Toward Predictive Kinetics for Ammonia Combustion and Emissions

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Rodger Cornell
(PhD 2022 - ARL)

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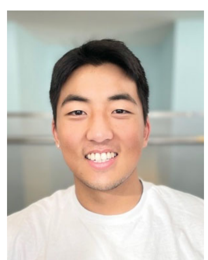
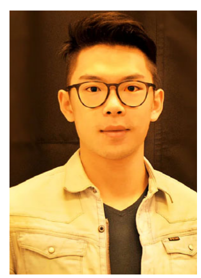
(PhD 2023)



Joe Lee
(PhD Candidate)



Lei Lei
(PhD 2020)

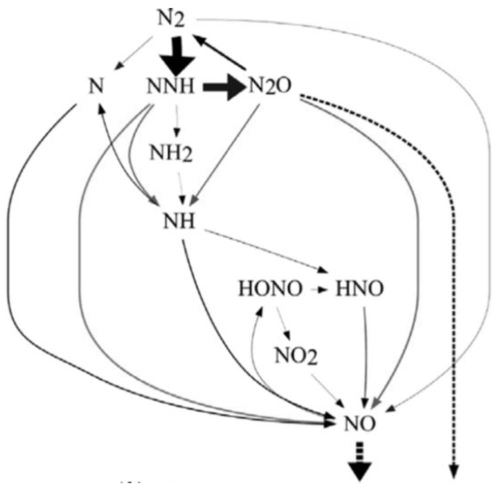
Avery Rambur
(MS Candidate)

Ella Kane
(PhD Candidate)

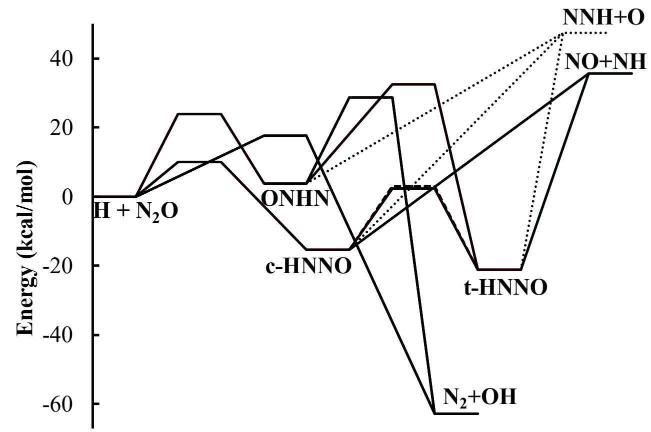
Jon Pankauski
(PhD Candidate)

Patrick Singal
(PhD Candidate)

Challenges in complex reactions worse for nitrogen

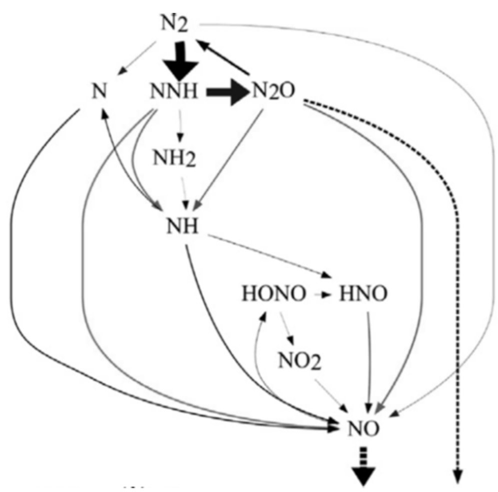


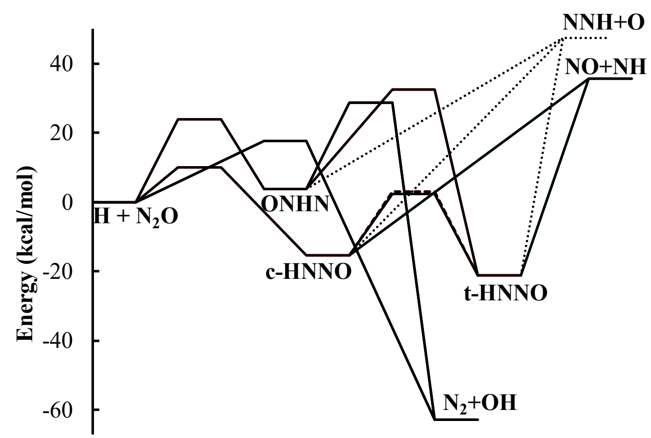
Key species can be formed
via multiple pathways



Key reactions have multiple wells/channels
with complex *T/P/X* dependence

Challenges in complex reactions worse for nitrogen





1. Experimental data alone are often insufficient to confirm *both* chemistry/physics *and* relevant parameters
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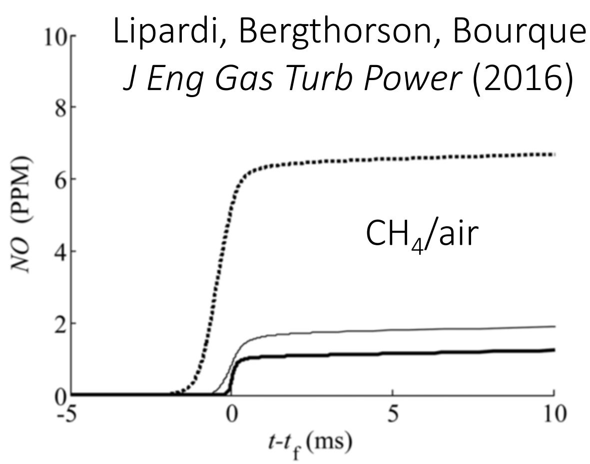
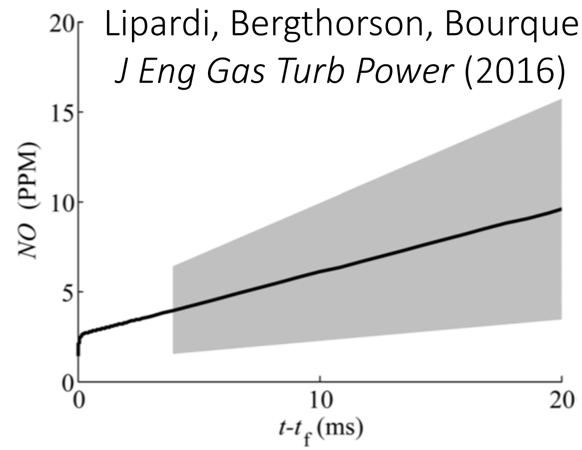
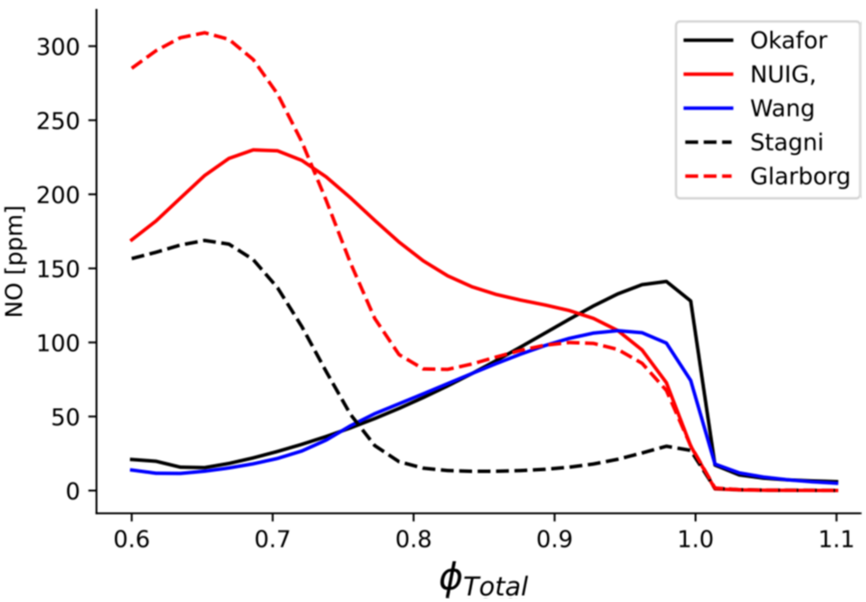
Challenges impede engineering design



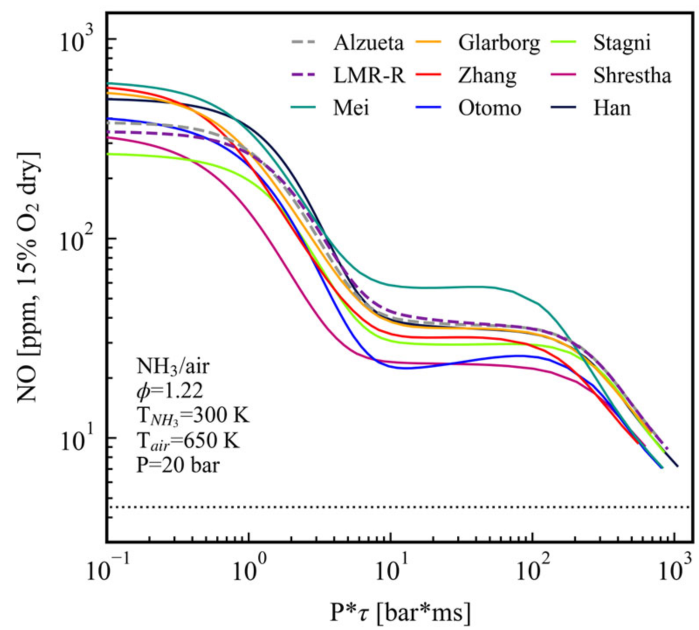


"NO_x predictions using currently available combustion models are <u>too variable and uncertain</u> to be used as reliable gas-turbine engine design tools."

Challenges impede engineering design

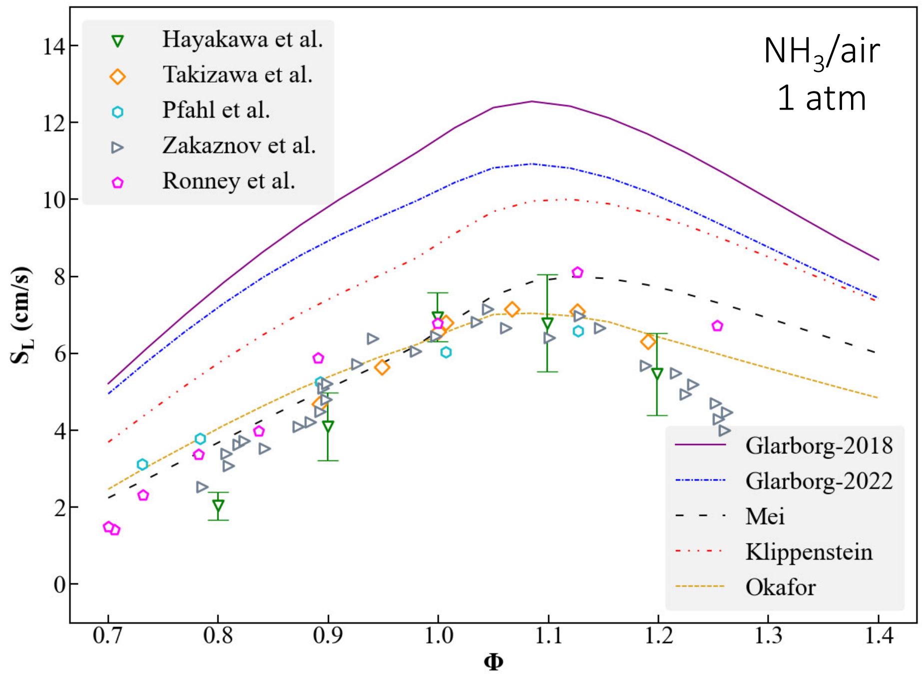


Rich-Quench-Lean combustion
of NH_3/CH_4 with 50% H_2O at 40 atm
Raslan, Yang, Durocher, Guthe, Bergthorson
J Eng Gas Turb Power (2024)



