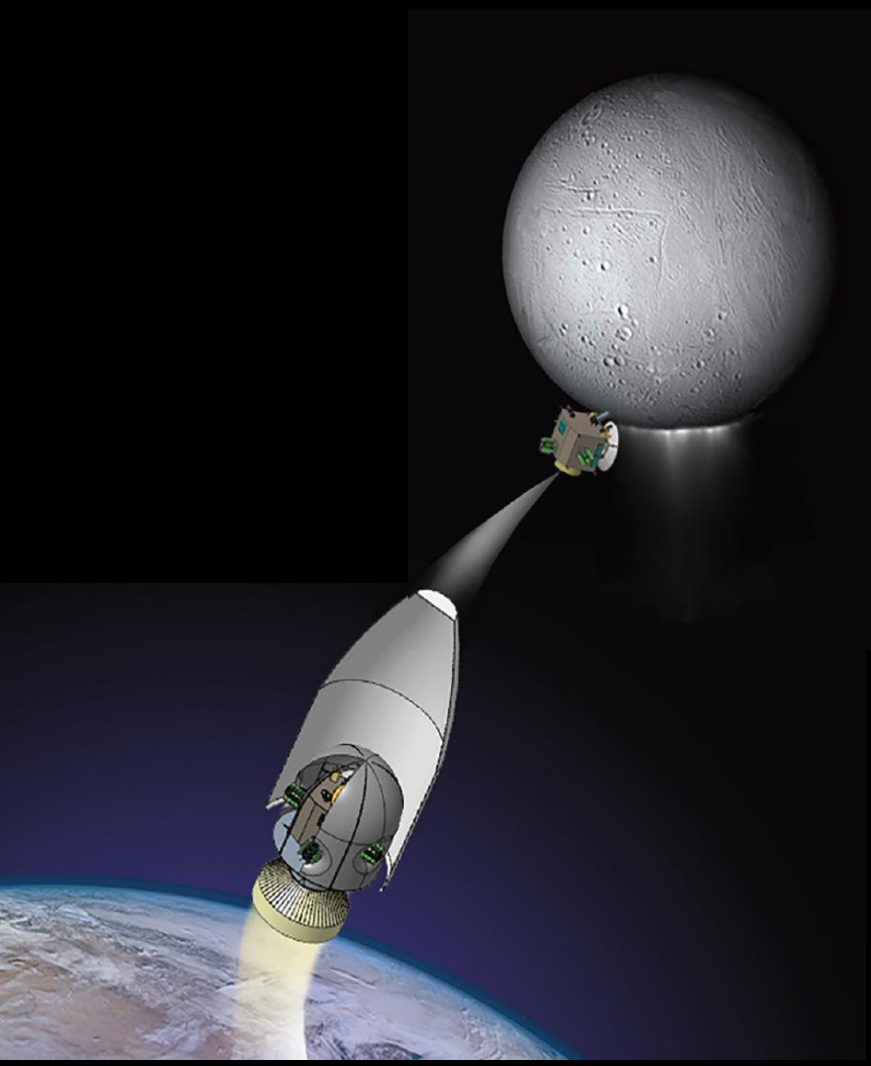# Addressing the Physics of Adsorption and Desorption of molecules from the sub-monolayer to multilayer films

