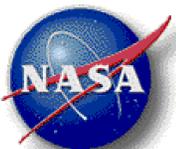


Calculation of State-Specific Rate Coefficients for Non-equilibrium Hypersonics Applications:

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

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Hypersonics: Physics and Chemistry

- Hypersonic flight

- Spacecraft or projectile entering the atmosphere at very high Mach number (velocity >10 km/s for Earth)
- Shock wave forms in front of the object creating a layer of compressed gases

- Physics and chemistry

- Description of the shock layer must include real gas properties including excitation of internal modes of atoms and molecules, diffusion and convection, emission of photonic radiation, ionization, chemical reactions
- At the same time, the object can undergo ablation, outgassing, spallation; all of which inject new heavy particle species into the shock boundary layer at the spacecraft surface
- Mixing of boundary layer and shock layer species can result in additional interactions.



Characteristics of Earth Entries

- Free stream $T < 300$ K & low Pressure at 50-90 km altitude (region of highest heat flux during re-entry)
- For a 10 km/s shock, translational energy peaks at $T > 20,000$ K just behind the shock, but internal modes are not immediately excited, so $T \gg T_{int}$
- Away from the shock, $T = T_{int} \approx 10,000$ K and $P \sim 0.1-0.3$ bar
- At the boundary layer, $P \sim 1$ bar and $T = 3000-5000$ K and the surface temperature $\approx 2000-3000$ K



Outline

I. Introduction to chemistry models for hypersonics

What are the shortcomings of the old chemistry models?

II. Methods for computing reaction rate coefficients from first principles

- Potential energy surfaces (PES)

Map out the interatomic forces between atoms.

- Quasiclassical trajectories (QCT)

Simulate collisions using classical mechanics & Monte Carlo sampling.

III. Analysis

- 0-d Master Equations and Euler equations 1-d Shock model

Determine “phenomenological” rate coefficients.

IV. Conclusions



Chemistry models for hypersonic re-entry flows

- In this flow regime, fluid dynamics, radiation, and non-equilibrium chemistry are highly coupled:
 - Vibration-Rotation-Translation energy transfer (VRT), dissociation, ionization convert kinetic energy to internal energy of the atoms and molecules in the flow
 - This internal energy is converted to radiative energy by photoemission
- The time required for these internal energy modes to equilibrate with translational energy must be known in order to predict the radiative heat flux impinging on the vehicle



The Entry Systems Modeling project in NASA's Space Technology Mission Directorate is supporting development of a new high-fidelity chemistry model for hypersonic flows



Motivation – Why improved chemistry models are necessary

- 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)
- The detailed chemistry & physics models currently in use for simulations of shock structure in hypersonic flows were developed in the 1980s (**Chul Park, JTHT 2(1), 8 (1988)**)
- 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



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”

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

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

- Assumes rotation and vibration are separable and internal energy relaxation and dissociation are not coupled (*quasi-steady state approximation*)



Example of non-equilibrium overshoot at the shock

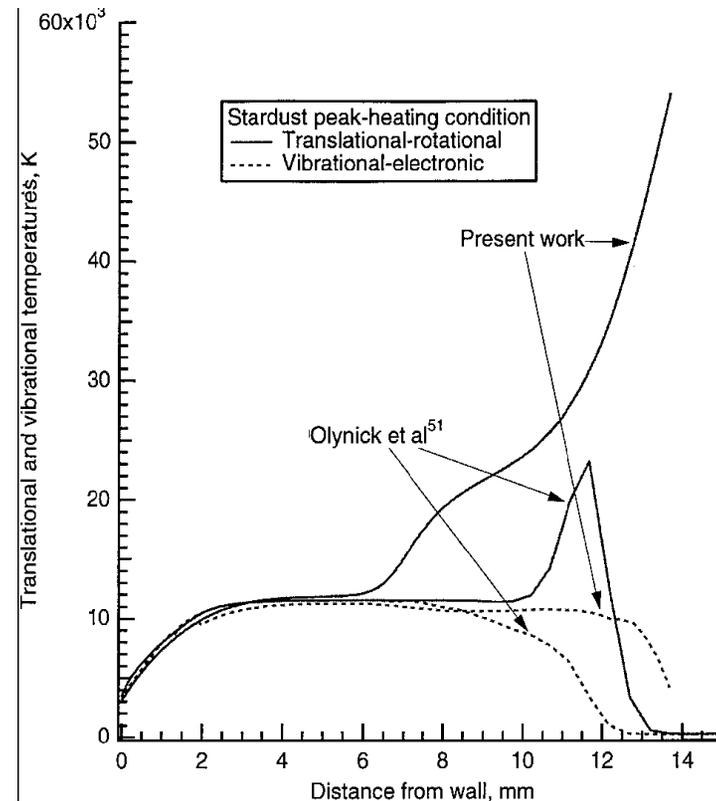
- Immediately after the shock $T \gg 10,000$ K and $T_{VIB} \sim 300$ K
 - $T_{ROT} = T$ results in prompt dissociation & atomic excitation

