

# Calculation of State-Specific Rate Coefficients for Non-equilibrium Hypersonics Applications:

*from  $H\Psi = E\Psi$  to  $k(T) = A*\exp(-E_A/RT)$*

Richard Jaffe, David Schwenke and Galina Chaban,  
NASA Ames Research Center

Moffett Field, California

Marco Panesi, Department of Aerospace Engineering,  
University of Illinois, Urbana-Champaign, Illinois



# Motivation

- The detailed chemistry & physics models currently in vogue for simulations of shock structure in hypersonic flows were developed in the 1980s
- Since that time, Navier-Stokes and Schrödinger equation solvers are  $\sim 10^6$  times more powerful, *but we are still using the same crude chemistry & physics models*
- For the last few years, NASA has been trying to remedy this situation

*Currently supported by Hypersonic-Entry Descent & Landing project in NASA's Space Technology Mission Directorate*



# Outline

## I. Introduction

*What are the shortcomings of the old models?*

## II. Methods for computing reaction rate coefficients from first principles

- Potential energy surfaces (PES)

*Map out the interatomic forces.*

- Quasiclassical trajectories (QCT)

*Simulate collisions using classical mechanics & Monte Carlo sampling.*

## III. Analysis

- 0-d Master Equations model

*Determine “phenomenological” rate coefficients.*

## IV. Conclusions



# Introduction

- The Apollo heatshield was designed with large safety margins, because hypersonic phenomena were not well understood
- Early observations and aerothermodynamics calculations clearly showed that thermodynamic and chemical equilibrium were not maintained in the bow shock layer during reentry

*Non-equilibrium radiation overshoot was observed, (predominantly atomic lines of nitrogen and oxygen)*

- During the 1980s an empirical “2-temperature” chemistry model was developed

*Most of the parameters were obtained from older shock tube experiments*



# 2-Temperature Chemistry Model

- Partitioning of internal energy modes

$$T_{rot} = T \quad \leftarrow T_{electron}^? \quad \rightarrow \quad T_{vib} = T_{electronic}$$

- Landau-Teller model used for post-shock internal energy relaxation

$$\frac{dE_{vib}(T_V)}{dt} = \frac{[E_{vib}(T) - E_{vib}(T_V)]}{\tau_V}$$

- Internal energy relaxation decoupled from “chemistry”

$$T_{ave} = T^s \times T_{vib}^{1-s} \quad (\text{usually } T_{ave} = (T \times T_{vib})^{1/2})$$

$$k_{diss}(T, T_{vib}) = A \cdot \exp(-E_A/RT_{ave}) \text{ or } (BT_{ave}^c) \cdot \exp(-E_A/RT_{ave})$$

- Developed mostly by Chul Park at NASA Ames



# Non-Equilibrium Overshoot at the Shock

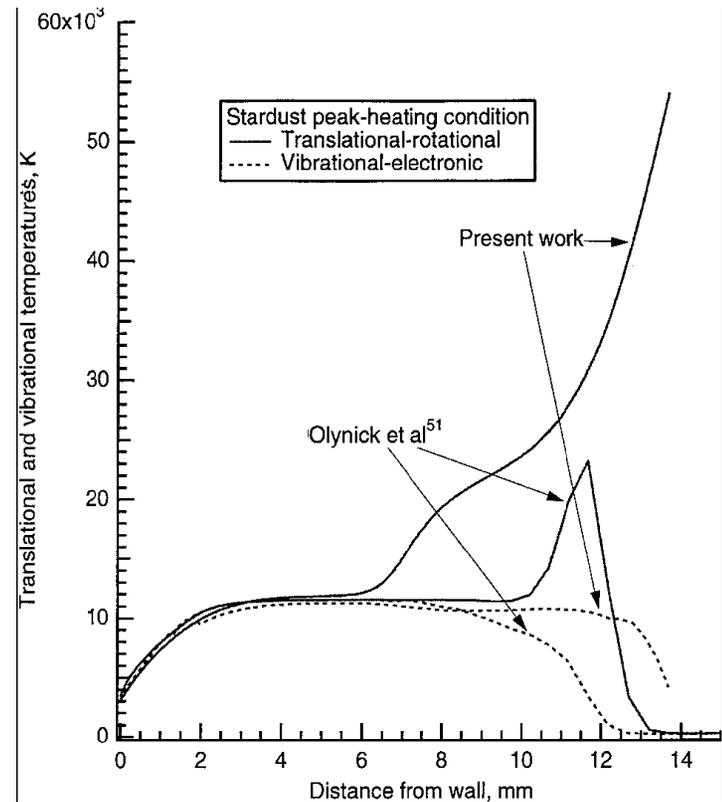
- Immediately after the shock  $T \gg 10,000$  K and  $T_{VIB} \sim 300$  K
  - For  $T_{ROT} = T$  prompt dissociation & atomic excitation

*Radiation overshoot*

- Closer to surface  $T = T_{VIB} \sim 10,000$  K

*Thermal equilibrium*

- Maximum  $T \sim 20,000$  K for  $T_{ROT} = T$  and  $\sim 60,000$  for  $T_{ROT} \neq T$



