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Ab initio Quantum Chemical and Experimental Reaction Kinetics Studies in the Combustion of Bipropellants

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March 24, 2017

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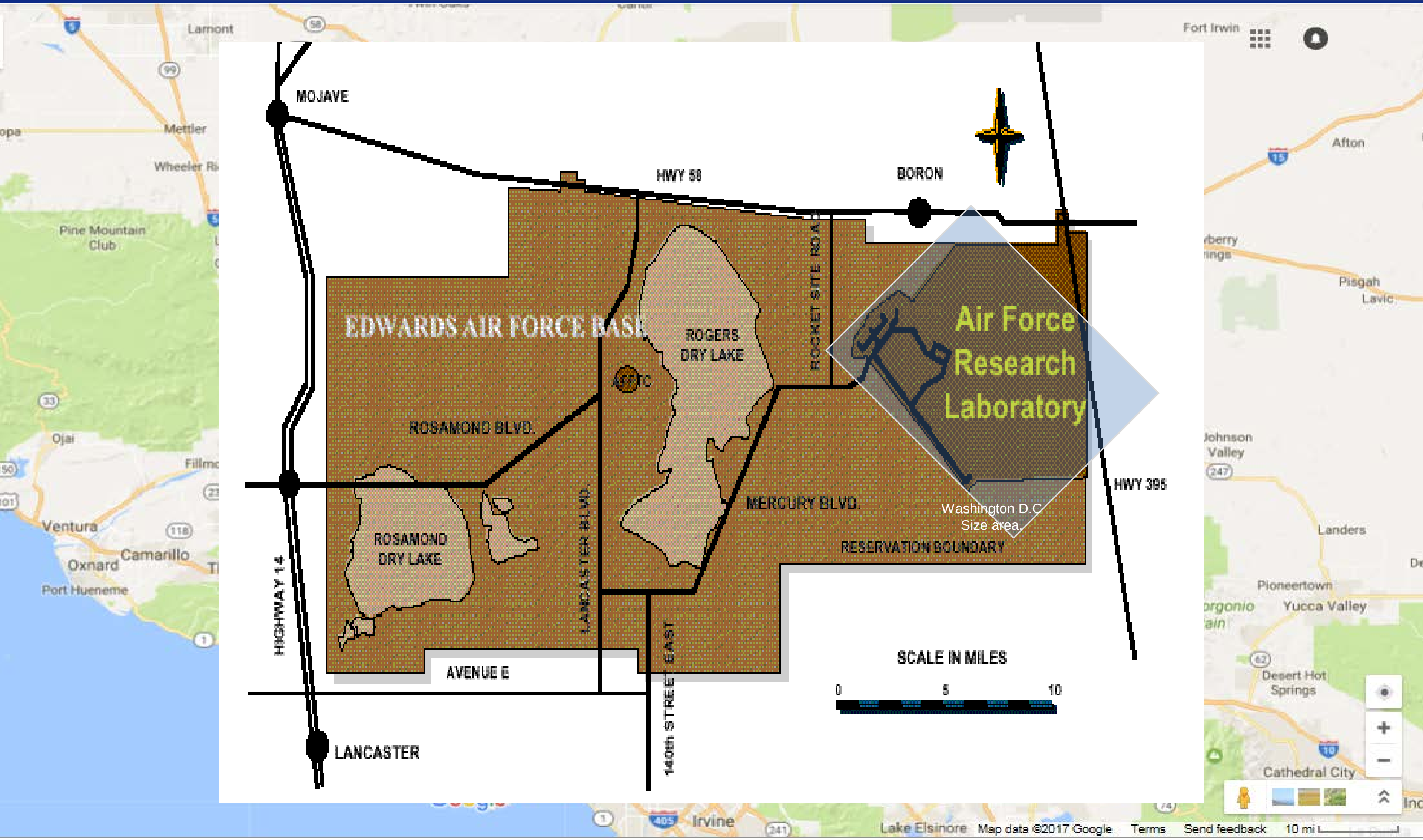
Where and how big is AFRL at Edwards AFB?



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Premier Rocket Test Facilities (+$3B) In Beautiful Mojave Desert, CA

A Cool Place to Work for a Place That's Hot!

Edwards AFB Accolades too Many But, e.g., Visit the URLs……

http://www.af.mil/News/ArticleDisplay/tabid/223/Article/137793/rocket-test-stand-gets-facelift.aspx

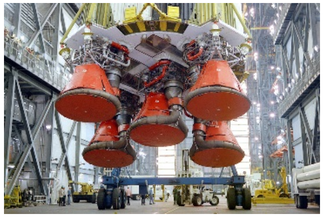
http://www.militarymuseum.org/EdwardsAFB.html

Murphy's Laws

"If anything can go wrong, it will"
Phrase born in 1949, EAFB
Capt. Edward A. Murphy
Engineer working on AF Project MX981
How much sudden deceleration
a person can stand in a crash

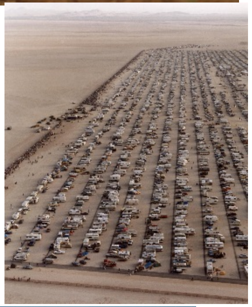
F-1 Engine Testing EAFB Rocket Site

Saturn V



Testing and Early Landings EAFB

EAFB Rocket Site Viewing



Chuck Yeager

First human to officially break the sound barrier
October 14, 1947, EAFB
Flew the experimental Bell X-1
A rocket-engine powered airplane
Mach 1 at an altitude of 45,000 ft

Apollo, KSC Transporter

Shuttle Takeoff, KFC

EAFB's success is KSC's success!

Our Partners in Propulsion Research & Technology Development

DEPARTMENT OF DEFENSE · UNITED STATES OF AMERICA

AIR FORCE RESEARCH LABORATORY

AMRDEC

NAWC Weapons Division · NAVAL AIR WARFARE CENTER

NASA

AEROJET ROCKETDYNE

ROCKET PROPULSION FOR THE 21ST CENTURY · RELIABILITY · COST · CAPABILITY · RP21 • 3X

Orbital ATK

BUSEK

NORTHROP GRUMMAN Space Technology

ORBITEC · A SUBSIDIARY OF SNC SIERRA NEVADA CORPORATION

AFRL ROCKET LAB

Rocket Propulsion for the 21st Century (RP21) Goals

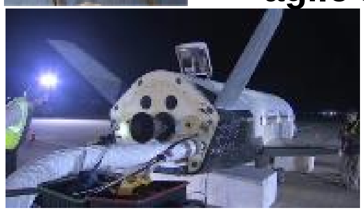
Boost and Orbit Transfer Propulsion	2017	2027	Status
• Reduce Stage Failure Rate* (RP)	75%	75%	Baseline (B)
• Improve Mass Fraction (Solid)	18%	38%	5%
• Increase ISP % (Solid/Liquid* (RP))	2%/0%	5%/4%	1%/B
• Increase Thrust to Weight % (Liquid, (RP))	103%	103%	10%
• Reduce Engine Turn Time(Reusable)	<8hrs	<4hrs	B
• MTBO/MTBR (Missions, Liquid)	50/100	50/100	10%
• Decrease Motor Health State Uncertainty	20%	50%	10%
Spacecraft Propulsion			
• Increase Efficiency (ET/ES/EM)	15%/15%/10%	65%35%/30%	B/B/B
• Decrease EP System Dry Mass (ET/ES/EM)	0%/50%/50%	75%/90%/90%	B/B/25%
• Decrease Flexible Prop.System Wet Mass	35%	65%	B
• Increase Chemical Prop. Density Isp	5%	15%	<1%
• Decrease Chemical Prop. Dry Mass	10%	40%	B
Tactical Propulsion*			
• Increase Total Impulse (RS&Smokey/MS)	20%/33%	35%/45%	B
• 4 Pulse motors			
• RS/Smokey Total Impulse Penalty	10/Mf	0	B
• Minimum Smoke Increase Total Impulse	5%	25%	B
• Increase Density Isp	5%	7%	B
• Insensitive Munitions*	See JIMTP & Backup Information		