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 $T_{ROT} \neq T$



Stardust return capsule trajectory: T , T_{VIB} along stagnation streamline for 59.9 km & 11.15 km/s (Park et al., JTH 15(1), 76 (2001))



Molecular Species of Interest

- Earth
 - N_2 , O_2 , NO, N_2^+ , NO^+ (emission in shock layer)
 - C_2 , CO, C_2H , C_3H , C_3 , C_4 , etc. (absorption in boundary layer)
- Mars
 - CO_2 (IR), CO (IR, VUV), CN (UV-Vis), N_2 (UV)

(green denotes free stream species)

Treatment of Rotation in N₂

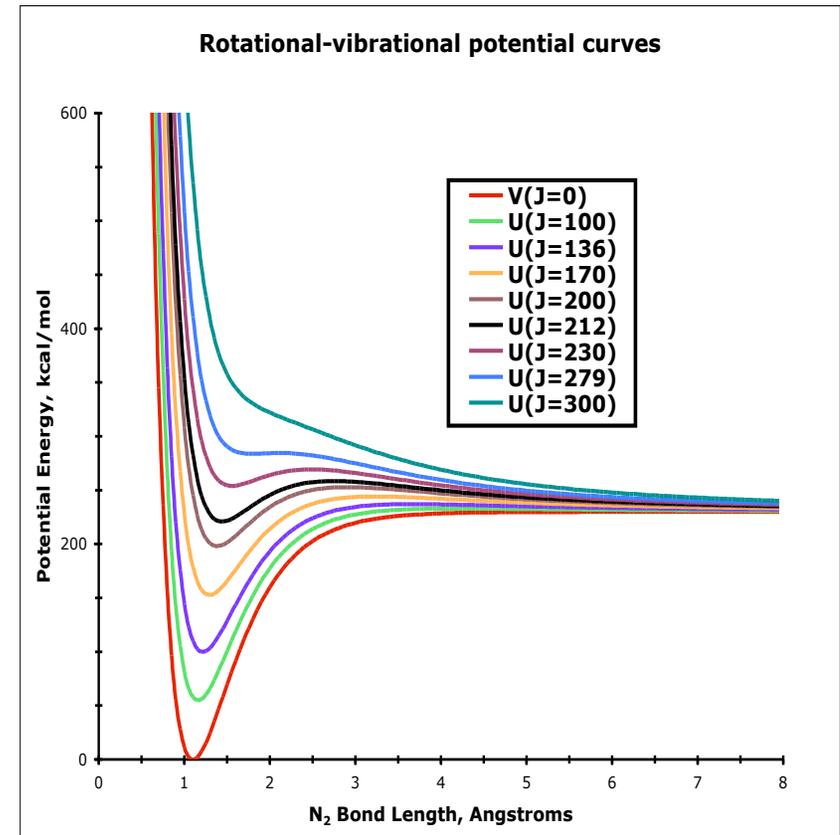
- **Rotation and vibration are not separable!**

For high rotation quantum numbers (J), dissociation energy is reduced, rotational and vibrational spacings become comparable

