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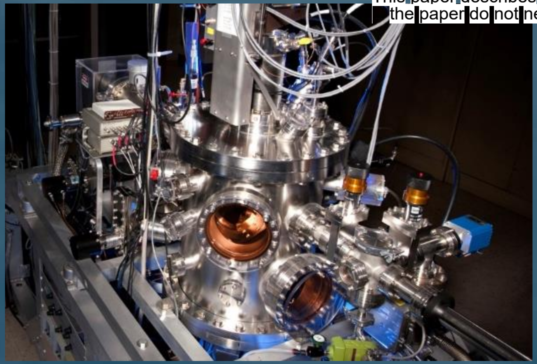

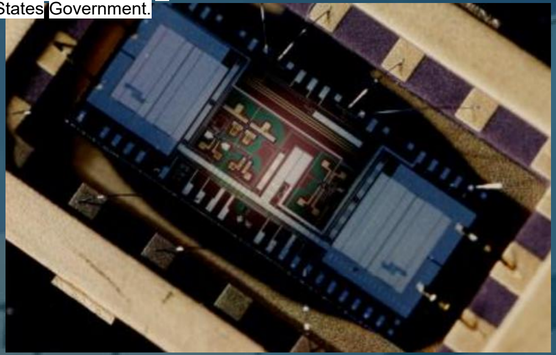

Sandia National Laboratories

Ion and neutral time-of-flight spectroscopy for deciphering hydrogen-surface interactions

R. D. Kolasinski, C. –S. Wong, and J. A. Whaley

Sandia National Laboratories, Plasma & Reacting Flow Science Department, Livermore, CA

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Overview

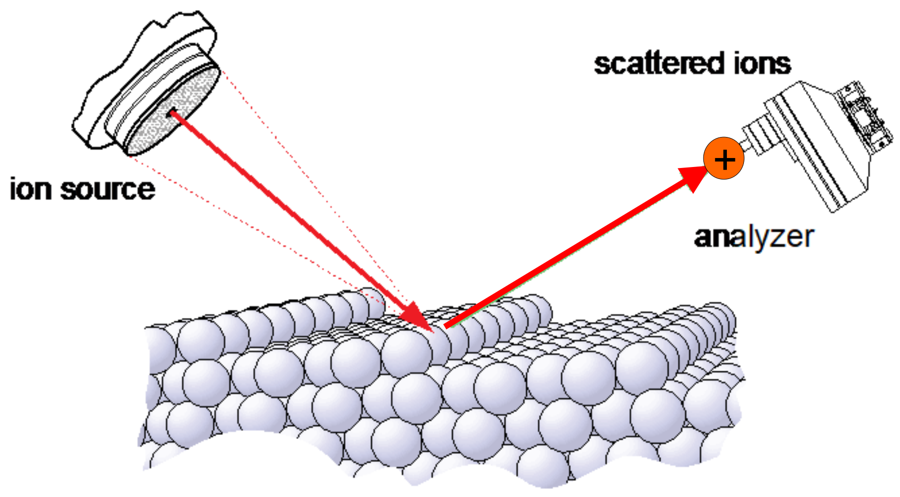
Motivation: The interaction between hydrogen and surfaces strongly affects how it migrates into the bulk

Technical Challenge: Chemisorbed hydrogen is difficult to detect using conventional surface analysis

In this talk:

- Using direct recoil spectroscopy to decipher the structure of chemisorbed H on W(111)
- Development of impact collision ion scattering spectroscopy techniques to analyze surface structure
- New ion scattering instrumentation for real-time measurement of surface composition in a high-pressure environment

Low energy ion scattering



Scattering from substrate atoms

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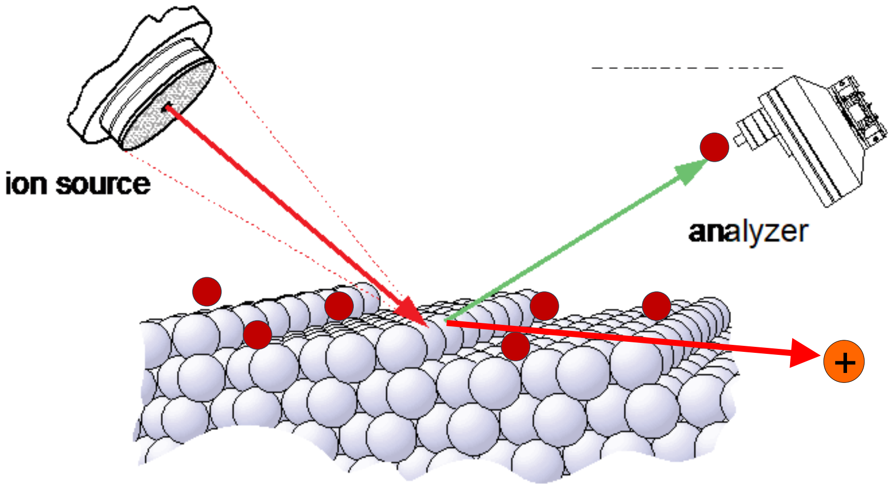
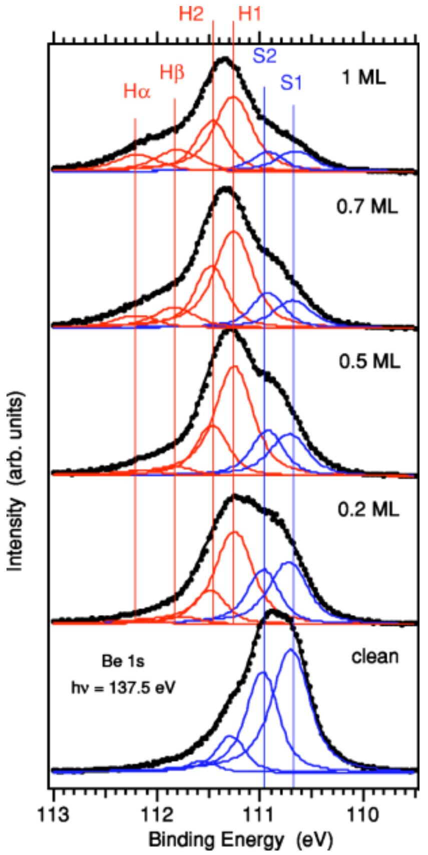
Direct recoil spectroscopy

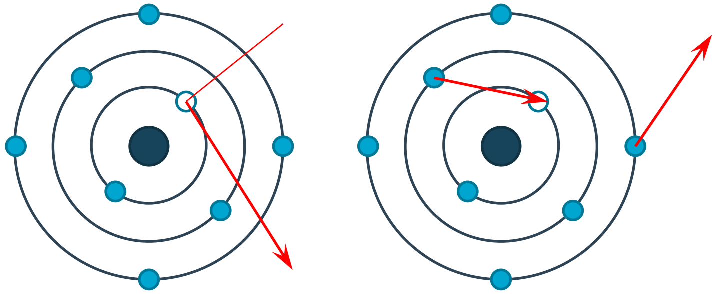


Detection of recoiled hydrogen

Detection of hydrogen is challenging for many conventional surface science techniques

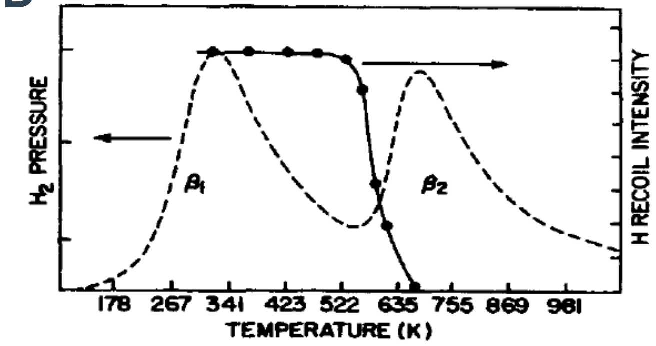
XPS





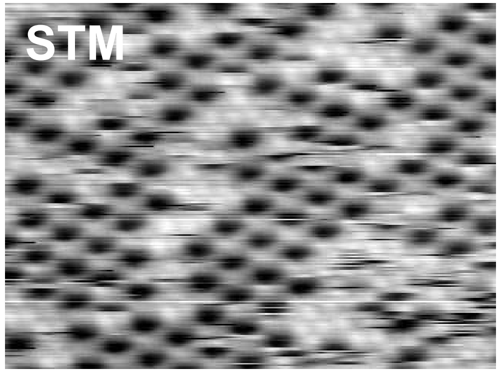
AES

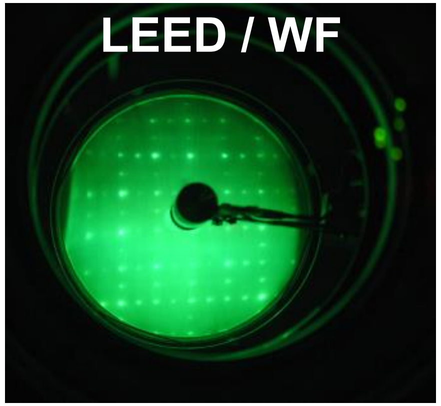
TPD



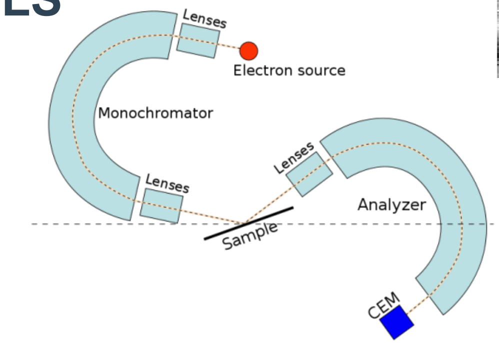
Technical challenges:

- Detection impossible with AES, indirect with XPS
- Detectable signal may be overwhelmed by substrate (LEED, STM, HREELS)
- Ambiguous/difficult to interpret. (TPD)



