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On the Development of a New Nonequilibrium Chemistry Model for Mars Entry

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Motivation

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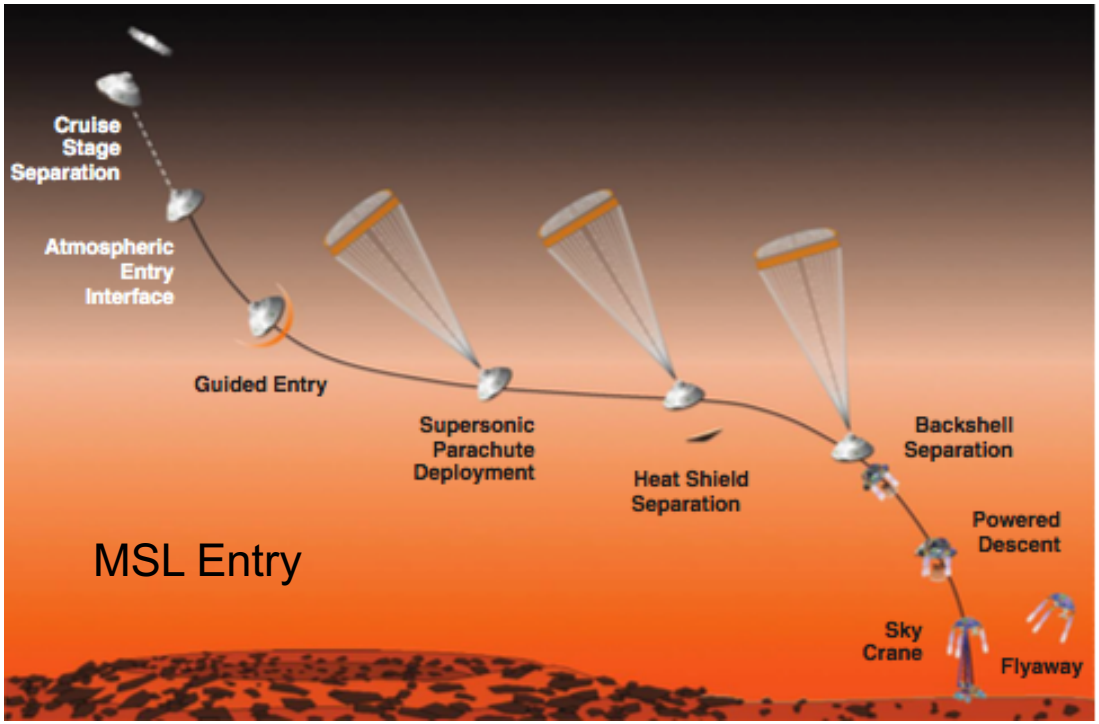
- NASA has been embarked on a program of scientific exploration of Mars by landing increasingly larger and heavier payloads
  - Prediction of thermal load used to determine TPS requirements
  - Testing in ground facilities and CFD simulations play critical roles



Nonequilibrium chemistry model currently in use is 20+ years old and based on mostly 35+ year old experiments

We are critically examining this "legacy" model and developing a new model based on computational chemistry and physics

Our objective is to reduce the uncertainty in predictions of thermal loads for Mars entry

Outline

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- Legacy nonequilibrium chemistry model
- Computational approach for developing a new model
- Rate Coefficients
  - Chemical rections for Mars entry
  - Uncertainty Quantification
  - CO dissociation
- Comparison with other models
  - Convective heating
  - Radiative Flux
- Next steps in developing the nonequilibrium chemistry model
- Conclusions

Legacy Mars Chemistry Model

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- Nonequilibrium between translational and internal energy modes of the flowfield species in the bow shock layer
  - After shock wave gas is compressed and heated
  - Two temperatures ($T = T_r$ and $T_v = T_{el\text{-}st}$)
  - First order relaxation equation describes evolution of T_v from the shock to thermal equilibrium ($T_v = T$); governed by relaxation time τ_v
  - Dissociation reactions modeled by Arrhenius rate expression using an average temperature $T_{av} = (T \cdot T_v)^{1/2}$
  - Rate coefficient parameters originally taken from 1960's-70's shock tube experiments, but subjected to empirical adjustment
- Developed by Chul Park at NASA Ames 1986-1992 (Park et al, JTHT **8**, 9-23 (1994))
- Recent modification of parameters by Johnston and Brandis (JSQRT **149**, 303-317 (2014))

Mars Entry: What Collisional Processes are Important?

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- Mars atmosphere is ~96% CO_2, ~2% N_2 ~2% Ar
- Dissociation
  - CO_2 (5eV) very fast and nearly complete
  - CO (11 eV) slow, rate determining process
- Heterogeneous exchange reactions provide lower energy (i.e. faster) routes for CO_2 and CO dissociation
  - $CO_2 + O \rightarrow CO + O_2$
  - $CO + O \rightarrow C + O_2$
  - $CO + N \rightarrow O + CN$
  - $CO + C \rightarrow O + C_2$

For Mars entry at 6-8 km/s, the rate of CO dissociation is critical because CO 4th positive emission is the dominant source of radiative heating

New Paradigm for a Nonequilibrium Chemistry Model

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- ***Accurate*** quantum mechanics calculations to quantify interaction energy between atoms and molecules
  - Potential Energy Surface **(PES)** obtained from solution of Schrödinger equation
  - Repeated for many geometric arrangements of the atoms (for *n* atoms there are *3n-6* degrees of freedom)
  - Goal is ≤ ± 5 kJ/mol relative accuracy (~0.05 eV, ~400 cm^{-1})
- Classical mechanics simulations of heavy particle collisions to compute collision cross sections and rate coefficients
  - Compute trajectories of many individual collisions (Quasi-Classical Trajectory or **QCT** calculation)
  - Monte Carlo sampling used reproduce random or thermal collisional distributions

