Recent progresses on NH_3 combustion chemistry using optical diagnostics and their impact on kinetics model development

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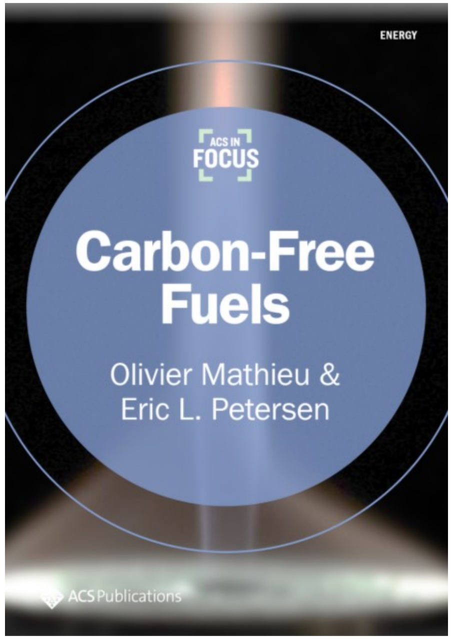
Ammonia Combustion Technical Working Group meeting agenda
January 9, 2024

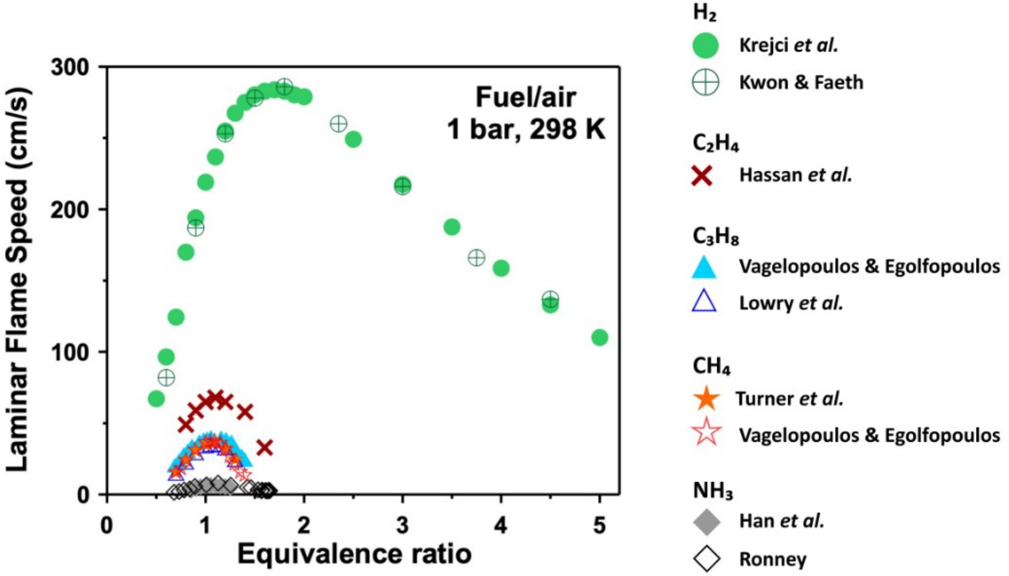
Introduction

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

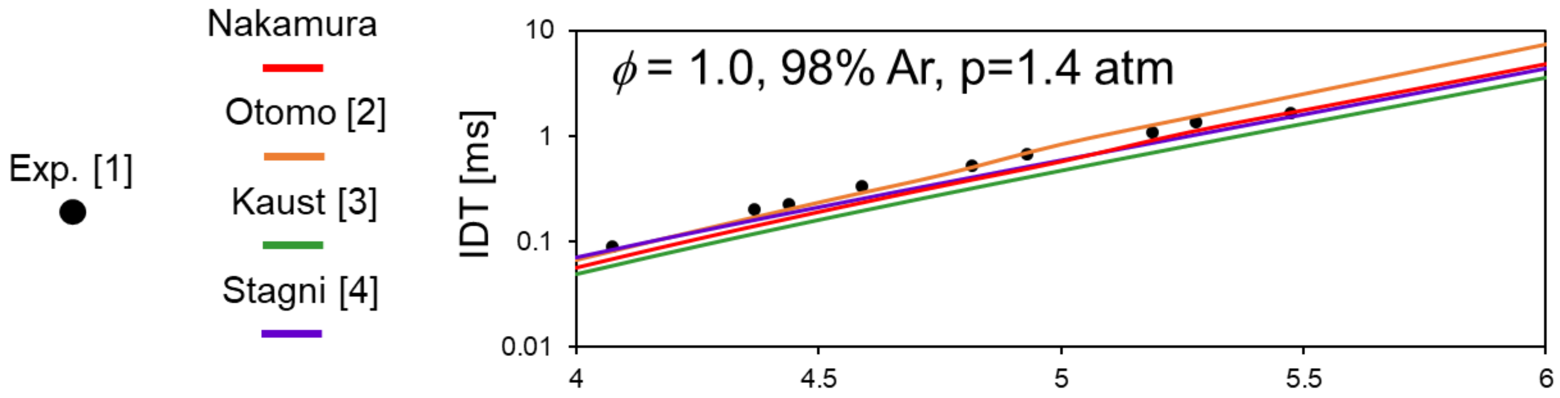
- Turbines and ICEs need to be designed around the fuel they use
- Global kinetics data (Ignition delay time, laminar flame speed) relate to key combustion properties in real-world applications => useful to set the dimensions
- Detailed chemistry needed for pollutants (NO, NO_2) and GHG (N_2O) emissions
- 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…

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

=> Models w/ different reaction schemes can achieve the same (good) predictions

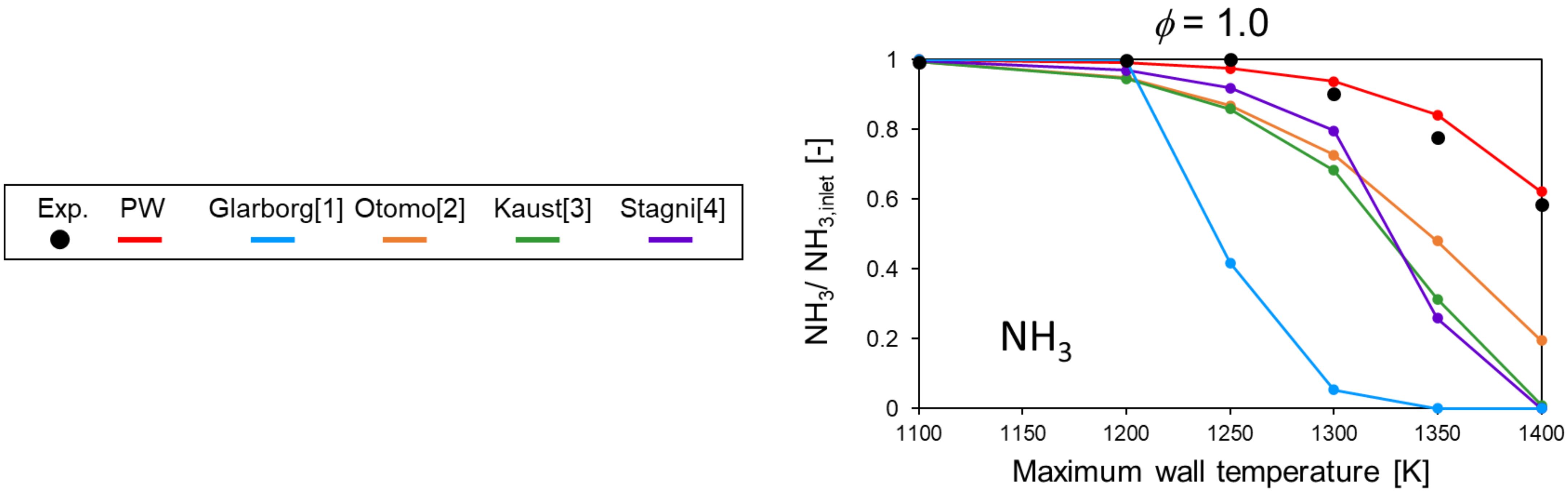


[1] O. Mathieu et al., Combust. Flame 162 (2015) 554-570. [2] J. Otomo et al., *Int. J. Hydrogen Energy*, 43 (2018) 3004–3014.
[3] X. Zhang et al., *Combust. Flame*, 234 (2021) 111653. [4] A. Stagni et al., *React. Chem. Eng.*, 5 (2020) 696–711.

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

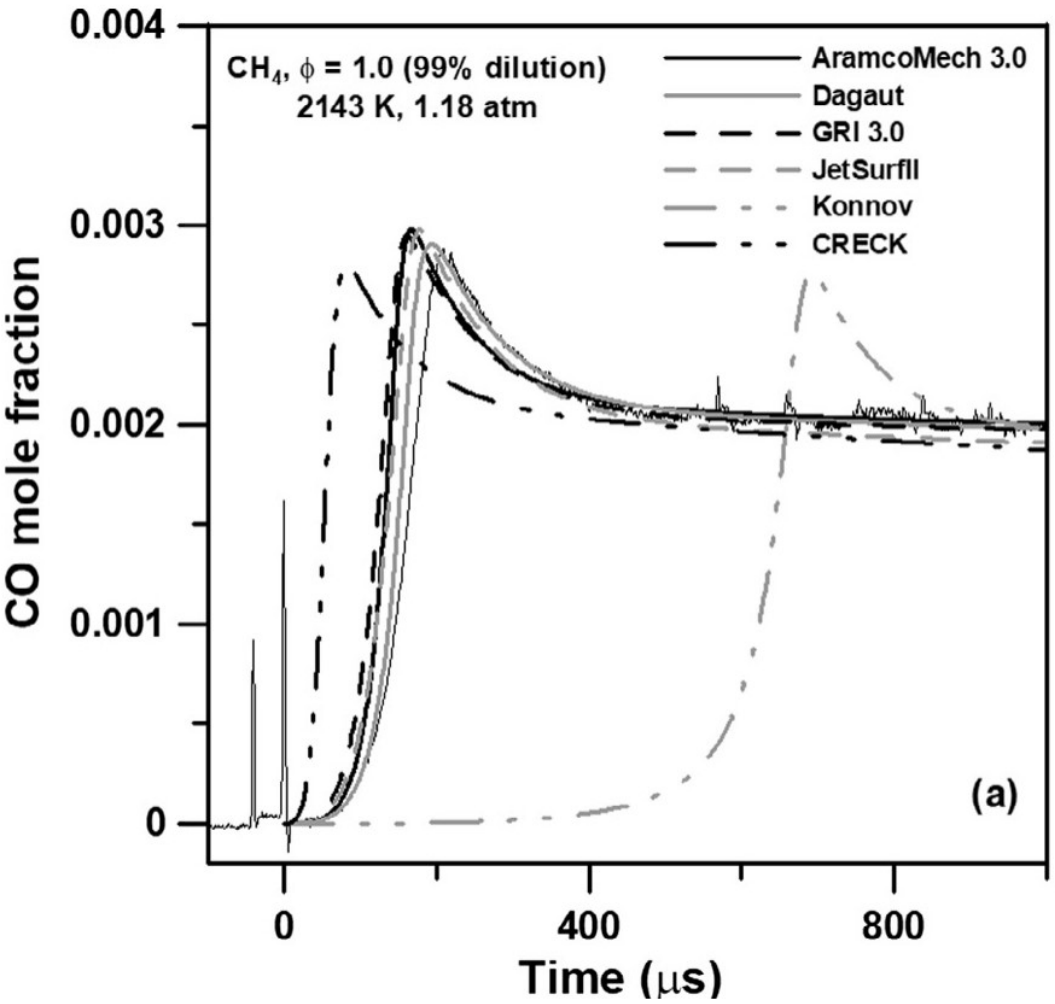


[1] P. Glarborg, J. A. Miller et al., *Prog. Energy Combust. Sci.*, 67 (2018) 31–68. [2] J. Otomo et al., *Int. J. Hydrogen Energy*, 43 (2018) 3004–3014.
[3] X. Zhang et al., *Combust. Flame*, 234 (2021) 111653. [4] A. Stagni et al., *React. Chem. Eng.*, 5 (2020) 696–711.