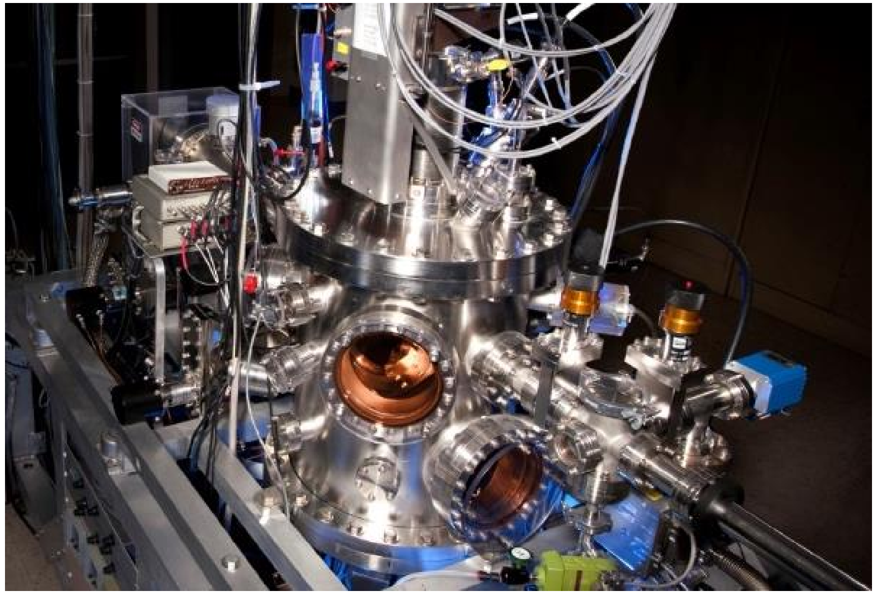


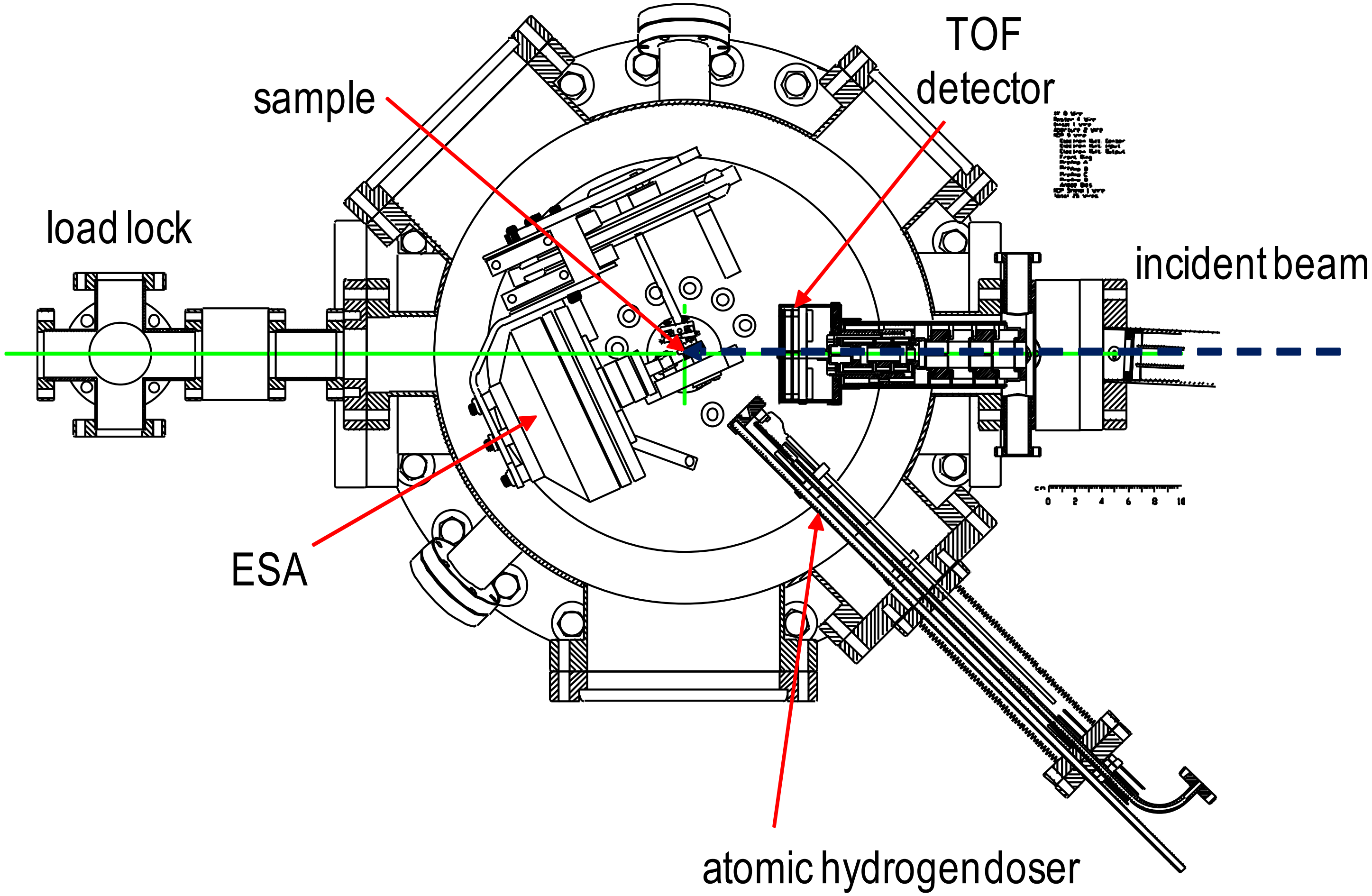
HREELS



Approach: Forward scattering used to detect recoiled H

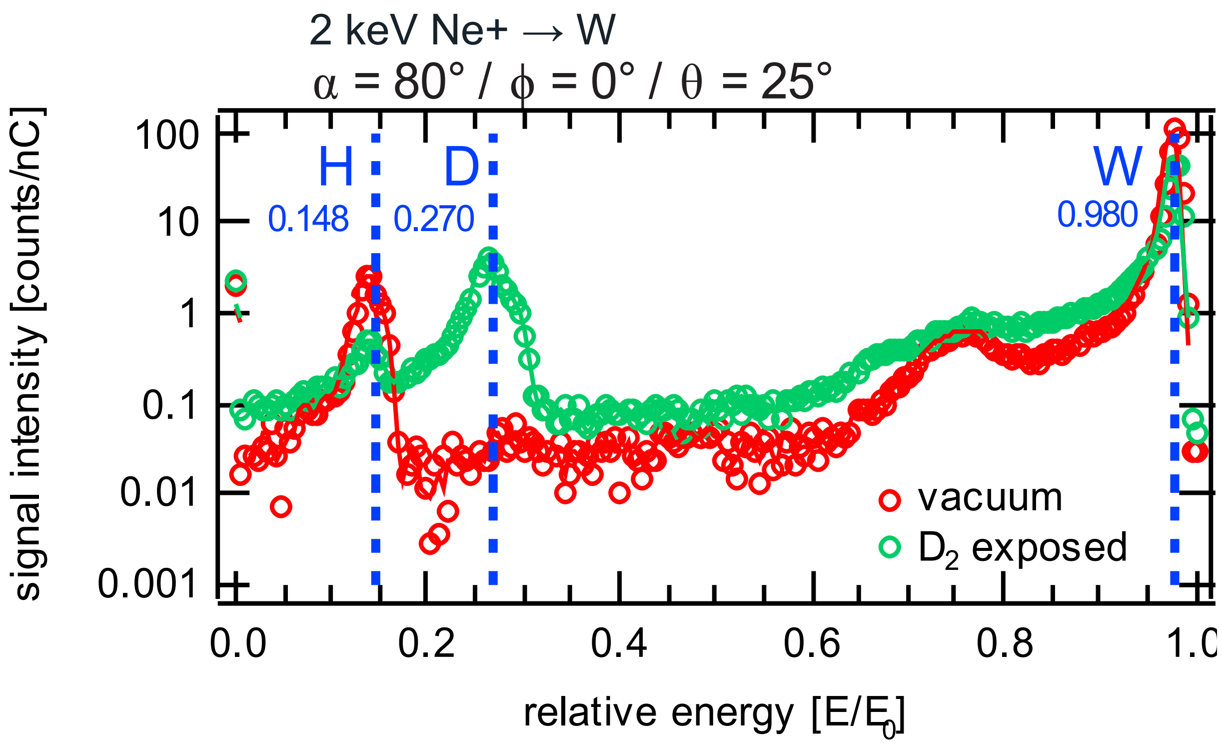
- Low energy ions: **< 3 keV He^+, Ne^+**
- Oblique incidence: **70° < α < 85°**
- Detection in far-forward direction
  - Scattering angle **θ < 45°**
- Atomic **H / D** dosing





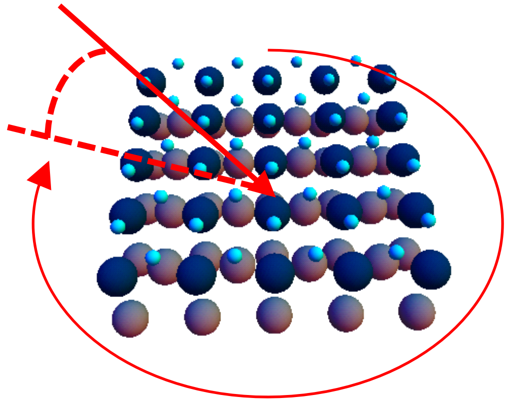
Above: Angle-resolved ion energy spectrometer

Multi-angle maps of H recoiled can provide deep insight into the structure of the chemisorbed H layer



