Spectroelectrochemical Studies of Surface Species in the Gold/Thiosulfate System

by

Kym Marjorie Watling, B. Sc. (Hons.)

A thesis submitted to Griffith Science, Environment, Engineering and Technology, Griffith University, Australia, for the degree of Doctor of Philosophy.

January 2007
Abstract

This thesis presents results of studies using the technique of surface-enhanced Raman scattering (SERS) spectroscopy to investigate surface processes occurring on gold during electrochemical experiments in thiosulfate solutions and during leaching in ammoniacal copper(II) thiosulfate systems. The gold SERS electrode was characterised using X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray analysis (EDX), linear sweep voltammetry (LSV) and cyclic voltammetry (CV). SEM investigations of the SERS activated gold surface showed the presence of electrodeposited dendrites with nanoscale features. XRD studies of the dendrites showed them to be polycrystalline with a large proportion of Au(111). Rotating disk electrode (RDE) studies of polished and SERS electrodes were undertaken in order to clarify the electrochemistry of various thiosulfate systems. The ex situ techniques of XPS and attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectroscopy were used to determine the presence of sulfur, copper and nitrogen on leached or electro-oxidised surfaces. Voltammetric methods were used to determine sulfur and copper surface coverages at various potentials in sulfide, thiosulfate and ammoniacal copper(II) thiosulfate media. The electro-oxidation of sulfide was examined as a model system in order to identify spectral features and coverage associated with various potential-dependent sulfur layers. In the hydrogen evolution region, a surface layer formed by underpotential deposition in acid and basic media was characterised by a gold-sulfur stretching band, $\nu_{\text{Au-S}}$, attributed in the literature to a monoatomic stretching mode of sulfur bonded to gold. The surface coverage in this potential region was limited to 0.35 ML, representing adsorption in a $(\sqrt{3}x\sqrt{3})R30^\circ$ structure. Bands were found to be absent that would have indicated the adsorption of $\text{SH}^-$ species as has been reported in the literature. A facile
change in the position of the $\nu_{\text{Au-S}}$ band with potential, unaccompanied by Faradaic processes, was seen when the adsorbed ($\sqrt{3}\times\sqrt{3})R30^\circ$ sulfur layer was examined in a sulfide-free solution. This may indicate a change in sulfur adsorption sites with potential in the hydrogen evolution region. At potentials above the $S^{\text{II}}/S^{\text{0}}$ reversible value in sulfide solutions, the surface coverage increased and $\nu_{\text{S-S}}$ bands were observed, indicating the formation of an adsorbed polysulfide species, $\text{Au-S}_n$. A change in the position of the $\nu_{\text{Au-S}}$ band was seen to accompany the formation of the $\nu_{\text{S-S}}$ bands. As coverage further increased, bands due to S-S-S bending, $\delta_{\text{S-S-S}}$, developed that were characteristic of cyclo-octasulfur, $S_8$. On removal from sulfide solution and rinsing, a characteristic SERS spectrum was observed ex situ. The spectrum showed a characteristic $\nu_{\text{S-S}}$ at 460 cm$^{-1}$ and $\nu_{\text{Au-S}}$ at 325 cm$^{-1}$ and was assigned to an adlayer of $S_8$ adsorbed on gold in a crown configuration, $\text{Au-S}_8$. Gold was polarised in thiosulfate solutions at a potential at which gold dissolution is known to occur. In situ SERS spectra showed bands characteristic of S-S bonding and $\text{Au}_2\text{S}$ to occur after 1 hr for thiosulfate with sodium and ammonium counter-ions and for both systems in the presence of ammonia. XPS studies of polished gold held in sodium thiosulfate under these conditions showed S 2p binding energies corresponding to metal sulfide and pyritic sulfur, $S_2^{2-}$. After 72 hrs at the mixed potential in air-saturated sodium thiosulfate, SERS investigations showed a spectrum with $\text{Au-S}_8$ characteristics. XPS studies on a polished electrode under these conditions showed a third type of S 2p binding with a binding energy between that of pyritic sulfur and $S_8$. The sodium thiosulfate system showed an adsorbed tetrathionate-like surface species, $\text{Au-S}_4\text{O}_6$, to be present at the mixed potential and to disappear with increased potential prior to the formation of bulk $S_8$ via an $\text{Au-S}_8$ intermediate. In the presence of the ammonium cation at high potentials, $\text{Au-S}_n$ bands appear in the presence of a more intense and
broad $\nu_{\text{Au-S}}$ characteristic of gold sulfide, $\text{Au}_2\text{S}$. This was assigned to a mixed gold sulfide/polysulfide phase, $\text{Au}_2\text{S}/\text{S}_n$. With addition of ammonia, the surface species $\text{Au-S}_4\text{O}_6$, $\text{Au}_2\text{S}/\text{S}_n$ and, tentatively, adsorbed $\text{NH}_3$ were observed above the mixed potential. For gold in air-saturated copper(II) ammoniacal thiosulfate media, bands due $\nu_{\text{S-S}}$ at 382 cm$^{-1}$ and symmetric S-O stretching, $\nu_{\text{symS-O}}$, at 1017 cm$^{-1}$ developed during leaching at the mixed potential. These modes diminished and, when rinsed and examined in water, were replaced by a single band at 255 cm$^{-1}$ assigned to a metal-sulfide stretch. In typical leach solutions, sulfur and copper coverages showed a 2:1 atomic ratio after leaching for 16 h. *Ex situ* ATR and XPS studies showed that ammonia was adsorbed to a surface copper sulfide. Kinetic studies using atomic absorption spectroscopy (AAS) to measure gold in solution showed that the ammoniacal copper(II) thiosulfate leaching solution exhibited higher dissolution rates in the presence of the sodium counter ion than the ammonium. Thiourea as an additive to thiosulfate solutions was seen to disrupt S-S bonding in both Au-S$_8$ and Au$_2$S/S$_n$ surface structures.
Declaration

The work contained in this thesis has not previously been submitted for a degree or diploma in any university. To the best of my knowledge and belief, this thesis contains no material previously published or written by another person except where due reference is made in the thesis itself.

=================================

Kym Marjorie Watling
Acknowledgements

I would like to thank and acknowledge many people for their unique and often-sought assistance in the generation of this work. Firstly, I thank my supervisor, Professor Greg Hope for his whip, wisdom and perpetual kindness. By feeding his students coffee, calamari, single malt whiskey and outrageous challenges, he has created within his research group a strong culture of learning and desire for dessert. Greg’s support and encouragement has seen his research group travel the world in the pursuit of scientific truth and adequate wine glasses. Sincere, humble thanks goes to Professor Ronald Woods, living legend in flotation science, for his finger-puppets, understanding, generosity and sublime wit. I am most grateful for the opportunity to have been guided by Prof. Woods in a work environment and amongst wider vistas. Extreme gratitude is due to Dr Matthew Jeffrey, CSIRO, Perth, and for patiently leading me through the black forests of electrochemistry and thiosulfate leaching, one pudding at a time. I gratefully acknowledge Dr. Jeffrey’s collaboration, advice and assistance with spectroelectrochemical experiments at Griffith University, also the use of his laboratories and rotating disk electrochemical rigs at Monash University. Fond thanks are extended to my collaborator, then Gretel Parker, now Dr Gretel Heber, for sharing many valuable thoughts, interpretations and the benefits of her extensive experience. I acknowledge Gretel’s assistance with shared experimental procedures and collaboration in studies of the model system. I thank my colleague, Mrs Carolyn Munce, for tolerance and support, advice and understanding that has been kindly and patiently distributed over many years. Grateful thanks are due to Dr Chris Brown, my co-supervisor and CRC for microTechnology group leader, for keeping his mind and door open and for calling me ‘chook’. I owe a debt of gratitude to Dr Llew Rintoul and
Associate Professor Peter Fredericks for their assistance with spectroscopy, both at our own Raman facility at Griffith University and at the QUT Centre for Instrumental and Developmental Chemistry. Receiving advice on all matters vibrational was always a charming and enlightening honour. A grand vote of thanks goes to Dr. Barry Wood of the Brisbane Surface Analysis Facility at Queensland University, for pushing X-ray photoelectron spectroscopy to its limit in order to find things of which there were so very little. Thanks too, to Dr. Narelle Brack for XPS undertaken at Latrobe University. I acknowledge Dr Thor Bostrom and staff at the Queensland University of Technology / Griffith University Analytical Electron Microscope Facility for their assistance with electron microscopy and kind advice, also Dr. Tony Raftery for X-ray diffraction experiments at the X-ray Analysis Facility within the same centre. I acknowledge the assistance of Mr Ross Stevens from the Griffith University Office of Technical Services, for much advice about chemistry and kind provision of materials and equipment. Sincere thanks go to the kind staff of the electrical and mechanical workshops, teaching laboratories and offices of what was the School of Science and is now the School of Biomolecular and Physical Sciences. For financial assistance, I acknowledge the Department of Employment, Science and Training for an Australian Postgraduate Award and the CRC for microTechnology for a Top-Up Scholarship. I must thank my friends, who have always provided an open veranda, ear and beverage in my time of need and the boys in Disgraceland for still being there. Warm thanks are humbly extended to Mrs. Betty Hope, Mrs. Elspeth Woods and Mrs. Marianne Jeffrey for their good humour, hospitality and valued advice. Finally, I’d like to express my gratitude to my son Adrick for his support and assistance during the writing process. His thoughtfulness, kindness, good humour, tolerance and wisdom have been my greatest blessings during the creation of this thesis.
This thesis is dedicated to the memory of my parents,

Marjorie and Norman Stanley Watling.
Publications Appearing During Candidature


## Contents

Abstract iii  
Declaration vii  
Acknowledgements ix  
Publications Appearing During Candidature xiii  
Abbreviations xxiii  
Figures xxv  
Tables xxxi

### 1. INTRODUCTION

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.1. Gold</td>
<td>2</td>
</tr>
<tr>
<td>1.2. Aims and Objectives</td>
<td>4</td>
</tr>
<tr>
<td>1.3. Approach and Methodology</td>
<td>5</td>
</tr>
<tr>
<td>1.4. Thesis Outline</td>
<td>7</td>
</tr>
<tr>
<td>1.5. Background</td>
<td>8</td>
</tr>
<tr>
<td>1.5.1. Disadvantages of Cyanide in Gold Leaching</td>
<td>8</td>
</tr>
<tr>
<td>1.5.2. Alternative Lixiviant for Gold</td>
<td>10</td>
</tr>
<tr>
<td>1.5.3. Thiosulfate Leaching</td>
<td>10</td>
</tr>
<tr>
<td>1.6. Techniques</td>
<td>13</td>
</tr>
<tr>
<td>1.6.1. Spectroelectrochemistry</td>
<td>13</td>
</tr>
<tr>
<td>1.6.2. Raman Spectroscopy</td>
<td>14</td>
</tr>
<tr>
<td>1.6.2.1. Normal Vibrational Modes</td>
<td>15</td>
</tr>
<tr>
<td>1.6.2.2. General Selection Rule</td>
<td>16</td>
</tr>
<tr>
<td>1.6.2.3. Mutual Exclusion Rule</td>
<td>16</td>
</tr>
<tr>
<td>1.6.2.4. Instrumentation</td>
<td>16</td>
</tr>
<tr>
<td>1.6.3. Surface Enhancement</td>
<td>17</td>
</tr>
<tr>
<td>1.6.3.1. Electromagnetic Effect</td>
<td>19</td>
</tr>
<tr>
<td>1.6.3.2. Chemical Effect</td>
<td>19</td>
</tr>
<tr>
<td>1.6.3.3. Nanoparticles</td>
<td>20</td>
</tr>
<tr>
<td>1.6.3.4. Surface Roughening</td>
<td>20</td>
</tr>
<tr>
<td>1.6.3.5. Oxidation-Reduction Cycling</td>
<td>21</td>
</tr>
<tr>
<td>1.6.3.6. Selection Rules</td>
<td>22</td>
</tr>
<tr>
<td>1.6.4. Ex situ Techniques</td>
<td>22</td>
</tr>
<tr>
<td>1.6.4.1. Attenuated Total Reflectance Infrared Spectroscopy</td>
<td>23</td>
</tr>
<tr>
<td>1.6.4.2. X-ray Photoelectron Spectroscopy</td>
<td>23</td>
</tr>
</tbody>
</table>
2. LITERATURE REVIEW

2.1. Chemistry of gold dissolution

- 2.1.1. Properties of Gold
- 2.1.2. Gold Oxides and Hydroxides
  - 2.1.2.1. Bulk Oxide Formation
  - 2.1.2.2. Surface Oxides
- 2.1.3. Aqueous Chemistry of Gold
  - 2.1.3.1. Nernst Equation
  - 2.1.3.2. Pourbaix Diagram
  - 2.1.3.3. Anodic Polarisation
- 2.1.4. Gold Lixivants
  - 2.1.4.1. Aqua Regia
  - 2.1.4.2. Halogen / Halide media
  - 2.1.4.3. Cyanide
  - 2.1.4.4. Thiocyanate
  - 2.1.4.5. Thiourea

2.2. Thiosulfate Leaching of Gold

- 2.2.1. Electrochemistry of Gold Dissolution in Thiosulfate
  - 2.2.1.1. Rotating Electrochemical Quartz Crystal Microbalance Studies
- 2.2.2. Ammoniacal Copper(II) Thiosulfate Leaching
  - 2.2.2.1. Role of Ammonia
  - 2.2.2.2. Role of Copper
  - 2.2.2.3. Effect of Oxygen
  - 2.2.2.4. Effect of pH
  - 2.2.2.5. Failure of Thiosulfate Leaching
- 2.2.3. Effect of Additives

2.3. Interaction of Sulfur with Gold

- 2.3.1. Gold-Sulfur Compounds
- 2.3.2. Electrochemistry of Sulfide Electroadsorption
  - 2.3.2.1. Prewave Region
  - 2.3.2.2. Protonation
  - 2.3.2.3. Sulfur Coverage of Prewave Region
  - 2.3.2.4. Oxidation Reactions
  - 2.3.2.5. Reduction Reactions
- 2.3.3. Stability of Polysulfides
- 2.3.4. Scanning Tunnelling Microscopy Studies
- 2.3.5. X-ray Photoelectron Studies

2.4. Raman Assignments of Reference Compounds

- 2.4.1. Sulfur compounds
  - 2.4.1.1. cyclo-Octasulfur S₈
  - 2.4.1.2. Polymeric and Disordered Sulfur
  - 2.4.1.3. Empirical Relationships in Homocyclic Sulfur Molecules
  - 2.4.1.4. Hydrogen Sulfides
  - 2.4.1.5. Gold-Sulfur Modes
  - 2.4.1.6. Copper-Sulfur Modes
  - 2.4.1.7. Polysulfides
- 2.4.2. Thiosulfate
- 2.4.3. Polythionates
- 2.4.4. Oxysulfur Anions
2.4.5. Thiourea ................................................................................. 74
  2.4.5.1. Copper-thiourea compounds ............................................. 75
2.4.6. Ammonia / Ammonium ................................................................. 75

2.5. SERS Substrates ............................................................................. 77
  2.5.1. Morphology of an Optimised Gold SERS Electrode .............. 77
  2.5.2. Fractality in SERS Substrates ............................................... 78
    2.5.2.1. Colloidal Aggregates of Nanoparticles ............................ 78
    2.5.2.2. Roughened Surfaces ...................................................... 78
    2.5.2.3. Dendritic Structures ...................................................... 79
  2.5.3. Electrochemical Faceting ...................................................... 80

2.6. SERS of Adsorbates on Gold ....................................................... 82
  2.6.1. Oxide Formation ................................................................. 82
  2.6.2. Thiolate Monolayers ........................................................... 82
  2.6.3. Sulfur on Gold ................................................................. 82
  2.6.4. Thiosulfate .......................................................................... 85
  2.6.5. Ammonia .......................................................................... 85
  2.6.6. Thiourea .......................................................................... 86

3. EXPERIMENTAL .......................................................................... 87
  3.1. Preamble .............................................................................. 88
  3.2. Reagents ............................................................................. 89
  3.2.1. Commercial Reagents ...................................................... 89
  3.2.2. Synthesised Compounds ................................................... 89
    3.2.2.1. Gold(I) Sulfide .............................................................. 89
    3.2.2.2. Sodium Polysulfide ...................................................... 90
  3.2.3. Solutions .......................................................................... 90
    3.2.3.1. Ammonia Solutions ..................................................... 90
    3.2.3.2. Sodium Sulfide Solutions .......................................... 90
    3.2.3.3. Ammoniacal Copper(II) Thiosulfate Solutions ............. 91
    3.2.3.4. pH of Thiosulfate Solutions ....................................... 91
  3.3. Electrochemistry ...................................................................... 92
  3.3.1. Spectroelectrochemical Cell ............................................... 92
    3.3.1.1. Nitrogen Purging ......................................................... 93
    3.3.1.2. Air Bubbling ............................................................... 93
    3.3.1.3. Oxygen Enrichment .................................................... 93
    3.3.1.4. Argon Purging ............................................................ 93
  3.3.2. Electrodes .......................................................................... 93
    3.3.2.1. Gold Working Electrodes .............................................. 94
    3.3.2.2. Ag/AgCl reference electrodes ..................................... 94
    3.3.2.3. Pt counter electrode .................................................... 95
    3.3.2.4. Potential Control ......................................................... 96
  3.3.3. Rotating Disk Electrochemistry ......................................... 96
  3.3.4. Electrochemical Coverage Experiments ........................... 98
  3.4. Raman Spectroscopy .............................................................. 99
    3.4.1.1. Renishaw System 100 Process Analyser ........................ 99
    3.4.1.2. Renishaw system RM2000 Research Microscope ............ 100
  3.4.2. Conventional Raman spectroscopy .................................... 100
    3.4.2.1. Solids ....................................................................... 100
    3.4.2.2. Solutions ................................................................. 101
3.4.3. Surface-Enhanced Raman Spectroscopy .................................. 101
  3.4.3.1. Substrate Activation ...................................................... 101
  3.4.3.2. Voltammetric SERS ...................................................... 103
  3.4.3.3. Potentiostatic SERS .................................................... 103
  3.4.3.4. Actively Leaching Surfaces ......................................... 103
3.4.4. Laser Degradation .......................................................... 104

3.5. Ammoniacal Copper(II) Thiosulfate Leaching .................. 105
  3.5.1. Ex situ Investigations ................................................... 105
  3.5.2. Kinetic Studies ........................................................... 105
  3.5.3. Attenuated Total Reflectance Infrared Spectroscopy ....... 106
  3.5.4. X-ray Photoelectron Spectroscopy .................................. 106
  3.5.5. Scanning Electron Microscopy ....................................... 107

4. ELECTRODE CHARACTERISATION ........................................ 109
  4.1. Preamble .............................................................................. 110
  4.2. SEM and EDX Microprobe Analysis .................................... 110
    4.2.1. The Highly Dendritic Surface ....................................... 111
    4.2.2. Standard Electrode Preparation .................................... 113
  4.3. Voltammetric Characterisation ......................................... 115
  4.4. X-ray Photoelectron Spectroscopy .................................... 116
    4.4.1. Polished Gold Electrode ............................................. 116
    4.4.2. Oxidation-Reduction Cycled Gold Electrode .................. 117
  4.5. X-ray Diffraction ............................................................ 120

5. ROTATING DISK ELECTROCHEMISTRY .................................. 121
  5.1. Preamble .............................................................................. 122
  5.2. Gold in Thiosulfate Solutions .......................................... 123
    5.2.1. Sodium Thiosulfate .................................................. 123
      5.2.1.1. Roughened and Polished RDEs ................................. 124
    5.2.2. Ammonium Thiosulfate .............................................. 126
  5.3. Additions to Sodium Thiosulfate Solutions ..................... 127
    5.3.1. Addition of Ammonia ................................................. 127
    5.3.2. Addition of Thiourea .................................................. 128
      5.3.2.1. Roughened and Polished RDEs .............................. 129
  5.4. Additions to Ammonium Thiosulfate Solutions ................ 130
    5.4.1. Addition of Ammonia ................................................. 130
    5.4.2. Addition of Thiourea .................................................. 131
      5.4.2.1. Roughened and Polished RDEs .............................. 133
    5.4.3. Summary of RDE results .......................................... 134

6. SERS SPECTROELECTROCHEMISTRY ..................................... 137
  6.1. Preamble .............................................................................. 138
  6.2. LSV under Spectroelectrochemical Conditions ................ 139
6.2.1. Sodium Thiosulfate .............................................................. 139
6.2.2. Sodium Thiosulfate + Ammonia ........................................... 140

6.3. Raman Spectroscopy of Reference Compounds 141

6.4. Concurrent SERS and Cyclic Voltammetry 146
6.4.1. Sodium Thiosulfate .............................................................. 147
6.4.2. Sodium Thiosulfate + Ammonia ........................................... 149

6.5. SERS Measurements at Stepped Potentials 152
6.5.1. Sodium Thiosulfate .............................................................. 152
   6.5.1.1. Laser Restructuring................................................................. 154
   6.5.1.2. Formation of Polythionates .................................................... 155
   6.5.1.3. Effect of pH ......................................................................... 155
   6.5.1.4. Extended Polarisation at High Potential ..................................... 155
6.5.2. Sodium Thiosulfate + Ammonia ........................................... 156
6.5.3. Ammonium Thiosulfate ........................................................ 158
6.5.4. Ammonium Thiosulfate + Ammonia ..................................... 159
6.5.5. Summary ............................................................................. 161

6.6. Time-Dependent SERS 162
6.6.1. Sodium Thiosulfate .............................................................. 162
6.6.2. Ammonium Thiosulfate ........................................................ 163
6.6.3. Sodium Thiosulfate + Ammonia ........................................... 164

6.7. Increased Thiosulfate Concentration 165
6.7.1. Stepped Potentials ................................................................. 165
6.7.2. Effect of pH .......................................................................... 167
6.7.3. Time-dependent SERS ........................................................ 169

6.8. Sodium Tetrathionate 171

6.9. Ammoniacal Copper(II) Thiosulfate Leaching 173
6.9.1. Cupric Tetra-ammine Sodium Thiosulfate............................ 173
6.9.2. Stability of SERS Surface During Leaching ............................. 175
6.9.3. Cupric Tetra-ammine Ammonium Thiosulfate ...................... 176

6.10. Sulfide as a Model System 178
6.10.1. SERS in Acidic Sulfide Media .............................................. 179
   6.10.1.1. Voltammetry on Polished Gold ............................................. 179
   6.10.1.2. Concurrent SERS and Voltammetry ......................................... 181
   6.10.1.3. Protonation of Chemisorbed Sulfide ....................................... 183
6.10.2. Investigation of Chemisorbed Sulfide in Sulfuric Acid ........... 185
6.10.3. SERS in Alkaline Sulfide Media ........................................... 187
   6.10.3.1. Voltammetry on Polished Gold ............................................. 187
   6.10.3.2. SERS and Voltammetry on Oxidation-Reduction Cycled Gold .... 188
6.10.4. Ex situ SERS of Chemisorbed Sulfide .................................. 191

6.11. Effect of Thiourea 193
6.11.1. Time-dependent SERS of Thiosulfate + Thiourea .................... 193
6.11.2. Stripping of Surface Layer after Oxidation in Thiosulfate ....... 194
6.11.3. Stripping of Chemisorbed Sulfide ......................................... 195
7. **EX SITU TECHNIQUES**

7.1. Preamble

7.2. Voltammetric Coverage Determination

7.2.1. Sulfide

7.2.2. Thiosulfate Solutions

7.2.3. Ammoniacal Copper(II) Thiosulfate

7.3. Leaching Rate in Ammoniacal Copper(II) Thiosulfate

7.4. X-ray Photoelectron Spectroscopy

7.4.1. Oxidation-Reduction Cycled Gold in Thiosulfate

7.4.1.1. Sodium Thiosulfate at 310 mV for 1 hr

7.4.1.2. Sodium Thiosulfate at the mixed potential for 72 hrs

7.4.2. Polished Gold in Thiosulfate

7.4.3. Ammoniacal Copper(II) Sodium Thiosulfate

7.4.3.1. Sulfur 2p Region

7.4.3.2. Volatility of Adsorbates

7.5. ATR-FTIR in Cupric Tetra-ammine Sodium Thiosulfate

8. **CONCLUSIONS**

8.1. Summary of Results

8.1.1. Rotating Disk Electrochemistry

8.1.2. SERS Substrate

8.1.3. Sulfide as a Model System

8.1.4. Thiosulfate with Additives

8.1.5. Thiourea

8.1.6. Ammoniacal Copper(II) Thiosulfate Leach Solutions

8.2. Future Work

8.3. Concluding Remarks

8.4. References
### Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Å</td>
<td>Angstrom</td>
</tr>
<tr>
<td>A</td>
<td>Ampere</td>
</tr>
<tr>
<td>AAS</td>
<td>atomic absorption spectroscopy</td>
</tr>
<tr>
<td>AES</td>
<td>Auger electron spectroscopy</td>
</tr>
<tr>
<td>a-S</td>
<td>photo-induced amorphous sulfur</td>
</tr>
<tr>
<td>ATR-FTIR</td>
<td>attenuated total reflectance Fourier transform infrared</td>
</tr>
<tr>
<td>Au-S₈</td>
<td>adsorbed cyclo-octasulfur</td>
</tr>
<tr>
<td>Au-Sₙ</td>
<td>adsorbed polymeric sulfur</td>
</tr>
<tr>
<td>BE</td>
<td>binding energy</td>
</tr>
<tr>
<td>BSE</td>
<td>backscattered electron</td>
</tr>
<tr>
<td>CCD</td>
<td>charged-coupled device</td>
</tr>
<tr>
<td>cm⁻¹</td>
<td>wavenumber</td>
</tr>
<tr>
<td>CTR</td>
<td>crystal truncation scattering</td>
</tr>
<tr>
<td>CV</td>
<td>cyclic voltammetry</td>
</tr>
<tr>
<td>δ</td>
<td>bending vibration</td>
</tr>
<tr>
<td>E</td>
<td>potential</td>
</tr>
<tr>
<td>E₉₃</td>
<td>potential vs. SHE</td>
</tr>
<tr>
<td>EDX</td>
<td>energy dispersive X-ray</td>
</tr>
<tr>
<td>EQCM</td>
<td>electrochemical quartz crystal microbalance</td>
</tr>
<tr>
<td>ESEM</td>
<td>environmental scanning electron microscope</td>
</tr>
<tr>
<td>EV</td>
<td>electron volt</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width half maximum</td>
</tr>
<tr>
<td>HREELS</td>
<td>high resolution electron energy-loss spectroscopy</td>
</tr>
<tr>
<td>I</td>
<td>current</td>
</tr>
<tr>
<td>IMFP</td>
<td>inelastic mean free path</td>
</tr>
<tr>
<td>IR</td>
<td>infrared</td>
</tr>
<tr>
<td>IRRAS</td>
<td>infrared reflection-absorption spectroscopy</td>
</tr>
<tr>
<td>kV</td>
<td>kilovolt</td>
</tr>
<tr>
<td>LEED</td>
<td>low energy electron diffraction</td>
</tr>
<tr>
<td>LSV</td>
<td>linear sweep voltammetry</td>
</tr>
<tr>
<td>M</td>
<td>molar (mol dm⁻³)</td>
</tr>
<tr>
<td>min</td>
<td>minute</td>
</tr>
<tr>
<td>ML</td>
<td>monolayer</td>
</tr>
<tr>
<td>µm</td>
<td>micron (10⁻⁶ m)</td>
</tr>
<tr>
<td>ν</td>
<td>stretching vibration</td>
</tr>
<tr>
<td>NA</td>
<td>numerical aperture</td>
</tr>
<tr>
<td>nm</td>
<td>nanometer (10⁻⁹ m)</td>
</tr>
<tr>
<td>OCP</td>
<td>open circuit potential</td>
</tr>
<tr>
<td>ORC</td>
<td>oxidation-reduction cycle</td>
</tr>
<tr>
<td>ppm</td>
<td>parts per million</td>
</tr>
<tr>
<td>pm</td>
<td>picometer (10⁻¹² m)</td>
</tr>
<tr>
<td>QCM</td>
<td>quartz crystal microbalance</td>
</tr>
<tr>
<td>R</td>
<td>Raman</td>
</tr>
<tr>
<td>RDE</td>
<td>rotating disk electrode</td>
</tr>
<tr>
<td>RHE</td>
<td>reversible hydrogen electrode</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Full Form</td>
</tr>
<tr>
<td>-------------</td>
<td>-----------</td>
</tr>
<tr>
<td>REQCM</td>
<td>rotating electrochemical quartz crystal microbalance</td>
</tr>
<tr>
<td>RSF</td>
<td>relative sensitivity factor</td>
</tr>
<tr>
<td>RT</td>
<td>room temperature</td>
</tr>
<tr>
<td>SAM</td>
<td>self-assembled monolayer</td>
</tr>
<tr>
<td>SCE</td>
<td>saturated calomel electrode</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscopy</td>
</tr>
<tr>
<td>SERS</td>
<td>surface enhanced Raman scattering</td>
</tr>
<tr>
<td>SFG</td>
<td>sum frequency generation</td>
</tr>
<tr>
<td>SHE</td>
<td>standard hydrogen electrode</td>
</tr>
<tr>
<td>SHG</td>
<td>second harmonic generation</td>
</tr>
<tr>
<td>S-\text{II}</td>
<td>sulfide including S^{2-}, HS^-, H_2S</td>
</tr>
<tr>
<td>SIMS</td>
<td>secondary ion mass spectrometry</td>
</tr>
<tr>
<td>S_\mu</td>
<td>polymeric sulfur, bulk solid</td>
</tr>
<tr>
<td>S_n</td>
<td>polymeric sulfur</td>
</tr>
<tr>
<td>S_x</td>
<td>polymeric sulfur, large disordered rings</td>
</tr>
<tr>
<td>SPR</td>
<td>surface plasmon resonance</td>
</tr>
<tr>
<td>STM</td>
<td>scanning tunnelling microscopy</td>
</tr>
<tr>
<td>UHV</td>
<td>ultra high vacuum</td>
</tr>
<tr>
<td>ULWD</td>
<td>ultra long working distance</td>
</tr>
<tr>
<td>UV</td>
<td>ultra violet</td>
</tr>
<tr>
<td>V</td>
<td>volts</td>
</tr>
<tr>
<td>vis</td>
<td>visible</td>
</tr>
<tr>
<td>vs.</td>
<td>versus</td>
</tr>
<tr>
<td>W</td>
<td>Watt</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
Figures