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



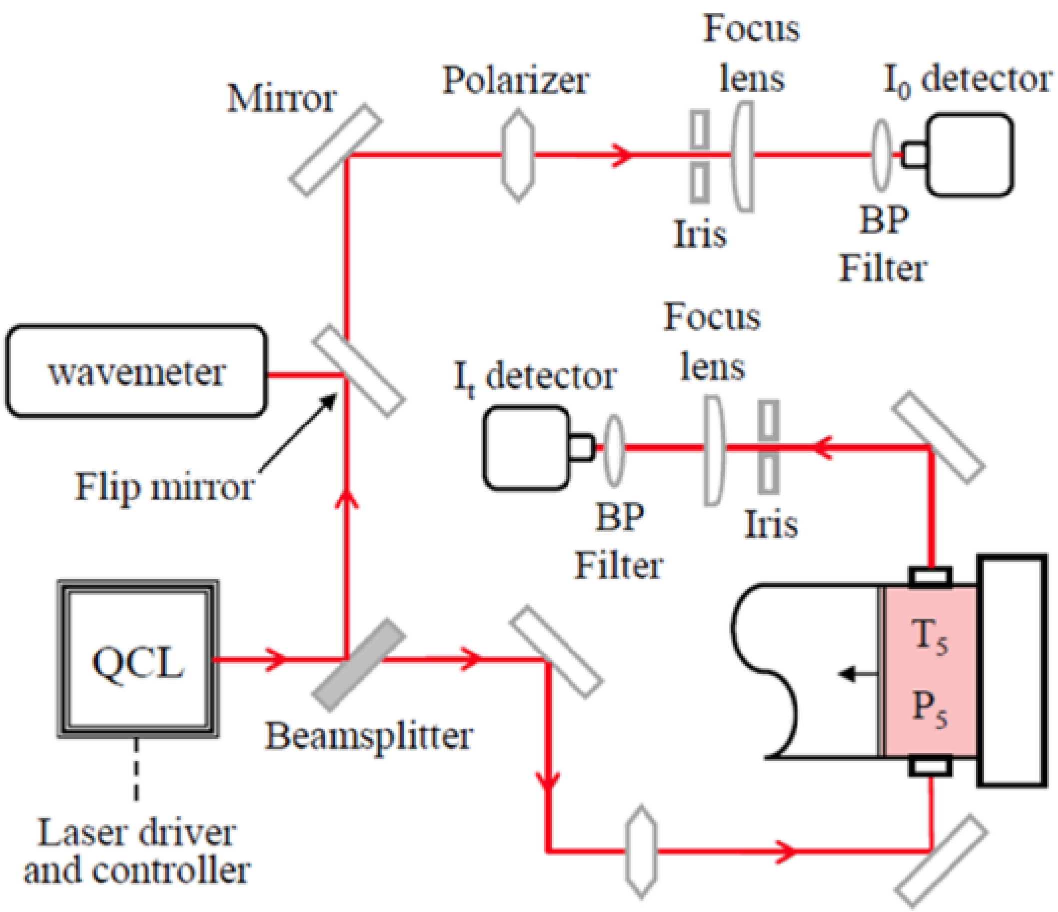
Experimental Method: Species Measurement in a ST

Absorption Laser Diagnostic

- *Quantum Cascade Lasers for:*
  - ***NH_3*** *(957.839 cm^{-1})*
  - ***N_2O*** *(2192.474 cm^{-1})*
  - ***H_2O*** *(1348.186 cm^{-1})*

