LANL Capabilities in Support of HyMARC and HySCORE

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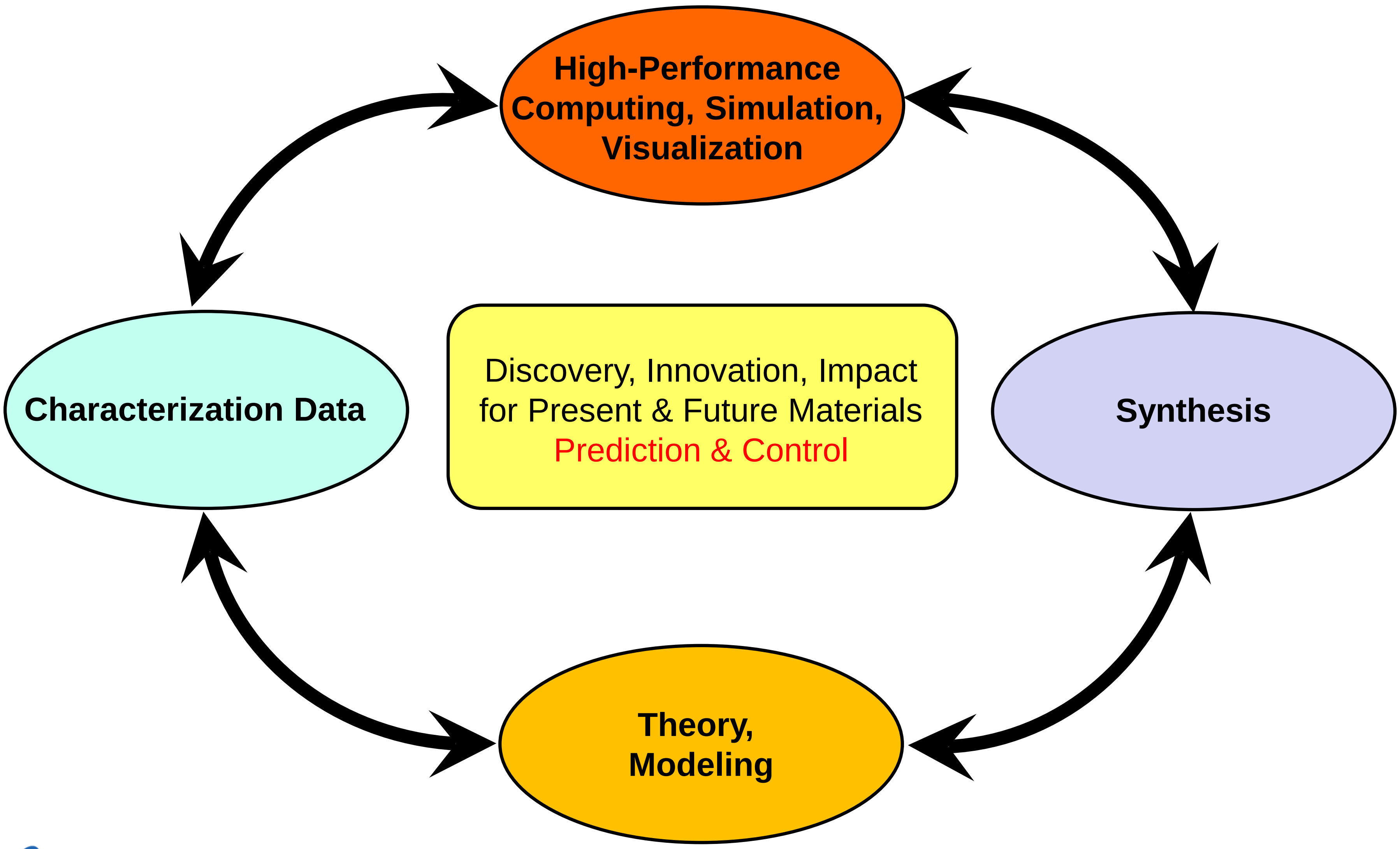
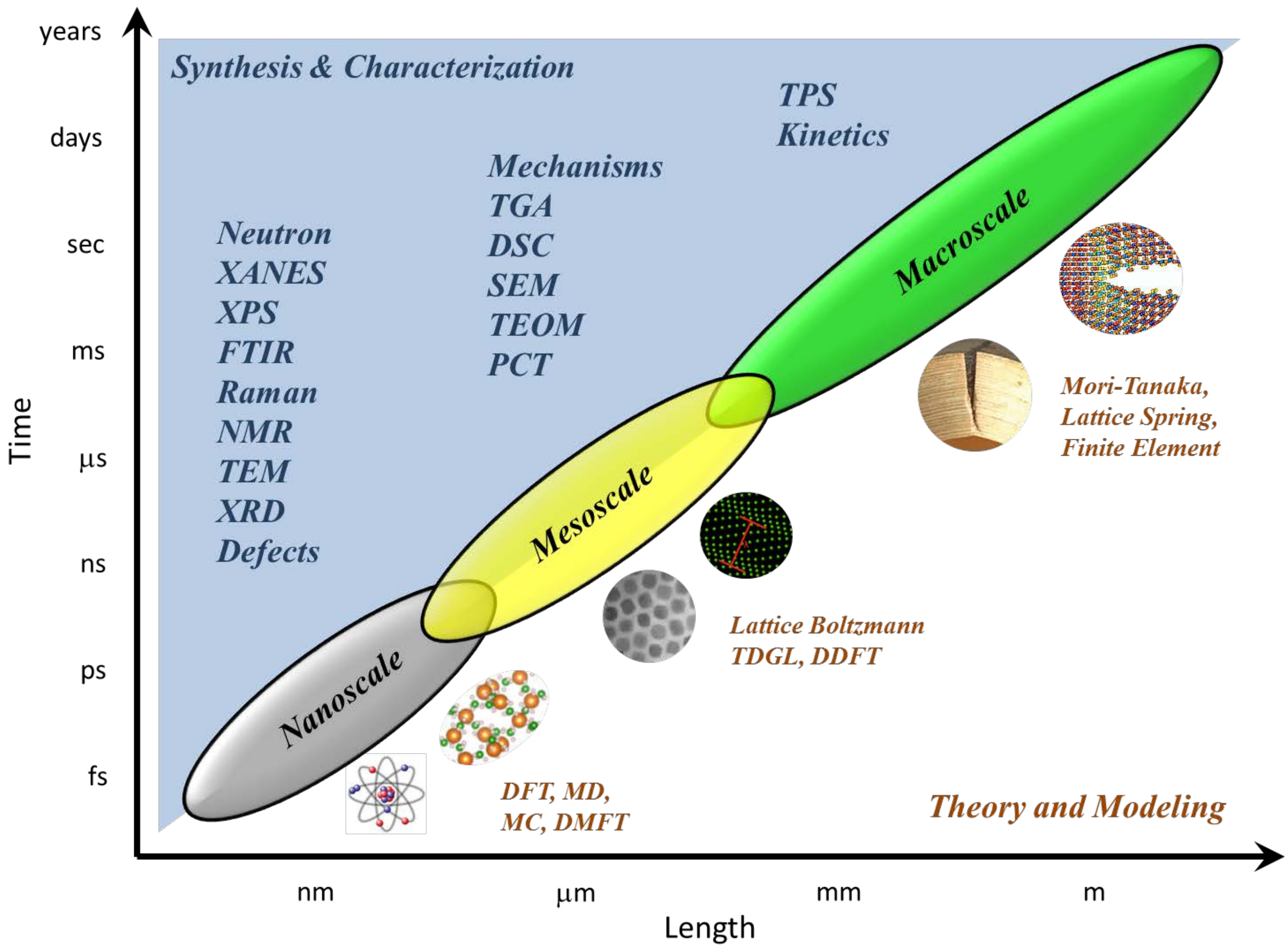
Los Alamos NATIONAL LABORATORY EST.1943

