
Uncertainty Analysis of Reaction Rates in a Finite-Rate Gas-Surface Model

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AFOSR FA9550-09-1-0157

AFOSR MURI Fundamental Processes in High Temp. Gas-Surface Interactions

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- Dr. Ioana Cozmuta (Co-PI on catalysis work)
- Prof. Adri van Duin

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 - Dr. Paolo Valentini
 - Paul Norman
 - Cory Sorensen
 - Savio Poovathingal



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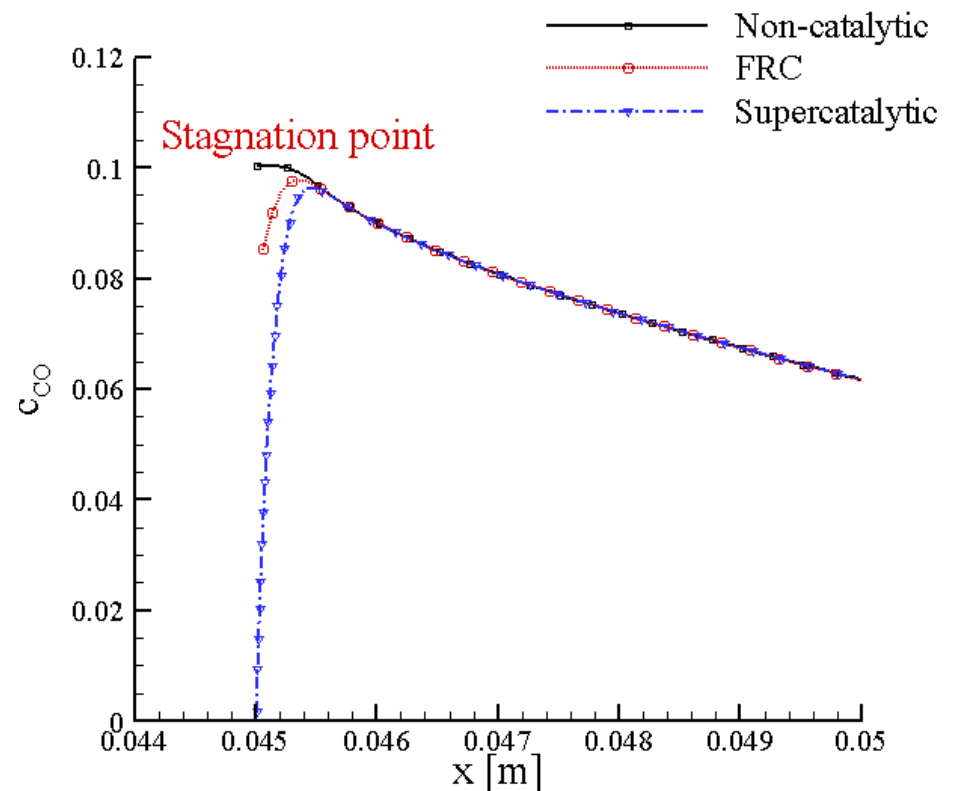
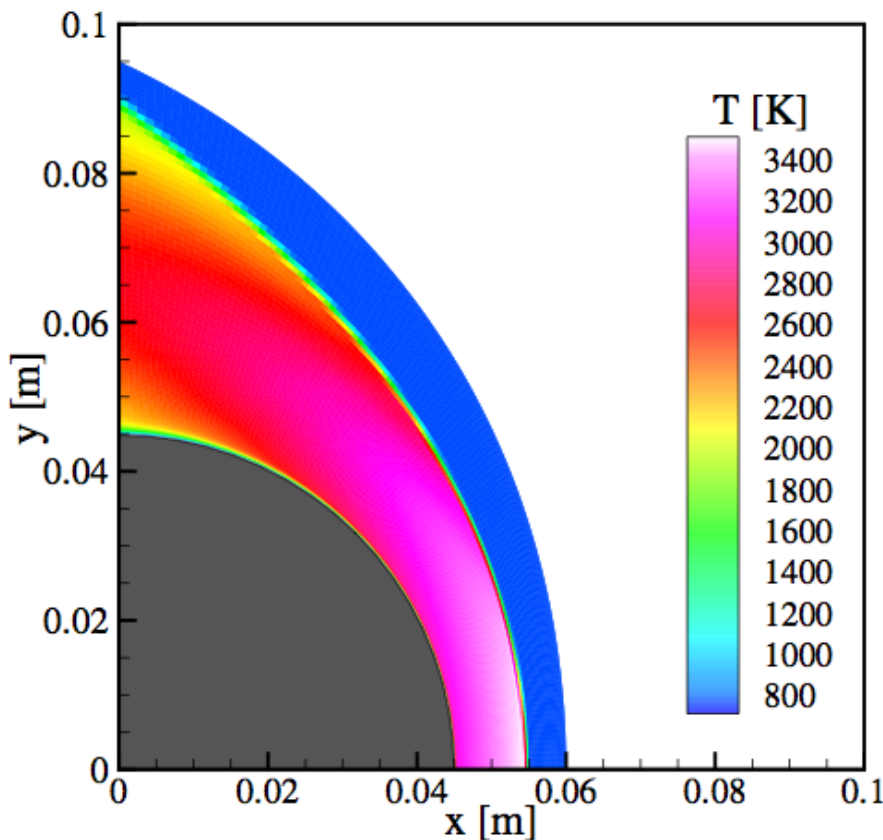


- 1) Finite-Rate Catalytic (FRC) wall boundary condition implemented in US3D CFD code. Uncertainty analysis performed.
- 2) Computational Chemistry simulations and the development of a FRC model for oxygen-silica catalysis under hypersonic conditions.
- 3) Preliminary results for oxidation of carbon-based surface ablators.

Finite-Rate Catalytic (FRC) Boundary Condition



- Finite-rate chemistry in the gas-phase *and* at the wall
- Modifies diffusion/chemistry in the boundary layer (coupled problem)
 - Ex. 2.7 km/s CO₂ flow ($T_w=500$ K)



Finite-Rate Model and Parameters



Example: Air-silica catalysis model⁵

- | | |
|--------------------------------------------|----------------------------|
| (1) $O + [s] \rightarrow O_s$ | <i>Adsorption Reaction</i> |
| (2) $N + [s] \rightarrow N_s$ | <i>Adsorption Reaction</i> |
| (3) $O + O_s \rightarrow O_2 + [s]$ | <i>E - R Reaction</i> |
| (4) $N + N_s \rightarrow N_2 + [s]$ | <i>E - R Reaction</i> |
| (5) $O + N_s \rightarrow NO + [s]$ | <i>E - R Reaction</i> |
| (6) $N + O_s \rightarrow NO + [s]$ | <i>E - R Reaction</i> |
| (7) $O_{s,m} + O_s \rightarrow O_2 + 2[s]$ | <i>L - H Reaction</i> |
| (8) $N_{s,m} + N_s \rightarrow N_2 + 2[s]$ | <i>L - H Reaction</i> |
| (9) $O_{s,m} + N_s \rightarrow NO + 2[s]$ | <i>L - H Reaction</i> |
| (10) $N_{s,m} + O_s \rightarrow NO + 2[s]$ | <i>L - H Reaction</i> |
| (11) $O_s \rightarrow O + [s]$ | <i>Desorption Reaction</i> |
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¹ Halpern and Rosner, *Journal of the Chemical Society*, 1978

² Deutschmann, O., Riedel, U., and Warnatz, J., *J. Thermophys. Heat transfer*, 1995

³ Thomel, J., Lukkien, J. J., and Chazot, O., *AIAA Paper 2007-4399*, June 2007

⁴ Valentini, Schwartzenruber, and Cozmuta, *AIAA Paper 2009-3935*, June 2009

⁵ Marschall, MacLean, and Barnhardt, "A Finite Rate Surface Reaction Model for DPLR", NASA 2011

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$$k_f = \left(\frac{\bar{v}}{4\Phi_{total}} \right) \gamma_o T^\beta \exp\left(-\frac{E_{er}}{RT} \right)$$

