Finite-rate oxidation model for carbon surfaces from molecular beam experiments

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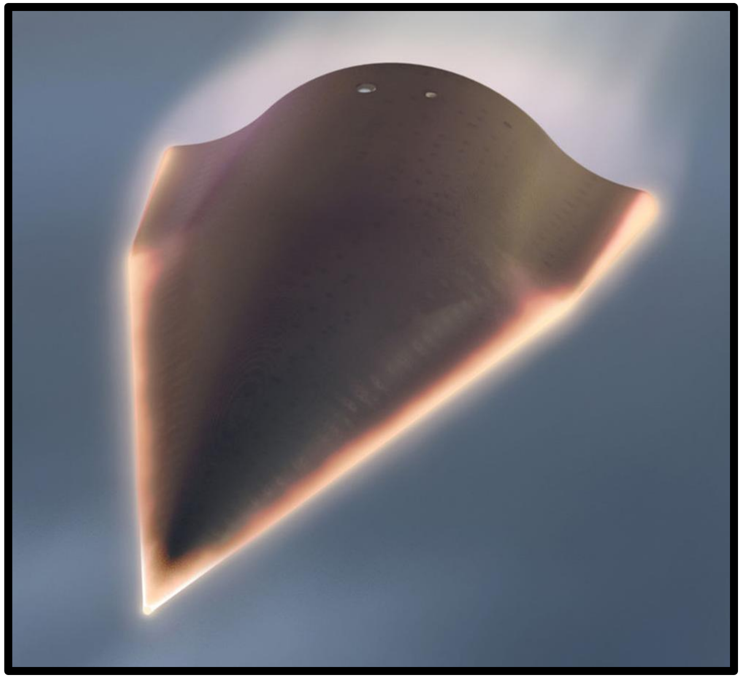
FA9550-10-1-0563: AFOSR MURI FY2010

Doctoral Dissertation Fellowship, UofMinnesota

Background:



Need: Understand surface ablation for thermal protection system (TPS) design. Challenging long-duration, high-altitude (nonequilibrium) flight conditions. Accurate ablation models are required within CFD simulations for vehicle design.

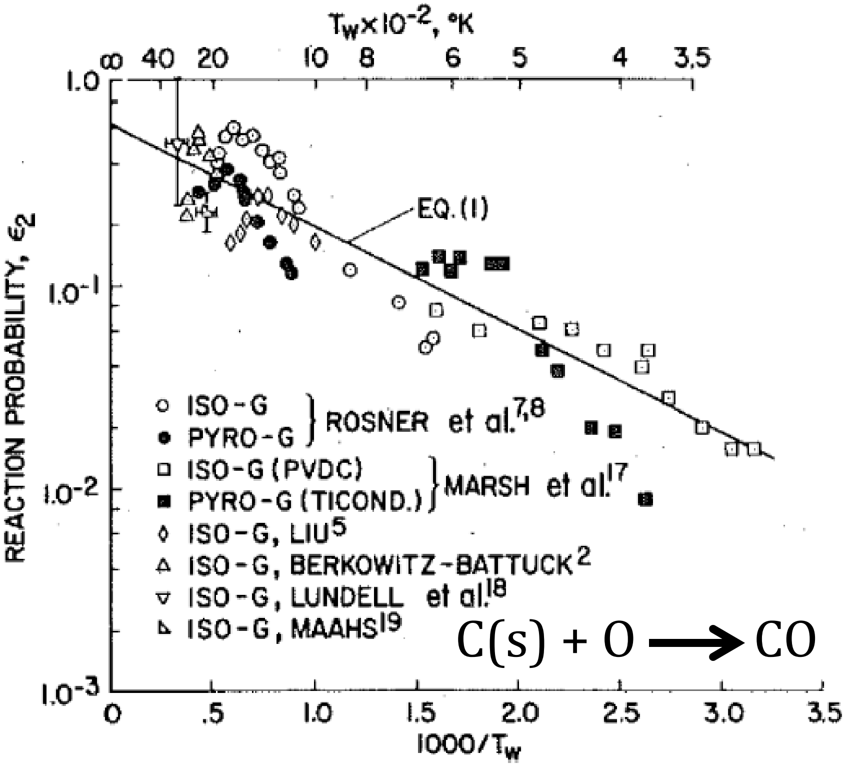
Problem: Wind-tunnel ablation experiments involve coupled gas-phase, gas-surface physics, which obscures fundamental processes. Current CFD models have large uncertainty.

Approach: Molecular Beam experiments combined with molecular simulation/theory to construct new gas-surface reaction models for CFD. Individual reaction mechanisms revealed and quantified.

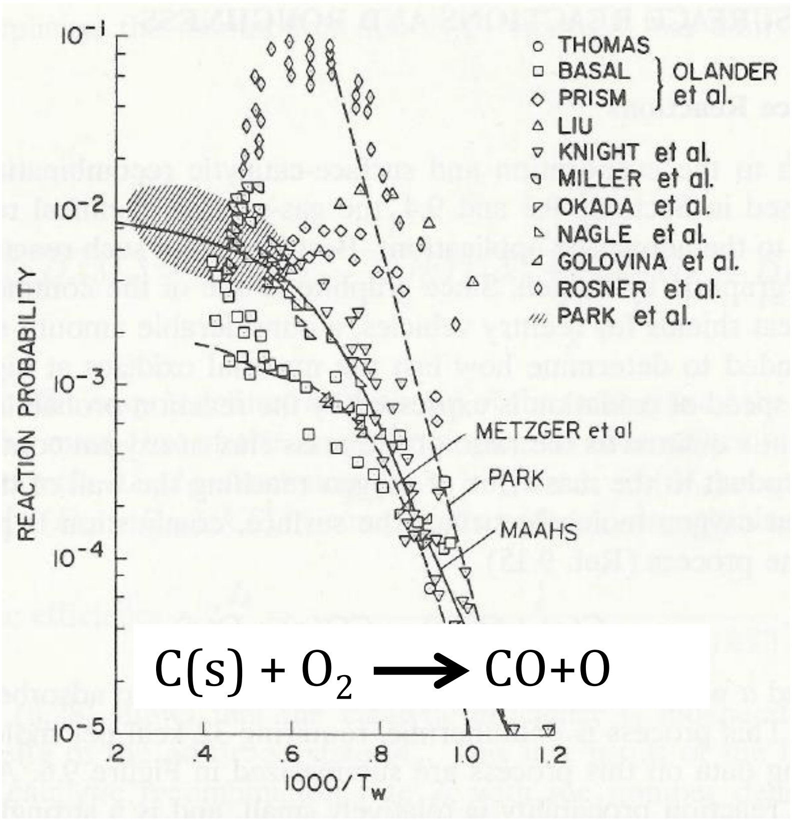
Existing Models: Park Model

Images and rates taken from: **Park C.**, “Effects of atomic oxygen on graphite ablation”, *AIAA Journal*, Vol. 14, No. 11, 1976, pp. 1640-1642.

Reaction	Rates	Reaction probability (γ)
$C(s) + O + O \rightarrow C(s) + O_2$	$\gamma \frac{P}{\sqrt{2\pi mkT}}$	0.63exp(-1160/T)
$C(s) + O_2 \rightarrow CO + O$	$\gamma \frac{P}{\sqrt{2\pi mkT}}$	$\frac{1.43\times10^{-3}+0.01exp(-1450/T)}{1+2\times10^{-4}exp(13000/T)}$
$C(s) + O \rightarrow CO$	$\gamma \frac{P}{\sqrt{2\pi mkT}}$	0.63exp(-1160/T)



$C(s) + O \longrightarrow CO$



$C(s) + O_2 \longrightarrow CO+O$

Existing Models: Zhluktov and Abe (ZA) Model

- **Surface coverage** model (required for wide temperature/pressure range).

Zhluktov S.V., Abe T., "Viscous Shock-Layer Simulation of Airflow Past Ablating Blunt Body with Carbon Surface", Journal of Thermophysics and Heat Transfer, Vol. 13, No. 1, 1999, pp. 50-59.

1. $O + (C) \Leftrightarrow (C - O)$ $\quad k_{f1} = \varepsilon_1 f_O$
2. $O_2 + 2(C) \Leftrightarrow 2(C - O)$ $\quad k_{r2} = \varepsilon_2 B(kT/h) e^{-T_{a2}/T}$
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10. $3(C) \Leftrightarrow C_3 + 3(C)$ $\quad k_{r10} = \varepsilon_{10} f_{C_3}$
11. $N + (C) \Leftrightarrow (C - N)$ $\quad k_{f11} = \varepsilon_{11} f_N$
12. $(C - N) + N \Leftrightarrow N_2 + (C)$ $\quad k_{r12} = \varepsilon_{12} f_{N_2} e^{-T_{a12}/T}$

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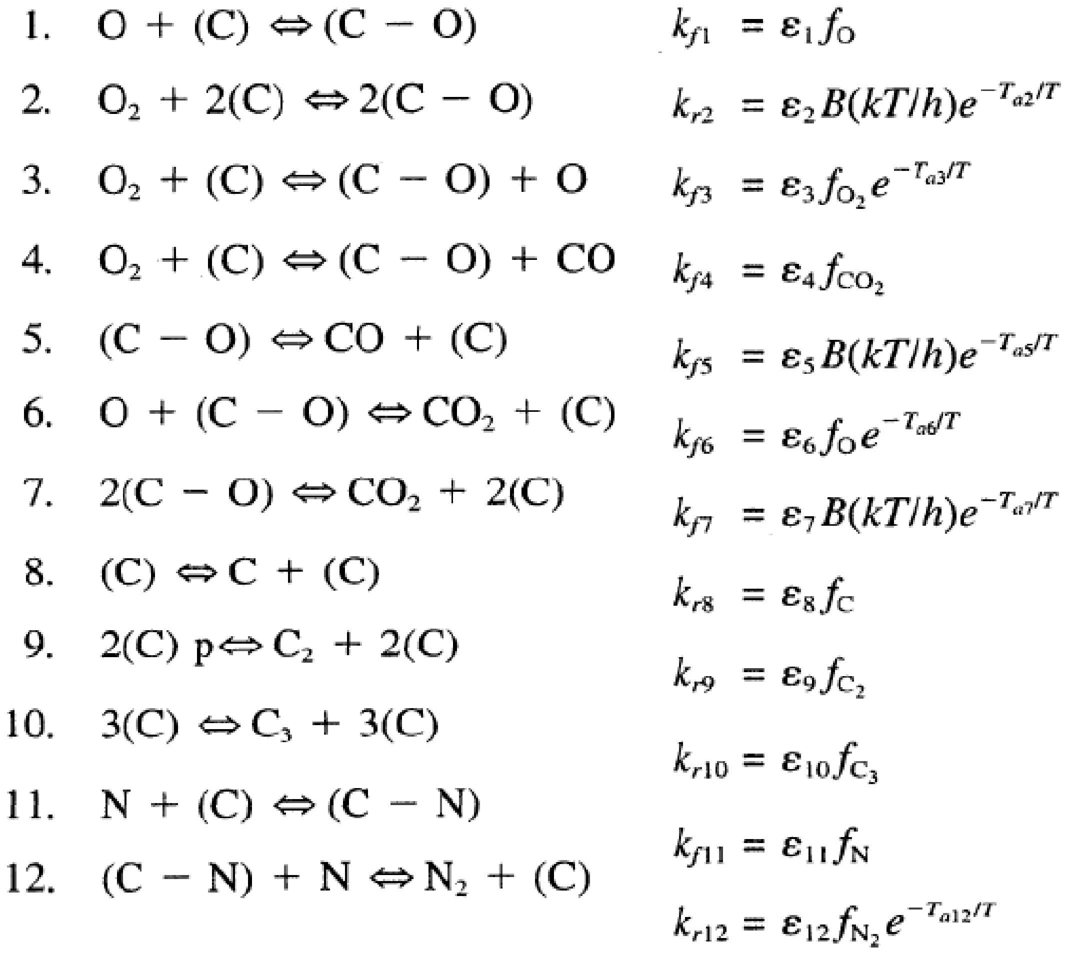