Figure 1-1: Potential waveform for SERS activating a gold electrode in 0.1 M KCl (Tian 2002). Potential V vs. SCE ............................................................. 21

Figure 1-2: Diagram of an ATR cell (Desai and Boeckl 2004)............................................................. 23

Figure 2-1: \( E_{\text{H}} \) – pH diagram for Au-H2O system at 25 °C (Vijh and Belanger 1977). ............................................................. 31

Figure 2-2: Cyclic voltammogram for a gold electrode in 0.5 M HClO4, from 0.05 to 1.7 V at a sweep rate of 50 mVs\(^{-1}\) (Tian and Conway 2004). ....... 33

Figure 2-3: Oxidation of thiourea to formamidine disulfide (Tian and Conway 2004)................................. 40

Figure 2-4: Linear sweep voltammogram in 0.2 M sodium thiosulfate showing oxidation of gold to gold thiosulfate. Accompanying mass change of gold electrode and calculated current are also shown (Chandra and Jeffrey 2004)................................. 43

Figure 2-5: Linear sweep voltammograms showing the effect of thiourea and potassium ethyl xanthate on the oxidation of gold in 0.2 M ammonium thiosulfate (Chandra and Jeffrey 2004)................................. 48

Figure 2-6: Structure of Au2S (Ishikawa et al. 1995)............................................................................... 50

Figure 2-7: Voltammograms for gold electrode in borate solution of pH 9.2 containing 1.6 x 10\(^{-4}\) M HS\(^{-}\). Triangular potential cycles at 20 mV s\(^{-1}\), with overlaid scans representing subsequent excursions to incrementally increased maximum potentials. The electrode was (a) stationary and (b) rotated at 10 Hz (Hamilton and Woods 1983)..................................................................... 51

Figure 2-8: \( E_{\text{H}} \)-pH diagram for the sulfur-water system at 25°C, 2 x 10\(^{-4}\) M for S\(^{\text{II}}\) species and 10\(^{-6}\) M for polysulfide species. Oxy-sulfur anions are not considered. Diagrams generated employing the CSIRO-NPL Thermodata system (Buckley et al. 1987). .................................................................................... 56

Figure 2-9: Example of sulfur adlayer domain on Au(111) after transfer to air (Gao et al. 1992b)..................................................................................... 58

Figure 2-10: Optimised geometry of the global minimum D\(_{4d}\) crown-S\(_{8}\) isomer (Wong et al. 2002)..................................................................................... 58

Figure 2-11: \textit{In situ} atomic resolution 6 x 6 nm\(^{2}\) STM images of electrodeposited sulfide, a) (\(3\sqrt{3}\times 3\sqrt{3}\))R30\(^{\circ}\) –800 mV; b) S\(_{3}\) –700 mV; c) S\(_{8}\) –600 mV vs. SCE 0.1 M NaOH, 3 mM Na\(_{2}\)S (Vericat et al. 2004).................................................. 59

Figure 2-12: STM micrograph of the c(4x2\(\sqrt{3}\)) structure adsorbed on the Au(111) electrode at -0.15 V vs. 3 M Ag/AgCl in 1.0 mM Na\(_{2}\)S\(_{2}\)O\(_{3}\), 1.0 mM KOH. The scan size is 7.5 x 7.5 nm\(^{2}\). ........................................................................ 60

Figure 2-13: ASTM standard spectrum for sulfur (McCreery 2005). ............................................................. 65

Figure 2-14: Raman spectra of polymeric sulfur. S\(_{x}\) - Large disordered rings; a-S - photo-induced amorphous sulfur; S\(_{\mu}\) - polymeric sulfur prepared by various methods (Eckert and Steudel 2003)................................................................................................. 66

Figure 2-15: Raman spectra of (a) polycrystalline, (b) glassy, (c) aqueous, and (d) molten Na\(_{2}\)S\(_{4}\). (Janz et al. 1976b). Detail of overtone region of polycrystalline spectrum shown in (e). ............................................................. 69

Figure 2-16: Raman spectra of Na\(_{2}\)S\(_{2}\)O\(_{3}\) and Na\(_{3}\)Au(S\(_{2}\)O\(_{3}\))\(_{2}\) from both solid phase and 0.1 M solutions ............................................................. 71

Figure 2-17: Raman spectrum of 1.0 M thiourea (Liu and Wu 2005)............................................................. 74

Figure 2-18: Resonance structures of thiourea (Reents et al. 1998). ............................................................. 75
Figure 2-19: SEM image of a SERS-optimised gold electrode oxidation-reduction
cycled in 0.1 M KCl (Liu et al. 2005). ............................................................ 77
Figure 2-20: Schematic representation of the development of a 3rd generation Menger
sponge fractal used for a porous roughened surface (Micic et al. 2004). . 79
Figure 2-21: Schematic representation of the development of a 3rd generation Koch
curve fractal used by to model a dendritic growth surface
(Micic et al. 2004). ..................................................................................... 79
Figure 2-22: SERS spectra of high coverage multilayer sulfur adsorbed on Au
from SO₂ in HClO₄, acquired during voltammetric cycle from
500 to –200 mV vs. RHE at 5 mVs⁻¹ (Quijada et al. 2000). ..................... 84
Figure 3-1: Spectroelectrochemical cell. A) gold working electrode, B) Ag/AgCl
reference, C) Pt auxiliary, D) solution purge inlet, E) over solution purge
inlet, F) purge outlet, G) syringe for reagent addition,
H) spectrometer objective, I) gold flag under 633 nm irradiation. .......... 92
Figure 3-2: Rotating disk electrochemical apparatus. Electrode, inset top right, shows
loss of SERS surface when electrode was polished too finely prior to
oxidation-reduction cycling................................................................. 97
Figure 3-3: Waveform generated by the automated ORC frequency generator........ 102
Figure 4-1: SEM images of SERS electrodes: a) standard preparation, 5 min ORC
with rinsing, b) highly-dendritic, 15 min ORC with soaking to minimise
loss of surface structures. ..................................................................... 110
Figure 4-2: EDX analysis of the highly-dendritic oxidation-reduction cycled gold
surface. .................................................................................................. 111
Figure 4-3: Backscattered scanning electron image of the highly-dendritic gold SERS
surface, magnification x8000................................................................. 112
Figure 4-4: Scanning electron image of the highly-dendritic gold SERS surface
showing nanoscale features................................................................ 112
Figure 4-5: Backscattered (left) and secondary (right) electron images of the standard
SERS electrode preparation. ................................................................. 113
Figure 4-6: EDX analysis of the standard gold SERS surface. ...................... 114
Figure 4-7: Scanning electron images of standard oxidation-reduction cycled gold
surface showing nanoscale features. Left image magnification x20000,
right image x40000............................................................................ 114
Figure 4-8: Cyclic voltammograms comparing the formation of gold oxide on a
polished gold (black) and oxidation-reduction cycled gold electrode (red)
in 0.1 M H₂SO₄, scan rate 40 mVs⁻¹. Note the scale of the oxidation-
reduction cycled electrode has been reduced by 1/3 to compare with
that of the polished electrode. ................................................................. 115
Figure 4-9: XPS survey scan of polished gold surface................................... 116
Figure 4-10: XPS survey scan of oxidation-reduction cycled gold surface ......... 118
Figure 4-11: XRD pattern of gold dendrite fragments from an oxidation-reduction
cycled gold electrode using a cobalt source. ................................. 120
Figure 5-1: Voltammogram of 0.1 M Na₂S₂O₃ recorded at 1 mV s⁻¹ with a gold
electrode rotated at 300 RPM................................................................. 123
Figure 5-2: Comparison of polished and oxidation-reduction cycled gold disk electrodes
rotated at 300 RPM in 0.1 M Na₂S₂O₃, LSV at 1 mV s⁻¹ ......................... 124
Figure 5-3: Comparison of polished and oxidation-reduction cycled gold disk electrodes
rotated at 300 RPM in 0.1 M Na₂S₂O₃, LSV at 1 mV s⁻¹. Detail of prewave region. ........................................................................ 125
Figure 5-4: Polished gold rotated disk electrodes in 0.1 M Na$_2$S$_2$O$_3$ and 0.1 M (NH$_4$)$_2$S$_2$O$_3$ at 300 RPM, sweep rate 1 mV s$^{-1}$. ............................ 126

Figure 5-5: Comparison of polished gold disk electrodes rotated at 300 RPM in 0.1 M Na$_2$S$_2$O$_3$; and 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$; scan rate 1 mV s$^{-1}$. .... 127

Figure 5-6: Polished gold disk electrodes rotated at 300 RPM in 0.1 M Na$_2$S$_2$O$_3$; 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$; and 0.1 M Na$_2$S$_2$O$_3$, 10 mM thiourea, scan rate 1 mV s$^{-1}$. ............................................................ 128

Figure 5-7: Polished gold disk electrodes rotated at 300 RPM in 0.1 M Na$_2$S$_2$O$_3$; 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$; and 0.1 M Na$_2$S$_2$O$_3$, 10 mM thiourea. Detail of thiourea prewave region. .................. 129

Figure 5-8: Polished gold disk electrodes rotated at 300 RPM in 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$; and 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$; scan rate 1 mV s$^{-1}$. ............................................................ 129

Figure 6-1: 0.1 M Na$_2$S$_2$O$_3$; and 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$ on oxidation-reduction cycled gold flag electrode, scan rate 1 mV s$^{-1}$ from –190 mV in the positive direction. Inset, RDE voltammetry at same scan rate on polished electrode in same solutions. ............................................................ 139

Figure 6-2: Solution Raman from aqueous oxy-sulfur anions 0.1 M Na$_2$S$_4$O$_6$; sat. Na$_3$Au(S$_2$O$_3$)$_2$; 1.0 M Na$_2$S$_2$O$_3$; 0.1 M Na$_2$SO$_4$; and from solid cyclo-octasulfur, α-S$_8$. ............................................................ 141

Figure 6-3: Raman spectra from gold sulfide and elemental cyclo-octasulfur (Irradiation density: 0.0031 kW cm$^{-2}$ and 0.31 kW cm$^{-2}$ respectively; 10 s x 100 accumulations and 0.2 s x 10 accumulations respectively). ........................................... 143

Figure 6-4: Raman spectrum of polysulfide solution prepared by dissolving Na$_2$S in deoxygenated water, adding S$_8$ as flowers of sulfur in the stoichiometric ratio of $2/8$ mol S$_8$ to 1 mol Na$_2$S and boiled for about 2 min until sulfur dissolved (Irradiation density: 0.31 kW cm$^{-2}$ 10 s x 10 accumulations). ........................................... 144

Figure 6-5: Solution Raman spectra of 1.0 M solutions of the sodium salts of disulfite, S$_2$O$_5^{2-}$; thiosulfate, S$_2$O$_3^{2-}$; sulfate, SO$_4^{2-}$; and oxygenated 0.1 M Na$_2$S$_2$O$_3$, 0.01 M CuSO$_4$, 0.4 M NH$_3$. ......................................................... 145

Figure 6-6: Cyclic voltammograms of 0.1 M Na$_2$S$_2$O$_3$ and 0.1 M (NH$_4$)$_2$S$_2$O$_3$ on ORC gold flag electrodes, from –290 mV scanned in the positive direction, scan rate 10 mVs$^{-1}$. ........................................................................... 146

Figure 6-7: SERS spectra acquired during cyclic voltammetry of Au in 0.1 M Na$_2$S$_2$O$_3$. Each scan represents data acquired during a ~70 mV voltammetric excursion, with the marked potential being the centre of the range. The lower scan was acquired at the starting potential. ......................... 147
Figure 6-8: Raman shift and current density vs. time-based potential. Dots represent SERS peaks observed during cyclic voltammetry of Au in 0.1 M Na$_2$S$_2$O$_3$. Data on RHS of diagram acquired during reverse scan. 148

Figure 6-9: SERS spectra acquired during cyclic voltammetry of Au in 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$. Each scan represents data acquired during a ~70 mV voltammetric excursion, with the marked potential being the centre of the range. The lowest scan was acquired at the starting potential. 149

Figure 6-10: Raman shift positions and current density vs. time-based potential. Dots represent SERS peak positions observed during cyclic voltammetry of Au in 0.1 M Na$_2$S$_2$O$_3$ with 0.4 M NH$_3$. Data on RHS of diagram represents current and SERS data acquired during reverse scan. 150

Figure 6-11: SERS spectra from gold electrode in 0.1 M$^3$ Na$_2$S$_2$O$_3$ recorded at the mixed potential and after holding at the applied potential for 2 min. 153

Figure 6-12: SERS spectra from gold electrode in 0.1 M Na$_2$S$_2$O$_3$ with 0.4 M NH$_3$ recorded at the mixed potential and after holding at applied potentials for 2 min. 156

Figure 6-13: SERS spectra from gold electrode in 0.1 M (NH$_4$)$_2$S$_2$O$_3$ recorded at the mixed potential and after holding at applied potentials for 2 min. 158

Figure 6-14: SERS spectra from gold electrode in 0.1 M (NH$_4$)$_2$S$_2$O$_3$, 0.4 M NH$_3$ recorded at the mixed potential and after holding at applied potentials for 2 min. 160

Figure 6-15: SERS spectra from gold electrode in 0.1 M Na$_2$S$_2$O$_3$ held for the marked times at A, 210 mV, and B, 310 mV. 163

Figure 6-16: SERS spectra recorded at 310 mV for (lower) 0.1 M Na$_2$S$_2$O$_3$ after 135 min, (middle) 0.1 M Na$_2$S$_2$O$_3$ after 202 min, (upper) 0.1 M Na$_2$S$_2$O$_3$ plus 0.4 M NH$_3$ after 160 min. 164

Figure 6-17: SERS spectra from a gold electrode in neutral 1.0 M Na$_2$S$_2$O$_3$ recorded at the mixed potential and after holding at the applied potential for 2 min. 166

Figure 6-18: SERS spectra from gold electrode in neutral, pH 9.2 and pH 10.5 solutions of 1.0 M Na$_2$S$_2$O$_3$ after holding at 350 mV for 2 min. 168

Figure 6-19: SERS spectra from gold electrode at the mixed potential in 1.0 M Na$_2$S$_2$O$_3$ at pH 10.5 recorded at 2, 5 and 10 min. Reference spectra of solid Au$_2$S and 0.1 M Na$_3$Au(S$_2$O$_3$)$_2$ are included for comparison. 170

Figure 6-20: Potential-dependent SERS spectra of gold in a 0.1 M sodium tetraionate solution and solution spectrum. 171

Figure 6-21: SERS spectra recorded in situ after 15 min in a solution of 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$, 0.01 M CuSO$_4$ in equilibrium with air and after transfer to water, then 0.1 M H$_2$SO$_4$. 174

Figure 6-22: Time-evolved SERS spectra from dendritic gold SERS surface leached in ammoniacal copper(II) sodium thiostasulfate solution, a) evolution of SERS signal to maximum at 20 min, b) diminution of SERS signal after 20 min. 175

Figure 6-23: SERS spectra recorded in situ after 15 min in 0.1 M (NH$_4$)$_2$S$_2$O$_3$, 0.4 M NH$_3$, 0.01 M CuSO$_4$ in equilibrium with air and after transfer to water, then to 0.1 M H$_2$SO$_4$. 177

Figure 6-24: Voltammograms at 20 mV s$^{-1}$ for a gold electrode in 0.1 M H$_2$SO$_4$ containing 2x10$^{-3}$ M Na$_2$S commenced at –290 mV and taken to different upper potential limits. 180

Figure 6-25: Triangular potential sweep voltammogram at starting from –290 mV at 2 mV s$^{-1}$ in 2 x 10$^{-3}$ M H$_2$S, 0.1 M H$_2$SO$_4$. 181
Figure 6-26: SERS spectra from a gold electrode in $2 \times 10^{-3}$ M H$_2$S, 0.1 M H$_2$SO$_4$ acquired during the 2 mV s$^{-1}$ voltammogram in Figure 6-25. The lowest scan is first of the series, from the start potential of $-290$ mV. ............ 182

Figure 6-27: High and low wavenumber regions Raman spectra of Au electrode in 0.1 M H$_2$SO$_4$ and $\sim 20 \times 10^{-3}$ M Na$_2$S held at various potentials............. 184

Figure 6-28: *in situ* SERS spectra after immersion of a gold SERS electrode stepped upward in potential in 0.1 M H$_2$SO$_4$ following removal from 0.1 M H$_2$SO$_4$, $2 \times 10^{-3}$ M Na$_2$S. The upper spectrum was acquired after the potential was decreased to $-240$ mV from 510 mV ....................................................... 185

Figure 6-29: Voltammograms at 20 mV s$^{-1}$ for a gold electrode in 0.05 M Na$_2$B$_4$O$_7$ containing $2 \times 10^{-3}$ M Na$_2$S, commenced at -1.09 V and taken to increasing upper potential limits (Parker *et al.* in preparation) ......................... 188

Figure 6-30: Triangular potential sweep voltammogram at 2 mVs$^{-1}$ in 1 mM Na$_2$S, 0.05 M Na$_2$B$_4$O$_7$ starting from $-690$ mV. ............................................................. 189

Figure 6-31: SERS spectra recorded after holding the potential of a gold electrode in $10^{-3}$ M Na$_2$S, 0.05 M Na$_2$B$_4$O$_7$ solution, pH 9.2, after holding the potential at the specified value for 2 min. ................................................................. 189

Figure 6-32: *ex situ* SERS spectra from a gold electrode withdrawn from 1 mM Na$_2$S in 0.05 M Na$_2$B$_4$O$_7$ solution, pH 9.2, upon removal from cell, rinsing and drying in air. ............................................................................................ 191

Figure 6-33: Time-dependent gold SERS spectra of 10 mM thiourea, 0.1 M Na$_2$S$_2$O$_3$ at 210 mV.......................................................... 193

Figure 6-34: SERS spectra from gold held in 0.1 M Na$_2$S$_2$O$_3$ at 210 mV, followed by returning to the OCP and adding solid thiourea to make the solution 0.1 M Na$_2$S$_2$O$_3$, 10 mM Tu. The potential was stepped to 210 mV after 20 min at OCP ................................................................. 195

Figure 6-35: SERS spectra from a gold electrode removed after holding in 1 mM Na$_2$S in 0.05 M Na$_2$B$_4$O$_7$ solution, pH 9.2, for 1 hr at $-290$ mV then placing in a solution of 0.01 M thiourea in 0.1 M sodium thiosulfate and holding at the marked potentials for the specified times ............................................. 196

Figure 7-1: Reference oxide monolayer stripping peak for polished gold flag electrode used for sulfide electrode-oxidation studies. Negative-going linear sweep from 1.81 to 0.21 V at 40 mVs$^{-1}$ after holding at 1.81 V for 100 s .......... 201

Figure 7-2: Triangular sweep voltammograms in 0.1 M H$_2$SO$_4$ from a gold electrode after holding at the specified potential for 100 s in 1 mM Na$_2$S, 0.05 M Na$_2$B$_4$O$_7$ solution, pH 9.2. .......................................................... 203

Figure 7-3: (A) A cyclic voltammogram from 0.21 V, initially in the positive-going direction, with potential limits of 0.21 V and 1.81 V, recorded after a gold electrode was held at 0.51 V for 15 min in 0.1 mol dm$^{-3}$ (NH$_4$)$_2$S$_2$O$_7$; negative-going linear potential sweep voltammogram after the electrode was then held at 1.81 V for 100 s in 0.1 mol dm$^{-3}$ H$_2$SO$_4$ (dashed line). Scans at 40 mV s$^{-1}$. (B) SERS spectra recorded in real time at each of the potentials marked on the voltammogram; these potentials are: initial positive-going scan, A 0.41 V, B 1.14 V, C 1.48 V; return scan, D 1.34 V, E 1.21 V, F 0.81 V; second positive-going scan G 0.41 V. .... 206

Figure 7-4: SERS spectra acquired for gold in various thiosulfate solutions at 310 mV prior to coverage determination in acid................................. 208

Figure 7-5: SERS spectra acquired for gold in various thiosulfate solutions at 510 mV prior to coverage determination in acid................................. 209
Figure 7-6: SERS spectra acquired for gold in various thiosulfate solutions at (A) 710 mV, (B) 810 mV & (C) 710 mV prior to coverage determination in acid............................................................................... 210

Figure 7-7: A linear potential sweep voltammogram at 1 mV s\(^{-1}\) after immersion for 15 min in 0.1 M Na\(_2\)S\(_2\)O\(_3\), 0.4 M NH\(_3\), 0.01 M CuSO\(_4\); and transfer to 0.1 M H\(_2\)SO\(_4\) (— - - - - - - -); a subsequent cyclic voltammogram at 40 mV s\(^{-1}\) commenced at 710 mV in the positive-going direction, with potential limits of 1.81 V and 210 mV (———); a following negative-going linear potential sweep voltammogram after the electrode was then held at 1.81 V for 100 s ( — — — ). ............................................................. 212

Figure 7-8: Leaching kinetics of gold in cupric tetra-ammine sodium (Na\(^{+}\)) and ammonium (NH\(_4\)\(^{+}\)) thiosulfate solutions as determined by AAS............ 214

Figure 7-9: SERS spectra from a gold electrode prior to XPS examination: in situ at 310 mV in 0.1 M Na\(_2\)S\(_2\)O\(_3\) solution and ex situ immersed in water and after drying in air. ............................................................................................ 217

Figure 7-10: Al K\(_\alpha\) XPS survey scan of gold SERS electrode after polarising at 310 mV in 0.1 M Na\(_2\)S\(_2\)O\(_3\) for 1 hr. ............................................................... 218

Figure 7-11: Detail of sulfur 2p region of Al K\(_\alpha\) XPS scan from gold SERS electrode after polarising at 310 mV in 0.1 M Na\(_2\)S\(_2\)O\(_3\) for 1 hr. ............................... 219

Figure 7-12: SERS spectra from a gold electrode prior to XPS examination, in situ at the mixed potential in 0.1 M Na\(_2\)S\(_2\)O\(_3\) solution after 72 hrs, ex situ after rinsing and drying in air. ..................................................... 221

Figure 7-13: Al K\(_\alpha\) XPS survey scan of gold SERS electrode leaching in 0.1 M Na\(_2\)S\(_2\)O\(_3\) at the mixed potential in air for 72 hrs. ................................. 222

Figure 7-14: Detail of sulfur 2p region of Al K\(_\alpha\) XPS scan from a gold SERS electrode after leaching in 0.1 M Na\(_2\)S\(_2\)O\(_3\) at the mixed potential in air for 72 hrs. 223

Figure 7-15: S 2p\(_{3/2}\) region of XPS spectrum of gold polarised in 0.1 M Na\(_2\)S\(_2\)O\(_3\) at (A) 210 mV and (B) 310 mV. ............................................................... 224

Figure 7-16: Al K\(_\alpha\) XPS detail spectra of: a) Cu 2p; b) N 1s regions for gold leached for 1 hr in a solution of 0.1 mol dm\(^{-3}\) Na\(_2\)S\(_2\)O\(_3\), 0.4 mol dm\(^{-3}\) NH\(_3\), 0.01 mol dm\(^{-3}\) CuSO\(_4\). Pass energy 40 eV, X-ray power 225 W. This sample (A) had spent minimum time under vacuum. ........................................ 226

Figure 7-17: Al K\(_\alpha\) XPS detail spectra of S 2p regions for gold leached for 1 hr in a solution of 0.1 mol dm\(^{-3}\) Na\(_2\)S\(_2\)O\(_3\), 0.4 mol dm\(^{-3}\) NH\(_3\), 0.01 mol dm\(^{-3}\) CuSO\(_4\). Sample A had spent minimum time under vacuum, with sample B having spent a further hour under vacuum. Pass energy 40 eV, X-ray power 225 W. ............................................................................................. 227

Figure 7-18: ATR-FTIR spectrum of rinsed and air-dried gold after leaching for 1 hr in sodium thiosulfate leach solution. ..................................................... 230
Tables

Table 2-1: Electronic structures of various valence states of gold, common geometries and examples of gold compounds for each valence state (Puddephatt 1987) ................................................................. 27
Table 2-2: Ionisation energies for copper, silver and gold (eV) (Puddephatt 1978) .... 27
Table 2-3: Some physical, thermodynamic and structural properties of gold........... 28
Table 2-4: Standard redox potentials and stability constants for the oxidation of gold in various ligands .................................................................................................................. 35
Table 2-5: XPS binding energies of various copper and sulfur compounds (Moulder et al. 1995) ........................................................................................................ 61
Table 2-6: Vibrational assignments and experimental wavenumbers for S₈ in CS₂. Wavenumber value calculated for inactive mode (Eckert and Steudel 2003). R – Raman, IR – infrared .................................................. 65
Table 2-7: IR and Raman modes of Au-S bonds in gold-sulfur compounds (Bowmaker 1999) .................................................................................................................. 68
Table 2-8: Raman assignments of the thiosulfate ion in solution (Haigh et al. 1993; Meyer et al. 1980) ........................................................................................................ 70
Table 2-9: Raman assignments for solid potassium polythionates, n = 3-6 (Steudel et al. 1988) ........................................................................................................ 73
Table 2-10: Quantitative Raman modes of some oxysulfur anions in solution (Meyer et al. 1980) ........................................................................................................ 74
Table 3-1: List of reagents ...................................................................................... 89
Table 4-1: XPS Quantification of a polished gold electrode .................................... 117
Table 4-2: XPS Quantification of an oxidation-reduction cycled gold electrode .... 118
Table 5-1: Comparison of oxidation peak potentials and maximum currents observed in RDE voltammograms for various thiosulfate systems. First column, shows currents for each system at 250 mV, the potential at which gold is known to oxidised in thiosulfate solutions (Chandra and Jeffrey 2004). Remaining cells represent peak positions and respective current maxima for the various systems ........................................................................................................... 135
Table 7-1: Sulfur coverage on a smooth gold electrode held at the marked potential for 100 s in 1 mM Na₂S in 0.05 M Na₂B₄O₇, pH 9.2 as determined by voltammetry in 0.1 M H₂SO₄ ........................................................................ 204
Table 7-2: Sulfur coverage on gold electrode determined by voltammetry .......... 207
Table 7-3: Sulfur and copper coverage on gold electrode in cupric tetra-ammine sodium thiosulfate leach solution as determined by voltammetry. .......... 213
Table 7-4: Sulfur and copper coverage on gold electrode in cupric tetra-ammine ammonium thiosulfate leach solution as determined by voltammetry ...... 213
Table 7-5: Quantification of XPS survey scan for a gold SERS electrode polarised for 1 hr at 310 mV in 0.1 M Na₂S₂O₃ ........................................................... 219
Table 7-6: Quantification of XPS survey scan for a gold SERS electrode after leaching in 0.1 M Na₂S₂O₃ at the mixed potential in air for 72 hrs. .......................... 222
Table 7-7: Binding energies and percentages of S 2p types on gold leached for 1 hr in a solution of 0.1 mol dm⁻³ Na₂S₂O₃, 0.4 mol dm⁻³ NH₃, 0.01 mol dm⁻³ CuSO₄. Sample (A) had spent minimum time under vacuum, with sample B having spent a further hour under vacuum ................................................... 228
Table 7-8: Nitrogen, sulfur and copper intensities on gold electrode in cupric tetra-ammine sodium thiosulfate leach solution as determined by XPS ........ 229
1. INTRODUCTION
1.1. **Gold**

Australia has recently replaced South Africa as the world’s second largest producer of gold, after the USA (Baker 2005). Our exports of non-monetary gold amounted to $5,642 million in 2004-5, ranking fourth in exports after coal, iron ore and crude petroleum (Baker 2005). In some situations the gold industry is being restrained by the lack of suitable leaching technology, particularly for carbonaceous and refractory ores. Rising gold prices are currently being accompanied by a global increase in exploration and investment in the development of extraction technologies. Unmined areas in Africa, Asia, South America and Russia have become a focus of major gold producing companies, with potential for environmental damage and dissent between mining companies and regional authorities who oppose the use of cyanide (Werbowski 2006). The development of an environmentally acceptable and commercially viable alternative to cyanide would be of great advantage to the gold recovery industry.