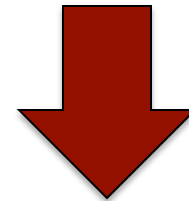
Eley - Rideal

$$\gamma_{er,O} = \gamma_{er,N} = 0.001$$

$$\beta_O = \beta_N = 0$$

$$E_{er,O} = E_{er,N} = 9000 J/mol$$

$$(\Phi_{total}) \text{ is set to } 7.5 \times 10^{-6} \text{ mol/m}^2$$



Elementary atomistic quantities

¹ Halpern and Rosner, *Journal of the Chemical Society*, 1978

² Deutschmann, O., Riedel, U., and Warnatz, J., *J. Thermophys. Heat transfer*, 1995

³ Thomel, J., Lukkien, J. J., and Chazot, O., *AIAA Paper 2007-4399*, June 2007

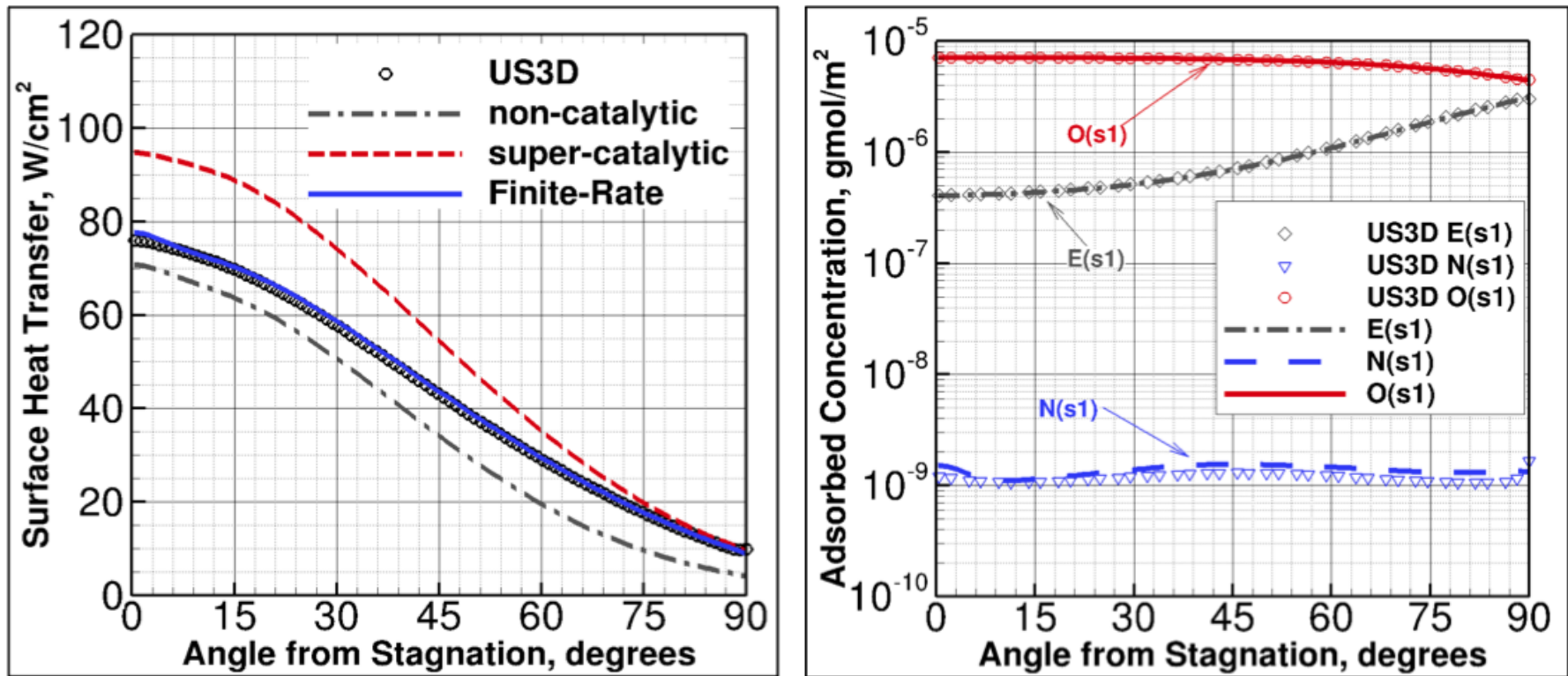
⁴ Valentini, Schwartzenruber, and Cozmuta, *AIAA Paper 2009-3935*, June 2009

⁵ Marschall, MacLean, and Barnhardt, "A Finite Rate Surface Reaction Model for DPLR", NASA 2011

US3D – DPLR Code-to-Code Validation



- Excellent agreement despite completely different implementation procedures
 - Ex. 6 km/s air flow over 1m radius cylinder ($T_w=2250$ K)



MacLean, Marschall, and Driver, **AIAA Paper 2011-3784**, Honolulu, HI.

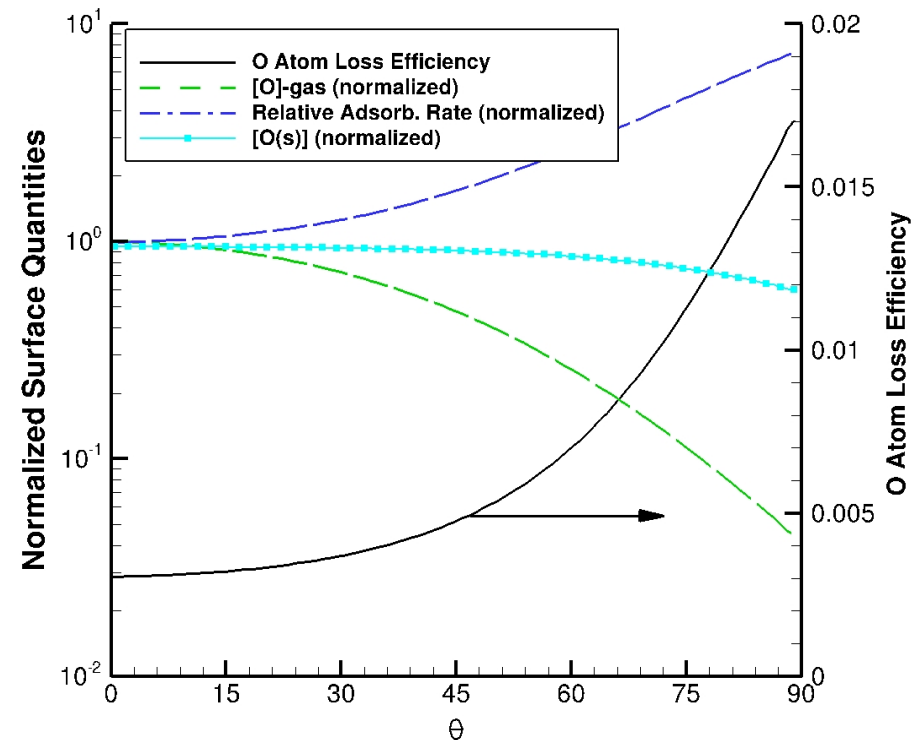
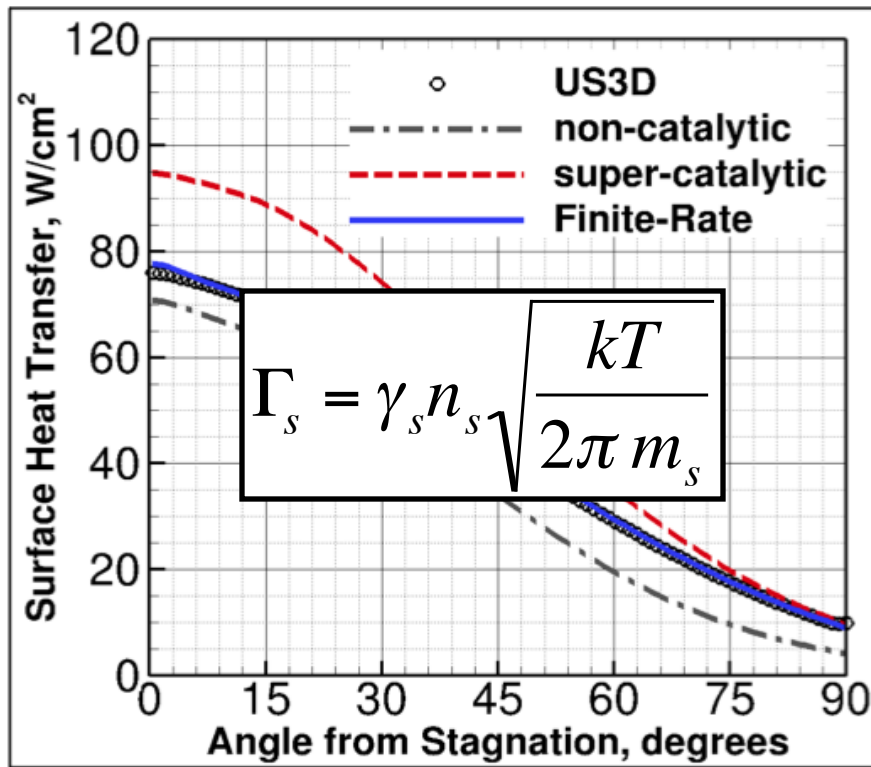
Sorensen, Valentini, and Schwartzentruber, **AIAA Paper 2011-3643**, Honolulu, HI.

