

# The Effects of Temperature and Oxidation on D Retention in Solid and Liquid Li Films on Molybdenum Plasma-Facing Components

Angela M. Capece

56<sup>th</sup> Annual Meeting of the APS Division of Plasma Physics  
New Orleans, LA

October 31, 2014



# Acknowledgements



## Co-authors:

- John Roszell, Princeton University
- Charles Skinner, PPPL
- Bruce Koel, Princeton University

## Contributors:

- Bob Kaita, PPPL
- Mike Jaworski, PPPL
- John Schmitt, PPPL
- Dick Majeski, PPPL

## Funding:

- **DOE** (FES), PPPL LDRD, *Fundamental Studies of Deuterium Retention in Solid and Liquid Metals*

# Outline



## I. Motivation:

## II. Our Approach:

- Using surface science test stands to understand PFCs in tokamak environments

## III. D Retention in Li Films on TZM

- What is the role of:
  - Temperature?
  - Oxidation?

## IV. Conclusions:

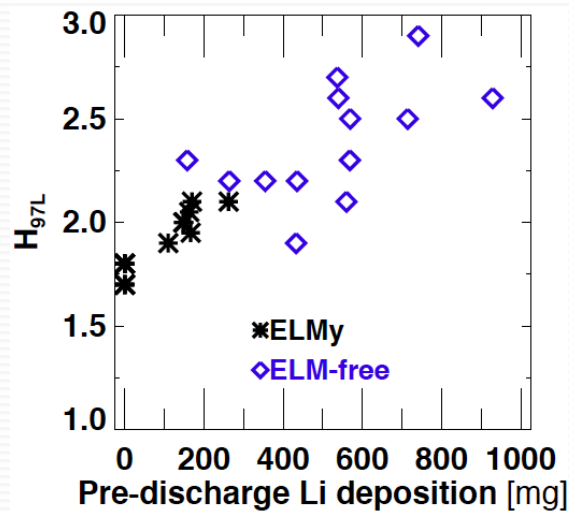
- Two regimes:
  - (1) At low temperature, D retention is highest in  $\text{Li}_2\text{O}$  films,
  - (2) At high temperature, D retention is highest in metallic Li films

# Li films improve plasma performance and confinement time in LTX and NSTX



## NSTX

*R. Maingi et al., PRL 107, 145004, 2011.*



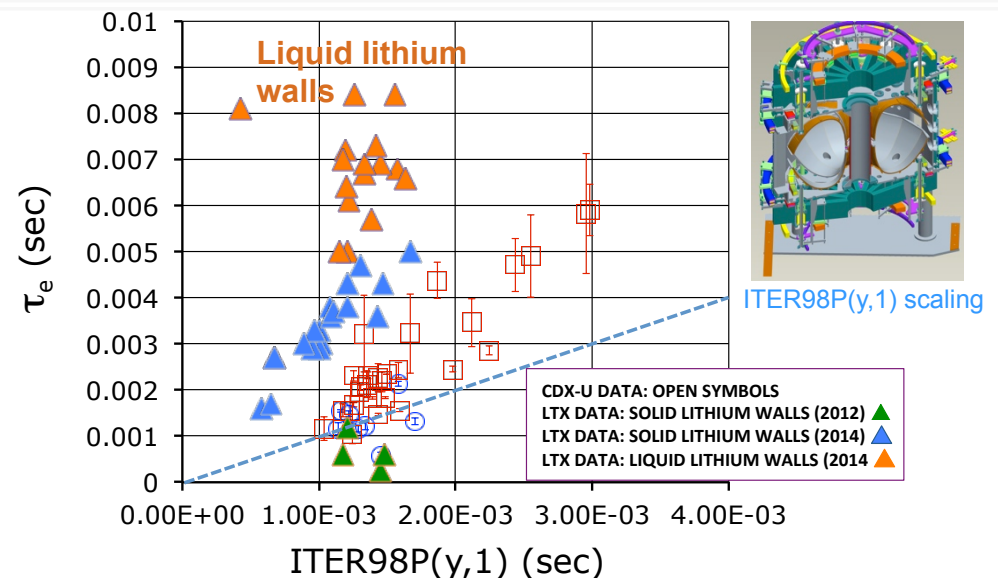
H factor increases with Li dose

Li causes reduction in:

- Divertor recycling
- Edge neutral density
- Electron transport

## Lithium Tokamak Experiment

*J. Schmitt, Invited talk Y12.3*



Confinement time increases 10x with liquid Li  
Low recycling with large-area Li walls

# We don't understand what happens at the surface



- Why does Li improve plasma performance?

# We don't understand what happens at the surface

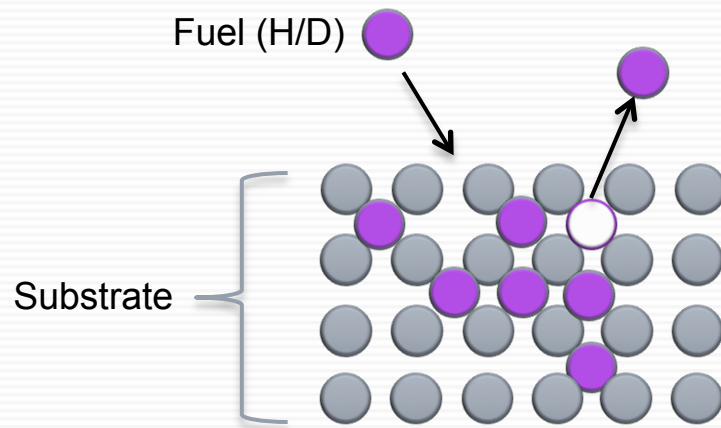


- Why does Li improve plasma performance?

Working hypothesis: Deuterium retention

High D retention → Low D recycling → High edge temperature → Reduced temperature gradients

- Recycling Process:



# We don't understand what happens at the surface



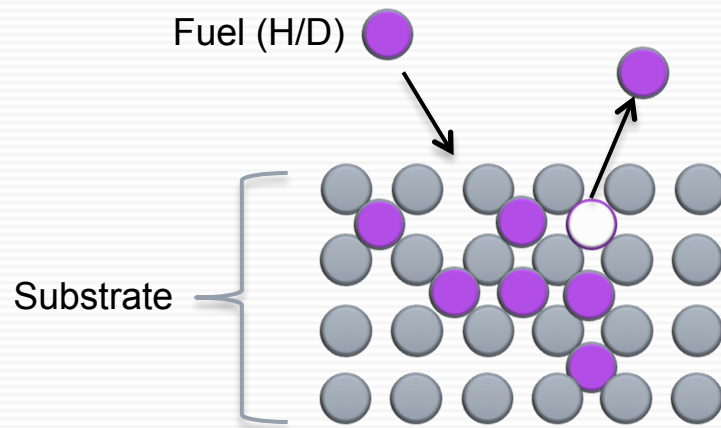
- Why does Li improve plasma performance?

Working hypothesis: [Deuterium retention](#)

How is D retained in Li?

High D retention → Low recycling → High edge temperature → Reduced temperature gradients

- Recycling Process:

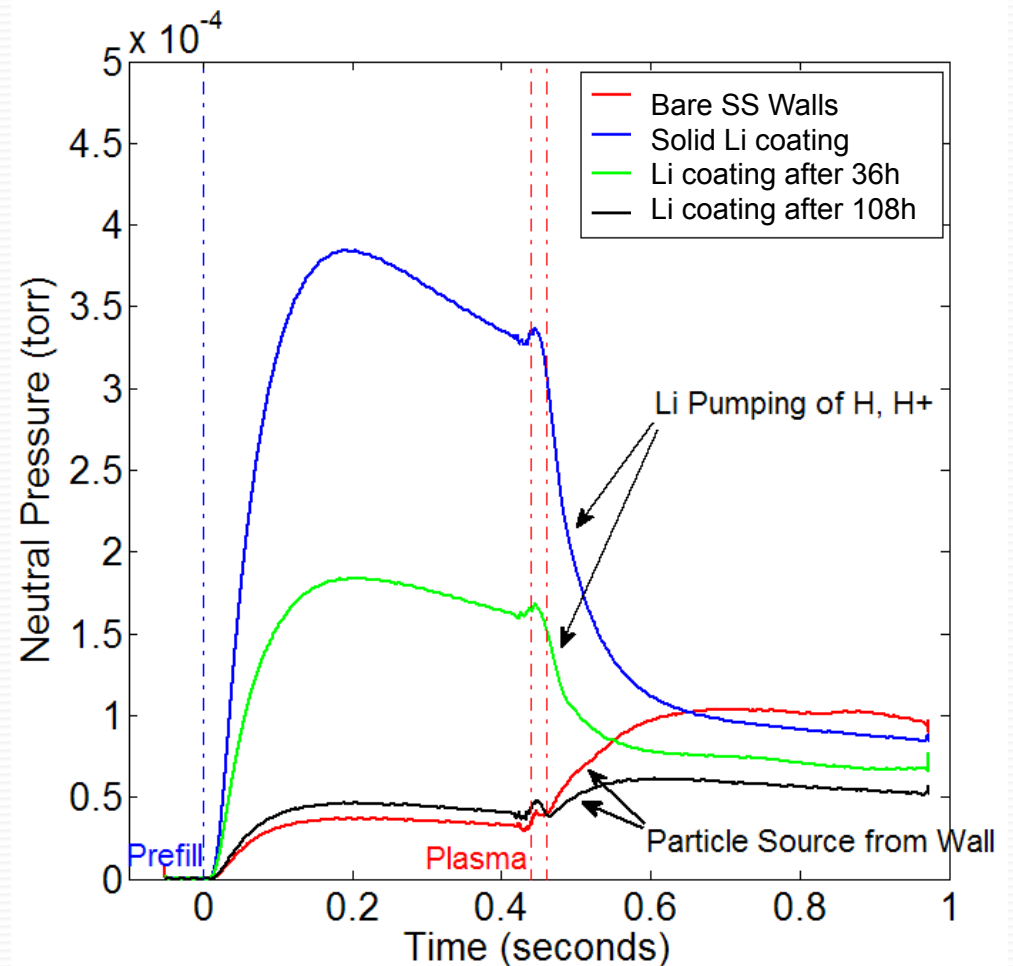


1. Through volumetric conversion of Li to LiD  
(*Baldwin & Doerner*)
2. Through complexes that involve oxygen  
(*Krstic, Allain, Taylor*)

# H pumping fraction is correlated with wall temperature and composition on LTX



- Hot, oxidized Li: lower H pumping
- Cold, oxidized Li: better H pumping
- With e-beam system:  
When Li is metallic, hot shells give improved plasma performance