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Contamination Control for Life Detection Team:
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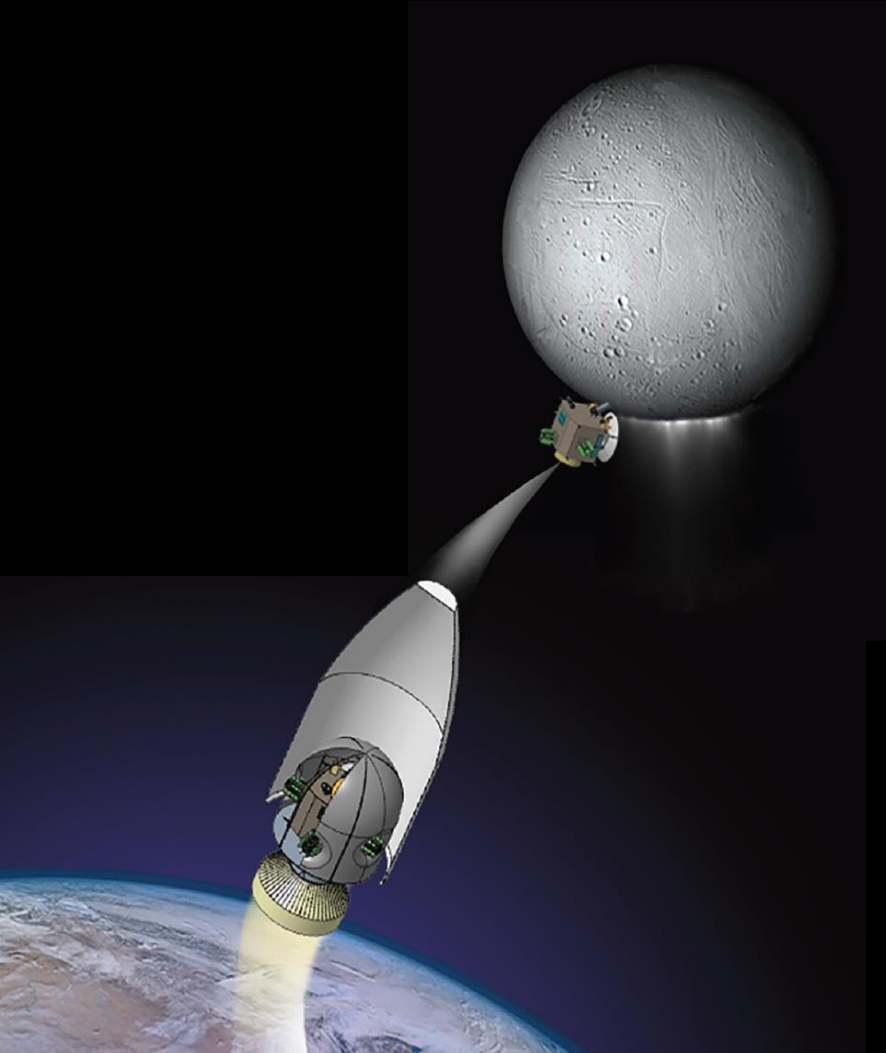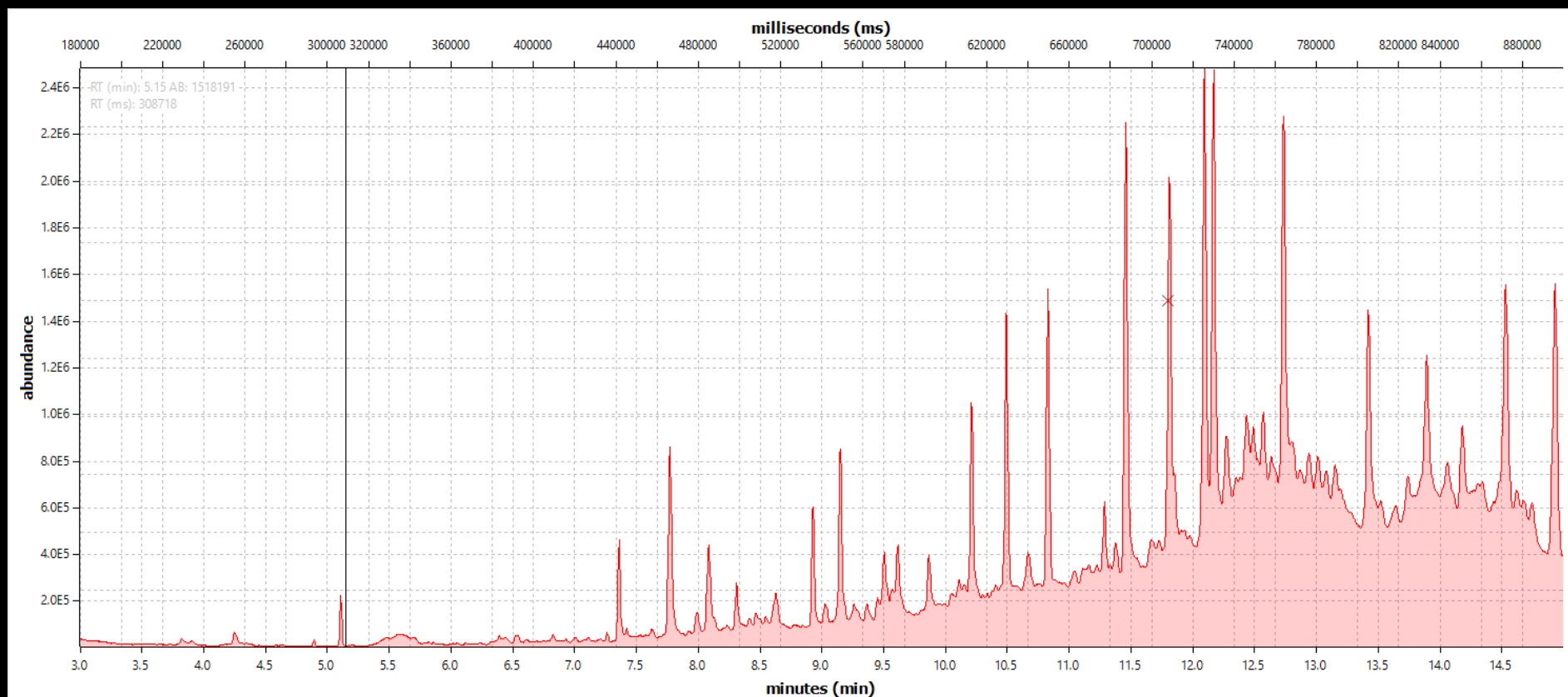NASA CCMPP 2021

Questions

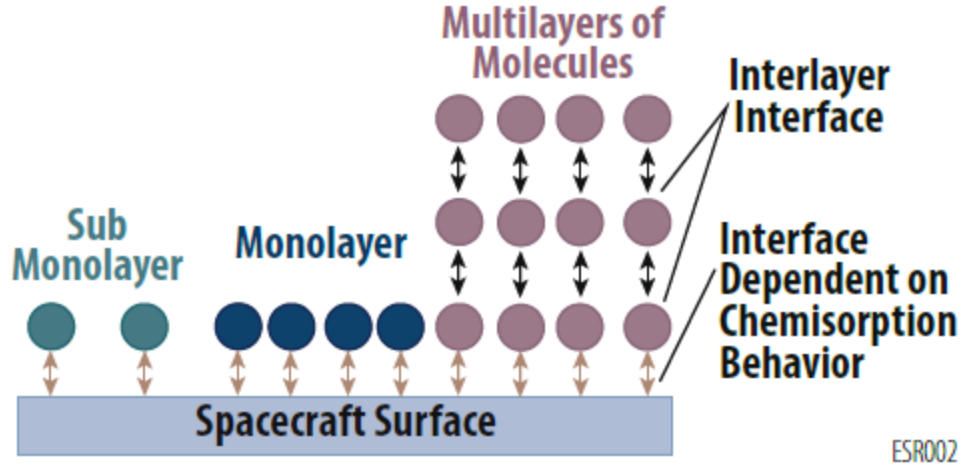1. How do we improve the fidelity of modeling of outgassing at extremely low molecular contamination levels for Astrobiology?

