X-ray Illumination in Solar Energy Conversion: Highlights of ANSER EFRC Work at the APS

Argonne-Northwestern Solar Energy Research (ANSER) Center

David M. Tiede
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Argonne National Laboratory

NORTHWESTERN UNIVERSITY

Argonne-Northwestern ANSER Solar Energy Research Center

Argonne NATIONAL LABORATORY

http://www.ANSERCenter.org

ANSER Center Institutions

CSE:
Chen, Poluektov, Tiede
MSD:
Elam, Martinson, Pellin
CNM
Wiederrecht

27 PI's Total

The ANSER Center joins established strengths at Northwestern University and Argonne National Laboratory (ANL) with those of senior personnel at Yale University, the University of Illinois at Urbana-Champaign, and the University of Chicago (UC) in molecular and nanostructured assemblies, materials, catalysts, and phenomena integral to solar energy conversion and storage.

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ANSER Research Subtasks

Subtask 1
Bio-inspired ***Molecular Materials for Solar Fuels***
Tiede, Ratner
Batista, Brudvig, Crabtree, Rauchfuss, Stupp, Wasielewski

Subtask 2
Interface Science for
Organic Photovoltaics
Marks, Chen
Chang, Freeman, Hersam, Mason, Poeppelmeier, Poluektov, Yu

Subtask 3
Nanostructured
Architectures for Photovoltaic and Solar Fuels Energy Conversion
Hupp, Kanatzidis
Pellin, Elam, Martinson, Schatz, Odom, Wiederrecht

ANSER Center Objectives

Develop a Fundamental Understanding of

- the interaction of light and charge with molecules and materials
- the energy levels and electronic structures of molecules and materials
- the dynamics of photoinduced charge generation, separation, and transport with unparalleled temporal and spatial resolution
- the interfaces at which charge generation, separation, transport, and selective chemical reactions occur
- the properties of unique materials, from self-assembling, bio-inspired materials for hydrogen fuel production from water to transparent conductors and nanostructured hard and soft materials for solar electricity generation.

Unique ANSER Center Identity

- **ANSER Center research is noted for placing a strong emphasis on combining cutting-edge time-resolved spectroscopic and structural techniques, e.g. x-ray, laser, EPR, to understand the mechanistic details of solar energy conversion to both *fuels and electricity*.**

- **This is made possible by ANSER's unique personnel portfolio, which includes a critical mass of researchers with strong backgrounds in both structure and spectroscopy as well as synthesis and materials fabrication.**

- **The ANSER Center focuses on both solar *fuels* and *electricity* using complementary approaches that provide solutions for both technologies.**

- **The ANSER Center focuses on multiple, hierarchical approaches to these problems with the goal of providing a fundamental science support base for DOE's Energy Innovation Hub, JCAP.**

APS in ANSER Research

Argonne-Northwestern ANSER Solar Energy Research Center

Subtask 1
Bio-inspired ***Molecular Materials for Solar Fuels***

Tiede, Ratner
Batista, Brudvig, Crabtree,
Rauchfuss, Stupp, Wasi…ki

Focus:
- Light-driven transition metal catalysis
- Time-resolved

Subtask 2
Interface Science for ***Organic Photovoltaics***

Marks, Chen
Cha… Hersam, Mason,
…uektov, Yu

Focus:
- Light-driven charge separation
- Thin film materials, interfaces

Subtask 3
***Nanostructured** Architectures for Photovoltaic and Solar Fuels*
Energy Conversion

Hupp, Kanatzidis
Pellin, Elam, Martinson, Schatz,
Odom, Wiederrecht

X-ray spectroscopy (XANES, XAFS)
X-ray scattering (HEXS-PDF)

Grazing incidence X-ray scattering (GISAXS)

Subtask 1: Bio-inspired Molecular Materials for Solar Fuels

Subtask 1 Leaders: David Tiede (ANL) and Mark Ratner (NU)

Subtask 1 Members:

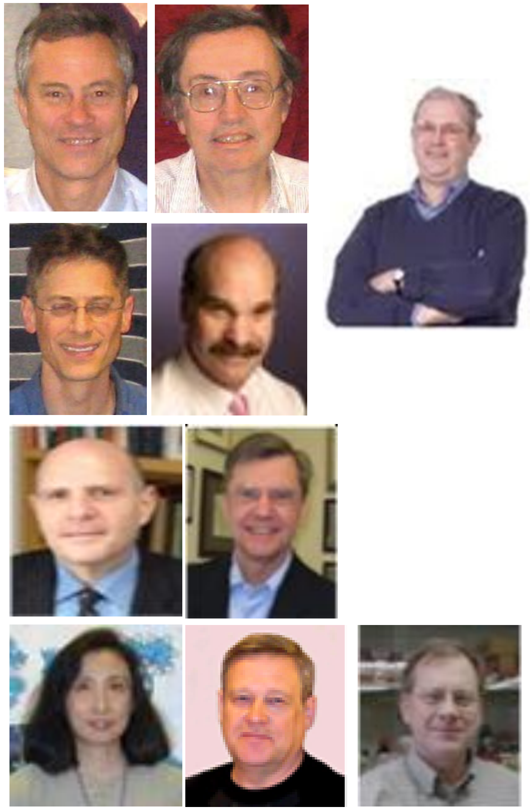
Gary Brudvig & Bob Crabtree (Yale)
⇒ design, synthesis & characterization of water-oxidation catalysts

Tom Rauchfuss (UIUC)
⇒ design, synthesis & characterization of proton-reduction catalysts

Victor Batista (Yale) & Mark Ratner (NU)
⇒ theoretical characterization

Sam Stupp & Mike Wasielewski (NU)
⇒ self-assembly of light-harvesting and catalytic modules
⇒ develop light-harvesting & charge separation modules wired to catalysts

Lin Chen, Oleg Poluektov & David Tiede (ANL)
□ spectroscopic and structural characterization



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Scope of work:

- Homogeneous: molecular, solution
- Inhomogeneous: thin films

Experiment:

Water-oxidation catalysts: e- source, O_2 evolving

- Ir-Cp* complexes solution (Crabtree, Brudvig groups, Yale)
- Ir-oxide electrode films (Crabtree, Brudvig groups, Yale)
- 1st row transition complex models (Crabtree, Brudvig groups, Yale)

Water-reduction catalysts: H_2 fuel evolving

- Fe-Fe hydrogenase mimics (Rauchfuss group, UIUC)
- Co-Cp complexes (Rauchfuss group, UIUC)
- “Dubois” Ni catalysts (Tiede, ANL and Wasielewski group, NU)

Hierarchical assemblies: i.e., linked to light

- Photosensitizer-catalyst assemblies (Wasielewski group, Subtask 1)
- Semiconductor-catalyst/photosensitizer (Yale group, Subtask 3)

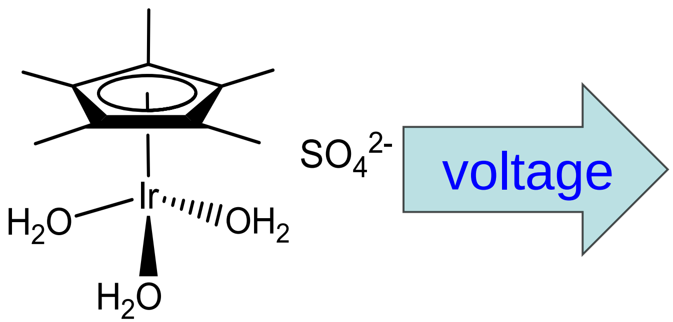
Theory:

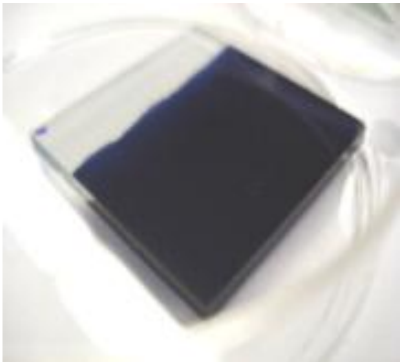
- **Use of X-ray structural data for testing/development of coordinate models (Batista, Yale)**

Example: Characterization Ir-oxide Blue Layer Catalyst Film

J. Blakemore, R. Crabtree, G. Brudvig, Yale University

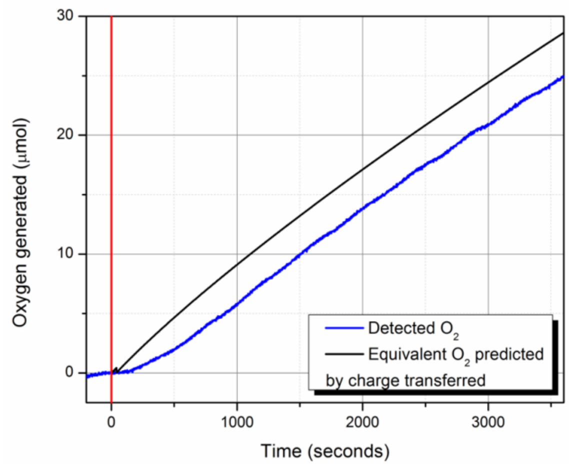
Solution Precursors





Highly active water-splitting catalyst amorphous film ($0.45 per ft²!)

Faradaic yield of O2 is ~ 100%



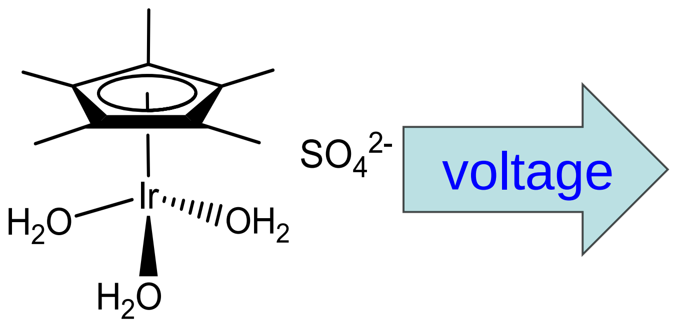
Same slope: stoichiometric oxygen evolution

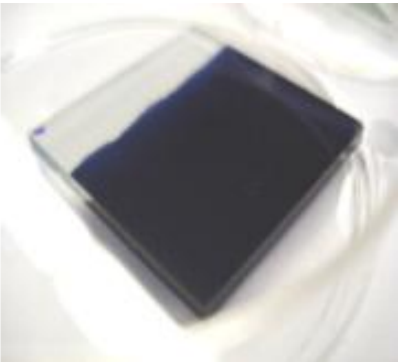
Best O_2 catalyst to-date

Example:
Characterization Ir-oxide Blue Layer Catalyst Film

J. Blakemore, R. Crabtree, G. Brudvig, Yale University

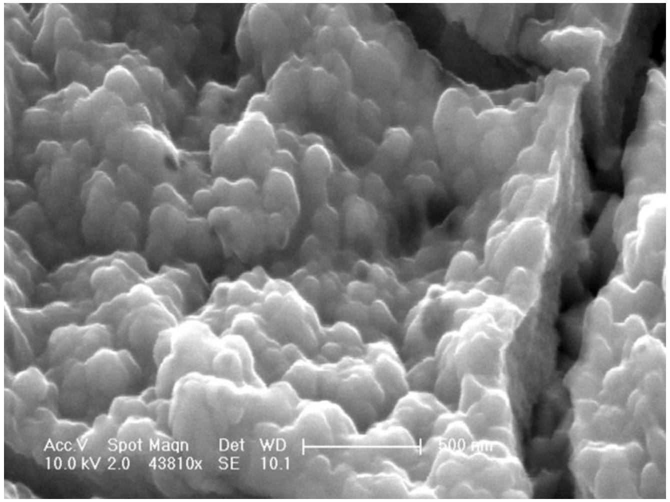
Solution Precursors





Highly active water-splitting catalyst amorphous film ($0.45 per ft^2!)

SEM:



- *Amorphous*
- *Insoluble film*
- *Difficult to characterize*
- *Reoccurring motif: "heterogenized" solar catalyst films*

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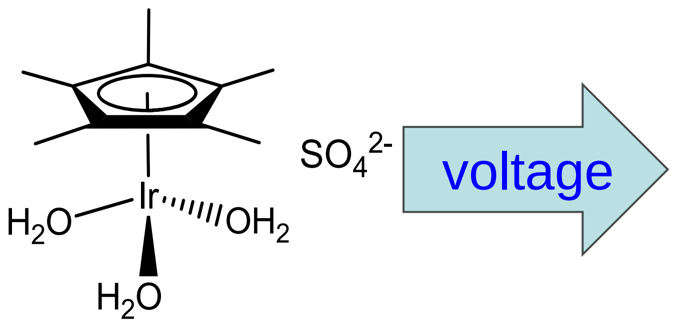
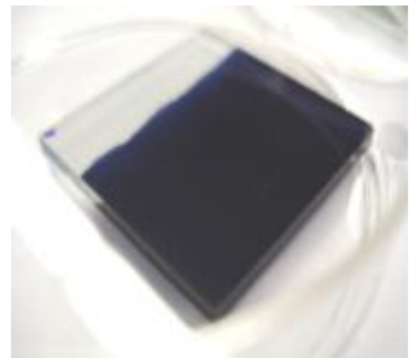
Example: Characterization Ir-oxide Blue Layer Catalyst Film

J. Blakemore, R. Crabtree, G. Brudvig, Yale University

Solution Precursors





Highly active water-splitting catalyst amorphous film ($0.45 per ft²!)

Mechanistic questions:

- What is this film?
- How did it form?
- How and why does it work so well?

- Can concepts here be used for development of 1st row transition metal catalysts? (feedback to cat. synthesis: Yale, UIUC, NU)

Solar Fuels Catalysts X-ray Characterization

Approach:
Multiple length-scale, *in-situ* Structure Characterization:

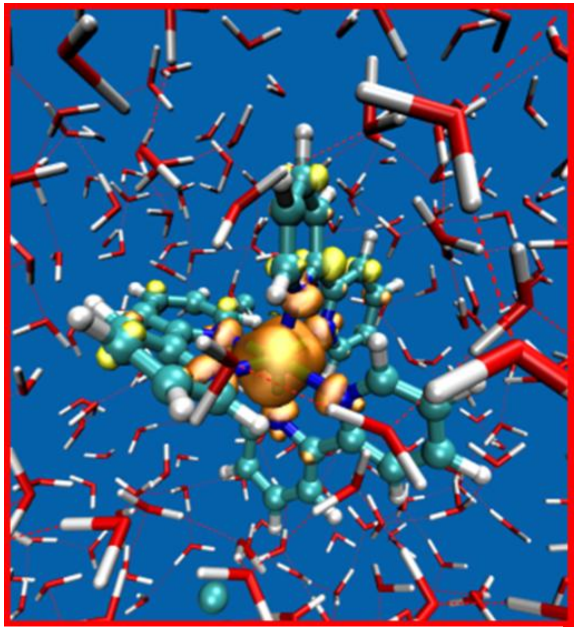
a) X-ray absorption spectroscopy (XAS) and fine structure (XAFS)- Lin Chen

- Metal atom oxidation state
- Electronic structure
- Inner sphere atomic structure

b) High Energy X-ray Scattering (HEXS) and Pair Distribution Function (PDF) Analyses- D. Tiede

- Inner and outer sphere atomic structures
- Ensemble structure
- Solvent interactions

Multi-Scale addressed theoretically



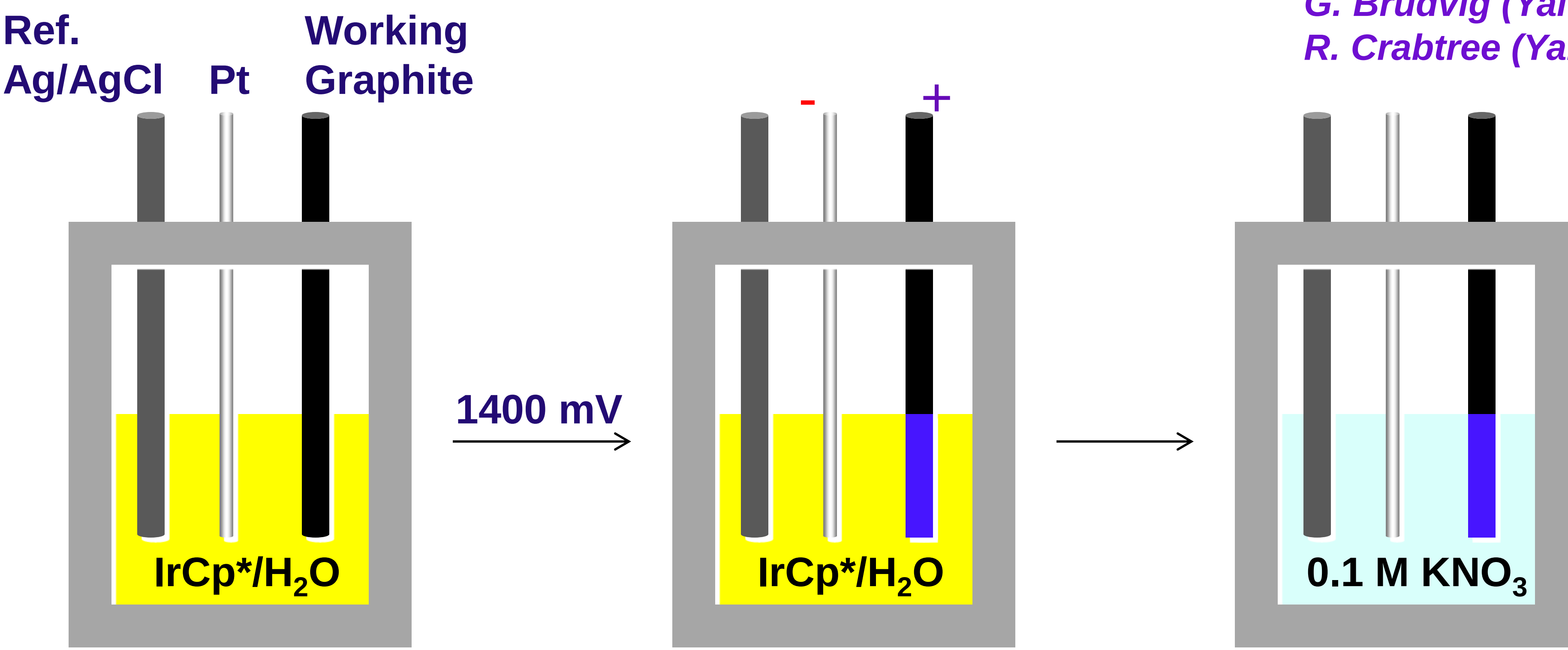
QM-MM/MD model $[Fe(bpy)_3]^{+2}$ in water
Daku and Hauser, JPC. Lett. (2010) 1:1830

Combination:

- Enables Multiple Length-Scale Structure Characterization
- Relate *in-situ* structure to catalysis → mechanism, design
- Extendable to pump-probe time-resolved:
    - follow the trail: electron transfer, structure, function

In-situ XAFS: Redox Cycling

M. Mara (NU)
J. Huang (ANL)
L. Chen (ANL-NU)
J. Blakemore (Yale)
G. Brudvig (Yale)
R. Crabtree (Yale)



- IrCp* precursor was electrodeposited onto the graphite working electrode at 1.4 V
- Precursor solution was replaced with 0.1 M KNO_3 solution and film structure was varied as a function of applied voltage

Metal-centered structure change linked to catalysis

M. Mara (NU)
J. Huang (ANL)
L. Chen (ANL-NU)
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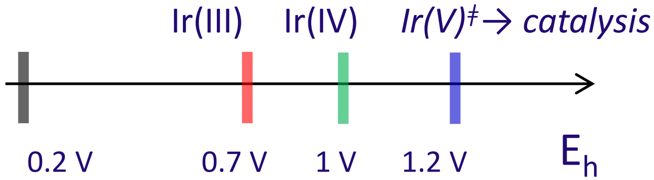
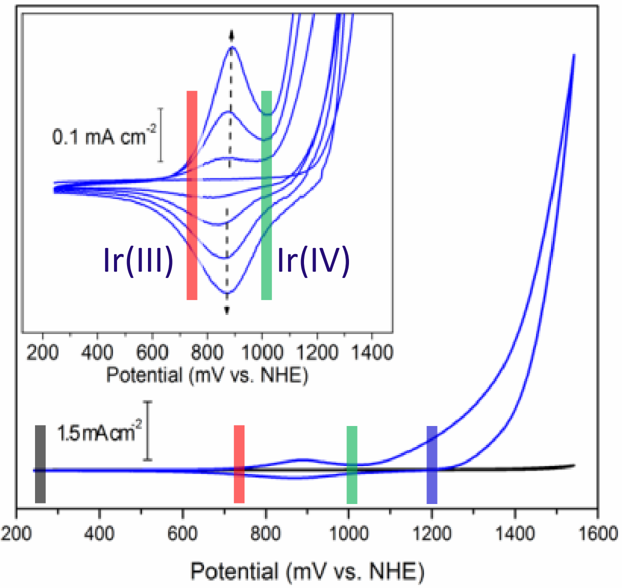
G. Brudvig (Yale)
R. Crabtree (Yale)

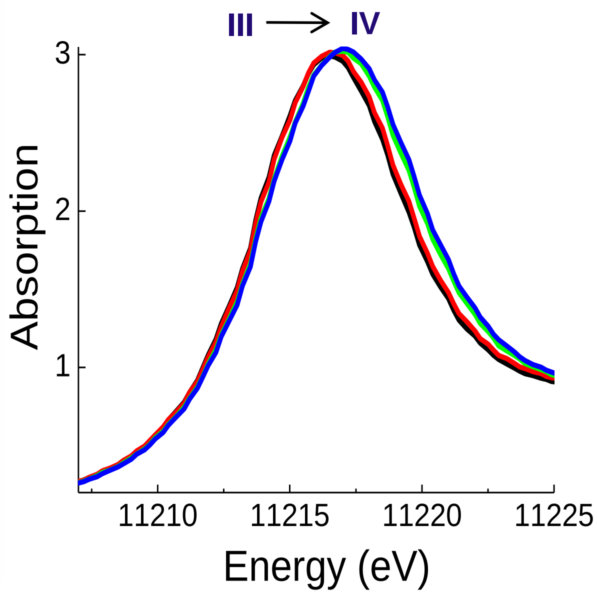


E-chem



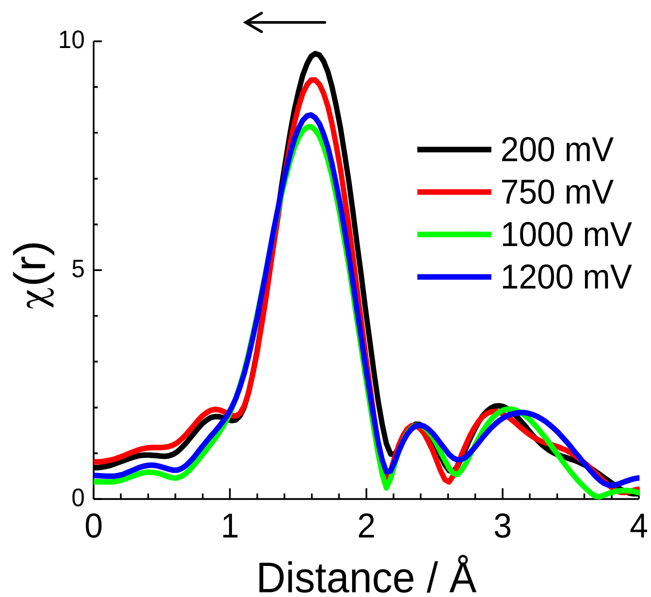
XANES

5d L-edge absorption



XAFS

Metal-center structure



Find:

- No accumulation of Ir(V) with on-set of catalysis
- Coordination structure change linked Ir(III) → Ir(IV) redox transition
- CW echem technique not capture transition state(s) !

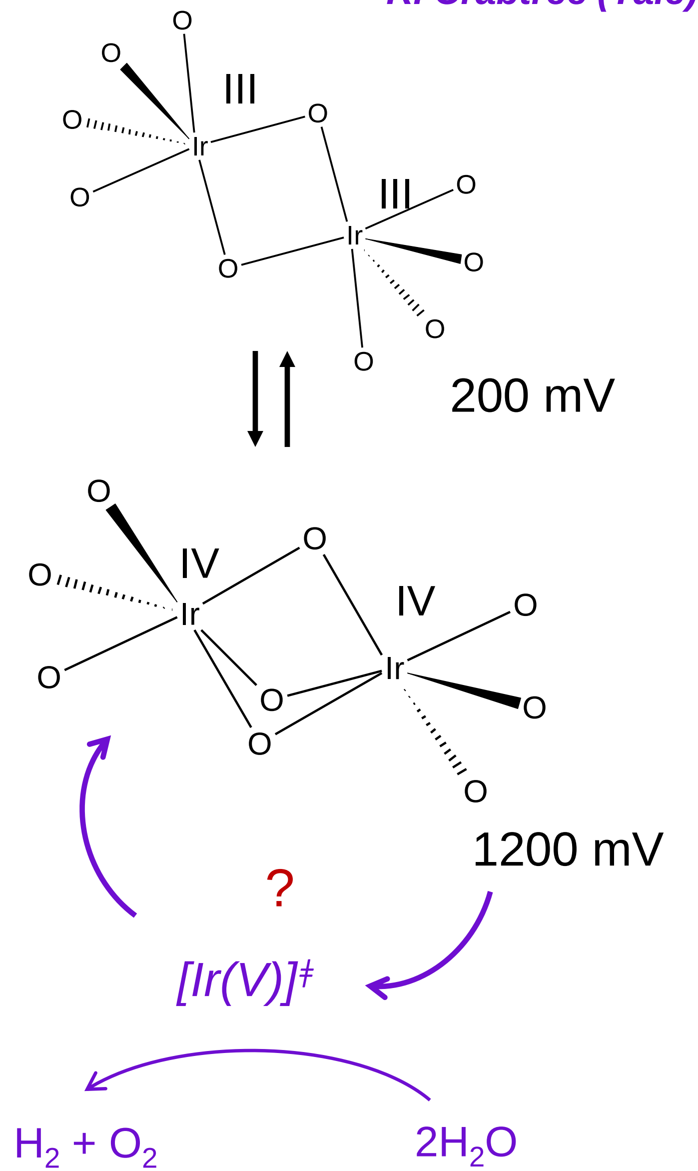
Voltage-Dependent Structural Changes

M. Mara (NU)
J. Huang (ANL)
L. Chen (ANL-NU)
J. Blakemore (Yale)
G. Brudvig (Yale)
R. Crabtree (Yale)

Oxidation state driven changes Ir(III) → Ir(IV):

- Ir-O bridging and Ir-Ir distances decrease
- Ligand geometry: *di-to-tris- μ-oxo*

Structural Parameters		
	200 mV	1200 mV
Ir-O (bridging)	1.97 Å n = 2	1.94 Å n = 3
Ir-O (terminal)	2.11 Å n = 4	2.11 Å n = 3
Ir-Ir	3.02 Å	2.99 Å
Ir-O (outer)	3.81 Å	3.73 Å



- Metal-centered, inner sphere structure characterization

Characterization of multi-scale structure in BL: HEXS-PDF

D. Tiede (ANL)
O. Kokhan (ANL)
J. Blakemore (Yale)
G. Brudvig (Yale)
R. Crabtree (Yale)

High Energy X-ray Scattering (HEXS):

- 60 keV to 100 keV X-rays
  - *High energy synchrotron X-ray light sources (APS)*

- Offers highest resolution (d ~ 0.15 Å) PDF analysis

Pete Chupas
Karina Chapman
APS
Beamline 11-ID-B

Characterization of multi-scale structure in BL: HEXS-PDF

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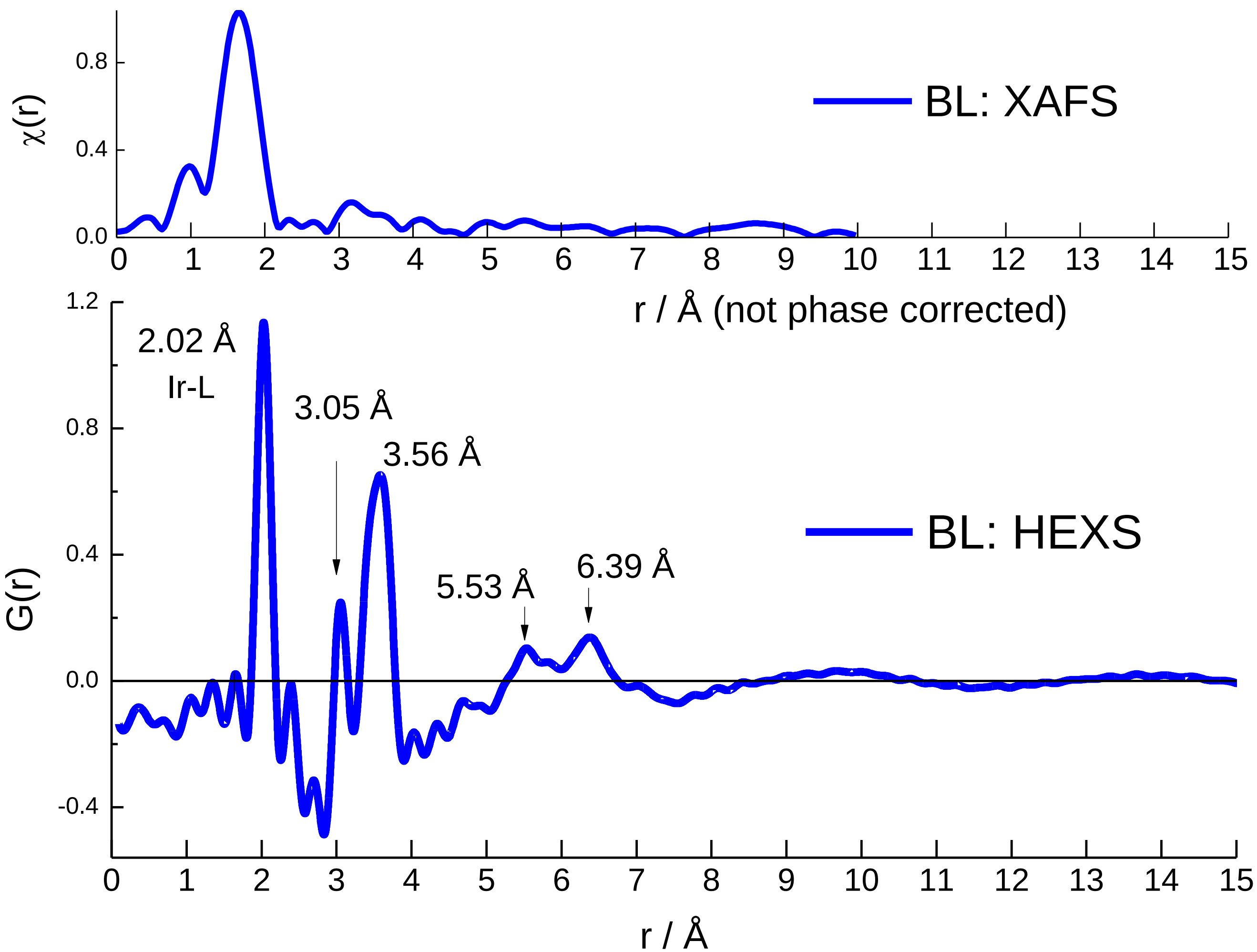

- **ANSER taking lead in developing combined XAFS/HEXS analyses approaches for solar fuels catalysts**

XAFS:
- Metal-centered, exclusive
- Distance phase (path) sensitive

HEXS:
- All atom
- Distance phase (path) independent
- Multi-scale 0.1 Å to 100s nm

Combination:
- Two independent direct measures of structure
- Two different “selection” rules (*i.e.*, complementary information)
- Enhanced resolution of structure

Characterization of multi-scale structure in BL: HEXS-PDF

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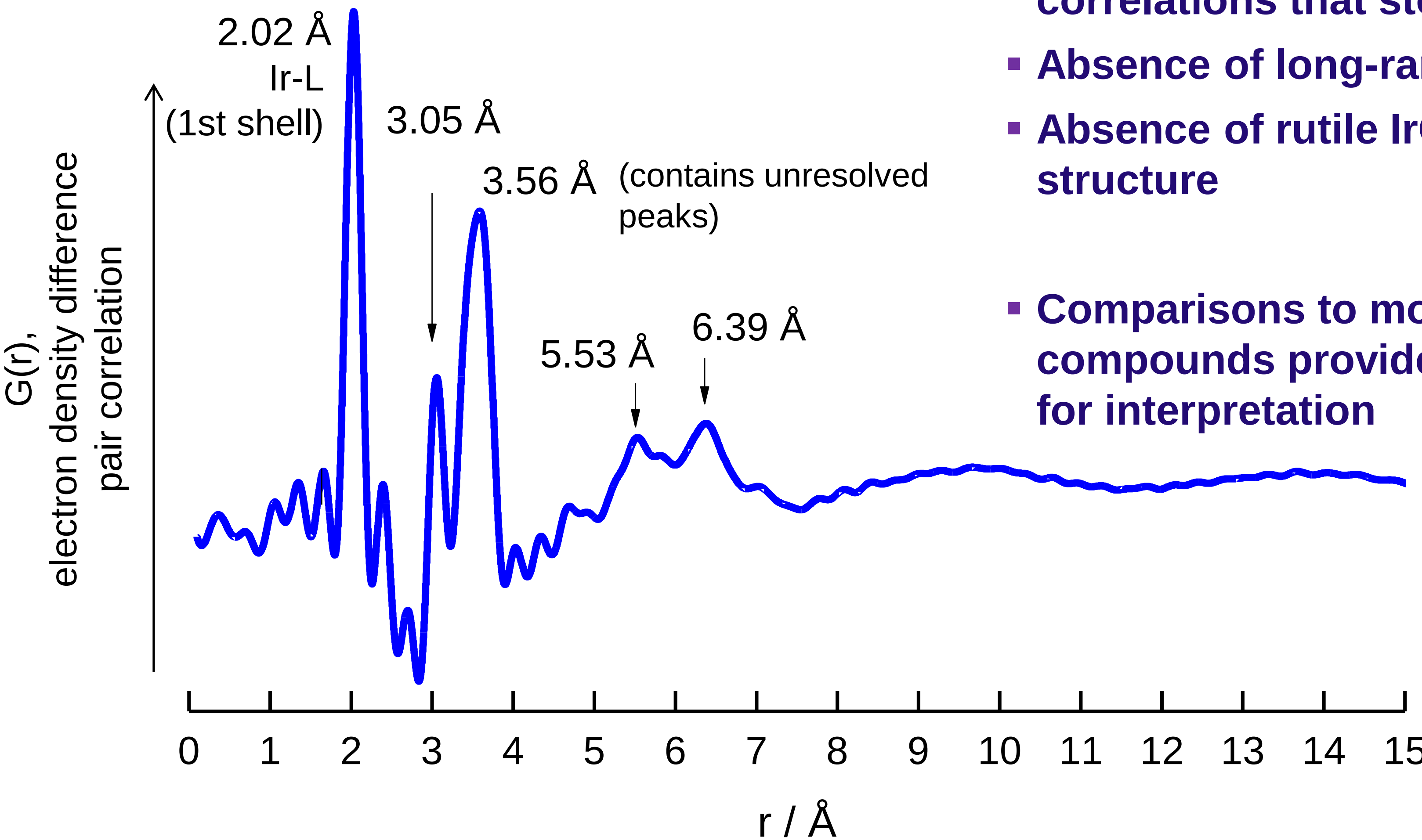
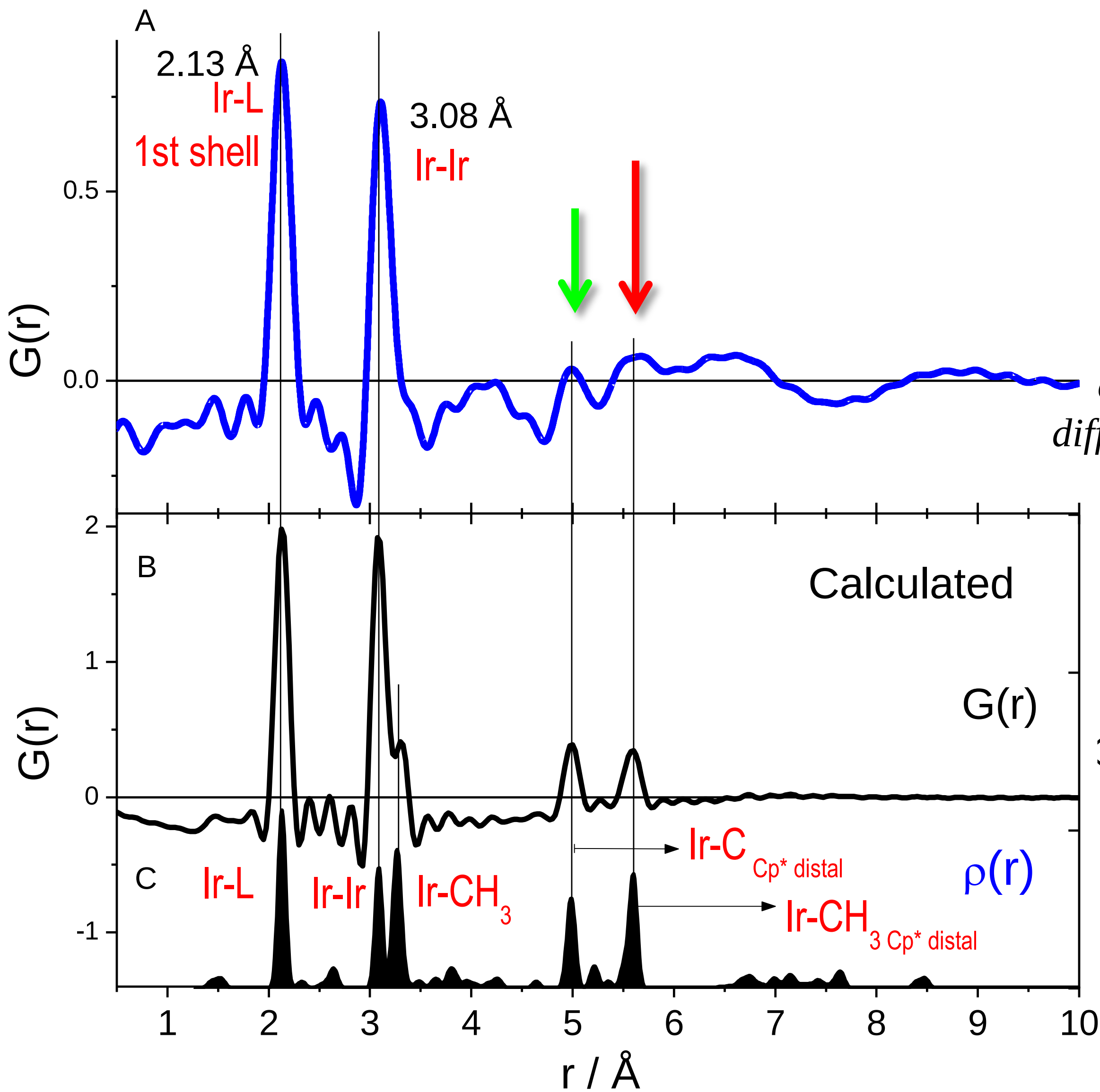


BL HEXS:

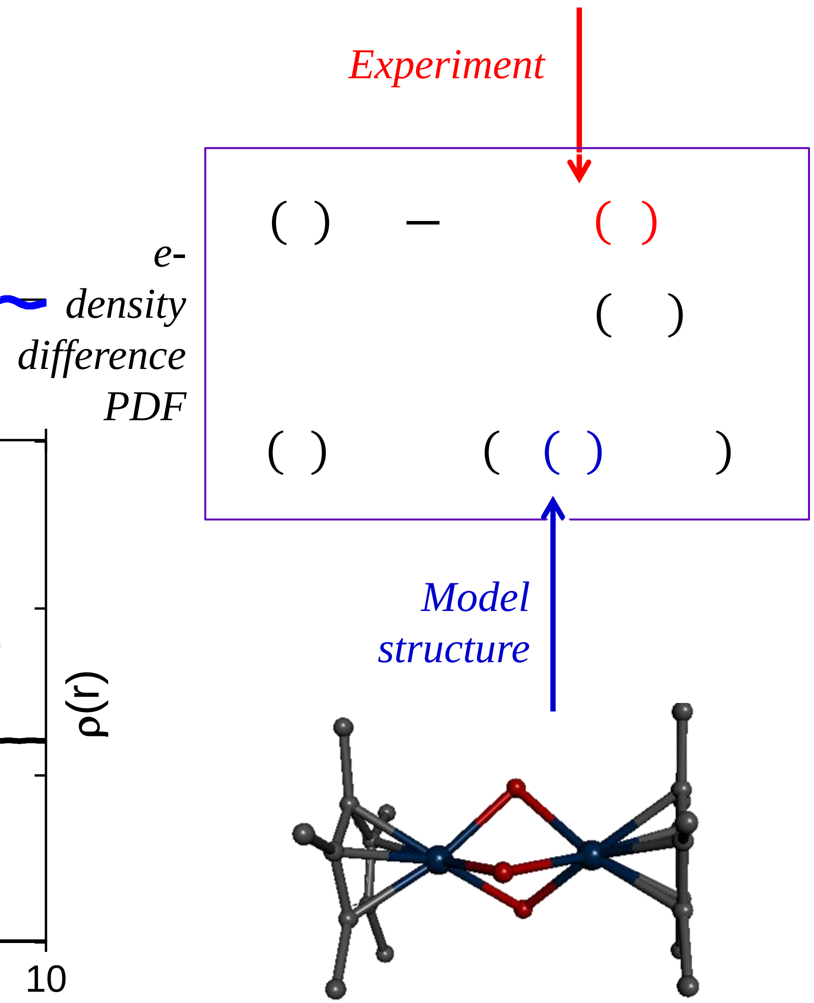
- **Distinct pattern of pair correlations that stop by 7 Å.**
- **Absence of long-range order**
- **Absence of rutile IrO_2 structure**

- **Comparisons to model compounds provide guide for interpretation**

HEXS of solution-state IrCp* complexes

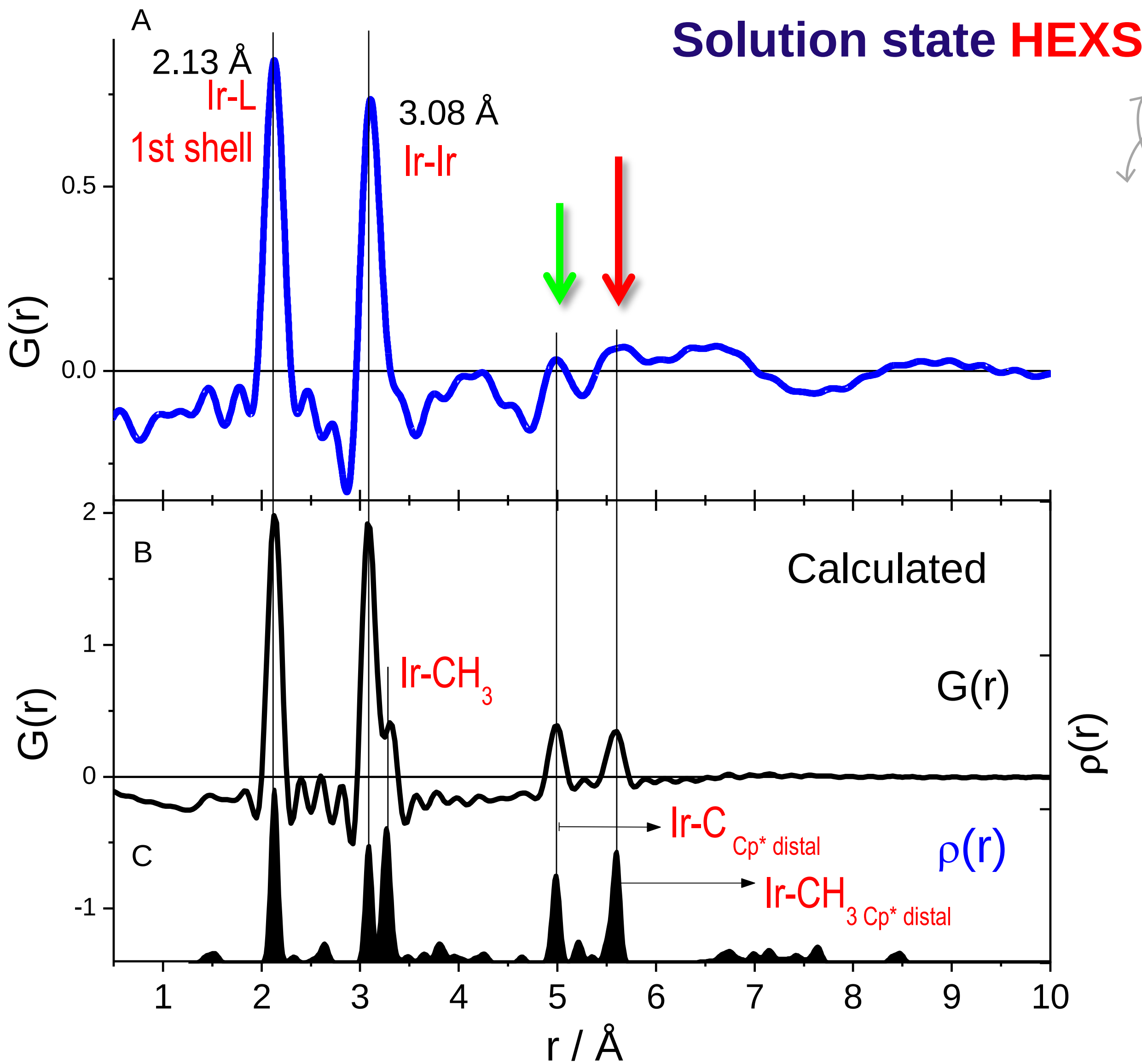


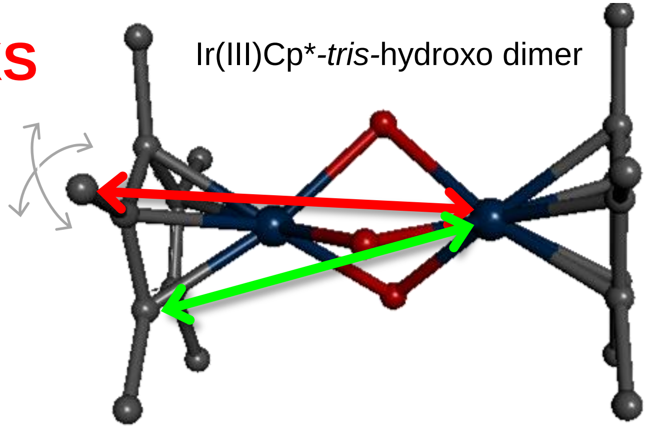
Solution state HEXS



Ir(III)Cp*-*tris*-hydroxo dimer

HEXS of solution-state IrCp* complexes

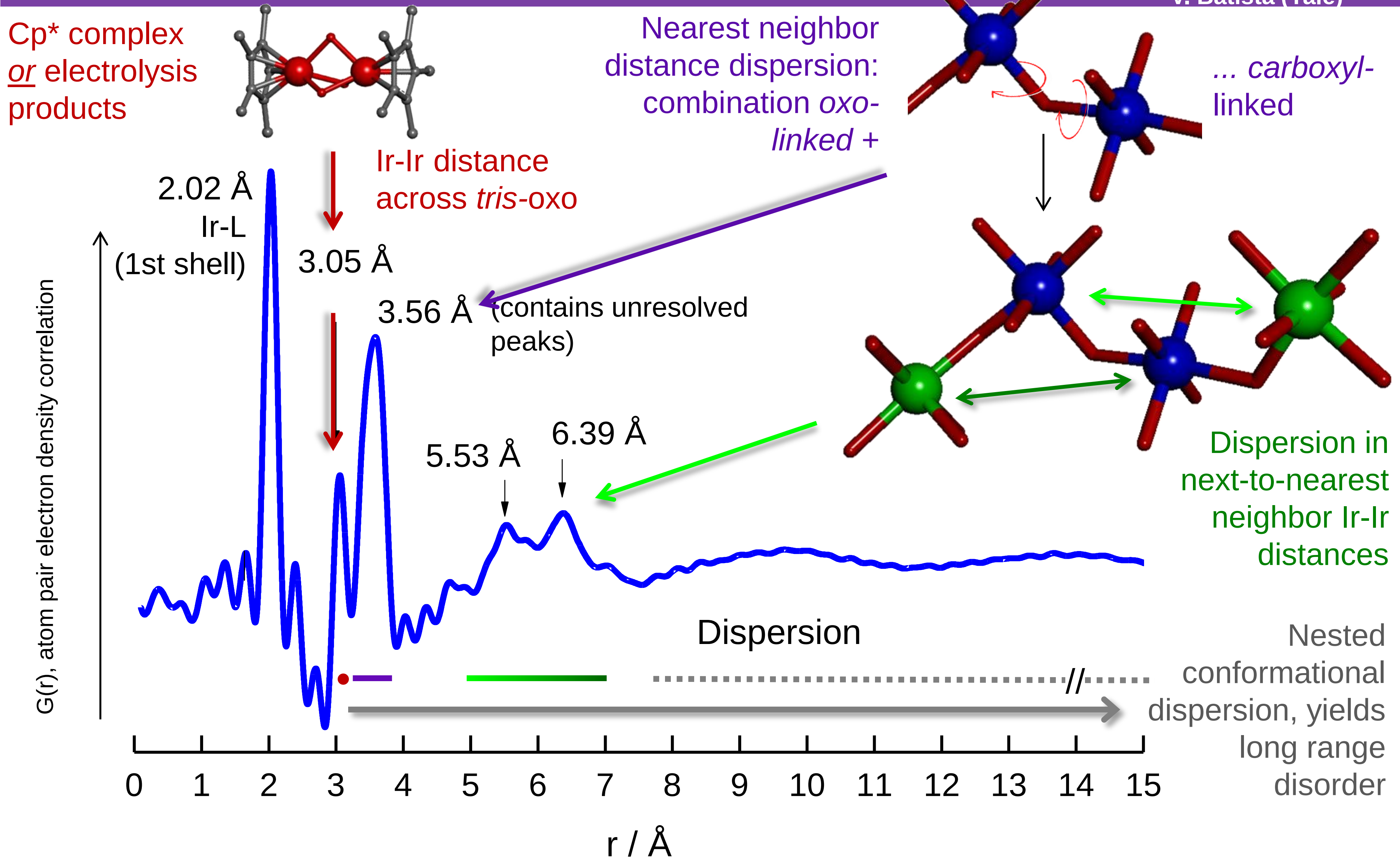




- **HEXS-PDF direct, X-ray method to achieve atomic scale resolution in solution**
- **Resolve effects of thermal factors and structural disorder**
- **Suitable to provide quantitative benchmarks for comparison to computational models**

Nested Disorder in BL:

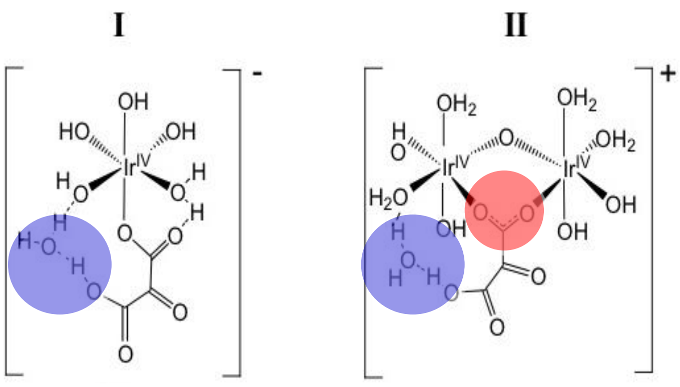
D. Tiede (ANL)
O. Kokhan (ANL)
J. Blakemore (Yale)
G. Brudvig (Yale)
R. Crabtree (Yale)
V. Batista (Yale)

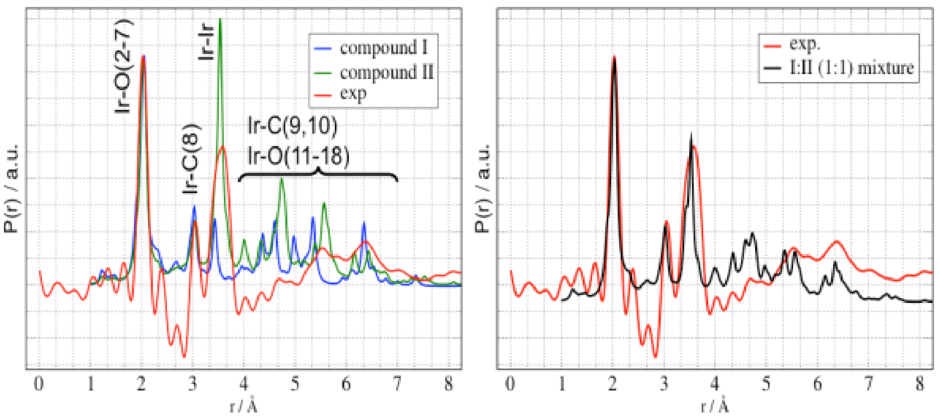


First Principles Modeling of Ir Blue Layer Film: Benchmarking to X-ray Data

Victor Batista:

- Simulated annealing, Monte Carlo (MC)
- Density functional theory (DFT) calculations
- Comparison to analogous coordination chemistry





- Comparison of model **PDF** to experimental **G(r)** suggests BL can be described as 1:1 combination of structures **I** and **II.** **Introduces:**
  - Carboxyl bridged Ir-Ir
  - Acid-base chemistry for proton-coupled electron transfer catalysis

- This is the start of 1st principles modeling. On-going work developing further support for this model

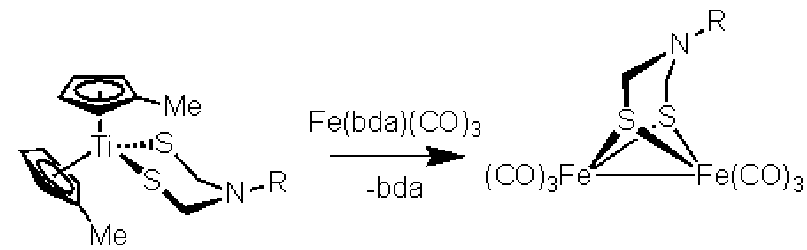
- Mark Ratner: presentation

Substituted FeFe complexes for enhanced H_2 catalysis and stability

T. Rauchfuss, UIUC

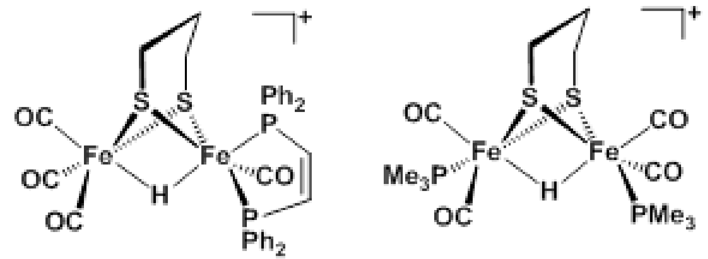
Novel Synthetic Routes to Hydrogen-Evolution Catalysts

- Titanocene carriers for dithiolate complexes



Phosphine FeFe derivatives

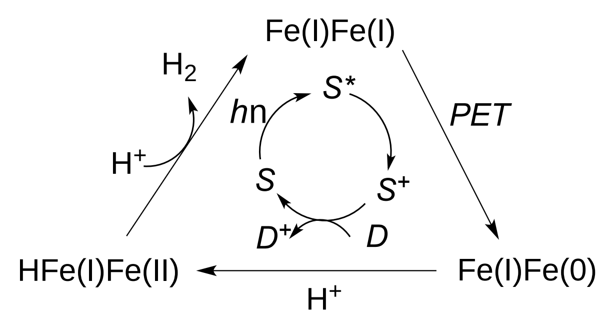
- Enhanced metal-carbonyl bonding
- Enhanced photostability



$[HFe_2(pdt)(dppv)(CO)_4]^+$ $[HFe_2(pdt)(PMe_3)_2(CO)_4]^+$

FeFe hydrides for photosensitized and photochemical hydrogen production

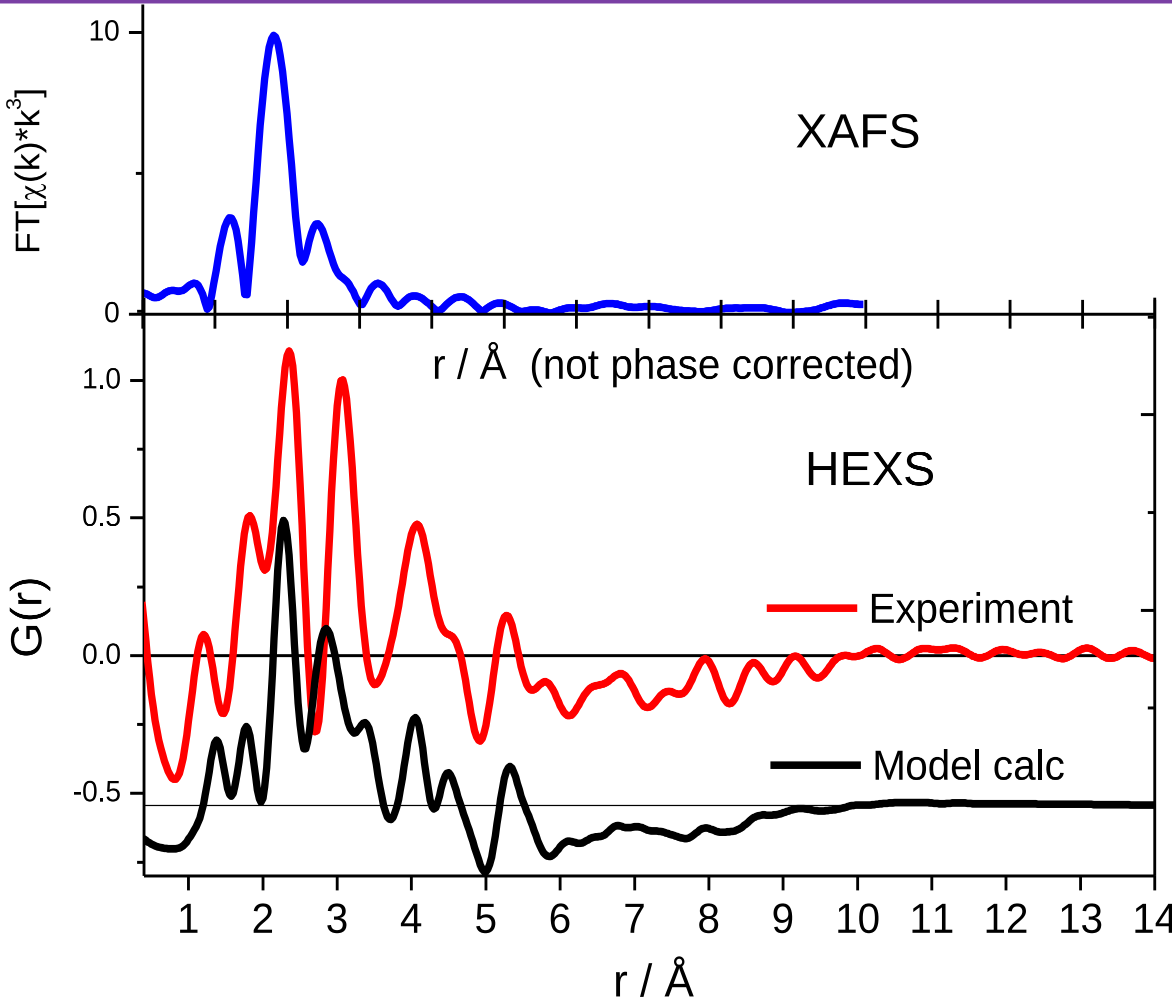
- Amanda Smeigh presentation
  M. Wasielewski (NU)

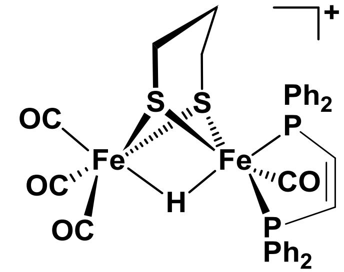


- **Multiple length-scale X-ray structural characterization**

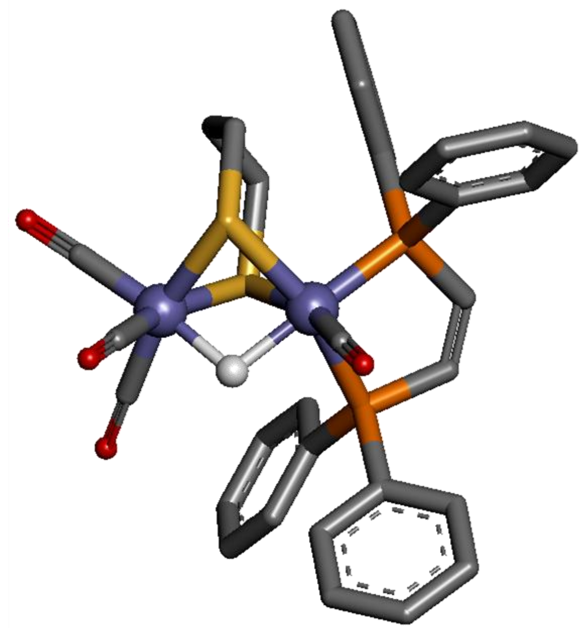
Combined XAFS and HEXS DiFe-Hydride

D. Tiede
J. Huang
M. Mara
L. Chen
W. Wang
T. Rauchfuss





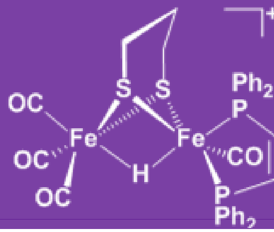
$[HFe_2(pdt)(dppv)(CO)_4]^+$



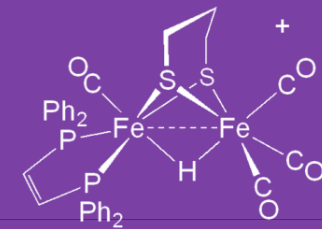
New opportunities *in-situ*, high-resolution structure characterization:

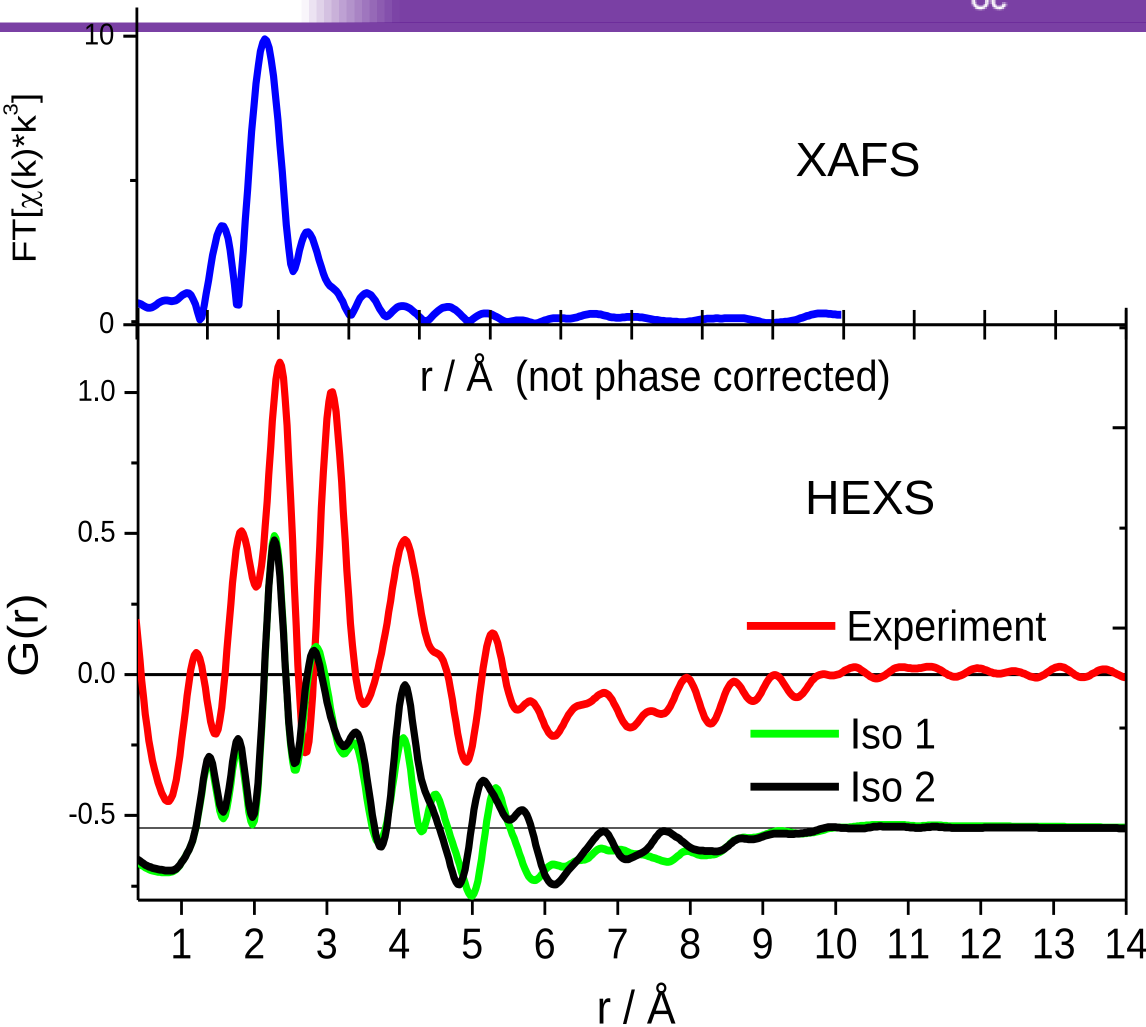
- Model structure refinement
- Catalysis-linked coordination change

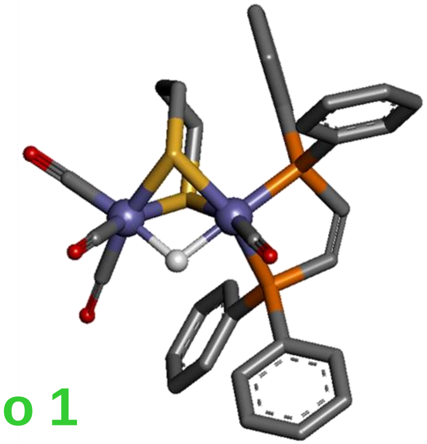
Isomers:



vs

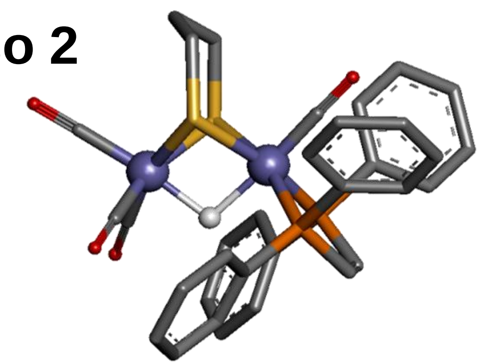






Iso 1

Iso 2



<u>*New*</u> opportunities *in-situ*, high-resolution structure characterization:

- Model structure refinement
- Detailed catalysis-linked coordination structure change

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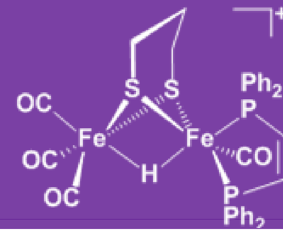
Isomers:



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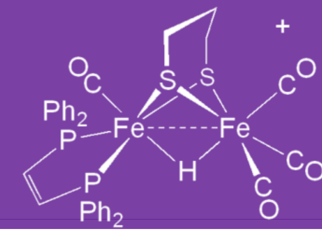
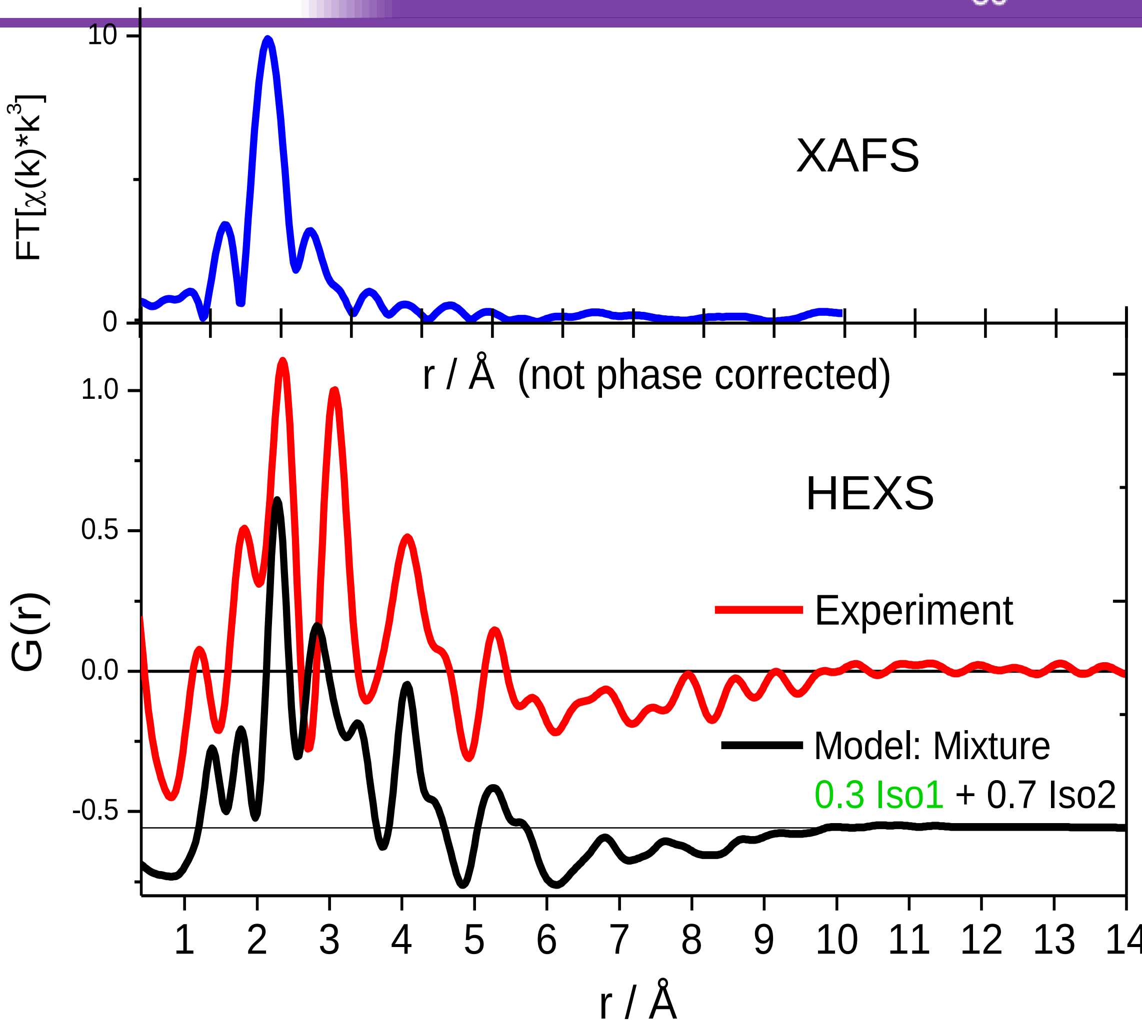
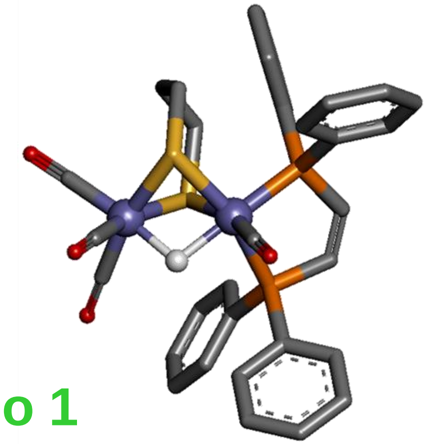
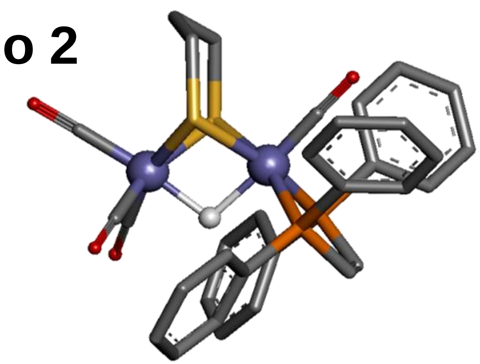






Iso 1

Iso 2



New opportunities *in-situ*, high-resolution structure characterization:

- Model structure refinement
- Detailed catalysis-linked coordination structure change

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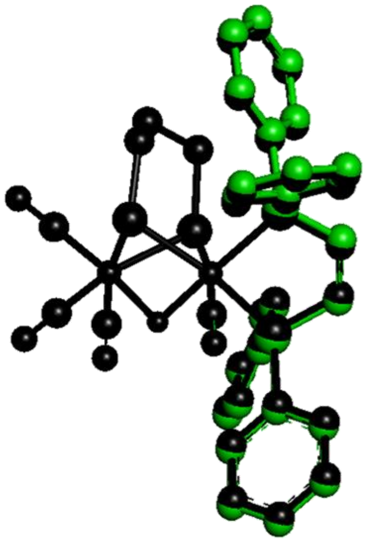
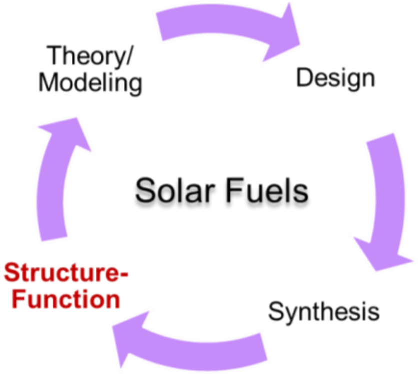
Conclusions: Solar Fuels Catalyst X-ray Characterization

- **Combined XAS-HEXS provides multi-scale measure structure**
- **New opportunities in-situ, high-resolution structure-function analyses:**



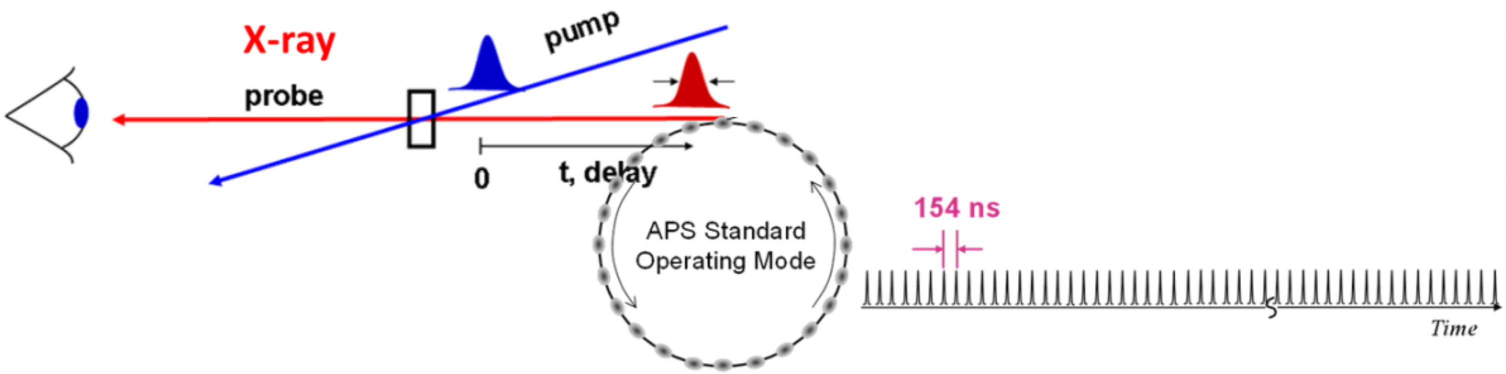
  - **Model structure refinement**
  - **Measure detailed, catalysis-linked coordination structure change**
  - **Applicable to both *in-situ* homogeneous and heterogeneous catalysis**

  - **Unique feature of ANSER:**
    - **multi-scale atomic approach to solar fuel catalyst structure-function analysis**
  - **Provide quantitative benchmarks modeling, solar catalyst design iteration**



Moving forward: Solar Fuels Catalyst X-ray Characterization

- **XAFS-HEXS determined structure for water-splitting, water-reduction catalyst theory (Batista, Ratner), design, synthesis (Brudvig, Crabtree, Rauchfuss)**
- **Real-time and Pump-probe time-resolved, in-situ X-ray characterization: structure following single-turnover, sequential single-electron transfer chemistry. Capture intermediate state structures (Chen, Tiede)**



- **Multi-scale (XAFS-HEXS) characterization of hierarchical assemblies**
  - **Subtask 1 - Linked photosensitizer-catalyst assemblies (Wasielewski, Brudvig, Crabtree, Rauchfuss, Stupp)**
  - **Subtask 2 - TCO films (Mason, Chang, Poeppelmeier)**
  - **Subtask 3 - Chalcogel-based films (Kanatzidis)**

Argonne-Northwestern ANSER Solar Energy Research Center

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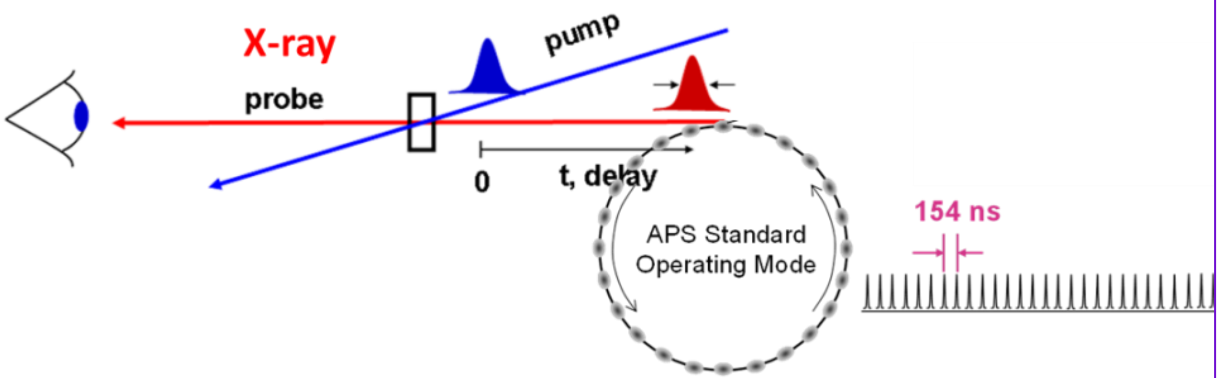

APS:
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Naran Dashdorj

Pete Chupas
Karina Chapman

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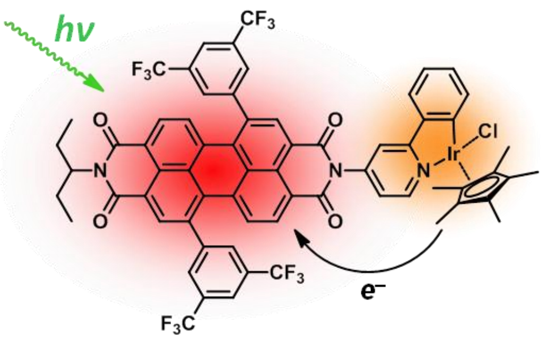
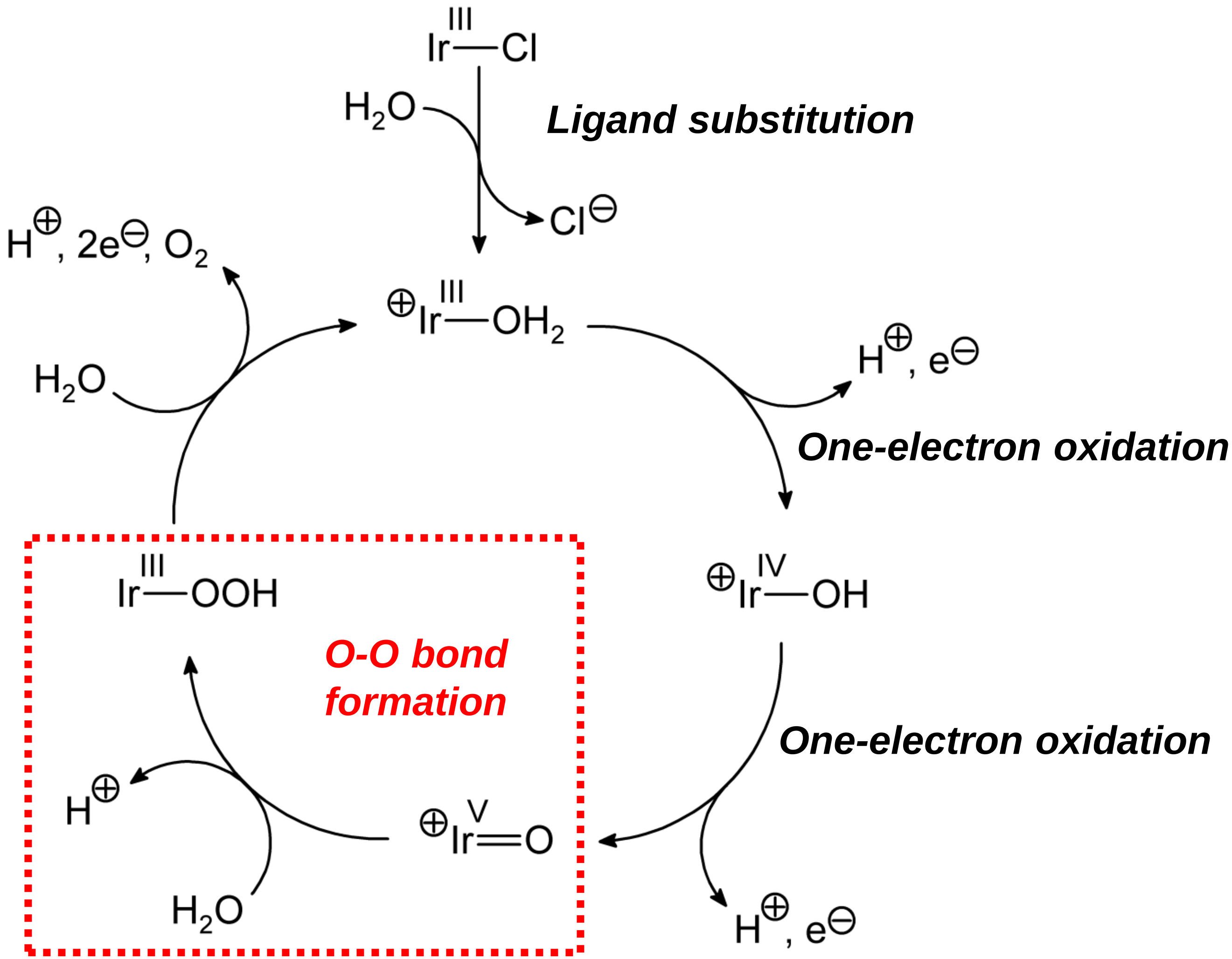
Thanks!

….. Questions, Comments?

Proposed Mechanism for Oxygen Evolution



charge separation module wired to water-oxidation catalyst
(**Wasielewski**, NU)



James Blakemore, **Brudvig**, **Crabtree** *et al.* (2010) *J. Am. Chem. Soc.* 132, 16017.