A DSMC Surface Chemistry Model for Carbon-Based Ablators

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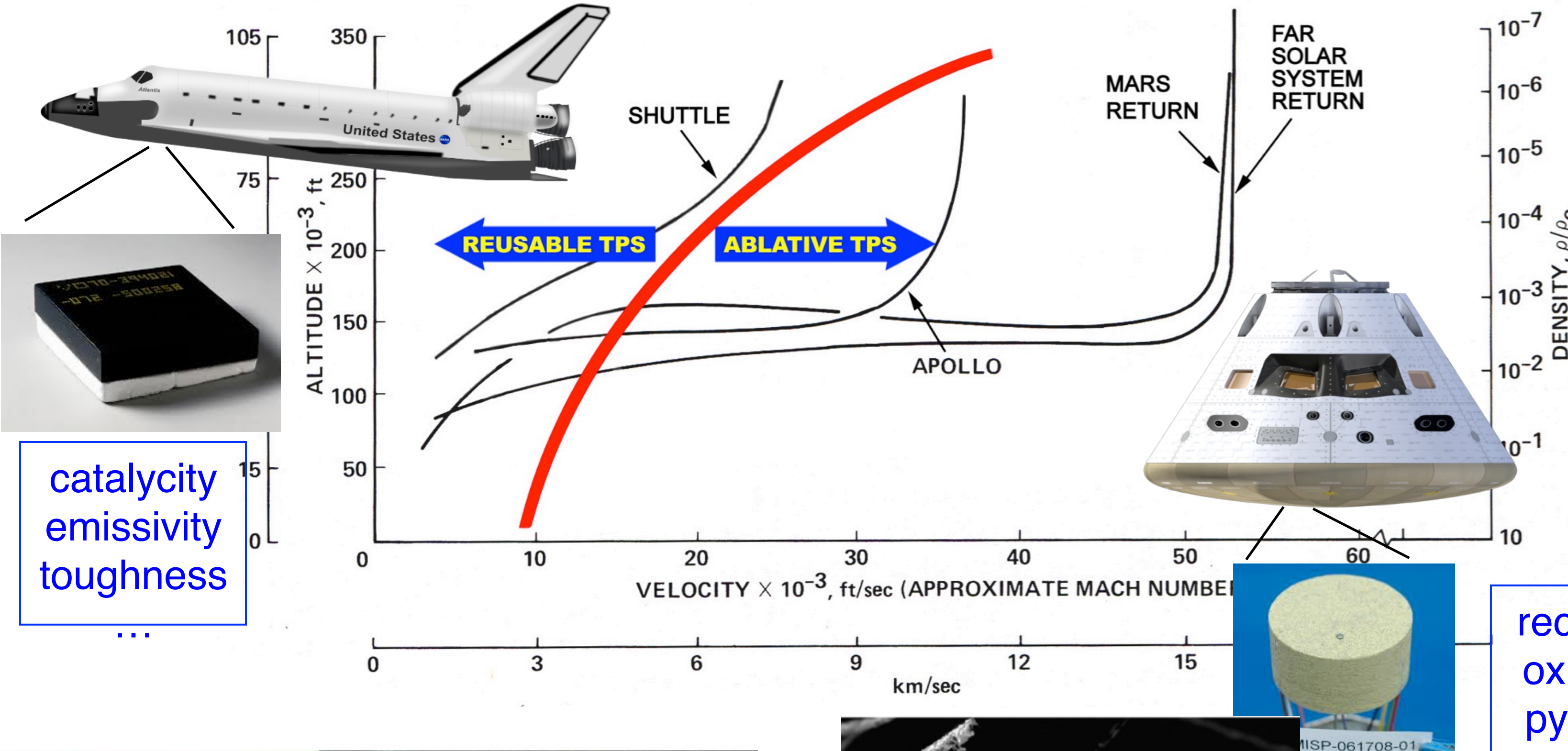
Outline

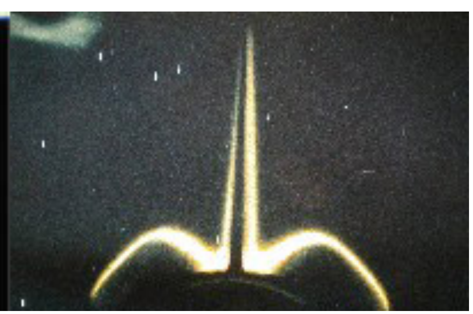
1. Context/Motivation
2. Surface scattering experiments (Murray-Minton)
3. DSMC surface scattering simulation
4. Existing models (Park, ZA, Alba, Poovathingal-Schwartzentruber-Murray-Minton)
5. Transformation of finite-rates to DSMC Surface Reaction Probabilities
6. Comparison of simulation results from different models to experiments
7. Conclusions