# Our Objective

- Develop a “physics-based” hypersonics model for high-speed Earth entry ( $> 10$  km/s), validated against experimental data
- Determine rate coefficients for dissociation, exchange and energy transfer reactions
  - $N_2$  dissociation for Earth entry
  - CO dissociation for Mars entry
- Try to avoid preconceived assumptions about temperature
  - We have succeeded for internal energy modes, but still assume Maxwellian distribution for translation



# Methods - PES

- With all the advances in computer hardware and quantum chemistry software, achieving chemical accuracy ( $\sim 4$  kJ/mol) is still out of reach for 4-atom cases (e.g.,  $N_2+N_2$ )
  - We chose to employ a hybrid approach for the  $N_4$  PES
  - Multi-Reference Configuration Interaction (MRCI) for geometries where the N-N bonds were greatly stretched
  - Single-reference method (CCSD(T)) for other geometries
  - Accurate empirical diatomic potential function for  $N_2$
- Energy computed for 1000s of geometries and fit to an analytic function for use in QCT calculations
- For the  $N_3$  PES only the MRCI method was used and combined with the empirical diatomic potential

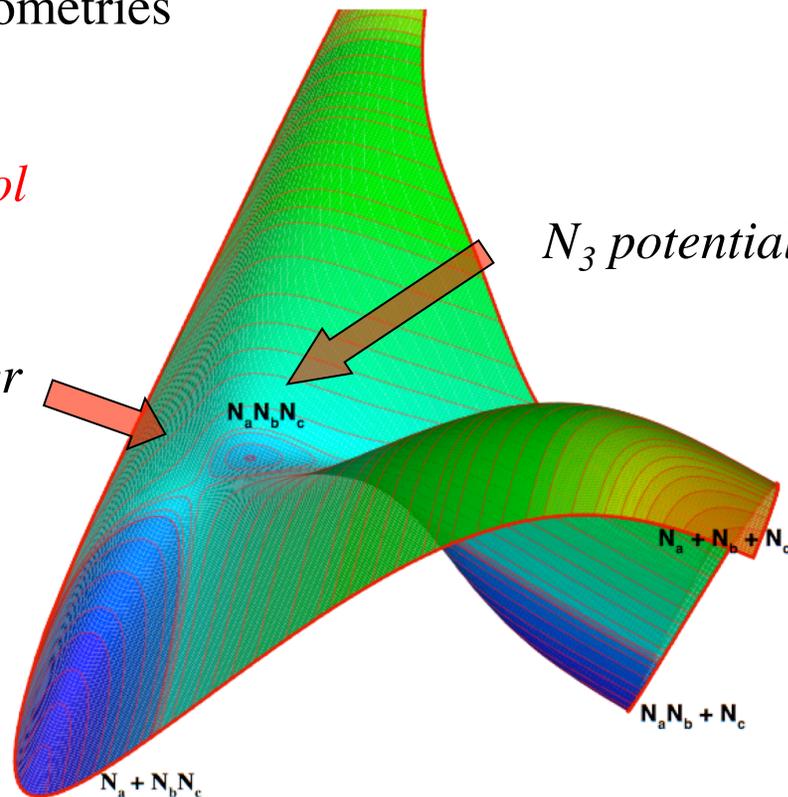


# Potential Energy Surface for $N_2 + N$ Collisions

Analytic representation of quantum chemistry energies for a grid of  $N_3$  geometries

*Relative energies  
accurate to  $\pm 2$  kcal/mol*

*Exchange reaction barrier*



color key  
**blue - low energy**  
**red - high energy**



# Methods - QCT

- Hamilton's equations of motion ( $q_i$ ,  $p_i$  are coordinates and momenta;  $H$  is total energy)

$$\frac{dq_i}{dt} = \frac{\partial H}{\partial p_i} \quad \frac{dp_i}{dt} = -\frac{\partial H}{\partial q_i} = -\frac{\partial V_{PES}}{\partial q_i}$$

- Simulate collisions like  $N + N_2$  or  $N_2 + N_2$ 
  - Initial conditions correspond to  $N_2(v, J)$  with random orientation, rotation and vibration phase, impact parameter ( $b$ ) and relative collision velocity ( $V_R$ )
  - State-to-state cross section obtained from a large sample of trajectories

$$S_R(v_i, J_i, v_f, J_f, V_R) = 2\pi \int_0^{b_{max}} P_R(V_R, b) b db$$

- State-to-state rate coefficient obtained by integration of Boltzmann-weighted cross section over collision energy ( $E_R$ )



