How oxygen and water affect hydrogen absorption in nickel

SAND2020-9918C

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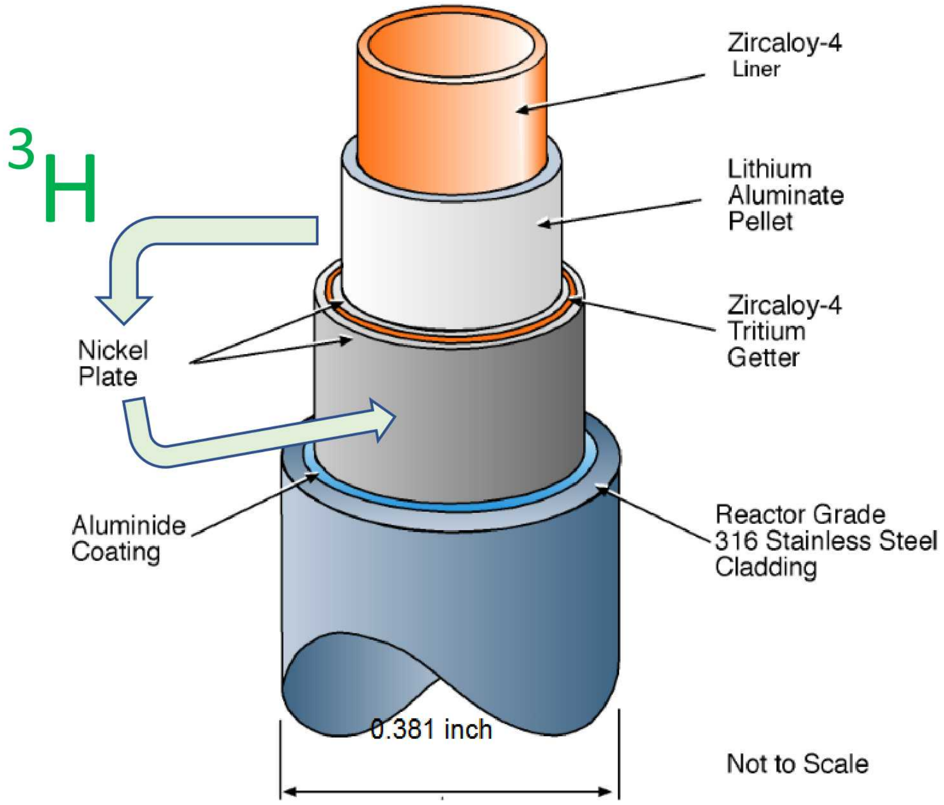
Budget: Spent: $57k (out of $100k) Extension granted until Dec31, 2020



K.A. Burns et al., PNNL-22086, (2012).

Nickel plating regulates the tritium flow from the pellet to the getter:

- Too fast flow leads to not-uniform growth of hydride in the getter.
- Too slow leads to tritium gas build up in the pellet.

Oxygen & water on the surface of the Ni can influence the flow hydrogen into and out of the Ni.

Our study aims at providing insight into the relevant surface mechanisms.

Sandia National Laboratories

This work is supported by the Tritium Science Program funded by the NNSA Tritium Sustainment Program.

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Key hypothesis:

<u>Small amounts</u> of surface oxygen (and maybe water) can reduce hydrogen uptake by the nickel surface

Key challenges:

1. Need precisely-controlled nickel surfaces
2. Need techniques sensitive to small amounts of surface hydrogen

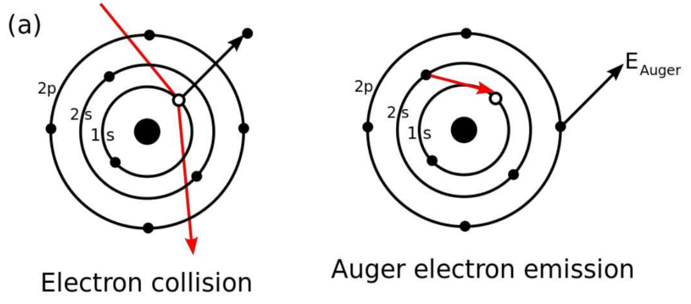
Typically, surface techniques are either …

- "blind" to hydrogen: XPS or AES

or…

- Weak signal, often convoluted with substrate contributions: STM, LEED, Helium atom scattering (HAS)

AES



Taken from wikipedia.org

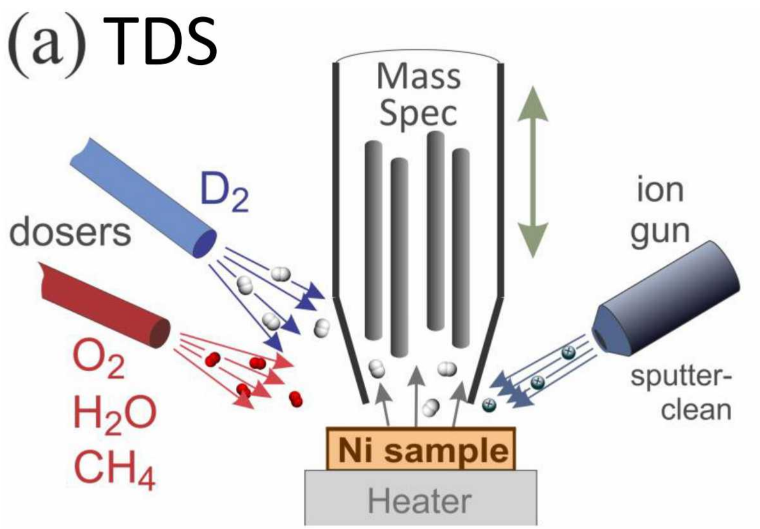
Our approach:

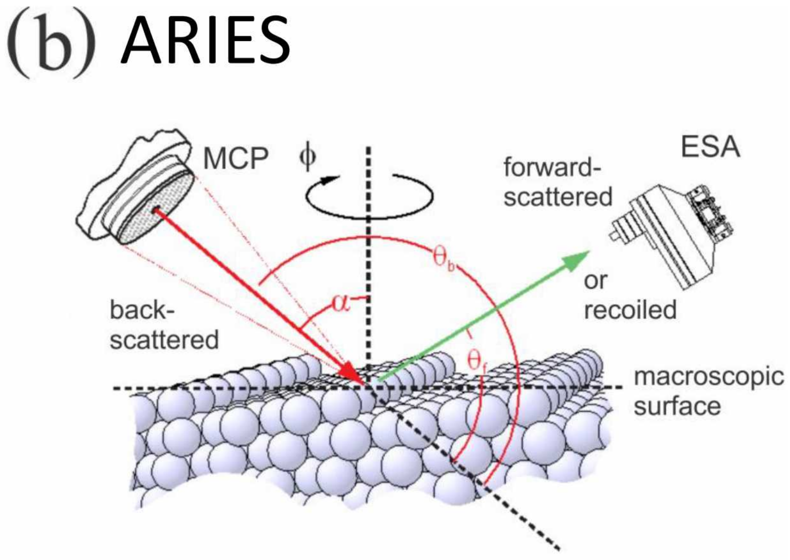
First address this well-defined question:

- How does O_2 on the surface of Ni affect its hydrogen adsorption?

- Work on precisely controlled Ni surfaces.
- Employ two techniques with sub-monolayer sensitivity to hydrogen:

UHV Setups:





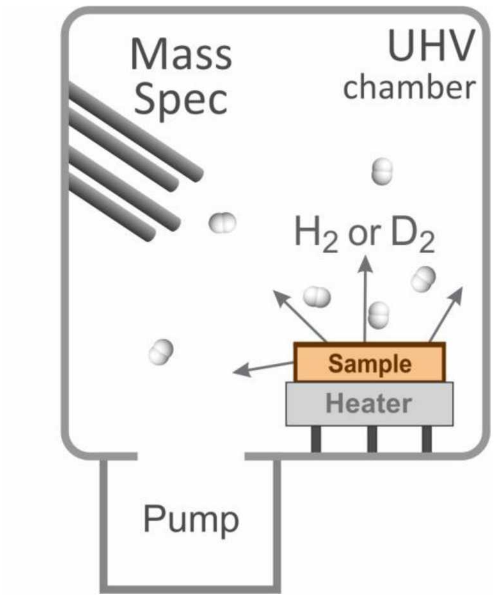
Thermal Desorption Spectroscopy (TDS)

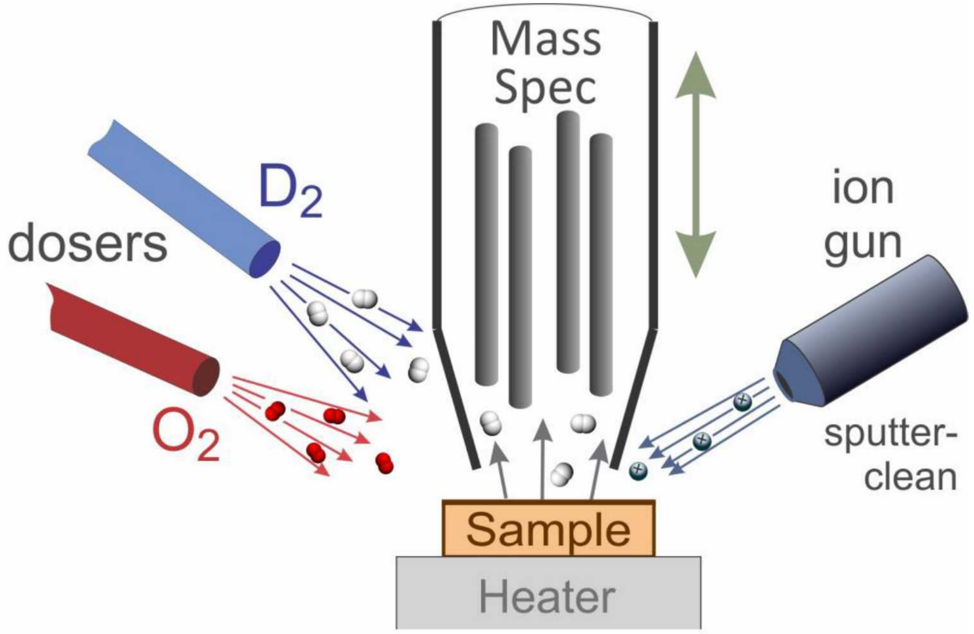
Our new setup:

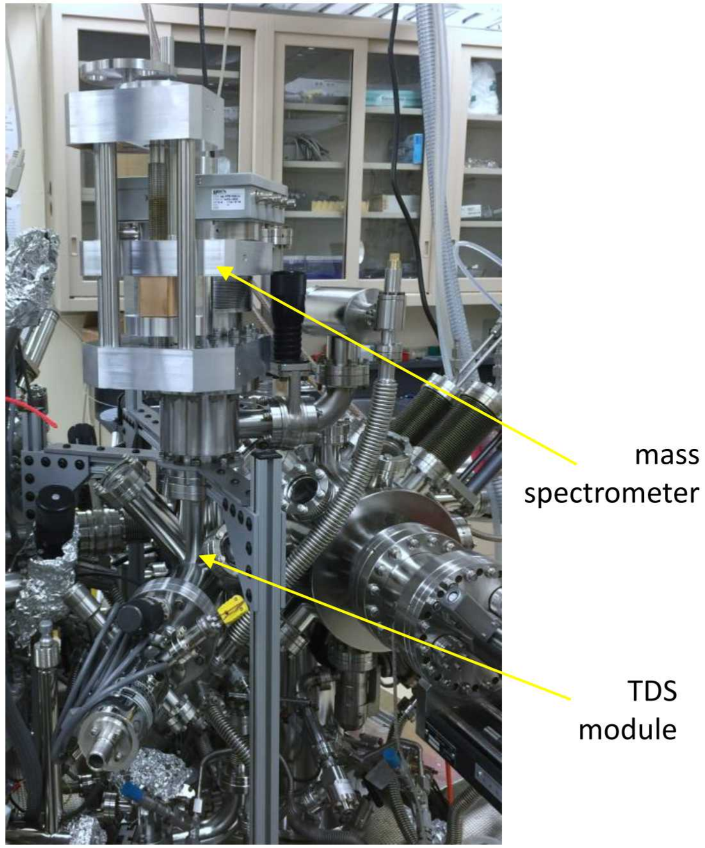
- Precise control of sample surface
- extremely sensitive measurements of H_2 or D_2 release

Designed with Josh Whaley
Commissioned & tested with Chen Wang

Conventional setup:







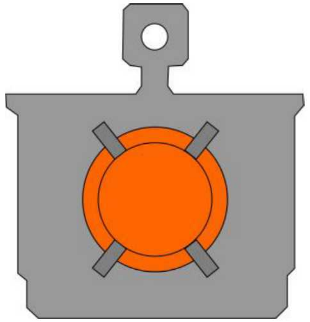
Upgrades completed within this TPBAR project:

1. **Special exposure chamber** (D_2, O_2, H_2O) dedicated to TDS, which separates gas exposure from TDS module

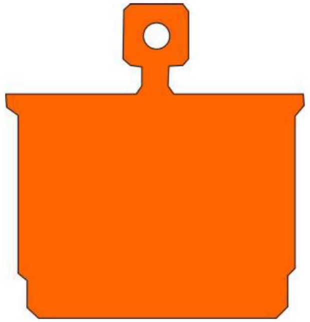
   >> eliminates possible desorption contributions from heating stage

2. **Sample holders as samples**

Instead of:



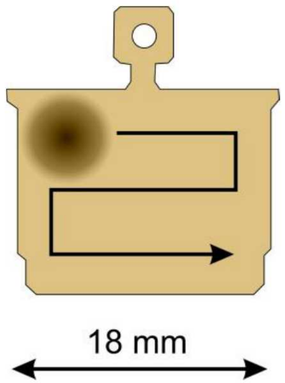
Machine sample holders out of sample material, i.e., Ni:



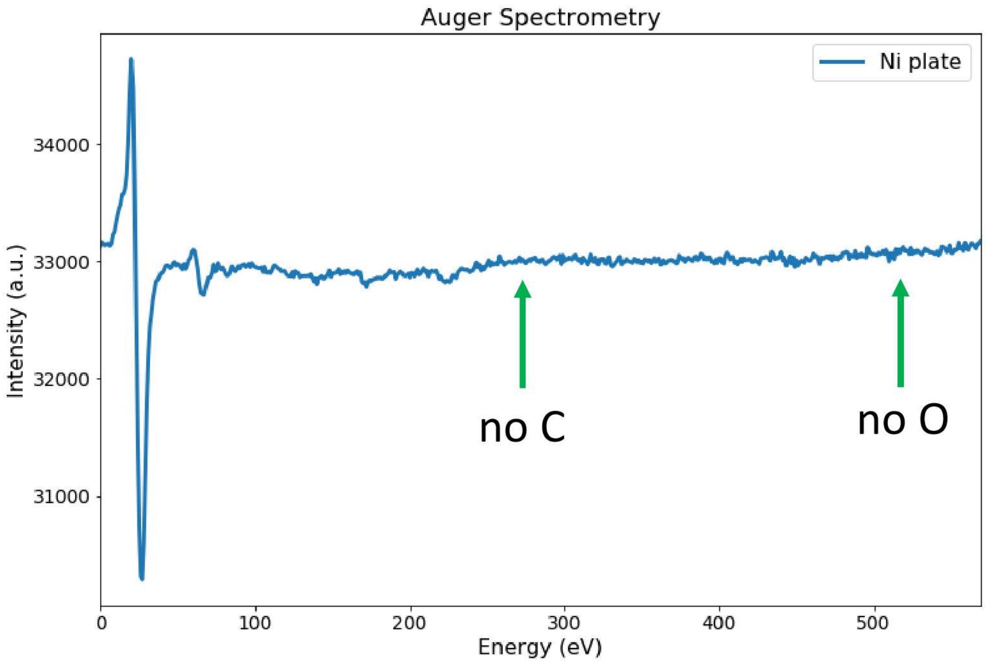
>> nothing but the sample is transferred from deposition chamber into TDS

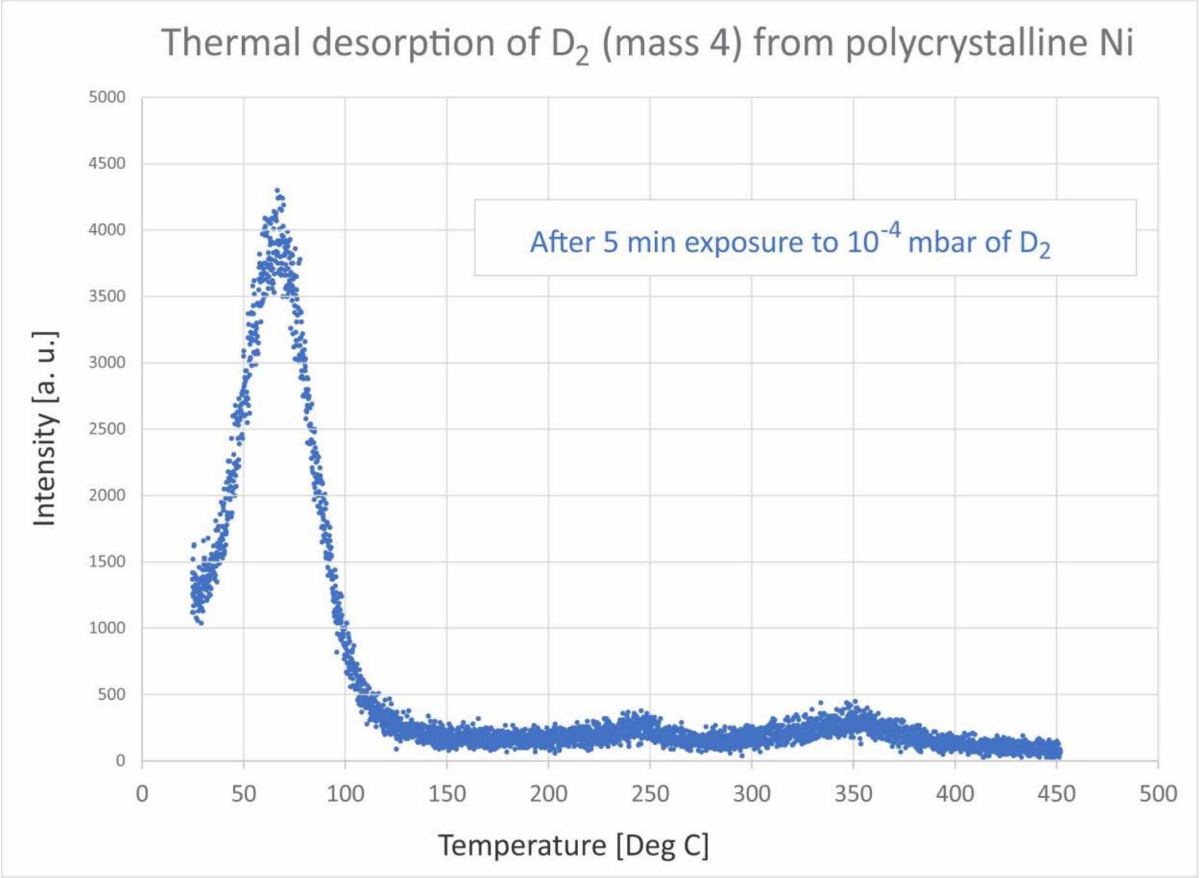
1. & 2. >>> only the Ni sample is being exposed to the gas environment we want to study, e.g., D_2, O_2, H_2O.

