NETL AMMONIA COMBUSTION TECHNOLOGY GROUP MEETING

Argonne NATIONAL LABORATORY

THEORY INFORMED KINETICS FOR NH_3 OXIDATION AND PYROLYSIS

Stephen J. Klippenstein, Clayton Mulvihill

Jim Miller, Peter Glarborg, Raghu Sivaramakrishnan

January 14, 2025

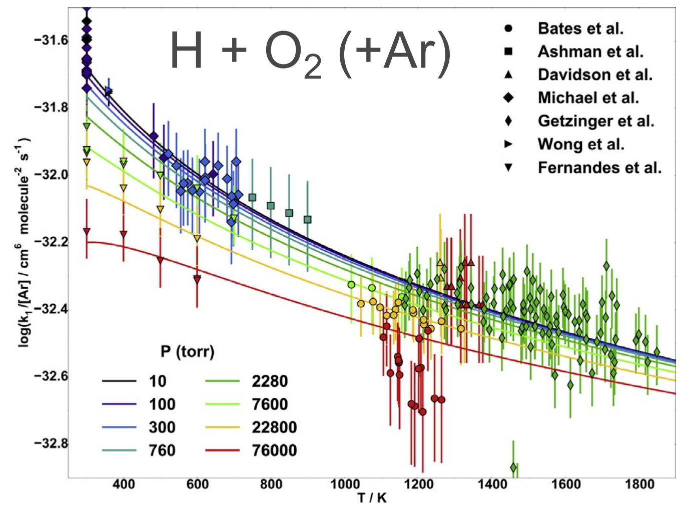
Theory Informed Kinetics (ThInK)

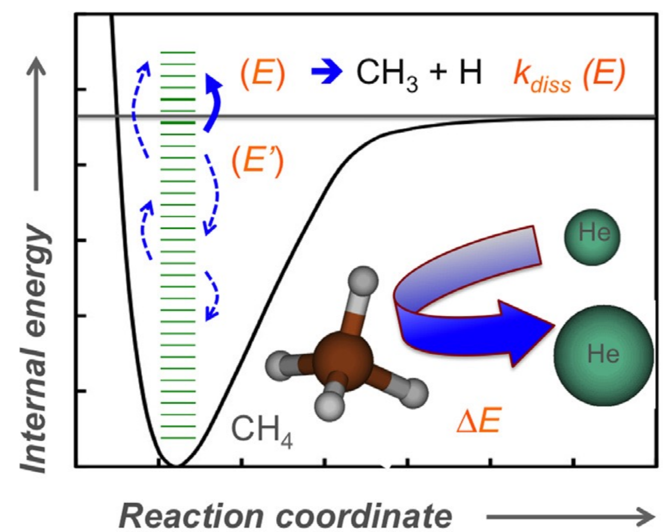
Spectacular Progress in First Principles Theor. Kin.
Accuracy Rivals or Exceeds Many Experiments
Generally can predict to better than factor of two
Often 20 % uncertainties

High Level Composite Ab Initio Methods

- CCSD(T), CCSDT(Q), Anharmonicities,
- Core-Valence, Relativistic, DBOC
- Multi Reference Methods

Sophisticated Variational Methods – VRC-TST
Multiple-Well Multiple-Channel Master Equation
First Principles Energy Transfer
Non-thermal Effects
Roaming Channels





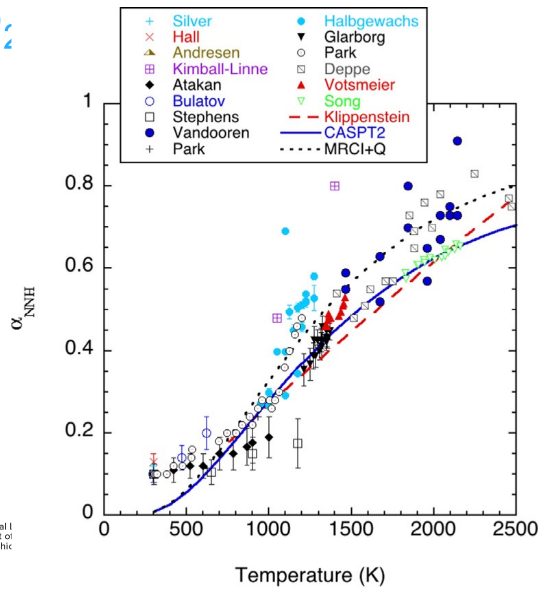
Theory Informed Kinetics (ThInK)

1. NOx Mechanism

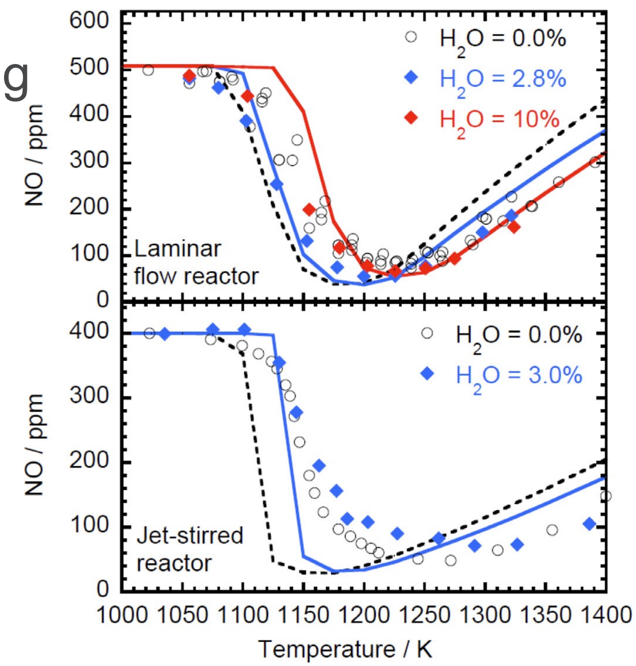
Glarborg, Miller, Ruscic, SJK; PECS, 67 (2018) 31-68.

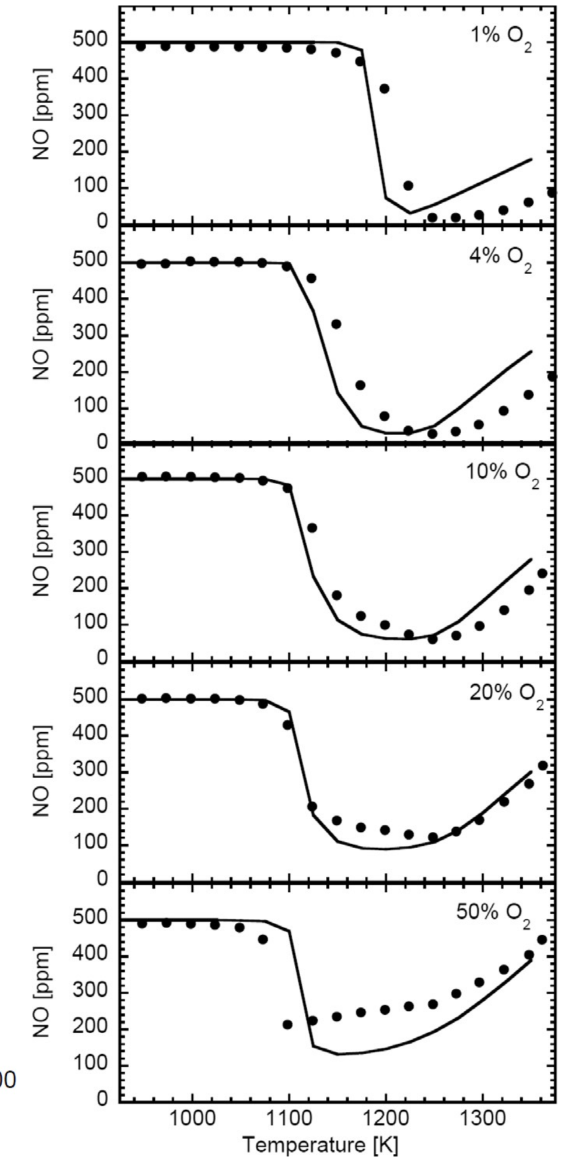
$NH_2 + NO$	Thermal deNOx
$CH + N_2$; $NCN + H$	Prompt NO
NNH; $NNH + O_2$; $NNH + O$	Role of NNH
$NH + NO$, $N_2O + H$	
$NH_2 + O_2$	
$NH_2 + NO_2$	

$NH_2 + NO$ Branching



SNCR With NH_3





Theory Informed Kinetics (ThInK)

2. NH_3 Oxidation
Peter Glarborg, Jim Miller, SJK
Fails miserably for NH_3 Flame Speeds
NH_2 + HO_2, NH_2 + O, HNO + NH_2, H + HNNO
HNO + M, NH_2 + H + M, NH_2 + NH_2 + M (Jasper)
Resolution – Raghu Sivaramakrishnan
Mike Burke – importance of NH_3 and H_2O as colliders and Mixture Effects

3. NH_3 Pyrolysis
Synthesis by Pulsed Heating and Quenching
Liangbing Hu and Dongxing Liu (Maryland), Emily Carter and Yiguang Ju (Princeton), Ahren Jasper and SJK (Argonne)
Preparing Fully Theoretical Model for NH_3 Pyrolysis; N_xH_y
With Clayton Mulvihill (Baylor)

Theory Informed Kinetics (ThInK)

4. NH_3 + CoFuel Oxidation

Yiguang Ju: $NH_3 + CH_3OH$

- $NH_2 + CH_3OH$; $NH_2 + CH_2O$ Proc. Combust. Inst. 40, 105489 (2024).

Henry Curran: $NH_3 + CH_4$

- $NH_2 + H_2NO$
- $CH_3 + H_2NO$
- $R + H_2NO$
- $CH_3 + NH_2$ Zhu, SJK, Curran, Zhou, Combust. Flame, submitted (2024).

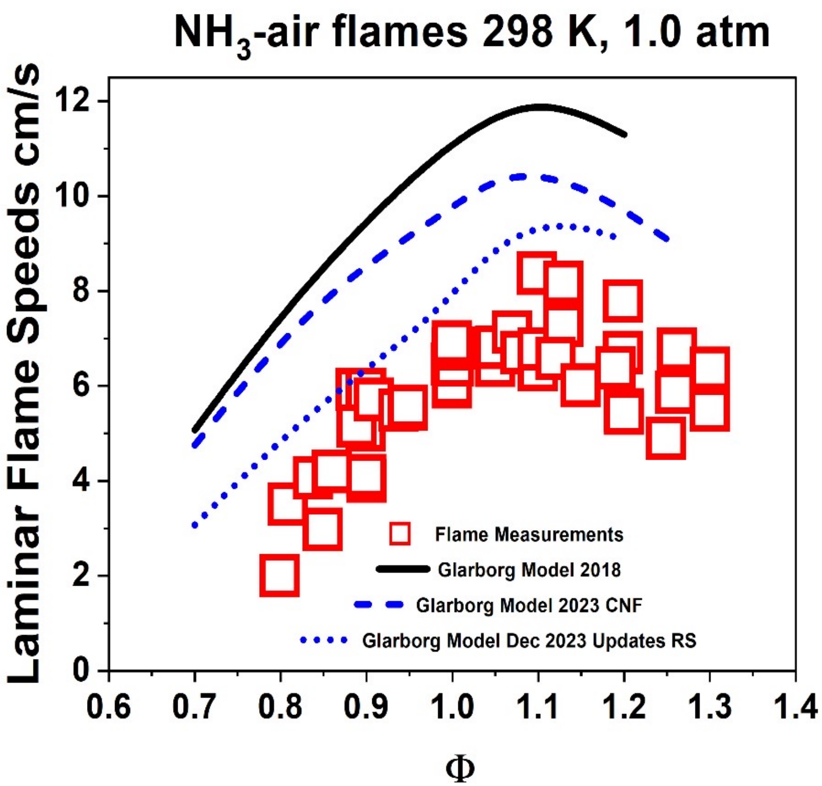
5. N_2O Chemistry

- N_2O Dissociation Mulvihill
- $N_2O + O = NO + NO$
- $N_2O + O = N_2 + O_2$
- HNNO + H = … Glarborg

