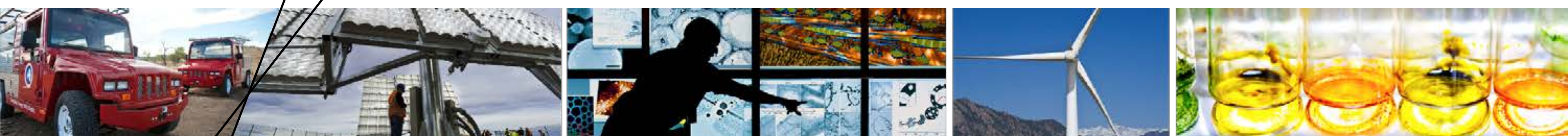
Structural Characterization for H_2 storage



NREL: Steven Christensen, Katherine Hurst, Philip Parilla, Thomas Gennett

SLAC/SSRL: Dimosthenis Sokaras, Dennis Nordlund, (Tsu-Chien Wang)

Core-level spectroscopy

- **Core-level spectroscopy: electronic structure via excitation of core electrons**
  - X-ray absorption Spectroscopy (XAS)
  - X-ray Emission Spectroscopy (XES)
  - Photoemission Spectroscopy (PES) – XPS / UPS
  - Inverse Photoemission Spectroscopy (IPES)
- **Applications:**
  - Composition: XPS, XES (XRF)
  - Electronic structure (DOS)
  - Physical structure
  - ‘Chemical environment’
  - Band level alignment

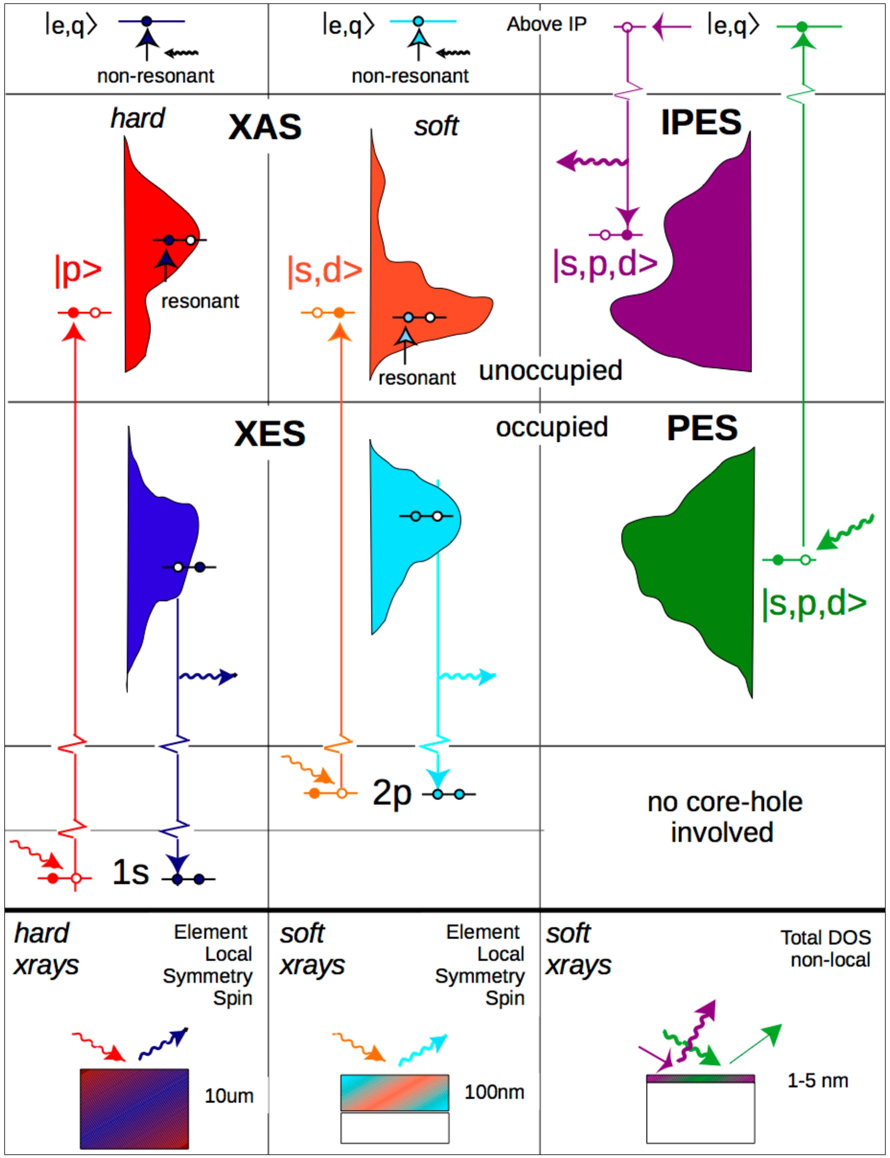
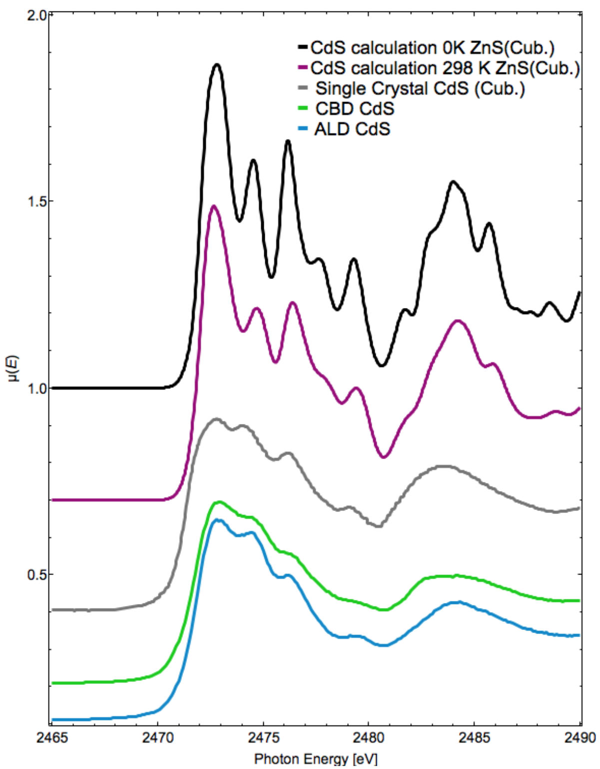