The ammoniacal copper(II) thiosulfate leaching system has the potential to replace cyanide as a lixiviant for the recovery of gold from its ores, but, for common ores, the leaching reaction fails. This long-standing industrial problem has prevented thiosulfate from becoming an acceptable replacement for cyanide. The failure of thiosulfate leaching is thought to be due to a passivation of the gold by a surface species during dissolution (Aylmore and Muir 2001; Breuer and Jeffrey 2003c; Wan and LeVier 2003).

Gold is considered the most noble of metals due to its lack of reactivity with oxygen and sulfur and is not found in nature as a sulfide (Puddephatt 1978). Paradoxically, however, gold has a very strong specific interaction with sulfur as a surface species. Thiols adsorbed onto gold are model systems for the rapidly developing area of self-assembled monolayers (SAMs) (Schreiber 2000). The sulfide ion is the smallest
member of the thiol family and the adsorption of sulfide on gold can be considered a model system for thiol adsorption. In a similar fashion, sulfide on gold can be used as a model system for studies of thiosulfate electro-adsorption.
1.2. **AIMS AND OBJECTIVES**

The aim of this work is to characterise surface reactions on gold in thiosulfate and sulfide solutions in order to provide a basis for the elucidation of the surface processes that passivate gold during leaching in ammoniacal copper(II) thiosulfate systems.

The spectroelectrochemical combination of *in situ* electrochemical and SERS spectroscopy techniques was selected as the primary technique used in order to characterise gold-sulfur surface interactions in both thiosulfate and sulfide solutions, with *ex situ* techniques such as XPS and ATR-FTIR used to provide complementary information. A significant objective of this research has been to examine the adsorption and electro-oxidation of sulfide on gold in order to provide a framework for interpretation of the surface interactions of gold with thiosulfate. The comparison of these spectroelectrochemical results to literature STM studies of electrooxidation of sulfide and thiosulfate is a significant step toward the determination of nature of passivating sulfur surface species on gold.

Characterisation of actively dissolving and passivated surface states serves a practical role in research into the surface passivation that has hampered commercial development of the thiosulfate leaching process. It is envisaged that this work will contribute to the development of thiosulfate as an environmentally acceptable, cost-effective alternative to cyanide in the gold recovery industry.
1.3.** Approach and Methodology**

Dissolution and adsorption reactions both involve surface processes and in order to observe these processes, surface techniques are required. Electrochemistry can be used to monitor the transfer of electrons during adsorption and dissolution processes. The usefulness of electrochemistry is limited by its inability to provide information regarding the nature of the compounds undergoing these reactions, thus ancillary techniques for molecular identification are required.

SERS is a technique that is uniquely appropriate to studies of adsorbates on the coinage metals Au, Ag and Cu, the substrates upon which it has the greatest effect. It provides vibrational structural information on the bonding of surface species and, coupled with electrochemical techniques, is an important tool used to investigate the molecular characteristics of the surface chemistry of gold dissolution and adsorption processes. SERS excels as a surface analysis technique that can be used to readily detect, *in situ*, sub-monolayers of adsorbed species on gold and silver electrodes (Hope et al. 2001; Woods et al. 2000), and has been applied to the investigation of the surface bonding of halides and pseudo halides (such as cyanide) to gold and silver (Gao et al. 1992a; Watling et al. 2005). Gold exhibits surface-enhancement when roughened electrochemically, making SERS a particularly suitable method for use in electrochemical studies of the adsorption and dissolution processes.
The following approaches and analytical methods were used to form the experimental basis for this thesis:

- Characterise the gold SERS substrate by SEM to determine the morphology of the electrogenerated surface structure; XRD to examine substrate crystallinity; and EDX and XPS to determine bulk and surface composition, respectively.
- Acquire RDE voltammetry of gold in thiosulfate and modified thiosulfate solutions using SERS and polished electrode.
- Perform simultaneous voltammetry and SERS of gold in thiosulfate, modified thiosulfate and sulfide solutions under spectroelectrochemical conditions.
- Acquire time-dependent and stepped-potential SERS studies of gold in thiosulfate, modified thiosulfate and sulfide solutions.
- Perform SERS leaching studies of gold in air-saturated ammoniacal copper(II) thiosulfate solutions at the mixed potential.
- Determine sulfur surface coverage of gold held at various potentials in thiosulfate, modified thiosulfate and sulfide solutions; and of copper and sulfur on gold leached in ammoniacal copper(II) thiosulfate solution using electrochemical techniques.
- Undertake kinetic studies using AAS to determine gold concentration in ammoniacal copper(II) thiosulfate leach solution.
- Perform *ex situ* examination of recovered gold using XPS to determine compositional and chemical state information; and ATR-FTIR to gain complementary vibrational information regarding surface species.
1.4. **Thesis Outline**

The thesis comprises eight chapters. Chapter one is an introduction, which presents the background to the impetus for research into gold dissolution in thiosulfate. It also provides a brief background to instrumental techniques including XPS, ATR-FTIR, vibrational spectroscopy and the nature of surface enhancement. Chapter two reviews the literature of the chemistry of gold dissolution processes, including ammoniacal copper(II) thiosulfate leaching and the interaction of sulfur with gold. It reviews vibrational and SERS literature regarding compounds that may be expected under leaching and passivated conditions. Literature results of electrochemical, XPS and STM studies of the interaction of sulfur compounds with gold are also presented. Chapter three provides experimental details for the techniques used for this thesis and chapter four reports the results of the characterisation of the SERS substrate using techniques including SEM, EDX, XPS and voltammetry. The results of experiments are presented and discussed in chapters five through seven. Rotating disk electrochemical studies of polished and roughened gold electrodes in various thiosulfate solutions are presented in chapter five; *in situ* SERS spectroelectrochemical studies of gold in sulfide, thiosulfate and ammoniacal copper(II) thiosulfate leaching solutions in chapter six; and the results of experiments using *ex situ* techniques such as ATR-FTIR, XPS and electrochemical coverage determination in chapter seven. Conclusions, recommendations for further work and references are presented in chapter eight.
1.5. BACKGROUND

The main impetus for undertaking the work for this thesis has been the need for a replacement for cyanide as a leaching agent (lixiviant) for gold. Thiosulfate is seen as the most likely alternative, but it is currently not competitive with cyanide due to problems with leaching efficiency. This section details the problems associated with the use of cyanide, lists the range of alternative lixivants under consideration by industry and presents the impediments that have prevented the adoption of thiosulfate as an alternative leaching agent. A background is also given into the various surface-specific experimental techniques that were used in order to investigate the surface chemistry of the thiosulfate leaching process.

1.5.1. Disadvantages of Cyanide in Gold Leaching

A lixiviant is a liquid medium that selectively leaches a desired metal rapidly and completely from its ore (or other material); and from which the metal can be recovered in a concentrated form (InfoMine 2006). Cyanide has been the gold mining industry’s lixiviant of choice for over 100 years, due to its low cost and the efficiency of gold recovery. Cyanide is an inexpensive raw material and its process applications are well characterised and readily controllable due to the vast amount of industrial experience gained during its extensive use. There is currently no ideal replacement for the cyanide process for treating gold ores, despite intensive research conducted over recent years. Cyanidation remains the most effective leaching system for gold but, due to cyanide’s acute toxicity, it remains a major environmental and public health concern.

Cyanide heap leaching was introduced as ore grades declined during the 1970s in response to a need to optimise yields from poor quality ore reserves. The heap leaching process introduced exposed heaps and tailings dams, which bought with them an
increased risk of environmental exposure and a heightened public awareness regarding the toxicity of cyanide. Well-documented and publicised incidents involving cyanide tailing spillages have included BHP’s Ok Tedi mine in New Guinea (Faulkner 2005); Cambior/Golden Star’s Omai spillage in Guyana, 1995; Esmerelda/Auril at Baia Mare, Romania 2001-2 (MPI 2006; UNEP 2002); and recently Lafayette’s spills at Rapu-Rapu in the Philippines, Oct. 2005 (Greenpeace 2006). Accidents involving the production or transportation of cyanide have also gained media attention, illustrating that not only does the end-use of cyanide in the mining industry present a potential environmental hazard, but also its manufacture and delivery. Reported incidents include the spillage of 1 tonne of sodium cyanide from a helicopter en route to Placer Dome’s Tolukuma mine in PNG, 2000 (UNEP 2002) and cyanide discharge into the river Elbe from the Draslovka chemical plant in the Czech region of Bohemia in January 2006 (CPTC 2006). Reports of hijacking of cyanide during transportation have emerged in the United States, the incidents being perceived by government officials as potential acts of terrorism (Rosenhek 2004).

Cyanide tailings and transportation accidents are now perceived as commonplace by the general public and media and have led to an increase in the global public awareness of the environmental consequences of cyanide usage in the gold mining industry. The industry dependence on cyanide has major implications in the future of both Australian and global gold and chemical industries and environmental management. There is increasing public and political pressure on gold mining companies around the world to address the issue of cyanide use, or face the possibility of mine closure or bans. The development of a safe and cost-effective alternative lixiviant for the gold industry is both an altruistic and lucrative challenge.
1.5.2. Alternative Lixiviants for Gold

Alternative gold lixiviants include halogen/halide media, thiourea, thiocyanate, thiosulfate, ammonium polysulfide, malononitrile and cyanamide (Adams et al. 1999). Some of these alternatives have found use in specialist ore leaching applications, such as the thiourea leach that was used at the New England Antimony mine, Hillgrove, NSW; the Newmont flash chlorination facility for carbonaceous ores at Carlin, Nevada, USA; and Newmont’s ammonium thiosulfate (ATS) leaching and recovery process for gold and silver at their Malozemoff Technical Facility, Nevada (Adams et al. 1999; 2003).

Factors that discourage the use of these alternative lixiviants include higher reagent costs, comparatively inefficient leaching and, perhaps surprisingly, the potential of even greater environmental/workplace hazards due to corrosive reagents and long-lived toxic effluent. Thiourea has been in the past classified as a carcinogen and the toxicity of its related compounds is, in many cases, undetermined. Of the alternatives, thiosulfate appears to be the safest and most likely to be made commercially viable.

1.5.3. Thiosulfate Leaching

Thiosulfate is an oxyanion of sulfur, similar in structure to the sulfate ion, but with a second sulfur atom taking the place of one oxygen atom. It is widely used: as photographic fixer due to its affinity for silver ions; for removal of chlorine in paper and textile bleaching; and its ammonium salt is used as a fertiliser in sulfur deficient soils. It has also been used medicinally as a treatment for ringworm, as an arthritis medication and as an antidote to cyanide and arsenic poisoning (Aylmore and Muir 2001; Puddephatt 1978).
Thiosulfate leaching of gold involves a complex solution and electrochemical system consisting of ammonia, oxygen, and with copper present in both its oxidation states (Aylmore and Muir 2001). Although the process is of considerable benefit and finds use in the processing of preg-robbing and carbonaceous ores (Bhakta 2003; Wan and LeVier 2003), it cannot currently compete with cyanidation under normal leaching conditions. The leaching kinetics are poor due to an intransigent passivation that has been suggested to be due to the formation of a surface layer (Aylmore and Muir 2001; Breuer and Jeffrey 2003c). Despite the success of their ammonium thiosulfate leaching research facility (Wan and LeVier 2003), construction of a commercial plant by Newmont has not been forthcoming. This may indicate that the process is as yet not economically viable and that further research is required in order to improve the efficiency of the process.

Most of the thiosulfate leaching research to date has focussed on the copper-ammonia–thiosulfate system, described also as ammoniacal copper(II) thiosulfate and cupric tetra-ammine thiosulfate leaching systems. In this system, thiosulfate is the lixiviant and copper(II) and ammonia form the cupric tetra-ammine complex that acts as the oxidant. Although it has been shown that gold can be readily leached in this way, a number of key problems have been identified. Many of these involve the complex solution chemistry of the leaching process. These include competitive oxidation of thiosulfate to tetrathionate by dissolved oxygen (Breuer and Jeffrey 2003a), catalysis of this reaction by copper(II) (Breuer and Jeffrey 2003b), precipitation of copper sulfide in oxygen deficient solutions, ageing of thiosulfate solutions, volatility and loss of ammonia, the decomposition of thiosulfate under acid conditions (Wan and LeVier 2003) and reliance of the leaching rate on the Nernstian dependence of the standard potential for copper reduction on the solution ratio of copper(II) / copper(I) (Jeffrey et al. 2003).
Aside from these complex solution chemistry problems, the formation of a passivating species comprising sulfur on the surface has been proposed by various authors (Aylmore and Muir 2001; Breuer and Jeffrey 2003c; Wan and LeVier 2003). The nature of the surface species causing this passivation will be investigated in this thesis.
1.6. **TECHNIQUES**

The techniques required for this study must be surface-specific, amenable to aqueous solutions and able to provide evidence regarding the nature of surface species in order to augment electrochemical data. Raman spectroscopy is a laser-based scattering technique that can provide a fingerprint spectrum of the molecular vibrations of a substance, such as bond stretching and bending; cyclic ring breathing modes, rocking and torsional or skeletal deformations. In solids, optical and acoustic lattice phonons can also be seen by this method. Raman can be used in solutions as, unlike infrared, it is relatively insensitive to water. The Raman Effect is inherently very weak, with solution concentrations for detection commonly in the millimolar to molar range. In order to gain surface specificity, the Raman signal emanating from adsorbates must be amplified in the order of $10^6$. This can be done using the technique of SERS, in which a specifically nanostructured gold, silver or copper surface can cause the required signal enhancement.

Other techniques described in this section include the *ex situ* techniques of ATR-FTIR and XPS. Although these cannot be used *in situ*, they give information regarding the complementary infrared vibrational characteristics; and chemical state information; respectively, of the gold surface after removal from solution and exposure to the ambient environment.

1.6.1. **Spectroelectrochemistry**

Spectroelectrochemistry combines solution electrochemistry and spectroscopic techniques to investigate adsorbates on electrode-solution interfaces under potential control or to monitor changes in solution chemistry during electrochemical experiments. In this study, the spectroscopy of the surface was examined during electrochemical
studies. Processes amenable to study by this method include thin films, conducting polymers and the chemistry of mineral recovery by flotation. Spectroscopic techniques suitable for use in surface studies of electrochemical systems include SERS, infrared reflection-absorption spectroscopy (IRRAS) and non-linear techniques including visible-infrared sum frequency generation (SFG) and second harmonic generation (SHG) (Weaver and Wasileski 2000). The Raman technique is proving to be one of the most rapidly developing and widely accepted of the electrochemical surface spectroscopic methods.

1.6.2. Raman Spectroscopy

Raman scattering, or the Raman Effect, is the inelastic scattering of incident radiation caused by electronic polarisation in the molecule induced by the incident beam (Nakamoto 1997a). The mechanism involves the scattering of light rather than the absorption of radiation as in infrared. The effect was predicted by a number of physicists (Dirac 1927; Kramers and Heisenberg 1925; Smekal 1923) and was observed experimentally by C. V. Raman in 1927 (Raman and Krishnan 1928). The Raman Effect can be greatly intensified on specifically prepared metallic substrates, the phenomenon known as the SERS effect (Kneipp et al. 1999).

Raman spectra can be gathered from all states of matter, including gaseous and molten material. Systems range from industrial instruments with remote fibre-optic coupled probe heads to microprobe research microscopes. Portable spectrometers are capable of providing onsite determination of unknown compounds for forensic, customs and security purposes using spectral libraries to match to known compounds.
Covalently bonded, easily polarisable materials are the most sensitive to Raman spectroscopy, with strong scatterers such as diamond and silicon being commonly used as calibration reference standards. Samples that do not respond to Raman spectroscopy include those with metallic or completely ionic bonding, as well as some point group structures with forbidden Raman transitions. Bonds between heavy metal atoms and larger non-metallics may be unable to be detected if the frequency of the bond is below the detection limit of the spectrometer. Similarly as for infrared, alkali halides are Raman-transparent and can be used as pressed sample mounts. Water is a weak Raman scatterer; therefore solution electrochemistry is well suited to examination by Raman spectroscopy.

1.6.2.1. Normal Vibrational Modes

The number of vibrational states of a polyatomic molecule depends on the degrees of freedom of motion of each atom. A molecule containing \(N\) atoms has \(3N\) degrees of freedom, three of which are translational modes, which can be excluded. In a non-linear molecule, three modes are due to rotations about the three perpendicular axes and can also be excluded. In a linear molecule only two degrees of freedom are due to rotation, as the molecule can be thought of as lying along one of the axes. The remaining degrees of freedom are due to the ‘internal motions’ or vibrations of the molecule. Of these there are \(3N - 6\) modes for a non-linear molecule and \(3N - 5\) modes for a linear molecule, where \(N\) is the number of atoms in the molecule. These correspond to stretching (or valence) modes characterised by changes in bond length, and bending (or deformation) modes involving changes in bond angles. Stretching modes can be described as symmetric or antisymmetric, and the deformational modes are variously described as bending, scissoring, rocking, wagging and twisting modes, in-plane or out-of-plane deformations relative to planar molecules (Baranska et al. 1987).
1.6.2.2. General Selection Rule

The complementary nature of Raman scattering and infrared absorption is described by the general selection rule, which states that if a vibration causes a change in the dipole moment of a bond, then it will be active in the infrared spectrum; if the vibration produces a change in the polarisability of the bond, it will be active in the Raman spectrum (Ferraro and Nakamoto 1994). The more polar the bond, for example hydroxyl and carbonyl groups, the stronger the absorption in the infrared; while more covalent materials, such as diamond, silicon and sulfur, show greater intensity in Raman spectra than in infrared.

1.6.2.3. Mutual Exclusion Rule

The infrared / Raman mutual exclusion rule states that if the molecule has a centre of symmetry, then modes that are Raman active will be inactive in the infrared and any modes that are infrared active will be inactive in Raman (Ferraro and Nakamoto 1994). If a molecule does not have a centre of symmetry it will show activity in both Raman and infrared vibrational modes in inversely varying degrees in accordance with the general selection rule.

1.6.2.4. Instrumentation

Raman spectrometers consist of a coherent light source, a focusing system, a filtering system and a detector. In microprobe systems, lasers are coupled to an optical microscope, allowing selective focusing and diffraction limited spot sizes in the order of 0.5 to 3 μm, dependent on the frequency of the radiation. Electrochemical cells with optically flat windows can be easily fitted into a microscope stage, with the ability to capture micro-optic still and video images of the potential controlled. Microprobe spectrometers are coupled to a computer-controlled x, y, z stage in order to acquire
point by point Raman maps or perform confocal depth profiling, with spatial resolution of 1 μm and instrument resolution of ~5 cm⁻¹.

Common laser sources with wavelengths ranging from infrared to ultraviolet include NdYAG 1064 nm; Diode laser 830 and 785 nm; HeNe 633 nm; Ar 514.5 nm; and HeCd with dual wavelengths of 442 and 325 nm. Holographic notch filters or edge filters are used to filter spurious plasma lines from the incoming laser source and to filter the intense Rayleigh scattering from the sample. Raman scattered photons are collected by pixel array charge coupled devices (CCDs) Peltier cooled to −70° to minimise electronic noise (Andrews and Demidov 1995).

1.6.3. Surface Enhancement

SERS is a phenomenon in which applied electromagnetic radiation resonates with the surface plasmons of certain metals with specific morphologies, causing extremely strong electromagnetic fields to emanate from the metal surface. The resulting fields greatly enhance the vibrational Raman scattering cross-section for adsorbates on the metal surface or solution species within the field, generating signal intensities ranging from 10⁶ to 10¹⁴ times that of conventional Raman scattering (Kneipp et al. 1999; Moskovits 1985; Otto et al. 1992). SERS allows submonolayer detection of adsorbates and, under certain experimental conditions, the detection of single molecules (Kneipp et al. 1997; Nie and Emory 1997).

The SERS effect is generated by the scattering of radiation from a suitably roughened metal surface (Moskovits 1985); or from nanoparticles with spatial features less than the wavelength of the incident radiation (Moskovits 1985). The enhancement effect is dependent upon the types of substrate and adsorbate; the degree of roughening of the
electrode or the size and shape of the nanoparticle; and the frequency of the incident radiation. Electrochemical oxidation-reduction cycling and aggregation of colloidal nanoparticles are the two most common methods of activating metals as SERS substrates (Tian 2002), with silver, copper and gold displaying the most intense enhancement. Early experiments used the coinage metals gold, silver and copper as SERS substrates, roughened by an electrochemical oxidation-reduction cycle (ORC) (Fleischmann et al. 1974).

The first observation of SERS was by Hendra, Fleischmann and McQuillan through their electrochemical investigations of Argon 514.5 nm excitation of pyridine on roughened silver in 1974 (Fleischmann et al. 1974). The authors believed that the observed enhancement was due to the high surface area of the roughened electrode and the corresponding increase in the number of adsorbates present on the increased surface area. The enhancement effect was further studied by Jeanmarie and Van Duyne, who coined the term SERS, and independently by Albrecht and Creighton within the same year. Both groups concluded that the enormously strong signal measured from pyridine on the roughened electrode is caused by an enhancement of the Raman scattering efficiency rather than the increase in surface area (Albrecht and Creighton 1977; Jeanmarie and Van Duyne 1977).

Proposed surface enhancement mechanisms fall into two categories (Moskovits 1985; Tian 2002): electromagnetic effects, which enhance solution species in the vicinity of the metal surface, and chemical effects, which act upon adsorbates bonded to the metal surface. The study of enhancement effects involves electromagnetic and solid state properties of the substrates and resonance effects within the metal-adsorbate complex.
1.6.3.1. Electromagnetic Effect

Surface plasmon resonance (SPR) of conduction electrons within small metallic structures or gratings with an incident radiation exerts a local optical field enhancement in the surrounding solution. The strongest enhancements occur as ‘hot spots’ in gaps between interacting resonant substrate particles (Kneipp et al. 1999).

The resonant plasmon frequency depends on the size, shape and type of metal substrate. The incident laser wavelength is matched to this frequency to enable the optimum SERS effect. An electromagnetic ‘feedback’ effect has been described, in which the amplified Raman field of the molecule itself polarises the metal particle, further intensifying the molecular Raman scattering (Vo-Dinh 1998). The enhanced electromagnetic field decreases with distance from the substrate surface, therefore analyte molecules do not need to be adsorbed on the surface to undergo electromagnetic enhancement. The electromagnetic field is known to decay exponentially (Moskovits 1985).

The decay of electromagnetic enhancement with distance was demonstrated in experiments using polymer spacers. The authors found the enhancement to decrease by a factor of 10 with each subsequent 35-50 Å spacer thickness (Murray and Allara 1982).

1.6.3.2. Chemical Effect

Theories describing the chemical effect include the proposal of two charge-transfer mechanisms, the first suggesting a metal-molecule electronic transition which induces a resonance Raman effect; the second in which a photo-excited substrate electron transfers to a lowest unoccupied molecular orbital in the adsorbate, returning to the metal to emit a Stokes photon (Kneipp et al. 1999). An adatom model proposes additional SERS activity at sites with atomic scale roughness, due to electron-phonon interactions (Vo-Dinh 1998).
1.6.3.3. Nanoparticles

Typical nanoparticles for SERS range from 10 - 150 nm, and are usually associated as aggregates. Nanoparticles undergo a dipolar plasmon resonance similar to a surface plasmon when excited by radiation with wavelengths exceeding that of the size of the particle. The condition for resonance exists when

\[ \text{Re}[\varepsilon(\omega_R)] = -2\varepsilon_0 \]

(1-1)

where \( \varepsilon \) is the dielectric function of the conductor, \( \varepsilon_0 \) that of the ambient and \( \omega_R \) the resonant wavelength (Moskovits 1985). Higher multipolar frequencies may also be induced, but only the dipolar resonance is considered with respect to SERS (Moskovits 1985). Theoretical modelling for metal nanospheres and spheroids has lead to reasonable approximations for resonant frequencies of particles of various sizes and shapes (Kerker 1984).

1.6.3.4. Surface Roughening

A surface plasmon resonance cannot normally be induced by incident radiation on a flat conductive surface, but resonance can be achieved by introduction of a surface grating with wavelength, \( \Lambda \). The grating allows the parallel momentum of the incident photon to equal that of the plasmon plus integral multiples of \( 2\pi/\Lambda \) (Kahl and Voges 2000). Randomly roughening of the surface simulates a Fourier superposition of gratings, allowing certain modes of plasmon resonance to occur (Moskovits 1985). Raman bands from roughened SERS active substrates are completely depolarised, in contrast to those from molecules adsorbed on atomically smooth surfaces or single nanoparticles (Creighton 1990).
### 1.6.3.5. Oxidation-Reduction Cycling

The SERS effect was discovered using a silver substrate oxidation-reduction cycled in 0.1 ml dm\(^{-3}\) KCl (Fleischmann et al. 1974). The roughening of an electrode by oxidation-reduction cycling causes deposition of metal clusters in the reduction phase, leading to surface structures with features in the order of 50 - 250 nm (Roth et al. 1993). These structures possess degrees of submicron regularity with likely nanoscale disorder on the surface of the submicron features.

ORC procedures are well documented for various metals, such as Ag, Au, Cu, Pt, Rh, Fe and Co (Tian 2002). Tian describes the following recommended ORC process for gold in 0.1 mol dm\(^{-3}\) KCl, as graphically represented in Figure 1-1.

![Figure 1-1: Potential waveform for SERS activating a gold electrode in 0.1 M KCl (Tian 2002). Potential V vs. SCE.](image)

This method of oxidation-reduction cycling gold as a SERS substrate, using 0.1 mol dm\(^{-3}\) KCl as the activating electrolyte, has become widely accepted in the literature (Kudelski 2005; Liu et al. 2002; Yu and Liu 2006). Modifications of Tian’s method include variations of scan rate, vertex potentials, holding times and number of cycles.
1.6.3.6. Selection Rules

During SERS, normal vibrational selection rules are relaxed, allowing the activity of modes that are usually forbidden in conventional Raman scattering (Creighton 1990). Moskovits and co-workers proposed that, in the presence of a large electric field gradient, vibrational modes that are hyper-Raman active become Raman active and quadrupole-allowed vibrations become infrared active in some circumstances (Sass et al. 1981). It has been proposed that a Raman signal that depends upon the product of the polarisability and the field gradient, rather than the product of the field and the polarisability gradient, may be responsible for the presence of some normally forbidden infrared transitions observed in SERS (Ayars et al. 2000).

1.6.4. Ex situ Techniques

Examination of adsorbates on surfaces is commonly performed using ex situ Ultra High Vacuum (UHV) methods. Techniques such as Secondary Ion Mass Spectrometry (SIMS), Auger Electron Spectroscopy (AES) and XPS for compositional analyses; High Resolution Electron Energy-Loss Spectroscopy (HREELS) for vibrational studies; and SEM and Low Energy Electron Diffraction (LEED) for surface morphology and crystallography, provide useful information on the nature of adsorbates on surfaces.

Such techniques are limited, however, due to the opportunity for oxidation and volatilisation of surface species once removed from the aqueous environment. In this work, XPS was used to interrogate ex situ leaching samples in order to determine chemical state information of surface-bonded species. SEM and EDX were used to characterise the morphology and bulk composition, respectively, of the gold SERS substrate.
1.6.4.1. Attenuated Total Reflectance Infrared Spectroscopy

The development of the attenuated total reflectance technique (Harrick 1967) allowed surfaces to be investigated by infrared spectroscopy. Light propagating through an optically thin, non-absorbing medium forms a standing wave perpendicular to the total reflecting surface. If the sample absorbs a fraction of this radiation, the propagating wave interacts with the sample and its energy becomes attenuated, giving rise to reflection spectra, very similar to the absorption spectra (Garnett 1904). In ATR-FTIR, infrared radiation passes through an optically dense crystal and reflects at the surface of the sample. Figure 1-2 shows a diagram of an ATR cell contacting a sample.

![Figure 1-2: Diagram of an ATR cell (Desai and Boeckl 2004)](image)

The resultant spectrum reveals the functional groups present on the surface, or in films, to a depth of ~5 μm (Desai and Boeckl 2004).