Thermal desorption Spectroscopy (TDS) of D_2 on Ni



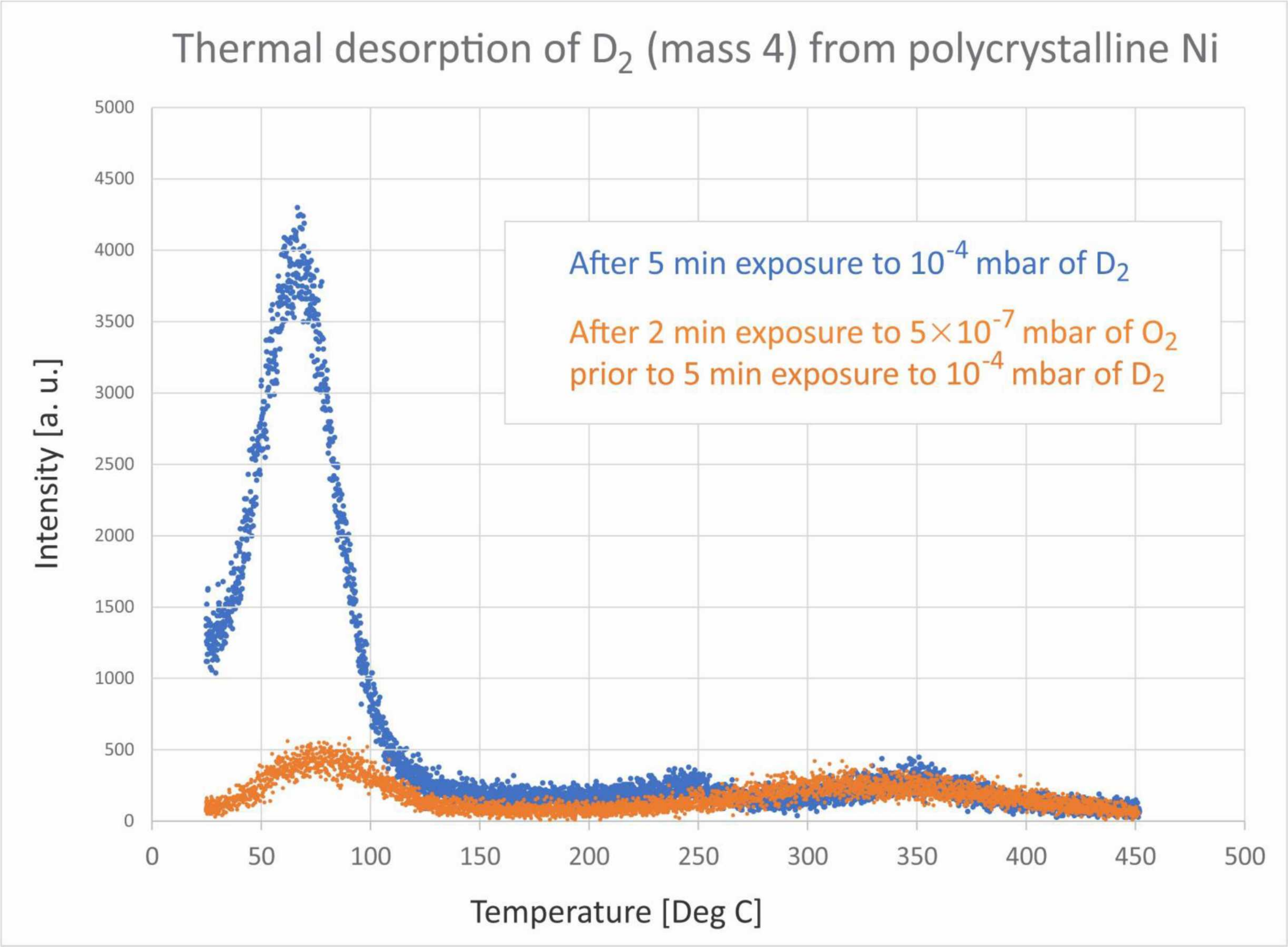
First, extensive Ar+ ion bombardment to make entire sample plate atomically clean:

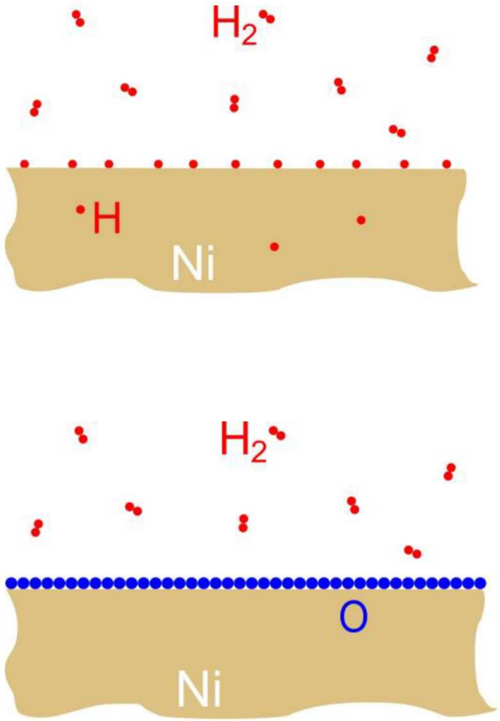




Peak at rather low Temp (~70 Deg C) >>>
We detect monolayer (or less) of D_2 at Ni surface.

TDS of D_2 on Ni pre-exposed to O2



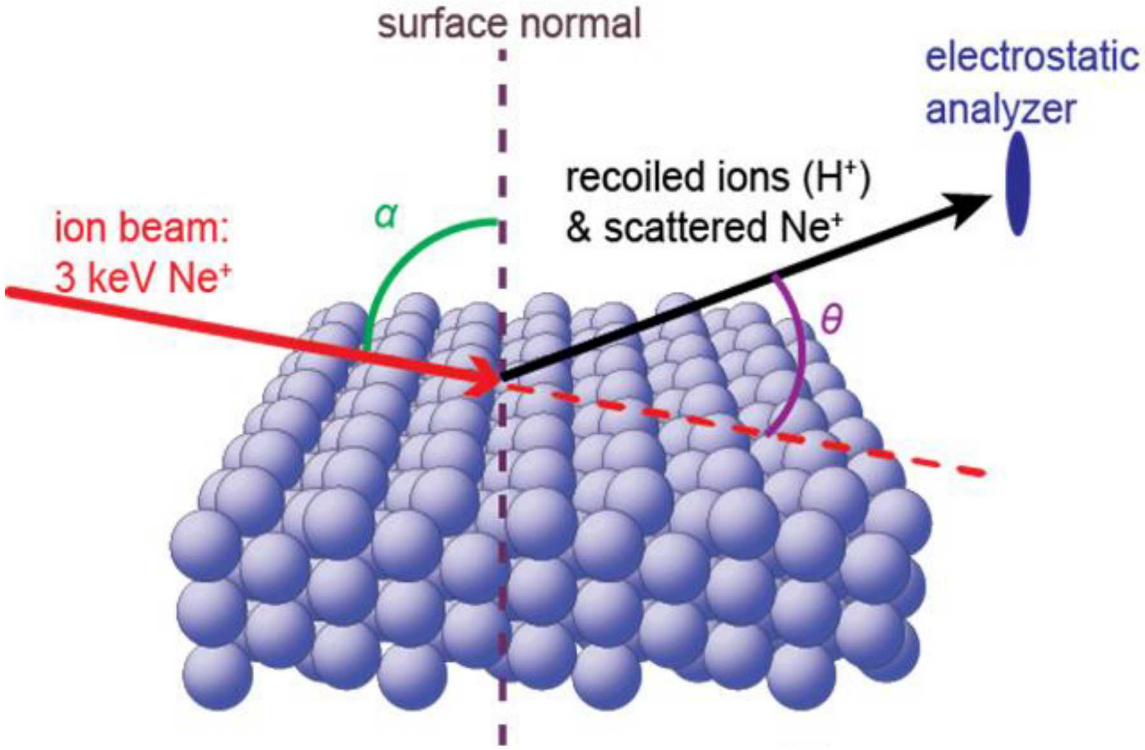


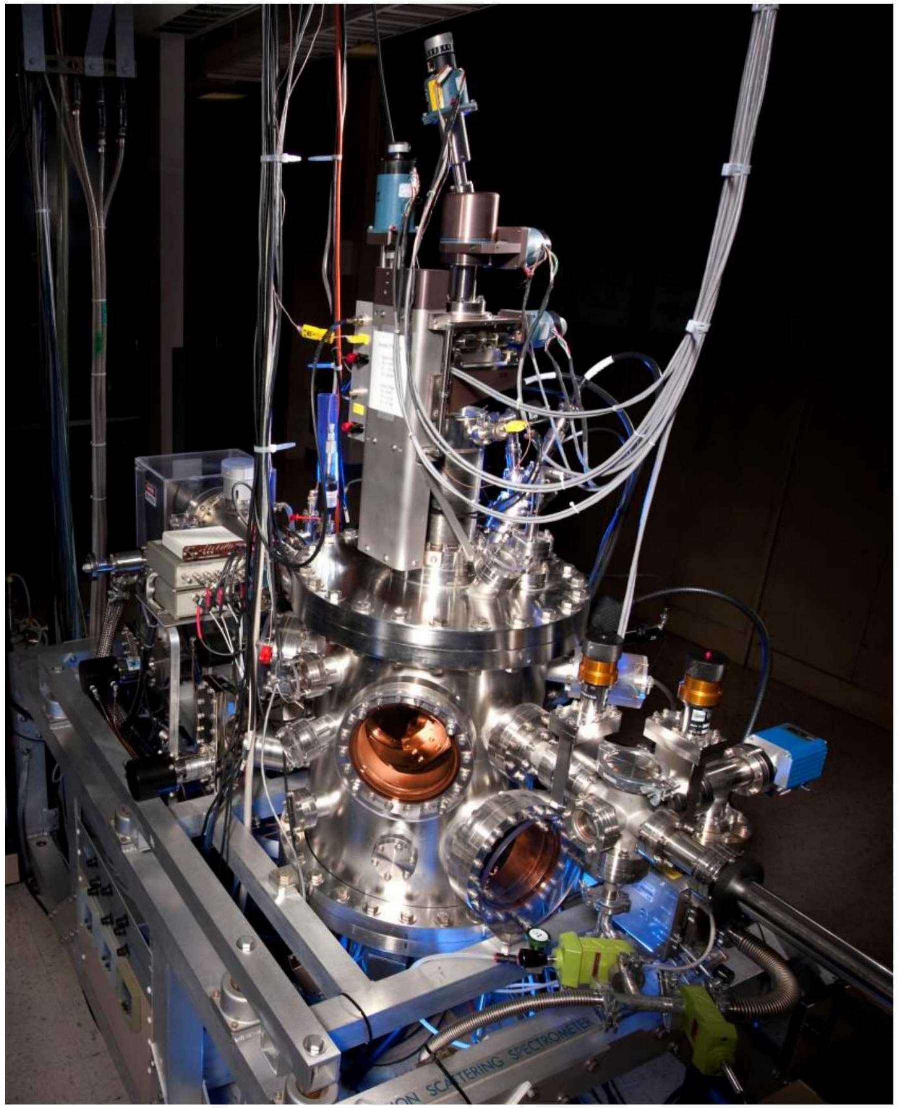
Small amount of oxygen blocks hydrogen adsorption!