Sorensen, Valentini, and Schwartzentruber, **J. Thermophysics and Heat Transfer**, In-press.

Pressure Dependence of Catalytic Efficiency



- Natural result of FRC model is that $\gamma = f(\text{surface coverage}) \sim f(\text{pressure})$
 - γ increases by 4x between $\theta=0^\circ$ and $\theta=90^\circ$ despite constant T_{wall}



MacLean, Marschall, and Driver, **AIAA Paper 2011-3784**, Honolulu, HI.

Sorensen, Valentini, and Schwartzentruber, **AIAA Paper 2011-3643**, Honolulu, HI.

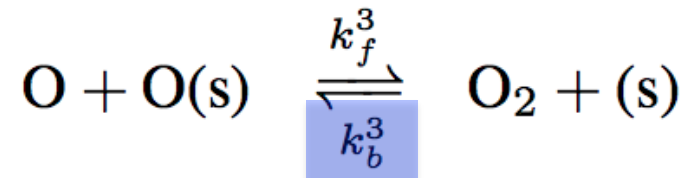
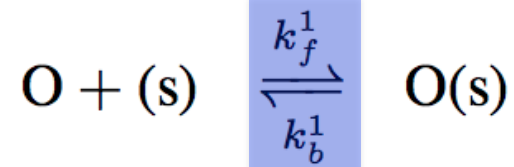
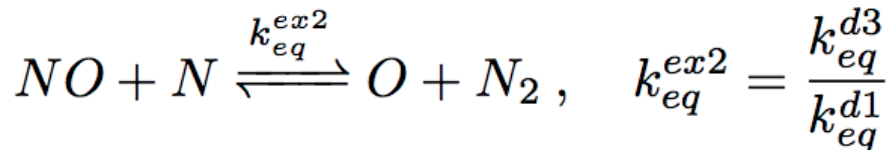
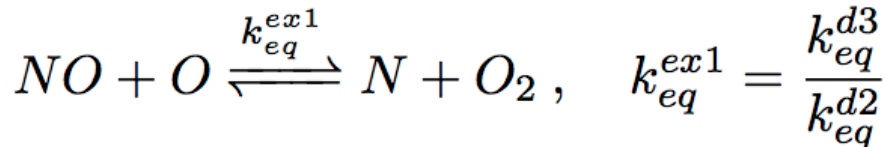
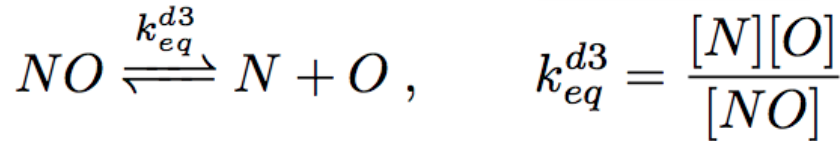
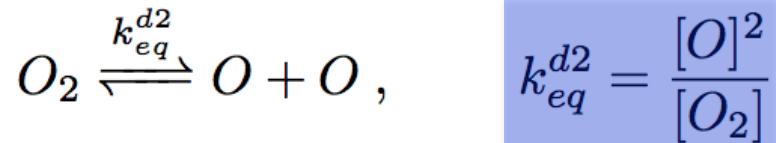
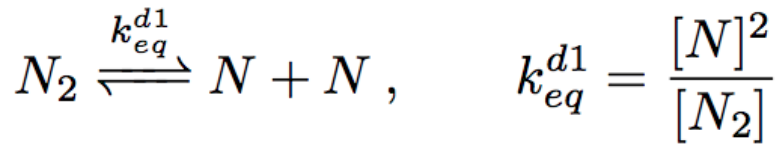
Sorensen, Valentini, and Schwartzentruber, **J. Thermophysics and Heat Transfer**, In-press.

Specifying Consistent Backwards Rates



Certain backwards rates must be set consistent with the *gas-phase* thermodynamics:

Park 90 model for air:



$$k_{eq}^1 = \frac{k_f^1}{k_b^1} = \frac{[O(s)]}{[O][s]}$$

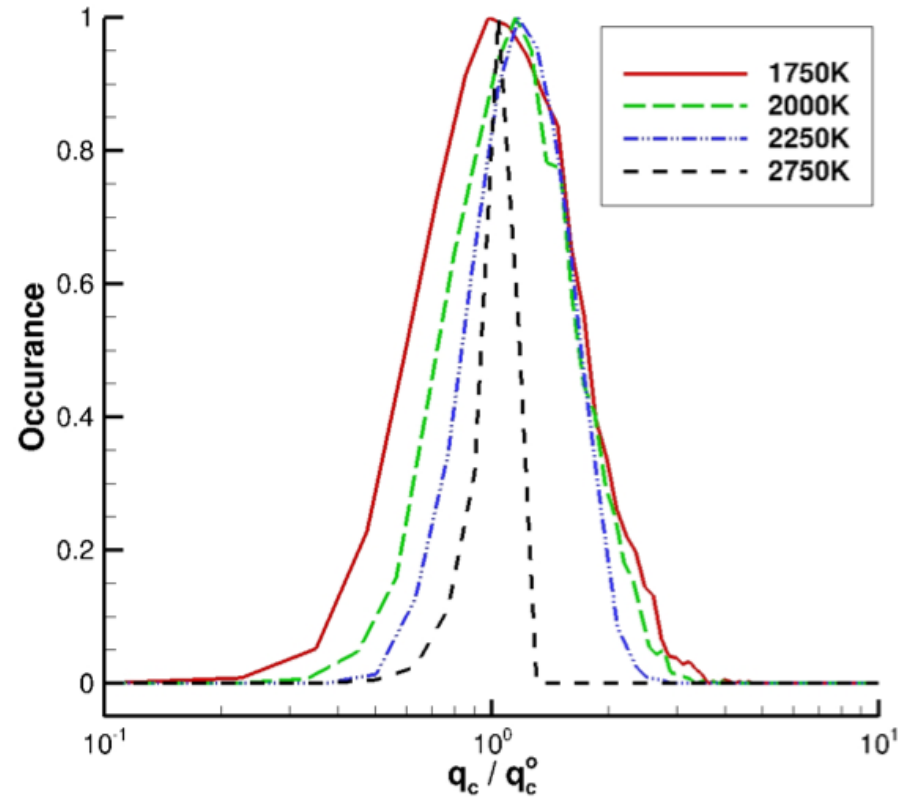
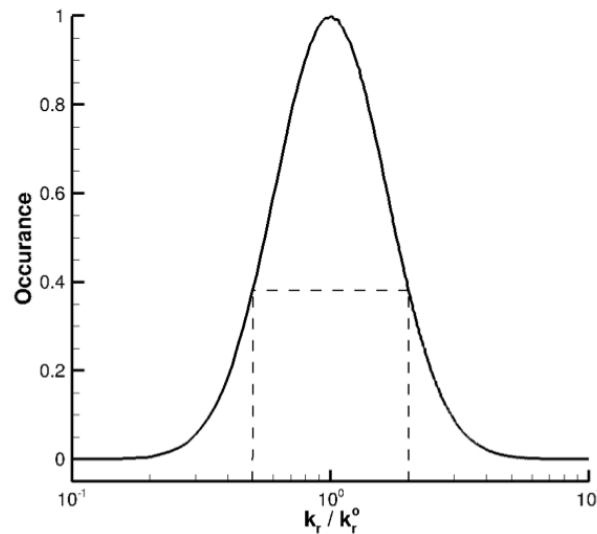
$$k_{eq}^3 = \frac{k_f^3}{k_b^3} = \frac{[O_2][s]}{[O][O(s)]}$$

$$k_b^3 = k_f^3 k_{eq}^1 k_{eq}^{d2}$$

Uncertainty Analysis (applied to rates)