Context: Planetary Entry

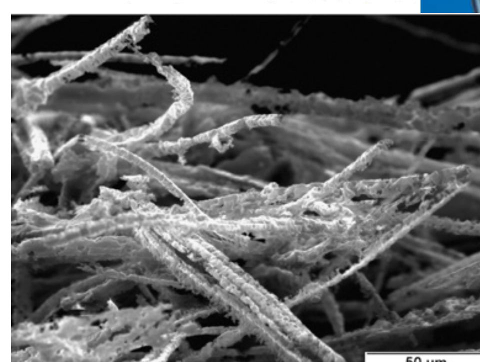


catalycity
emissivity
toughness
…

recession
oxidation
pyrolysis
…

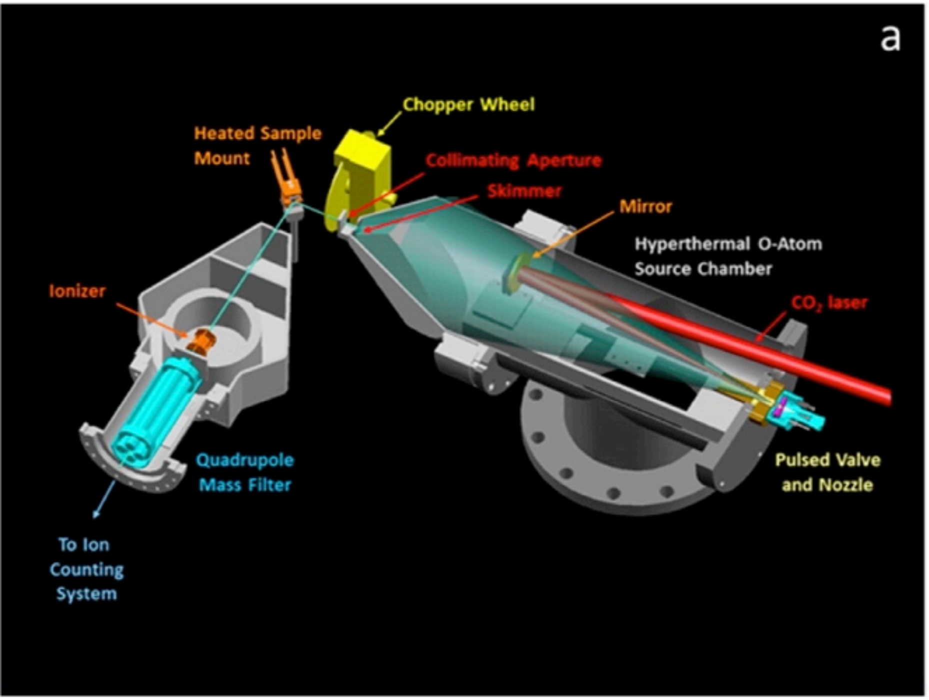


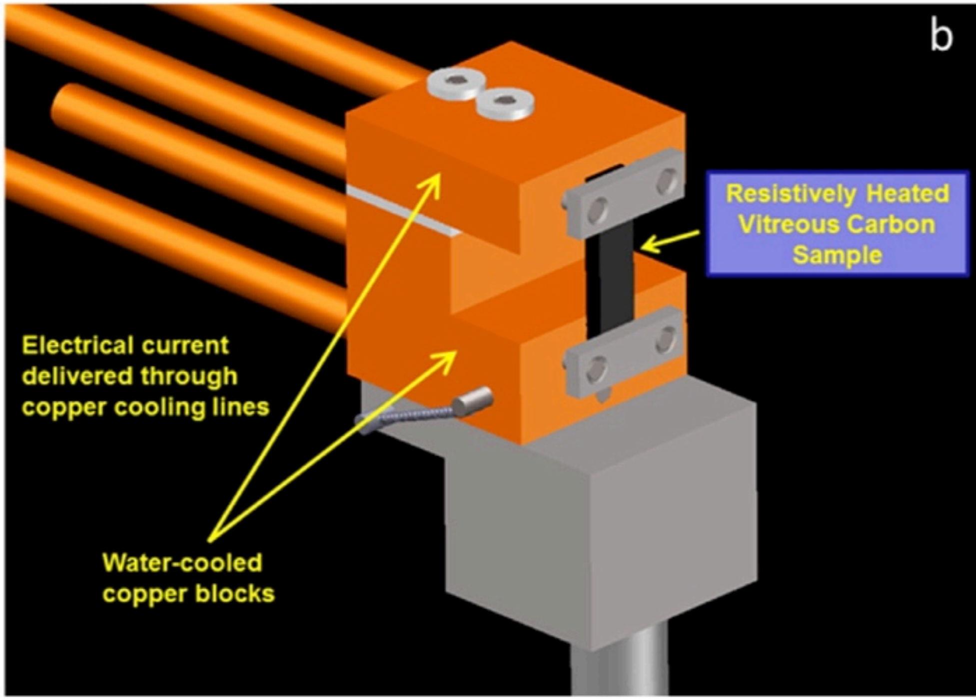
LEO: O at ~5eV



Courtesy: F. Panerai

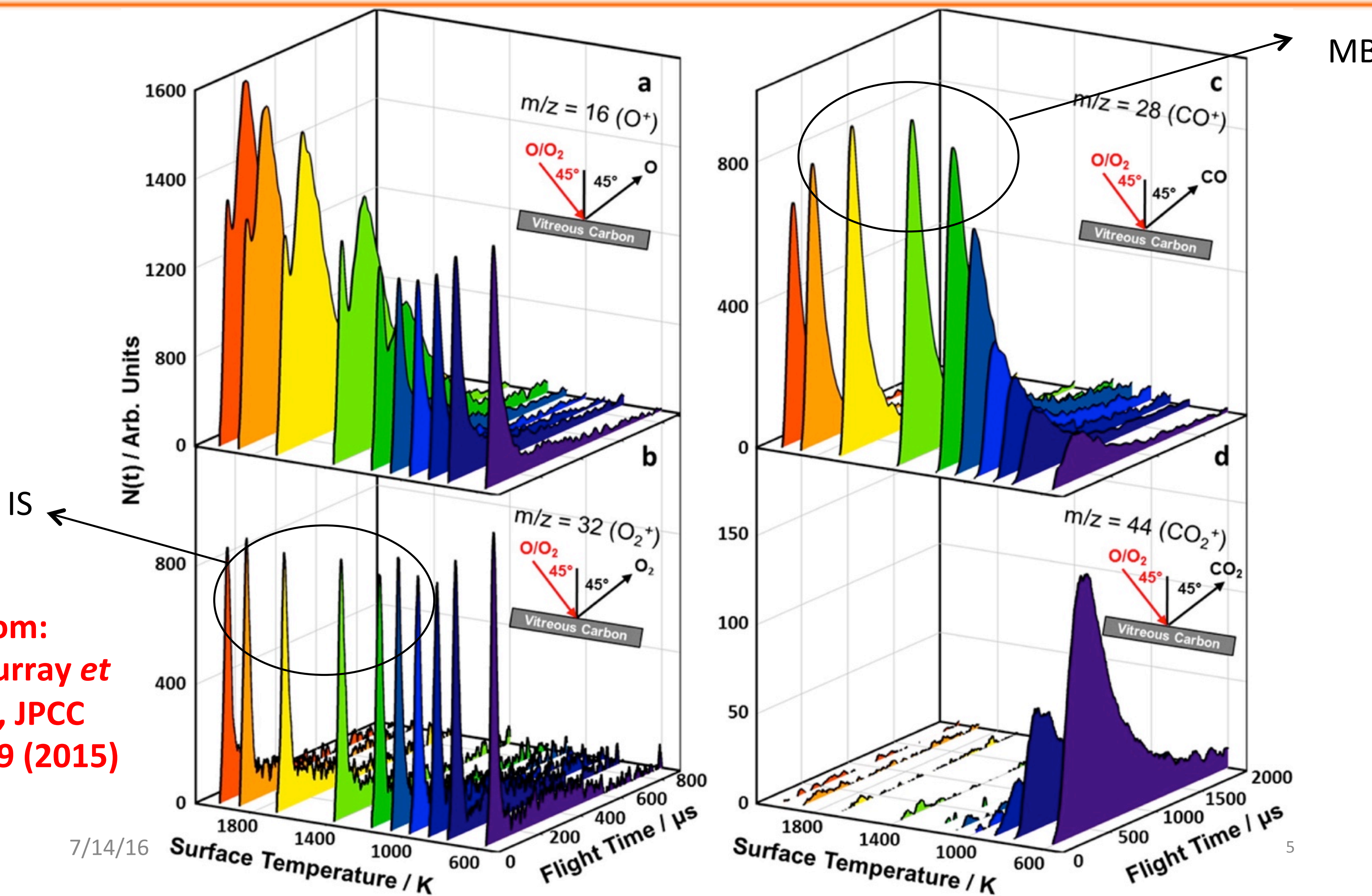
Experimental setup from Murray-Minton[5]





From: Murray *et al.*, JPCC 119 (2015) [5]

Experimental results from Murray-Minton[5]



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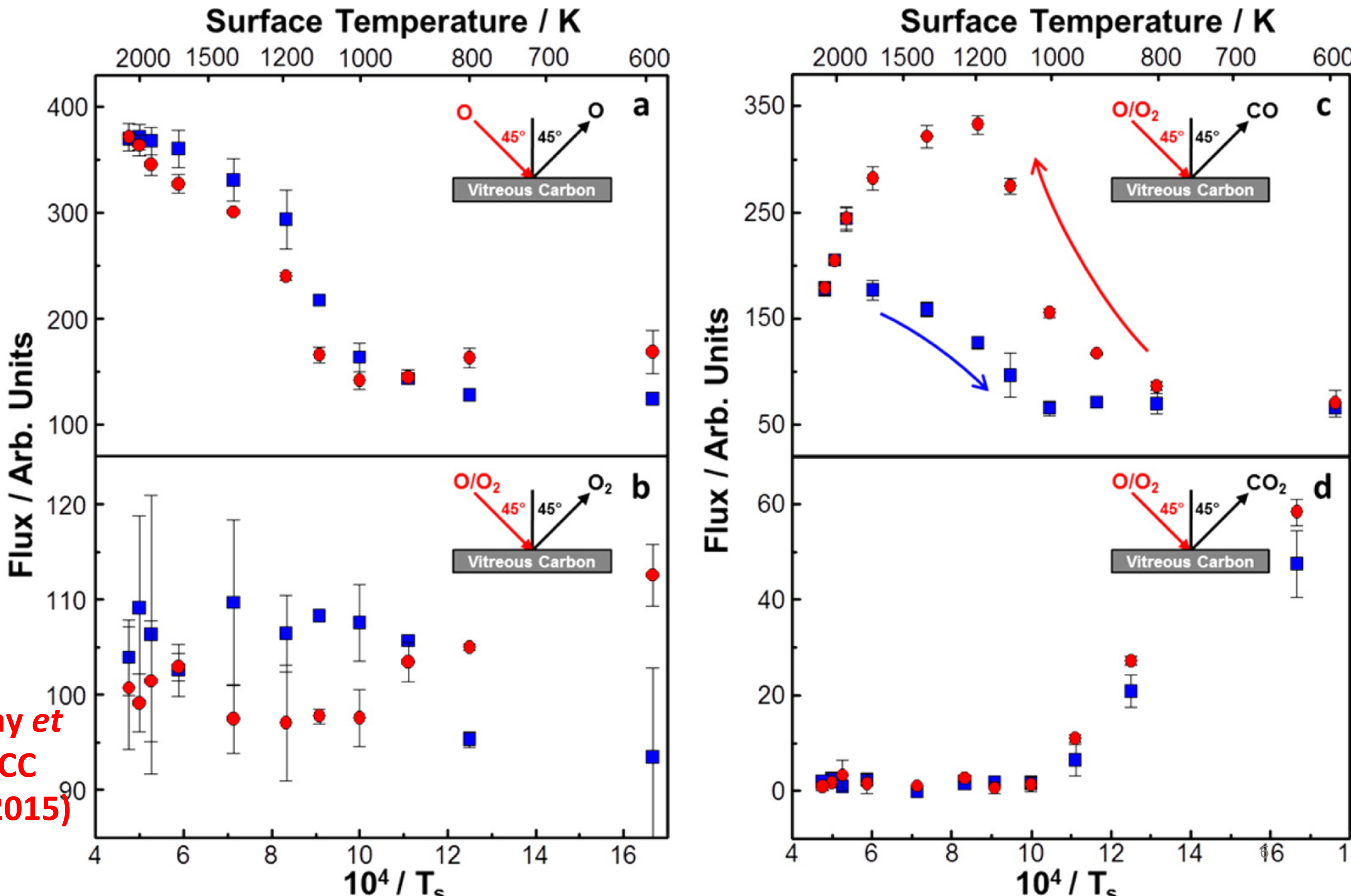