Hydrogen Storage Workshop
National Renewable Laboratory
4-5 Nov, 2015

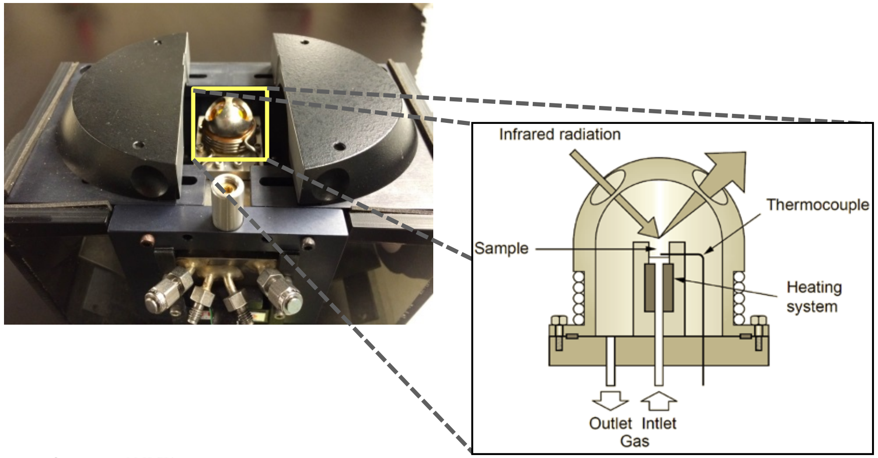
HyMARC-HySCORE



HyMARC-HyScORE

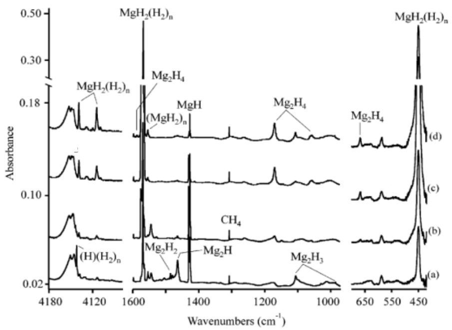


In Situ DRIFTS & *In Situ* Raman Characterization

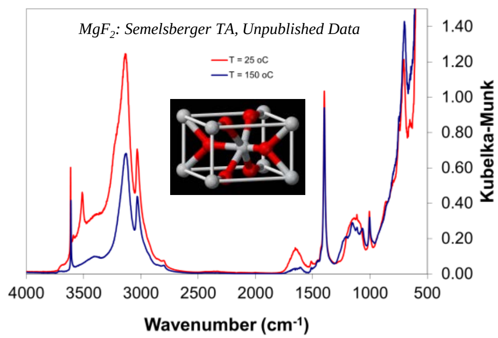


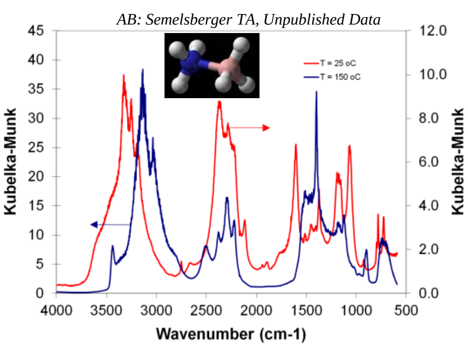
Capabilities

- Maximum Temperature: 900 °C
- Maximum Pressure: 100 bar (@ 700 °C)
- Temperature/Humidity chamber
- Reactive gases (H_2, O_2…)
- Small sample size (< 200µL)
- Glove box accessible
- MCT Detector



J. Phys. Chem. A, Vol. 108, No. 52, 2004

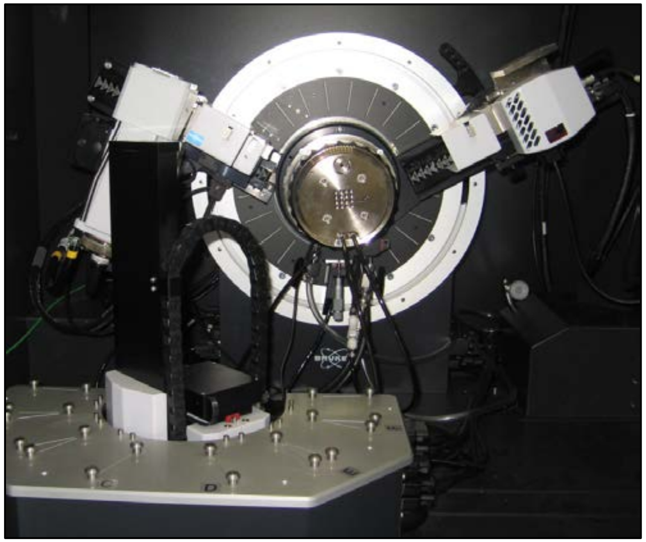




Information & Insights:

- Chemical identification
- Bond strengths
- Chemical structure
- Hydrogenation-dehydrogenation **mechanisms** as a function of P-C-T
- Direct inputs for modeling dynamics

In Situ XRD Characterization



Bruker D8 ADVANCE powder X-ray diffractometer

Capabilities

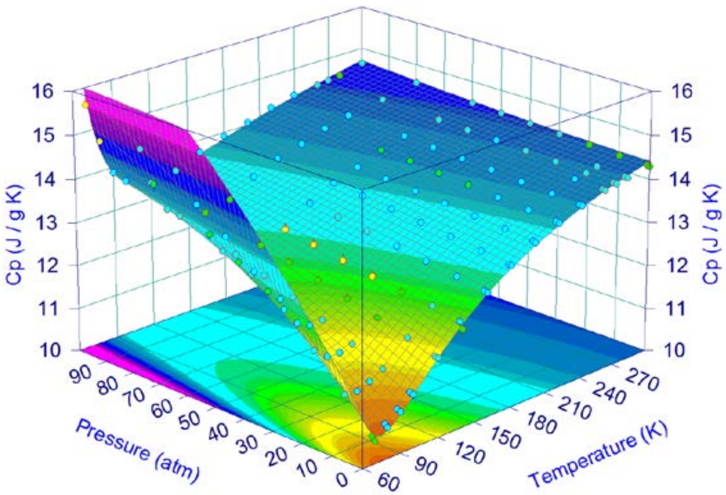
- Phase Identification (ICDD)
- Quantitative analysis with whole pattern fitting and relative intensities
- Heating stage to 1400 °C
- Temperature/Humidity chamber (95% RG to 60 °C)
- High Pressure (100 bar H2) and Temperature (900 °C)

