EPR spectroscopic studies of the electronic and atomic requirements in

Catalytic Water Oxidation by Ruthenium Complexes

Outline

- 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

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$

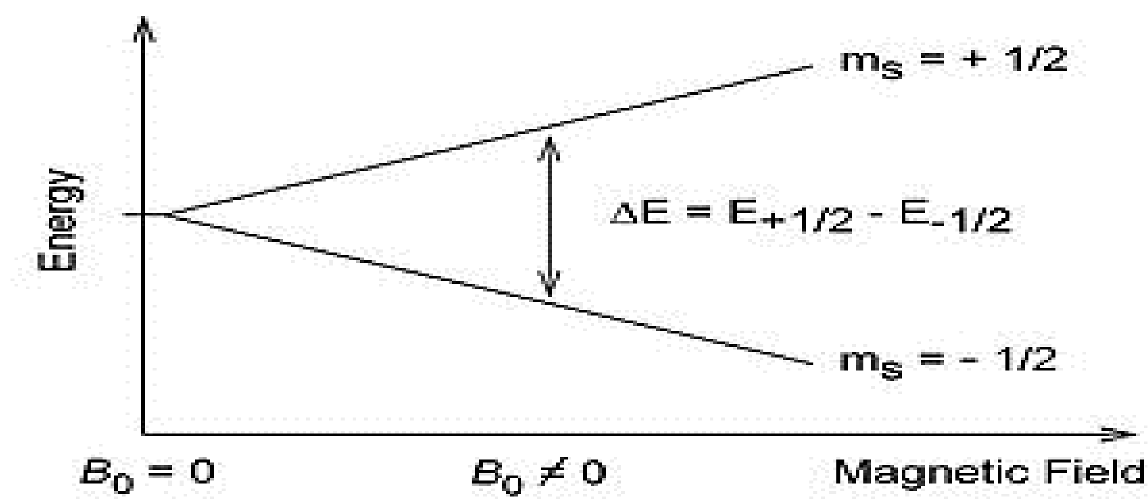
$$4Ce(IV) + 2H_2O \rightarrow 4Ce(III) + O_2 + 4H^+$$

What is EPR?

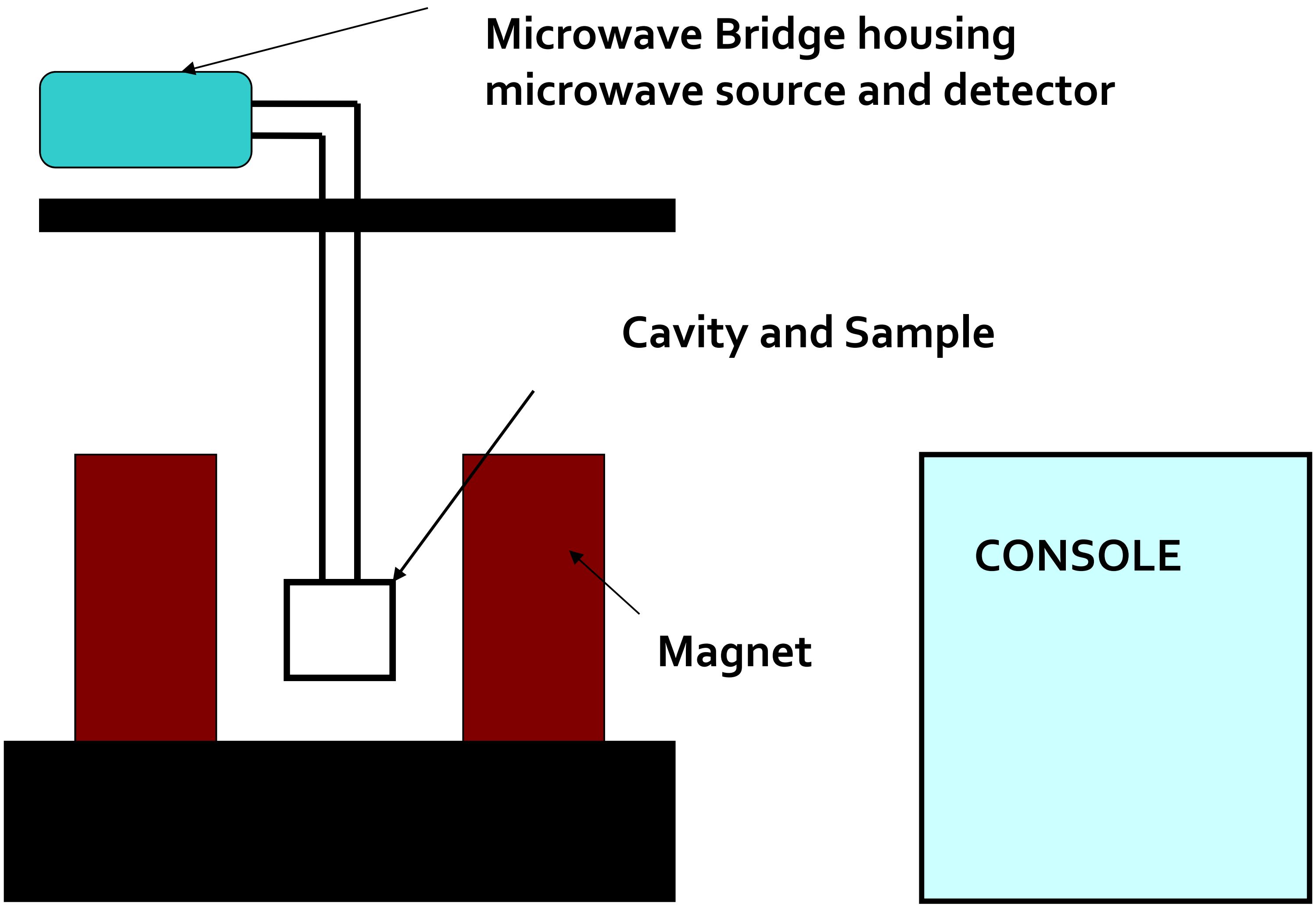
- Electron Paramagnetic Resonance
- technique for studying chemical species that have one or more unpaired electrons