1.6.4.2. X-ray Photoelectron Spectroscopy

XPS is a UHV technique based upon the photoelectric effect, whereby photons can induce electron emission from a solid, provided the energy of the irradiation, \( hv \), is greater than the work function, \( \phi \). The work function is defined as the minimum energy required to remove an electron from the highest occupied energy level in the solid to the ‘vacuum level’, in which the electron has zero kinetic energy, \( E_{\text{kin}} \) (Attard and Barnes 1998).
A monochromated beam of X-rays, commonly emitted from a magnesium or aluminium anode, incident upon the sample surface, causes photoemission from both core and valence electrons. The kinetic energy of the ejected photoelectrons are measured using an electrostatic energy analyser and the spectra are displayed in terms of the binding energy, $E_B$, which is calculated according to (Attard and Barnes 1998):

$$E_B = h\nu - E_{\text{kin}} - \phi$$  \hspace{1cm} (1-2).

The exact binding energy of an electron depends not only upon the level from which photoemission is occurring, but also upon the formal oxidation state of the atom and the local chemical and physical environment. Chemical state information can therefore be gained from shifts in the core level photoelectrons of chemically bound atoms from those of neutral unbound atoms. This ability to discriminate between different oxidation states and chemical environments is a major strength of the XPS technique (Attard and Barnes 1998).

XPS has a relatively high degree of surface sensitivity. The escape depth of photoelectrons from a specific solid depends on the Inelastic Mean Free Path (IMFP) of the ejected photoelectrons. In metals this is typically less than 1 – 2 nm (Riviera and Myhra 1998) and, for this reason, XPS is best described as a surface-sensitive, rather than surface-specific, technique.
2. LITERATURE REVIEW
2.1. CHEMISTRY OF GOLD DISSOLUTION

Gold is unique amongst metals as it is not attacked by atmospheric oxygen at any temperature (Puddephatt 1978). It not only has the highest oxidation potential of all metals, but also the highest electronegativity and electron affinity (Schmidbaur et al. 2005; Jansen and Mudring 1999). The oxidation potential of gold in water in the absence of complexing ligands is higher than the decomposition potential of water, therefore gold will not dissolve in water at any potential or pH. Gold can only dissolve in aqueous solution in the presence of a suitable oxidising agent and stabilising ligand.

2.1.1. Properties of Gold

Gold is an excellent conductor of heat and electricity and is soft and highly malleable. Metallic gold is yellow, while finely divided and nanoparticulate gold can be black, purple, ruby, blue or green, depending on the particle size and resultant plasmon resonance. The yellow colour of gold cannot be explained classically and is ascribed to a small band gap between 5d orbitals and a relativistically contracted 6s orbital.

Gold compounds can exist in a range of valence states from –1 to +5, with the common aurous, Au\(^+\), and auric, Au\(^{3+}\), states favouring soft and hard ligands, respectively. Gold forms compounds with halides; cyanide; various ligands containing sulfur, phosphorus or nitrogen; antimony; tellurium; organic ligands and alkali metals. The surface of gold is particularly attractive to thiol moieties, which can chemisorb to the metal, resulting in the formation of self-assembled monolayers for appropriate ligand structures (Schreiber 2000). Table 2-1 lists the electronic structures of various valence states of gold and examples of compounds and typical geometries of the in various states.
Table 2-1: Electronic structures of various valence states of gold, common geometries and examples of gold compounds for each valence state (Puddephatt 1987).

<table>
<thead>
<tr>
<th>valence</th>
<th>electronic structure</th>
<th>geometry</th>
<th>examples</th>
<th>comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>-I</td>
<td>[Xe] 4f¹⁰ 5d¹⁰ 6s²</td>
<td>lattice</td>
<td>AuM (M=Cs, Rb, K, Na)</td>
<td>isoelectronic with Hg</td>
</tr>
<tr>
<td>0</td>
<td>[Xe] 4f¹⁰ 5d¹⁰ 6s¹</td>
<td>fcc</td>
<td>metallic Au</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>[Xe] 4f¹⁰ 5d¹⁰</td>
<td>linear, trigonal planar, tetrahedral</td>
<td>Au(CN)₂⁻</td>
<td></td>
</tr>
<tr>
<td>II</td>
<td>[Xe] 4f⁹ 5d⁹</td>
<td>RₙAu-AuRₙ</td>
<td>Au₂I₂[μ-(CH₂)₂PMe₂]₂</td>
<td>paramagnetic</td>
</tr>
<tr>
<td>III</td>
<td>[Xe] 4f⁸ 5d⁸</td>
<td>square planar</td>
<td>AuCl₄⁻</td>
<td>diamagnetic</td>
</tr>
<tr>
<td>IV</td>
<td>[Xe] 4f⁷ 5d⁷</td>
<td>octahedral</td>
<td>none well characterised</td>
<td>proposed intermediates in organogold reactions</td>
</tr>
<tr>
<td>V</td>
<td>[Xe] 4f⁶ 5d⁶</td>
<td></td>
<td>AuF₅, AuF₆⁻</td>
<td>very strong oxidiser</td>
</tr>
</tbody>
</table>

Table 2-2 lists the first four ionisation energies for copper, silver and gold. The first ionisation energy of gold is considerably higher than that for copper or silver, requiring a much stronger oxidant. Upon dissolution however, the formation of the gold(III) valence state is generally favoured, and it can be seen from Table 2-2 that the third ionisation energy of gold is lower than those of silver and copper.

Table 2-2: Ionisation energies for copper, silver and gold (eV) (Puddephatt 1978).

<table>
<thead>
<tr>
<th></th>
<th>1st</th>
<th>2nd</th>
<th>3rd</th>
<th>4th</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>7.72</td>
<td>20.3</td>
<td>36.8</td>
<td>58.9</td>
</tr>
<tr>
<td>Ag</td>
<td>7.57</td>
<td>22.0</td>
<td>39.7</td>
<td>52</td>
</tr>
<tr>
<td>Au</td>
<td>9.22</td>
<td>20.1</td>
<td>30.5</td>
<td>43.5</td>
</tr>
</tbody>
</table>

A list of physical, thermodynamic and crystallographic properties of gold is presented in Table 2-3.
Table 2-3: Some physical, thermodynamic and structural properties of gold

<table>
<thead>
<tr>
<th>Property</th>
<th>units</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>79</td>
<td></td>
</tr>
<tr>
<td>Atomic weight</td>
<td>196.967 amu</td>
<td></td>
</tr>
<tr>
<td>Melting point</td>
<td>1063 °C</td>
<td></td>
</tr>
<tr>
<td>Enthalpy of fusion</td>
<td>12.677 kJ mol⁻¹</td>
<td></td>
</tr>
<tr>
<td>Boiling point</td>
<td>2660 °C</td>
<td></td>
</tr>
<tr>
<td>Enthalpy of vaporisation</td>
<td>330 kJ mol⁻¹</td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity</td>
<td>309.6 W m⁻¹K⁻¹</td>
<td>(Johnson and Davis 1975)</td>
</tr>
<tr>
<td>Specific heat</td>
<td>0.1289 J g⁻¹K⁻¹</td>
<td>(Allred &amp; Rochow, fluorine = 4.1)</td>
</tr>
<tr>
<td>Resistivity at 20 °C</td>
<td>2.35 μΩ cm</td>
<td></td>
</tr>
<tr>
<td>Ionic radius</td>
<td>gold(I) 1.37 Å</td>
<td></td>
</tr>
<tr>
<td></td>
<td>gold(III) 0.85</td>
<td></td>
</tr>
<tr>
<td>Electronegativity</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>Interatomic distance gold(0)</td>
<td>2.88 Å</td>
<td></td>
</tr>
<tr>
<td>Co-ordination number</td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>Atomic radius</td>
<td>1.44 Å</td>
<td></td>
</tr>
<tr>
<td>Most closely packed:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Lattice plane</td>
<td>3(110)</td>
<td></td>
</tr>
<tr>
<td>Lattice direction</td>
<td>3[112]</td>
<td></td>
</tr>
<tr>
<td>Twinning plane</td>
<td>(111)</td>
<td>(Smithells 1976)</td>
</tr>
<tr>
<td>Twinning direction</td>
<td>[112]</td>
<td></td>
</tr>
<tr>
<td>Preferred texture:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrodeposit</td>
<td>[110]</td>
<td></td>
</tr>
<tr>
<td>Casting - II to axis of crystal</td>
<td>[100]</td>
<td></td>
</tr>
<tr>
<td>Drawing - II to axis of wire</td>
<td>[100]:[111] ratio 1:1</td>
<td></td>
</tr>
<tr>
<td>Evaporated films</td>
<td>[110]:[111]</td>
<td></td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
<td></td>
</tr>
<tr>
<td>Space group</td>
<td>Fm3m</td>
<td>(Wyckoff 1963), Smyth and McCormick 1995)</td>
</tr>
<tr>
<td>Structure type</td>
<td>Face centred cubic</td>
<td></td>
</tr>
<tr>
<td>Asymmetric units, Z</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>Lattice parameter, a</td>
<td>4.07825 Å</td>
<td></td>
</tr>
<tr>
<td>Unit cell volume</td>
<td>67.83 Å³</td>
<td></td>
</tr>
<tr>
<td>Molar volume</td>
<td>10.214 cm⁻³</td>
<td></td>
</tr>
<tr>
<td>Density</td>
<td>19.285 g/cm⁻³</td>
<td></td>
</tr>
<tr>
<td>Specific gravity at 20 °C</td>
<td>19.32</td>
<td></td>
</tr>
</tbody>
</table>
2.1.2. **Gold Oxides and Hydroxides**

Gold is the most resistant of all metals to attack by air or molecular oxygen at all temperatures. The thermodynamically unstable oxide, \( \text{Au}_2\text{O}_3 \), can be formed from the metal only in highly reactive chemical environments (Irissou *et al.* 2005).

2.1.2.1. **Bulk Oxide Formation**

Gold has an inherently low affinity to oxygen and no binary oxides of appreciable stability are known (Jansen and Mudring 1999). The one well-defined oxide that has been synthesised and characterised is the gold(III) oxide, \( \text{Au}_2\text{O}_3 \) (Jansen and Mudring 1999). The enthalpy of formation, \( \Delta H_f^\circ \), of the oxide at 298 K is \(-13.0 \pm 2.4\) kJ mol\(^{-1}\) (Ashcroft and Schwarzmann 1972). The \( \text{Au}/\text{Au}_2\text{O}_3 \) couple acts as a true metal/metal oxide system with a standard reduction potential of 1.362 V (Gerke and Rourke 1927). The free energy of formation, \( \Delta G_f^{\circ}_{298} \), of \( \text{Au}_2\text{O}_3 \), calculated from the standard reduction potential, is \(+80.0\) kJ mol\(^{-1}\) (Buehrer and Roseveare 1927), indicating that the oxide is highly unstable. Gold(III) oxide decomposes to gold and oxygen above 160 °C and oxygen does not react with massive gold below this temperature (Johnson and Davis 1975).

Gold(III) hydroxide \( \text{Au} (\text{OH})_3 \) can be formed by adding sodium hydroxide to a solution containing tetrachloroaurate. The gold(III) hydroxide can be further dehydrated to gold oxyhydroxide \( \text{Au} (\text{O})\text{OH} \) and gold(III) oxide, \( \text{Au}_2\text{O}_3 \), is formed upon heating to constant weight at 140 – 150 °C (Johnson and Davis 1975). Hydrous gold(III) oxide contains 2.0-2.4 waters of crystallisation and requires hydrothermal treatment to form anhydrous \( \text{Au}_2\text{O}_3 \) (Jansen and Mudring 1999). The anhydrous oxide has been characterised as having an oxidation state of +3, an average bond length of 204.2 pm and a decomposition temperature of \( 296 \pm 5 \) °C (Jansen and Mudring 1999).
2.1.2.2. Surface Oxides

Surface oxides have been identified on gold following pulsed laser deposition in an O\textsubscript{2} environment (Irissou \textit{et al.} 2005); and following O\textsubscript{2} plasma treatment (Tsai \textit{et al.} 2003). Both studies showed evidence that the surface oxides formed by these methods were unstable and decomposed over time to metallic gold. Gold sputtered in various reactive gas mixtures (Ar-N\textsubscript{2}, Ar-O\textsubscript{2}, and Ar-CH\textsubscript{4}) was not seen to form gold oxide films (Pierson \textit{et al.} 2005).

2.1.3. Aqueous Chemistry of Gold

The stability of gold in aqueous solution can be visualised by use of a Pourbaix diagram, with reference to the Nernst Equation, from which the diagram is derived.

2.1.3.1. Nernst Equation

The Nernst equation relates the electrical potential of a system at equilibrium to its standard state potential, temperature and the activity of the products and reactants. For the reduction of the oxidised species M\textsuperscript{n+} to the reduced species, M,

\[ M^{n+} + ne^- \leftrightarrow M \]  \hspace{1cm} (2-1),

assuming that activity and concentration are equivalent, the Nernst equation expresses the half-reaction potential \( E \), as:

\[ E = E^0 + \frac{RT}{nF} \ln \frac{[M^{n+}]}{[M]} \]  \hspace{1cm} (2-2),

where \( E^0 \) is the standard reduction potential in V vs. SHE, \( R \) is the gas constant, \( F \) is Faraday’s constant and \( T \) the absolute temperature in degrees Kelvin.

2.1.3.2. Pourbaix Diagram

The Pourbaix diagram shows the regions of thermodynamic stability of a mixed system, such as gold in water, in terms of the pH and \( E_H \) of solution.
(Van Muylder and Pourbaix 1966), where $E_H$ is defined as potential, $E$, on the SHE scale. The regions relate only to stable species, whereas metastable states often occur in practice and the kinetics of any process is not taken into account. The boundaries of the regions of stability are calculated from the equilibrium constants of the reactions. These values are substituted into a modified Nernst equation in order to determine the equilibrium conditions potentials under which the solution species achieves a specific concentration with varying pH. The concentration is arbitrarily chosen to be $10^{-6}$ mol dm$^{-3}$ for simplified Pourbaix diagrams such as the one shown in Figure 2-1.

Figure 2-1: $E_H$ – pH diagram for Au-H$_2$O system at 25 °C (Vijh and Belanger 1977).

The solid lines represent the boundaries of the regions of stability in the gold / water system and the dotted lines represent the range of electrochemical stability of water.
The $E_H$ / pH boundaries of the water stability region arise from the Nernstian response of the following reactions to changes in pH (Weast 1984):

$$\frac{1}{2} \text{O}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{O} \quad E^\circ = +1.229 \text{ V (SHE)} \quad (2-3)$$

$$\text{H}^+ + e^- \rightarrow \frac{1}{2} \text{H}_2 \quad E^\circ = 0 \text{ V (SHE)} \quad (2-4).$$

The water stability boundaries limit the range of potentials that can be studied by voltammetry in aqueous solution. It can be seen from Figure 2-1 that gold(0) is thermodynamically stable with respect to its ion at all pH ranges within the range of stability of water, and accordingly, water should be oxidised before gold at all potentials. Gold is the only metal for which this occurs and thus is the most noble of the metals (Puddephatt 1978).

### 2.1.3.3. Anodic Polarisation

Gold surface oxides are known to form during anodic polarisation in aqueous media (Vijh and Belanger 1977). Various studies have been undertaken in order to determine the mechanism, coverage and type of oxide formation during anodic oxidation (Juodkazis et al. 2000; Rand and Woods 1971; Tian et al. 2003; Tremiliosi-Filho et al. 2005; Xia and Birss 2001; Zhang et al. 1993).

A cyclic voltammogram showing the formation of gold oxide is presented in Figure 2-2 (Tian and Conway 2004). The voltammogram shows the formation of oxide during an anodic peak beginning at ~1.23 V and ending at 1.7 V, the potential known as the ‘Burshtein minimum’ (Burshtein et al. 1967; Michri et al. 1972). This potential is assumed to correspond to the formation of a monolayer of oxygen species during the oxidation of gold and can be used to calculate the real surface area of a gold electrode (Tian and Conway 2004; Trassati and Petrii 1991).
Figure 2-2: Cyclic voltammogram for a gold electrode in 0.5 M HClO$_4$, from 0.05 to 1.7 V at a sweep rate of 50 mVs$^{-1}$ (Tian and Conway 2004).

Oxygen was found to be adsorbed at potentials greater than the Burshtein minimum without changing the characteristics of desorption (Rand and Woods 1973; Woods 1976). The authors found the method of the Burshtein minimum (Michri et al. 1972) to give surface areas that were 20% less than those obtained by the integration of the cathodic charged passed after anodically polarising a gold electrode at 1.8 V for 100 s (Rand and Woods 1971; 1973; Woods 1976).

There is general agreement that the formation of oxide on gold is a two-electron process. (Tian et al. 2003; Tremiliosi-Filho et al. 2005; Woods 1976; Xia and Birss 2001). Based upon this assumption, the charge passed by a monolayer of oxygen is reported to be 386 $\mu$C cm$^{-2}$ based on a 1:1 stoichiometry of adsorbed oxygen on a (100) plane of gold (Rand and Woods 1971), or 400 $\mu$C cm$^{-2}$ (Burshtein et al. 1967).
XPS studies of a gold electrode surface after anodic polarisation in the potential range of 1.3 to 2.1 V have shown the binding energies of gold and oxygen to be 85.9 and 530 eV, respectively (Juodkazis et al. 2000), assigned to the chemical states of gold(III) and oxygen(-II).

Electrochemical and Quartz Crystal Microbalance (QCM) studies of gold in 0.1 mol dm\(^{-3}\) H\(_2\)SO\(_4\) have suggested the growth of compact (\(\alpha\)-) and overlying hydrous (\(\beta\)-) oxide films upon anodic polarisation of gold (Xia and Birss 2001). The \(\alpha\)-oxide was suggested to comprise AuO at potentials up to 1.5 V, a mixture of AuO and Au\(_2\)O\(_3\) at higher potentials, becoming predominantly Au\(_2\)O\(_3\) at 2.0 V with a limit of formation of three monolayers (Xia and Birss 2001). A hydrous \(\beta\)-oxide, Au\(_2\)O\(_3\).\(n\)H\(_2\)O, was found between 2.1 and 2.6 V. The value of \(n\) was found to be between 1 - 10, with the hydration decreasing with time as the film thickens (Xia and Birss 2001).

### 2.1.4. Gold Lixiviants

A gold lixiviant system consists of a suitable oxidizing agent and a complexing ligand. Table 2-4 lists various ligands with the standard redox potentials and stability constants for the following reactions of gold in their presence:

\[
\begin{align*}
[Au(OH_2)]=^+ + 2L & \underset{\beta_2}{\overset{\beta_1}{\leftrightarrow}} [AuL_2]^+ + 2H_2O & E^{0}_{1,0} \\
[Au(OH_2)_4]^3^- + 4L & \overset{K}{\leftrightarrow} [AuL_4]^3^- + 4H_2O & E^{0}_{3,0} \\
3[AuL_2]^+ + 2L & \overset{K}{\leftrightarrow} [AuL_4]^3^+ + 2Au + 2L & E^{0}_{3,1}
\end{align*}
\]
Table 2-4: Standard redox potentials and stability constants for the oxidation of gold in various ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>( E_{1,0}^0 )</th>
<th>( \log \beta_2 )</th>
<th>compound</th>
<th>( E_{3,0}^0 )</th>
<th>( \log \beta_4 )</th>
<th>compound</th>
<th>( E_{3,1}^0 )</th>
<th>( \log K )</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(_2)O</td>
<td>+1.7 (^c)</td>
<td>0 (^d)</td>
<td>([Au(OH_2)_2]^+)</td>
<td>+1.50 (^c)</td>
<td>0 (^b)</td>
<td>([Au(OH_2)_4]^{2+})</td>
<td>+1.4 (^c)</td>
<td>10 (^c)</td>
</tr>
<tr>
<td>Cl(^-)</td>
<td>+1.15 (^c)</td>
<td>11 (^d)</td>
<td>AuCl(_2)</td>
<td>+1.00 (^c)</td>
<td>25.3 (^a)</td>
<td>AuCl(_4)</td>
<td>+0.93 (^c)</td>
<td>7.7 (^c)</td>
</tr>
<tr>
<td>Br(^-)</td>
<td>+0.96 (^c)</td>
<td>15 (^d)</td>
<td>AuBr(_2)</td>
<td>+0.86 (^c)</td>
<td>32.8 (^a)</td>
<td>AuBr(_4)</td>
<td>+0.81 (^c)</td>
<td>5 (^c)</td>
</tr>
<tr>
<td>SCN(^-)</td>
<td>+0.67 (^c)</td>
<td>20 (^d)</td>
<td>Au(SCN(_2))</td>
<td>+0.64 (^c)</td>
<td>43.9 (^a)</td>
<td>Au(SCN(_4))</td>
<td>+0.62 (^c)</td>
<td>0.32 (^c)</td>
</tr>
<tr>
<td>I(^-)</td>
<td>+0.56 (^c)</td>
<td>21 (^d)</td>
<td>AuI(_2)</td>
<td>+0.57 (^c)</td>
<td>47.7 (^a)</td>
<td>AuI(_4) (unstable)</td>
<td>+0.57 (^c)</td>
<td>2.3 (^d)</td>
</tr>
<tr>
<td>NH(_3)</td>
<td>+0.563 (^c)</td>
<td>21 (^d)</td>
<td>([Au(NH_3)_2]^+)</td>
<td>+0.325 (^c)</td>
<td>46, 30 (^a)</td>
<td>([Au(NH_3)_4]^{3+})</td>
<td>+0.206 (^c)</td>
<td>12 (^a)</td>
</tr>
<tr>
<td>S=C(NH(_2))(_2)</td>
<td>+0.380 (^d)</td>
<td>24 (^d)</td>
<td>Au[S=C(NH(_2))(_2)](^+)</td>
<td>+0.325 (^c)</td>
<td>46, 30 (^a)</td>
<td>([Au(NH_3)_4]^{3+})</td>
<td>+0.206 (^c)</td>
<td>12 (^a)</td>
</tr>
<tr>
<td>Se=C(NH(_2))(_2)</td>
<td>+0.20 (^d)</td>
<td>27 (^d)</td>
<td>Au[Se=C(NH(_2))(_2)](^+)</td>
<td>+0.325 (^c)</td>
<td>46, 30 (^a)</td>
<td>([Au(NH_3)_4]^{3+})</td>
<td>+0.206 (^c)</td>
<td>12 (^a)</td>
</tr>
<tr>
<td>S(_2)O(_3))(^2-)</td>
<td>+0.150 (^a)</td>
<td>28 (^d)</td>
<td>Au(S(_2)O(_3))(_2))(^3-)</td>
<td>+0.325 (^c)</td>
<td>46, 30 (^a)</td>
<td>([Au(NH_3)_4]^{3+})</td>
<td>+0.206 (^c)</td>
<td>12 (^a)</td>
</tr>
<tr>
<td>SO(_3))(^2-)</td>
<td>+0.083 (^a)</td>
<td>26.8, 16 (^a)</td>
<td>Au(SO(_3))(_2))(^3-)</td>
<td>+0.325 (^c)</td>
<td>46, 30 (^a)</td>
<td>([Au(NH_3)_4]^{3+})</td>
<td>+0.206 (^c)</td>
<td>12 (^a)</td>
</tr>
<tr>
<td>HS(^-)</td>
<td>−0.090 (^a)</td>
<td>30.1 (^a)</td>
<td>Au(HS(_2))</td>
<td>−0.10 (^b)</td>
<td>85 (^b)</td>
<td>Au(CN(_2))</td>
<td>+0.1 (^b)</td>
<td>−25 (^c)</td>
</tr>
<tr>
<td>S(^2-)</td>
<td>−0.460 (^a)</td>
<td>38.9 (^a)</td>
<td>AuS(^-)</td>
<td>−0.10 (^b)</td>
<td>85 (^b)</td>
<td>Au(CN(_2))</td>
<td>+0.1 (^b)</td>
<td>−25 (^c)</td>
</tr>
<tr>
<td>CN(^-)</td>
<td>−0.570 (^a)</td>
<td>39 (^d)</td>
<td>Au(CN(_2))</td>
<td>−0.10 (^b)</td>
<td>85 (^b)</td>
<td>Au(CN(_2))</td>
<td>+0.1 (^b)</td>
<td>−25 (^c)</td>
</tr>
</tbody>
</table>

\(^a\) (Jeffrey 1997) \(^b\) (Johnson and Davis 1975) \(^c\) (Puddephatt 1978) \(^d\) (Puddephatt 1987) \(^e\) (Senanayake 2004a)
2.1.4.1. Aqua Regia

The traditional solvent system for gold, and also platinum and palladium, is aqua regia, a mixture of concentrated nitric and hydrochloric acids in a volume ratio of 1:3 (Habashi 1970). In this system, nitric acid acts as the oxidising agent and chloride as the ligand. Gold is stabilised in solution as the planar tetrachloroauroate $\text{AuCl}_4^-$, with gold in its +3 oxidation state, as expected in the presence of a ‘hard’ non-polarisable ligand (Puddephatt 1978). This process is used in the purification of gold from gold-silver alloys containing a low percentage of silver (Habashi 1970), as a silver content greater than 8% will form insoluble silver chloride and passivate the process. This highly aggressive process, requiring silica based reaction vessels, is complicated by the presence of other metals and is not suited to the extraction of gold from its ores.

2.1.4.2. Halogen / Halide media

Gold dissolves in acidic halogen halide media according to the following reaction:

$$\text{Au} + \frac{3}{2} \text{X}_2 + \text{X}^- \leftrightarrow \text{AuX}_4^- \quad \text{X} = \text{Cl, Br, I} \quad (2-8)$$

The $\text{I}_2 / \text{KI}$ system finds contemporary use in this manner as a common industrial non-cyanide etchant for gold (Smithells 1976).

Chlorination was used as a method of dissolving gold from its ores prior to the introduction of cyanidation in the late 1800s (Adams et al. 1999). Its disadvantages, compared with cyanidation for gold leaching, include preferential chlorination of base metal sulfides, leading to high reagent consumption and variable gold recovery. Like aqua regia, it is unable to recover the silver content of gold ores due to the formation of insoluble silver chloride. The high cost of the halogens and their corrosive
nature also contribute to making the process economically unviable for conventional gold recovery (Adams et al. 1999). Chlorination becomes viable, however, for highly carbonaceous ores that are difficult to treat with cyanidation. A flash chlorination circuit was introduced to Newmont Mining’s Carlin Mine in Nevada in 1971, specifically to pre-treat carbonaceous ores prior to cyanidation (Heitt 2002).

Chlorination is an important step in the refinement of raw gold (Dahne 1999). Known as the Miller process, chlorine gas is bubbled through raw molten gold at 1100 °C. Base chlorides such as Zn, Fe and Pb are volatilised, while silver and copper chlorides form a slag which floats on the molten gold and can be removed. The gold reaches greater than 99% purity when the endpoint of the reaction is noted by the appearance of reddish gold chloride vapour.

