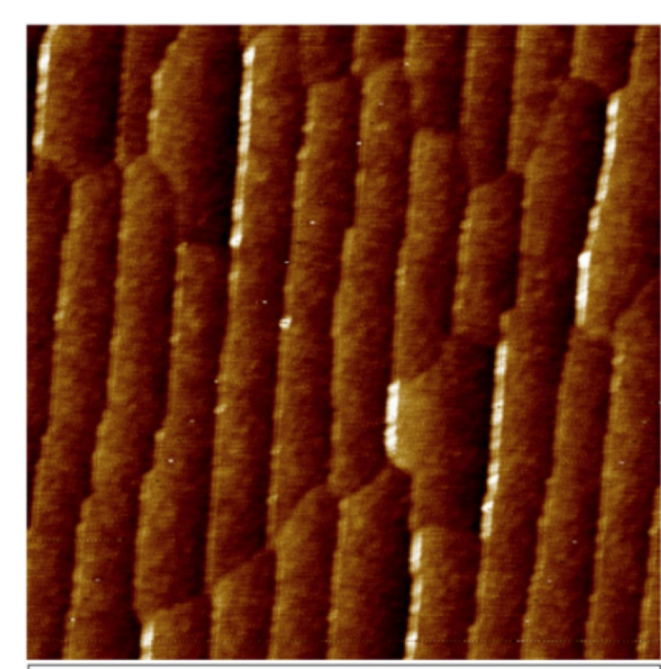
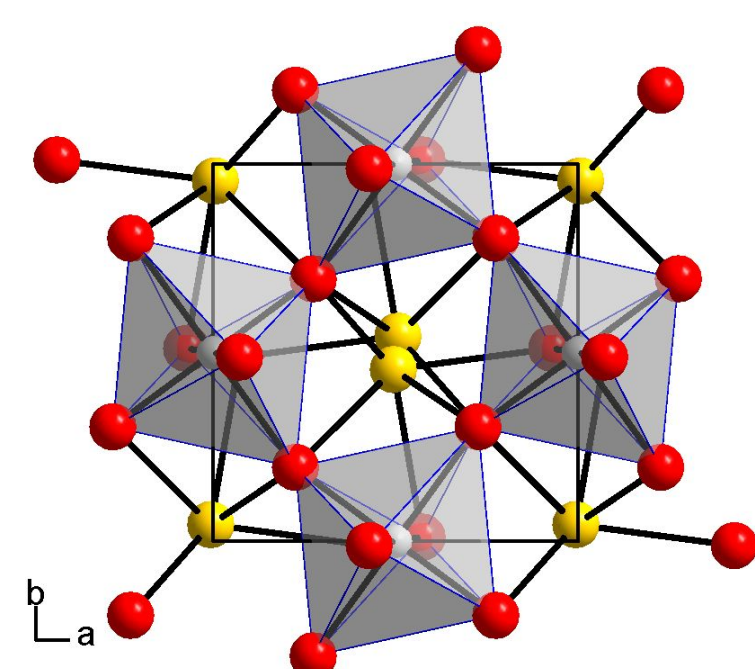


**Synopsis:** We examine the contribution of ion gauges and  $\text{LaMnO}_3$  perovskite single crystals in the kinetics of dehydrogenation/dehydration of 2-propanol to form acetone/propene. We also present a design for heating a molecular beam and an analysis of its thermic implications.

## Background and Motivation



1.2 nm  
-0.9 nm



Molecular Model (Right) of  $\text{LaMnO}_3$

- Perovskites have the general formula of  $\text{ABO}_3$ , typically composed of alkaline or lanthanide cations (A) and transition metal cations (B).
- Perovskites are chosen for study as catalysts due to their wide tunability of composition and consequently the acid-base and redox characteristics.
- This study is on the conversion of 2-propanol to acetone and propene via ion gauge- and catalysis-activated dehydr(ogen)ation reactions.

## Experimental Setup (SATIRA)

- All measurements are taken in ultra high vacuum (UHV) to control the chemical environment of the perovskite sample. We produce an effusive molecular beam by collimating our reactants with a glass capillary array (GCA) and two differential pumping stages.