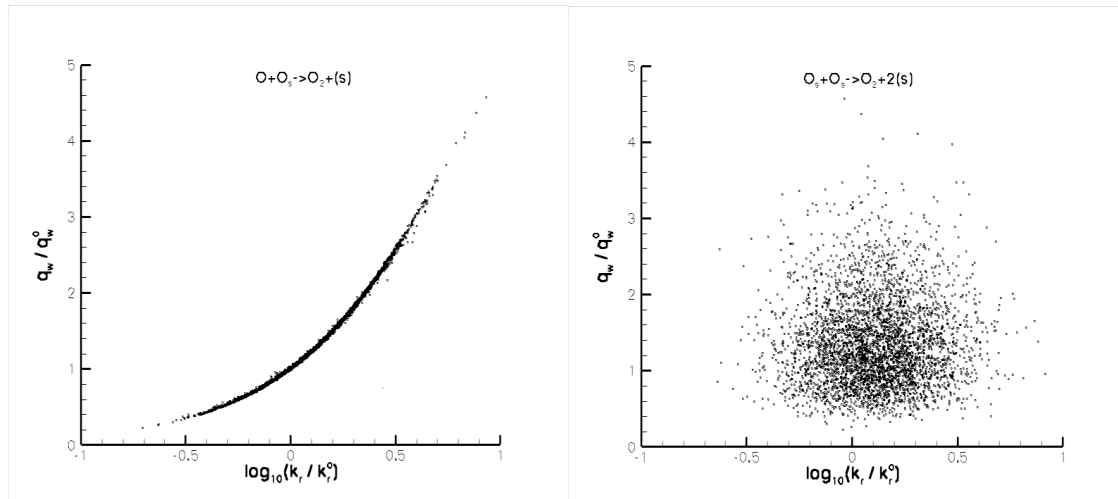
- Off-nominal rate sets determined by sampling each rate from a log-normal distribution centered at nominal value (~ 1 order of magnitude variation)
- 2000 US3D simulations (different rate sets) per wall temperature
- Chemical heat flux variation directly proportional to rate uncertainty (no unexpected non-linear coupling)
- However, magnitude of q_c variation diminishes as T_w increases as recombination becomes diffusion-limited



Rate Correlations

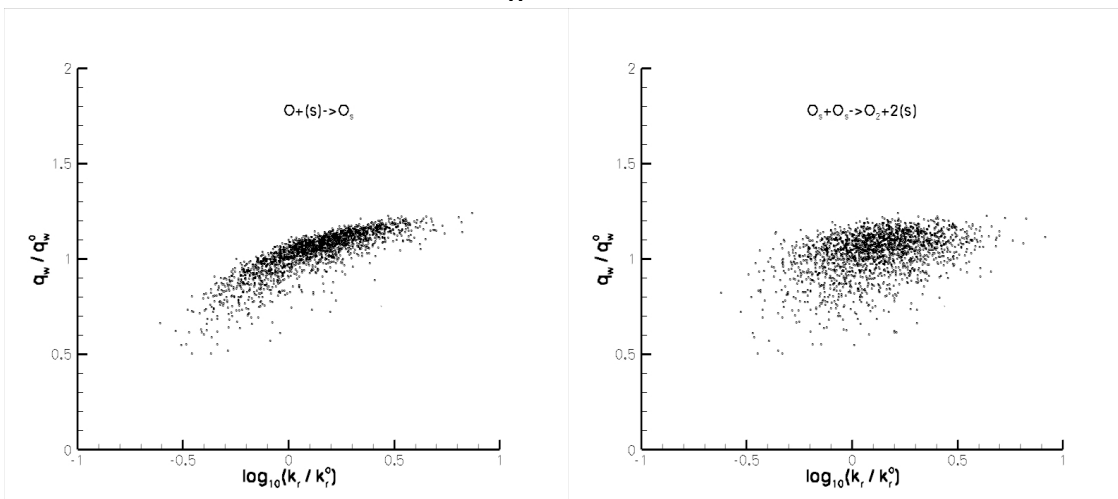


$T_w = 1750K$



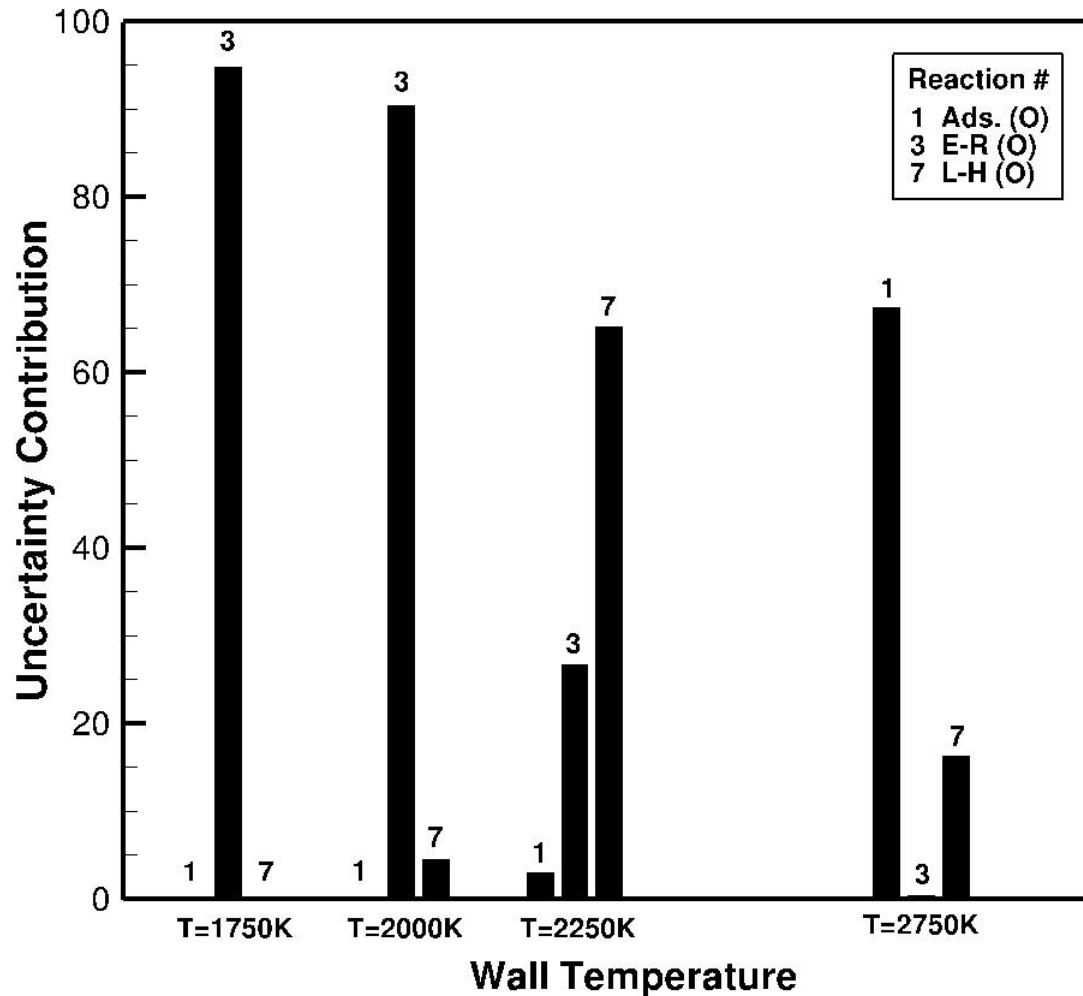
- Linear regression is used to determine the reactions' correlation to chemical heat flux
- E-R recombination is highly correlated to the heat flux at 1750K while reaction L-H oxygen shows no trend

