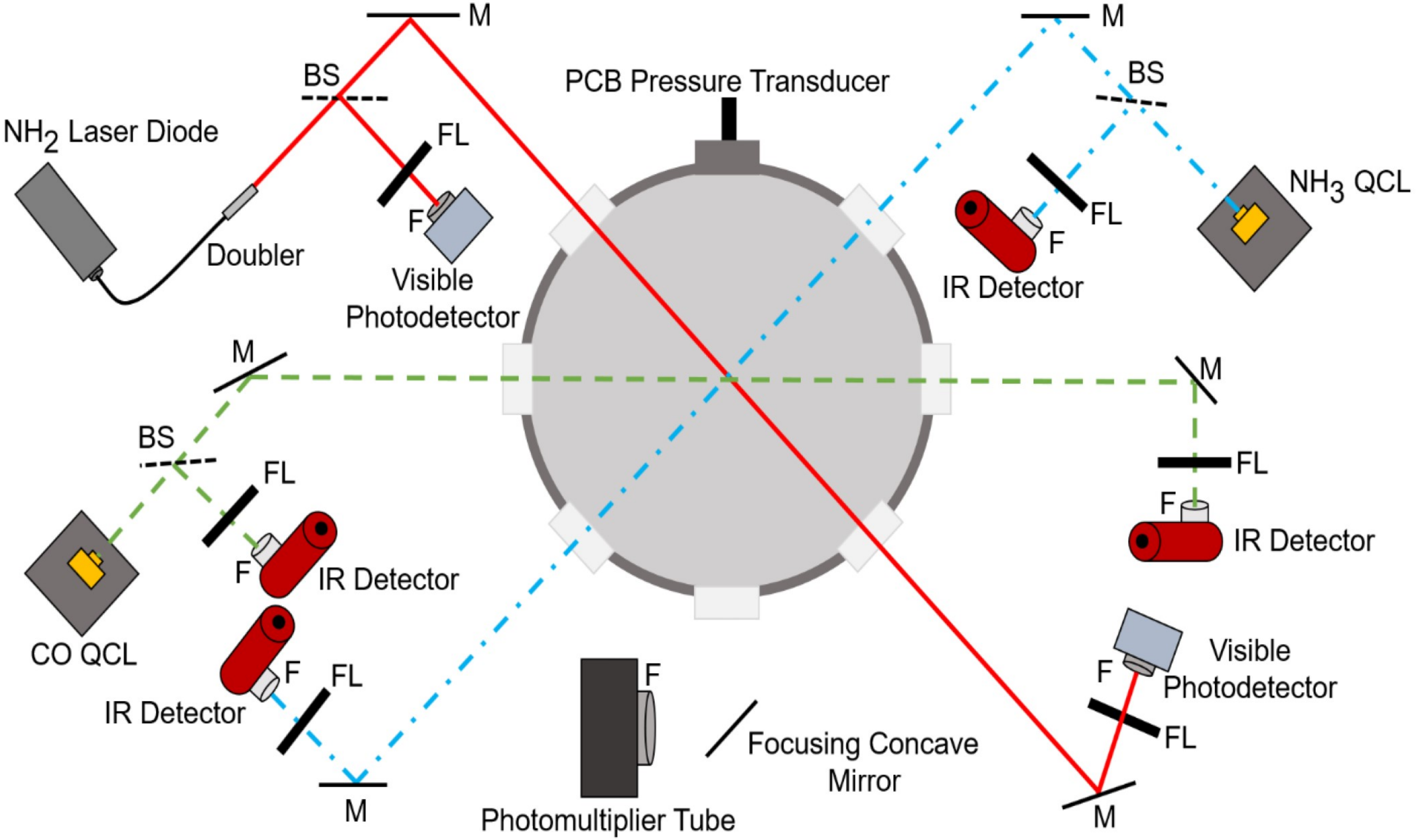
$$\frac{I_t}{I_0} = exp^{(-k_v PLX_{NH3})}$$



Experimental Method: Species Measurement in a ST

Simultaneous species

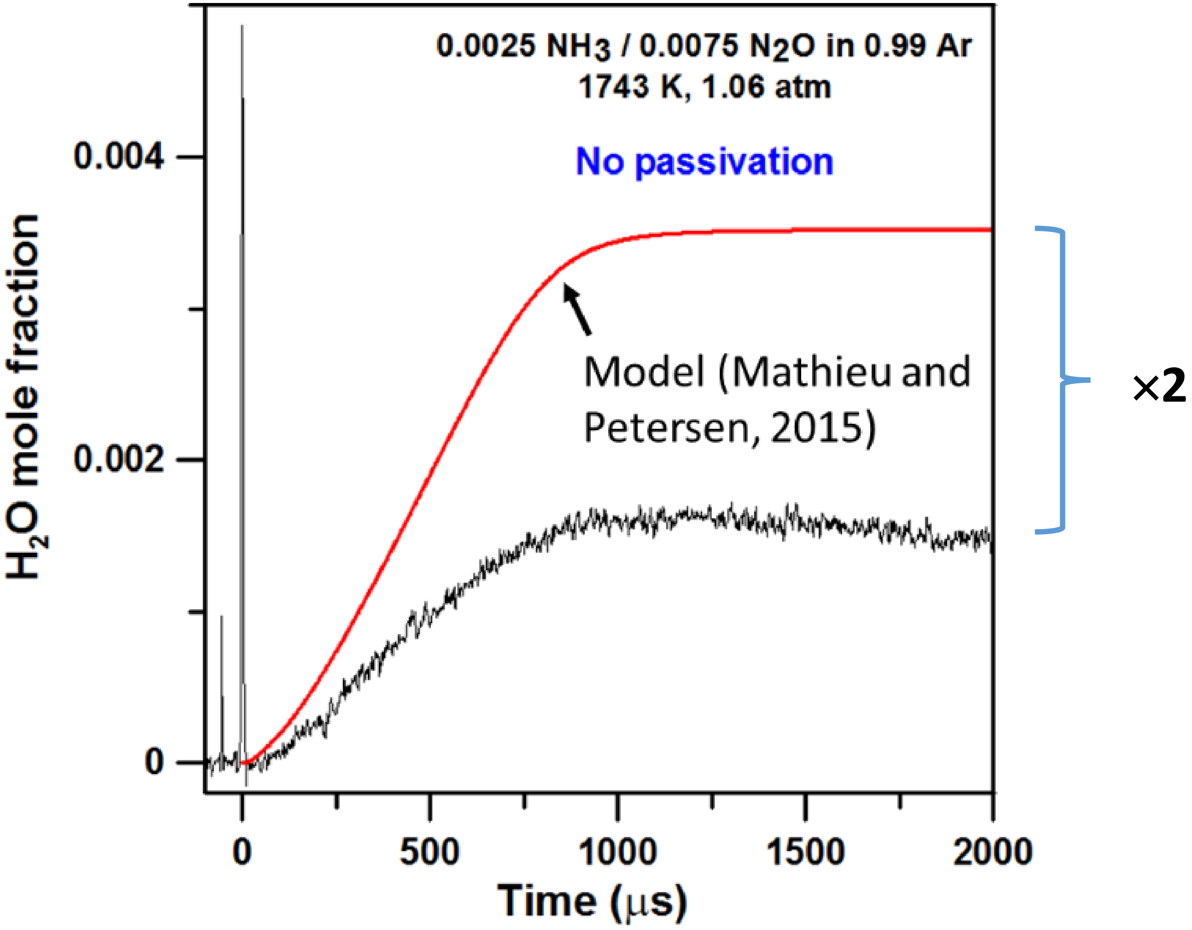
- ***NH_3*** *(957.839 cm^{-1})*
- ***NH_2*** *(16741.3 cm-1)*
- ***N_2O*** *(2062.026 cm^{-1})*