This strategy should yield rate coefficients accurate to ±20%

(Ref: Jaffe et al. "First principles calculation of heavy particle rate coefficients" in "Hypersonic nonequilibrium Flows: Fundamentals and Recent Advances", E. Josyula, ed, AIAA 2015)

Important Chemical Reactions for Mars Entry

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	Reaction	Experiment	PES	QCT rate coeff.
D1	CO_2+ M → **CO** + O + M M = CO_2, N_2, CO, O	Shocktube expts 1968-74 & 1984		
D2	*CO + M → C + O + M* *M = CO, O*	*Shocktube expts 1968-74 & 1984*	*NASA Ames 2016*	*NASA Ames 2016*
❊D3	N_2 + M → N + N + M M = N_2, N	Shocktube expts 1964-74 & 1993	NASA Ames 2010 U. Minnesota 2013	NASA Ames 2010-16 U. Minn. 2013-16
❊D4	O_2 + M → O + O + M M = N_2, CO, O	Expts 1960s, 84 Hanson 2016	Varandas 1988 Dawes 2011-13	Andrienko 2016
E1	CO_2 + O → **CO** + O_2	Ibragimova 1991		
E2	*CO + O → C + O_2*	*Hanson 1991*	*NASA Ames 2016*	*NASA Ames 2016*
❊E3	N_2 + O → NO + N	Michael 1992 Roth 1985	Sayos 2003-16	Sayos 2010-12 U. Minn 2016
❊E4	NO + O → O_2 + N	Fontijn 1998	Sayos 2002	Sayos 2003
E5	CO + N → **CN** + O		Nyman 2000-2008	
E6	CO + N → NO + C		Nyman 2000-2008	
E7	CN + O → NO + C	Roth 1990	Nyman 2000-2008	
E8	CO + C → **C_2** + O			

Uncertainty Quantification (UQ)

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- UQ used to identify critical reactions
  - Monte Carlo sensitivity analysis
    - 96 % CO_2/4% N_2 (free stream at 0.25 torr and 300 K)
    - 1-d shock at 7.75 km/s
    - Random sampling of rate coefficient and vibrational relaxation parameters
  - Two criteria considered: sensitivity to CO 4th positive radiative intensity and sensitivity to attaining chemical equilibrium (T/T_{eq} = 1.05)
- Repeated many times for statistical analysis
- Key reactions:

Reaction	Sensitivity to Radiative Flux	Sensitivity to Equilibration Time
$CO + O \rightarrow C + O + O$	55%	48%
$CO + CO \rightarrow C + O + CO$	25%	10%
$CN + O \rightarrow C + NO$	9%	24%
$CO + O \rightarrow C + O_2$	4%	8%

CO Dissociation

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- The radiative heat flux experienced by spacecraft entering the Martian atmosphere at 5-8 km/s is mostly due to the CO 4th positive band system (λ < 200 nm)
  - Radiative heating is therefore proportional to the mole fraction of CO in the bow shock layer
  - CFD-Radiative transport calculations using the T-T_v model (legacy Mars chemistry model) predict greater radiance than observed in tests run in the Electric Arc Shock Tube (EAST) at Ames
  - Johnston and Brandis (JQSRT, 2014) scaled some of the rate coefficient parameters to force agreement between CFD and EAST for CO 4th positive
- Ab initio PESs have been computed for CO + Ar and CO + O and used in QCT calculations of CO dissociation rate coefficients (Schwenke *et al.,* J Chem. Phys. submitted)
  - Experimental data for CO + Ar seem more reliable than for CO + O
  - Efficiency of different collision partners (M) for promoting dissociation has been expressed as ratio k(CO+M)/k(CO+Ar)

Rate Coefficient Ratios for CO Dissociation

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- Early experimental values (Baulch, based on pre-1972 shock tube experiments)
  - k_{CO+CO}/k_{CO+Ar} = 1-2 k_{CO+O}/k_{CO+Ar} = 15
- Park (1994) T-T_v model
  - k_{CO+CO}/k_{CO+Ar} = 10 k_{CO+O}/k_{CO+Ar} = 15
- Johnston and Brandis (2014)
  - k_{CO+CO}/k_{CO+Ar} = 10 k_{CO+O}/k_{CO+Ar} = 15
  - $k_{CO+Ar(JB)}/k_{CO+Ar(Park)}$ = 5
- Objectives of our QCT rate coefficient calculations:
  - Evaluate the accuracy of the experimental data used in the legacy model
  - Determine these rate coefficient ratios as a function of temperature
  - Study the importance of the exchange reactions in the shock layer

CO + Ar

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After nearly all of the CO_2 is dissociated, CO and O are the major species (with equal mole fraction)