2.1.4.3. Cyanide

In the cyanidation process, gold is stabilised by cyanide ligands as the linear dicyanoaurate(I), [Au(CN)₂]⁻. Cyanide is a highly polarisable soft ligand and gold is stabilised in the oxidation state of +1 (Puddephatt 1978). The high thermodynamic stability of the gold-cyanide complex, log k ~38.3 (Fleming et al. 2003) is reflected in its low standard reduction potential, E⁰ = –570 mV (Adams et al. 1999). This potential is sufficiently low to allow the oxidation of gold from gold(0) to gold(I) to be driven by the reduction of oxygen under ambient conditions. The reaction can be described in terms of two electrochemical half reactions: the oxidation of gold to the dicyanide coupled to the reduction of oxygen (Adams et al. 1999):

\[
\begin{align*}
\text{Au} + 2\text{CN}^- & \leftrightarrow \text{Au(CN)}_2^- + e^- \quad (2-9) \\
\text{O}_2 + 4\text{H}^+ + 4e^- & \leftrightarrow 2\text{H}_2\text{O} \quad (2-10)
\end{align*}
\]
giving an overall reaction:

$$4\text{Au} + 8\text{CN}^- + 2\text{H}_2\text{O} + \text{O}_2 \rightarrow 4[\text{Au(CN)}_2^-]^- + 4\text{OH}^- \quad (2-11).$$

The chemistry is complicated by various factors. The reaction rate depends upon a balance of pH, temperature, cyanide concentration and diffusion of cyanide and oxygen to the gold surface (Habashi 1970). Hydrocyanic acid, HCN, has a pKₐ of 9.3, therefore the pH of the solution must be kept alkaline (Habashi 1970) to prevent loss of available cyanide by the hydrolysis reaction,

$$\text{CN}^- + \text{H}_2\text{O} \leftrightarrow \text{HCN} + \text{OH}^- \quad (2-12),$$

and by reaction with carbonic acid formed from atmospheric CO₂,

$$\text{CN}^- + \text{H}_2\text{CO}_3 \leftrightarrow \text{HCN} + \text{HCO}_3^- \quad (2-13).$$

High alkalinity has been found to decrease the rate of dissolution (Habashi 1970), with an optimal pH of ~11. The concentration of the cyanide itself will also affect solution pH, with higher concentrations increasing alkalinity and contributing to decrease in reaction rate. Although the rate of reaction would be expected to increase with temperature, in this case the solubility of oxygen decreases and the rate of cyanide loss increases due to volatilisation. The optimal operating temperature has been found by experiment to be 85°C (Habashi 1970). Under normal atmospheric conditions, the rate of oxygen diffusion into the solution limits the reaction to an effective maximum cyanide concentration of $2.5 \times 10^{-3}$ mol dm$^{-3}$, above which the reaction rate does not increase (Habashi 1970). Common industrial leaching concentrations are 350–500 ppm (7-10 $\times 10^{-3}$ moles dm$^{-3}$), in which a slight excess of cyanide is present to counter the effect of competing (preg-robbing) ore elements such as copper and carbon.
2.1.4.4. Thiocyanate

Gold dissolves in thiocyanate in the presence of iron(III) as an oxidising agent, which itself is also complexed by thiocyanate (Adams et al. 1999). Oxidation of gold in acidic thiocyanate solutions can be expected to produce either the gold (I) complex $\text{Au(SCN)}_2^-$ or the gold (III) complex $\text{Au(SCN)}_4^-$ (Wan et al., 2003).

$$\text{Au(SCN)}_2^- + e^- = \text{Au} + 2\text{SCN}^- \quad (2-14)$$

$$\text{Au(SCN)}_4^- + 3e^- = \text{Au} + 4\text{SCN}^- \quad (2-15)$$

Thiocyanate is also oxidised at the leaching potential initially to (SCN)$_2$ and ultimately to $\text{SO}_4^{2-}$ and HCN, causing environmental and health hazards. Employing ferric ion as oxidant, thiocyanate forms relatively strong complexes with ferric ions, which reduces both the oxidizing potential of ferric ions and the concentration of free thiocyanate needed for the formation of complexes with gold. The silver compound, AgSCN, is insoluble and not recoverable by this method.

2.1.4.5. Thiourea

Thiourea in a slightly acid solution is able to dissolve gold (Plaskin and Kozhukova 1960) and in large concentrations can achieve leaching rates faster than those with cyanide (Adams et al. 1999). The use of an acidic leach would be an advantage in circuits involving bacterial oxidation of sulfide ores as, unlike the case for cyanide, the leach solution would not need to be made alkaline prior to leaching (Zhang et al. 2001). Gold dissolved in thiourea forms a positively charged species:

$$\text{Au} + 2\text{CS(NH}_2\text{)}_2 \leftrightarrow \text{Au(CS(NH}_2\text{)}_2)^+ + e^- \quad (2-16).$$
High potentials are needed to dissolve gold at an acceptable rate by this method, requiring strong oxidizing agents such as peroxide, iron(III) or ozone (Adams et al. 1999). The mechanism of gold dissolution involves the oxidation of thiourea to form formamidine disulfide, as seen in Figure 2-3, which appears to play a major role in the leaching process (Zhang et al. 2001).

An Electrochemical Quartz Crystal Microbalance (EQCM) study of the anodic dissolution of gold in various concentrations of thiourea in 0.5 mol dm\(^{-3}\) HClO\(_4\) (Tian and Conway 2004) showed that gold dissolved via a one electron process in the potential range of 450 – 650 mV. The peak potential for dissolution was found to be 600 mV. A peak at 1.27 V, which was seen to occur at thiourea concentrations above 3 x 10\(^{-5}\) mol dm\(^{-3}\), was attributed to the oxidation of thiourea to formamidine disulfide.

Despite the favourable kinetics of the thiourea leaching process, it has not been accepted as an economically and environmentally viable leaching system. Disadvantages of the system include: the need for tight controls on operating parameters; thiourea concentrations approximately three times that of cyanide required for equivalent leach rates; consumption of thiourea due to side reactions; concern regarding reported toxicity of thiourea; and the production of an acidic solution requiring neutralisation (Adams et al. 1999, Li and Miller, 2006).
2.2. **THIOSULFATE LEACHING OF GOLD**

Thiosulfate is considered the most likely alternative to cyanide as a commercial gold lixiviant. The thiosulfate leaching process has been the subject of applied and fundament research over the last 20 years, with a recent review outlining issues and impediments that currently prevent its acceptance as a commercial process (Muir and Aylmore 2004).

2.2.1. **Electrochemistry of Gold Dissolution in Thiosulfate**

The leaching of gold in a thiosulfate solution under normal atmospheric conditions is an electrochemical process consisting of oxidation and reduction half-reactions. The oxidation half-reaction is the oxidation of gold in thiosulfate, which has a standard reduction potential (Zhang and Nicol 2003) of 0.153 V, represented as:

\[
\text{Au} + 2\text{S}_2\text{O}_3^{2-} \rightarrow \text{Au} (\text{S}_2\text{O}_3)_2^{3-} + \text{e}^- \quad (2-17)
\]

The reduction half-reaction, with a standard potential of 0.401 V at pH 14, is the reduction of oxygen (Zhang and Nicol 2003):

\[
\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- \quad (2-18)
\]

Both reactions are summed to give an overall reaction:

\[
4\text{Au} + 8\text{S}_2\text{O}_3^{2-} + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Au} (\text{S}_2\text{O}_3)_2^{3-} + 4\text{OH}^- \quad (2-19)
\]

The potential of oxygen reduction is more positive than that of gold oxidation in thiosulfate therefore the reaction should occur spontaneously in the presence of oxygen. This is not the case, as the reaction has been found to progress very slowly.
The failure of thiosulfate to leach gold in the presence of oxygen has been attributed to the high overpotential required to reduce oxygen on gold (Aylmore and Muir 2001; Breuer and Jeffrey 2003c), coupled with the formation of a passivating sulfur layer on the gold surface, thought to be due to the decomposition of thiosulfate (Aylmore and Muir 2001).

2.2.1.1. Rotating Electrochemical Quartz Crystal Microbalance (REQCM) Studies

Electrochemical methods alone are not sufficient to determine the reactions occurring at metal surfaces, due to the possibility of more than one reaction occurring at the same potential. A technique that has proved useful in augmenting electrochemical information is the REQCM (Jeffrey et al. 2000). By use of this method, changes in the mass of the gold during leaching are related to measurements of electrochemical processes from a rotating disk electrode (RDE).

Figure 2-4 shows the current recorded during a linear sweep voltammogram of gold in thiosulfate accompanied by the change in mass of the gold as measured by the REQCM during leaching (Chandra and Jeffrey 2004). The calculated current expected from this change in mass is also plotted. In this experiment the gold oxidation reaction is isolated from the reduction reaction by purging the solution to remove oxygen. The excess in measured current over that calculated from the loss of mass from the electrode indicates that other processes not involving mass change are taking place in the same potential region. The authors propose that the other reaction taking place is the oxidation of thiosulfate to tetrathionate (Chandra and Jeffrey 2004).
2.2.2. Ammoniacal Copper(II) Thiosulfate Leaching

The complexity of this thiosulfate lixiviant system far exceeds that of the cyanide system. The process is catalysed by copper and requires the presence of ammonia as a secondary complexing ligand (Aylmore and Muir 2001). It involves a dual oxidation system involving oxygen and a copper(I)–copper(II) redox cycling process. The oxidation of gold and its stabilisation by thiosulfate leads to the formation of the dithiosulfate aurate(I) ion, Au(S₂O₃)²⁻, with stability log \( k \sim 28.6 \) (Fleming et al. 2003). Ideal leaching conditions for gold were obtained with solutions containing 0.1 mol dm⁻³
thiosulfate, $10 \times 10^{-3}$ mol dm$^{-3}$ CuSO$_4$, 0.4 mol dm$^{-3}$ ammonia and at pH $> 11.4$ at 30 °C (Breuer and Jeffrey 2000).

2.2.2.1. Role of Ammonia

The addition of ammonia to the thiosulfate solution increases the leaching rate, but its role in the system is as yet unestablished. Ammonia is thought by some authors to be preferentially adsorbed over thiosulfate, enabling the gold to be brought into solution as an ammine complex (Aylmore and Muir 2001). This theory has been disputed, as this reaction is not observed in electrochemical dissolution studies in ammonia alone (Breuer and Jeffrey 2003c). It is generally agreed however that ammonia alters the surface chemistry of the gold allowing dissolution to proceed (Aylmore and Muir 2001; Breuer and Jeffrey 2003c) and that ammonia also stops copper precipitation as its hydroxide at the pHs discussed.

2.2.2.2. Role of Copper

Copper plays a catalytic role in the dissolution of gold in thiosulfate (Aylmore and Muir 2001), increasing the dissolution rate by a factor of 20. It is stabilised by ammonia as the cupric tetra-ammine complex, Cu(NH$_3$)$_4^{2+}$, and can act as an electron acceptor via the reduction half-reaction:

$$\text{Cu(NH}_3\text{)}_4^{2+} + 3\text{S}_2\text{O}_3^{2-} + e^- \rightarrow \text{Cu(S}_2\text{O}_3\text{)}_3^{5-} + 4\text{NH}_3 \quad E^0 = 220 \text{ mV} \quad (2-20)$$

The standard potential for this reaction is 220 mV, allowing cupric tetra-ammine to oxidise gold to gold thiosulfate (Breuer and Jeffrey 2003c). The copper(I) complex is recycled to copper(II) by a rapid reaction with oxygen, according to (copper ligands ignored):

$$4\text{Cu}^+ + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 4\text{Cu}^{2+} + 4\text{OH}^- \quad (2-21)$$
The amount of copper(II) in solution varies during the leaching process, depending on the initial concentration and the relative rates of the copper reduction and oxidation reactions (Breuer and Jeffrey 2003c). The ratio of copper(II)/copper(I) determines the rate of gold leaching through a Nernstian dependence of the standard potential of the copper reduction reaction:

\[
E^0 = E_{Cu^{2+}/Cu^+}^0 + \frac{RT}{F} \ln \left( \frac{[Cu^{2+}]}{[Cu^+]}) \right) \quad (2-22)
\]

The stability of thiosulfate in solution is also affected by the copper(II) concentration. Thiosulfate can be oxidised by the copper(II) complex to form tetrathionate according to the reaction (Breuer and Jeffrey 2003c):

\[
2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} \rightarrow 2Cu(S_2O_3)_3^{5-} + S_4O_6^{2-} + 8NH_3 \quad (2-23)
\]

The presence of ammonia slows the kinetics of the reduction process, which proceeds far more quickly in its absence. Increasing levels of copper(II) in solution can therefore hinder the rate of leaching by decreasing the available thiosulfate and making less copper(II) available for gold leaching. This in turn affects solution potential via the Nernstian dependence of the copper(II)/copper(I) ratio described in (2-22) (Jeffrey et al. 2003).

It is noted that the copper tetra-ammine notation Cu(NH$_3$)$_4^{2+}$ is used for convenience only, as species of the type Cu(H$_2$O)$_{6-x}$(NH$_3$)$_x^{2+}$, with $x = 1$ or 2, more likely to occur given the ammonia concentrations used for this work. The aqueous Cu-NH$_3$-S$_2$O$_3^{2-}$ system shows extremely complex speciation and is itself the subject of intensive study (Senanayake 2004b).
2.2.2.3. Effect of Oxygen

Oxygen is required in order to regenerate copper(II) from copper(I). It is known to oxidise thiosulfate to tetrathionate, although very slowly without a suitable catalyst such as copper(II) (Jeffrey et al. 2003). In the presence of copper(II), the thiosulfate oxidation rate is proportional to the oxygen flow rate and acceptable leaching kinetics are seen with a low oxygen (2% O\textsubscript{2} in N\textsubscript{2}) aeration mixture (Jeffrey et al. 2003). In the absence of oxygen, the oxidation of copper(I) cannot take place, copper(II) cannot be regenerated and the leaching process ceases. The precipitation of copper sulfides from solution is commonly seen in such stagnant or oxygen deprived leaching solutions (Wan and LeVier 2003).

2.2.2.4. Effect of pH

Thiosulfate reacts with acid to liberate a range of products including primarily sulfur and sulfur dioxide, sulfite and sulfate, with hydrogen sulfide, sulfanes and polythionates also potential products at low pH (Schmidt et al. 1975). The pH of the leaching solution must therefore be kept alkaline to minimise decomposition and loss of thiosulfate. It was found that the effect of pH on the reaction between copper and thiosulfate was greater than upon the rate of gold leaching, suggesting that leaching be carried out at a pH greater than 11.4 to avoid degradation of thiosulfate (Breuer and Jeffrey 2000).

The ammonia / ammonium equilibrium is dependent upon solution pH according to

\[
\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{NH}_4^+ + \text{OH}^- \quad \text{pK}_a = 9.25 \quad (2-24).
\]
The ammonium ion does not complex copper(II), therefore the solution pH must be kept above the pK_a of the hydrolysis reaction in order to stabilise ammonia. Loss of ammonia due to volatilisation of NH_3 would result in a decrease of solution pH.

2.2.2.5. Failure of Thiosulfate Leaching

The complexity of the thiosulfate leaching system requires a high degree of control of variables such as pH, potential via the copper(II)/copper(I) ratio, ammonia/ammonium equilibrium, oxygen and thiosulfate concentrations. In trial heap leaching operations, difficulties were experienced with variable copper content within the ores; inability to aerate leaching heaps; varied pH within the ore; loss of ammonia and thiosulfate due to degradation; and an undefined ‘ageing’ of heap leach solutions after an extended period, causing the leaching process to stall (Wan and LeVier 2003). A sulfur-like coating on gold following passivation has been observed *ex situ* using XPS and Raman spectroscopies (Wan and LeVier 2003). The authors were not able to characterise the coating as *cyclo*-octasulfur, S_8, proposing instead an amorphous or incompletely crystallised sulfur coating.

2.2.3. Effect of Additives

The general failure of the thiosulfate-copper-ammonia system, along with the potential for environmental hazard due to ammonia is currently heading research toward alternative catalysts for gold oxidation by thiosulfate. Additives recently studied include thiourea and xanthate (Chandra and Jeffrey 2004), both of which contain sulfur. Of these two compounds, thiourea was found to increase the rate of leaching, while xanthate was found to passivate the leaching process, as illustrated in Figure 2-5.
The effect of alkali cations is also of interest (Chandra and Jeffrey 2004). To date, only REQCM studies of thiosulfate systems with these additives have been performed, making this a novel field for SERS research.
2.3. **Interaction of Sulfur with Gold**

The interaction of sulfide with gold provides a model system for understanding the electrochemical and spectroscopic characteristics of the adsorption and growth of deposited sulfur layers. The notation $S^{\text{II}}$ refers in this work to the pH-dependent range of sulfide species, including $\text{H}_2\text{S}$, $\text{HS}^-$ and $S^{2-}$. The information obtained from studies of sulfur layers formed by anodic oxidation of $S^{\text{II}}$ species on gold electrodes has proved to be valuable in characterising sulfur layers formed in a number of mineral processing systems. These include sulfur layers produced during the thiosulfate leaching of gold (Watling *et al.* 2006; Woods *et al.* 2006), sulfur generated in the photodecomposition of flotation collector species on gold surfaces (Hope *et al.* 2003), and sulfur formed by oxidation of sulfide mineral surfaces, using gold decoration to facilitate surface-enhancement of Raman scattering (Hope *et al.* 2006). The rigorous electrochemical behaviour and model attributes of the interaction of sulfur moieties with gold surfaces has also resulted in the $S^{\text{II}}$/gold system (Buckley *et al.* 1987; Gao *et al.* 1992a; Hamilton and Woods 1983; Hamilton and Woods 1984; Ho *et al.* 1996; Poirier 1997; Woods *et al.* 1989) being used as a model for the interaction and modification of gold surfaces with self-assembled monolayers (SAMs) of thiols and other organosulfur molecules. Since these compounds bind to gold through sulfur atoms, sulfide adsorbed on gold can be considered to be the shortest member of the thiol homologous series.

Despite the noble character of bulk metallic gold, its surface has been found to show a strong affinity for sulfur compounds due to free valencies of gold atoms exposed on the surface (Schmidbaur *et al.* 2005), allowing self-assembly of sulfur-functionalised monolayers and the adsorption of atmospheric sulfur. Due to the thermodynamic instability of the gold sulfide, sulfidation of the gold surface does not proceed into the
bulk metal, in contrast to the tarnishing of silver in which the sulfide is thermodynamically stable (Schmidbaur et al. 2005).

### 2.3.1. Gold-Sulfur Compounds

The reaction equation and standard reduction potential for the formation of gold(I) sulfide is as follows (Licht 1988):

\[
\text{Au}_2\text{S} + 2\text{e}^- \leftrightarrow 2\text{Au} + \text{S}^{2-} \quad \text{E}^\circ = -330 \text{ mV} \quad (2-25)
\]

The black-brown, very slightly soluble gold(I) sulfide, \(\text{Au}_2\text{S}\), \(pK_{sp} = 68.4\) (Puddephatt 1978), can be prepared from reaction of \([\text{Au(CN)}_2]^-\) with \(\text{H}_2\text{S}\). The compound has a positive Gibbs free energy of formation of +29 kJ mol\(^{-1}\) (Puddephatt 1978).

The sulfide \(\text{Au}_2\text{S}\) has a cuprite structure and is a bulky covalent crystal in which each gold atom has only two sulfur neighbours, as shown in Figure 2-6. Nearest neighbour interatomic distances are 217, 355 and 502 pm for Au-S, Au-Au and S-S, respectively.

![Figure 2-6: Structure of \(\text{Au}_2\text{S}\) (Ishikawa et al. 1995).](image)

The gold(III) sulfide, \(\text{Au}_2\text{S}_3\), formed by reacting \(\text{Au}_2\text{Cl}_6\) with \(\text{H}_2\text{S}\) in anhydrous ether, cannot be prepared in aqueous solution as it reduces to metallic gold (Puddephatt 1978).
2.3.2. Electrochemistry of Sulfide Electroadsorption

Voltammetric investigations of gold in sulfide solutions have shown that a prewave occurs at underpotentials to the corresponding $\text{S}^{2-}/\text{S}^0$ reversible potential at a range of solution pH (Buckley et al. 1987; Gao et al. 1992a; Hamilton and Woods 1983). The prewave has been attributed to sulfur binding to gold atoms on the metal surface (Hamilton and Woods 1983).

2.3.2.1. Prewave Region

Figure 2-7 presents voltammograms in borate at pH 9.2 of stationary and rotated gold electrodes in $1.5 \times 10^{-4}$ mol dm$^{-3}$ HS$^-$. The system was also examined at pH 6.8 and in 1.0 mol dm$^{-3}$ NaOH. The prewave is noted at ~-500 mV in Figure 2-7 and was found to occur at potentials ~30 mV more negative with each unit increase in pH (Hamilton and Woods 1983).

Figure 2-7: Voltammograms for gold electrode in borate solution of pH 9.2 containing $1.6 \times 10^{-4}$ M HS$. Triangular potential cycles at 20 mVs$^{-1}$, with overlaid scans representing subsequent excursions to incrementally increased maximum potentials. The electrode was (a) stationary and (b) rotated at 10 Hz (Hamilton and Woods 1983).
The prewave of sulfide in the presence of 1 mol dm$^{-3}$ NaOH featured two anodic and cathodic peaks. The charge passed in the anodic wave was found to be equal to that of the cathodic reduction, indicating the following reaction for deposition of sulfur on the gold surface:

$$S^{2-} \leftrightarrow S + 2e^-$$  \hspace{1cm} (2-26)

Figure 2-7 shows that both rotated and stationary electrodes pass the same current in the prewave region, indicative of a surface-specific reaction with a single reaction step (Hamilton and Woods 1983). The prewave has been observed by various authors, with agreement that it represents a surface species (Alanyalioglu et al. 2001; Briceno and Chander 1990a; 1990b; Buckley et al. 1987; Gao et al. 1992a; Lay et al. 2003; Lezna et al. 1990; Vericat et al. 2004).

### 2.3.2.2. Protonation

Various authors have discussed the possibility of protonation of the underpotential deposited sulfur submonolayer. Briceno and Chander studied polycrystalline gold in $2 \times 10^{-4}$ mol dm$^{-3}$ Na$_2$S at pH 9.3. The authors proposed that at potentials below the prewave an initial adsorption of hydrosulfide ions occurs without formal charge transfer and describe the process according to:

$$\text{Au} + \text{HS}^- \leftrightarrow \text{Au} \text{| HS}^-$$  \hspace{1cm} (2-27),

where $\text{Au} \text{| HS}^-$ represents adsorbed ions. The authors suggest that the specifically adsorbed hydrosulfide is then oxidised via a two-electron process at the prewave to form a chemisorbed deprotonated sulfide according to (Briceno and Chander 1990a):

$$\text{Au} \text{| HS}^- \leftrightarrow \text{Au} \text{| S}^0 + \text{H}^+ + 2e^-$$  \hspace{1cm} (2-28)

It has been suggested that the negative 450 mV shift in the reversible potential of the prewave between pH 2 and pH 12 represents a protonation equilibrium coupled to the
redox process (Gao et al. 1992a). In this scenario the oxidation and reduction peaks of the prewave represent deprotonation and protonation, respectively, of a previously adsorbed sulfide layer, which is described by the authors as follows:

\[(\text{HS}^-)_\text{ad} - 2e^- \leftrightarrow S_{\text{ad}} + \text{H}^+ \quad (2-29)\]

The authors provide SERS evidence (Gao et al. 1992a) that sulfur is adsorbed prior to the prewave oxidation due to the presence of vibrational modes attributed to Au-S bonding.

An investigation was undertaken into the electrochemistry of polycrystalline Au and monocrystalline Au(111) in 2 x 10⁻³ mol dm⁻³ Na₂S at pH 12 (Alanyalioglu et al. 2001). The authors support a deprotonation mechanism in the prewave region, occurring according to Equation (2-29). Two oxidation and reduction peaks were noted in the prewave of the polycrystalline system, while only one set of reversible peaks was seen in the case of Au(111). This was proposed to be due to two possible adsorption sites for SH⁻ on the polycrystalline system (Alanyalioglu et al. 2001).

The optical characteristics of the electrodorsorption of sulfide at pH 7 and 9.2 have been studied using simultaneous modulation reflectance spectroscopy and voltammetry (Lezna et al. 1990). The authors noted the presence of a broad reflectance peak commencing in the hydrogen evolution region and reaching a maximum ~200 mV below the potential of the oxidation prewave. This peak was seen to overlap with a second reflectance peak coincident with the prewave, indicative of a charge-transfer process. The authors suggest that these results indicate the initial adsorption of sulfide occurs in the hydrogen evolution region, prior to the prewave.
Evidence for a physisorbed $S^{2-}$ was reported in studies using crystal truncation scattering (Vericat et al. 2003). Using this technique, the authors were able to identify the presence of weakly bound sulfide species before anodic adsorption and after cathodic stripping. The authors propose that the weakly bound sulfide is stabilized on the surface by water or $Na^+$ co-adsorption and suggest that such weakly bound species are difficult to detect by scanning tunnelling microscopy (STM) due to tip interactions and high mobility and disorder (Vericat et al. 2003).

2.3.2.3. Sulfur Coverage of Prewave Region

The charge due to underpotential deposition of sulfur in the prewave potential region was found to be $\sim 90 \mu C \ cm^{-2}$ in $\sim 1.7 \times 10^{-4} \ mol \ dm^{-3} \ S^{II}$ solutions at pH 6.8, 9.2 and in 1 mol dm$^{-3}$ NaOH, equivalent to a fractional sulfur coverage of 0.4 monolayer, based upon a two-electron process (Hamilton and Woods 1983).

2.3.2.4. Oxidation Reactions

Comparison of the rotating disk and stationary electrode studies showed that the anodic peak observed in Figure 2-7, attributable to multilayer $S_8$ formation via the $S^{II}/S^0$ redox couple, was also seen to include current due to reactions that produced soluble species. These reactions were proposed (Hamilton and Woods 1983) to be: firstly, the formation of polysulfides as intermediates in the formation of sulfur according to:

$$xS^{2-} \rightarrow S_x^{2-} + (2x-2)e^- \quad (2-30)$$

$$S_x^{2-} \rightarrow S_x + 2e^- \quad (2-31),$$

and secondly, the oxidation of $S^{2-}$ to $SO_4^{2-}$ by following reaction:

$$S^{2-} + 4H_2O \rightarrow SO_4^{2-} + 8H^+ + 8e^- \quad (2-32)$$
Although not featured in Figure 2-7, the oxidation of sulfur to sulfate by this reaction was proposed to occur during oxidation at potentials greater than 1.0 V, accompanied by oxygen adsorption on gold (Hamilton and Woods 1983).

### 2.3.2.5. Reduction Reactions

Two peaks are seen during reduction of the sulfur multilayer (Hamilton and Woods 1983). The first reduction peak at –400 mV is the same in both the rotated and stationary systems, indicating a reduction of the sulfur multilayer to polysulfides by the reverse of reaction (2-31). The second reduction peak behaves as the reduction of a soluble species in the rotating disk studies, indicating that this peak is due to the reduction of polysulfide to sulfide by the reverse of reaction (2-30). By comparing the charge passed in the rotated and stationary systems, the value of $x$ in reactions (2-30) and (2-31) was deduced to be 5.0, 3.3 and 1.5 for sulfide systems at pH 13, 9.2 and 6.8, respectively (Hamilton and Woods 1983).

### 2.3.3. Stability of Polysulfides

Polysulfides are metastable species and as such are commonly not included in Pourbaix diagrams, despite their importance in the electrochemistry of sulfide systems. Figure 2-8 presents a $E_\text{H}$-pH diagram constructed to include polysulfide species over a pH range of 6 to 14 for a $2 \times 10^{-4}$ mol dm$^{-3}$ S$^{\text{II}}$ and $10^{-6}$ mol dm$^{-3}$ polysulfide system at 25 °C (Buckley et al. 1987).
The figure shows that the predominance of polysulfide increases with both the concentration of sulfide and increasing pH. According to Figure 2-8, the presence of polysulfides would be expected in a solution at pH 9.2 at potentials between -250 and -150 mV. The formation of sulfate, although thermodynamically favoured, has slow kinetics and requires high overpotentials to occur at a significant rate.
2.3.4. Scanning Tunnelling Microscopy Studies

Structural studies using electrochemical methods in conjunction with STM have been used to determine two-dimensional surface structures and sulfur coverages associated with sulfur adsorption on gold (Gao et al. 1992b); and to relate these structures to S 2p binding energies (Vericat et al. 2001) and surface X-ray diffraction data (Vericat et al. 2004).

STM studies of the electro-oxidation of gold were undertaken in 0.5 to 1 x 10^{-3} mol dm^{-3} Na2S solutions, with 0.1 mol dm^{-3} NaClO4 / 4 x 10^{-3} mol dm^{-3} HClO4 used as a supporting electrolyte (Gao et al. 1992b). Images of the Au(111) substrate were obtained at −500 mV vs. SCE in the hydrogen evolution region, with monomeric sulfur still observed at terrace edges. Above this potential, between -400 to –100 mV vs. SCE, a structure was observed with (√3x√3)R30° symmetry with respect to the Au(111) lattice, with an atomic spacing of 5.0 Å. The authors attribute this structure to an adsorbed monomeric sulfur with a fractional coverage of 1/3 ML (Gao et al. 1992b).

When the potential was increased to 0 V vs. SCE, the onset of current due to the solution sulfide to polysulfide oxidation processes was accompanied by the formation of a lattice of square or rectangular structures within 1 to 2 minutes (Gao et al. 1992b). The lattice was seen to co-exist with some regions of (√3x√3)R30° structure and areas in which a multilayer of disordered ring structures had formed.

When the electrode was withdrawn from solution and examined ex situ, an image of a network of crown-like ring structures was observed, as shown in the author’s STM image presented in Figure 2-9.
The crown-S\textsubscript{8} structure, illustrated in Figure 2-10 has been found by ab-initio calculations to possess the global energy minimum for isomers of S\textsubscript{8} (Wong et al. 2002). On visual comparison, this structure bears a structural similarity to the surface product observed in Figure 2-9.