2. Can we reduce molecular contamination down to femtomole levels in a sample?

High fidelity contamination transport modeling is critical to life detection missions.

Typical outgassing composition (a cold finger)

More than 50 different compounds detected, widely varying in adsorption energy

Multilayers of Molecules
Interlayer Interface
Sub Monolayer
Monolayer
Interface Dependent on Chemisorption Behavior
Spacecraft Surface
ESR002

upon their environment, needs to be addressed

With many molecular layers, the behavior will approach bulk behavior

As the number of molecular layers decreases, the behavior will diverge from bulk behavior

In the case of water on inorganic oxides, the first 3-5 layers are ice-like at room temperature. A solid like structure is formed.

To more closely approximate real behavior, it is necessary to address the material stack up

Graphic from "Eigenbrode et al., 2021, *Frontiers in Space Tech.*"

Approach to more closely model transport

1. Address the molecular composition of the contamination
   1. Estimate the actual contamination composition and physical properties through chemical analysis or statistical means
   2. Evaluate the behaviors of this contamination on surfaces of interest (surface and bulk sinks)
2. Address the number of molecular layers
3. Address the behavior of the contamination in the modeled contamination load

Material-Material interactions

- There is a scarcity of material-material interaction data for most common Aerospace Contaminants
- Brunauer, Emmett and Teller's 1938 paper discusses the behavior of molecules in multiple molecular layers
  - They suggest an approximation of the first molecular layer adsorption energy as being the enthalpy of sublimation
    - This is consistent with other models of non-reactive monolayer adsorption energies
  - Their approach also addresses the treatment of additional layers with different adsorption energies

"Adsorption of Gases in Multimolecular Layers" Brunauer, Emmett and Teller
Journal of the American Chemical Society, **60** (2) 309-319, 1938

Implementation

- Particle-In Cell, LLC's Contamination Transport Simulation Program (CTSP) v1.5 was used
- Four discrete representative molecules were chosen for the simulations (n-dioctyl phthalate, n-hexadecane, n-eicosane and n-pentacosane)
- Thermodynamic data for these species were utilized
- A material-material interaction routine was developed to address what the interaction of the individual contaminant is with the different surfaces
- In this work, only bare surface material and molecular contaminant surface interactions were chosen, however, the capability exists to expand the definitions further
- Enthalpies of sublimation were used for the first molecular layer and enthalpies of vaporization were used for subsequent layers.

Implementation (continued)

- The model evaluated was for an in-flight bake out of a component (ramp up, time and temperature)
- The Material-Material interaction and strictly enthalpy of vaporization models were run for comparison
- CTSP utilized a meshed spacecraft model
  - Initial loaded the four exemplary compounds onto each mesh element
  - The coverage of the mesh elements were tracked for each compound
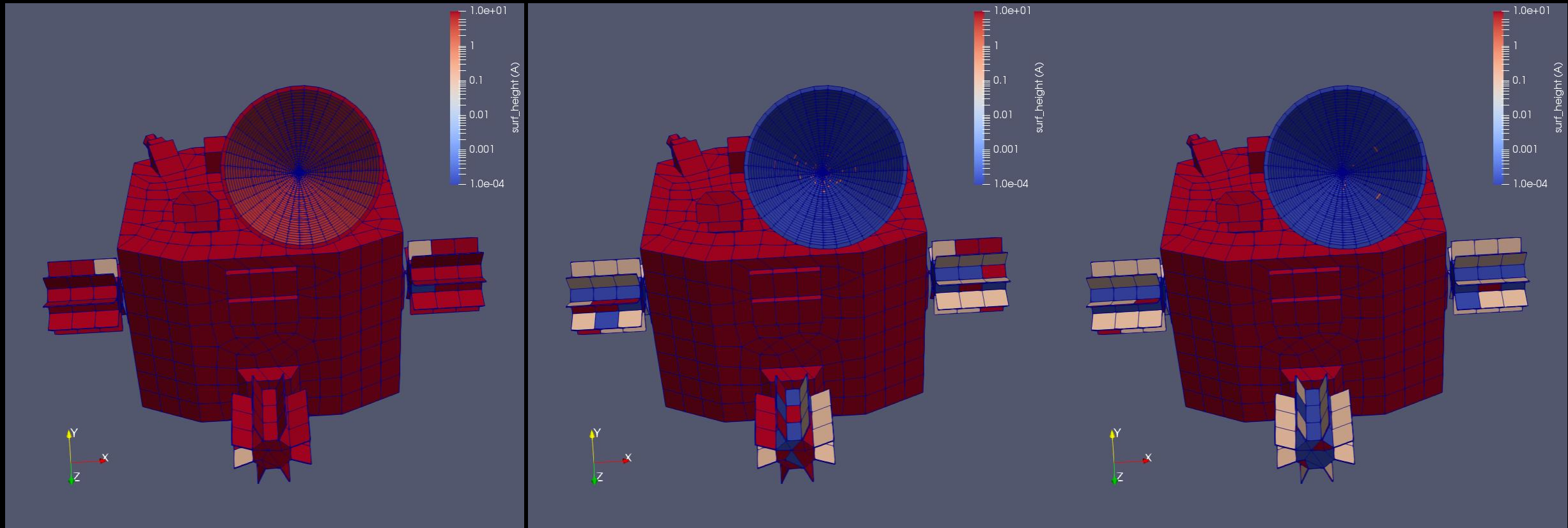 - Surface residence times were used for defining rates of desorption