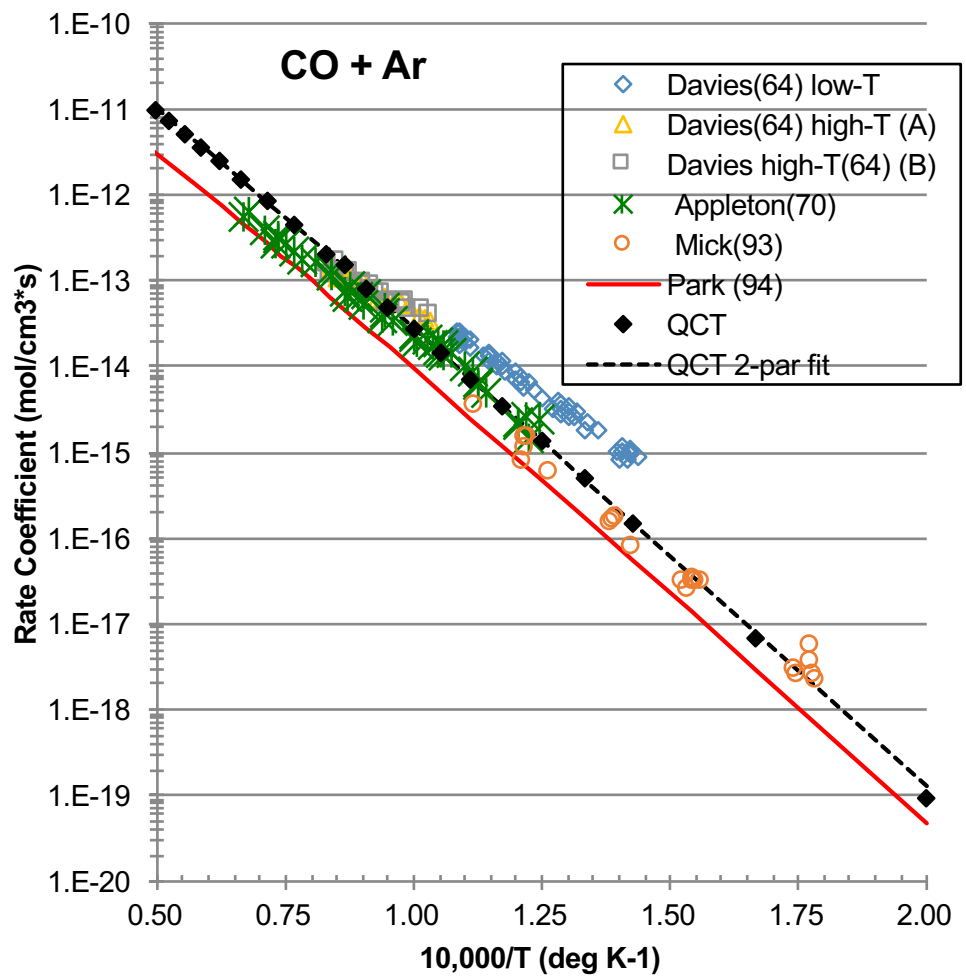
<u>Experimental data</u>

Davies (1964)	CO + Ar, CO,O
Appleton (1970)	CO + Ar, CO, O
Hanson (1974)	CO + CO, O
Mick & Roth (1993)	CO + Ar, CO

<u>Park (1994) T-T_v model</u>

<u>NASA Ames (2014-2015)</u> QCT

- Scatter in experimental data is small
- Very good agreement between QCT and Appleton and Mick and Roth expt.
- Fair to good agreement between QCT and Davies and Park (94)



CO + O (^{3}P)

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- Three triplet PESs with equal statistical weight govern CO + O (^{3}P) collisions
  - Lead to different non-linear CO_2 triplet electronic states (1 ^{3}A', 1 ^{3}A" and 2 ^{3}A") with O-C-O angle ~120°
  - 1 ^{3}A' has well depth ~75 kJ/mol (~0.8 eV); other states are more weakly bound
- Heterogeneous exchange reaction forming O_2 + C also possible on these PESs
  - Reaction is endothermic by 6.1 eV (low in comparison to the 11.2 eV dissociation energy of CO)
- All three PESs used for QCT calculations of CO dissociation and exchange reactions

CO + O Rate Coefficients (experiment)

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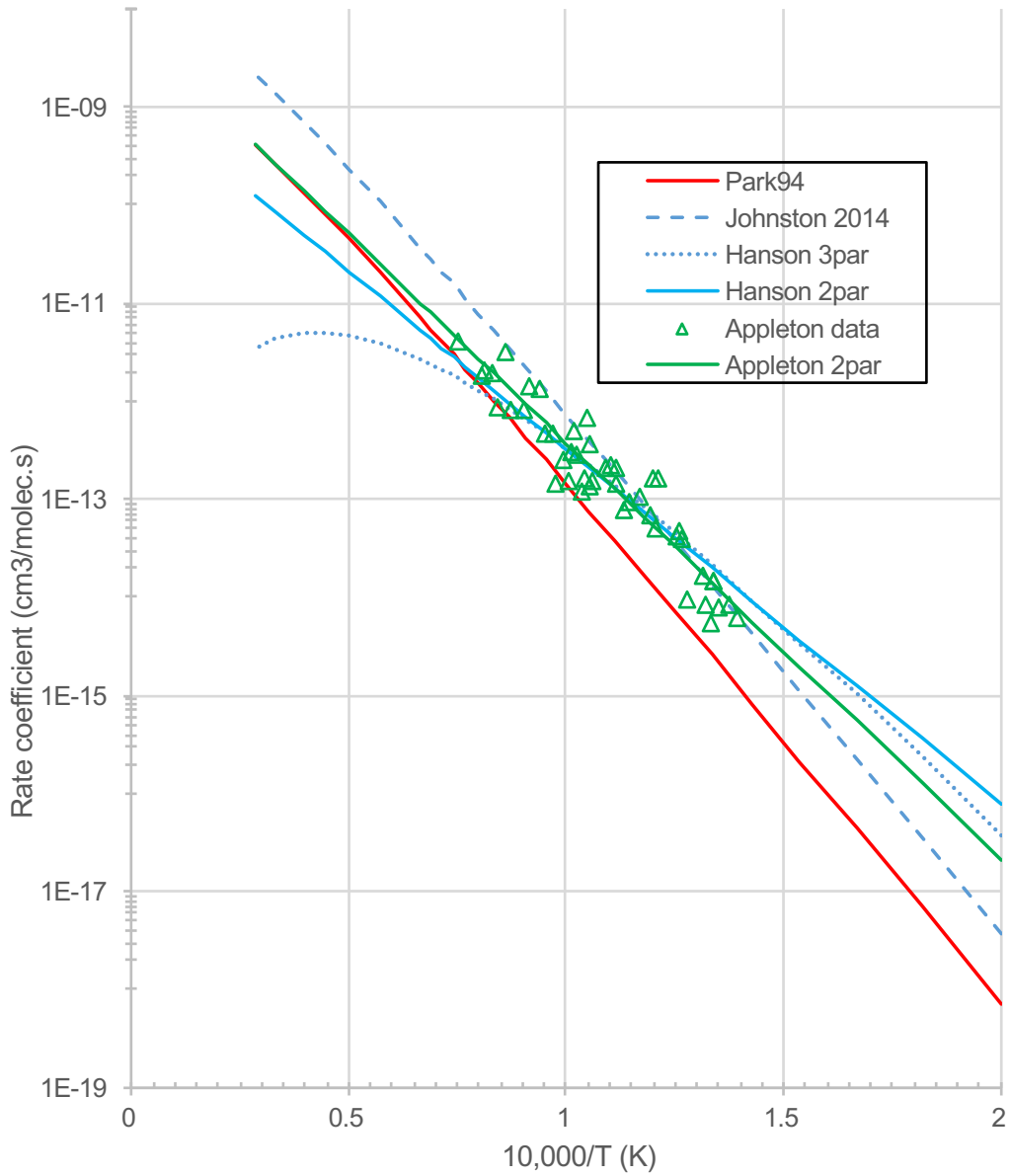