- Many long-lived vibration levels above dissociation limit (*quasibound*)

- New N₂ potential (R. Leroy, et al., *J Chem Phys* **125**, 164310 (2006)) from experimental measurements

$v_{\max} = 60$ and $J_{\max} = 279$
9390 ro-vibrational levels



$$V_J(r) = V_{J=0}(r) + J(J+1)B_{rot}(r_e/r)^2$$



Our Objective

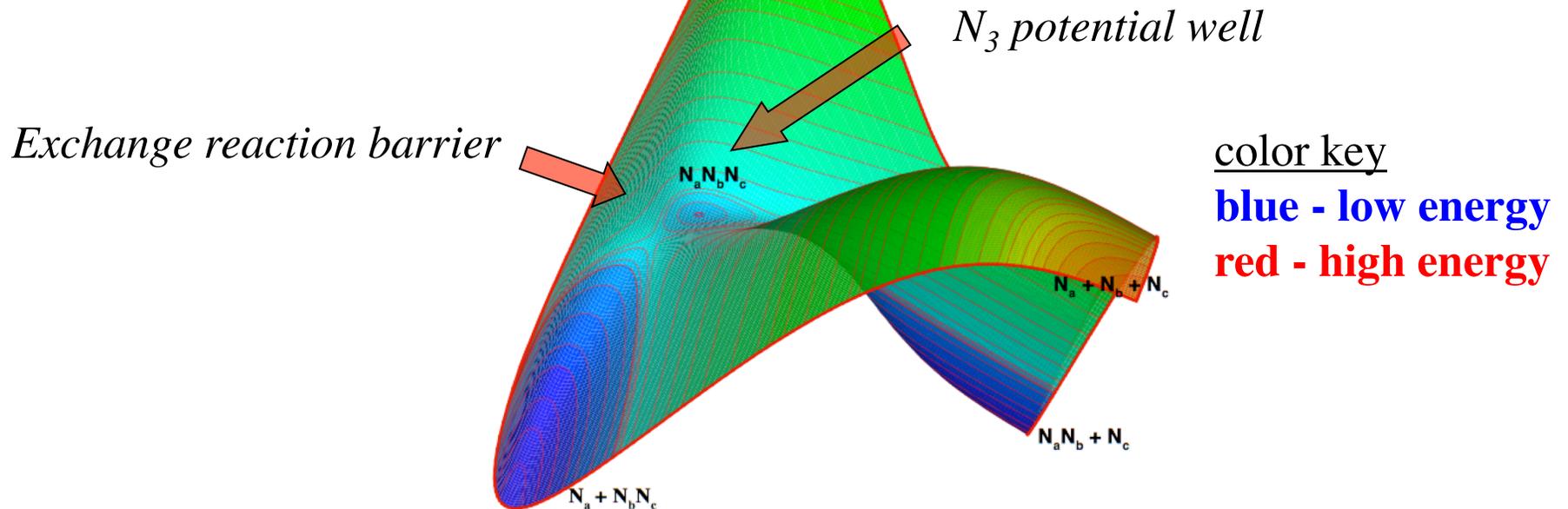
- Develop a “physics-based” hypersonics model for high-speed Earth entry (10-14 km/s), validated against experimental data
- Determine rate coefficients for dissociation, exchange and energy transfer reactions
 - N_2 dissociation for Earth entry
 - CO_2 and CO dissociation for Mars entry
- Try to avoid preconceived assumptions about temperature
 - We have succeeded for internal energy modes, but we still assume Maxwellian distribution for translation



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 ± 2 kcal/mol*



Quantum Mechanics Refresher

- Electronic Schrödinger equation (shown for clamped nuclei)

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) \right] u(\mathbf{r}) = Eu(\mathbf{r})$$

- V (potential)
 - electron-electron, electron-nucleus and nucleus-nucleus Coulomb interaction for potential energy calculations
 - diatomic potentials or triatomic PES for ro-vibrational energy level calculations
- Wavefunction (u) and energy (E) determined by basis set expansion methods

