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# Investigation of the High-Energy Oxidation of FiberForm from DSMC Analysis of Molecular Beam Experiments

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## Overview of the Effort

A collaborative effort between the University of Illinois at Urbana-Champaign (UIUC), NASA Ames Research Center (ARC) and Montana State University (MSU) succeeded at developing a new finite-rate carbon oxidation model [2] from molecular beam scattering experiments on vitreous carbon (VC) [1]. We now aim to use the direct simulation Monte Carlo (DSMC) code SPARTA to apply the model to each fiber of the porous fibrous Thermal Protection Systems (TPS) material FiberForm (FF). The detailed micro-structure of FF was obtained from X-ray micro-tomography and then used in DSMC. Both experiments and simulations show that the CO/O products ratio increased at all temperatures from VC to FF. We postulate this is due to the larger number of collisions an O atom encounters inside the porous FF material compared to the flat surface of VC. For the simulations, we particularly focused on the lowest and highest temperatures studied experimentally, 1023 K and 1823 K, and found good agreement between the finite-rate DSMC simulations and experiments.

## Molecular Beam Experiments

A hyperthermal O/$O_2$ beam composed of approximately 90% O and 10% $O_2$ is directed at a carbon sample at an incident angle of 45º. The number density as a function of arrival time at the detector, N(t), for the products exiting the surface was collected at various final angles that were in the plane of the beam and the surface normal. Angular flux distributions at each final angle can be obtained from the time-of-flight (TOF) distributions.



*Molecular beam experimental setup [1]*
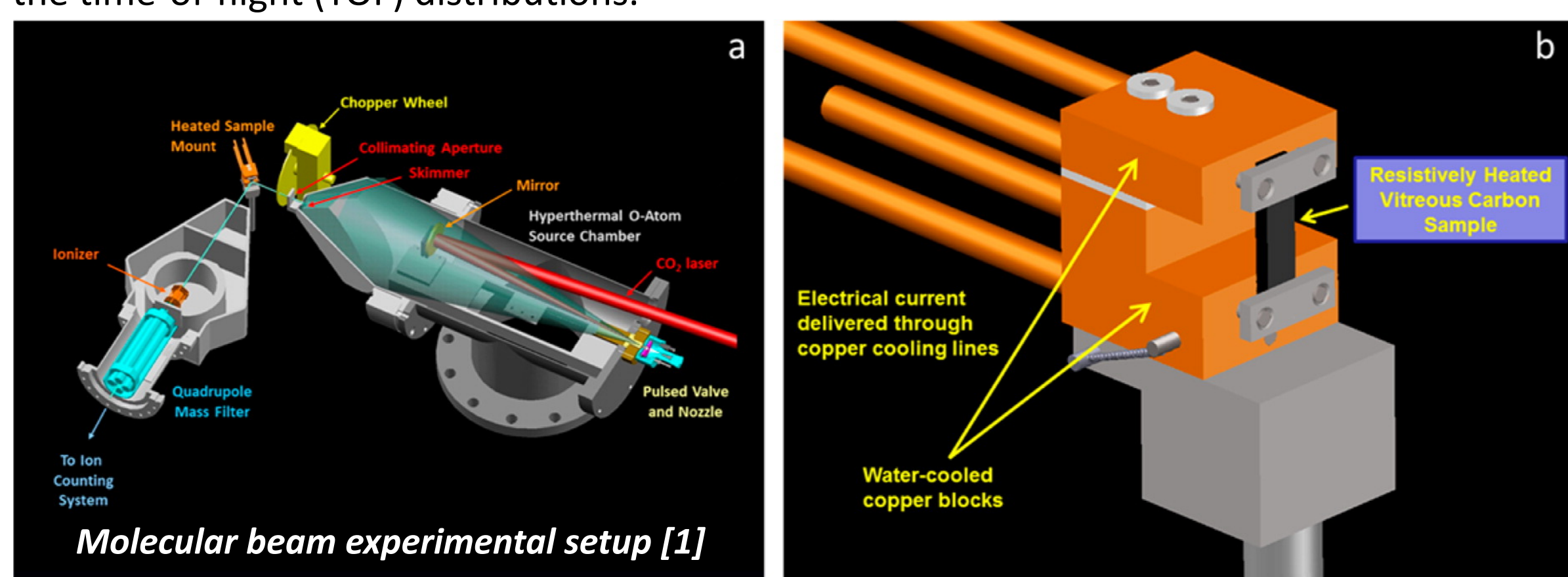
## Finite-Rate Model from VC experiments [2]