Residence time- sublimation and vaporization

Normal hydrocarbon carbons vs residence time @ 20°C
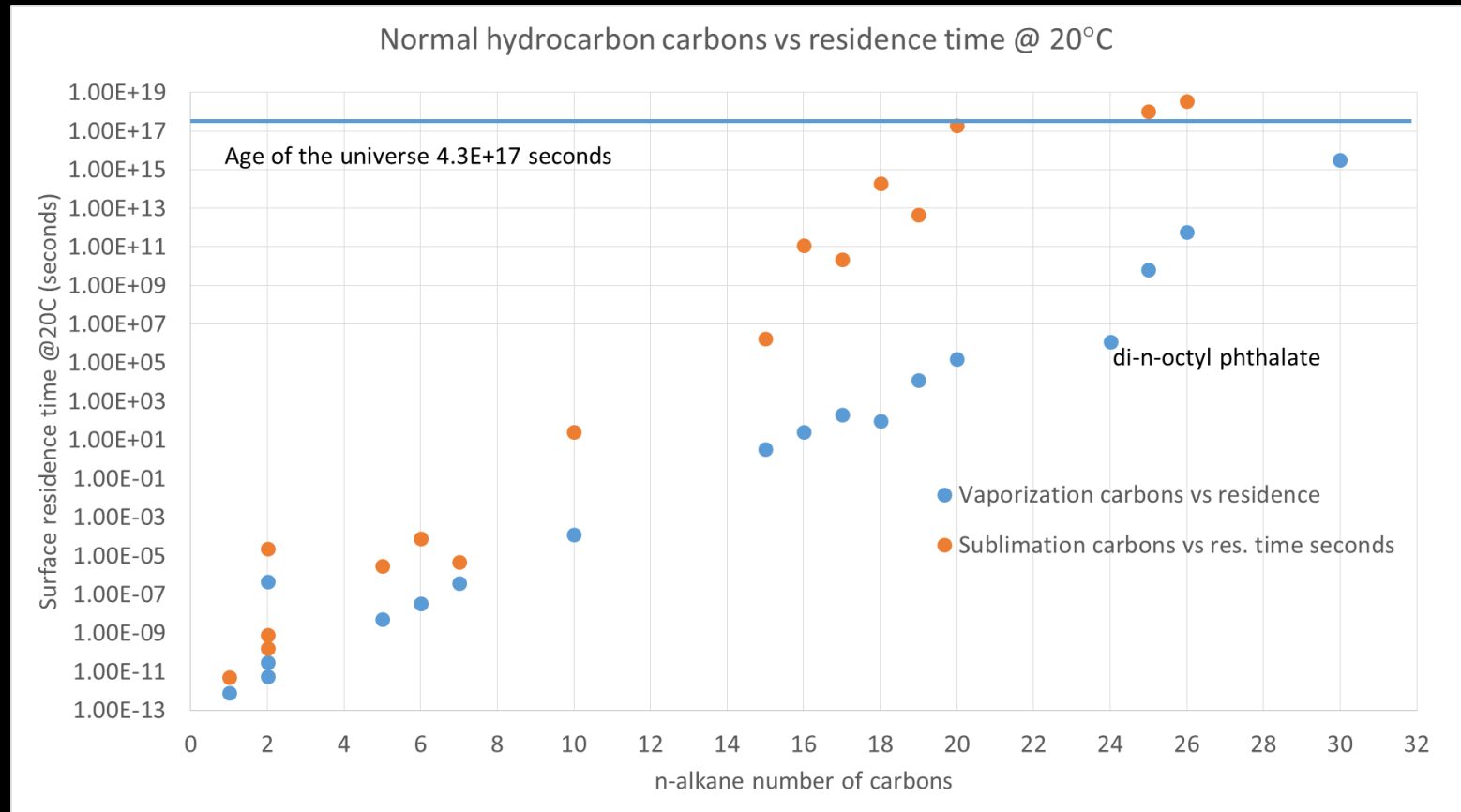
There are significant differences in the surface residence times between sublimation and vaporization

Based upon $\tau_{res} = \tau_0\, e^{\left(\frac{\Delta H_{desorption}}{RT}\right)}$

Standard model (Collector cone only)

Time 0   30 minutes   60 minutes

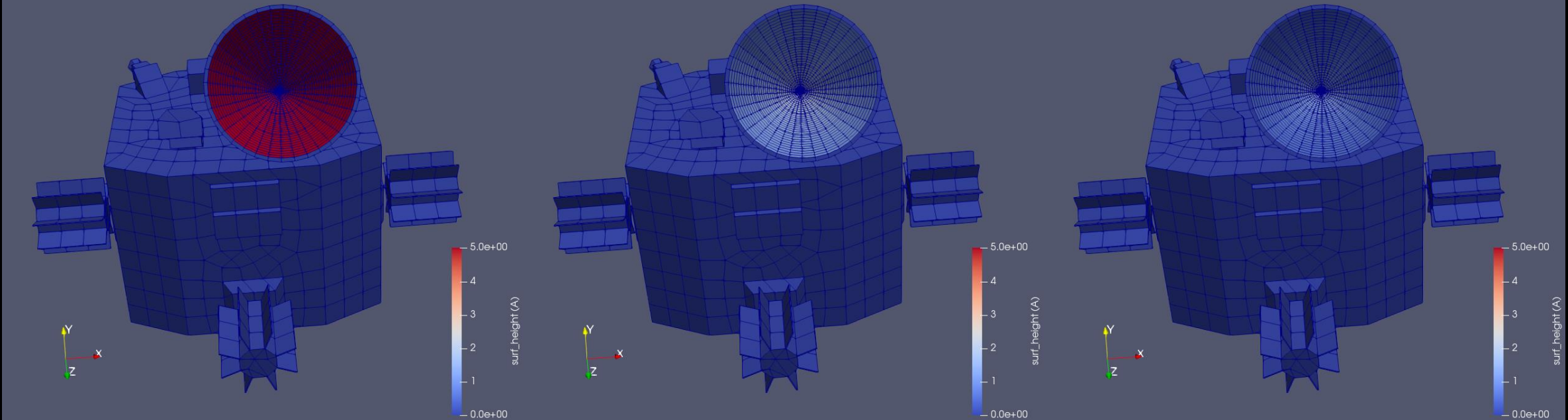Approximately 1×10^{-12} of loading remaining at 60 minutes