Methods - PES

- With all the advances in computer hardware and quantum chemistry software, achieving chemical accuracy (~ 4 kJ/mol) is still difficult 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



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)



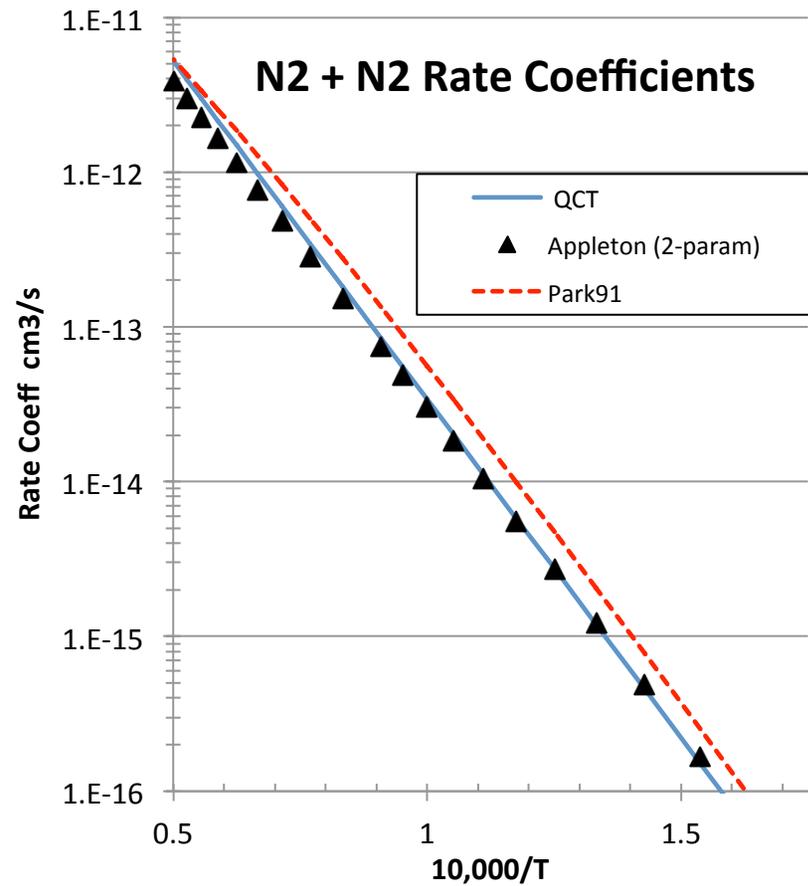
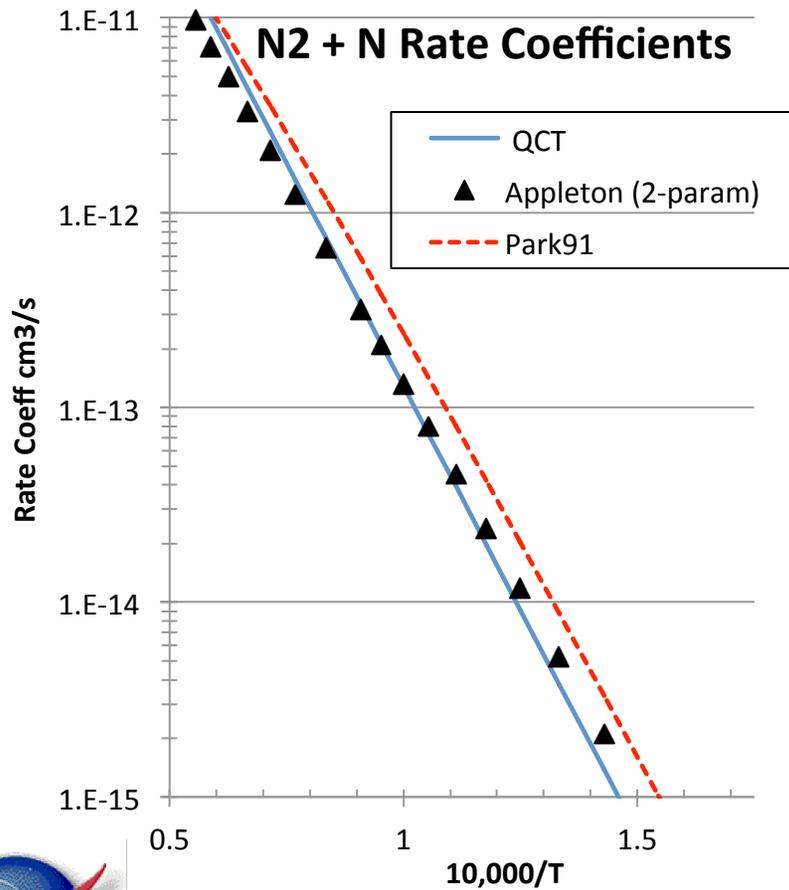
State-specific Rate Coefficients