Beer-Lambert relation

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

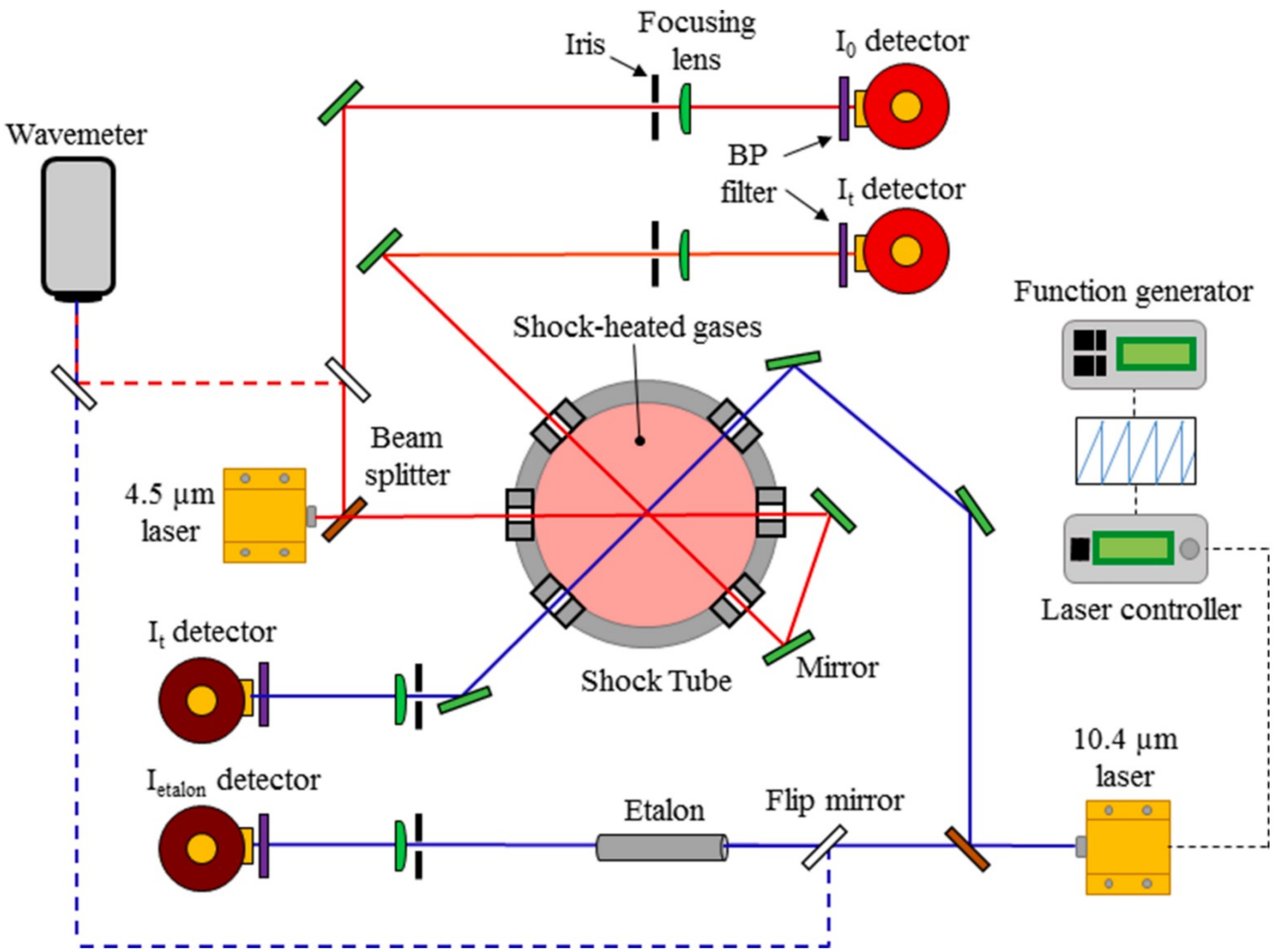


Experimental Method: Species Measurement in a ST

Simultaneous species

- ***NH_3*** *(957.839 cm^{-1})*
- ***N_2O*** *(2192.474 cm^{-1})*

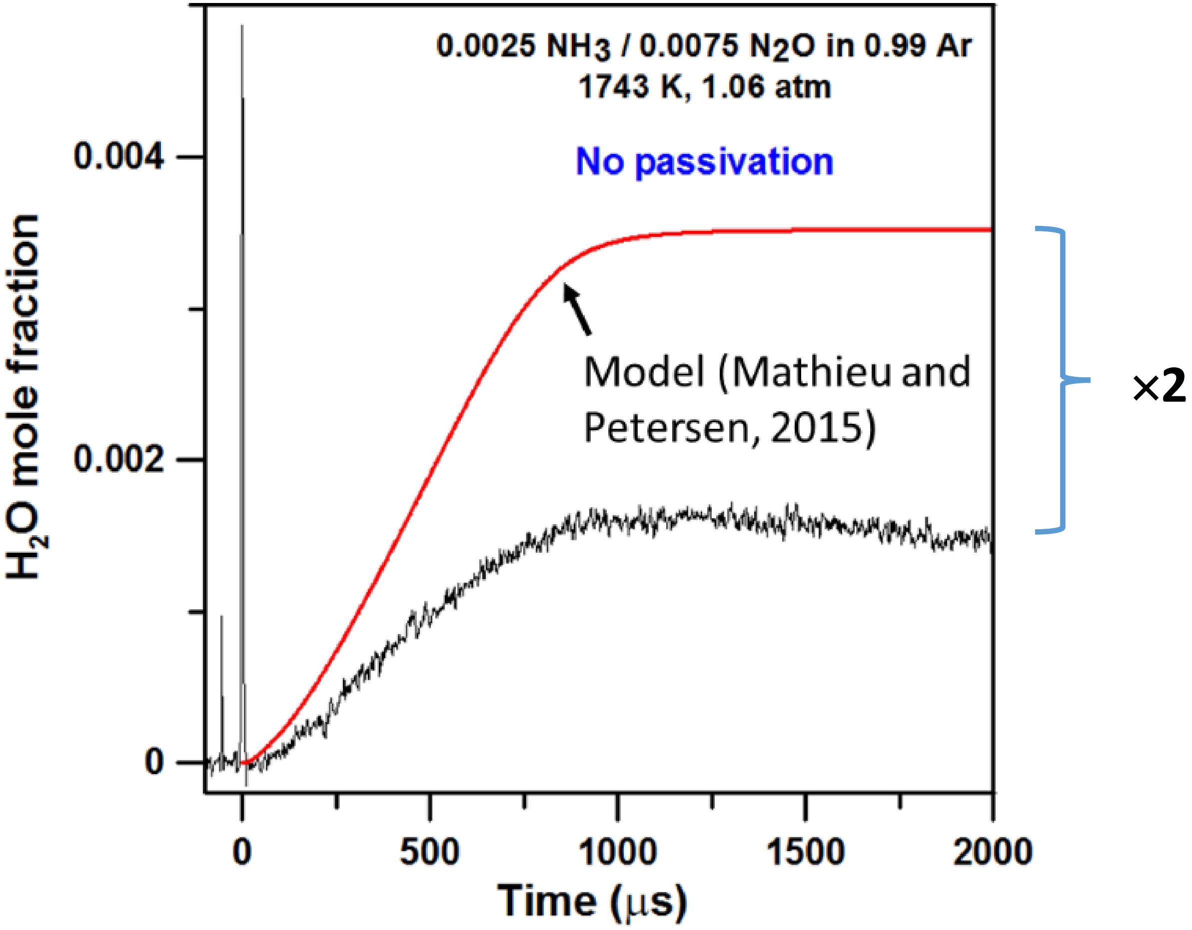
Necessitate double pass



Experimental Method: Mixture preparation

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

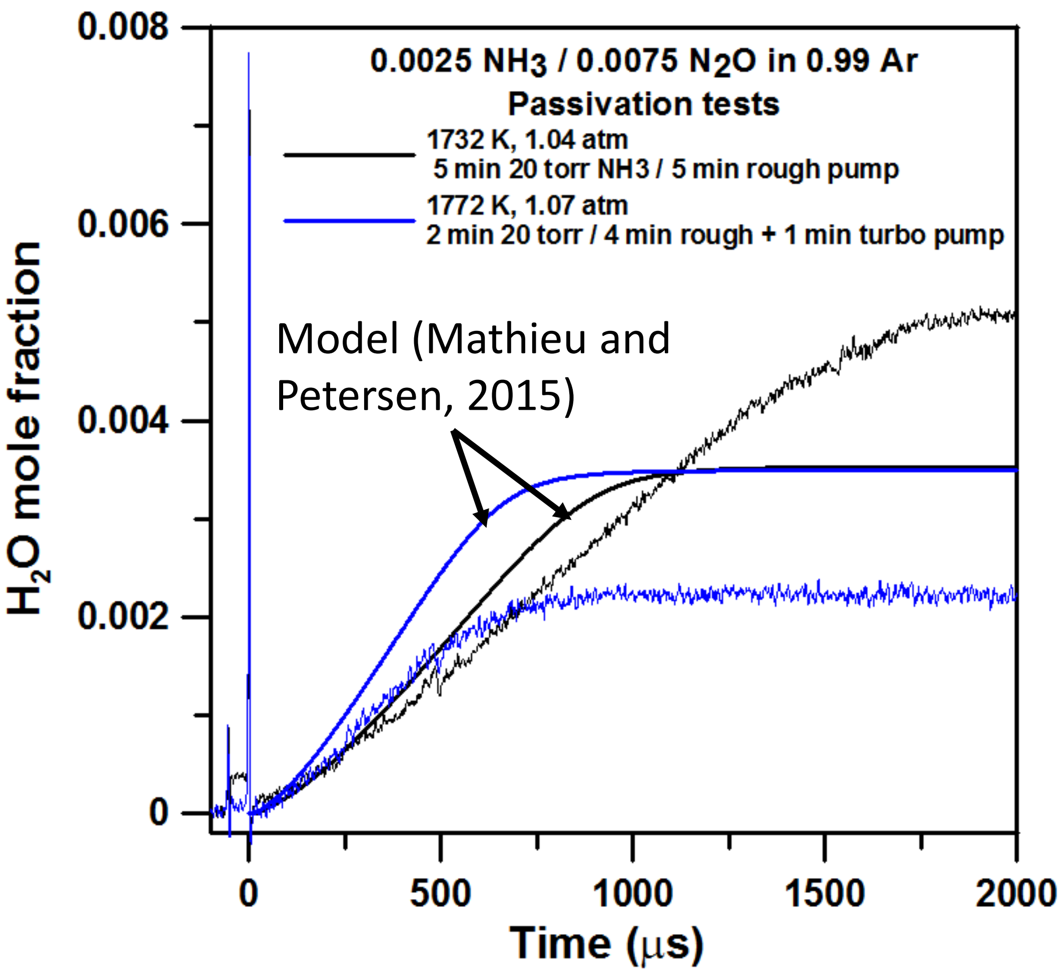
- **NH_3 adsorb on stainless steel => loss of NH_3 in initial mixture**



Experimental Method: Mixture 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**



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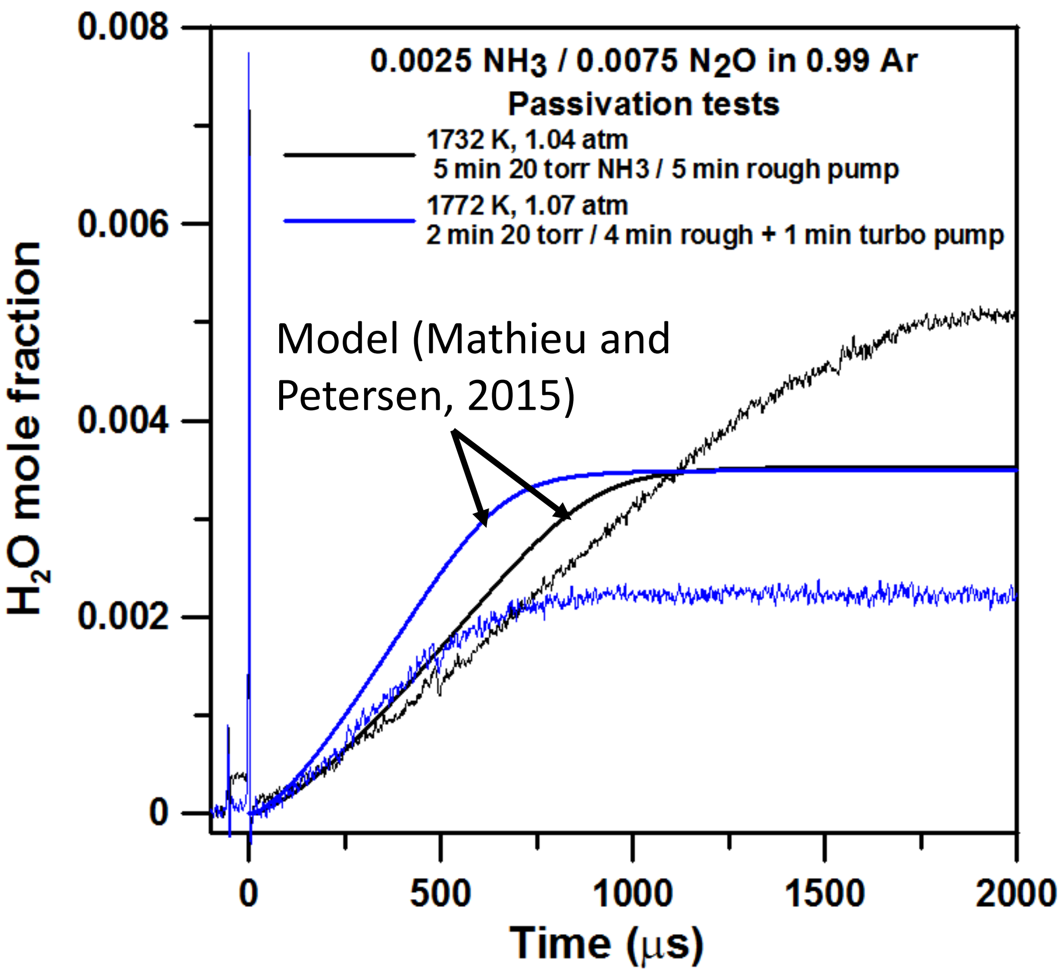
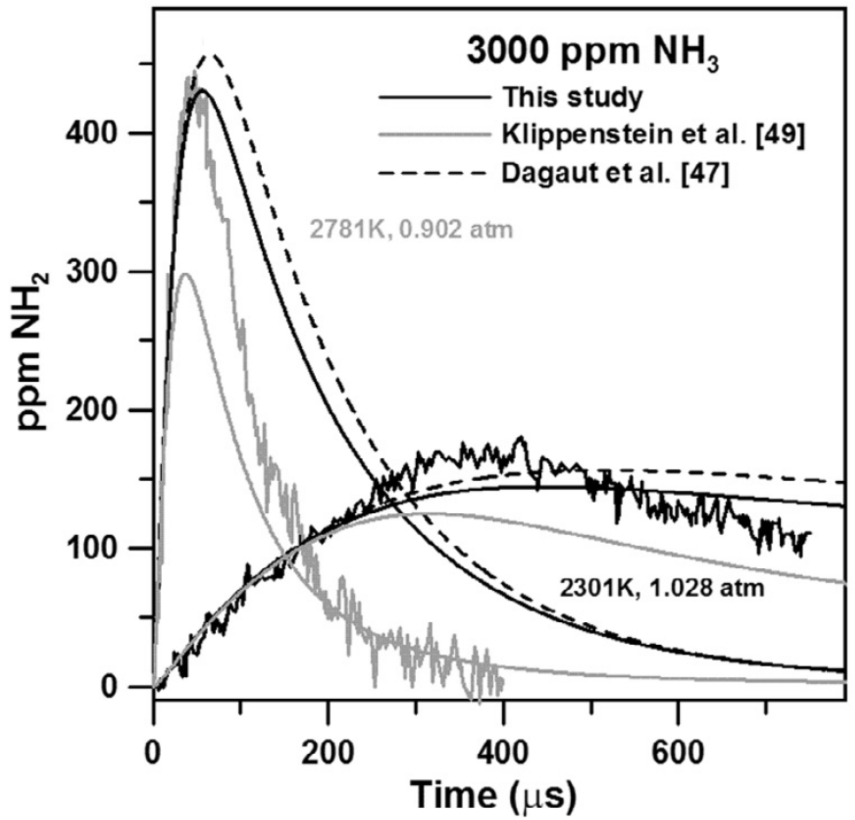
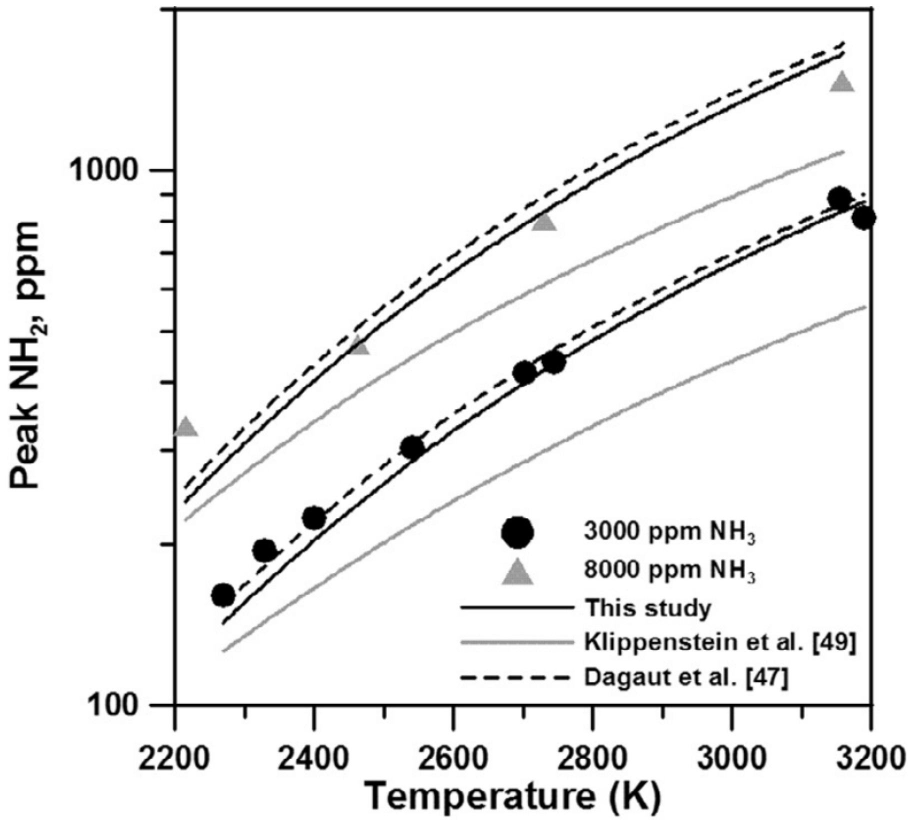