*J.C. Schmitt et al., JNM 438, S1096 (2013)*



# H pumping fraction is correlated with wall temperature and composition on LTX

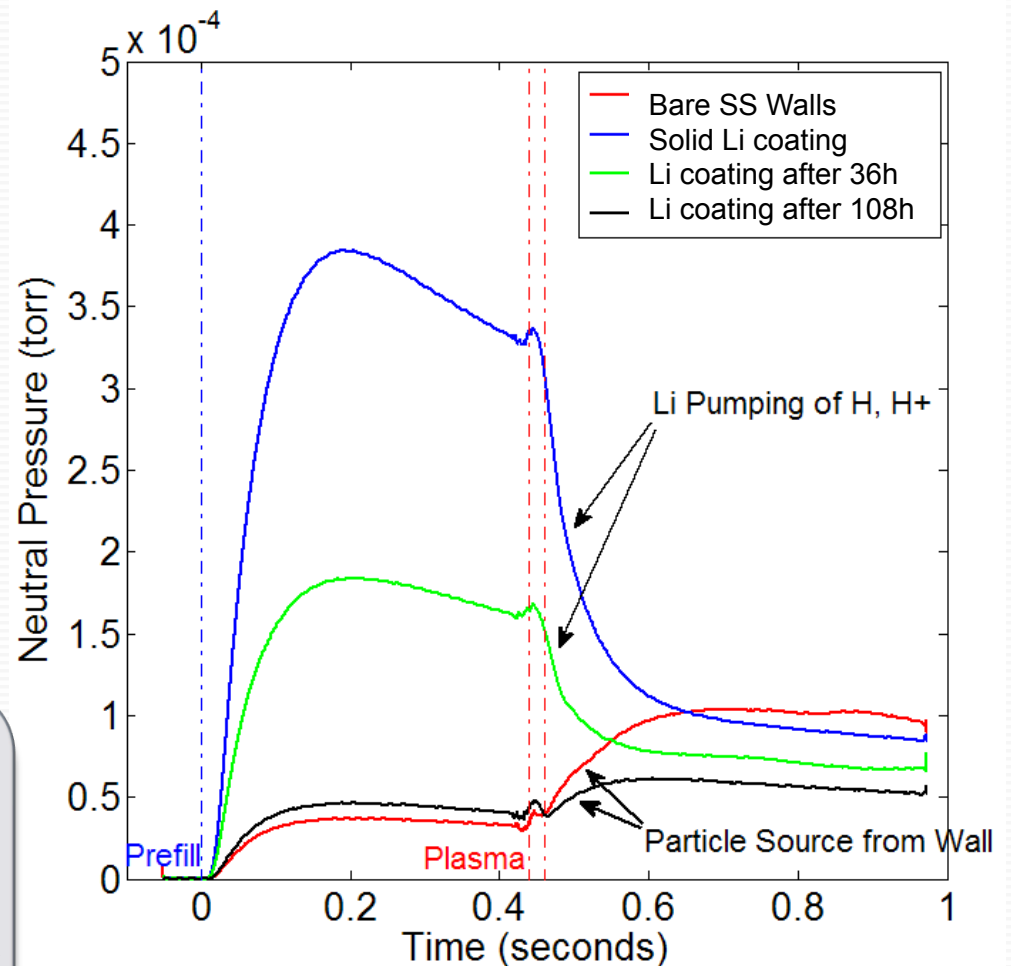


- Hot, oxidized Li: lower H pumping
- Cold, oxidized Li: better H pumping
- With e-beam system:  
When Li is metallic, hot shells give improved plasma performance

## Key Question:

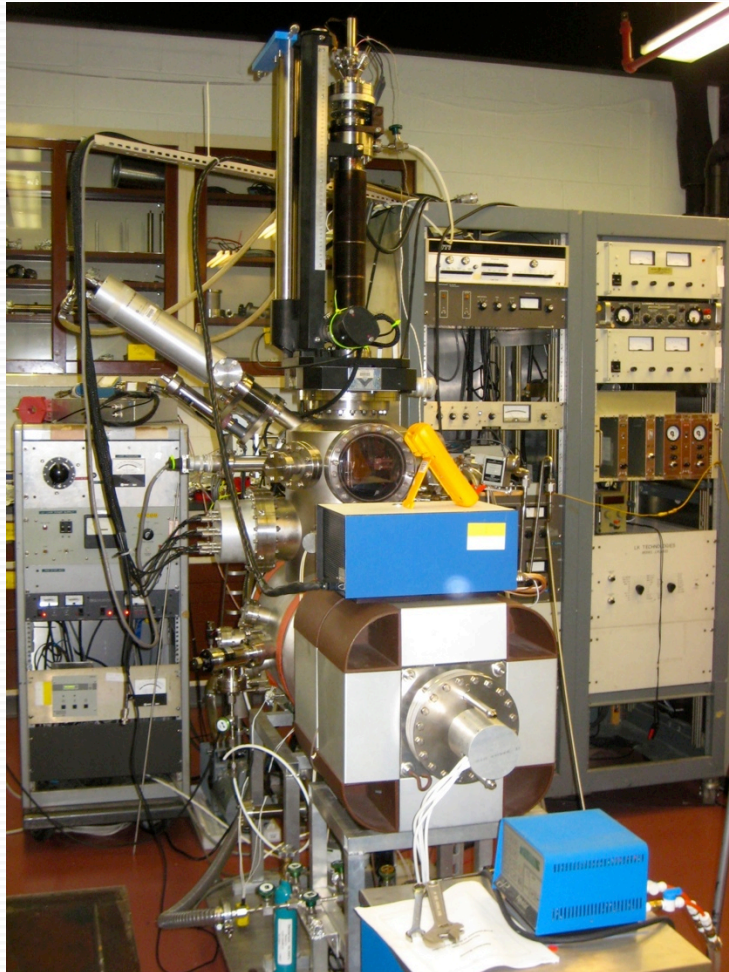
How is the pumping ability of Li affected by temperature & oxidation?

Our goal: To elucidate this data under carefully controlled conditions.



*J.C. Schmitt et al., JNM 438, S1096 (2013)*

# Surface science provides fundamental information needed to understand plasma-wall interactions



*Test stand instrumentation in the Surface Science & Technology Lab at PPPL*

Key variables affecting chemistry at surface:

- Pressure (residual gases)
- Temperature (plasma heating)
- Composition (Mo, Li, D, etc.)

Lab-based surface science experiments enable independent control of all variables

*...something we cannot achieve in a tokamak or linear plasma device!*

Isolate effects of:

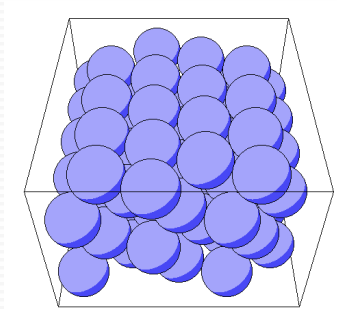
- Chemistry
- Incident particle fluxes and energies
- Substrate temperature
- Surface composition
- Morphology

Start simple, i.e. single effects, and add complexity to bridge gap between model systems and tokamak environment

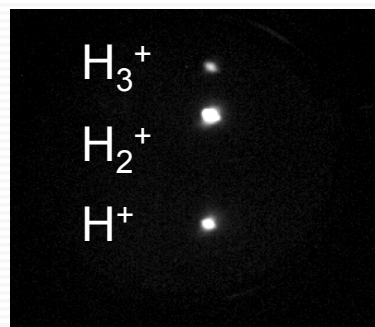
# Our capabilities span from the simple to the complex



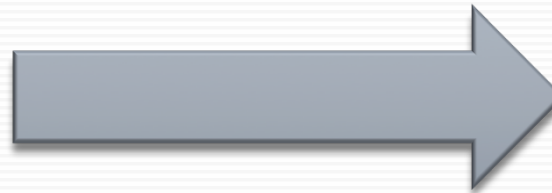
## Simple Model Experiments



Mo(110) crystal



Monoenergetic ion beam  
(Image of He ions on phosphor screen)

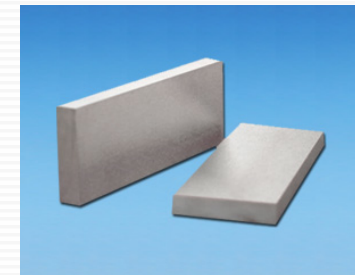


Grain boundaries  
Alloying elements: Ti, Zr, C  
Surface roughness

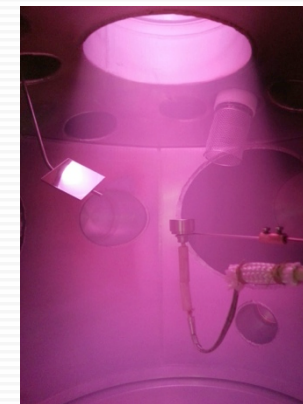


Multiple species:  $H^+$ ,  $H_2^+$ ,  $H_3^+$   
Increased flux:  $10^{12} \rightarrow 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$   
Atoms, ions, or atoms + ions

## More Complex Systems



TZM Mo alloy

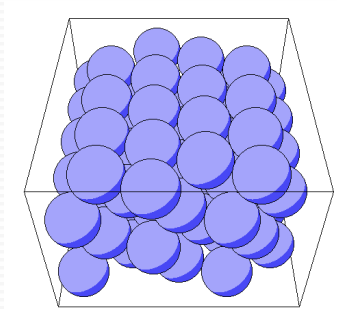


ECR plasma source

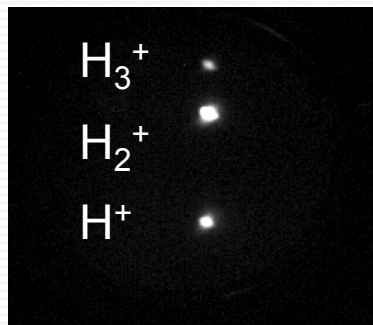
# We will focus on more complexity in this talk



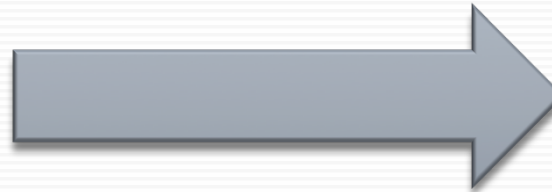
## Simple Model Experiments



Mo(110) crystal



Monoenergetic ion beam  
(Image of He ions on phosphor screen)

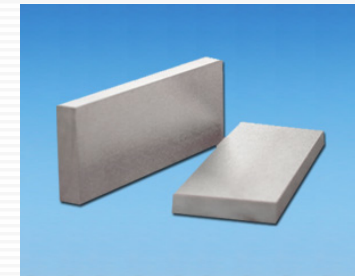


Grain boundaries  
Alloying elements: Ti, Zr, C  
Surface roughness

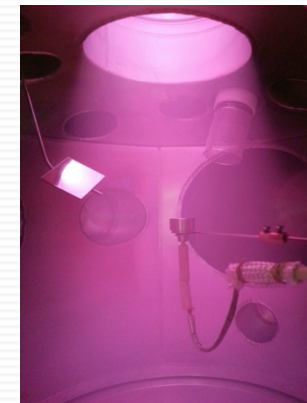


Multiple species:  $H^+$ ,  $H_2^+$ ,  $H_3^+$   
Increased flux:  $10^{12} \rightarrow 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$   
Atoms, ions, or atoms + ions