* Additional Backup goal information exists

In-Space Propulsion (RQRS) R&D
Basic Science to Flight Demo

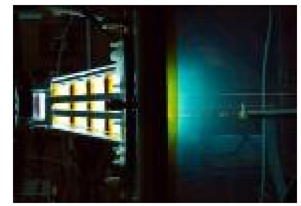
Sustainment **Resiliency** **Superiority**

Hall Effect Thruster (HET)



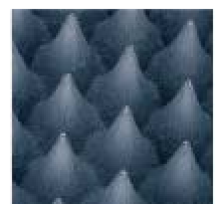
- XR-5A thrusters
- Customer: AFSPC
- Rapid tech transition via agile space experiments

High Power (>100 kW class) EP (FRCs)



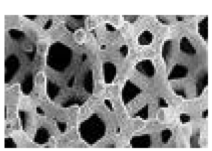
- *Extremely low mass, high thrust*
- *multimode compatible*

Densified Ionic Liquid Electrosprays (DILE)



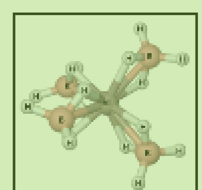
- *Cube sat applications*
- *Extremely high efficiency, scalable thrust*

AF-M315E Transition (GPIM)



- Replacement of hydrazine with higher performance non-toxic propellant
- Customer: NASA/AF/Industry
- Developing family of thrust levels ¼ to 20 lbf

Next-gen Adv Biprop Thruster (ABT)



- *More performance*
- *Vol-limited spacecraft*

ROCKET LAB

STEM Students
How to Work at AFRL EAFB?

- **Ph.D**
  - **NRC Post-doc**
    - http://nrc58.nas.edu/RAPLab10/Opportunity/Opportunity.aspx?LabCode=13&ROPCD=133003&RONum=B7679
- **Graduate Students**
  - **AF SFFP**
    - http://nrc58.nas.edu/RAPLab10/Opportunity/Opportunity.aspx?LabCode=13&ROPCD=133003&RONum=B7679
  - **AFIT**
    - http://afsffp.sysplus.com/SFFP/contact/afit-wright-patterson-afb.aspx
  - **SMART**
    - http://www.asee.org/fellowship-programs/graduate
  - **USAFA**
    - http://afsffp.sysplus.com/SFFP/contact/usafa-colorado-springs-co.aspx
- **Under Graduate Students**
  - **Pathways**
    - https://www.usajobs.gov/GetJob
- **Student-teachers**
  - **STAR**
    - http://starteacherresearcher.org/sites.html

Our Interest in Combustion Kinetics of Bipropellants

- Understand Auto-ignition Chemistry
  - Occurs at Low Temperature-Pressure Conditions
- Understand Fuel Pyrolysis
  - Competes With Oxidation
- Understand Fuel Oxidation
  - Competes With Pyrolysis
- Construct Comprehensive Reaction Kinetics Models
  - Discover Other Auto-igniting Bipropellant Systems

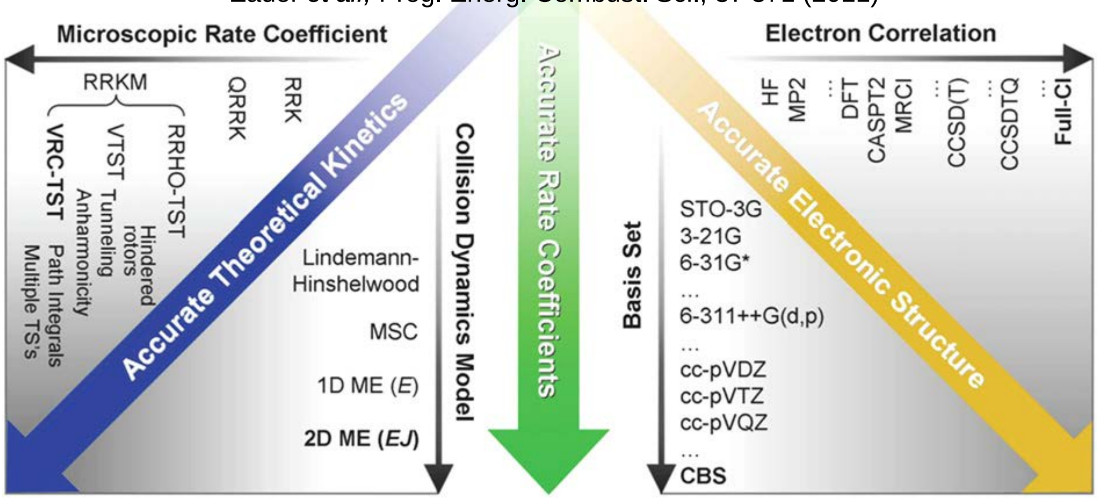
CH_3NHNH_2/N_2O_4

Improve Propulsion Capabilities Over the Current State-of-the-art CH_3NHNH_2/N_2O_4

Why Quantum Chemical Reaction Kinetics Studies?

- Only Option When Experiments are not Possible or Limited
  - Combustion Conditions of P & T too Extreme to Probe
- Accuracy (E_a) can be as Good or Better Than Experiments
  - Thermochemical Accuracy Possible
  - Ideal for Branching Ratio Predictions for Closely Competing Reactions
- Can be a Cost Effective Alternate to Experiments
  - Hardware & Software Efficiencies Improving Constantly
- A Balanced Approach to Kinetics Calculations Recommended

Zador *et al.,* Prog. Energ. Combust. Sci., 37 371 (2011)



$N_2H_3 + NO_2$ Reaction Kinetics Perspective

- Radical Chemistry Modelling
  - N_2H_4/NO_2 Auto-ignition

- Recent Works
  - Only Theoretical Studies
    - See Raghunath *et al.*, Adv. Quantum Chem., **69**, 253 (2014)............$k_{298\ K,\ 1atm}$ = (2.3×10^{-11})
    - See Daimon *et al.*, Sci. Tech. Energetic Materials, **74**, 17 (2013).......$k_{298\ K,\ 1atm}$ = (1.6×10^{-14}) ?
    - See Daimon *et al.*, J. Propul. Power, **30**, 707 (2014)………………… $k_{298\ K,\ 1atm}$ = (1.9×10^{-11})

      Also, See Kanno *et al.*, J. Phys. Chem., A, **119**, 7659 (2015)