- Considerable scatter in the Appleton data
- Fairly good agreement between Appleton (8,000-15,000 K) and Hanson (5500-9000 K) data
- Hanson 3-parameter fit is not suitable for exptrapolation
- Park and Johnston recommendations bracket the experimental results

CO + O Rate Coefficients (only dissociation)

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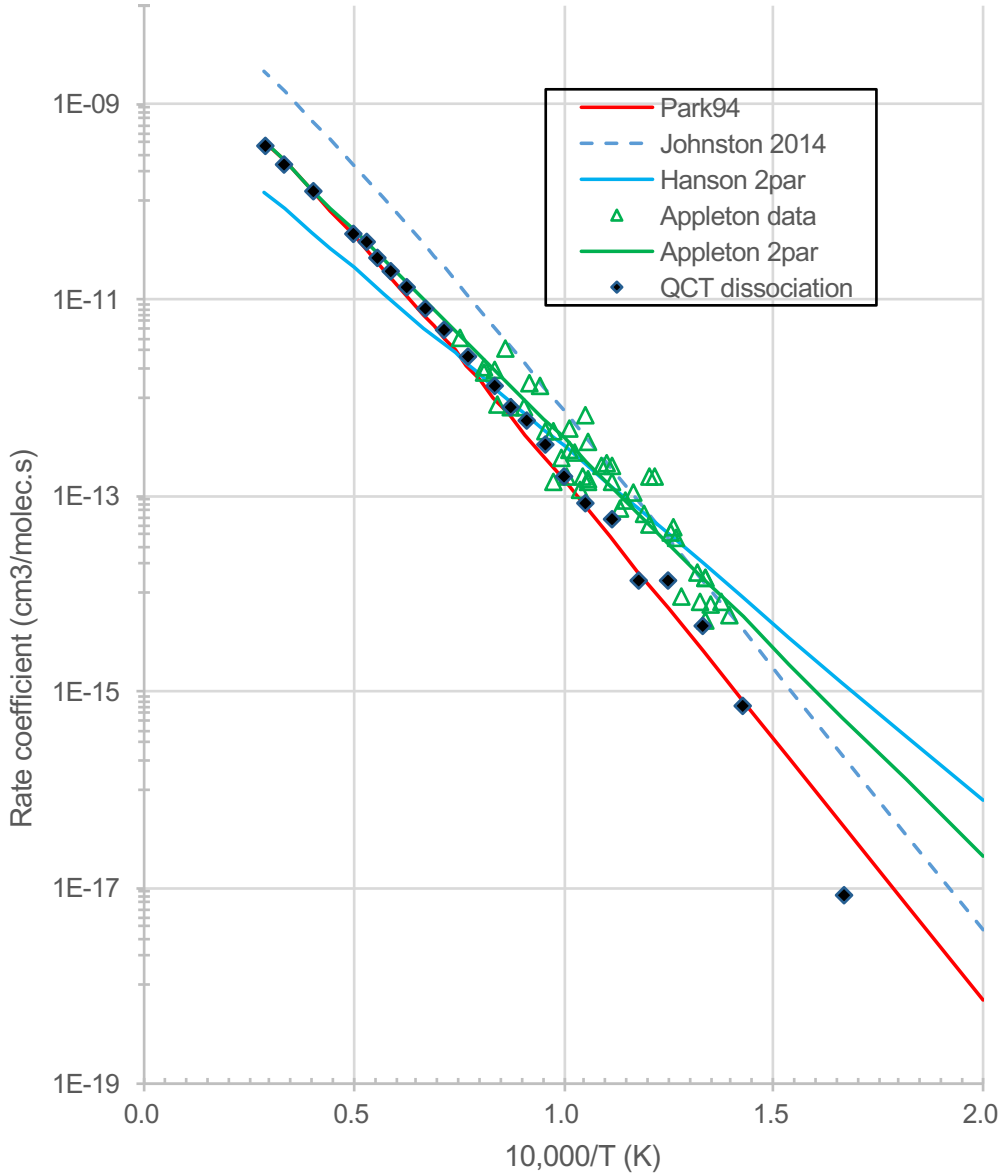

