EPR spectroscopic studies of the electronic and atomic requirements in

Catalytic Water Oxidation by Ruthenium Complexes
Introduction to my project
EPR
  - What is EPR?
  - How does it work?
Data
  - Temperature Dependence
  - Power Dependence
  - Analysis of EPR Spectra
Oxygraph
  - Overview
  - Graphs
Water Splitting

- Utilization of sun light requires solar capture, light-to-energy conversion and storage
- Ruthenium complexes are capable of water splitting

\[ 2H_2O \rightarrow O_2 + 4H^+ + 4e^- \]

\[ 4Ce(IV) + 2H_2O \rightarrow 4Ce(III) + O_2 + 4H^+ \]
What is EPR?

- Electron Paramagnetic Resonance technique for studying chemical species that have one or more unpaired electrons
How does EPR work?

- Magnetic moment makes electron act like a bar magnet
- Apply external magnetic field
- Unpaired electrons can move between their two spin states
- Net absorption of energy, and it is this absorption which is monitored and converted into a spectrum
EPR Spectrometer

Microwave Bridge housing microwave source and detector

Cavity and Sample

Magnet

CONSOLE
EPR signal – First derivation of absorption signal

Size of EPR signal used to measure concentration
Knowledge of the $g$-factor can give information about a paramagnetic center's electronic structure.

- Isotropic: $g_x = g_y = g_z$
- Uniaxial: Two principal values coincide but the third is different
- Rhombic: $g_x \neq g_y \neq g_z$

Some important classes of paramagnetic systems that show such anisotropy include:

1. Free Radicals
2. Transition ions surrounded by ligands
3. Point Defects
Orientations

Fig. 1. Schematic representation of g-tensor and the consequential e.p.r. spectra
Ru 3 Solution

Actual and Simulated Ruthenium 3 solution

\[ \Delta E = h\nu = g\beta B \]
Rhombic Ru 3
Power Dependence

Power dependence curves of 3,4 and 4,4 OOH

- 3,4 at 20 K
- 4,4 at 20 K
- 3,4 at 140 K
- 4,4 at 140 K
Temperature Dependence

Temperature Dependence of 4,4 OOH

Temperature Dependence of 3,4
Curie’s Law (general overview)

- This relation was discovered experimentally by Pierre Curie.
- It only holds for high temperatures, or weak magnetic fields.

\[ M = C \cdot \frac{B}{T}, \]

\[ C = \frac{N g^2 \mu_B^2 J(J+1)}{3k_B} \]
### Curie’s Law

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<th>B/T</th>
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<tr>
<td>0.0175</td>
<td>2.517E+11</td>
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**correlation= 0.997337449**
Curie’s Law 3,4

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correlation= 0.985821465
Temperature Dependence Curves of 3,4 and 44OOH

Temperature (K)

Intensity

$10^6$

20 40 60 80 100 120 140

Temperature (K)

Intensity

$10^6$

20 40 60 80 100 120 140

3,4

4,4
O₂ Evolution Measured with Hansatech Oxygraph

Hansatech Oxygraph System for Photosynthesis & Respiration Measurement in Liquid-Phase.
Oxygen Evolution

Oxygen Evolution of Ruthenium Catalysts

Time (Seconds)
Low Concentration Ru

![Graph showing the g-factor vs. intensity for different concentrations of Ru. The graph includes a legend for each curve representing different concentrations: 4x10^-5 Ru3, 4x10^-5 Ru4, 4x10^-5 Ru5, 4x10^-5 Ru4 20 min later, 4x10^-5 Ru5 20 min later, and Empty Cavity.](image-url)
Where is this Project headed?

- Understand critical electronic, energetic and geometric requirements of the water oxidation reaction
- This will constitute major steps towards development of future light-to-fuel energy solutions
- XANES and EXAFS analysis at Argonne National Lab.
Thanks!

- I would like to thank my advisor, Professor Yulia Pushkar, and graduate student, Dooshaye Moonshiram, for working with me this summer!
Questions?