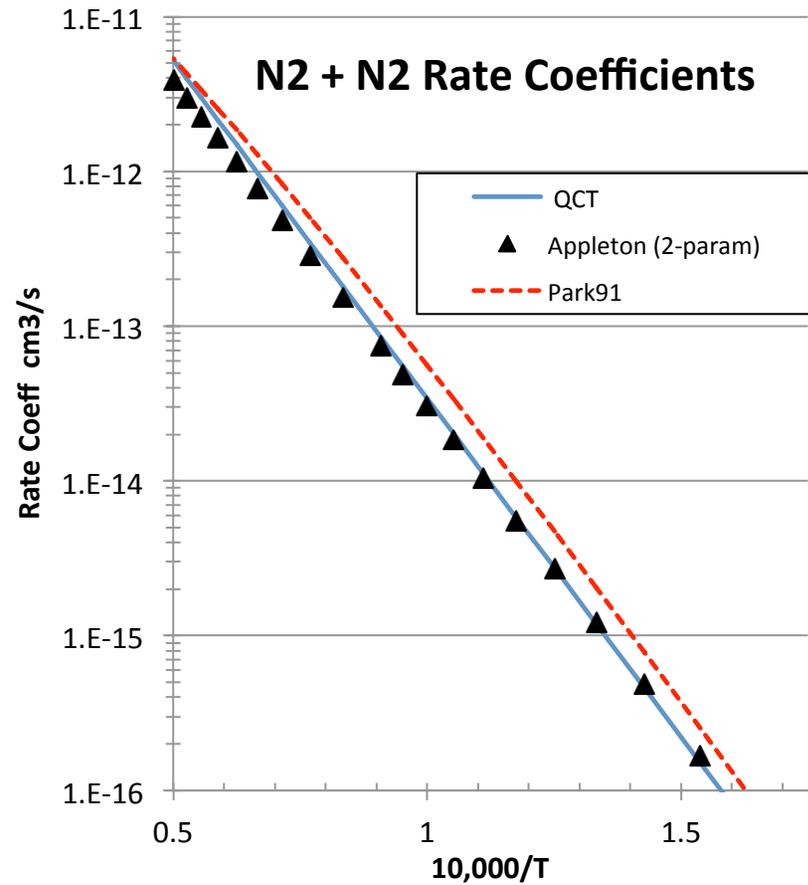
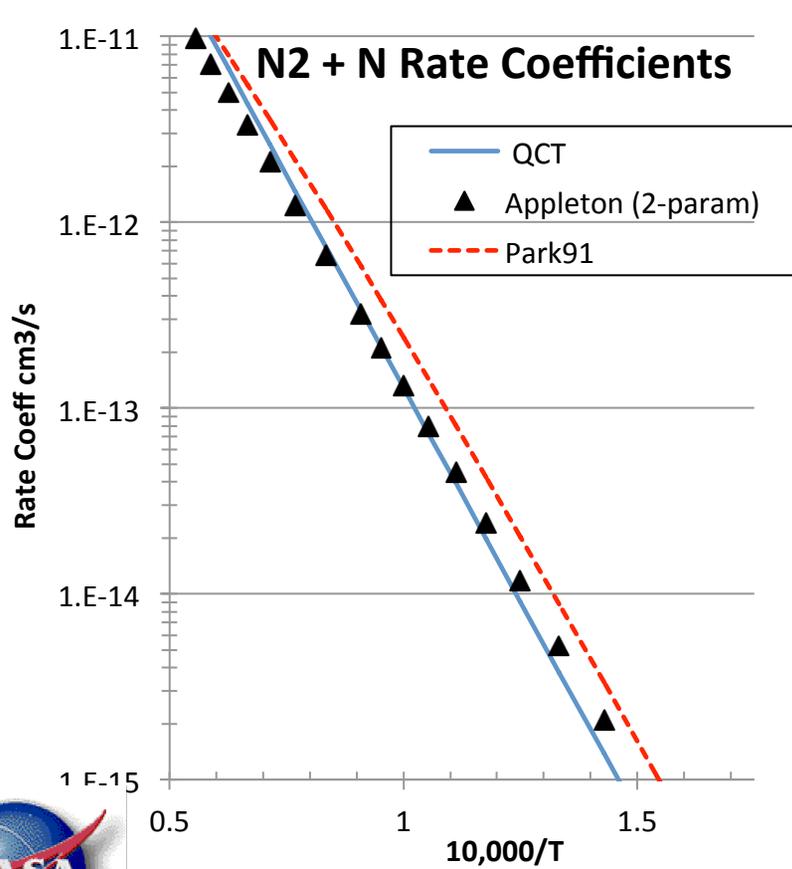
# State-specific Rate Coefficients

- $N_2 X^1\Sigma_g^+$  has 9390 rovibrational levels with the Leroy potential – *we have obtained state-specific rate coefficients for all of them*
- For inelastic collisions rate coefficients exhibit relatively large values for  $|\Delta v| > 1$
- Inclusion of exchange reactions enhances this effect
- Largest contributions to dissociation rate coefficient come from rovibrational levels near and above the dissociation energy
- *Quasi-bound levels contribute ~40% to thermal rate coefficient for  $T > 10,000$  K*