- Good agreement between QCT dissociation rate coefficient and Park model
- Agreement between QCT dissociation rate coefficient and expt is poor
- k_{CO+O}/k_{CO}+Ar ~3-5 for QCT not 15 as in Park model

CO + O Rate Coefficients (dissoc. + exchange)

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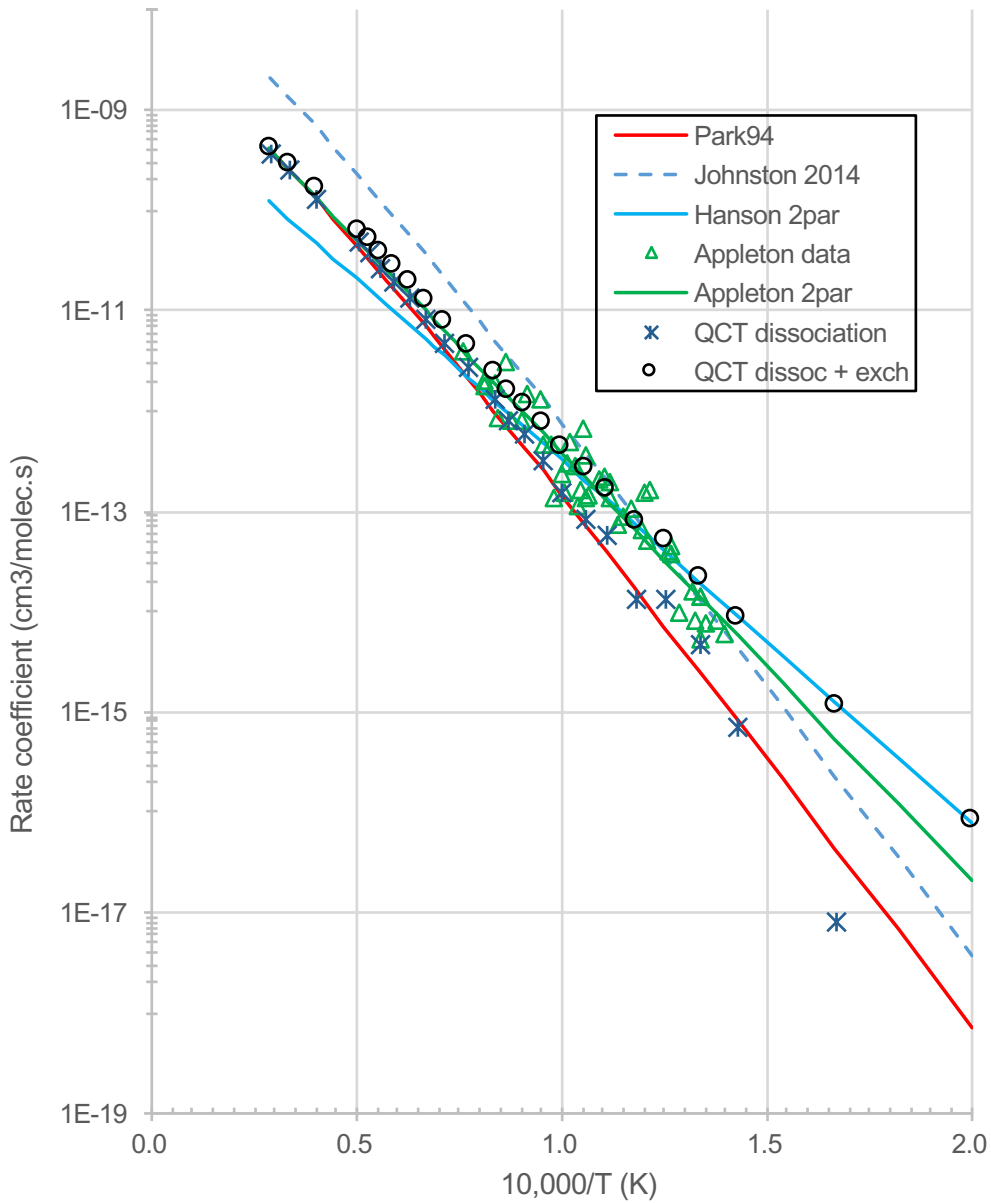

- Addition of hetero exchange rate coeff to dissociation greatly improves agreement with expt (especially at lower temperatures
- Good agreement with Johnston scaled value ~8,000 K, but temperature dependence is quite different
- Exchange is the dominant CO removal process for T< 8000K

This exchange reaction was not previously thought to be important

Key Points for CO Dissociation

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- Experimental data look quite good!
  - However, it is advantageous to use experimental data points (if available), not just Arrhenius expressions
- Heterogeneous exchange reaction provides an important pathway for CO removal, especially for T < 10,000 K
  - Converts CO to O_2, which is readily dissociated at these temperatures
  - Experimental CO dissociation rate coefficients implicitly include this reaction by having spuriously large dissociation rates and larger temperature exponents
  - When combined with dissociation, agreement betwee QCT and experimental results is excellent
- QCT rate coefficients needed for CO + CO to complete work on this set of reactions