$T_w = 2750K$



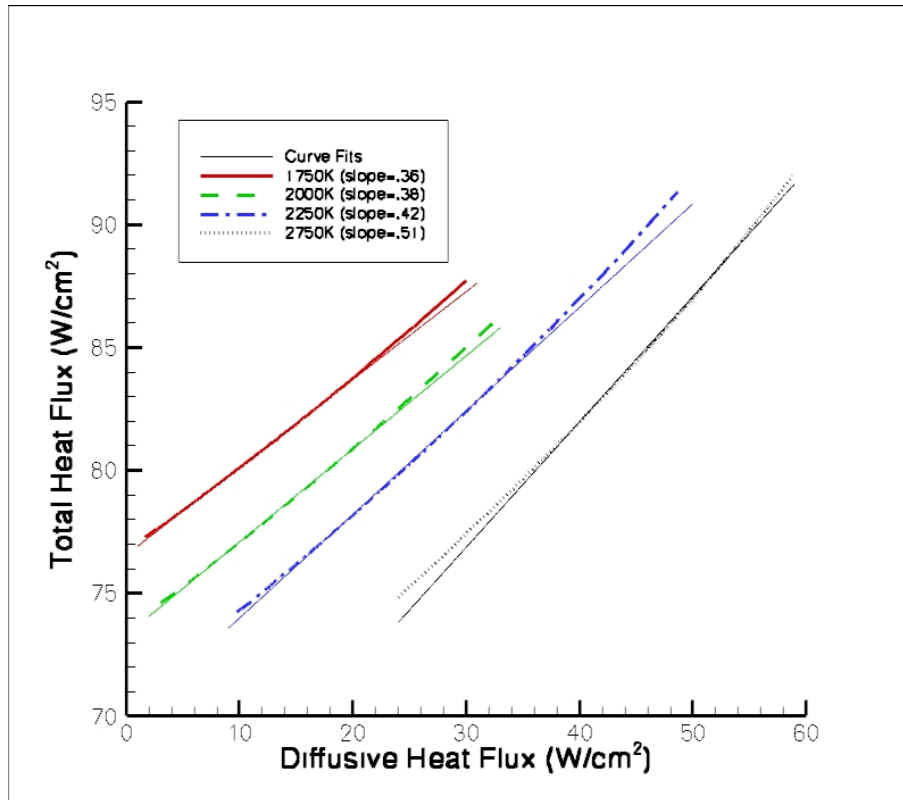
- Adsorption of oxygen and L-H oxygen are both correlated to the heat flux at 2750K

Dominant Rate Progression with Temperature



- E-R is most correlated to heat flux at temperatures below 2000K
- Above 2000K, L-H becomes most correlated
- Around 2750K, adsorption of oxygen becomes most correlated
- All reactions which are most correlated involve oxygen only

Conductive, Chemical, and Total Heat Flux



- Total heat flux is the sum of trans-rot and vibrational conductive terms plus chemical contribution
- An increase in chemical heat flux (due to rate uncertainty) does not lead to the same increase in total heat flux
- Due to an altered boundary layer state (more diatomic molecules), which lowers the conduction heat flux
 - Note: We assume full energy accommodation

$$q_w = \underbrace{\left(\kappa \frac{\partial T}{\partial n} \right)_w + \left(\kappa_v \frac{\partial T_v}{\partial n} \right)_w}_{\Delta q_{conductive}} + \underbrace{\rho_w \sum_i D_i h_i \left(\frac{\partial c_i}{\partial n} \right)_w}_{\Delta q_{chem}}$$

$$\Delta q_{conductive} = -(1 - \text{slope}) \Delta q_{chem}$$

Conclusions Regarding Finite-Rate Model



- 1) Backwards surface reaction rates should be determined in a consistent manner with adsorption/desorption/*gas-phase* equilibrium constants.
- 2) $\gamma_{\text{O}} = \text{fcn}(T_w, \text{ and } \textit{coverage})$, possibly parameterized by partial pressure of oxygen.
- 3) Uncertainty in chemical heat flux is directly linked to the dominant mechanism at that wall temperature and its associated uncertainty.
- 4) Uncertainty in chemical heat flux decreases (for same rate variation) as wall temperature increases due to diffusion-limited chemistry.
- 5) An increase in chemical heat flux due to rate uncertainty leads to only a fraction of that increase in total heat flux (reactivity alters the boundary layer and therefore the conductive heat flux).

In general, uncertainty in heat flux is ‘well-behaved’ for a given set of mechanisms. The problem lies in omitting mechanisms and/or applying in diffusion limited situations (heat flux insensitive to rates).

Computational Chemistry (Oxygen-Silica)



- Silica is a significant component in both ablative and non-ablative thermal protection systems because of its good insulating properties.
- Many TPS materials, including Space Shuttle Tiles, SiC, and Ultra High Temperature Ceramics (UHTCs) form layers of primarily **SiO₂** (stoichiometric) when exposed to atomic oxygen[1-3].
- There is little experimental evidence as to the structure of a silica surface exposed to high T due to the difficulties of *in situ* measurements.

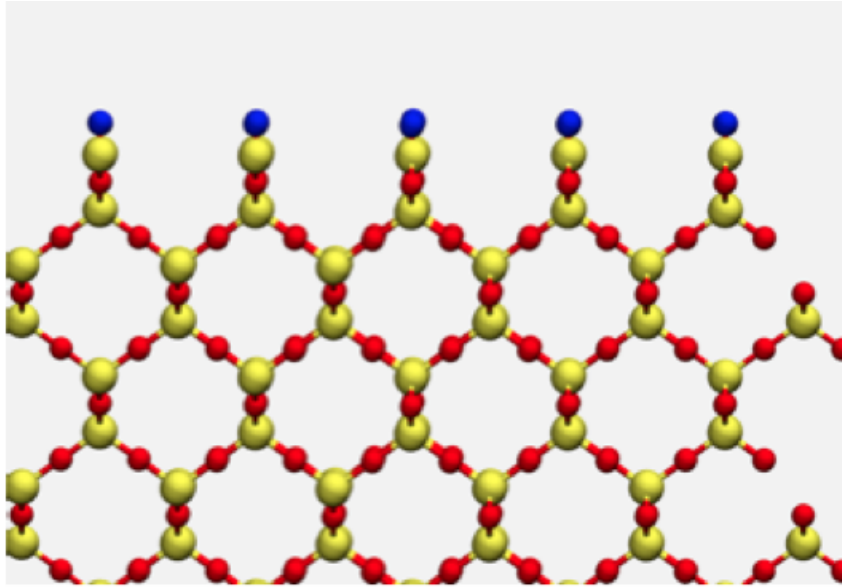
- Goals:**
- 1) What are the in-situ surface structures for silica surfaces?**
 - 2) What are the dominant catalytic mechanisms for dissociated oxygen interacting with such surfaces?
(for example, we observe no high-T LH reactions...)**
 - 3) What are the associated rates?**

[1] E. Jumper and W. Seward. *Journal of Thermophysics and Heat Transfer*, 1994

[2] M. Balat-Pichelin et al., *Chemical Physics*, 2003

[3] D. Alfano et al., *Journal of European Ceramic Society*, 2010

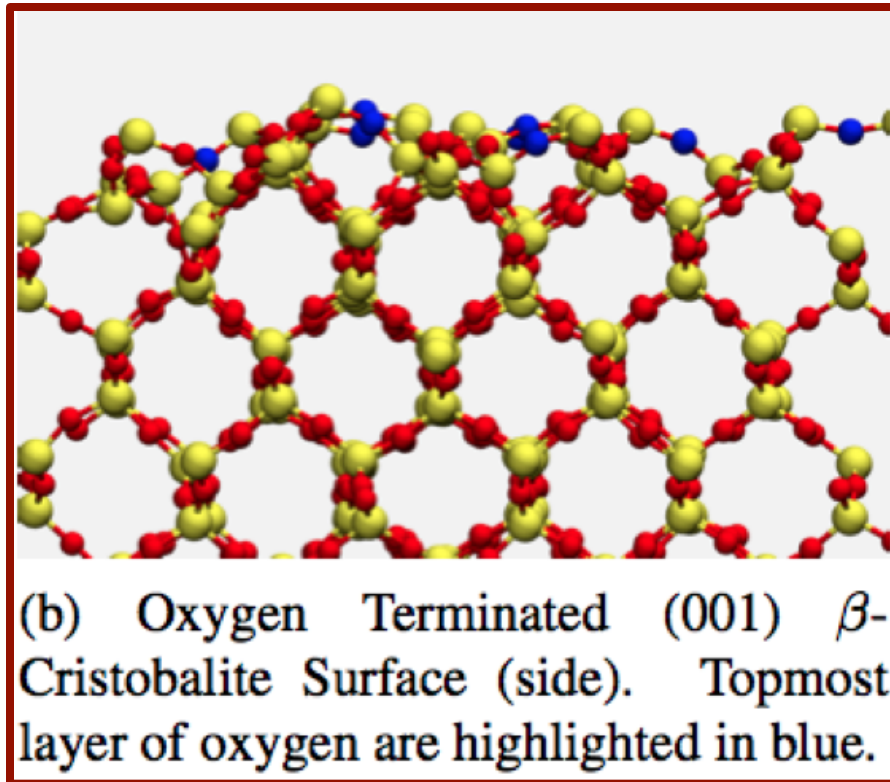
Prior Oxygen-Silica Research



(b) Oxygen Terminated (001) β -Cristobalite Surface (side). Topmost layer of oxygen highlighted in blue.