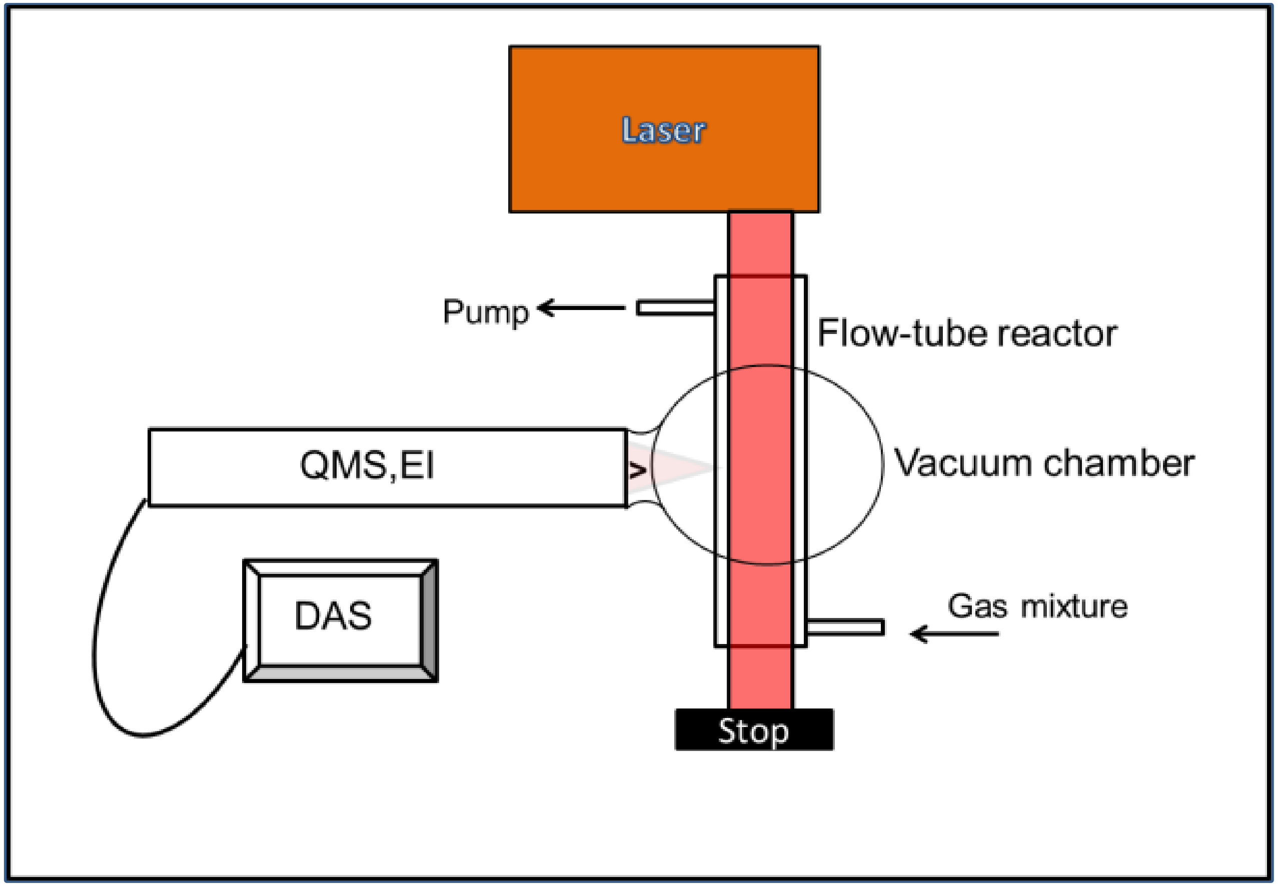
      $CH_3NNH_2 + NO_2 \rightarrow$ Products, k = (2.2×10^{-13})

      trans-$CH_3NHNH + NO_2 \rightarrow$ Products k = (1.4×10^{-12})

      cis-$CH_3NHNH + NO_2 \rightarrow$ Products k = (1.2×10^{-12}) cm^3 $molecule^{-1}$ s^{-1}

- This work (submitting for publication)
  - Pulsed Laser Photolysis - Flow Tube Mass Spec Experiments
    - First Experimental Determination
  - *Ab initio* Chemical Kinetics
    - Multi-reference Second-order Perturbation and Coupled-cluster Methods: PES (Potential Energy Surface)
    - Rice–Ramsperger–Kassel–Marcus Theory and Master Equation Simulations: k(*E*,*J*)

Pulsed Laser Photolysis Flow Tube Apparatus



N_2H_3 Source & Flow Tube Chemistry

$N_2H_4 + h\nu \rightarrow N_2H_3 + H$	$\sigma_{193\ nm} = 450 \times 10^{-20}\ cm^2\ molec^{-1}$	1
$NO_2 + H \rightarrow NO + OH$	$k_2 = 1.3 \times 10^{-10}\ cm^3\ molecule^{-1}\ s^{-1}$	2
$N_2H_4 + H \rightarrow N_2H_3 + H_2$	$k_3 = 1.4 \times 10^{-13}\ cm^3\ molecule^{-1}\ s^{-1}$	3
$N_2H_4 + OH \rightarrow N_2H_3 + H_2O$	$k_4 = 3.6 \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$	4
$N_2H_3 + NO_2 \rightarrow N_2H_2 + HONO$	k_5	5
$N_2H_3 + NO_2 \rightarrow$ other products	k_6	6
$HONO \rightarrow$ loss	$k_7 = 1\ s^{-1}$	7
$N_2H_3 \rightarrow$ loss	$k_8 = 10\ s^{-1}$	8
$H \rightarrow$ loss	$k_9 = 10\ s^{-1}$	9
$OH \rightarrow$ loss	$k_{10} = 10\ s^{-1}$	10

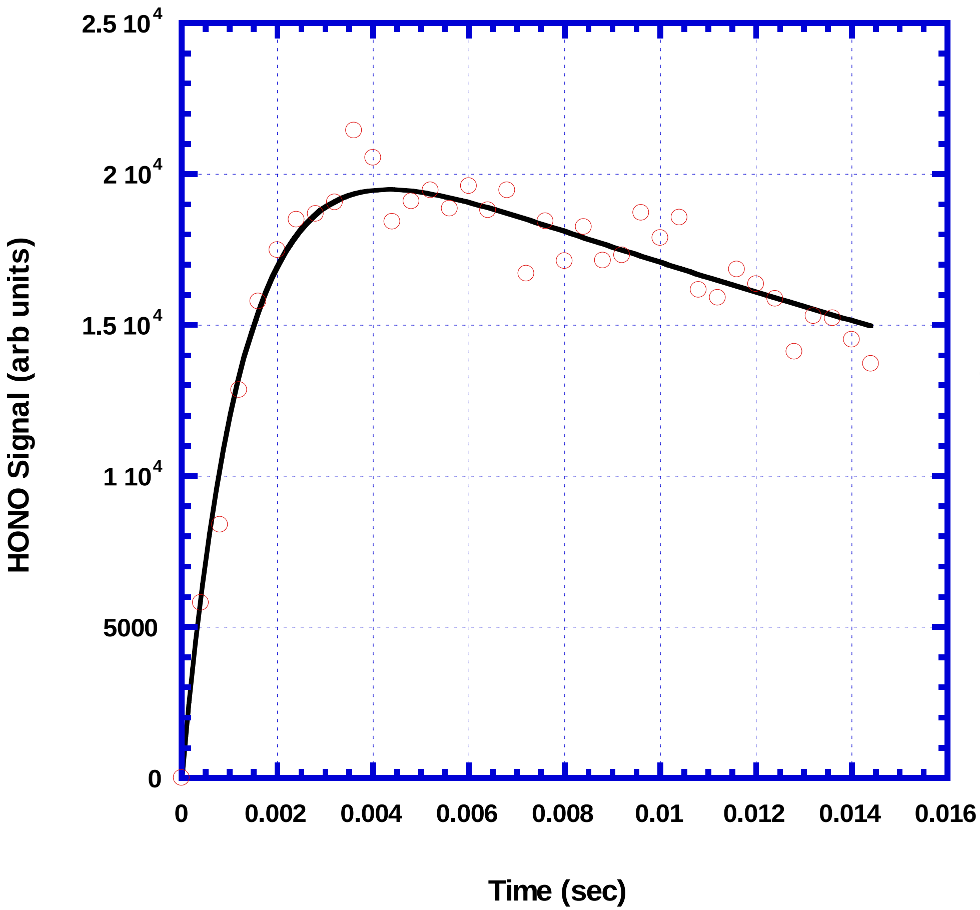
$$[HONO] = (k_5[NO_2][N_2H_3]_o)\{e^{-k_7 \cdot t} - e^{-k' \cdot t}\}/(k' - k_7)$$