Example ion energy spectrum for H and D adsorption on W

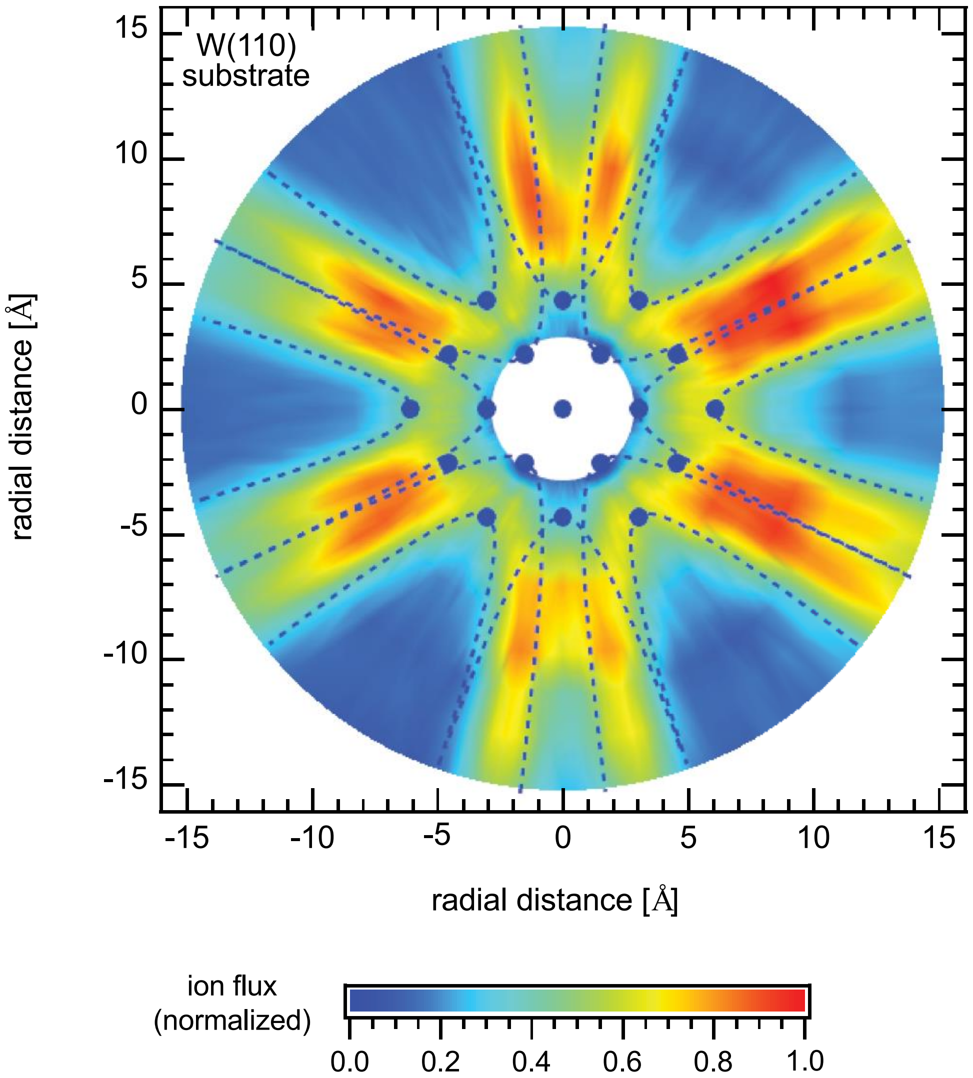
Multi-angle maps created by varying ion beam incidence angle and crystal azimuth



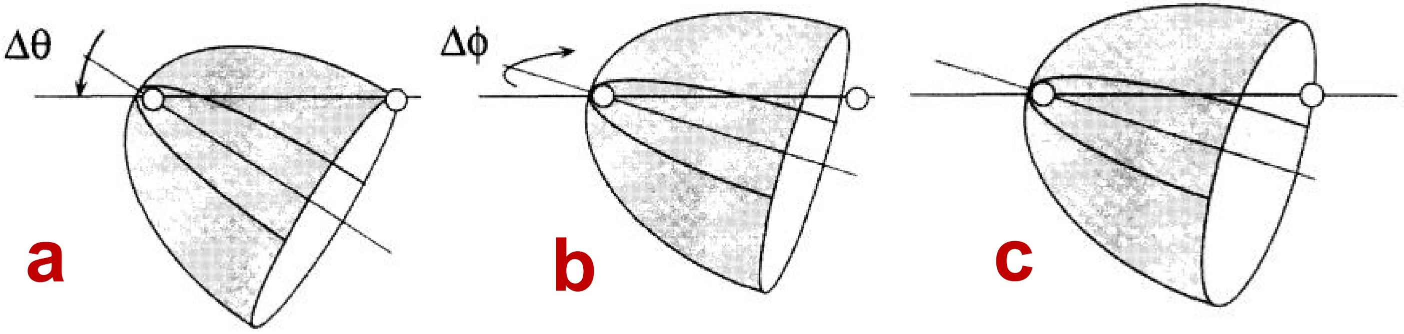
Measure scattered and recoiled fluxes over many orientations

- Provides a much more comprehensive data set for comparison with models
- Limitations: requires lengthy acquisition time, increases ion dose to sample

Multi-angle map of Ne+ forward scattered from the W(110) surface



- Patterns trace out shadow cone intersections with neighboring atoms
- Can be rendered in real space

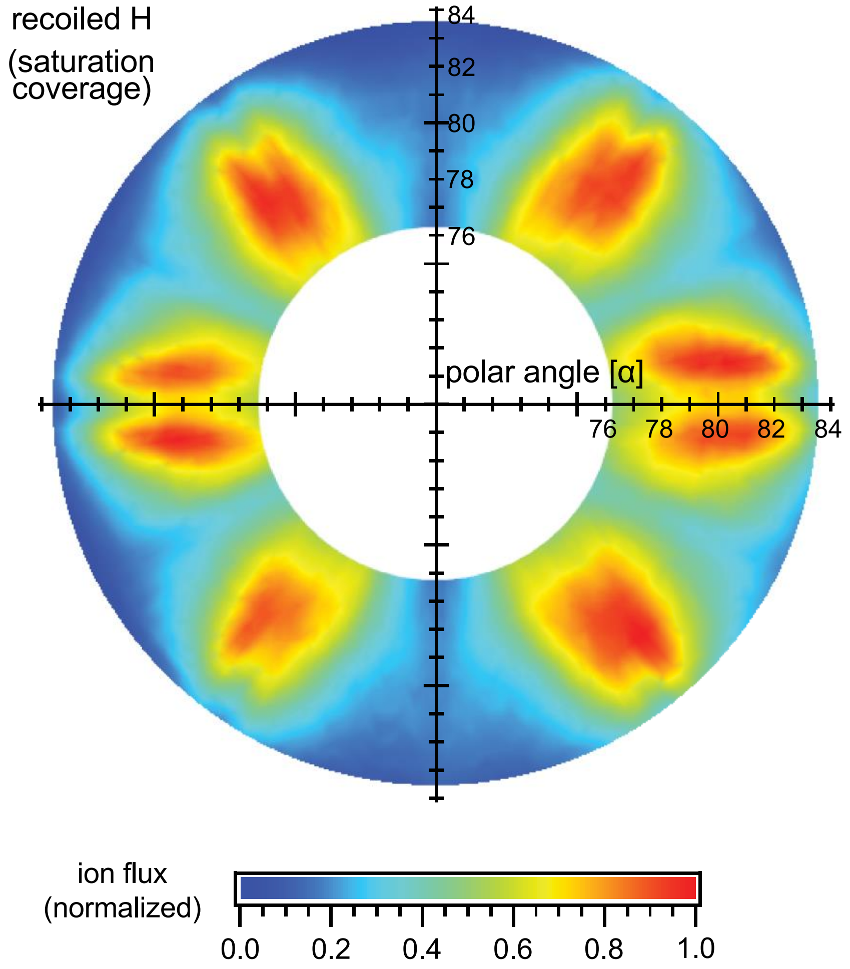


R. G. Agostino, *Surf. Sci.* **384** (1997) 36.

Observations

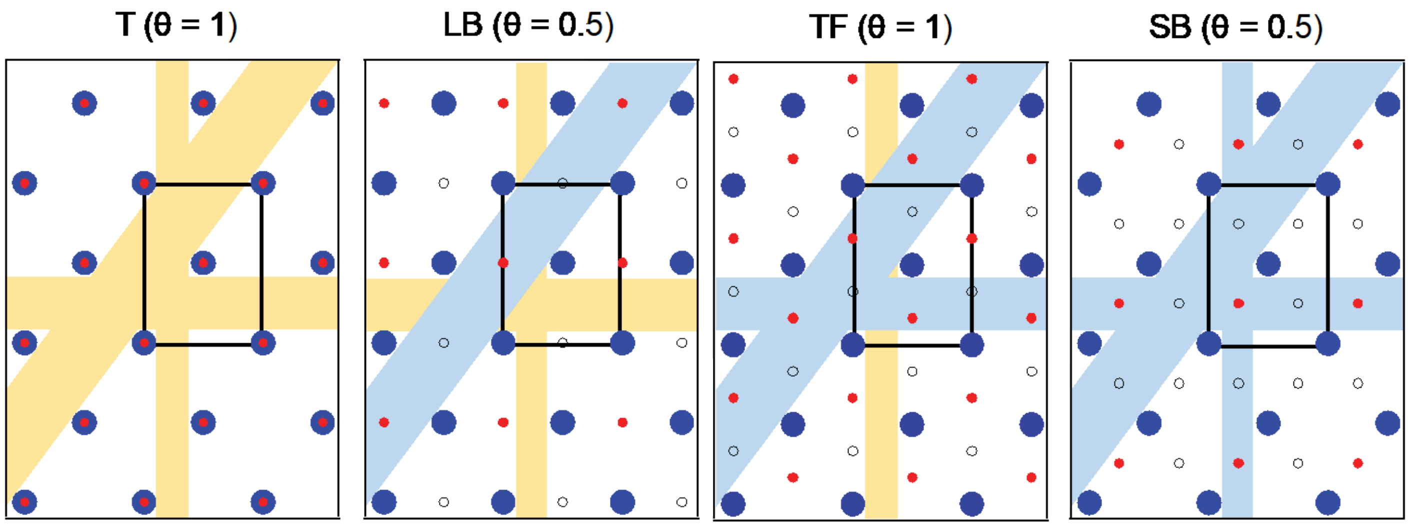
- Pattern consistent with non-reconstructed, clean surface.
- W atoms effective at deflecting Ne^+ along open surface channels.

