This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

SAND2023-03912C

Sandia National Laboratories

Chemisorbed hydrogen on tungsten materials: atomic scale analysis using low energy ion beams

Robert D. Kolasinski, Chun-Shang Wong, Antonio Cruz, and Josh A. Whaley
Sandia National Laboratories, Plasma & Reacting Flow Science Dept., Livermore, CA 94550 USA

OVERVIEW

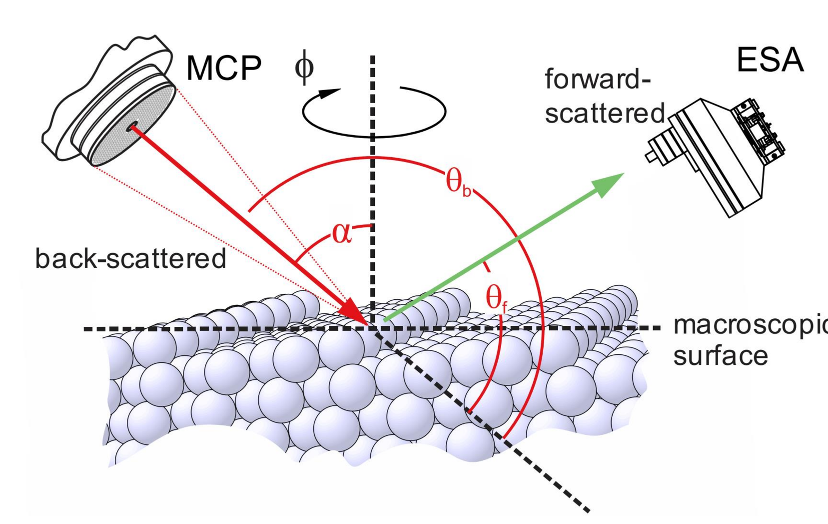
In this study, we use two forms of low energy ion beam analysis, low-energy ion scattering (LEIS) and direct recoil spectroscopy (DRS), to probe the atomic-scale behaviour of hydrogen on surfaces. These measurements involve dosing the surface with atomic or molecular hydrogen while probing the surface with low energy ions (typically 500 eV - 3 keV He^+, Li^+, or Ne^+). The recoiled H intensity varies surface orientation, enabling us to determine the chemisorbed hydrogen surface binding configuration. Recently, we have pursued the use of multi-angle scattering maps, which involve acquiring scattered and recoiled particle fluxes over a large angular sector. When coupled with binary collision or molecular dynamics simulations, the surface configuration can be determined with high precision < 0.02 nm [1]. We have applied these techniques to a variety of materials [2, 3].

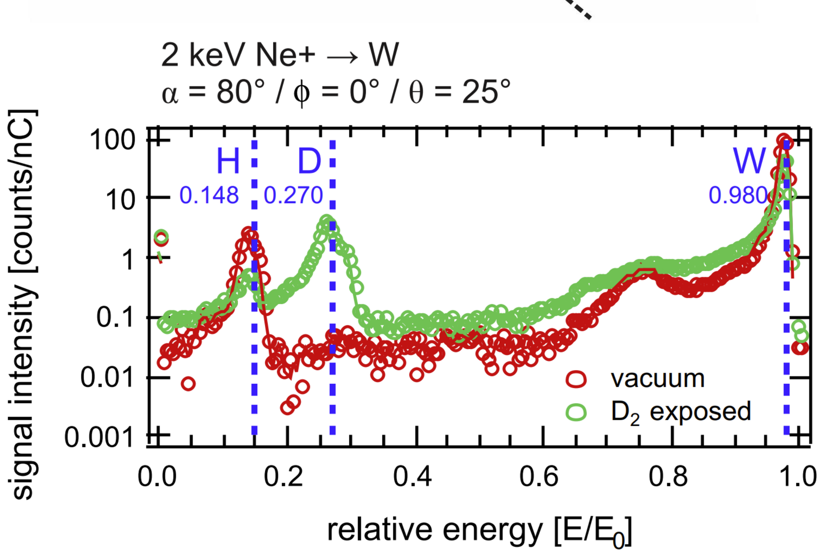
Like most surface analysis techniques, both LEIS and DRS are generally used at low pressures typical of ultra-high purity vacuum systems, usually < 10^{-4} Pa. In this work, we developed modifications to these techniques to allow them to be extended to higher pressures and more complex exposure environments. For these measurements, we use a time-of-flight (TOF) spectrometer that includes a differentially-pumped ion source and flight tubes. This equipment was attached to an ultra-high vacuum chamber where the scattered and recoiled particles are sampled at angles of 65° and 160° relative to the incident ion beam, enabling detection of both forward and back-scattered particles simultaneously. Initial characterization of 10 keV Li^+ scattered from Au, W, Pd, Ni, and Al surfaces at pressures of 5×10^{-2} Pa and above revealed minimal attenuation of the scattered signal and good mass resolution. Preliminary results from experiments to study adsorption and implantation of hydrogen onto / into different tungsten materials will be presented.