<u>To complete by Dec 31:</u>

- Quantify amount of oxygen needed to block hydrogen
- Same type of study with water

Angle-resolved ion energy spectroscopy (ARIES)





Low energy ion scattering (LEIS):

Notation: X(QS), Detects projectile ion Ne^+, scattered from the surface atom X

Direct recoil spectroscopy (DRS):

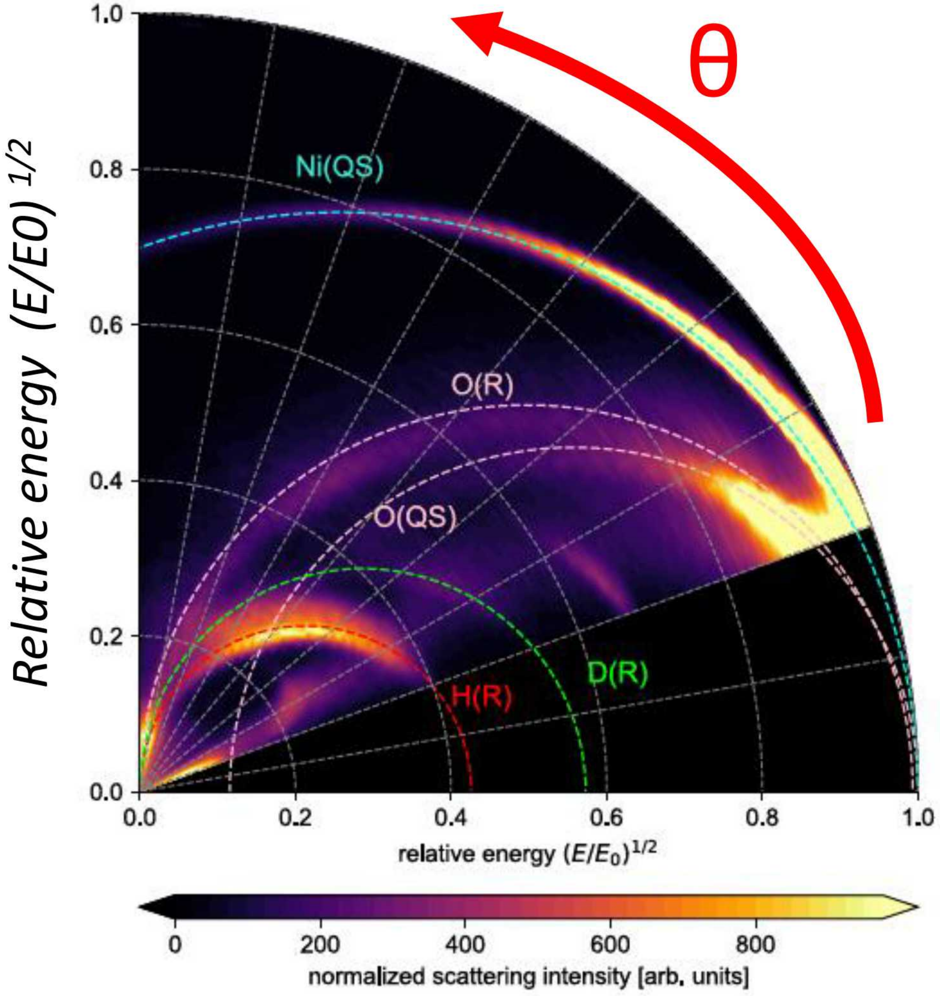
Notation: X(R), Detects surface atom X, recoiled by the projectile into the detector.

like H(R) (recoiled hydrogen)

Measure clean Ni foil in residual UHV

3 keV Ne+ beam α=80 Deg from normal

"Collision circle plot" for scattering angles $20° \leq \theta \leq 90°$ …



… assigns circular arcs to collision processes:

Strongest signals from H(R), Ni(QS) and O(R)

Energies of scattered & recoiled ions, assuming elastic collisions, conservation of energy & momentum

$$\frac{E_S}{E_0} = \left(\frac{\cos\theta \pm \sqrt{\mu^2 - \sin^2\theta}}{1+\mu} \right)^2$$

$$\frac{E_R}{E_0} = \frac{4\mu}{(1+\mu)^2} \cos^2\theta$$

E_s = energy of scattered ion

E_R = energy of recoiled ion

E_0 = energy of incident ion (3 keV)

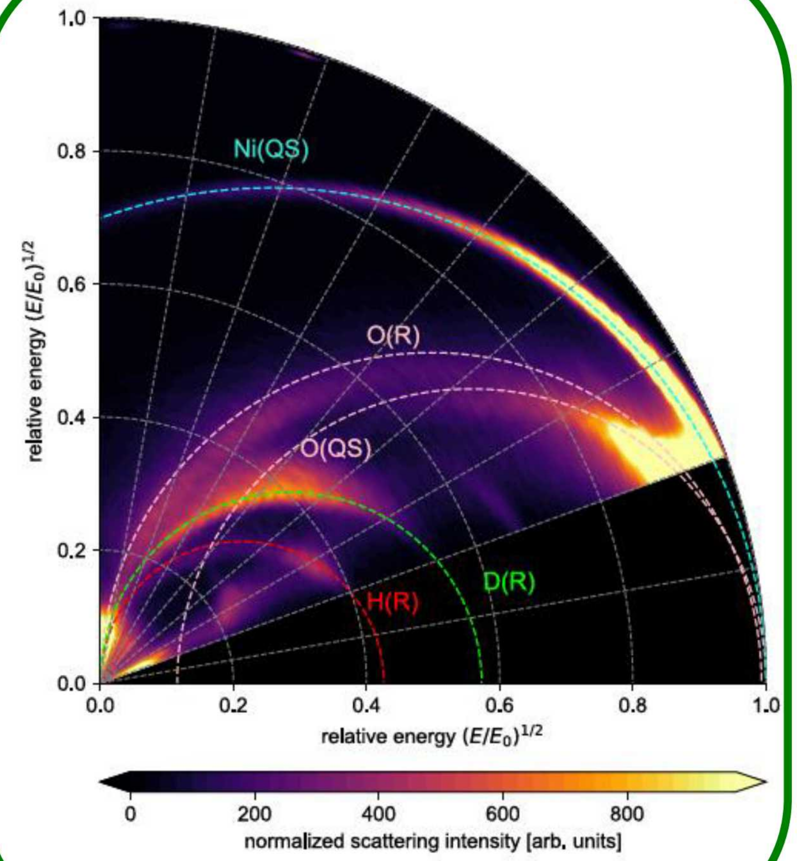
ϑ = scattering angle

μ = mass ratio of target atom to incident ion

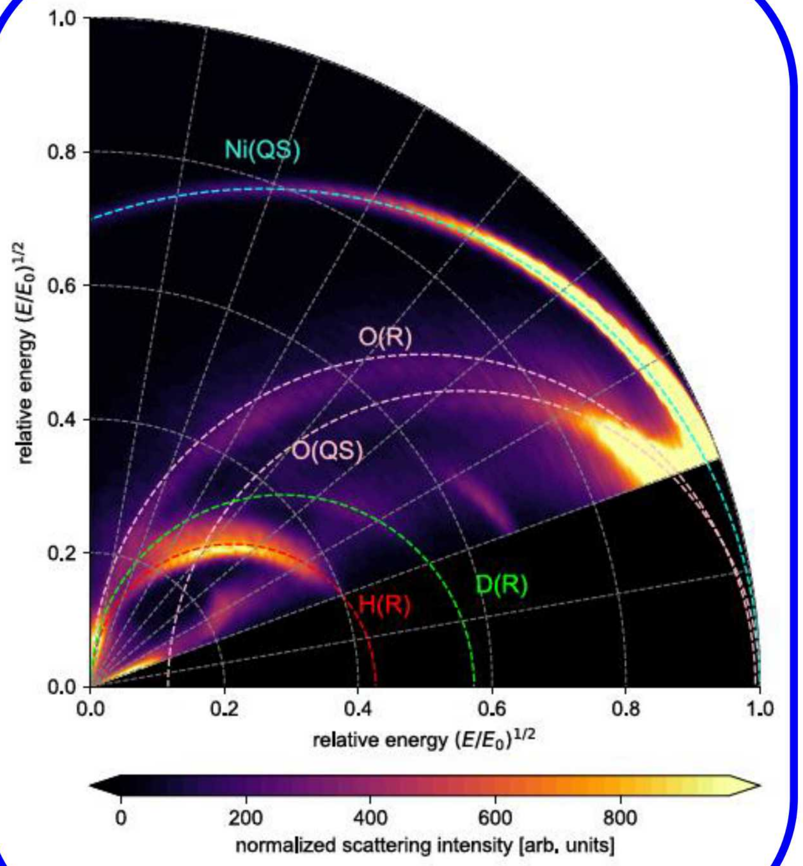
Collision-circle plots for different gaseous environments…

(Dosing gasses into the chamber via a leak valve)