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- But how to parameterize all of the rate coefficients? Typical ablation experiments involved coupled gas-phase and gas-surface processes.
- **We propose to use Molecular Beam experiments.**

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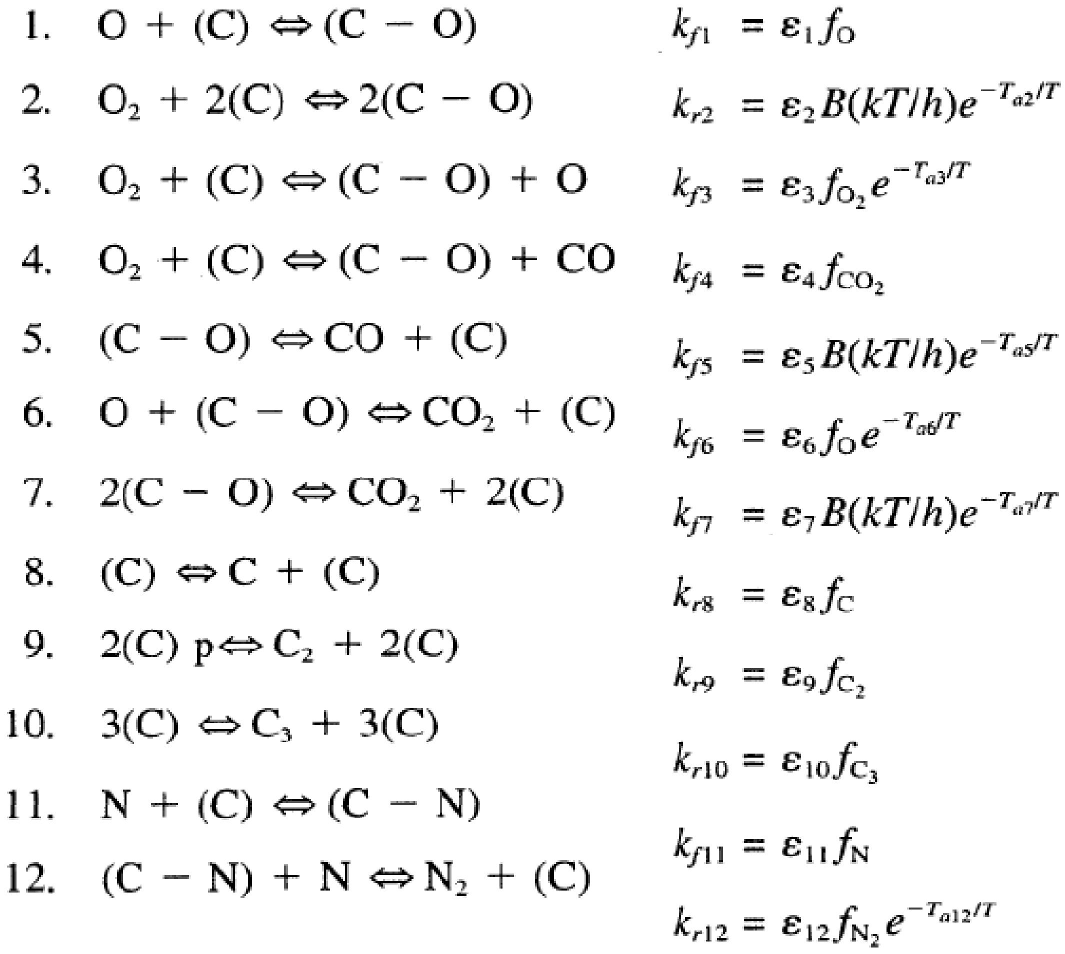

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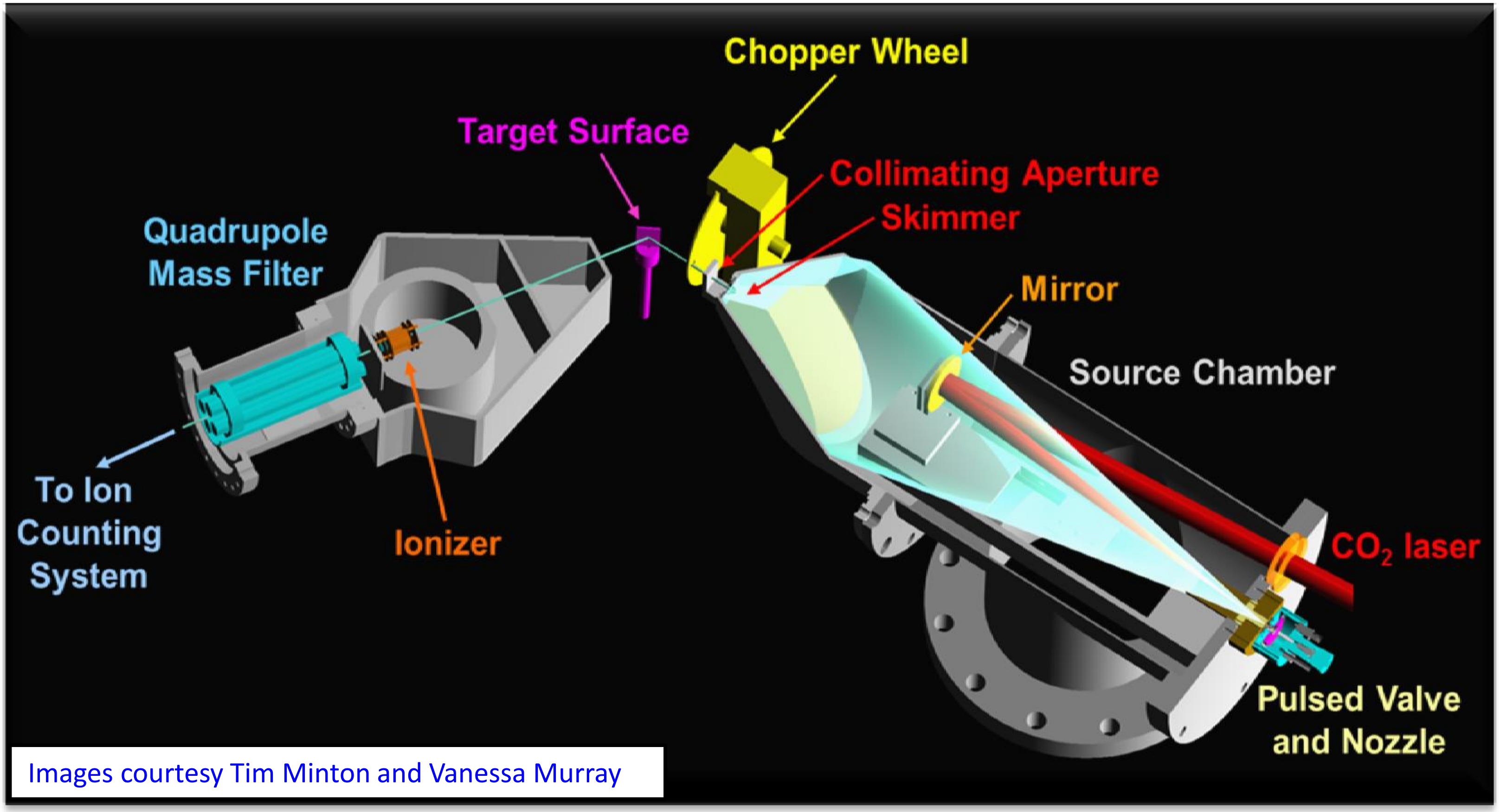
Molecular Beam Experiments (Minton group – Montana State)



Images courtesy Tim Minton and Vanessa Murray

Can we use Molecular Beam data for boundary layer flows?

Two significant results from Molecular Beam (MB) experiments (Minton group, Montana State) changed our approach:

1) Majority of reaction products were observed to scatter *thermally* (despite the high-energy 5eV beam O atom source).
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   - if experimental surfaces had low coverage at all conditions, this would have made its use for boundary layer flows (high p) questionable
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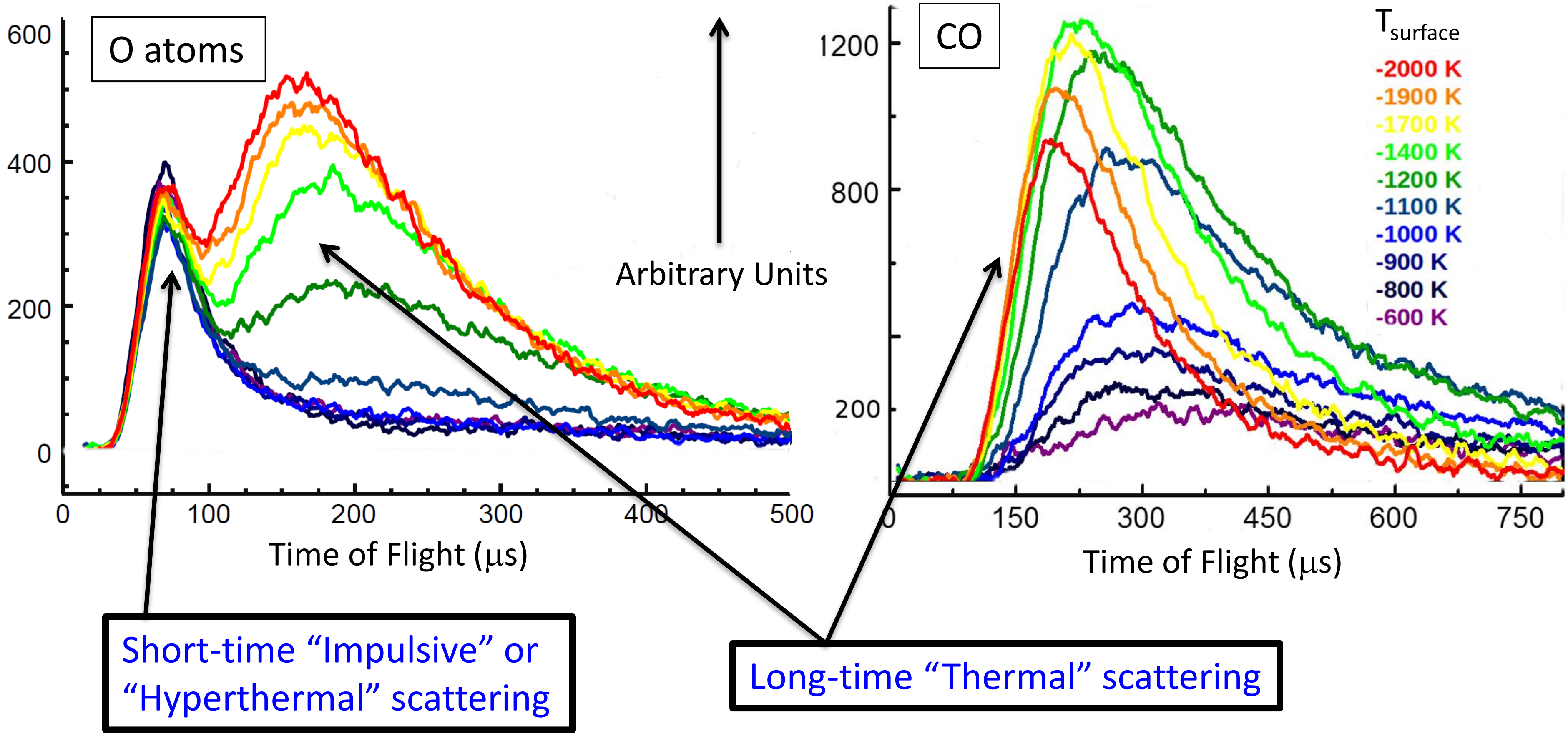
These two results enable individual reaction rates, for use in CFD-type ablation models, to be determined using Molecular Beam data.