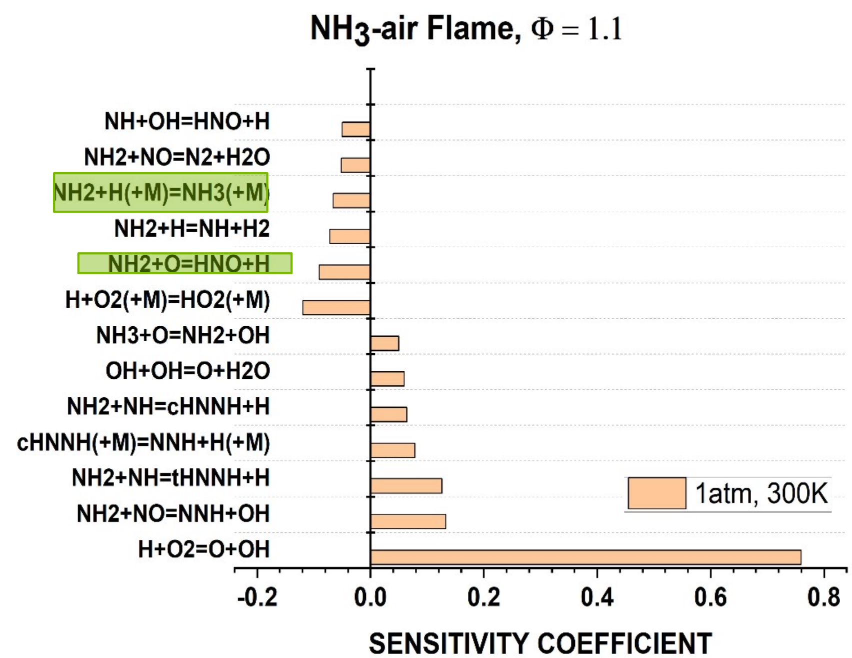
NH_3 FLAME SPEEDS

NH_3 Flame Speeds

Raghu Sivaramakrishnan - 2023



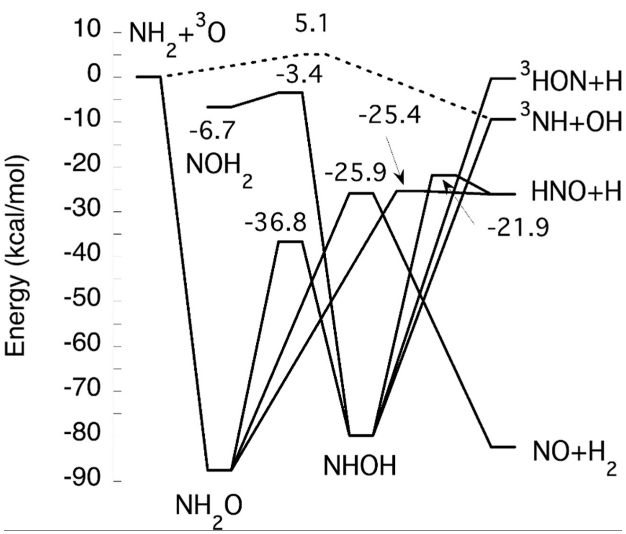
Glarborg, Miller, Ruscic, Klippenstein
Modeling Nitrogen Chemistry in Combustion
Prog. Ener. Combust. Sci. 67 (2018) 31-68



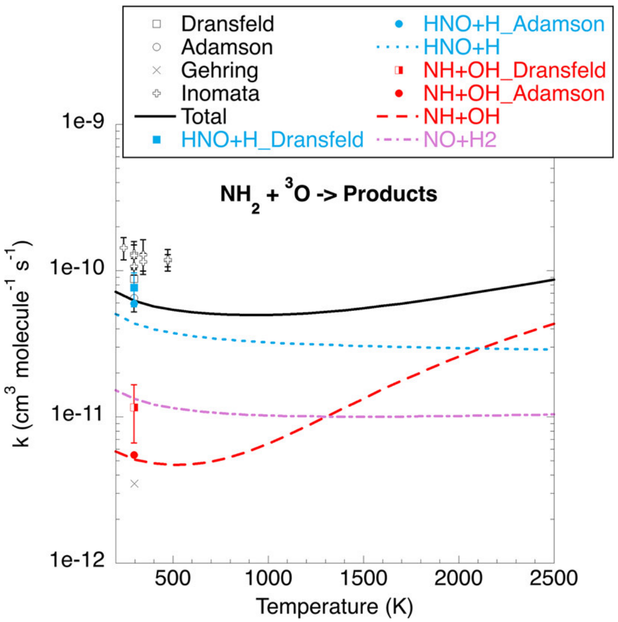
Glarborg
The $NH_3/NO_2/O_2$ System: Constraining Key Steps in Ammonia Ignition and N_2O Formation
Combust. Flame 257 (2023), 112311.

NH_2 + O

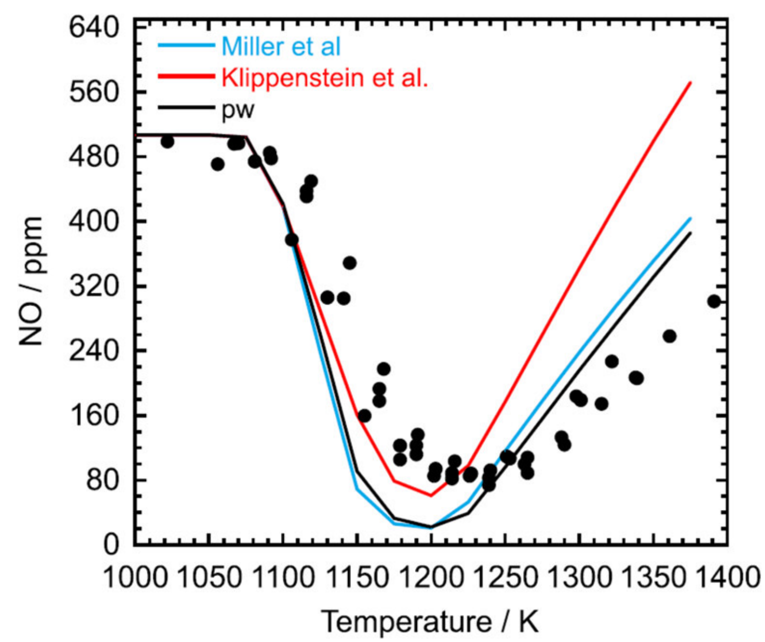
CCSD(T)-F12/CBS(TZ-F12,QZ-F12) freqs.
ANL1' energies ~CCSDTQ(P)/CBS + rel. + DBOC + anh.
VRC-TST for NH_2+O; NH + OH; VTST for NH_2O = H+HNO; etc



NO + H_2 is new channel



Reduction of NO by NH_3



SJK, Mulvihill, Glarborg
Theoretical Kinetics Predictions for Reactions on the NH_2O
Potential Energy Surface, J. Phys. Chem. A 127 (2023) 8650-8662.

NH_2 + H (+ M) NH_2 + NH_2 (+M)

Jasper
Trajectory Simulations
MP2/CBS

Table 1. Calculated Third-Body Efficiencies Relative to M = N_2[a]

system	*T* (K)	M = N_2	Ar	O_2	NH_3	CH_4	CO_2
NH_3(+M)	300	1.00	0.32	0.50	4.39	3.15 (2.60[a])	3.54 (2.83[a])
	1000	1.00	0.41	0.59	8.11	5.38	5.44
	2000	1.00	0.45	0.70	9.90	6.36	5.76
N_2H_4(+M)	300	1.00	0.50 (0.77[a], 0.4[b])	0.61	2.93 (4.0[b])		
	1000	1.00	0.59	0.69	4.87		
	2000	1.00	0.70	0.80	6.02		

[a]These are compared with available experimental results given in parentheses taken from [a]Altinay and MacDonald[37−39] or [b]Van Khe et al.[45]

Additional Estimates of Third Body Collider Efficiencies for H_2O

On the Rate Constant for NH_2 + HO_2 and Third-Body Collision Efficiencies for NH_2 + H (+M) and NH_2 + NH_2 (+M)

J. Phys. Chem. A, 125, 1505 (2021)

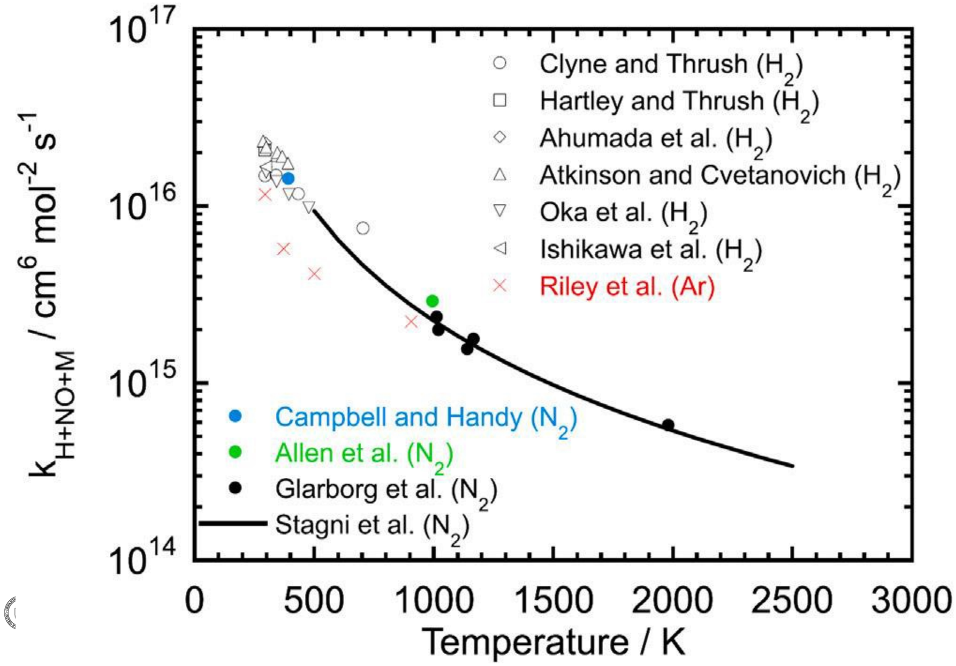
Glarborg, Hashemi, Cheskis, Jasper

H + NO (+M) = HNO (+M)

Calculated third body efficiencies for HNO(+M) relative to M = Ar.

T/K	M = Ar	He	N_2	H_2	NH_3
300	1.00	1.23	1.83	3.20	5.35
600	1.00	1.37	1.65	3.12	5.82
1000	1.00	1.67	1.73	3.07	6.18
1500	1.00	1.60	1.52	2.58	5.87
2000	1.00	1.53	1.54	2.40	5.73
2500	1.00	1.70	1.55	2.23	5.90

Jasper
Trajectory Simulations
MP2/CBS



An experimental, theoretical, and kinetic modeling study of post-flame oxidation of ammonia
Jian, Hashemi, Wu, Glarborg, Jasper, SJK
CNF, 261, 113325 (2024).

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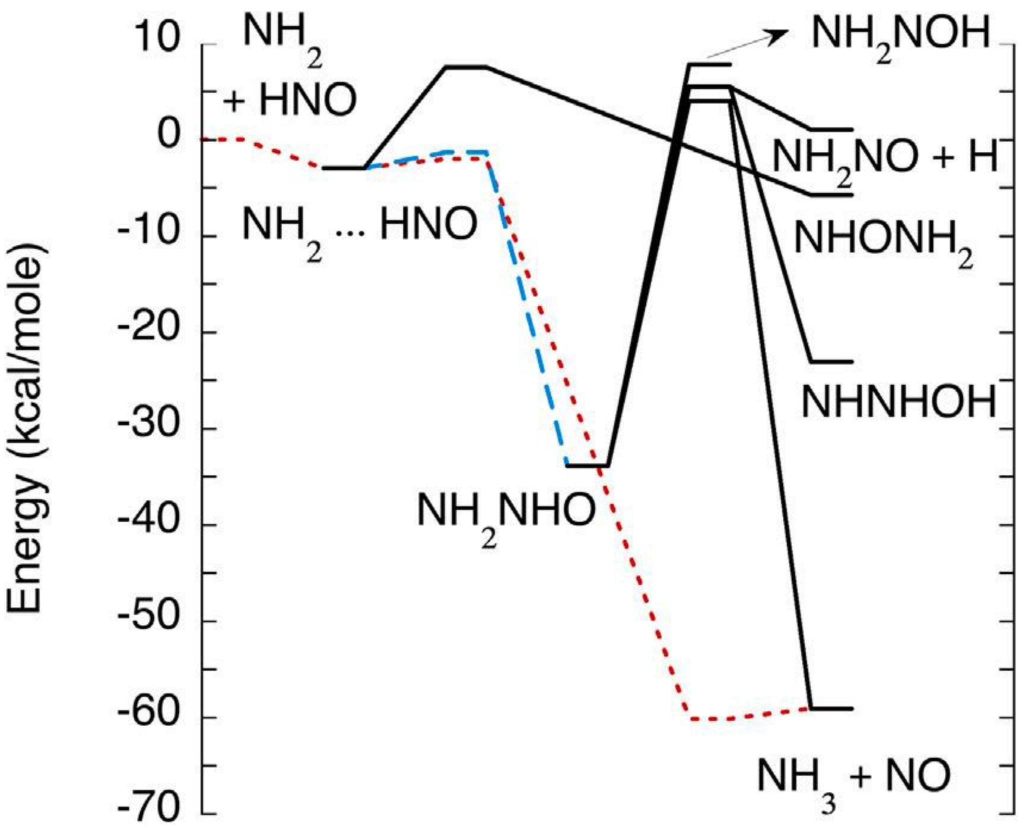
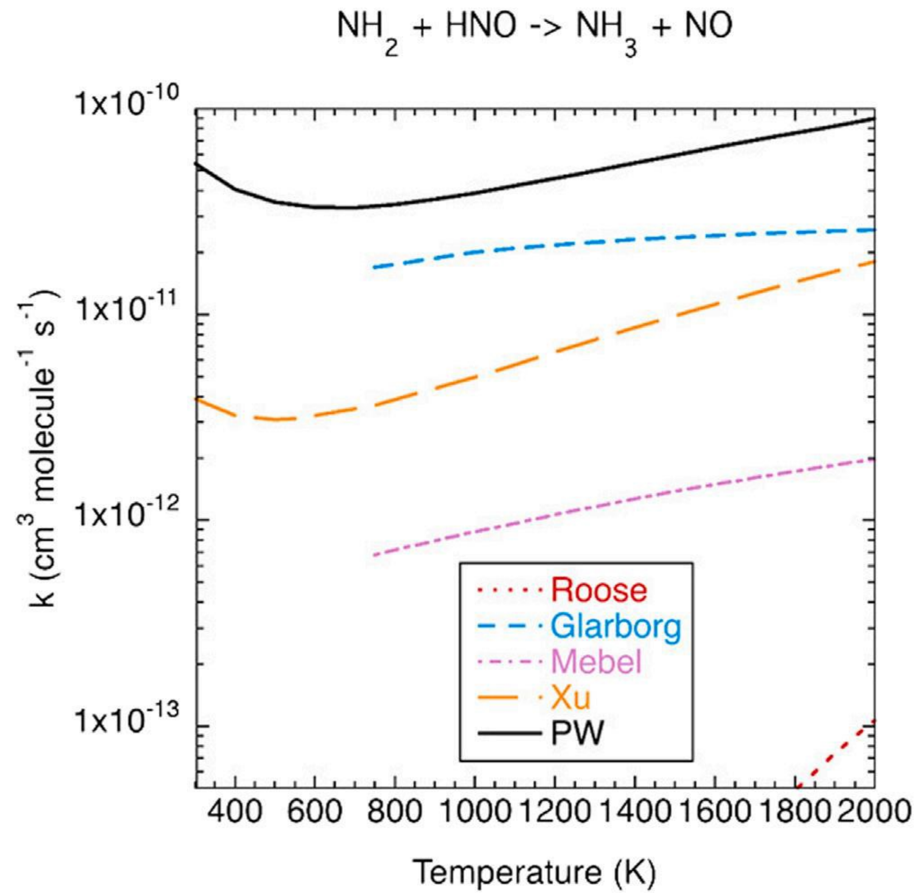
NH_2 + HNO