Chemisorbed hydrogen can be mapped in a similar manner using direct recoil spectroscopy



Surface Channeling

- Ne^+ ions interact with an extended region of the surface at oblique incidence
- Enhanced recoiled H flux detected along surface channels where H is binding
- Can be used for identification of binding site



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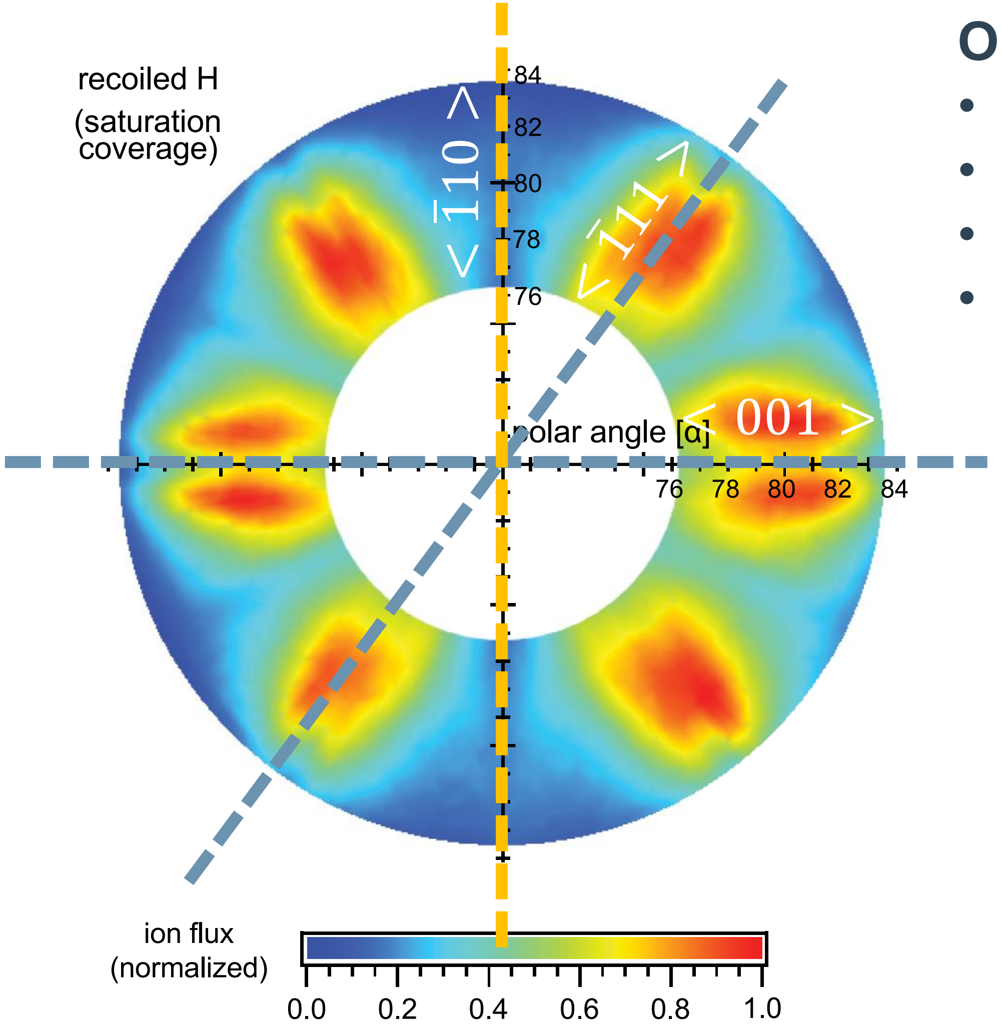
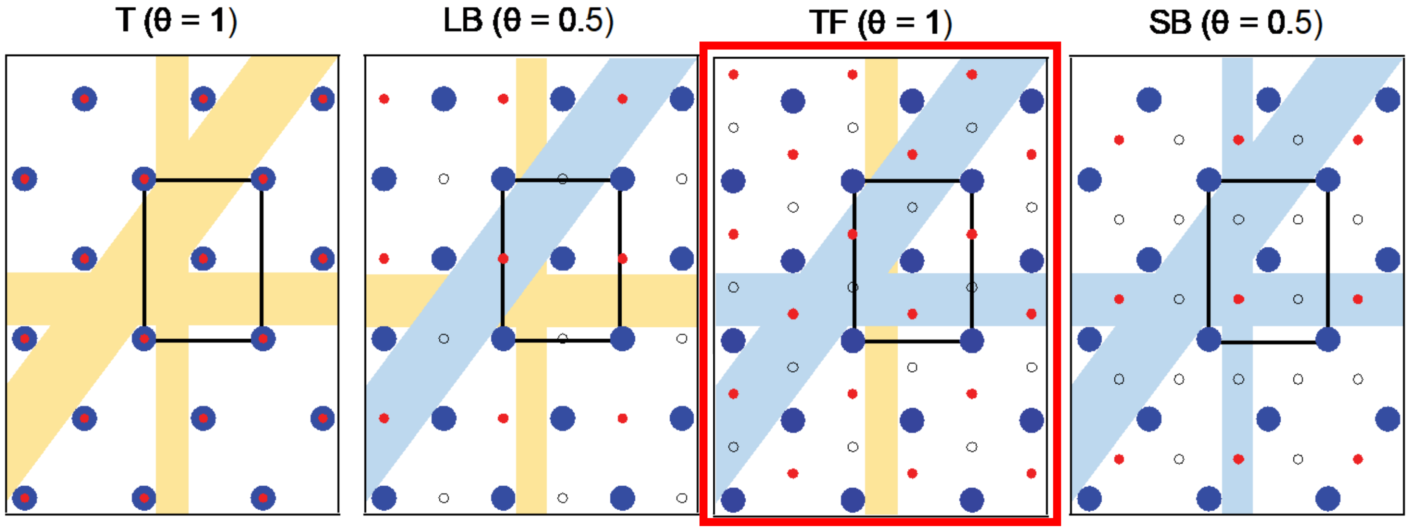


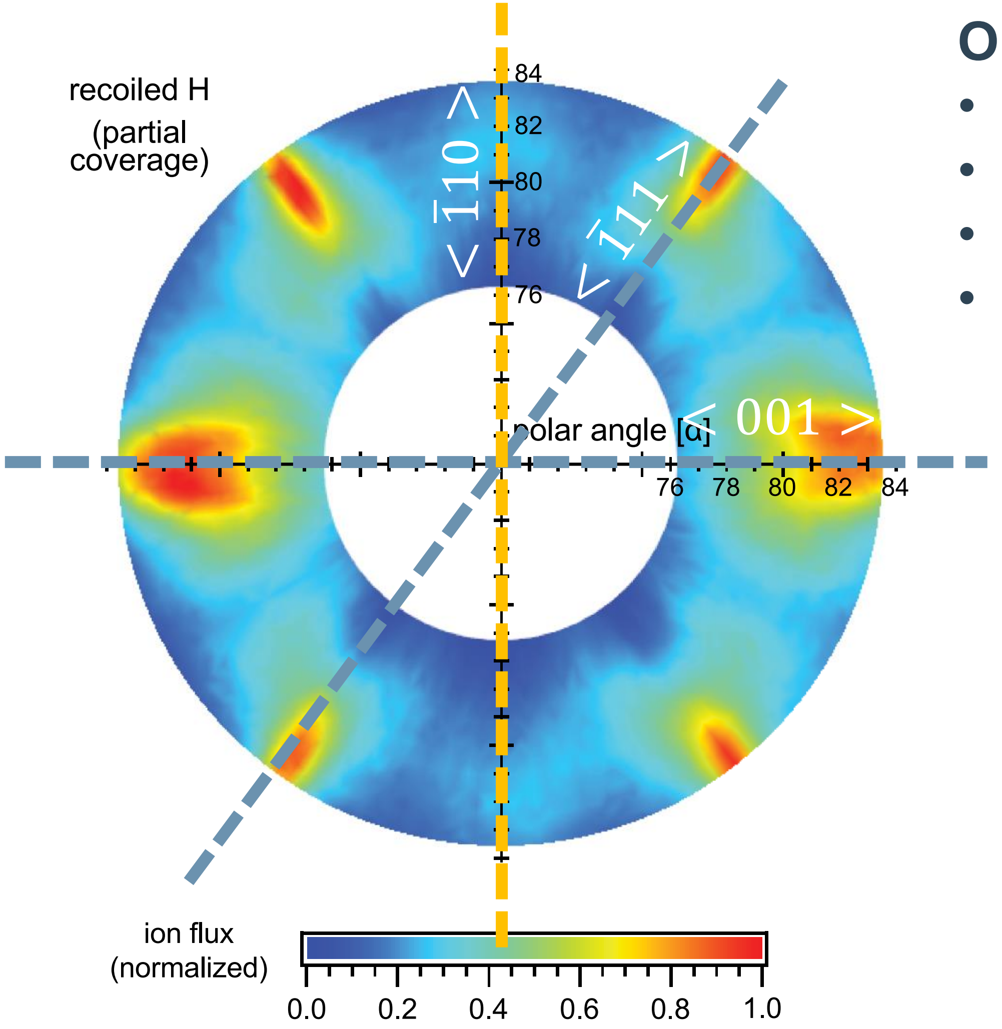
Observations

- H chemisorbs on W(110) with no dissociation barrier.
- Recoiled H observed along $<001>$ and $<\bar{1}11>$ channels
- No recoils observed along $<\bar{1}10>$ channels
- Consistent with binding to three fold hollow sites as predicted by DFT.