Experimental Method: pre-experiment preparation

NH_3 absorption on stainless steel is a big issue w/ dilute mixtures

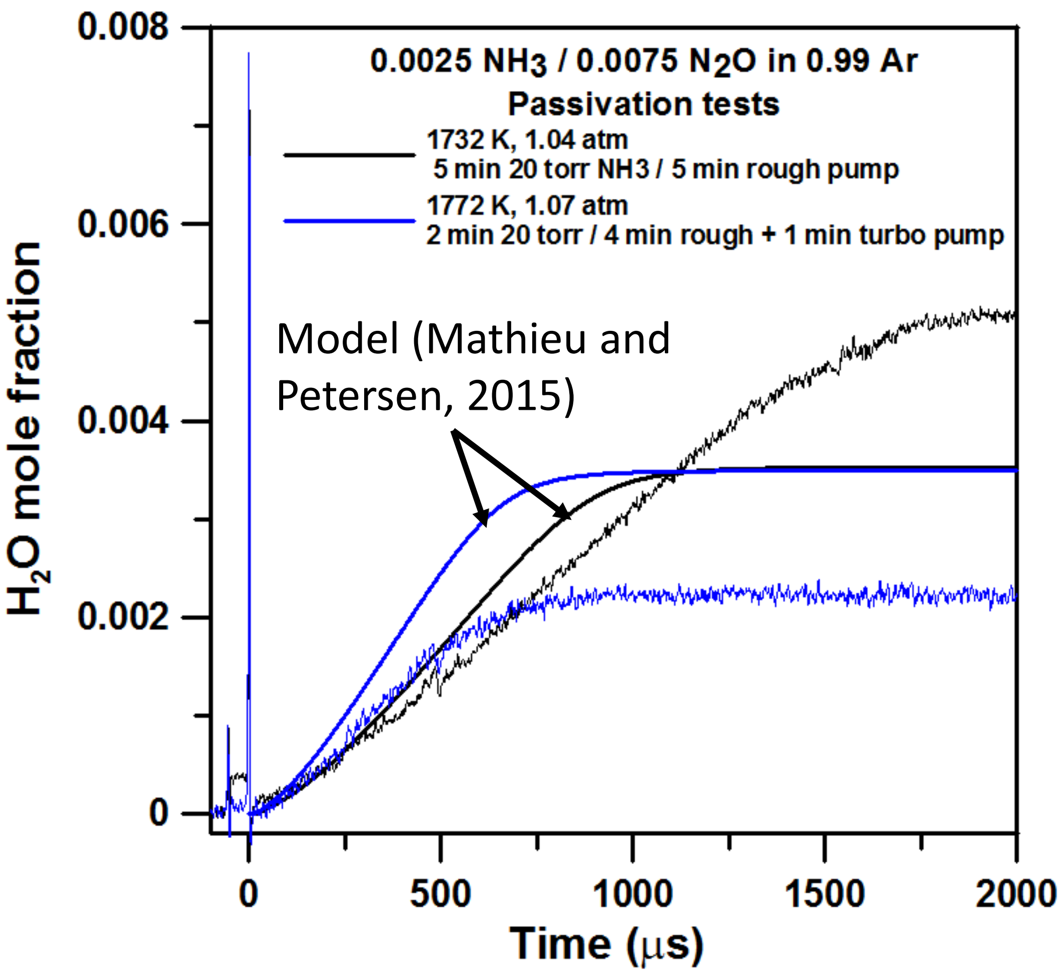
- **NH_3 adsorb on stainless steel => loss of NH_3 in initial mixture**



Experimental Method: pre-experiment preparation

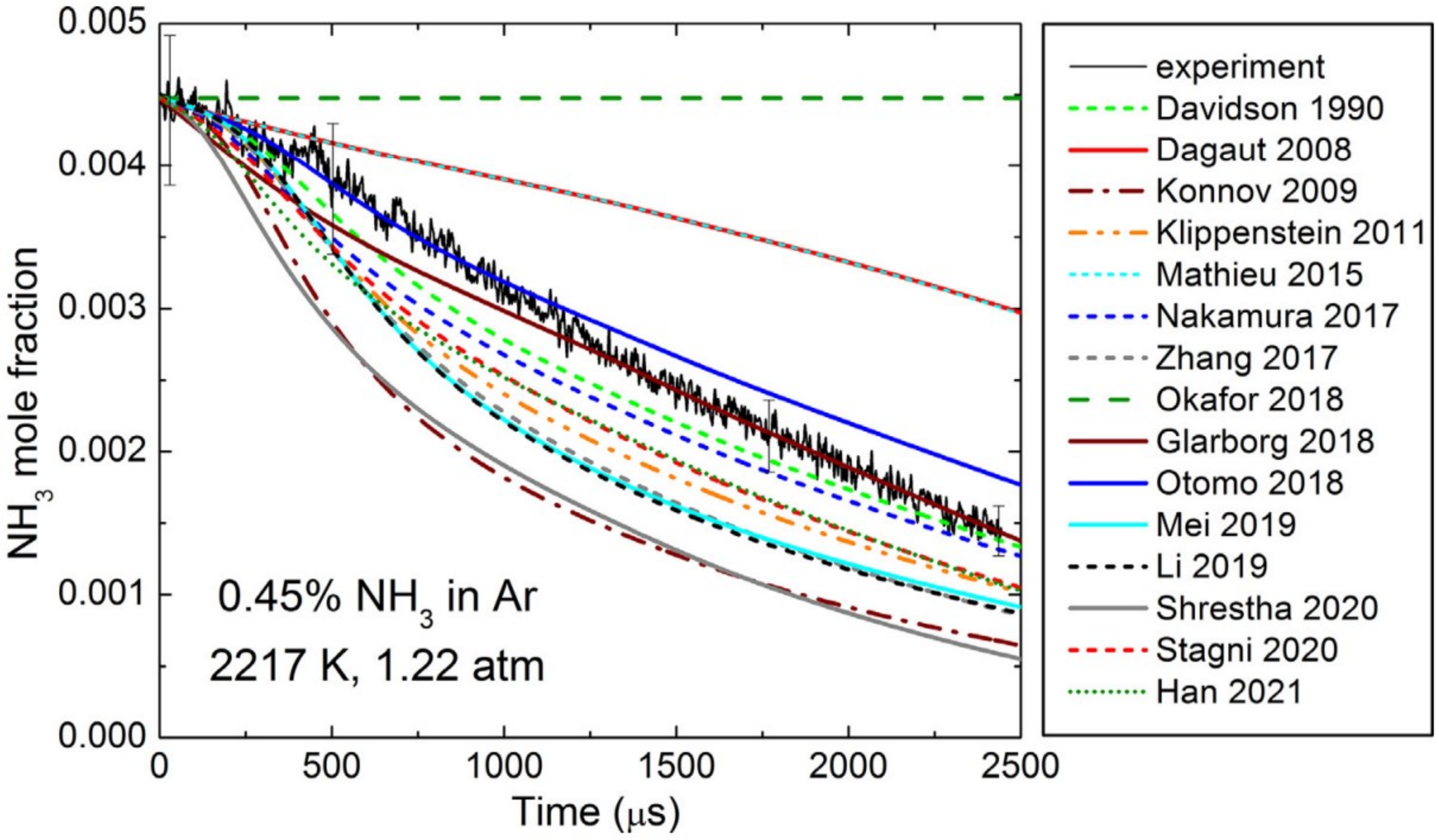
*Importance of surface passivation but **more** important to measure NH_3*

- **Passivation to mitigate this issue (introduce NH_3 to saturate surface and then vacuum/introduce the dilute mixture)**
- **Good and consistent passivation hard to obtain for dilute mixtures**
- **=> NH_3 measurement highly desired**