Molecular Beam Results: Time-of-Flight (TOF) Distributions

- Beam contains 93% O and 7% O_2
- Beam pulse lasts only ~1 μs and occurs every 0.5 seconds (2 Hz)
- TOF distributions for various $T_{surface}$ (single scattering angle of 15 degrees) averaged under steady-state operation (~15min of beam operation)

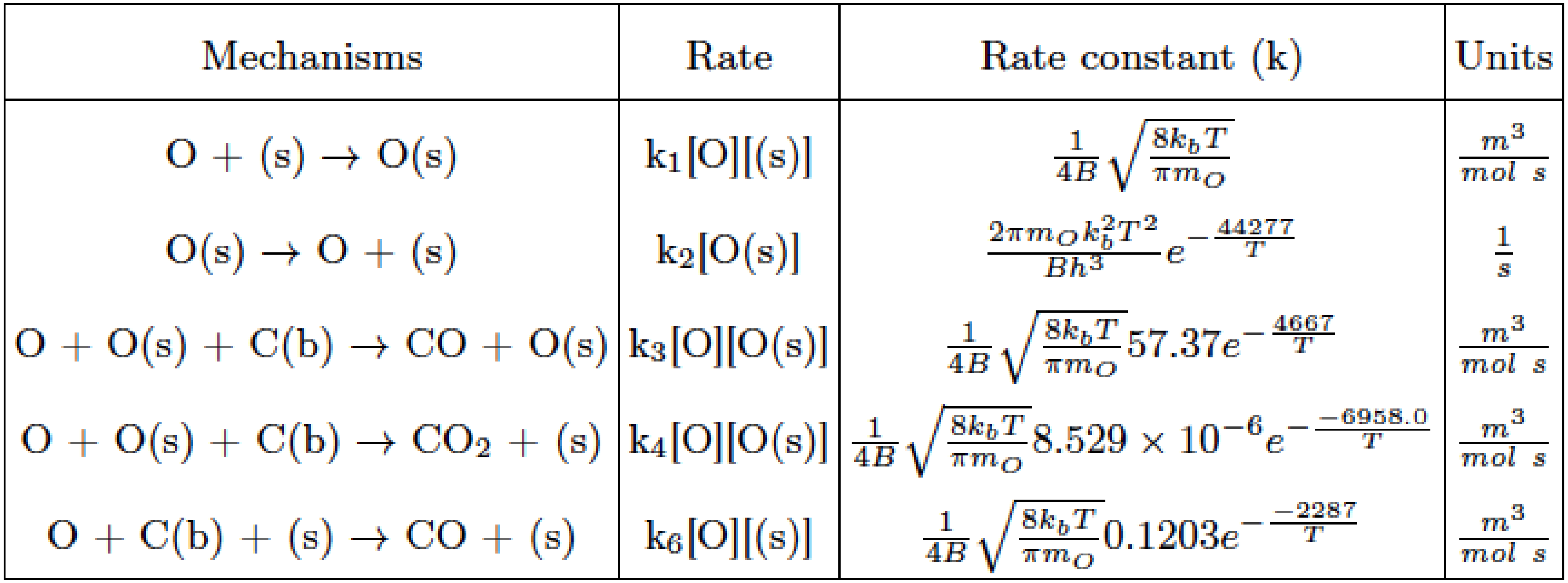


Short-time "Impulsive" or "Hyperthermal" scattering

Long-time "Thermal" scattering

New CFD Model Based on Molecular Beam Data

Using *only* the Molecular Beam data, we have constructed a preliminary oxygen-carbon gas-surface model:



Mechanisms	Rate	Rate constant (k)	Units
$\mathrm{O} + (\mathrm{s}) \rightarrow \mathrm{O(s)}$	$\mathrm{k_1[O][(s)]}$	$\frac{1}{4B}\sqrt{\frac{8k_bT}{\pi m_O}}$	$\frac{m^3}{mol\ s}$
$\mathrm{O(s)} \rightarrow \mathrm{O} + (\mathrm{s})$	$\mathrm{k_2[O(s)]}$	$\frac{2\pi m_O k_b^2 T^2}{Bh^3} e^{-\frac{44277}{T}}$	$\frac{1}{s}$
$\mathrm{O} + \mathrm{O(s)} + \mathrm{C(b)} \rightarrow \mathrm{CO} + \mathrm{O(s)}$	$\mathrm{k_3[O][O(s)]}$	$\frac{1}{4B}\sqrt{\frac{8k_bT}{\pi m_O}} 57.37 e^{-\frac{4667}{T}}$	$\frac{m^3}{mol\ s}$
$\mathrm{O} + \mathrm{O(s)} + \mathrm{C(b)} \rightarrow \mathrm{CO_2} + (\mathrm{s})$	$\mathrm{k_4[O][O(s)]}$	$\frac{1}{4B}\sqrt{\frac{8k_bT}{\pi m_O}} 8.529 \times 10^{-6} e^{-\frac{-6958.0}{T}}$	$\frac{m^3}{mol\ s}$
$\mathrm{O} + \mathrm{C(b)} + (\mathrm{s}) \rightarrow \mathrm{CO} + (\mathrm{s})$	$\mathrm{k_6[O][(s)]}$	$\frac{1}{4B}\sqrt{\frac{8k_bT}{\pi m_O}} 0.1203 e^{-\frac{-2287}{T}}$	$\frac{m^3}{mol\ s}$

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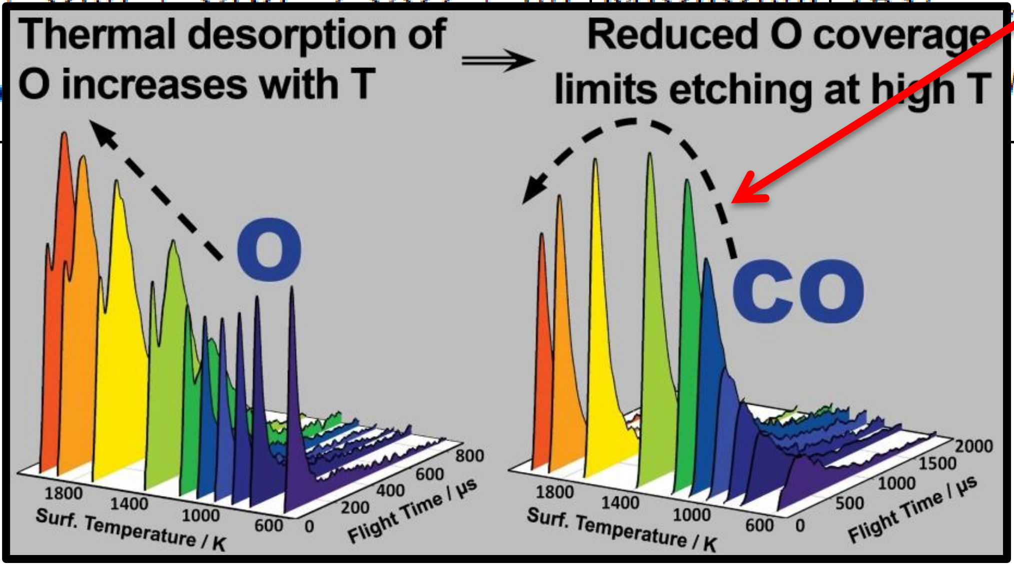

Thermal desorption of O increases with T $\Longrightarrow$ **Reduced O coverage limits etching at high T**

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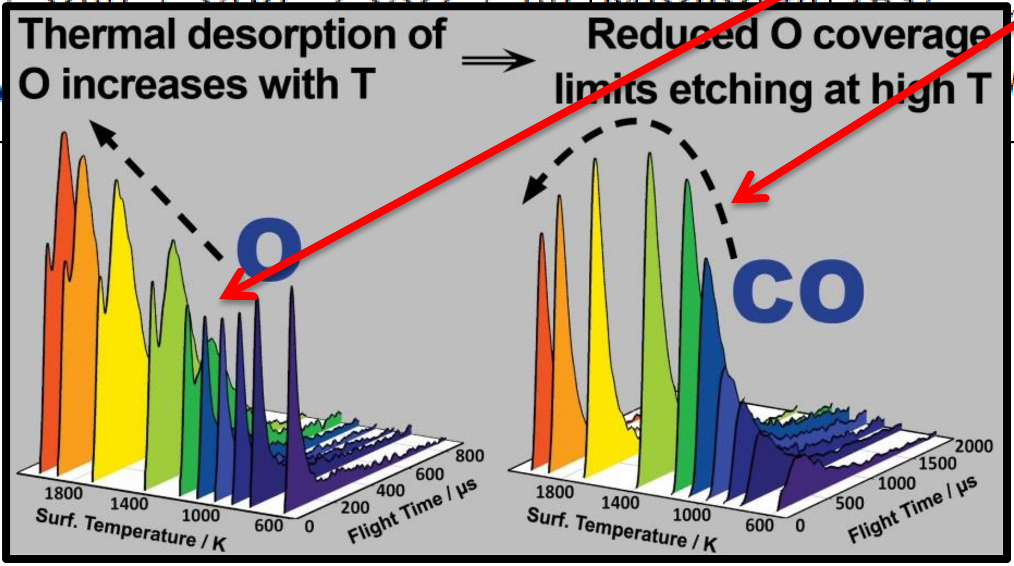


O Atom Desorption Energy:

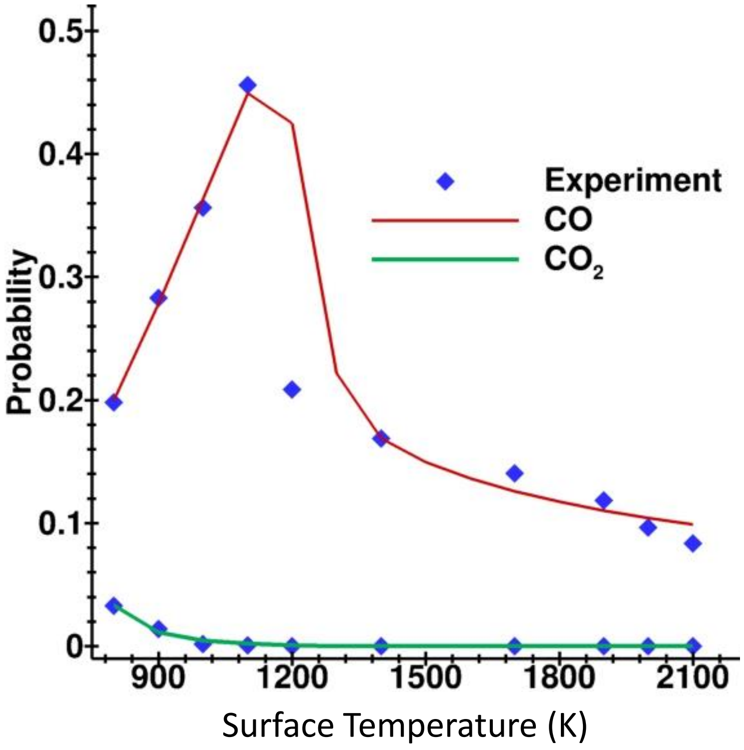
Z-A model: E_d = 45,000 K

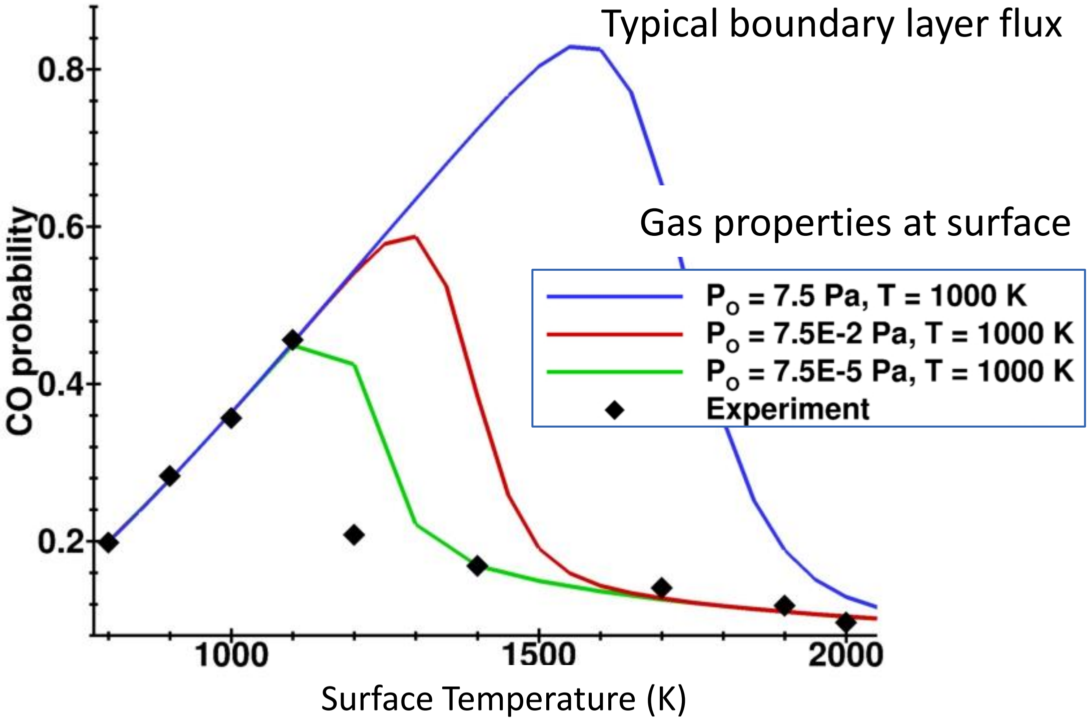
New model: : E_d = 44,277 K !!

New CFD Model Based on Molecular Beam Data

A finite-rate model accounting for surface coverage (similar to Z-A model) does in fact fit the MB data accurately (bottom-left figure). Very interesting.

Surface coverage model is based only on MB data, yet it should be applicable to much higher fluxes (bottom-right figure). Remarkably, these predictions are in reasonable agreement with existing models/literature for boundary layer (high flux) conditions.





Validation with Experiment

In fact, a maximum in CO production was observed experimentally!!

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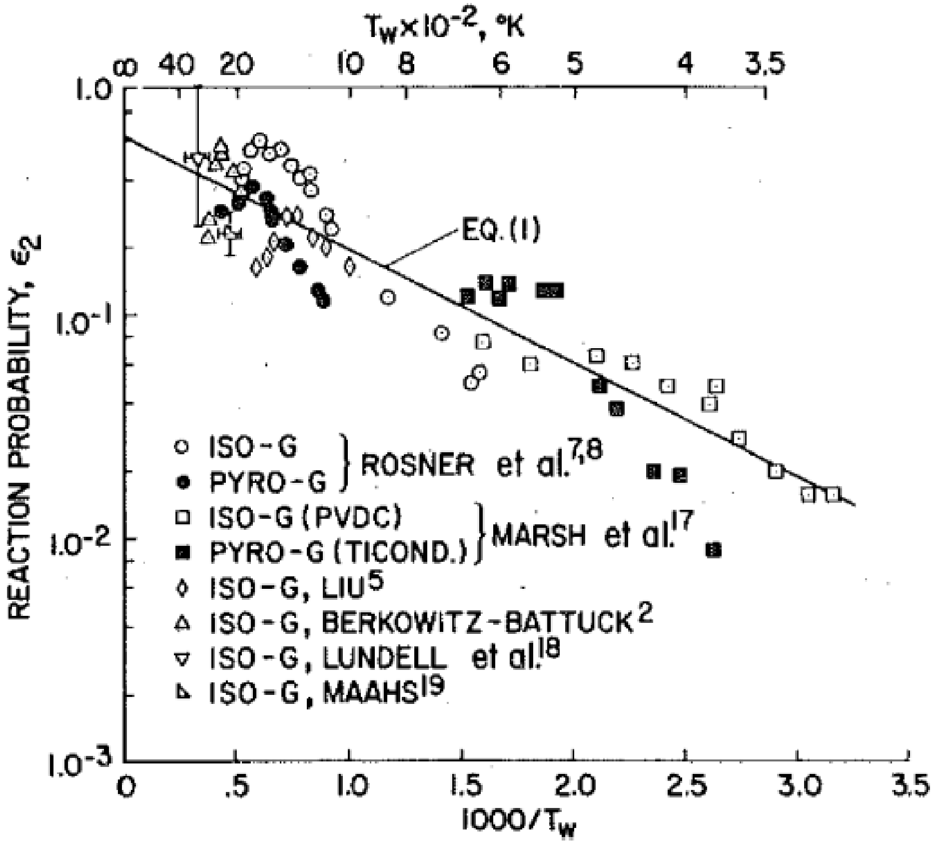

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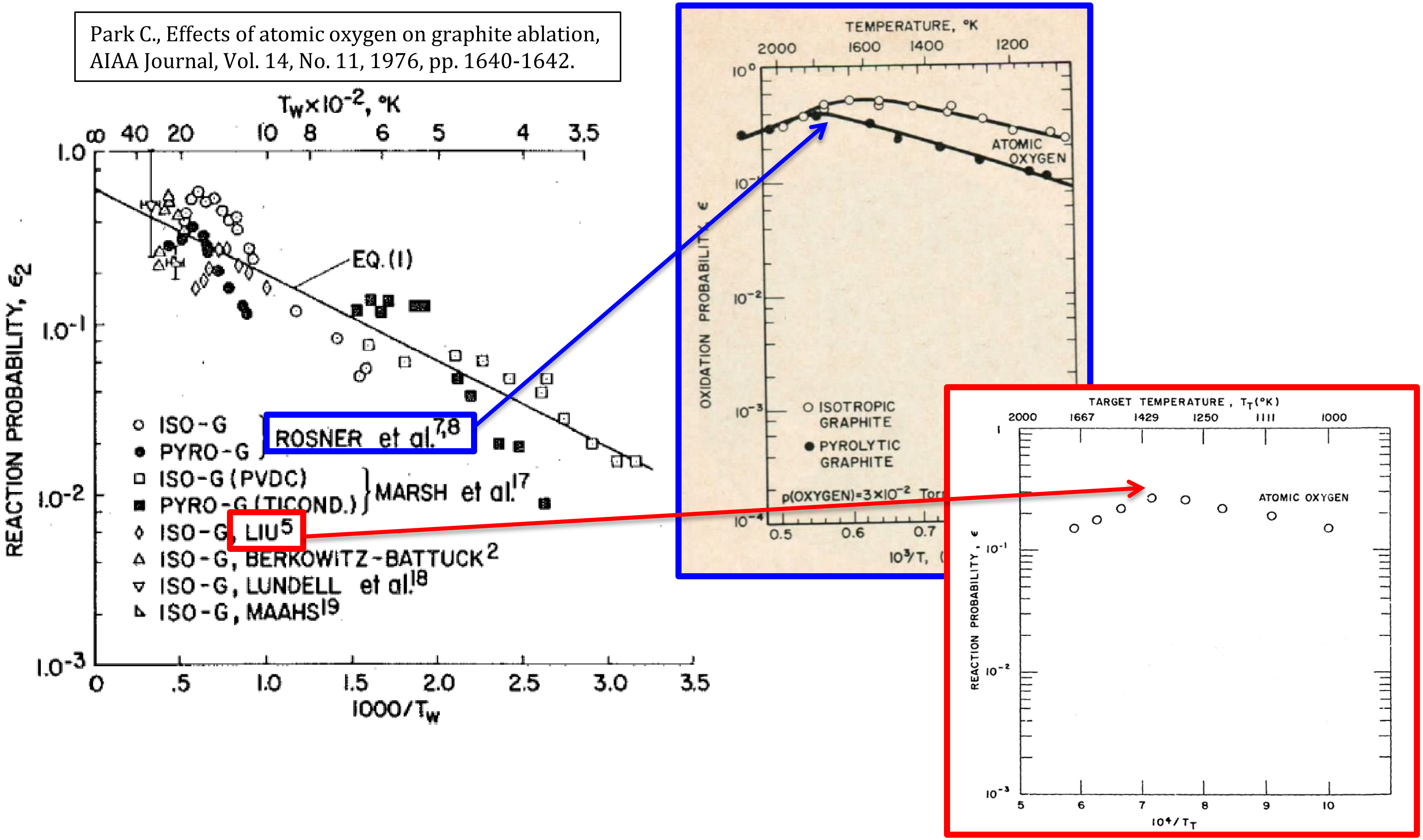