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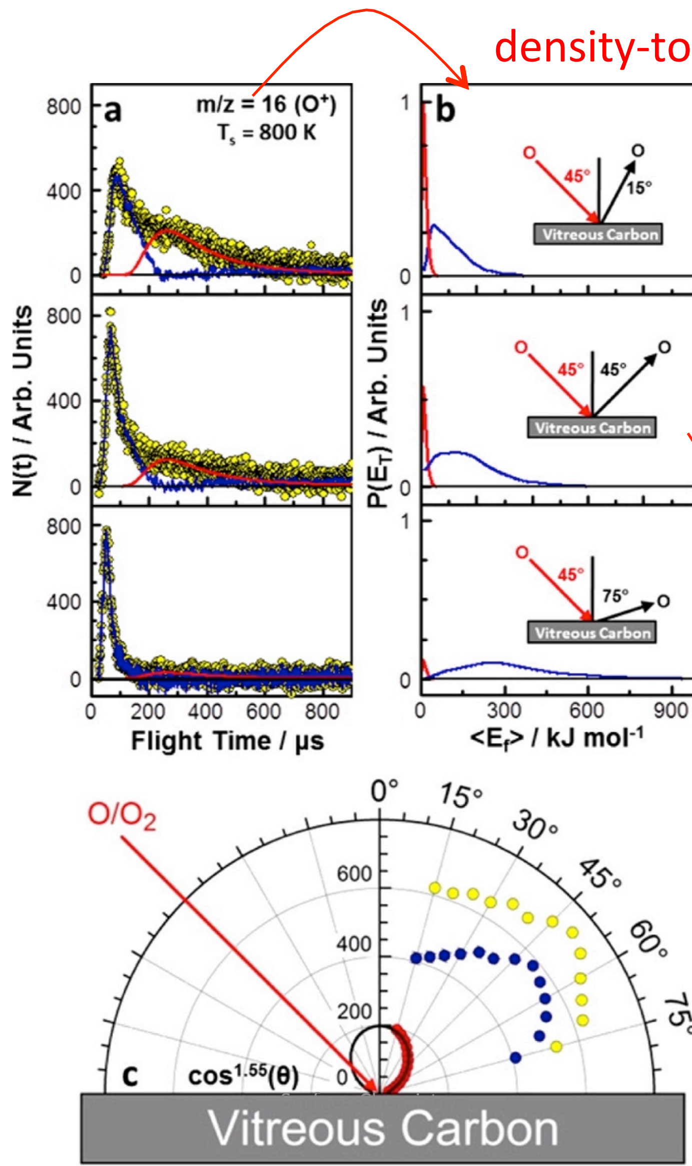
Experimental results from Murray-Minton[5]

density-to-flux conversion

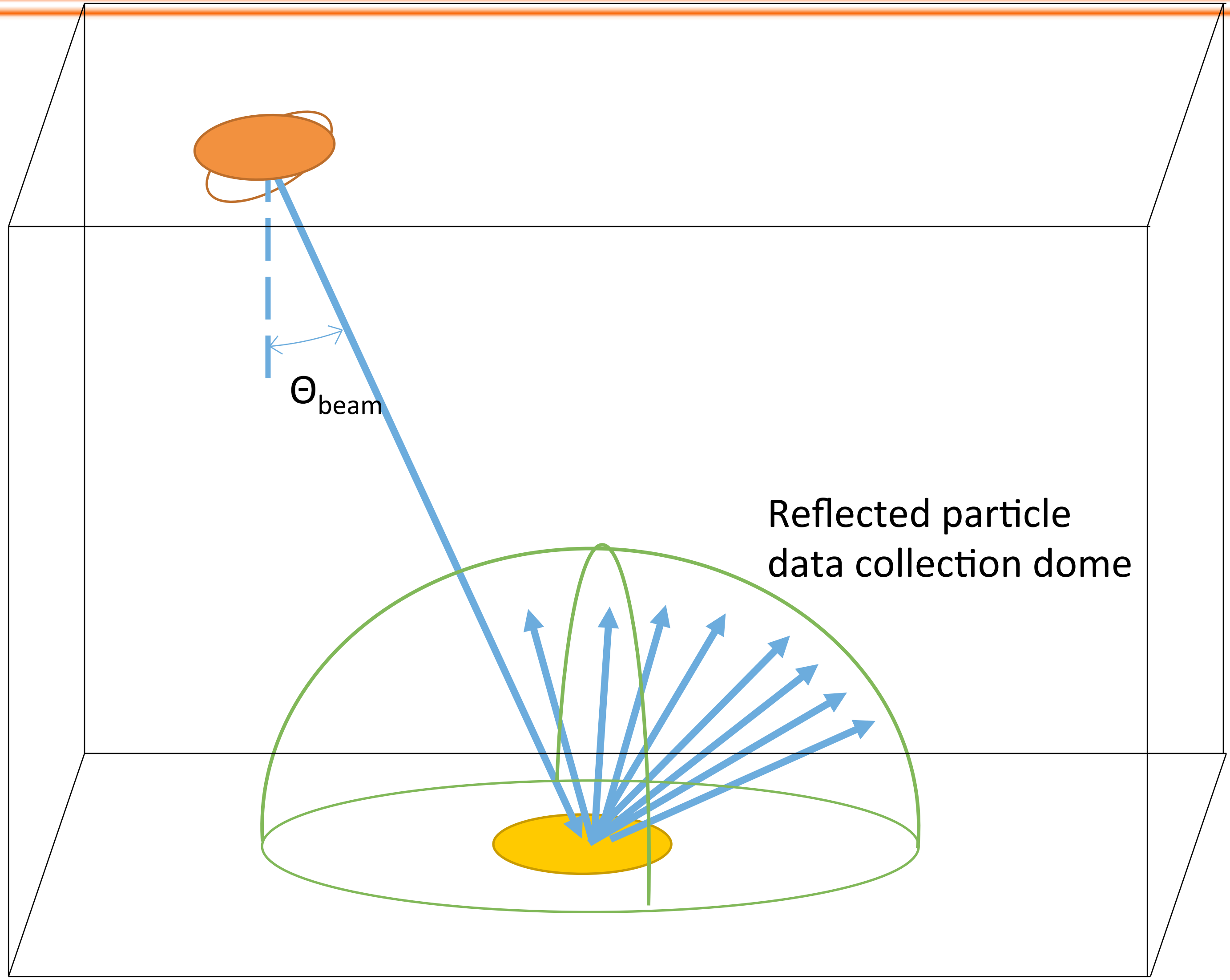


P(E_T) integrated

FLUX-INTEGRATED ANGULAR DISTRIBUTION

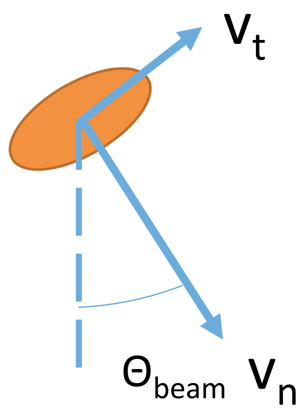
From: Murray *et al.*, JPCC 119 (2015) [5]

DSMC setup

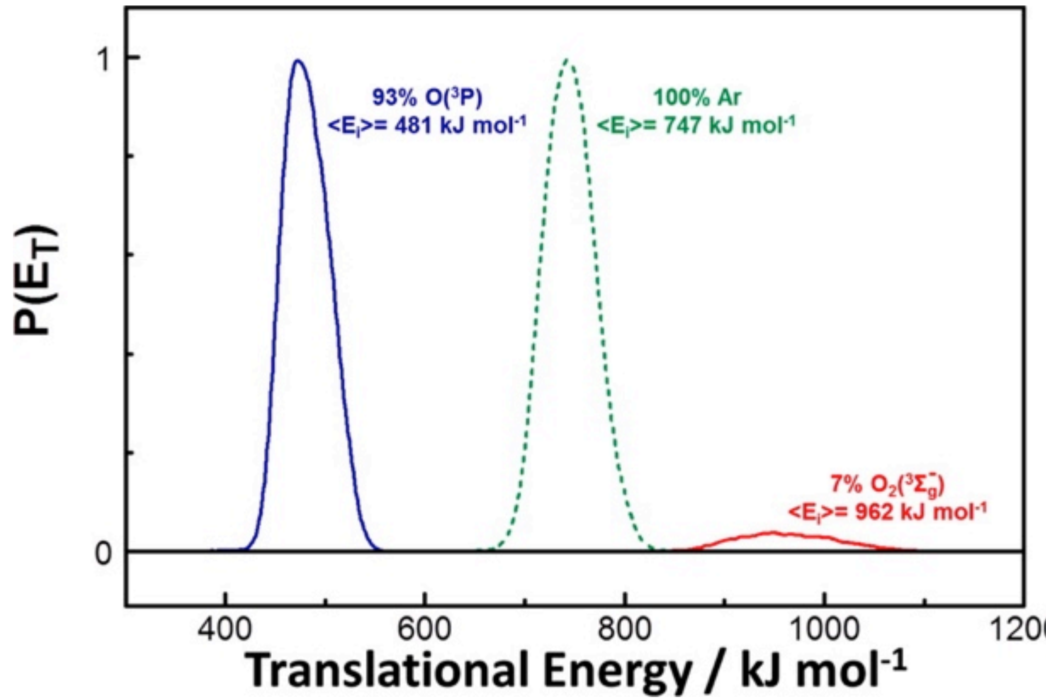


DSMC Setup - Beam

Velocity of the particles from the beam



- V_n is drawn from the distribution based on the experiment.
- V_t and V_{out} are decided based on the beam spread.
- V_x, V_y, and V_z is then calculated from geometry.



