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SRNL Ultrafast Spectroscopy Materials Characterization

Dr. Scott McWhorter
SRNL EERE Program Manager

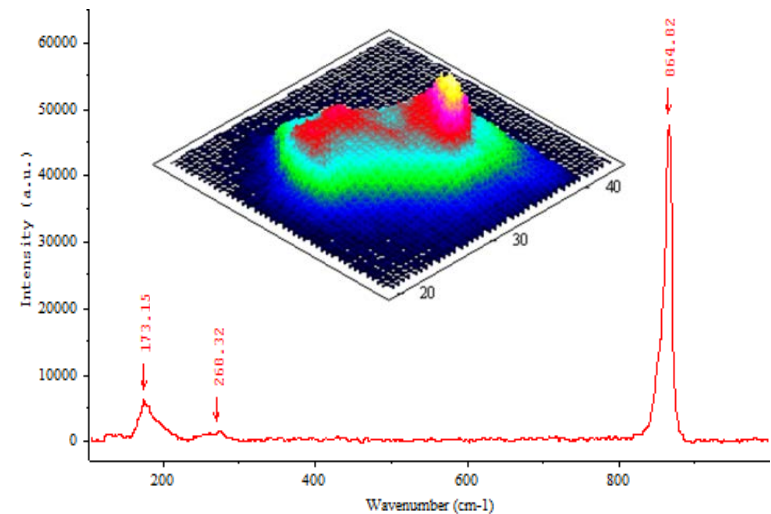
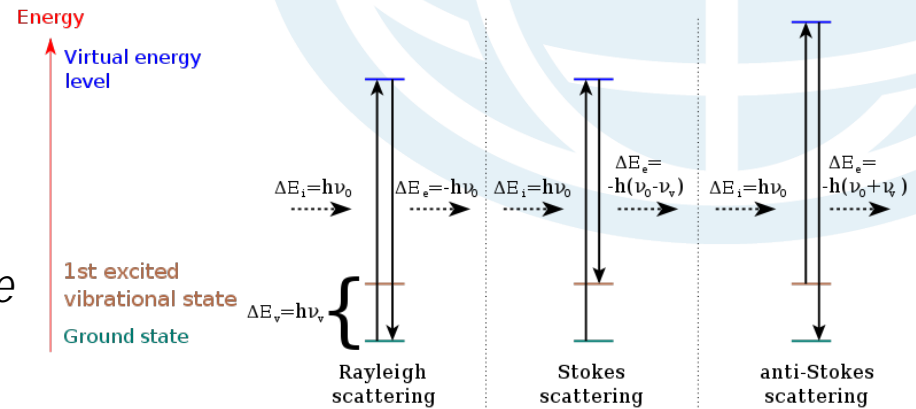
Hydrogen Storage Lab Meeting