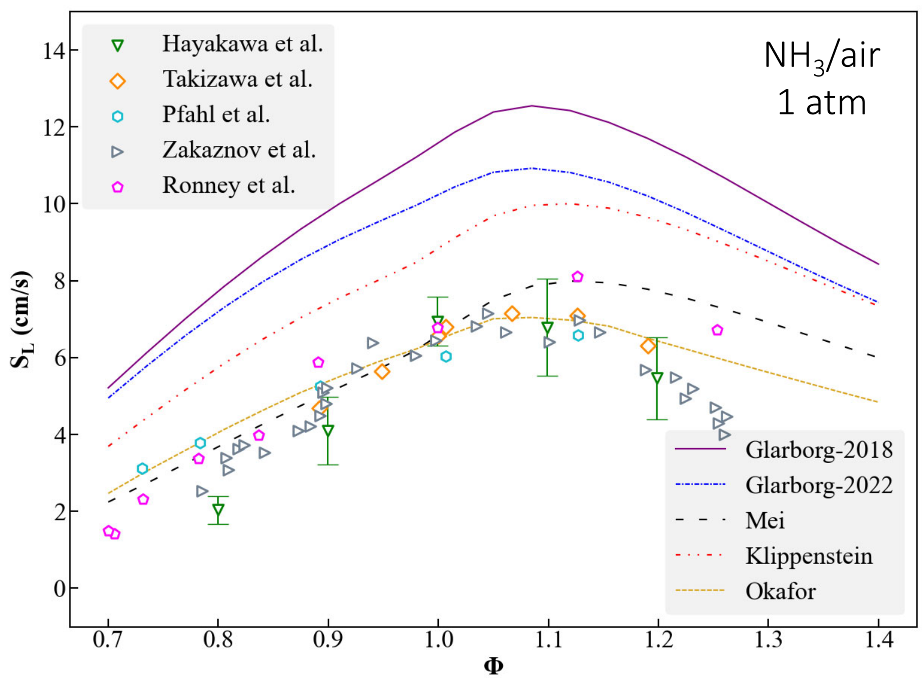
Rich-Relaxation combustion
of NH_3 for ϕ = 1.22 at 20 atm
(similar to: Gubbi, Cole, Emersen, Noble, Steele,
Sun, Lieuwen *ACS Energy Lett* (2023))

When models get it “right”…



Gubbi, Cole, Emersen, Noble, Steele, Sun, Lieuwen
ACS Energy Lett (2023)

When models get it "right"…often for wrong reasons



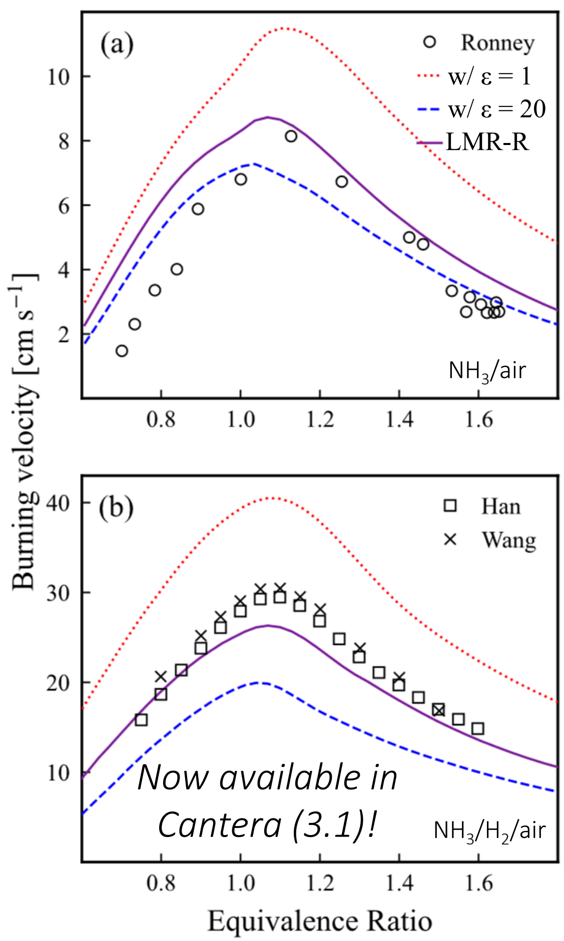
Gubbi, Cole, Emersen, Noble, Steele, Sun, Lieuwen
ACS Energy Lett (2023)

None of the models shown account for very high NH_3 third body efficiency!

System	300 K	1000 K	2000 K
HO_2 (+M)			
He:Ar	0.90 (0.82)[a]	1.17	1.34
N_2:Ar	1.71 (1.95)[a]	1.58 (1.79)[b]	1.20 (1.38)[c]
H_2:Ar	3.69 (2.52)[a]	3.07	1.71
CO_2:Ar	13.7	8.94 (4.29)[b]	3.03 (5.0)[c]
NH_3:Ar	20.4	17.9	18.7
H_2O:Ar	23.3 (22.7)[a]	22.2 (18.9)[b]	21.3 (23.0)[c]
NH_3 (+M)			
N_2:Ar	3.15[f]	2.47	2.25
O_2:Ar	1.55	1.48	1.70
CO_2:Ar	11.2[f]	13.4	14.3
NH_3:Ar	13.9	20.0	22.2
CH_4:Ar	9.94[f]	13.3	14.3
H_2O:Ar	14.0	23.6	27.9

Third-body efficiencies from
ab initio trajectory calculations
Jasper *Faraday Discuss* (2022)

When models get it “right”…



Now available in Cantera (3.1)!

Singal, Lee, Lei, Speth, Burke *PCI* (2024)

LMR-R properly accounts for third-body efficiencies

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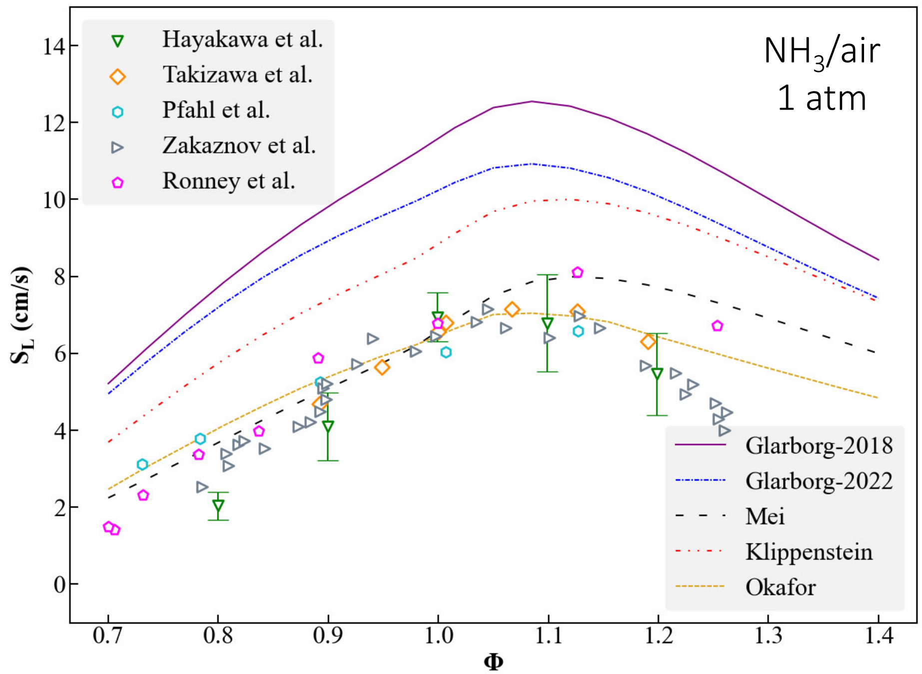

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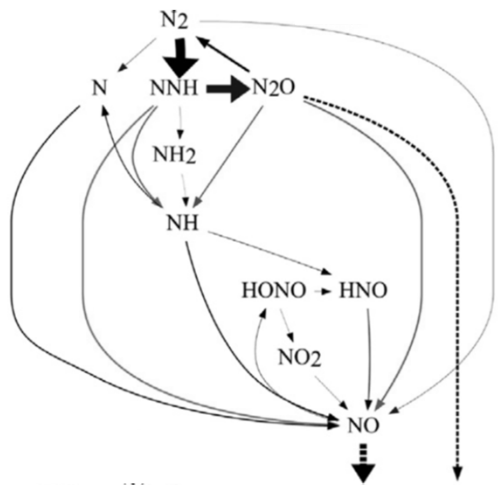

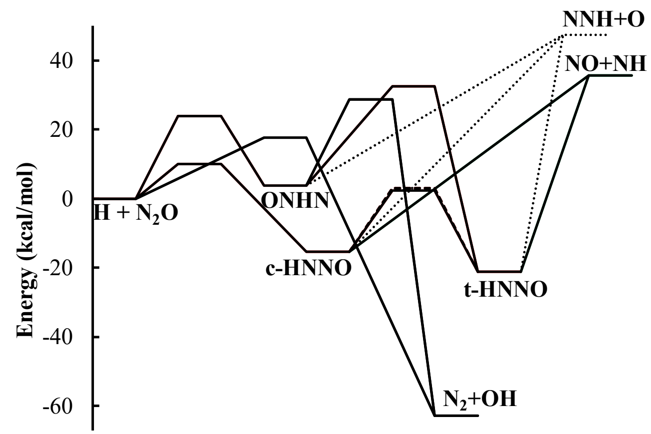

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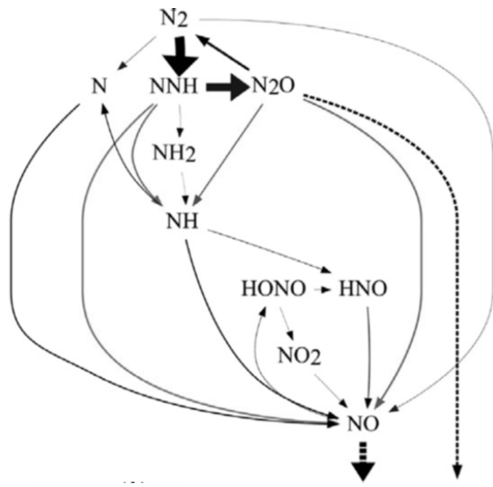
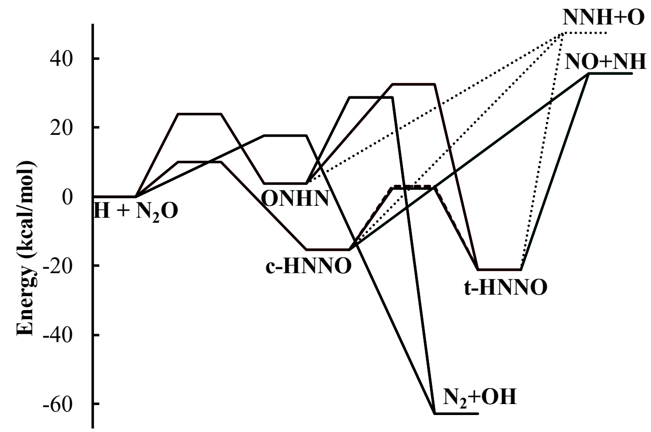
Opportunities to address challenges