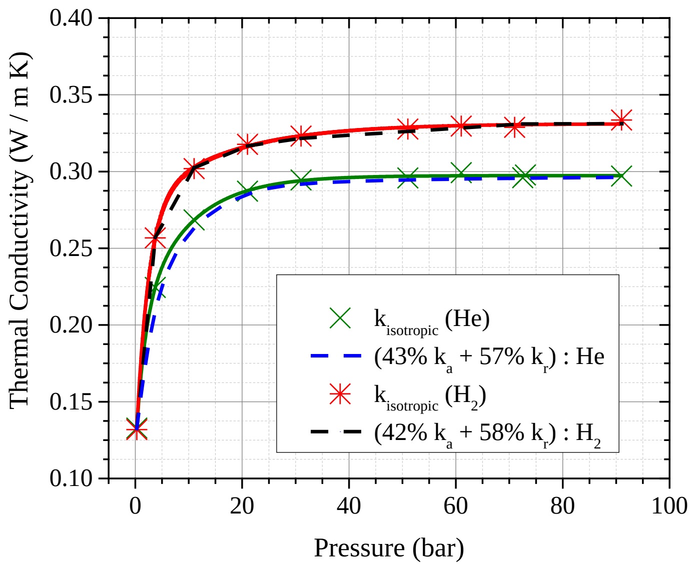
Information & Insights:

- Crystal structure as a function of pressure, composition, & temperature (PCT)
- Phase diagrams
- Hydrogenation-dehydrogenation **mechanisms**
- Direct inputs for modeling dynamics

Brian L. Scott (LANL): 458 publications, >7900 citations

In Situ Thermal Conductivity Measurements





Semelsberger TA, Veenstra M, Dixon C. Room Temperature Thermal Conductivity Measurements of Neat MOF-5 Compacts with High Pressure Hydrogen and Helium Int J Hydrogen Energy, Submitted

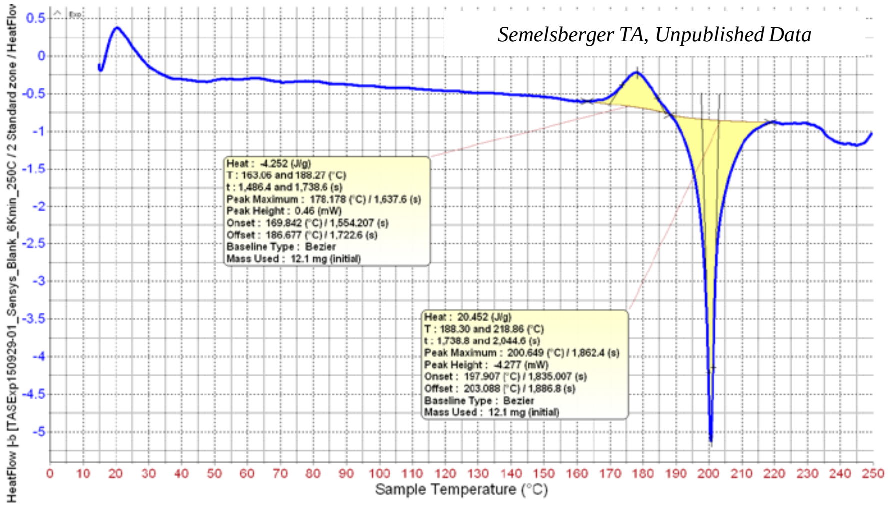
Capabilities

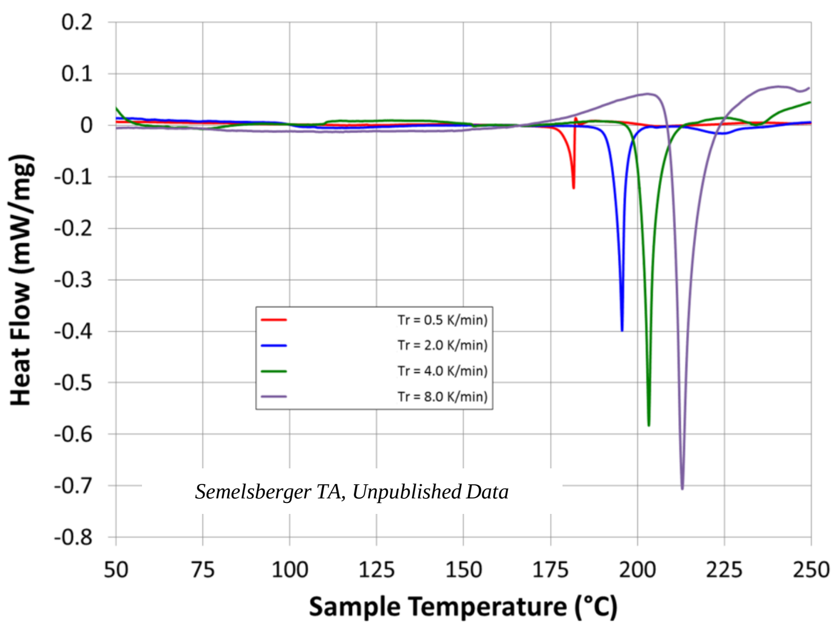
- Thermal conductivity and thermal diffusivity
- Isotropic or anisotropic measurements
- Temperature range: -196 °C – 900 °C
- Pressure range: Vac – 100 bar
- Powders or engineered compacts
- Wide range of adsorbates or reactive gases

Information & Insights:

- *In situ* thermal conductivity measurements under real-life operating conditions
- Thermal conductivity as a function of pressure, composition, temperature, adsorbate, and degree of hydrogenation/dehydrogenation