## More Complex Systems

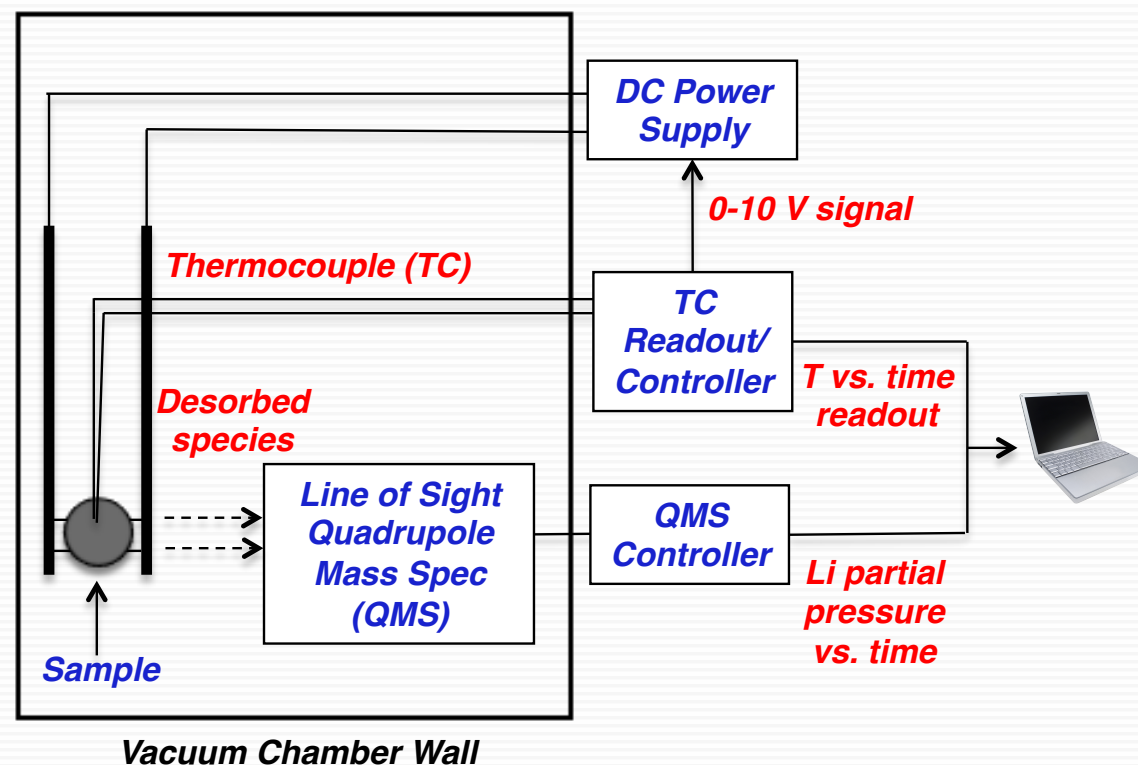
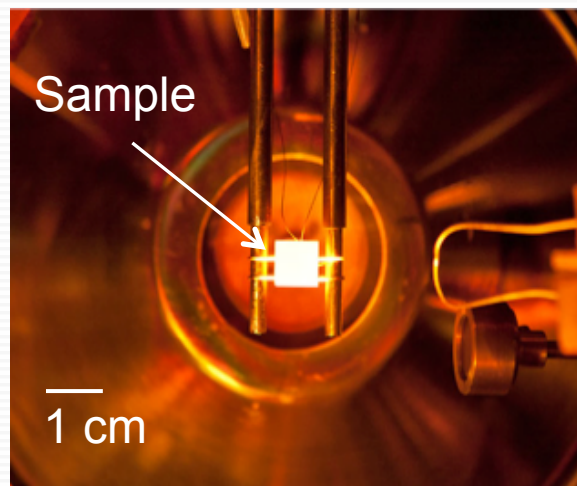


TZM Mo alloy



ECR plasma source

# Temperature programmed desorption gives desorption energy, rate constants, & quantity desorbed

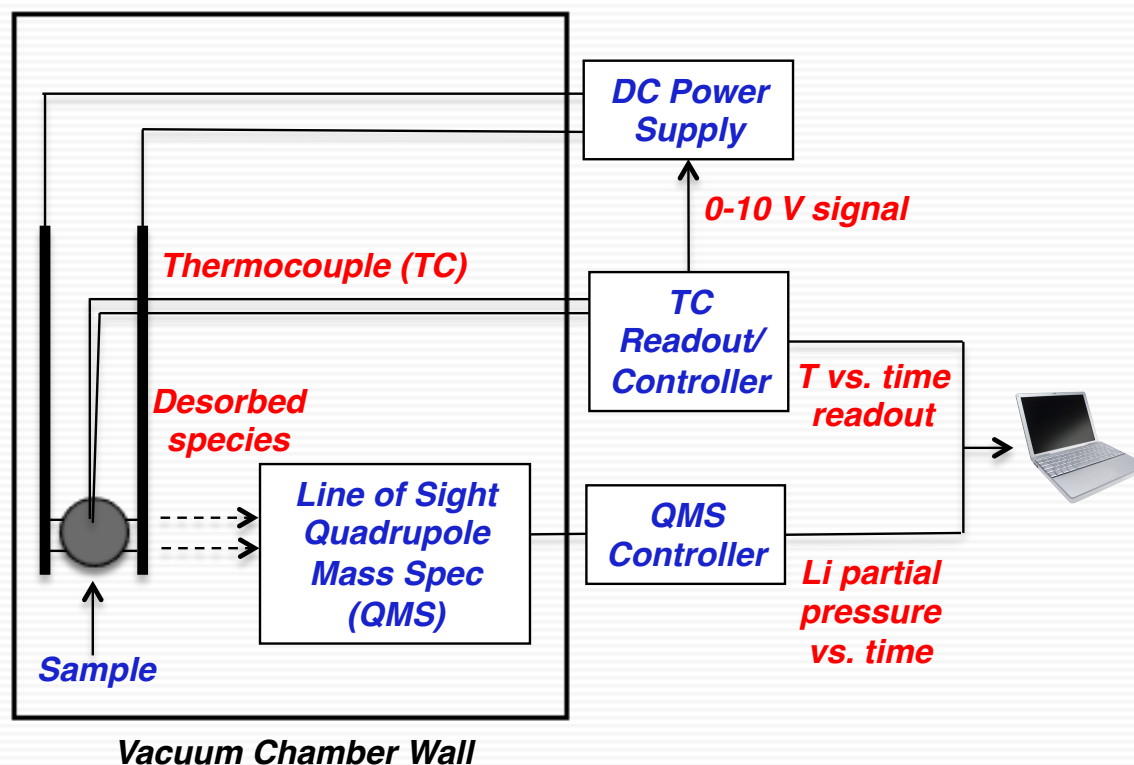
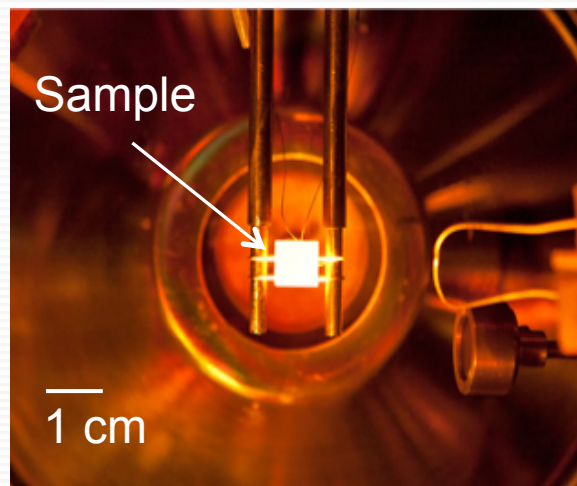


## Temperature Programmed Desorption (TPD) Technique:

- Linear temperature ramp applied to sample
- Partial pressure of desorbing species measured
- Temperature of desorption peak relates to binding energy
- Area under pressure vs. time curve proportional to number of atoms desorbed



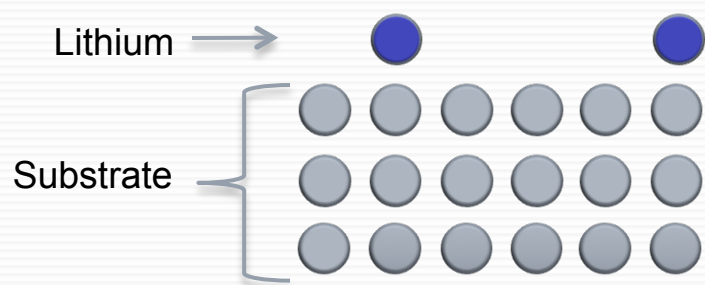
Temperature programmed desorption gives desorption energy, rate constants, & quantity desorbed



Area under pressure vs. time curve  $\rightarrow$  # of atoms desorbed

**TPD can be used to measure D retention!**

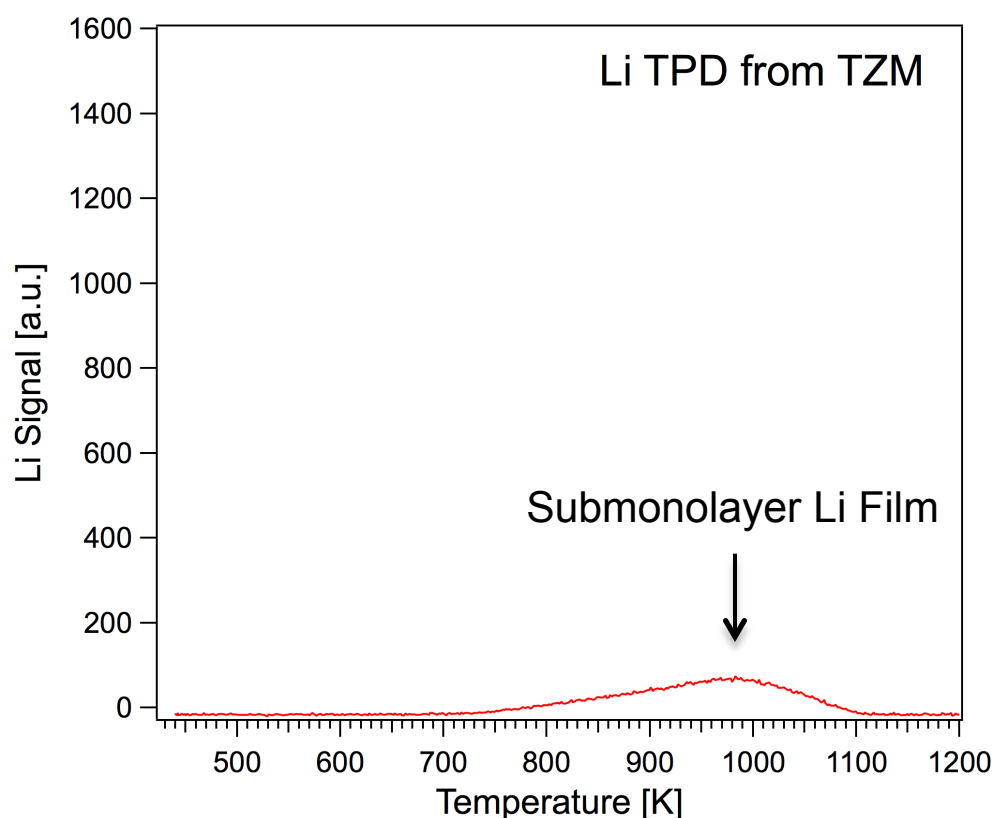
# TPD shows that Li is stable on TZM up to 1000 K



- Submonolayer Li film on TZM stable up to 1000 K
- Represents Li-Mo bonding
- Desorption energy  $\sim 2.7$  eV