$$k' = (k_5 + k_6)[NO_2] + k_8$$

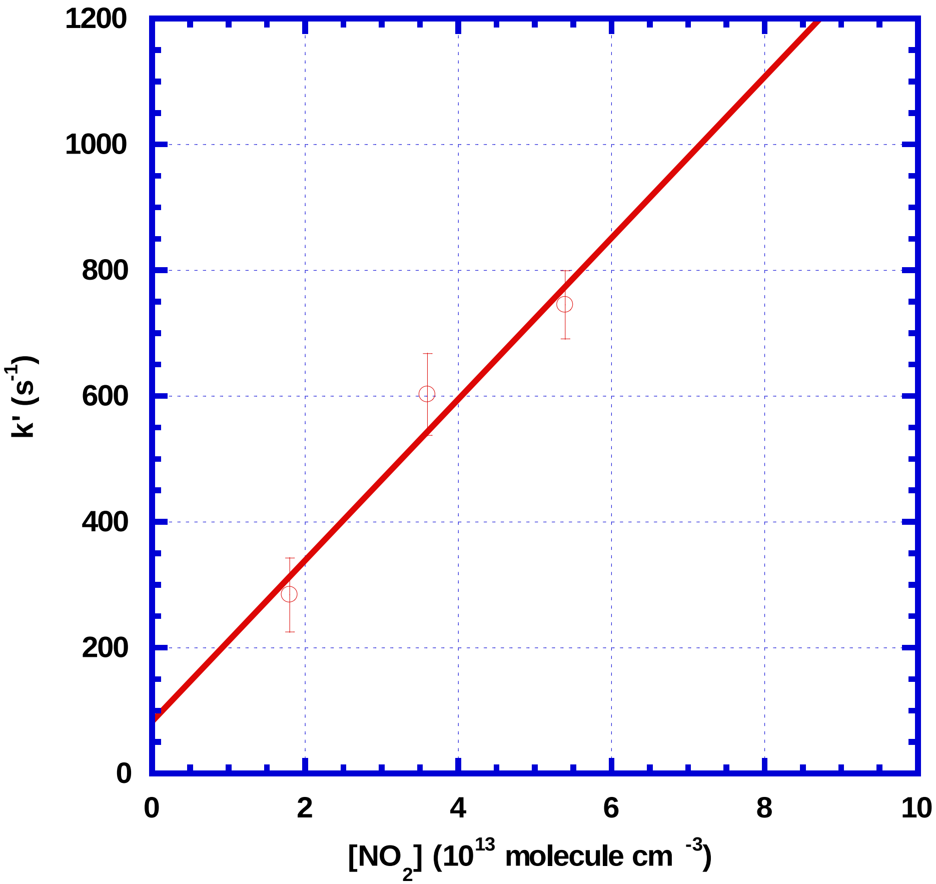
$[N_2H_4] = 5 \times 10^{14}$, $[H] = 5 \times 10^{12}$, $[NO_2] = 1 \times 10^{13}$ to 5×10^{13} molecule cm^{-3}

$N_2H_3 + NO_2$ Reaction Kinetics

Typical [HONO] Temporal Profile

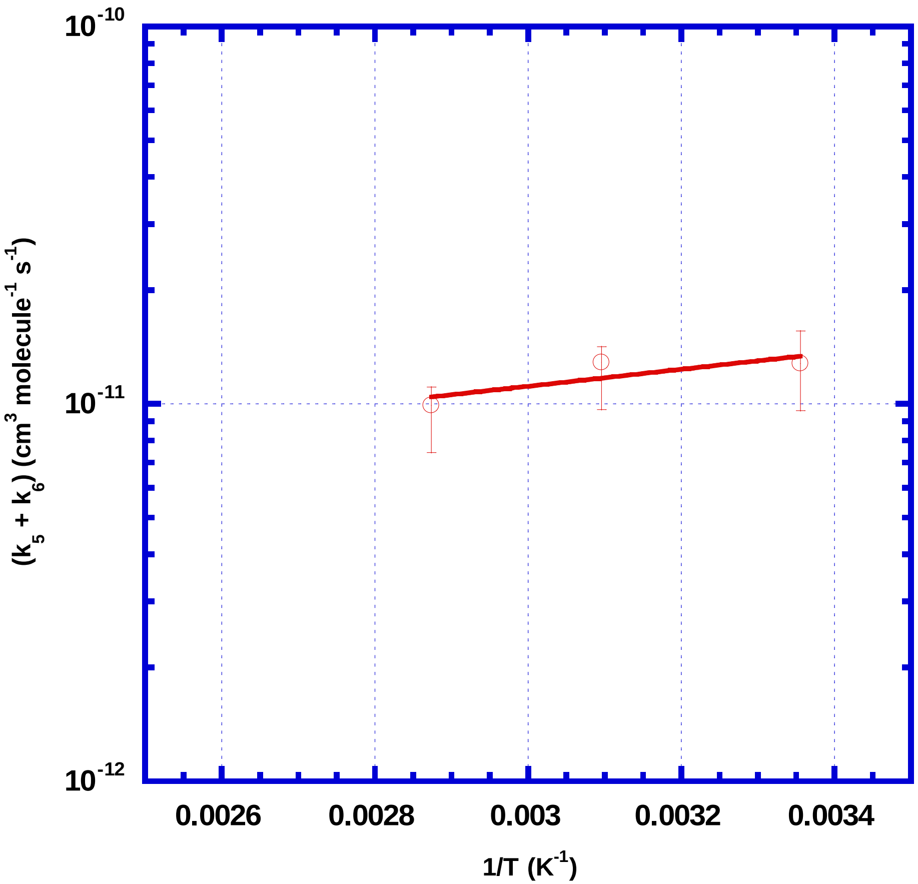


Second-order Plot



$k_{298\ K,\ 2\ Torr\ N_2} = (1.23 \pm 0.25) \times 10^{-11}\ cm^3\ molecule^{-1}\ s^{-1}$