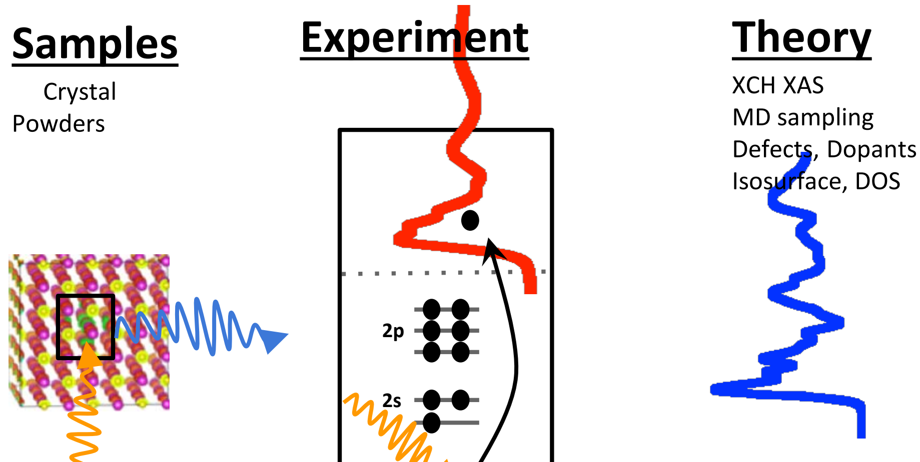
Figure: Dennis Nordlund, SLAC

Feedback driven characterization model

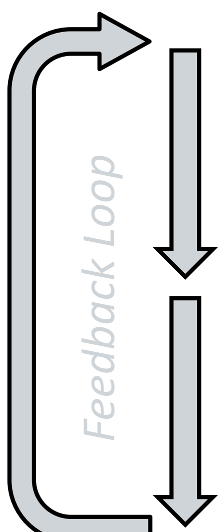
Calculated and Experimental XAS S 1*s* of CdS