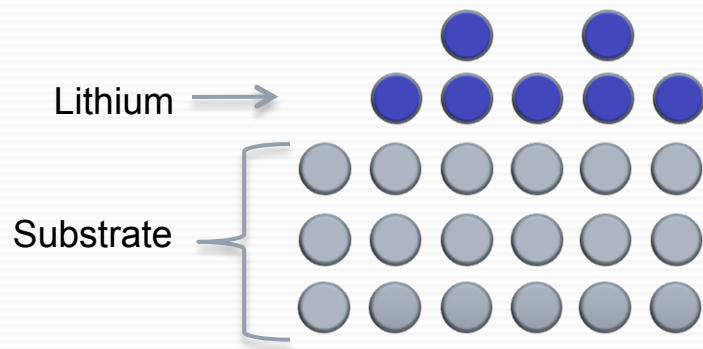
$$\frac{E^*}{RT} = \frac{1}{2} + Y - \ln Y + \frac{\ln Y}{Y} - \frac{\ln Y}{2Y^2} (2 - \ln Y)$$

$$Y = \ln \left( \frac{v_0 \cdot T}{\beta} \right)$$

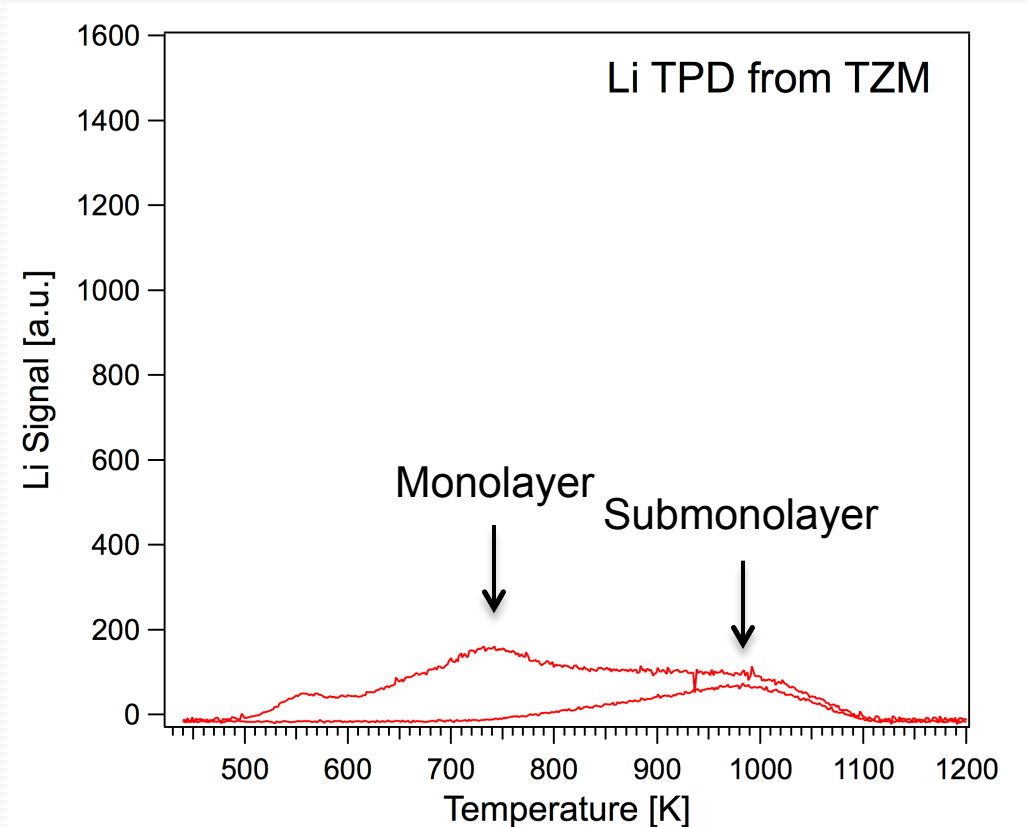


*C.H. Skinner et al., JNM 438, S647 (2013)*

# Area under Li TPD curve increases with Li dose



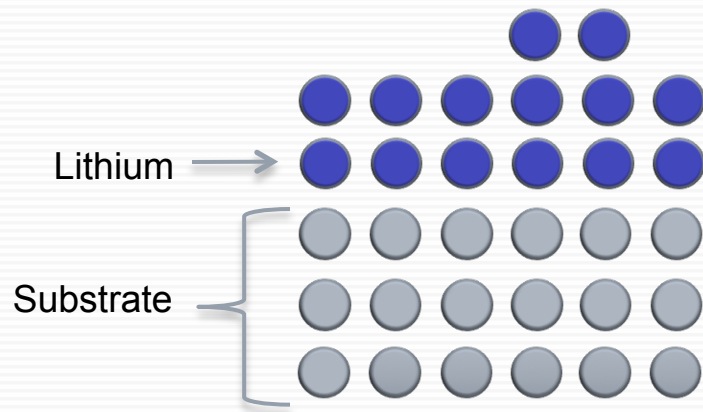
- Area under Li TPD curve increases with Li dose
- Dipole interactions lower the desorption energy
- Desorption energy of monolayer  $\sim 2$  eV
- $E_d$  is a function of coverage



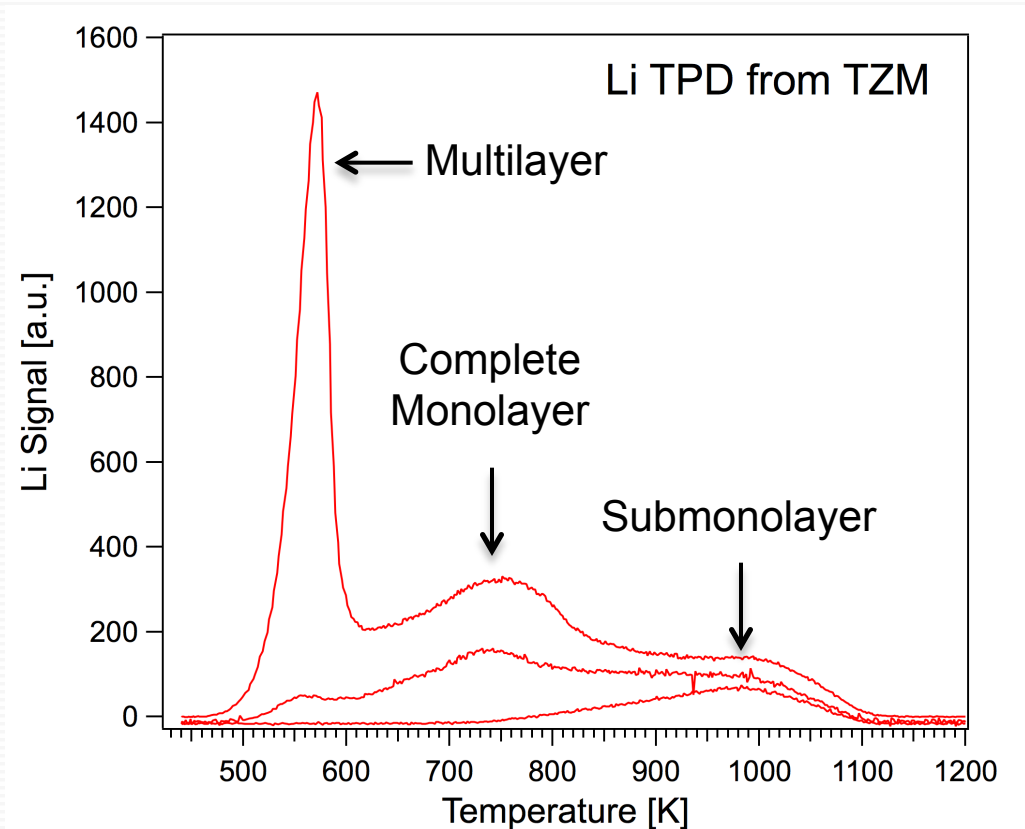
*C.H. Skinner et al., JNM 438, S647 (2013)*



# Thick Li layers evaporate at 500 K



- Thick Li films (multilayer) evaporate at 500 K
- Multilayer film represents Li-Li bonding
- Cohesive energy of metallic Li  $\sim 1.7$  eV



*C.H. Skinner et al., JNM 438, S647 (2013)*

# Li film on TZM is exposed to D plasma from ECR source



## Experimental Parameters:

### Sample:

TZM Mo Alloy (99% Mo, 0.5% Ti, 0.08% Zr)

*Li film thickness:* 5 monolayers (ML)

*Wall temperature:* 315–460 K (42–187°C)

**Chamber Pressure:**  $2 \times 10^{-9}$  Torr

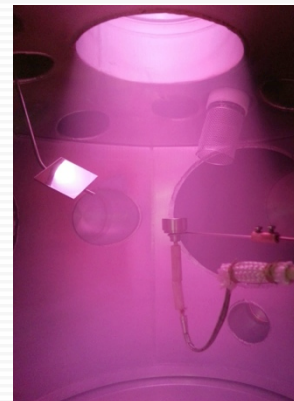
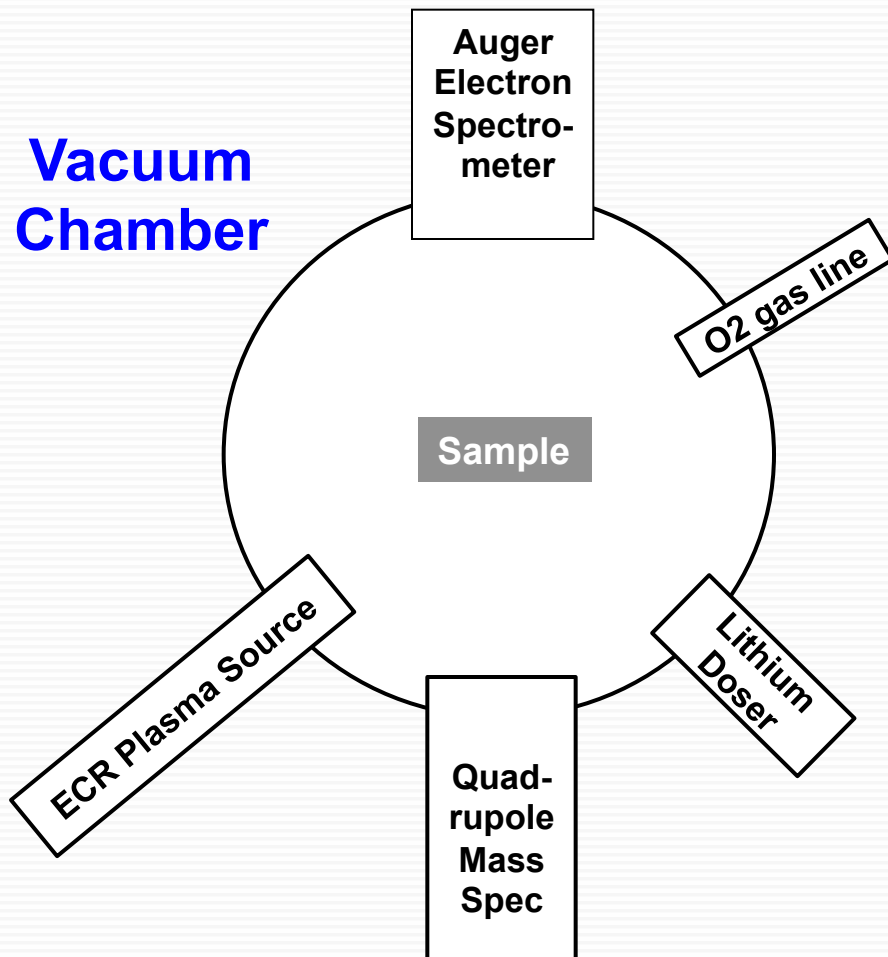
**$D_2^+$  ion energy:** 250 eV per  $D_2^+$  ion