- Assume that oxide layers formed on SiC are β -Cristobalite (SiO_2 polymorph)
- Furthermore, cleave this bulk material to form a surface and place adsorbed atoms arbitrarily on surface

Prior Oxygen-Silica Research



- Assume that oxide layers formed on SiC are β -Cristobalite (SiO_2 polymorph)
- Furthermore, cleave this bulk material to form a surface and place adsorbed atoms arbitrarily on surface
- Such surfaces are highly unphysical (high energy dangling bonds)
- Stable (**non-catalytic**) reconstructions observed in our MD simulations and experimentally

Surface Coverage on High-T Amorphous SiO₂

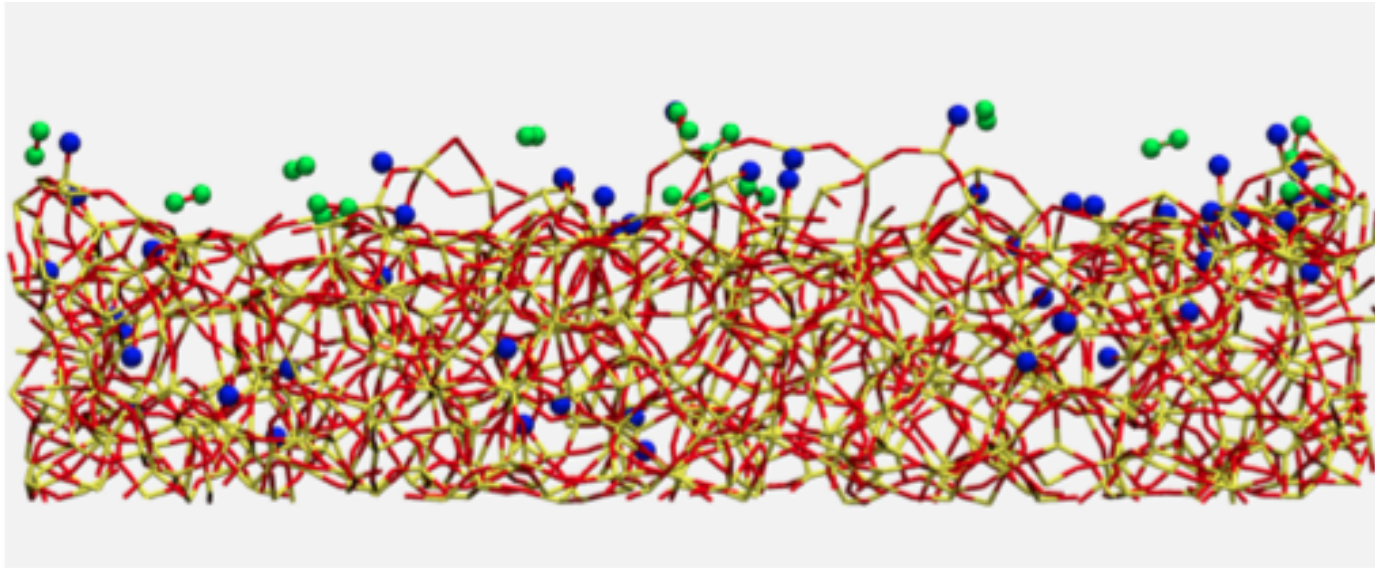


Figure 14 – Visualization of annealed amorphous SiO₂ after exposure to dissociated oxygen at high pressure. Defects are highlighted. Blue = (≡Si-O·). Green = (≡Si-O₂).

- There is experimental and computational evidence for the existence of the ≡Si-O defect [1-3], and the stable/non-catalytic (Si-O-Si) reconstructions [4]

[1] D. Griscom and L. FriebeL., *Physical Review B*, 1981

[2] E. O'Reilly et al., *Physical Review B*, 1983

[3] V. Bermudez et al., *Physical Review B*, 1979

[4] O. Sneh and S. George, *Journal of Physical Chemistry*, 1995

Surface Coverage on High-T Amorphous SiO₂

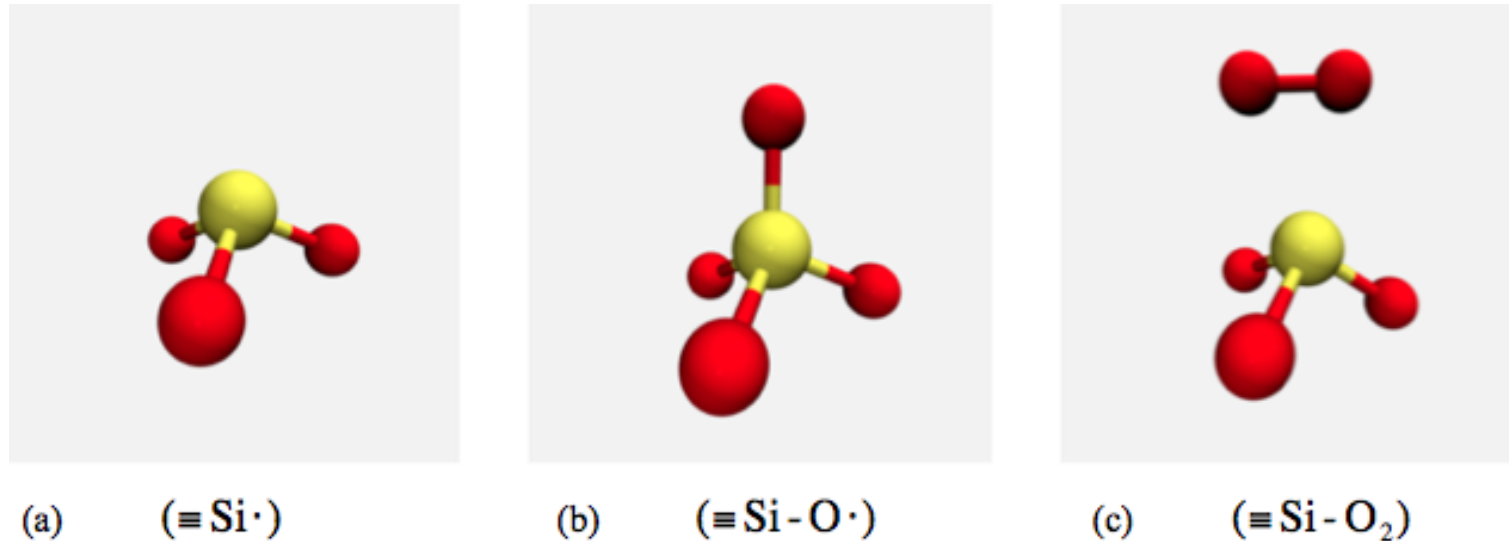


Figure 13 – Defects observed on annealed amorphous SiO₂ surfaces exposed to dissociated oxygen.