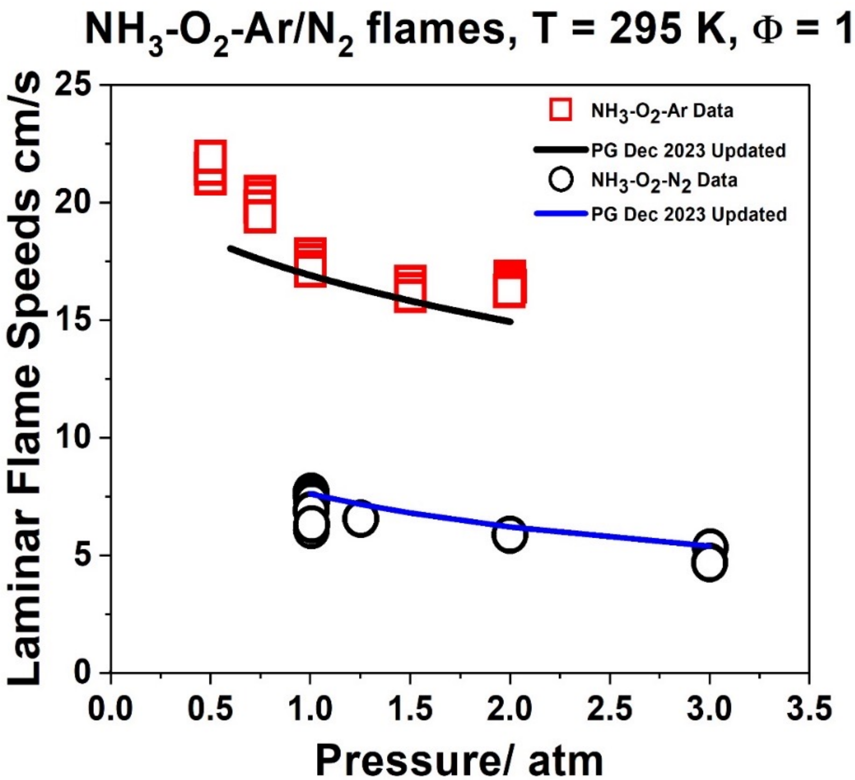


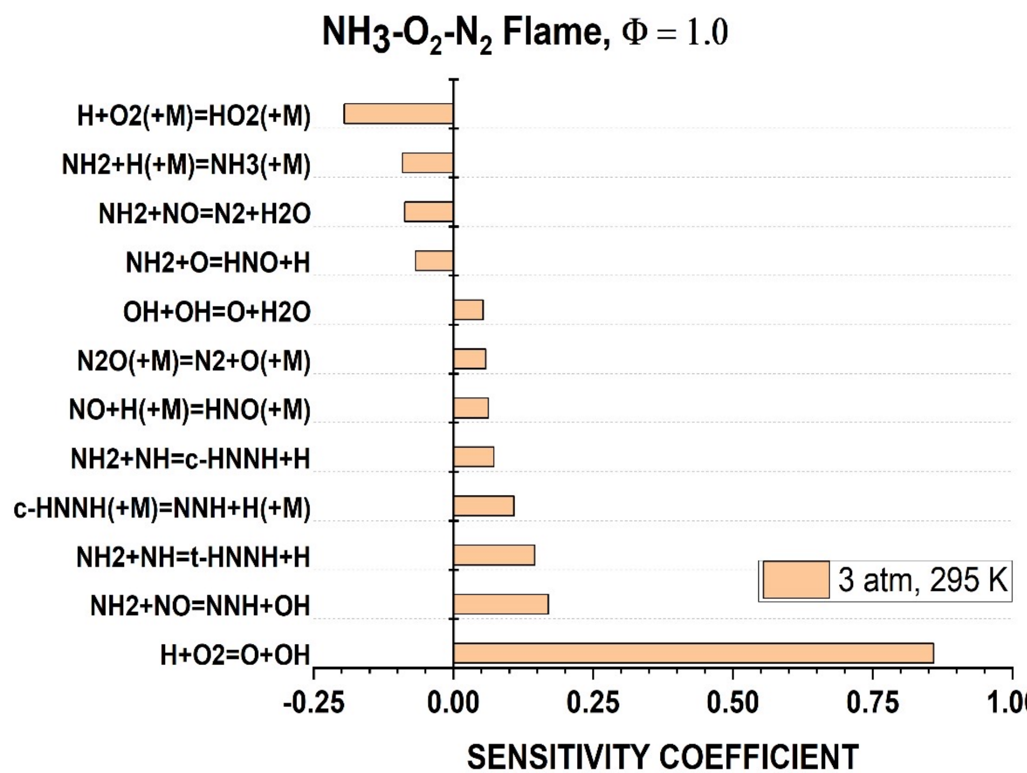
An experimental, theoretical, and kinetic modeling study of post-flame oxidation of ammonia
Jian, Hashemi, Wu, Glarborg, Jasper, SJK
CNF, 261, 113325 (2024).

CCSD(T)-F12/cc-pVTZ-F12 vibs.
ANL0 energies
VRC-TST for NH_2… HNO
VTST for NH_2…HNO = NH_2NHO or NH_3 + NO



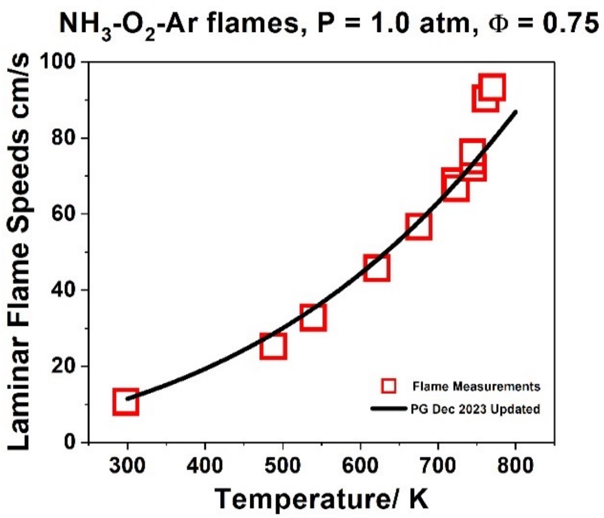
FLAME SPEEDS WITH DIFFERENT DILUENTS

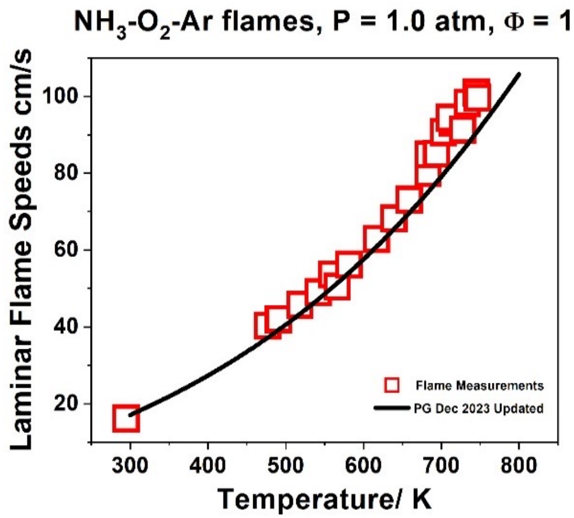


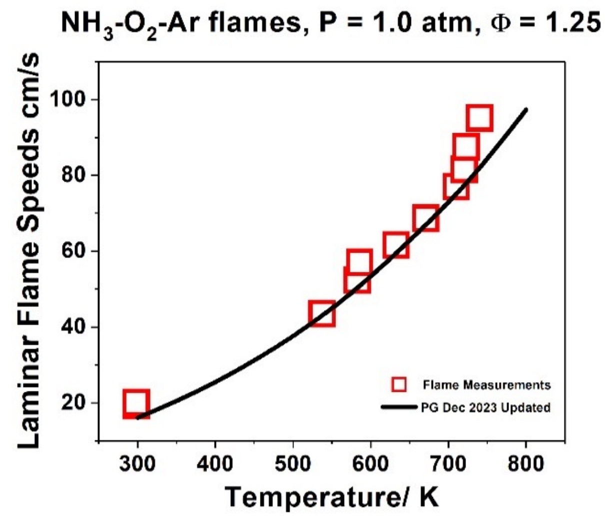


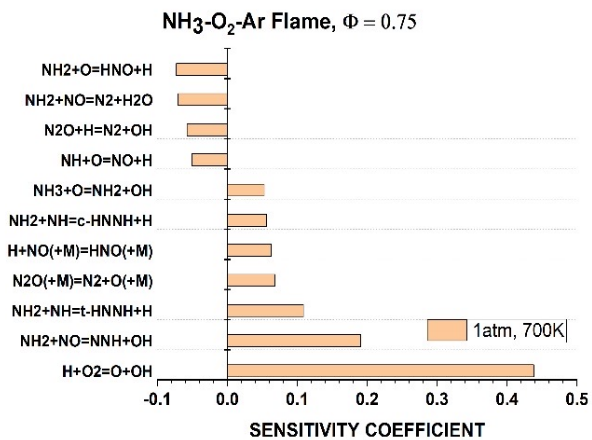
Data is from Figures 2a and 4b Figueroa-Labastida et al. CNF 260 (2024) 113256

TEMPERATURE DEPENDENT FLAME SPEEDS

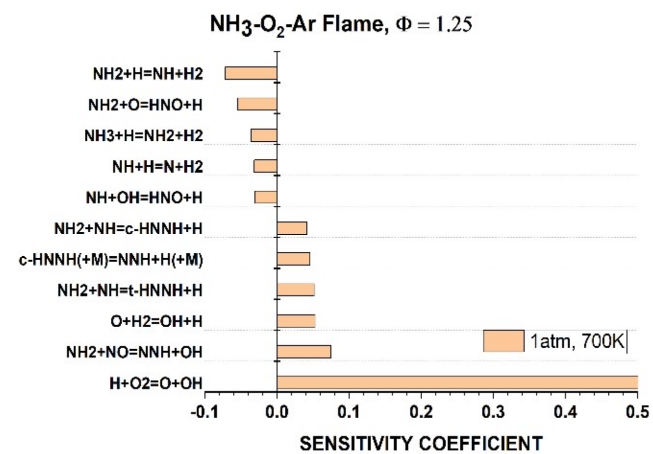






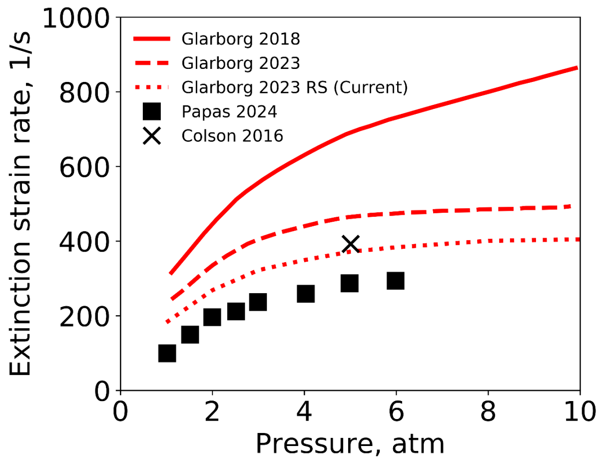


Data taken from Figures 7a-c Figueroa-Labastida et al. CNF 260 (2024) 113256.