**$D_2^+$  ion flux:** of  $1 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$

**Exposure time:** 100 s

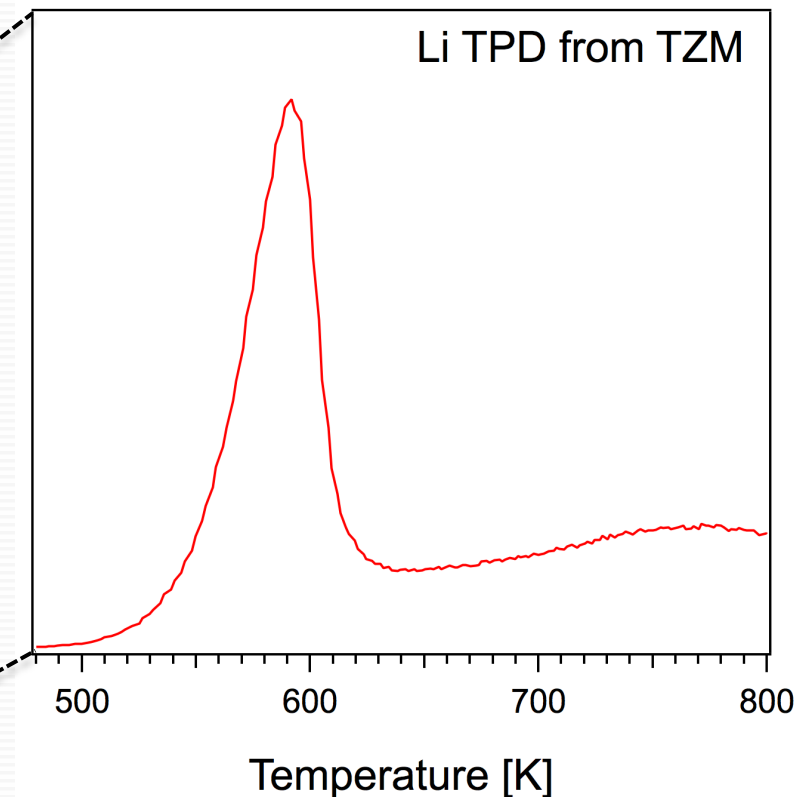
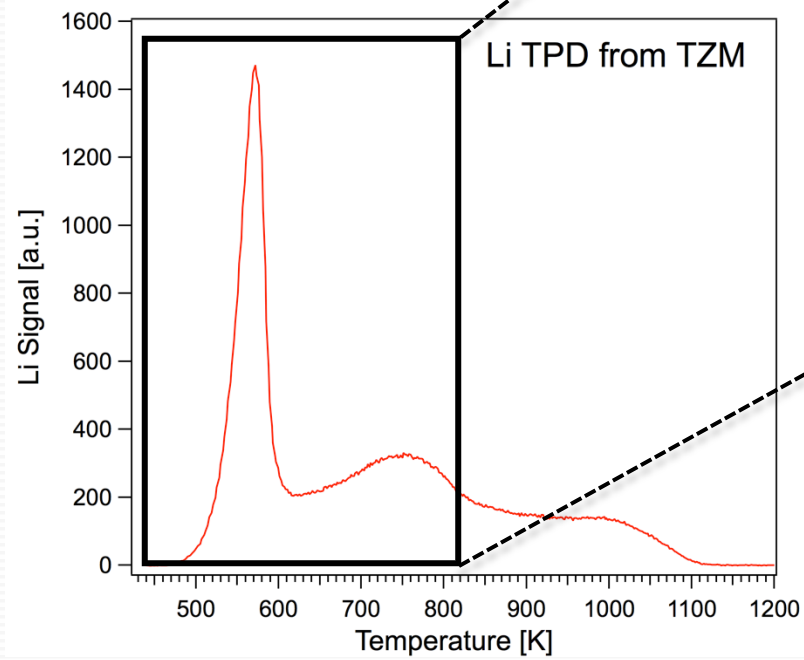
**Fluence:**  $2 \times 10^{15} \text{ D cm}^{-2}$

**$D_2$  exposure:**  $5 \times 10^{-5}$  Torr for 100 s (5000 L)

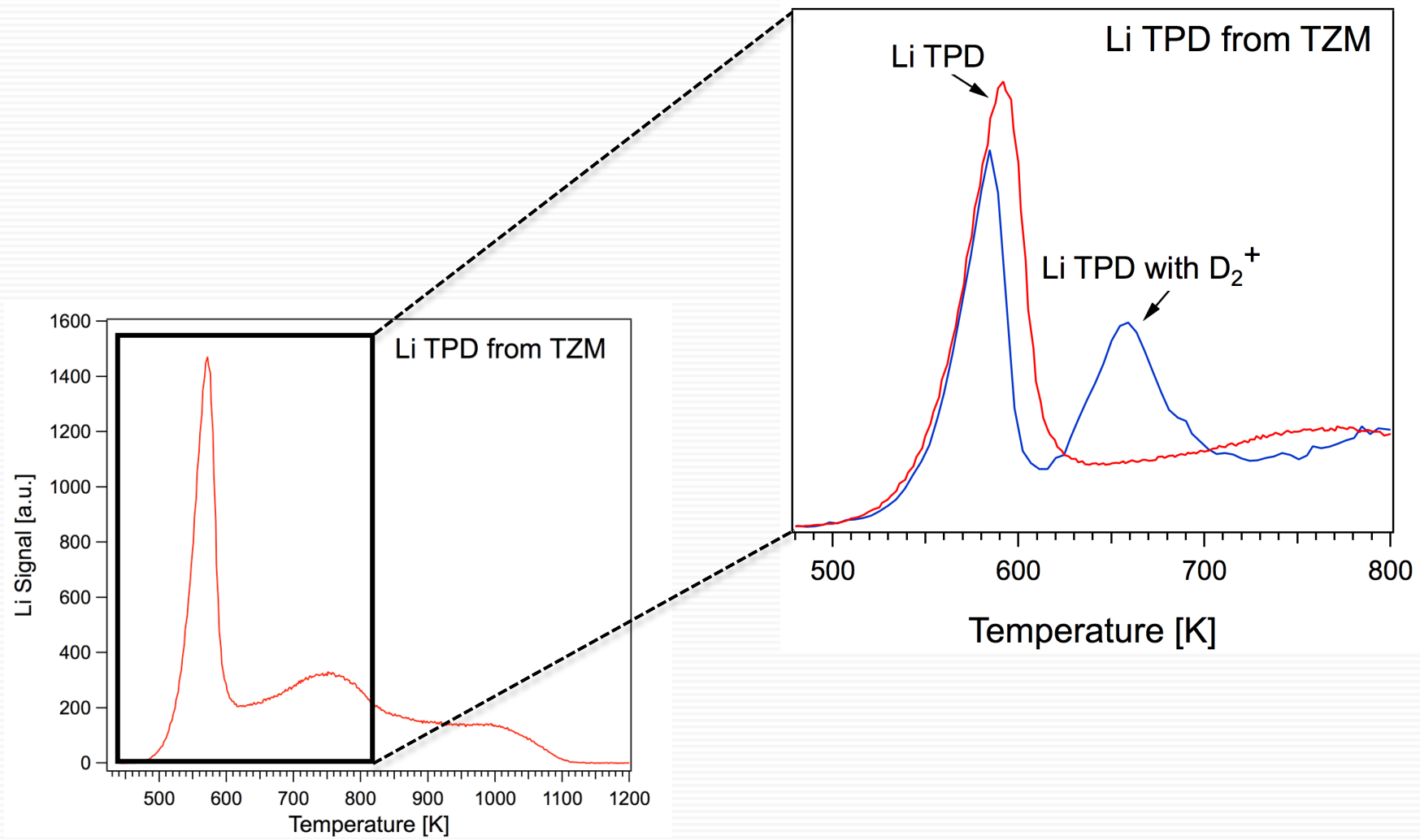


**ECR Plasma Source**

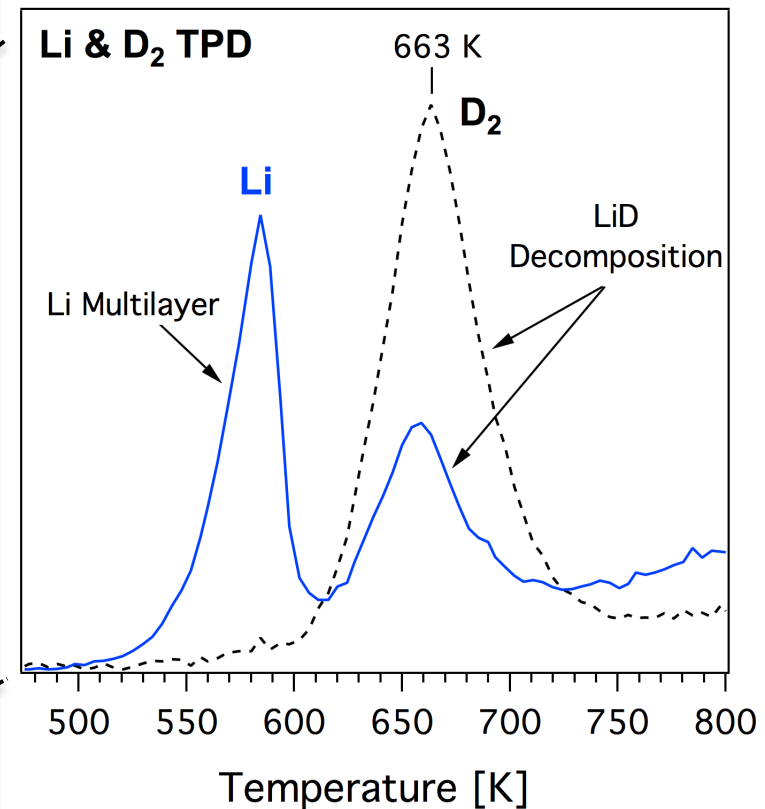
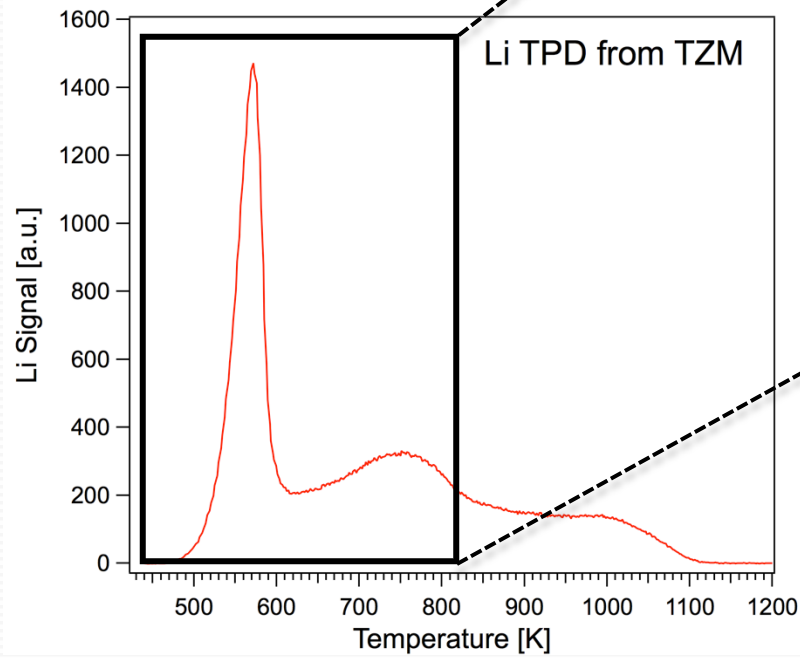
# D retained as LiD after exposure to $D_2^+$ from ECR plasma source



