

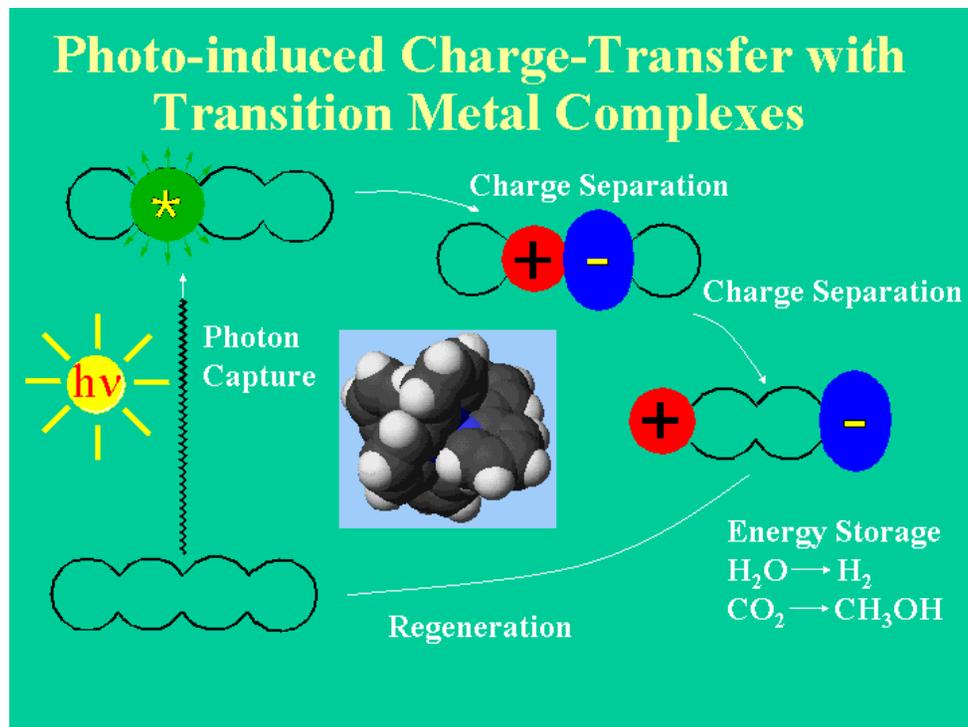
# Photo- and Radiation Induced Processes

- \* **Research Focus in Photochemistry**
- \* **Time-Resolved Infrared Spectroscopy**
- \* **Pulse Radiolysis (LEAF)**

The **T**hermal, **P**hoto- and **R**adiation-Induced Reactions  
in Condensed Media Group

<http://www.bnl.gov/chemistry/programs/TPR.asp>

# Research Focus



The long-term storage of solar energy as fuels or valuable chemicals requires efficient coupling of light absorption and chemical transformation processes. Mechanistic studies of systems which couple photo-induced electron-transfer processes to the bond-forming reactions required in the photogeneration of hydrogen and the photoreduction of carbon dioxide to useful chemicals are a major focus.

# Ongoing Projects

- \* **CO<sub>2</sub> Reduction**

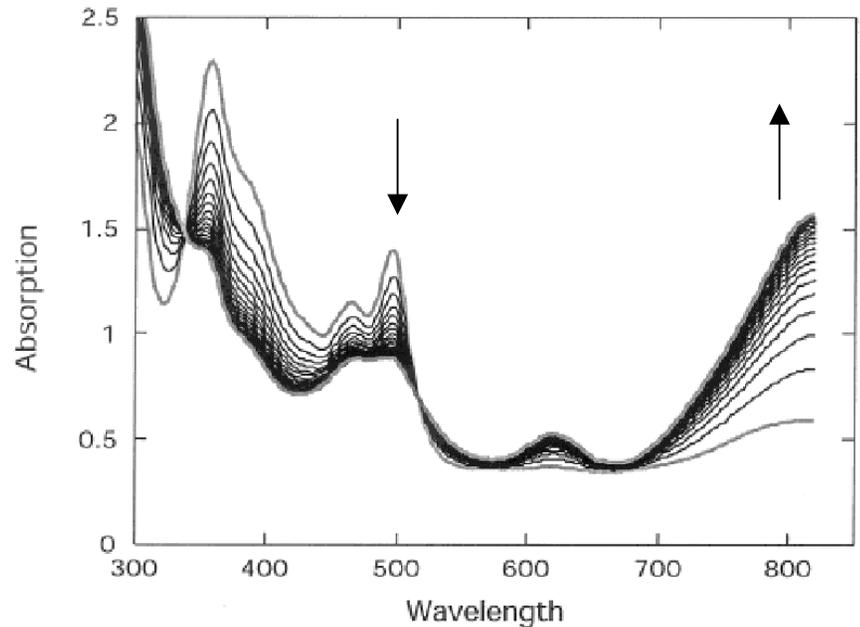
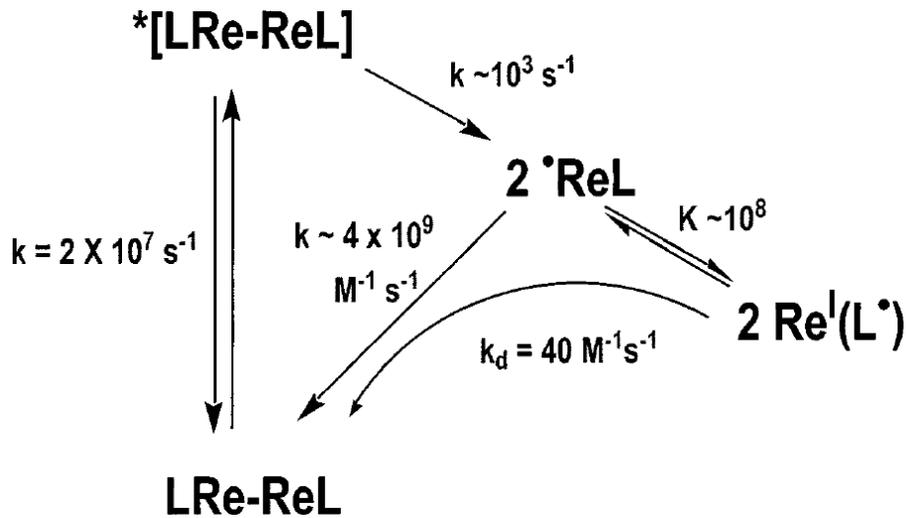
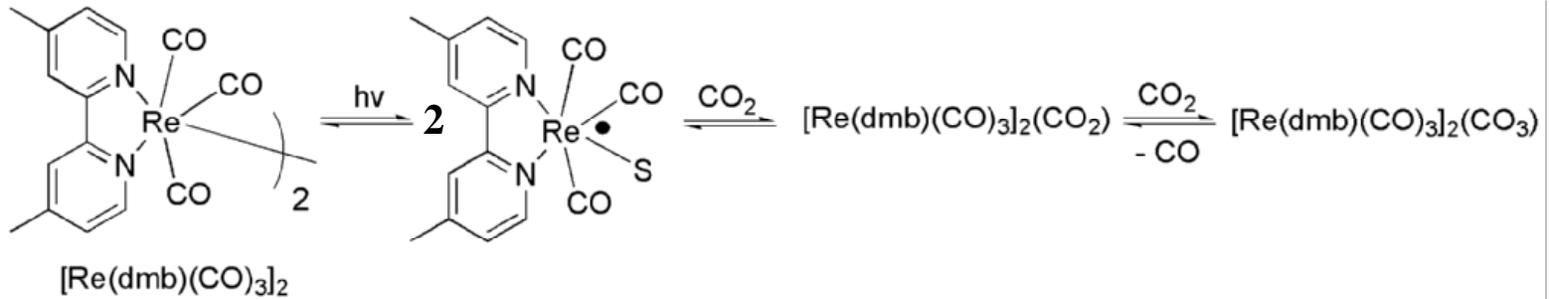
- \* **Small Molecule Activation**

**H<sub>2</sub> and H<sup>+</sup> (implications for H<sub>2</sub> generating reactions, catalytic hydrogenation and hydroformylation)**

**CH<sub>4</sub> and other hydrocarbons (through C-H bond activation to give liquid fuels and industrially important chemicals)**

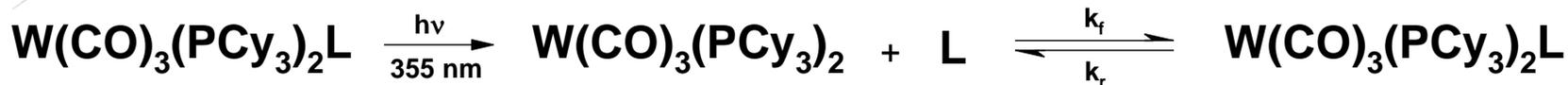
**N<sub>2</sub> and NO (to ammonia under mild conditions)**

# CO<sub>2</sub> Photo-Reduction

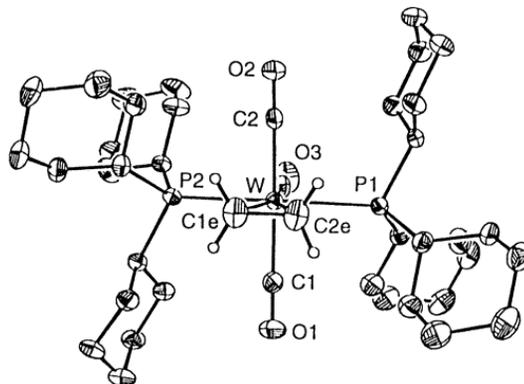


E. Fujita et al.

# H<sub>2</sub> and N<sub>2</sub> Binding

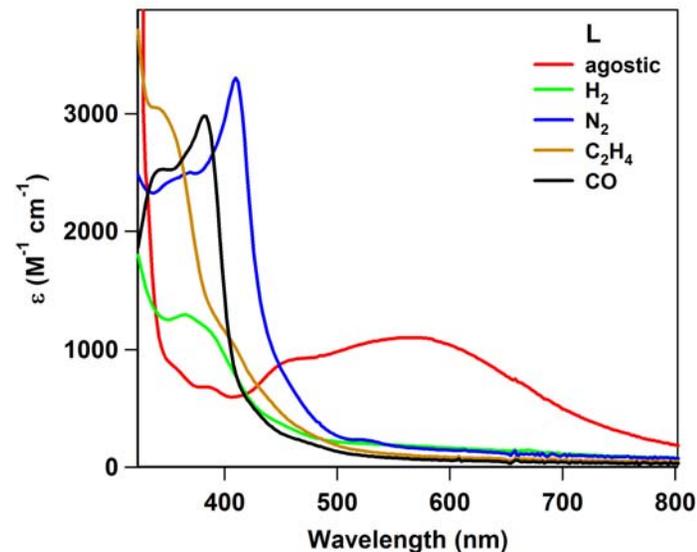


**W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>**  
reversibly reacts with  
**H<sub>2</sub>, D<sub>2</sub>, N<sub>2</sub>, C<sub>2</sub>H<sub>4</sub>, H<sub>2</sub>O,**  
**MeOH, CH<sub>3</sub>CN,**  
**pyridine, and CO.**



**Table:** Rate and calculated equilibrium constants for the reaction of various ligands, L with W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> to form W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>L in toluene at 25 °C.

L	k <sub>f</sub> (M <sup>-1</sup> s <sup>-1</sup> )	k <sub>r</sub> (s <sup>-1</sup> )	calcd. K (mol <sup>-1</sup> )
N <sub>2</sub>	3.0 x 10 <sup>5</sup>	99	3000
H <sub>2</sub>	1.9 x 10 <sup>6</sup>	950	2000
D <sub>2</sub>	1.5 x 10 <sup>6</sup>	680	2200
C <sub>2</sub> H <sub>4</sub>	3.4 x 10 <sup>4</sup>	570	60

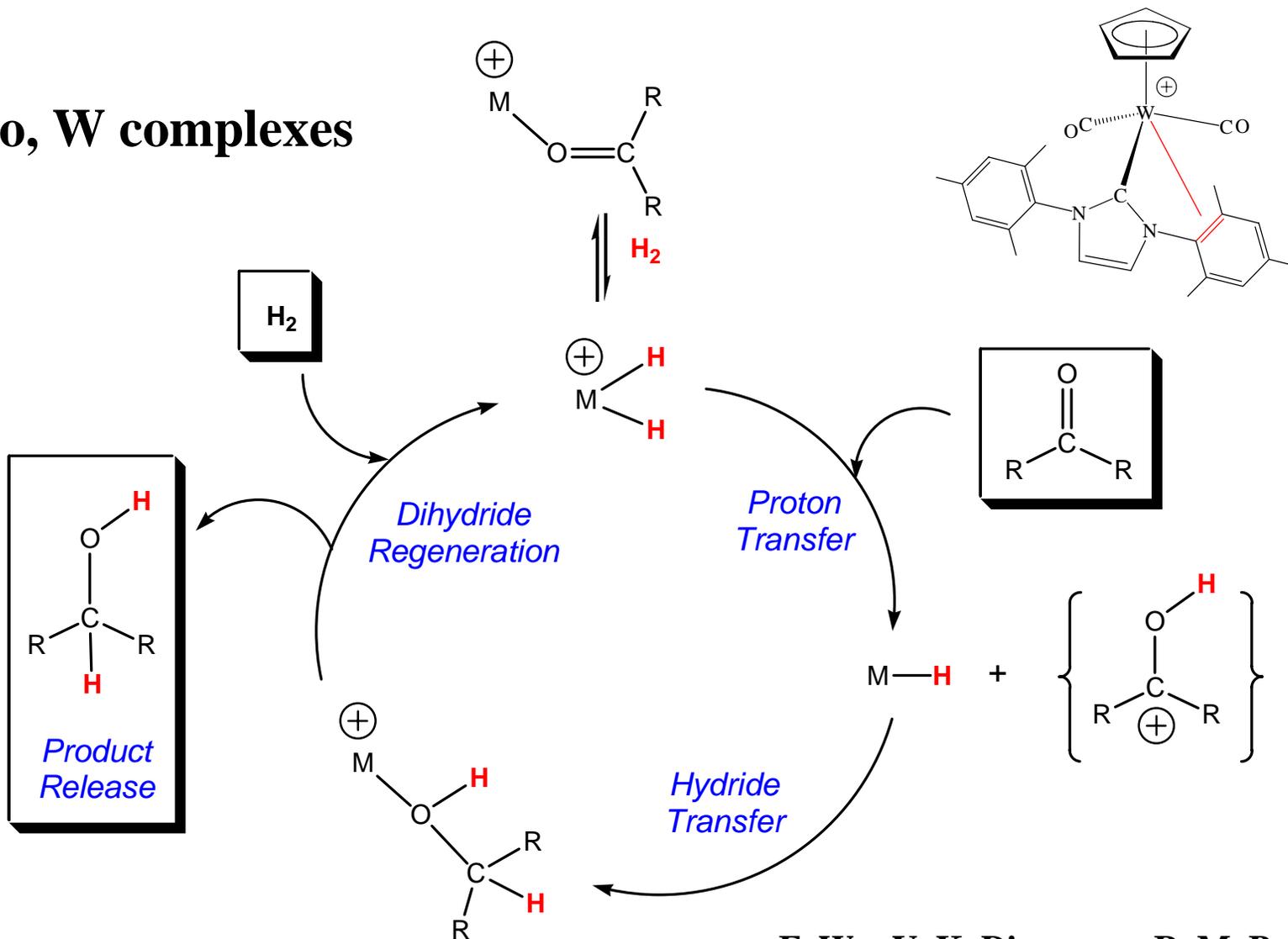


**Figure:** UV-vis absorption spectra of W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub> (agostic) and W(CO)<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>L in toluene.

# Ionic Hydrogenation

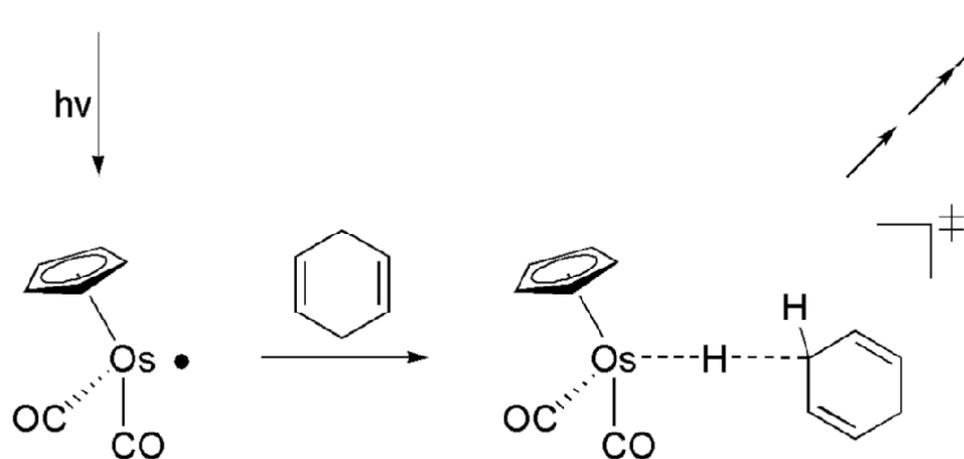
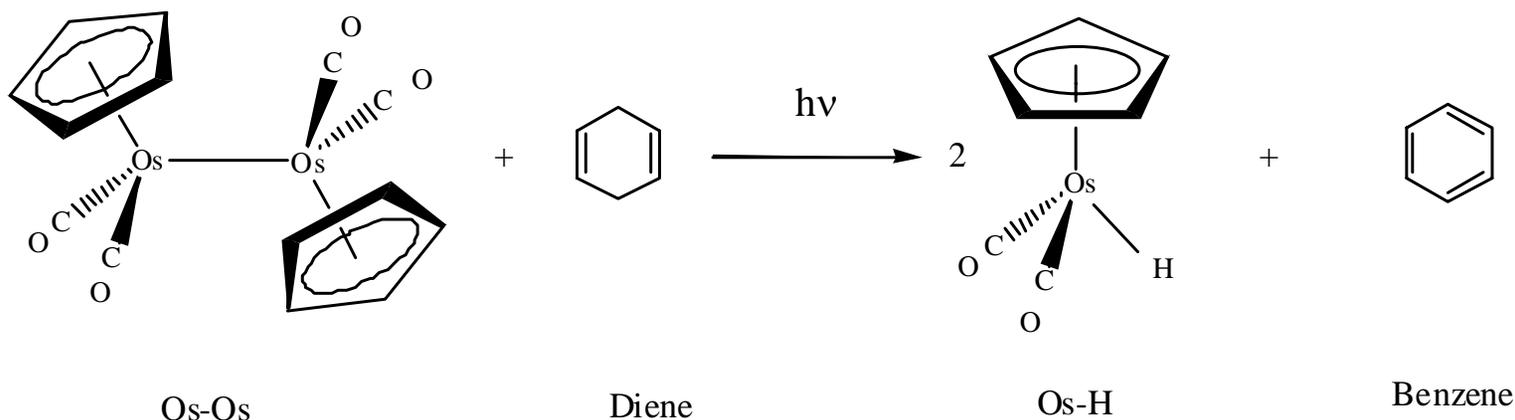
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**M= Mo, W complexes**



F. Wu, V. K. Dioumaev, R. M. Bullock

# C-H Bond Activation



**via hydrogen atom transfer**

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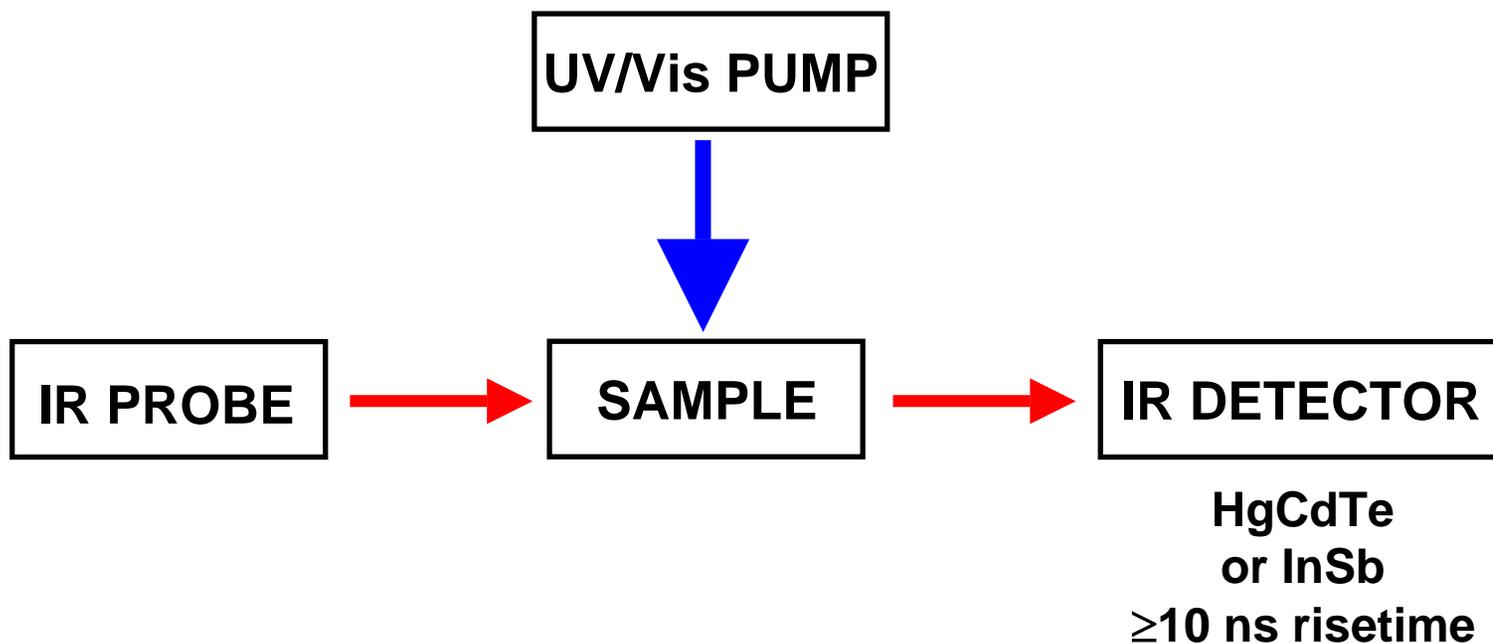
# Goals and Methods

- **To identify transient species and the reaction pathways for small molecule activation**
  - **Properties of redox active catalysts with vacant sites**
  - **Interaction with small molecules**
  - **Kinetics and thermodynamics of bond formation and cleavage**
- **Tools**
  - **Vacuum-line techniques**
  - **Ultra-pure dry solvents**
  - **Emission spectroscopy**
  - **UV-vis and FTIR spectroscopy**
  - **X-ray crystal structures, XANES, EXAFS**
  - **Pulse radiolysis**
  - **NMR ( $^1\text{H}$  and  $^{13}\text{C}$ )**
  - **Electrochemistry**
  - **CW photolysis**
  - **GC, LC/MS and FAB MS**
  - **Time-resolved IR and flash photolysis**



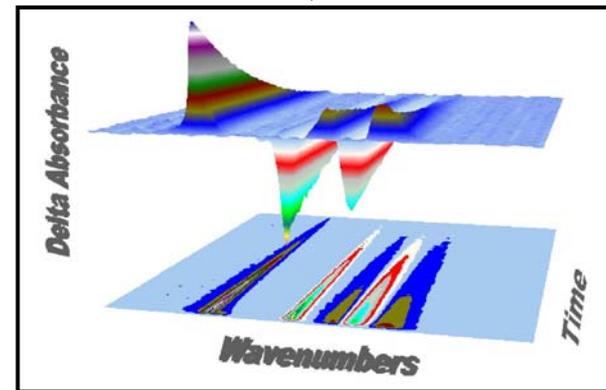
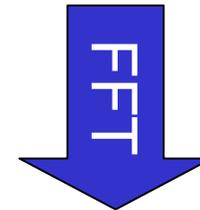
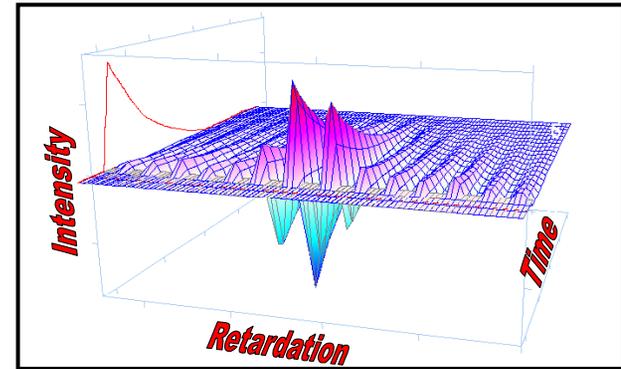
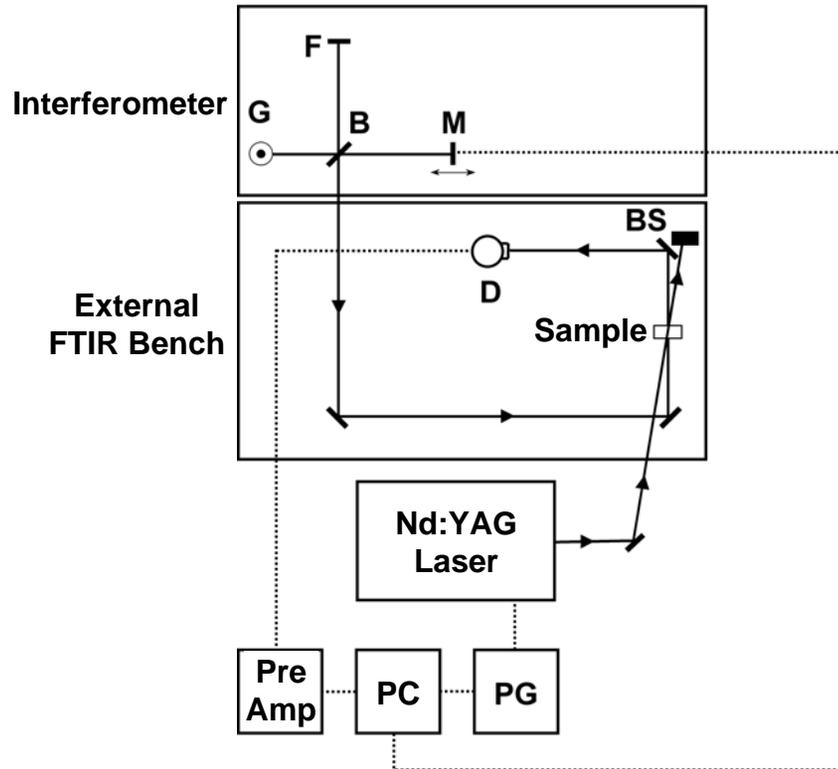
IR & UV-vis  
Spectra

# TRIR Spectroscopy



# Step-Scan FTIR

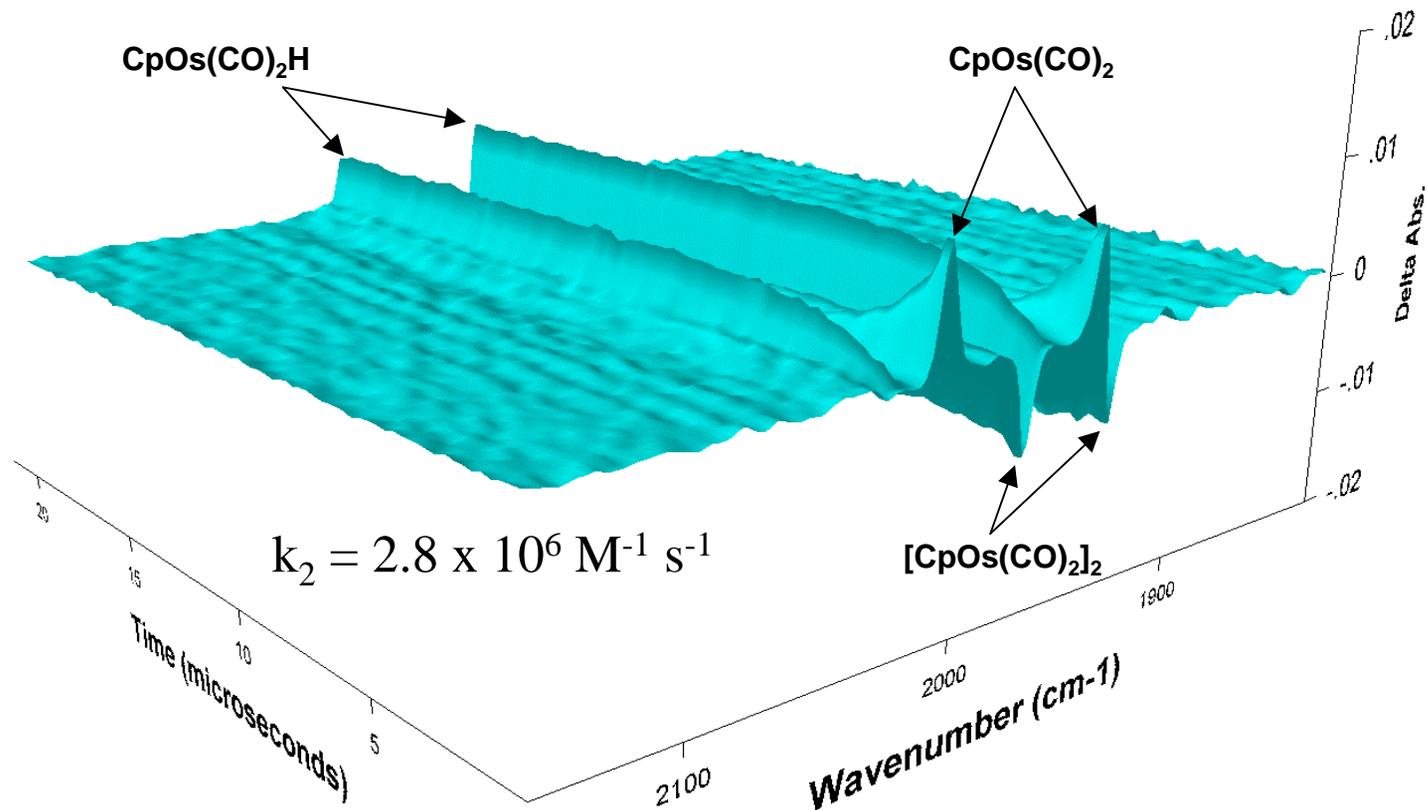
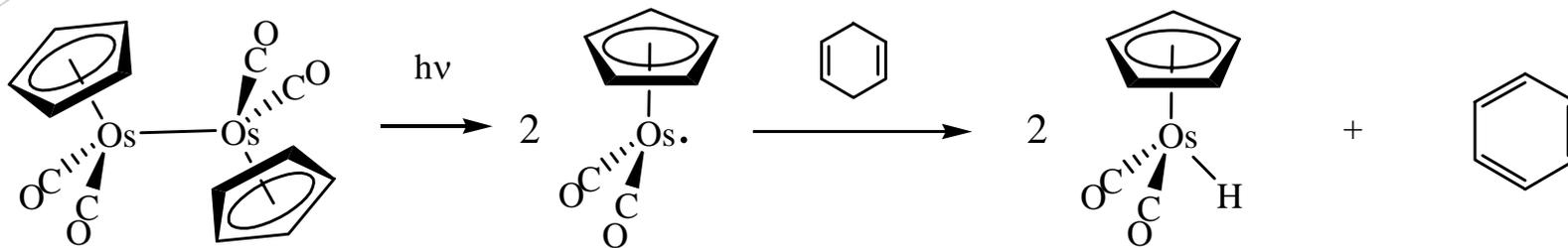
## Time-resolved interferograms



## Time-resolved FTIR spectra

# Carbon-to-Metal H Atom Transfer

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