Importance of accurate NH_3 measurement

Models are validated against data w/ passivation => <u>How good are they?</u>

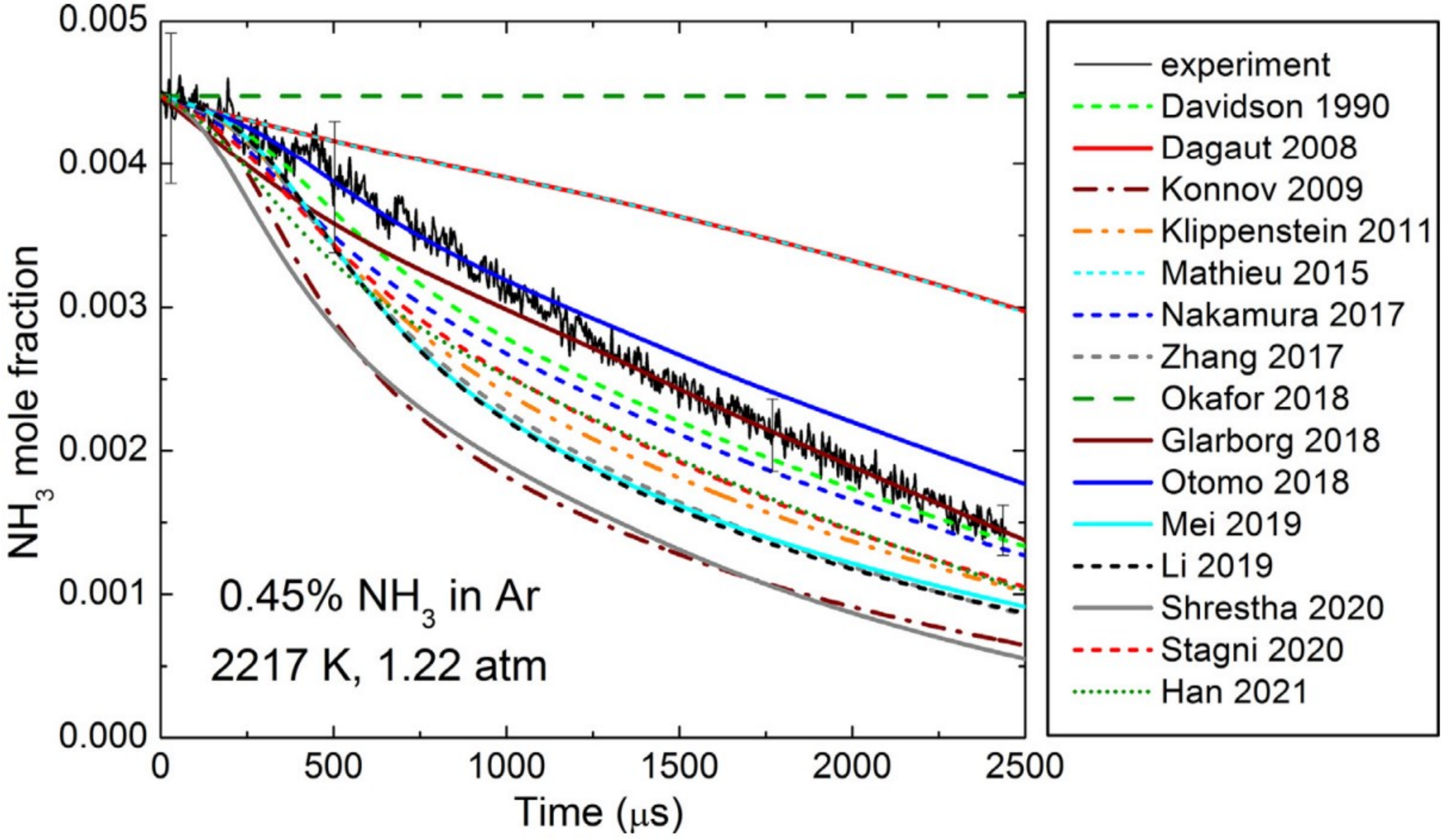




Data: D.F. Davidson, K. Kohse-Hoinghaus, A.Y. Chang, R.K. Hanson, Int. J. Chem. Kinet. 22 (1990) 513–535.

Experimental results

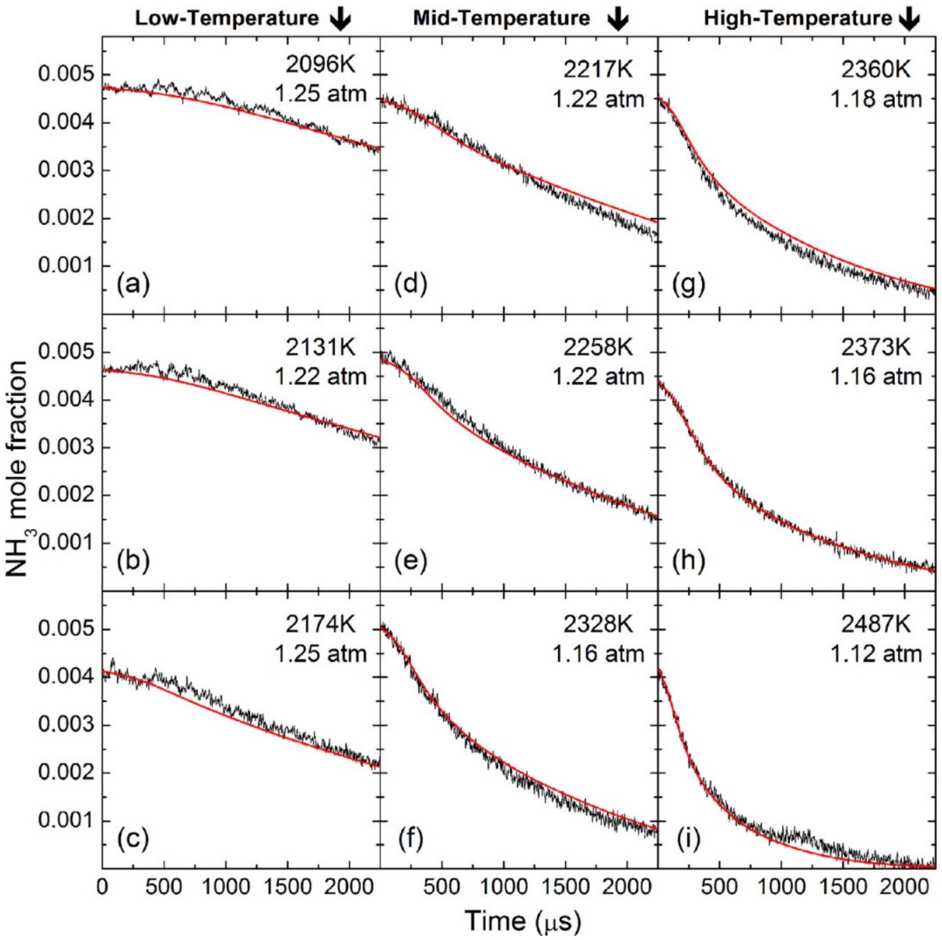
NH_3 Pyrolysis – Alturaifi et al., CNF 2022