*Talk by K. Swaminathan Thu 08/31 2:05pm on the finite-rate model*

The detailed TOF information of the scattered products was used to distinguish between the time scales of the various reaction mechanisms. In general, the Langmuir-Hinshelwood (LH) mechanism is a thermal surface mechanism consisting of 3 major steps: adsorption, formation and desorption. Since the reaction takes place on the surface, the reactants must first adsorb on surface sites. The second step is the formation step, in which the reactants interact with carbon to form products on the surface. Finally, these products are desorbed as gas-phase species. The LH mechanisms employed in this model are further classified as 3 different types (herein referred to as LH(1-3)) and are distinguished based on the time scales of the CO/CO2 formation and desorption processes:

- LH1. Rapid formation and desorption (prompt mechanism)
- LH2. Slow formation with rapid desorption (formation limited)
- LH3. Rapid formation with slow desorption (desorption limited)

A total of 9 reactions were inferred from analysis of the experimental data: adsorption, desorption of O, LH3 formation and desorption of 2 types of CO, and LH1 formation of O, CO and $CO_2$. CO{a} is weakly bound and exits the surface quickly, while CO{b} is strongly bound to the surface and desorbs much more slowly.

| Mechanisms | Reaction | Rate constant (k) |
|---|---|---|
| Adsorption | $O + (s) \longrightarrow O(s)$ | $\frac{1}{4\hbar}\sqrt{\frac{8k_bT_g}{\pi m}} * 0.87$ |
| LH3 CO{a} formation | $O + (s) + O'(s) + C(b) \longrightarrow CO\{a\}(s) + O'(s)$ | $\frac{1}{4\hbar}\sqrt{\frac{8k_bT_g}{\pi m}} * 3.8027 \, exp(-\frac{4243.3}{T_s})$ |
| LH3 CO{b} formation | $O + (s) + O'(s) + C(b) \longrightarrow CO\{b\}(s) + O'(s)$ | $\frac{1}{4\hbar}\sqrt{\frac{8k_bT_g}{\pi m}} * 8.7351 \, exp(-\frac{1468.2}{T_s})$ |
| LH1 O formation | $O(IS) + (s) \longrightarrow O(TD) + (s)$ | $\frac{1}{4\hbar}\sqrt{\frac{8k_bT_g}{\pi m}} * 3.0237 \, exp(-\frac{3034.5}{T_s})$ |
| LH1 CO formation | $O + (s) + O'(s) + C(b) \longrightarrow CO + (s) + O'(s)$ | $\frac{1}{4\hbar}\sqrt{\frac{8k_bT_g}{\pi m}} * 73.006 \, exp(-\frac{5978.8}{T_s})$ |
| LH1 $CO_2$ formation | $O + O(s) + 4O'(s) + C(b) \longrightarrow CO_2 + (s) + 4O'(s)$ | $\frac{1}{4\hbar}\sqrt{\frac{8k_bT_g}{\pi m}} * 53.097 \, exp(-\frac{231.41}{T_s})$ |
| Desorption | $O(s) \longrightarrow O + (s)$ | $270567.8 \, exp\left(-\frac{5275.6}{T_s}\right)$ |
| LH3 CO{a} desorption | $CO\{a\}(s) \longrightarrow CO\{a\} + (s)$ | $8573.7 \, exp\left(-\frac{2375.8}{T_s}\right)$ |
| LH3 CO{b} desorption | $CO\{b\}(s) \longrightarrow CO\{b\} + (s)$ | $0.70598 \, exp\left(-\frac{1743.1}{T_s}\right)$ |