Z. Piazza, R. Kolasinski, et al. *J. Phys. Chem. C* (2021)



Binding site does not appear to change with H coverage



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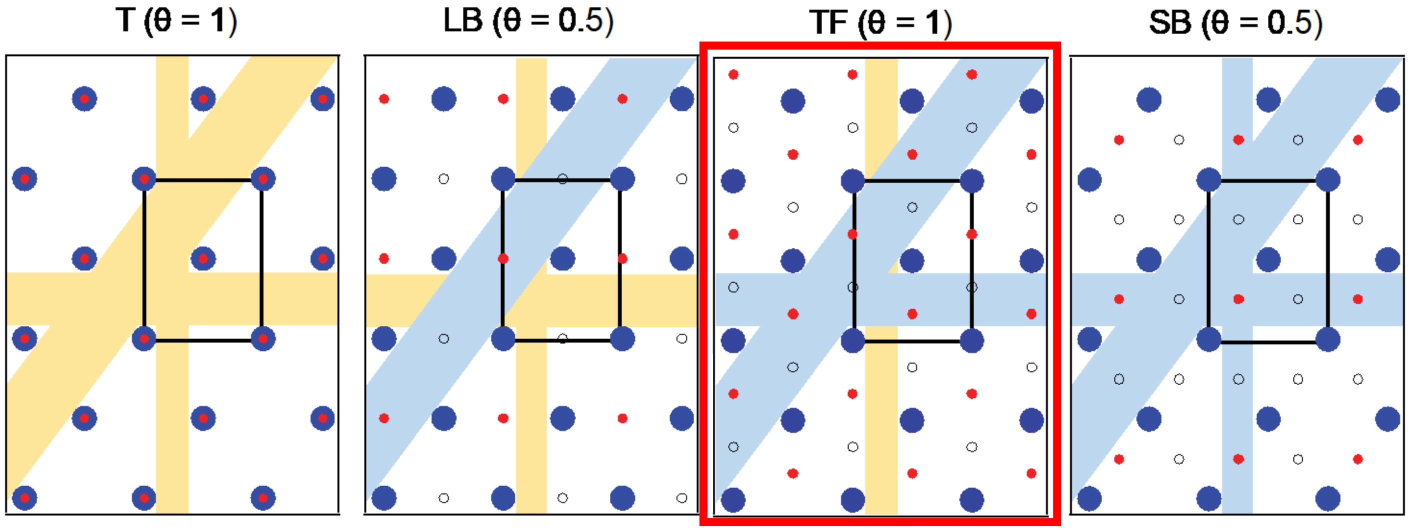
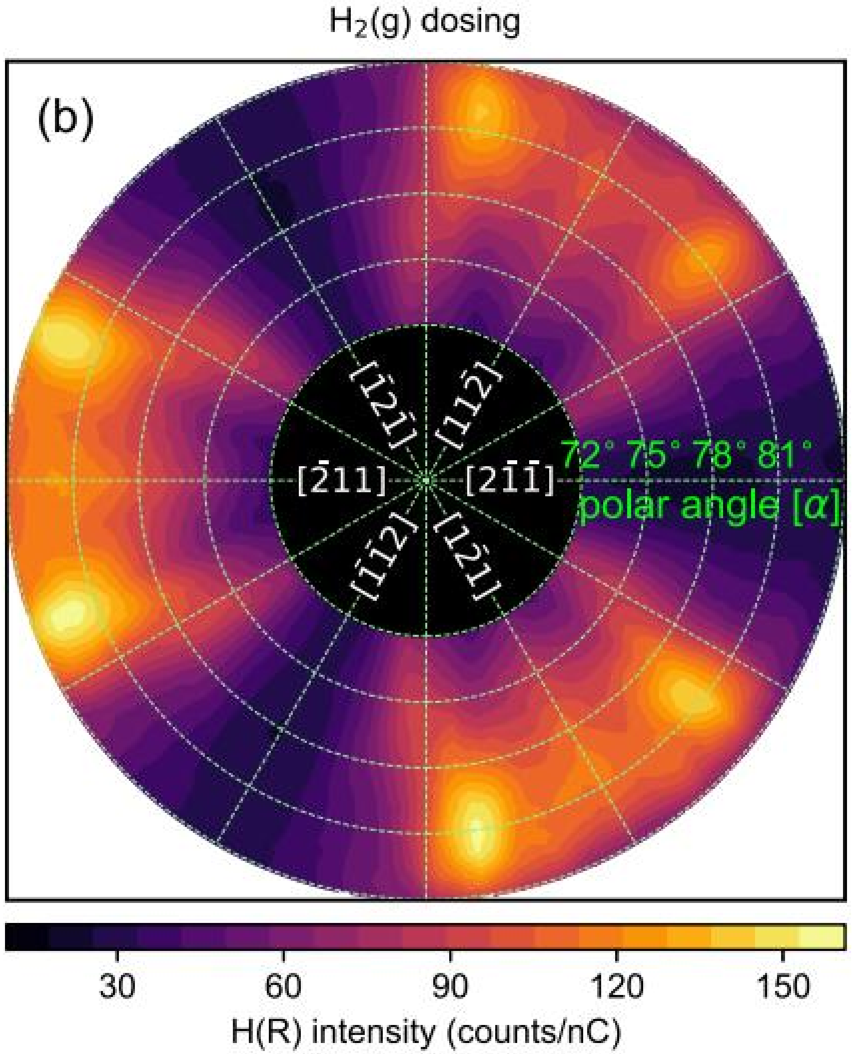
Z. Piazza, R. Kolasinski, et al. *J. Phys. Chem. C* (2021)



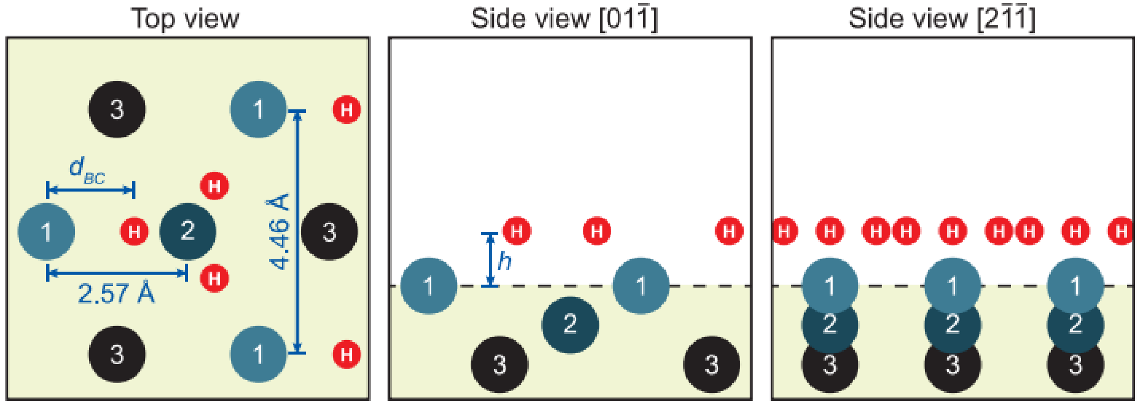
H chemisorption on W(111) requires a more complex interpretation



Technical challenges

- Top 3 layers of W atoms contributed to measurement
- Bond-centered binding geometry for chemisorbed H
- Can not be interpreted using simpler surface channeling model

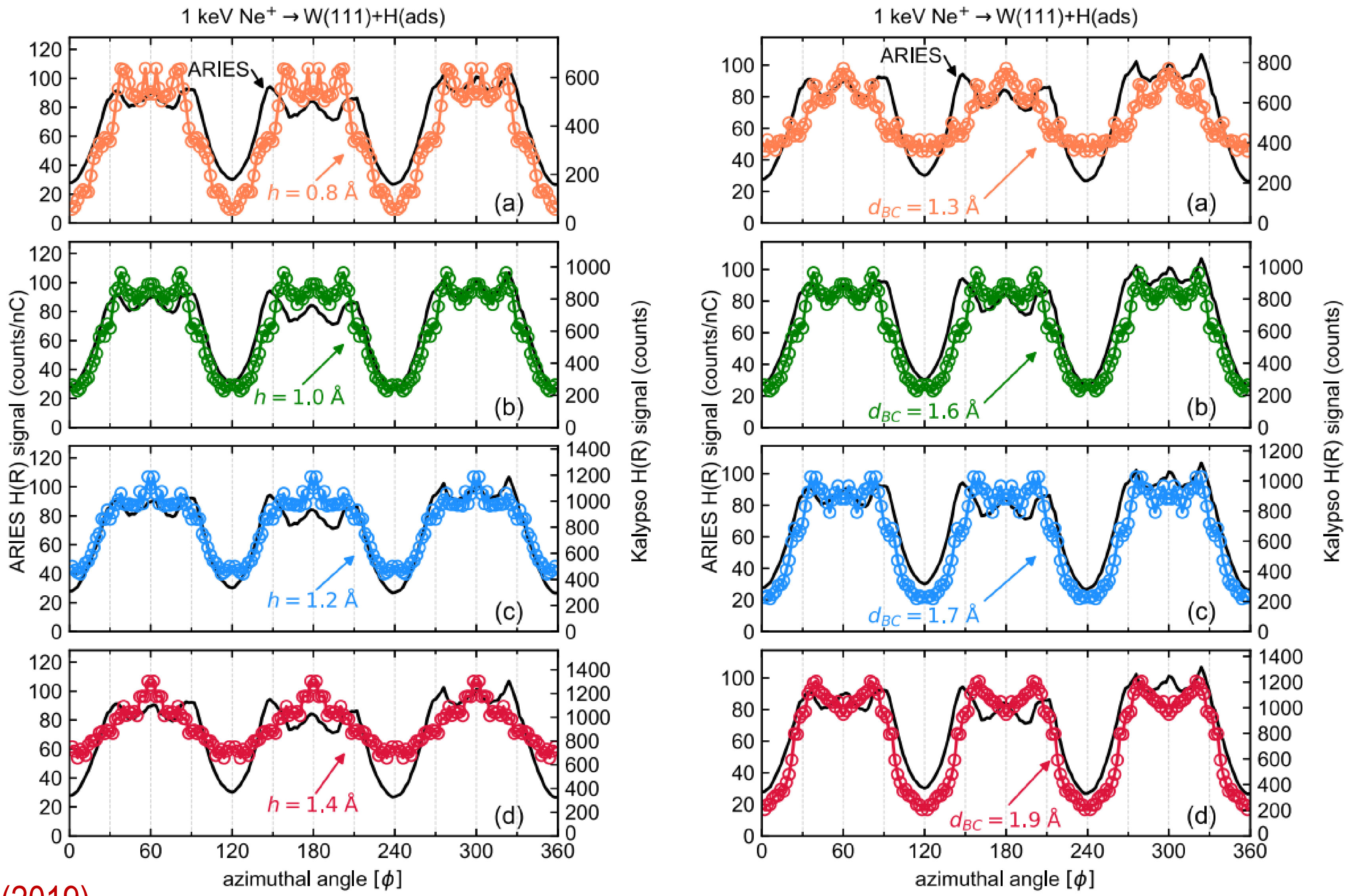
C. –S. Wong, J. A. Whaley, Z. Bergstrom, B. D. Wirth, and R. Kolasinski, *Phys. Rev. B* (2019)