Experimental results

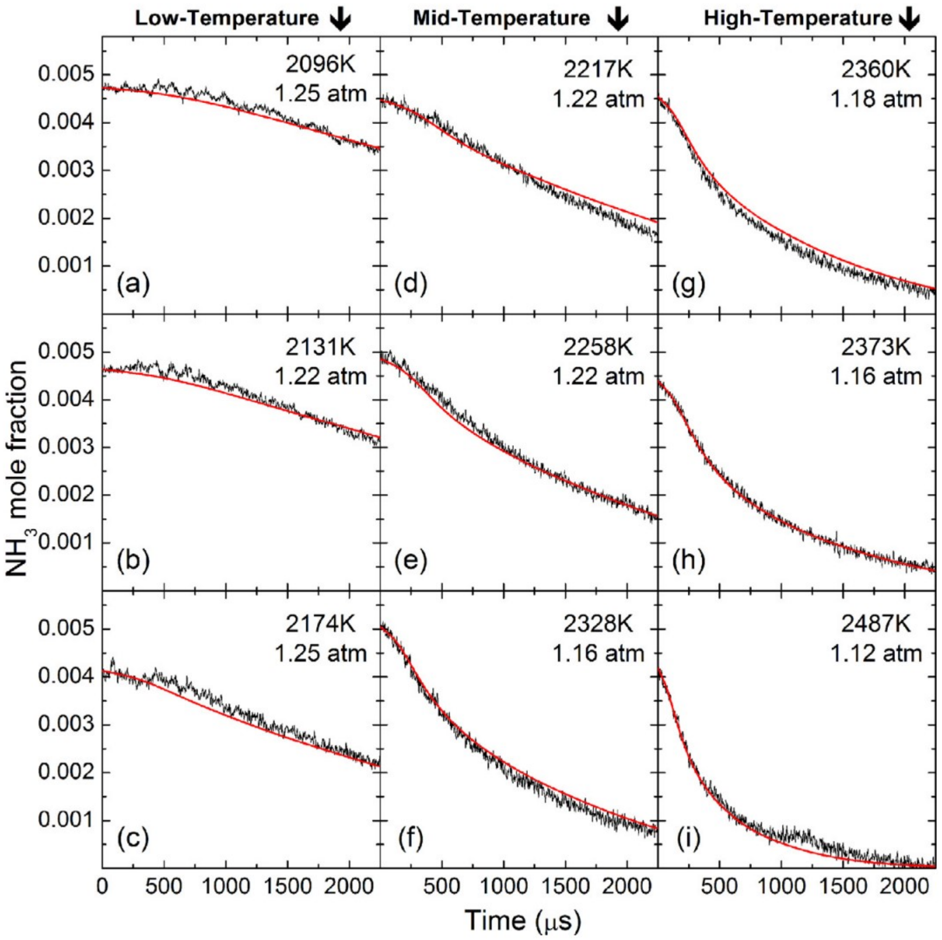
NH_3 Pyrolysis – Alturaifi et al., CNF 2022