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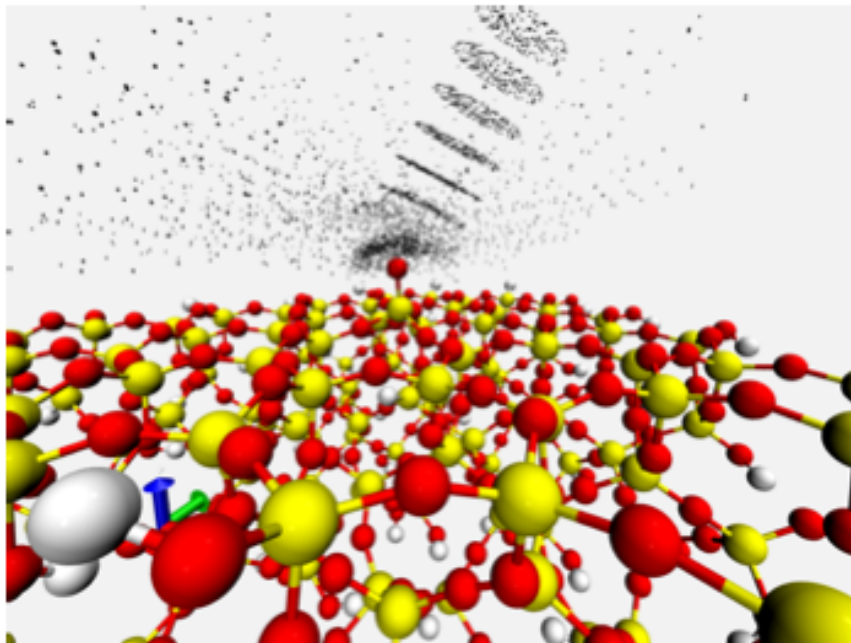
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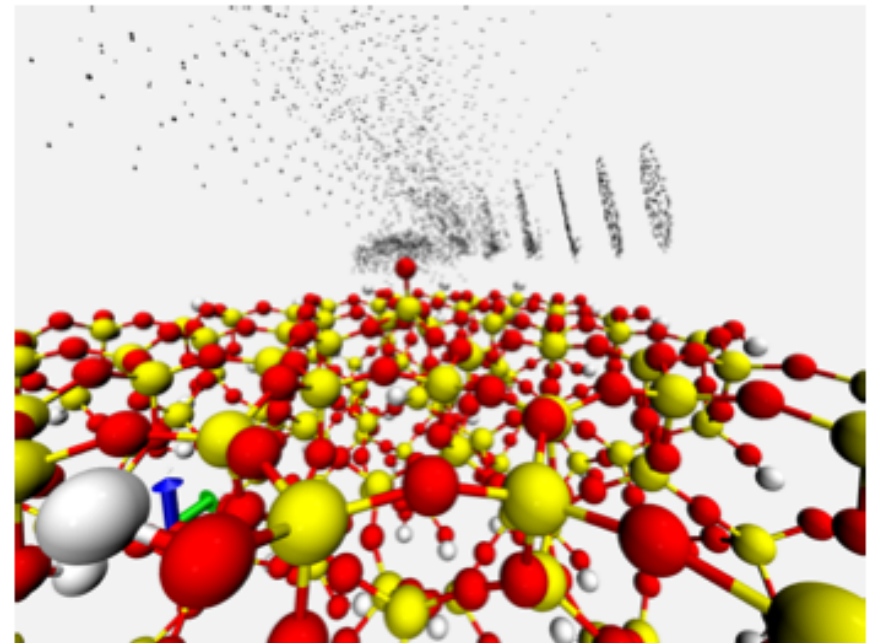
Individual Collision-Defect Simulations



- Isolate each defect and compute average **activation energies** and **steric factors** for reactions due to gas-phase collisions
- $T_{\text{wall}} = T_{\text{gas}}$ (Maxwell-Boltzmann velocities at random angle)



(a) $\phi = 30$



(b) $\phi = 75$

Finite-Rate Model via Computational Chemistry



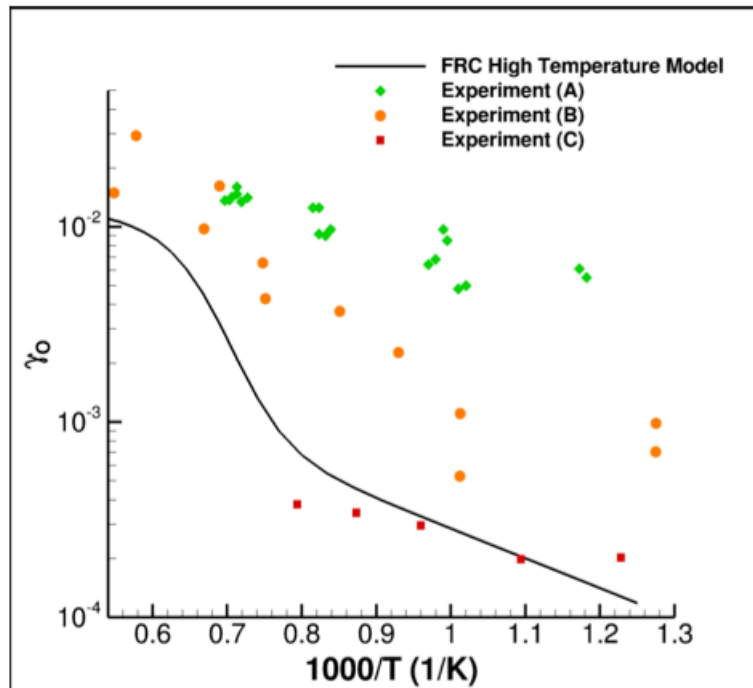
$O + E_c \rightleftharpoons O_c$	Atomic Oxygen Adsorption	(1)
$O + O_c \rightleftharpoons O_2 + E_c$	Eley Rideal Recombination	(2)
$O + O_c \rightleftharpoons O_{2c}$	Molecular Oxygen Formation	(3)
$O + O_{2c} \rightleftharpoons O_2 + O_c$	Molecular Oxygen Replacement	(4)
$O_{2c} \rightleftharpoons O_2 + E_c$	Molecular Oxygen Desorption	(5)
$O + E_f \rightleftharpoons O_f$	Atomic Oxygen Physisorption	(6)
$O_f + E_c \rightleftharpoons E_f + O_c$	Physisorbed to Chemisorbed	(7)
$O_f + O_c \rightleftharpoons E_f + E_c + O_2$	Langmuir Hinshelwood Recombination	(8)

Rate	Rate Equation	Functional Form	A	E_a (eV)
r_1^f	$k_1^f [O][E_s]$	$(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_1^f e^{-E_1^f/(K_B T)})$	1.0	0.0
r_1^r	$k_1^r [O_s]$	$A_1^r e^{-E_1^r/(K_B T)}$	$10^{-15} \text{ (s}^{-1}\text{)}$	4.25
r_2^f	$k_2^f [O][O_s]$	$(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_2^f e^{-E_2^f/(K_B T)})$	0.169	0.401
r_2^r	$k_2^r [O_2][E_s]$	$(\bar{c}_{O_2}/4) \times (2\pi r_s^2) \times (A_2^r e^{-E_2^r/(K_B T)})$	0.663	1.27
r_3^f	$k_3^f [O][O_s]$	$(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_3^f e^{-E_3^f/(K_B T)})$	1.13	0.253
r_3^r	$k_3^r [O_{2s}]$	$A_3^r e^{-E_3^r/(K_B T)}$	$10^{-15} \text{ (s}^{-1}\text{)}$	4.14
r_4^f	$k_4^f [O][O_{2s}]$	$(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_4^f e^{-E_4^f/(K_B T)})$	0.172	0.303
r_4^r	$k_4^r [O_2][O_s]$	$(\bar{c}_{O_2}/4) \times (2\pi r_s^2) \times (A_4^r e^{-E_4^r/(K_B T)})$	0.716	1.18
r_5^f	$k_5^f [O_{2s}]$	$A_5^f e^{-E_5^f/(K_B T)}$	$1.20 \times 10^{14} \text{ (s}^{-1}\text{)}$	2.71
r_5^r	$k_5^r [O_2][E_s]$	$(\bar{c}_{O_2}/4) \times (2\pi r_s^2) \times (A_5^r e^{-E_5^r/(K_B T)})$	1.0	0.0
r_6^f	$k_6^f [O][E_f]$	$(\bar{c}_O/4) \times (2\pi r_s^2) \times (A_6^f e^{-E_6^f/(K_B T)})$	1.0	0.0
r_6^r	$k_6^r [E_f]$	$(A_6^r e^{-E_6^r/(K_B T)})$	$10^{15} \text{ (s}^{-1}\text{)}$	0.130
r_7^f	$k_7^f [O][O_f][E_c]$	$(2\pi r_s \Lambda_D) \times (\bar{c}_O/4) \times P_{rc} \times (A_7^f e^{-E_7^f/(K_B T)})$	1.0	0.0
r_8^f	$k_8^f [O][O_f][O_c]$	$(2\pi r_s \Lambda_D) \times (\bar{c}_O/4) \times P_{rc} \times (A_8^f e^{-E_8^f/(K_B T)})$	1.0	0.2