# D retained as LiD after exposure to $D_2^+$ from ECR plasma source

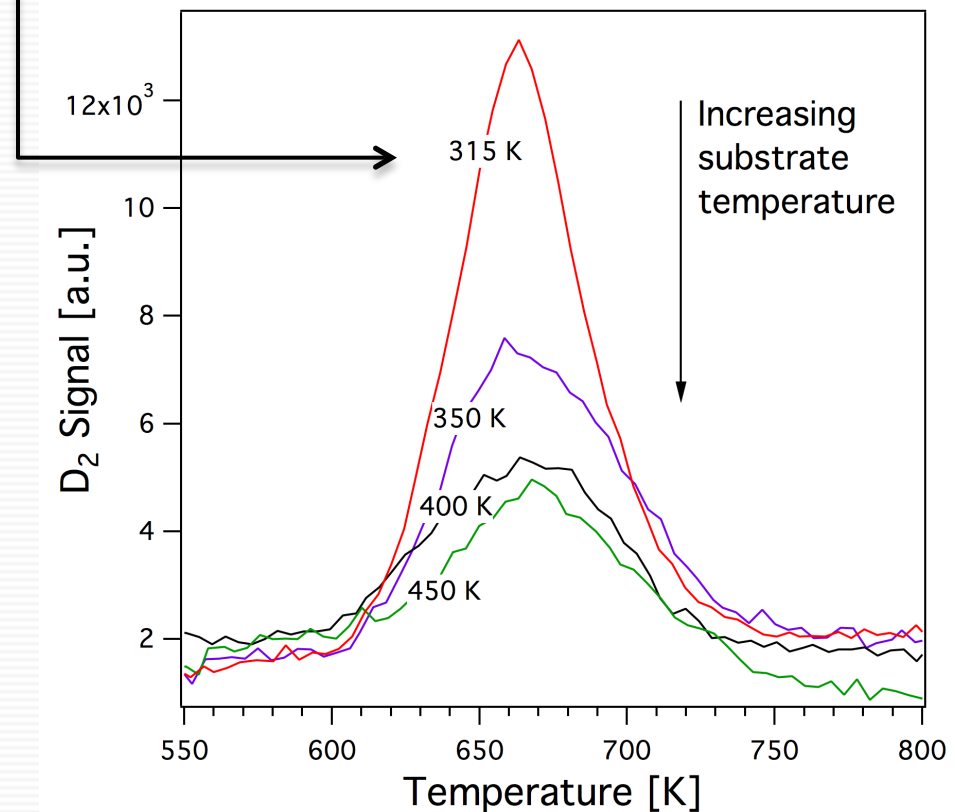
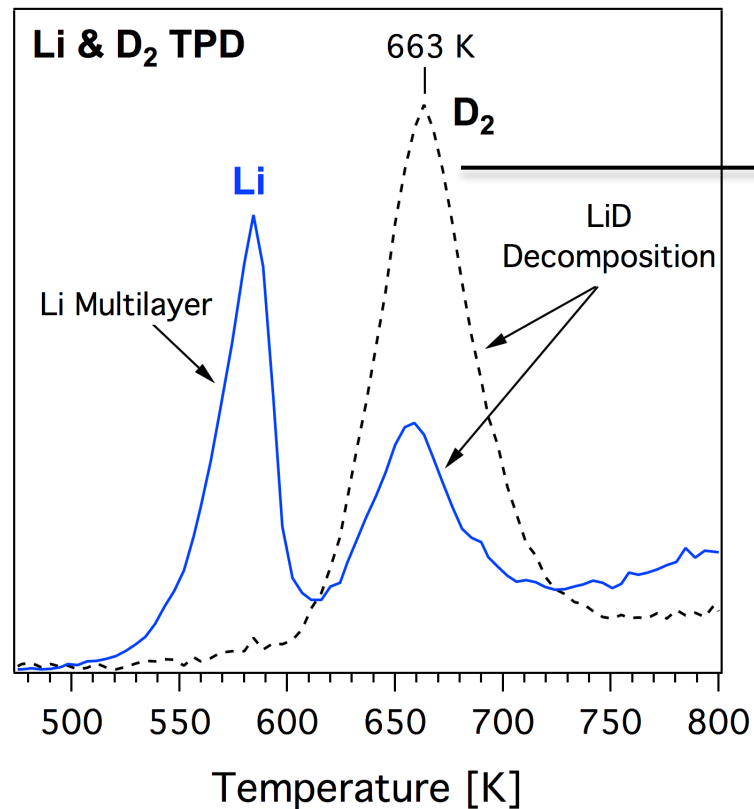


# D retained as LiD after exposure to $D_2^+$ from ECR plasma source

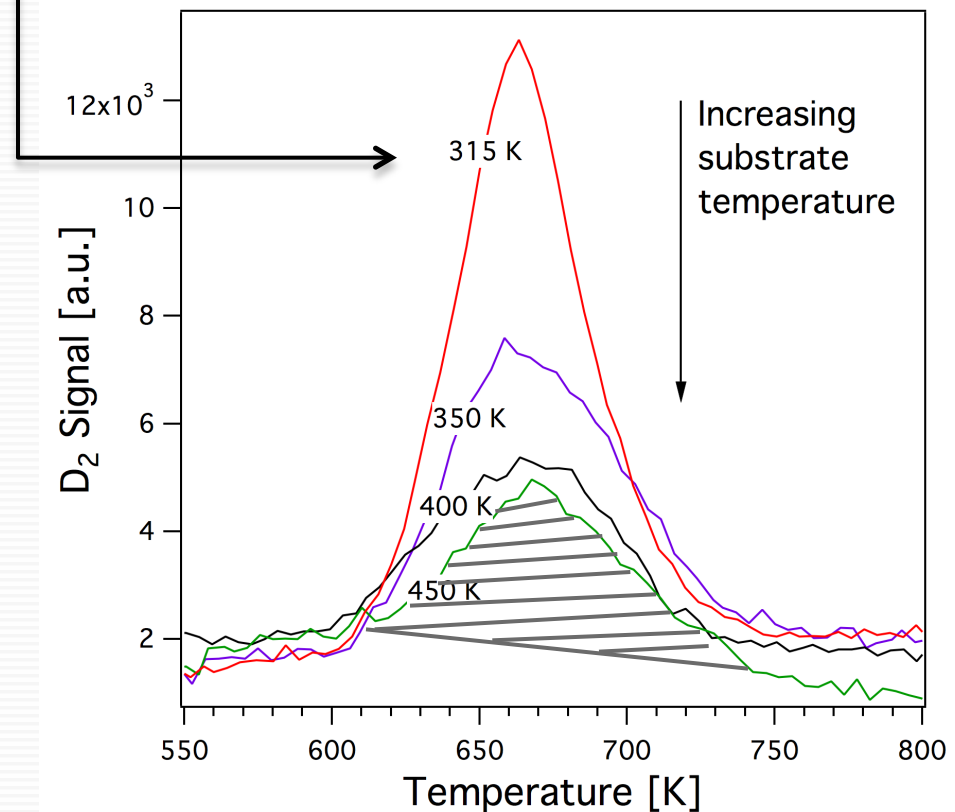
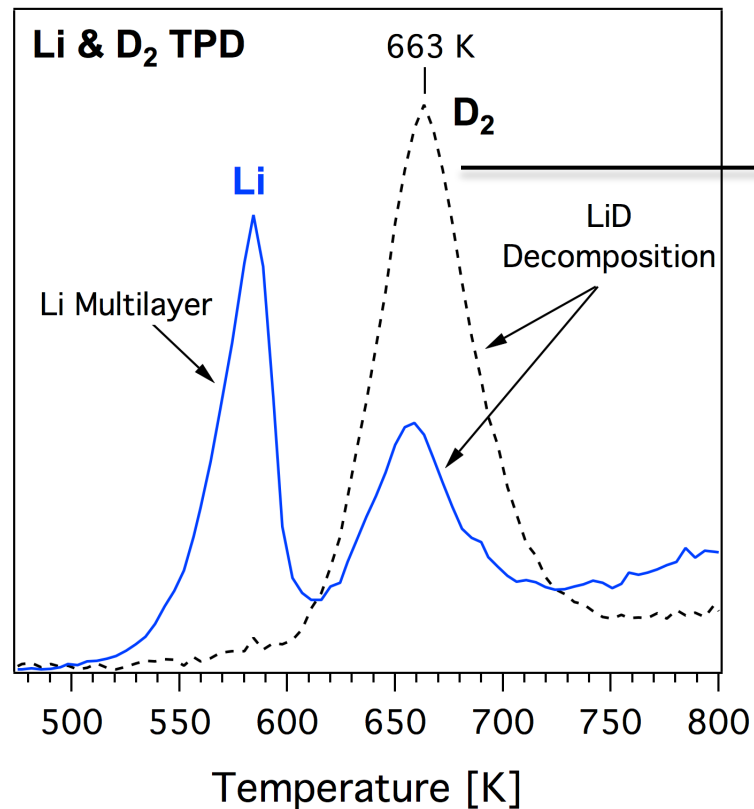