November 4-5, 2015

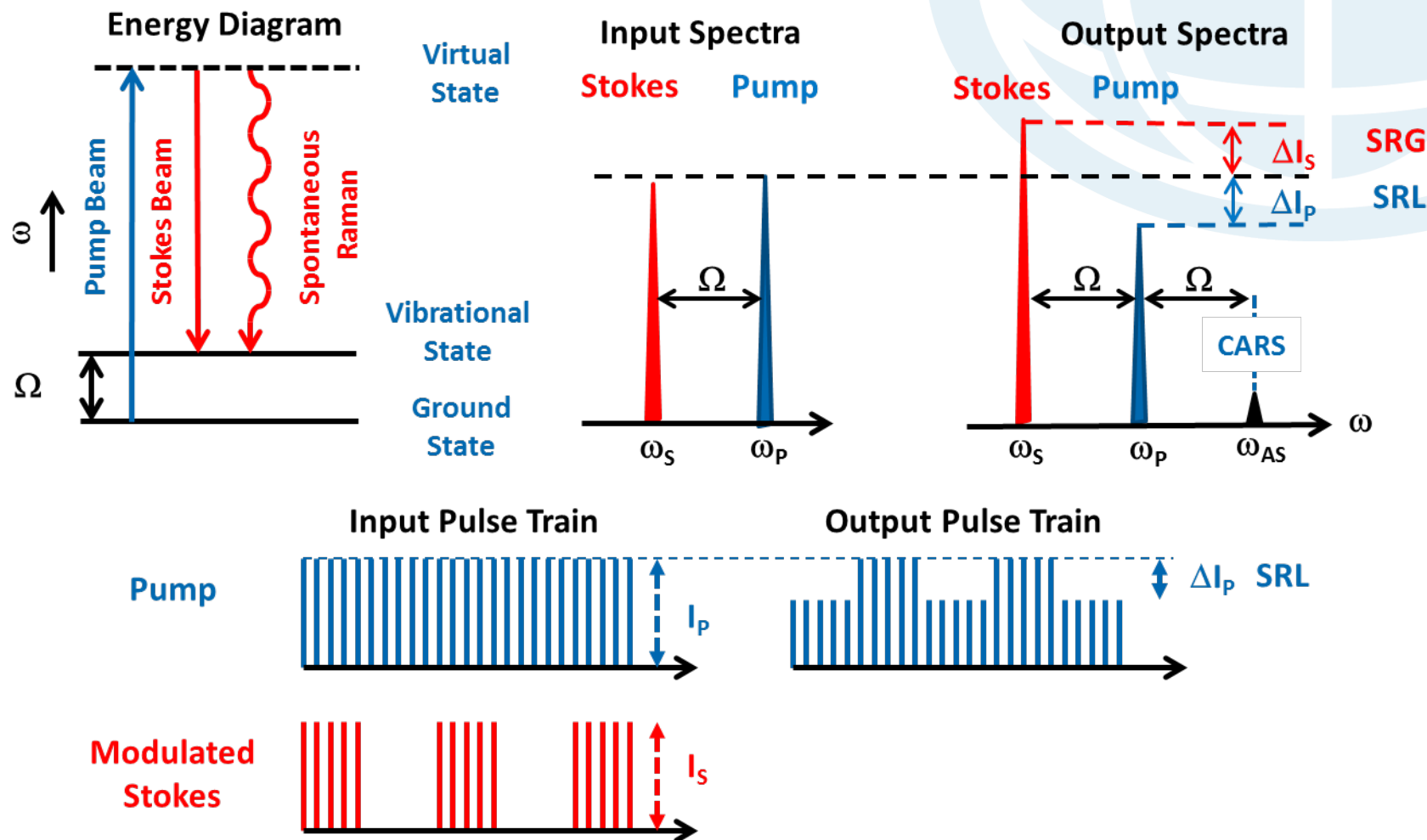
Background

- **Spontaneous Raman Spectroscopy**

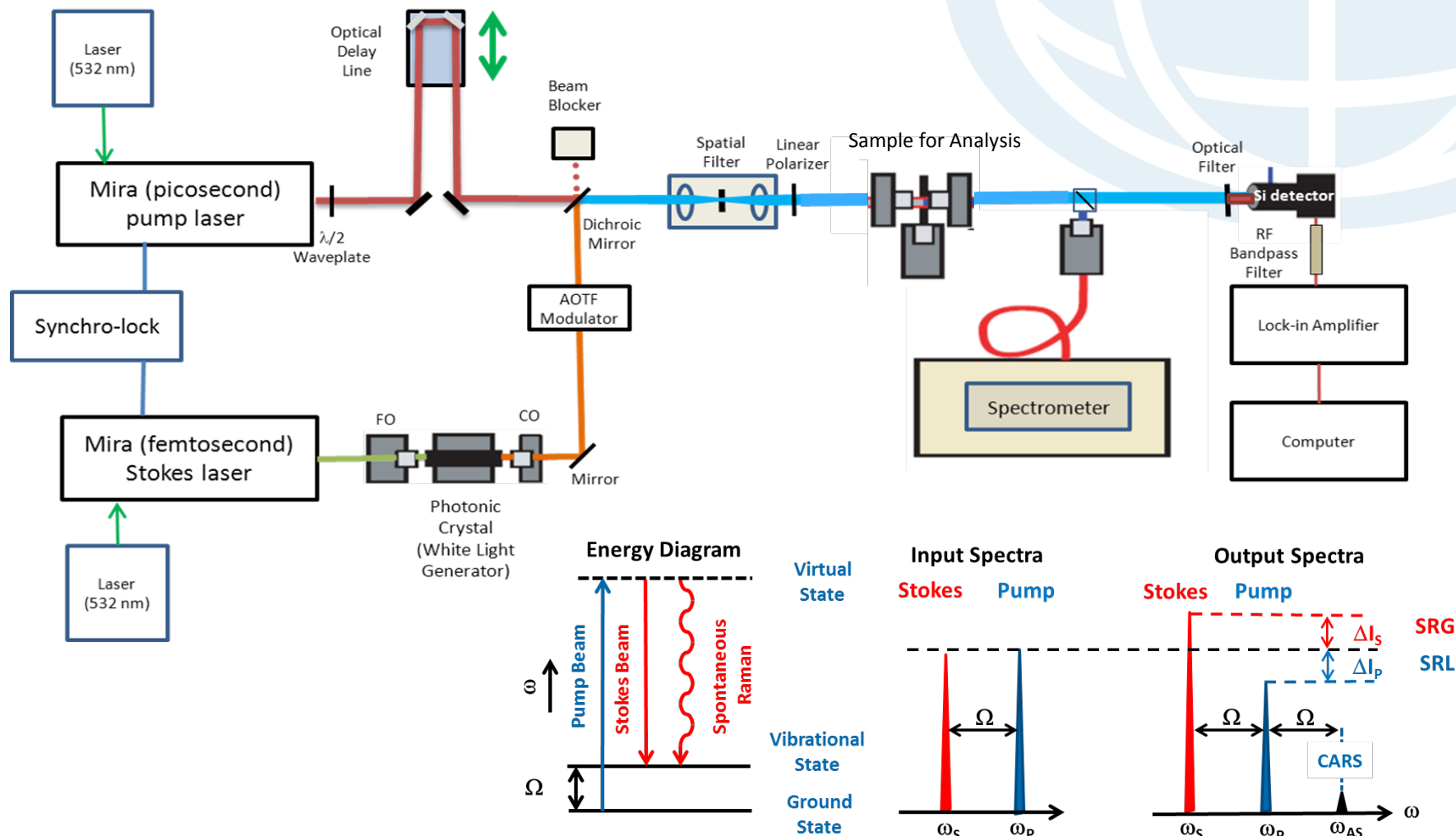
- *Spectroscopic technique for molecular characterization of materials.*
- *Similar to infrared spectroscopy.*
- *Inelastic interaction between photon/molecule*
 - 1 photon in a million undergoes inelastic scattering
- *Weak signal*
 - Long integration times
 - Fluorescence can overcome the signal
 - Slow imaging speeds.
- **What do we need to do to improve the technique?**
 - *Enhance signal dramatically*
 - Overcome fluorescence
 - Reduce time to acquire signal
 - Imaging becomes possible and much faster.