More recent STM studies (Lay et al. 2003; Vericat et al. 2004) reveal similar structures to those seen by Gao and Weaver (Gao et al. 1992b). Examples of structures observed under alkaline conditions, using 3 x 10\textsuperscript{-3} mol dm\textsuperscript{-3} Na\textsubscript{2}S in 0.1 mol dm\textsuperscript{-3} NaOH (a pH at which the formation of polysulfides would be expected) are shown in Figure 2-11 (Vericat et al. 2004). The presence of a rectangular array of adsorbed S\textsubscript{8} between -780 and –550 mV vs. SCE, shown in Figure 2-11C. The authors estimated the coverage of this layer as \textfrac{2}{3} ML. On lowering the potential to –850 mV vs. SCE, the
structure was seen to transform to a \((\sqrt{3}\times\sqrt{3})R30^\circ\) structure with fractional sulfur coverage of \(\frac{1}{3}\) ML, shown in Figure 2-11A. Crystal truncation scattering (CTR) studies by the authors provided evidence that the \((\sqrt{3}\times\sqrt{3})R30^\circ\) S layer was adsorbed in three-fold hollow sites (Vericat et al. 2003). The transformation was seen to be reversible, with structures such as hexagonal clusters of sulfur triplets, shown in Figure 2-11B, seen occasionally during transformation from the \((\sqrt{3}\times\sqrt{3})R30^\circ\) structure back to the adsorbed \(S_8\). All three structures were seen to co-exist at the open circuit potential (OCP) due to the slow kinetics of the transformation.

Figure 2-11: in situ atomic resolution 6 x 6 nm² STM images of electrodeposited sulfide, a) \((\sqrt{3}\times\sqrt{3})R30^\circ\) –800 mV; b) \(S_3\) –700 mV; c) \(S_8\) –600 mV vs. SCE 0.1 M NaOH, 3 mM Na₂S (Vericat et al. 2004).

The structures were seen to desorb from terraces at –920 mV vs. SCE, with adsorbates desorbing from edge sites by \(\sim –1.1\) V vs. SCE. In the reverse process, adsorption was seen to occur at the step edges and terraces at similar potentials as for desorption. The terrace site adsorption and desorption potentials corresponded to the oxidation and reduction prewaves, respectively for Au(111) in the same solution (Vericat et al. 2004).

A study of the formation of S atomic layers on Au from \(0.2 \times 10^{-3}\) mol dm\(^{-3}\) K₂S in \(1 \times 10^{-3}\) mol dm\(^{-3}\) Na₂SO₄, found a \(\frac{1}{3}\) ML \((\sqrt{3}\times\sqrt{3})R30^\circ\) structure between –850 and –400 mV vs. Ag/AgCl, with the sulfur atoms bound to 3-fold hollow sites of Au(111) (Lay et al. 2003). The authors report a \((3\sqrt{3}\times3\sqrt{3})R30^\circ\) structure which they suggest
may be a precursor to the formation of adsorbed S\textsubscript{8} rings. The restructuring and templating of the Au(111) surface by a (4x4) structure was reported (Lay et al. 2003). The (4 x 4) structure was seen to co-exist with the (√3x√3)R30° and, upon desorption, a (4 x 4) template was retained by the gold surface. Upon sulfide readsorption, a more highly ordered (4 x 4) structure was seen to appear on the templated regions, showing a similar structure to that described as S\textsubscript{3} (Vericat et al. 2003; Vericat et al. 2004).

An investigation of electro-oxidation in thiosulfate solutions has been reported (Lay et al. 2003). The authors found a c(4x2√3) structure at the OCP of -0.2 V vs. Ag/AgCl (-0.245 V vs. SCE), as presented in Figure 2-12. The structure was seen to oxidatively desorb when the potential was increased to -0.05 V vs. Ag/AgCl (-0.095 V vs. SCE).

![Figure 2-12: STM micrograph of the c(4x2√3) structure adsorbed on the Au(111) electrode at -0.15 V vs. 3 M Ag/AgCl in 1.0 mM Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, 1.0 mM K\textsubscript{2}O. The scan size is 7.5 x 7.5 nm\textsuperscript{2}.](image)

A (2 x 2) structure was reported in sulfide and thiosulfate solutions (Lay et al. 2003). The layer was associated with 1/2 ML coverage and each unit cell appeared to contain one dimer. The image was distorted, suggesting the dimers were not in stable sites and were mobile upon imaging.
2.3.5. X-ray Photoelectron Studies

The surface of a sulfur-coated gold electrode has been examined using a combination of XPS and electrochemical techniques (Buckley et al. 1987). The authors polarised a gold foil electrode for 30 s at –200 mV in 2 x 10^{-4} mol dm^{-3} Na_{2}S in order to deposit sulfur at a potential between that of prewave adsorption and bulk sulfur formation. The XPS spectrum showed the presence of more than one sulfur environment, which was fitted with two doublets. One type of sulfur showed a 2p_{3/2} binding energy of 161.2 eV and accounted for ~65% of the overall sulfur peak intensity. This major doublet was found to have a binding energy associated with metal sulfides (Buckley et al. 1987; Moulder et al. 1995). The S 2p_{3/2} binding energy reported for sulfur in Cu_{2}S is 161.5 eV (Gebhardt et al. 1986).

The second type of sulfur showed a binding energy of 162.3 eV, similar to that observed for pyritic sulfur, S_{2}^{2−} (Buckley et al. 1987). When polarised at 200 mV, a potential at which bulk sulfur is expected to form, two doublets were observed at 2p_{3/2} binding energies of 161.3 and 162.9 eV, with the higher binding energy accounting for 63% of the intensity (Buckley et al. 1987). Table 2-5 presents binding energies of some copper and sulfur compounds. It can be seen that, with increasing potential, binding energies approach, but do not reach, the S^{0} 2p_{3/2} energy of 164.0 eV (Moulder et al. 1995).

Table 2-5: XPS binding energies of various copper and sulfur compounds (Moulder et al. 1995).

<table>
<thead>
<tr>
<th>Sulfur</th>
<th>S 2p_{3/2}</th>
<th>Copper</th>
<th>Cu 2p_{3/2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>S^{2−}</td>
<td>160.0 – 164.0</td>
<td>CuS</td>
<td>931.9 – 933.2</td>
</tr>
<tr>
<td>S_{8}</td>
<td>163.5 – 164.0</td>
<td>Cu_{2}S/Cu_{2}O</td>
<td>932.2 – 932.7</td>
</tr>
<tr>
<td>SO_{3}^{−}</td>
<td>165.5 – 167.5</td>
<td>Cu</td>
<td>932.5 – 932.8</td>
</tr>
<tr>
<td>SO_{2}</td>
<td>167.0 – 168.0</td>
<td>CuO</td>
<td>933.5 – 934.0</td>
</tr>
<tr>
<td>SO_{4}^{2−}</td>
<td>174.5 – 177.0</td>
<td>CuSO_{4}</td>
<td>934.9 – 935.5</td>
</tr>
</tbody>
</table>
Elemental sulfur is known to vaporise under UHV conditions above 200 K (Klauber et al. 2001) and binding energies at 163.0 eV have been described as modified sulfide on the assumption that elemental sulfur would not exist under vacuum (Grano et al. 1977). Evaporative loss of a lower binding energy 2p3/2 species at 162.9 eV has been noted to occur at a significantly slower rate. The authors attributed this binding energy as being due to monolayer sulfur on gold (Buckley et al. 1987).

Experiments to determine the coverage of butanethiol on gold have used the ratio of sulfur to gold to achieve a quantitative value of the fractional monolayer (Hutt and Leggett 1997). This ratio was chosen to eliminate the attenuation of both the gold and sulfur signals by the overlying butyl layer and was found to be 0.084 ± 0.003 for a full self assembled monolayer (SAM). This layer was reported to correspond to a (√3x√3)R30° lattice of butanethiol on Au(111).

Rodriguez et al. reported high resolution photoemission spectra acquired from S2 gas adsorbed on polycrystalline and gold (111) substrates (Rodriguez et al. 2003). The authors observed a set of three doublets for adsorption of small doses of S2 at 300 K, at 160.8 eV (dominant), 161.6 and 163.4 eV (very weak). Upon annealing to 500 K, the doublet with the 160.8 eV intensity gained intensity and was shown to be associated with surfaces that displayed a (√3x√3)R30° LEED pattern (Rodriguez et al. 2003). The associated sulfur coverage was calculated from the area under the S 2p doublets as ~1/3 ML. The authors assigned this type of surface sulfur to S atoms bonded to three-fold hollow sites of Au(111). Density functional calculations found this to be the most stable site for S on Au(111) at low coverages.
With increasing S coverage, the authors found S 2p features above 163 eV to gain intensity and assigned these to the presence of $S_n$ aggregates, where $n = 2$. The authors described the reaction occurring above $1/3$ ML in the following equation:

$$nS \rightarrow S_n$$

(2.33),

with evidence for $n > 2$ at S coverages greater than a monolayer. The authors reported that sulfur atoms bonded to Au(111) at room temperature were highly mobile and able to form S-S bonds at moderate and high sulfur coverages. As the coverage increased the authors note a weakening of the Au-S bonds, which facilitates changes in adsorption site. At 1 ML S coverage, the a-top sites were found to be more stable than the fcc hollows (Rodriguez et al. 2003). As the sulfur coverage increases, therefore, sulfur atoms can move to the more stable a-top sites.
2.4. Raman Assignments of Reference Compounds

Literature assignments of the nature and position of conventional Raman modes for various species of interest have been documented for comparison with those obtained from SERS spectroelectrochemical studies.

2.4.1. Sulfur compounds

2.4.1.1. cyclo-Octasulfur $S_8$

At ambient temperature, cyclo-octasulfur can crystallise as orthorhombic $\alpha$-$S_8$, monoclinic $\beta$-$S_8$ or monoclinic $\gamma$-$S_8$ (Steudel and Eckert 2003). Commercially available sulfur samples predominantly consist of $\alpha$-$S_8$, with random-coil polymeric sulfur, $S\mu$, and cyclo-heptasulfur, $S_7$, generally present as impurities. The $S_7$ is responsible for the characteristic bright yellow colour of commercial sulfur, as pure orthorhombic $\alpha$-$S_8$ is greenish-yellow (Steudel and Eckert 2003). The isolated $S_8$ molecule has a $D_{4d}$ point group symmetry and exhibits seven observable Raman-active vibrations (Eckert and Steudel 2003).

Table 2-6 details mode symmetries (Becucci et al., 1997) and experimental values of the vibrational modes of $S_8$ in CS$_2$ at room temperature (Eckert and Steudel 2003). In an orthorhombic $\alpha$-$S_8$ crystal, the number of Raman-active vibrations increases due to the lowered site symmetry (Eckert and Steudel 2003). Despite the increased complexity, the spectrum of $S_8$ is characterised by intense bending modes, $\delta_{S-S-S}$ at $\sim$150 cm$^{-1}$ and $\sim$220 cm$^{-1}$, and a S-S stretching mode, $\nu_{S-S}$ at $\sim$ 470 cm$^{-1}$, the relative intensities of which can be seen in Figure 2-13 (McCreery 2005).
Sulfur powder, 99.98% [Aldrich #41,498-0], is one of eight compounds adopted by the American Society for Testing and Materials subcommittee on Raman spectroscopy as Raman frequency standards (ASTM E 1840) (McCreery 2005). The ASTM E 1840 standard sulfur spectrum, collated from Raman spectra obtained by at least six different experimentalists, using both FT and dispersive Raman spectrometers, is presented in Figure 2-13 (McCreery 2005).

Table 2-6: Vibrational assignments and experimental wavenumbers for \( S_8 \) in \( CS_2 \). Wavenumber value calculated for inactive mode (Eckert and Steudel 2003). R – Raman, IR – infrared.

<table>
<thead>
<tr>
<th>vibration</th>
<th>mode symmetry</th>
<th>type</th>
<th>Energy cm(^{-1})</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \nu_1 )</td>
<td>A(_1)</td>
<td>stretch</td>
<td>476</td>
<td>R</td>
</tr>
<tr>
<td>( \nu_2 )</td>
<td>A(_1)</td>
<td>bend</td>
<td>218.5</td>
<td>R &amp; IR</td>
</tr>
<tr>
<td>( \nu_3 )</td>
<td>B(_1)</td>
<td>stretch</td>
<td>(424)</td>
<td>inactive</td>
</tr>
<tr>
<td>( \nu_4 )</td>
<td>B(_2)</td>
<td>bend</td>
<td>243</td>
<td>IR</td>
</tr>
<tr>
<td>( \nu_5 )</td>
<td>E(_1)</td>
<td>stretch</td>
<td>471</td>
<td>IR</td>
</tr>
<tr>
<td>( \nu_6 )</td>
<td>E(_1)</td>
<td>bend</td>
<td>191</td>
<td>IR</td>
</tr>
<tr>
<td>( \nu_7 )</td>
<td>E(_2)</td>
<td>stretch</td>
<td>476</td>
<td>R &amp; IR</td>
</tr>
<tr>
<td>( \nu_8 )</td>
<td>E(_2)</td>
<td>bend</td>
<td>152.5</td>
<td>R &amp; IR</td>
</tr>
<tr>
<td>( \nu_9 )</td>
<td>E(_2)</td>
<td>torsion</td>
<td>86</td>
<td>R &amp; IR</td>
</tr>
<tr>
<td>( \nu_{10} )</td>
<td>E(_3)</td>
<td>stretch</td>
<td>444</td>
<td>R</td>
</tr>
<tr>
<td>( \nu_{11} )</td>
<td>E(_3)</td>
<td>bend</td>
<td>248</td>
<td>R &amp; IR</td>
</tr>
</tbody>
</table>

Figure 2-13: ASTM standard spectrum for sulfur (McCreery 2005).
2.4.1.2. Polymeric and Disordered Sulfur

The Raman spectrum of polymeric sulfur, $S_\mu$, features one strong and one weak band in the stretching region at 460 and 425 cm$^{-1}$, respectively, and two weak bending modes at $\sim$275 and 260 cm$^{-1}$ (Eckert and Steudel 2003). Raman spectra from two different preparations of polymeric sulfur are shown in Figure 2-14. A planar zigzag structure has been used to model the vibrational spectrum, but not all modes have been reproduced, hence the model may be too simplistic (Eckert and Steudel 2003).

Figure 2-14: Raman spectra of polymeric sulfur. $S_x$ - Large disordered rings; a-S - photo-induced amorphous sulfur; $S_\mu$ - polymeric sulfur prepared by various methods (Eckert and Steudel 2003).

Highly disordered solid forms of sulfur include $S_x$, a mixture of large rings formed from liquid sulfur; and amorphous sulfur, a-S, formed from photo-induced ring-opening in $\alpha$-$S_8$ at high temperatures (Eckert and Steudel 2003). Both of these disordered forms
of sulfur bear spectral similarities to polymeric sulfur, as illustrated by Figure 2-14. Broad Raman bands are characteristic of the disordered forms of sulfur, as the entire vibrational density of states gains optical activity due to loss of translational symmetry (Eckert and Steudel 2003).

2.4.1.3. Empirical Relationships in Homocyclic Sulfur Molecules

In homocyclic sulfur ring structures, the stretching vibrations have been found to depend mainly on the bond distance, while bending modes are determined by the size and symmetry of the ring (Eckert and Steudel 2003). Both stretching and bending modes can be calculated using the empirical formulae in equations (2-34) and (2-35).

\[ r_{SS} = 2.53 - 1.04 \times 10^{-3} \cdot \nu_{SS} \]  
\[ \delta_{S-S-S} = 400 - 22.8 \cdot n \]

where \( r_{SS} \) is bond length in angstroms, Å, and \( \nu_{SS} \) is wavenumber, cm\(^{-1}\).

2.4.1.4. Hydrogen Sulfides

The S-H stretching modes of the dihydrogen sulfide molecule, H\(_2\)S, have been observed in a high-pressure aqueous system as a single Raman band at \( \sim 2590 \) cm\(^{-1}\) (Bondarenko and Gorbaty 1997). The S-H stretch of the hydrosulfide ion, HS\(^-\), was observed at 2570 cm\(^{-1}\) in a low-temperature study of sulfide/hydrosulfide equilibrium (Meyer et al. 1983).

2.4.1.5. Gold-Sulfur Modes

Comprehensive Raman assignments of gold sulfides are not available in the literature but assignments of gold–sulfur stretching modes, \( \nu_{Au-S} \), have been reported for a variety
of compounds (Bowmaker 1999). Table 2-7 presents vibrational modes observed in various compounds containing gold-sulfur bonds. Bands due to gold-sulfur stretching, $\nu_{\text{Au-S}}$, were seen to appearing in two spectral regions in both Raman and infrared, from 270–280 cm$^{-1}$ and 310–345 cm$^{-1}$, challenging the concept of a single gold-sulfur vibration (Bowmaker 1999).

**Table 2-7: IR and Raman modes of Au-S bonds in gold-sulfur compounds (Bowmaker 1999).**

<table>
<thead>
<tr>
<th>compound</th>
<th>$\nu_{\text{sym} \text{Au-S}}$</th>
<th>$\nu_{\text{antisym} \text{Au-S}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Au(SCN)}_2]^{-}$</td>
<td>306 R</td>
<td>310 IR</td>
</tr>
<tr>
<td>$[\text{Au(SMe)}_2]^{-}$</td>
<td>334 R</td>
<td>342 IR</td>
</tr>
<tr>
<td>$[\text{Au(SBu')}_2]^{-}$</td>
<td>244 R</td>
<td>310-340</td>
</tr>
<tr>
<td>IR studies only</td>
<td></td>
<td></td>
</tr>
<tr>
<td>$[(\text{SMe})_2\text{AuX}]^{-}$</td>
<td>270-279</td>
<td>330-345 (R, IR)</td>
</tr>
</tbody>
</table>

**2.4.1.6. Copper-Sulfur Modes**

At least five stable phases of Cu$_x$S, being covellite (CuS), anilite (Cu$_{1.75}$S), digenite (Cu$_{1.8}$S) djurleite (Cu$_{1.95}$S) and chalcocite (Cu$_2$S), are known to exist between the stoichiometry of $x = 1 – 2$ (Wang *et al.* 2003). The structural formulae of covellite is not consistent with its stoichiometry as a copper(II) sulfide, with XPS studies of covellite showing copper to be present largely as copper(I) (Goh *et al.* 2006). The Raman spectrum of covellite shows a strong band at 475 cm$^{-1}$ due to stretching modes of sulfur dimers within the lattice and a small lattice mode at 267 cm$^{-1}$ (Iishi-*et-al.*-1993). The comparatively sulfur-deficient chalcocite Cu$_2$S does not exhibit any bands in the 300 - 800 cm$^{-1}$ spectral range (Tacconi *et al.* 1996).

**2.4.1.7. Polysulfides**

Literature studies of Raman spectroscopy of polysulfides, S$_n^{2-}$, have focused upon crystalline compounds with emphasis on the effect of counter-ions on the anion
geometry (El Jaroudi et al. 1999) and crystalline, glassy and molten states of Na\(^+\), K\(^+\) and Ba\(^{2+}\) cation systems (Janz et al. 1976a; Janz et al. 1976b; Janz et al. 1976c). Their solution spectrum of aqueous Na\(_2\)S\(_4\) is presented in Figure 2-15.

Figure 2-15: Raman spectra of (a) polycrystalline, (b) glassy, (c) aqueous, and (d) molten Na\(_2\)S\(_4\). (Janz et al. 1976b). Detail of overtone region of polycrystalline spectrum shown in (e).

The authors reported a predominant S-S stretching band at 446 cm\(^{-1}\), weaker stretching bands at 410- and 484 cm\(^{-1}\) (Janz et al. 1976b) and weak bands at 194 and 256 cm\(^{-1}\), which may be attributed to bending modes. A marked broadening of the S-S stretching bands was observed in the polysulfide solution as compared with the crystalline state, supporting previous observations of disproportionation of polysulfides in solution (Schwarzenbach and Fischer 1960). In their study, S\(_5^{2-}\) was found to be stable in solution, while the lower polysulfides disproportionated to S\(_5^{2-}\), S\(_4^{2-}\) and SH\(^-\) (Janz et al. 1976b). The anions S\(_3^{2-}\) and S\(_2^{2-}\) were not detected within the equilibrium mixtures used (Schwarzenbach and Fischer 1960), but a complex equilibrium mixture
of all polysulfides up to octa-sulfide have been reported in studies of nucleophilic degradation of S\textsubscript{8} by HS\textsuperscript{−} and OH\textsuperscript{−} (Steudel 2003b).

2.4.2. Thiosulfate

The molecular formula of the thiosulfate ion is S\textsubscript{2}O\textsubscript{3}^{2−}. It is structurally similar to the tetrahedral sulfate ion, SO\textsubscript{4}^{2−} but with one oxygen atom replaced by sulfur, reducing its symmetry from tetrahedral to C\textsubscript{3v} (Haigh \textit{et al.} 1993). When complexed with gold(I), thiosulfate is known to bind to gold through its terminal sulfur atom (Baggio and Baggio 1973). Various authors have undertaken Raman studies of the thiosulfate ion and related oxyanions (Gabelica 1980; Haigh \textit{et al.} 1993; Rintoul \textit{et al.} 1997; Woods \textit{et al.} 2006). Table 2-8 presents Raman assignments and detection limits of the thiosulfate ion in solution.

![Table 2-8: Raman assignments of the thiosulfate ion in solution (Haigh \textit{et al.} 1993; Meyer \textit{et al.} 1980)](image)

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Vibrational notation</th>
<th>Raman shift cm\textsuperscript{−1}</th>
<th>Detection limit mol dm\textsuperscript{−3}</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-O symmetric stretch</td>
<td>ν\textsubscript{1} A\textsubscript{1} ν\textsubscript{symS-O}</td>
<td>1002</td>
<td>0.005</td>
</tr>
<tr>
<td>S-O symmetric bend</td>
<td>ν\textsubscript{2} A\textsubscript{1} δ\textsubscript{symS-O}</td>
<td>672</td>
<td>0.02</td>
</tr>
<tr>
<td>S-S stretch</td>
<td>ν\textsubscript{3} A\textsubscript{1} ν\textsubscript{S-S}</td>
<td>451</td>
<td>0.003</td>
</tr>
<tr>
<td>S-O antisymmetric stretch</td>
<td>ν\textsubscript{4} E ν\textsubscript{antisymS-O}</td>
<td>1125</td>
<td>0.04</td>
</tr>
<tr>
<td>S-O antisymmetric bend</td>
<td>ν\textsubscript{5} E δ\textsubscript{antisymS-O}</td>
<td>541</td>
<td>0.02</td>
</tr>
<tr>
<td>S-O-S rock</td>
<td>ν\textsubscript{6} E ρ\textsubscript{S-O-S}</td>
<td>339</td>
<td>0.01</td>
</tr>
</tbody>
</table>

The effects of cation variation on solid and solution Na\textsuperscript{+} and NH\textsubscript{4}\textsuperscript{+} thiosulfate and solid K\textsuperscript{+} and Cs\textsuperscript{+} thiosulfate were reported from studies using low energy 1064 nm FT Raman (Haigh \textit{et al.} 1993). The authors paid particular attention to the variation of the antisymmetric S-O stretching mode as an indicator of coordination i.e. free ion, single or bridged S bonding, or bonding through oxygen.
Gabelica provides a structural study of solid metal thiosulfate complexes, describing the effects of bonding to various metals upon the frequencies of the S-O and S-S stretching modes (Gabelica 1980). The author claimed that preferential bonding of a metal with a soft acid character will occur through the sulfur atom. The resulting bond order perturbation would result in a shift of the $\nu_{\text{symS-O}}$ and $\nu_{\text{antisymS-O}}$ modes toward higher wavenumbers together with a decrease in wavenumber of the $\nu_{\text{S-S}}$ band (Gabelica 1980).

![Raman spectra of Na$_2$S$_2$O$_3$ and Na$_3$Au(S$_2$O$_3$)$_2$ from both solid phase and 0.1 M solutions.](image)

Figure 2-16 presents Raman spectra from crystalline and 0.1 mol dm$^{-3}$ solutions of sodium thiosulfate (Woods et al. 2006). It can be seen from Figure 2-16 that the spectrum of crystalline sodium thiosulfate displays bands at 431 cm$^{-1}$ and 1019 cm$^{-1}$, which are assigned to $\nu_{\text{S-S}}$ and $\nu_{\text{symS-O}}$ (Gabelica 1980; Haigh et al. 1993), respectively.
The bands shift to 445 cm\(^{-1}\) and 999 cm\(^{-1}\), respectively, when the thiosulfate ion is in solution, suggesting a lengthening of the S-O bond and contraction of the S-S bond.

### 2.4.2.1. Gold Thiosulfate

Solid and 0.1 mol dm\(^{-3}\) solution spectra of trisodium gold(I) dithiosulfate, Na\(_3\)Au(S\(_2\)O\(_3\))\(_2\), are shown in Figure 2-16 (Woods \textit{et al.} 2006). The \(\nu_{S-S}\) and \(\nu_{\text{symS-O}}\) bands appear at 415 cm\(^{-1}\) and 1039 cm\(^{-1}\), respectively, from the gold thiosulfate complex in the solid sodium compound and at 418 cm\(^{-1}\) and 1019 cm\(^{-1}\), respectively, from the gold complex ion in solution. A sharp \(\delta_{\text{symS-O}}\) is seen in the solid at \(\sim 670\) cm\(^{-1}\), broadening and shifting downward in wavenumber to \(\sim 660\) cm\(^{-1}\) in solution. Little change is seen in the wavenumber of the \(\nu_{S-S}\) in the gold complex upon solvation, indicating minimal effect upon the S-S bond length. A comparative lengthening of the S-O bond in the complex upon solvation is, however, indicated by the decrease in wavenumber of \(\nu_{\text{symS-O}}\). The difference between \(\nu_{S-S}\) for the gold thiosulfate complex and that of the thiosulfate ion reflects a lengthening of the S-S bond when thiosulfate is bound to gold.

### 2.4.3. Polythionates

Raffo sols, comprising sulfur and polythionates (sulfane disulfonates) formed by acid decomposition of thiosulfate, feature the vibrational modes of S\(_8\) and a characteristic S-S stretch at 393 cm\(^{-1}\) (Steudel \textit{et al.} 1988). It was suggested by the authors that this band represents the S-S bond adjacent to the SO\(_3^-\) group. Table 2-9 lists experimentally determined Raman bands for the potassium salts of tri-, tetra-, penta- and hexa-thionate (Steudel \textit{et al.} 1988).
Table 2-9: Raman assignments for solid potassium polythionates, \( n = 3-6 \) (Steudel et al. 1988)

<table>
<thead>
<tr>
<th>Trithionate ( \text{K}_2\text{S}_3\text{O}_6 )</th>
<th>Tetrathionate ( \text{K}_2\text{S}_4\text{O}_6 )</th>
<th>Pentathionate ( \text{K}_2\text{S}_5\text{O}_6\cdot1.5\text{H}_2\text{O} )</th>
<th>Hexathionate ( \text{K}_2\text{S}_6\text{O}_6 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>153 vs</td>
<td>206 s, b</td>
<td>153 m</td>
<td></td>
</tr>
<tr>
<td></td>
<td>220 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>233 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>251 m</td>
<td>255 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>262 s</td>
<td>284 s</td>
<td>291 m</td>
<td></td>
</tr>
<tr>
<td>325 w</td>
<td>300 s, b</td>
<td>303 m</td>
<td>299 sh</td>
</tr>
<tr>
<td></td>
<td>374 m</td>
<td>318 w</td>
<td></td>
</tr>
<tr>
<td></td>
<td>384 s</td>
<td>384 vs</td>
<td>389 s</td>
</tr>
<tr>
<td></td>
<td>396 m</td>
<td></td>
<td></td>
</tr>
<tr>
<td>443 m</td>
<td></td>
<td>440 m</td>
<td></td>
</tr>
<tr>
<td>455 s</td>
<td></td>
<td>450 sh</td>
<td></td>
</tr>
<tr>
<td>477 m</td>
<td>472 m</td>
<td>470 vs</td>
<td></td>
</tr>
<tr>
<td>518 m</td>
<td>501 s</td>
<td></td>
<td></td>
</tr>
<tr>
<td>530 vw</td>
<td>534 m</td>
<td>524 w</td>
<td></td>
</tr>
<tr>
<td>542 vw</td>
<td>546 m</td>
<td>550 w</td>
<td></td>
</tr>
<tr>
<td>552 vw</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>620 w</td>
<td>636 m, b</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>657 m</td>
<td>655 w</td>
<td></td>
</tr>
<tr>
<td>680 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>692 w</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>984 m</td>
<td>948 w</td>
<td>1040 vw</td>
<td></td>
</tr>
<tr>
<td>1062 vs</td>
<td>1045 s</td>
<td>1037 vs</td>
<td>1053 m</td>
</tr>
</tbody>
</table>

### 2.4.4. Oxysulfur Anions

A comprehensive quantitative study (Meyer et al. 1980) examined 10 oxysulfur anions in aqueous solutions, listing relative and absolute scattering intensities and assignments of vibrational modes. Species covered by this study were thiosulfate, sulfite, bisulfite, disulfite, sulfur dioxide, sulfate, bisulfate, dithionate, dithionite and tetrathionate. Raman shifts for the most characteristic modes listed by Meyer et al. are presented in Table 2-10.
Table 2-10: Quantitative Raman modes of some oxysulfur anions in solution (Meyer et al. 1980).