Graphics from "Eigenbrode et al., 2021, *Frontiers in Space Tech.*"

Improved Physics Model (Collector cone only)

All Species @ 0 seconds

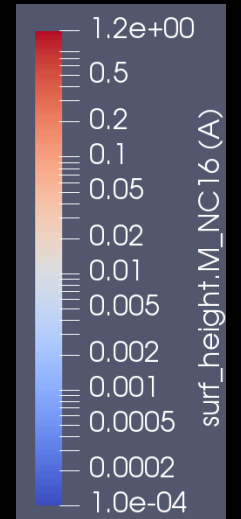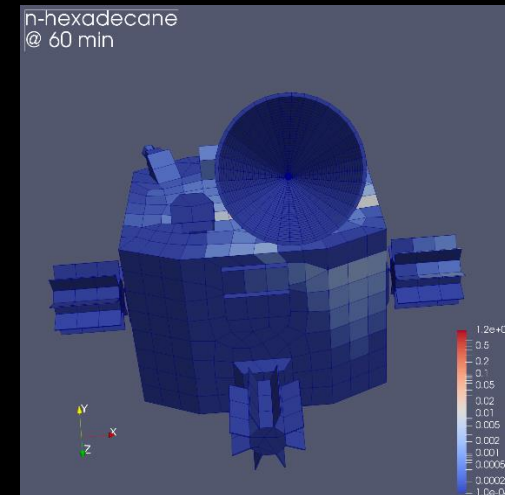All Species @ 30 minutes
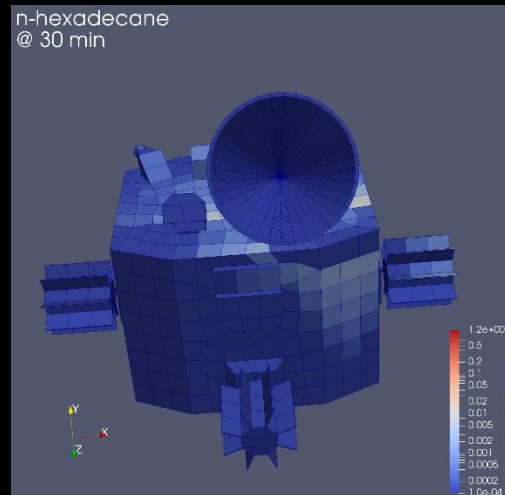
All Species @ 60 minutes

Time 0

30 minutes

60 minutes

Approximately 12% of contamination load remaining at 60 minutes, primarily the nC25 hydrocarbon

Graphics from "Eigenbrode et al., 2021, *Frontiers in Space Tech.*"

Comparison of n-C16 loss between standard model and improved model
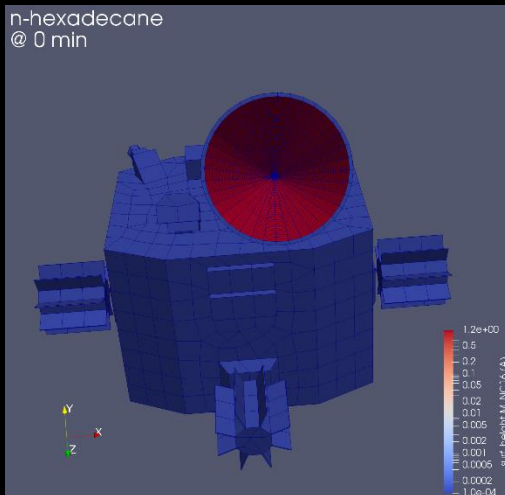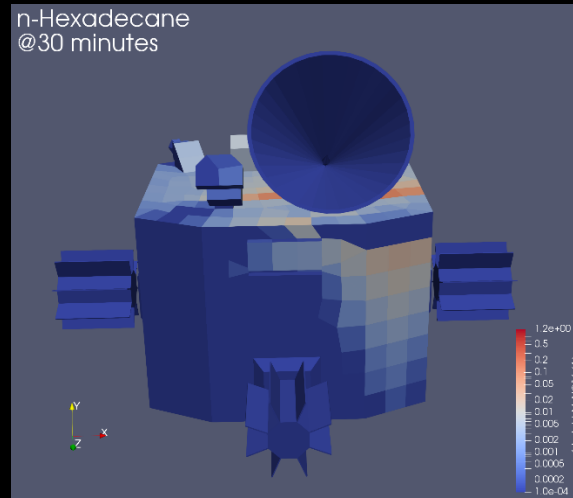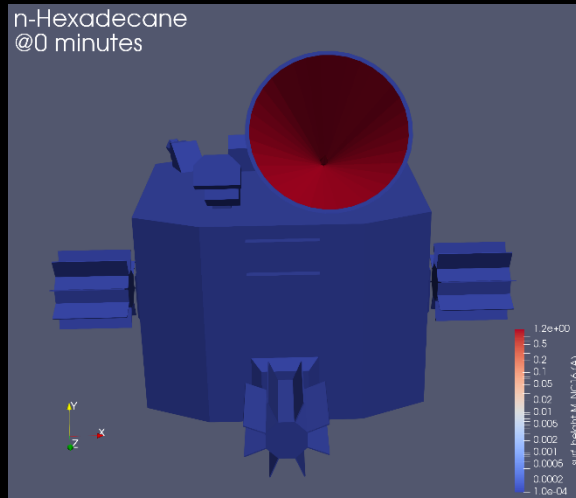
Graphics from "Eigenbrode et al., 2021, *Frontiers in Space Tech.*"