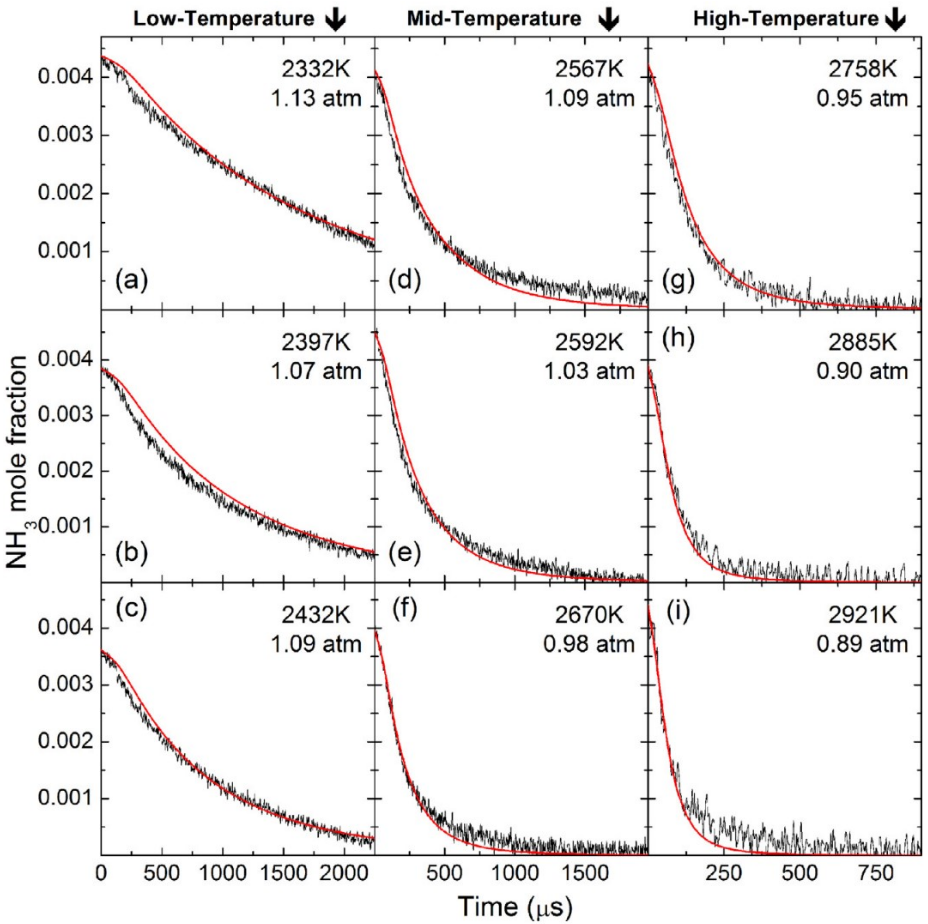
No model able to predict NH_3 pyrolysis

Experimental results

47 reactions pyrolysis model developed



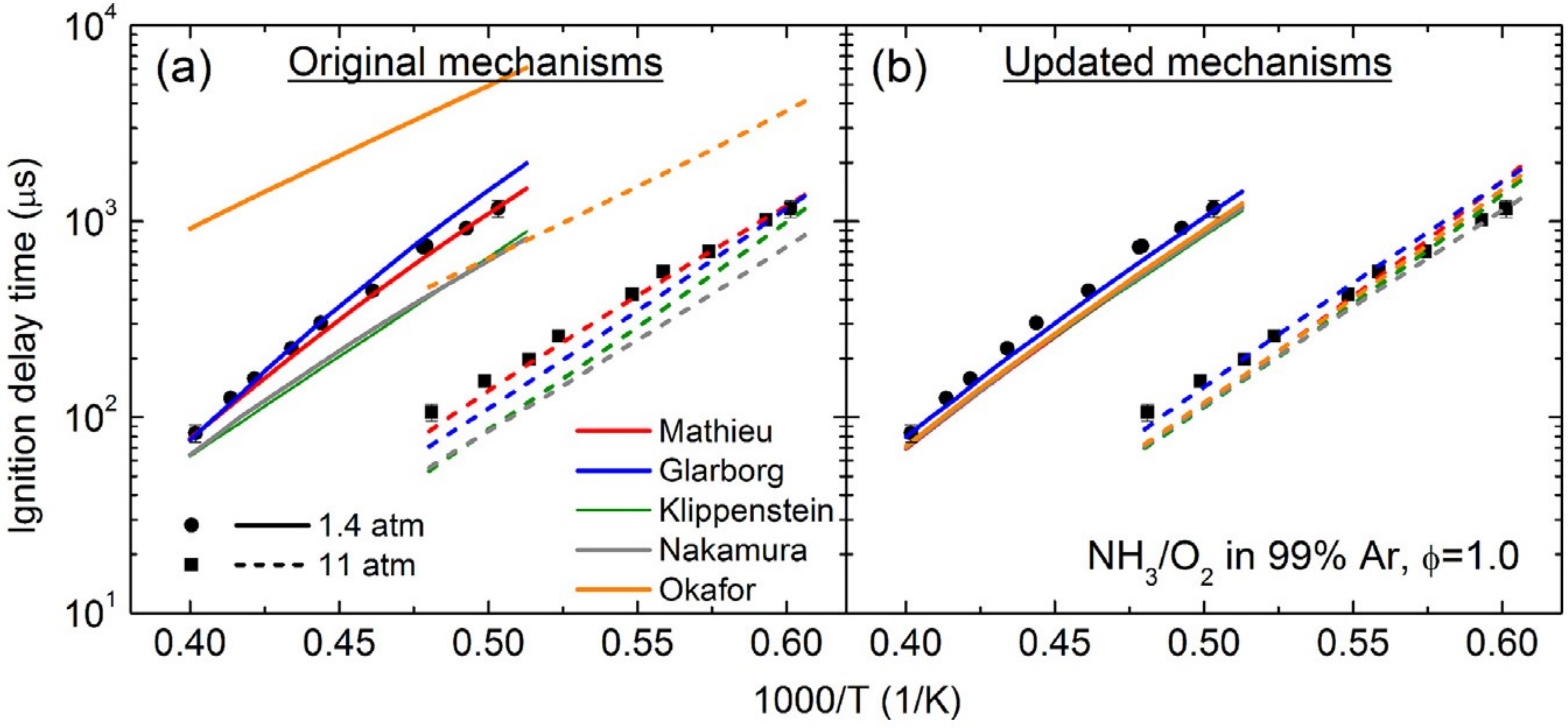
0.5% NH_3 in Ar



0.42% NH_3 /2% H_2 in Ar

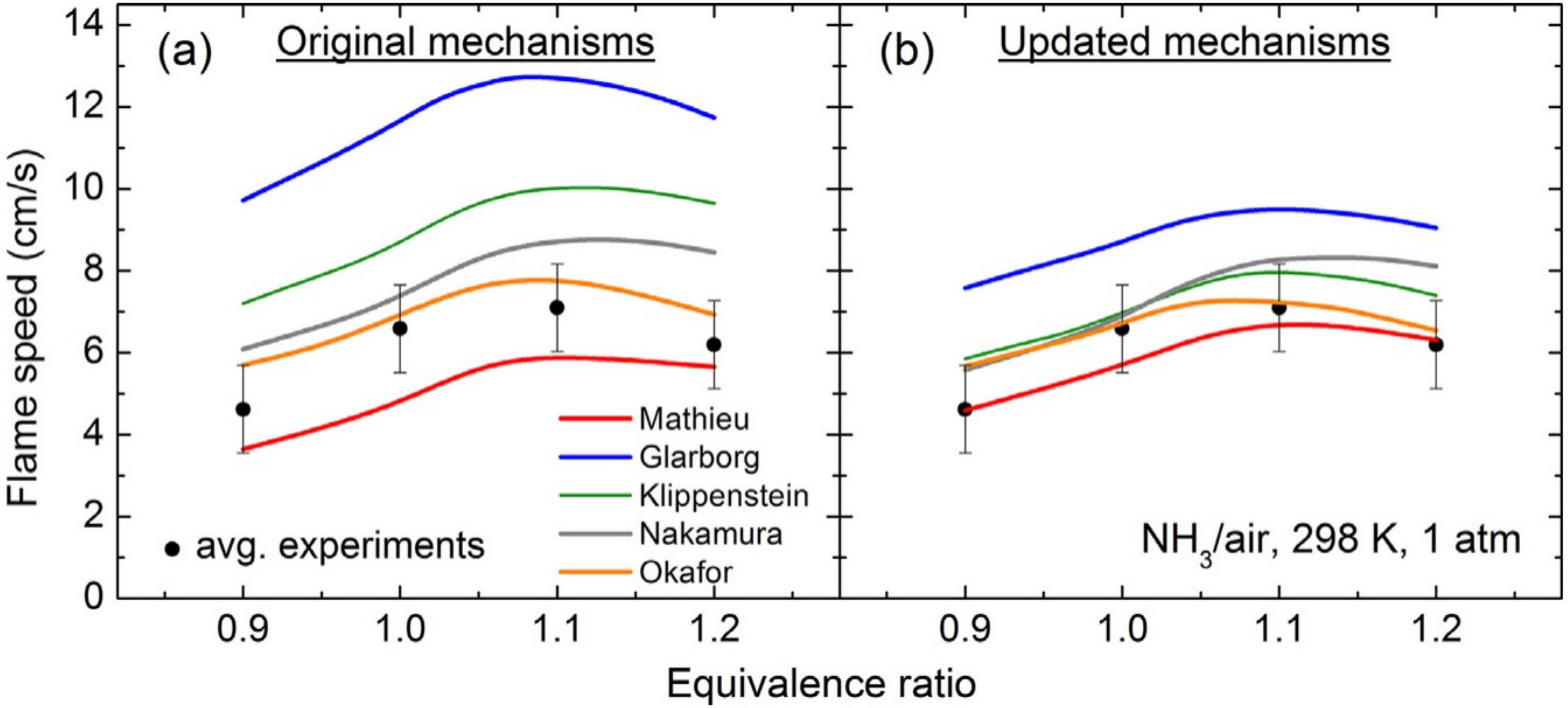