The beam meets the sample in the scattering chamber and bombards it with reactants.

We measure the reaction products with a mass spectrometer positioned directly underneath the sample holder.

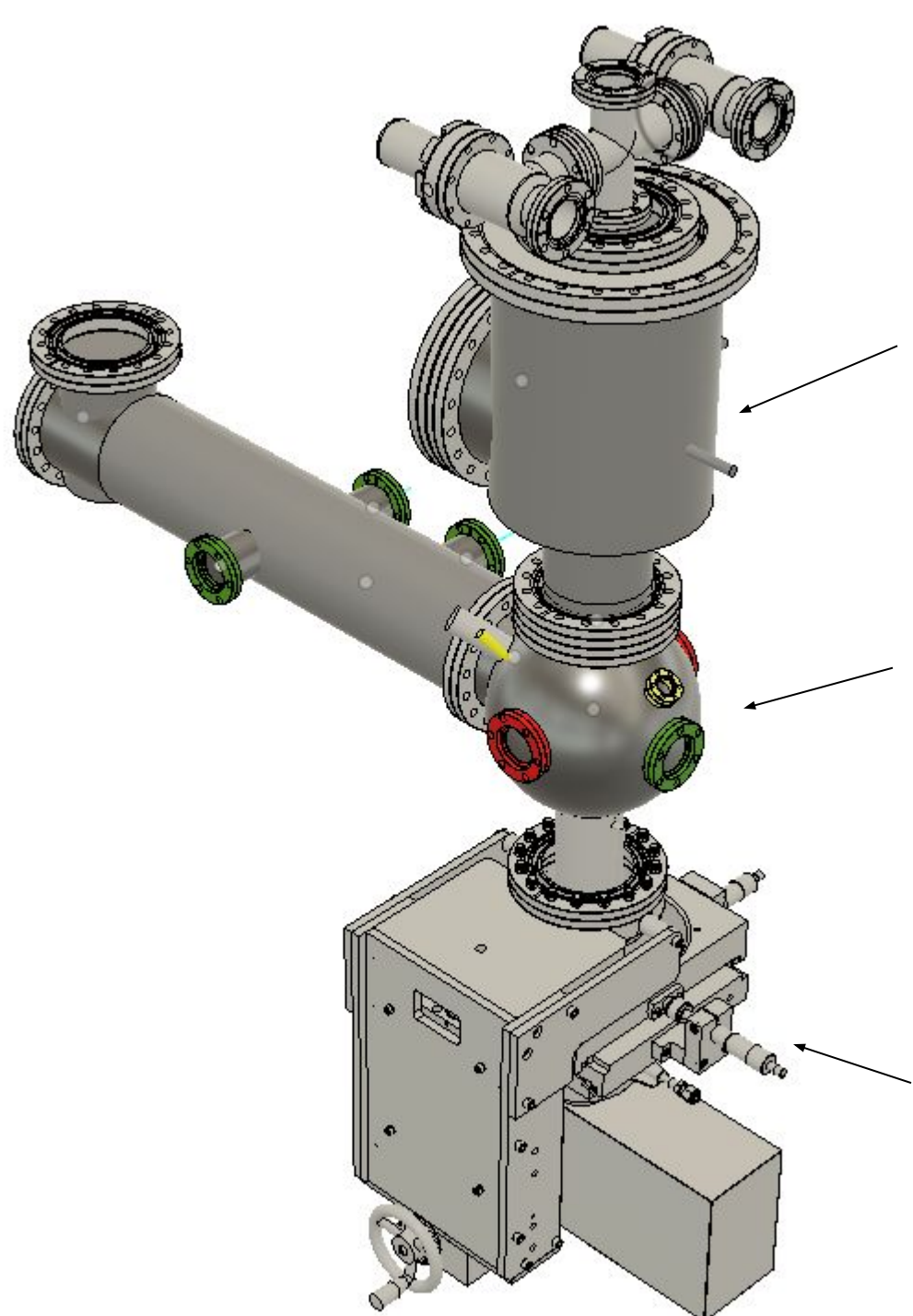
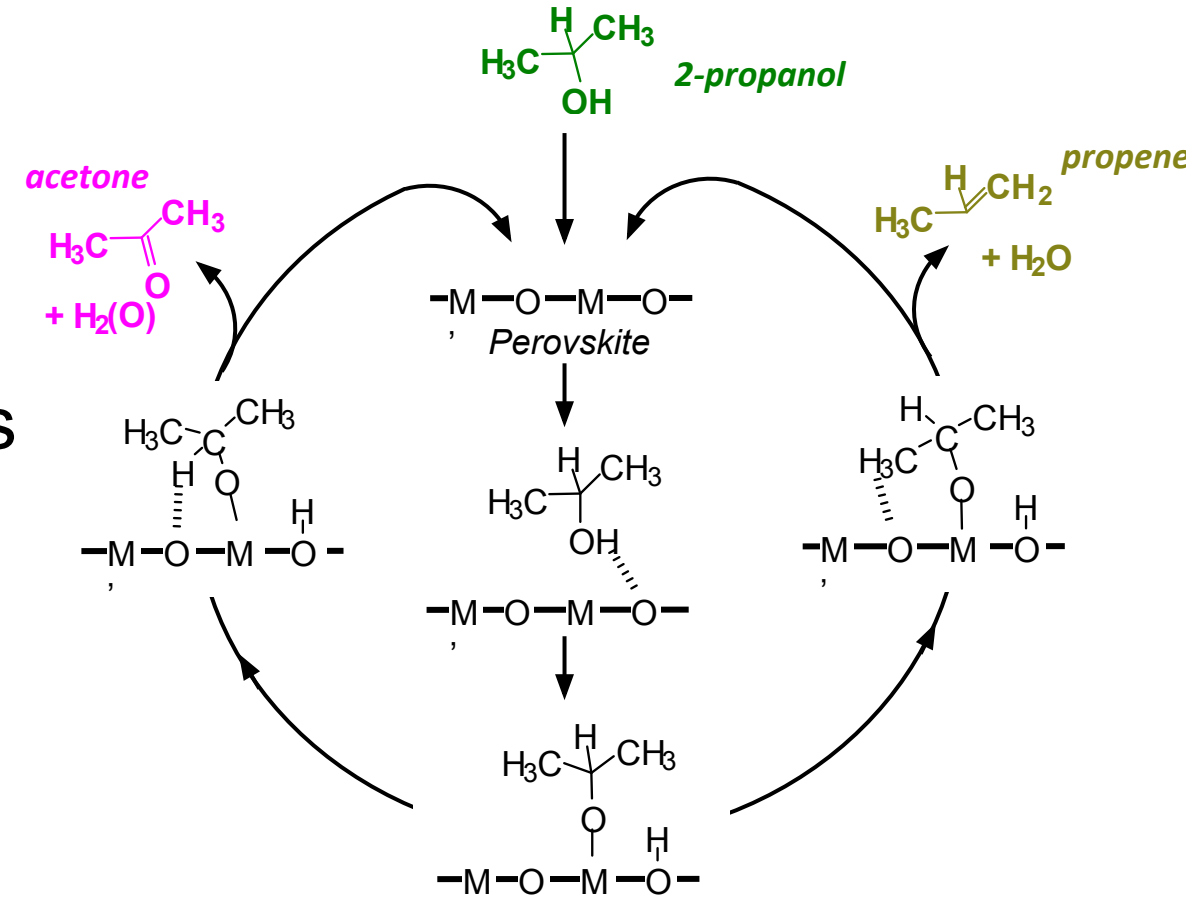