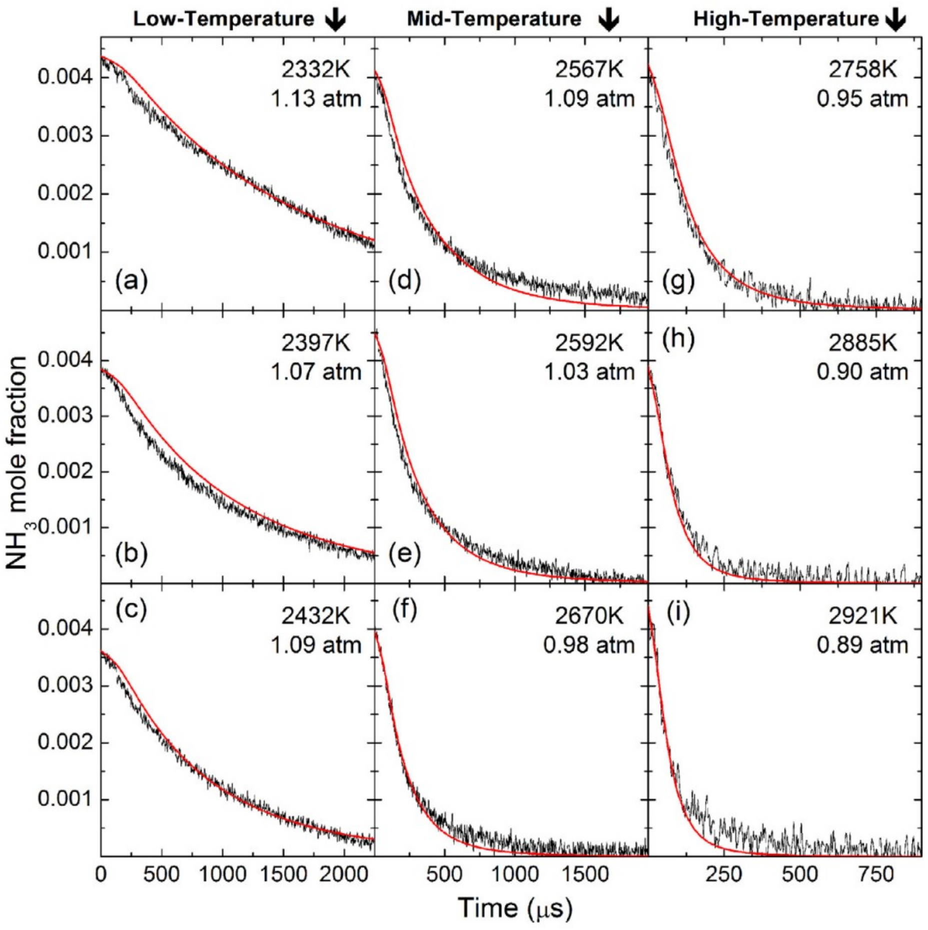
No model able to predict NH_3 pyrolysis

Experimental results

47 reactions pyrolysis model developed



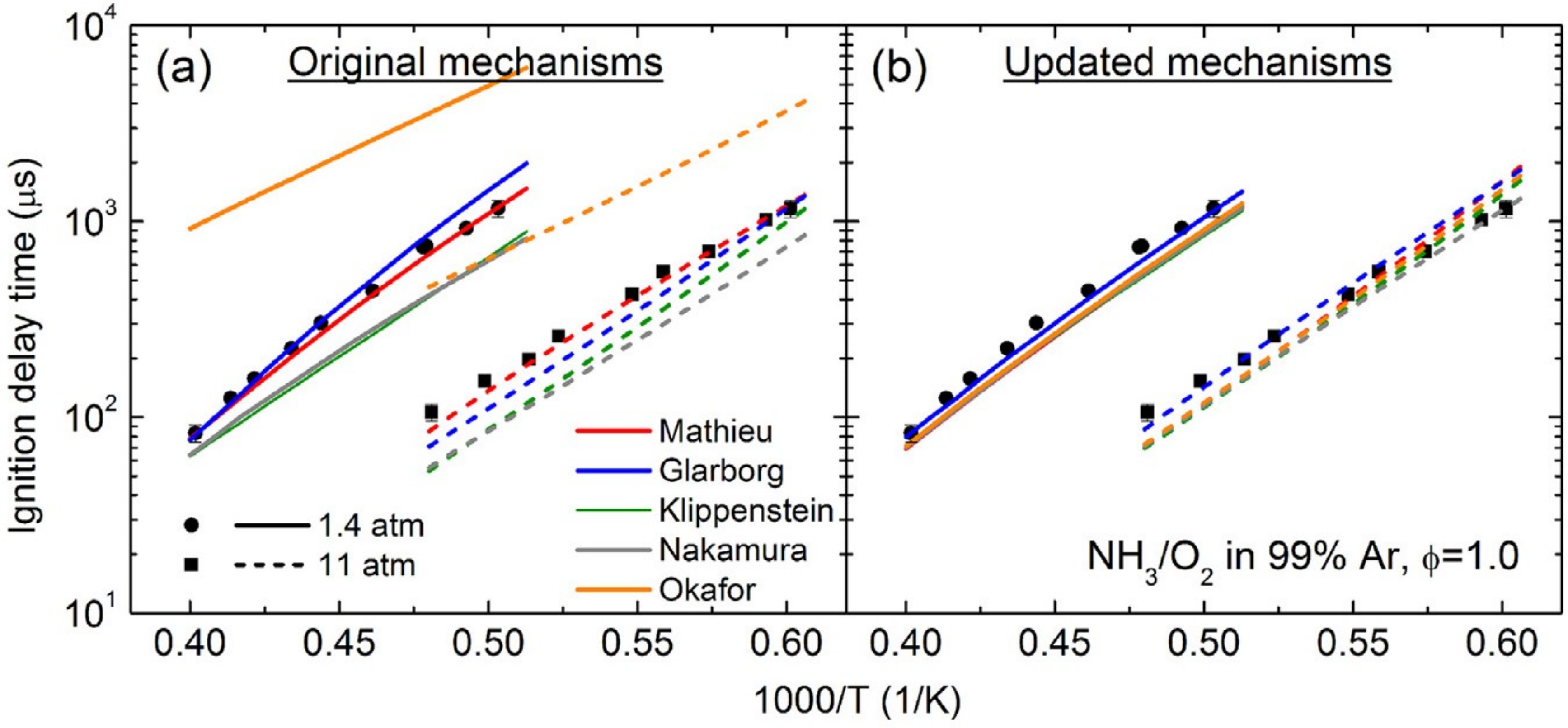
0.5% NH_3 in Ar



0.42% NH_3 /2% H_2 in Ar

Experimental results

Critical importance of NH_3 pyrolysis to model NH_3 oxidation



Experimental results

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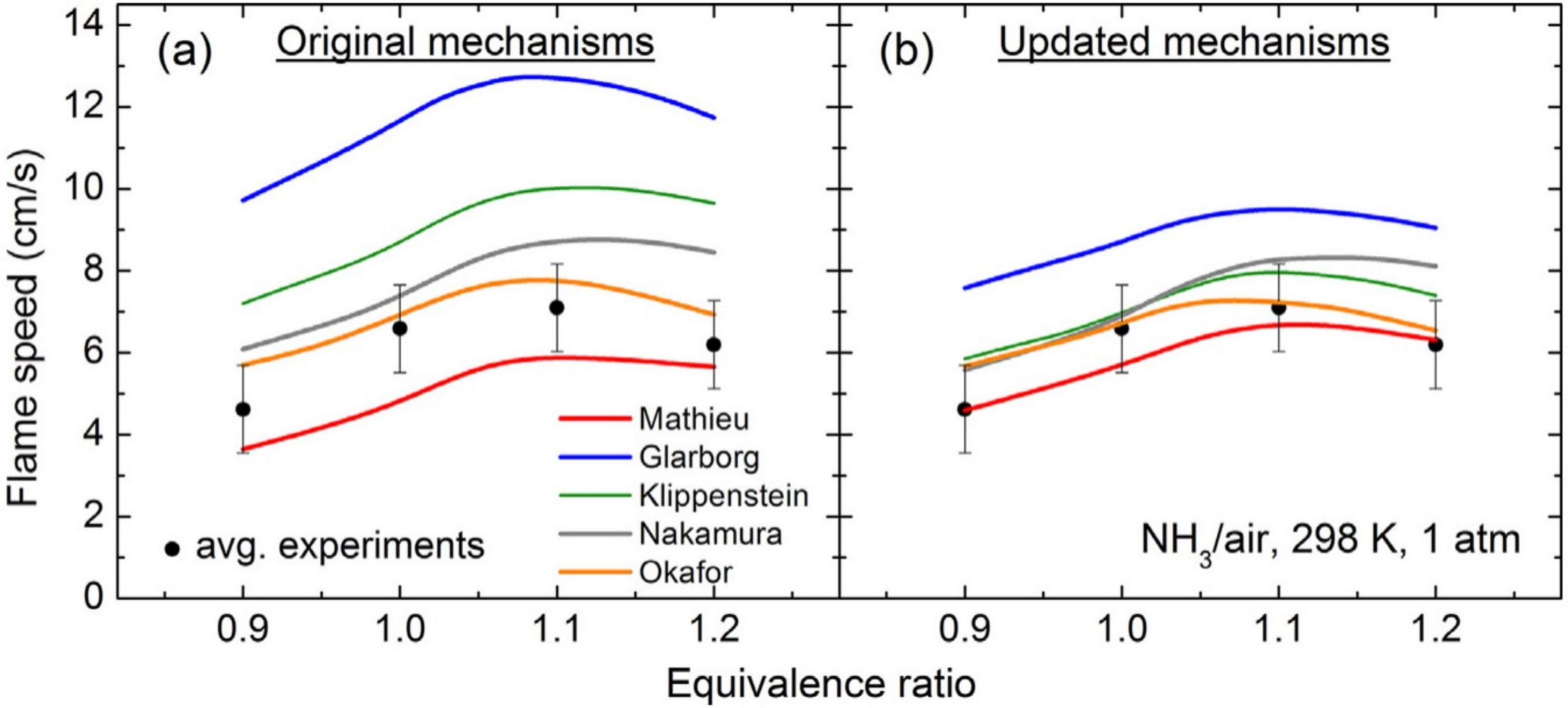
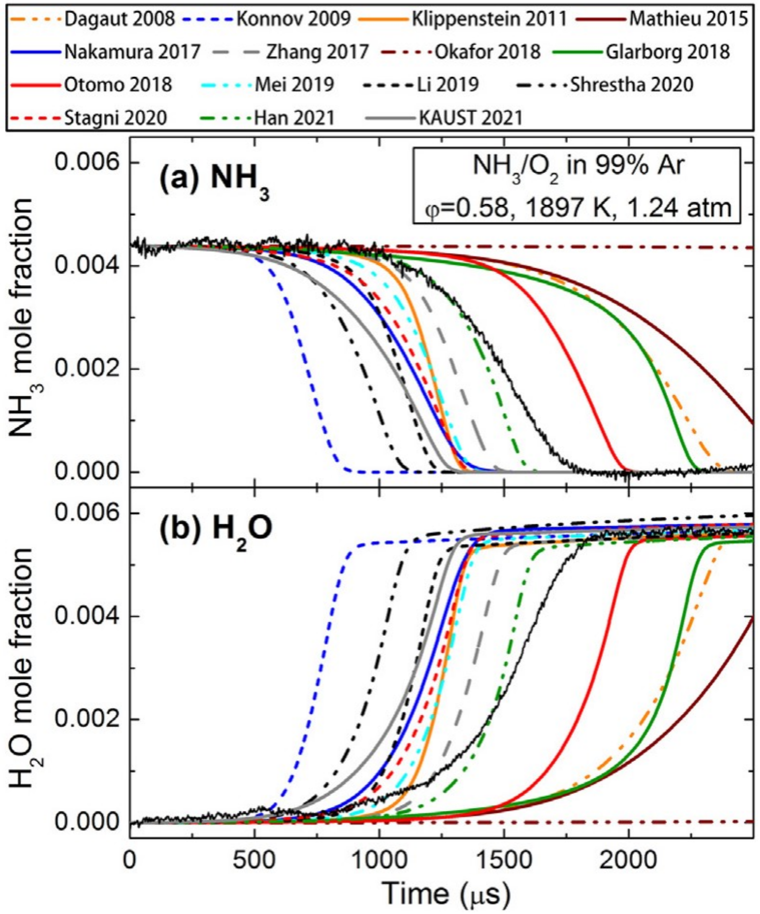
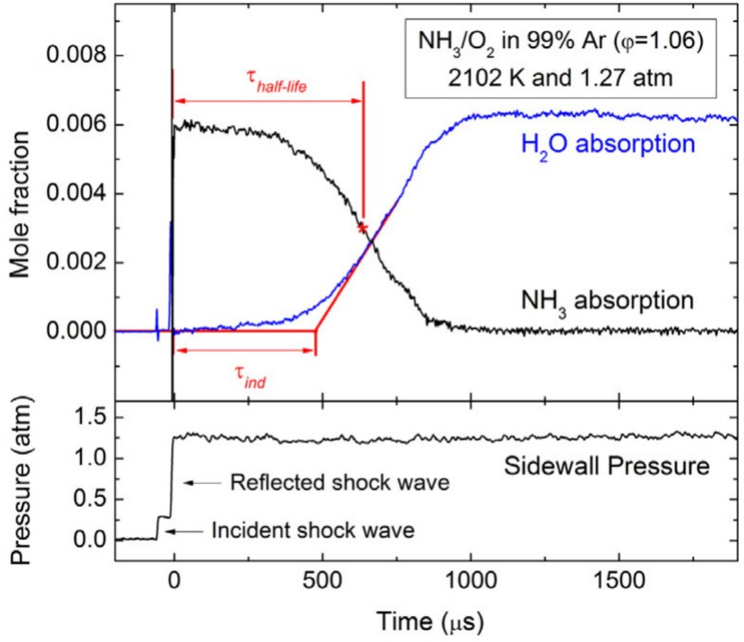
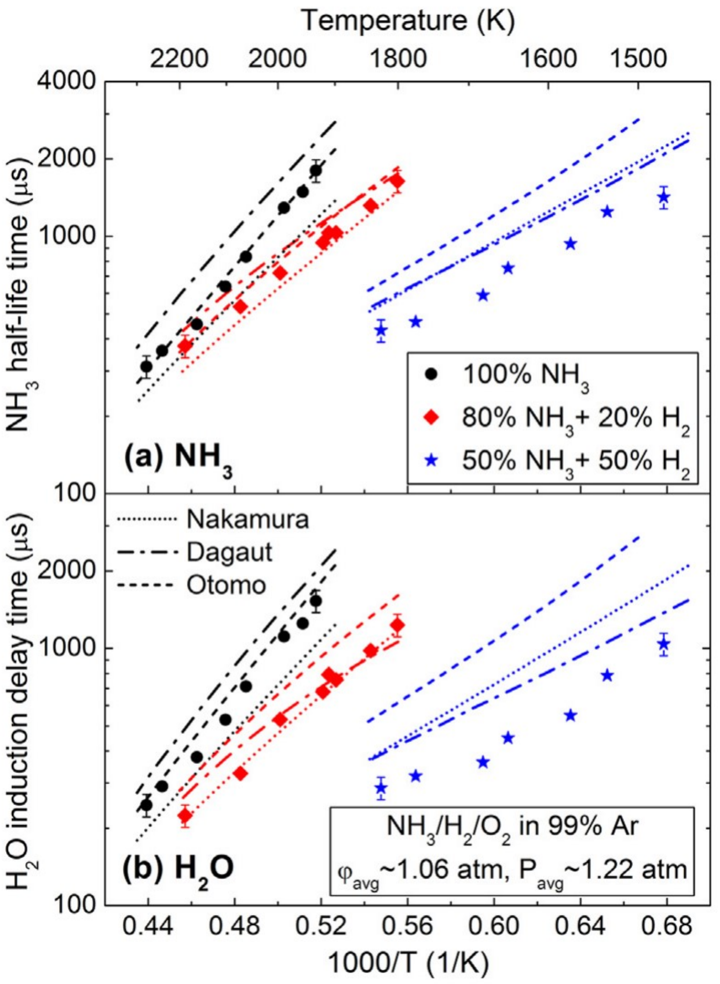