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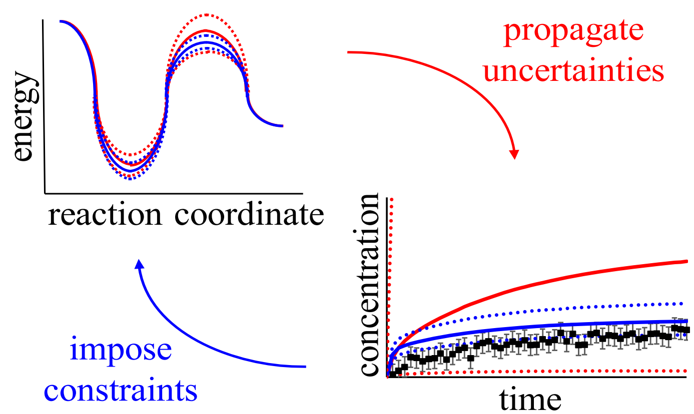
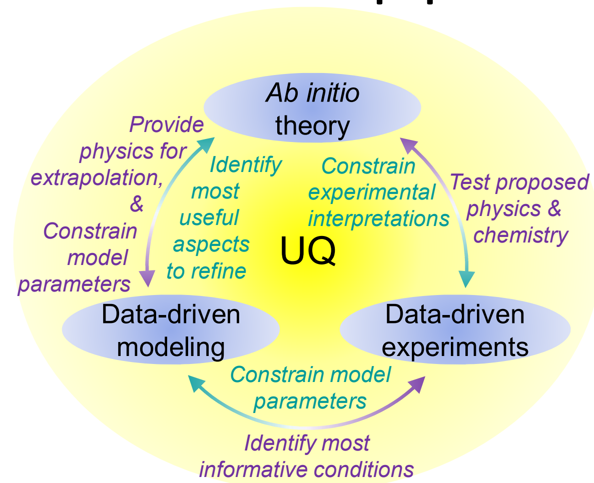
1. Ab initio theory can characterize chemistry/physics, constrain parameters and experimental interpretations, and extrapolate
2. Bayesian design can pinpoint experiments to accentuate pathways, differentiate among mechanisms, and predict Quantities of Interest
3. Multiscale data-driven modeling using theoretical and experimental data can evaluate consistency and can extrapolate

A multiscale physics-based, data-driven approach





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1. Deep dives on reactions relevant to N_2O emissions from NH_3 combustion

2. Multi-scale data-driven models using theoretical and experimental data for NH_3 combustion

N_2O formation and consumption

N_2O production:

$$NH + NO \longrightarrow N_2O + H \text{ (high-T)}$$

$$NH_2 + NO_2 \longrightarrow N_2O + H_2O \text{ (vs. } H_2NO + NO\text{)}$$

N_2O consumption:

$$N_2O \xrightarrow{+M} O + N_2 \text{ (high-T)}$$

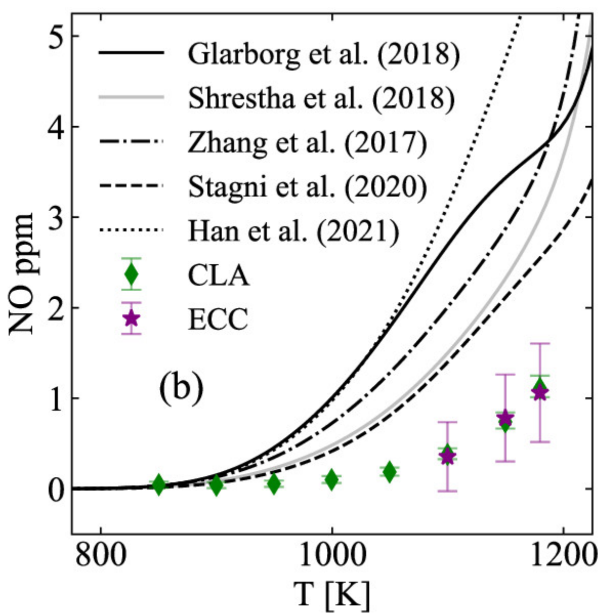
$$N_2O + NH_2 \longrightarrow N_2H_2 + NO$$

$$N_2O + H \longrightarrow N_2 + OH$$

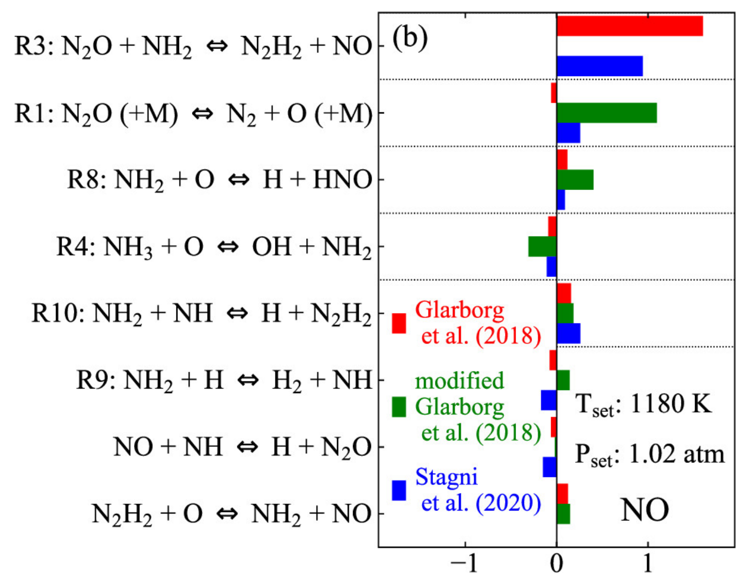
$$N_2O + O \longrightarrow NO + NO$$

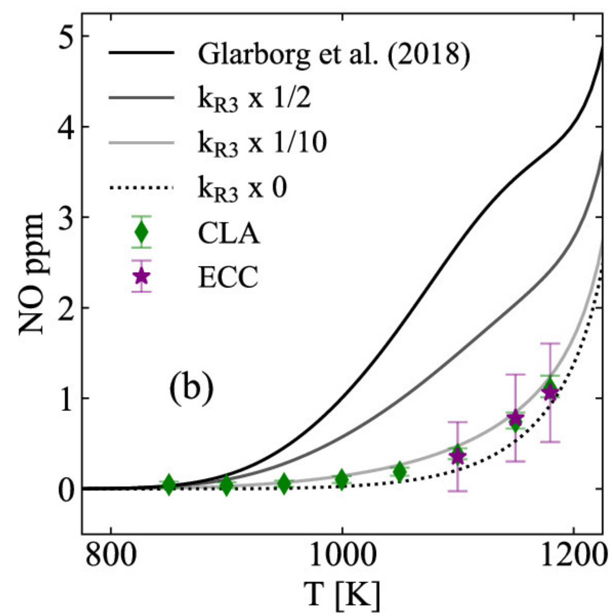
$$\longrightarrow N_2 + O_2$$

$NH_2 + N_2O = N_2H_2 + NO$ is too fast is most models



$NH_3/N_2O/N_2$ in JSR





(Supported by later theory from Klippenstein showing higher barrier than earlier estimates)

Cornell, Barbet, Burke *ENF* (2021)

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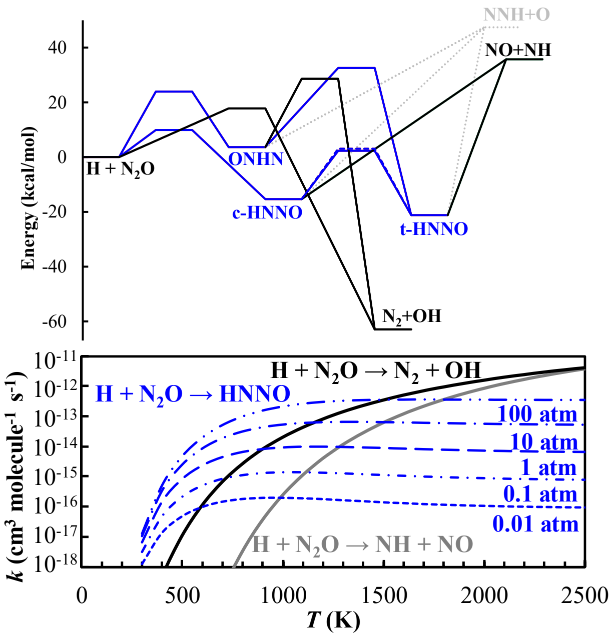
$$\cancel{N_2O + NH_2 \longrightarrow N_2H_2 + NO}$$

$$N_2O + H \longrightarrow N_2 + OH$$

$$N_2O + O \longrightarrow NO + NO$$

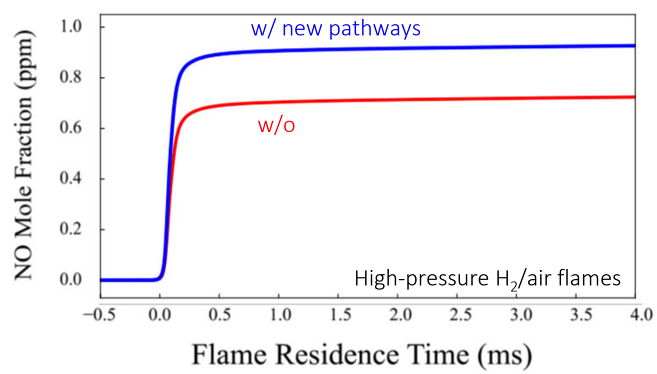
$$\longrightarrow N_2 + O_2$$

H + N_2O forms a lot of HNNO (missing from models)



Meng, Lei, Lee, Burke
PCI (2023)

$$
\begin{aligned}
&\text{HNNO} + \text{O}_2 &&\not\longrightarrow \\
&\text{HNNO} + \text{H} &&\longrightarrow \text{NH}_2 + \text{NO}, \ldots \\
&\text{HNNO} + \text{O} &&\longrightarrow \text{HNO} + \text{NO}, \ldots \\
&\text{HNNO} + \text{OH} &&\longrightarrow \text{HNOH} + \text{NO}, \ldots
\end{aligned}
$$



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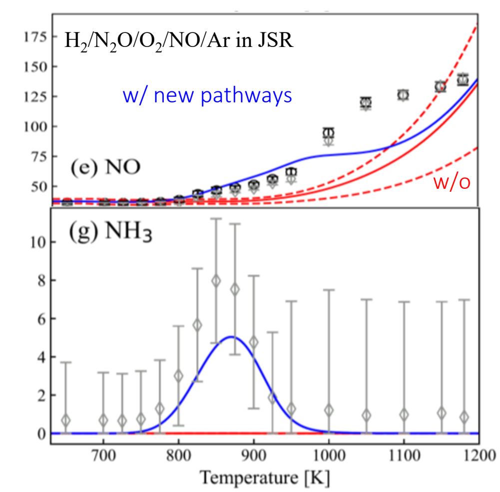
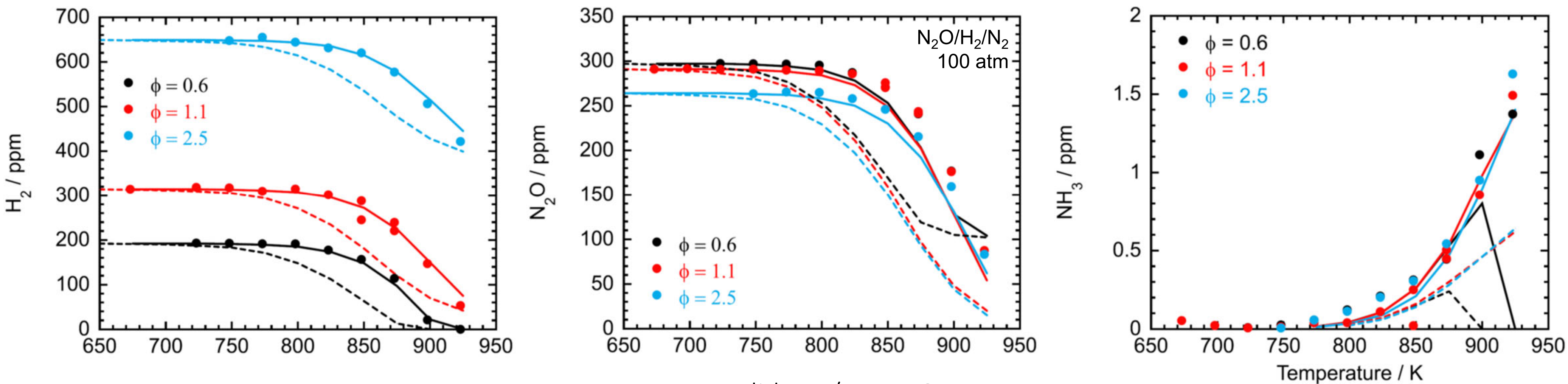