Investigating the processing of CdS used in thin film solar cells.
In collaboration w/ David Prendergast LBNL



$$\langle \Psi_f | \hat{\epsilon} \cdot \boldsymbol{r} | \Psi_{1s} \rangle$$

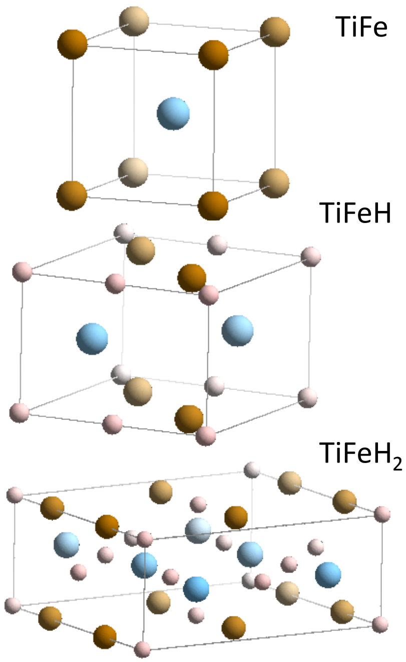


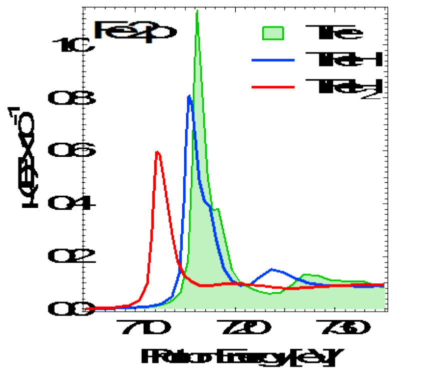
Theoretical Modeling Schematic

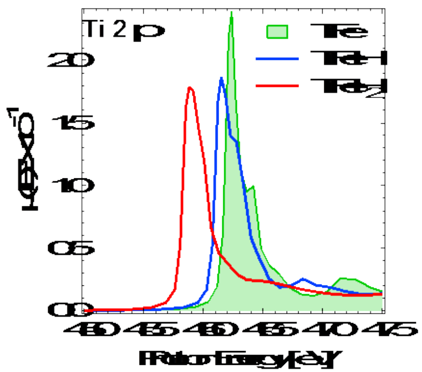
- *Develop structure*
  - Crystal Structure
  - Molecular Dynamics (*ab initio*, empirical)
  - Monte Carlo Simulations
- *Simulate XAS/XES spectra*
  - DFT within XCH approximation for *K*-edges
  - DFT within BSE approximation for *L*-edges (new)
  - DFT within GS approximation for XES (new)
- *Compare to experimental data*