Experimental results

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

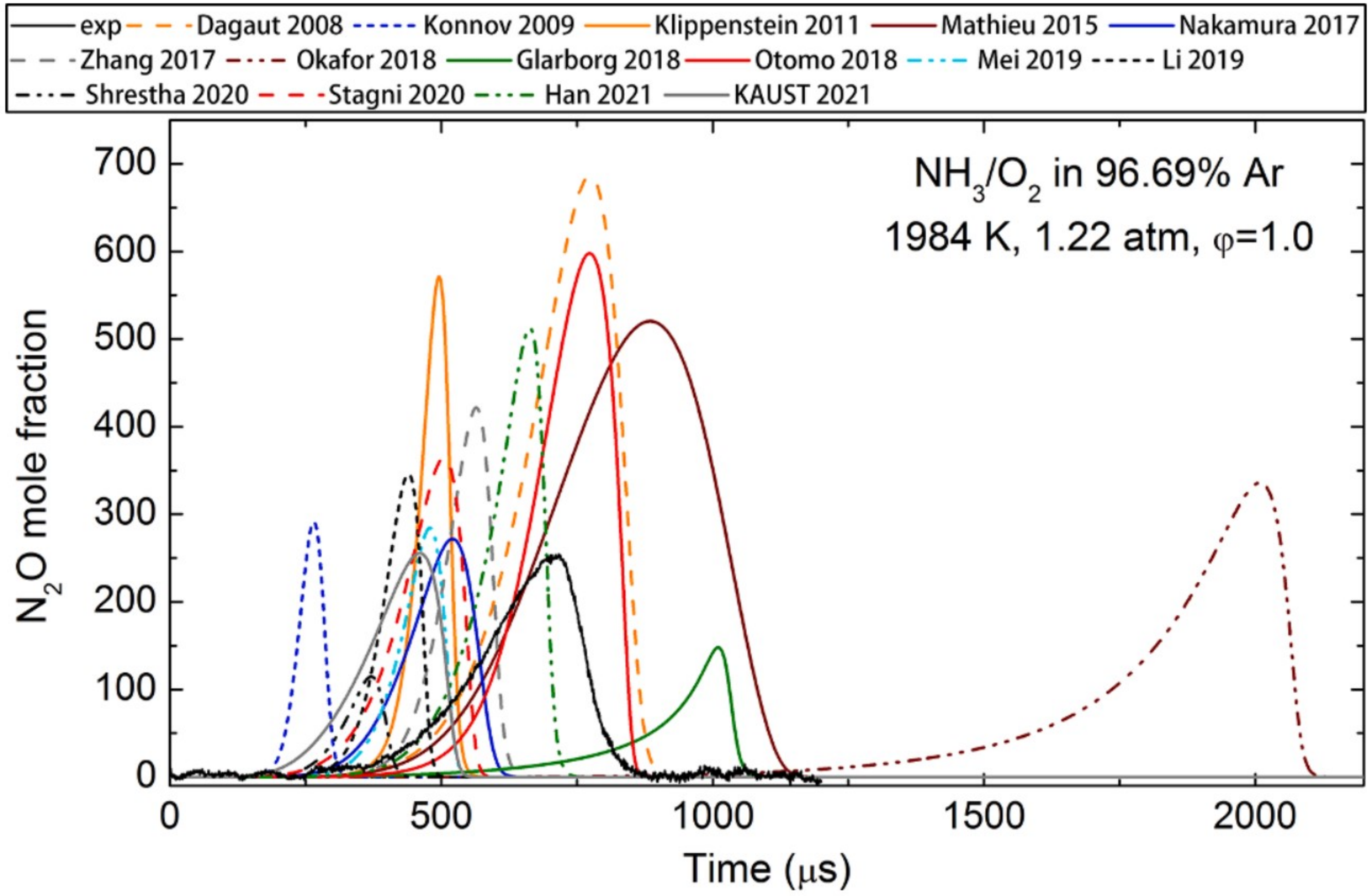






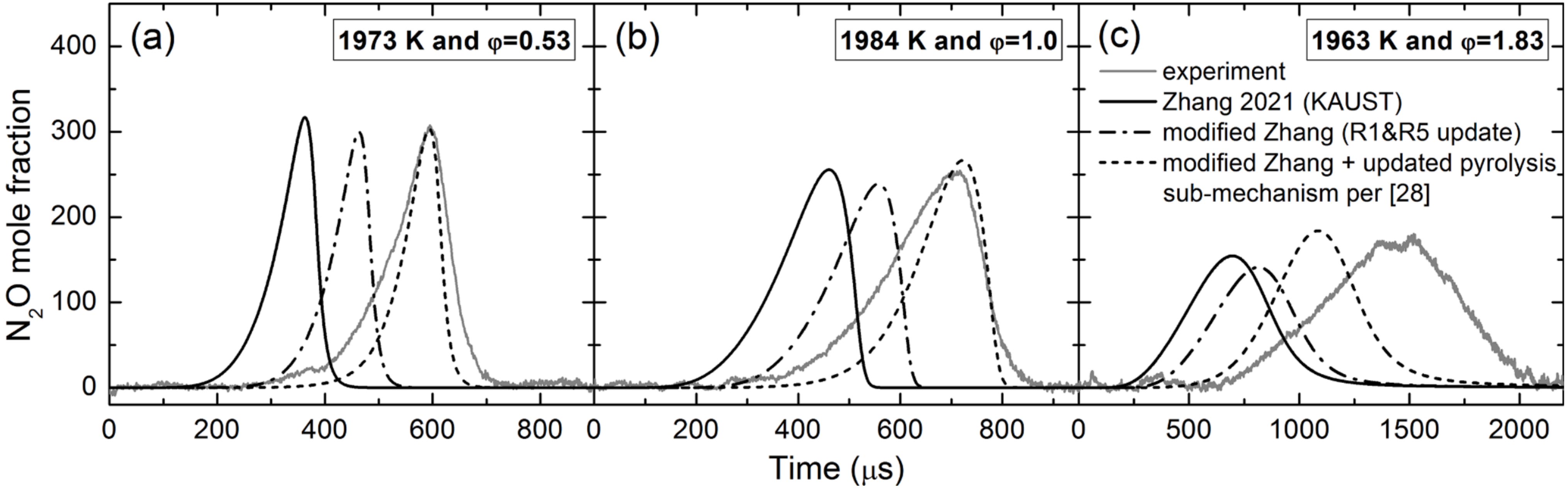
Experimental results

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

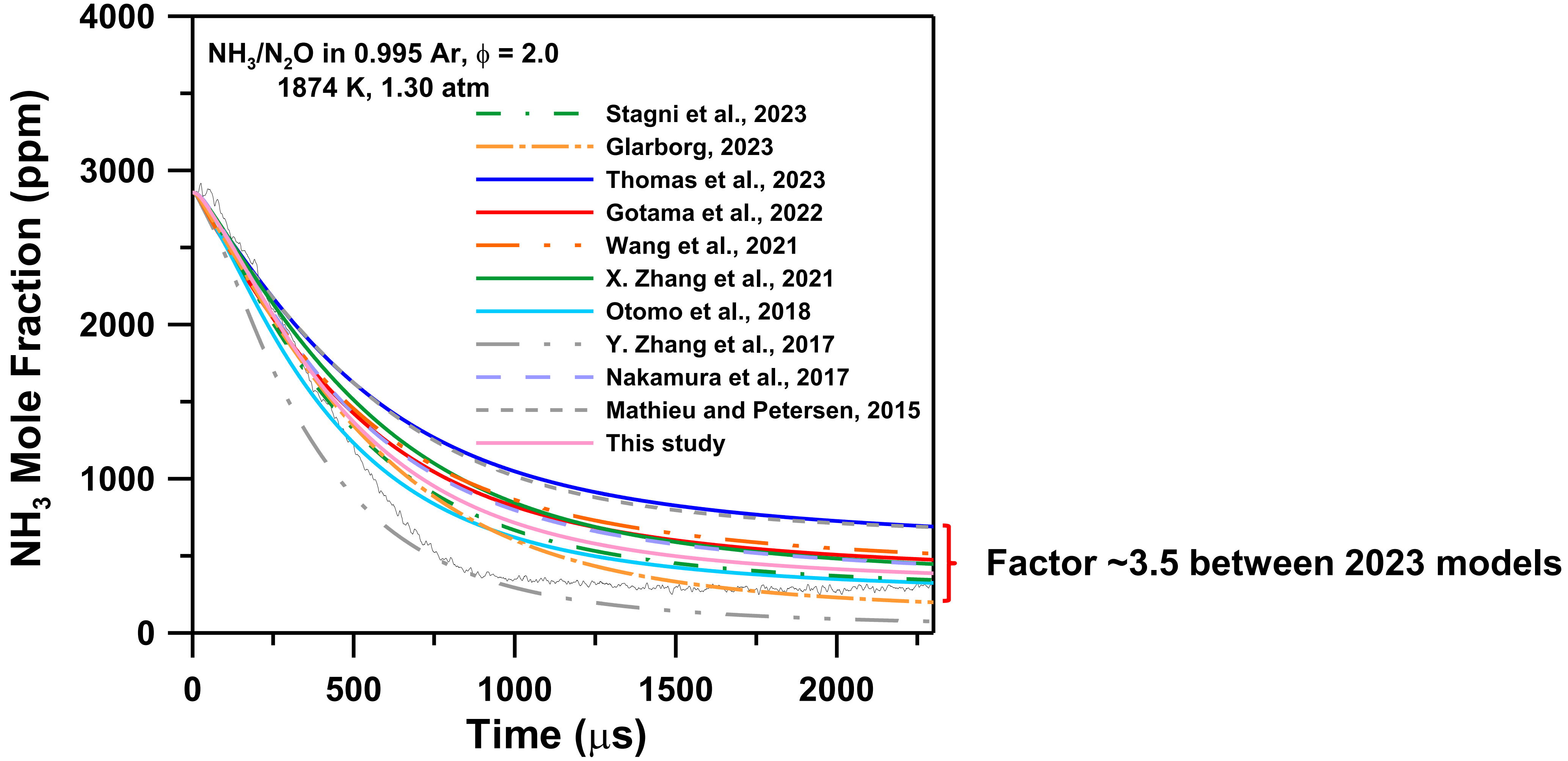


R1: $NH_3 + O_2 \rightleftarrows NH_2 + HO_2$

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

Model Comparisons

NH_3 oxidation from N_2O - WIP



Chemiluminescence Diagnostic