Temperature Dependence of $N_2H_3 + NO_2$ Reaction

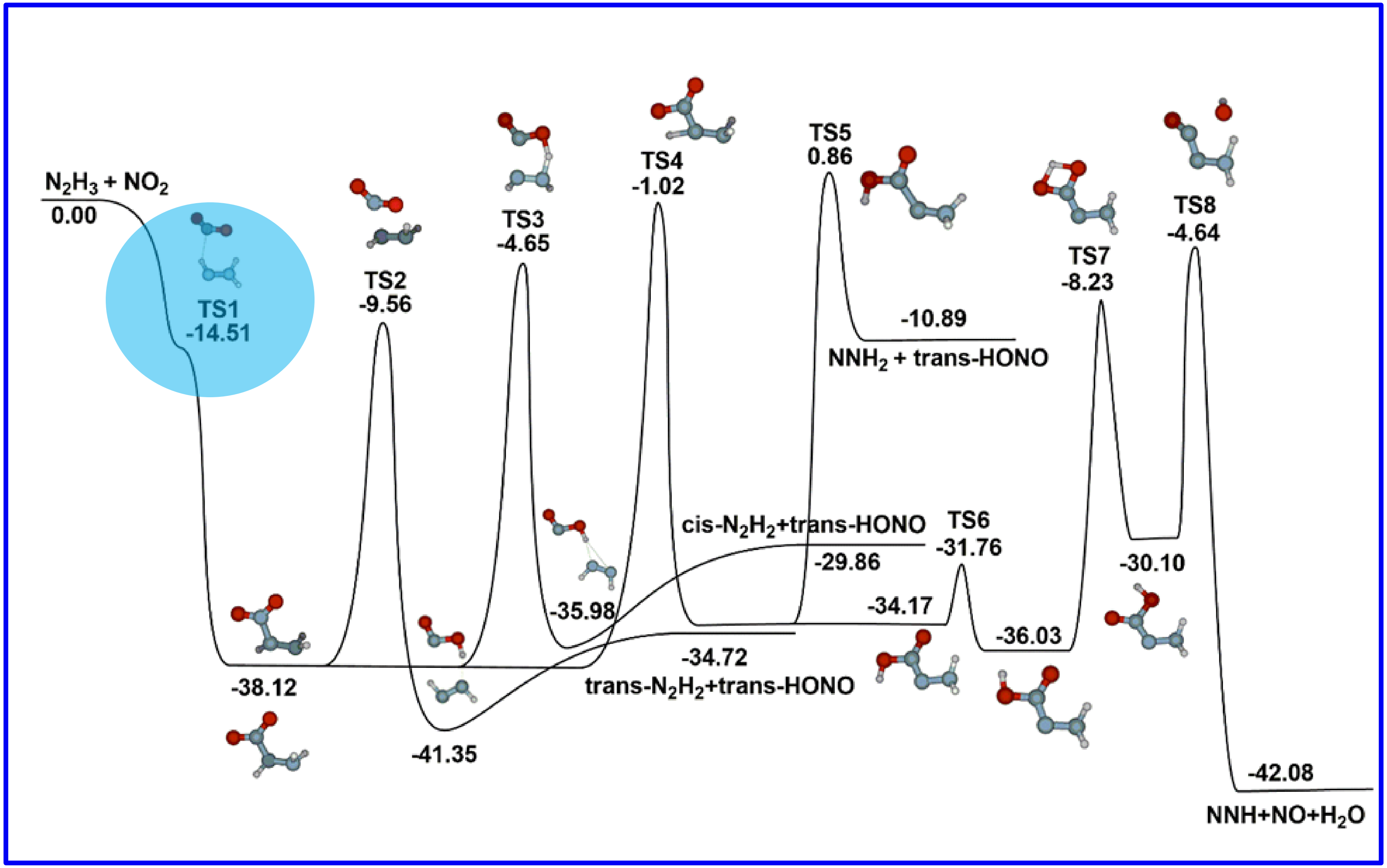


$$(k_5 + k_6)_{2\text{-Torr-}N_2} = (2.36 \pm 0.47) \times 10^{-12} \exp((520 \pm 350)/T)\ \text{cm}^3\ \text{molecule}^{-1}\ \text{s}^{-1}$$

Ab initio Quantum Chemistry Approaches for $N_2H_3 + NO_2$ Reaction

- Previous Work used Single-reference Methods (e.g. CCSD(T))
- However, Reaction is not a Simple H-abstraction Process
- There is Strong Electron Repulsion Between N and O-atoms
- The Significant Multi-reference Character of the Wavefuntion in the TSs for Addition and Bond Breaking With Loose Geometries Needs Proper Treatment
- Here in addition, we Apply CASPT2 With Dunning's Augmented Correlation Consistent Basis Set to Characterize the PES

Potential Energy Surface for $N_2H_3NO_2$ Adduct Formation

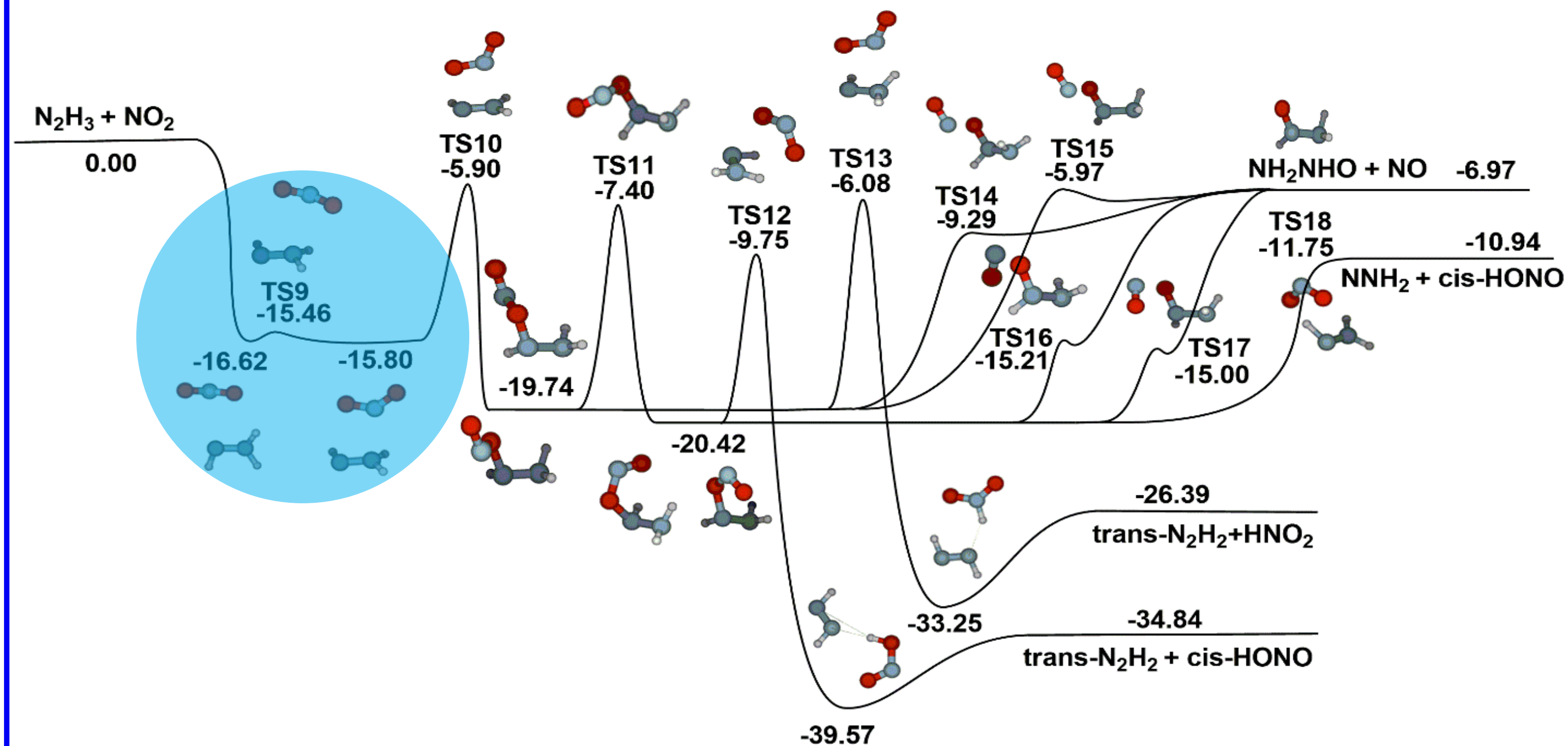


Zero-point corrected energies (kcal/mol, at 0 K), relative to entrance channel

CASPT2/aug-cc-pVTZ

CCSD(T)/cc-pV∞Z

Potential Energy Surface for N_2H_3ONO Adduct Formation



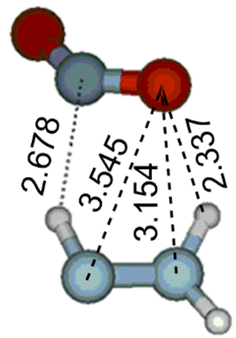
Zero-point corrected energies (kcal/mol, at 0 K), relative to entrance channel

CASPT2/aug-cc-pV∞Z

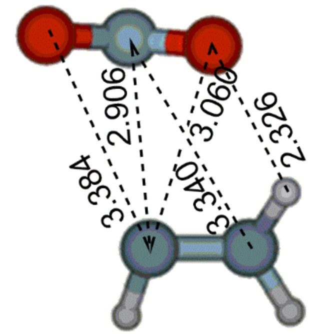
CCSD(T)/cc-pV∞Z

TSs and Complex Structures Involved in N_2H_3 Addition to NO_2

- **Pseudo-planar**
  6-member ring structure
- **NO_2 interaction**
  With 2 H-atoms of N_2H_3
- **TS Stabilization**
  Two H-bonds formed