Lee, Barbet, Meng, Cornell, Burke
CNF (2023)

HNNO pathways important to N_2O at high pressure



solid = w/ HNNO
dashed = w/o HNNO

Glarborg, Fabricius-Bjerre, Joensen, Hashemi, Klippenstein *CNF* (2025)

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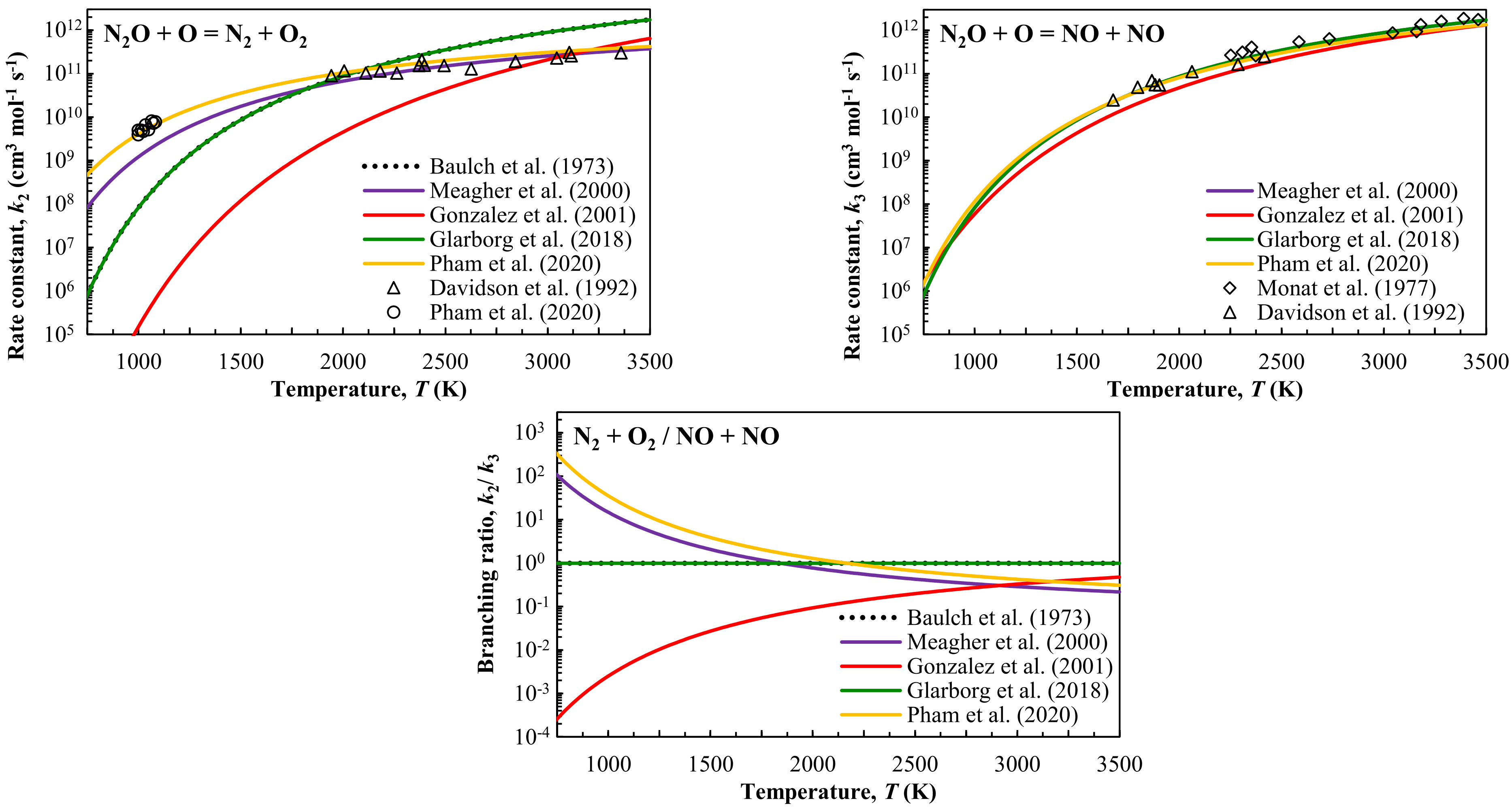
$$N_2O + H \longrightarrow N_2 + OH$$
$$+ \quad \xleftrightarrow{+M} HNNO$$

$$N_2O + O \longrightarrow NO + NO$$
$$\longrightarrow N_2 + O_2$$

Disagreement about products (and rates) of $N_2O + O$



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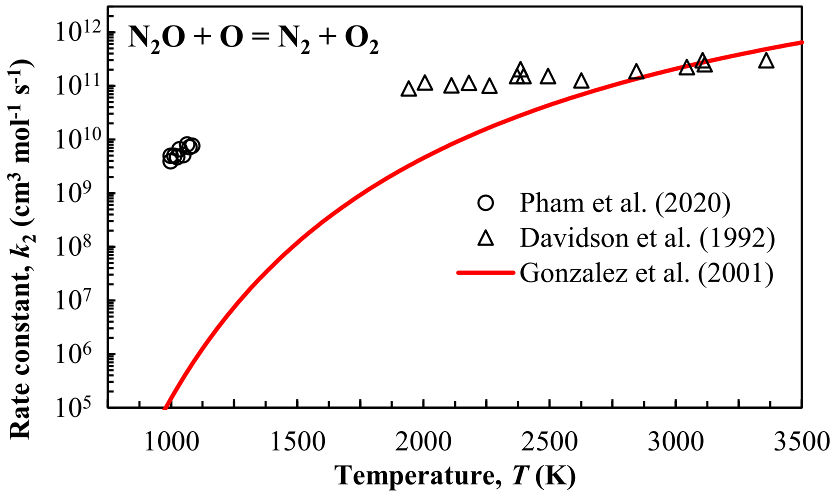

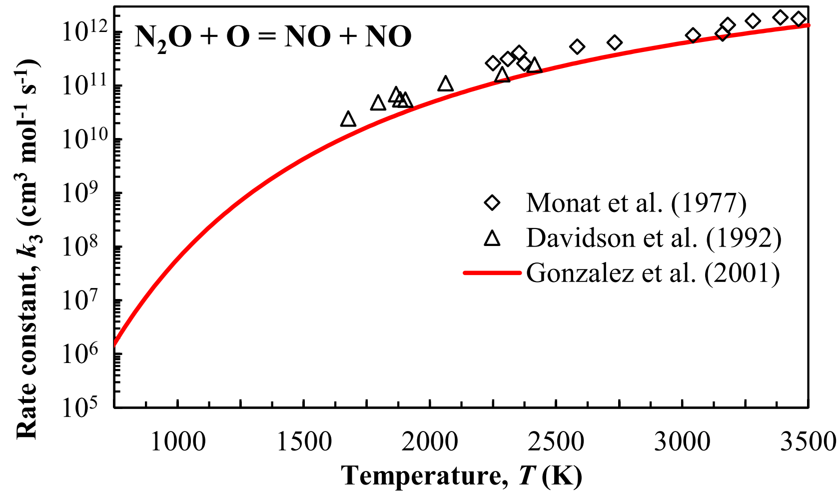

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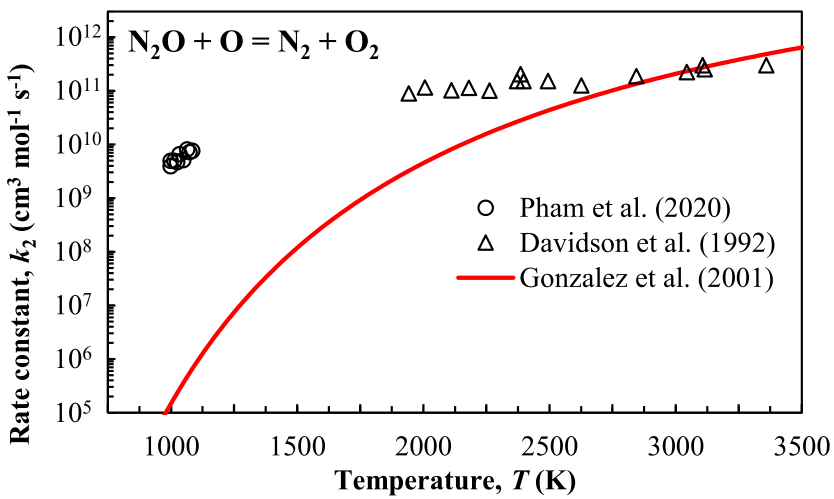
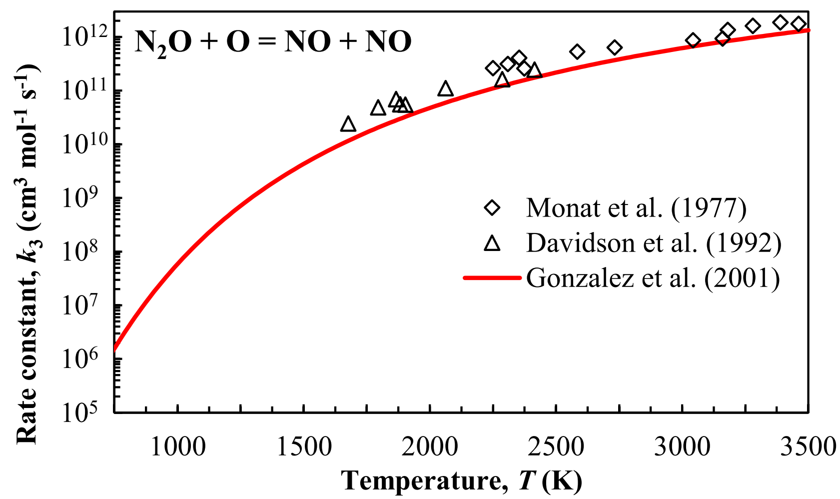
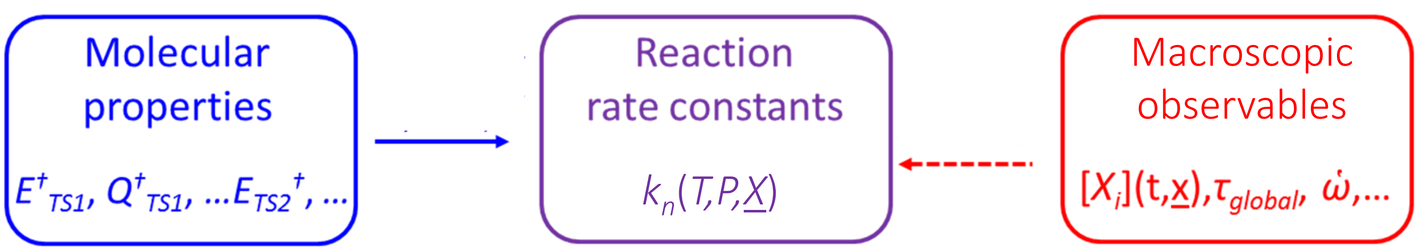
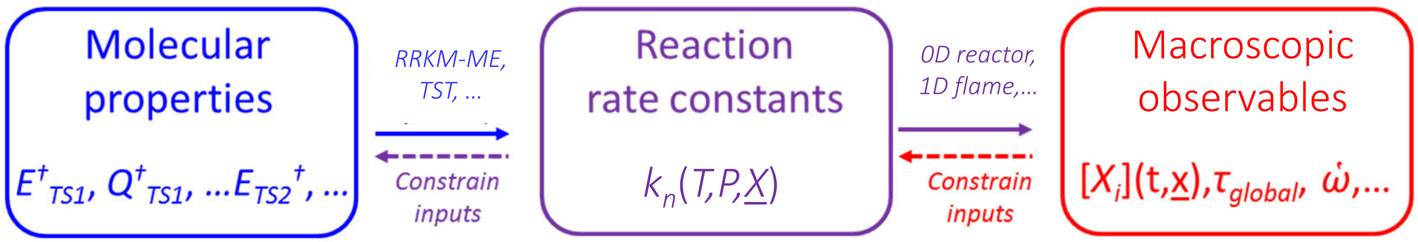
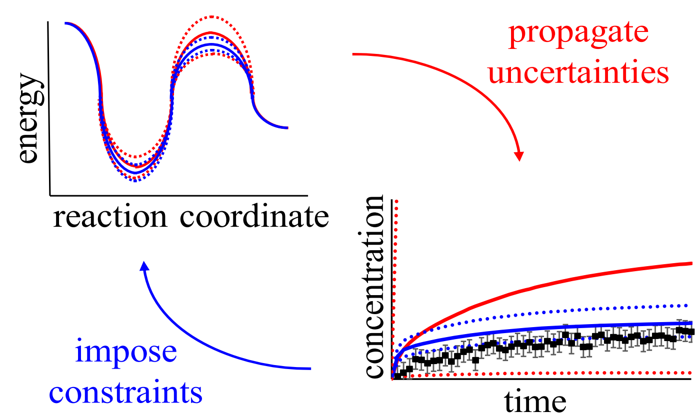