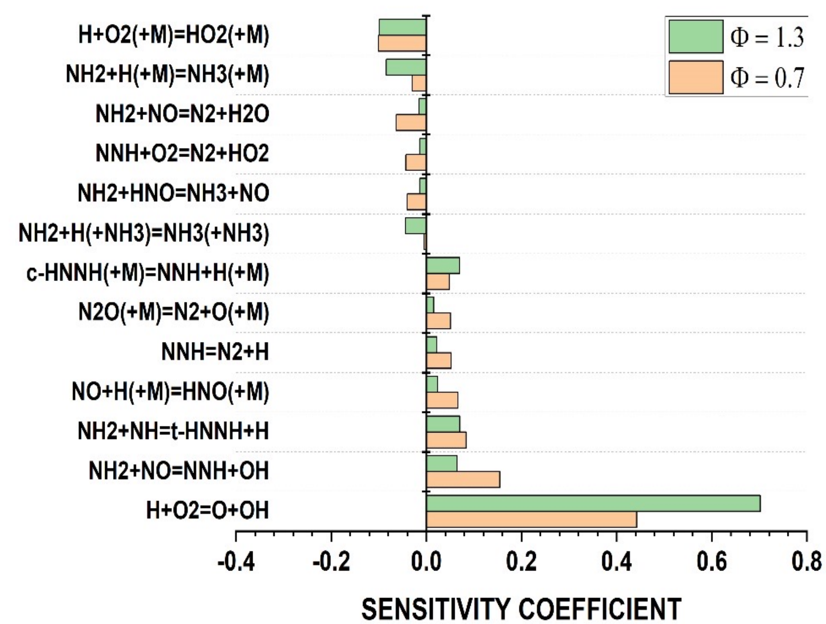
PRESSURE DEPENDENT FLAME SPEEDS

NH_3-air counterflow, T = 300 K, ϕ = 1

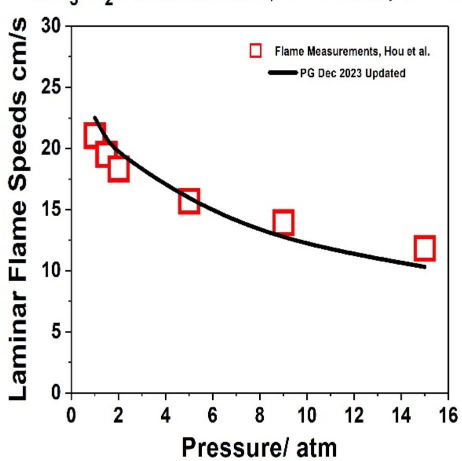


Data from Hou et al. Fuel 320 (2022) 123913.

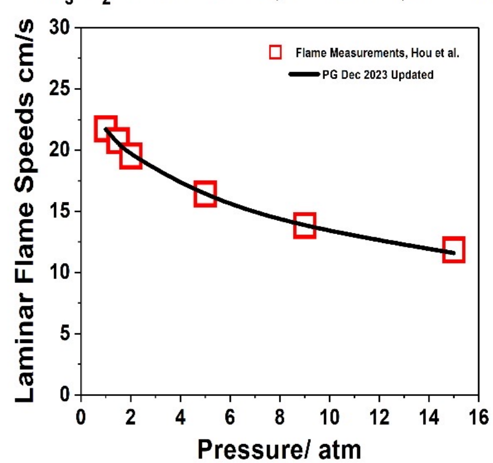
NH_3-O_2-Ar-He Flames, P = 9 atm, T = 300 K



NH_3-O_2-Ar-He flames, T = 298 K, Φ = 0.7



NH_3-O_2-Ar-He flames, T = 298 K, Φ = 1.3



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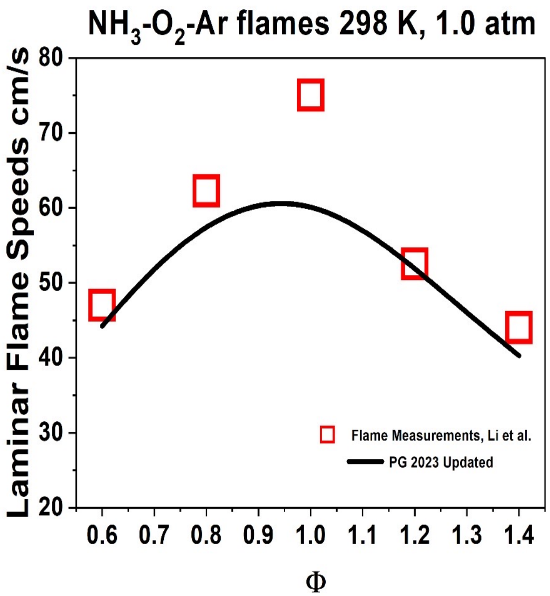
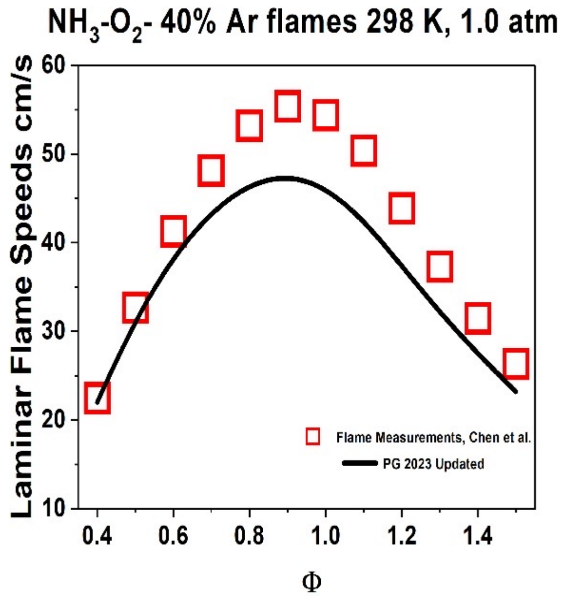
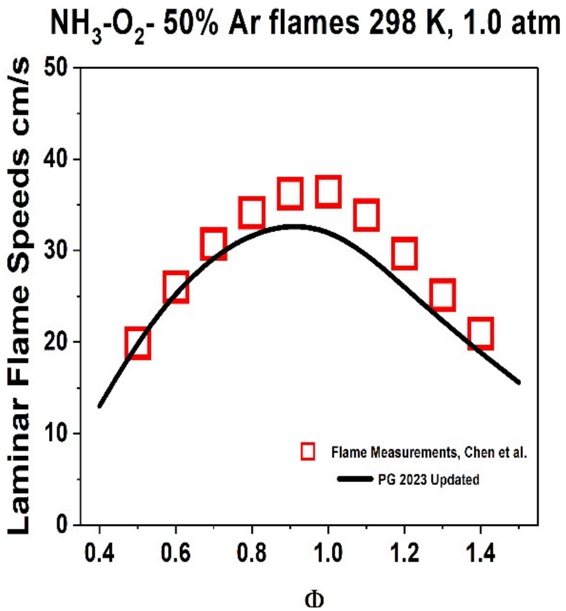
DILUTION DEPENDENT FLAME SPEEDS





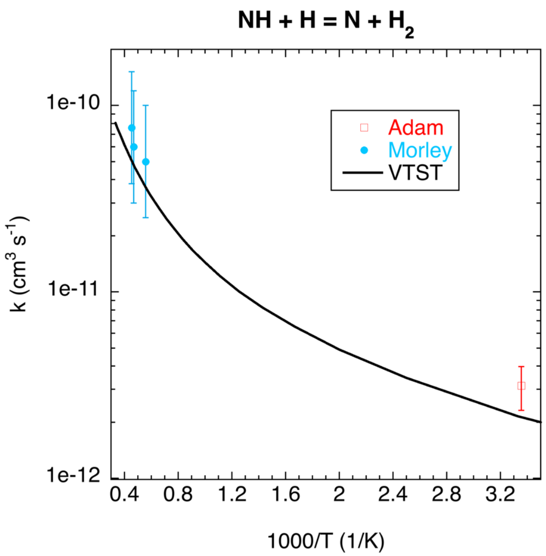


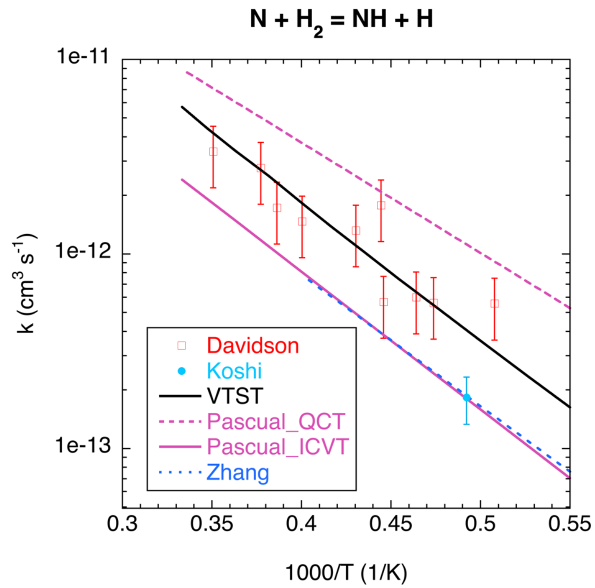
Data taken from Figure 7 Li et al. Int. J. Hydrogen Ener. 46 (2021) 21249.

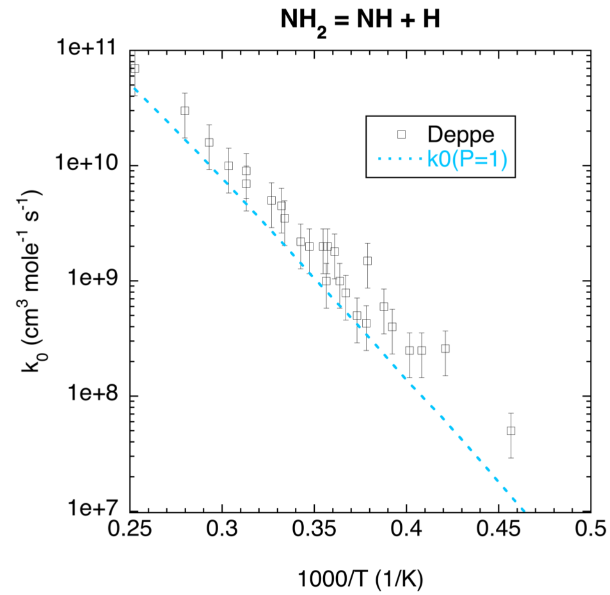
Data taken from Figures 3a-b Chen et al. CNF 255 (2023) 112930.