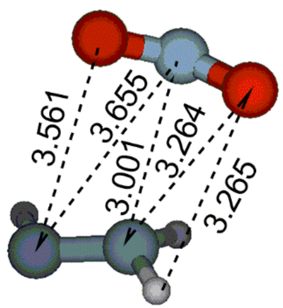


TS1

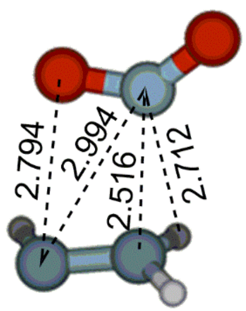


NH_2NH--NO_2 complex

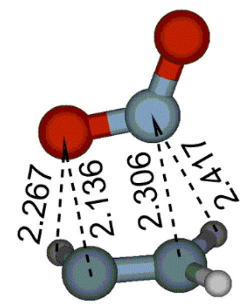
- **Pseudo-planar**
  5-member ring structure
- **One H-bond**
- **Loose geometry**



TS9



$NHNH_2$--NO_2 complex



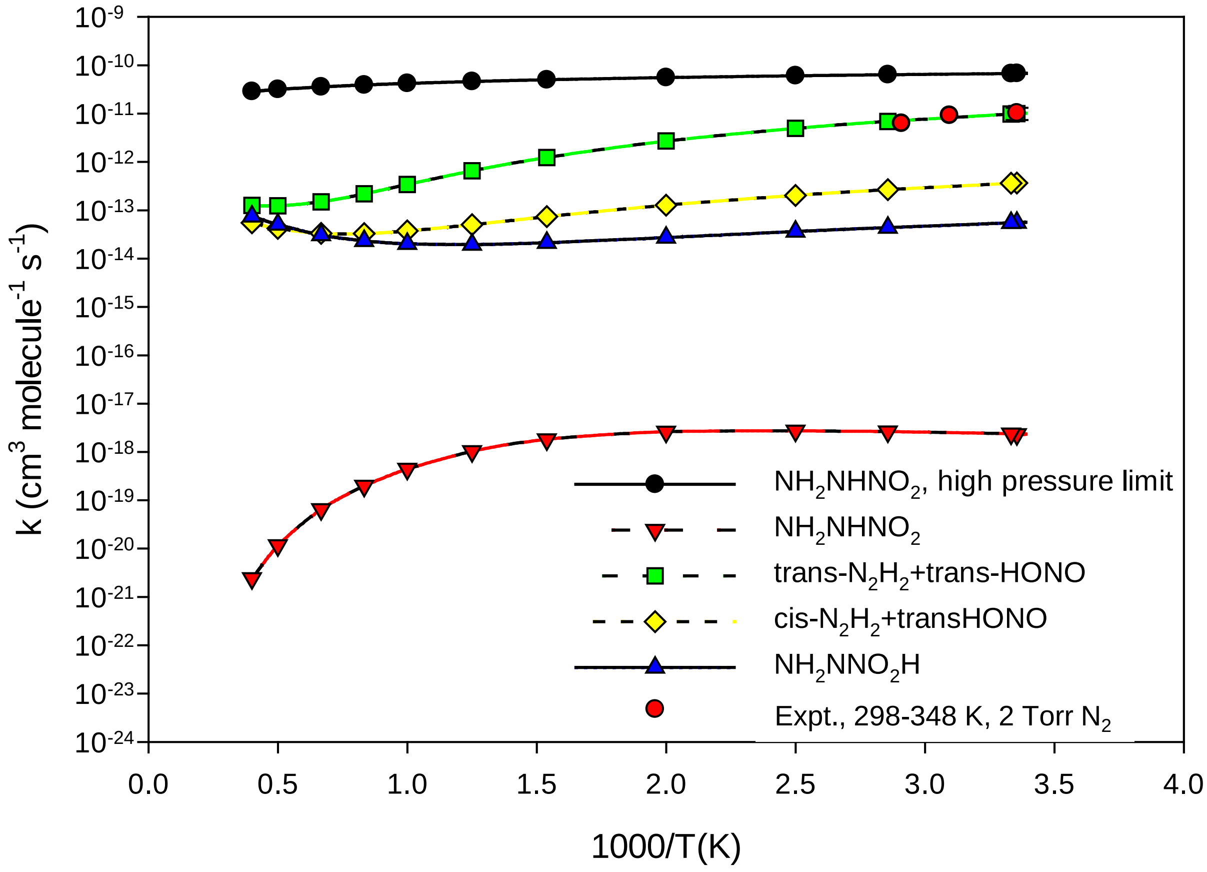
TS10

- **Planar**
  4-member ring structure
- **Loose geometry**

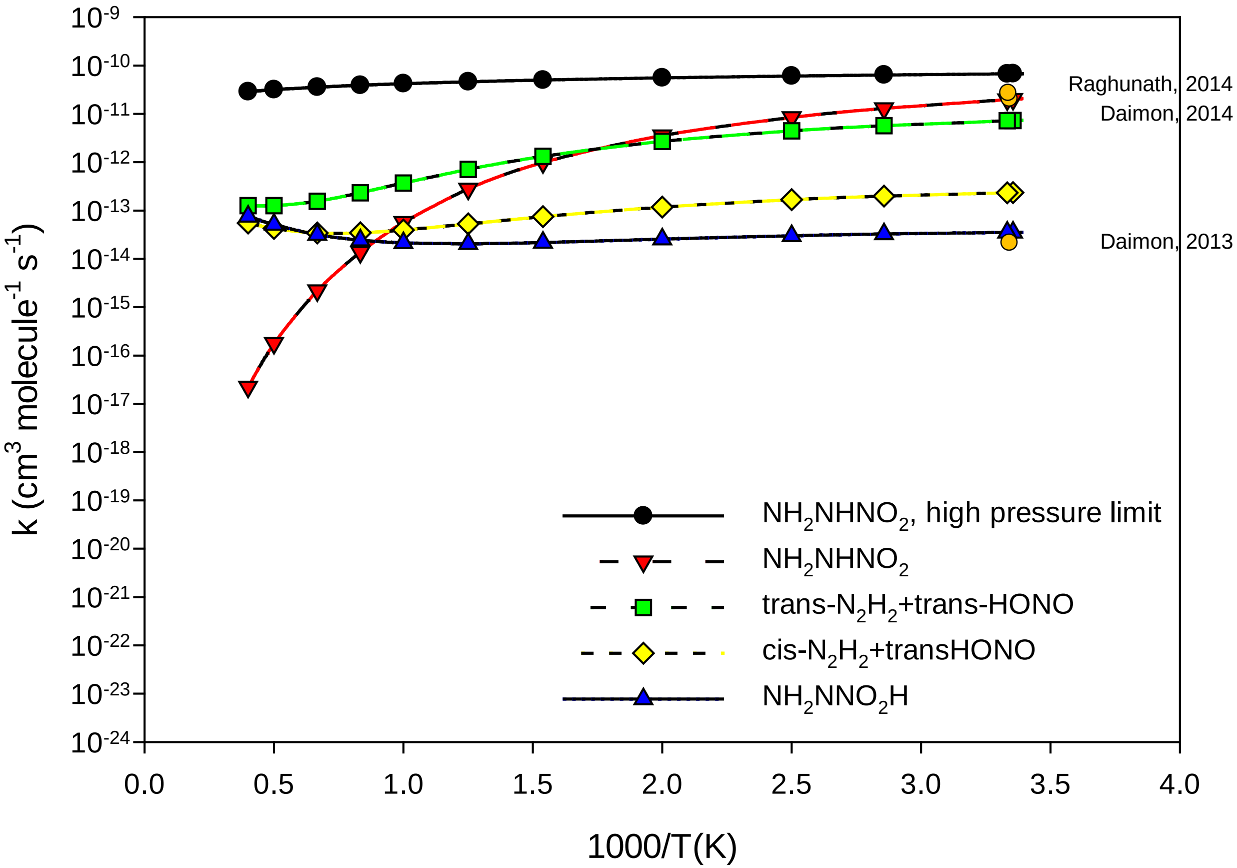
RRKM and Multi-well Simulations

- Rice–Ramsperger–Kassel–Marcus (RRKM) Theory Together With Multi-well Master Equation Simulations Carried out to Compute the Phenomenological Thermal Decomposition Rate Coefficients (Klippenstein and Co-workers, VARIFLEX, Version 2.0)
- ΔE_{down} = 125 × $(T/300)^{0.85}$ cm^{-1} Energy Transfer Model Used
- TST With Rigid-rotor Harmonic-oscillator Assumption Including Tunneling Corrections Used to Calculate High-pressure Limit
- Good Agreement With Experiment Observed