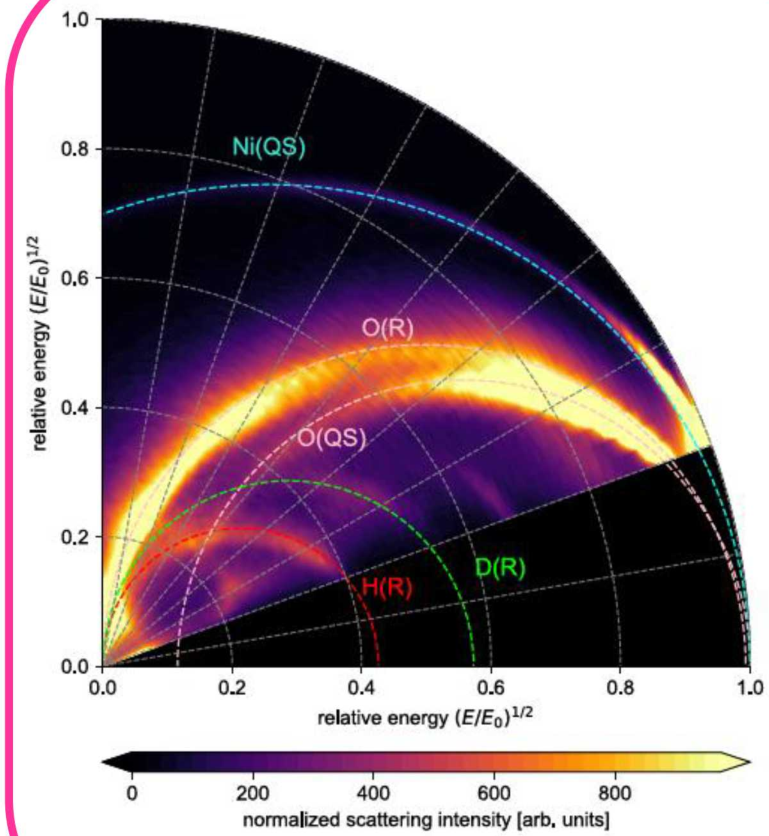
Dosing with D_2



Clean Ni foil



Dosing with O_2

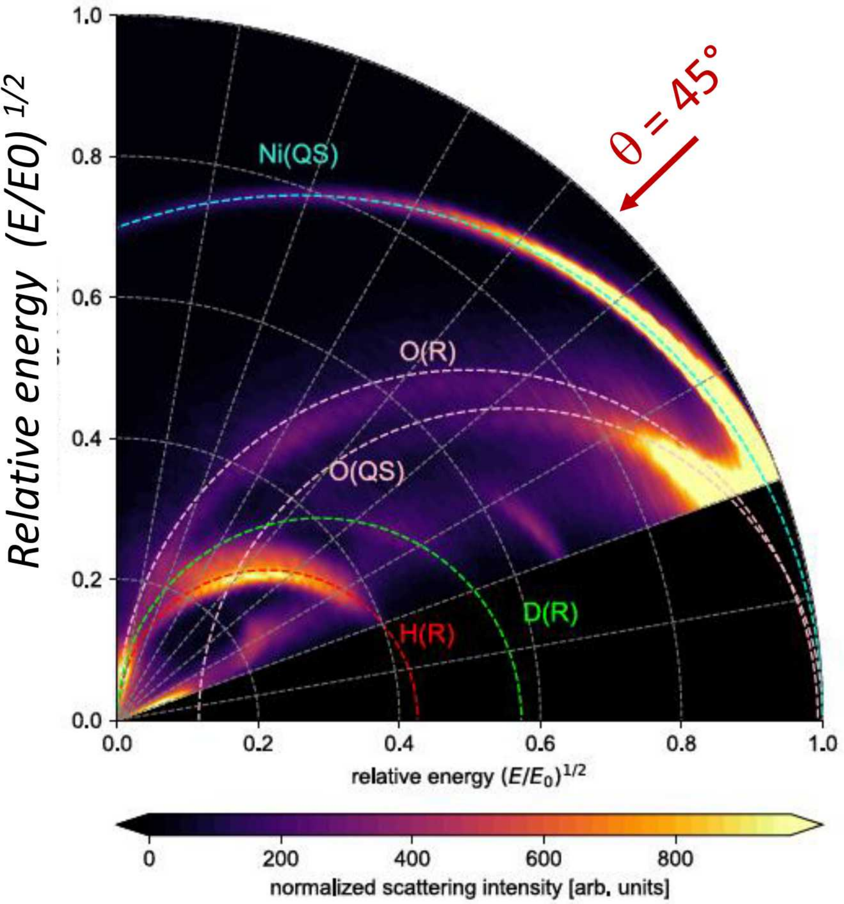


… allow assignment of collision processes relevant during gas exposure.

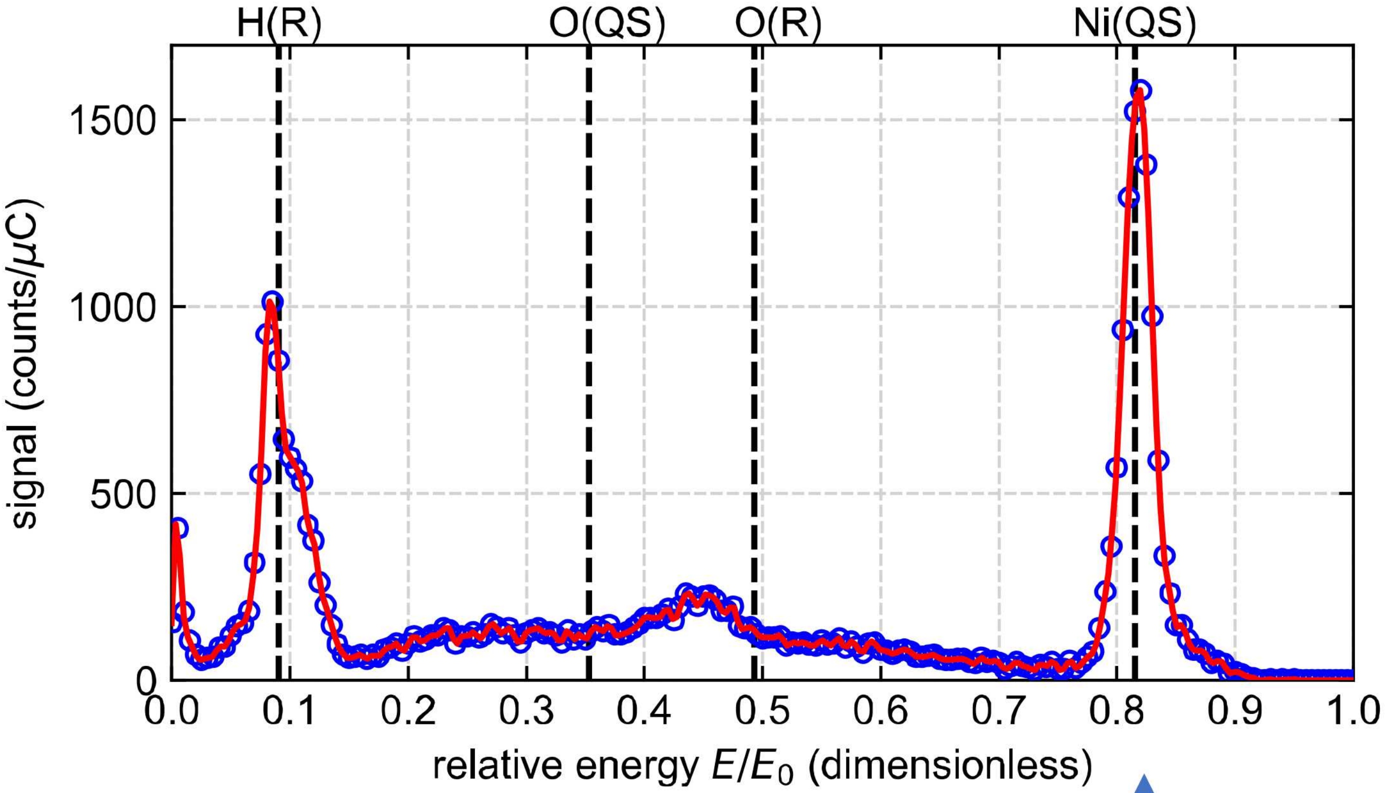
Baseline ion energy spectrum on Ni foil in “residual UHV”

3 keV Ne+ beam $\alpha = 80$ Deg from normal

Clean Ni surface



Fixed scattering angle θ = 45°



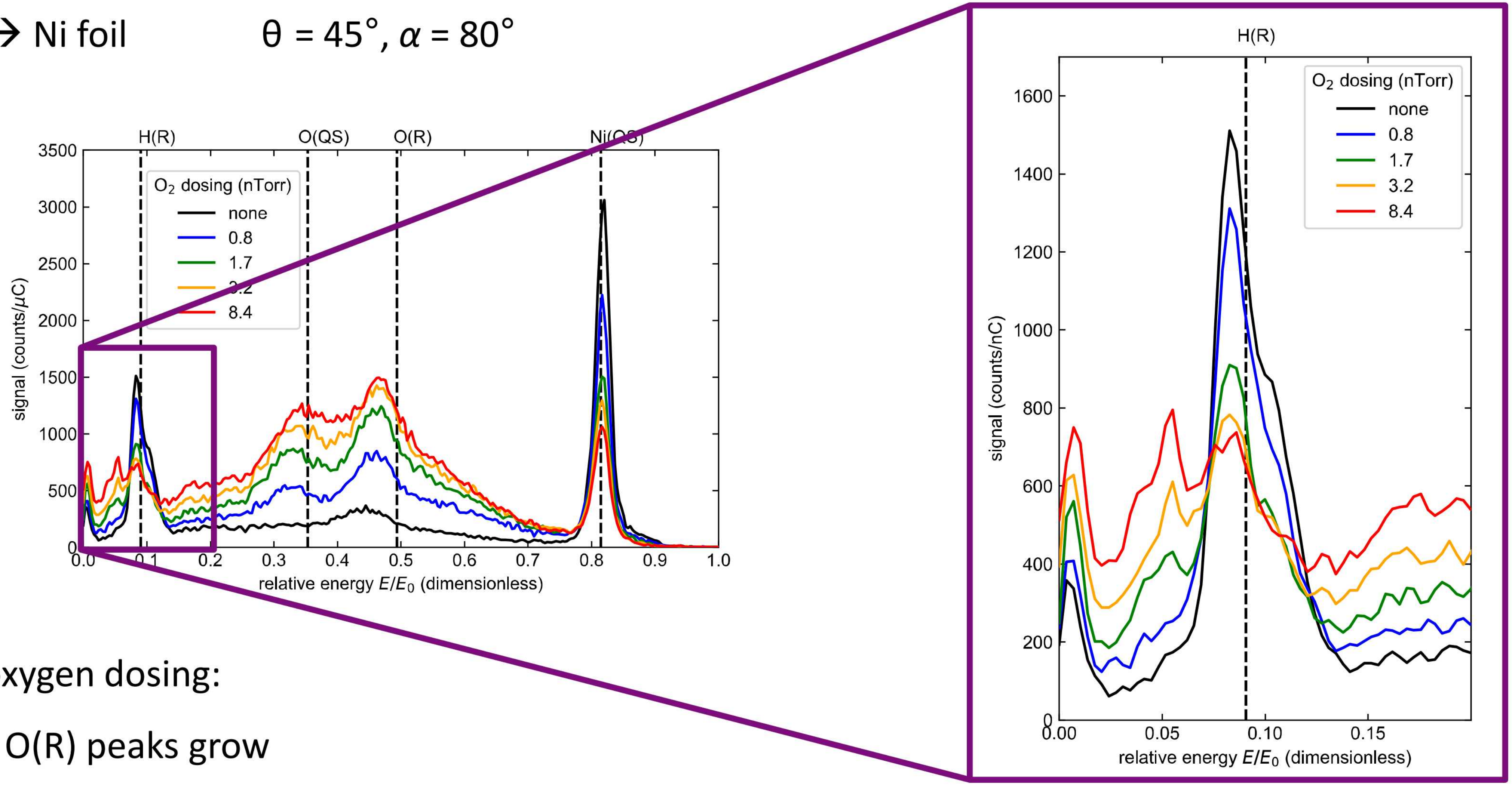
Recoiled H

Trace amounts of impurities (mostly O, possibly some C)