- $N_2 X^1\Sigma_g^+$ 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*



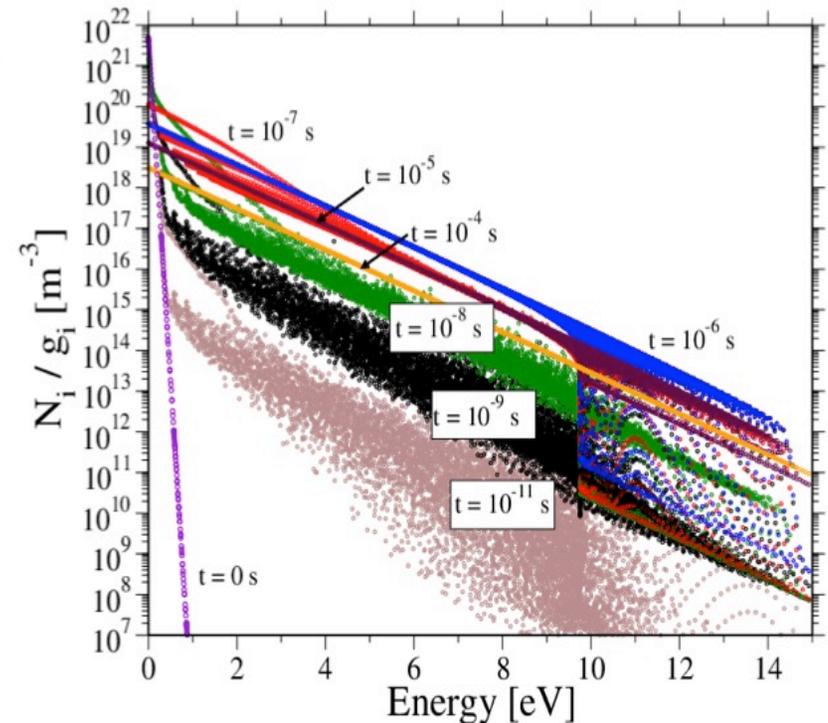
Thermal Rate Coefficients

- Thermal dissociation rate coefficients agree well with experimental data (Appleton, J. Chem. Phys. 47, 3231 (1967))