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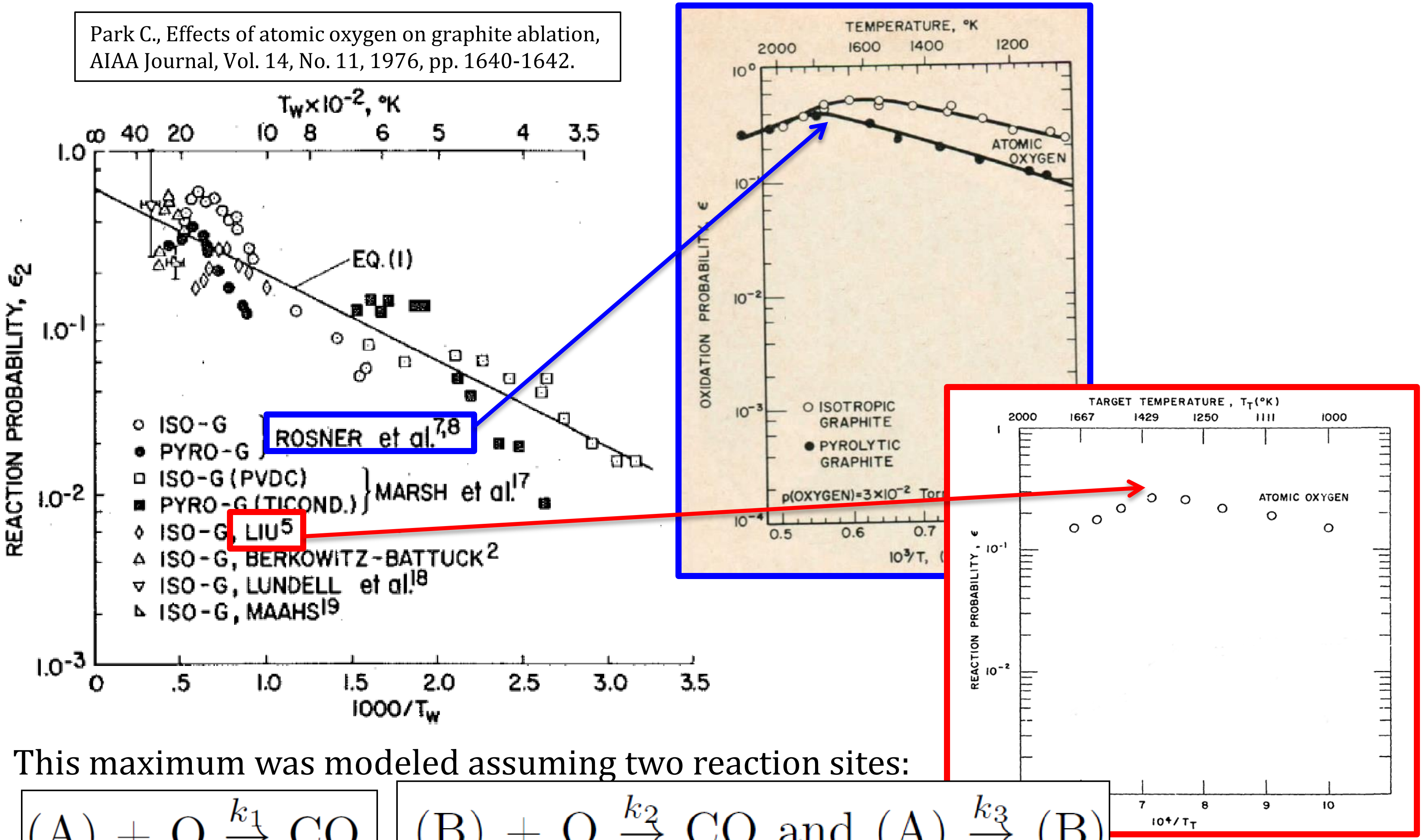
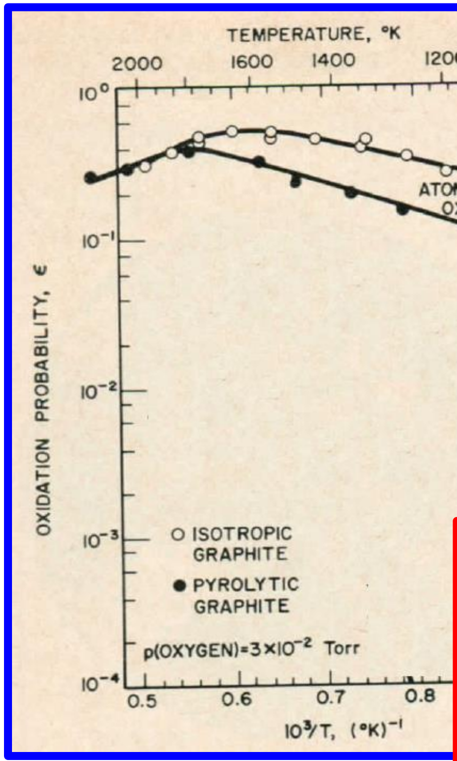


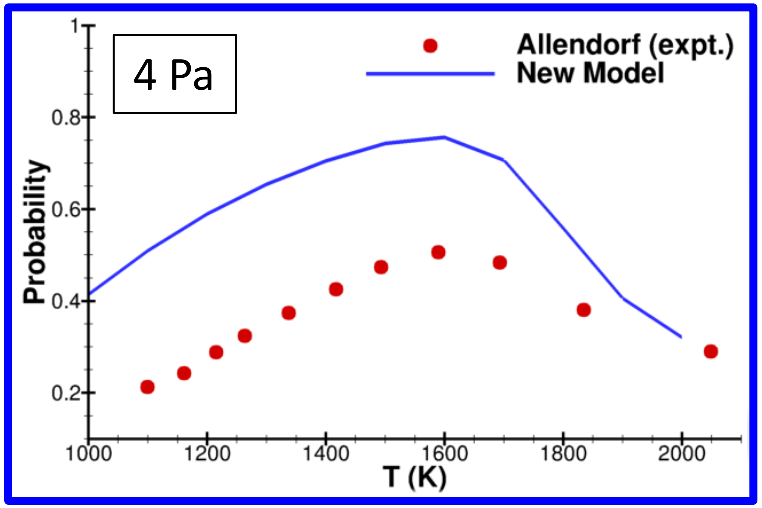
This maximum was modeled assuming two reaction sites:

$$\boxed{(A) + O \overset{k_1}{\to} CO,} \quad \boxed{(B) + O \overset{k_2}{\to} CO \text{ and } (A) \overset{k_3}{\to} (B)}$$

Validation with Experiment

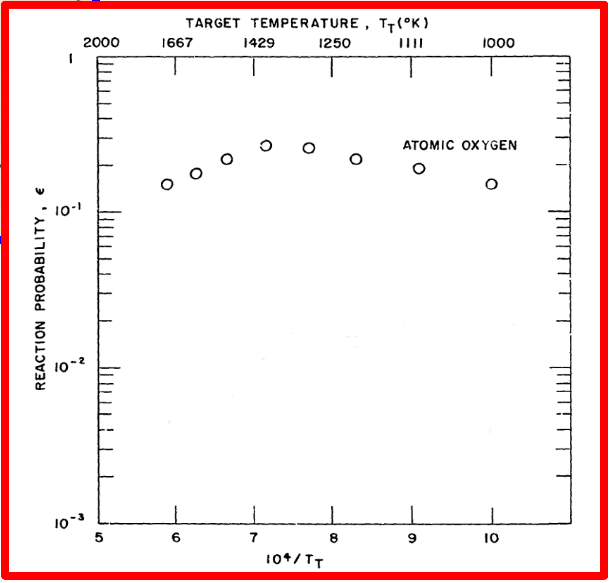
Our new model predicts maximum CO probability at similar $T_{surface}$ seen in both experiments at significantly different pressures (due to surface-coverage modeling).

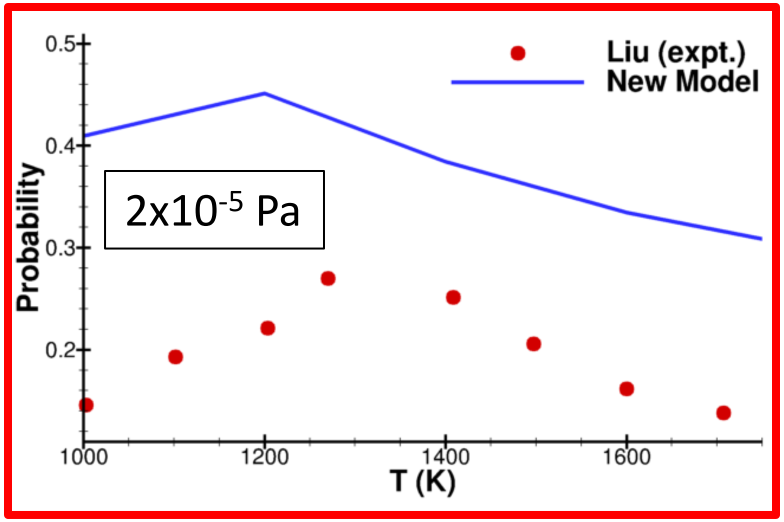




Allendorf, H. D., and D. E. Rosner. "Comparative studies of the attack of pyrolytic and isotropic graphite by atomic and molecular oxygen at high temperatures." *AIAA journal* Vol. 6, No. 4 (1968): 650-654.

Liu, George Nung-Keung, "High Temperature Oxidation of Graphite by a Dissociated Oxygen Beam", MIT-TR-186. MASSACHUSETTS INST OF TECH CAMBRIDGE AEROPHYSICS LAB, 1973.

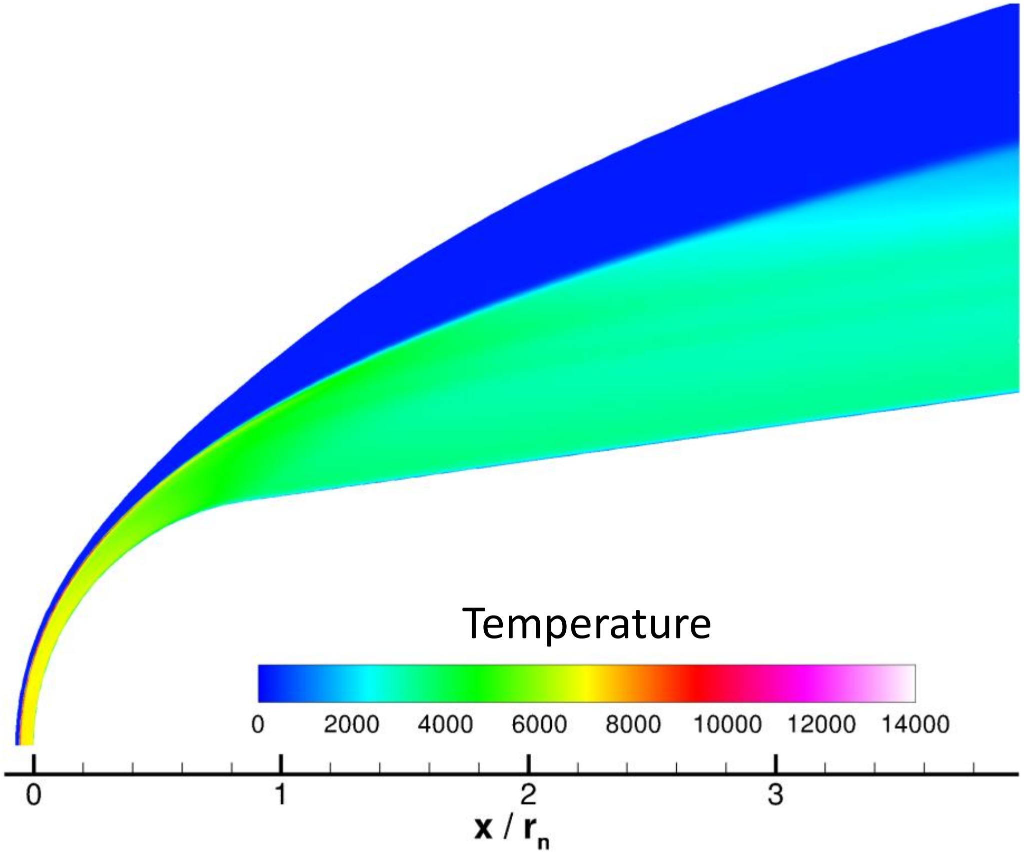




CFD solutions for flow over a sharp leading edge

Simulations performed by Graham V. Candler (University of Minnesota)