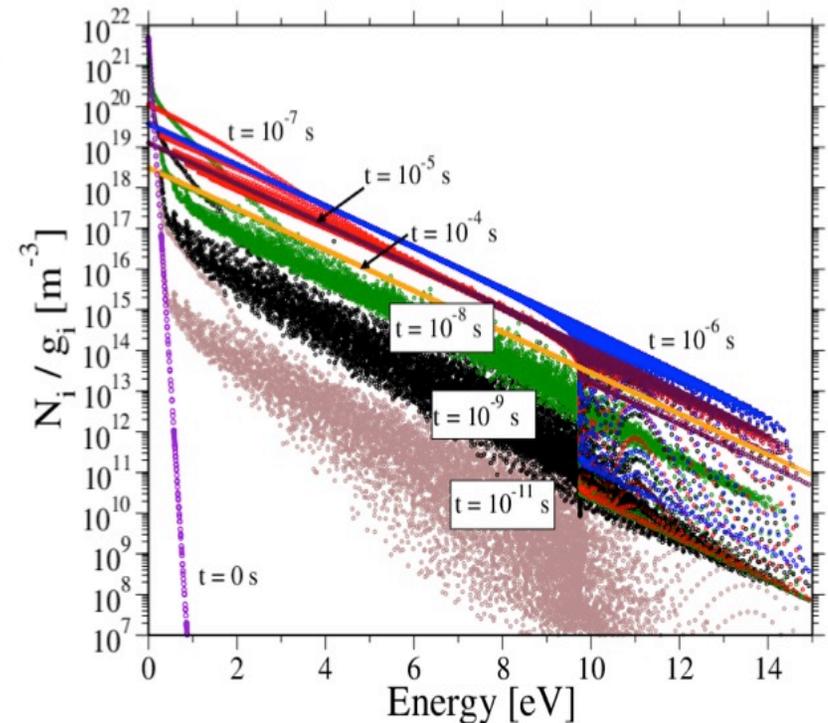
# Thermal Rate Coefficients

- Thermal dissociation rate coefficients agree well with experimental data (Appleton)



# Analysis – 0-d Master Equations

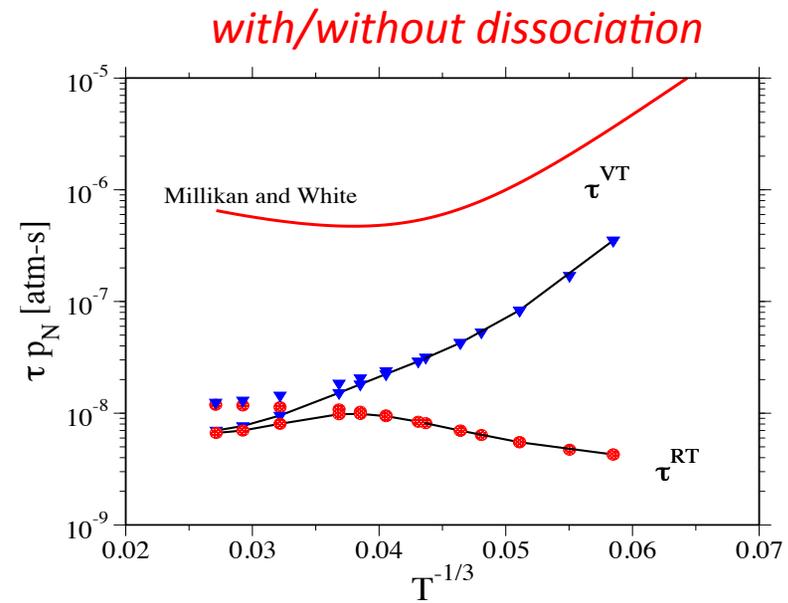
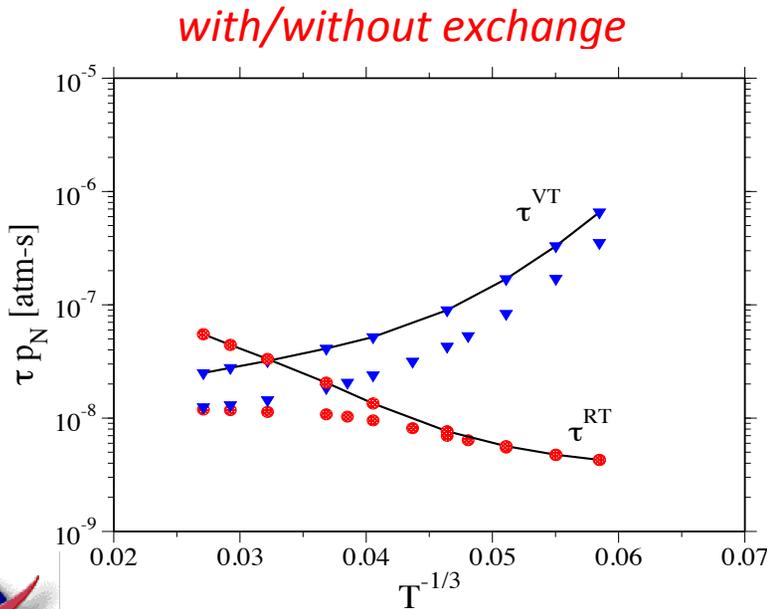
- Master Equation simulate  $N_2$  relaxation-dissociation
  - All state-specific reactions for  $N_2 + N$  dissociation, exchange and energy transfer included (9390 ro-vibration levels)
  - Start with 97%  $N_2 + 3%$  N at 300 K and impose and maintain a high value of T
- Follow the evolution of the  $N_2$  rovibrational population from  $t = 0$  to  $10^{-3}$  s



Panesi et al., J. Chem. Phys. 138, 044312 (2013)

## N<sub>2</sub> Relaxation Times ( $\tau$ )

- For N<sub>2</sub> + N collisions Exchange reactions speed up relaxation (decrease  $\tau_V$  and  $\tau_R$ )
  - $\tau_V \approx \tau_R$  for  $T > 10,000$  K
- Dissociation decreases  $\tau_V$  and  $\tau_R$  for  $T \geq 20,000$  K
- Empirical Millikan-White  $\tau_V \geq 10x$  larger than present values



