

# Combine X-ray Scattering and Spectroscopy

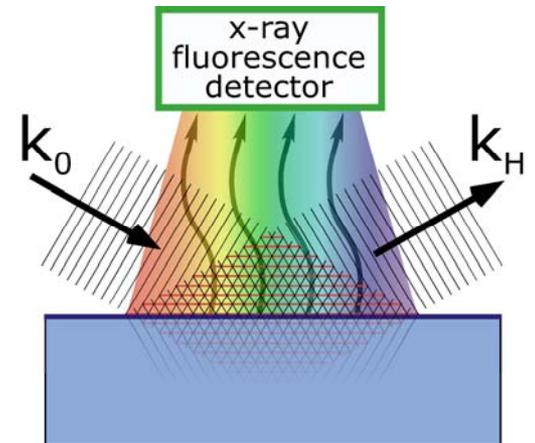
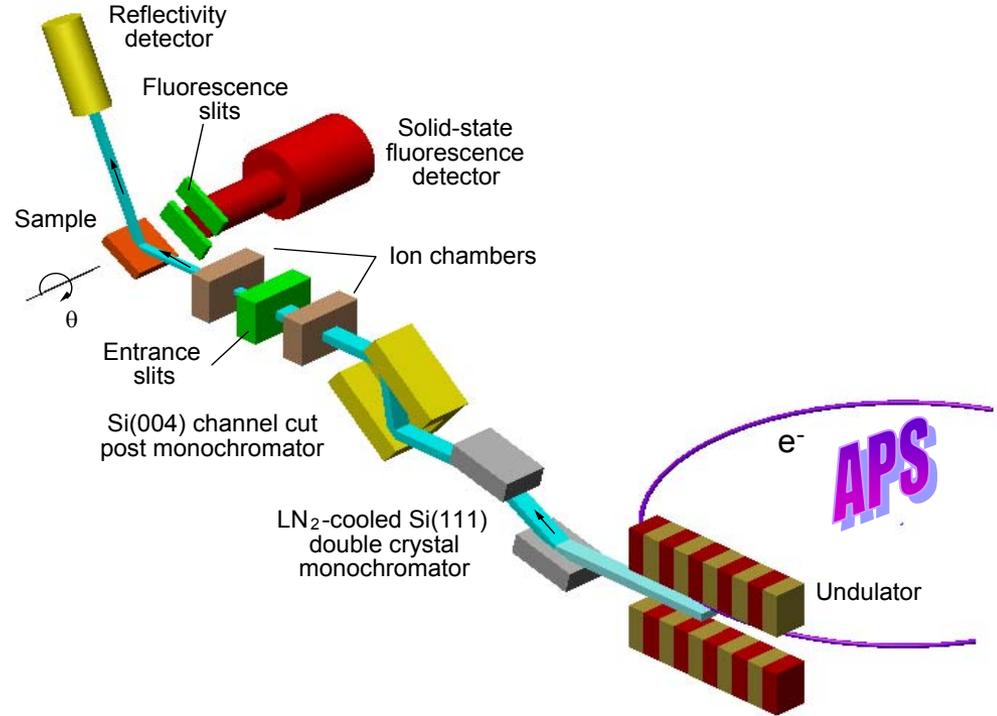
To Achieve:  
Site-Specific Spectroscopy  
or  
Element -specific structure

Examples:

XSW : X-ray Standing Waves

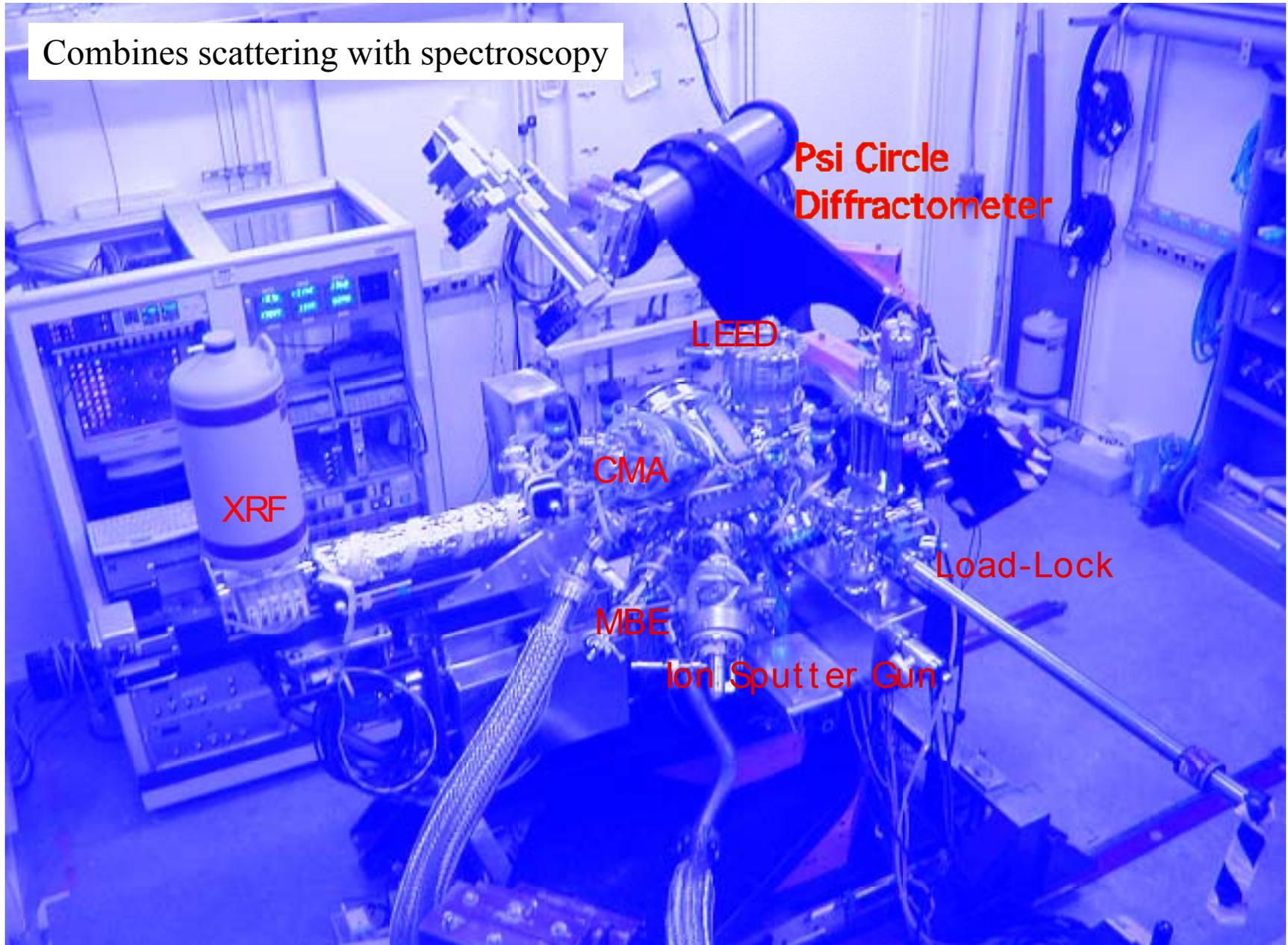
RAXR: Resonant Anomalous X-ray Reflectivity:

Goal: Real-Space Atomic-Imaging



# X-Ray UHV Surface Chamber at DND-CAT APS / ANL

Combines scattering with spectroscopy



# XSW Generated by Dynamical Bragg Diffraction from Single Xtal

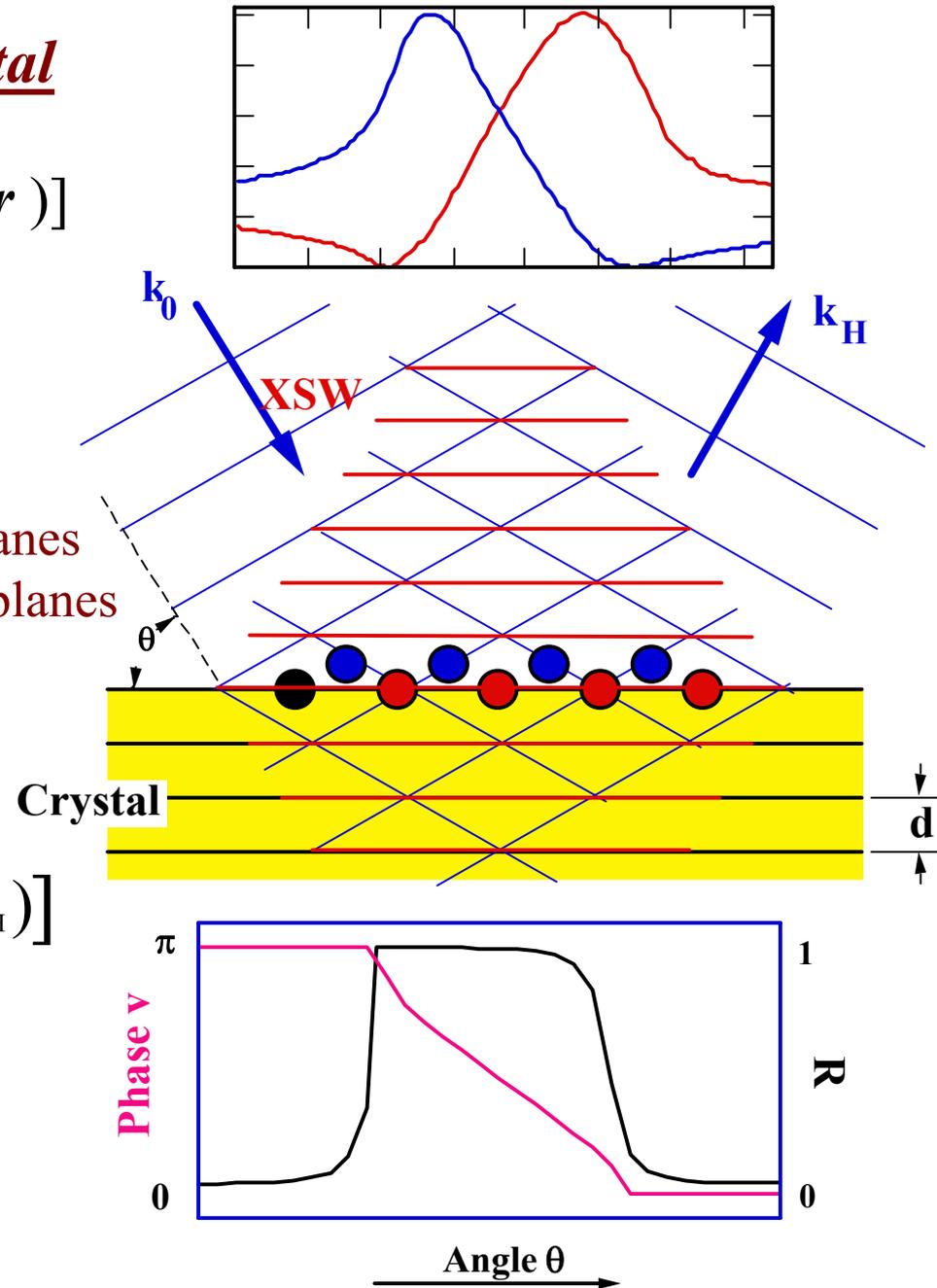
$$I = I_0 [1 + R + 2\sqrt{R} \cos(\nu - 2\pi \mathbf{H} \cdot \mathbf{r})]$$

$$\mathbf{H} \cdot \mathbf{r} = \Delta d / d$$

- 180° XSW phase shift → d/2 inward shift
- Low-angle side → Nodes on diffraction planes
- Hi-angle side → Antinodes on diffraction planes

$$Y(\theta) = [1 + R(\theta) + 2f_H \sqrt{R(\theta)} \cos(\nu(\theta) - 2\pi P_H)]$$

XRF Yield(Y) measures hkl Fourier Amplitude ( $f_H$ ) and phase ( $P_H$ ) of atomic distribution



# X-ray Standing Wave Atomic-Imaging

By summation of XSW measured Fourier components

$$\rho(\mathbf{r}) = 1 + 2 \sum_{\substack{H \neq -H \\ H \neq 0}} f_H \cos[2\pi(P_H - H \cdot \mathbf{r})]$$

