

## Advancing the in-situ characterization of light elements via X-ray absorption spectroscopy using superconducting detectors

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Catalysts are substances that increase the rate of, or lower the energy required for, a chemical reaction, without being consumed in the process. Catalysts have a unique potential to incentivize green energy by reducing the cost of clean fuel production and enabling the economic utilization of greenhouse gases. New generations of catalysts are being developed to enable these applications by efficiently transforming carbon dioxide and methane into valuable chemical feedstocks such as carbon monoxide and methanol. In order to accelerate catalysis development, it is critical to have an accurate picture of the interaction between the reactants and the catalytic surface [1]. A comprehensive understanding of electronic structure can explain why certain geometries and elements favor catalysis, while other configurations suffer from gradual poisoning or degradation.

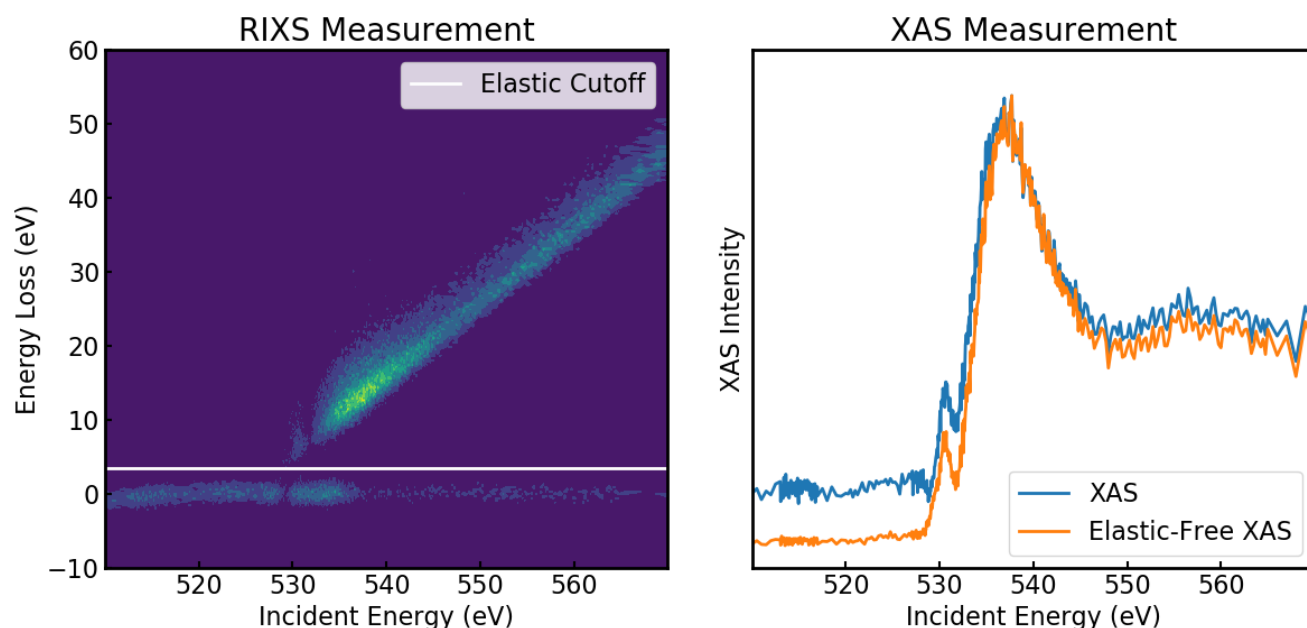
X-ray spectroscopy is a set of element-specific techniques where tunable X-rays are used to excite an electron from the inner orbitals of an atom, and emitted photons or electrons are measured to glean information about the electronic structure of the atom. X-rays provide a way to focus on the electronic structure of one element at a time, making these techniques invaluable for probing the complex multi-element environments. X-ray absorption spectroscopy (XAS) is sensitive to the oxidation state, symmetry, and spin of the probed element [2]. For example, XAS can distinguish between high-spin and low-spin configurations, or between octahedral and tetragonal geometries. Measurements of the carbon K-edge have been used to investigate carbon speciation [3], and bond orientation [4].

These strengths make X-ray spectroscopy, in theory, one of the best techniques available to probe catalysts in-situ. Unfortunately, the K-edges of the light elements lie in the soft X-ray regime, where high-vacuum is required to avoid attenuating photons and electrons. Many catalytic reactions take place at high temperatures and pressures that are not compatible with typical spectroscopic instruments. Furthermore, reactions typically take place at metal sites on the catalysis surface, which may cover only a fraction of a monolayer. Most X-ray spectroscopic techniques cannot be applied to systems where the pressure is over 1 Torr, the temperature is over 600 K, and the sample is less than 10% of a monolayer, making fundamental measurements of real systems rare. New X-ray spectroscopic instruments are required that are compatible with these requirements.

Transition-edge sensors (TES) are sensitive X-ray detectors with high efficiency and good energy resolution [5]. Compared to common X-ray detectors such as silicon-drift detectors or proportional counters, a TES detector has more than 50x better energy resolution. Compared to highly energy-resolving grating spectrometers, they have over 100x the collecting efficiency. These detectors allow us to remove all sources of background from measurements of light elements, including nearby spectroscopic lines, and even elastic scattering. This capability enables measurements of even dilute samples through a silicon-nitride window, which will make it possible to characterize dilute catalytic reactions at high temperatures and pressures.

We are planning to pair advanced TES detectors with a state-of-the-art synchrotron and an in-situ measurement cell to produce a unique catalysis characterization facility at the NIST beamlines at the National Synchrotron Radiation Lightsource (NSLS-II). This facility will be purpose-built to investigate

the orientation and electronic structure of light elements on catalytic surfaces, realizing the promise of x-ray spectroscopy for in-situ catalysis characterization.



**Figure 1.** Left: Resonant inelastic X-ray scattering from an oxygen sample behind a SiN window. The SiN window contributes a substantial but variable elastic scattering. However, the elastic scattering can be clearly separated from the non-resonant oxygen fluorescence from the sample. Right: The energy resolving power of a TES is used to subtract the elastic scattering background from the oxygen sample, leading to a cleaner signal.

#### References

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