- Hypersonic flow over 8^0 cone with 10cm radius leading edge (using the US3D code)
- 5-species reacting air, U = 7km/s, prescribed $T_{surface}$ variation around geometry



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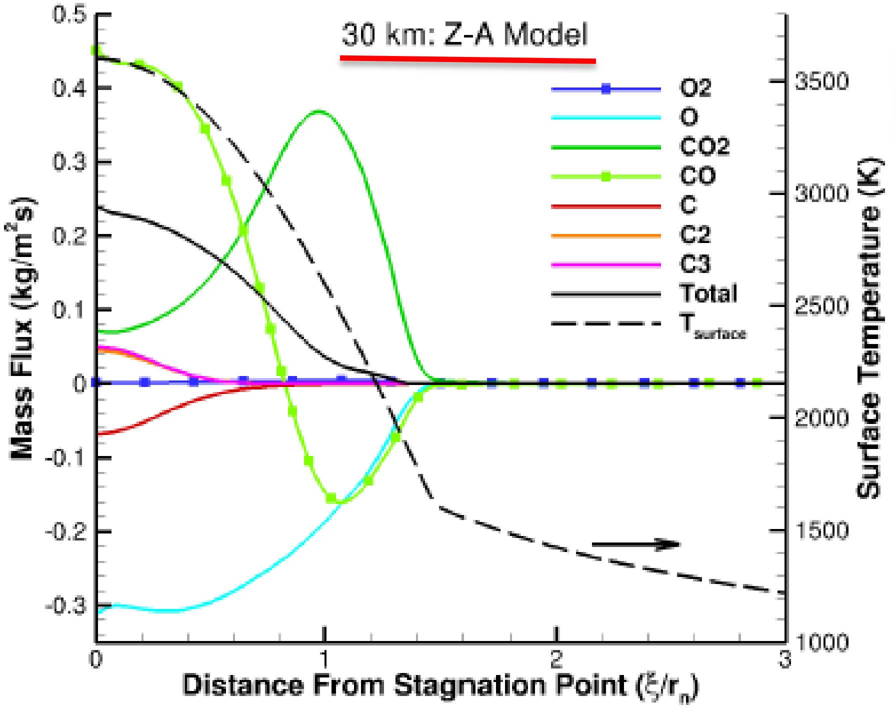

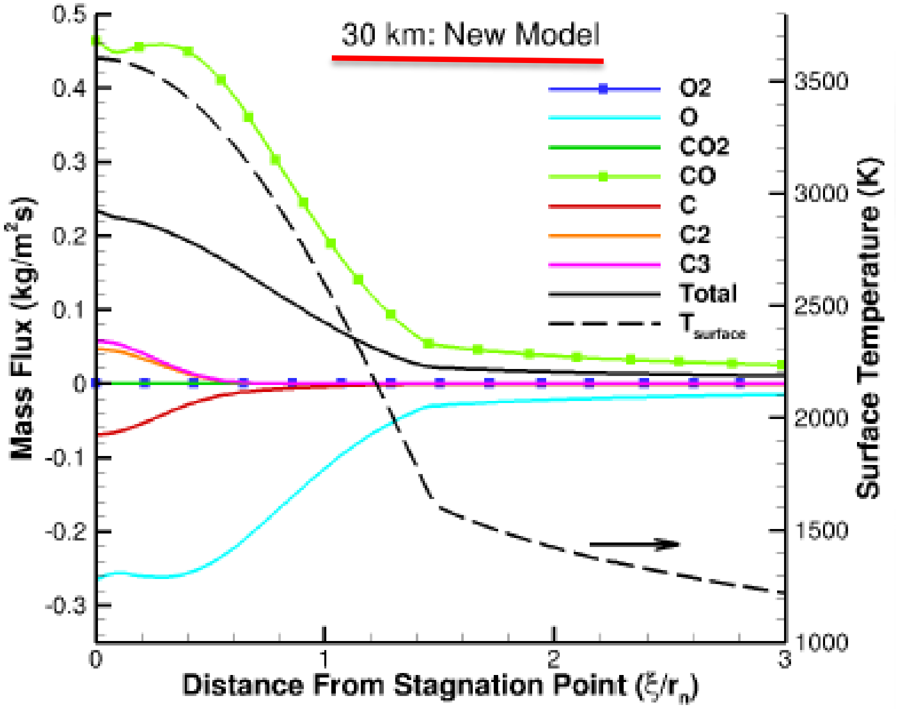

- Total mass loss is similar between models, *species fluxes are completely different*.
- ZA-model: All CO_2 for T<3000K and all CO for T>3000K
- New-model: All CO at any T with negligible CO

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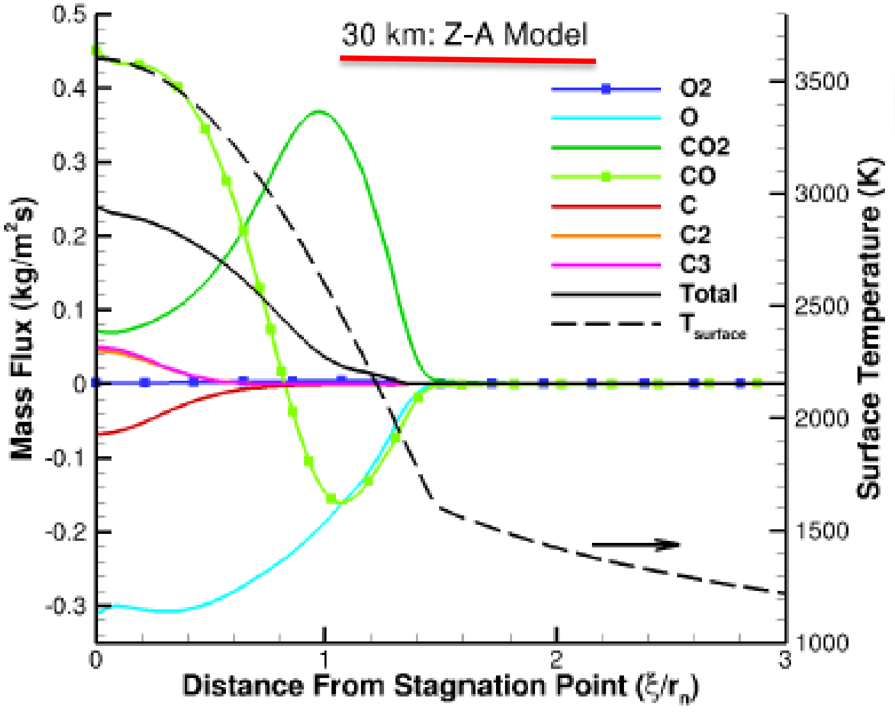

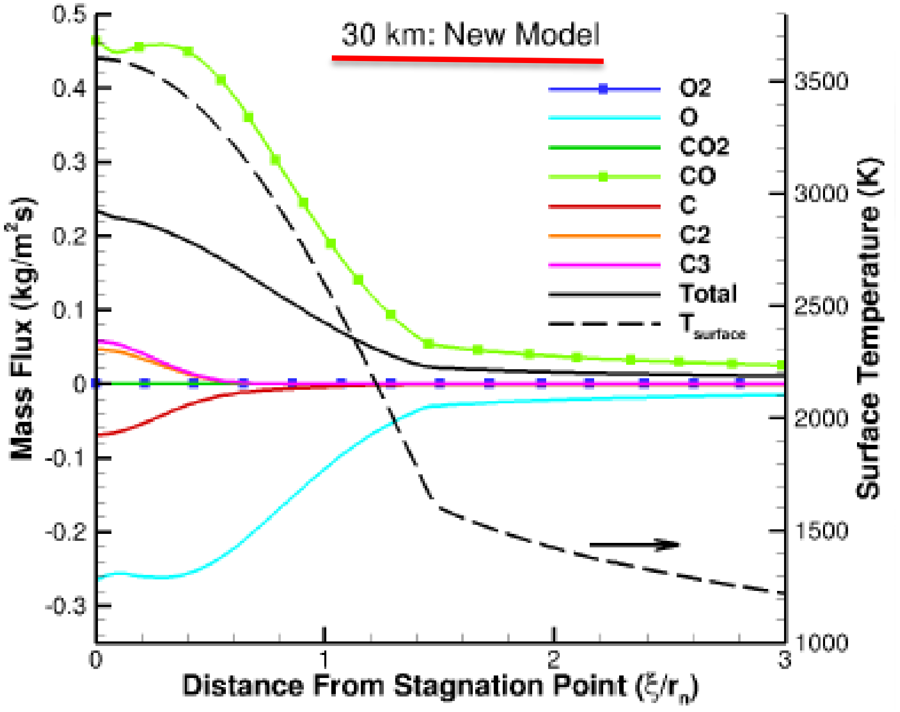

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- ZA-model: All CO_2 for T<3000K and all CO for T>3000K
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- $P_{CO} >> P_{CO2}$ is consistent with recent CFD/Experimental results of Dr. Chris Alba *et al.*:

C.R. Alba, R.B. Greendyke, J. Marschall, Development of a Nonequilibrium Finite-Rate Ablation Model for Radiating Earth Reentry Flows, Journal of Spacecraft and Rockets, 2016, Vol.53, No. 1, pp. 98-120.

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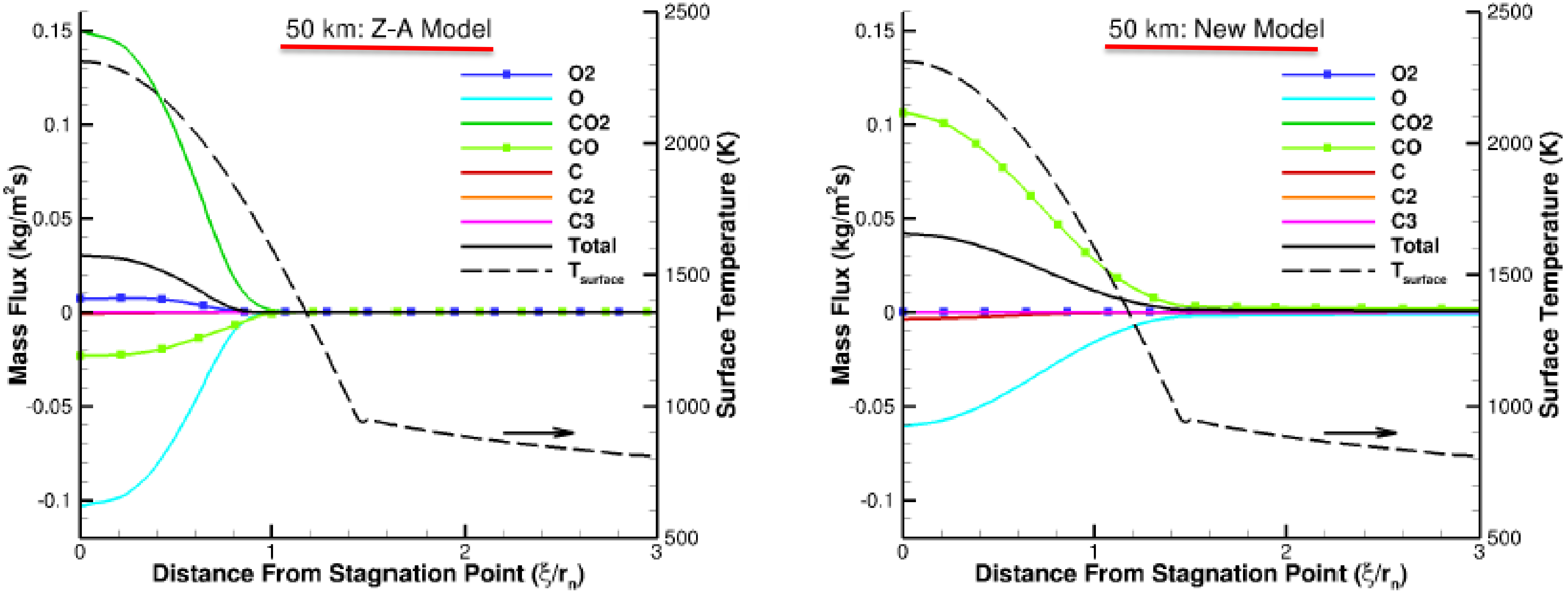

- At higher altitudes (stronger nonequilibrium), the total mass loss is higher with the new model [solid black line].
- Again, the species fluxes are completely different. Notice how the ZA-model predicts CO *adsorption* leading to CO_2 production.