In Situ Thermal Analysis Under Elevated T & P





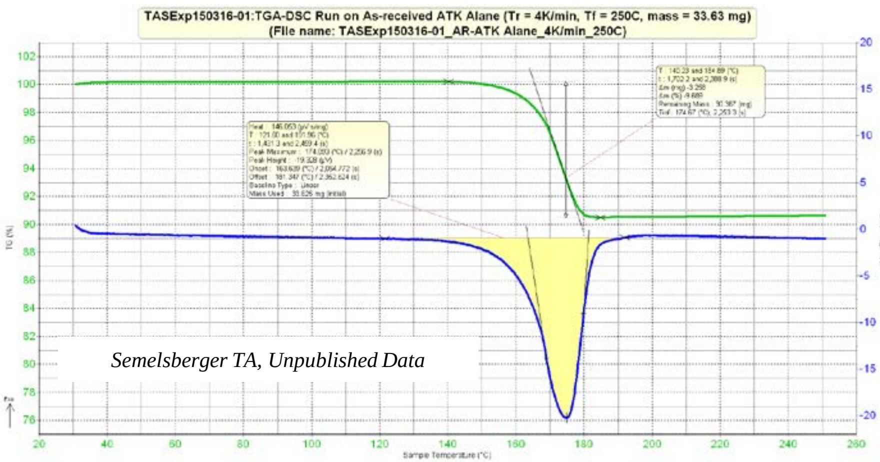
Capabilities

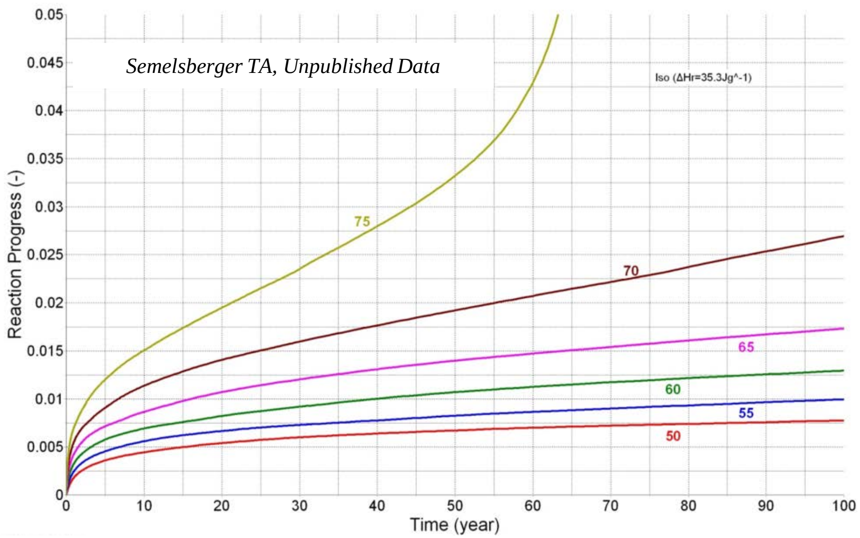
- Temperature Range: -180 °C – 830 °C
- Maximum Pressure: 400 bar (@ 600 °C)
- Sample size (100 μL–12 mL)
- Glove box accessible
- Reactive gases (H_2, O_2…)
- Batch or continuous flow operation

Information & Insights:

- Heats of hydrogenation-dehydrogenation reaction as a function of Pressure, Composition, & Temperature
- Hydrogenation-dehydrogenation kinetics(conversion, selectivity, yields..)
- Heat Capacities (-180 °C – 830 °C)
- Direct inputs for modeling

In Situ EGA Analysis: TGA-DSC-IR-RGA-GC





Capabilities

- Temperature Range: -150 °C –1600 °C
- Maximum Pressure: vacuum-ambient
- Sample size: < 35g (<3.4 mL)
- Glove box accessible
- Reactive gases (H_2, O_2…)
- Batch or continuous flow operation

Information:

- Heats of hydrogenation-dehydrogenation reaction
- Hydrogenation-dehydrogenation kinetics (conversion, selectivity, yields..)
- Hydrogen Capacity (net usable)
- Gas-phase impurities
- Direct inputs for modeling dynamics

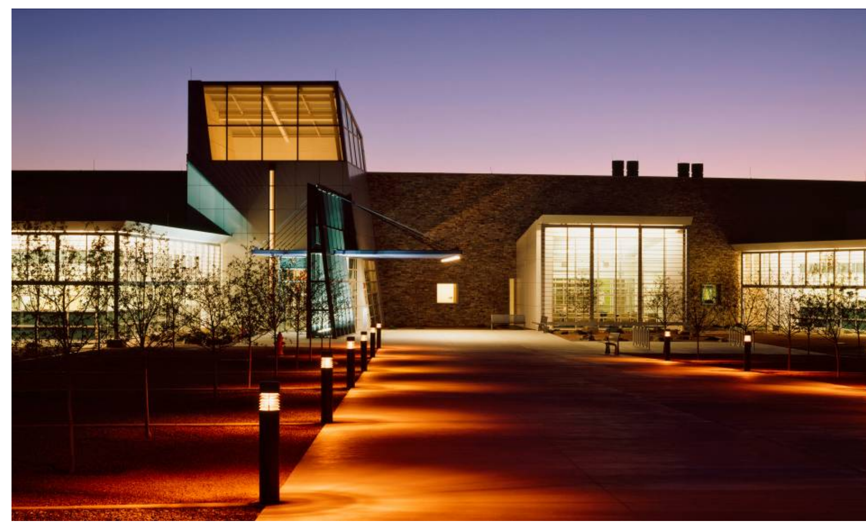
Additional Techniques

- PCT
- BET/Micropore/Mesopore Analysis
- Chemisorption/Titration
- TPD/TPO/TPR/TPRxn
- HP “TGA”
- Batch or continuous flow operation
- Synthesis
- High-performance computing
- SEM
- TEM
- ……

Ultrafast Spectroscopy for Hydrogen Storage Research

Dmitry Yarotski, Rohit Prasankumar, George Rodriguez, Abul Azad, Richard Sandberg, Steve Gilbertson, Antoinette Taylor

Los Alamos National Laboratory



Current Challenges

HyMARC goal is … to understand phenomena and kinetics

Large gap in knowledge and characterization:

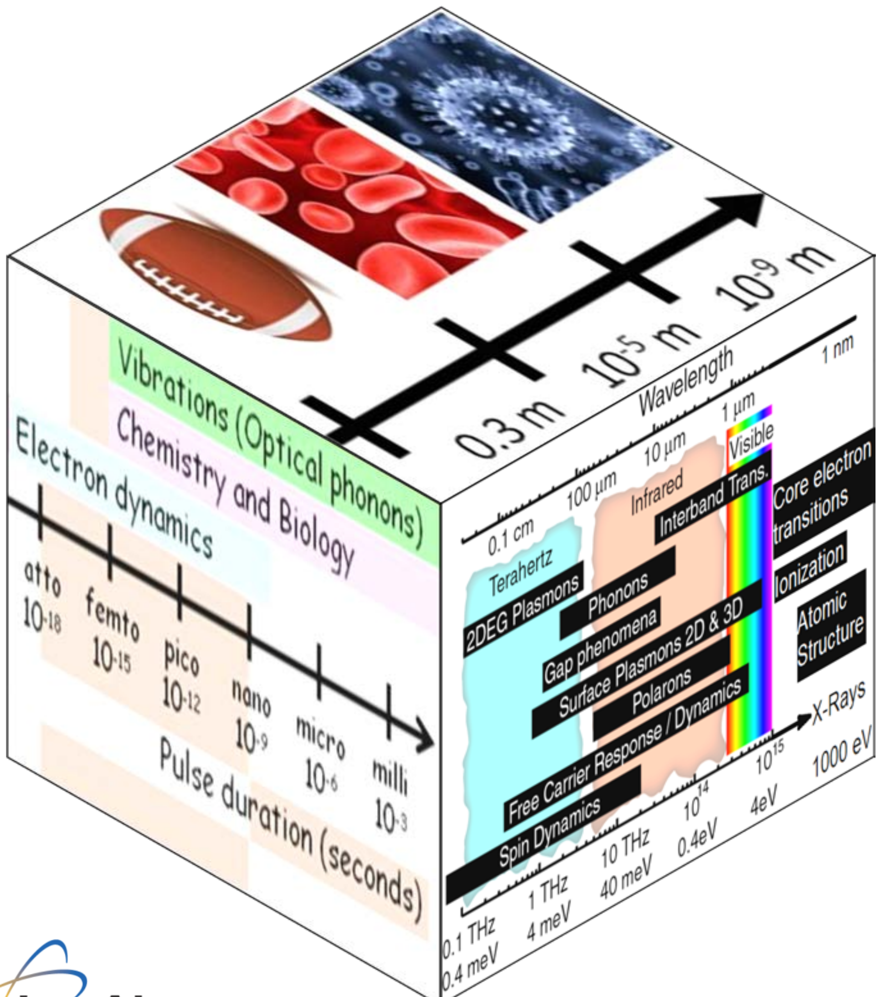
- Characteristic timescales and dynamics of underpinning processes
- Very few time-resolved studies exist in H_2 fuel/storage research