Analysis – 0-d Master Equations

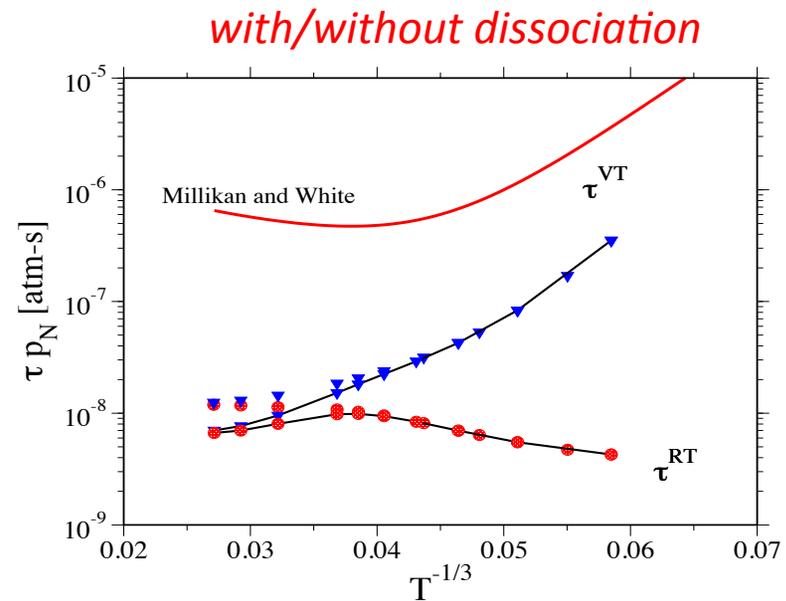
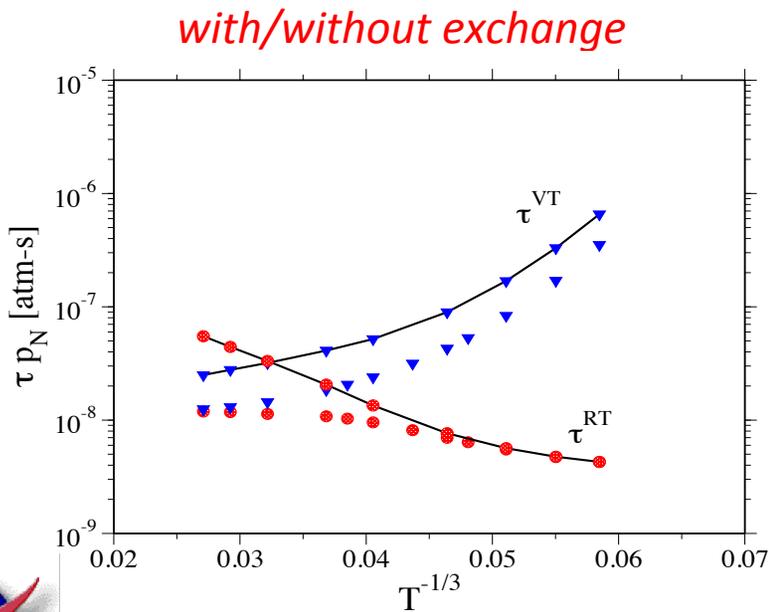
- Master Equation simulate N_2 relaxation-dissociation
 - All state-specific reactions for $N_2 + N$ dissociation, exchange and energy transfer included (9390 ro-vibration levels)
 - Start with 97% $N_2 + 3%$ N at 300 K and impose and maintain a high value of T
- Follow the evolution of the N_2 rovibrational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



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

N₂ Relaxation Times (τ)

- For N₂ + N collisions Exchange reactions speed up relaxation (decrease τ_V and τ_R)
 - $\tau_V \approx \tau_R$ for $T > 10,000$ K
- Dissociation decreases τ_V and τ_R for $T \geq 20,000$ K
- Empirical Millikan-White $\tau_V \geq 10x$ larger than present values