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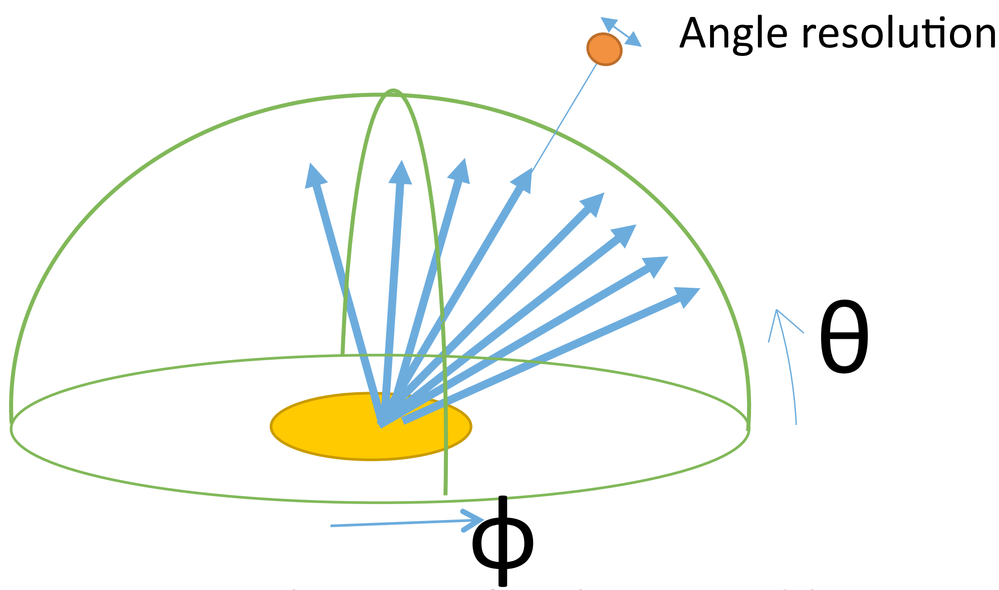
DSMC Setup - Beam

Reflected particle data collection

- Information of all the particles leaving the dome is not recorded.
- An angle resolution is specified and the information of the particles leaving inside the solid angle is only recorded
- Count, Energy distribution (EDF) and Time-Of-Flight (TOF) of each species is recorded at specified angles - θ and ϕ



Modeling Considerations

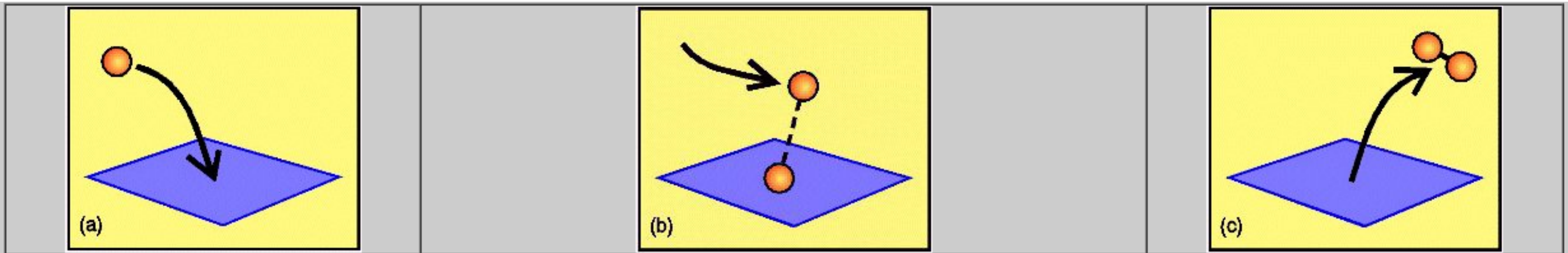
- The composition of the beam is similar to that of the experiment
  93% O, 7%O_2 by volume.

- Once the surface is saturated, all the atoms are scattered impulsively without getting adsorbed.

- All the experimental results are collected at steady state. Steady state is attained when
  1. The surface gets saturated
  2. Rate of adsorption = Rate of desorption + Rate of product formation

Surface reactions

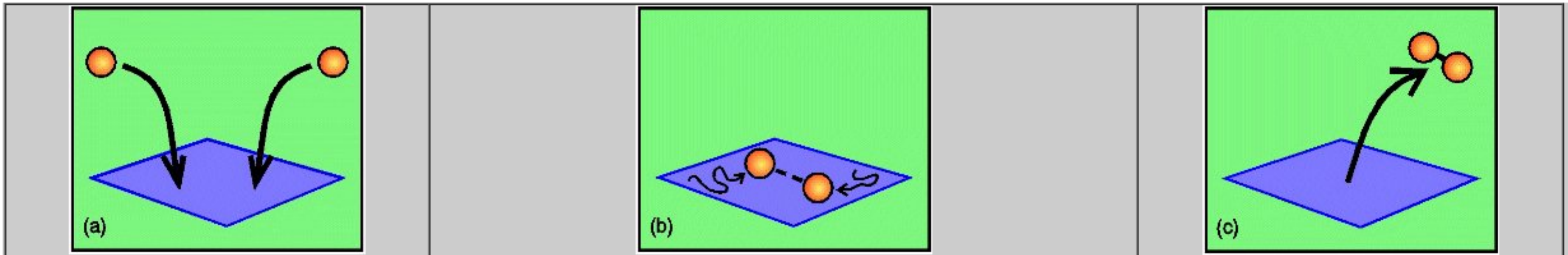
Eley- Rideal (ER) mechanism – A(s) + B -> AB + (s)



An atom adsorbs onto the surface.	Another atom passes by which interacts with the one on the surface.	A molecule is formed which desorbs.

From: UCL Center for Cosmic Chemistry and Physics

Langmuir-Hinshelwood (LH) mechanism – A(s) + B(s) -> AB + 2(s)



Two atoms adsorb onto the surface.	They diffuse across the surface and interact when they are close.	A molecule is formed which desorbs.

Existing models

Park (1976) [1]

- First air-carbon ablation model

Zhluktov-Abe (ZA) (1999) [2]

- Finite-rate model with 7 forward and reverse rates that are thermodynamically constrained for each process.

Alba (2015) [3]

- Modified ZA model: same reactions, 3 rates are different
- Based on high-speed flow experiments, measured CN radiation emission

Poovathingal-Schwartzentruber-Murray-Minton (PSMM) (2016) [4]

- Based on Murray-Minton's hyperthermal O/O_2 beam experiments [5]

Modeled Reactions

	Reaction	Type	Z-A/Alba	PSMM	This work
1f	$A + (s) \rightarrow A_s$	Adsorption	x	x	x
1b	$O_s \rightarrow O + (s)$	Desorption	x	x	x
2f	$2O_s \rightarrow O_2 + 2(s)$	LH	x		
2b	$O_2 + 2(s) \rightarrow 2O_s$	Dissociative Ads	x		
3f	$O_2 + (s) \rightarrow O + O_s$	Dissociative Ads	x		
3b	$O + O_s \rightarrow O_2 + (s)$	ER	x		
4f	$CO + O_s \rightarrow CO_2 + (s)$	ER	x		
4b	$CO_2 + s \rightarrow CO + O_s$	Dissociative Ads	x		
5f	$O_s + C_b \rightarrow CO + (s)$	LH	x		x
5b	$CO + s \rightarrow O_s + C_b$	Dissociative Ads	x		
6f	$O + O_s + C_b \rightarrow CO_2 + (s)$	ER	x	x	
6b	$CO_2 + (s) \rightarrow O + O_s + C_b$	Dissociative Ads	x		
7f	$2O_s + C_b \rightarrow CO_2 + 2(s)$	LH	x		x
7b	$CO_2 + 2(s) \rightarrow 2O_s + C_b$	Dissociative Ads	x		
8	$O + C_b + (s) \rightarrow CO + (s)$	ER		x	
9	$O + O_s + C_b \rightarrow CO + O_s$	ER		x	