MultiScale Informatics (MSI) combines physics and data across multiple scales





Burke *IJCK* (2016)

Analysis considers uncertainties and theoretical/experimental data for *all* reactions

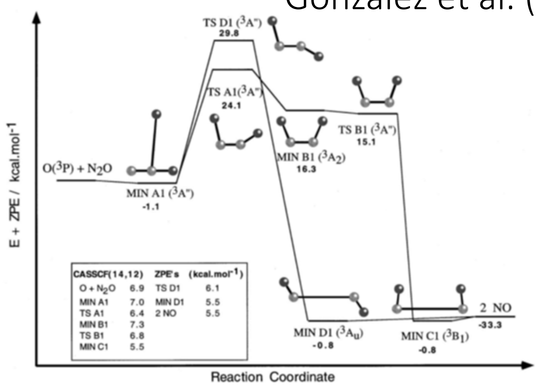
$$N_2O \xleftrightarrow{+M} N_2 + O \quad (1)$$

$$N_2O + O \longleftrightarrow N_2 + O_2 \quad (2)$$

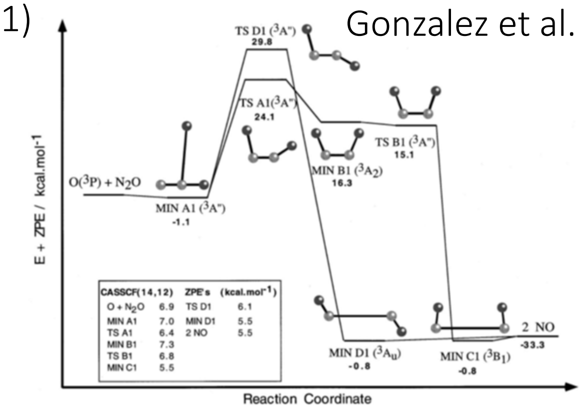
$$N_2O + O \longleftrightarrow NO + NO \quad (3)$$

$$NO + O \xleftrightarrow{+M} NO_2 \quad (4)$$

$$NO_2 + O \longleftrightarrow NO + O_2 \quad (5)$$



Gonzalez et al. (2001)



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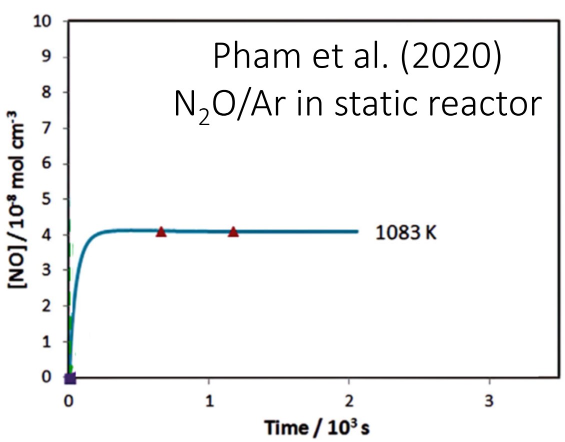
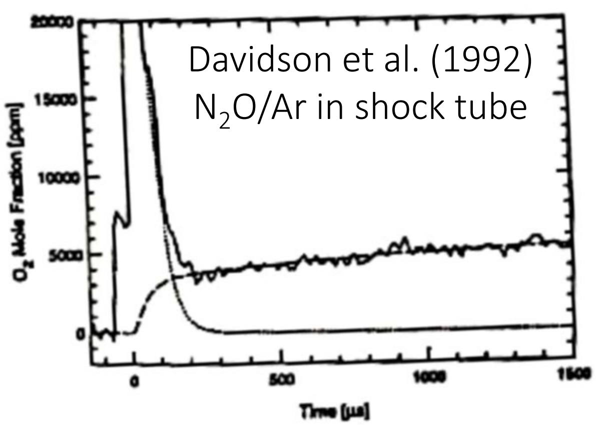
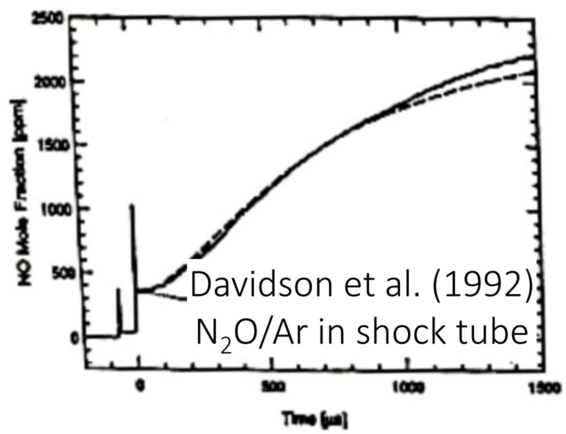


Pham et al. (2020)
N_2O/Ar in static reactor



Davidson et al. (1992)
N_2O/Ar in shock tube



Davidson et al. (1992)
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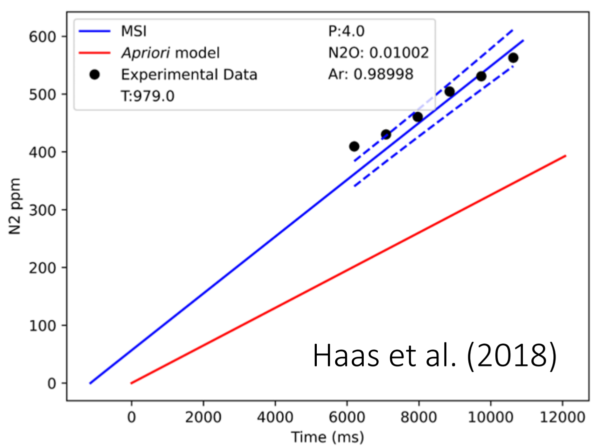
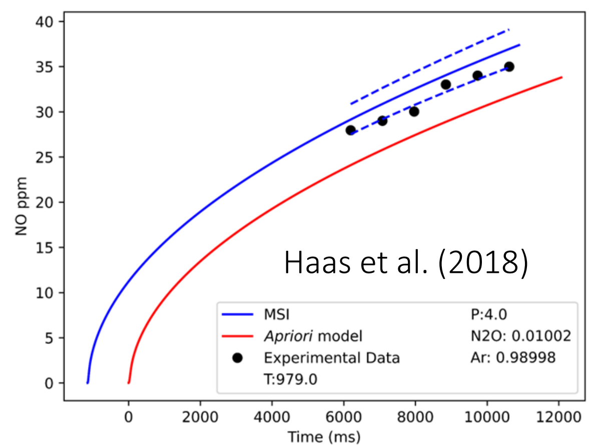
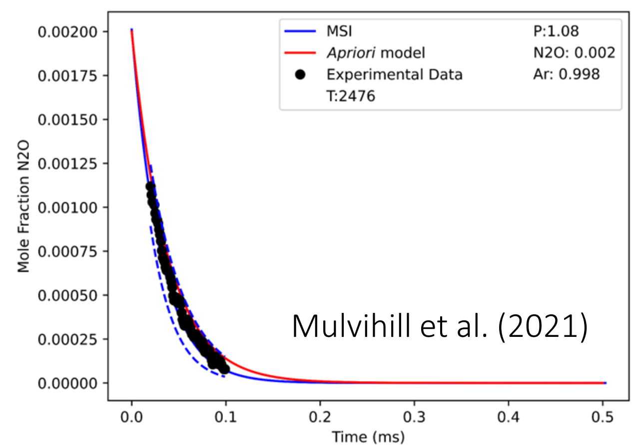
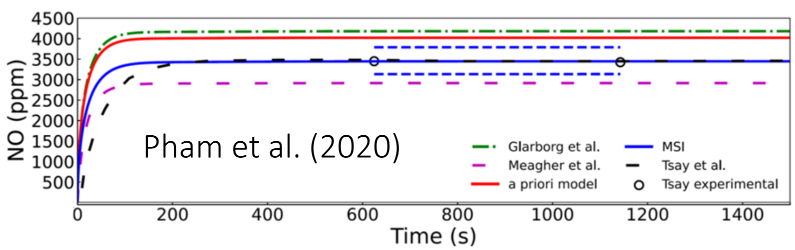
Lee, Barbet, LaGrotta, Meng, Lei, Haas, Burke *CNF* (2024)