[1] C. -S. Wong, R. D. Kolasinski, and J. A. Whaley, *Surf. Sci.* **729** (2023) 122229.
[2] C. -S. Wong, J. A. Whaley, Z. J. Bergstrom, Brian D. Wirth, and Robert D. Kolasinski, *Phys. Rev. B* **100** (2019) 245405.
[3] R. D. Kolasinski, J. A. Whaley, and D. K. Ward, *Surf. Sci.* **677** (2018) 176.

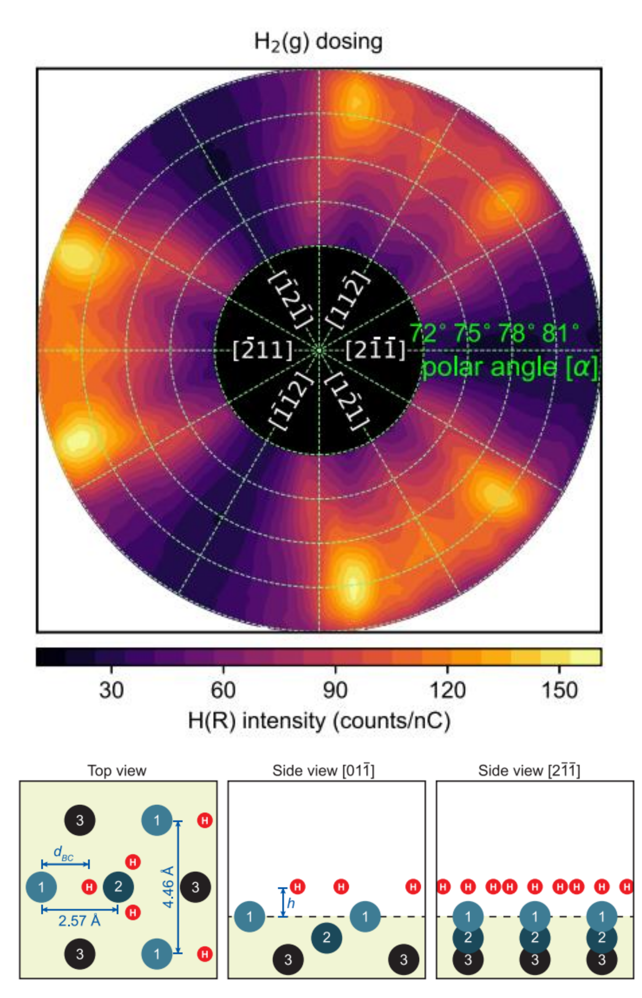
INTRODUCTION / PREVIOUS WORK

Previously, we have used LEIS / DRS to detect the atomic configuration of hydrogen on surfaces. This was accomplished by measuring scattered / recoiled ion fluxes over a wide range of orientations. This enables us to put together multi-angle scattering maps, which can be compared directly with binary collision and MD models.





Ion scattering / recoil spectra for W surface before and after dosing with D_2 gas.



Example of multi-angle map showing recoiled H distributions as a function of different azimuthal and polar angles. These data are compared with simulations to determine the H binding site.