Calculated XAS – assessing the possible

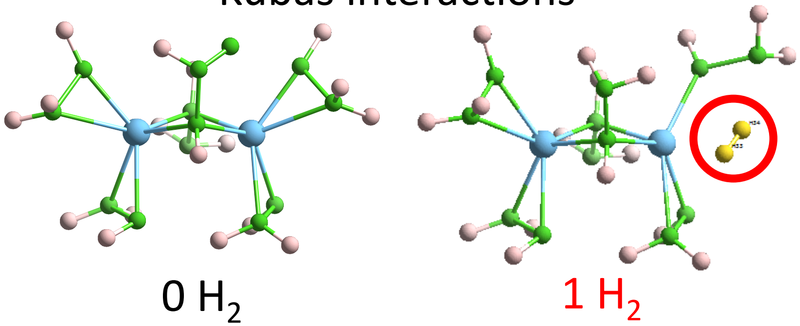
Metal hyrdrides



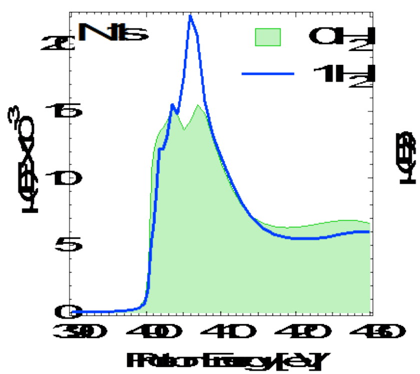


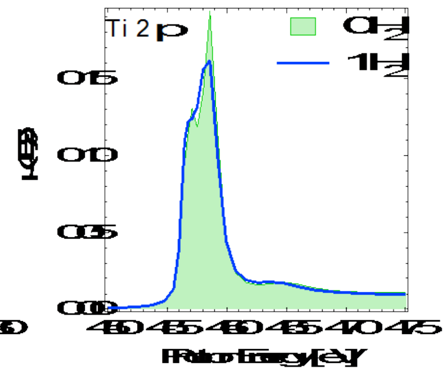


Kubas interactions



Ti (III) hyrdrazine complexes. DFT structures: C.V.J. Skipper et al., *J Phys Chem C* **116** (2012) 19134.





- **Starting with model systems – we can evaluate possible experiments**
- **Calculated XAS – predicts the possible changes to the local electronic and physical structure with and without H_2**

Calculated w/ FEFF

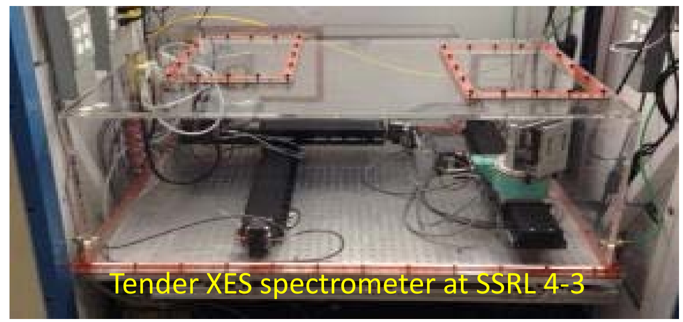
SSRL-NREL Experimental capabilities

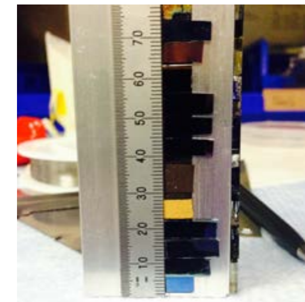
XRS/XAS XAS/XES

Soft < 1.5 keV Tender (1.5-5 keV) Hard > 6 keV

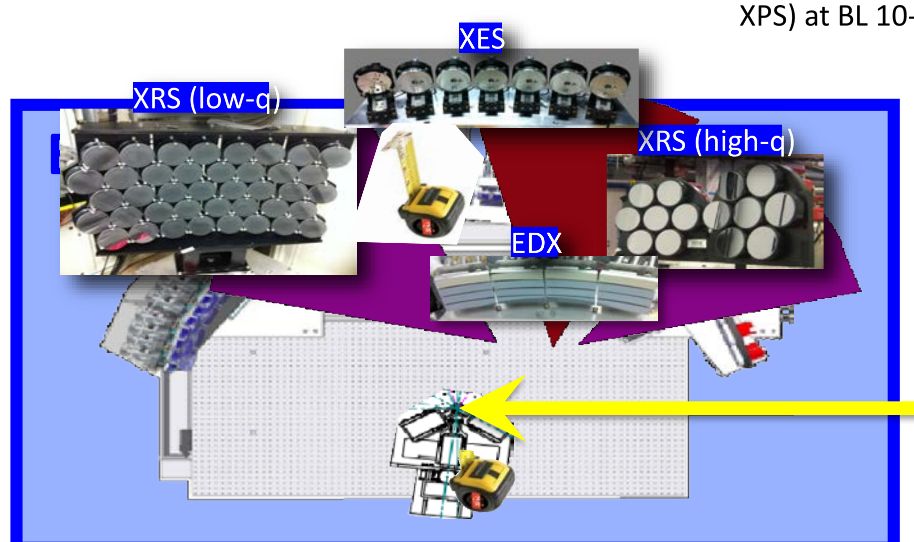
1*s*: B, C, N, O 2*p* TMs: Ti, V, Ni, 1*s*: Al, Si, P, S 3*p* TMs: Mo, Ru, Pd 1*s* TMs: Fe, Co, Ni 2*p*: Pt, Ir