<table>
<thead>
<tr>
<th>Anion</th>
<th>Wavenumber, cm⁻¹ (detection limit, mol dm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>sulfate SO₄²⁻</td>
<td>1104 (0.1) 981 (0.007) 613 (0.1) 451 (0.03)</td>
</tr>
<tr>
<td>hydrogensulfate HSO₄⁻</td>
<td>1230 (0.1) 1050 (0.004) 885 (0.02)</td>
</tr>
<tr>
<td>dithionate S₂O₆²⁻</td>
<td>1206 (0.01) 1092 (0.001) 710 (0.003) 550 (0.01) 320 (0.05) 281 (0.002)</td>
</tr>
<tr>
<td>sulfur dioxide SO₂</td>
<td>1340 (0.06) 1144 (0.03) 540 (0.3)</td>
</tr>
<tr>
<td>sulfite SO₃²⁻</td>
<td>966/933 (0.01) 620 (0.2) 470 (0.02)</td>
</tr>
<tr>
<td>hydrogensulfite HSO₃⁻</td>
<td>1021 (0.003)</td>
</tr>
<tr>
<td>disulfite S₂O₅²⁻</td>
<td>1052 (0.0002) 655 (0.0003) 424 (0.0005) 235 (0.00005)</td>
</tr>
<tr>
<td>dithionite S₂O₄²⁻</td>
<td>1052/997 (0.02) 584 (0.003) 461 (0.002) 232 (0.0008)</td>
</tr>
<tr>
<td>thiosulfate S₂O₃²⁻</td>
<td>1125 (0.04) 1002 (0.005) 672 (0.02) 541 (0.02) 451 (0.003) 339 (0.01)</td>
</tr>
<tr>
<td>tetrathionate S₄O₆²⁻</td>
<td>1230 (0.04) 1040 (0.009) 640 (0.03) 522 (0.05) 390 (&lt;0.009) 260 (0.0098)</td>
</tr>
</tbody>
</table>

2.4.5. Thiourea

The Raman spectrum of a 1.0 mol dm⁻³ thiourea solution is presented in Figure 2-17 (Liu and Wu 2005). The bands represent the vibrational modes due to N-C-N bending, δₜₜ 483 cm⁻¹; C=S stretching, νₛₛ 732 cm⁻¹; symmetric NH₂ wagging, ρₚₚ 1096 cm⁻¹; and N-C-N symmetric and antisymmetric stretching, νₛₚₚₚₚ 1405 cm⁻¹ and νₜₜₜₜ 1495 cm⁻¹ (Brown et al. 1995; Liu and Wu 2005).
The thiourea molecule consists of a delocalised \( \pi \) system involving three canonical forms as shown in Figure 2-18. Bonding to a metal via the sulfur atom forces the molecule to adopt the orientation of structures II and III, shifting the frequency of the C-S stretch to a lower wavenumber value characteristic of a single bond (Brown et al. 1995; Reents et al. 1998).

![Figure 2-18: Resonance structures of thiourea (Reents et al. 1998).](image)

2.4.5.1. Copper-thiourea compounds

Copper-thiourea compounds have been well characterised and show Cu-S stretching modes, \( \nu_{\text{Cu-S}} \), in both IR and Raman between 200 – 280 cm\(^{-1}\) (Bombicz et al. 2004; Bott et al. 1998). The wavenumber of \( \nu_{\text{Cu-S}} \) shows a strong dependence on the copper co-ordination environment and is empirically related to the Cu-S bond length by the following relationship in which \( r \) is Cu-S bond length in Å (Bott et al. 1998).

\[
\nu = 31180 \, r^{-5.94}
\] (2-36)

2.4.6. Ammonia / Ammonium

Ammonia has a \( C_{3v} \) symmetry with 4 modes active in both infrared and Raman (Handy et al. 1999). The A\(_1\) modes, which are strong in Raman, are the symmetric N-H stretch, \( \nu_{\text{sy mn-N-H}} \), which occurs at 3336 cm\(^{-1}\) in gas phase (Handy et al. 1999) and ~3300 in solution (Ujike and Tominaga, 2002); and the symmetric NH\(_3\) bending mode,
$\delta_{\text{symN-H}}$. In the gas phase, $\delta_{\text{symN-H}}$ is split due to molecular inversion of the ammonia molecule, occurring at 932 and 968 cm$^{-1}$, while in ammonia solutions the vibration is observed as a single band at $\sim$1050 cm$^{-1}$. The remaining E modes, which are strong in infrared but weak in Raman, are the $\nu_{\text{antisymN-H}}$ at $\sim$3443 cm$^{-1}$ in gas phase and 3400 cm$^{-1}$ in solution; and the $\delta_{\text{antisymN-H}}$ at 1627 cm$^{-1}$ in gas phase and 1650 cm$^{-1}$ in solution.

The ammonium ion, NH$_4^+$, is of tetrahedral symmetry, T$_d$, and has 2 infrared and 4 Raman modes, both of which are also infrared active (Agullo-Rueda et al. 1988). The strongest Raman mode is the A$_1$ symmetric N-H stretch, $\nu_{\text{symN-H}}$, at 3040 cm$^{-1}$. A weak E deformation mode, $\delta_{\text{symN-H}}$, is Raman active at 1680 cm$^{-1}$. The T$_2$ modes showing strong infrared activity give very weak Raman bands for the antisymmetric N-H stretch, $\nu_{\text{antisymN-H}}$, at 3145 cm$^{-1}$ and the antisymmetric deformation, $\delta_{\text{antisymN-H}}$, at 1400 cm$^{-1}$ (Agullo-Rueda et al. 1988; Nakamoto 1997b).
2.5. SERS SUBSTRATES

2.5.1. Morphology of an Optimised Gold SERS Electrode

Electrochemically roughening a gold electrode using a similar procedure to that described by Tian has been shown to produce nanoscale gold deposits on the electrode surface. Figure 2-19 is an electron micrograph (Liu et al. 2005) showing the morphology of a polished gold electrode subjected to 25 oxidation-reduction cycles in 0.1 mol dm$^{-3}$ KCl. The scan rate was 0.5 V s$^{-1}$ in both positive and negative directions, with lower and upper potentials of –280 mV and 1.22 V vs. Ag/AgCl respectively. The electrode was held at the lower potential for 10 s and the upper potential for 5 s. The authors report that this roughening procedure was found in an earlier study to give optimal SERS of adsorbed polypyrrole (Liu et al. 2002).

Figure 2-19: SEM image of a SERS-optimised gold electrode oxidation-reduction cycled in 0.1 M KCl (Liu et al. 2005).
Figure 2-20 shows the formation of nanoparticulate clusters of deposited gold, with individual particles of ~20 nm diameter. A surface with this morphology conforms to early grating theories of SERS enhancement (Kahl and Voges 2000; Moskovits 1985). Interaction of incident light with such gratings allows the transfer of momentum from the incoming photons to the surface plasmons, satisfying a condition for resonance.

2.5.2.  Fractality in SERS Substrates

Fractals structures possess self-similar, or self-affine, scaling properties that are ubiquitous in nature (Sanchez-Gil and Garcia-Ramos 1998). Electromagnetic theories of both nanoparticulate and roughened SERS substrates were found to benefit from consideration of the fractal implications of both types of morphology.

2.5.2.1.  Colloidal Aggregates of Nanoparticles

In the case of nanoparticles, theories derived from discrete electromagnetic dipole approximations were insufficient to explain the significant enhancements and ‘hot spots’ observed due to colloidal aggregation of single spherical or spheroidal nanoparticles. The self-affine nature of colloidal aggregation allows the structure to be considered and treated mathematically as a fractal, as can aggregation due to vapour deposition of island films (Sanchez-Gil et al. 2000).

2.5.2.2.  Roughened Surfaces

Electromagnetic field enhancements from randomly roughened surfaces have mostly been modelled on the assumption of a Gaussian correlation function for the surface profile (Sanchez-Gil and Garcia-Ramos 1997). This assumption is not valid in most cases as random surface roughness generally exhibits complex multiscale features common to fractal structures. Roughened surfaces modelled as Menger sponge fractals
in order to calculate field enhancement showed an attenuation of field strength (Mickey et al. 2004), a result which appears at odds with the highly-regarded performance of this type of surface as a SERS substrate.

2.5.2.3. Dendritic Structures

Dendritic structures formed at a surface from diffusion-limited aggregation during an electrodeposition process are not true fractals. They are more correctly described as pseudo or pre-fractals (Mickey et al. 2004) as the scaling ability of the self-similarity of these structures is limited by the mechanical stability of the dendrites. Dendritic structures modelled as a Koch curve fractal predicted that the highest SERS activity would arise from molecules adsorbed at high apexes of the dendritic aggregates and that the enhancement was independent from the angle of laser incidence in the range of 0 – 90° (Mickey et al. 2004).

Figure 2-21: Schematic representation of the development of a 3rd generation Koch curve fractal used by to model a dendritic growth surface (Mickey et al. 2004).
Dendritic gold substrates have appeared in recent literature in applications such as semiconductor-supported biomimetic superhydrophobicity substrates (Wang et al. 2006) and have been seen to play a role in the formation of silicon nanowires (Peng and Zhu 2003).

2.5.3. Electrochemical Faceting

Electrodeposition on single crystal metal surfaces results in various growth processes, including spirals and faceting arising from screw dislocations in the single crystal surfaces. In a polycrystalline surface, the individual grains can be considered as single crystal microsubstrates joining at grain boundaries. Abnormal growth, expected at the grain boundaries of a polycrystalline surface, would be negligible due to the relatively small area occupied by the grain boundaries as compared with the grains. It is therefore reasonable to extend theories of deposition and growth of single crystals to that of polycrystalline systems (Bockris et al. 2000).

The electric field of a hypothetically flat surface can be considered uniform. The formation of roughness on the surface changes the potential, with the field becoming concentrated on projections. This leads to faster growth at the points of higher field strength, with sufficient irregularity leading to differential growth velocities of different crystal faces (Bockris et al. 2000). The formation of preferred crystallographic orientation of grains in polycrystalline metals under potential control is known as electrochemical faceting, and by adjusting the periodic perturbation of the applied potential, different preferred orientations can be achieved (Arvia et al. 1986).
The electrodeposition of dendrites initially results from a microspiral or other pointed growth from a flat substrate surface (Bockris et al. 2000). When the radius of curvature of the tip of the microspiral is much less than the diffusion layer thickness, a point sink occurs. In this case, the limiting current density becomes much higher on the tip. It is further argued by that the concentration and activation overpotentials are much less at the spiral tip, causing electrodeposition to occur there more rapidly than in the rest of the substrate (Bockris et al. 2000).
2.6. SERS OF ADSORBATES ON GOLD

The following section reviews SERS literature for the various adsorbate systems studied in this thesis. Previous work by our group on SERS of cyanides and chlorides on gold has been reported (Jeffrey et al. 2005; Watling et al. 2005).

2.6.1. Oxide Formation

SERS studies of metal-oxide bonding during electro-oxidation of platinum, rhodium, ruthenium and gold have been undertaken (Zhang et al. 1993). A broad vibrational band centred at ~570 cm\(^{-1}\) was seen by the authors upon oxide formation on a gold electrode in 0.1 mol dm\(^{-3}\) HClO\(_4\). The band was seen to sharpen and shift to 550 cm\(^{-1}\) prior to reduction of the oxide layer (Zhang et al. 1993). Under alkaline conditions, a band at 420 cm\(^{-1}\) was seen to occur prior to the formation of the higher wavenumber mode seen in acidic conditions. The lower frequency mode was assigned to a surface hydroxide (Zhang et al. 1993).

2.6.2. Thiolate Monolayers

Studies of adsorbed thiols on gold are numerous (Chen and Li 2006) and lay outside the scope of this work. A recent review of the characterisation of thiolate-based monolayers by vibrational spectroscopy was reported (Kudelski 2005). In this review, metal-sulfide modes were assigned within a range of 200 – 360 cm\(^{-1}\).

2.6.3. Sulfur on Gold

Electrochemical studies of S\(^{\text{II}}\) oxidation on gold in acidic and basic electrolytes were complemented by real-time surface-enhanced Raman studies (Gao et al. 1992a). The authors noted a small reversible anodic peak at underpotentials to the oxidation of
sulfide to polysulfide and bulk S$_8$, and attributed this prewave to a
deprotonation / protonation reaction involving a specifically adsorbed hydrosulfide ion.
SERS features accompanying underpotential deposition included the appearance of
broad bands at $\sim$270 cm$^{-1}$ and $\sim$310 cm$^{-1}$, which were attributed to $\nu_{\text{Au-SH}}$ and $\nu_{\text{Au-S}}$
bands, respectively, but the authors did not report spectra from the region in which the
corresponding $\nu_{\text{S-H}}$ bands would be expected.

Beyond the prewave, at $-0.4$ V vs. SCE, just prior to the commencement of the main
oxidation peak, a broad $\nu_{\text{S-S}}$ stretching band appeared at $\sim$ 450 cm$^{-1}$, with the higher
wavenumber $\nu_{\text{Au-S}}$ band at $\sim$305 cm$^{-1}$ retained in the $4 \times 10^{-3}$ mol dm$^{-3}$ Na$_2$S solution at
pH 12 (Gao et al. 1992a). As the potential was further increased, the 450 cm$^{-1}$ band
sharpened and shifted upwards by $\sim$10 cm$^{-1}$, concurrent with the development of a
second stretching mode at $\sim$ 470 cm$^{-1}$. This band was predominant by 150 mV vs. SCE,
accompanied by bending modes at 220 and 150 cm$^{-1}$, suggesting the formation of S$_8$.
Similar behaviour was seen in $2 \times 10^{-3}$ mol dm$^{-3}$ Na$_2$S at pH 2, with the exception of
development of the 470 cm$^{-1}$ band. In the acid case, the band at 450 cm$^{-1}$ became
sharper at higher potentials and only traces of bending modes were observed.

The results of Gao et al. bear remarkable similarity to the findings of Quijada et al.,
from electrochemical SERS studies of SO$_2$ reduction of on gold under acid conditions
(Quijada et al. 2000). A series of spectra from this study is presented in Figure 2-22.
Figure 2-22: SERS spectra of high coverage multilayer sulfur adsorbed on Au from SO$_2$ in HClO$_4$, acquired during voltammetric cycle from 500 to –200 mV vs. RHE at 5 mVs$^{-1}$ (Quijada et al. 2000).
An early study of electro-oxidation of $10^{-3}$ mol dm$^{-3}$ $(\text{NH}_3)_2\text{S}$ in 1.0 mol dm$^{-3}$ NaOH at 700 mV vs. RHE (Baltruschat et al. 1988) assigned a stretching mode at 474 cm$^{-1}$ and bending modes at 220 and 150 cm$^{-1}$ to adsorbed polysulfides with $n = 2 – 3$. They proposed that the 220 cm$^{-1}$ mode may be due to Au-S-S bending and the 150 cm$^{-1}$ mode to Au-S stretching. These assignments are not in agreement with other authors and appear to be due to the formation of S$_8$.

### 2.6.4. Thiosulfate

Studies of SERS of thiosulfate on silver substrates have been reported in the literature (Doering and Nie 2002; Gonnison et al. 1998; Rintoul et al. 1997) with a potential-dependent study of the adsorption of thiosulfate on silver showing strong SERS spectra and a clear chemisorption / physisorption threshold of $-200$ mV for 5 x $10^{-3}$ mol dm$^{-3}$ thiosulfate (Gonnison et al. 1998). SERS studies of thiosulfate on gold in the current literature have largely arisen from work undertaken for this thesis (Jeffrey et al. 2005; Watling et al. 2006; Woods et al. 2005; Woods et al. 2006).

### 2.6.5. Ammonia

Potential-dependent SERS studies of the adsorption of ammonia on gold and palladium electrodes have been reported (de Vooys et al. 2001). The authors found a mode at 365 cm$^{-1}$, consistent with a metal-ammonium stretching vibration, to appear at 200 mV vs. RHE. The band was seen to shift to 385 cm$^{-1}$ as the potential was stepped to 800 mV. The vibrational mode was not retained on transfer to an ammonia free solution indicating a relatively weak ammonia-gold interaction (de Vooys et al. 2001).
2.6.6. Thiourea

Various studies of SERS of thiourea have been undertaken on copper (Brown et al. 1995; Loo 1982), silver (Kim and Kim 2005; Loo 1982; Reents et al. 1998) and platinum surfaces (Zheng et al. 2005). In a study of thiourea on gold (Holze and Schomaker 1990), a broad feature at ~225 cm$^{-1}$ was attributed to a gold-sulfur stretch, $\nu_{\text{Au-S}}$. The carbon-sulfur stretch, $\nu_{\text{C-S}}$, was found to have shifted to 707 cm$^{-1}$ as compared with 732 cm$^{-1}$ for thiourea in solution, which indicates adsorption of thiourea on gold via the sulfur atom (Holze and Schomaker 1990). The NH$_2$ rocking mode, $\rho_{\text{NH}_2}$, was shifted from 1090 cm$^{-1}$ in solution to 1099 cm$^{-1}$, indicating that this mode was disturbed upon adsorption (Holze and Schomaker 1990).
3. EXPERIMENTAL
3.1. PREAMBLE

Simultaneous surface-enhanced Raman spectroscopy and electrochemistry were the primary *in situ* techniques used to identify vibrational characteristics and electrochemical processes of surface adsorbates on gold in thiosulfate and sulfide media. These *in situ* studies were complemented by *ex situ* techniques including ATR-FTIR, XPS, XRD, SEM and EDX; and by kinetic studies using AAS in order to determine the gold loss from the electrode over time. Electrochemical techniques were used to quantify adsorbate coverage.

The morphology of the gold SERS substrate was examined by SEM, with XRD used to determine the crystalline orientation of the SERS surface. XPS was used to determine the composition of the substrate before and after roughening; and, along with ATR-FTIR, to examine polished electrodes after leaching in ammoniacal copper(II) sodium thiosulfate solution, for residual adsorbates.

Kinetic studies of gold leached using ammoniacal copper(II) sodium and ammonium thiosulfate solutions were undertaken using rotated disk electrodes. Atomic absorption spectroscopy was used to determine the solution concentration of gold during the leaching process.
3.2. REAGENTS

3.2.1. Commercial Reagents

All commercial reagents were of AR grade unless otherwise stated. Table 3-1 presents a list of the reagents used in this study.

Table 3-1. List of reagents

<table>
<thead>
<tr>
<th>reagent</th>
<th>formula</th>
<th>manufacturer</th>
<th>grade</th>
</tr>
</thead>
<tbody>
<tr>
<td>ammonia solution</td>
<td>NH₃/NH₄OH</td>
<td>Pronalys</td>
<td>AR</td>
</tr>
<tr>
<td>ammonium persulfate</td>
<td>(NH₄)₂S₂O₅</td>
<td>Analar</td>
<td>AR</td>
</tr>
<tr>
<td>ammonium thiosulfate anhydrous</td>
<td>(NH₄)₂S₂O₃</td>
<td>Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>cupric sulfate pentahydrate</td>
<td>CuSO₄·5H₂O</td>
<td>Vipul</td>
<td>AR</td>
</tr>
<tr>
<td>gold</td>
<td>Au</td>
<td>Johnson Matthey</td>
<td>99.99%</td>
</tr>
<tr>
<td>gold sodium thiosulfate dihydrate</td>
<td>Na₃Au(S₂O₃)₂·2H₂O</td>
<td>Alfa Aesar</td>
<td>99.9%</td>
</tr>
<tr>
<td>hydrochloric acid</td>
<td>HCl</td>
<td>Univar</td>
<td>AR</td>
</tr>
<tr>
<td>nitric acid</td>
<td>HNO₃</td>
<td>BDH</td>
<td>AR</td>
</tr>
<tr>
<td>potassium chloride</td>
<td>KCl</td>
<td>Chem Supply</td>
<td>AR</td>
</tr>
<tr>
<td>quinhydrone</td>
<td>C₆H₆O₂·C₆H₄O₂</td>
<td>Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>sodium carbonate</td>
<td>Na₂CO₃</td>
<td>BDH</td>
<td>AR</td>
</tr>
<tr>
<td>sodium dithionate hydrous</td>
<td>Na₂S₂O₃ + H₂O</td>
<td>BDH</td>
<td>LR</td>
</tr>
<tr>
<td>sodium hydrogen carbonate</td>
<td>NaHCO₃</td>
<td>Univar</td>
<td>AR</td>
</tr>
<tr>
<td>sodium hydroxide</td>
<td>NaOH</td>
<td>M&amp;B</td>
<td>AR</td>
</tr>
<tr>
<td>sodium metabisulfite</td>
<td>Na₃S₂O₅</td>
<td>Univar</td>
<td>AR</td>
</tr>
<tr>
<td>sodium sulfate anhydrous</td>
<td>Na₂SO₄</td>
<td>Univar</td>
<td>AR</td>
</tr>
<tr>
<td>sodium sulfite anhydrous</td>
<td>Na₂S</td>
<td>Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>sodium sulfite anhydrous</td>
<td>Na₂SO₃</td>
<td>Analar</td>
<td>AR</td>
</tr>
<tr>
<td>sodium tetraborate decahydrate</td>
<td>Na₂B₄O₇·10H₂O</td>
<td>Sigma Aldrich</td>
<td>AR</td>
</tr>
<tr>
<td>sodium tetrathionate dihydrate</td>
<td>Na₂S₂O₄·2H₂O</td>
<td>Sigma</td>
<td>AR</td>
</tr>
<tr>
<td>sodium thiosulfate pentahydrate</td>
<td>Na₂S₂O₃·5H₂O</td>
<td>Chem Supply</td>
<td>AR</td>
</tr>
<tr>
<td>sulfur</td>
<td>S₈</td>
<td>Chem Supply</td>
<td>AR</td>
</tr>
<tr>
<td>sulfurous acid</td>
<td>H₂SO₄</td>
<td>Univar</td>
<td>AR</td>
</tr>
<tr>
<td>thiourea</td>
<td>CS(NH₂)₂</td>
<td>Fisons</td>
<td>AR</td>
</tr>
</tbody>
</table>

3.2.2. Synthesised Compounds

Solid gold(I) sulfide and solutions of sodium polysulfide were prepared as reference compounds for Raman investigations.

3.2.2.1. Gold(I) Sulfide

Gold(I) sulfide, Au₂S, was prepared by adding Na₃Au(S₂O₃)₂ to a solution of Na₂S in ultrapure water, filtering the resulting precipitate and washing with ultrapure water.
The solid was a dark brown colour. Though stable under 633 nm irradiation, it was seen to decompose rapidly under 442 nm irradiation leaving a residue of elemental gold.

3.2.2.2. Sodium Polysulfide

Sodium polysulfide solutions were prepared by dissolving Na$_2$S in deoxygenated water and adding S$_8$ as flowers of sulfur in the stoichiometric ratios of $^{1/8}$:1 S$_8$ to Na$_2$S and $^{2/8}$:1 S$_8$ to Na$_2$S. The solutions were boiled for ~2 min until the sulfur had dissolved. The resultant solutions exhibited a dark-red colouration.

3.2.3. Solutions

All solutions were prepared using ultrapure water from a Permutit Australia Hi-Pure Water System with a typical resistivity of 18 MΩ cm. Sulfide, thiosulfate and ammoniacal copper(II) thiosulfate solutions were prepared within 2-4 hours of use.

3.2.3.1. Ammonia Solutions

Sodium tetraborate and hydrochloric acid were used as primary and secondary standards, respectively, for standardising ammonia solutions.

3.2.3.2. Sodium Sulfide Solutions

In order to minimise the formation of solution polythionates due to the presence of oxygen, the following precautions were taken for sodium sulfide addition to both acidic and alkaline solutions. Anhydrous sodium sulfide was added directly to a supporting electrolyte that had been deaerated by N$_2$ bubbling in the spectroelectrochemical cell for at least 1 hr. The sulfide was weighed directly into a syringe body prior to insertion of the barrel, which pushed the sulfide to the end of the chamber and largely excluded air. The syringe was then attached to pre-purged tubing and the solution was drawn into the
syringe. The sulfide solution was then pumped into the cell and the syringe rinsed with solution at least 10 times in order to thoroughly disperse the sulfide into the cell. In acidic solutions purging was ceased and the cell sealed after sulfide addition to minimise H\textsubscript{2}S gas release. The solution was further mixed by physically agitating the cell. In the case of alkaline solutions nitrogen purging was continued in order to stir the solution.

3.2.3.3. Ammoniacal Copper(II) Thiosulfate Solutions

The following procedure was adopted for the preparation of ammoniacal copper(II) thiosulfate leaching solutions in order to prevent the formation of copper thiosulfate compounds. Copper(II) sulfate was added to a volumetric flask filled halfway with ultrapure water. Ammonia was then added to stabilise the copper(II) as a tetra-ammine complex prior to addition of solid sodium or ammonium thiosulfate. The solution was then adjusted to volume with ultrapure water. To minimise loss of ammonia, leaching solutions were oxygenated prior to use by vigorous shaking for 2 min in a closed oversized container with an air volume four times that of the solution volume.

3.2.3.4. pH of Thiosulfate Solutions

The 0.1 mol dm\textsuperscript{-3} sodium thiosulfate solutions used showed a neutral pH, with the ammonium thiosulfate solutions of same concentration slightly more acidic with a pH of 6. With the addition of 0.4 mol dm\textsuperscript{-3} ammonia, the pH of the sodium and ammonium thiosulfate solutions became 11.4 and 9.8, respectively. The addition of 0.01 mol dm\textsuperscript{-3} CuSO\textsubscript{4} to both the ammoniacal sodium and ammonium thiosulfate solution did not result in a change in pH.
3.3. ELECTROCHEMISTRY

Electrochemical experiments were conducted in a specially designed borosilicate electrochemical cell with an optically flat transparent window to enable Raman analysis.

3.3.1. Spectroelectrochemical Cell

The cell was cylindrical, 120 mm long and 35 mm diameter, with a solution volume of 70 ml. A photograph of the spectroelectrochemical cell is presented in Figure 3-1. The cell features four B10 inlet ports and one B19 port close to the window. Two gas ports of 3 mm OD and 1.5 mm ID were located in two of the B10 inlets. A syringe was fitted to a B10 inlet for addition of sodium sulfide. Laboratory glassware and glass components of the electrochemical cell were cleaned in 7 % HNO₃ (Aristar) for 48 hrs and rinsed repeatedly with ultrapure water.

![Figure 3-1: Spectroelectrochemical cell. A) gold working electrode, B) Ag/AgCl reference, C) Pt auxiliary, D) solution purge inlet, E) over solution purge inlet, F) purge outlet, G) syringe for reagent addition, H) spectrometer objective, I) gold flag under 633 nm irradiation.](image-url)
3.3.1.1. Nitrogen Purging

A nitrogen purge was applied, when required, in order to reduce the oxygen concentration in the cell. Deaeration was achieved by bubbling high purity nitrogen (Linde, 4.0) through a modified pipette inserted into a B10 feed-through fitting, positioned close to the centre of the cell, for at least 30 min prior to conducting experiments. A positive nitrogen pressure was maintained over the cell during the measurement phase in quiescent solutions. This was achieved by use of a second gas inlet, which allowed gas to flow above the solution surface.

3.3.1.2. Air Bubbling

In experiments where air bubbling was necessary, the house vacuum was applied to a gas port. Air was then drawn into the solution through an open pipette inserted through a B10 feed-through, with all other inlets sealed.

3.3.1.3. Oxygen Enrichment

Oxygen enrichment was undertaken by bubbling instrument grade oxygen (BOC) through the electrolyte solution in the cell.

3.3.1.4. Argon Purging

Rotating disk electrode studies undertaken at Monash University utilised an argon purge (99.999% Linde) to purge solution oxygen.

3.3.2. Electrodes

A three-electrode electrochemical configuration was used, consisting of a gold working electrode, an Ag/AgCl reference electrode and a platinum wire counter electrode. The cell was assembled with reference and counter electrodes in place and the
electrolyte was deaerated within the cell for at least 30 min prior to immersion of the
gold electrode.

3.3.2.1. Gold Working Electrodes

Fine gold (Johnson Matthey 99.99 %) working electrodes consisted of a rectangular
gold flag with an exposed area of ~2 cm². The electrodes were formed by beating a
gold bead and trimming to shape after melting to attach a fine gold braid made from
interwoven strands of 0.5 mm diameter gold wire (Johnson Matthey, 99.99%).

Fresh surfaces for each experiment were generated by grinding on 15 μm grit size
P1200 SiC paper, sonicating in ultrapure water and then heating at 450 °C in a furnace
for at least 30 min to remove any adsorbed species from the surface. After removal
from the furnace, the electrode was quenched in ultrapure water and rinsed repeatedly
prior to SERS preparation.

The gold flag electrode was angled at ~20° from vertical to enable the bottom electrode
edge to contact the glass window, allowing a distance gradient between the glass
window and the electrode surface. The incident radiation was applied normal to the
glass window.