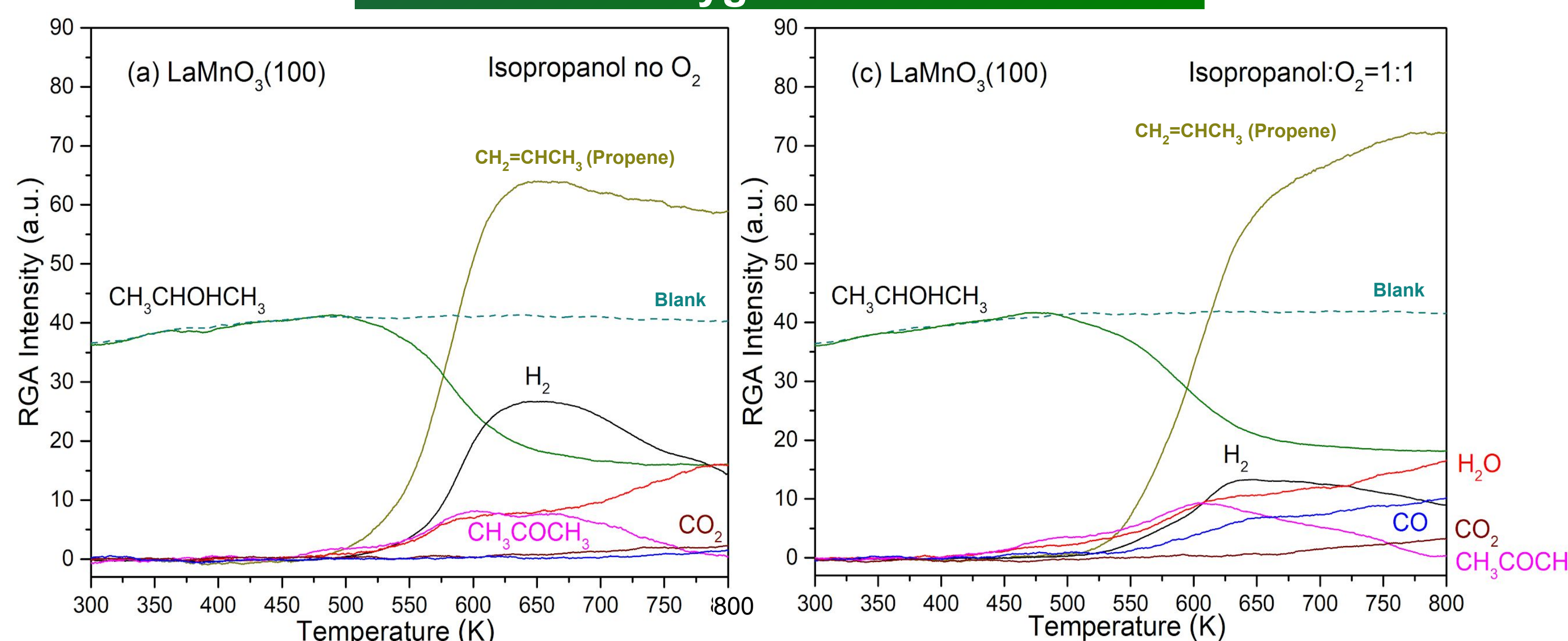
Figure: A Section of Our UHV Chamber

## Reaction Mechanism

- 2-propanol loses its hydroxyl hydrogen as it adsorbs onto the polar surface of the catalyst
- The resultant intermediates can either recombine and desorb or form products acetone or propene via dehydrogenation.