NH_3 PYROLYSIS

NH_2 KINETICS







Geometries and Vibrational Frequencies

- CCSD(T)-F12/cc-pVQZ-F12

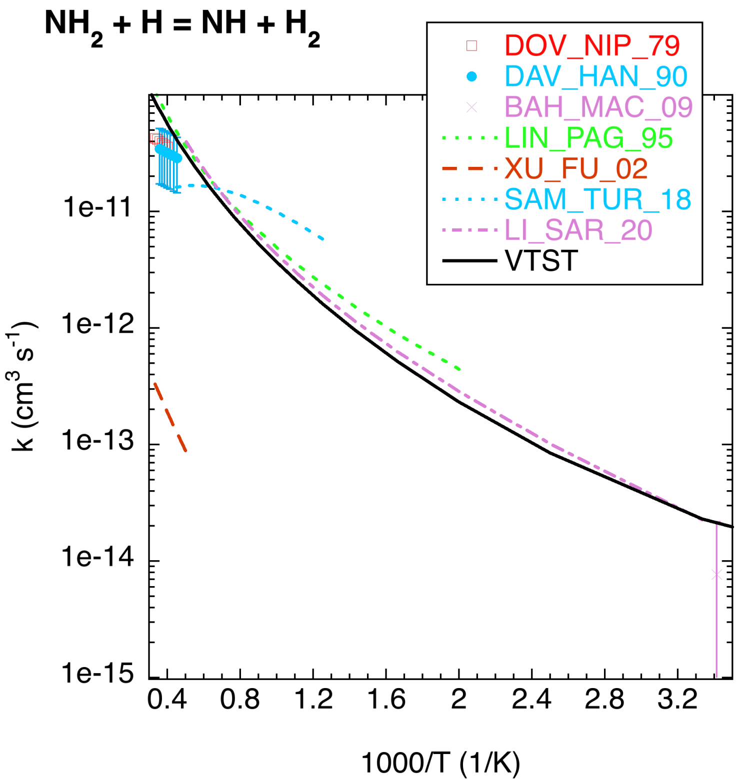
Energies

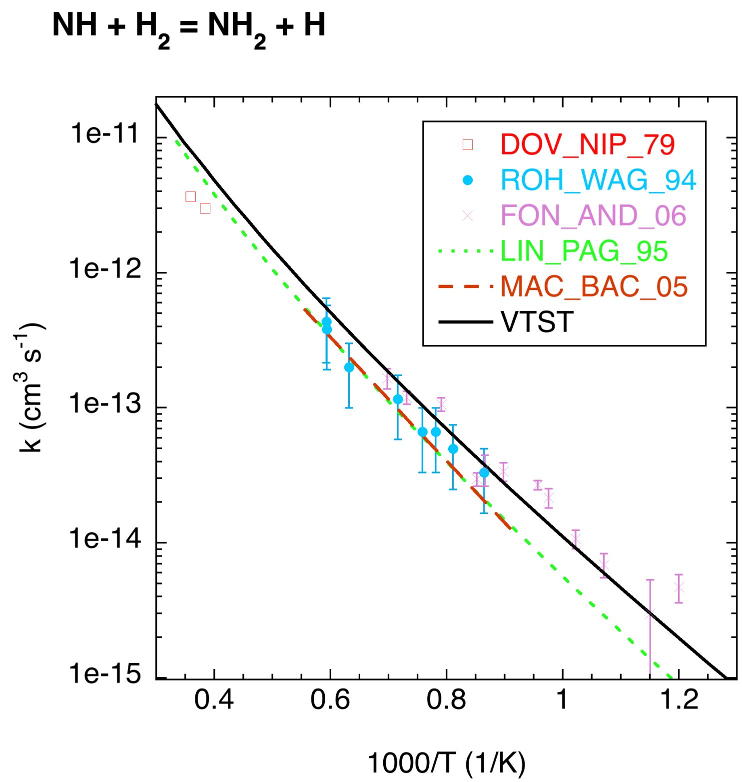
- CCSD(T)-F12/CBS(QZF,5ZF)
- CCSDT(Q)/cc-pVTZ
- CCSDTQ(P)/cc-pVDZ
- Core-Valence; CCSD(T)/CBS(TZ,QZ)
- Relativistic; CCSD(T)/atz
- Diagonal Born-Oppenheimer
- Anharmonic; CCSD(T)/TZ

Rates

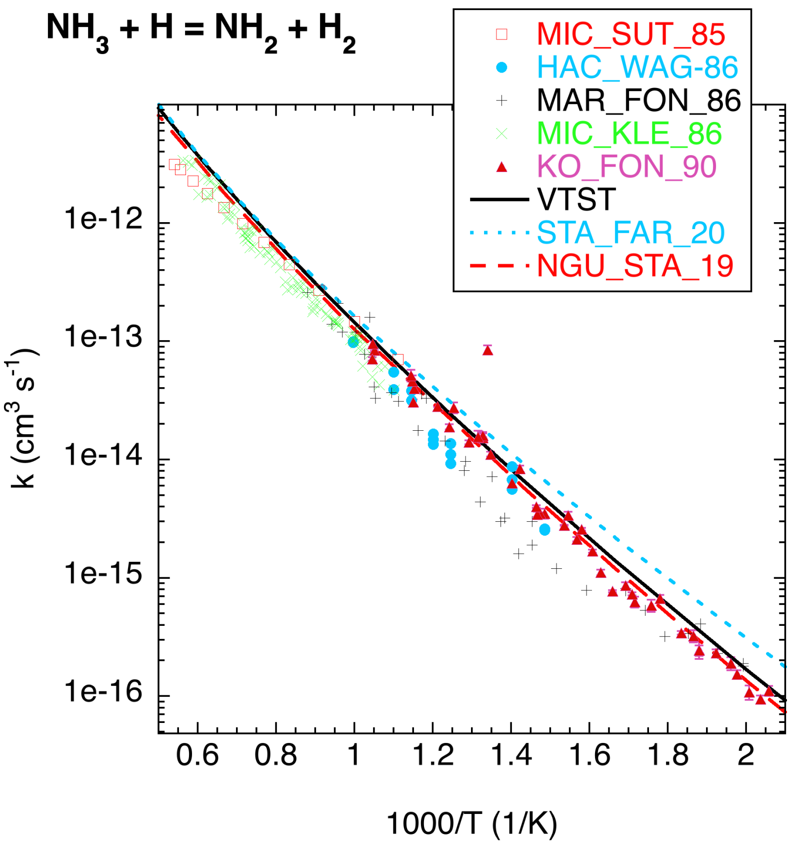
- VTST
- Anharmonic State Counts
- 1 Dimensional ME

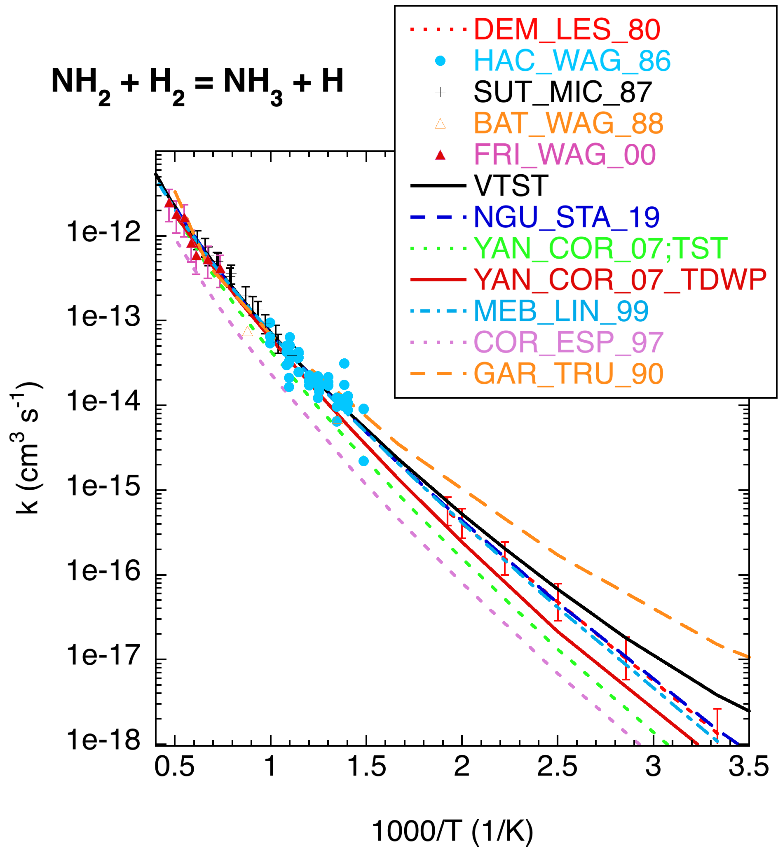
NH_3 KINETICS



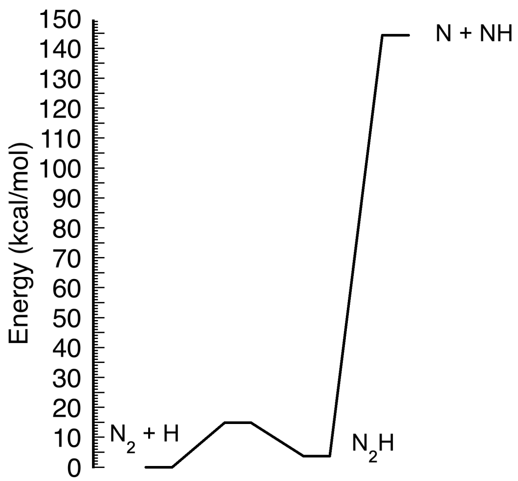


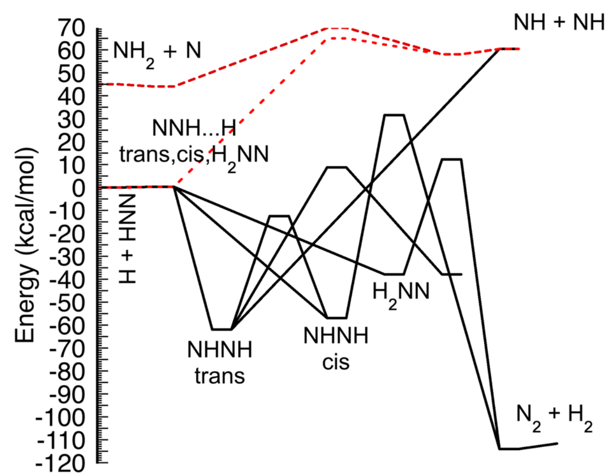
NH_4 KINETICS

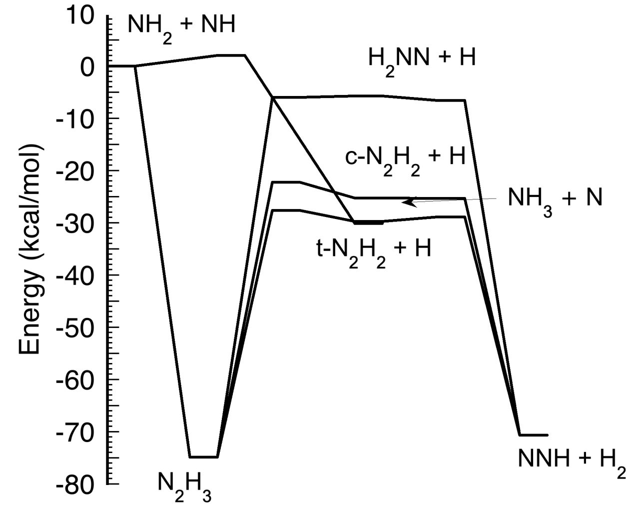


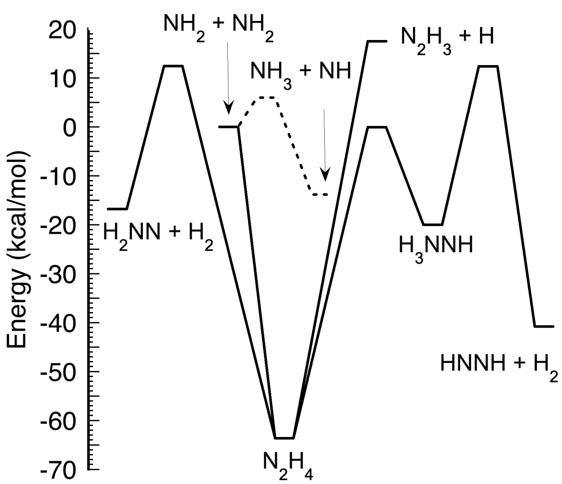


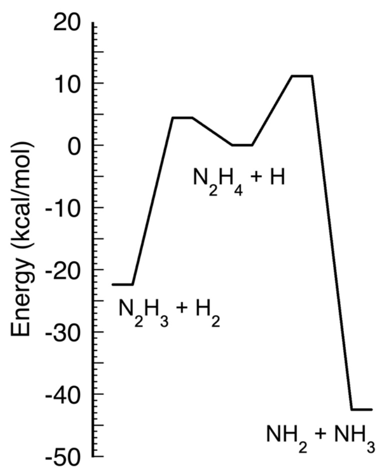
N_2H_X POTENTIAL ENERGY SURFACES











CCSD(T)-F12/CBS(TZ-F12,QZ-F12) freqs.
ANL1' energies
~ CCSDTQ(P)/CBS + rel. + DBOC + anh.
VRC-TST for rad-rad
VTST for rad-mol

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N_2H_X POTENTIAL ENERGY SURFACES

Table 1: Basis Set Convergence (kcal/mol)

Species	A5Z	A6Z	CBS	CBSF12	Delta CBS
N_2H_2;t + H	0	0	0	0	0
N_2H_2;t + H = N_2H_3	2.01	1.96	1.91	1.90	-0.01
N_2H_3	-51.94	-52.00	-52.08	-52.12	-0.04
N_2H_2;t + H = NNH + H_2	3.01	2.99	2.97	2.97	0.00
NNH + H_2	-37.59	-37.60	-37.62	-37.61	0.00
N_2H_2;c + H	5.42	5.40	5.38	5.40	0.02
N_2H_2;c + H= N_2H_3	7.64	7.58	7.50	7.51	0.01
N_2H_2;c + H= NNH + H_2	5.85	5.81	5.75	5.78	0.03
H_2NN + H	24.95	24.90	24.84	24.81	-0.03
H_2NN + H = N_2H_3	No S.P.				
H_2NN + H = NNH + H_2	24.68	24.62	24.54	24.52	-0.02
NH_2 + ^{3}NH	29.76	30.08	30.46	30.45	-0.01
NH_2 + ^{3}NH = NH_3 + ^{4}N	31.34	31.65	32.02	32.01	-0.01
NH_3 + ^{4}N	-2.84	-2.42	-1.91	-1.95	-0.04