Ne^+ scattered from Ni

Effect of oxygen on hydrogen adsorption

3 keV Ne^+ → Ni foil θ = 45°, α = 80°

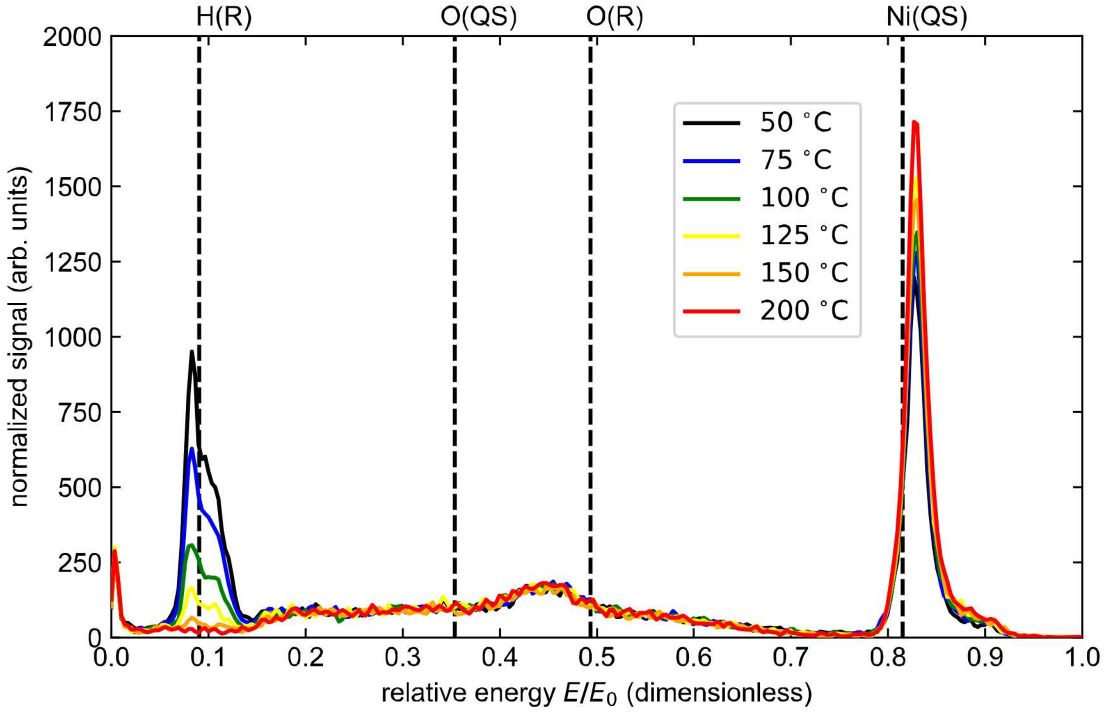


With increasing oxygen dosing:

1. O(QS) & O(R) peaks grow
2. Ni peak diminishes as O coverage increases
3. H peak decreases down to background level

Temperature effect on H adsorption with & without O_2 dosing

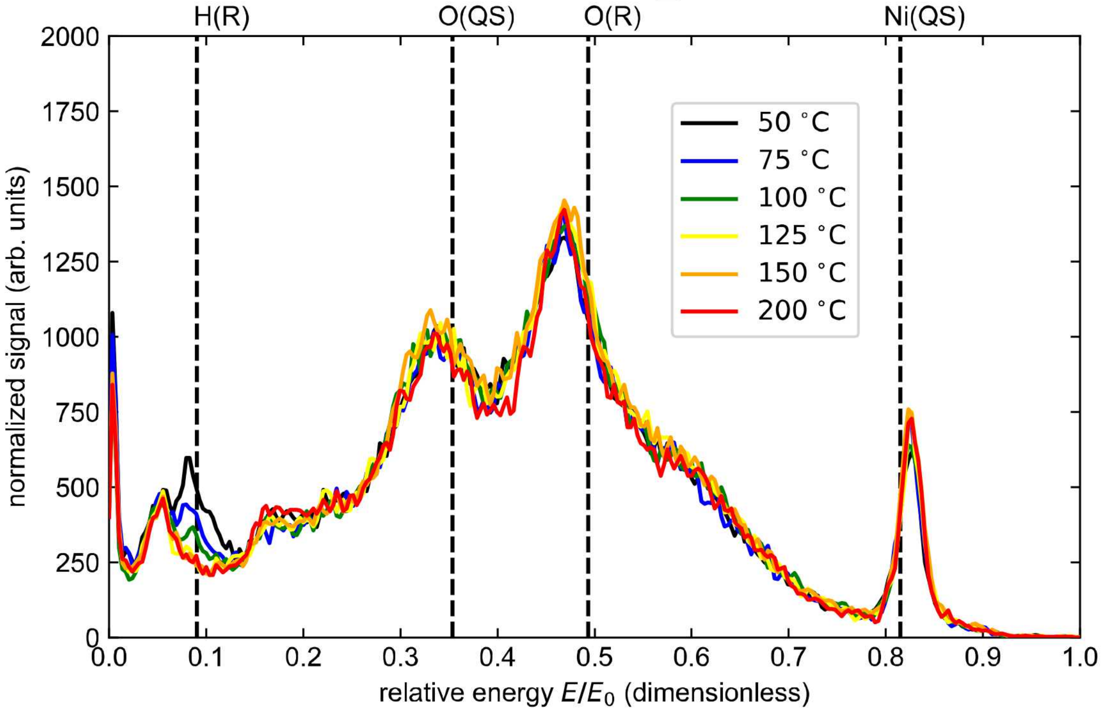
No O_2 dosing



With increasing temperature:

1. H peak diminishes
2. Ni peak increases (due to less surface H)
3. No changes from 200 °C to 400 °C

With 2 nTorr O_2 dosing

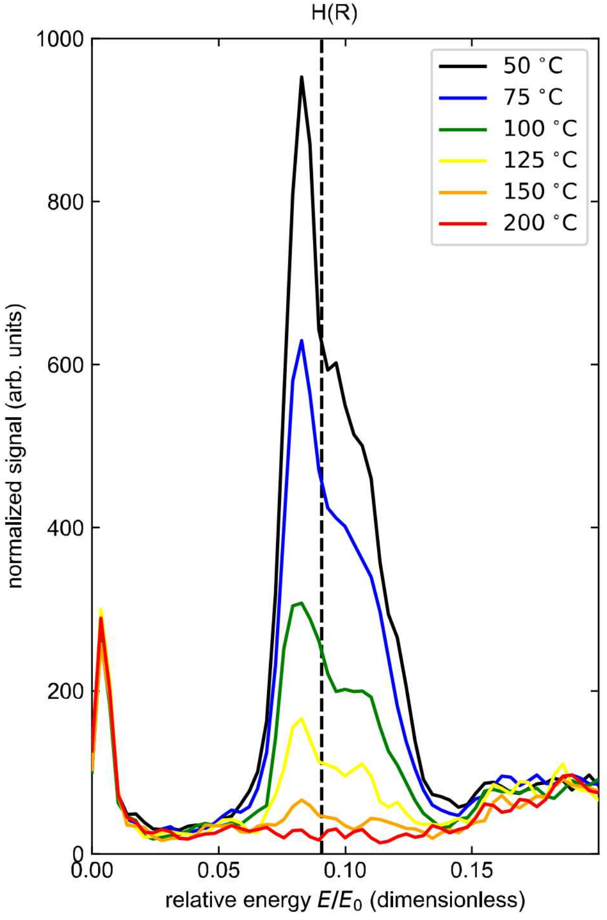


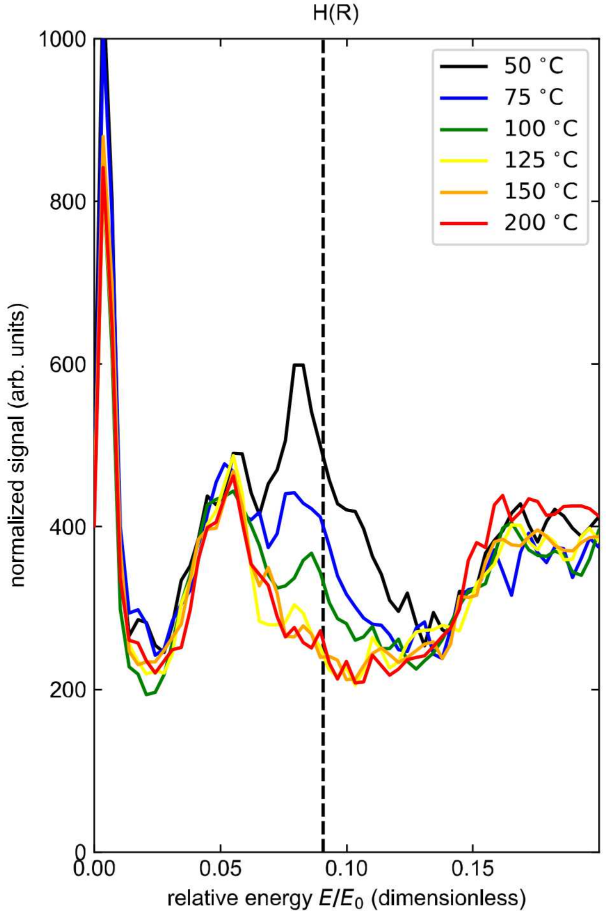
With increasing temperature:

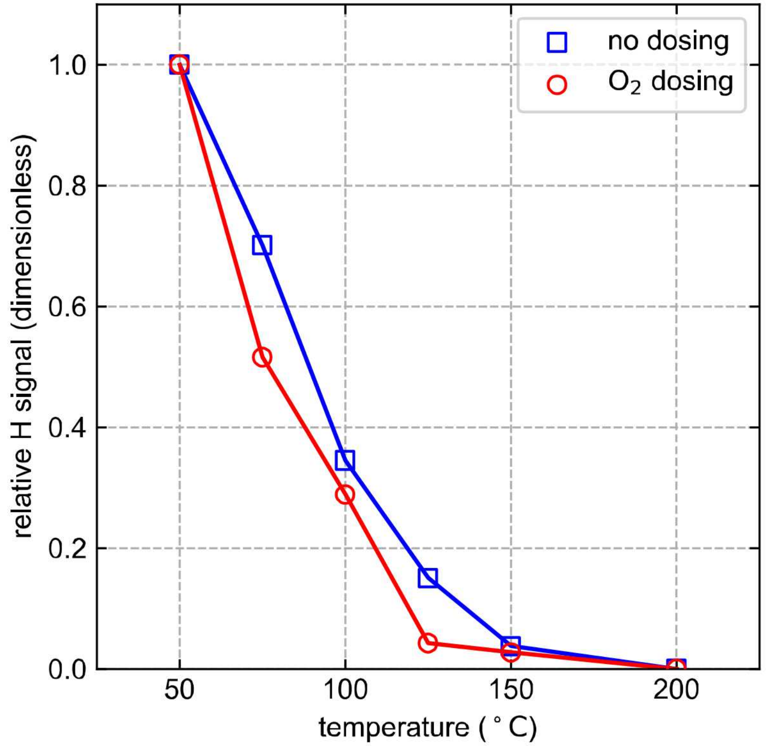
1. H peak diminishes
2. O peaks remains unchanged (up to 400 °C)
3. Ni peak increases slightly

Temperature effect on H adsorption with & without O_2 dosing (cont.)