Use in CFD Simulations

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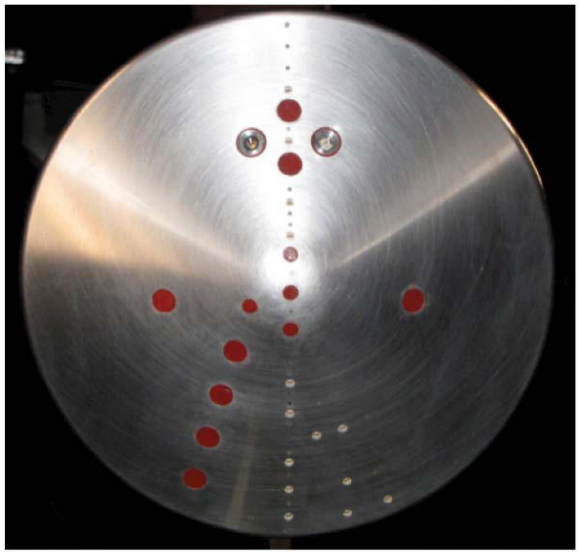
- Used new rate coefficient data in simulations of convective heating for LENS XX shock tunnel tests
  - Pure CO_2 flow impinging on 12” diameter model
  - Flow enthalpies up to 43 MJ/kg
  - Compared Park94 model with new CO rate coefficients from present work to the Johnston modification of the original Park model in DPLR simulations



Simulation vs LENS XX Test Data

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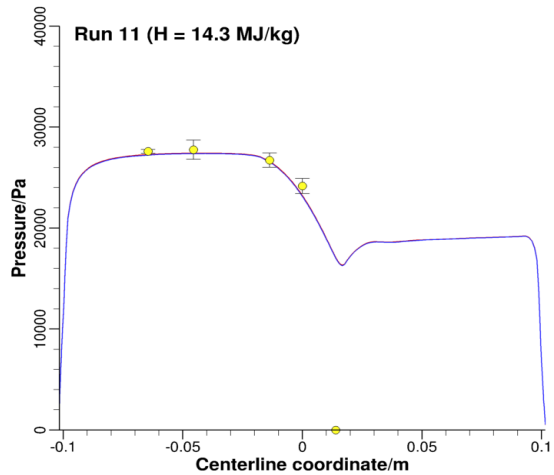
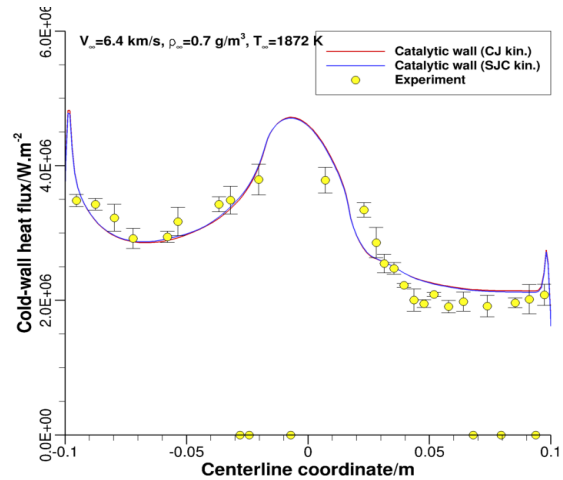
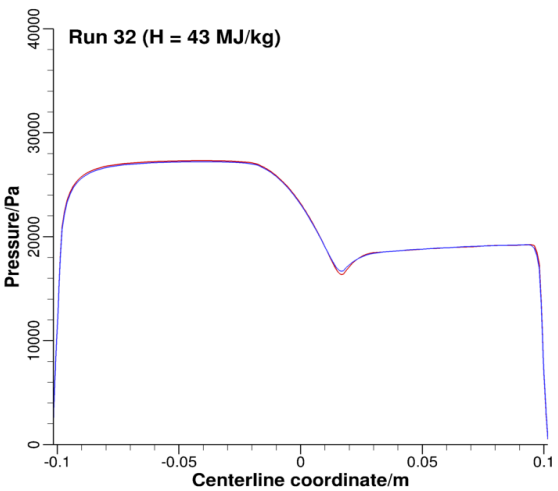
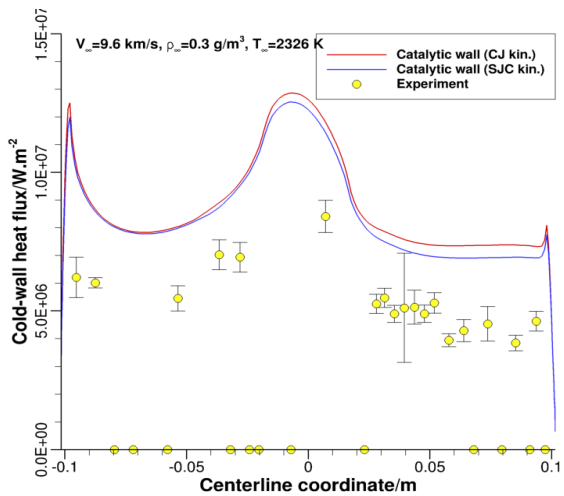
Moderate enthalpy (14.3 MJ/kg):

- Convective heat flux predictions for the models are barely distinguishable
- CFD and test data in good agreement
- This condition applicable to Mars entry









High enthalpy (43 MJ/kg):

- Heat flux prediction lower for new rate coefficients
- Agreement between CFD and test data is not good
- This condition is applicable to Venus entry