Comparison of n-C20 loss between standard model and improved model
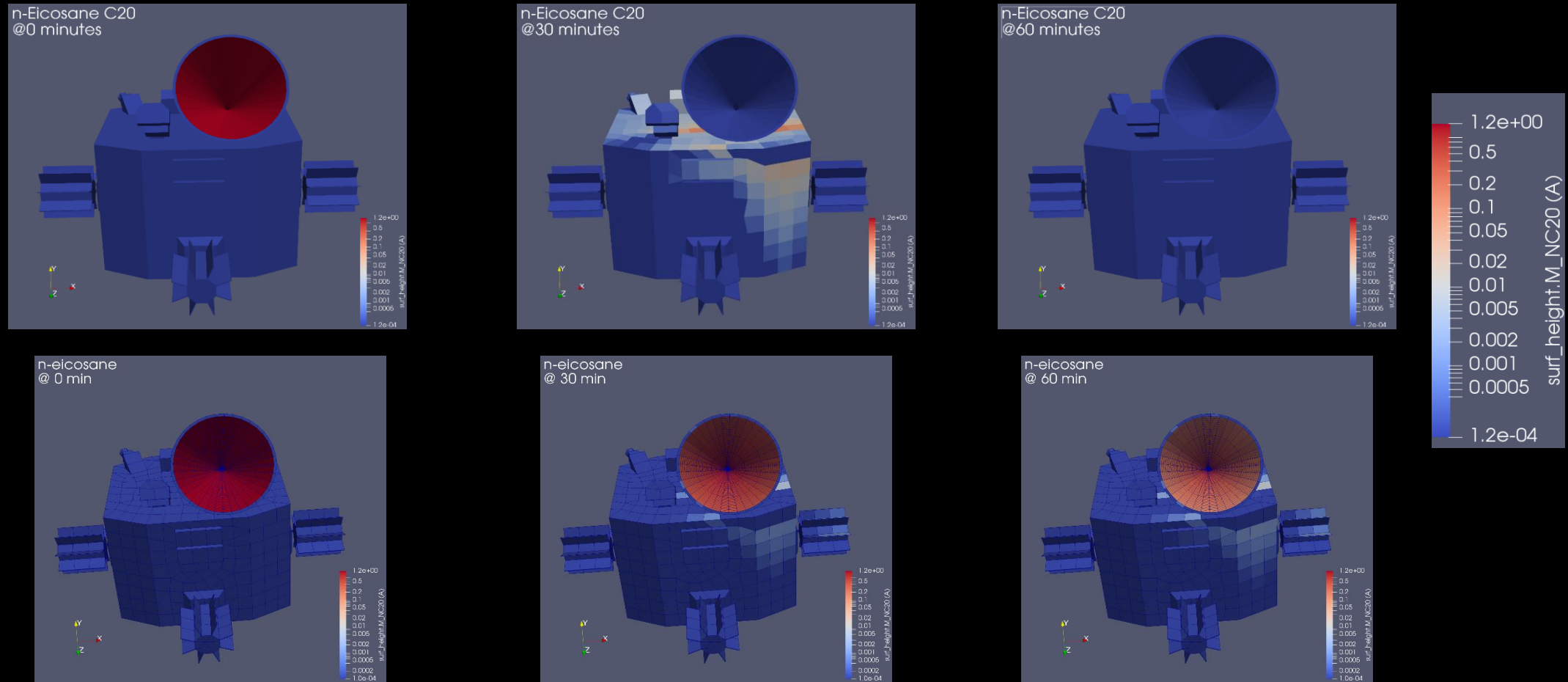
Graphics from "Eigenbrode et al., 2021, *Frontiers in Space Tech.*"

Summary

- Brunauer, Emmett and Teller's development for multilayer adsorption was incorporated into molecular transport modeling
- Their estimation of the adsorption energy for the first molecular layer and subsequent layers was utilized
- Both models utilized the rate reduction due to the source area
- The improved physics model is more consistent with long duration high temperature bake out of surface contaminated high vacuum systems