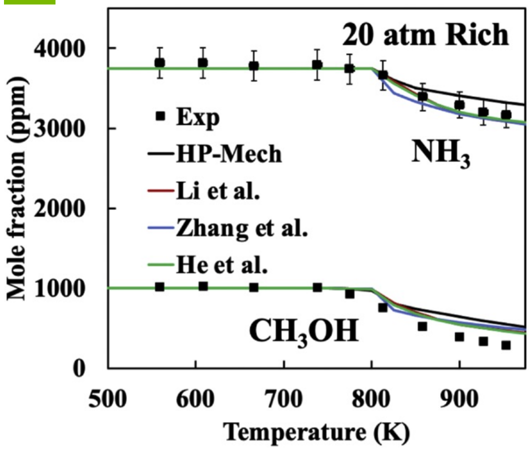
Table 2: Corrections

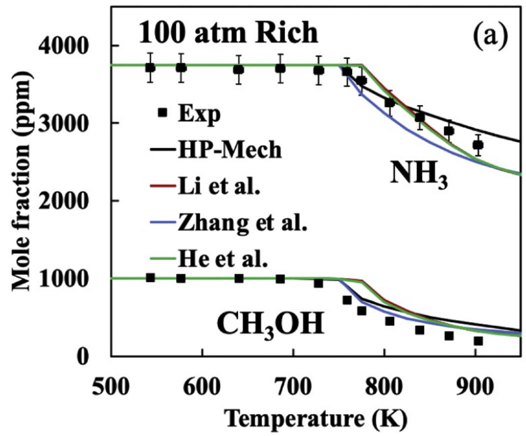
Species	T(Q) DZ	T(Q) TZ	Q(P) DZ	Core-Val.	Rel.	DBOC	Har. ZPE
N_2H_2;t + H	0	0	0	0	0	0	0
N_2H_2;t + H = N_2H_3	-0.36	-0.43	0.00	0.01	0.00	0.02	0.88
N_2H_3	0.16	0.12	0.00	-0.27	0.13	-0.07	7.17
N_2H_2;t + H = NNH + H_2	-0.26	-0.26	0.01	0.04	-0.03	0.17	-1.54
NNH + H_2	-0.35	-0.17	0.01	-0.04	-0.07	0.09	-3.17
N_2H_2;c + H	-0.03	-0.01	0.00	0.05	-0.01	0.01	-0.38
N_2H_2;c + H = N_2H_3	-0.29	-0.35	0.00	0.05	0.00	0.03	0.57
N_2H_2;c + H= NNH + H_2	-0.22	-0.23	0.02	0.06	-0.03	0.10	-0.81
H_2NN + H	0.04	-0.01	0.01	-0.12	0.05	0.03	-0.78
H_2NN + H = N_2H_3	No S.P.						
H_2NN + H = NNH + H_2	-0.15	-0.21	0.02	-0.11	0.05	0.12	-0.82
NH_2 + ^{3}NH	0.39	0.05	-0.03	0.30	-0.10	0.09	-1.10
NH_2 + ^{3}NH = NH_3 + ^{4}N	0.05	-0.26	-0.02	0.31	0.31	0.12	-0.25
NH_3 + ^{4}N	0.44	0.19	-0.01	0.09	-0.07	-0.10	3.80

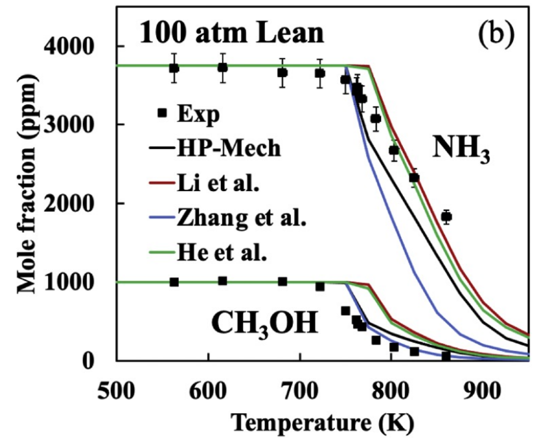
NH_3 + CO-FUELS

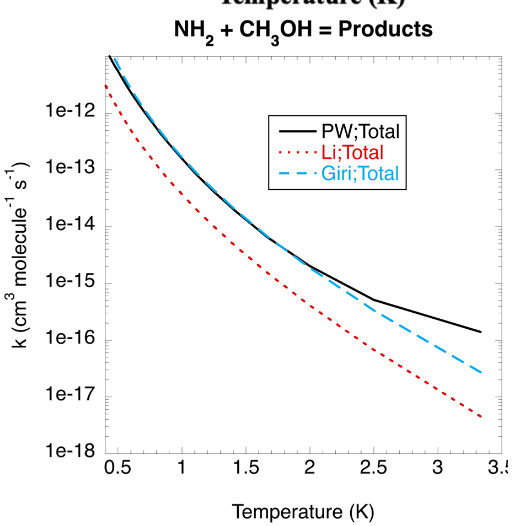
NH_3/CH_3OH OXIDATION

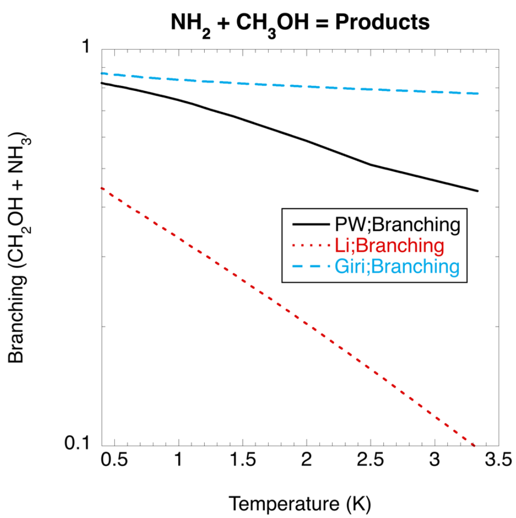
Wang, Mei, Liu, Thawko, Mao, Zhao, Glarborg, SJK, Ju, Proc. Combust. Inst. 40, 105489 (2024)

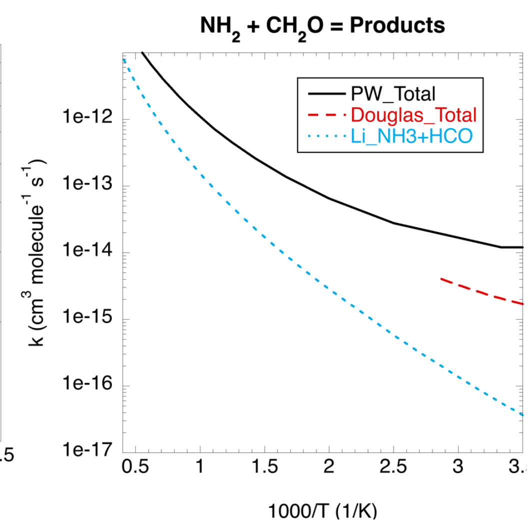


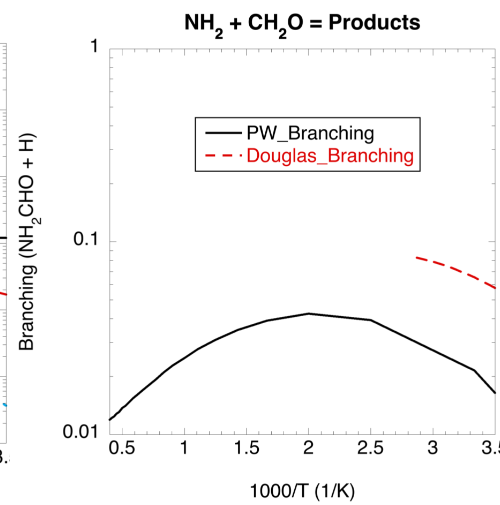




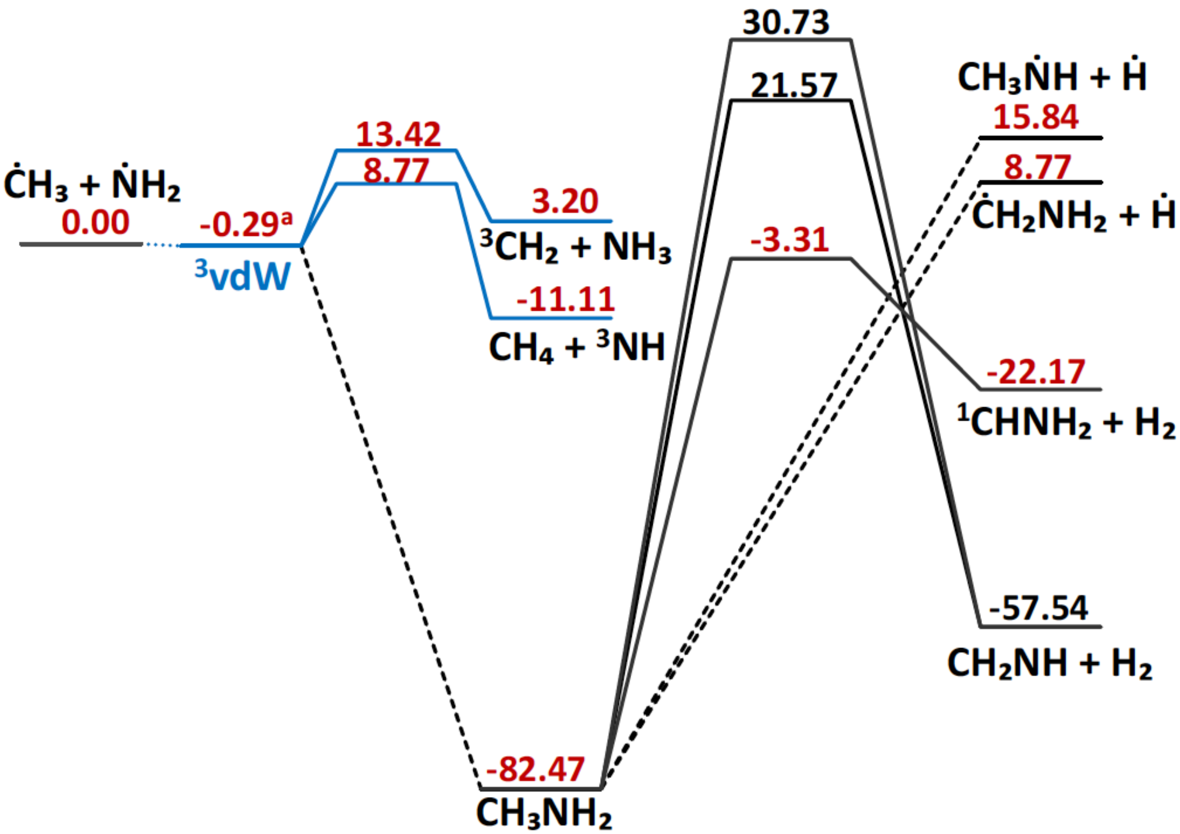








CH_3 + NH_2 POTENTIAL ENERGY SURFACE



ANL0F

CCSD(T)-F12/cc-pVTZ-F12

CCSDT(Q)/cc-pVDZ

Core-Valence

Rel.

Anharm.