Use in CFD Simulations

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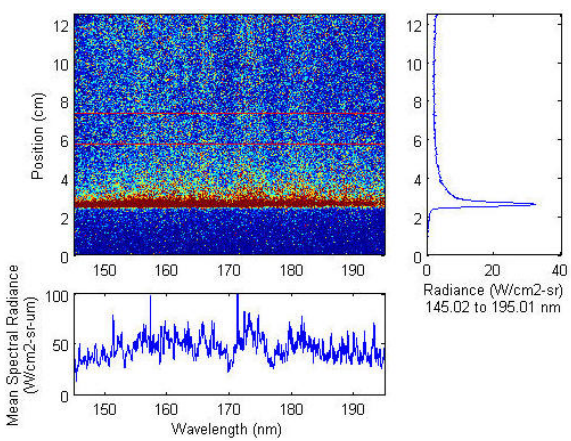
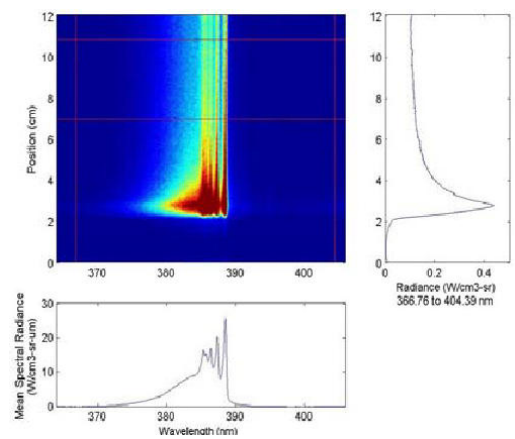
- Used new rate coefficient data in simulations of CO 4th positive and CN violet integrated intensities from EAST tests
  - 96% CO_2/4% N_2 in Electric Arc Shock Tube at NASA Ames
  - Flow enthalpy up to 43 MJ/kg
  - Compared Park94 with new CO rate coefficients from present work with Johnston modification and the original Park model in LAURA-HARA simulations



CN violet ▸▸
◂◂ CO 4th+



Simulation vs EAST Test Data

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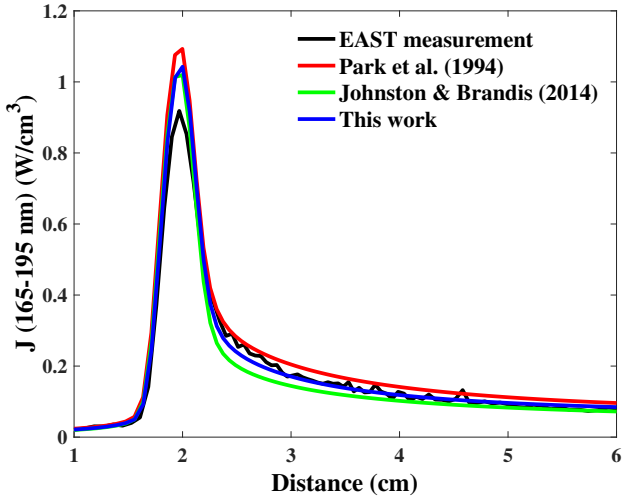
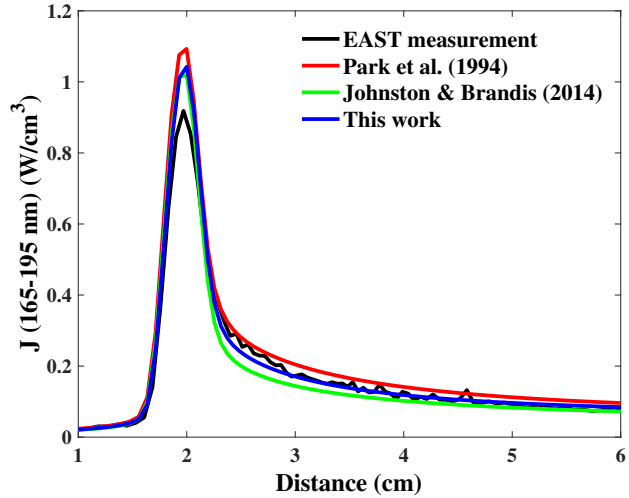
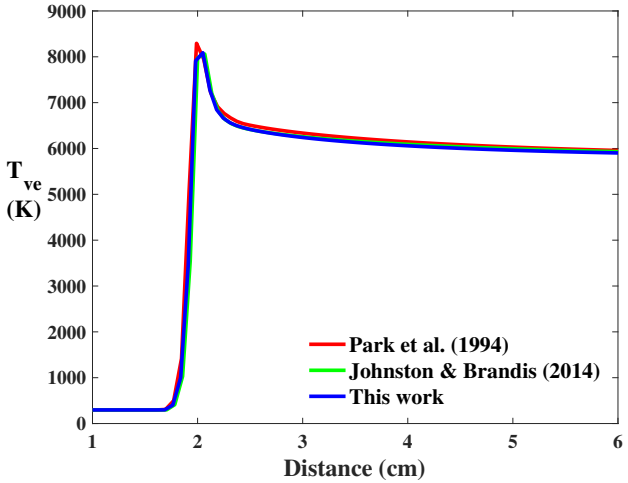
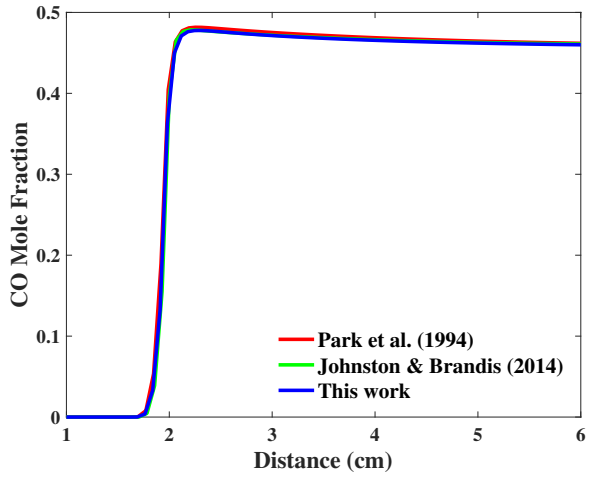
P_0 = 0.25 torr and shockspeed = 6.43 km/s