Conclusions

1) Clearly, the same macroscopic result (i.e. surface recession) can be obtained with many different model parameterizations. Too many “knobs” to turn…

2) A new experimental method of creating/validating CFD ablation models is introduced. Molecular Beam data can uniquely determine *individual* mechanisms and rates, in contrast to plasma wind-tunnel measurements where all processes are coupled.

3) The observations of thermal reaction mechanisms and surface coverage dependence make Molecular Beam data directly relevant to hypersonic flows.

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Chemistry and Biochemistry,
Montana State University, Bozeman, MT

FA9550-10-1-0563: AFOSR MURI FY2010
Doctoral Dissertation Fellowship, UofMinnesota

New AFOSR Grant (starting in Fall 2016)

“Nonequilibrium Gas-Surface Interactions at High Temperature”

Aerothermodynamics (Dr. Ivett Leyva)

Aerospace Materials for Extreme Environments (Dr. Ali Sayir)

Tom Schwartzentruber – Minnesota
Graham Candler – Minnesota
Tim Minton – Montana State
Erica Corral – Arizona
John Perepezko – Wisconsin

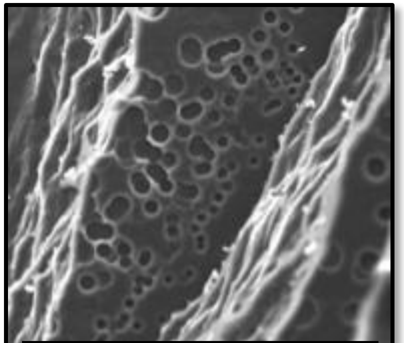
Brief Overview:

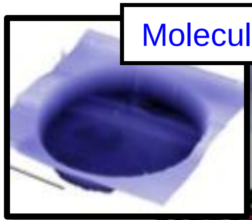
- Further oxygen-carbon molecular beam experiments
- Finalize/validate oxygen-carbon CFD model
- Molecular beam and torch testing of ceramic (SiC-based) TPS
- CFD modeling of ceramic (SiC-based) TPS, validated models
- Fabrication of new TPS materials and coatings for testing in various facilities

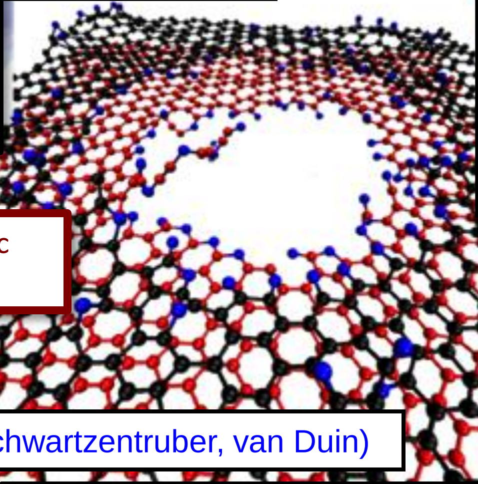
BACKUP SLIDES

Last Year: A general mechanism for carbon oxidation

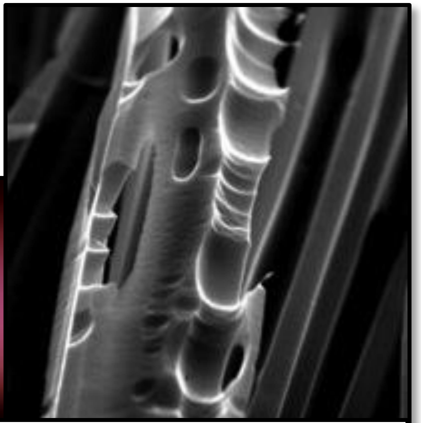
- “Etch pits” observed across a range of experimental facilities and carbon materials (HOPG to Fiber Preform)
- Below the microstructure scale, carbon atoms removed from graphitic ‘edges’; a general mechanism

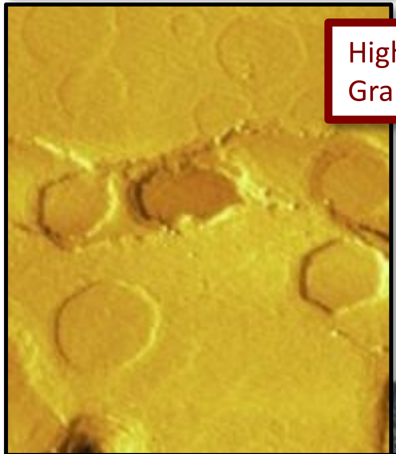

TGA Furnace (Corral)


Molecular Beam (Minton)


Simulations (Schwartzentruber, van Duin)

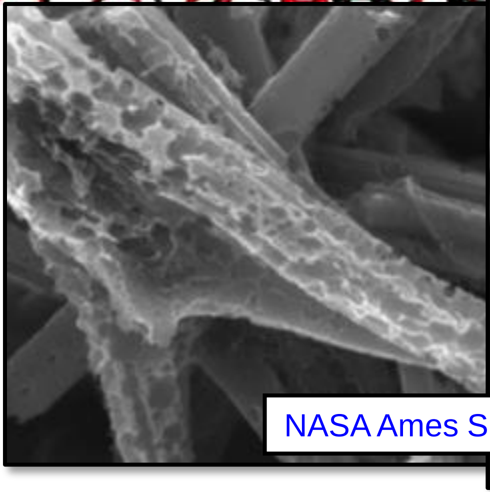

Plasmatron (von Karman Institute)




Highly Oriented Pyrolytic Graphite (HOPG)

Diffusion Reactor (Marschall)


Carbon Fiber Pre-form

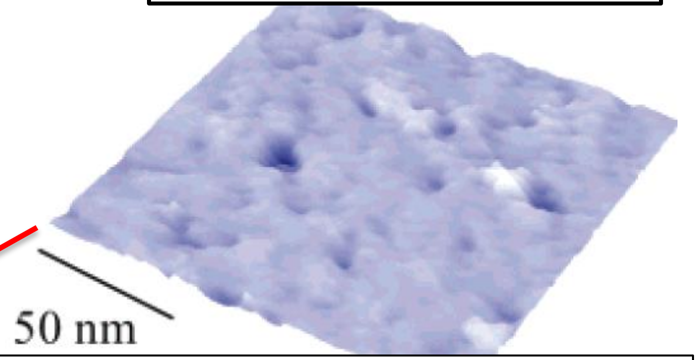



NASA Ames Sidearm Reactor (Mansour, Panerai, et al.)

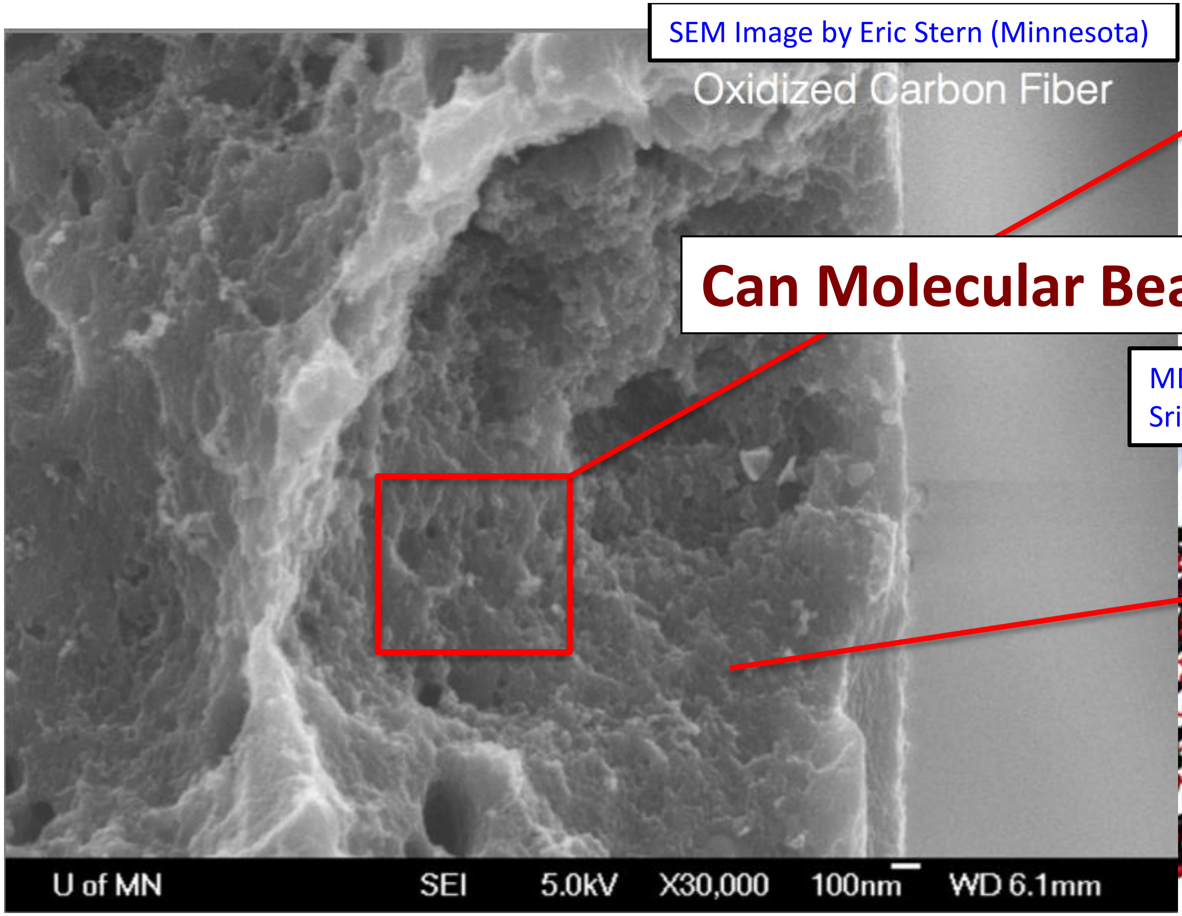
Relevant Length Scales

- Molecular Dynamics domain is the size of ~1 pixel on image below…
- Carbon surfaces used in Molecular Beam experiments are representative of surface structure well-above the atomic scale.