MRCI tests

VRC-TST

1DME

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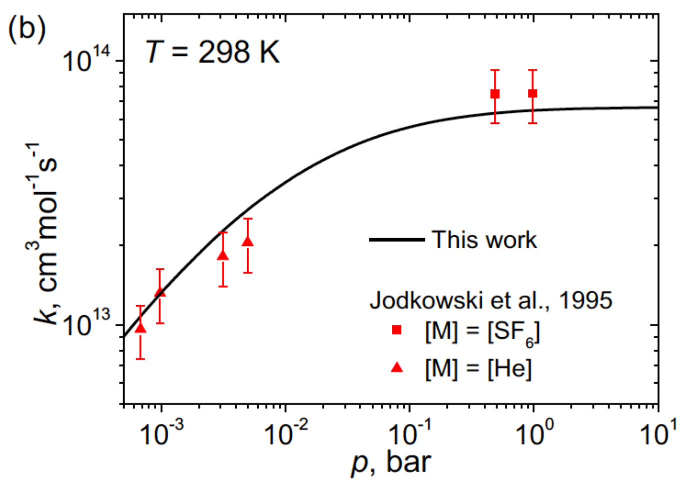
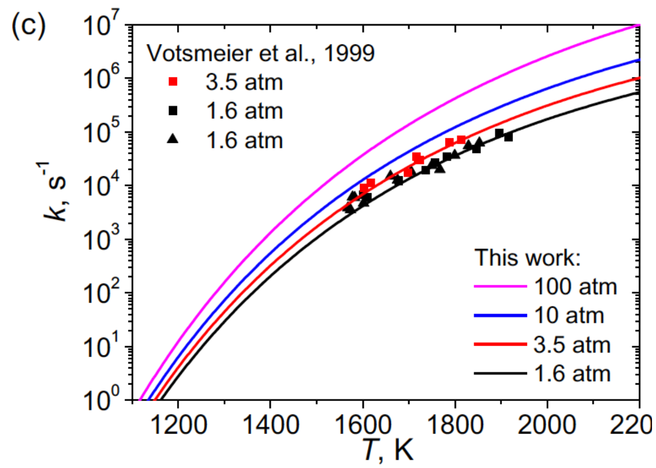
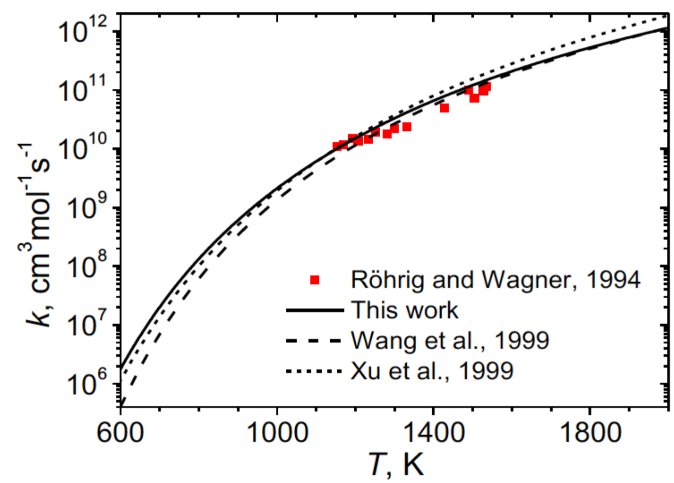
$CH_3 + NH_2 = CH_3NH_2$



$CH_3NH_2 = CH_3 + NH_2$



$CH_4 + {}^3NH = CH_3 + NH_2$



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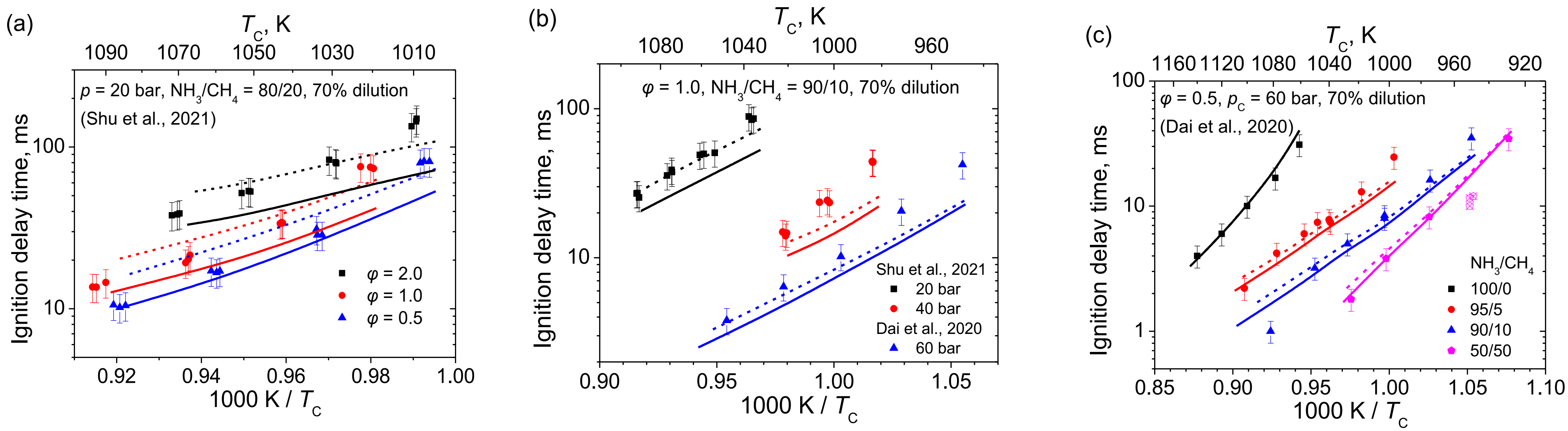
NH_3/CH_4 IGNITION DELAY TIMES



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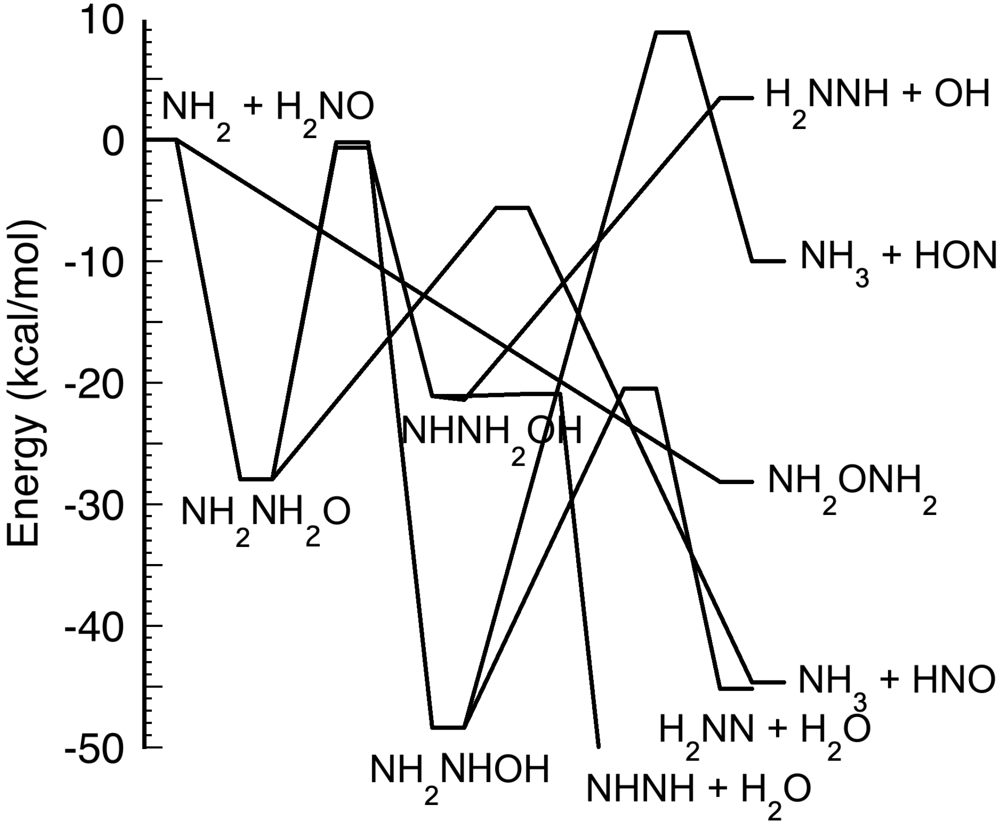
$NH_2 + H_2NO$



OPT/Freq/ZPE/Conformer: CCSD(T)-F12/cc-pVTZ-F12
SPE: CCSD(T)-F12/CBS-F12 + CCSDT(Q)/cc-pVDZ + Core-Valence/CBS(TZ,QZ) + Relativistic(ATZ) + Anharm(B2PLYPD3/TZ) + Born-Oppenheimer

Dominant Path:

$NH_2 + H_2NO = NH_2NH_2O$
$NH_2NH_2O = NH_3 + HNO$
Effectively Just Abstraction

Other Paths:

< 2%

Abstraction Rate:

Preliminary Rate ~ 4-5 times less than from Stagni
Significant Multireference Effects
T(Q) Correction = -2.8 kcal/mol
ANL0 Like Barrier at -5.6 kcal/mol

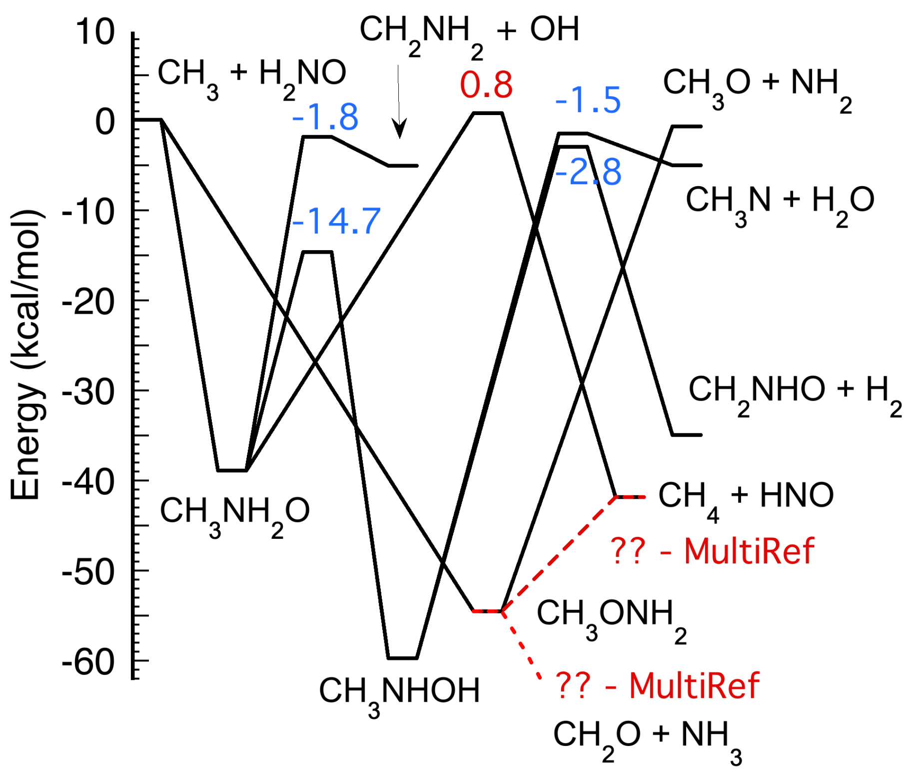
Stagni

CASPT2 Barrier at -8.7 kcal/mol
Spin-Splitting corrected Barrier at -8.0 kcal/mol

Next Step

CI+QC Barrier with Spin Splitting

$CH_3 + H_2NO$



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Dominant Path:

$CH_3 + H_2NO = CH_3NH_2O$

Secondary Paths:

$CH_3 + H_2NO = CH_3ONH_2$

$CH_3NH_2O = CH_3NHOH$
$CH_3NHOH = CH_4 + HNO$

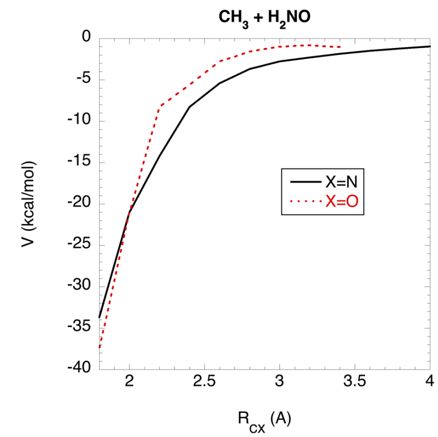
$CH_3NHOH = CH_3N + H_2O$

Other Paths:

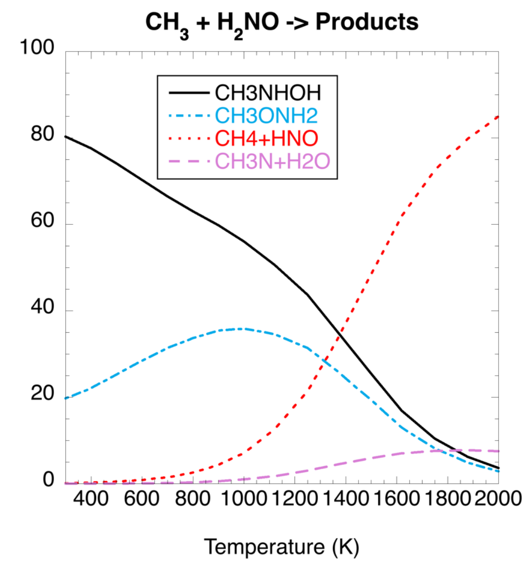
< 1%

What happens to CH_3NHOH and CH_3ONH_2?