## FiberForm Microstructure

FiberForm is a rigid anisotropic material with an average porosity around 87%. We acquired micro-CT images of a 3 mm diameter cylindrical sample using a 3D X-ray microscope at Stanford University and extracted a 0.5 mm thick slab of material from the reconstructed dataset. The final voxel size of the sample used for the simulation was 3.302 mm, and the surface comprised of approximately 16 million triangles.
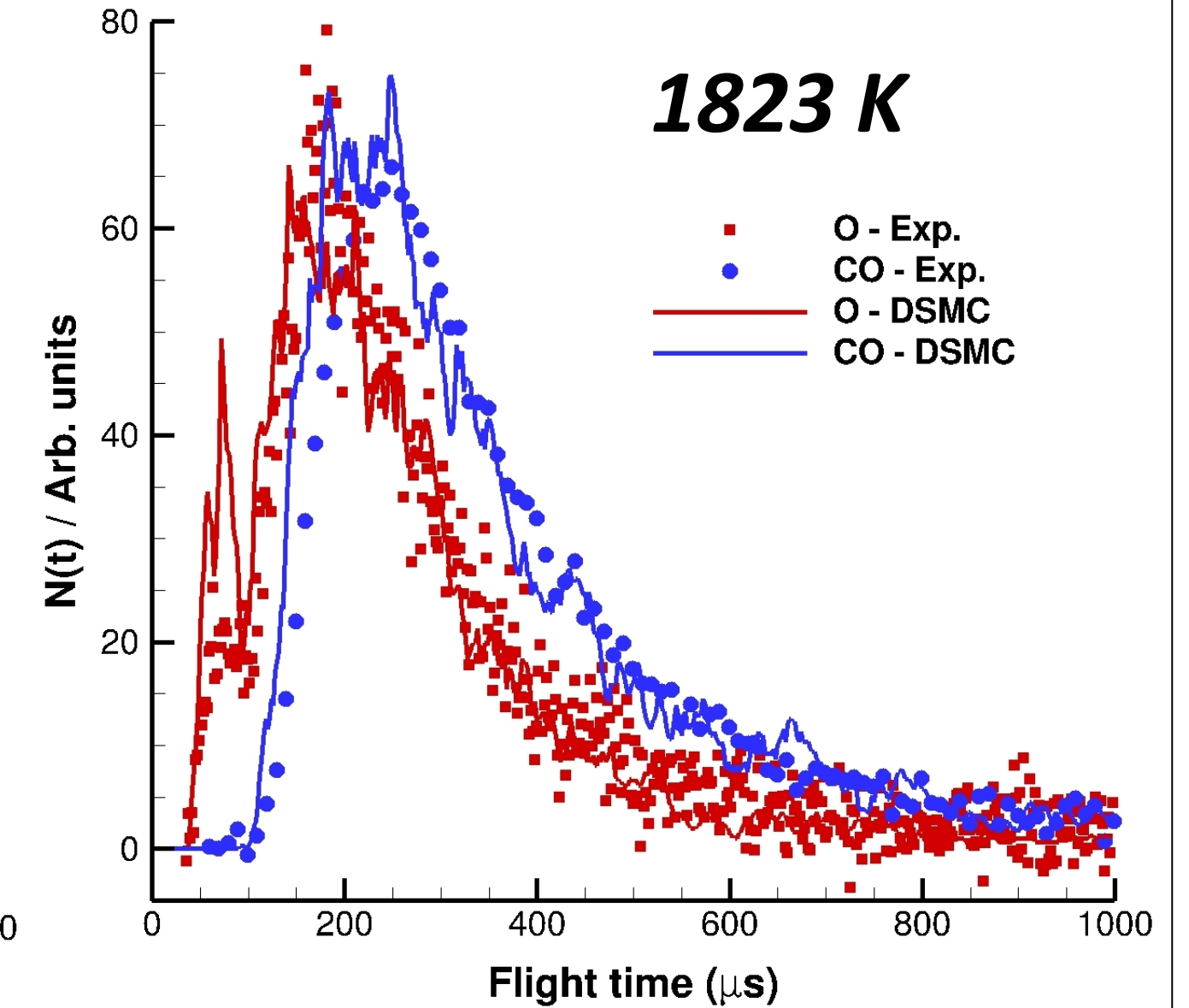