Experimental results

Critical importance of NH_3 pyrolysis to model NH_3 oxidation



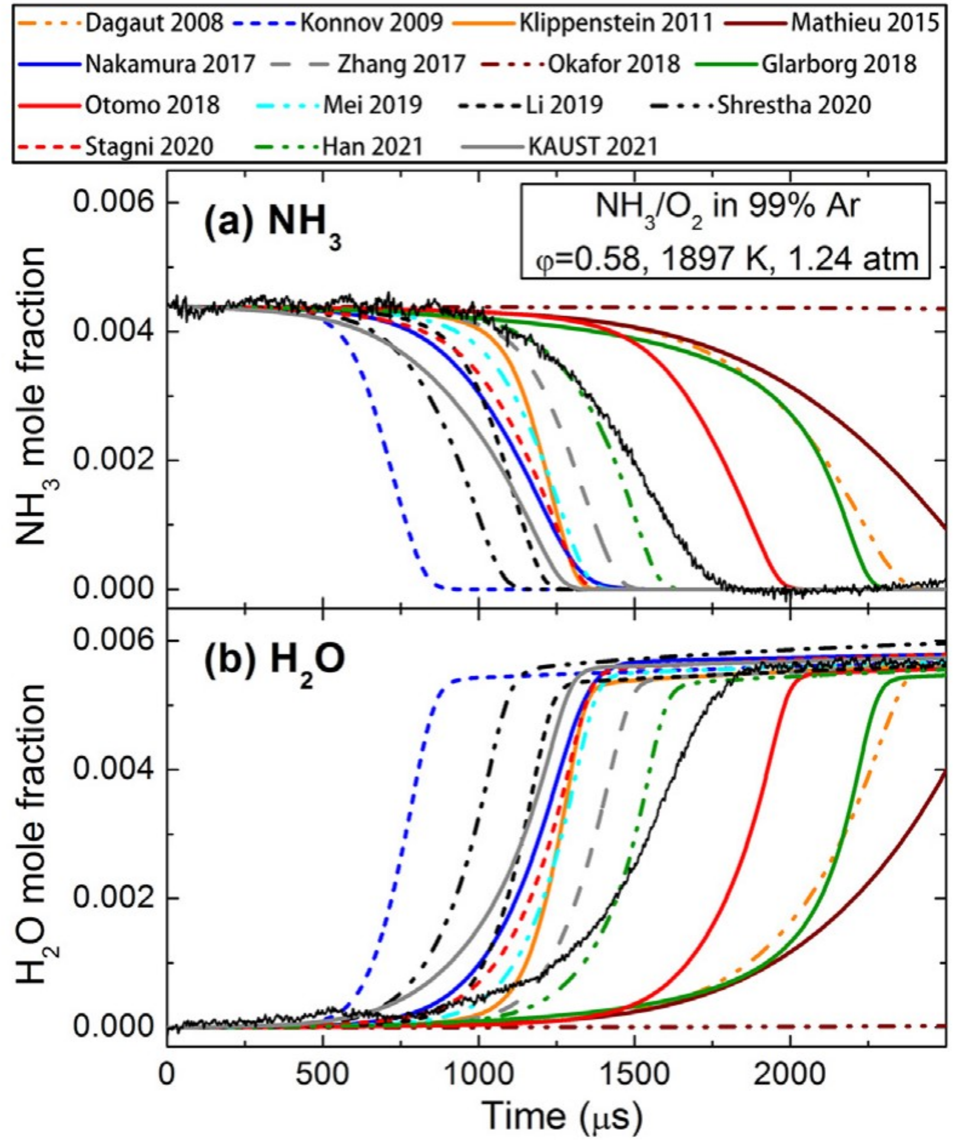
Experimental results

Critical importance of NH_3 pyrolysis to model NH_3 oxidation



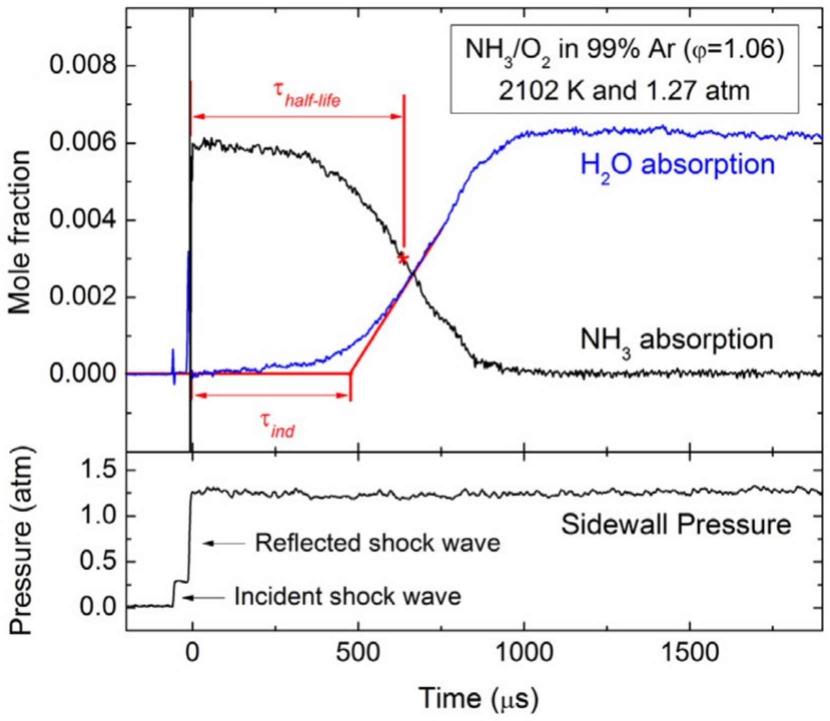