- New Li peak observed near 650 K
- Peak corresponds to LiD decomposition

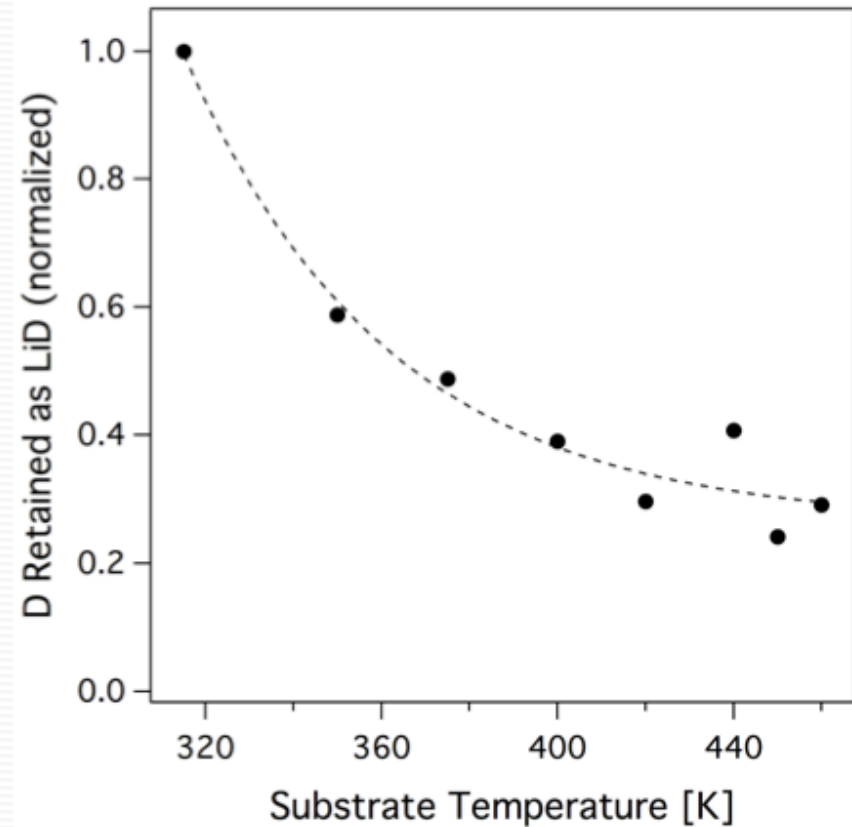
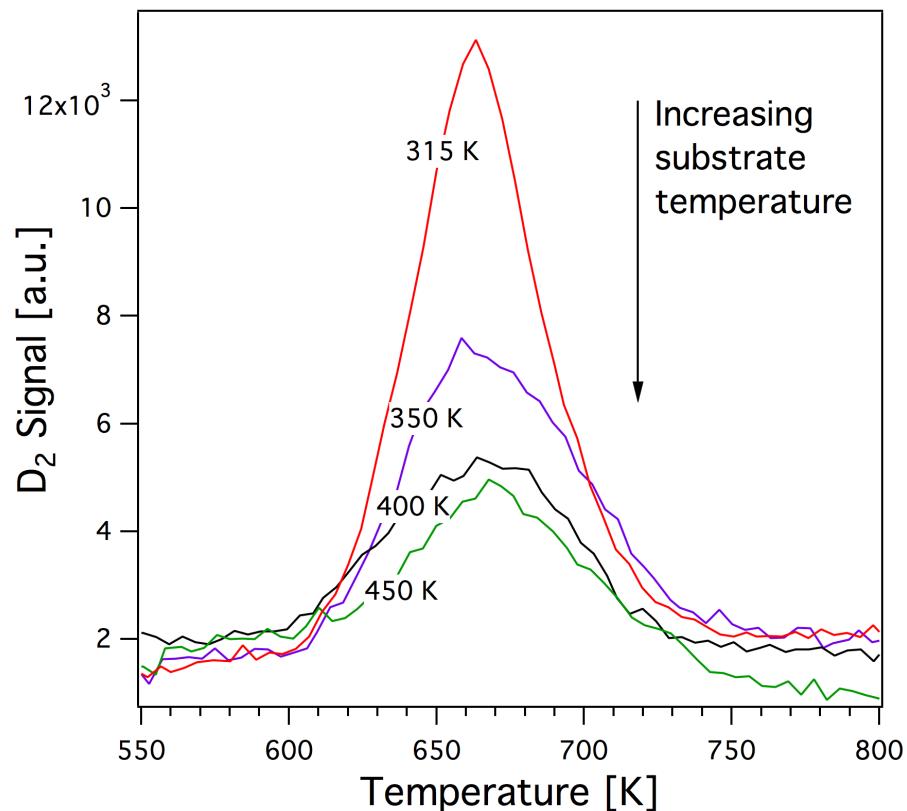
# D retention in ultrathin Li films decreases with substrate temperature from 315-460 K



# D retention in ultrathin Li films decreases with substrate temperature from 315-460 K



# D retention in ultrathin Li films decreases with substrate temperature from 315-460 K



D retention in ultrathin metallic Li drops exponentially with temperature up to 460 K



# $D_2^+$ is $10^4$ times more effective than $D_2$ gas at forming LiD



What is the effect of  $D_2$  gas?

- Operate experiment without plasma

**Ion fluence:**

$2 \times 10^{15} D^+$  ions  $cm^{-2}$

$\sim 2$  monolayers

$D_2$  gas exposure

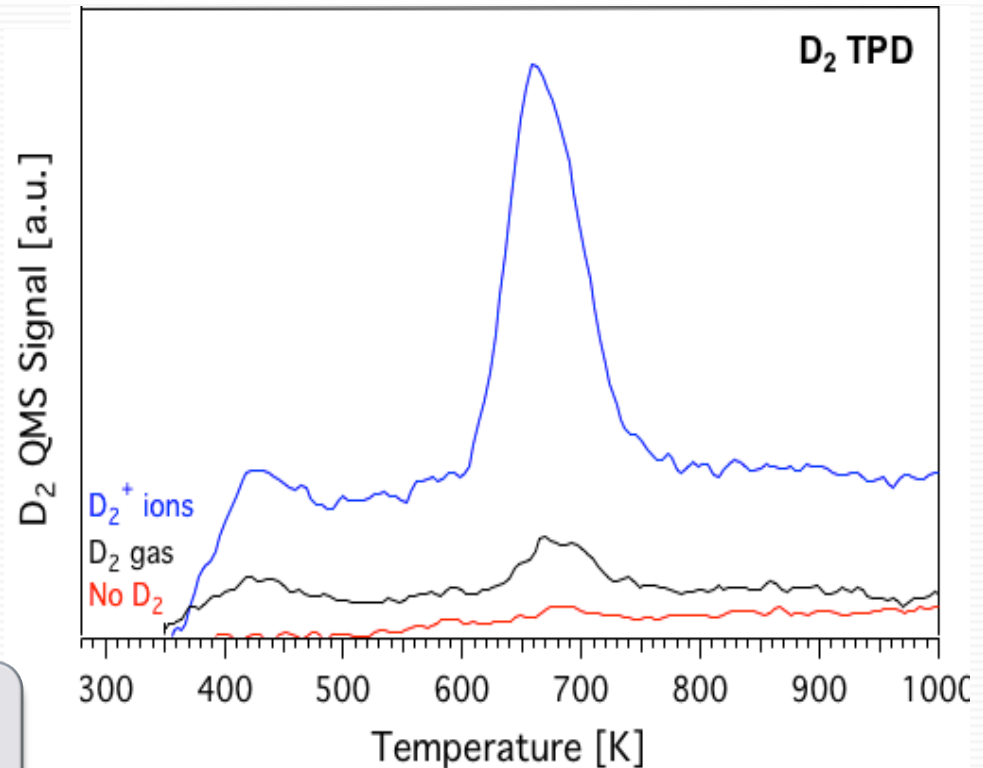
$5 \times 10^3$  L (1 L =  $10^{-6}$  Torr-s)

$\sim 5 \times 10^3$  monolayers

$\sim 2000\times$  as much  $D_2$  as  $D^+$

But we make  $10\times$  less LiD

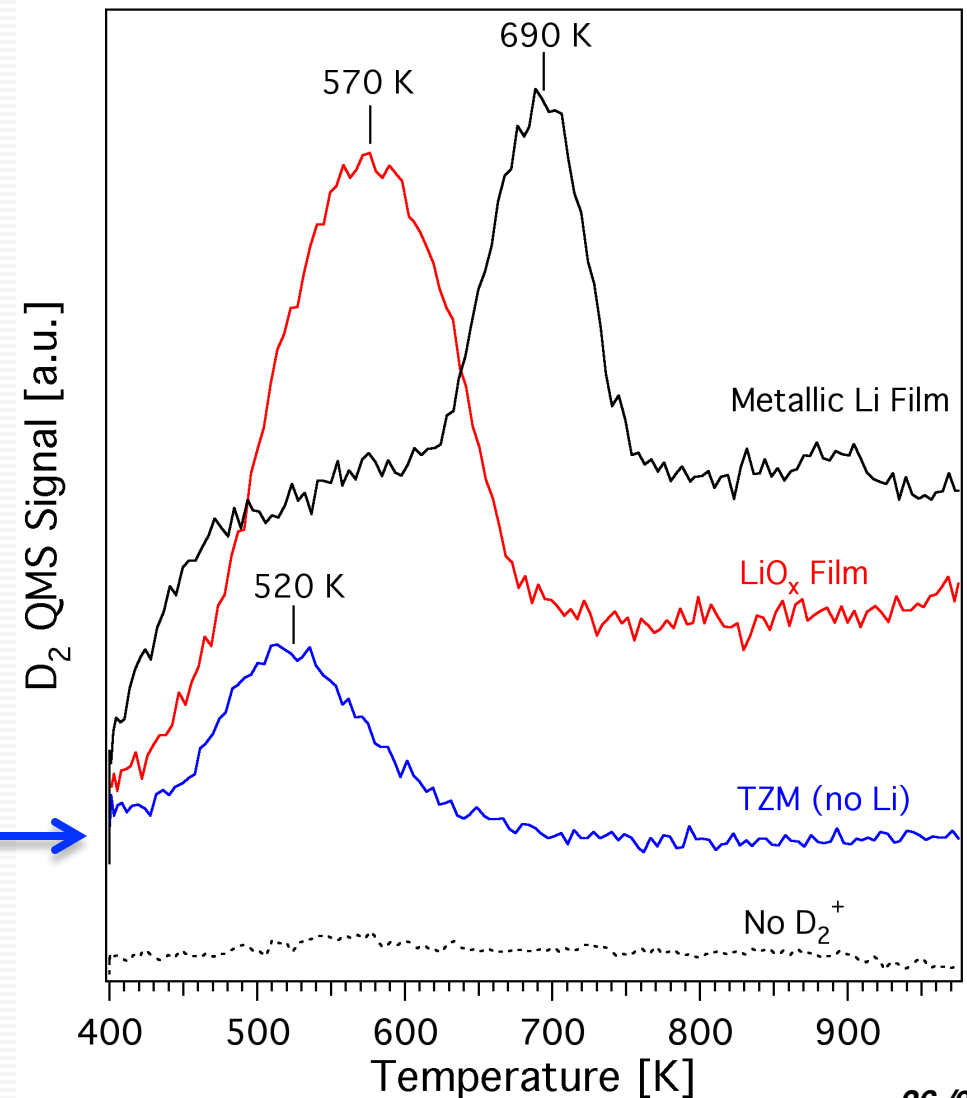
$D_2^+$  ions are  $10^4$  times more effective than  $D_2$  gas at forming LiD!