Specific interests:

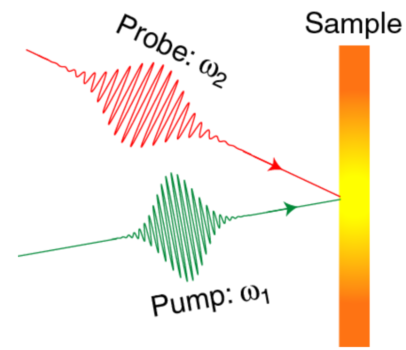
- Benchmark semi-classical and fully quantum MD/QMD simulations that span fs-ns timescales
- (De/Re)Hydrogenation reaction dynamics, intermediate states
- Phase transitions, phase coexistence/separation
- Electron and ion diffusion at and across interfaces
- Heat flow/dissipation
- Investigate all of the above *in situ*, under pressure (>700 MPa) and temperature extremes

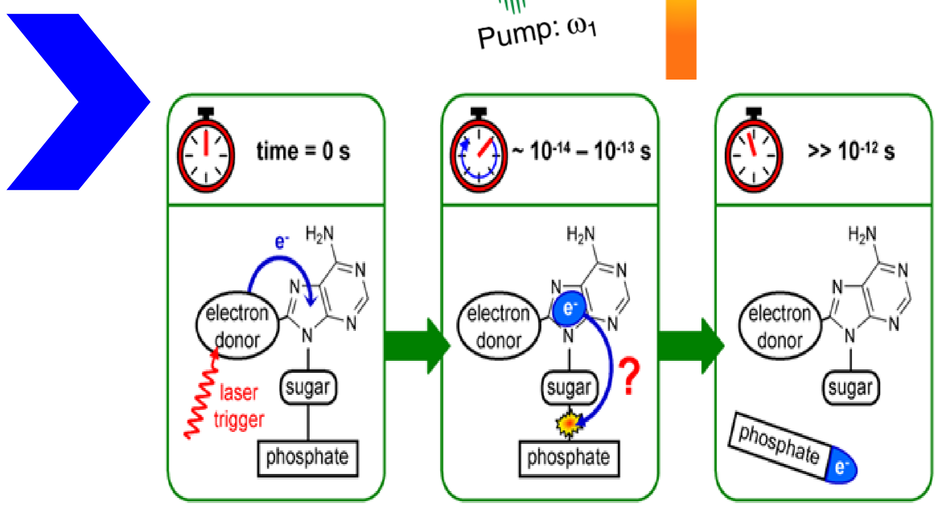
Why Ultrafast Spectroscopy?

- Ultrafast (10-100 fs) spectroscopy can **resolve** non-equilibrium dynamics (reaction, transport etc.) at the fundamental time and spatial scales of electronic and nuclear motion



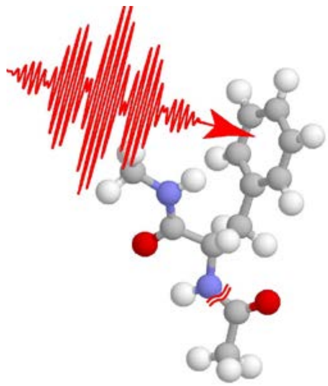
- Remote – *in situ* probe storage materials under relevant dynamic and static conditions

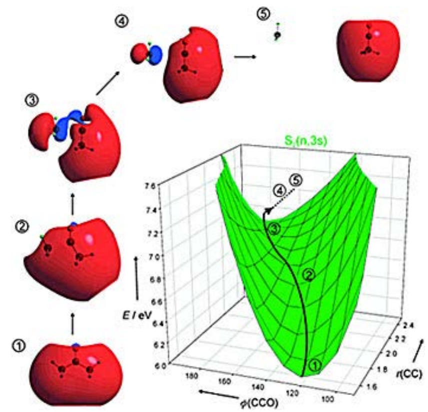




Ultrafast Coherent Manipulation

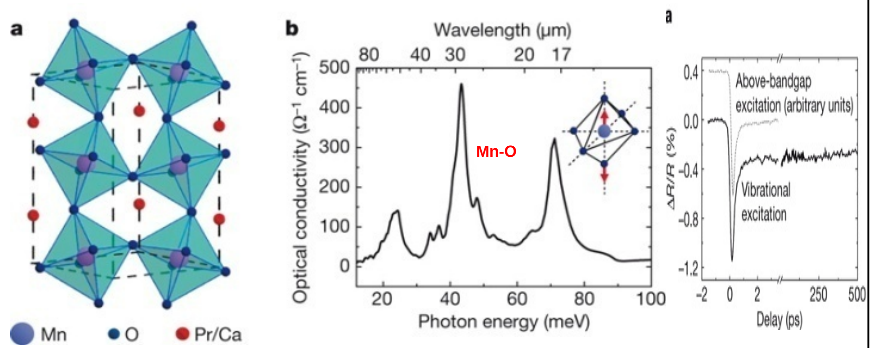
Coherently drive specific electronic/atomic motion/bond to reveal its effect on material performance. Induce phase transitions. Create non-thermally accessible phases

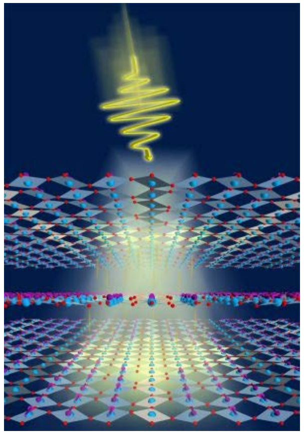


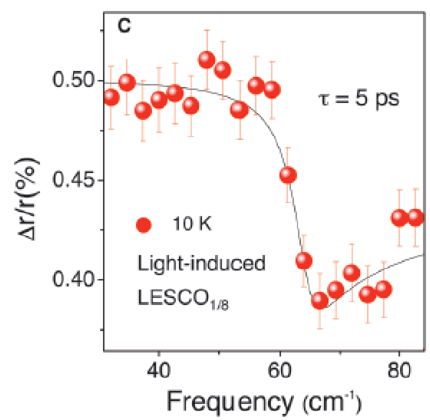


*www.lms.caltech.edu

Rini, Nature 449, 72 (2007)