Modeled Reactions

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1f	$A + (s) \rightarrow A_s$	Adsorption	x	x	x
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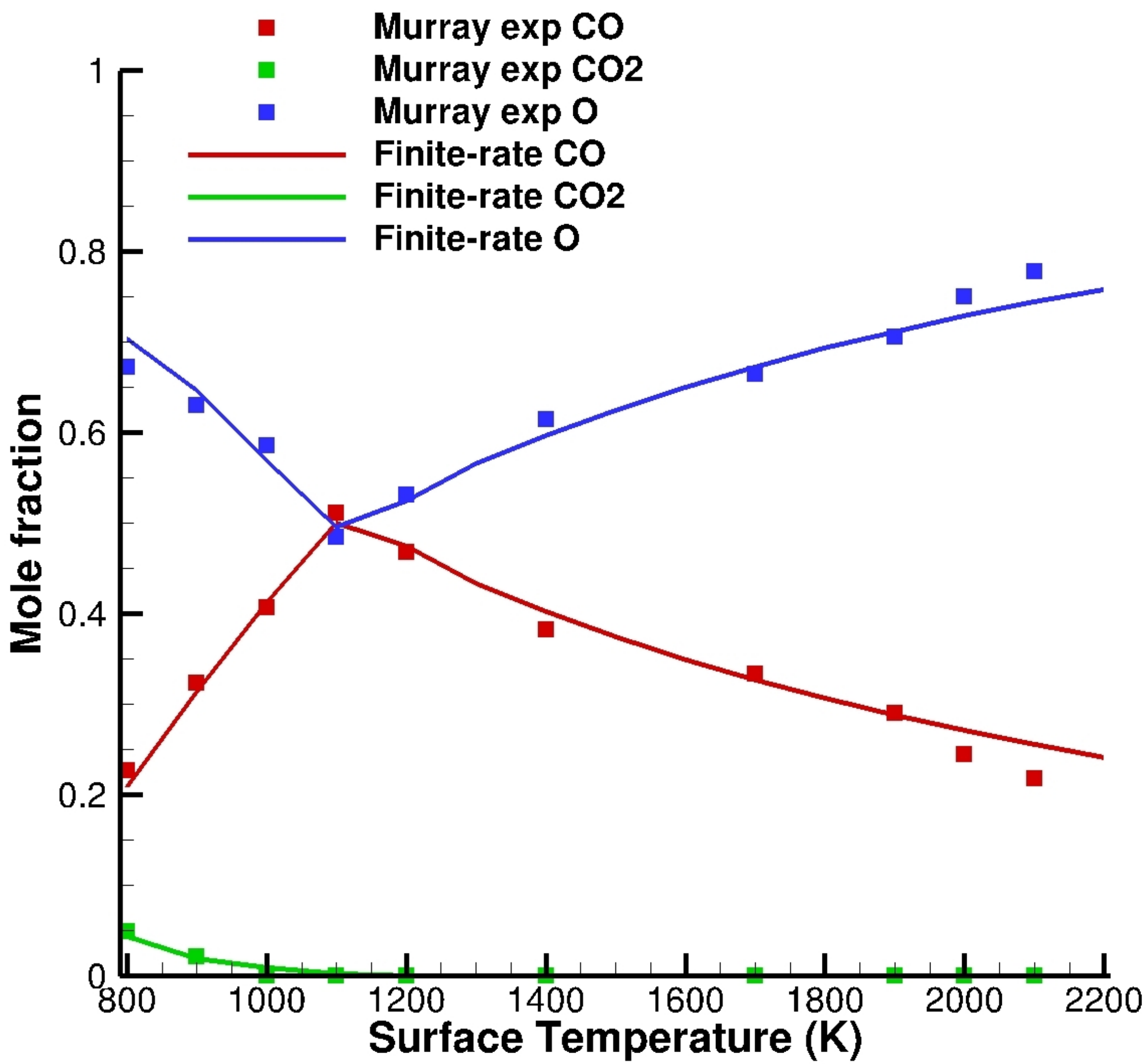
2f	$2O_s \rightarrow O_2 + 2(s)$	LH	x		
2b	$O_2 + 2(s) \rightarrow 2O_s$	Dissociative Ads	x		
3f	$O_2 + (s) \rightarrow O + O_s$	Dissociative Ads	x		
3b	$O + O_s \rightarrow O_2 + (s)$	ER	x		
4f	$CO + O_s \rightarrow CO_2 + (s)$	ER	x		
4b	$CO_2 + s \rightarrow CO + O_s$	Dissociative Ads	x		
5f	$O_s + C_b \rightarrow CO + (s)$	LH	x		x
5b	$CO + s \rightarrow O_s + C_b$	Dissociative Ads	x		
6f	$O + O_s + C_b \rightarrow CO_2 + (s)$	ER	x	x	
6b	$CO_2 + (s) \rightarrow O + O_s + C_b$	Dissociative Ads	x		
7f	$2O_s + C_b \rightarrow CO_2 + 2(s)$	LH	x		x
7b	$CO_2 + 2(s) \rightarrow 2O_s + C_b$	Dissociative Ads	x		
8	$O + C_b + (s) \rightarrow CO + (s)$	ER		x	
9	$O + O_s + C_b \rightarrow CO + O_s$	ER		x	

Finite-rate chemistry



Transformation of rates into DSMC probabilities

- **<u>Gas-surface reactions:</u>**
  - Adsorption: $O + (s) \rightarrow O_s$

$$P_{ads} = S_0(N_{sites} - N_{O_s})\frac{F_N}{S_P}$$

  - Eley-Rideal: $O + C_b + (s) \rightarrow CO + (s)$

$$P_{ER} = 2k_{ER}\frac{N_{O_s}F_N}{S_P}\frac{1}{v_n}$$

Adapted from: Molchanova *et al.*, RGD29 (2014) [6]

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Transformation of rates into DSMC probabilities

- **Surface reactions:**
  - Desorption: $O_s \rightarrow O + (s)$ $\quad \nu_{des} = k_{des}$

$$\tau_{des} = -\frac{log(Rn)}{\nu_{des}}$$

  - LH CO formation: $O_s + C_b \rightarrow CO + (s)$ $\quad \nu_{LH} = k_{LH} N_{O_s}$
  - LH CO_2 formation: $2O_s + C_b \rightarrow CO_2 + 2(s)$

$$\nu_{LH} = k_{LH} \frac{N_{O_s}(N_{O_s} - 1)}{2} \frac{F_N}{S_P}$$

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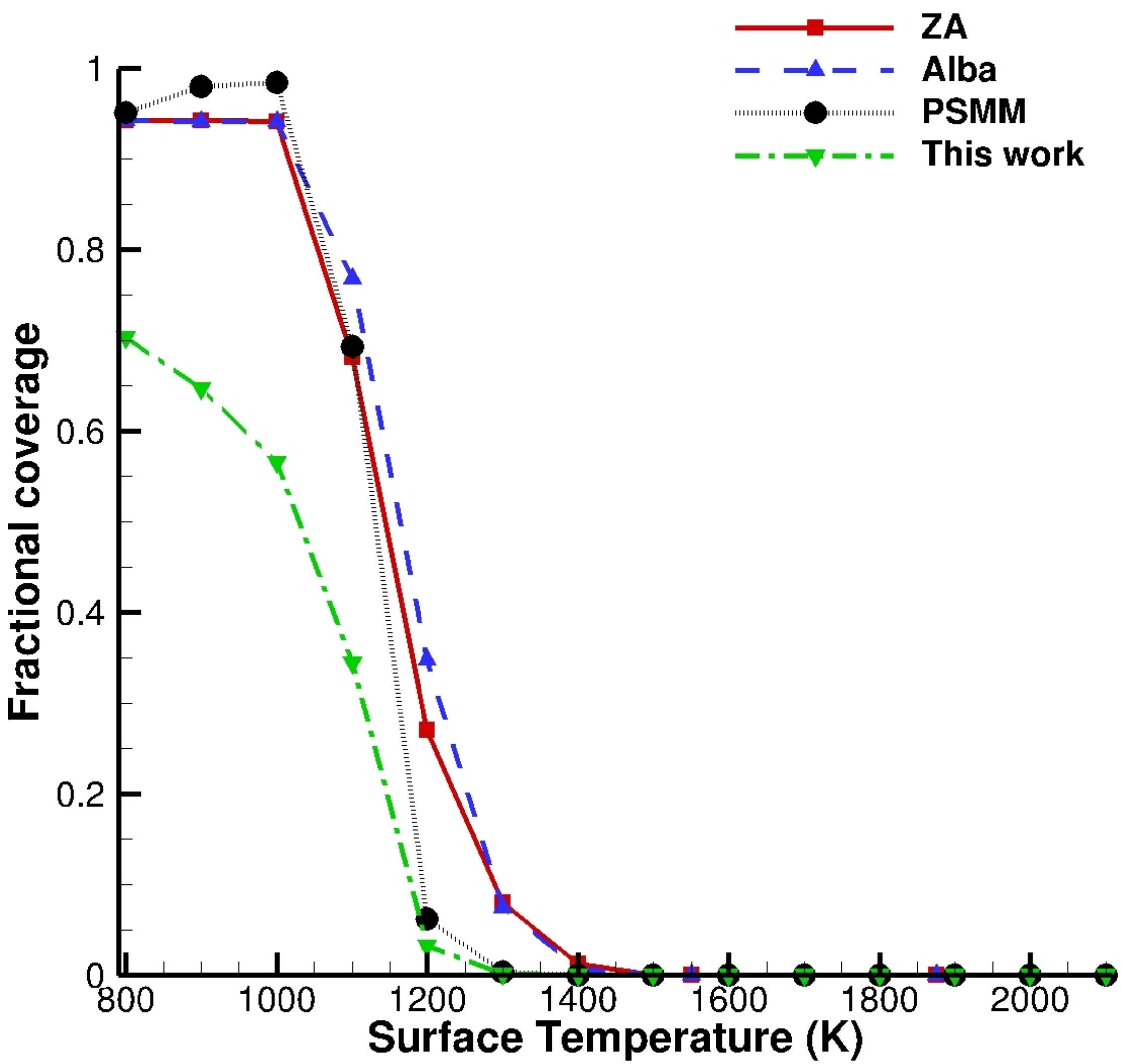
Surface Coverage