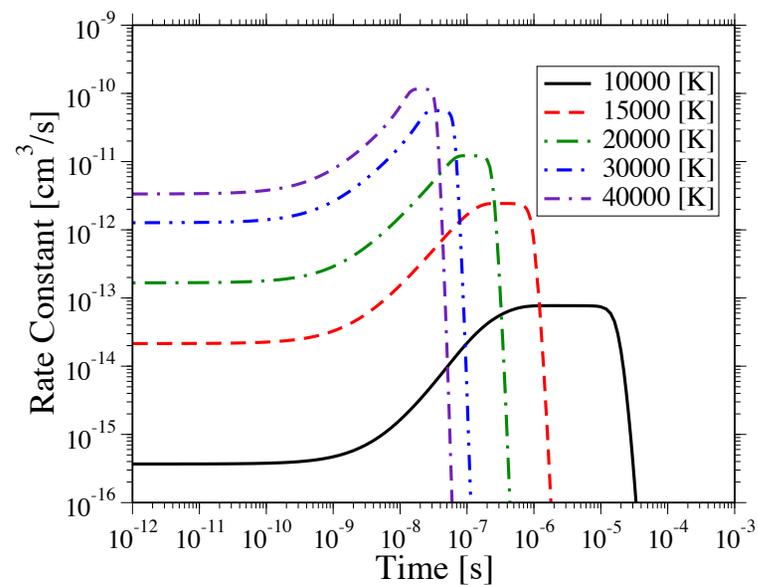
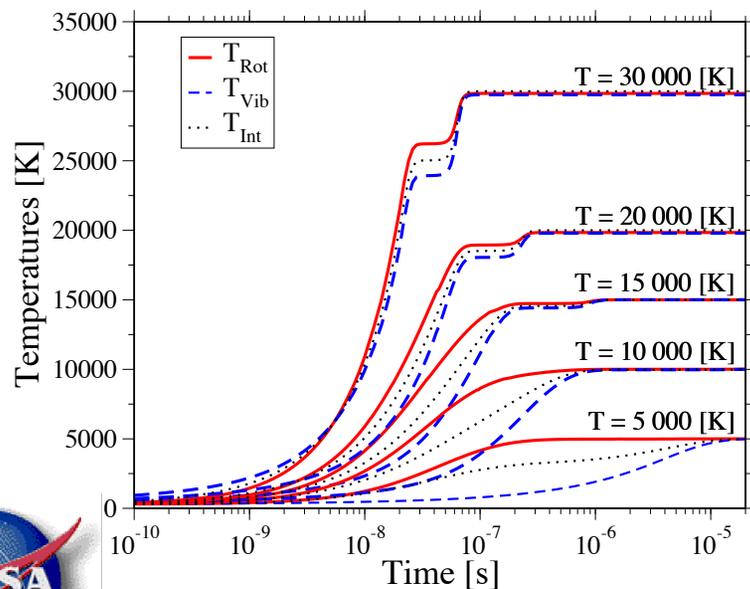
$\tau$  Computed by the e-folding method



# QSS?

- Quasi-Steady State behavior is observed in Master Equation results
  - $T_V$  &  $T_R$  reach plateaus at values less than  $T$  for  $T > 10,000$  K
  - “Global” dissociation rate coefficient also plateaus

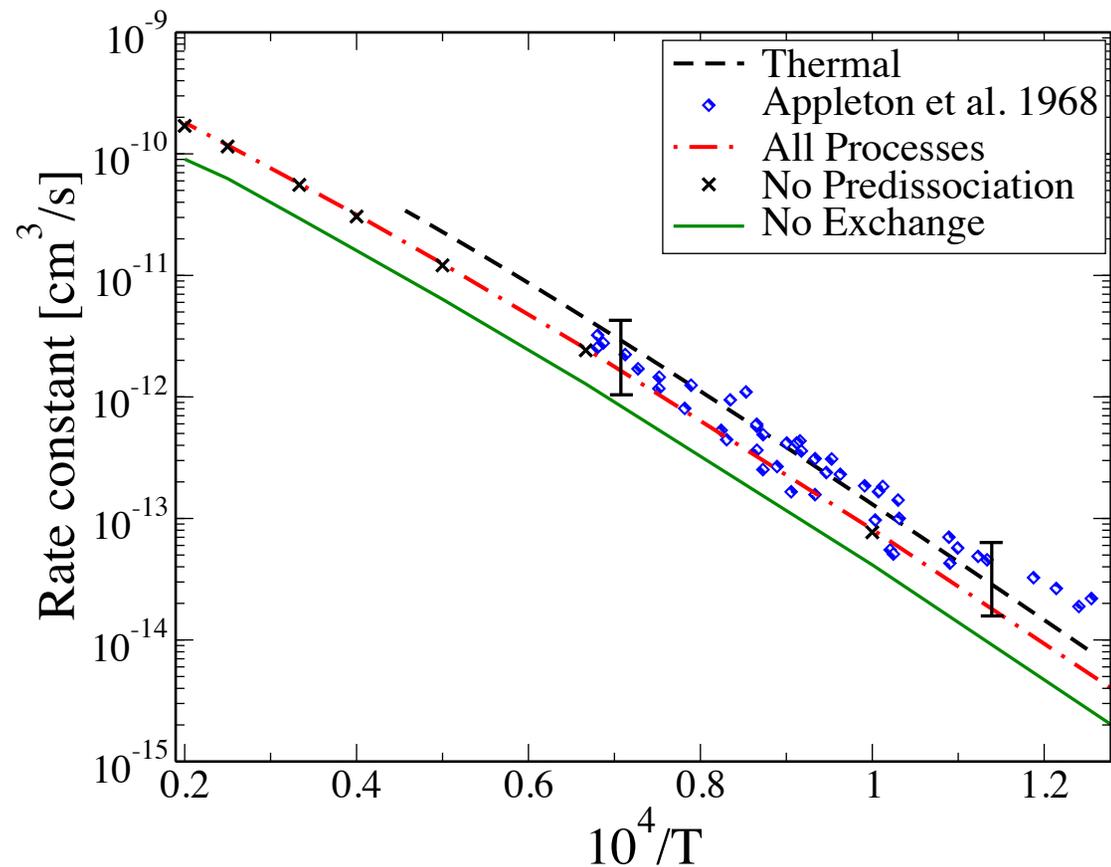
*For high  $T$ , most dissociation occurs before QSS is realized*
- $\tau_V \approx \tau_R$  at high- $T$  evident from plot of  $T_V$  &  $T_R$  vs  $t$