Compare H(R) peaks:



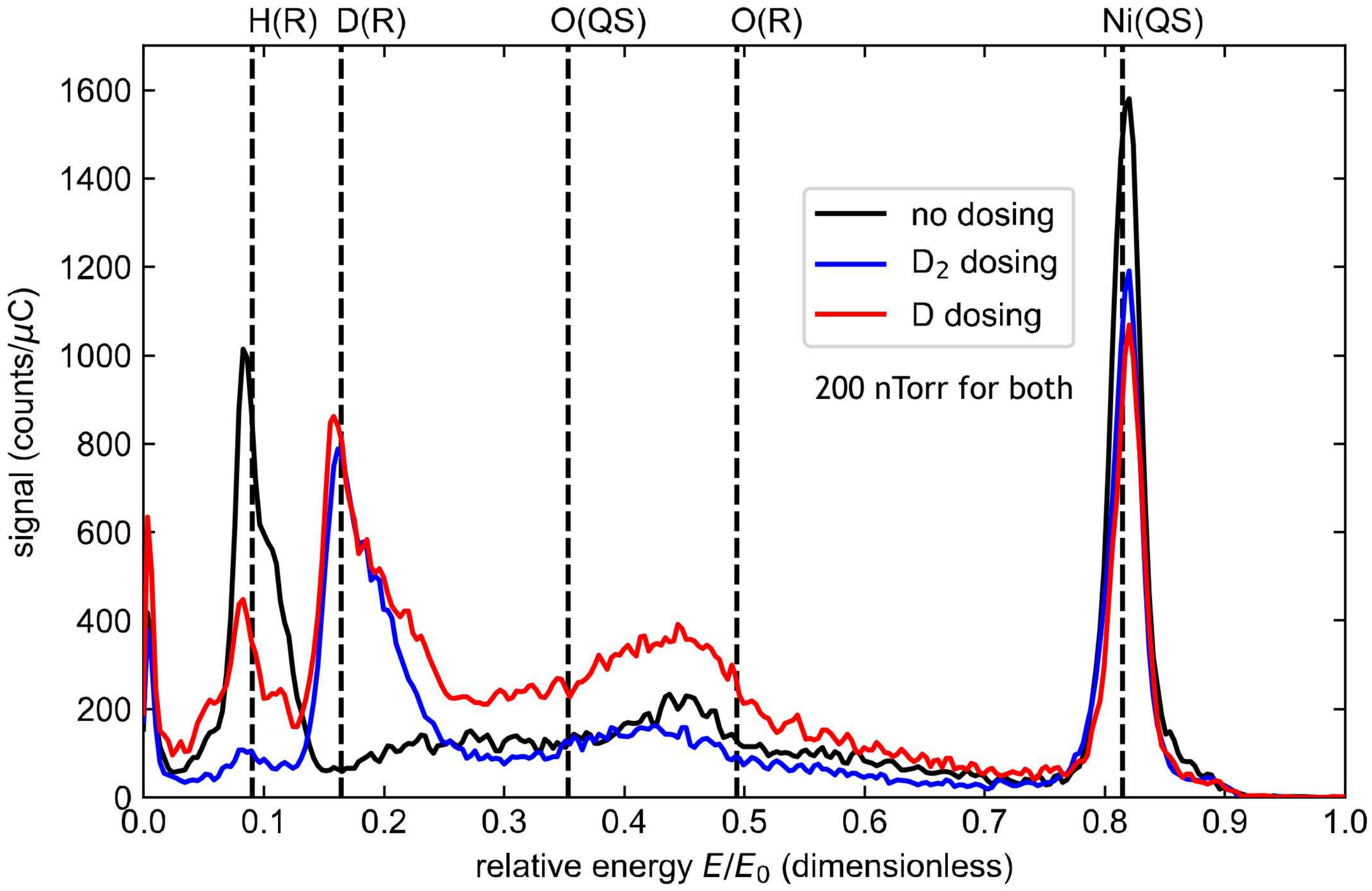




Surface H diminishes more rapidly for increasing temperature with O_2 present

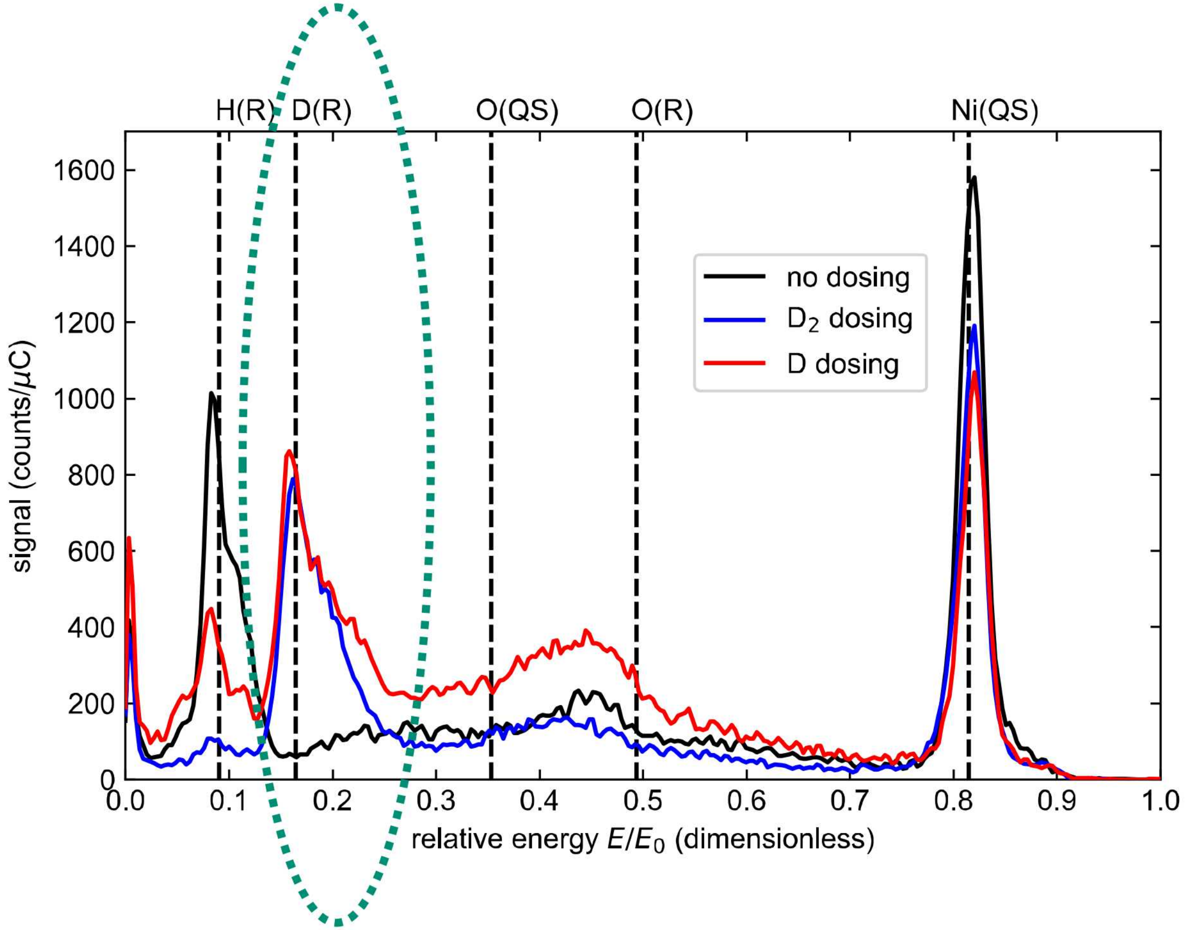
Repulsion by co-adsorbed O ?

Examining dissociation: comparison of dosing with D_2 vs D

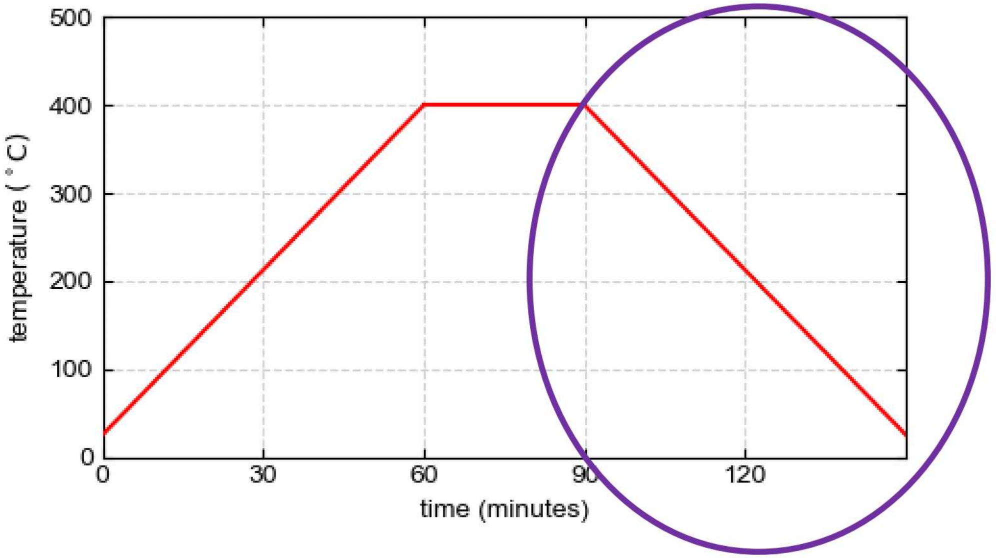


- D_2 and D have similar uptake on Ni
- not a significant barrier for D_2 dissociation at the surface
- background for D is larger due to impurities outgassed by H cracker