Experiments vs Alba

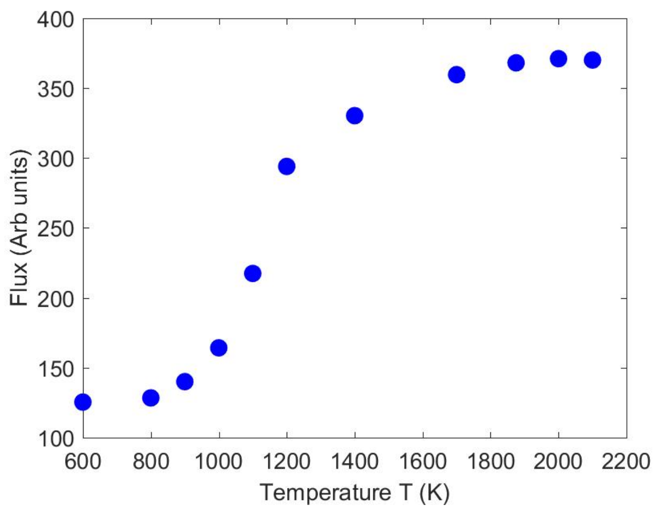
$\Theta = 45°$

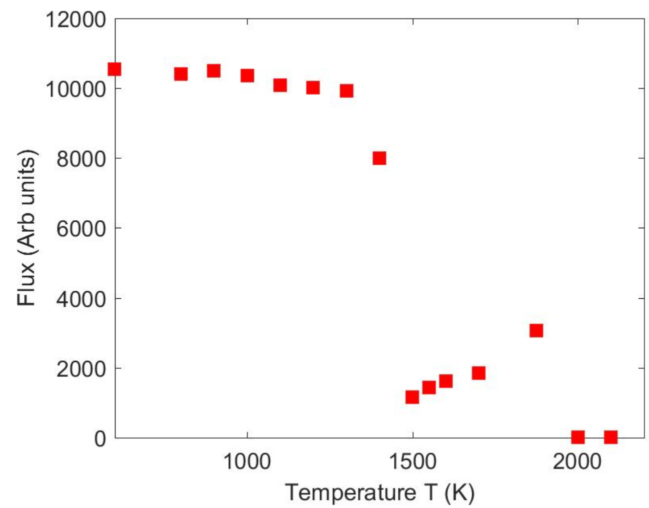
$\Phi = 0°$

Experiment

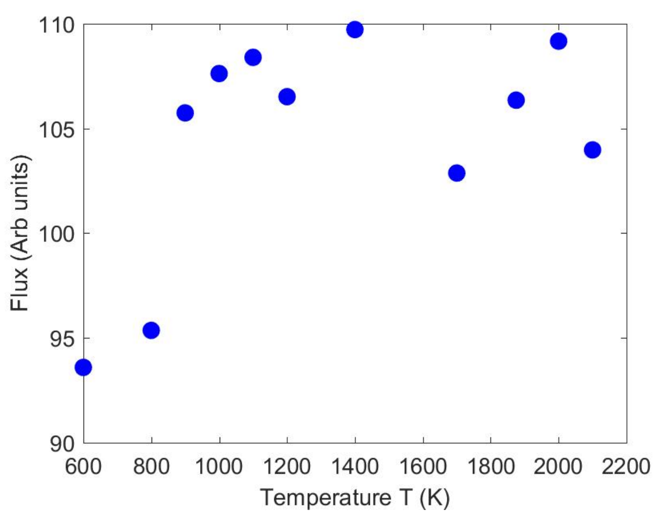
DSMC Alba

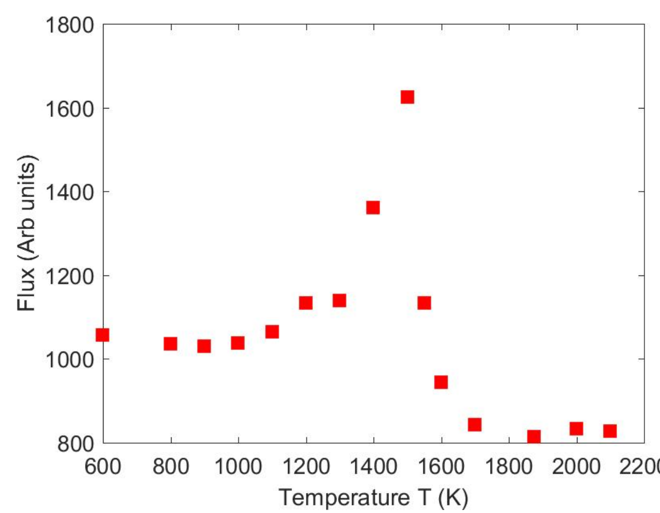
O





O_2





Experiments vs Alba

$\Theta = 45°$

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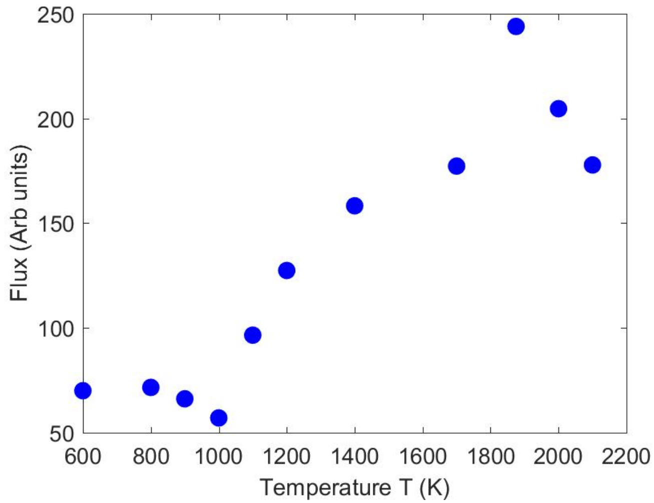
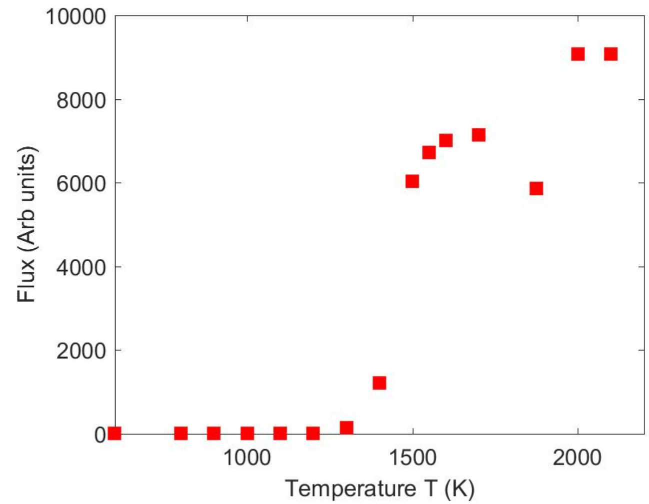
Experiment