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

INSTRUMENTATION

We have developed a new instrument for the study of hydrogen-surface interactions. Basic characteristics of this system are listed below.

Ion Sources:
- 20 keV alkali ion source (Li^+, Na^+, and Cs^+)
- 5 keV Ar^+ sputter source

Diagnostics:
- Time-of-flight tubes mounted at scattering angles of 165° and 65° (for forward and back-scattering measurements).
- Electronics allow for ~800 ps time resolution
- High resolution QMA (0-50 amu) for TDS / SIMS, w/ direct line-of-sight to sample
- Large-angle micro-channel plate for imaging backscattered ion distributions

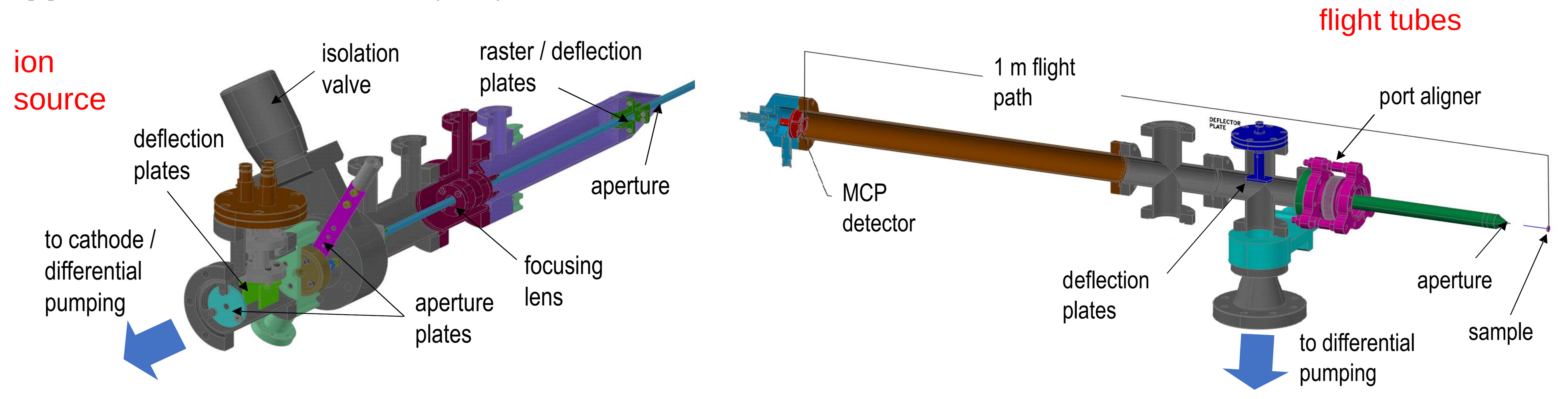
Manipulator:
- Annealing up to 1800 °C for 1 hr, LN_2 cooling

ADAPTATION FOR MEASUREMENTS AT ELEVATED PRESSURES

Increasingly, there has been an emphasis on developing surface characterization techniques that can operate under non-ideal conditions (e.g. technical surfaces at elevated pressures / temperatures). A recent example has been the development of ambient-pressure XPS [4], where differential pumping is used to increase transmission efficiency and collect photoelectrons close to the surface.

In this case, we take a similar approach to adapt LEIS and DRS to operate at higher pressures, by relying on differentially pumped time-of-flight tubes to analyze the scattered and recoiled ion energies.

[4] H. Bluhm et al. *MRS Bulletin* **32** (2007) 1022.