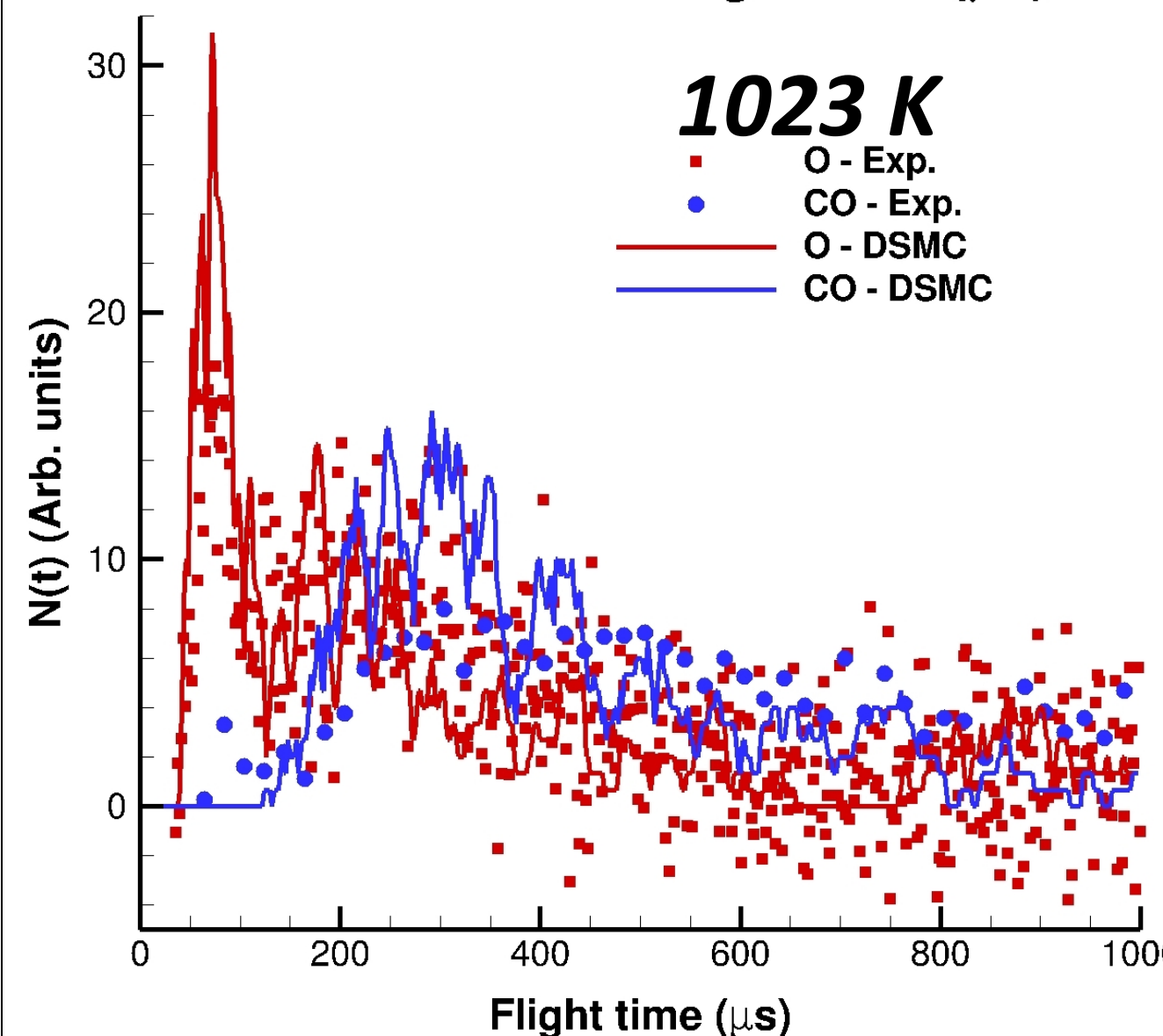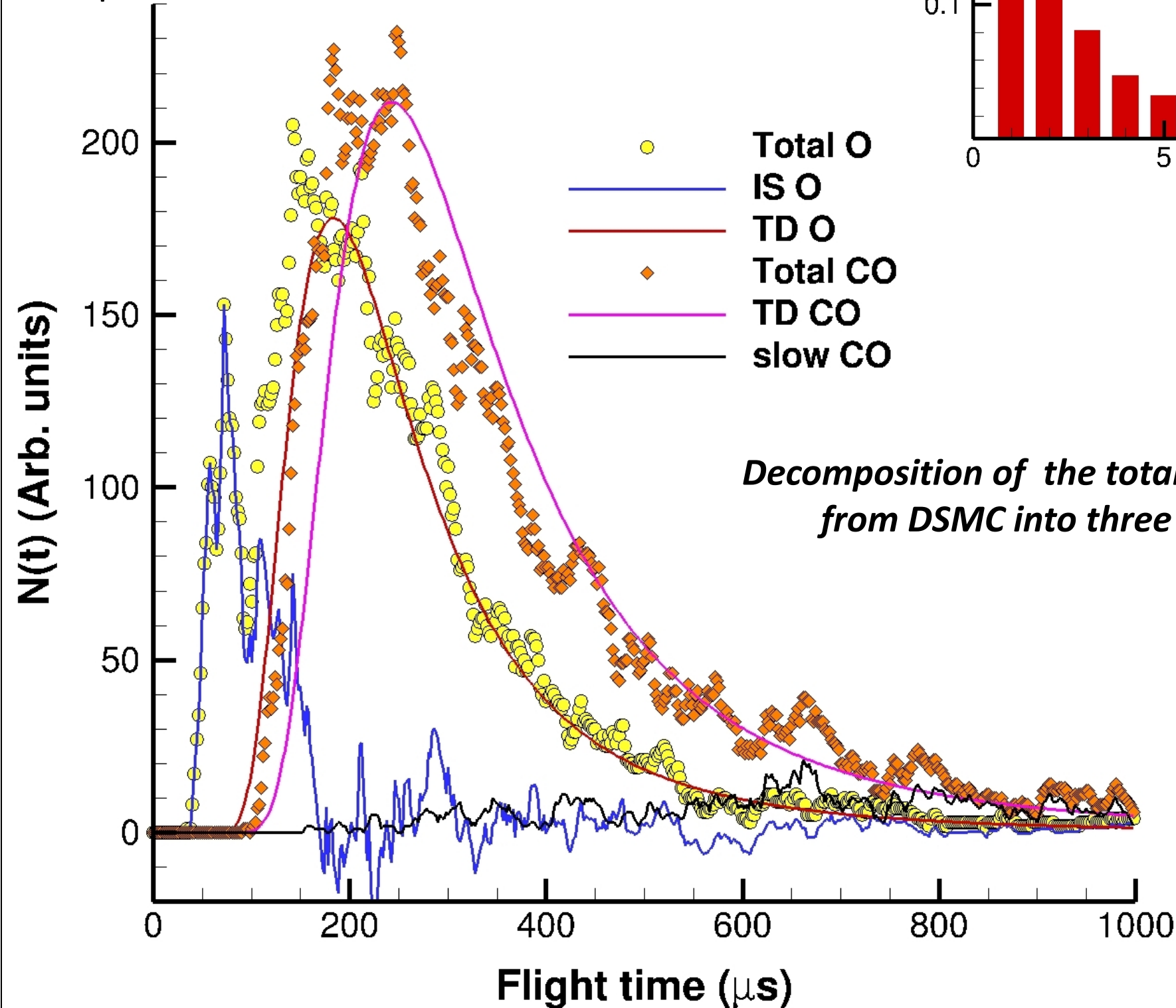