Experimental results

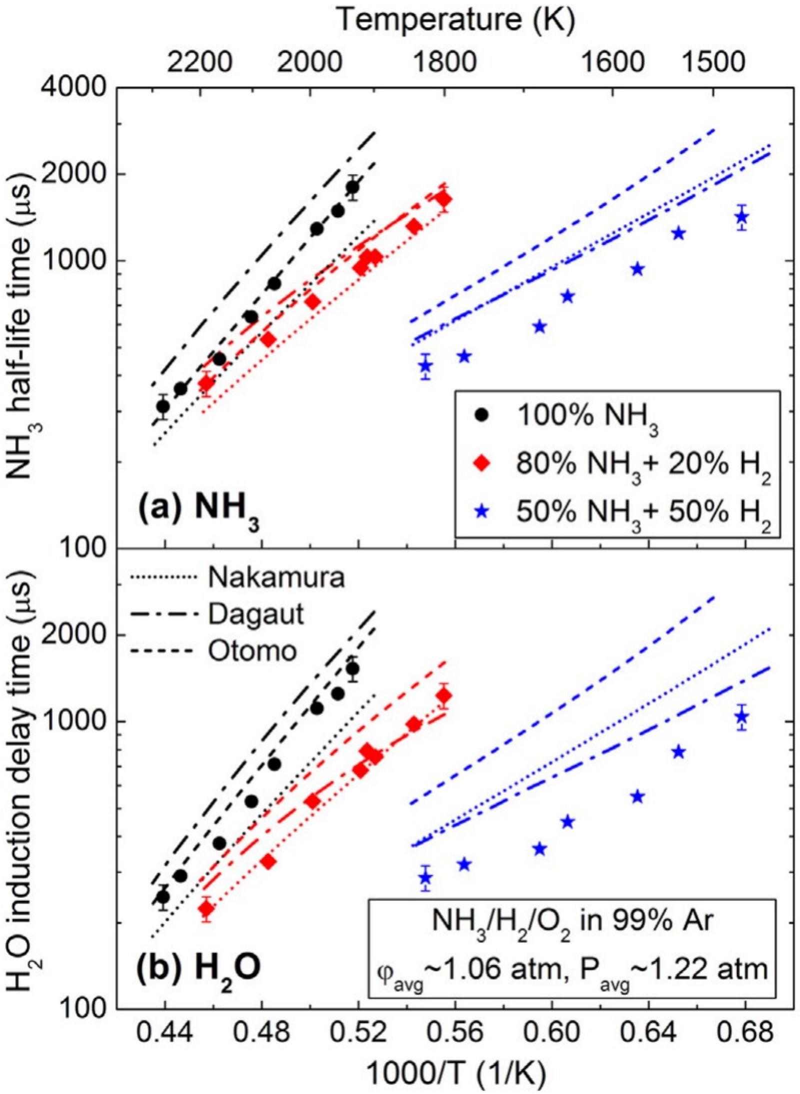
NH_3 and NH_3/H_2 Oxidation – Alturaifi et al., PROCI 2022



Experimental results

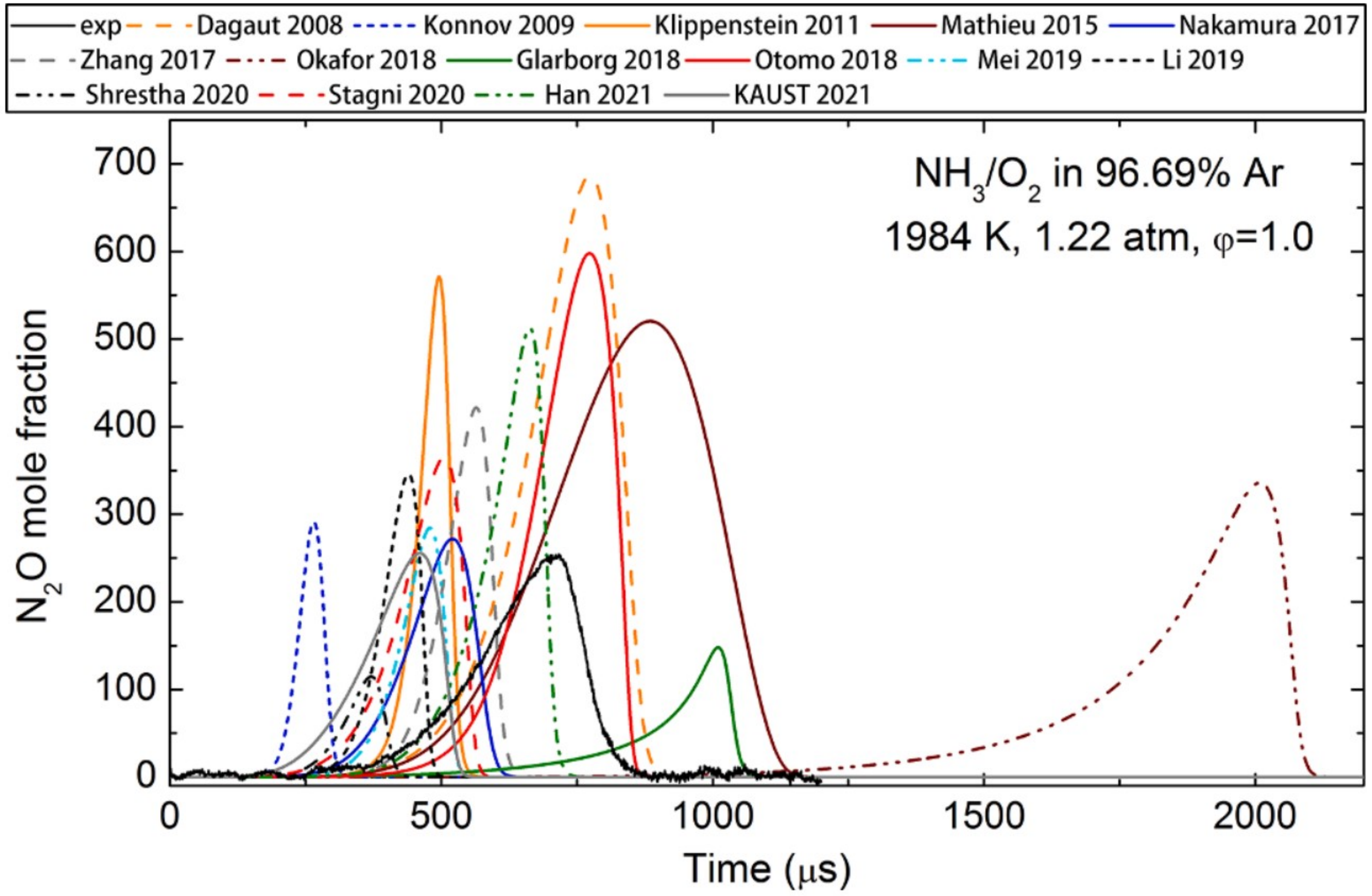
NH_3 and NH_3/H_2 Oxidation – Alturaifi et al., PROCI 2022