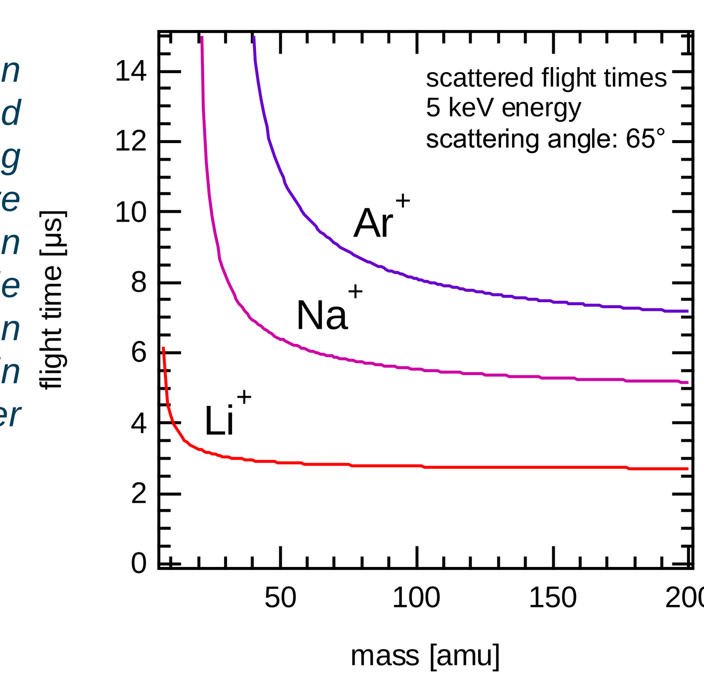
PRELIMINARY RESULTS

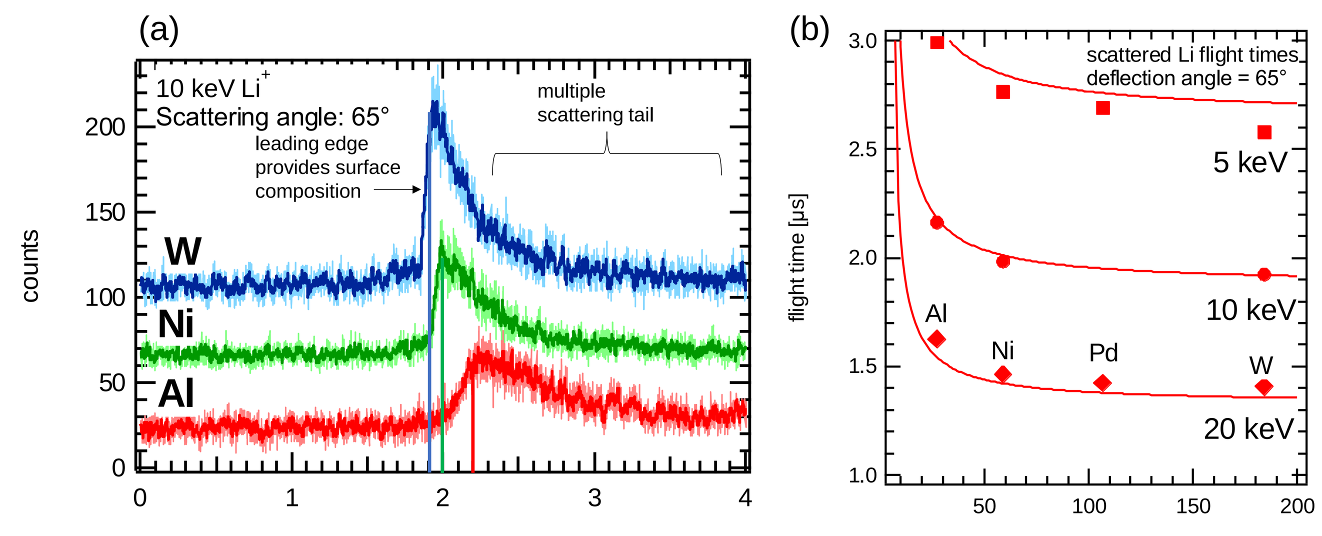
The pressure limit for the MCP detectors used for ion detection and high voltage ion optics is roughly 5×10^{-6} Torr. In addition, attenuation of the incident ion beam (due to scattering as it passes through the higher-pressure gas environment) is another concern. The amount of signal attenuation is expected to obey the following relationship:

$$I = I_0 e^{-dp\sigma/kT}$$

Here, I and I_0 are the initial and attenuated particle intensities. In addition, d is the distance traversed by the energetic particles in a gas of pressure p, and σ is the collision cross section between the energetic particles and the gas species. Because the attenuation depends exponentially on distance d, we kept the total distance between the ion gun exit and the flight tube entrance as small as practical (50 mm).