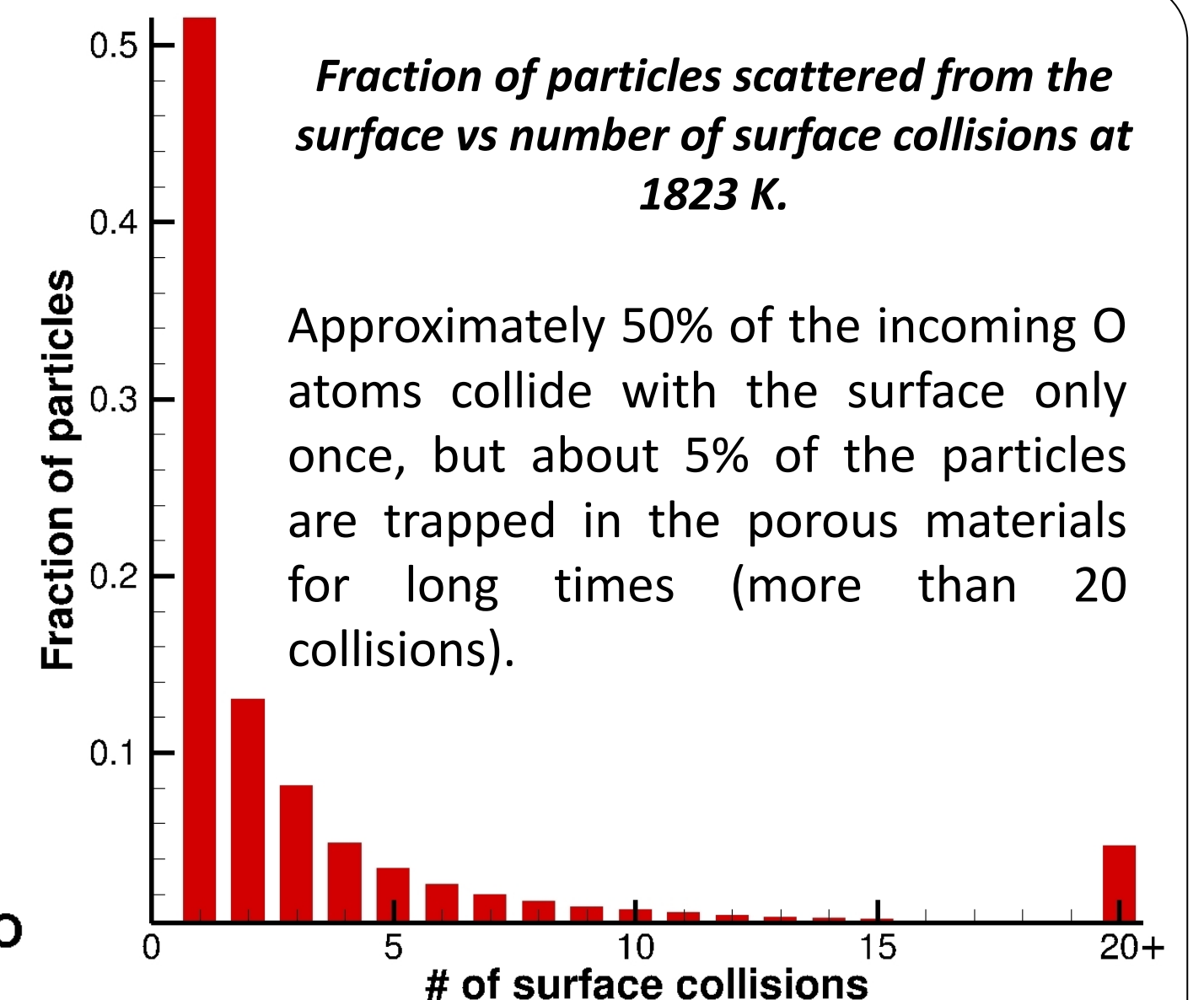*Computational surface