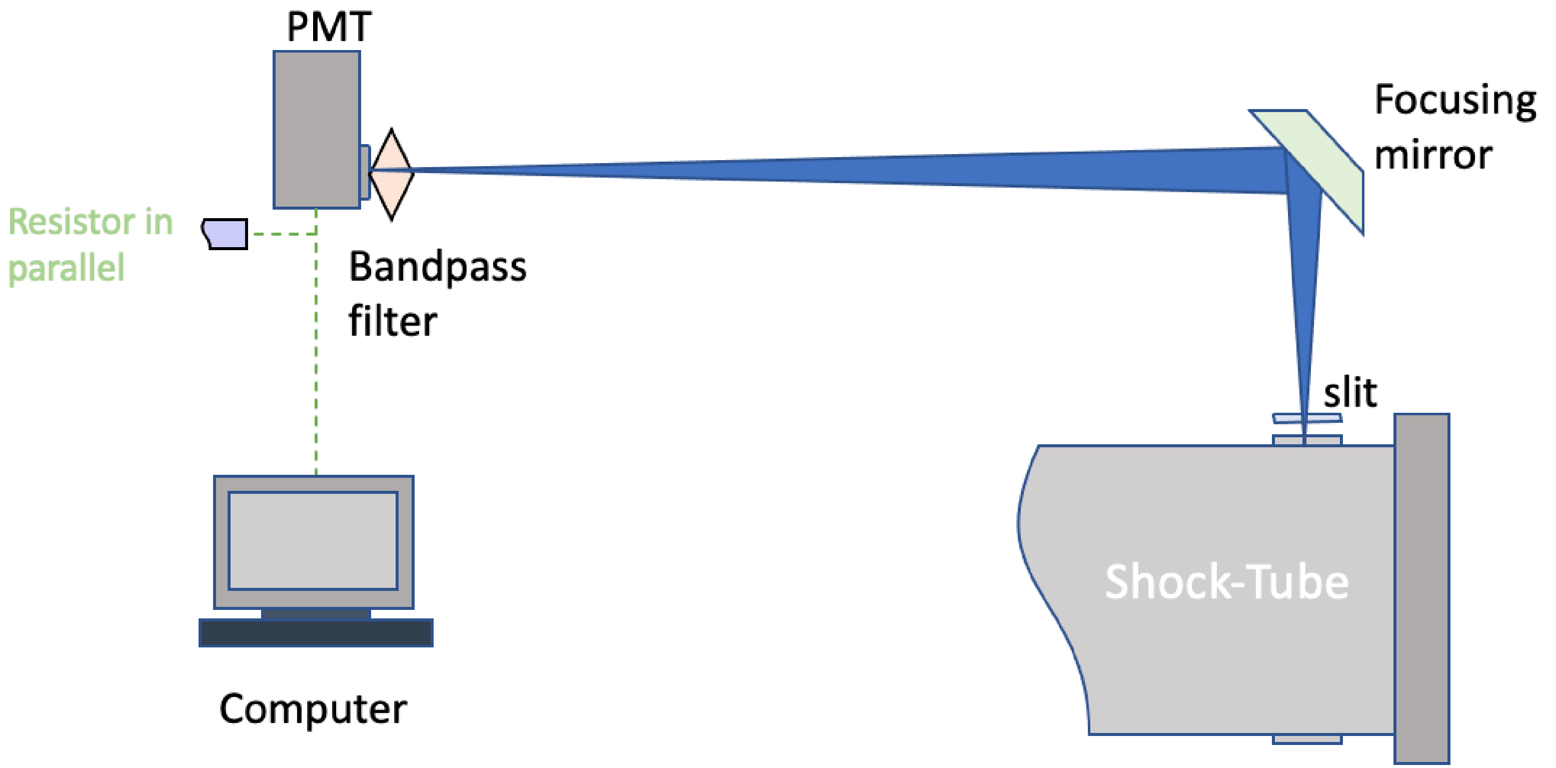
Light emission from de-excitation of a radical at a specific wavelength

- Inexpensive
- Robust
- Reliable
- Allow determining where combustion takes place
- Can potentially allow for equiv. ratio diagnostic

Chemiluminescence Diagnostic

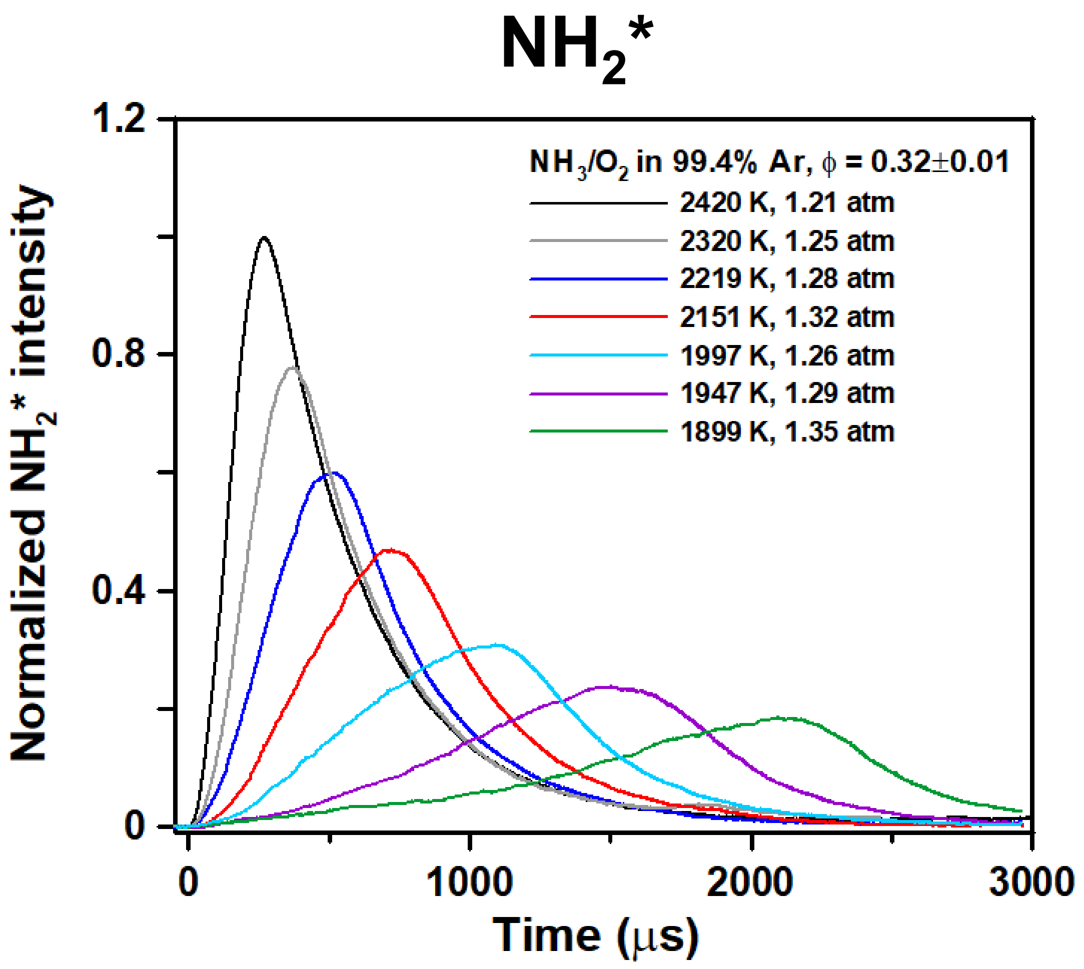
NH_2 and NH* chemiluminescence measured using a PMT*

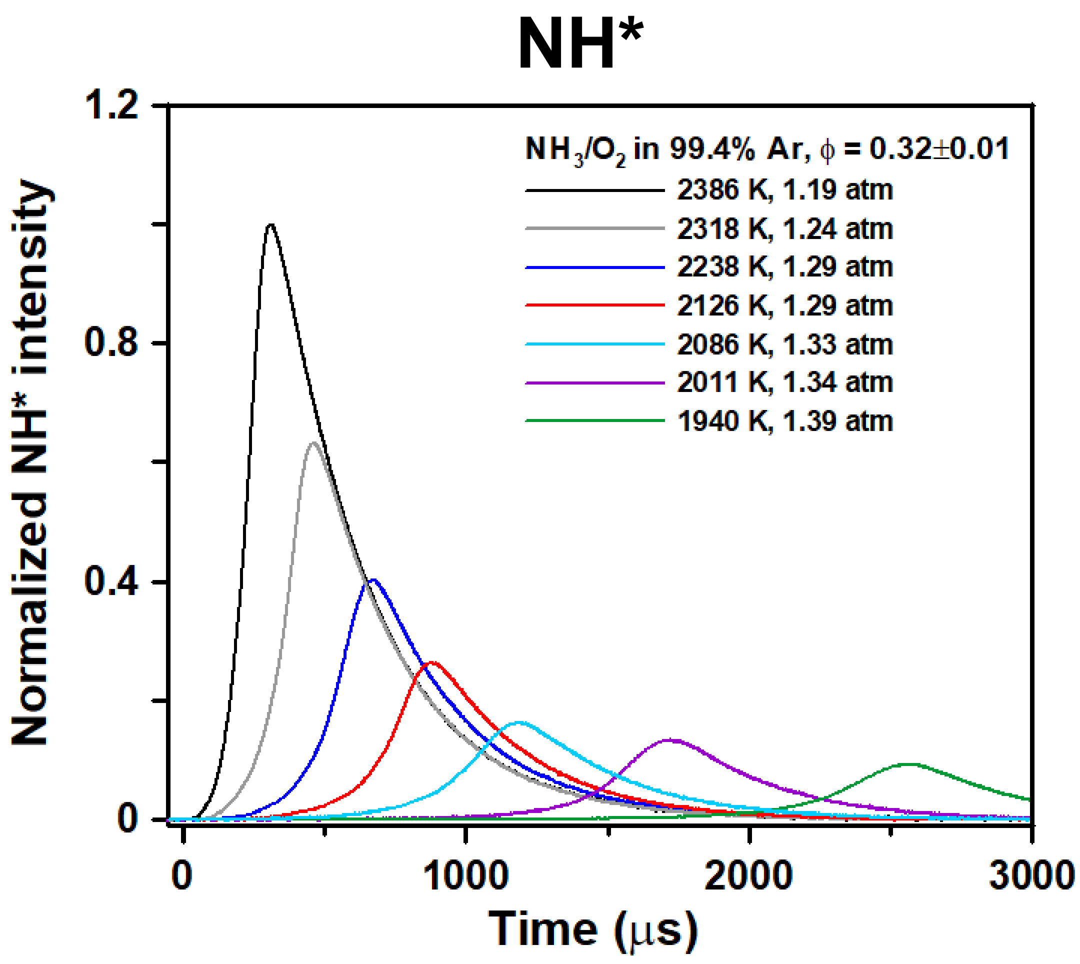
Filters for NH_2* and NH* were centered at 633 nm and 337 nm respectively.