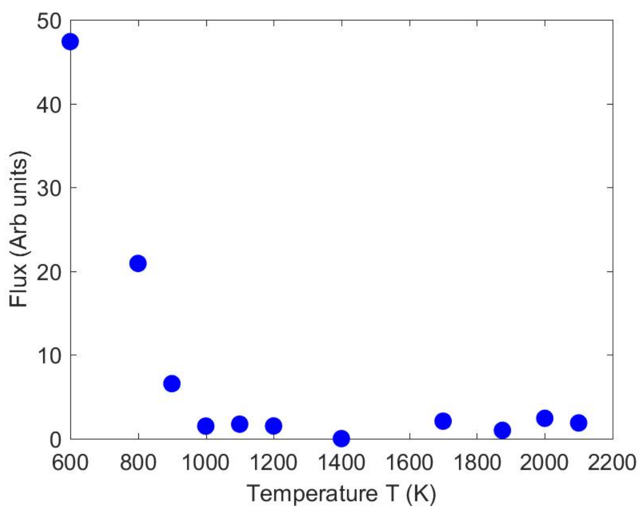
DSMC Alba

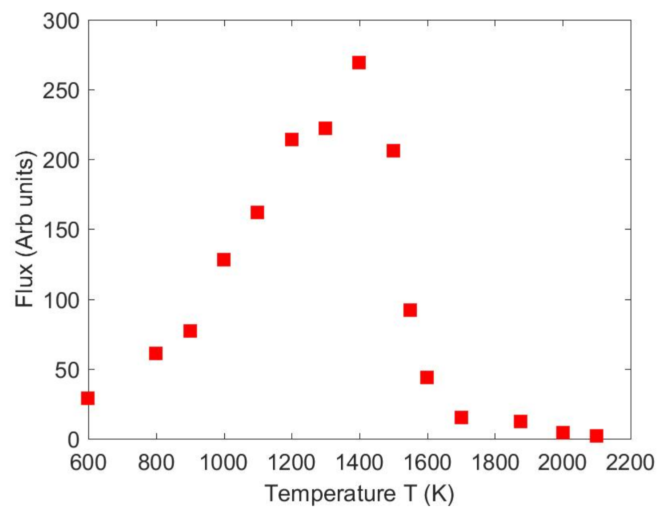
CO



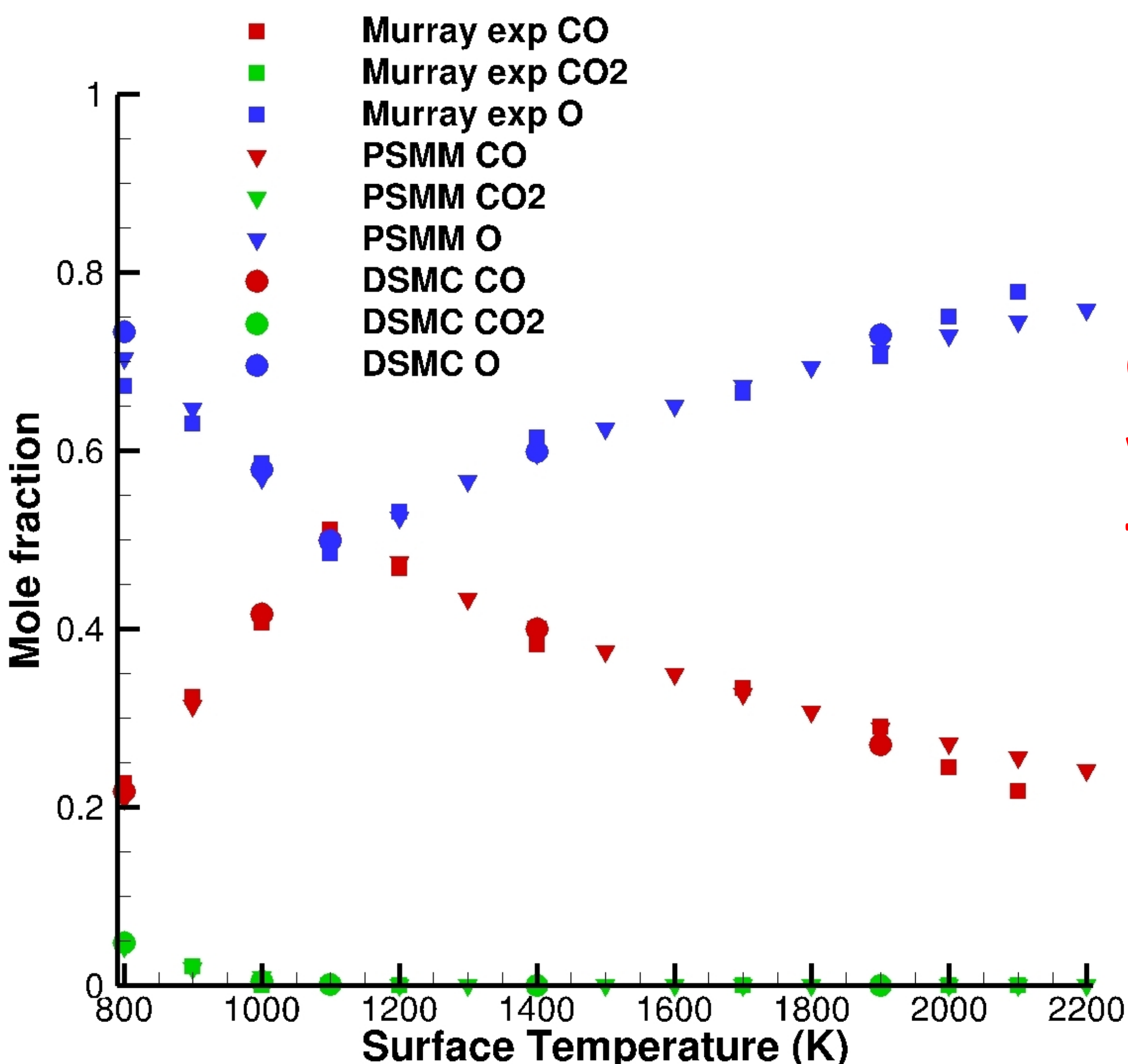


CO_2





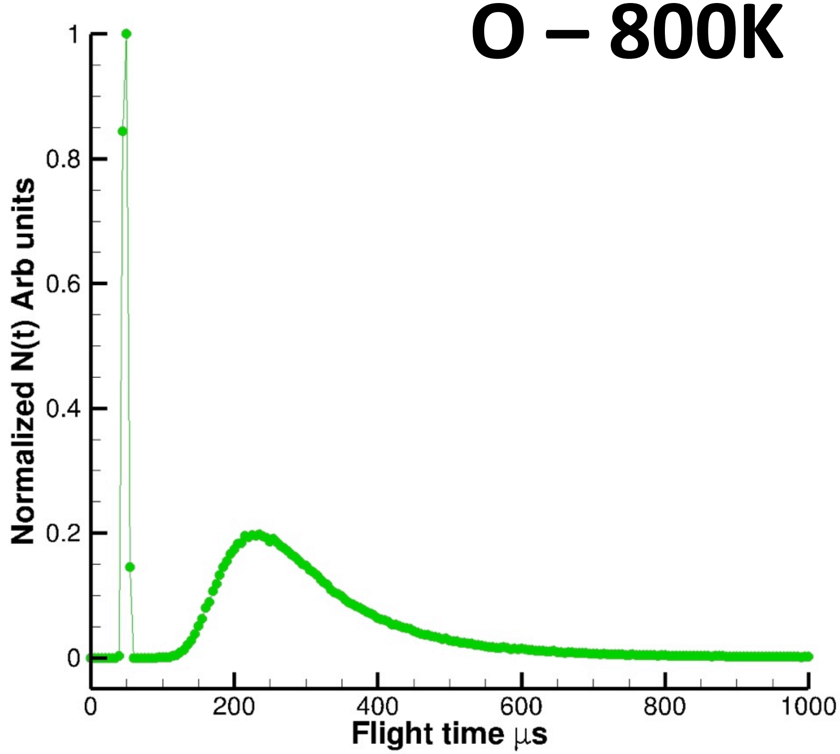
PSMM vs This work vs experiments

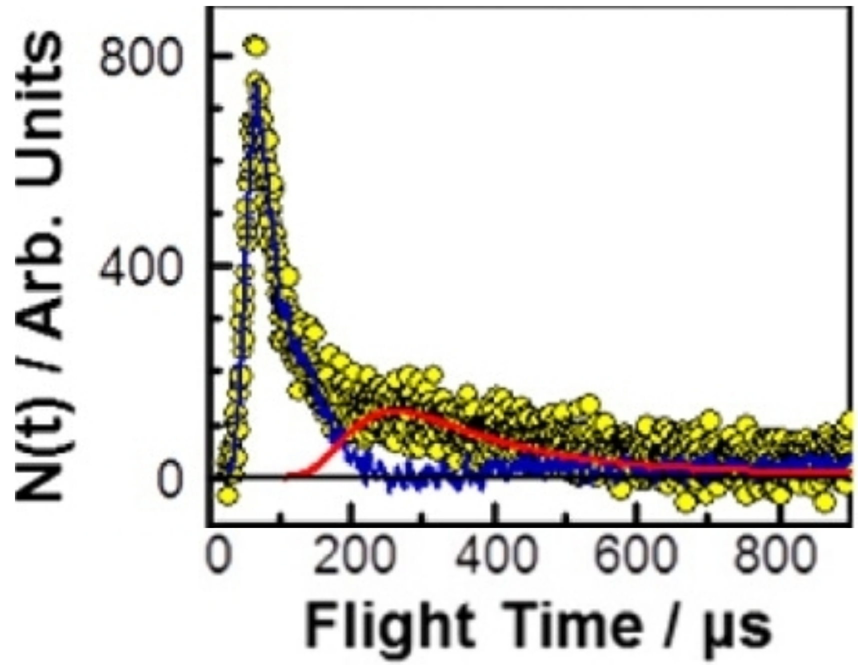


! We can fit the same experimental results with rates derived from different processes !