used for the simulation*
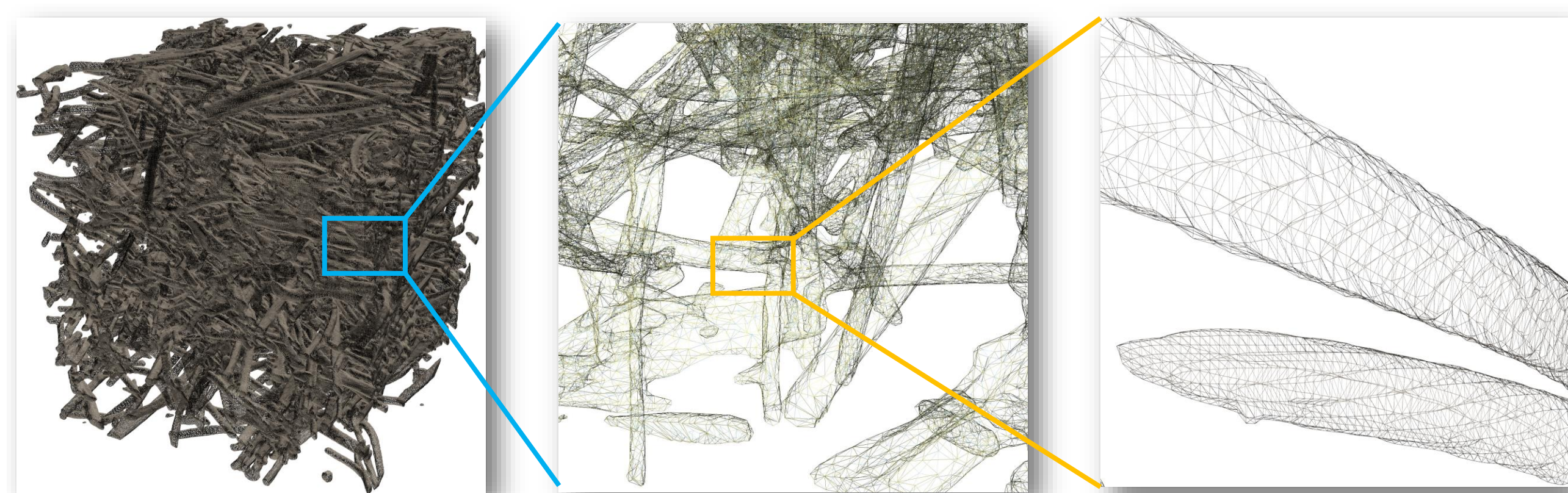