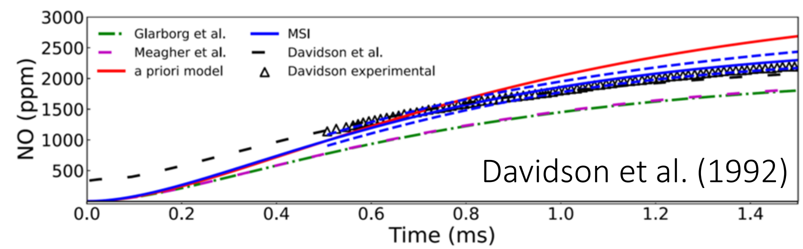
MSI model broadly consistent with data

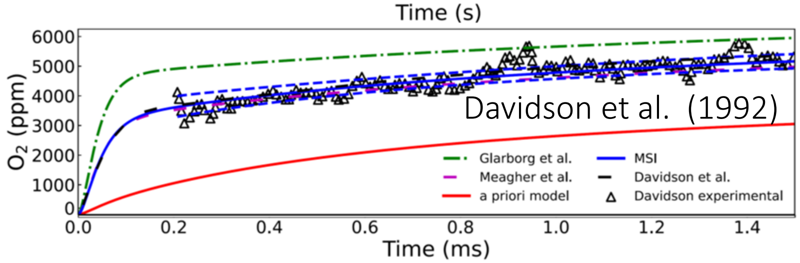






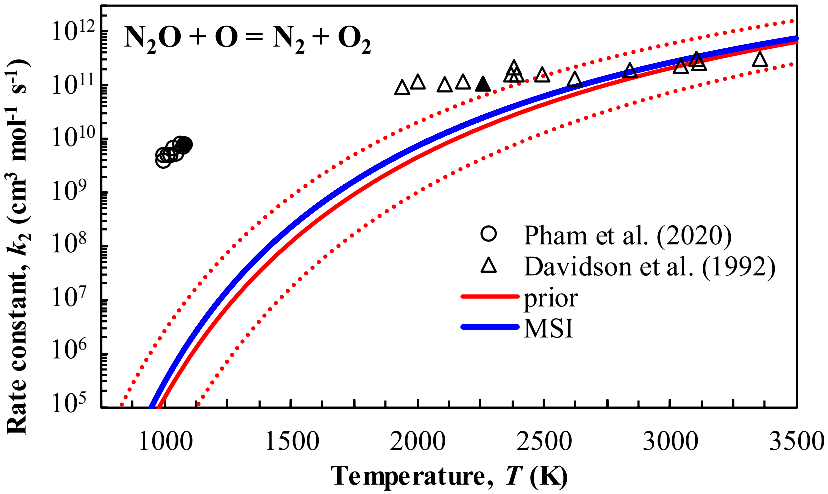


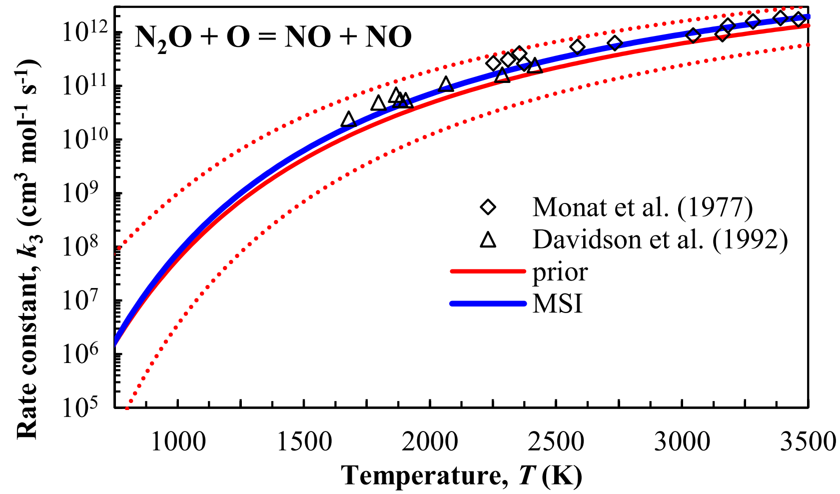


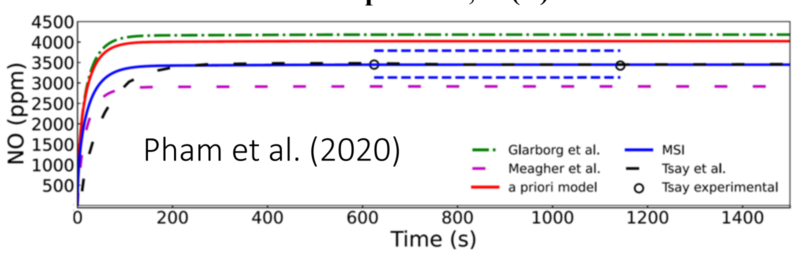


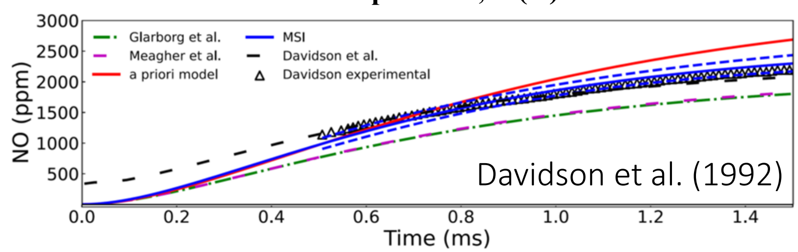
Lee, Barbet, LaGrotta, Meng, Lei, Haas, Burke *CNF* (2024)

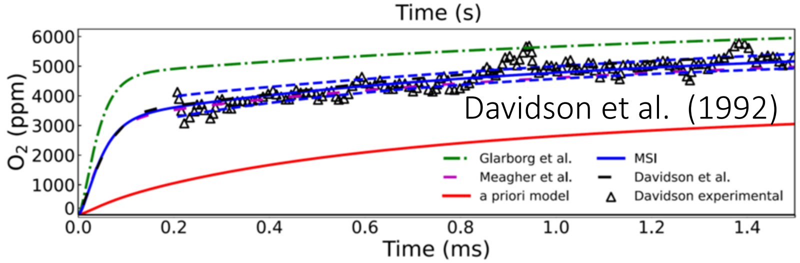
MSI model shows lower $N_2O + O = N_2 + O_2$ rate





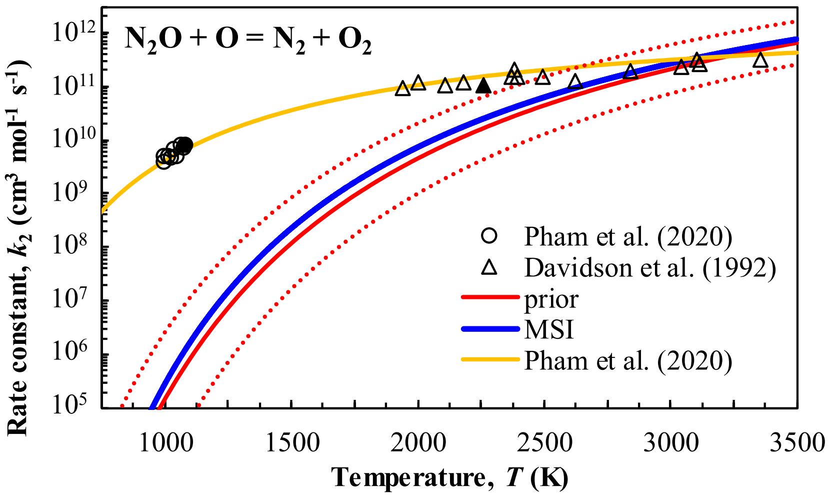


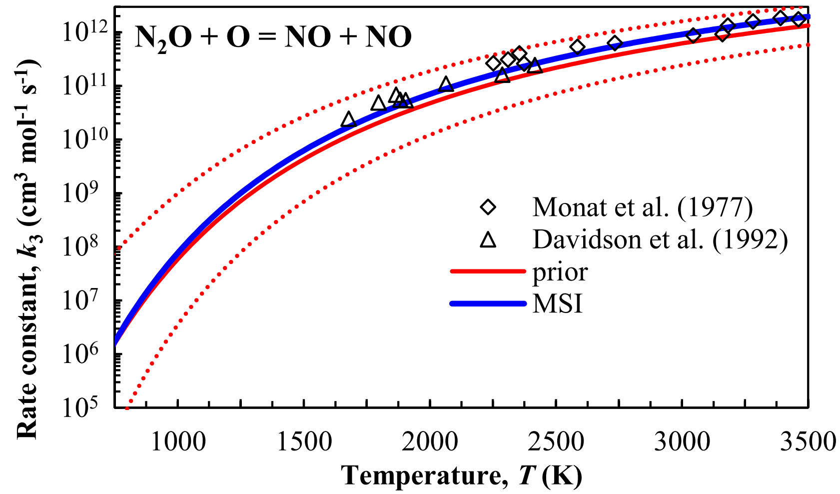


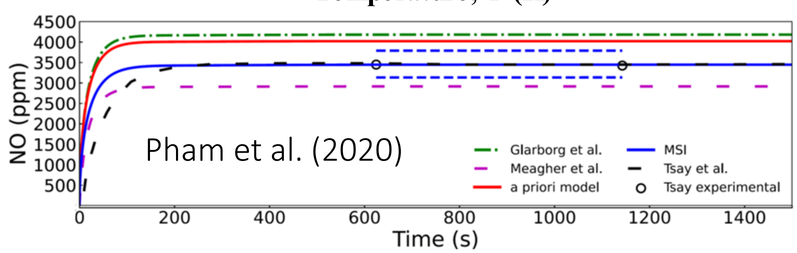


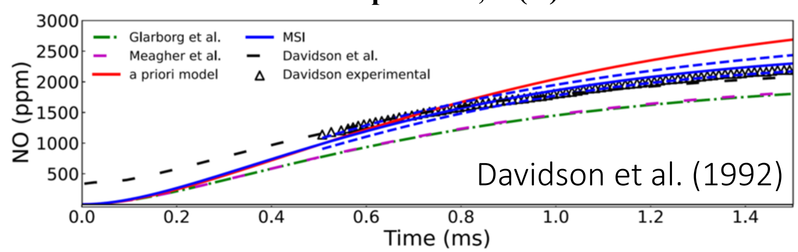
Lee, Barbet, LaGrotta, Meng, Lei, Haas, Burke *CNF* (2024)

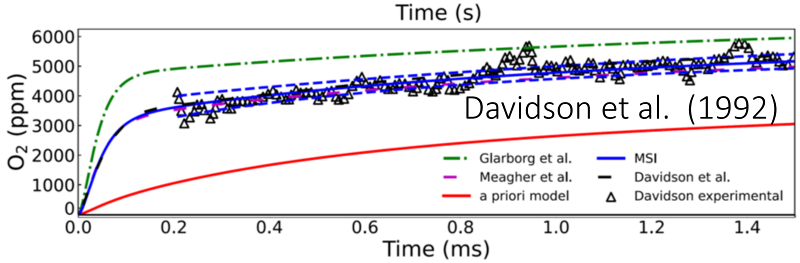
Experiments fail to constrain $N_2O + O = N_2 + O_2$





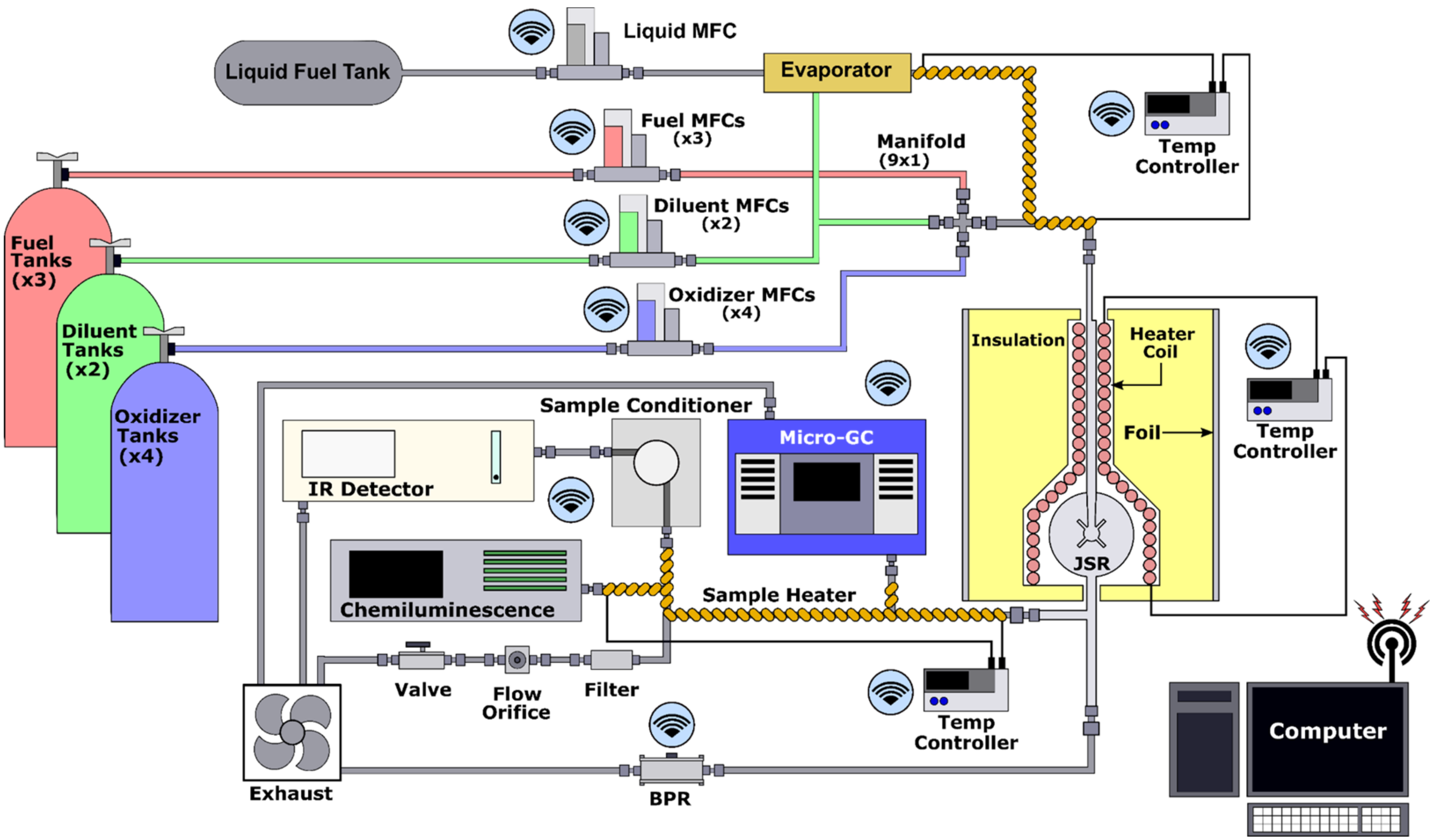






Lee, Barbet, LaGrotta, Meng,
Lei, Haas, Burke *CNF* (2024)