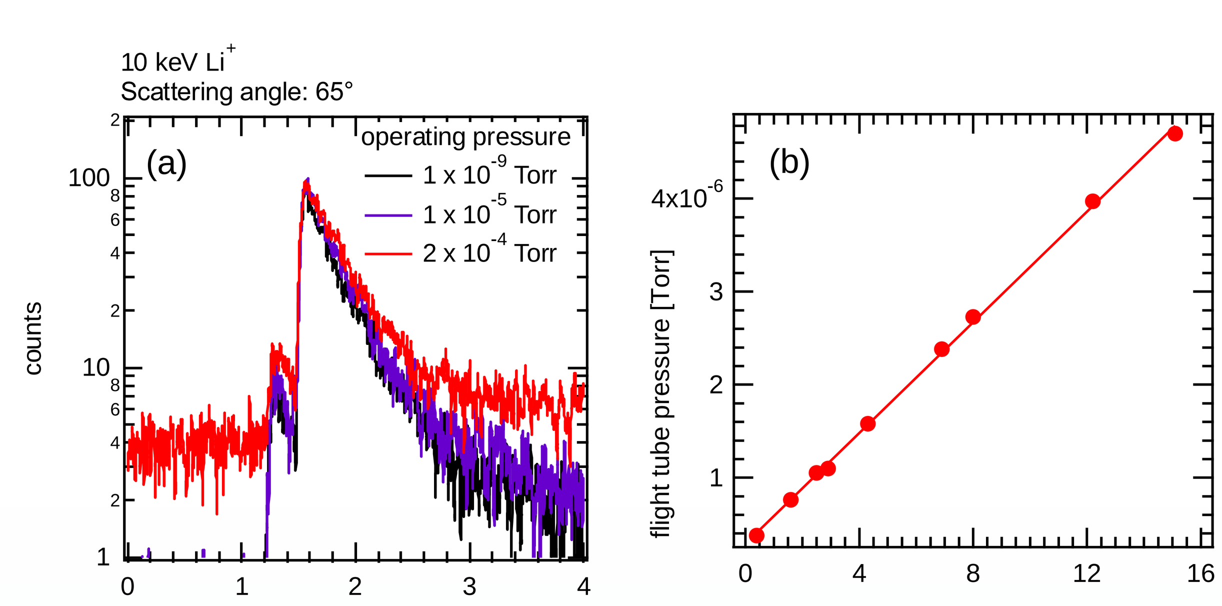
Selection of the ion species can be tailored for the surface being analyzed. Li+ ions are well suited for detection of lighter metals, while heavier ions provide an increased variation in flight times at larger masses.





Experimental data (a) showing representative TOF data for 10 keV Li^+ scattered from different materials. The sharp leading edge of each peak, arising from single elastic collisions between the incident ions and the surface, is used as a reference to determine the surface composition. In panel (b), we show how the measured peak positions (symbols) match with theoretical predictions (solid curves).

Experimental data showing how ISS data is affected by varying neutral gas pressures. The partial pressure of 2×10^{-4} Torr is comparable to neutral pressure in the Tritium Plasma Experiment. In panel (a), TOF spectra are plotted for 10 keV Li^+ ions incident on a W surface for varying Ar gas pressures, showing minimal attenuation of the signal. Likewise, panel (b) shows differential pumping performance tests using a smaller 1 mm entrance aperture. Even when the ambient pressure in the analysis chamber is 16 mTorr, the pressure within the flight tubes is still within the acceptable range for our detection equipment (< 5×10^{-6} Torr).



SUMMARY / OUTLOOK

The work described here provides reasonable confidence that our approach can be applied to high-pressure environments. Carrying these results over to a case where the surface is also exposed to high particle flux will be a focal point of forthcoming work. Additional challenges include advanced ion source and detector development that will greatly improve the sensitivity and resolution of our TOF system, as well as modifications that will enable operation in an environment where high magnetic and electric fields are present. Finally, the instrumentation will be tested using different plasma sources to verify its ability to analyze surface composition under such conditions.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

Sandia National Laboratories

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.