H chemisorption on W(111) requires a more complex interpretation

Modelling approach

- MD needed to account for scattering at oblique incidence
- Quantitative comparison with experiments possible, allows bond length to be precisely calculated



C. –S. Wong, J. A. Whaley, Z. Bergstrom, B. D. Wirth, and R. Kolasinski, *Phys. Rev. B* (2019)

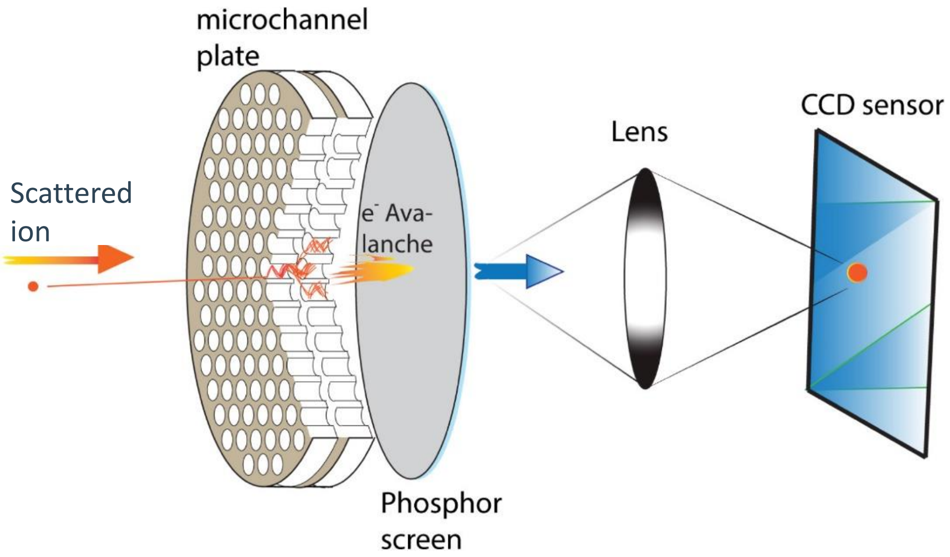
Time of flight spectroscopy can help address limitations of prevailing techniques

Limitations of existing instrumentation:

- Multi-angle maps require up to 24 hrs. to acquire
  - Prevents time-resolved measurements of H behavior
  - Substantial ion dose to sample, limits ability to probe sensitive targets
- Electrostatic analyzer detects only charged particles
  - Modelling of neutralization is complex, making challenging to model the experimental results precisely

Potential benefits of time of flight spectroscopy (TOF):

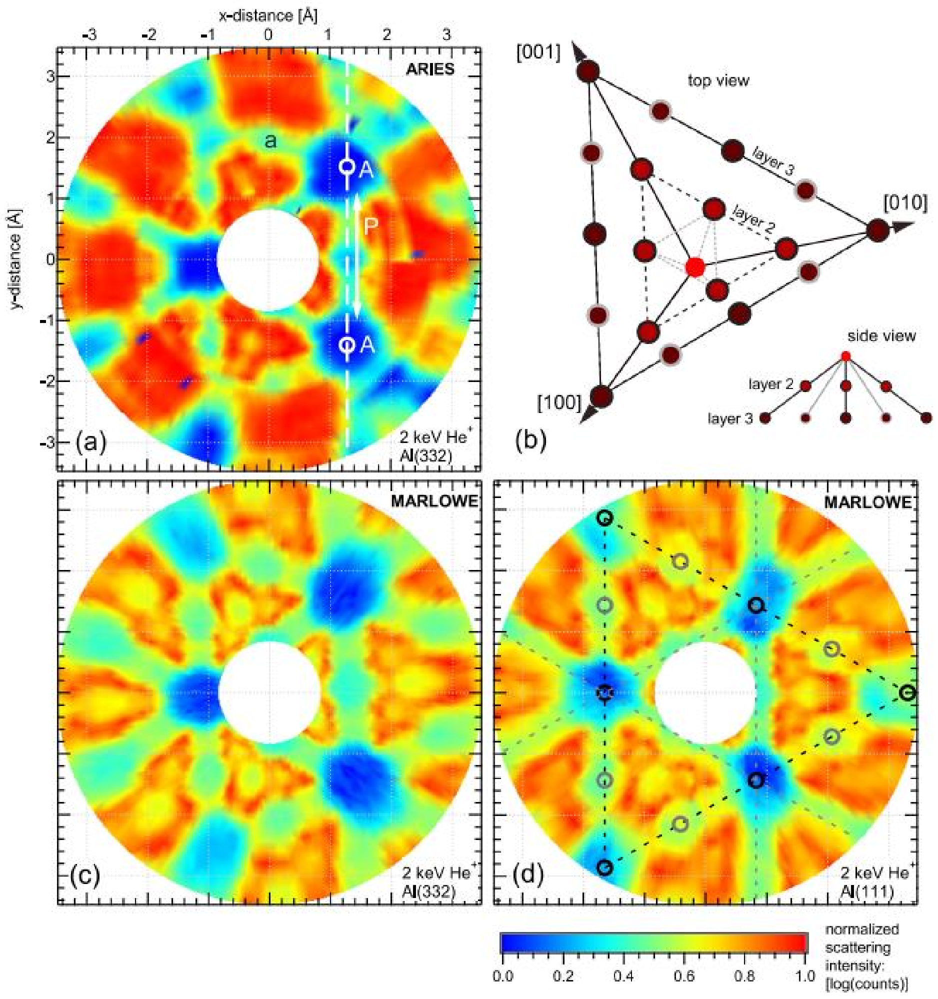
- Many ways to limit ion dose to samples
  - Uses pulsed beam with low duty cycle, high sensitivity detectors
  - A large microchannel plate detector can image many particles simultaneously
- Detects both ion and neutral particles
- Lower mass resolution is a disadvantage compared with an electrostatic analyzer



Using a high-speed camera to image MCP detector with phosphor screen

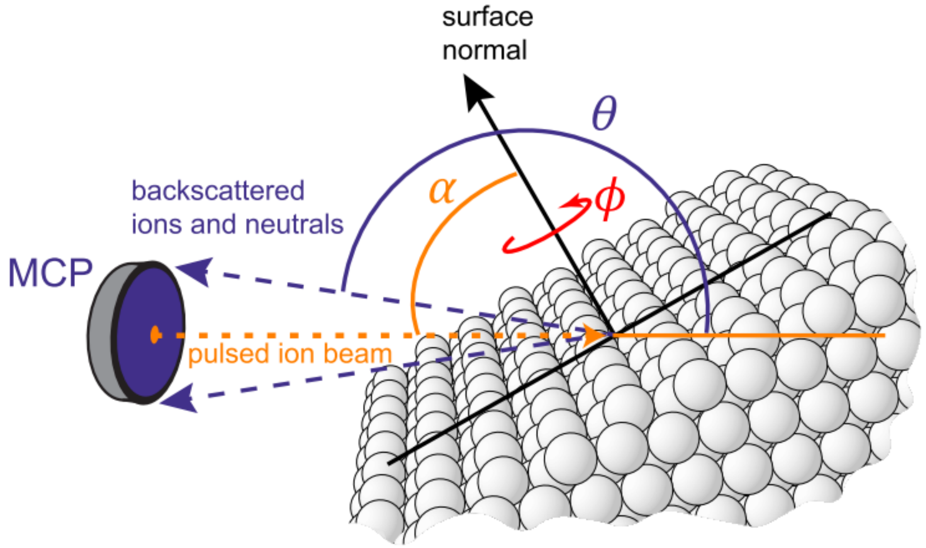
B. Kim, S. Bae, H. Chio, et al, Nucl. Instrum. Meth. B **899** (2018) 22.

Time of flight spectroscopy



He backscattering maps from Al surfaces
R. D. Kolasinski, J. A. Whaley, D. Ward, *Surf. Sci.* (2019)

C. –S. Wong, et al., *J. Phys. Condens. Matter* (2020)



Recent work

- TOF meas. of low-energy He channeling into W, Al
- FAN-style model developed to analyze shadowing and blocking patterns

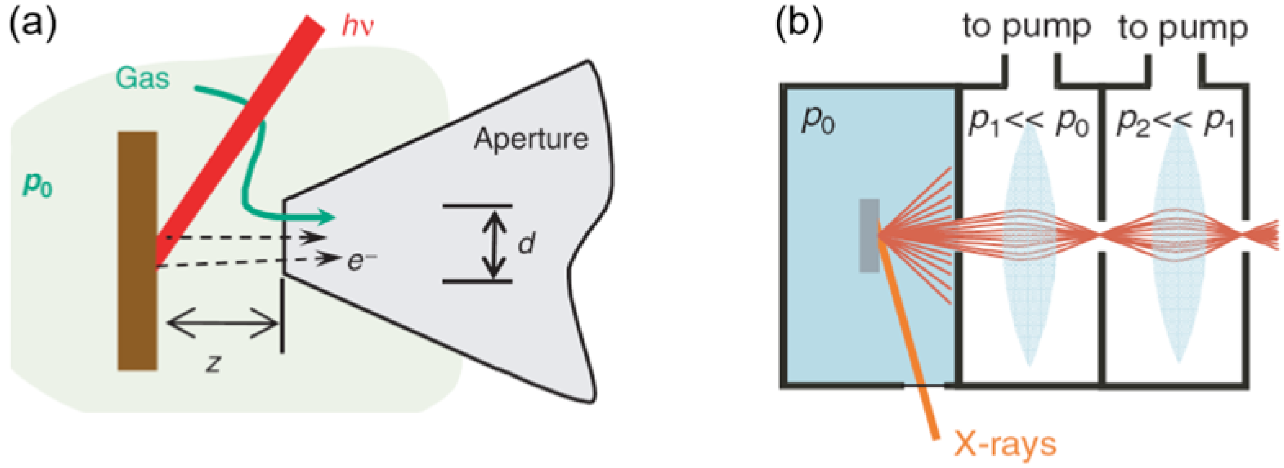
New instrumentation under development

- Includes a large-angle MCP detector to collect pattern from backscattered ions
- Additional longer flight tubes are differentially pumped to allow for measurements at high pressures