Experimental results

Chemiluminescence plots, normalized to the highest temperature.





Reaction determination: NH_2*

Reactions exothermic enough to produce NH_2 were found.*

Difference in energy between ground and excited state of NH_2 :

$$\Delta E = \frac{N_A hc}{\lambda} = 189.818\ \mathrm{kJmol^{-1}}$$

$\boldsymbol{N_A}$= Avogadro′s Number (6.022 x 1023 $\mathrm{mol^{-1}}$),

h = Planck's constant (6.626 x 10−34 J.s),

c = speed of light (3 x 108 m/s),

λ = wavelength

Reaction	Heat of reaction (kJ mol^{-1})
$NNH+NH \leftrightarrows N_2+NH_2$	- 421.980
$H_2NN+O \leftrightarrows NH_2+NO$	- 272.524
$N_2H_3+NH \leftrightarrows N_2H_2+NH_2$	- 197.03
$NH_2+M \leftrightarrows NH+H+M$ (in reverse)	- 390.758

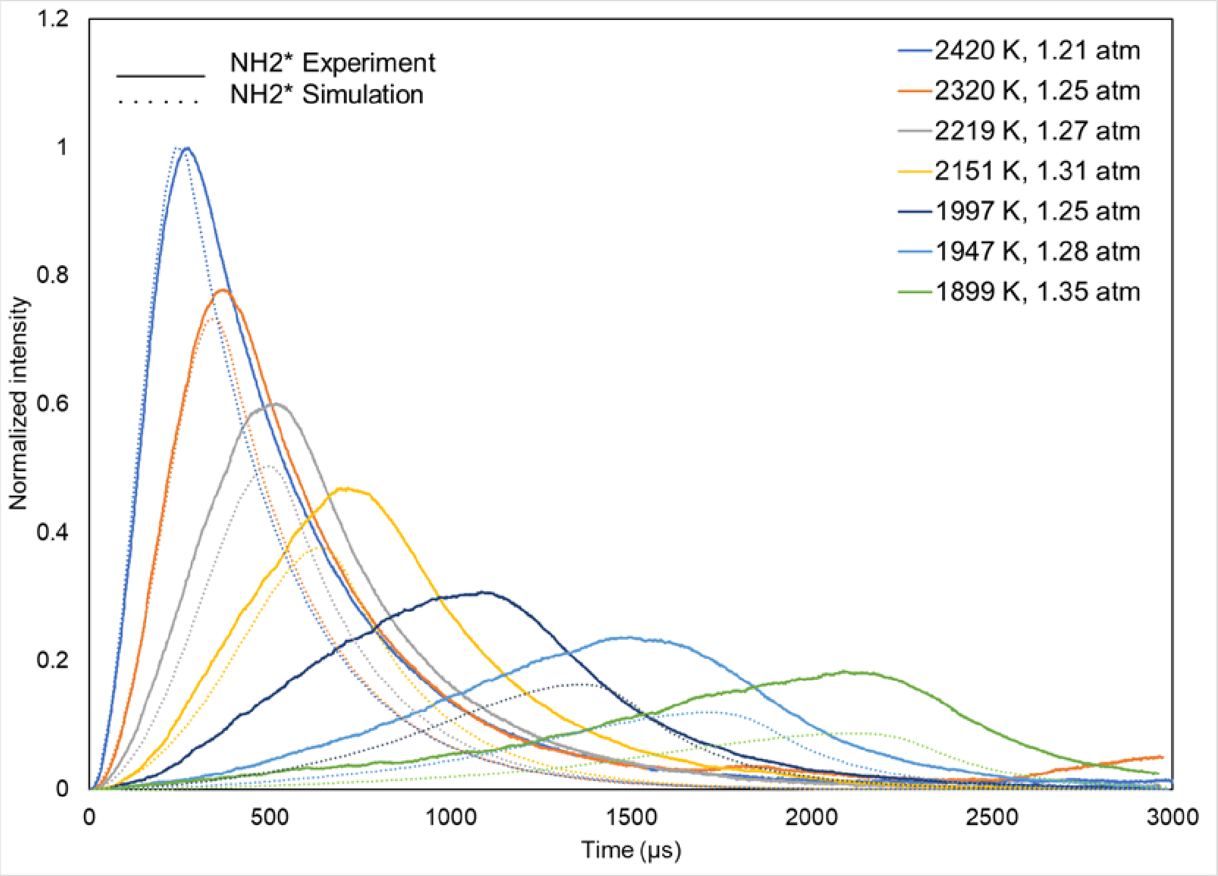
De-excitation Reactions

De-excitation reactions added

NH_2^*	NH^*
$NH_2^* \leftrightarrows NH_2$	$NH^* \leftrightarrows NH$
$NH_2^* + Ar \leftrightarrows NH_2 + Ar$	$NH^* + Ar \leftrightarrows NH + Ar$
$NH_2^* + O_2 \leftrightarrows NH_2 + O_2$	$NH^* + O_2 \leftrightarrows NH + O_2$
$NH_2^* + H_2O \leftrightarrows NH_2 + H_2O$	$NH^* + H_2O \leftrightarrows NH + H_2O$
$NH_2^* + N_2 \leftrightarrows NH_2 + N_2$	$NH^* + N_2 \leftrightarrows NH + N_2$
$NH_2^* + H_2 \leftrightarrows NH_2 + H_2$	$NH^* + H_2 \leftrightarrows NH + H_2$
$NH_2^* + H \leftrightarrows NH_2 + H$	$NH^* + H \leftrightarrows NH + H$
$NH_2^* + NH_2^* \leftrightarrows NH_2 + NH_2$	$NH^* + NH^* \leftrightarrows NH + NH$

Model (Stagni, 2023 + p.w.) vs Experiment NH_2*

Relatively accurate modeling



WIP: can presently model accurately shock tube **OR** flame data (CNRS Orleans)

=> Need to have good NH_2 chemistry

Future directions

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

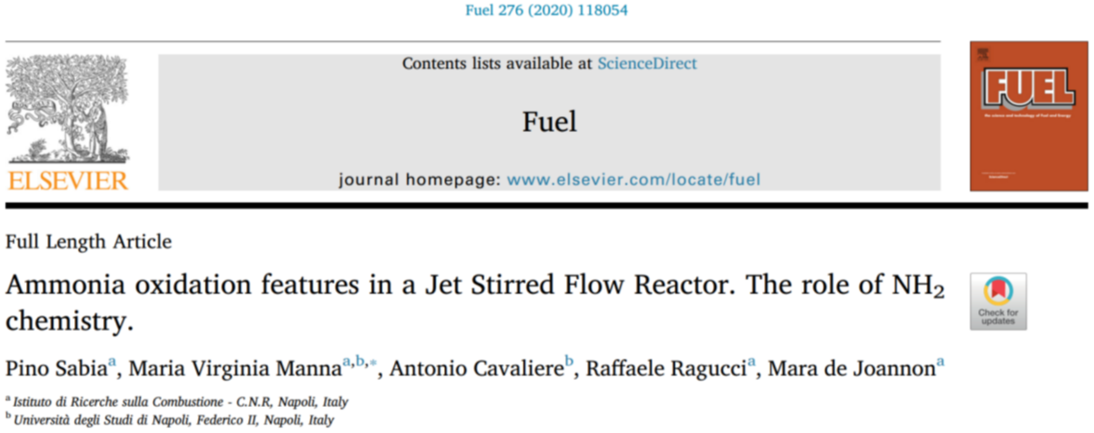
Combustion radicals:

- Difficult and costly to measure
- radical-radical interactions very hard for high-level calculation

Future directions

NH_2 diagnostic being 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: $NH_2 \rightarrow NH \rightarrow N_2H_2 \rightarrow NNH \rightarrow N_2$



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Full Length Article

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

Pino Sabia[a], Maria Virginia Manna[a,b,*], Antonio Cavaliere[b], Raffaele Ragucci[a], Mara de Joannon[a]

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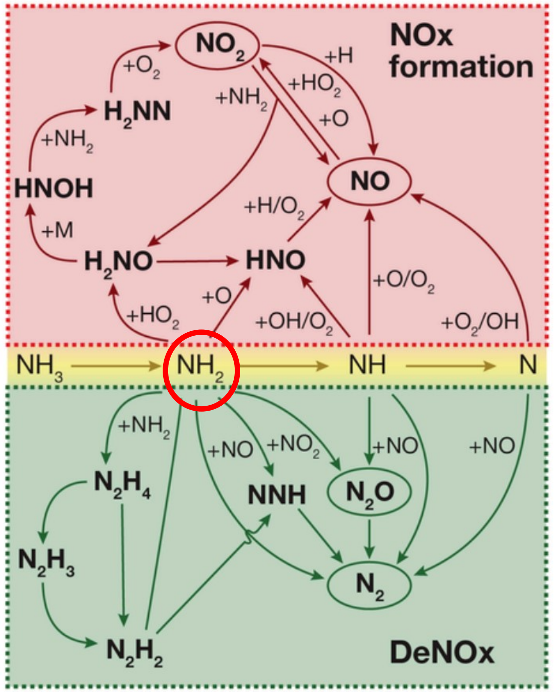
[b] Università degli Studi di Napoli, Federico II, Napoli, Italy



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

Conclusions

- **Results showed:**
  - Critical importance of accurate NH_3 measurement in dilute experiments in stainless steel combustion apparatuses
  - Critical importance of 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)
  - NH_2 diagnostic under development

Acknowledgments

National Science Foundation

- **National Science Foundation (Award # 20308433)**

TURBOMACHINERY LABORATORY
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Experimental Method: Shock Tube Facility

Stainless Steel Shock Tube