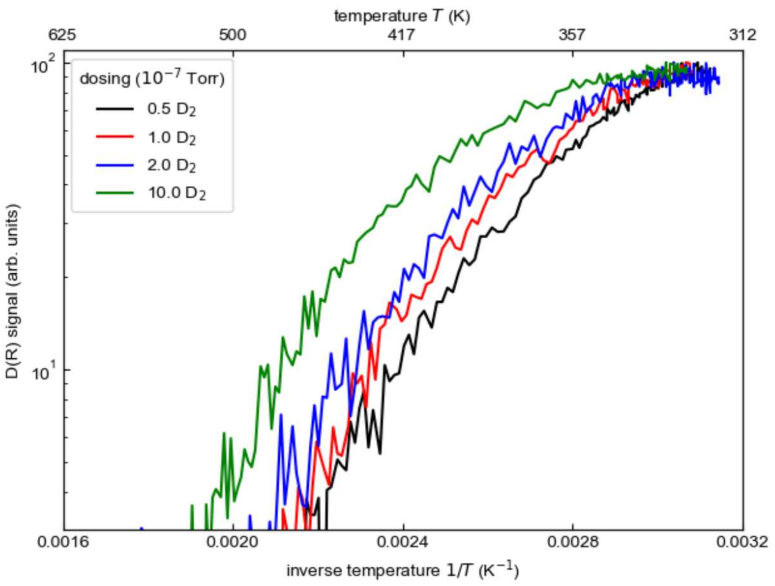
Temperature effect on hydrogen uptake

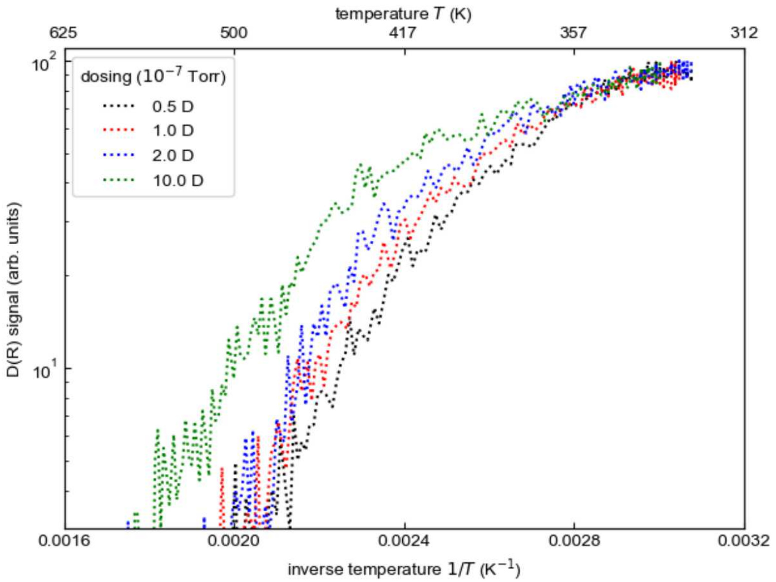


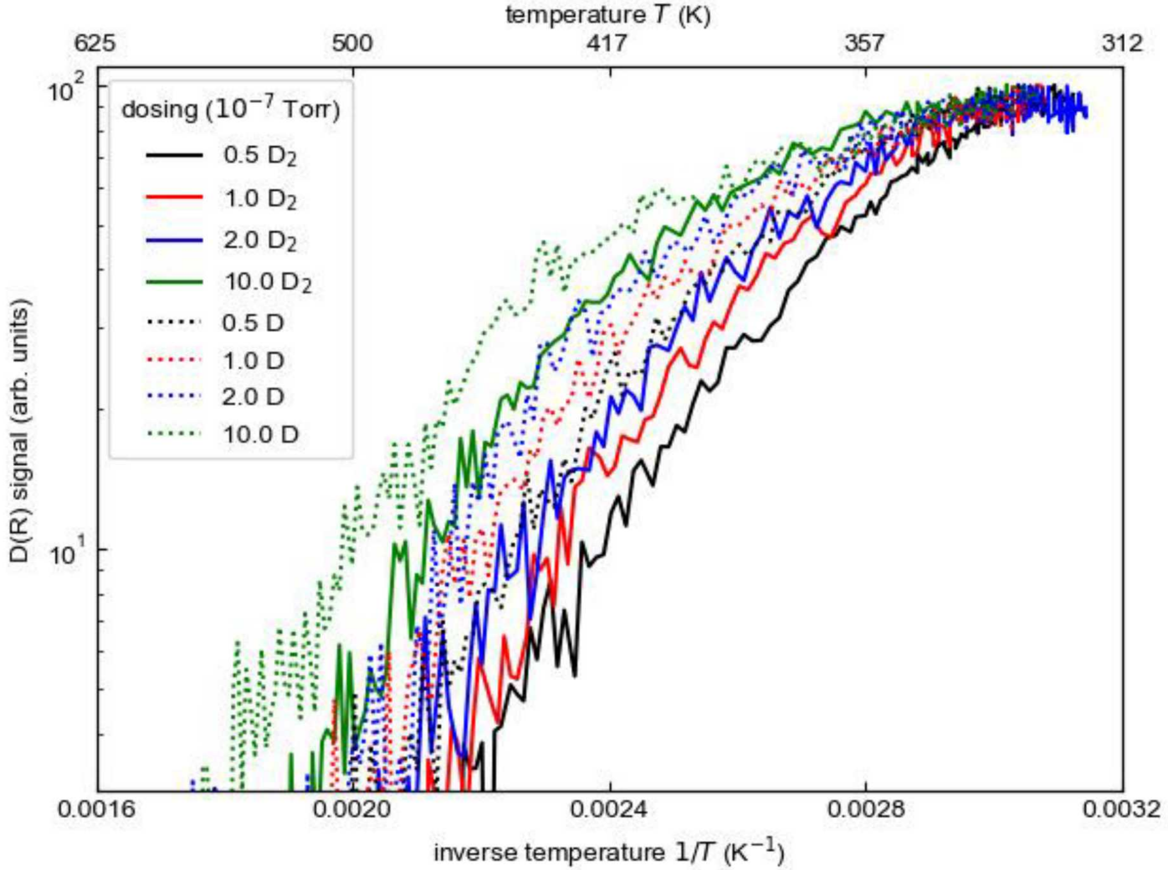
isobar measurements of hydrogen uptake by monitoring D(R) while ramping down temperature



Isobars comparing D and D_{2c}







For both D and D_2 dosing

- Isobar curves generally obey Arrhenius relation
- Higher pressure → adsorption at higher temperatures

D adsorbs at higher temperature/lower pressure than D_2

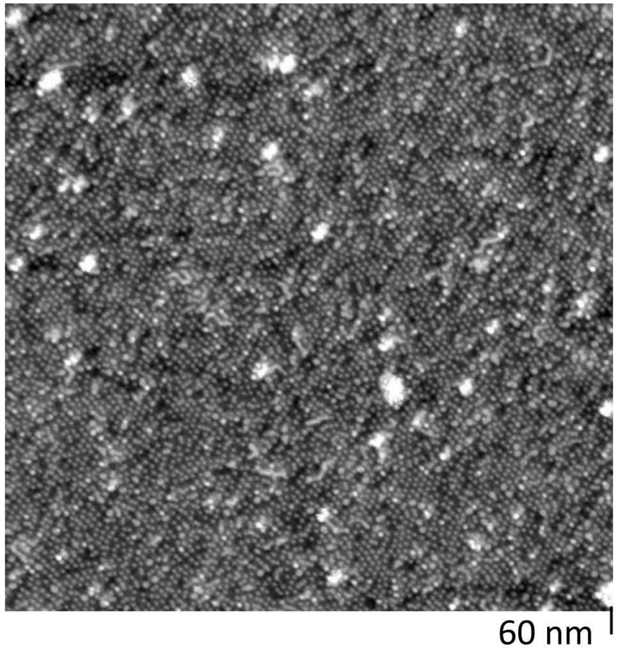
Summary:

- Demonstrated extreme H-sensitivity of TDS and ARIES
- **Both techniques showed that minute amounts of oxygen can block H-uptake by the Ni surface**
- ARIES: Quantified effect of Temp and dissociation on H-uptake

Outlook:

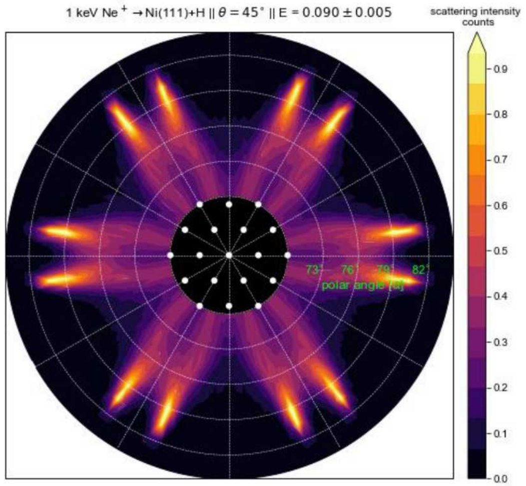
- Include other contaminants (H_2O, CH_4)
- H & O adsorption on Ni single crystals

H/Pd (3x3)
Individual
H vacancies



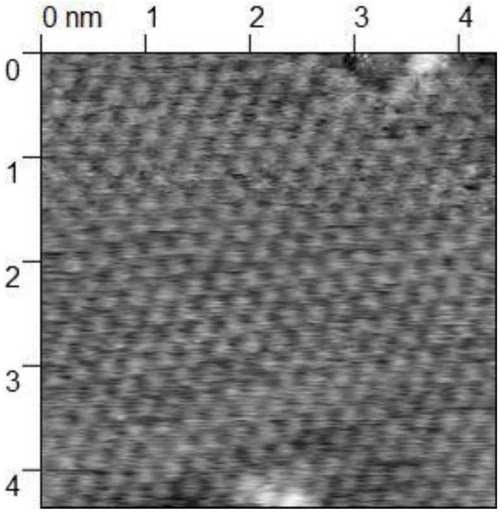
60 nm

Combine ARIES with modeling



simulated H/Ni(111) map for three-fold adsorption site

Leverage our new capability to image hydrogen with STM:



H/Pd (1x1)
Individual H atoms