Adapting UHV surface science techniques to a high pressure environment

Standard UHV technique: XPS
***In-operando* adaptation:** differential pumping to increase transmission efficiency, collect photoelectrons close to surface to minimize scattering

Example: Ambient pressure XPS



Bluhm, H. et al. *MRS Bulletin* **32** (2007) 1022

Optical techniques for composition:

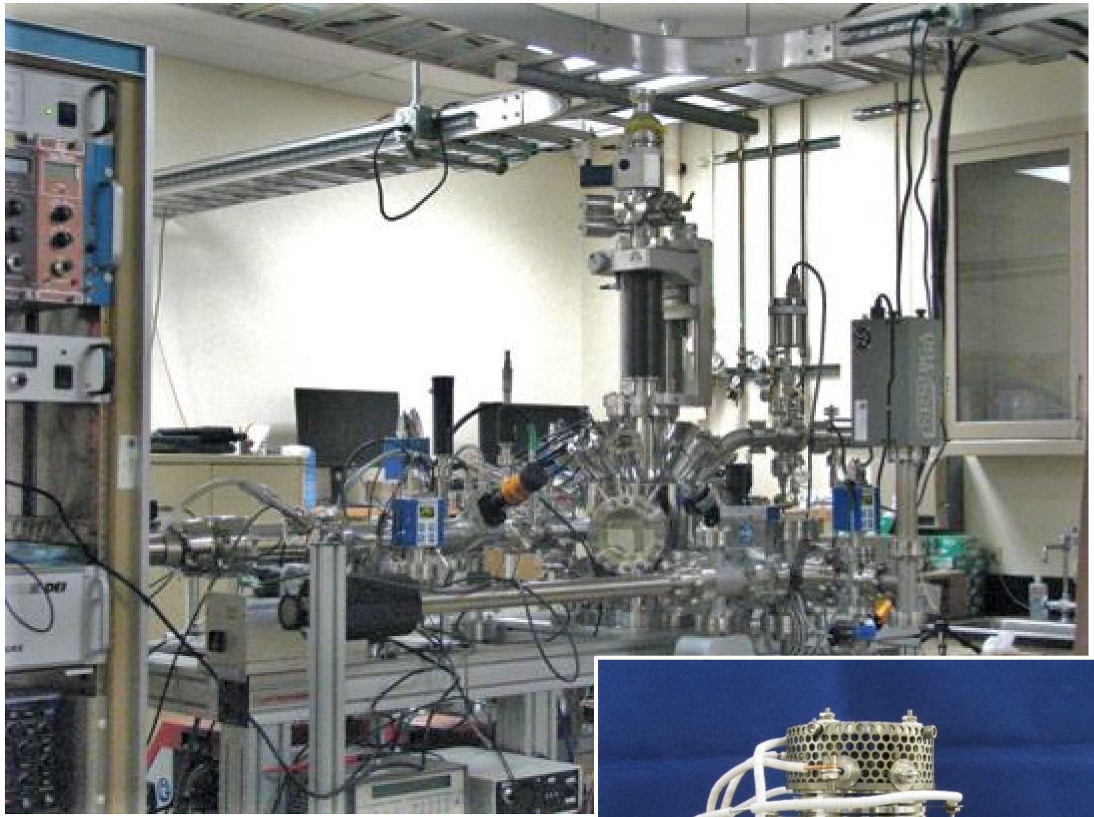
- Optical spectroscopy to detect sputtered particles
- Laser-based diagnostics (LIBS)

Fewer techniques available for detection of hydrogen

- Can ion scattering / direct recoil spectroscopy be adapted?

Instrument with differentially pumped flight tubes to allow for higher pressure operation

New instrument for high-resolution depth profiling



High-resolution Extrel mass spectrometer

Instrument designed at Sandia (on-line June 2022)

Optimized for:

- 20 keV alkali ion source for high resolution profiling of H, He, and oxide layers
- High resolution QMA (0-50 amu) for TDS / SIMS
    - Direct line-of-sight to sample

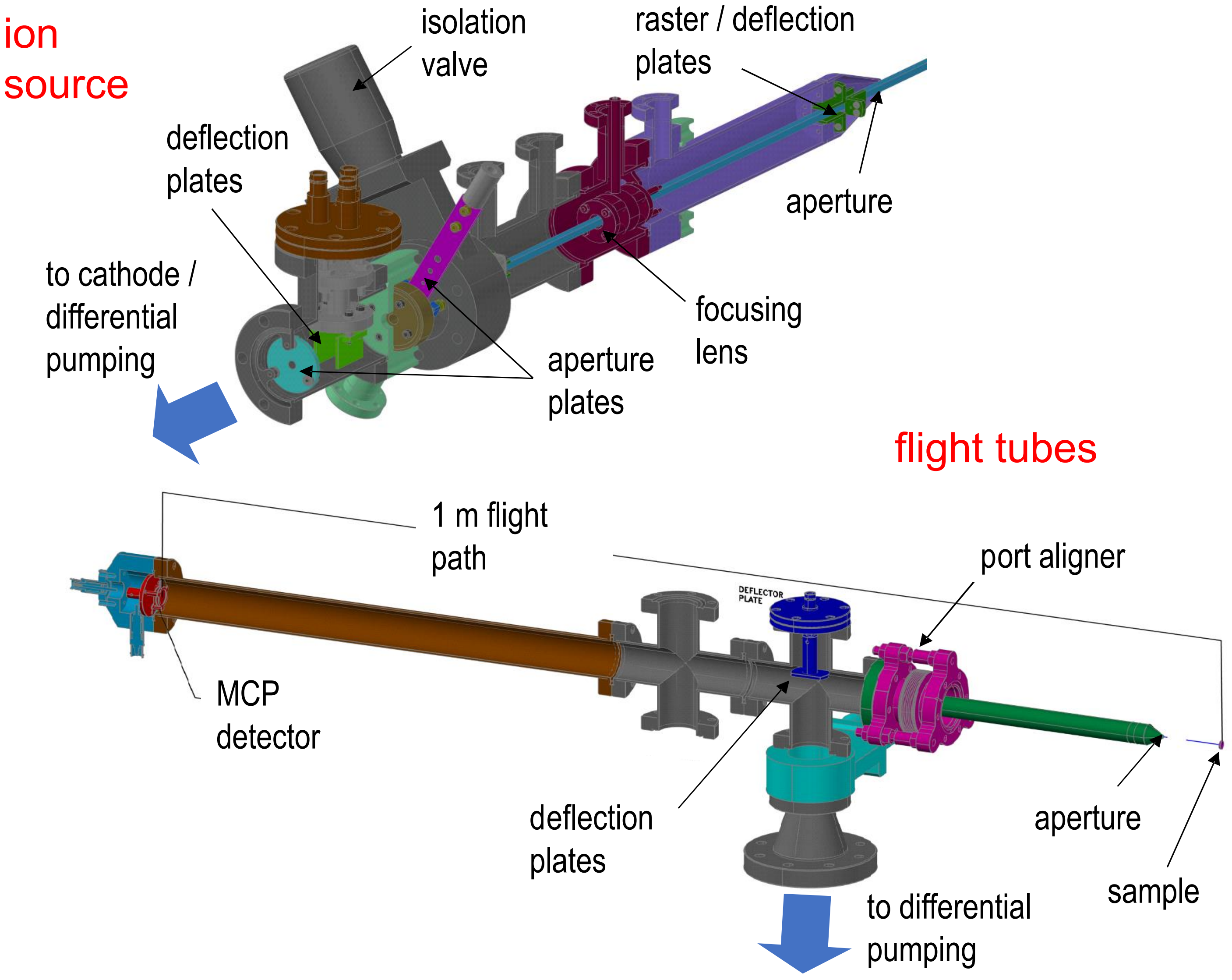
Instrumentation:

- Annealing up to 1800 °C for 1 hr
- Large-angle micro-channel plate for imaging backscattered ion distributions

Unique feature: differentially-pumped detection system

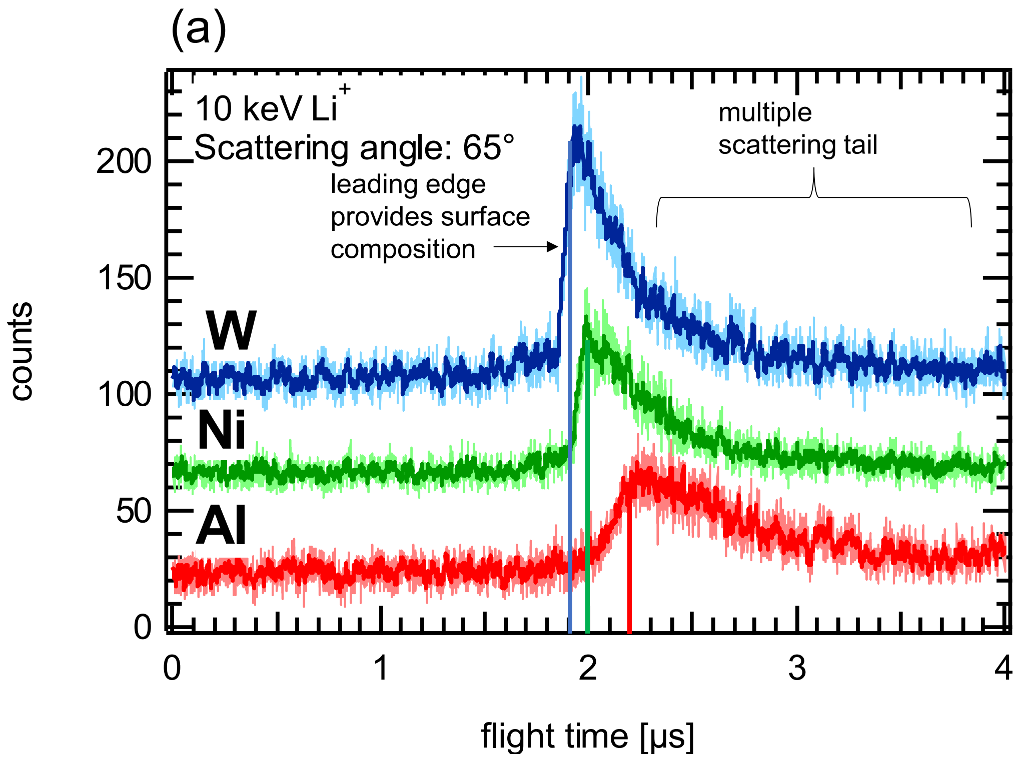
- Enables surface measurements in an elevated pressure environment (~1 mTorr)