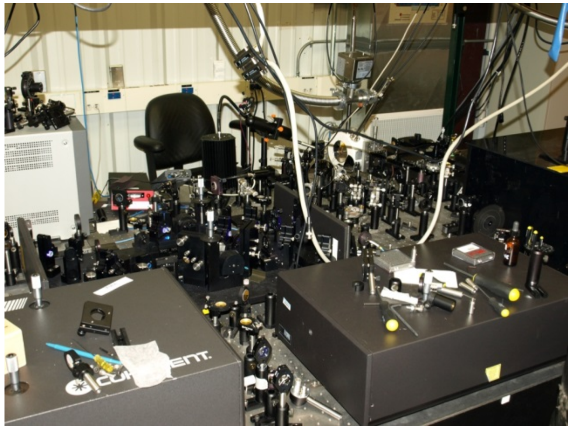


Fausti, Science 2011

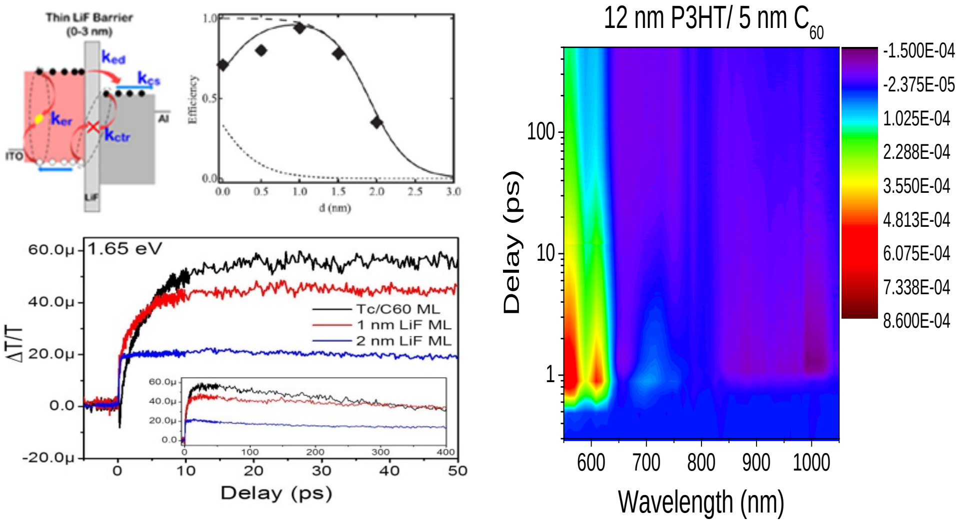
Why Los Alamos?

- Ultrafast Spectroscopic capabilities matched by very few in the world
- Multiple femtosecond laser systems covering THz to soft X-Ray
- Wide range of environmental conditions – temperature, pressure, fields
- Extensive expertise in applying these capabilities to a broad range of systems spanning soft matter/polymers, metals to gas plasmas

Broadband Optical Pump-Probe Spectroscopy



Ultrafast Charge Transfer at Photovoltaic Device Interfaces



Sampat et al., J. Phys. Chem C, 2015

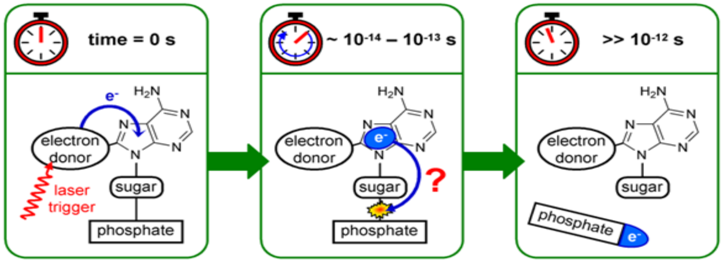
Capabilities

- TR-Raman, Transient Absorption, TR-SHG, TR-Kerr
- Sensitivity better than $\Delta R/R(\Delta T/T)<10^{-7}$
- Multiple 10-100 fs systems with 10 nJ to 4 mJ (~TW/cm^2) energies
- **Spectral coverage from 0.26 to 20 µm**
  - Visible and Infrared optical parametric amplifiers
  - Difference frequency generation
  - Harmonic generation
- Variable temperature 4K ÷ 1000K
- High pressure cells
- Two split-coil magnets for H = 0 ÷ 8 T
- Fourier Transform Infrared Spectrometers (4 ÷ 400K, 100 ÷ 45,000 cm^{-1})

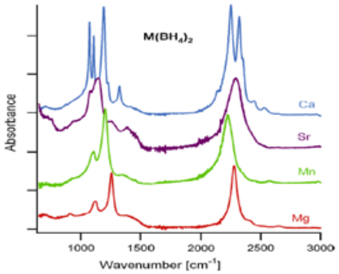
Applications for HyMARC

❖ UV, Visible, IR absorption

- Induce kynetics with heat, photon or field. Probe bond/phase dynamics
- (De/Re)hydrogenation kynetics/energy
- Reaction dynamics/Intermediate states
- Phase transitions
- Nature of adsorbants, mechanisms



* Gareth Roberts

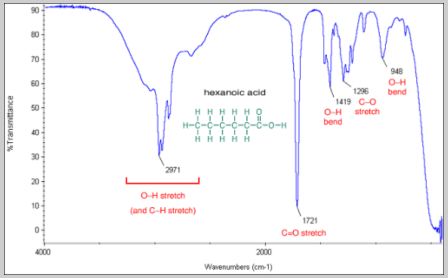


D'Anna et al, Spectrochimica Acta A, 2011

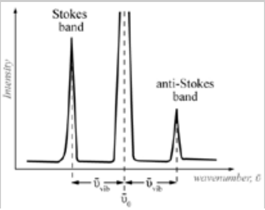
❖ CW and time-resolved, spontaneous and stimulated Raman

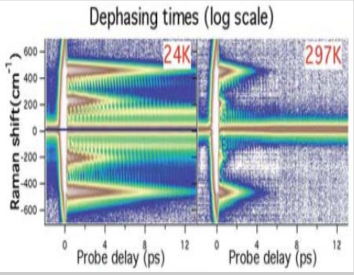
- Component signatures
- Reaction dynamics