# Dissociation Rate Coefficient for $N_2 + N$

- Global and thermal dissociation rate coefficients ( $k^D$  and  $k^{D*}$ , respectively) in good agreement with experimental data (Appleton)

- Neglect of exchange reaction lowers  $k^D$  by factor of 2
- Quasi-bound levels make negligible contribution to  $k^D$



# What the Master Equation Study tells us

- For the non-equilibrium overshoot region  $T \neq T_{\text{ROT}}$ 
  - $T \geq 20,000 \text{ K}$ ,  $\tau_V \approx \tau_R$  and  $T_{\text{VIB}} = T_{\text{ROT}} = T_{\text{int}}$  is a good approximation
  - Strong coupling between internal energy relaxation and dissociation
  - Maximum in  $T$  is much higher because rotational modes are not excited
- Under these conditions, the dissociation rate coefficient is 1/3 lower than the thermal one
  - Exchange reaction lowers  $\tau$  and increases  $k^D$



# Conclusions

- Accurate potential energy surfaces have been determined for  $N_3$  and  $N_4$  based on ab initio quantum mechanics calculations
  - Used in Quasi-Classical Trajectory calculations to obtain state-to-state rate coefficients for collisional processes important for hypersonic reentry conditions
- We have determined a full set of state-to-state rate coefficients for  $N_2 + N$  collisions
  - Excellent agreement with experimental data for thermal equilibrium conditions
  - Enables us to carry out a detailed study of non-equilibrium relaxation (Master Equation calculations)
  - A major assumption of the 2-temperature model ( $T_R = T$ ) is shown to be invalid for these conditions



## Conclusions (2)

- Similar calculations for  $N_2 + N_2$  collisions have been carried out
  - Good agreement is found for dissociation rate coefficients at thermal equilibrium
  - Calculations of non-equilibrium effects are on-going
- These state-to-state rate coefficients are being used in the development of coarse-grain reduced dimensionality models (stay for the next talk) that can be used in CFD calculations

*More detailed studies of the shock structure are needed to better characterize the non-equilibrium region*