*Triangulated image of a FiberForm sample obtained from X-ray imaging using microtomography*
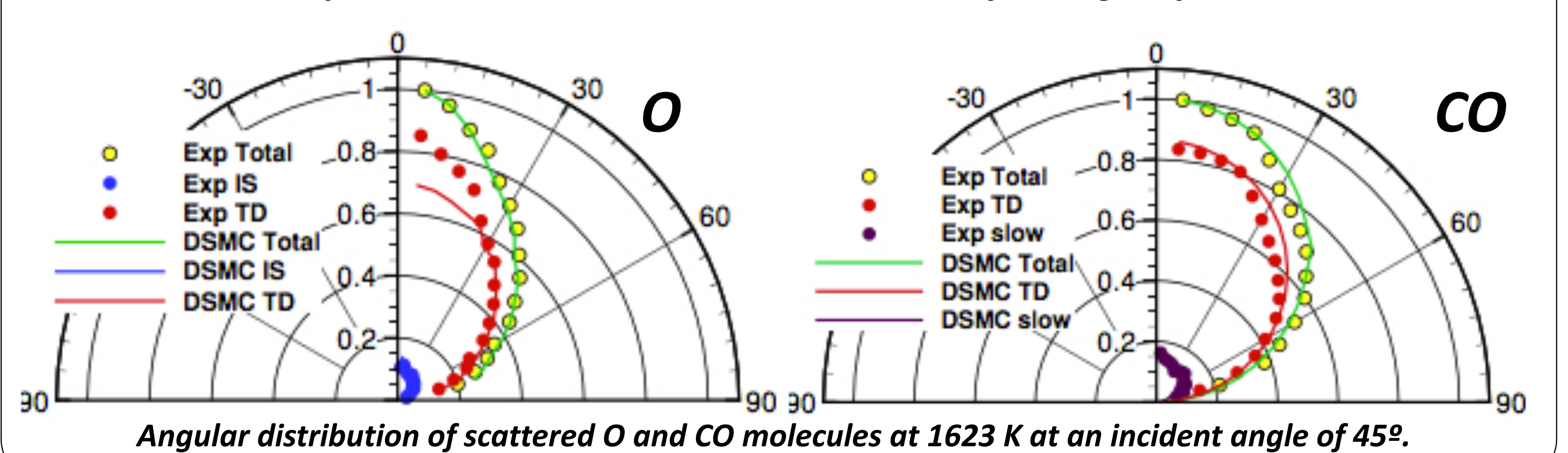
## Results