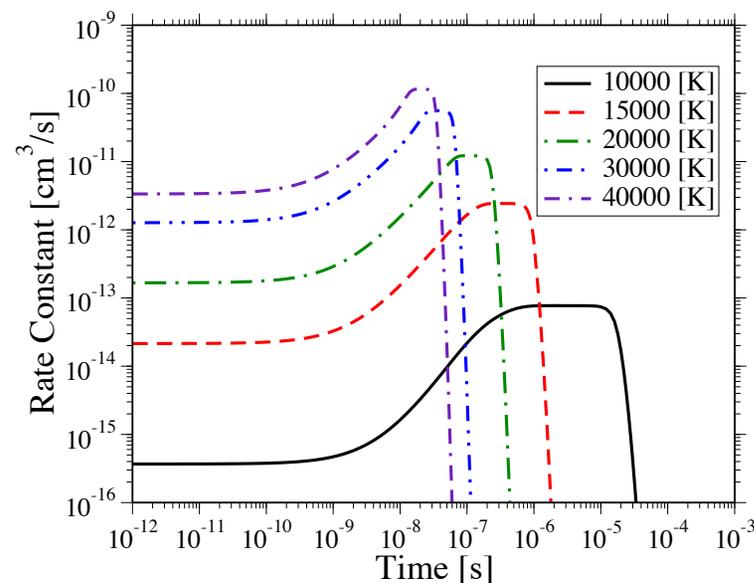
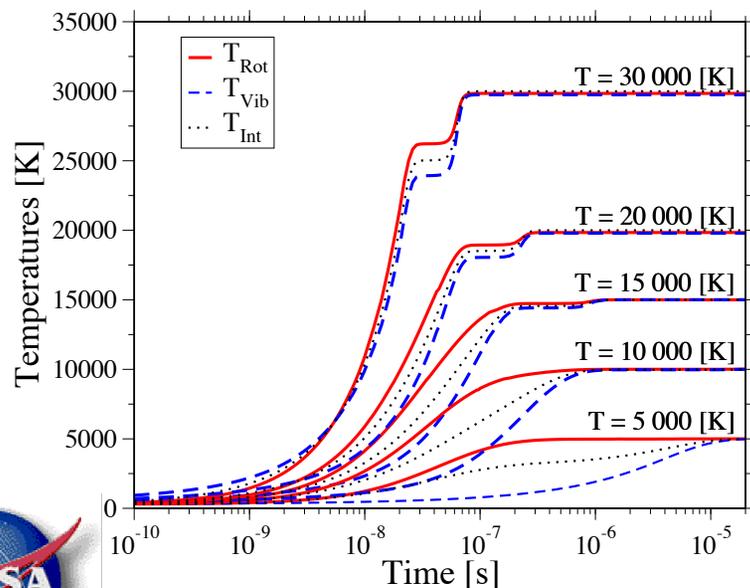


τ Computed by the e-folding method

Entry Systems & Technology Division

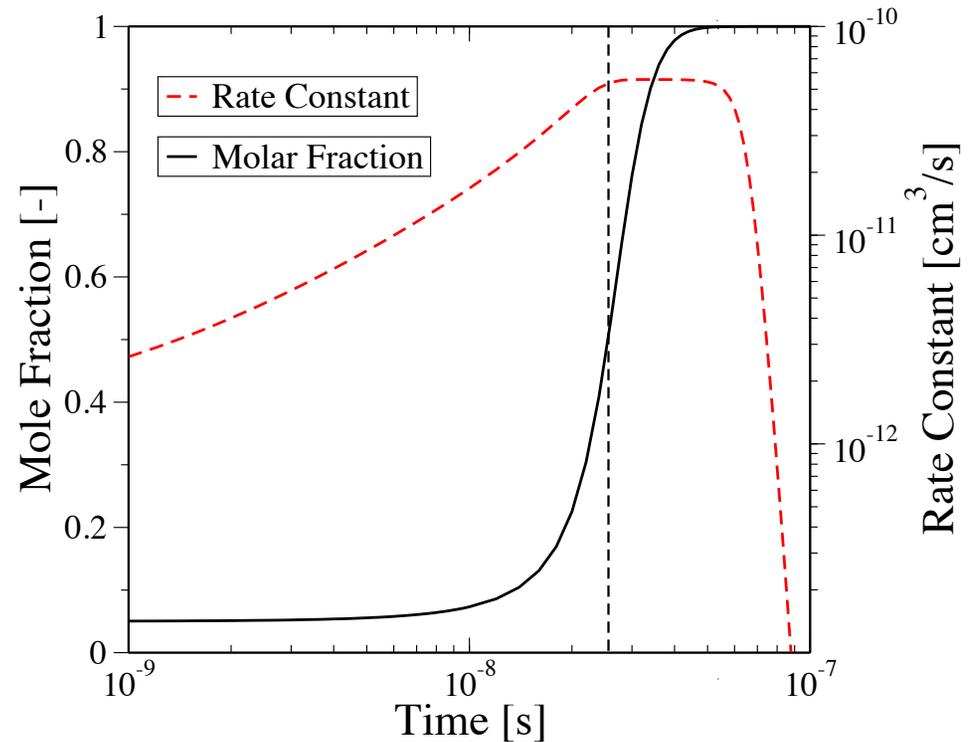
QSS?

- 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
- $\tau_V \approx \tau_R$ at high- T evident from plot of T_V & T_R vs t



QSS?

- For high T, half the dissociation occurs before QSS is realized
- Example: $T = 30,000$ K
 - Dissociation starts $\sim 10^{-9}$ s
 - QSS starts $\sim 2.5 \times 10^{-8}$ s when $X_N \approx 0.5$ & $T_{\text{VIB}} = T_{\text{ROT}} = 23,000$ K



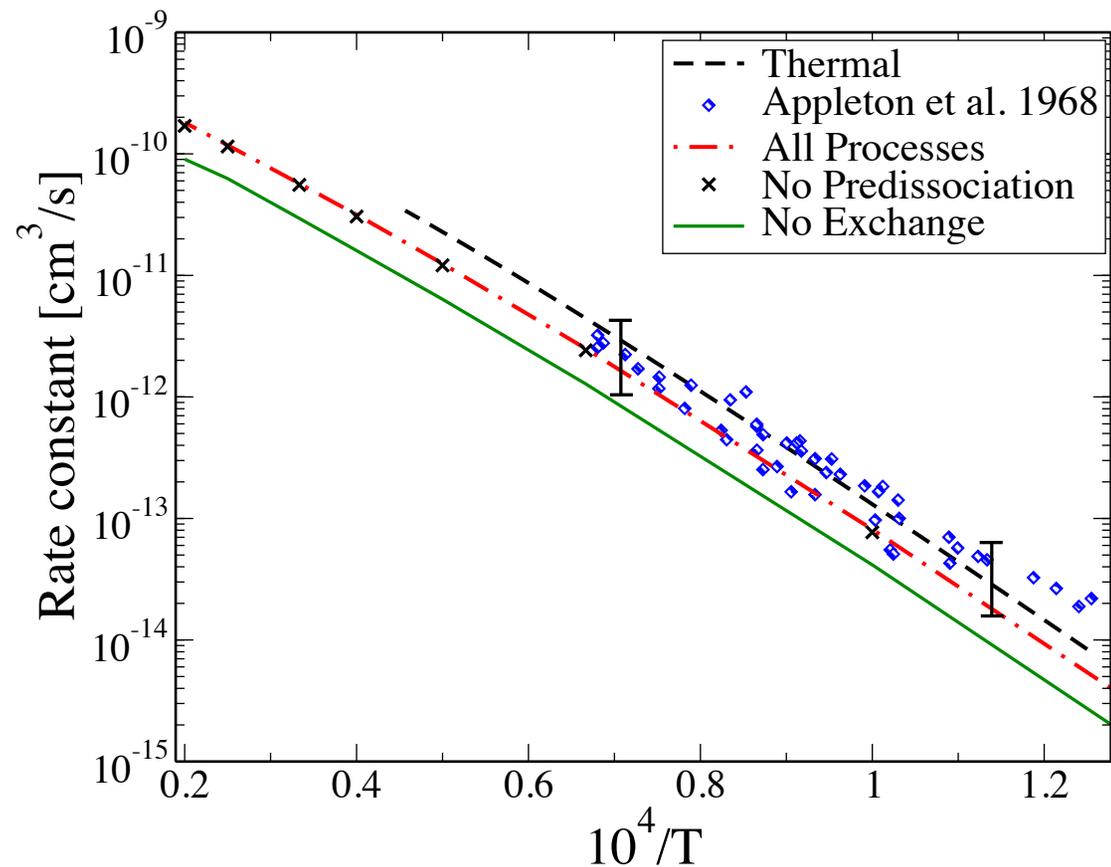
At $T = 30,000$ K only 50% of N_2 dissociation is at QSS conditions



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
- Predissociation (i.e., tunneling): $(N_2(qb) \rightarrow N + N$ makes 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 τ 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 & 1-d Euler 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 that can be used in CFD calculations

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



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