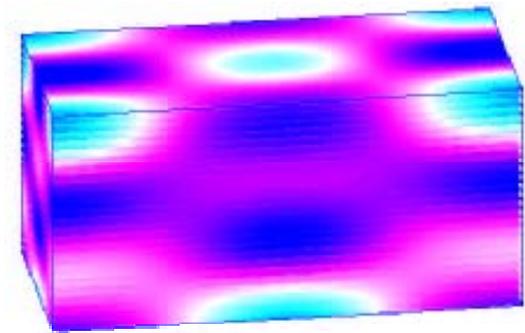
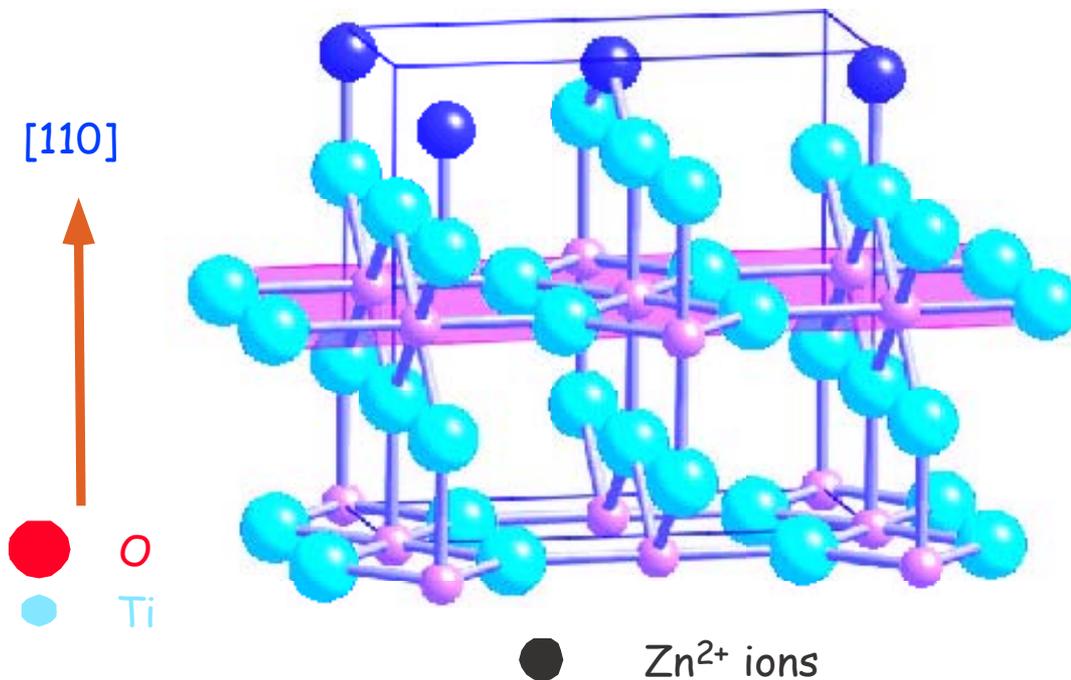