Based on experimental results, it is assumed that $O_2$ is non-reactive for the purpose of this work. Similarly, it is assumed that CO molecules formed as reactions products do not participate in subsequent reactions with the carbon surface.

In order to obtain the Thermal Desorption (TD) component of TOF signals, a Maxwell-Boltzmann at t=0 is fitted at the surface temperature.



*Fraction of particles scattered from the surface vs number of surface collisions at 1823 K.*

Approximately 50% of the incoming O atoms collide with the surface only once, but about 5% of the particles are trapped in the porous materials for long times (more than 20 collisions).

Total O
IS O
TD O
Total CO
TD CO
slow CO

*Decomposition of the total TOF signal of O and CO at 1823 K from DSMC into three components: IS, TD and slow*



1023 K
O - Exp.
CO - Exp.
O - DSMC
CO - DSMC

1823 K
O - Exp.
CO - Exp.
O - DSMC
CO - DSMC

*TOF of scattered O and CO molecules at incident and final angles of 45º.*



O
Exp Total
Exp IS
Exp TD
DSMC Total
DSMC IS
DSMC TD

CO
Exp Total
Exp TD
Exp slow
DSMC Total
DSMC TD
DSMC slow

*Angular distribution of scattered O and CO molecules at 1623 K at an incident angle of 45º.*

## References

1. Murray V et al, Inelastic and Reactive Scattering Dynamics of Hyperthermal O and $O_2$ on Hot Vitreous Carbon Surfaces, *Journal of Physical Chemistry C* **119** (26) (2015), pp. 14780-14796.
2. Swaminathan-Gopalan K et al, DSMC Analysis of Molecular Beam Experiments for Oxidation of Carbon Based Ablators, *55th AIAA Aerospace Sciences Meeting* (2017), AIAA 2017-1845.
3. Borner A et al, Detailed DSMC Surface Chemistry Modeling of the Oxidation of Light-Weight Carbon Preform Ablators , *47th AIAA Thermophyics Conference* (2017), AIAA 2017-3687.

## Acknowledgements