Branching Rate Coefficients (2 Torr N_2) & High Pressure Limit Versus T



Branching Rate Coefficients (1 Atm N_2) & High Pressure Limit Versus T



CH_3NH Perspective

- CH_3NHNH_2 (Bipropellant Fuel)
  - Pyrolysis and Oxidation Compete in Combustion Processes
    - Facile Bond Breaking: $CH_3NHNH_2 \rightarrow CH_3NH + NH_2$
      - Previously, NH_2 Monitored, Li *et al.,* Combustion Flame, 161, **16**, (2014)
    - However, Fate of CH_3NH not Well Understood
      - Important for Kinetics Modelling Simulations

- CH_3NH (Decomposition, Source of H-atoms?)

$CH_3NH \rightarrow$ TS1 $\rightarrow CH_3 + NH$

$\rightarrow$ TS2 $\rightarrow CH_2{=}NH + H$

$\rightarrow$ TS3 $\rightarrow CH_2NH_2$

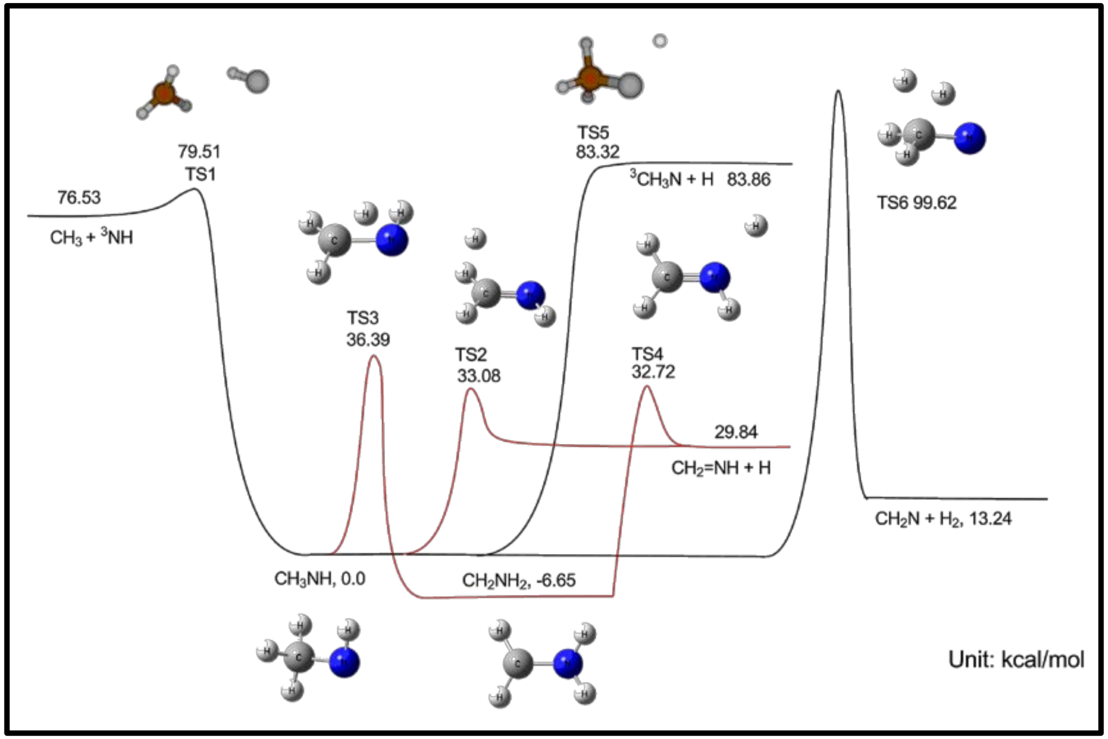
$CH_2NH_2 \rightarrow$ TS4 $\rightarrow CH_2{=}NH + H$

$CH_3NH \rightarrow$ TS5 $\rightarrow CH_3N + H$

$\rightarrow$ TS6 $\rightarrow CH_2{=}N + H_2$

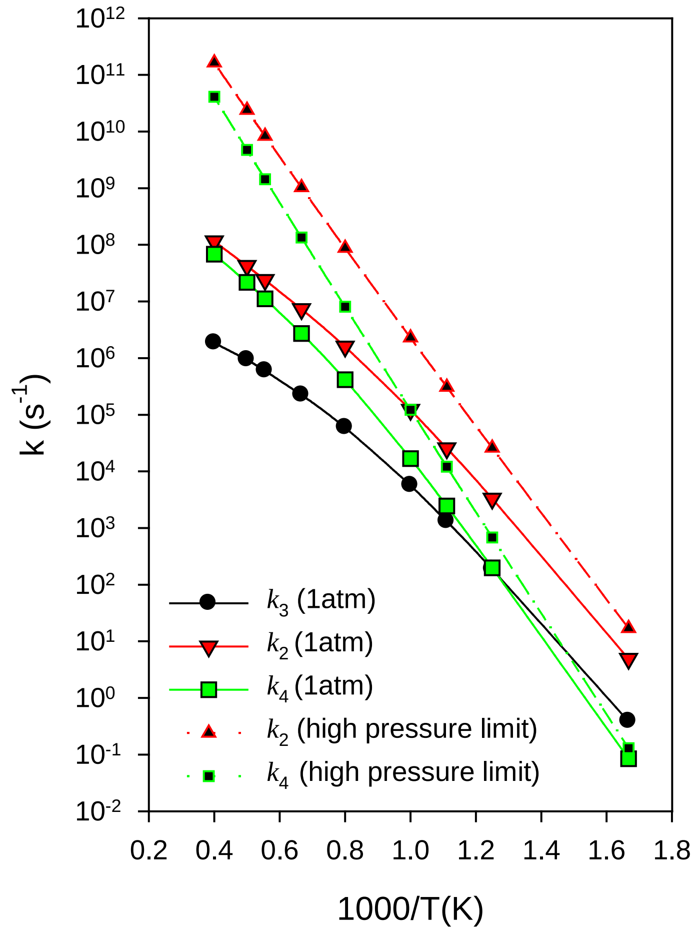
- This work
  - Multi-reference *ab initio* Methods Used to Characterize Bond Breaking Processes
  - RRKM and Multi-well Simulations Carried out to Compute Reaction Rates

CH_3NH Dissociation PES



CASPT2 Theory for N-H and C-N Bond Breaking

RRKM and Multi-well Simulations for CH_3NH Decomposition



Dominant Channel:

$CH_3NH \rightarrow TS2 \rightarrow CH_2{=}NH + H$

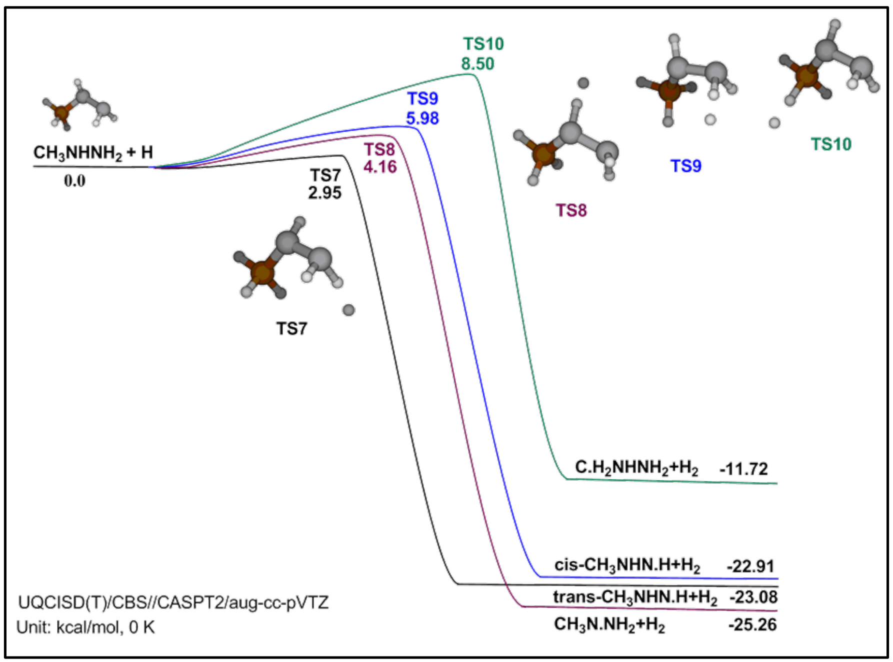
CH_3NHNH_2 + H
Reaction Kinetics Summary

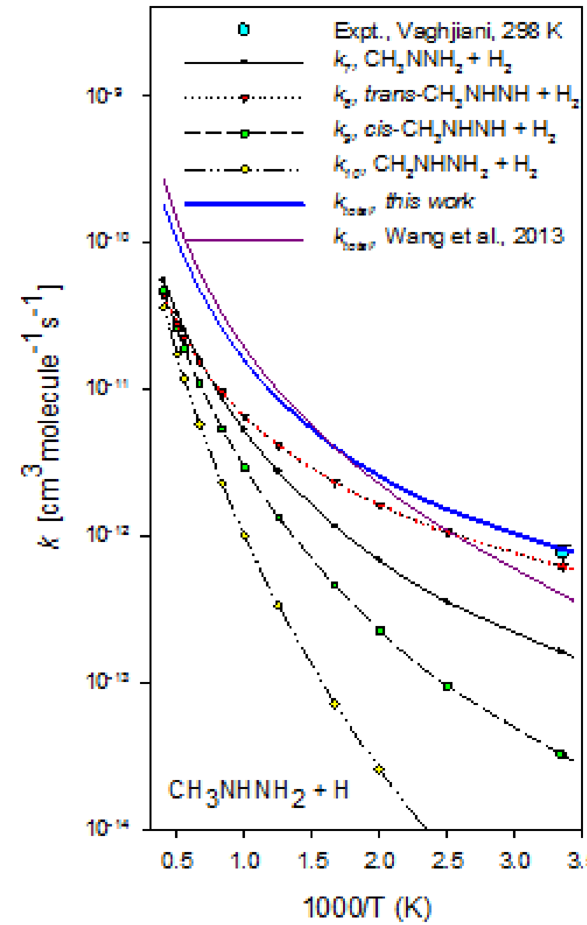
CH_3NHNH_2 + H → TS7 → CH_3NNH_2 + H_2

→ TS8 → trans-CH_3NHNH + H_2

→ TS9 → cis-CH_3NHNH + H_2

→ TS10 → CH_2NHNH_2 + H_2





Conclusions

- $N_2H_3 + NO_2$ Reaction Kinetics
  - Fast addition reaction
  - Direct detection of HONO product confirmed
  - Weak -ve temperature dependence of rate coefficient (k) seen
  - Multi-reference methods employed to accurately determine stationary energies of the PES
  - Calculated k in agreement with experiment

- CH_3NH Decomposition
  - CH_2=NH + H channel dominates

- CH_3NHNH_2 + H Reaction Kinetics
  - Agreement seen in absolute rate coefficient between theory and experiment
  - Theory provides insight regarding at which site H-abstraction dominates

- High-level *ab initio* quantum chemical calculations and direct *real-time* kinetics measurements can provide unparalleled-details regarding the nature of the reaction mechanism of a chemical system of interest

Acknowledgements

DOD HPC DEPARTMENT OF DEFENSE HIGH PERFORMANCE COMPUTING MODERNIZATION PROGRAM

THE NATIONAL ACADEMIES *Advisers to the Nation on Science, Engineering, and Medicine*

NERSC

Questions?

Solid Rocket Motors
Area 1-32
• Pad 1 & 2
• 1Mlbf thrust
• 450Klbf, unique 6DOF Thrust Stand
• SOTA data acquisition system with 420 channels
• Motor sizes up to first stage ICBMs
• Extensive upgrades 2000s
Development Test History
• MM III PAP
• Sargent
• Atlas V
• Super Strypi
• MANY others
LEO-7 & LEO-46
Super Strypi (SPARK) Nanosat Launcher
AFNWC Advanced 1st, 2nd & 3rd Stage
Atlas V Strap-on
Altitude/Spacecraft
Development History
• Multiple MDA systems
• Minuteman
• Agena
• MANY others
SPEF
Area 1-42
Cells A, B, D
• SPEF
• Up to 50Klbf thrust
• DOF Thrust Stand
• SOTA data acquisition system with 576 channels
• 30ft diameter spacecraft altitude chamber
• Comprehensive time-resolved diagnostics (best in nation)
• Diffusion pumps
• Test large, high power Electric & Ionic Liquid Propulsion thrusters
Cell E
• Multi-Newton Chemical spacecraft thrusters to 200lbf thrust solids
• World class diagnostics system & thrust stand
In-space Laboratory
• 7 altitude chambers for in-space testing
E-Cell
For more information contact:
AFRL/RQR, 5 Pollux Dr, Edwards AFB, CA 93524
661-275-5230
RDT&E Testing Capability
Rocket Propulsion Division
Edwards AFB, CA
Approved for Public Release, Distribution Unlimited, PA clearance # 15416
>30 RDT&E Activities Supported since 1990
Technology Transition Cycle
S&T Maturation
Commercial RDT&E
Industry
Gov't RDT&E
Testing Customers (partial)
NASA
DARPA
ORS
ULA
United Launch Alliance
Sandia National Laboratories
LOCKHEED MARTIN
BOEING
Orbital ATK
BUSEK
AEROJET ROCKETDYNE
NORTHROP GRUMMAN
Other Contractors
Ball
Liquid Rocket Engines
Area 1-120
Stand 1-A & 1-D
• 1.6Mlbf Thrust stand
• Vacuum jacketed (VJ) LO2 (cryogenic) run tank, 75,000 gallon, 165 psig
• VJ LH2 (cryogenic) Run Tank, 90,000 gallon, 165 psig
• RP-1 run tank, 60,000 gal. 150 psig
• SOTA data acquisition system with 1200 channels
• Extensive upgrades 1990s
Development Test History
• Saturn V F-1
• Delta IV RS-68
Example Run times
RS-68: 2-3 minutes
RD-68 Development
Development problems are in start-steady state-stop (transients), not long duration
Stand 2-A
• Component and engine test stand
• Two position, ground level test stand
• Maximum thrust of 2,000,000 lbf
• Horizontal or 45 degree down
• LO2 Vacuum Jacketed Run Tank; 2,000 gallon, 8,500 psig
• LH2 Vacuum Jacketed Run Tank; 3,800 gallon, 8,500 psig at 77 K
• RP-1 Run Tank, 2000 gallon, 6,600 psig
• SOTA data acquisition system with 1200 channels
• Extensive upgrades 1990-current
AFRL USET
AFRL HCB
DARPA FALCON
Development Test History
• Saturn V F-1
• DARPA FALCON
• AFRL USET turbopump
• AFRL Hydrocarbon Boost Demo (HCB)