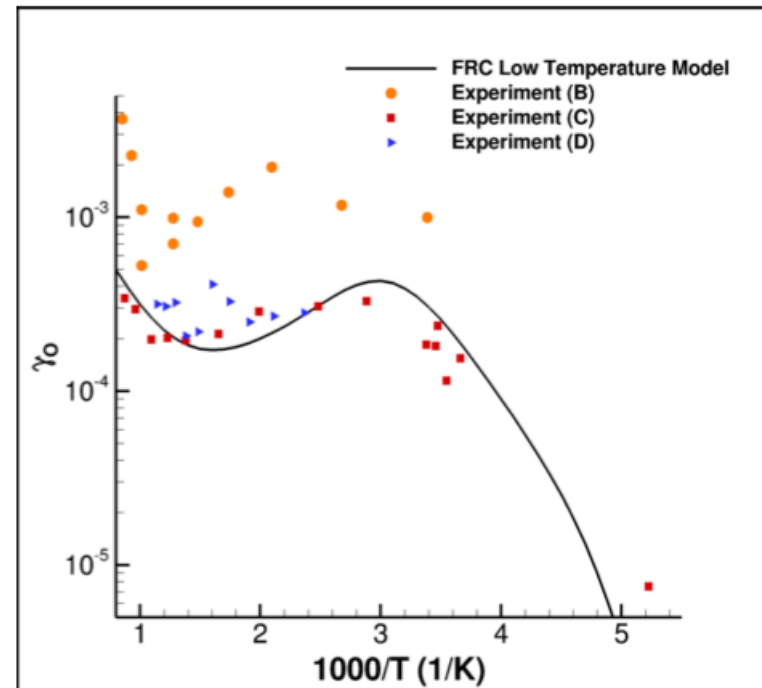
Finite-Rate Model vs. Experiment



- Exponential trend of $\gamma(T)$ in general agreement with experiment
 - a direct result of dominant defects/mechanisms/activation energies
- Magnitude of γ influenced by surface roughness (currently fit to experiment)



(a) High Temperature FRC Model



(b) Low Temperature FRC Model

[A] Balat-Pichelin, M., Badie, J., Berjoan, R., and Boubert, P., "Recombination coefficient of atomic oxygen on ceramic materials under earth re-entry conditions by optical emission spectroscopy," *Chemical Physics*, Vol. 291, No. 2, 2003, pp. 181–194.

[B] Stewart, D. A., "Surface Catalysis and Characterization of Proposed Candidate TPS for Access-to-Space Vehicles," NASA Technical Memorandum 112206, 1997.

[C] Kim, Y. C. and Boudart, M., "Recombination of O, N, and H Atoms on Silica: Kinetics and Mechanism," *Langmuir*, Vol. 7, 1991.

[D] Marschall, J., "Experimental Determination of Oxygen and Nitrogen Recombination Coefficients at Elevated Temperature Using Laser-Induced Fluorescence," AIAA, Baltimore, MD, 1997.

Waiting for final results based on new DFT data specific to these reactions.

Carbon-based Surface Ablators



- Molecular beam experiments on Highly-Oriented Pyrolytic Graphite

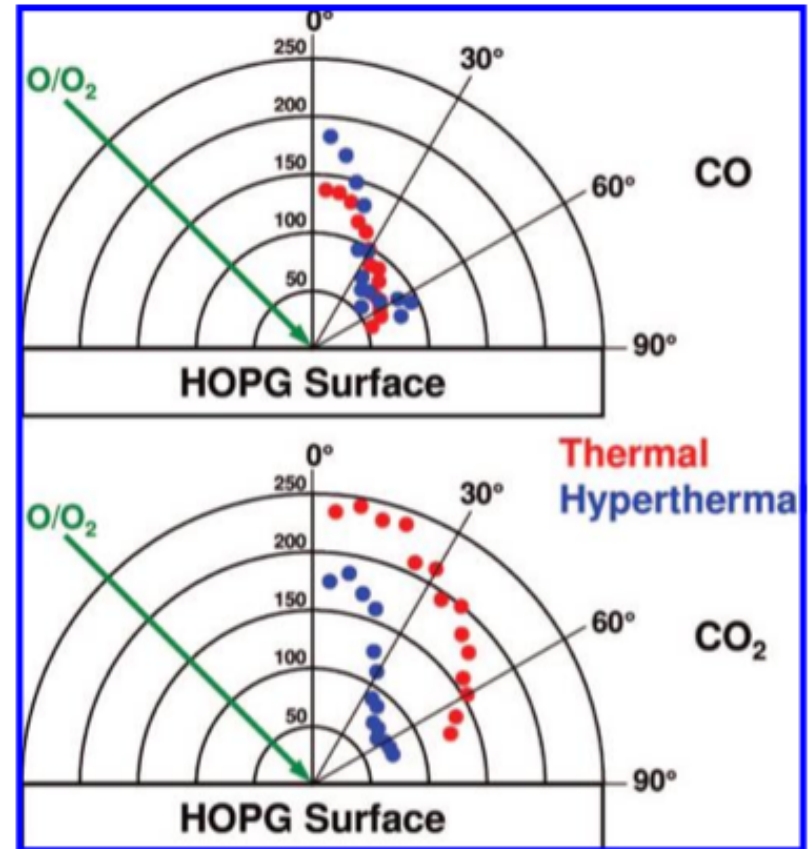
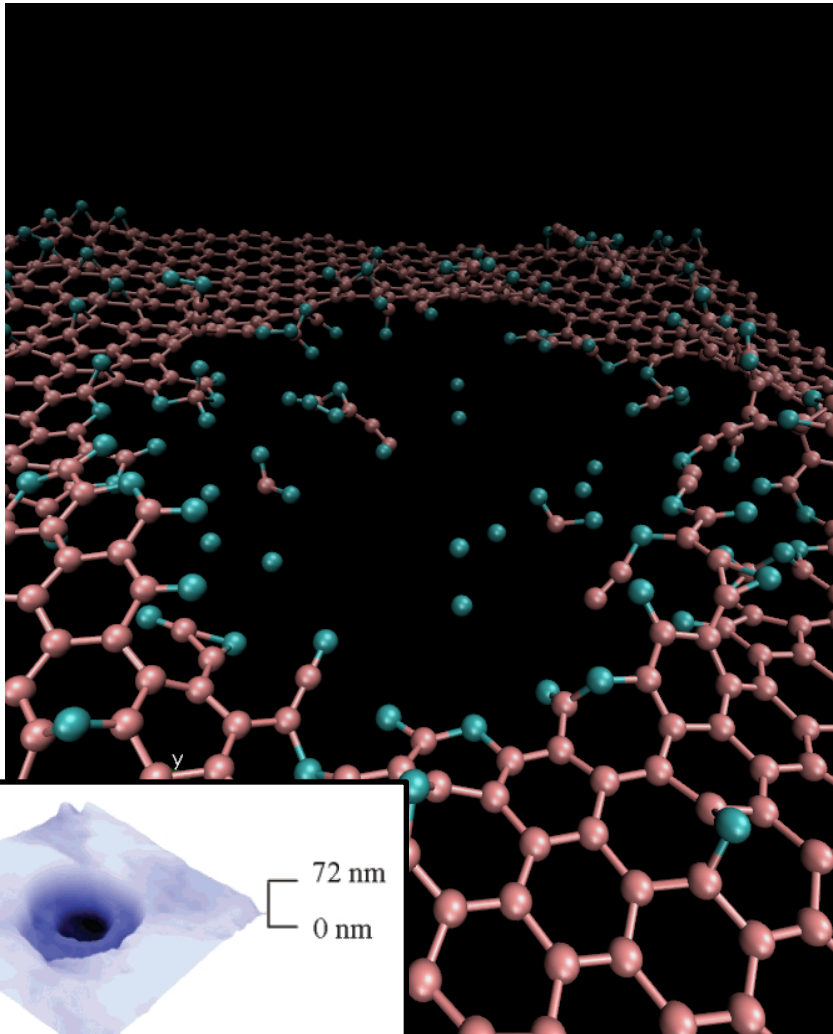


Figure 3. Relative flux of scattered CO (top panel) and CO₂ (bottom panel) as a function of θ_s , with $\theta_i = 45^\circ$. Red circles represent the flux of the thermal components and blue circles represent the flux of the hyperthermal components.

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