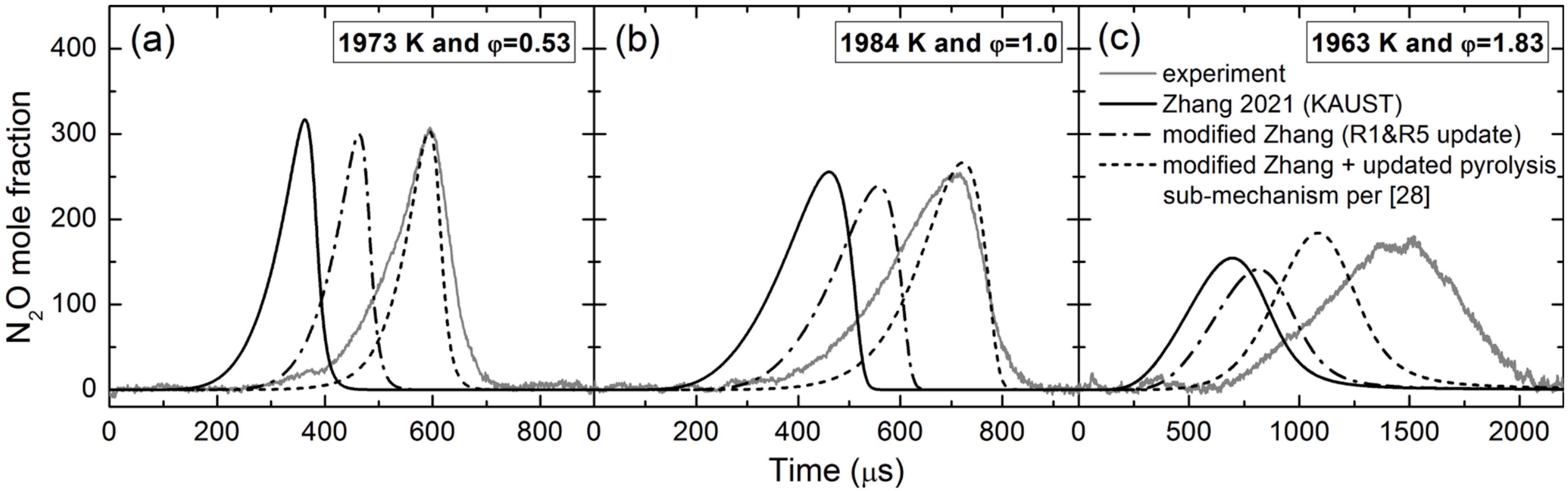
Experimental results

N_2O from NH_3 Oxidation – Alturaifi et al., Fuels Communication, 2022



Experimental results

N_2O from NH_3 Oxidation – Alturaifi et al., Fuels Communication, 2022

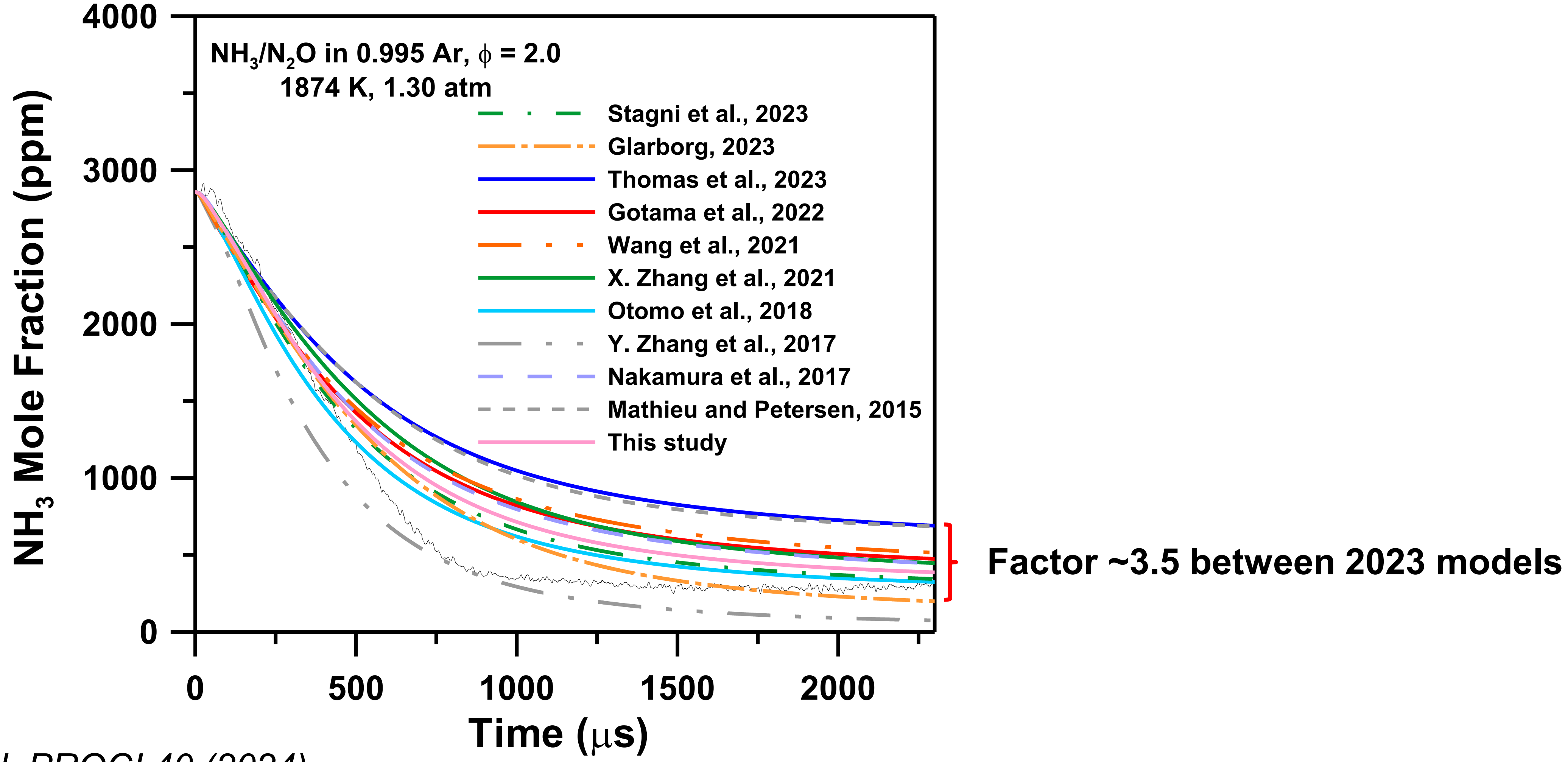


R1: $NH_3 + O_2 \rightleftarrows NH_2 + HO_2$

R5: $NH_3 + O \rightleftarrows NH_2 + OH$

Model Comparisons

NH_3 oxidation from N_2O

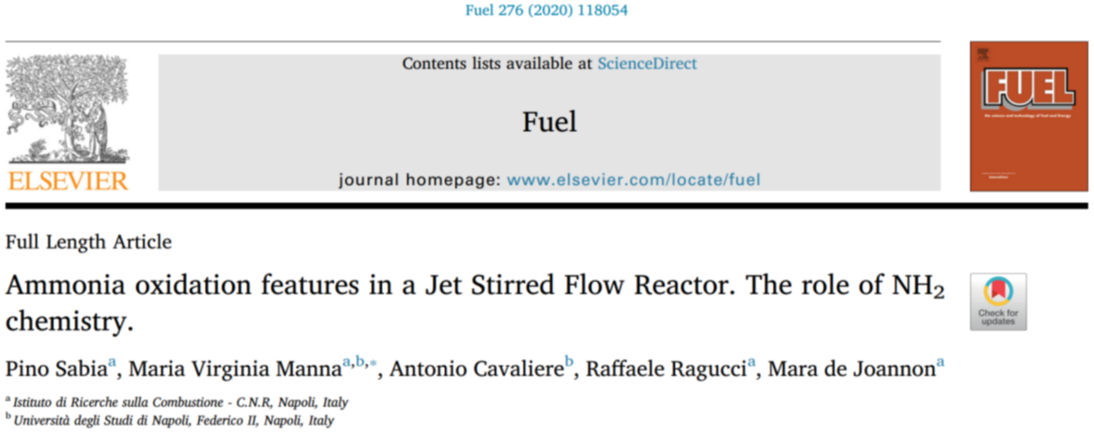


Mathieu et al. PROCI 40 (2024)

Latest results

NH_2 diagnostic developed at TAMU

- **Key species in ammonia combustion**
- **Several reaction pathways identified in literature:**
  - Path 1: $NH_2 \rightarrow NH \rightarrow N_2O \rightarrow N_2$,
  - Path 2: $NH_2 \rightarrow HNO \rightarrow NO \rightarrow N_2$,
  - Path 3: $NH_2 \rightarrow NH \rightarrow N_2H_2 \rightarrow NNH \rightarrow N_2$


Fuel 276 (2020) 118054

Contents lists available at ScienceDirect

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Full Length Article

Ammonia oxidation features in a Jet Stirred Flow Reactor. The role of NH_2 chemistry.

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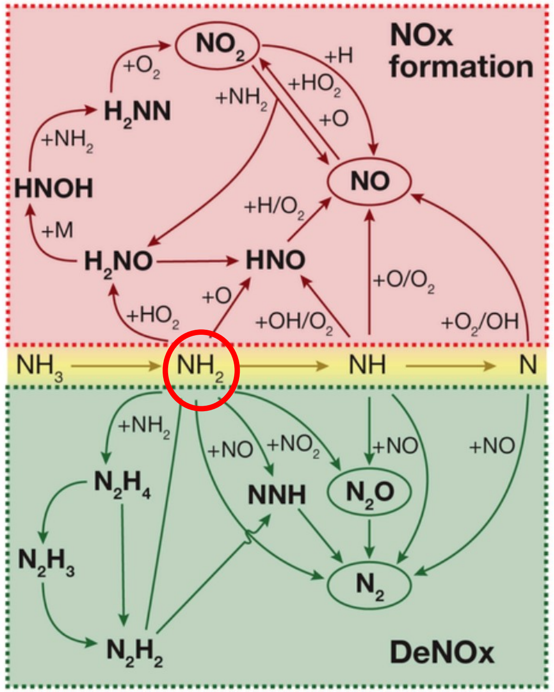
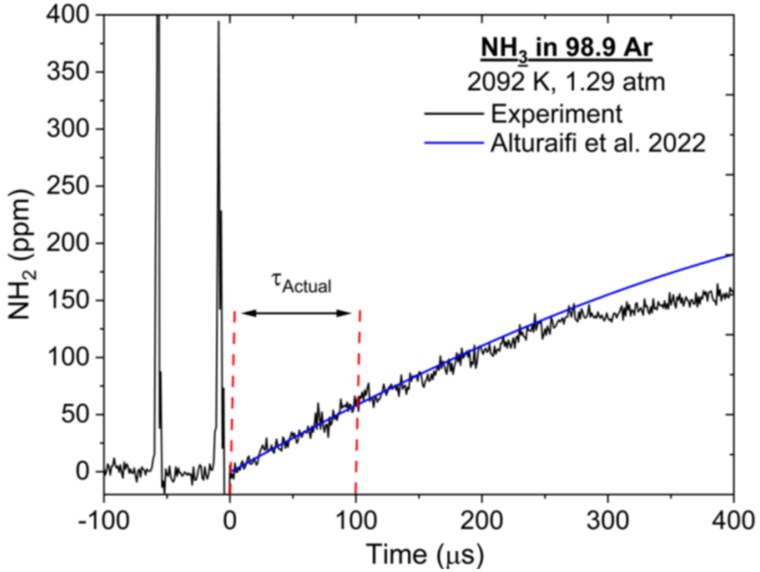


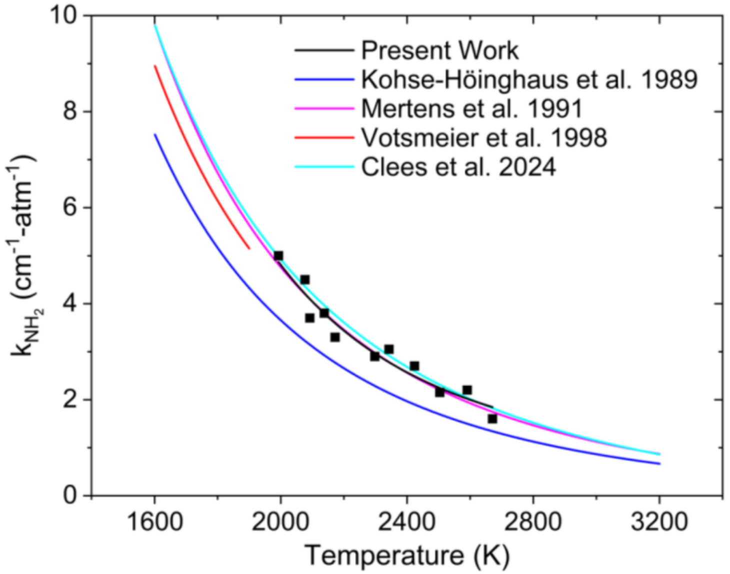
- **Simultaneous N_2O and NH_2 diagnostics to better assess the relative importance of these pathways**