Addn to N preferred over O



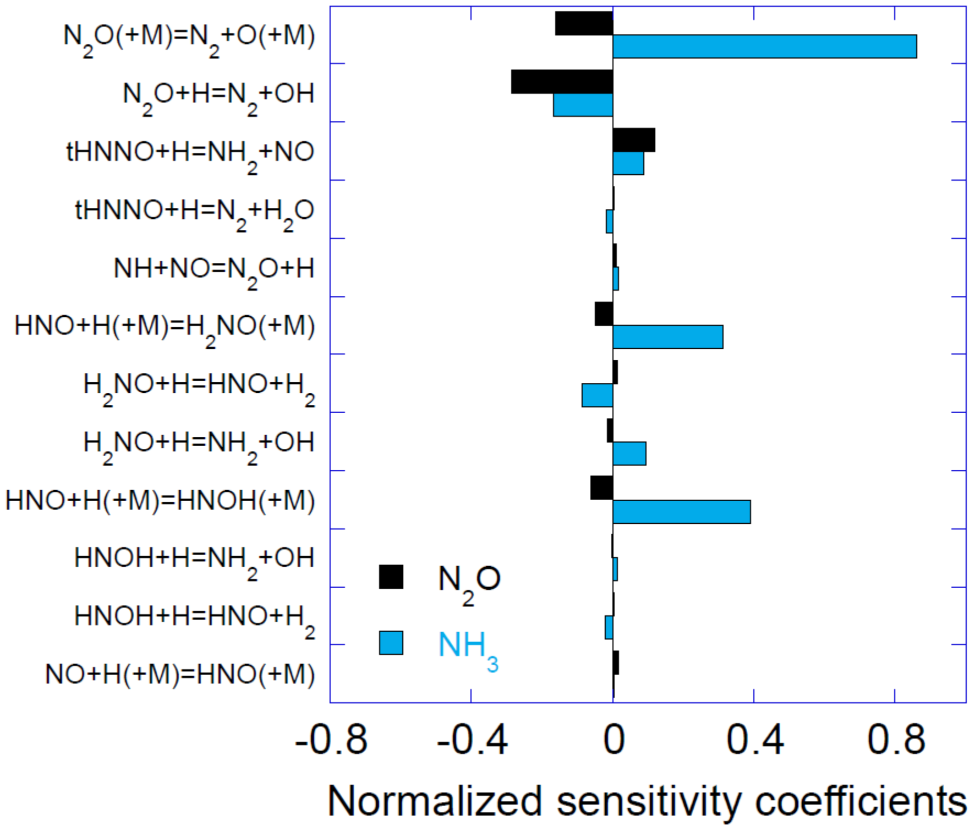
Preliminary Results



N_2O CHEMISTRY

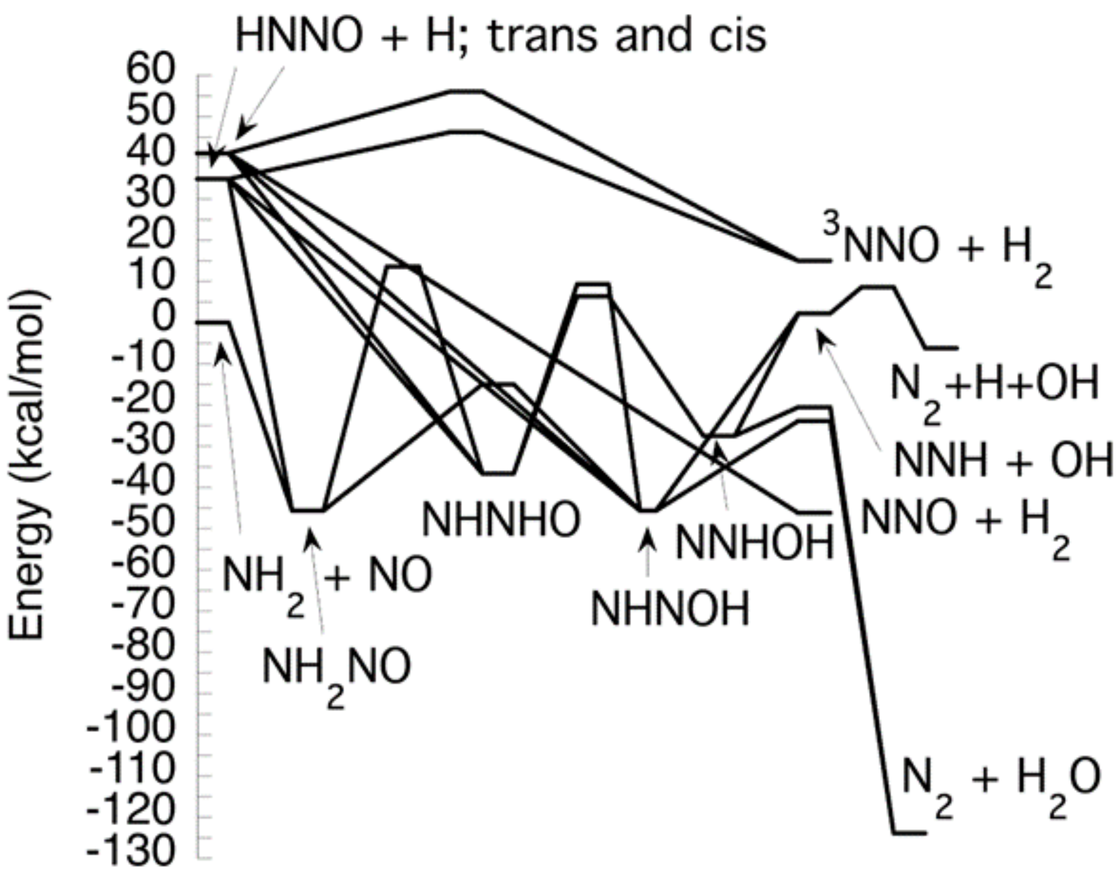
HNNO + H

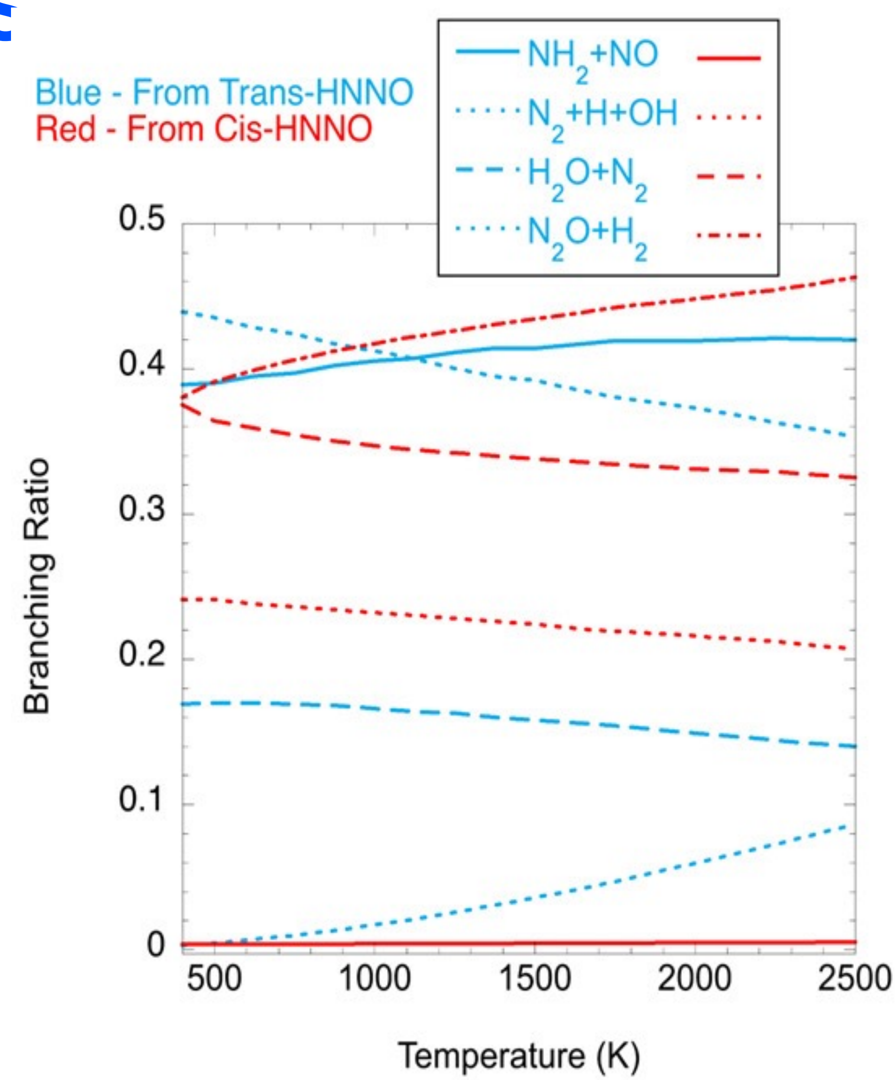
Meng, Lei, Burke, On the Role of HNNO in NOx Formation, Proc. Combust. Inst. 39, 551-560 (2023).



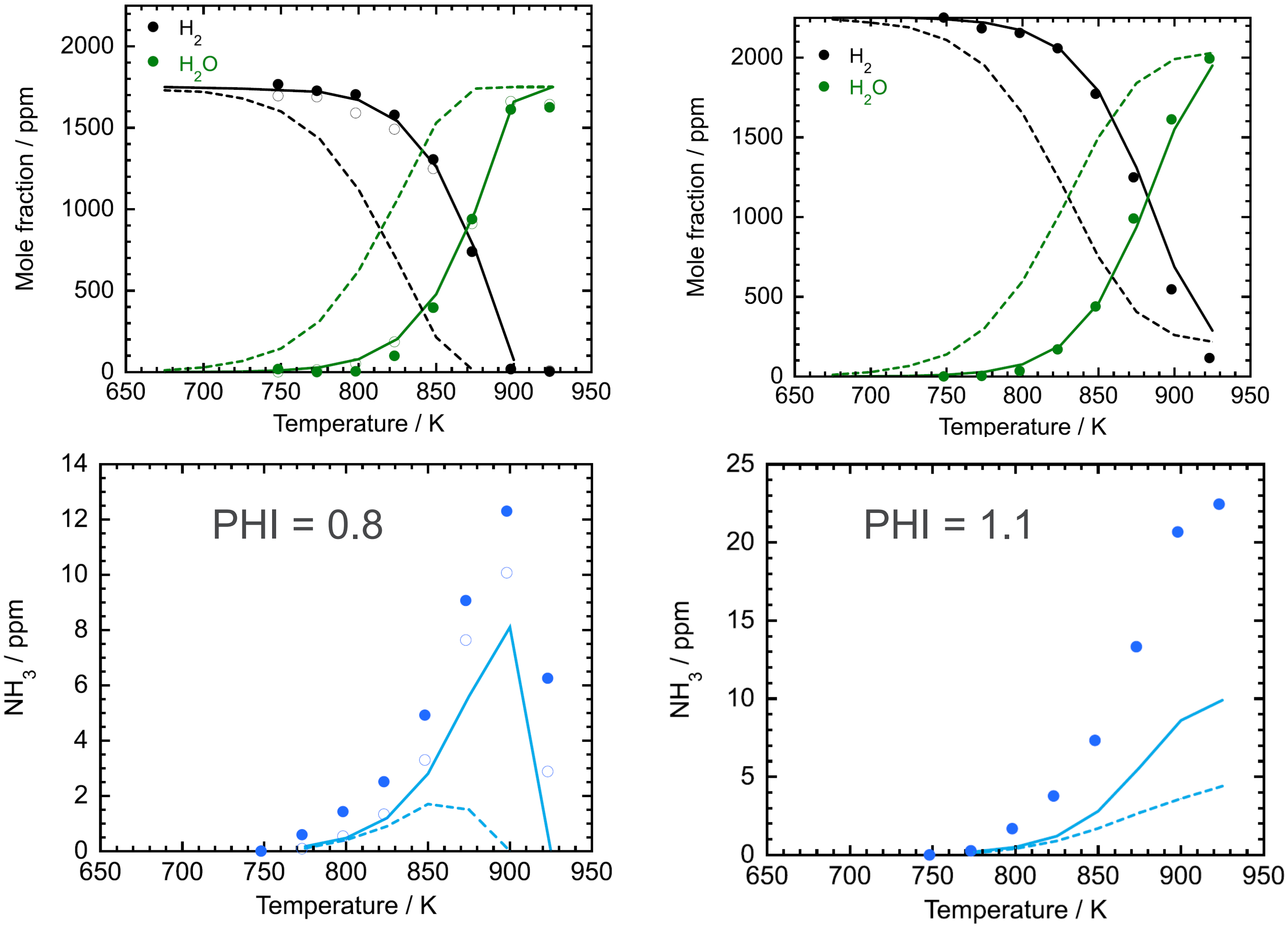
Experimental and kinetic modeling study of the N_2O-H_2 system: Implications for N_2O + H
Glarborg, Fabricius-Bjerre, Joensen, Hashemi, SJK
CNF, 271, 113810 (2024).

HNNO + H RATE CONSTANTS





EFFECT OF HNNO CHEMISTRY ON NH_3 OXIDATION



With (solid)
Without (dashed)

HNNO chemistry

ACKNOWLEDGEMENTS

DOE-BES CSGB Gas Phase Chemical Physics (Wade Sisk)

- Core Program - Chemical Dynamics in the Gas Phase
- Argonne-Sandia Consortium on Pressure Dependent Chemistry

DOE-BES CSGB Solar Photochemistry (Jennifer Roizen)

- A Programmable Non-Equilibrium Electrified Ammonia Synthesis for Efficient Hydrogen Storage

Collaborators

Jim Miller	
Peter Glarborg	(DTU)
Raghu Sivaramakrishnan, Ahren Jasper	(Argonne)
Clayton Mulvihill	(Baylor)
Yiguang Ju	(Princeton)
Henry Curran/Chong-Wen Zhou	(Galway)