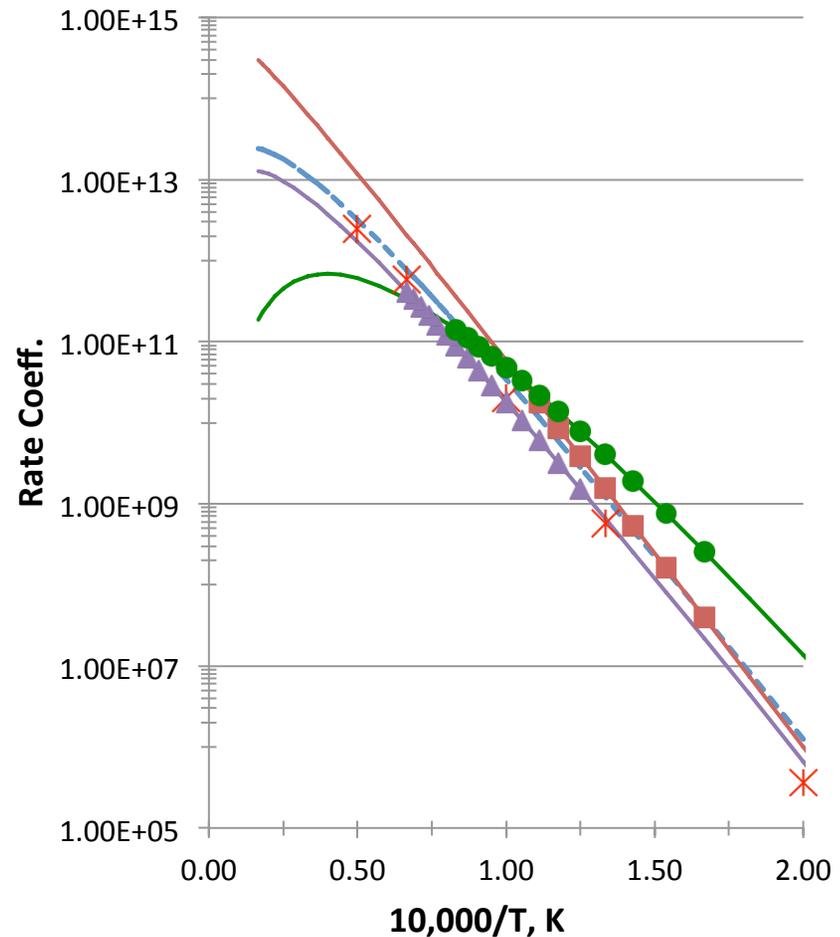


# Supporting material

# Thermal Dissociation Rate Coefficient

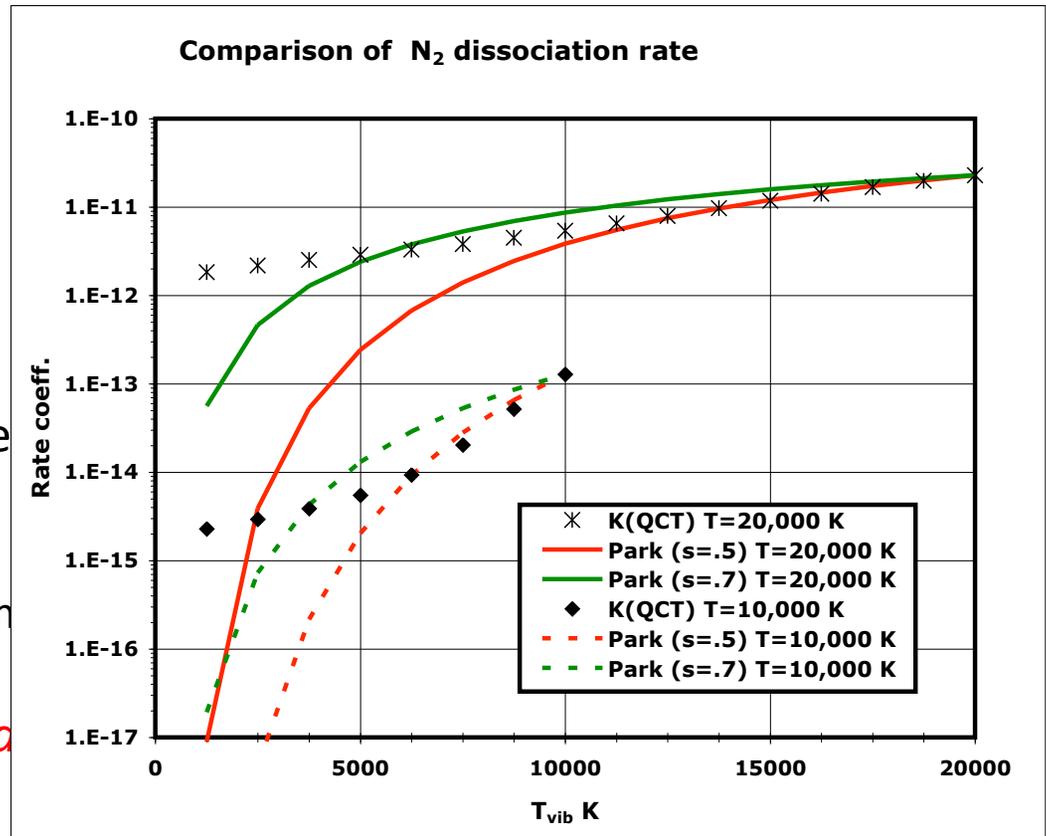
- $N_2 + N_2$  dissociation rate coefficient agrees well with shock-tube results of Byron and Appleton
- No evidence for curvature in fit to Arrhenius expression