Latest results

NH_2 diagnostic developed at TAMU

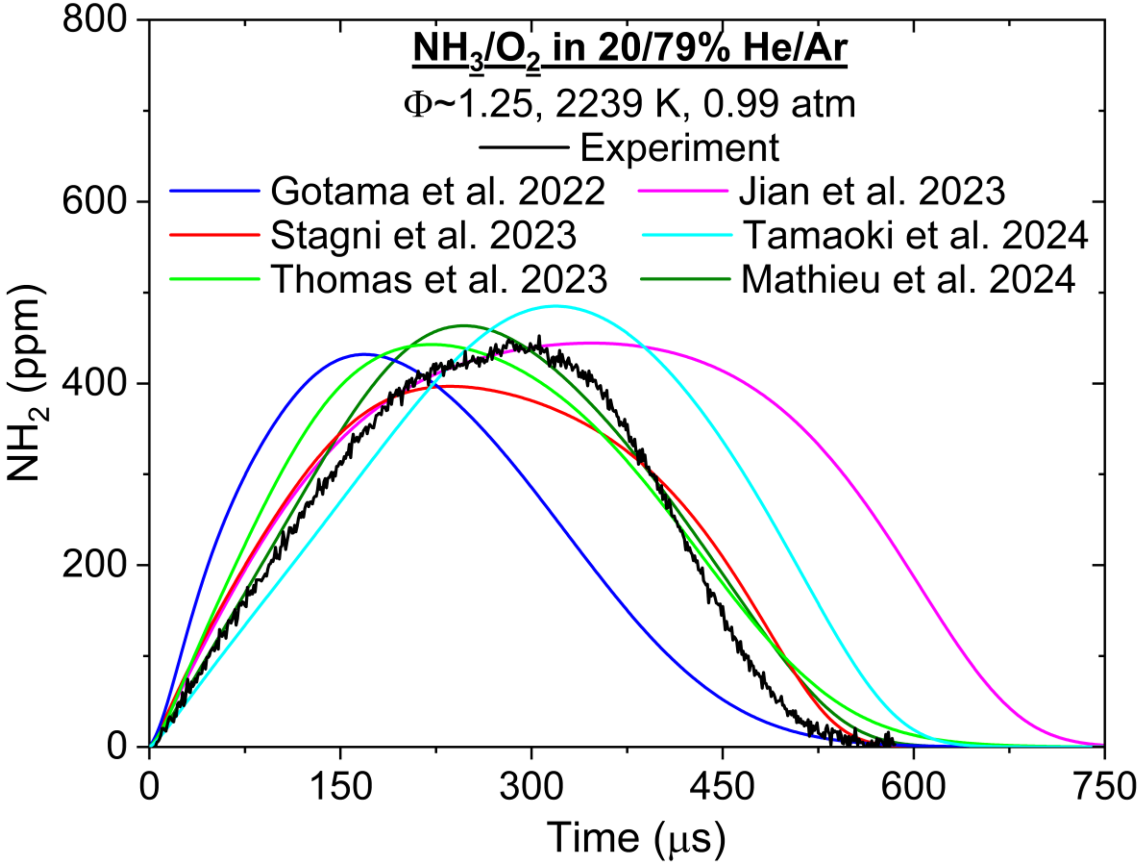
- **How to calibrate the diagnostic (absorption coefficient)?**
- **NH_2 needs to be produced at known concentration**
  - $CH_3NH_2 \rightarrow CH_3 + NH_2$ @ ST conditions
    - CH_3NH_2 used in Methamphetamine production…
- **Same method as in Kohse-Höinghaus et al. (1989)**
  - Using NH_3 detailed kinetic mechanism
    - NH_3 pyrolysis mechanism (Alturaifi et al., 2022)
  - Consider NH_2 predictions as long as no predicted consumption occurs

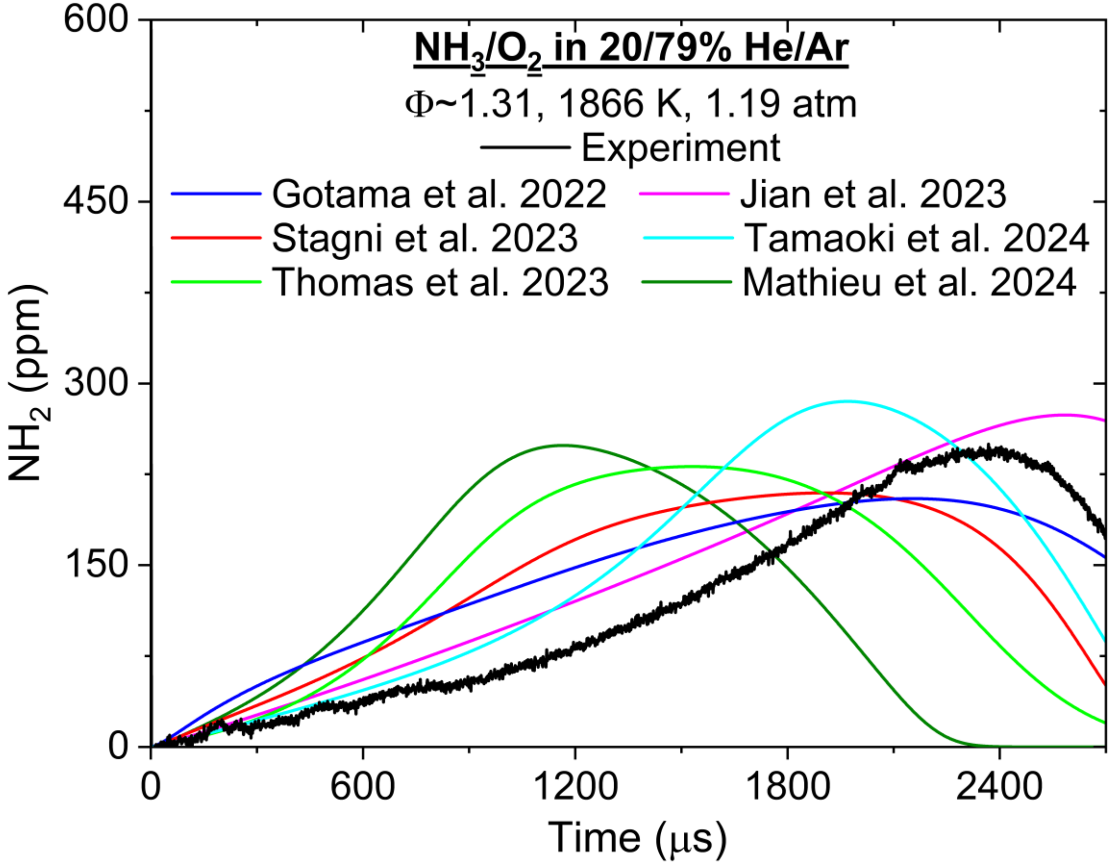




Latest results

NH_2 measurements at TAMU





G.J. Gotama, A. Hayakawa, E.C. Okafor, et al. *Combust. Flame* 236 (2022) 111753.
D.E. Thomas, K.P. Shrestha, F. Mauss, W.F. Northrop, *Proc. Combust. Inst.* 39 (2023) 1803–1812.
J. Jian, H. Hashemi, H. Wu, P. Glarborg, *Appl. En. Combust. Sci.* 14 (2023) 100137.
A. Stagni, S. Arunthanayothin, M. Dehue, et al. *Chem. Eng. J.* 471 (2023) 144577.
O. Mathieu, C.M. Gregoire, E. L. Petersen, *Proc. Combust. Inst.* 40 (2024) 105250.
K. Tamaoki, Y. Murakami, K. Kanayama, T. Tezuka, M. Izumi, H. Nakamura, *Comb. Flame* 259 (2024) 116177.

Conclusions

- **Results showed:**
  - Critical importance of:
    - Accurate measurements
    - Pyrolysis chemistry
  - Models still in need of improvements
    - Large discrepancies between models
    - Overall, latest models are the most accurate
  - More data & more work on the models are necessary (radicals)

Future directions

- Ammonia pyrolysis (NH_3 + NH_2)
- NH_2 + N_2O during NH_3 combustion

NH_3 combustion radicals need to be measured

HCs combustion: CO_2, H_2O, CO, H_2, CH_4, CH_2O, CH_3OH, C_2H_2, C_2H_4, C_2H_6, C_2H_5OH, CH_3CHO….

NH_3 combustion: N_2, H_2, H_2O, N_2O, NOx. N_2H_x: instable/dangerous to work with

=> NH_3 combustion chemistry for radicals more critical than for HCs

Acknowledgments

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