$\text{Li}_2\text{O}$  retains more D, but film is less thermally stable than LiD



D is implanted in uncoated TZM

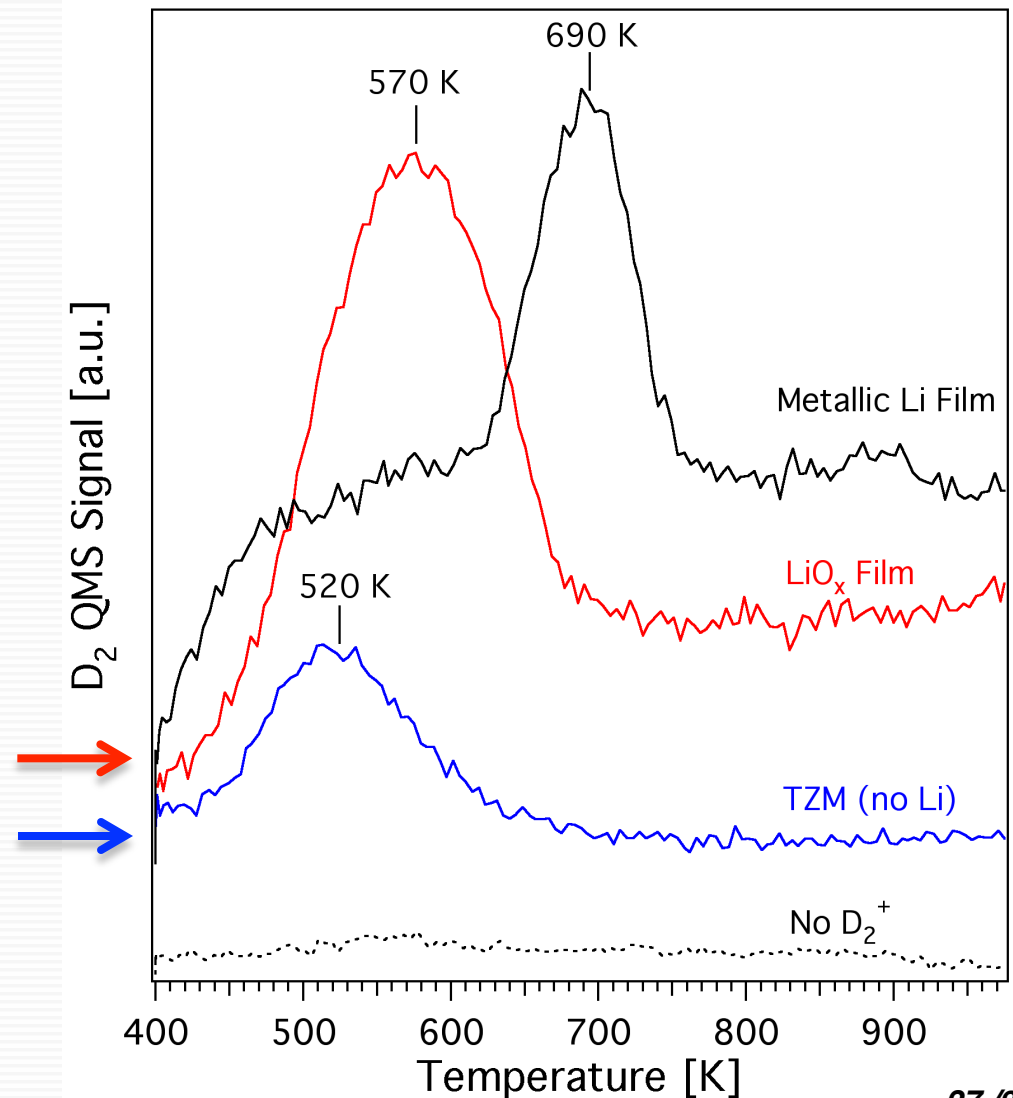


# $\text{Li}_2\text{O}$ retains more D, but film is less thermally stable than LiD



4 to 5x more  $\text{D}_2$  retained in  $\text{Li}_2\text{O}$  than TZM

D is implanted in uncoated TZM



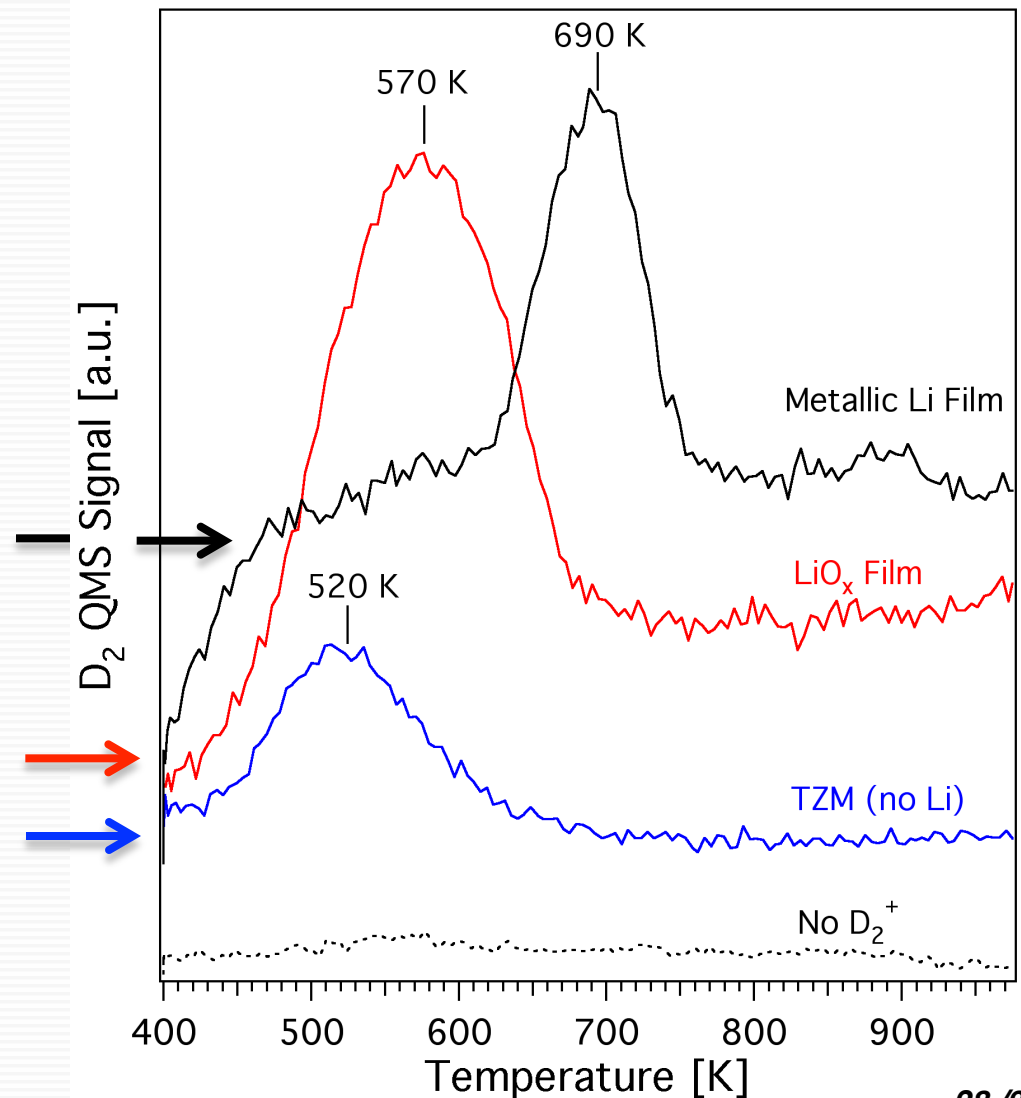
# $\text{Li}_2\text{O}$ retains more D, but film is less thermally stable than LiD



2x less  $\text{D}_2$  retained in metallic Li,  
but more thermally stable!

4 to 5x more  $\text{D}_2$  retained in  $\text{Li}_2\text{O}$   
than TZM

D is implanted in uncoated TZM



# $\text{Li}_2\text{O}$ retains more D, but film is less thermally stable than LiD



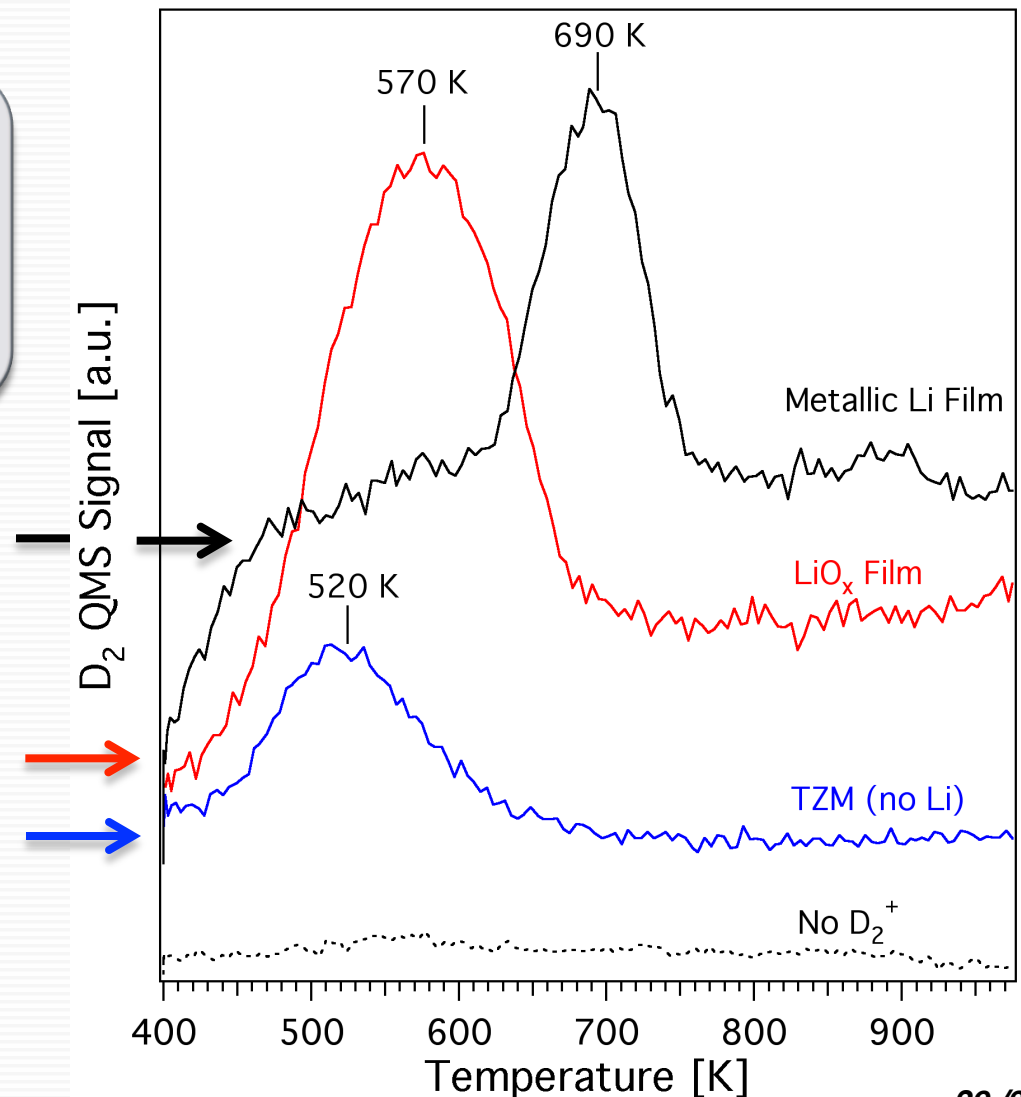
$T < 130^\circ\text{C}$ ,  $\text{Li}_2\text{O}$  is best for D retention

$T > 130^\circ\text{C}$ , Metallic Li is needed for D retention

2x less  $\text{D}_2$  retained in metallic Li, but more thermally stable!

4 to 5x more  $\text{D}_2$  retained in  $\text{Li}_2\text{O}$  than TZM

D is implanted in uncoated TZM



# Conclusions



**$T < 130^{\circ}\text{C}$ ,  $\text{Li}_2\text{O}$  is best for D retention**

**$T > 130^{\circ}\text{C}$ , Metallic Li is needed for D retention**

## **D retention in metallic Li films drops exponentially up to 460 K**

- $\text{D}_2^+$  are  $10^5$ x more effective than  $\text{D}_2$  gas at forming LiD
- Oxygen inhibits LiD formation at the surface

## **Oxidation improves D retention in Li films on TZM below 400 K**

- D retention in  $\text{Li}_2\text{O}$  films is 2x higher than in metallic Li at 400 K
- D retained in  $\text{Li}_2\text{O}$  films is released at 400 K
- At elevated temperatures, metallic Li film is needed to retain D

## **Results are consistent with LTX**

- Li does not pump  $\text{D}_2$  well
- Bare metal acts as particle source
- Cold  $\text{Li}_2\text{O}$  films will retain D