This work vs experiments

O – 800K

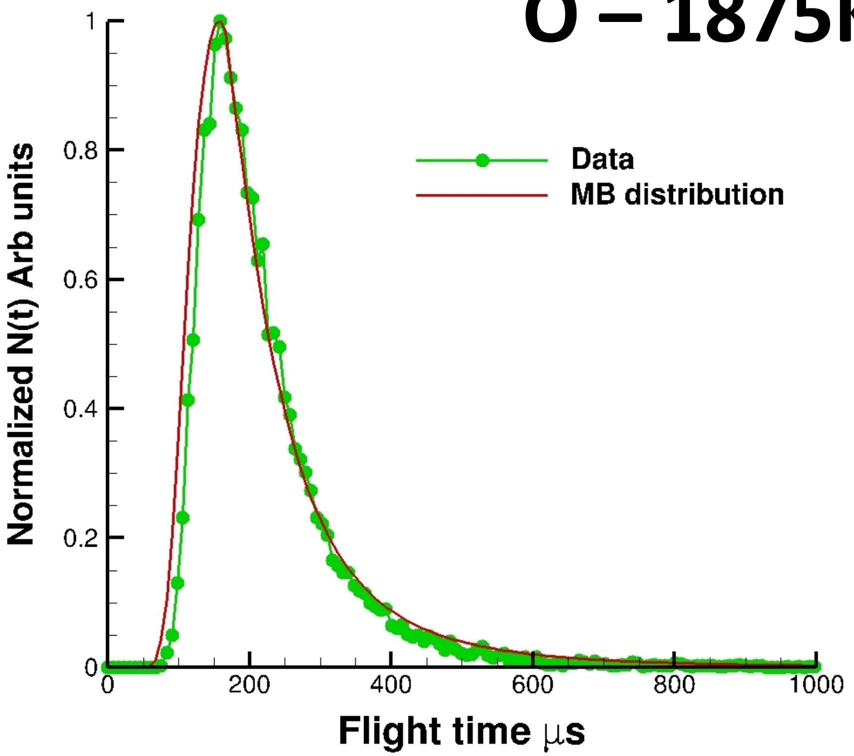


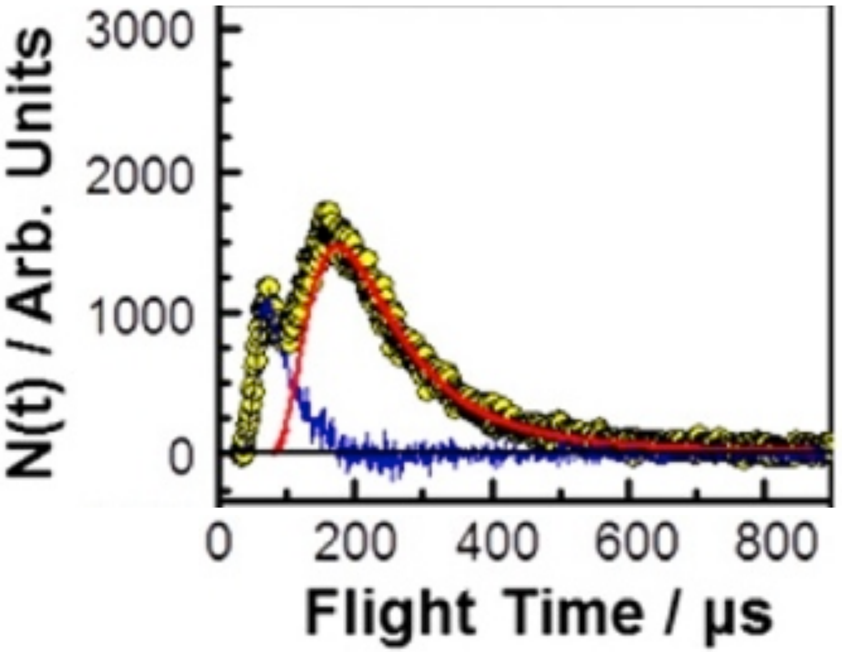


From: Murray *et al.*, JPCC 119 (2015) [5]

This work vs experiments

O – 1875K





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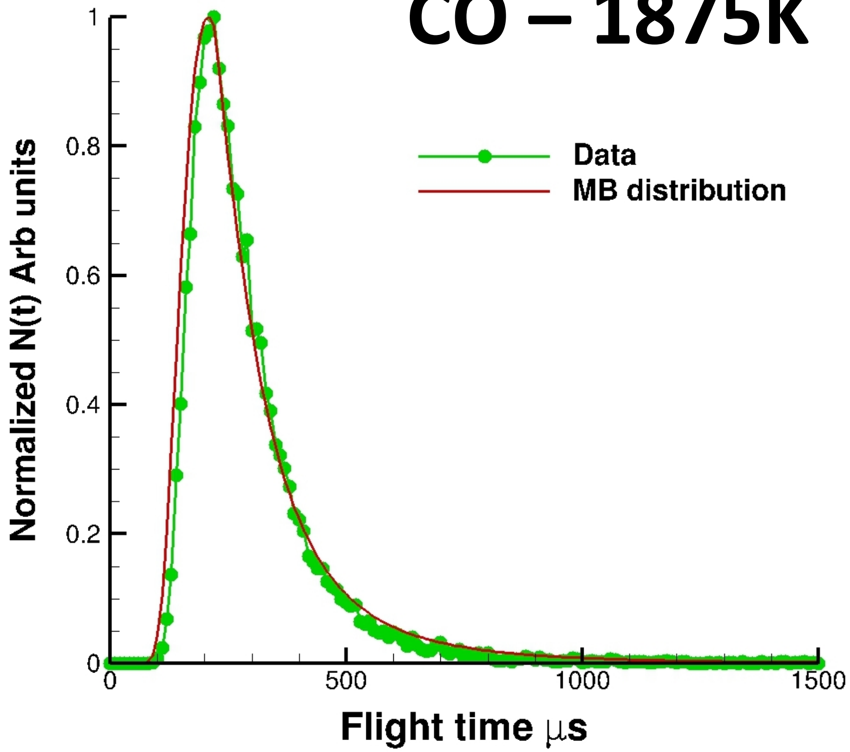
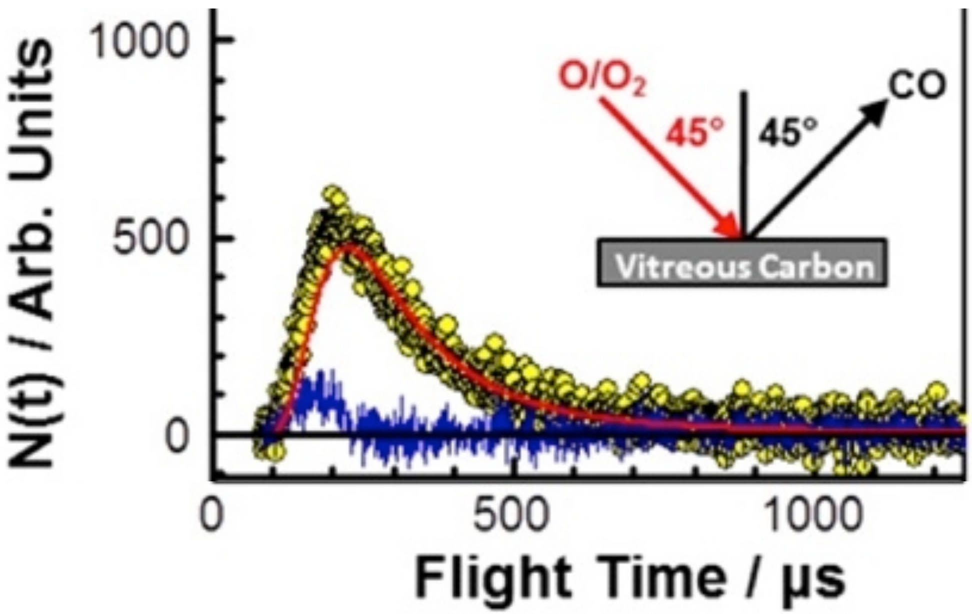
This work vs experiments

CO – 1875K





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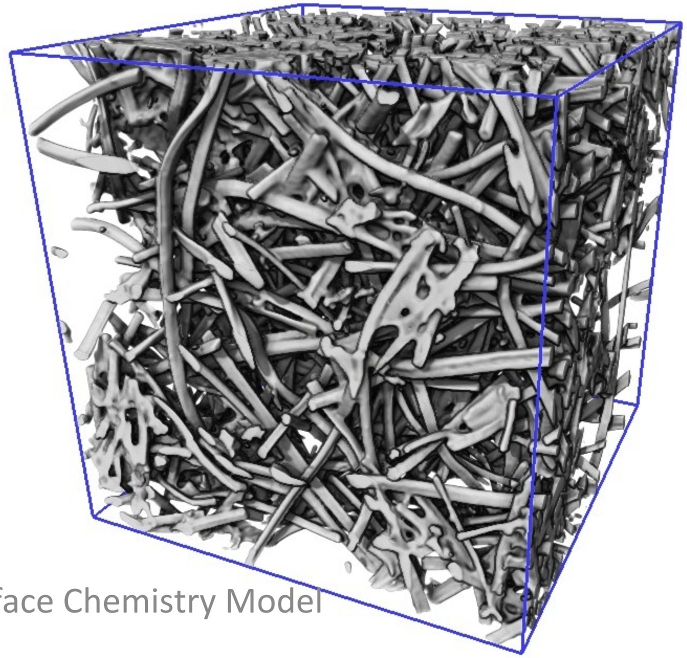
Conclusions

- Multiple oxygen-carbon oxidation models investigated [1-4].
- Murray-Minton's experimental results on vitreous carbon [5] used as baseline
- ZA and Alba perform poorly when compared with experimental results
- **PSMM and This work are able to fit the experimental data with finite-rates derived from different reactions**
- PSMM and This work have similar features (O TOF at all temperatures) and differences (CO-CO_2 TOF)
- Next:
  - Improve the model (energy barrier, CLL)
  - Look at oxidation of FiberForm



References

1. Park, "Effects of atomic oxygen on graphite ablation", *AIAA J.*, Vol. 14 (11), (1976).
2. Zhluktov and Abe, "Viscous shock-layer simulations of airflow past ablating blunt body with carbon surface", *JTHT*, Vol. 13 (1), (1999).
3. Alba *et al.*, "Numerical modeling of Earth reentry flow with surface ablation", *J. Spacecraft and Rockets*, Vol. 53 (1), 2016.
4. Poovathingal *et al.*, "Finite-rate oxidation model for carbon surfaces from molecular beam experiments", *AIAA Aviation*, AIAA 2016-3842 (2016).
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6. Molchanova *et al.*, "A detailed DSMC surface chemistry model", 29th RGD, pp. 131-138 (2014).

Acknowledgments

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- SANDIA National Laboratories for help with SPARTA (Drs. Steve Plimpton and Michael Gallis): www.sparta.sandia.gov

… and thanks for your attention!