Conclusions
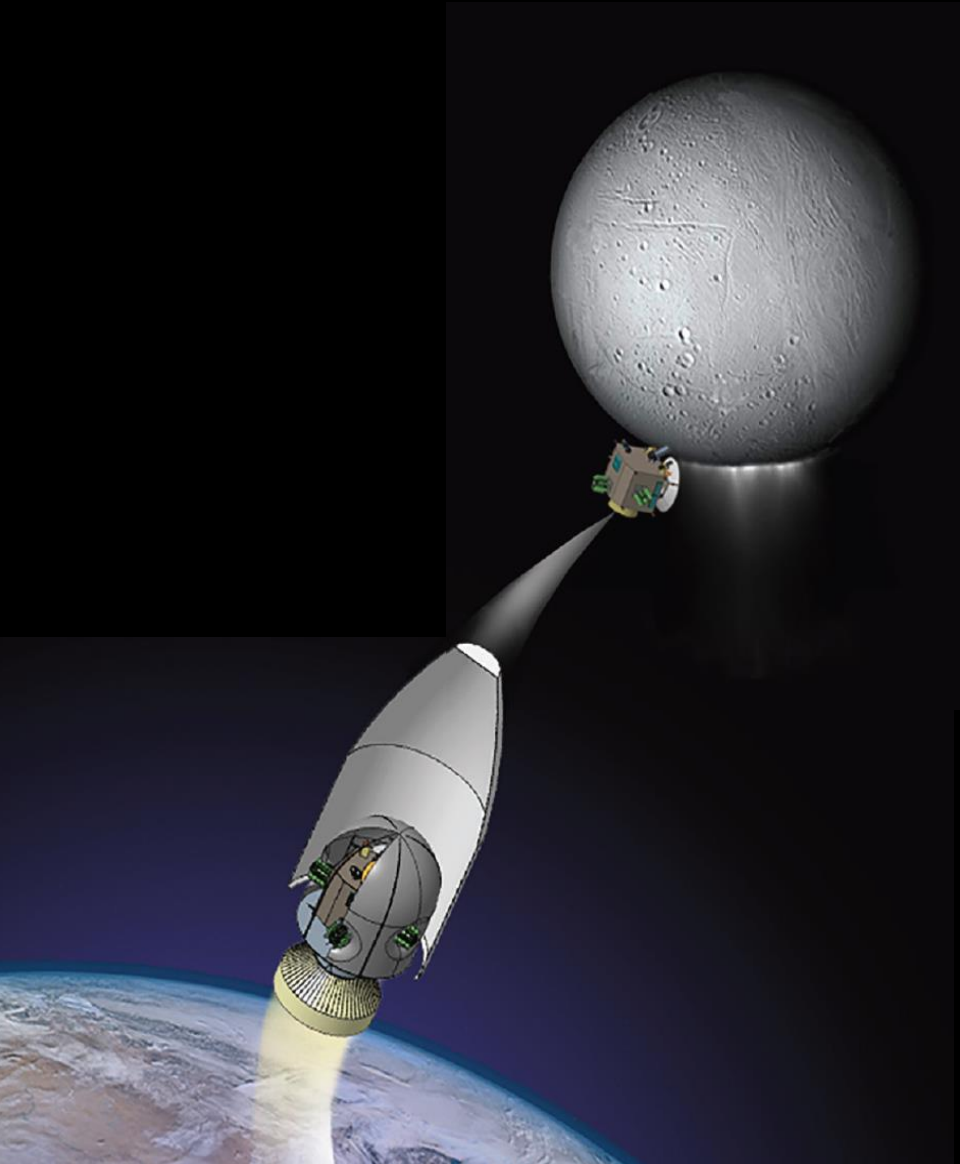
- The techniques developed in this study will enable future life detection and other highly contamination sensitive missions to provide scientific results with higher confidence in their validity.

- The improved Physics model addressing the variation of adsorption energies has higher fidelity than standard approaches
- Allows higher fidelity modeling for Astrobiology missions
- Models containing multiple species are possible
- Further improvements with additional data are possible
- Treating specific material-material interactions is possible

Backup Charts

Detailed Molecular Adsorption/Desorption

- **Below about five monolayers of organic contamination on a surface, the behavior of molecules on the surface is significantly different from in the bulk material.**
  - In the case of water on an inorganic oxide surface, in the first three monolayers of water on the surface, the adsorbed water is "ice like" at room temperature. (David B. Asay, 2005)
- **Details of the equilibrium behavior of molecular adsorption on surfaces was described by Brunauer, Emmett and Teller (BET) in 1937.**
  - The equilibrium state is defined by the arrival rate and accommodation being equal to the source area and the evolution rate or surface residence time and area
  - The energetics and thus rate behavior of the first or first few molecular layers is in virtually all cases different from any and all additional layers.
- **The propagation of the energy perturbation to additional molecular layers can be accounted for within the BET framework.**
  - Within the BET framework, Chemisorption as well as physisorption can be dealt with.
- **Divergence of the actual adsorption behavior on a real surface is to be expected due the dispersion in the surface energy.**

BET graphical description

The adsorption energy in the first monolayer is the highest
The adsorption energy in the second monolayer is second highest
This continues until the energy converges to vaporization energy of bulk liquid