Simulation vs EAST Test Data

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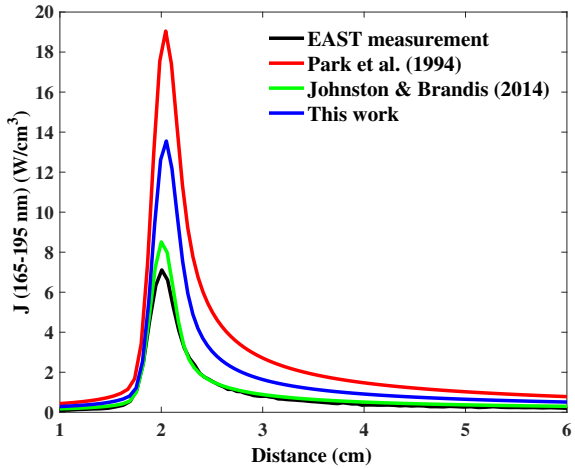
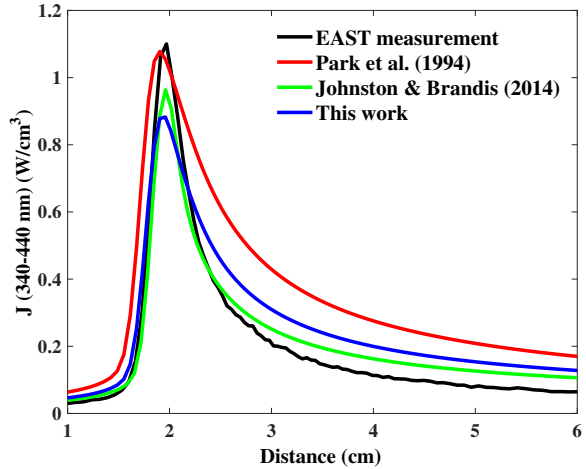
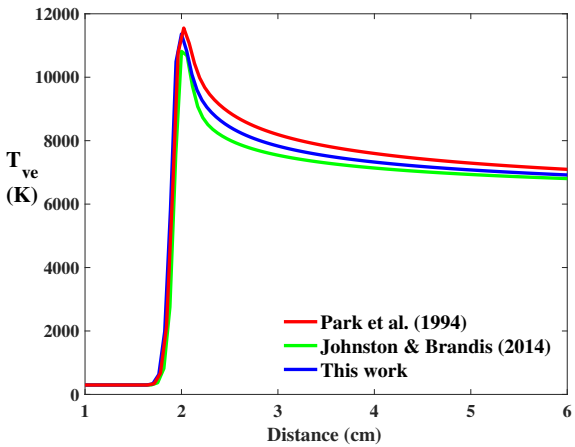
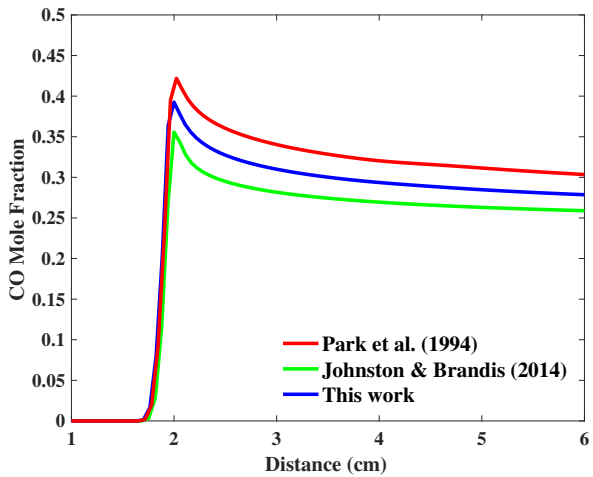
P_0 = 0.1 torr and shockspeed = 7.98 km/s









On-going Work

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- Potential energy surfaces:
  - PES for CO + CO collisions to enable determination of rate coefficients for CO dissociation by CO + CO collisions
- Rate coefficients:
  - QCT calculations for CO + N reactions forming CN + O and NO + C
  - QCT calculations for O_2 dissociation and Zel'dovich reactions (N_2 + O and NO + O) using published PESs
- Analysis of quasi-steady state (QSS) models and internal energy relaxation (τ_v, τ_{int}) using coarse-grained QCT methods developed by Prof. Panesi at U. Illinois at Urbana-Champaign
- Examination of alternative multi-temperature models and other approaches to describing nonequilibrium flows

Conclusions

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- The effort to create a new physics-based model for describing nonequilibrium phenomena in Mars entry flowfields is bearing fruit
- Potential energy surfaces and thermal rate coefficients for dissociation and exchange reactions have been computed for many of the important chemical reactions
  - Independent calculations for N_2 dissociation from two research groups show remarkable agreement
  - Rate coefficients for different dissociation reactions show limitations and successes in the older data from shock tube experiments
- Work is progressing toward creation of a data base of QCT rate coefficients for the complete set of heavy particle reactions for modeling Earth and Mars entry
  - Relaxation parameters (τ_v) and thermochemical data (specific heats, enthalpies and entropies) are also being computed
- We are also examining alternatives to the T-T_v model using coarse-grained QCT calculations

Acknowledgements

The imag

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- U. Illinois Collaborators
  - (Prof) Marco Panesi
  - Simone Venturi
  - Robyn Mcdonald

Mars tourism is coming!

NASA's Mars Exploration Program seeks to understand whether Mars was, is, or can be a habitable world. Missions like Mars Pathfinder, Mars Exploration Rovers, Mars Science Laboratory and Mars Reconnaissance Orbiter, among many others, have provided important information in understanding of the habitability of Mars. This poster imagines a future day when we have achieved our vision of human exploration of Mars and takes a nostalgic look back at the great imagined milestones of Mars exploration that will someday be celebrated as "historic sites."

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