- **Developed several spectrometers/optics for XAS, XRS, XES in multiple energy ranges**
- **Developed *in-situ* methodologies**
- **High throughput capabilities for *ex-situ***

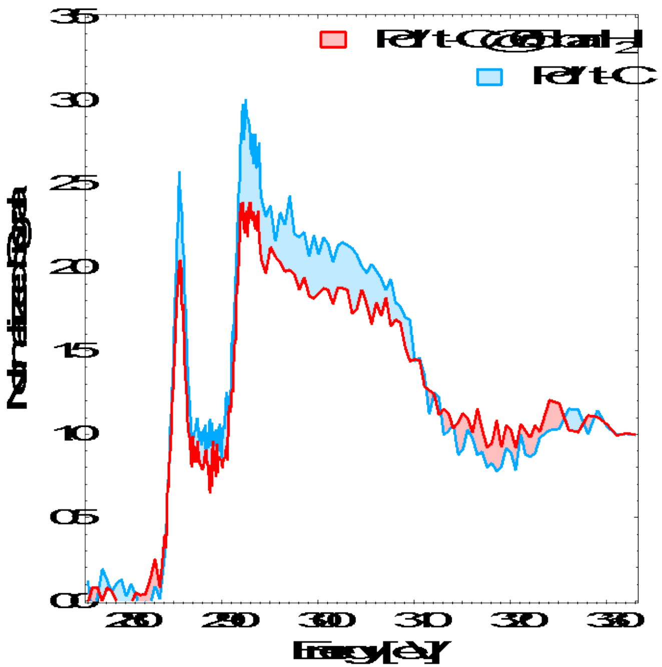


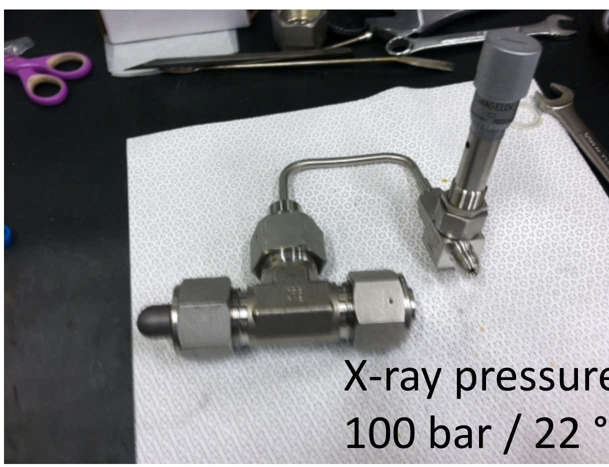


High throughput sample holder enables ~100 samples per run for soft X-ray characterization (XAS, XPS) at BL 10-1 / SSRL.



Operando X-ray spectroscopy for H_2 storage





X-ray pressure cell:
100 bar / 22 °C
30 bar / 300 °C

- **What chemical and structural changes can be expected for elevated pressures and temperatures?**
- **What chemical and structural changes can be observed?**
- **Developed a pressure cell that enables:**
  - o **Hard X-ray XAS / XES**
  - o **Soft X-ray XAS via XRS**
- **Operando measurements can give a fundamental knowledge for H_2 storage mechanisms**

Acknowledgement

- This work was supported by the Fuel Cell Technologies Program within the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy.