

Analysis of NO formation during Earth entry using the Quasi Classical Trajectory Method

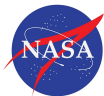
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Mentors: Dr. Richard L. Jaffe,
Dr. David W. Schwenke

NASA Ames Research Center

NASA Ames Summer Internship 2017



High Temperature Air Chemistry in Hypersonics

Goal: Understanding high-temperature, non-equilibrium chemistry for hypersonic flows

1. Prediction of the thermo-chemical non-equilibrium state
2. Atomic oxygen and nitrogen dictate heat shield oxidation and ablation
3. Improve thermal protection system design

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Current Focus:

What can we learn from QCT, besides obtaining rate constants, through $N_2 + O$ interactions ?

Quasi Classical Trajectory Approach

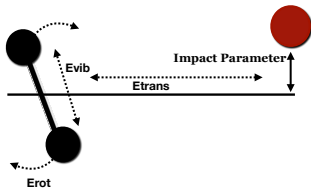
1. Initialize reactants (quantized)

- ▶ relative velocity of approach
- ▶ impact parameter
- ▶ Internal energy state
- ▶ Randomize orientations of atoms

2. Integrate Hamilton's equations of motion

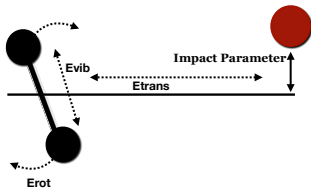
3. Analyze outcomes

4. Run lots of these calculations and analyze outcomes (statistically)



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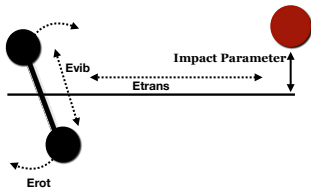


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For this work, REAQCT Code, developed at University of Minnesota has been used.

Potential Energy Surface for N_2+O

N_2+O interactions require two surfaces (A'' and A' , ground triplet)

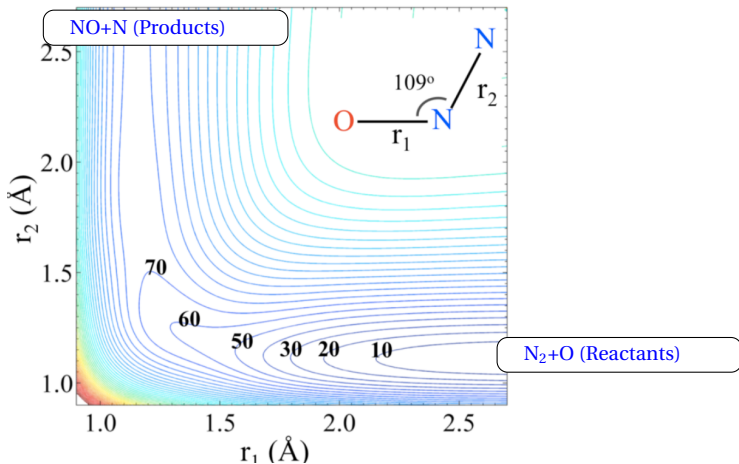


Figure: Contour plot for a possible NON geometry (Energies in kcal/mol)

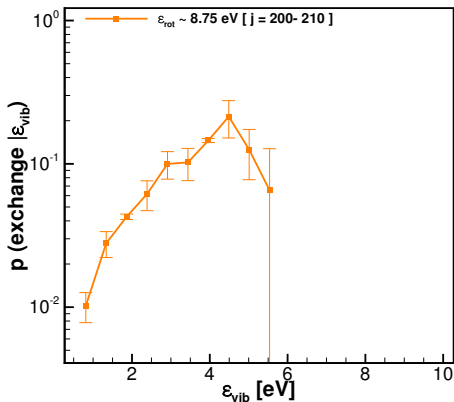
Lin, W, Varga, Z., Song, G., Pauku, Y. and Truhlar, D.G., 2016. Global triplet potential energy surfaces for the $N_2(X^1\Sigma^+)+O(3P)\rightarrow NO(X^2\pi)+N(4S)$ reaction. The Journal of chemical physics, 144(2), p.024309

NO formation analysis based on molecular energies

Translational energy, $\epsilon_{trans} \approx 1.0$ eV

$N_2(\epsilon_{vib}, \epsilon_{rot}) + O \rightarrow NO + N$

Dissociation energies: ϵ_d
= 9.91 eV (N_2) and 5.6 eV (NO)



Vibrational energy effect

- linear variation at lower energies
- nearly constant at higher energies

Figure: Exchange reaction probability vs. vibrational energy

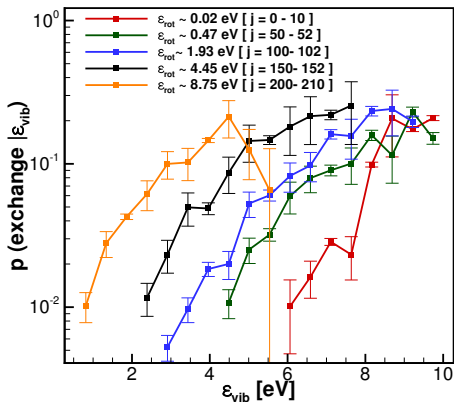
NO formation analysis based on molecular energies

Translational energy, $\epsilon_{trans} \approx 1.0$ eV

$N_2(\epsilon_{vib}, \epsilon_{rot}) + O \rightarrow NO + N$

Dissociation energies: ϵ_d

= 9.91 eV (N_2) and 6.62 eV (NO)



Vibrational energy effect

- linear variation at lower energies
- nearly constant at higher energies

Rotational energy effect

- makes up for threshold energy

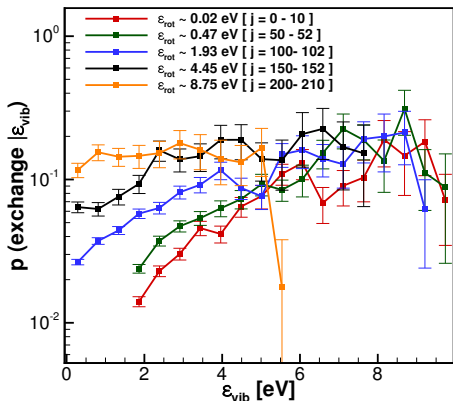
Figure: Exchange reaction probability vs. vibrational energy

NO formation analysis based on molecular energies

Translational energy, $\epsilon_{trans} \approx 3.0$ eV



Dissociation energies: ϵ_d
= 9.91 eV (N_2) and 5.6 eV (NO)



Vibrational energy effect

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Rotational energy effect

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Translational energy effect

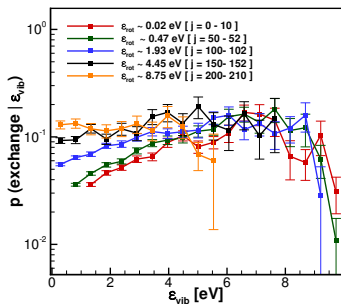
- Increase in ϵ_{trans} increases reaction probability

Figure: Exchange reaction probability vs. vibrational energy

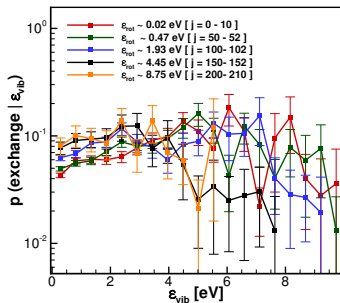
NO formation analysis based on molecular energies

Translational energy, $\epsilon_{trans} \approx 5.0$ eV

Translational energy, $\epsilon_{trans} \approx 8.50$ eV



(a)



(b)

Figure: Exchange reaction probability vs. vibrational energy,
 $N_2(\epsilon_{vib}, \epsilon_{rot}) + O \rightarrow NO + O$