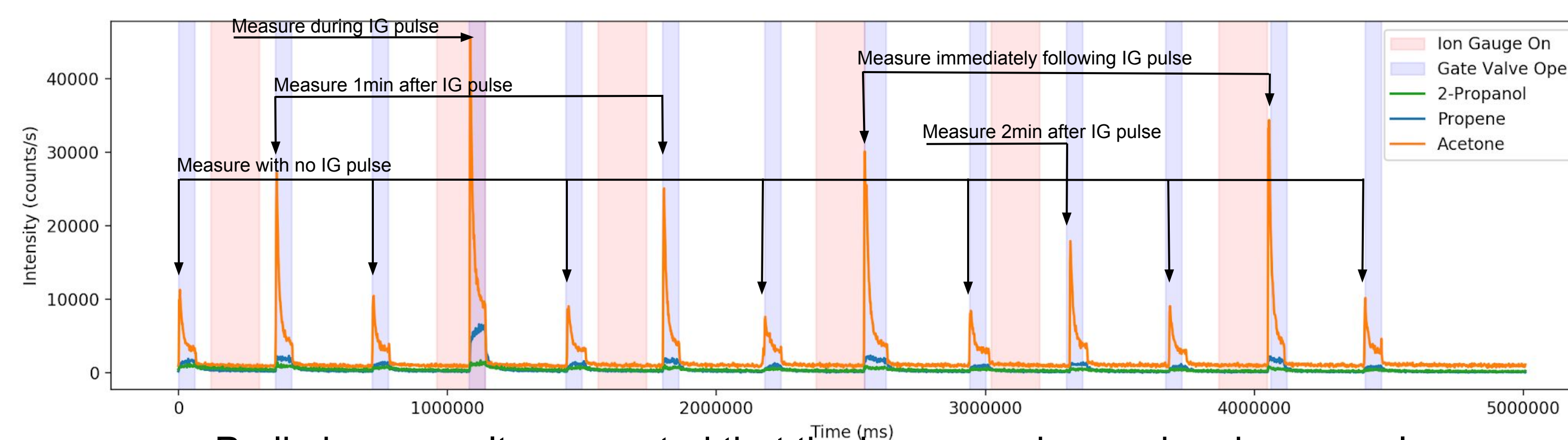


## Effect of Oxygen Concentration



- The above figure shows that the relative production efficiency of propene to acetone can be modulated by coexposure of oxygen to catalyst *in-situ* and varying the temperature.
- The conversion of 2-propanol into acetone +  $\text{H}_2\text{O}$  may require an additional O atom from the catalyst's surface (Langmuir-Hinschelwood).
- Back-filling our chamber with  $\text{O}_2$  can result in a lower steady state vacancy and likely fills these holes, enabling another acetone reaction to occur.

## Ion Gauge Contribution



- Preliminary results suggested that the ion gauge in our chamber was also contributing to production.
- In this measurement, we dosed our chamber with  $5 \times 10^{-5}$  Torr 2-Propanol, and sampled it at regular 6-minute intervals with a mass spectrometer.
- The intensity of our propene signal changes linearly as a function of when the ion gauge was on last. The "overlapping" pulse (4th pulse, purple) exists on the same trendline, suggesting any amplification effect is minimal, and that the ion gauge does in fact activate genuine product reactions.

## Acknowledgements

- We thank Yafen Zhang for providing the continuous-exposure temperature-programmed reaction data.
- This work was supported primarily by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Chemical Sciences, Geosciences, and Biosciences Division.
- This work was supported in part by the U.S. Department of Energy, Office of Science, Office of Workforce Development for Teachers and Scientists (WDTS) under the Science Undergraduate Laboratory Internship Program.

AFM Image from Effect of Sr Substitution in  $\text{LaMnO}_3(100)$  on Catalytic Conversion of Acetic Acid to Ketene and Combustion-Like Products, Yafen Zhang, David R. Mullins, and Aditya Savara, The Journal of Physical Chemistry C 2019 123 (7), 4148-4157

## Beam Heating Enhancement

- We have recently completed an upgrade that enables us to change the kinetic energy of the reactants incident on the sample by heating them in the molecular beam stage.
- This will help us to further distinguish the behavior of our ion gauge from "real" catalytic activity.
- Vented Screws are used throughout the design to prevent "virtual leaks".