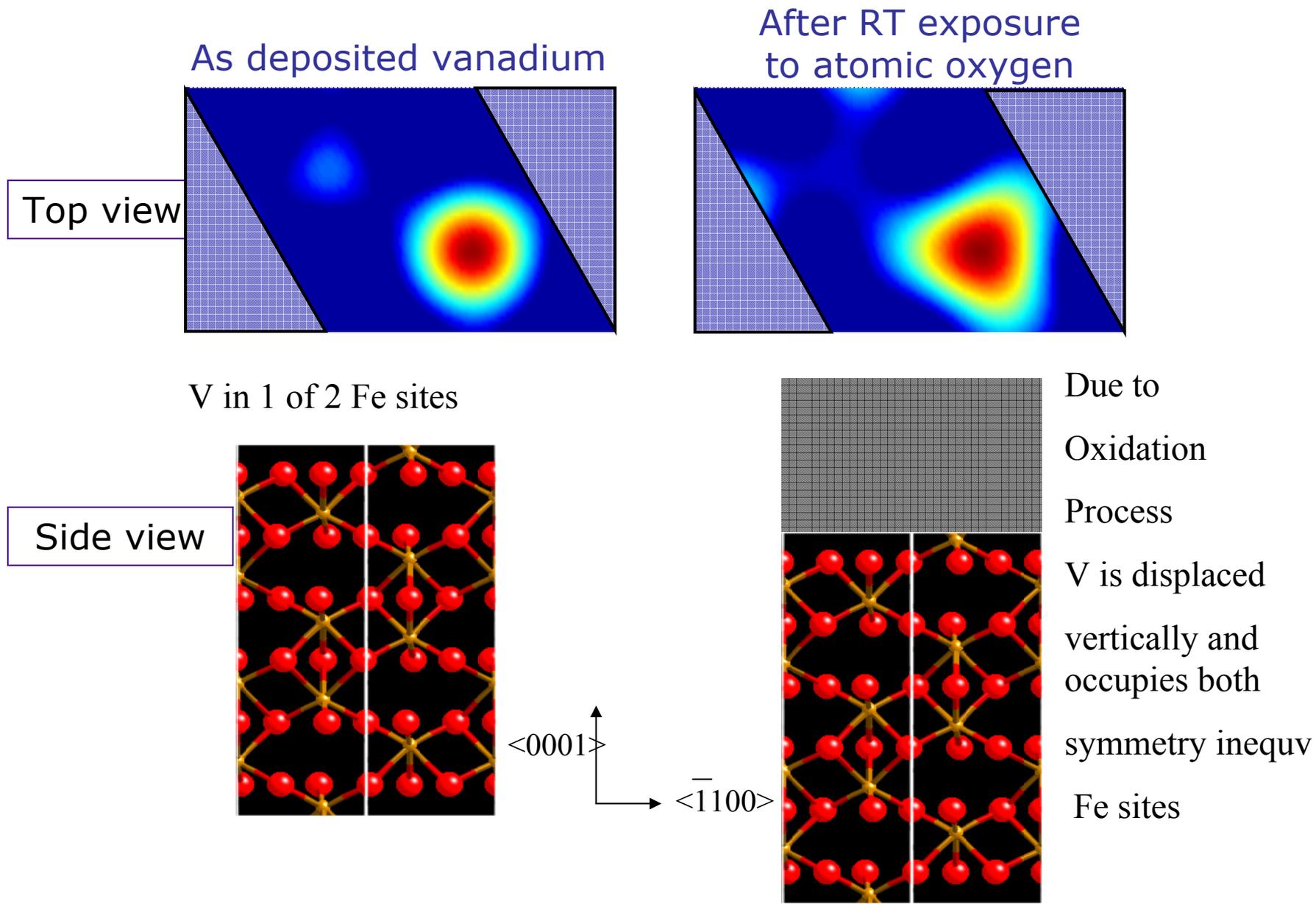


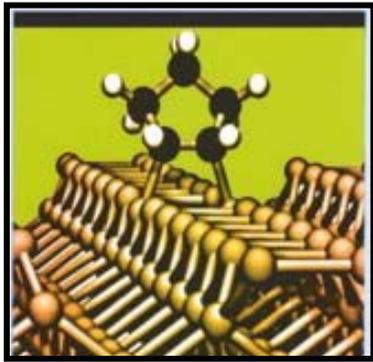
Image of Zn<sup>2+</sup> ion  
distribution on TiO<sub>2</sub>(110)

# XSW Imaging of $\text{VO}_x / \text{Fe}_2\text{O}_3(0001)$

w/ P. Stair NU



## How are atoms arranged within molecular / inorganic structures ?



Nanolythographic patterning of  
Bromostyrene / Si(001)

w/ M. Hersam / NU

SPM ⇨ Top View Only, single molecule sensitivity

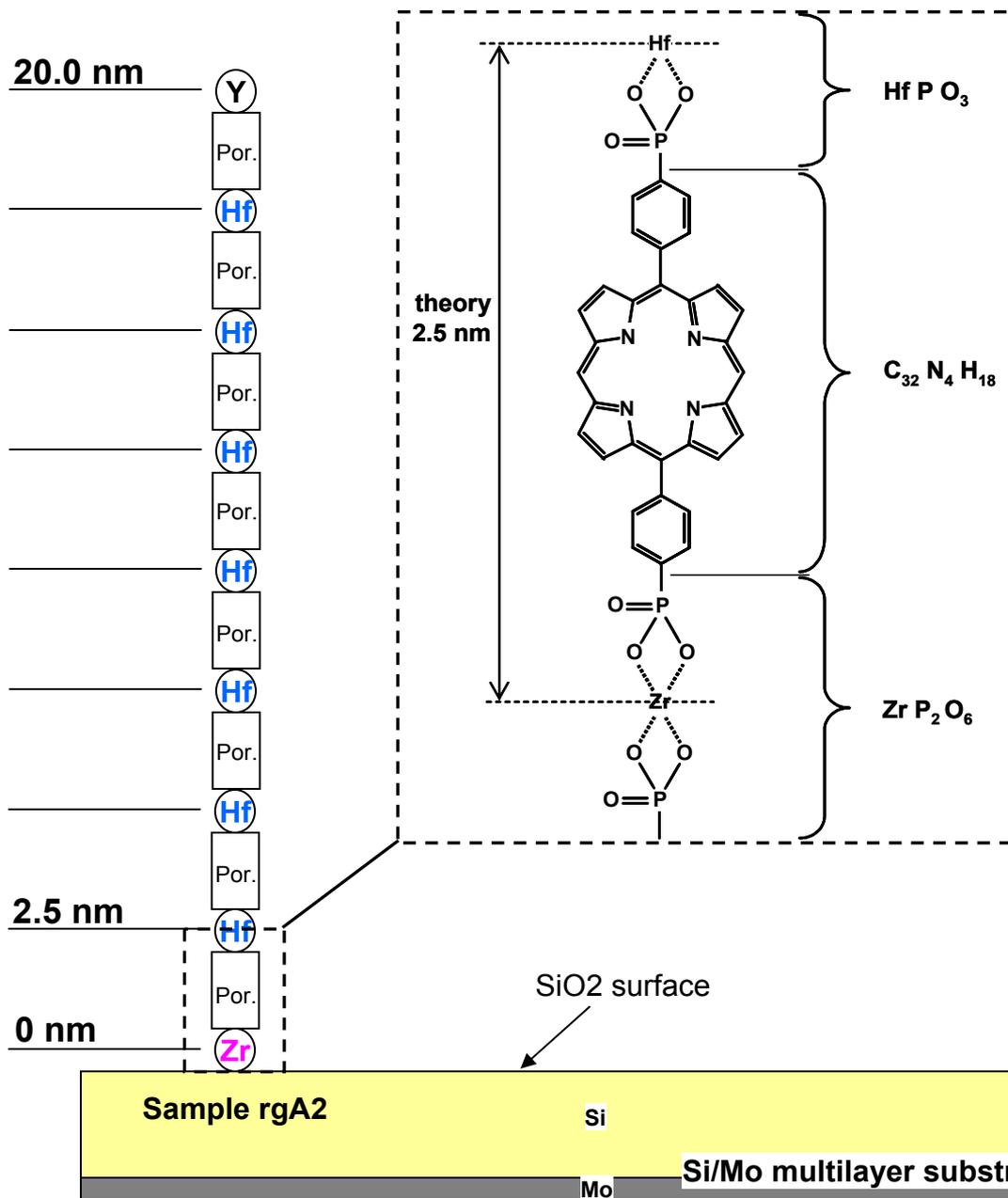
X-Ray ⇨ Top to Bottom View, but needs molecular layer

XSW ⇨ Where are XRF selected atoms located relative to Si lattice? ( $\pm 0.05 \text{ \AA}$ )

XRR & GIXS ⇨ How are the molecules packed?

XPS ⇨ Is there a C-Si covalent bond?

# Metal-Organic Self-Assembled Multilayers



- XRR -> Film Thickness, etc.
- XSW -> Profiles of metal atoms

Porphyrin multilayers on  
Si/Mo multilayer mirror  
w/ J. Hupp & S. Nguyen / NU

Long-Period XSW  
generated by Bragg  
diffraction from 20 nm  
period Si/Mo multilayer

# Biomolecular Adsorption at a Charged Surface

- Complex balance between energy and entropy

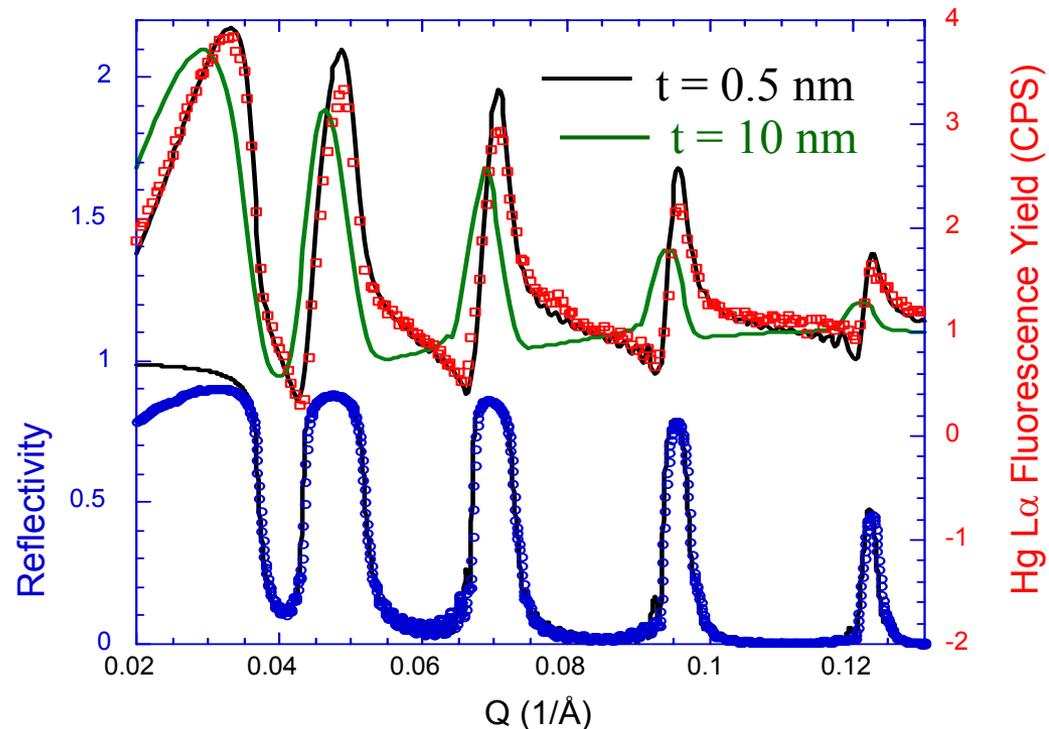
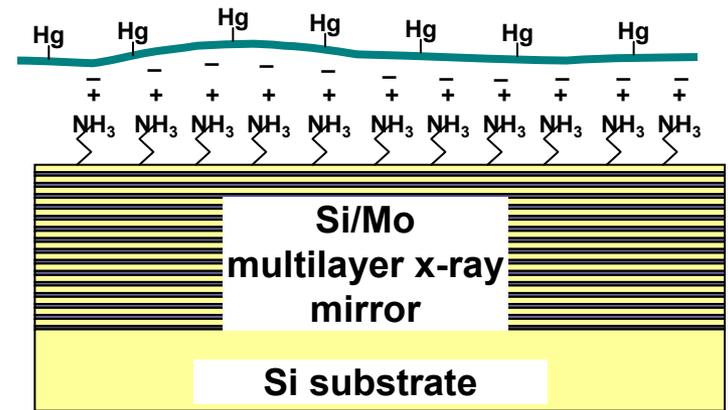
Eg: Synthetic RNA molecule Hg-Poly(U)

Specific example;

Hg-Poly(U) adsorbed to amine-functionalized SiO<sub>2</sub> surface.

Hg modeled as 0.5 nm thick layer.

- Can observe polyanions and counter ions
- Compared to theory with long- and short-range electrostatic effects (Olvera/NU).

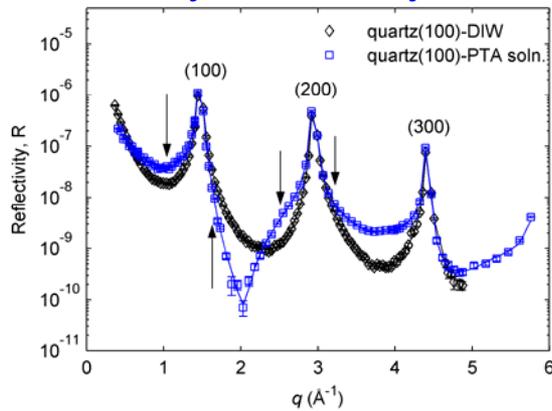


$t$  = thickness of Poly(U) layer

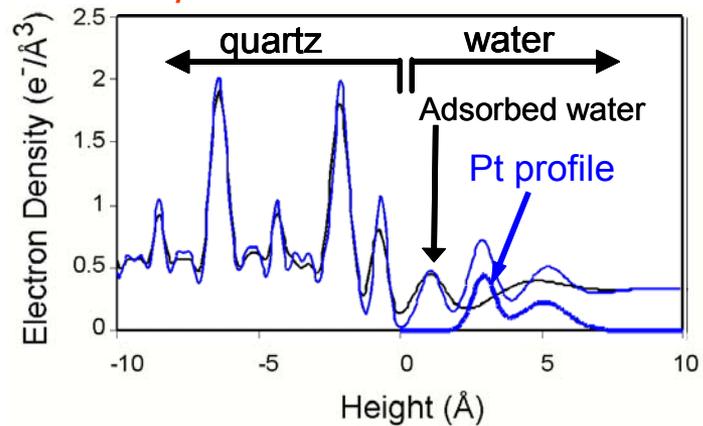
# Resonant Anomalous X-ray Reflectivity: from Paul Fenter / ANL

Example: Probing adsorption of  $\text{Pt}(\text{NH}_3)_4$  at the quartz-water interface\*

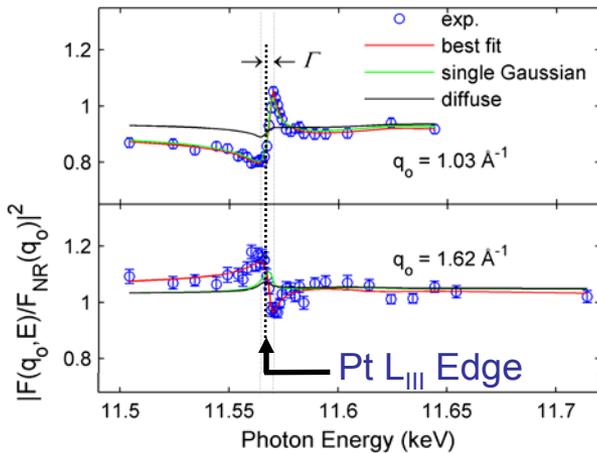
## X-ray Reflectivity Data



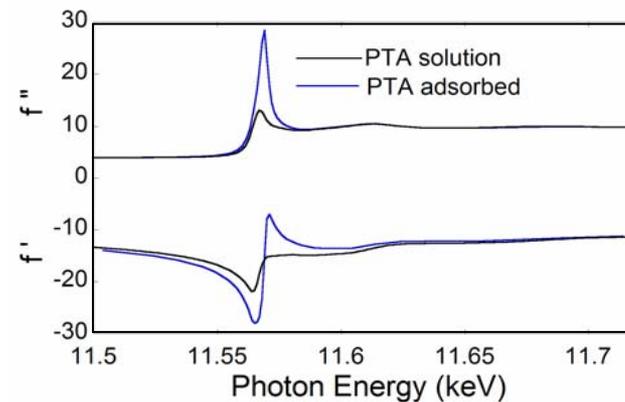
## Element-Specific Interfacial Sub-Structure



## Resonant Anomalous Spectra



## Interface-Specific Spectroscopy



- *Simultaneously* probes the geometric and spectroscopic structures of interfaces
- Provides elemental sub-profiles and interface-specific XANES spectra

\*C. Park, P. Fenter, N. C. Sturchio and J. R. Regalbuto, *PRL*, **94** 076104 (2005)