Exchange Reaction Comparison: $N_2 + O$ and $N_2 + N$ System

Translational energy, $\epsilon_{trans} \approx 3.00$ eV

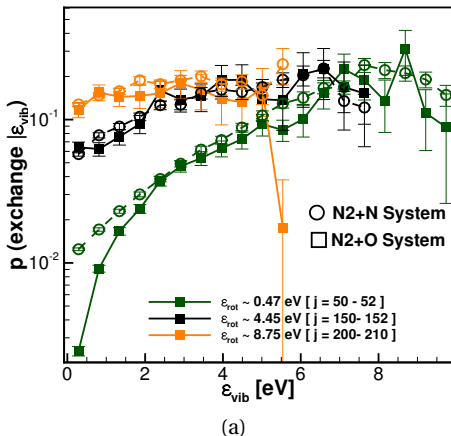
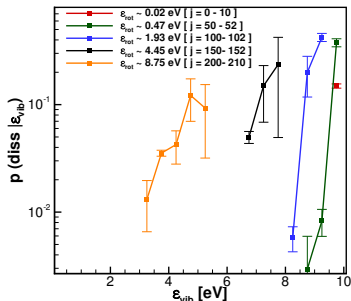


Figure: Exchange reaction probability vs. vibrational energy,

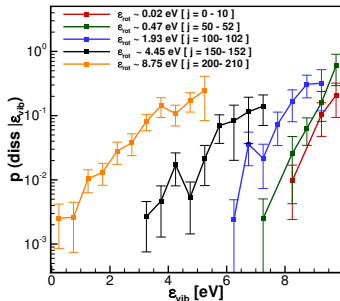
N₂ dissociation analysis based on molecular energies

Translational energy, $\epsilon_{trans} \approx 1.0$ eV



(a)

Translational energy, $\epsilon_{trans} \approx 3.0$ eV



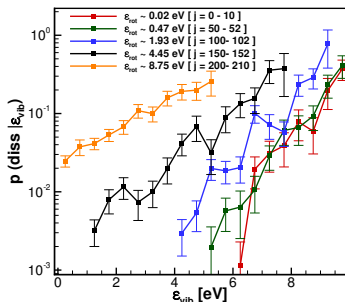
(b)

Figure: Dissociation reaction probability vs. vibrational energy,
 $\text{N}_2(\epsilon_{vib}, \epsilon_{rot}) + \text{O} \rightarrow \text{N} + \text{N} + \text{O}$

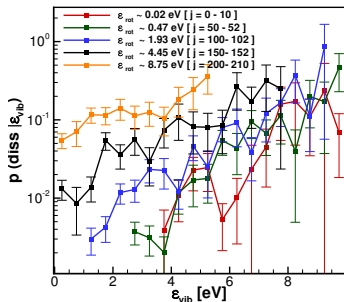
N_2 dissociation analysis based on molecular energies

Translational energy, $\epsilon_{trans} \approx 5.0$ eV

Translational energy, $\epsilon_{trans} \approx 8.50$ eV



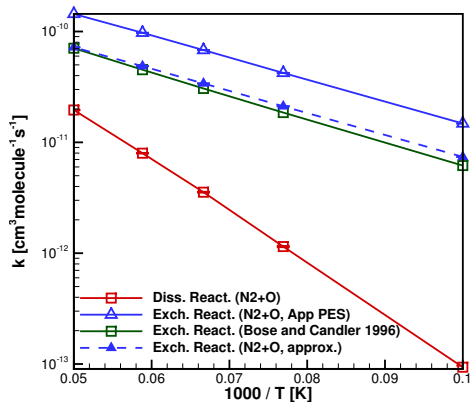
(a)



(b)

Figure: Dissociation reaction probability vs. vibrational energy,
 $N_2(\epsilon_{vib}, \epsilon_{rot}) + O \rightarrow N + N + O$

Reaction Rate Constants for Various Temperatures



$$k = \frac{1}{3} [k(A'') + k(A')]$$
$$k(A')/k(A'') \approx \frac{1}{2}, T > 12,000K$$
$$\Rightarrow k(\text{approx.}) \approx k(A'')/2$$

Figure: Reaction Rate Constants

Conclusions

- Reaction cross-sections for exchange and dissociation reactions strongly depend on vibrational energy
- Reaction cross-sections for dissociation has stronger dependence on vibrational energy
- On logarithmic scale, linear variation with vibrational energy for both reactions was shown
- The reaction cross-sections for interactions are not chaotic, in fact they have very simple trends. This is true for non-reactive interactions too (not shown in presentation)
- Simple trends are strong motivation to build simple models consistent with QCT information.

Thank you

Questions?