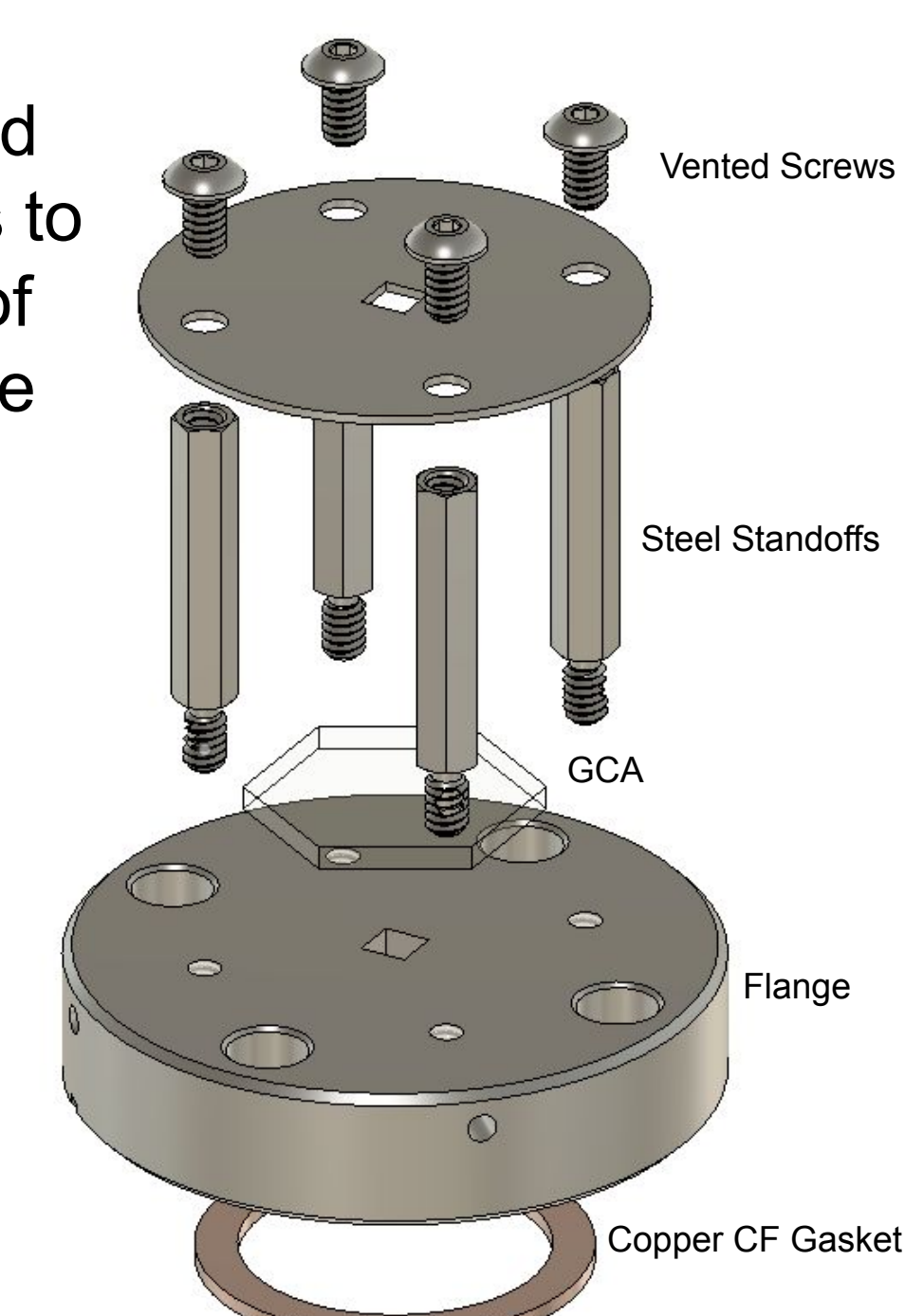
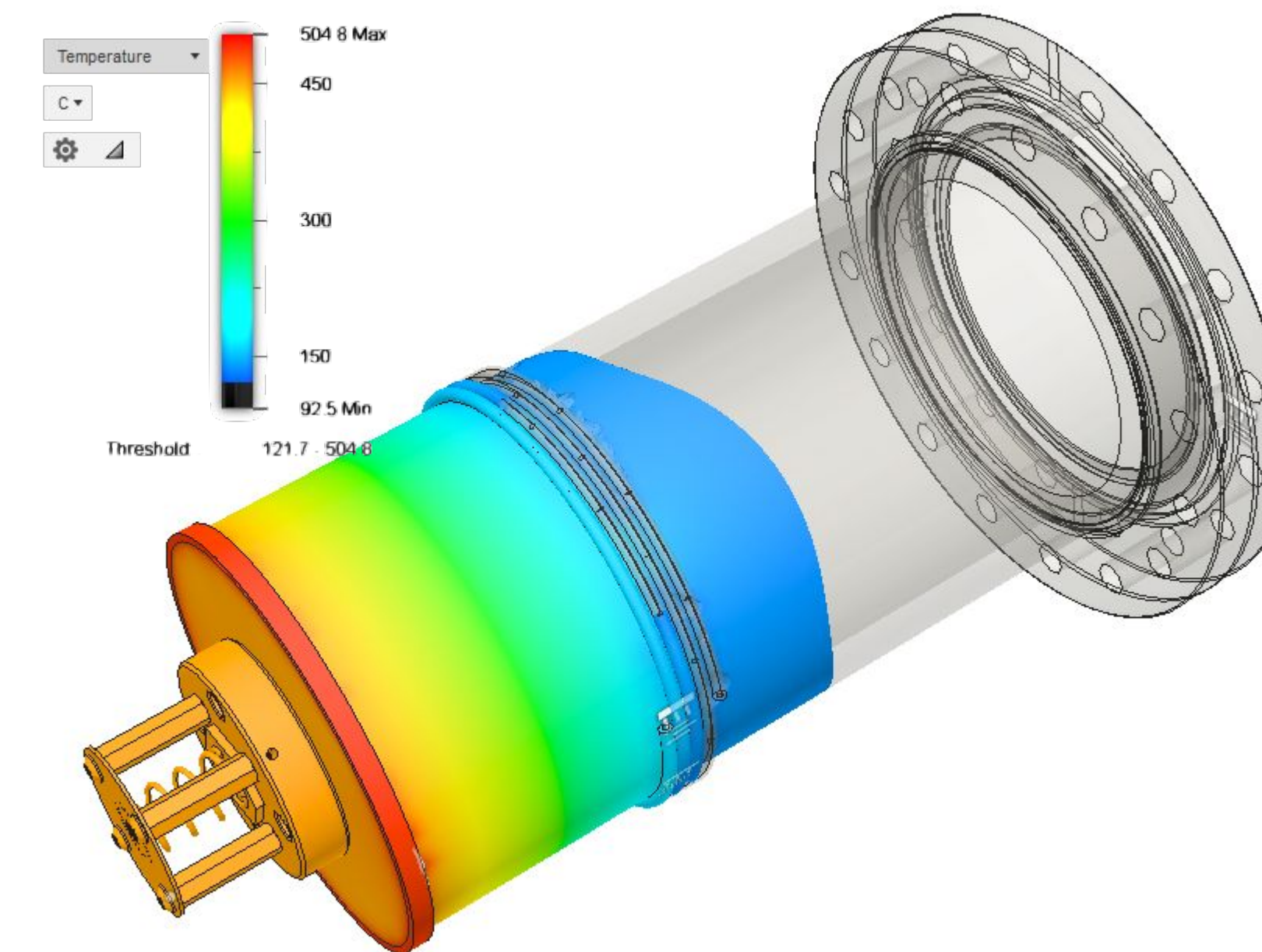


Figure: Exploded View of the GCA Assembly

## Thermal Analysis



- In order to determine the amount of cooling required, we solved the heat equation computationally via the finite element method with Neumann (temperature) and Dirichlet (heat flux) boundary conditions.
- A maximum temperature of  $100^\circ\text{C}$  is required at the flange to protect sensitive instrumentation above it.

## Conclusions

- We conclude that ion gauges have the ability to act as "catalysts" themselves, in converting 2-propanol to acetone and propene products.
- Our beam heating enhancement will enable us to study the reaction rates of molecules impinging on our sample as a function of their initial kinetic energies, as part of a broader agenda to further characterize the reaction kinetics of catalytic conversions.