Nicholson, Minton, Sibener, *J. Phys. Chem. B* 2005, 109, 8476-8480

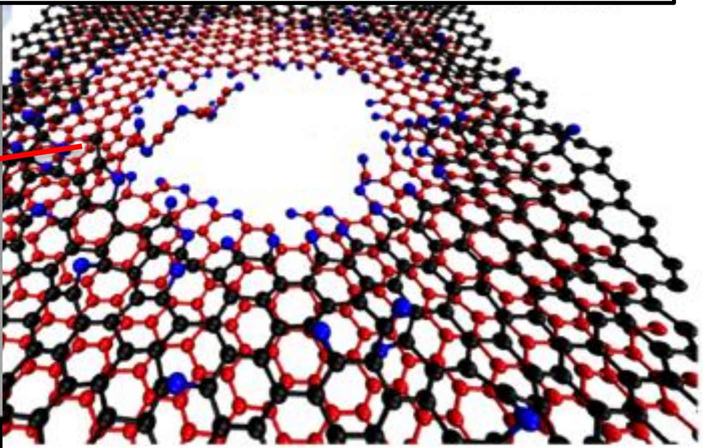


SEM Image by Eric Stern (Minnesota)



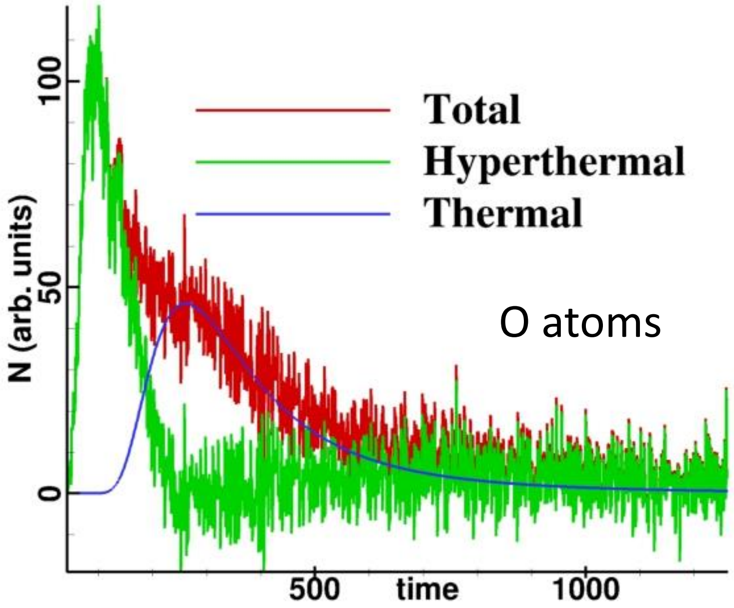
Can Molecular Beam data be used directly?

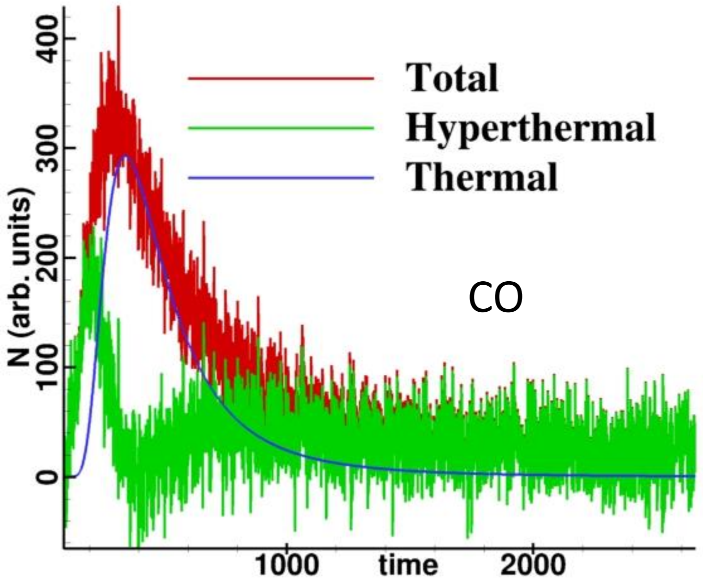
MD Simulations: Poovathingal, Schwartzentruber, Srinivasan, van Duin, *J. Phys. Chem. A*, 2013.

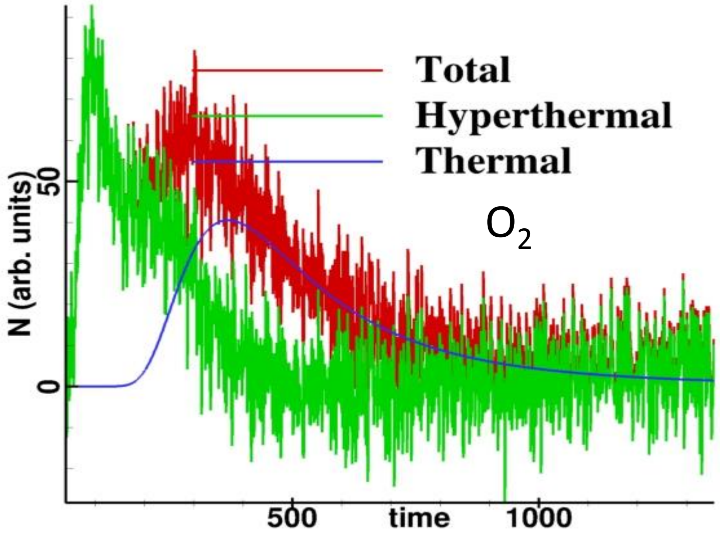


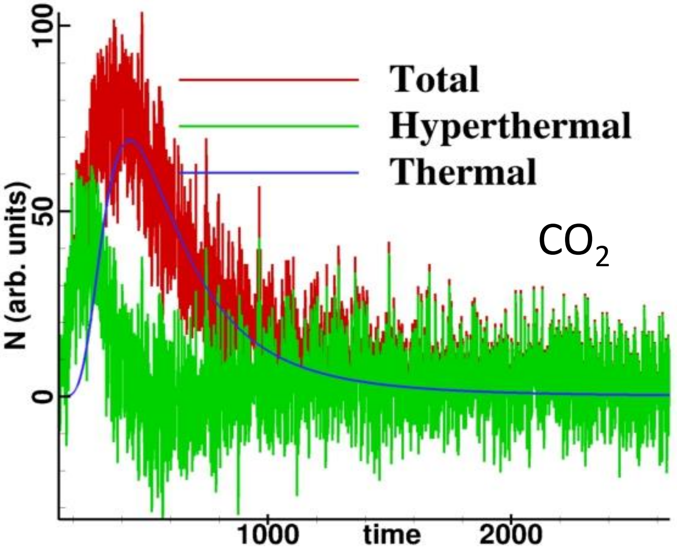
Molecular Beam Results: Time-of-Flight (TOF) Distributions

- TOF distributions are accurately fit with a Maxwell-Boltzmann distribution corresponding to $T_{surface}$ (thermal scattering is dominant, especially for CO/CO_2)







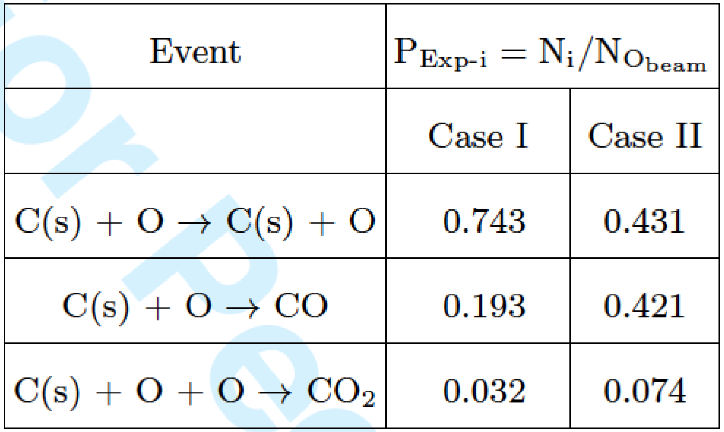


Reaction Probabilities from Molecular Beam Data

Molecular Beam scattering occurs under steady-state conditions.

We therefore assume that the amount of oxygen in the beam flux is equal to the amount of oxygen observed to scatter from the surface (O, O_2, CO, CO_2).

Thus, we can readily calculate probabilities of forming each reaction product.



Event	$P_{\text{Exp-i}} = N_i / N_{O_{\text{beam}}}$	
	Case I	Case II
$C(s) + O \rightarrow C(s) + O$	0.743	0.431
$C(s) + O \rightarrow CO$	0.193	0.421
$C(s) + O + O \rightarrow CO_2$	0.032	0.074

Case 1: Keep hyperthermal O

Case 2: Ignore hyperthermal O

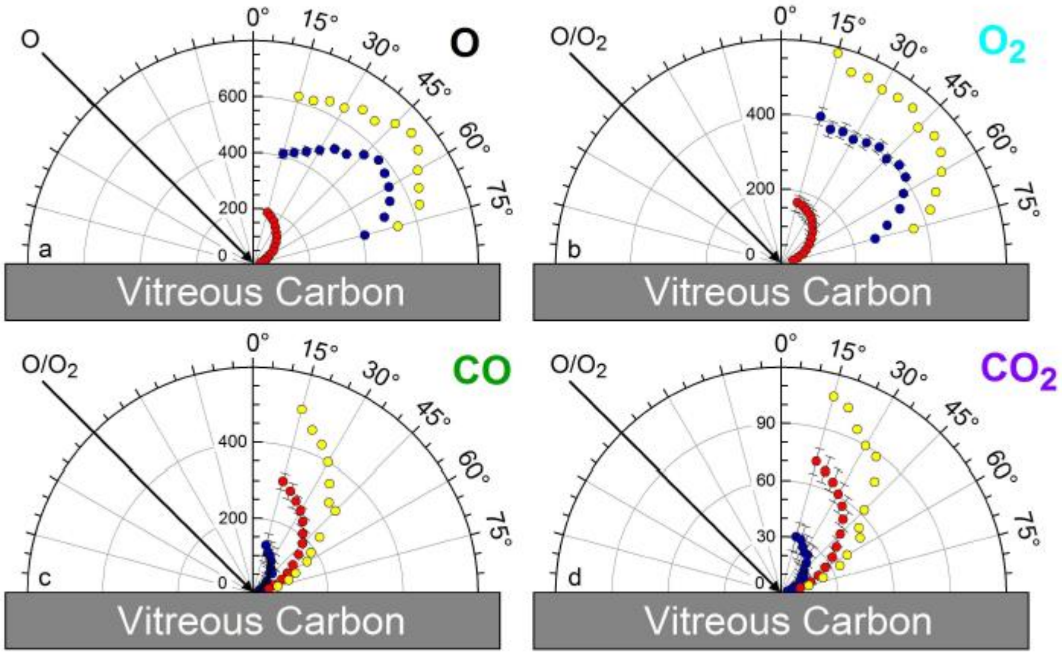
Regardless of small assumptions:

Mainly CO production (little CO_2).

Reaction prob. is high (> 0.1).

O_2 is essentially non-reactive.

Tsurface = 800 K



Reactant flux (N_i): thermal component (red), hyperthermal component (blue), total (yellow).