Adsorption Energy

E_1
E_2
E_3
: :
E_L

~E_L

E_1 E_2 E_3
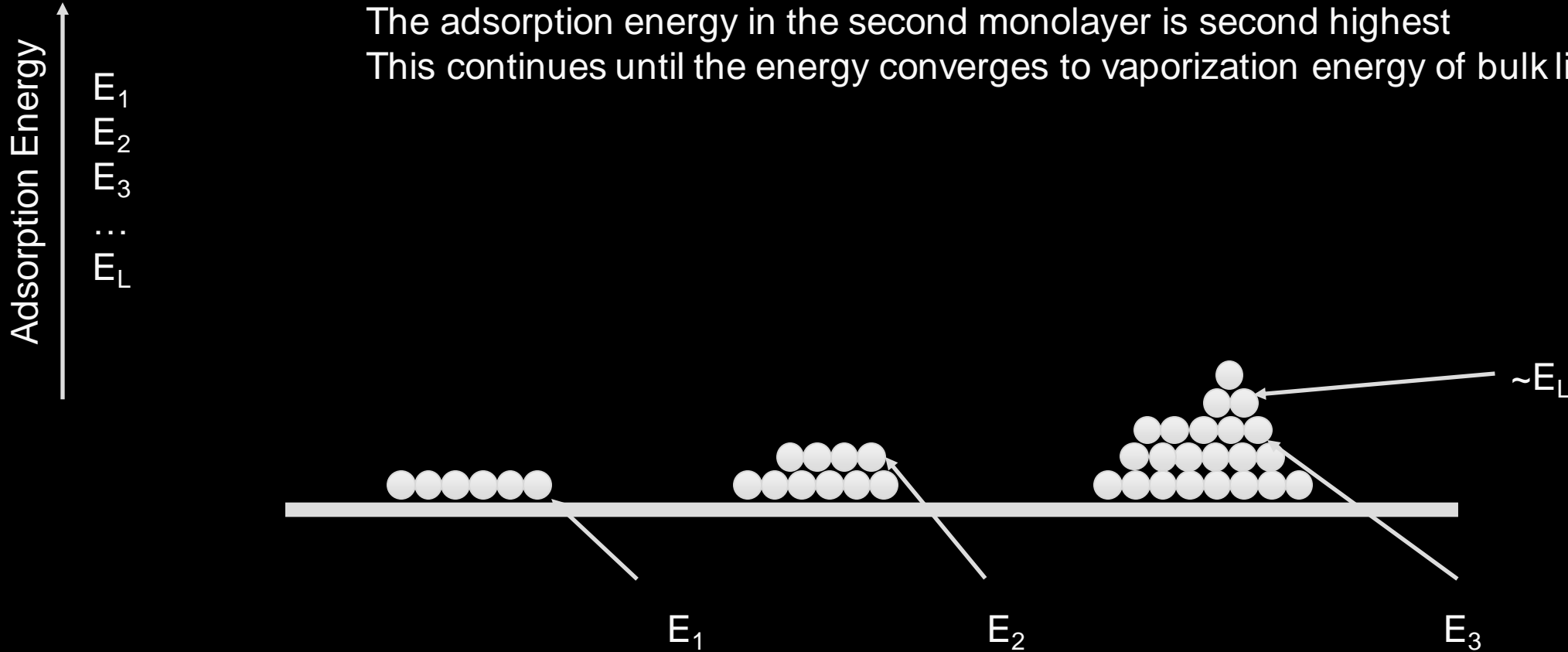
Adsorption Kinetics

- **The rate of adsorption of a material on a specific surface is based upon**
  - **The rate of arrival of the material to the surface**
    - Material cannot accumulate faster than it is supplied to the surface
    - This is in effect a function of the partial pressure of the material in the gas phase
    - The numerical rate per unit area is often described by the Hertz-Knudsen equation

$$\frac{1}{A}\frac{\mathrm{d}N}{\mathrm{d}t} \equiv \varphi = \frac{\alpha p}{\sqrt{2\pi m k_{\mathrm{B}} T}} = \frac{\alpha p N_A}{\sqrt{2\pi M R T}},$$

  - **The accommodation of the molecules**
    - This is the probability that the molecules at this energy will adsorb on the surface
  - **The area**
    - This area is the area of the specific type of target surface (whether this is bare, is a monolayer, a multilayer, etc.)
- In the BET approach, the adsorption rate is represented as

$$a_1 p s_0$$

  - a_1 is the accommodation or sticking factor, p is the partial pressure, and s_0 is the bare exposed surface area

Desorption Kinetics

- **The rate of desorption of a material from a specific surface is based upon**
  - The fractional area of the specific surface layer of molecules, in this case bare surface
  - The frequency of potential desorption events, whether probable of not
  - The energy of the specific desorption process
  - The temperature, defines what proportion of the molecules exceed that energy
- **In the BET approach, the desorption rate is represented as**

$$b_1 s_1 e^{-E1/RT}$$

  - b_1 is the frequency of the potential desorption events, s_1 is the fractional area of the specific surface, E1 is the energy of the specific desorption process, R is the gas constant, and T is the temperature
  - This is basically the surface residence time multiplied by the fractional area

Adsorption/ Desorption Equilibrium

- **The BET Equilibrium description adsorption and desorption is**

$$a_1 p s_0 = b_1 s_1 e^{-E1/RT}$$

- **Using the BET terminology, the subscripts describe the molecular layer property**
  - $a_1 = 1 - s_1$ The total area minus the area covered by one layer is the fraction that is bare
  - E_1 is the adsorption energy for the first molecular layer
- **The quantity material on a surface is the sum of the adsorption and desorption behavior of all the layers**
  - Due to the direct relation between one layer and the next layer in the definition of the rate of adsorption and desorption, it is possible to simplify the equation from the individual layer level to an infinite number of molecular layers
- **Known differentiation between layer behaviors can be accounted for**

Points to Ponder

- The accommodation of molecules is an average value
- The desorption energy is a function of the surface energy
- The surface energy is an average energy
  - At the extremes of the levels of coverage for a layer, the adsorption behavior should be expected to diverge from the average
  - A 2 eV point defect is equivalent to a 192 kJ per mole difference in surface energy, which is huge!
- Physical constraints
  - A molecule adsorbed onto a uniform clean surface loses at least one degree of freedom
  - Addition of further restrictions in the physical adsorption process results in loss of additional degrees of freedom. Physical imperfections, lattice defects, excitons,…
- Water adsorbed on silicon dioxide is locked into a solid like physical state (Ice like) at room temperature through at least three molecular layers

BET assumption: heat of desorption from a bare surface is approximately the heat of sublimation