Optimal experiments in computer-controlled setup



Barbet, Lee, LaGrotta, Cornell, Burke *CNF* (2024)

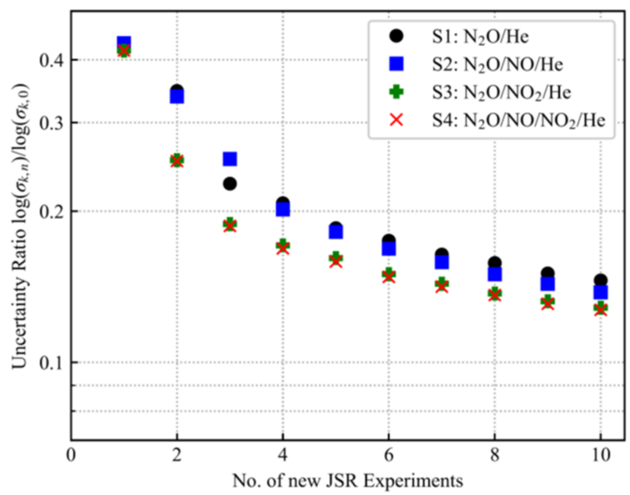
Optimal design to reduce uncertainty in $k_{N2O+O=N2+O2}$ considering actual experimental limitations and uniquely diverse chemical space

Mixture composition	5.85-20.0% N_2O (±2%) 0.00-250 ppm NO (±2%) 0.00-422 ppm NO_2 (±2%) balance He
Residence time	0.45s,1.0 s (±5%)
Pressure	15.00 psi (±1%)
Temperature	1050,1100 K (±1%)

Observable	N_2O[1]	N_2[1]	NO[1]	NO[2]	NO_2[2]	O_2[1]
Calibration	multi-point	multi-point	multi-point	1500 ppm ±2.3%	50.0 ppm ±6.4%	multi-point
Drift	±2.5%	±3%	±1.5%	±1%	±1.5%	—
Linearity	±1%	±3%	±1%	±3%	±1%	—
Noise (1σ)	±7[a]/1[b]%	±2%	±7[a]/1[b]%	±1%	±0.5%	±4%
Resolution	25 ppb	1 ppm	25 ppb	1 ppm	25 ppb	20 ppm

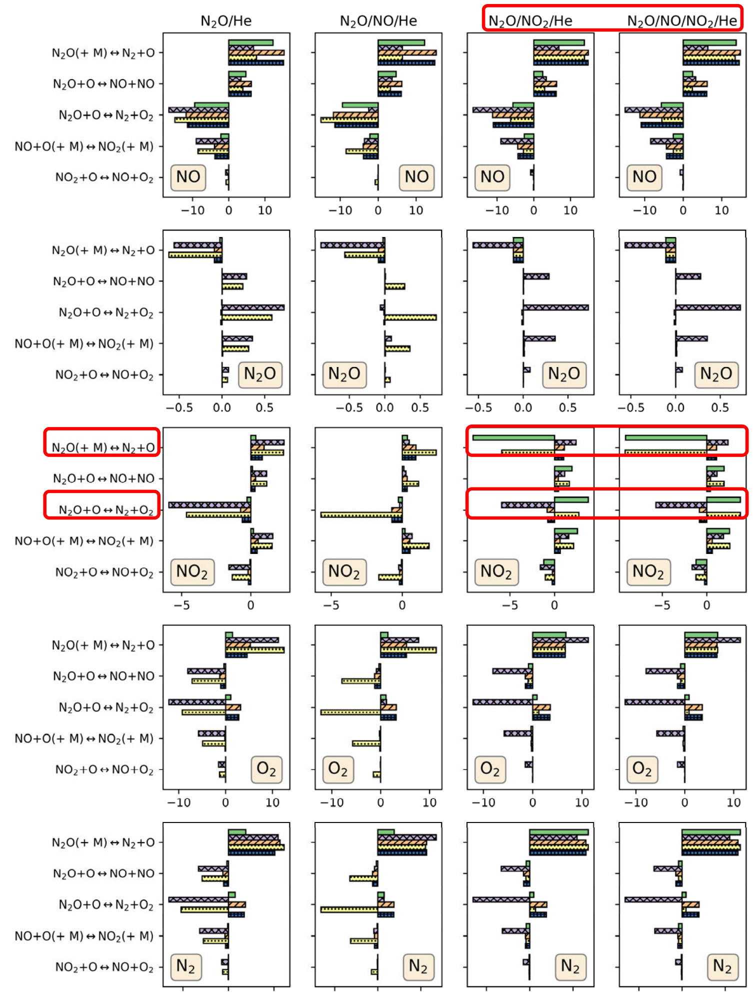
Barbet, Lee, LaGrotta, Cornell, Burke *CNF* (2024)

Optimal design identifies the value of NO_2 addition

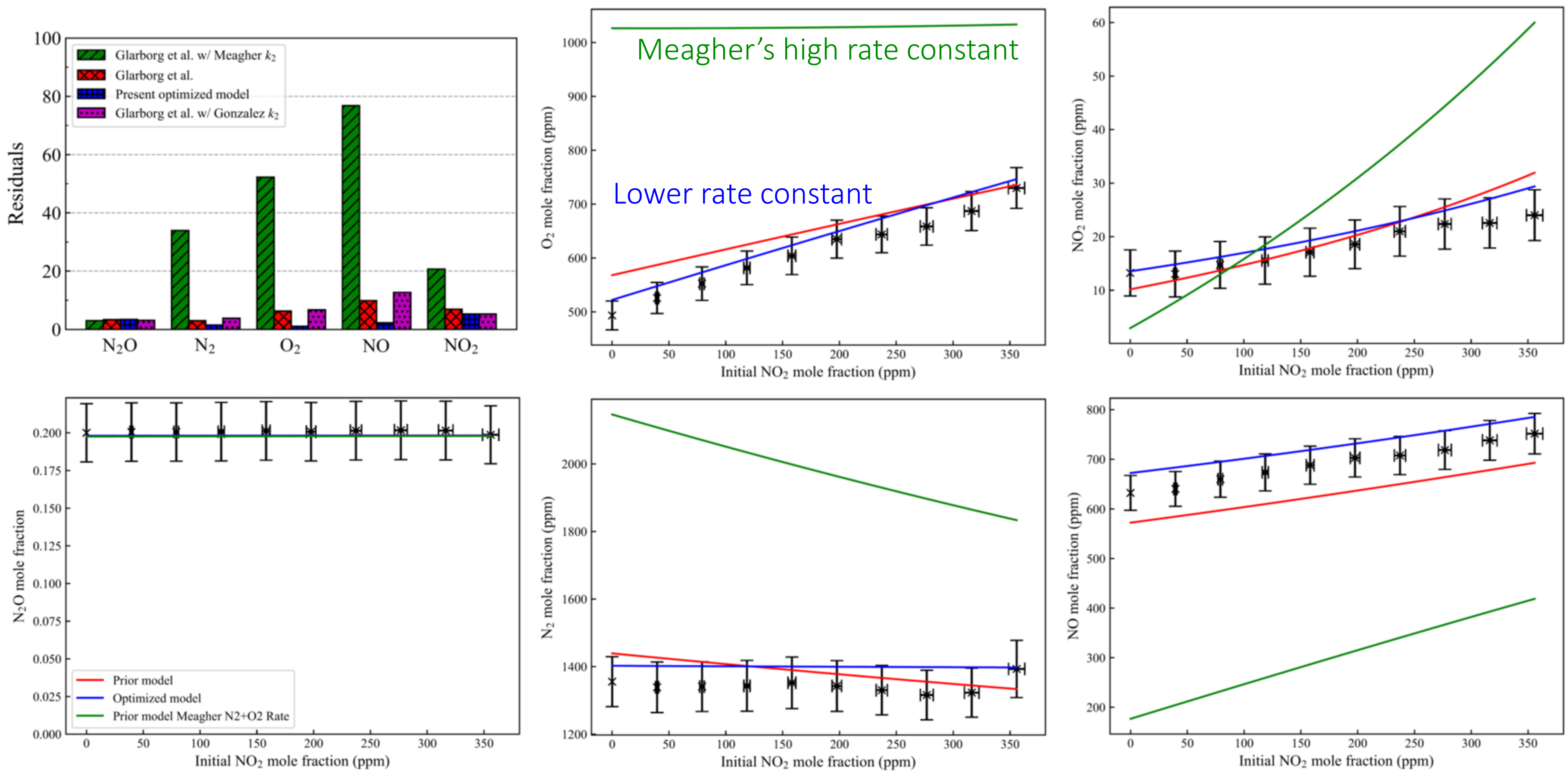


ID	T(k)	τ(s)	N_2O(%)	NO(ppm)	NO_2(ppm)
1	1050	0.45	20.0	0	356
2	1100	1.5	20.0	250	0
3	1050	0.45	20.0	0	0
4	1050	0.45	20.0	10	356
5	1050	0.45	20.0	10	0
6	1100	1.5	6.82	250	180
7	1050	0.45	20.0	11.5	356
8	1050	0.45	20.0	0	10
9	1100	1.5	6.82	250	214
10	1050	0.45	20.0	11.5	0

Barbet, Lee, LaGrotta, Cornell, Burke *CNF* (2024)



Measurements at these conditions definitively rule out higher rate constants for $N_2O + O = N_2 + O_2$



N_2O formation and consumption

N_2O production:

$$NH + NO \longrightarrow N_2O + H \text{ (high-T)}$$

$$NH_2 + NO_2 \longrightarrow N_2O + H_2O \text{ (vs. } H_2NO + NO)$$

N_2O consumption:

$$N_2O \xrightarrow{+M} O + N_2 \text{ (high-T)}$$

$$\cancel{N_2O + NH_2 \longrightarrow N_2H_2 + NO}$$

$$N_2O + H \longrightarrow N_2 + OH$$

$$+ \quad \xleftrightarrow{+M} HNNO$$

$$N_2O + O \longrightarrow NO + NO$$

$$\cancel{\longrightarrow N_2 + O_2}$$

Ongoing massive MSI analysis of theoretical and experimental data for nitrogen kinetics