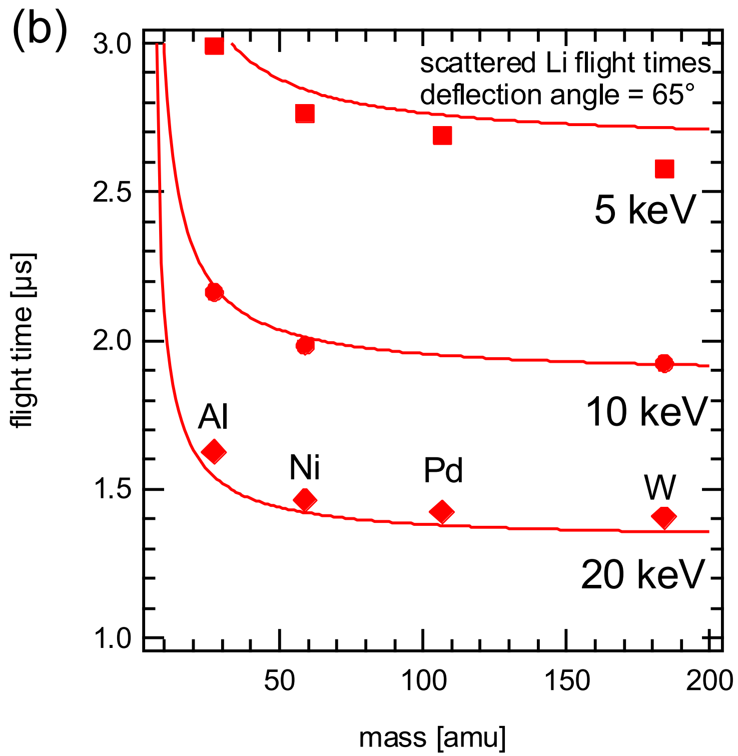
Ion source and flight tubes are differentially pumped to enable high pressure operation

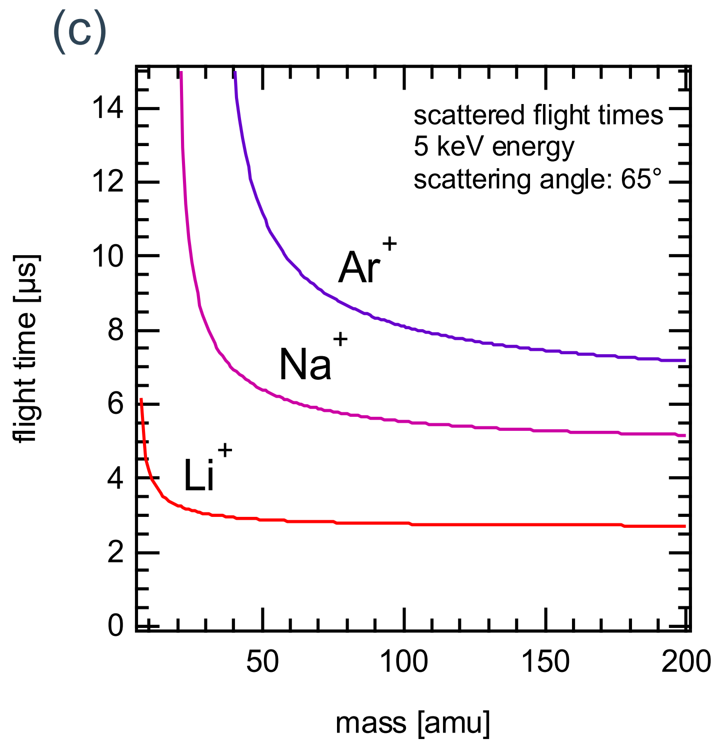


- Both the ion source and flight tubes contain high voltage electrodes that must be differentially pumped to prevent arcing.
- Small apertures provide isolation from high pressure environment in process chamber.
- Focusing lenses can be adapted to many commercial ion source.
- Flight tube includes deflection plates for measurement of ion / neutral fraction

Preliminary results show expected flight time dependence on energy, target mass

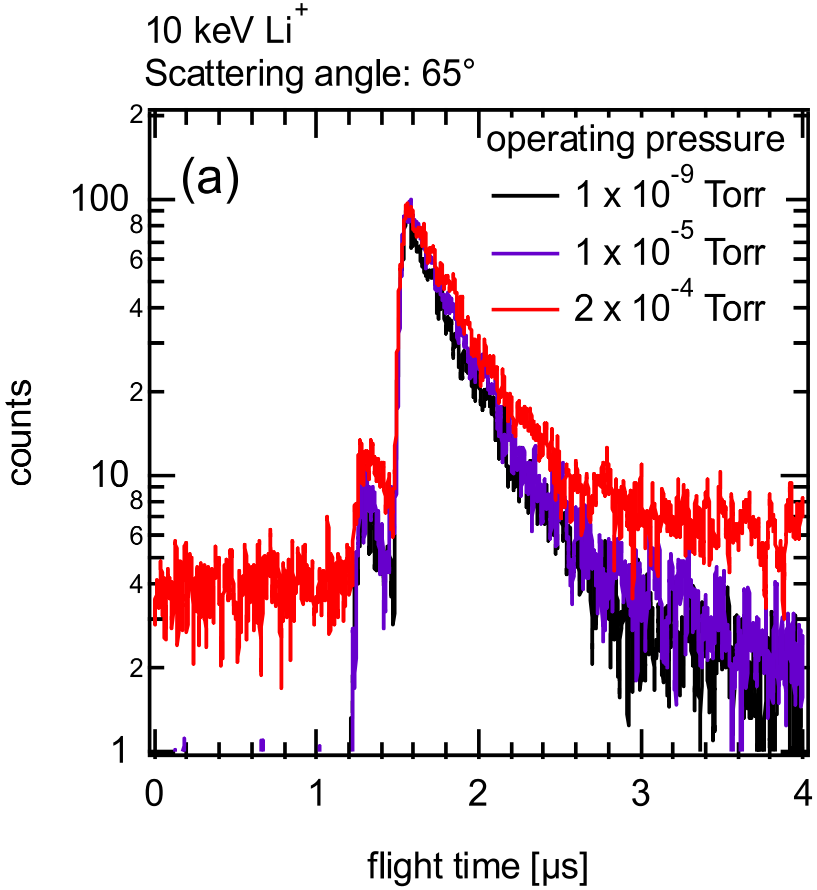


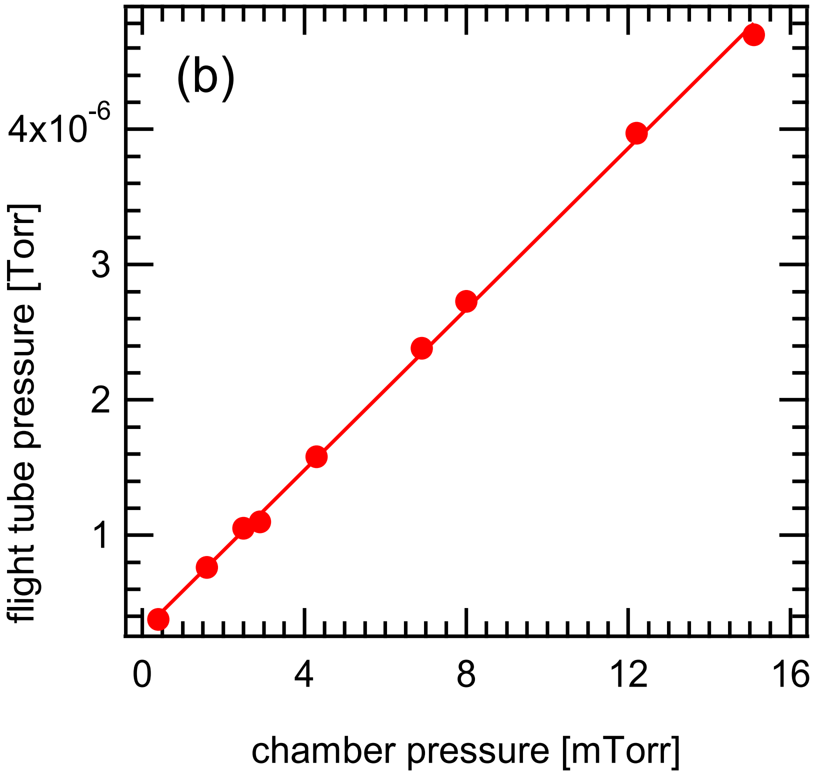




- Flight times measured using a multi-channel scaler (requires ~10 nm resolution at 20 keV beam energy)
- Peak positions matched well with theoretical predictions.
- Sensitivity to different masses varies depending on ion species used.

Demonstration measurements at elevated pressures





- Initial experiments at elevated pressures show minimal degradation of signal up to 0.2 mTorr.
- Attenuation of measured signal at these pressures is also minimal.
- Ion feedback likely the main limitation as pressure increases.
- Use of smaller apertures, higher intensity beams could allow the technique to be applied to even higher pressures

Concluding remarks

- Multi-angle mapping technique developed for characterization of adsorbed H isotopes
- An MD model simulates surface collisions accurately, allows for quantitative comparisons with experiments on W(111)+H system
- Time of flight spectroscopy addresses many limitations existing instrumentation (based on the use of an electrostatic analyzer)
- Preliminary measurements using differentially-pumped TOF system appear promising, provide the ability to measure surface composition at pressures up to 0.2 mTorr.

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- J. P. Allain (Penn State University)

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Thank you for your attention!