Legend  
■ Byron  
△ Appleton  
○ Hanson  
★ QCT  
Dashed Park model



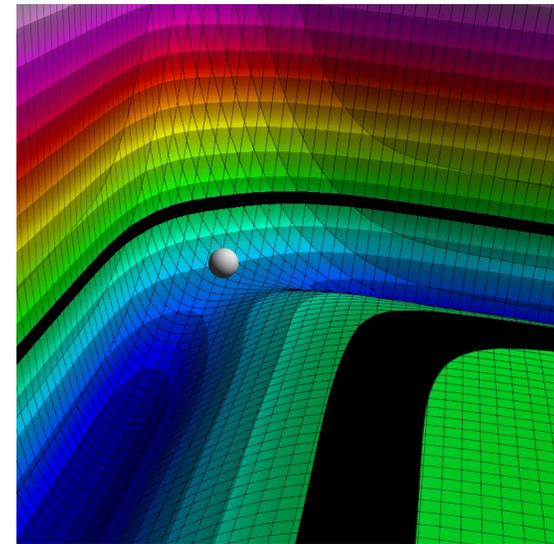
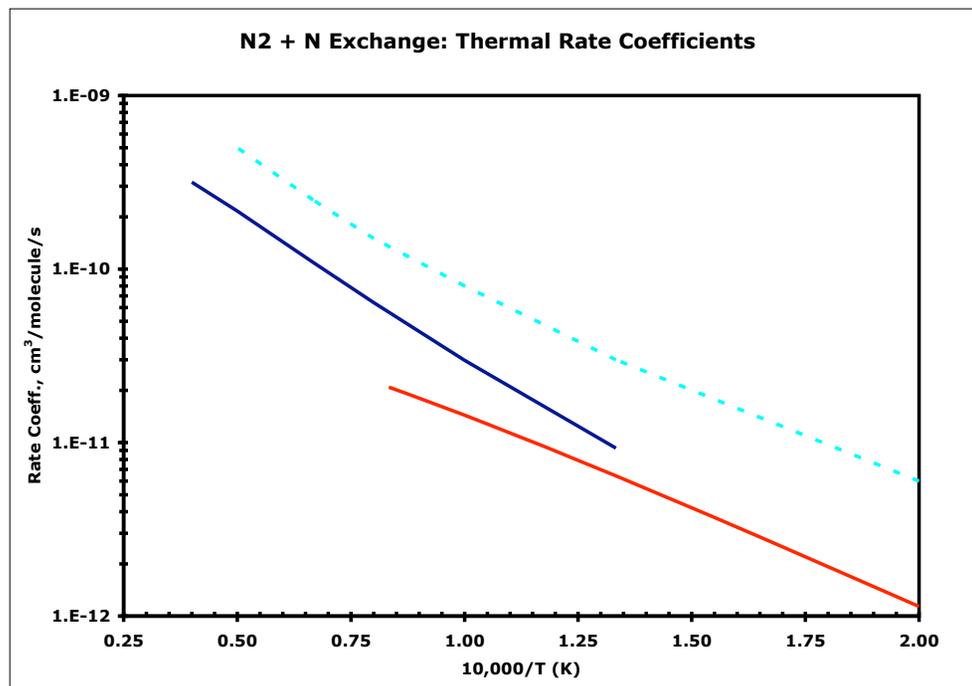
# Park's 2-Temperature Model for N<sub>2</sub> Dissociation

- Park's 2-T empirical model to account for  $T_{vib} < T$ 
  - Empirical
  - $T_{ave} = T^s \times T_{vib}^{(1-s)}$
  - Originally Park used  $s = 0.5$
  - Current model uses  $s = 0.7$
- Model cannot be adjusted to agree with QCT data for full range of  $(T, T_{vib})$ 
  - Rate coefficients fall off too much when  $T_{vib} \ll T$
- *Differences with QCT values indicate dissociation is more strongly dependent on rotation than vibration*



# Details of exchange reaction

- Activation energy for exchange is much less than for dissociation
  - 45 vs 225 kcal/mol
- Results in much larger changes in rotation-vibration energy than do inelastic collisions



Exchange barrier on the N<sub>3</sub> PES

*Blue line - QCT*

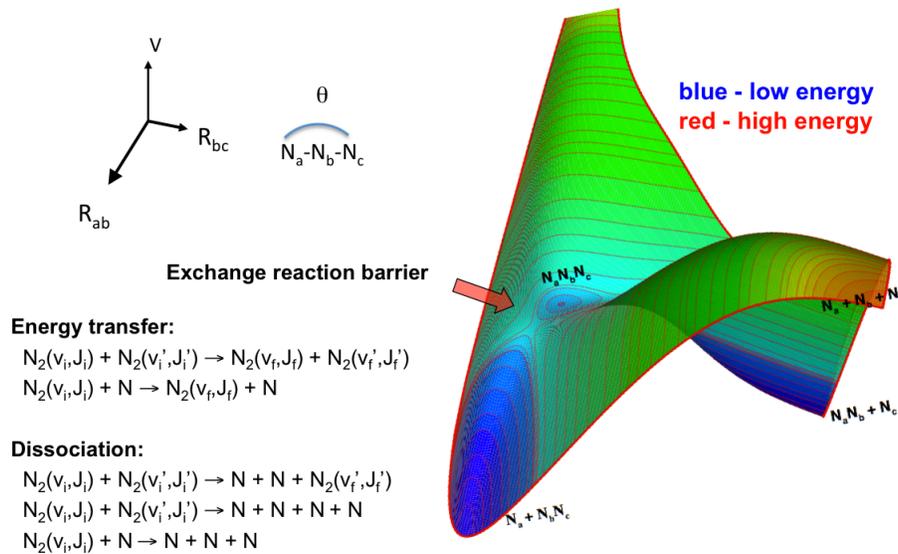
*Red line - quantum mech (Wong)*

*Dashed line - QCT (Capitelli empirical PES)*

# Comments On The Development of Chemistry Models for Hypersonic Atmospheric Entry

Richard Jaffe  
 Aerothermodynamics Branch  
 Entry Systems Technology Division  
 NASA Ames Research Center  
 Moffett Field, CA 94035

Development of High-Fidelity Physics-Based Models to describe hypersonic flight through the atmospheres of Earth and Mars is underway at NASA Ames Research Center. The goal is to construct chemistry models of the collisional and radiative processes that occur in the bow shock and boundary layers of spacecraft during atmospheric entry that are free of empiricism. In this talk I will discuss our philosophy and describe some of our progress. Topics to be covered include thermochemistry, internal energy relaxation, collisional dissociation and radiative emission and absorption. For this work we start by solving the Schrödinger equation to obtain accurate interaction potentials and radiative properties. Then we invoke classical mechanics to compute state-specific heavy particle collision cross sections and reaction rate coefficients. Finally, phenomenological rate coefficients and relaxation times are determined from master equation solutions.



**$N_3$  Potential Energy Surface for angle  $\theta = 115^\circ$**