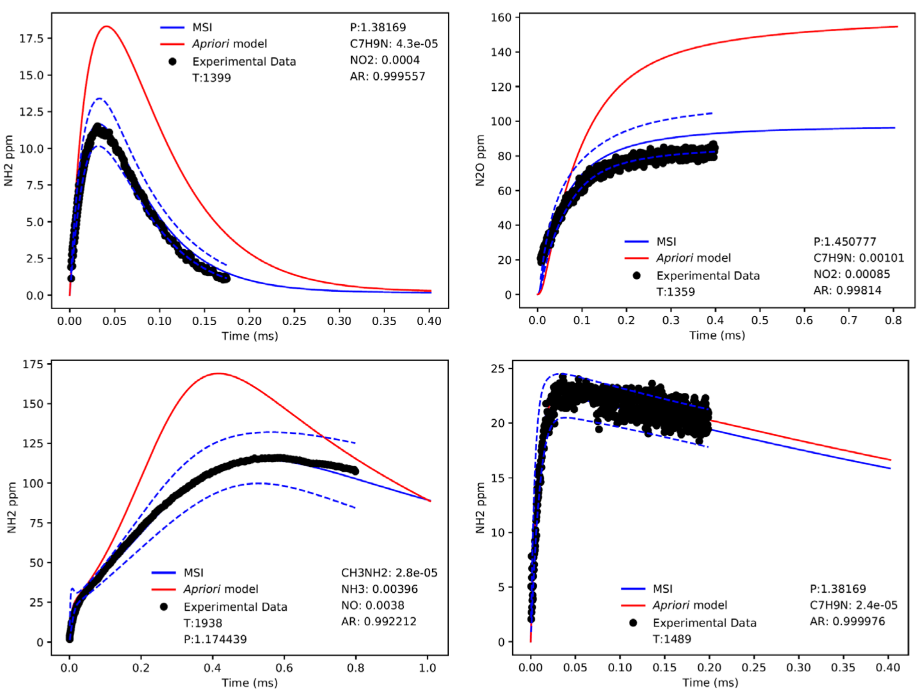
- Expansive dataset:
  - Theoretical data for several 10s of reactions
  - Experimental data from 100s of experiments

- Primary focus thus far:
  - Subset of key reactions important to NH_3 oxidation by $NO/NO_2/N_2O$
    - NH_3 + H/O/OH/O_2, NH_2 + NO, NH_2 + NO_2, NH_2 + N_2O, H_2NO + OH/NO_2/O_2/HO_2, …

  - (Strong but incomplete overlap with NO_x formation from H_2 and NH_3 oxidation by O_2)

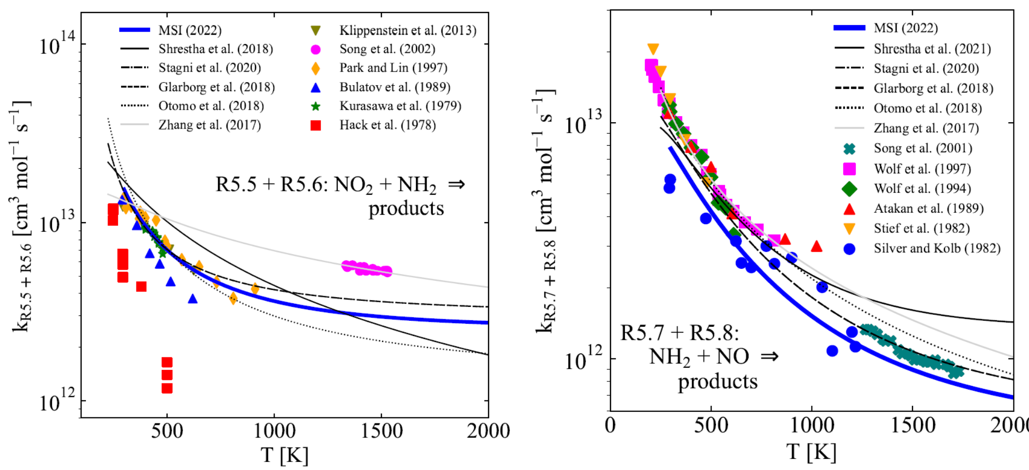
Cornell, Lee, LaGrotta, Burke (in prep)

MSI model gives alternative (self-consistent) explanations of data used to determine rate constants



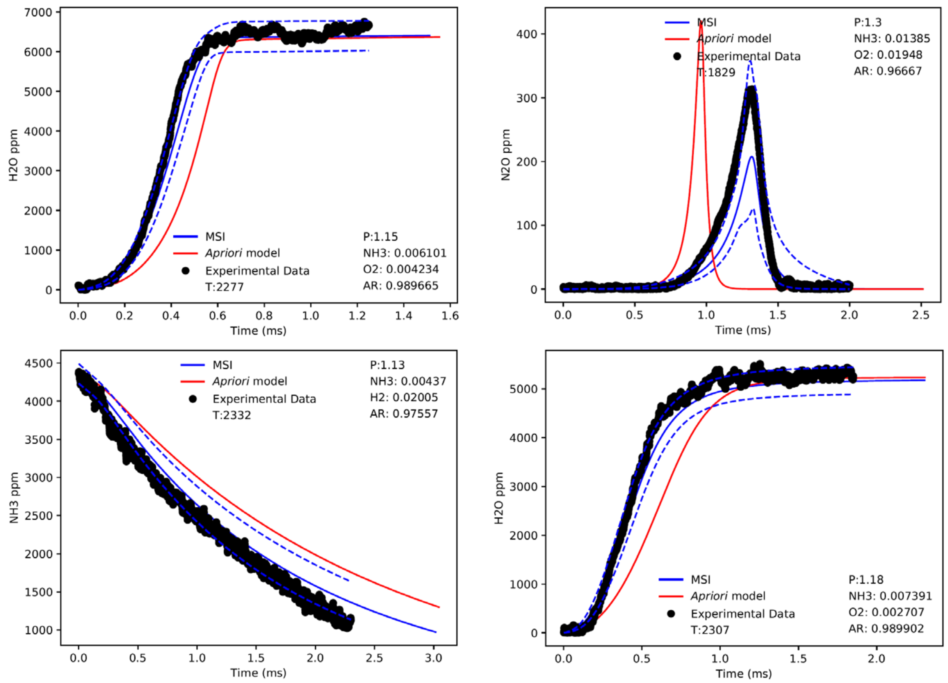
Song, Golden, Hanson, Bowman

IJCK (2001); *PCI* (2002); *JPCA* (2002); *JPCA* (2002)



Cornell, Lee, LaGrotta, Burke (in prep)

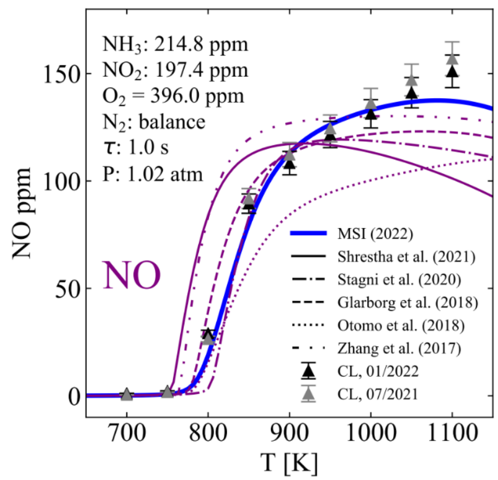
MSI model better reproduces training data

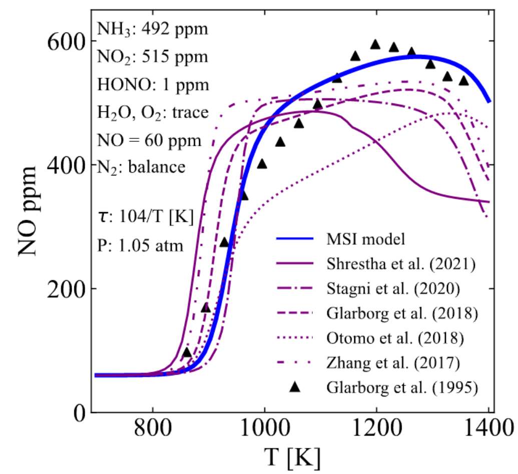


Alturaifi, Mathieu, Petersen

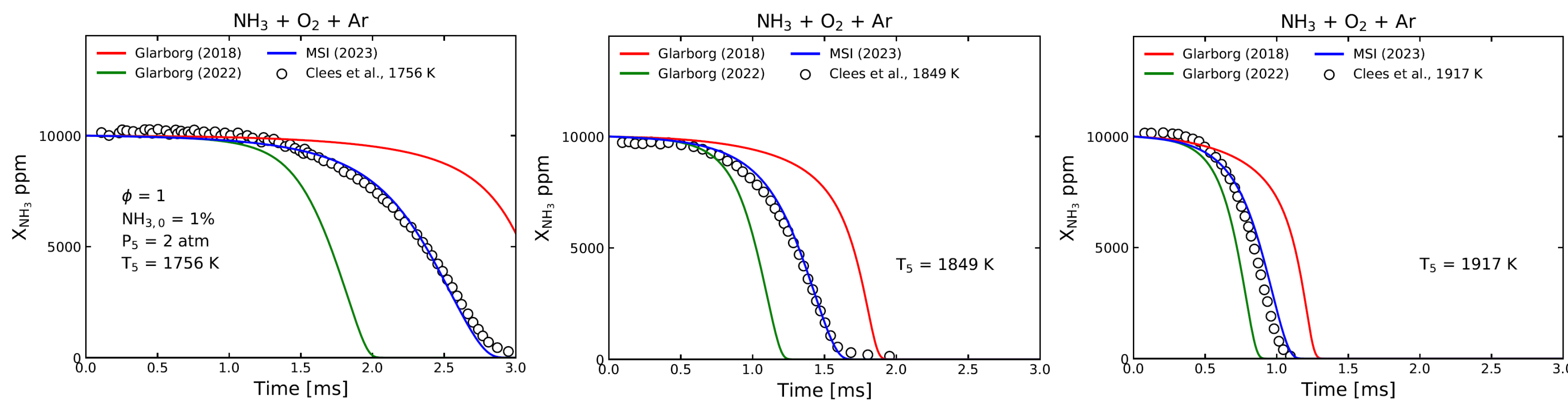
Fuel Comm (2022); *CNF* (2022); *PCI* (2023)

MSI model accurately *predicts* non-training data





Cornell, Barbet, Lee, Burke *AECS* (2023) Glarborg, Dam-Johansen, Miller *IJCK* (2023)



Clees, Rault, Figueroa-Labastida, Barnes, Ferris, Hanson *US Combust Meeting* (2023); *CNF* (2024)

Conclusions

- N_2O consumption pathways are very different than previously thought
  - $N_2O + O = N_2 + O_2$ and $N_2O + NH_2 = N_2H_2 + NO$ are too slow to matter
  - $N_2O + H = HNNO$ (excluded from models) is a major pathway at high pressure
- Rate constants for key reactions in NH_3 oxidation may be different than thought
  - $NH_2 + NO$, $NH_2 + NO_2$, …
- Multi-component pressure dependence important to full-strength mixtures
- Multiscale physics-based, data-driven approach useful for deriving new insights

Big open questions

- What other surprises are in store? what other reactions/species are missing?
- How do the kinetics change with pressure and *composition*?
- How much can we trust ammonia models right now?
- How do NH_3 and HCs interact? Synergistic/antagonistic? what new pathways emerge?

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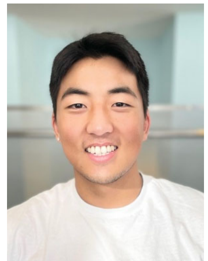
(PhD 2022 - ARL)

Carly LaGrotta
(PhD 2023)



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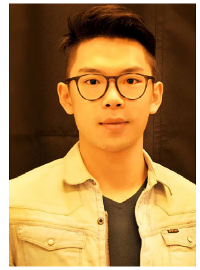
(PhD Candidate)



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Thank you!

Questions?

ACS PRF# 56409-DNI6

NSF CFS #1706252
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NSF CAREER #1944004

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