Stimulated Raman Scattering Technical Approach

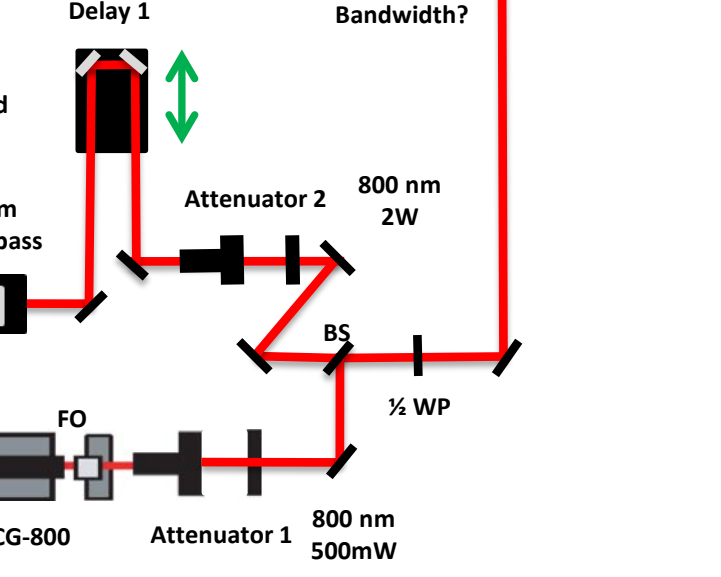


Picosecond and Femtosecond Lasers SRS Setup



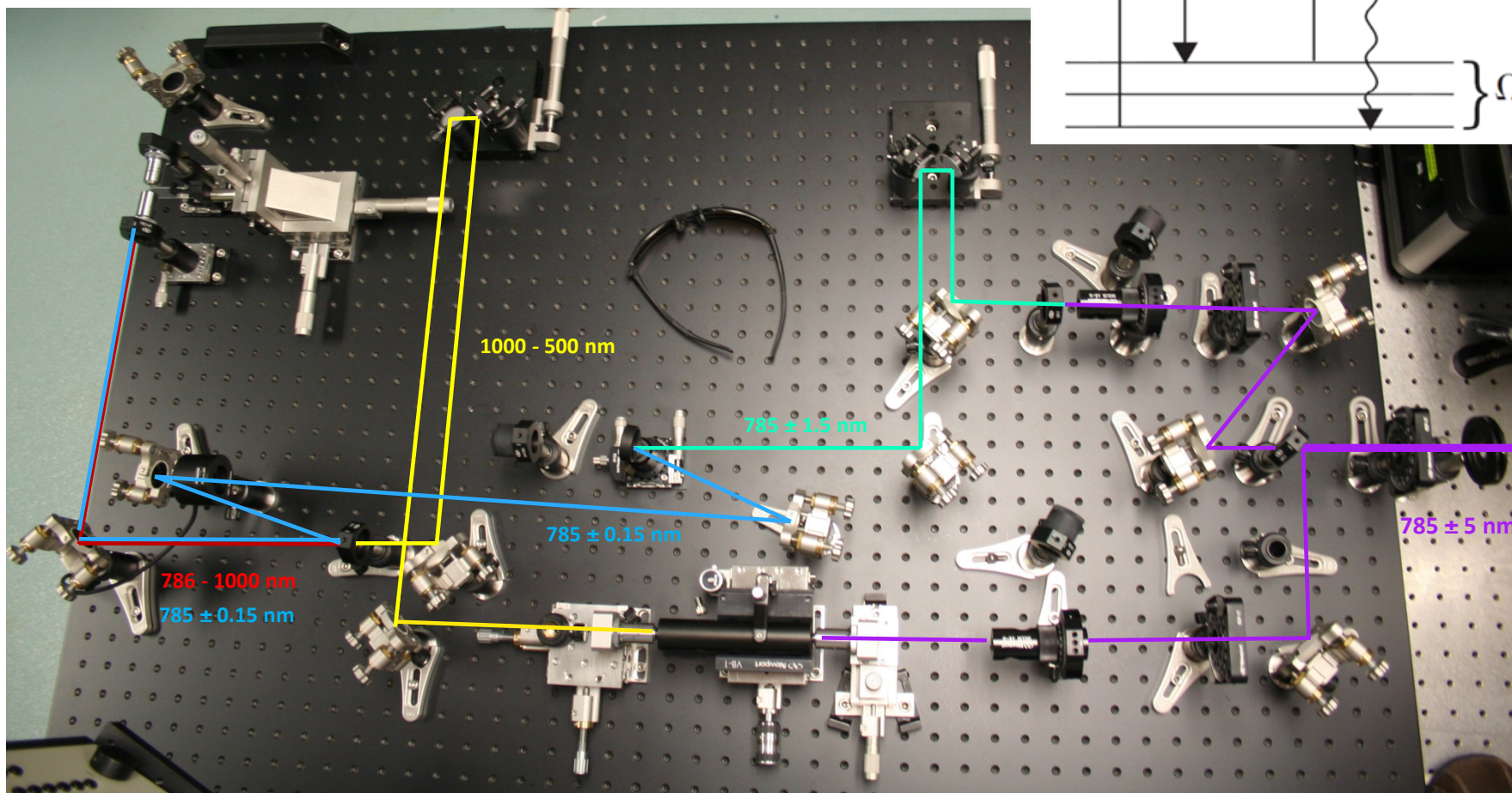
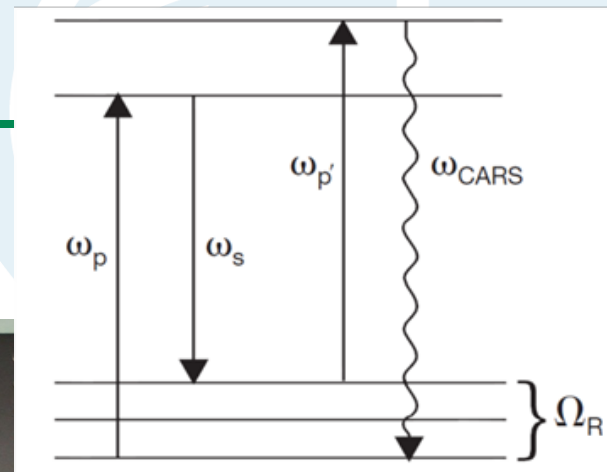
Mira 900 D
Ti:Sapphire Laser

800 nm
2.5 W

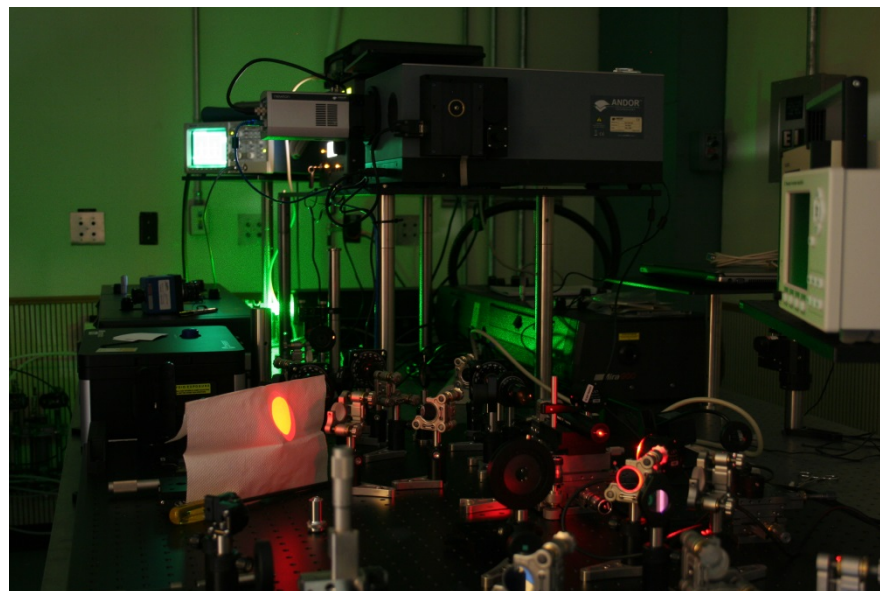
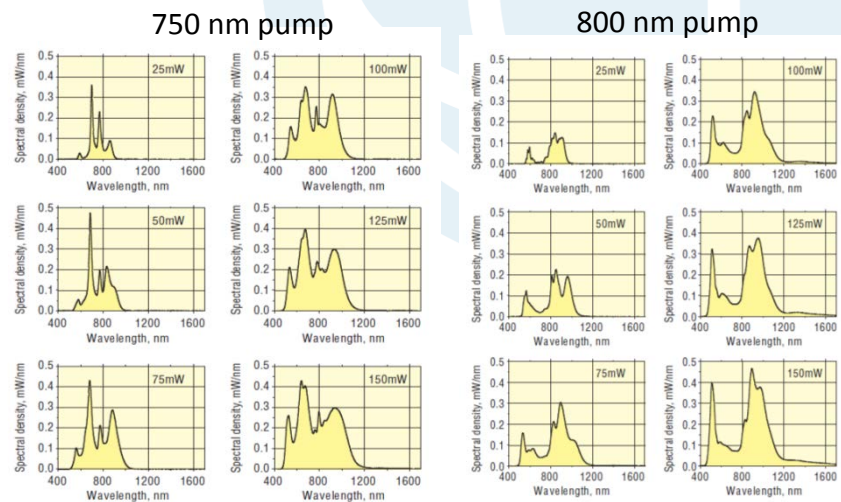
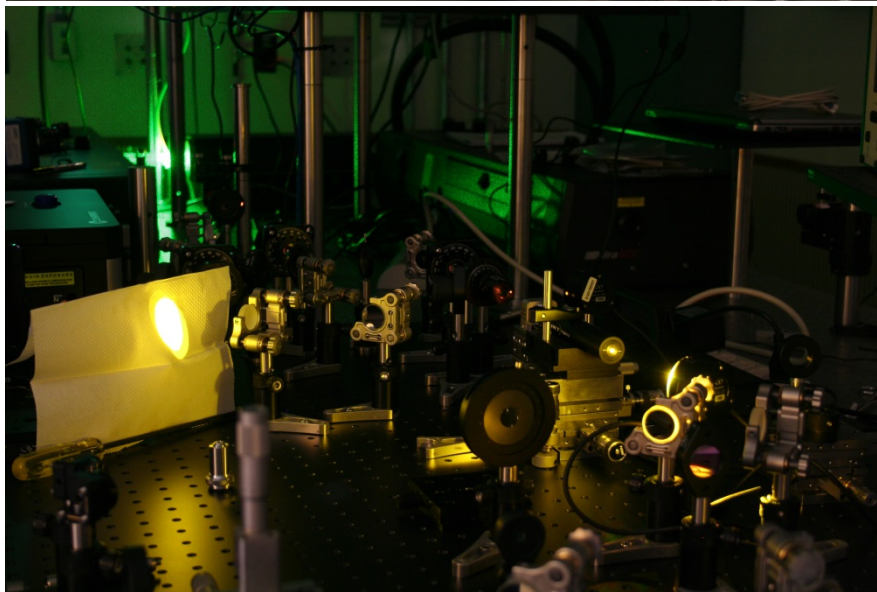
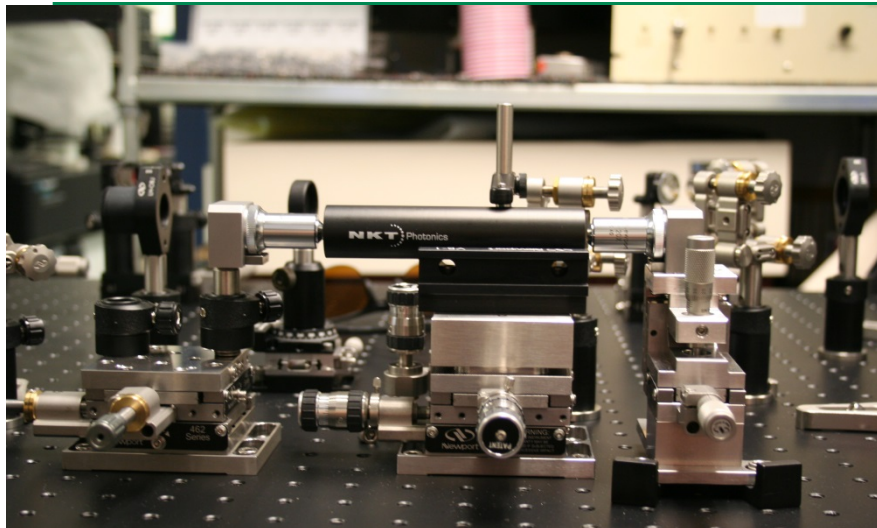


SRL is the preferred setup since photodiode responsivity is higher for the pump wavelength.

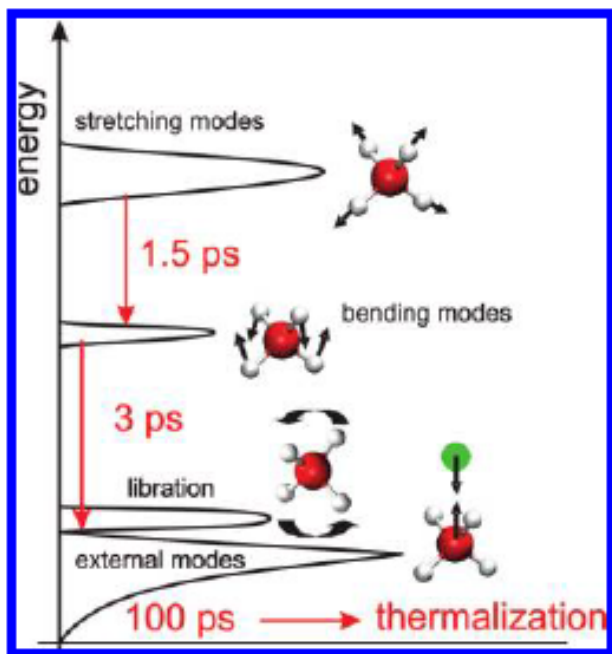
Broadband CARS Setup



Broadband CARS Setup



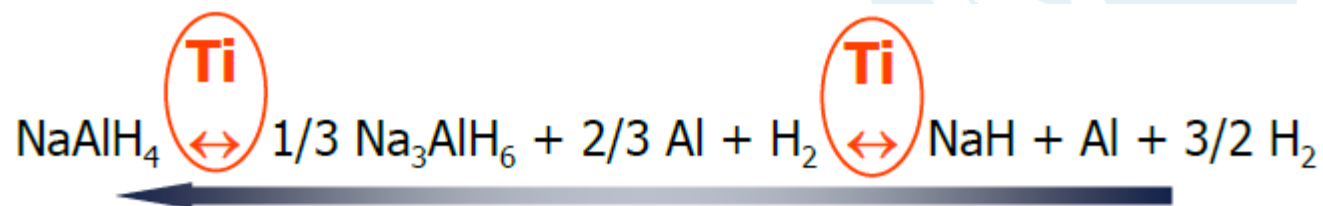
Ultrafast Interrogation of Metal Hydrides



- Understanding the dynamics of complex anions
 - Temperature-dependent reorientation occurring on the ps timescale can reveal kinetic limiting phases

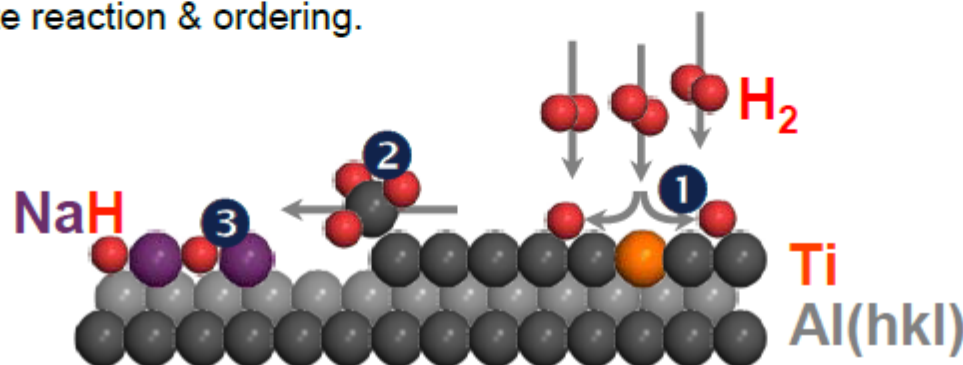


Ultrafast Interrogation of Metal Hydrides



Elementary reaction steps (at surfaces)

- 1 Ti catalyzed H_2 dissociation on depleted material (Al)
 - 2 Formation of mobile species & mass transport.
 - 3 Solid state reaction & ordering.
- } Relevant to new hydrides (**Alane**)





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High Pressure Differential Scanning Calorimetry (HPDSC)

Ragaiy Zidan

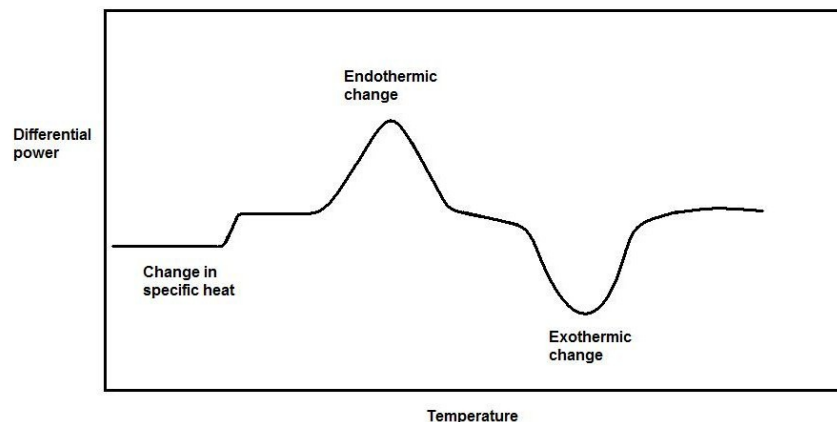
Team:

Joseph Teprovich, Patrick Ward, Scott McWhorter, Scott Greenway

High Pressure Differential Scanning Calorimetry (HPDSC)

Differential Scanning Calorimetry allows for the analysis of thermodynamic and kinetic properties of materials including:

- Phase Changes
- Temperature of Reactions
- Melting Points
- Enthalpy (via integration)
- Activation Energy
- Specific Heat of a material



High Pressure DSC Can be operated under constant volume or constant pressure conditions and can be utilized to give additional information about:

- Enthalpy and Entropy for broad peak reactions in which the enthalpy cannot be obtained by integration. (via Van't Hoff plot of T_{eq} at various constant pressures using on set point)
- Information about structural changes at high pressures.
- Information about thermodynamic changes at high pressures.

HPDSC Instrumental Setup

The HPDSC instrument at Savannah River National Laboratory used a piston driven high pressure gas manifold to ensure constant pressures up to 400 bar. This gas manifold is attached in tandem to high pressure DSC crucibles rated to 400 bar which can be used to measure thermograms of air sensitive materials. The DSC is a Setaram SynSys Evo with a heating block capable of reaching 600 °C.



Investigating Phases Formation and Thermodynamic Properties under Higher Hydrogen Pressure

- Several automotive companies announced the commercialization of hydrogen fuel cell cars based on high-pressure hydrogen tanks (700 bars)
- High Pressure Differential Scanning Calorimeter (HP DSC) can be used to gain a fundamental understanding of the changes in thermodynamic properties and kinetics of novel materials under high hydrogen pressure (400 bars)
- The possible alteration of the thermodynamics of some materials pointed out by Reilly and Wiswall and was utilized later in the destabilization of borohydrides later by Vajo *et al.* can be investigated
- Understating the alteration of thermodynamic properties (e.g. enthalpy and entropy) of these materials under higher pressure could lead to a higher hydrogen storage density system by taking advantage of the available high pressure
- A HP DSC study can relate the exothermicity of the formation of these alloys to the lowering of the dehydrogenation temperature of the whole system
- Understanding the behavior of materials during hydrogenation and dehydrogenation can lead to voiding thermodynamic sink



Destabilization Mechanisms of Hydrides to Shift The Thermodynamics at High Temperatures.

- Many alloys disproportionate to a metal and a hydride when hydrogenated where the resulting product is reversible
 - An example of this class of system is magnesium hydride (MgH_2) mixed with nano scale aluminum particles which dehydrogenates forming an alloy at $< 250^\circ \text{C}$ (versus $> 300^\circ \text{C}$ for bulk MgH_2) with enhanced kinetics. This reversible reaction is based on the following solid state atomic exchange $12\text{MgH}_2 + 17\text{Al} \rightleftharpoons \text{Mg}_{12}\text{Al}_{17} + 12\text{H}_2$
 - Hydrogen release from this composite is assisted by the formation of $\text{Mg}_{12}\text{Al}_{17}$ alloy, an exothermic formation that leads to a lower ΔH of the whole system.
 - As an example, $\text{Mg}_{12}\text{Al}_{17}$ can be hydrogenated at higher pressure to shift the equilibrium forming MgH_2 and Al and the same can apply to alloys such as Mg_xSi_y , CaAl , Li_xCy etc.
- Phase diagrams of the components forming the alloy and the hydride can be investigated to determine a clear path to practical hydrogenation temperatures and pressures of these destabilized systems
- Understanding the behavior of materials and phase formation during hydrogenation and dehydrogenation under high pressure can lead to optimization of stoichiometric (x,y)

Reversibility and Destabilization

- Reversibility and destabilization of hydride materials as a function of high pressure (400 bars) has not been thoroughly studied
- Studying the formation, the disproportionation, and the intermediate phases of these alloys enables us to control the alteration of thermodynamic properties and leads to a more detailed understanding of the reversibility of many complex hydrides
- Fundamental understanding of many complex hydrides (e.g. borohydrides and amides) is needed when they are combined with destabilizing agents especially under higher pressure
- Phase diagrams of the formation of these reversible alloys from composites can be determined as a function of temperature and pressure
- Hindered mass transport and slow kinetics could have prevented the use of some of these composites/alloys in the past
- Enhancement of mass transport, reversibility and kinetics is expected under high pressure and can be monitored using HP DSC

HPDSC Applications

The behavior of many materials differ under high pressure conditions. HPDSC allows for the measurement of these changes at high pressures. This allows for the analysis of the thermodynamic behavior of hydrogen storage materials under high pressures. Examples are:

- Enthalpy and Entropy changes at high pressure
- Difference in phase change conditions at high pressures
- Qualitative information about kinetics from the broadness of de/rehydrogenation peaks (at various pressures)
- Pressure induced phases due to the change in specific heat
- Allows for the observation of hydrogenation of many materials which require high pressures not obtainable by conventional DSC
- Dehydrogenation at higher pressure can avoid thermodynamic sinks and can be monitored by HP DSC
- Formation of exothermic reaction in the steps of hydrogenation can be recognized and investigated under HP