- CW and dynamic non-contact thermometry
- Heat generation and dissipation



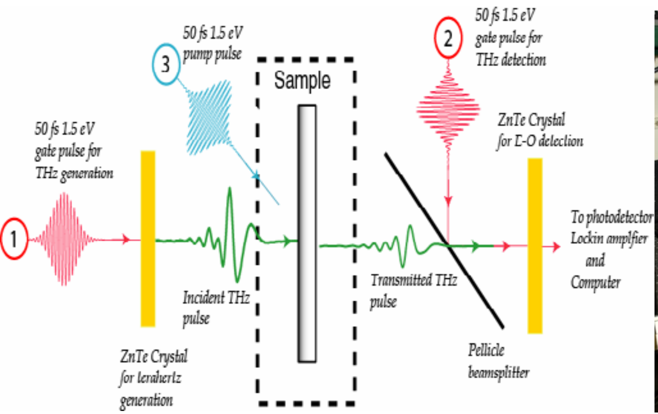
$$\frac{I_{AS}}{I_S} \propto \exp(-\hbar\omega / kT)$$

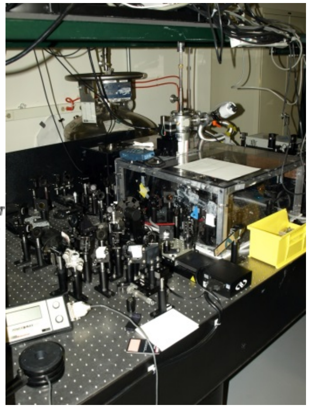




*McGrane (LANL)

Optical Pump – THz Probe Spectroscopy

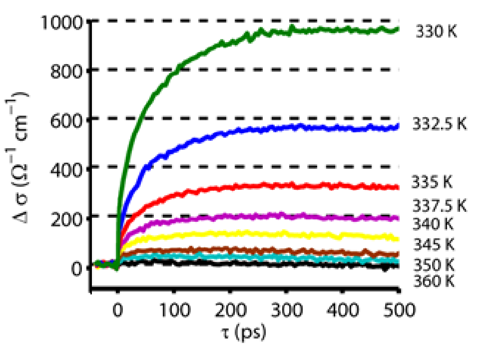




Capabilities

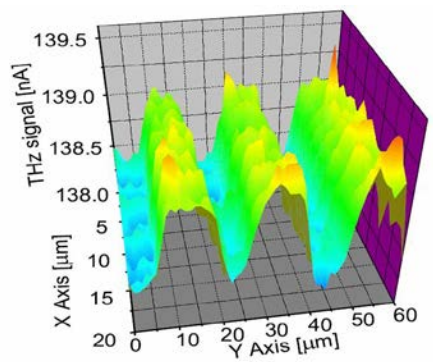
- Coherent detection of amplitude and phase
- Non-contact probe of static and ultrafast **transport** properties
- Broad frequency range of 0.1 - 5 THz
- Multiple sub-ps systems for angle-dependent transmission/reflection studies
- Amplified systems for higher THz energies
- Variable temperature 4K ÷ 700K
- Magnetic fields 0 ÷ 8 T
- THZ apertureless NSOM, < 100 nm

Metal-Insulator transition in VO_2



Hilton et al., Phys. Rev. Lett., 2007

THz NSOM on Si/Au

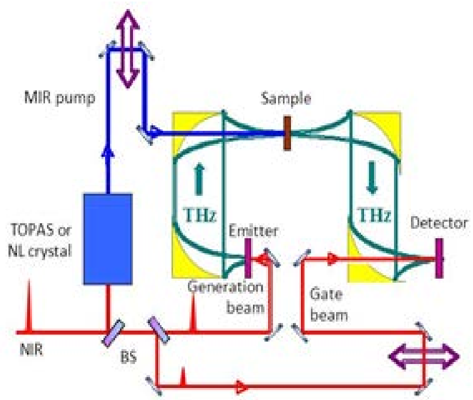


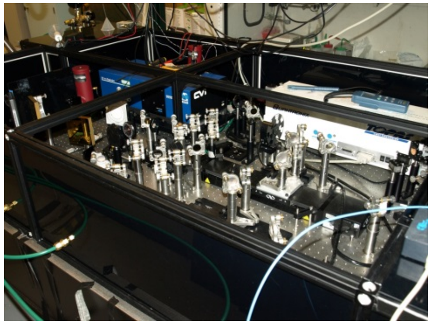
*Chen (LANL)

Applications:

- Vibrational signatures, excited state dynamics
- Ionic transport, scattering and loss channels
- Nanoscale characterization with NSTM

Mid-IT/THz Pump – Broadband Probe

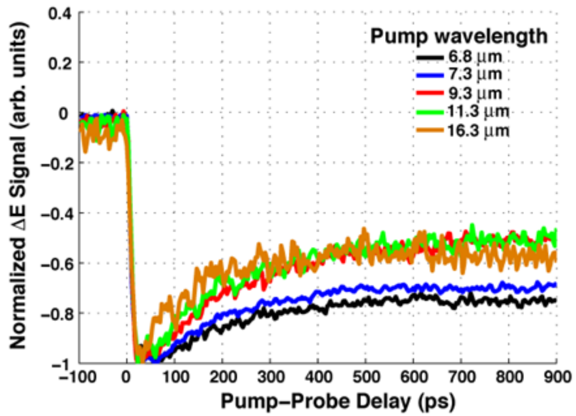




Capabilities

- Selective low-energy mode excitation
- Mid-IR Pump - THz probe system:
  - Amplified 3 mJ, 1.5 eV, 30 fs pulses
  - 0.5 - 20 µm excitation or probe
  - 0.1 ÷ 3THz probe
- THz pump – THz/SHG/KR/Optical probe
  - Amplified 3 mJ, 1.5 eV, 100 fs pulses
  - THz generation: ~1 MV/cm at 1 THz
  - DFG of two tunable OPAs: up to ~1 MV/cm at 10÷70 THz
- Variable temperature 4K ÷ 700K

Charge dynamics in small-bandgap InSb

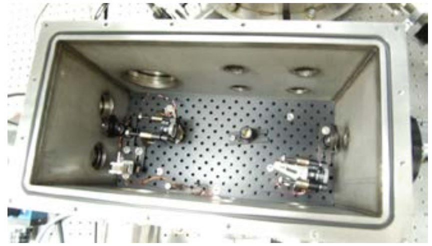


*Dani (LANL)

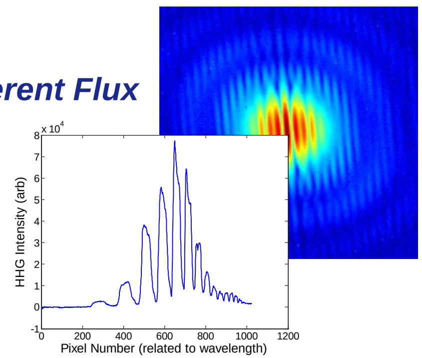
Applications:

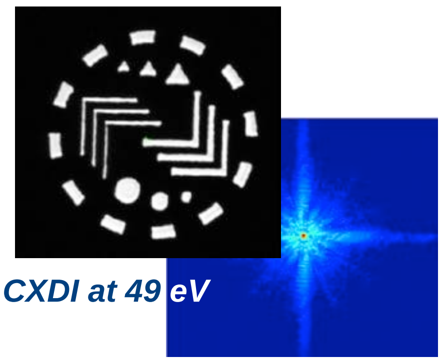
- Phonon-driven reaction/ionic transport initiation with THz and IR
- Influence of particular reaction channel or chemical bond on the device performance

Coherent X-Ray Diffraction Imaging



Coherent Flux





CXDI at 49 eV

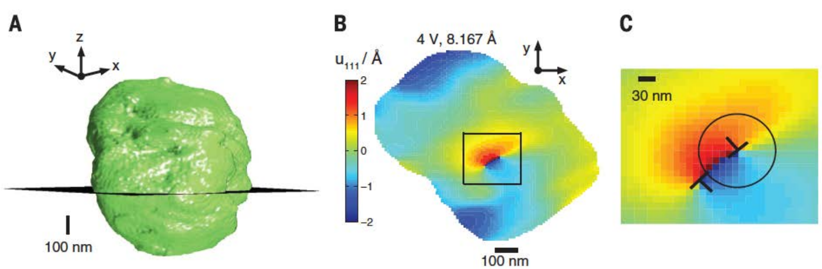
Sandberg (LANL)

Capabilities

- Bright, tunable flux at 20÷100 eV photon energies (> 10^8 ph/harmonics)
- 30 fs time-resolution
- Flexible optical bench for various imaging setups
- ~ 100 nm spatial resolution
- Variable temperature 4K ÷ 700K
- Access APS Bragg CXDI station for **mesoscale strain mapping** in catalyst nanoparticles

Single dislocation imaged in operating battery particle:

Ulvestad et al., Science 348, 1344–1347 (2015).

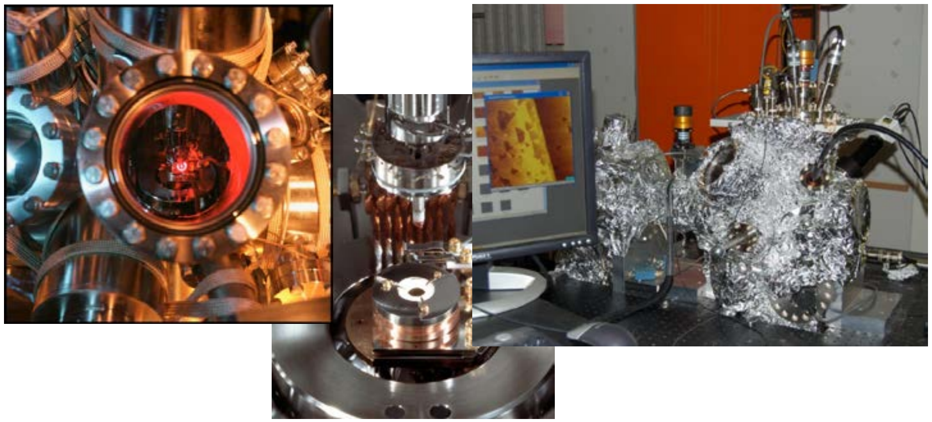


Applications:

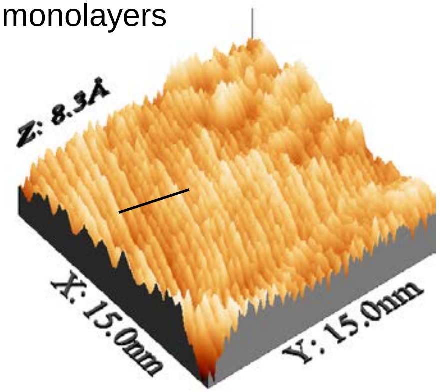
- Dynamics of catalyst nano/microparticle geometry and composition (M-edges)
- Bragg CXDI allows mapping of particle strain and shape changes during catalytic reaction

Scanning Probes Capabilities

VT UHV Scanning Probe Microscope allows unambiguous characterization of the electronic, magnetic and other properties of materials at the atomic length scales

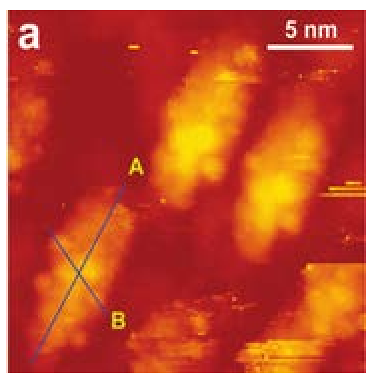


Self-assembled oligothiophene monolayers



Kuo et al., submitted

DNA wrapped carbon tubes



D.A. Yarotski et al., Nano Lett. (2009)

Parameters:

- Ambient or UHV environment
- Variable sample temperature, T=25÷600 K with 0.1 K stability
- Sample preparation:
  - Ion bombardment and thermal annealing for substrate preparation
  - Pulsed valve for *in situ* injection of the biological solutions
  - Thermal evaporator for monolayer deposition
- Wide range of operation modes: STM (electronics), AFM (morphology), Scanning Thermal Microscopy (for heat source/leak mapping in the devices)
- Coupled to ultrafast laser system for studies of dynamic photo-induced phenomena

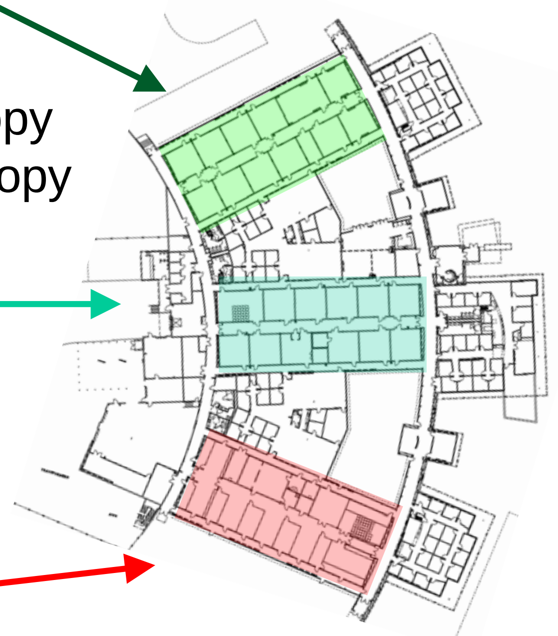
Also available at the Center for Integrated Nanotechnologies (CINT)

Characterization Wing
- TEM, SEM
- Low Temp Transport
- Scanning Probe Microscopy
- Ultrafast Laser Spectroscopy

Synthesis Wing
- Molecular Beam Epitaxy
- Chem & Bio labs
- Molecular films

Integration Lab
- E-beam lithography
- Photolithography
- Deposition & Etch
- SEM/FIB

Core Facility



Gateway to Los Alamos
- Scanning Probe Microscopy
- SEM, STEM
- Nano-indenter
- Pulsed Laser Deposition
- Ultrafast Spectroscopy
- Computer Cluster
- Visualization Lab