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

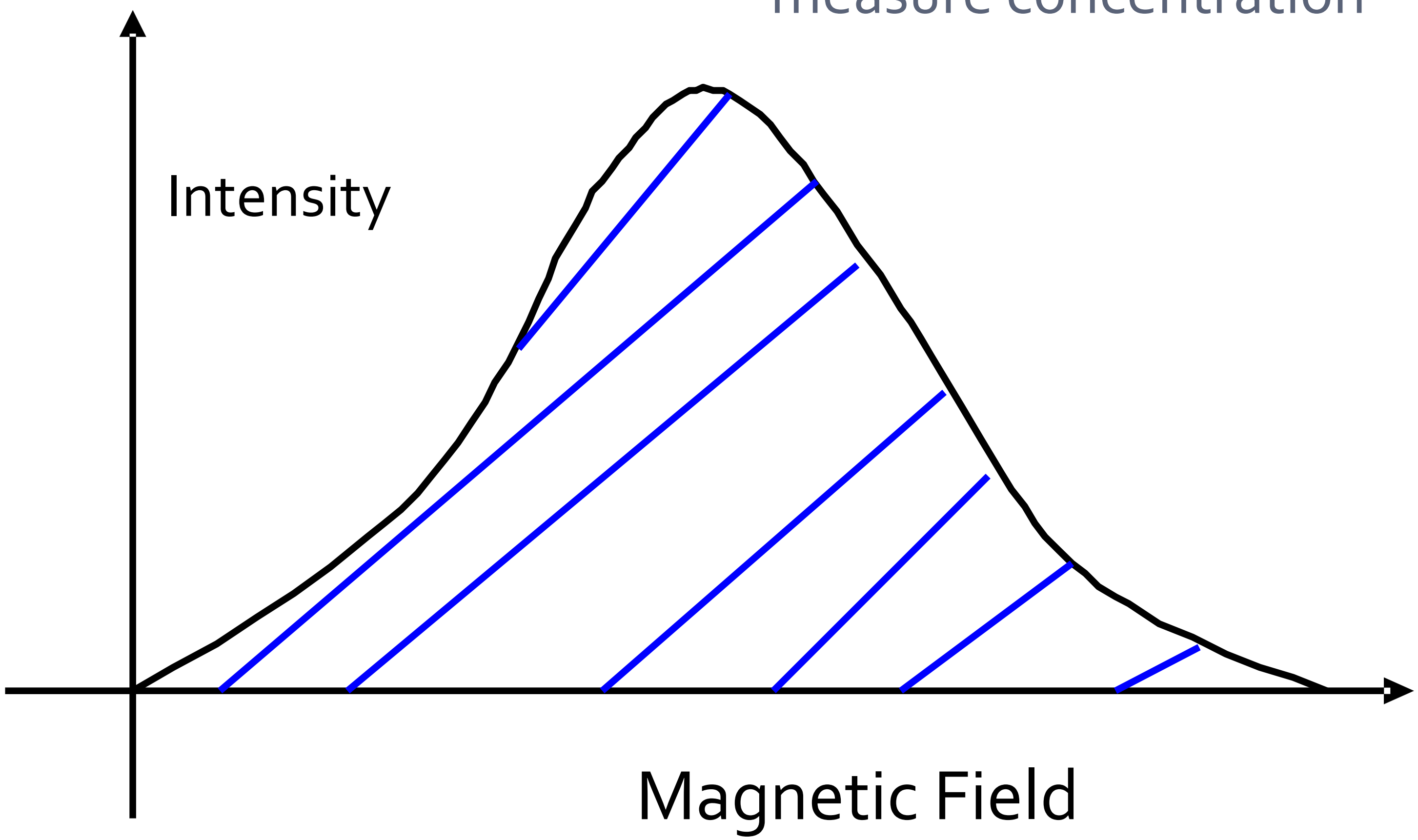


EPR Spectrometer



EPR signal – First derivation of absorption signal

Size of EPR signal used to measure concentration



G Factor

- Knowledge of the *g-factor* can give information about a paramagnetic center's electronic structure.
- Isotropic: gx = gy = gz
- Uniaxial: Two principal values coincide but the third is different
- Rhombic: gx ≠ gy ≠ gz

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

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

Orientations

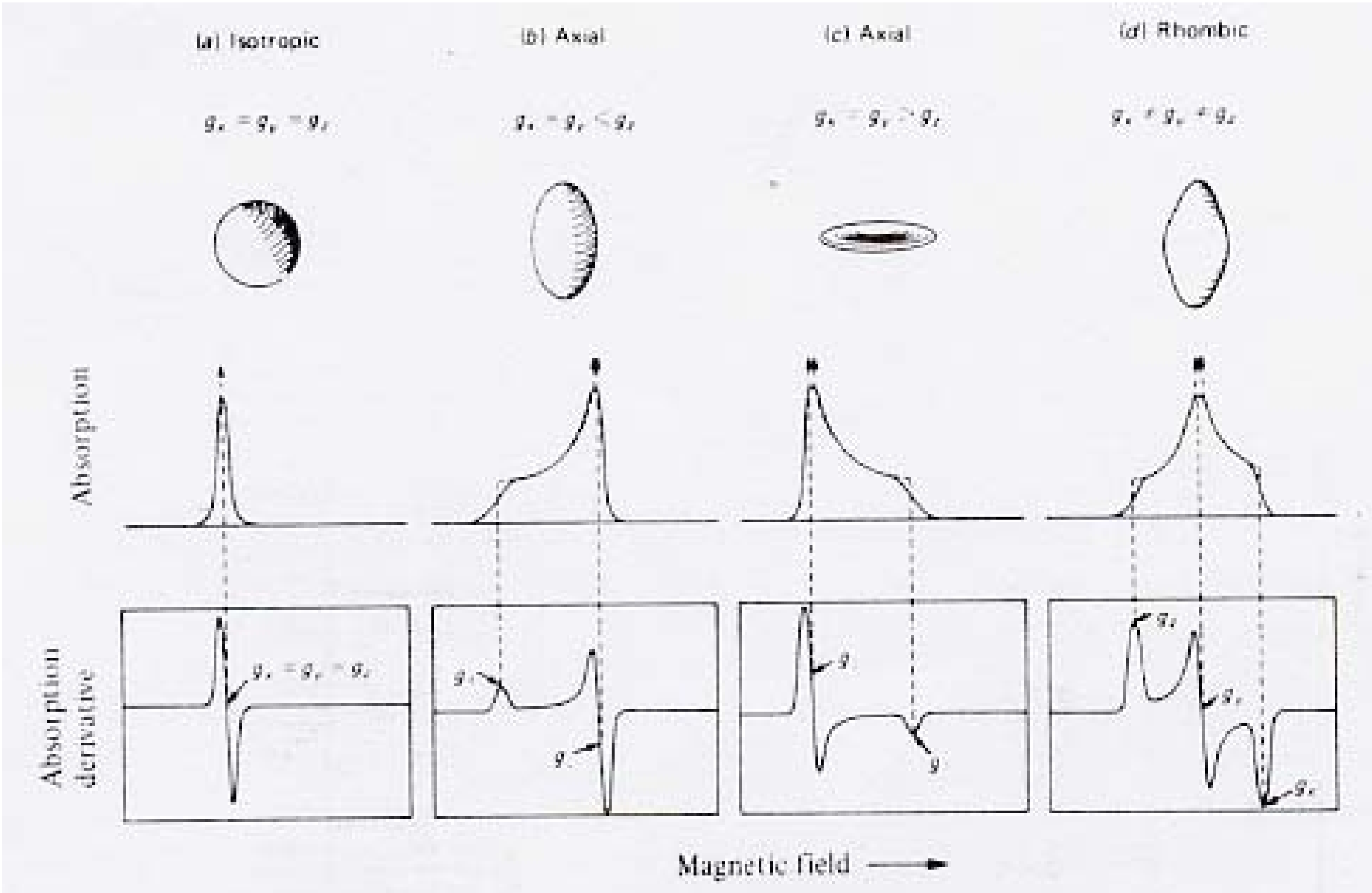
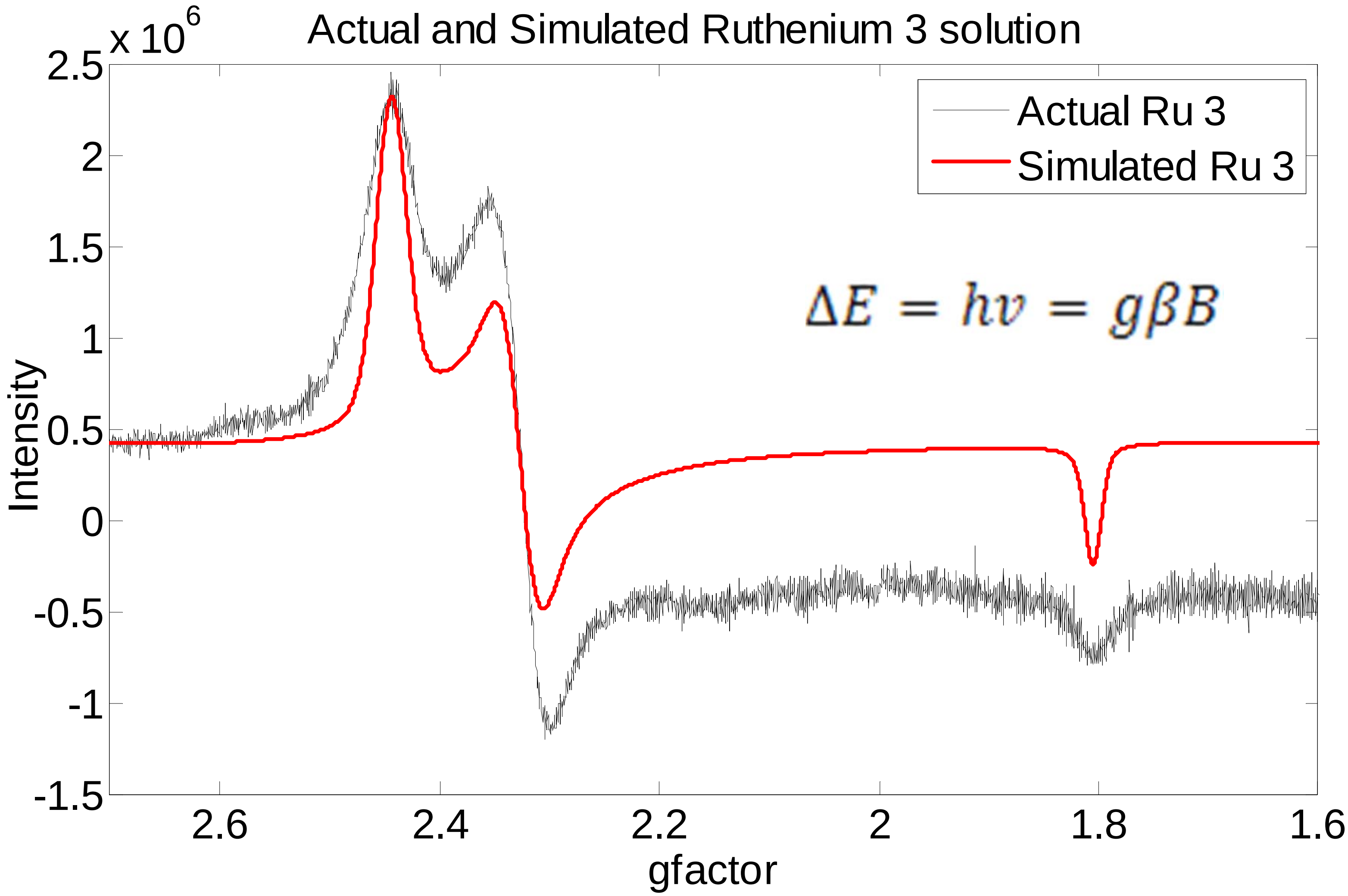


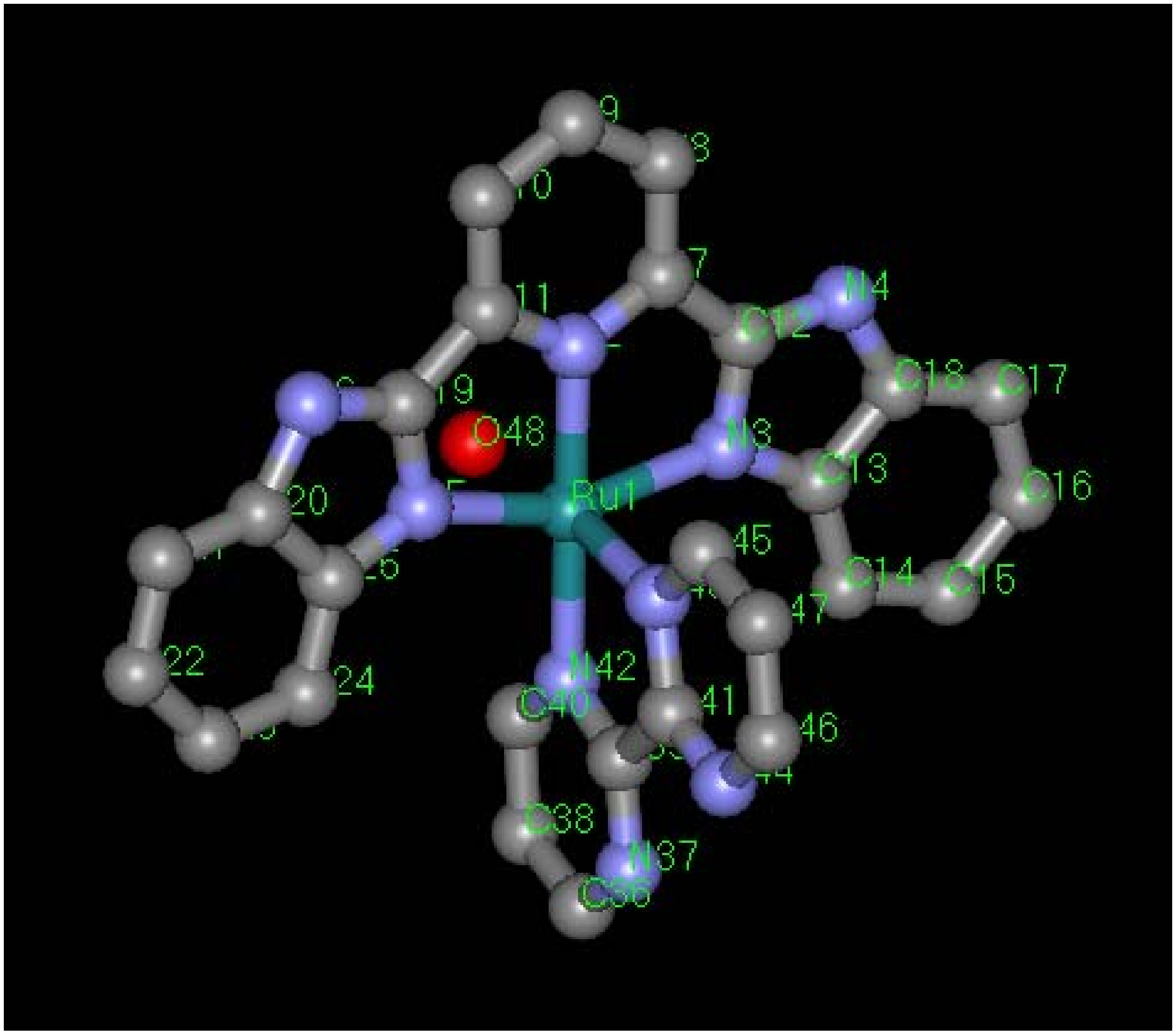
Fig. 1. *Schematic representation of g-tensor and the consequential e.p.r. spectra*

Ru 3 Solution

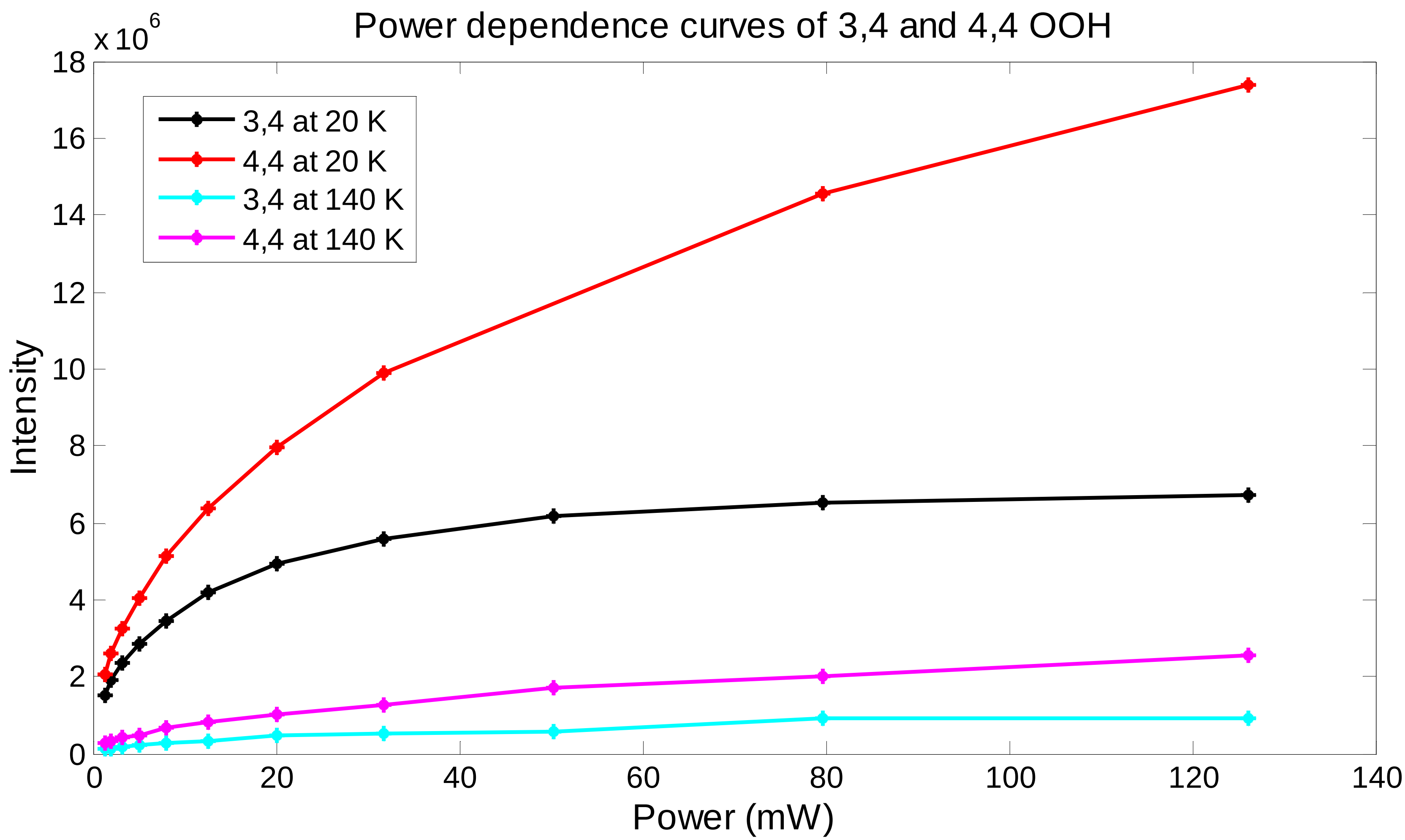


$$\Delta E = hv = g\beta B$$

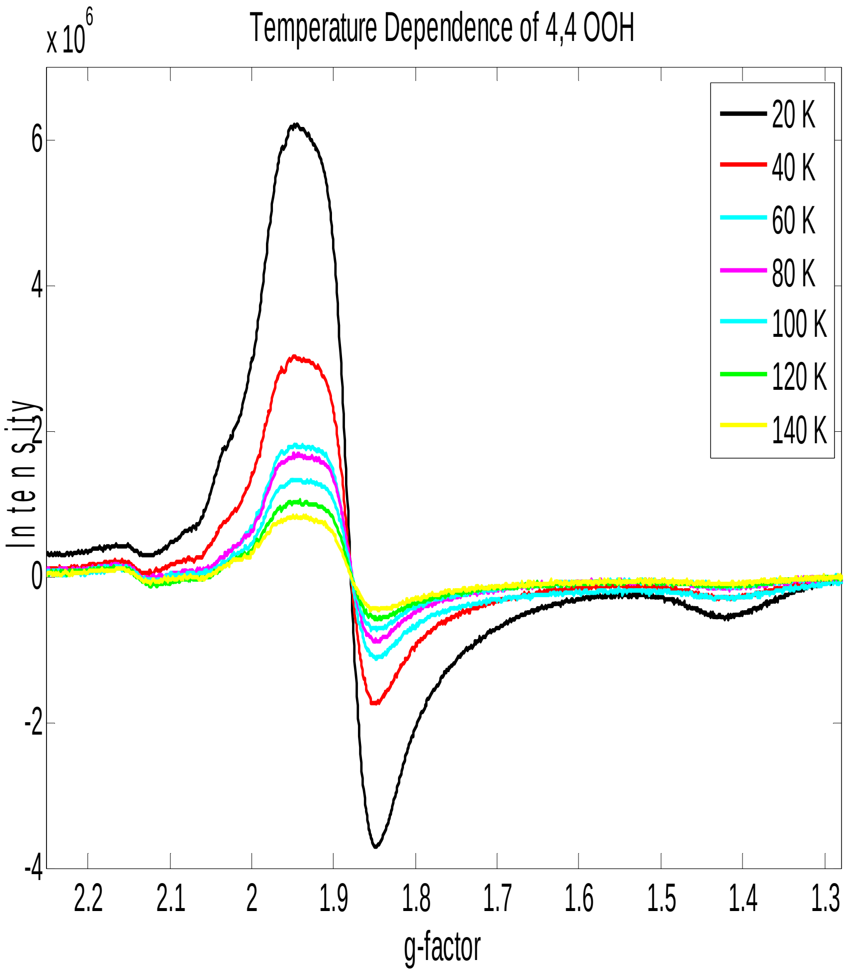
Rhombic Ru 3

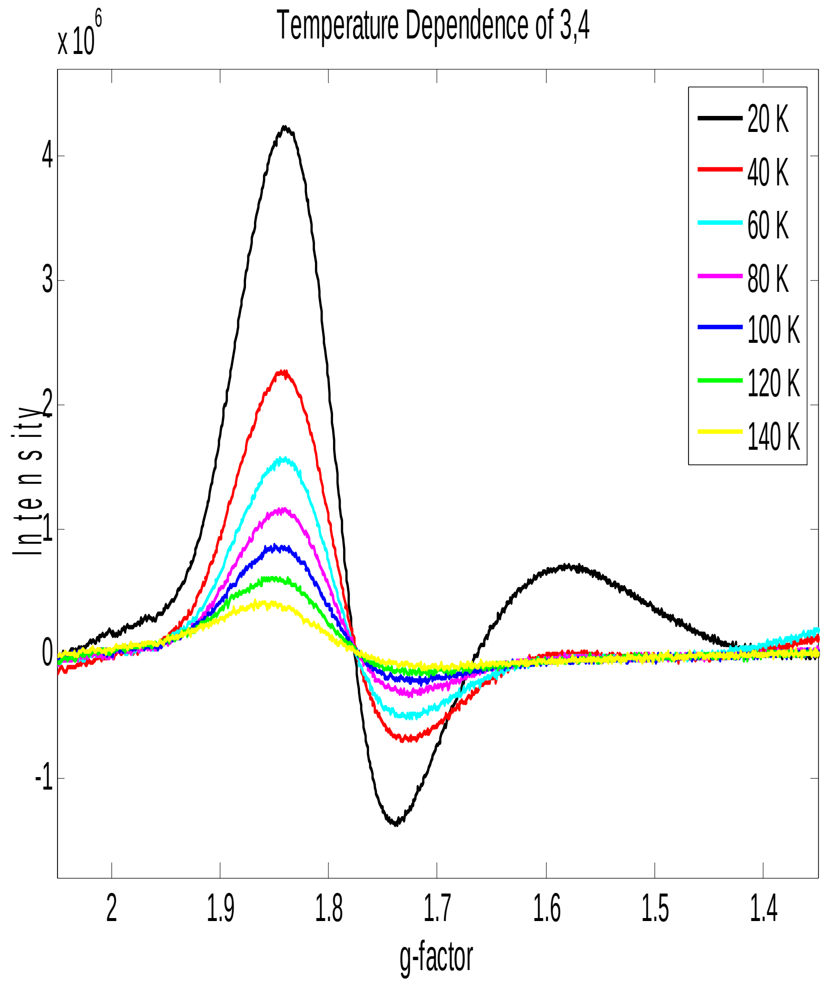

N4
C12
C18
C17
O48
N3
C13
C16
Ru1
45
C14
C15
47
N42
C40
41
46
C38
N37
22
24
20
19
11

Power Dependence



Temperature Dependence





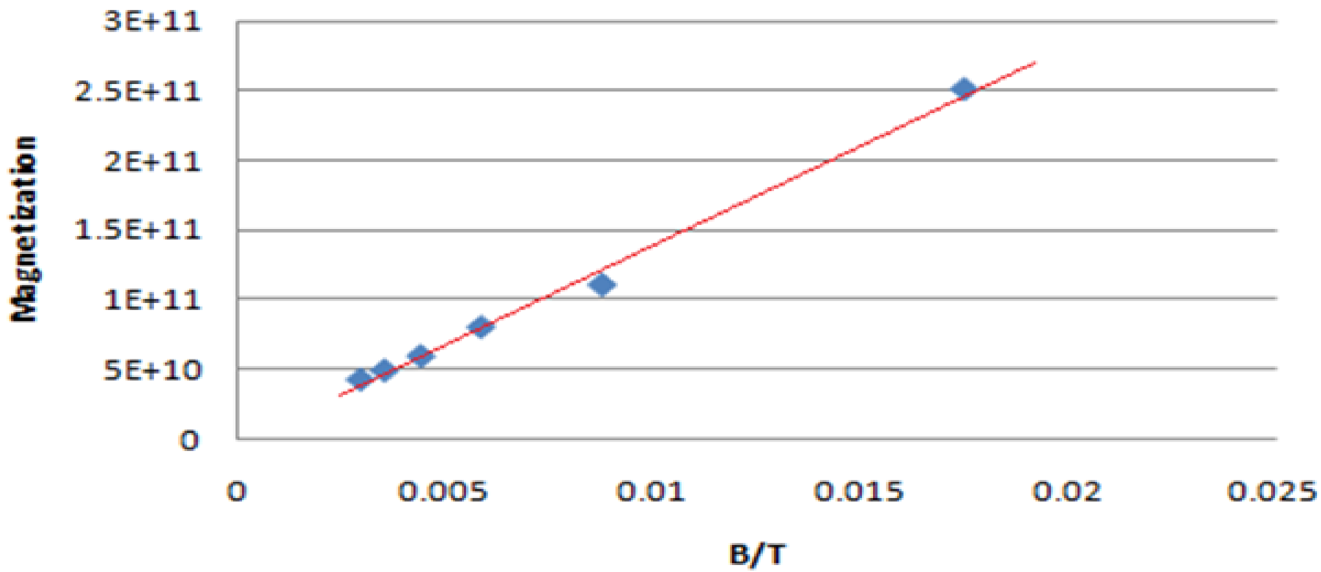
Curie's Law (general overview)

$$\mathbf{M} = C \cdot \frac{\mathbf{B}}{T},$$

$$C = \frac{N g^2 \mu_B^2 J(J+1)}{3k_B}$$

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

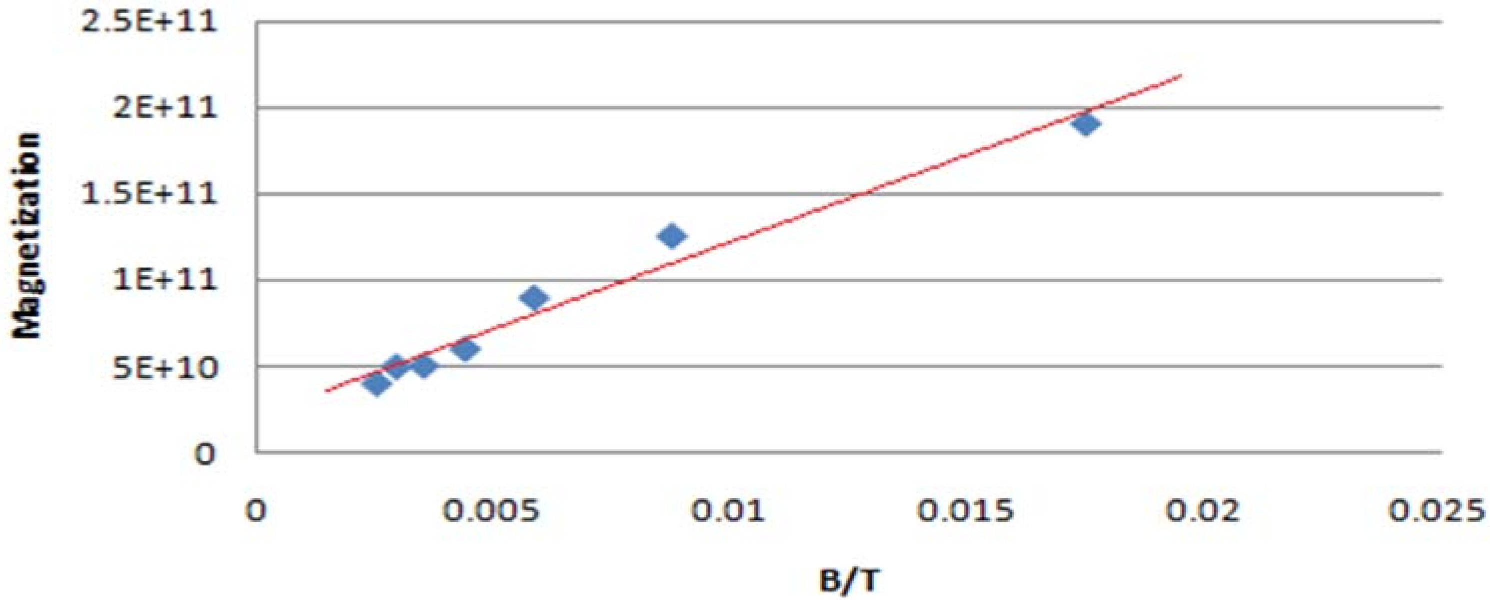
Curie's Law 44 OOH



B/T	Intensity
0.0175	2.517E+11
0.00875	1.105E+11
0.005833333	79990000000
0.004375	58950000000
0.0035	48540000000
0.002916667	42010000000

correlation= **0.997337449**

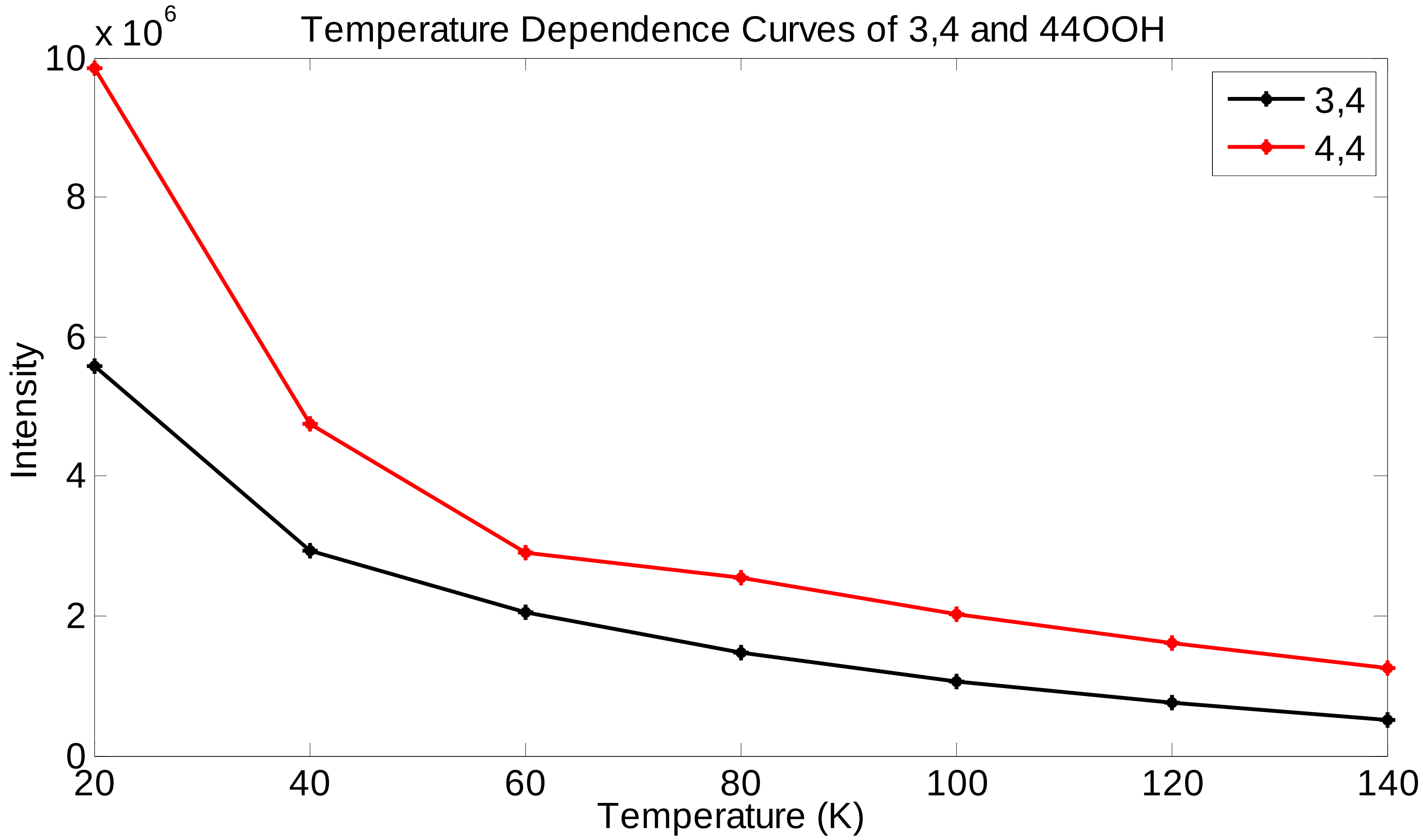
Curie's Law 3,4



B/T	intensity
0.0175	1.901E+11
0.00875	1.253E+11
0.005833333	89750000000
0.004375	60380000000
0.0035	50670000000
0.002916667	50130000000
0.0025	40490000000

correlation= **0.985821465**

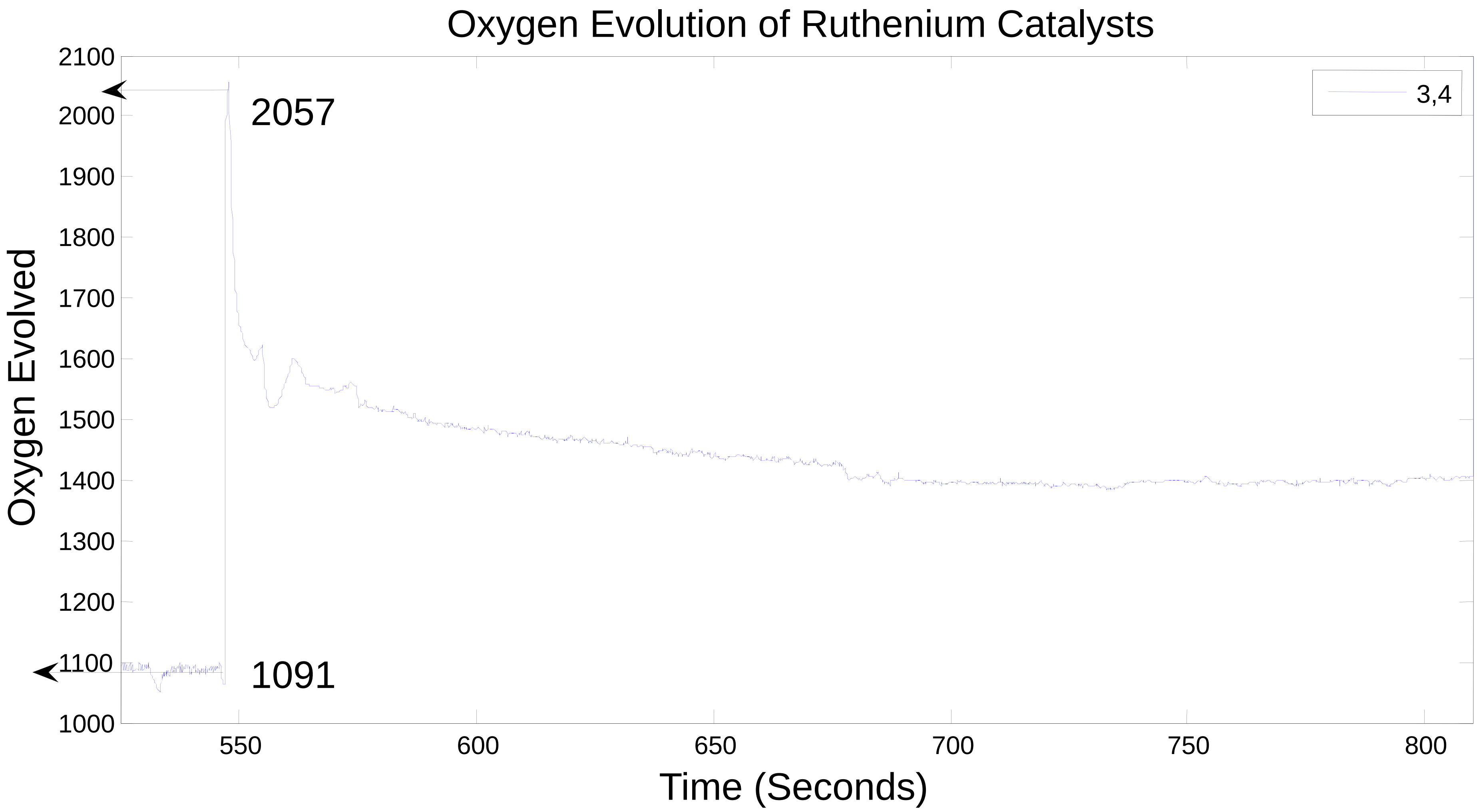
Temperature Dependence



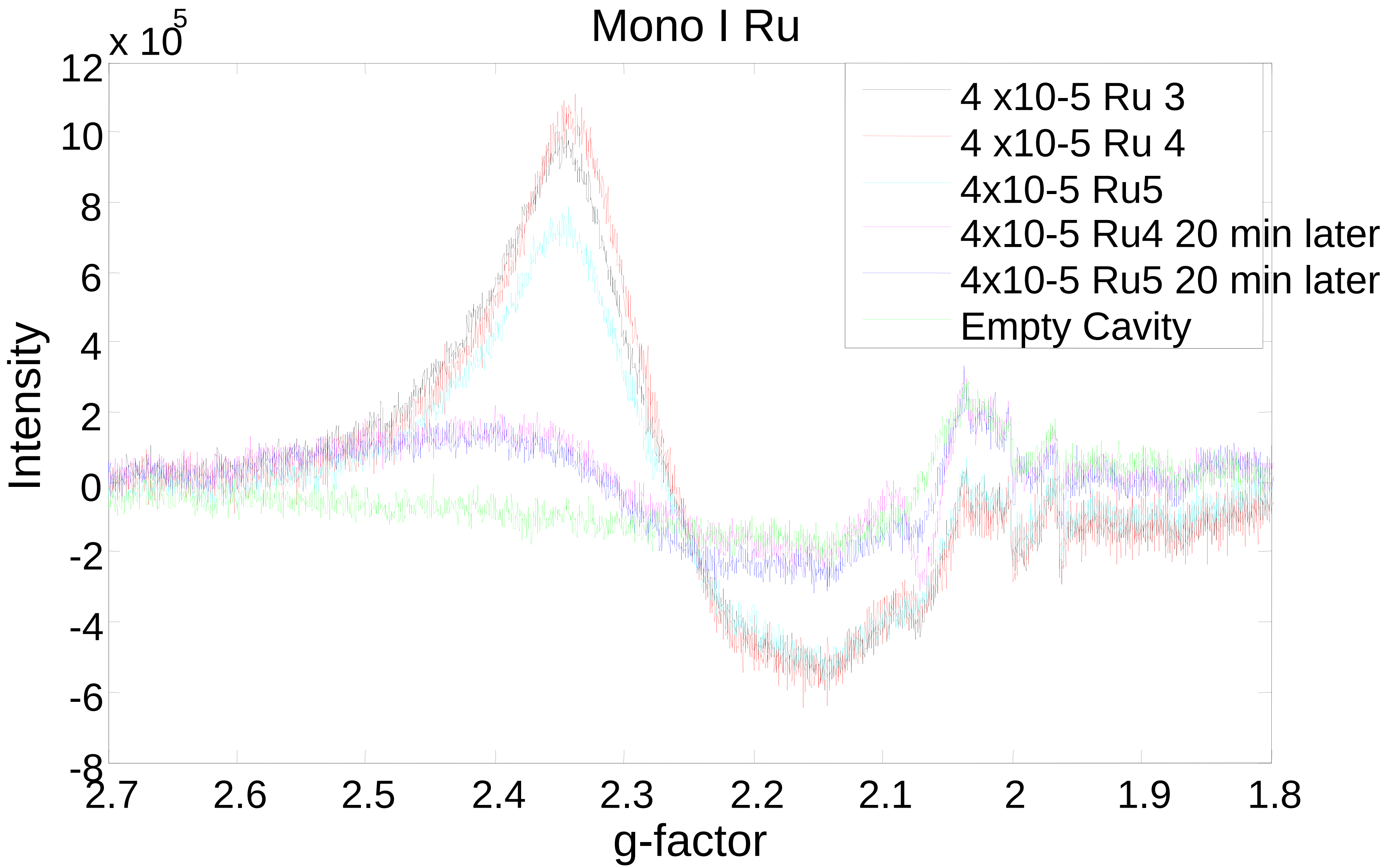
O_2 Evolution Measured with Hansatech Oxygraph

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

Oxygen Evolution



Low Concentration Ru



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?