3.3.2.2. Ag/AgCl reference electrodes

A Cypress Systems EE008 Ag/AgCl/3.0 mol dm⁻³ KCl electrode was used as a primary
reference. Secondary Ag/AgCl reference electrodes were prepared by growing AgCl on
an Ag wire from a 1.0 mol dm⁻³ KCl acidified to pH 1 with HCl. For secondary
references, AgCl-plated wire was immersed in 3.0 mol dm⁻³ KCl solution in a junction
comprising a B10 feed-through with a Teflon tube and Vycor frit (PAR G0100).
These electrodes were used for oxidation-reduction cycling and for solutions which were not harmful to the Ag/AgCl reference electrode (Rogers 2006). All reference electrodes were stored in 3.0 mol dm$^{-3}$ KCl solutions in sealed containers when not in use.

Cypress electrodes were used with protection of a double junction for sulfide and ammoniacal thiosulfate solutions, which have the potential to damage Ag/AgCl reference electrodes (Rogers 2006). The Cypress electrode was sealed in a junction comprising a B10 feed-through with a Teflon tube and Vycor frit (PAR G0100), similar to that used for preparation of the reference electrode. The double junction was filled with a supporting electrolyte, commonly sodium sulfate solution, of similar ionic strength to the solution under investigation. Reference electrodes were located within 2 cm of the gold working electrode.

The response of the reference electrodes was regularly checked against the potential of a platinum electrode in saturated quinhydrone at pH 7 (Seto 1997). The reaction temperature was 22°C, resulting in an Ag/AgCl reference potential of 0.210 V on the standard hydrogen electrode (SHE) scale (Galster 1991). Potentials have been reported in the SHE scale unless otherwise specified.

### 3.3.2.3. Pt counter electrode

The Pt counter electrode was constructed from a 1 mm diameter pure platinum wire (Johnson Matthey, 99.998%) sealed into a B10 feed-through. The electrode was located at the rear of the cell, approximately 10 cm from the working electrode, and the surface area exposed to the solution was ~1 cm$^2$. Similarly to the reference, the counter electrode was also isolated from reactive solutions such as sulfide and thiosulfate to
avoid unwanted reactions. The counter electrode was sealed in a fritted glass chamber containing a supporting electrolyte of similar ionic strength, commonly sodium sulfate solution. The electrode was stored in 7% HNO₃ when not in use.

3.3.2.4. Potential Control

Potential control of the working electrode in the spectroelectrochemical cell was established using an ADInstruments potentiostat controlled by a Maclab/4e analogue-digital converter interfaced to a PC running ADInstruments EChem software. The potential applied between the reference and working electrodes was monitored by a digital voltmeter to observe any deviations from the value of the potential applied by the potentiostat.

3.3.3. Rotating Disk Electrochemistry

Rotating disk electrode (RDE) studies of the voltametric behaviour of smooth and oxidation-reduction cycled gold surfaces were undertaken at Monash University in the laboratory of Dr. Matthew Jeffrey. The cell comprised a custom-made internal glass section of 100 ml volume, housed within an external glass section, which included a water jacket. The cell contained five ports, three of which were used for the working electrode, the counter electrode and a gas line, leaving two available for additions or other measurements. A threaded port for a Luggin capillary was fitted beneath the cell.

The working electrode was a gold disk of 6 mm diameter recessed in Teflon and rotated at 300 rpm using Pine MSRX rotator. The electrode was polished with β-alumina for a smooth surface. Roughened surfaces were also prepared in order to compare the electrochemical characteristics of polished and oxidation-reduction cycled gold surfaces. The roughened surfaces were sanded with P1200 SiC paper prior to
oxidation-reduction cycling between 1.2 V and -0.3 V in 1.0 mol dm$^{-3}$ KCl, acidified to pH 1 with HCl. The use of a finer grade of paper, P2400 SiC, was found to destabilise the SERS surface, causing it to be easily removed under a gentle stream of ultrapure water. An electrode treated in this fashion, with a visible pattern of light and dark areas due to loss of the SERS surface, is shown in the inset of Figure 3-2.

The platinum counter electrode (Johnson Matthey, 99.998%) was isolated from the electrolyte solution in a glass tube fitted with a fine sintered glass frit. The saturated calomel (242 mV vs. SHE) reference electrode was housed in the Luggin capillary to prevent ions leaking from the reference electrode entering the working solution and to place the reference as close as possible to the centre of the rotating working electrode while minimising distortion of the solution flow. Potential measurements acquired relative to the SCE are reported on the SHE scale in this thesis. Voltammograms from rotated electrodes were recorded at 20-21°C using a PAR273 potentiostat.

Figure 3-2: Rotating disk electrochemical apparatus. Electrode, inset top right, shows loss of SERS surface when electrode was polished too finely prior to oxidation-reduction cycling.
3.3.4. Electrochemical Coverage Experiments

Sulfur and copper coverages were determined by integrating the anodic charge passed during oxidation of residual surface species after various treatments in thiosulfate and sulfide media. The experiments were carried out using smooth gold electrodes that were subjected to grinding, sonication and furnace treatment only. Coverage experiments using the SERS substrate were also undertaken to compare with values from the smooth electrode.

The electrodes were cycled in deaerated 0.1 mol dm$^{-3}$ H$_2$SO$_4$ until the voltammetry was reproducible, prior to rinsing and immersion in the solution of interest. They were then held at a set potential in the solution of interest for 100 s, prior to withdrawal from the cell under potential control and immersion in ultrapure water. The coated electrodes were gently and thoroughly rinsed by immersing in a vial of water then rotating at 60 rpm in a fresh beaker of ultrapure water and a final rinse in fresh water before transfer to a cell containing 0.1 mol dm$^{-3}$ H$_2$SO$_4$.

To oxidise the residual sulfur species on the surface, a triangular potential scan at 40 mV s$^{-1}$ was applied from the rest potential, which was commonly ~ 410 mV. The upper limit of the scan was 1.81 V, the lower potential limit was 210 mV. For samples from solutions containing copper, the triangular sweep was commenced at 210 mV in order to record the stripping of copper sulfide. Following the triangular sweep for copper and / or sulfur determination, the charge due to the reduction of a monolayer of oxide was determined. The gold electrode was held at 1.81 V for 100 s, and then a negative-going scan was applied at 40 mV s$^{-1}$, ending at 210 mV.
3.4. **RAMAN SPECTROSCOPY**

Raman spectra for this thesis were acquired on two systems, a Renishaw System 100 Process Analyser and a Renishaw System RM2000 Research Microscope. The Renishaw system 100 was the primary spectrometer used for the studies in this thesis and was used for collecting all *in situ* electrochemical and SERS spectra and solution samples as well as for some solid samples. The Renishaw system RM2000 was used to examine some solid samples.

### 3.4.1.1. Renishaw System 100 Process Analyser

The Renishaw System 100 Process Analyser used 632.8 nm excitation from a Renishaw RL633 HeNe laser, delivered horizontally to the sample via a multimode optical fibre. The light was focused through an ultra-long working distance x 20 Olympus LMP Plan Fl lens with a numeric aperture of 0.4 and focal length 1.0 cm to a measured spot size of 50 μm. Full power recorded at the sample was 6 mW, with reduced power settings of 10% and 1% used when required.

Raman scattered radiation was collected at 180° geometry through the same lens used for laser delivery. The Rayleigh peak of the collected light was removed using a holographic notch filter in early experiments and an edge filter in later experiments after the notch filter was replaced due to degradation. The Raman shifted signal was dispersed by a 1800 line mm⁻¹ single pass grating and detected using a Peltier-cooled CCD detector with spectral resolution of 2 cm⁻¹. The spectrometer was referenced daily to the 520 cm⁻¹ lattice vibration of silicon and calibrated using an internal neon line source. SERS spectra were generally accumulated in static mode, with scans centred at 670 cm⁻¹ to allow the acquisition of spectra in the range of 50 – 1200 cm⁻¹, with the
lower wavenumber limit dependent on the efficacy of the holographic notch or edge filter at the time of recording.

3.4.1.2. Renishaw system RM2000 Research Microscope

The Renishaw system RM2000 microRaman spectrometer used 441.6 nm excitation from an 80 mW Kimmon HeCd laser, or 514 nm excitation from a 15 mW Spectra Physics model 163C Argon ion laser, delivered vertically to the sample through the objective of a Leica LMDM microscope. The light was focused through a x50 Leica N Plan lens with a numeric aperture of 0.75.

Raman scattered radiation was collected at 180° geometry through the same lens used for laser delivery. The Raman-shifted signal was Rayleigh-filtered using holographic notch filters and dispersed by a 2400 line mm⁻¹ single pass grating. The signal was detected using a Peltier-cooled CCD detector with spectral resolution of 1 cm⁻¹. The spectrometer was referenced daily to the 520 cm⁻¹ lattice vibration of silicon and calibrated using a neon source.

3.4.2. Conventional Raman spectroscopy

Both solids and solutions were examined using conventional Raman scattering to obtain standard Raman spectra of compounds without SERS enhancement.

3.4.2.1. Solids

Spectra of solid samples were acquired by directly focusing the beam on the solid, which was either placed directly on a glass slide or packed into a capillary tube. The focus was monitored by CCD camera and the spot size for acquisition was 50 μm.
Three summed accumulations of 10 s exposures were adequate for medium to strong Raman scatterers.

3.4.2.2. Solutions

Solution spectra were obtained by recording from the solution held in a glass vial. The solutions were typically 1.0 mol dm$^{-3}$ with saturated solutions used if weak Raman scattering was observed. Three to ten accumulations of 10 s exposures were generally sufficient to achieve an adequate signal to noise ratio. Solutions within the spectroelectrochemical cell were examined simply by moving the cell sideways using the manual x,y,z stage controller to shift the laser spot from the electrode to the surrounding solution while maintaining the same plane of focus.

3.4.3. Surface-Enhanced Raman Spectroscopy

The experiments undertaken for this thesis required observation of both dissolution and adsorption processes by SERS. In the case of dissolution studies, an extremely robust electrode is required to withstand exposure to dissolution processes while maintaining SERS activity. In order to meet this criterion, a more concentrated 1.0 mol dm$^{-3}$ KCl electrolyte was used to allow greater dissolution of gold and therefore a higher concentration of tetrachloroaurate dissolution product in the electrical interface. The electrolyte was acidified to prevent passivation by the surface oxide, Au$_2$O$_3$.

3.4.3.1. Substrate Activation

The SERS electrode was freshly prepared for each experiment. Prior to activation, the electrodes were abraded on P1200 SiC paper. After abrasion and sonication in ultrapure water, the electrode was placed in a furnace for at least 30 min prior to quenching and storage in ultrapure water prior to activation.
The gold electrode was activated external to the electrochemical cell by applying oxidation-reduction cycles in 1.0 mol dm$^{-3}$ KCl solution, acidified with HCl to pH 1, in equilibrium with air. A three-electrode system was used, as described for electrochemical measurements. The ORC was carried out by automatically applying 0.5 s pulses for 5 min between the same potentials and ending at the lower value. The potentials were applied using a Pine Instruments model RDE4 potentiostat operated in single channel mode, controlled by a custom-designed frequency generator designed and built by the Griffith University Electronics Workshop. Figure 3-3 shows the waveform generated by the automatic ORC generator.

![Waveform generated by the automated ORC frequency generator.](image)

The potential difference between the working and reference electrodes was monitored using a digital voltmeter. The frequency generator featured a duty cycle in which the deposition step was longer than the dissolution step to minimise loss of gold by diffusion of tetrachloroaurate from the electrochemical interface. The cycle ended on
the lower potential. This was found to displace chloride from the Au surface prior to rapid removal of the electrode. The electrode showed a bronze colouration and a hydrophilic surface after activation and was rinsed and stored in ultrapure water following activation for ~10 min prior to introduction to the cell.

3.4.3.2. Voltammetric SERS

This technique involved the collection of SERS spectra during the acquisition of a voltammetric scan. Spectra were collected for 5–10 s during potential scans, with a rest time of 1-2 s between scans allowing an acquisition range of 20-50 mV per scan. The number of scans acquired over a potential ramp ranged from 50-150, with the initial scan commenced while the electrode was held at the lower potential limit.

3.4.3.3. Potentiostatic SERS

Spectra were recorded as a function of time from electrodes held at constant potential in various solutions. These scans were able to be collected for longer acquisition times than those acquired during voltammetry. Typical collections were 10 co-added acquisitions of 10 s exposures, giving a total collection time of 100 s. Due to the longer collection times, Raman spectra acquired at held potentials had a superior signal to noise ratio than those acquired during voltammetric excursions.

3.4.3.4. Actively Leaching Surfaces

The leaching of the gold SERS surface presented a challenge for the collection of SERS data over time, as the activity of the SERS surface decreased with the dissolution of the nanostructured surface. Spectra obtained from gold SERS electrodes during leaching were recorded at the mixed potential in quiescent leach solution in equilibrium with air unless otherwise specified. It was found that the SERS signal decreased significantly
after 15 min of active leaching; therefore this was considered the maximum time for SERS interrogation in these systems. SERS spectra were acquired as 10 co-added acquisitions of 10 s exposures, giving a total collection time of 100 s.

3.4.4. Laser Degradation

The possibility of laser degradation of the sample during analysis of sulfur species is of concern. Indicators of laser damage commonly include a visible blackening of the sample after analysis as observed under optical microscopy, changes in band positions and intensity during the period of observation and visible movement of the focused laser spot during interrogation due to decomposition of the surface.

If any indicators of laser damage were observed in solid samples the laser power was decreased and the spot moved to a new position to observe the response. Once a non-destructive laser power was found, the collection times were increased until a satisfactory signal was achieved. In spectroelectrochemical studies, changes in spectral characteristics after laser re-positioning were reported when observed.
3.5. **AMMONIACAL COPPER(II) THIOSULFATE LEACHING**

In addition to *in situ* leaching experiments on gold SERS electrodes, experiments were performed on abraded gold coupons for *ex situ* investigations by using XPS and ATR-FTIR, and on an abraded gold stub for kinetic studies.

3.5.1. *Ex situ* Investigations

Leaching for studies using XPS and ATR-FTIR was carried out using 5 mm x 3 mm coupons of fine gold (Johnson Matthey 99.99%) prepared by abrading on P1200 SiC paper, followed by sonication in ultrapure water. The coupons were suspended in 50 ml of ammoniacal copper(II) thiosulfate leaching solutions with ~50 cm$^2$ of solution surface exposed to air and gently agitated at ~60 rpm on an orbital shaker for 1 hr prior to gentle rinsing and evaporation in air in preparation for analysis.

3.5.2. Kinetic Studies

Kinetic studies were undertaken using a rotating cylindrical fine gold (Johnson Matthey 99.99 %) stub of 6.8 mm diameter. The surface was abraded using P1200 SiC paper prior to sonication in ultrapure water. The surface of the stub was immersed in 50 ml of ammoniacal copper(II) sodium and ammonium thiosulfate solutions in equilibrium with air, with a solution surface area of 50 cm$^2$. A Pine Instruments MSRX Rotator was used to maintain a rotation speed of 300 rpm. Samples of 5 ml volume were taken each hour for five hours, with a final sample taken after 18 hr. Gold concentrations were determined as soon as practicable after sampling using a Varian A10 Atomic Absorption Spectrophotometer. The 242.8 nm emission line of a gold lamp was used, with gold standards in the range of 2 – 20 ppm prepared from Na$_3$Au(S$_2$O$_3$)$_2$ dissolved in the relevant sodium or ammonium thiosulfate leach matrix.
3.5.3. Attenuated Total Reflectance Infrared Spectroscopy

For ATR-FTIR experiments, a 5 mm x 3 mm coupon of fine gold (Johnson Matthey 99.99%) was abraded with P1200 SiC paper and subjected to ammoniacal copper(II) sodium thiosulfate leaching for 1 hr prior to rinsing in ultrapure water. Spectroscopic investigations of the surface of the leached coupon were undertaken using a Thermo Nicolet Nexus 870 FTIR spectrometer with an Avatar KRS5 ATR attachment.

3.5.4. X-ray Photoelectron Spectroscopy

XPS studies on polished and SERS activated 5 mm x 3 mm fine gold coupons (Johnson Matthey 99.99%) were carried out at Latrobe University, Victoria, after leaching or potentiostatic treatment in various thiosulfate solutions. The experiments were undertaken using a Kratos Axis Ultra X-ray photoelectron spectrometer with monochromated Al K\(\alpha\) radiation operating at 150 W over an analysis area of 0.7 x 0.3 mm. Pass energies were 160 eV for wide scans and 20 eV for regions, with detection in hybrid mode. Binding energies were referenced to Au4f\(_{7/2}\) at 83.8 eV.

XPS studies were also performed at the University of Queensland on a Kratos Axis Ultra X-ray Photoelectron Spectrometer using Al K\(\alpha\) radiation operating at 150 W or 225 W. Pass energies were 160 eV for wide scans and 20 or 40 eV for detail. Samples were soaked in HNO\(_3\) prior to furnace treatment and, following removal from the furnace, were treated with NH\(_3\)/H\(_2\)O\(_2\) prior to leaching experiments to remove any copper impurities from the surface. After leaching, the samples were rinsed well with ultrapure water and air dried prior to XPS analysis.
3.5.5. Scanning Electron Microscopy

A fine gold coupon, 3 mm x 5 mm, was spot-welded to a gold wire of diameter 0.5 mm. The sample was subjected to standard oxidation/reduction cycling preparation, rinsed, stored in ultrapure water for 10 min then removed and allowed to air dry. SEM of the surface of the SERS electrode was carried out using an FEI Quanta 200 Environmental SEM at the Queensland University of Technology / Griffith University Analytical Electron Microscopy Facility (QUT/GU AEMF). The presence of impurities in the oxidation-reduction cycled surface such as contaminating metals and residual KCl was examined using EDX analysis and backscattered electron (BSE) imaging.
4. ELECTRODE CHARACTERISATION
4.1. PREAMBLE

The SERS electrode was examined using a variety of techniques in order to determine the morphology, composition and electrochemical properties of the oxidation-reduction cycled surface.

4.2. SEM AND EDX MICROPROBE ANALYSIS

Electrodes were prepared for visual characterisation by scanning electron microscopy and compositional analysis by EDX analysis. An electrode was subjected to a 5 min ORC (standard preparation) and another to excessive ORC pulsing for 15 min to maximise the electrodeposition growth (highly-dendritic). The standard electrode was rinsed and stored in water for 10 min as per normal conditions before removal to air. In order to preserve the fragile electrogenerated surface, the highly-dendritic electrode was not rinsed but instead was stored in ultrapure water for 24 hrs to gently remove solution species such as potassium and chloride from the roughened surface. Figure 4-1 shows the comparison between the visual appearance of the electrodeposits on the standard and highly-dendritic samples imaged at the same magnification.

Figure 4-1: SEM images of SERS electrodes: a) standard preparation, 5 min ORC with rinsing, b) highly-dendritic, 15 min ORC with soaking to minimise loss of surface structures.
Linear striations from the abrasive can be seen in both images, with the highly-dendritic sample showing an obvious increase in electrodeposited surface features from that of the standard preparation.

4.2.1. The Highly Dendritic Surface

EDX analysis of an area 50 x 50 $\mu m^2$ of the highly-dendritic sample showed a high purity gold surface, as shown in Figure 4-2. Residual KCl from the ORC process was not detected by this method.

![Figure 4-2: EDX analysis of the highly-dendritic oxidation-reduction cycled gold surface.](image)

Figure 4-3 shows a backscattered scanning electron micrograph, taken at medium magnification, of a characteristic cluster of dendrites on the surface of the highly-dendritic sample. Attributes of the dendrites include a fragile skeletal structure and an increase in diameter at the tips. Some dendrites display a fishbone structure while others had a more globular appearance. A scanning electron micrograph at higher magnification is shown in Figure 4-4. In this image the scale of the features can be seen to have features less than 100 nm. The globular ends and fine skeletal structure of the dendrites are clearly apparent.
Figure 4-3: Backscattered scanning electron image of the highly-dendritic gold SERS surface, magnification x8000.

Figure 4-4: Scanning electron image of the highly-dendritic gold SERS surface showing nanoscale features.
4.2.2. Standard Electrode Preparation

The electron micrograph in Figure 4-5 shows the resulting macrostructure of an electrode subjected to the normal ORC procedure as described in Section 3.4.3.1. This electrode was stored in ultrapure water for only 10 min and would therefore be more likely to have retained residual KCl from the ORC procedure. In order to establish if KCl was detectable on the surface, backscattered electron micrographs were obtained and compared with the SEM image. Figure 4-5 shows the comparison of low magnification SEM and BSE images. The darkening of regions within the dendritic forms suggested that some lighter elements were present within the dendritic clusters.

![Figure 4-5: backscattered (left) and secondary (right) electron images of the standard SERS electrode preparation.](image)

The EDX analysis shown in Figure 4-6 was performed in a spot in which was seen to be dark in backscatter mode. The analysis shows a trace of potassium and chlorine, but the signal was weak and inconclusive. It would appear that at the level of KCl present, EDX does not have sufficient surface sensitivity to provide confirmation.
The dendritic structures on the surface of a standard preparation electrode exhibit more robust features than that of the highly-dendritic sample. It is possible that finer structures were dislodged during the rinsing process. Figure 4-7 shows dendritic features from the standard preparation surface, including some fine dendrites that were retained on the surface.

Figure 4-7: Scanning electron images of standard oxidation-reduction cycled gold surface showing nanoscale features. Left image magnification x20,000, right image x40,000.
4.3. **Voltammetric Characterisation**

A comparison of the voltammetric response of oxide formation on polished and oxidation-reduction cycled electrodes is shown in Figure 4-8. The voltammogram represents the first cycle in degassed 0.1 mol dm$^{-3}$ sulfuric acid at a scan rate of 40 mVs$^{-1}$, commencing from 0.5 V in the positive direction.

![Figure 4-8: Cyclic voltammograms comparing the formation of gold oxide on a polished gold (black) and oxidation-reduction cycled gold electrode (red) in 0.1 M H$_2$SO$_4$, scan rate 40 mVs$^{-1}$. Note the scale of the oxidation-reduction cycled electrode has been reduced by $1/3$ to compare with that of the polished electrode.](image)

Both electrodes show a peak representative of the formation of a passivating oxide at 1.45 V, with the polished electrode showing a more pronounced oxidation prewave. It is possible that this is indicative of a difference in crystallinity or composition. The reduction peak of the oxidation-reduction cycled electrode occurs at a lower potential than that of the polished electrode. The reduction current observed in the oxidation-reduction cycled electrode below 800 mV may be attributed to oxygen entrapment within the dendritic surface. The increase in surface area of the roughened electrode was reflected in a current approximately three times that of the polished.
4.4. **X-ray Photoelectron Spectroscopy**

Both polished and oxidation-reduction cycled electrodes were prepared for XPS analysis. The electrodes were subjected to the standard P1200 SiC grinding, sonication and furnace treatment at 450 °C. Oxidation-reduction cycled electrodes were prepared by the method described in Section 3.4.3.1. Polished electrodes were finished to a mirror surface using α and β alumina on a Struers DP nap with sonication in ultrapure water between alumina grades. Electrodes were thoroughly rinsed in ultrapure water to remove soluble impurities, with polished electrodes subjected to further sonication to remove residual alumina.

4.4.1. **Polished Gold Electrode**

Figure 4-9 shows the survey scan acquired from the polished gold surface. The scan shows a gold spectrum with impurities due to copper, silicon, carbon and oxygen.

![XPS survey scan of polished gold surface](image)

**Figure 4-9: XPS survey scan of polished gold surface**
Detail scans were acquired in order to quantify the gold, copper, carbon and oxygen present. The presence of copper indicates an impurity within the fine gold that may have migrated to the grain boundaries and surface during treatment in the oven. The presence of silicon indicates residual SiC particles may have lodged in the gold surface from the coarse grinding stage. Detection of traces of aluminium by this method is not reliable due to the close proximity of the 2s and 2p photoelectron peaks, at 119 and 74 eV respectively, to the Au 5s at 110 eV and 5p at 75 eV (Briggs and Seah 1990). The presence of alumina on the surface was not detected.

The results of quantification for gold, copper, carbon and oxygen are presented in Table 4-1. The peaks were fitted to detailed scans using a Gaussian-Lorenzian lineshape and a Shirley background. Quantification of the copper peak is considered to give an approximate value due to poor signal to noise ratio, approaching the limit of detection of the instrument. It can be seen from Table 4-1 that the polished electrode had a large amount of carbon and oxide contamination, which was likely to have been acquired during the polishing stage.

<table>
<thead>
<tr>
<th>BE (eV)</th>
<th>FWHM (eV)</th>
<th>Raw Area (CPS)</th>
<th>Relative Sensitivity Factor (RSF)</th>
<th>Atom%</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu 2p₃/2</td>
<td>933.0</td>
<td>3.395</td>
<td>32505.0</td>
<td>5.321</td>
<td>0.6</td>
</tr>
<tr>
<td>O 1s</td>
<td>532.0</td>
<td>3.438</td>
<td>150720.0</td>
<td>0.780</td>
<td>16.7</td>
</tr>
<tr>
<td>C 1s</td>
<td>285.0</td>
<td>3.133</td>
<td>185685.0</td>
<td>0.278</td>
<td>65.3</td>
</tr>
<tr>
<td>Au 4f 7/2</td>
<td>85.0</td>
<td>6.292</td>
<td>863037.5</td>
<td>6.250</td>
<td>17.4</td>
</tr>
</tbody>
</table>

**4.4.2. Oxidation-Reduction Cycled Gold Electrode**

The electrode subjected to oxidation-reduction cycling showed an absence of copper and silicon impurities. Carbon and oxygen are evident but their concentration was greatly reduced compared with that of the polished sample. The quantification of gold,
carbon and oxygen is presented as Table 4-2. The peaks were fitted to detailed scans using a Gaussian-Lorenzian lineshape and a linear background. Quantification of the oxygen peak is considered to be an approximate value due to poor signal to noise ratio, approaching the limit of detection of the instrument.

Table 4-2: XPS Quantification of an oxidation-reduction cycled gold electrode.

<table>
<thead>
<tr>
<th></th>
<th>BE (eV)</th>
<th>FWHM (eV)</th>
<th>Raw Area (CPS)</th>
<th>RSF</th>
<th>Atom%</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>532.0</td>
<td>3.284</td>
<td>21035.0</td>
<td>0.780</td>
<td>6.8</td>
<td>0.9</td>
</tr>
<tr>
<td>C 1s</td>
<td>285.0</td>
<td>3.196</td>
<td>33950.0</td>
<td>0.278</td>
<td>34.7</td>
<td>3.5</td>
</tr>
<tr>
<td>Au 4f (7/2)</td>
<td>84.0</td>
<td>3.044</td>
<td>995630.0</td>
<td>6.250</td>
<td>58.5</td>
<td>95.6</td>
</tr>
</tbody>
</table>

A trace of sulfur was noted in the XPS scan as small peaks due to S 2s and 2p\(_{3/2}\) at 229 and 166 eV respectively. As this sample was not subjected to any sulfide or sulfoxyl anion in solution, it is thought that this may be attributed to adsorption of SO\(_2\) produced within the laboratory environment.

![XPS survey scan of oxidation-reduction cycled gold surface](image)

**Figure 4-10: XPS survey scan of oxidation-reduction cycled gold surface**

It can be seen from the comparative data that the oxidation-reduction cycled sample surface exhibited substantially higher purity than the polished sample, indicating that
the dissolution / electrodeposition process reduces inherent impurities within gold itself, minimises interference from particulate inclusions such as SiC particles and reduces contamination by carbonaceous matter.

The surface area of the oxidation-reduction cycled electrode was shown in Figure 4-8 to be greater than that of the polished electrode, due to the higher currents seen during voltammetry Figure 4-8. The higher surface area of the oxidation-reduction cycled electrode appeared more prone to adsorption of atmospheric contaminants than the polished electrode. When used for electrochemical experiments, the electrode is transferred wet from the ORC solution, rinsed with DDI water and stored in DDI water until immersion in solution, minimising the opportunity for atmospheric contamination.
4.5. X-ray Diffraction

The dendritic surface of the SERS electrode was removed by sonication, rinsed thoroughly with ultrapure water and analysed by XRD using a Philips PW1050 with a cobalt source. Figure 4-11 presents the XRD pattern. The dendritic surface structures showed evidence of polycrystalline orientation with Au(111) predominant at 44.6° and a smaller peak due to Au(200) at 52.0°. Peaks due to 220 and 311 crystal faces were not observable using cobalt radiation as they were beyond the 2θ end point of the scan. The sample was prepared as an unknown and may have undergone some loss of structure during preparation.

Figure 4-11: XRD pattern of gold dendrite fragments from an oxidation-reduction cycled gold electrode using a cobalt source.
5. ROTATING DISK ELECTROCHEMISTRY
5.1. PREAMBLE

A rotating disk electrode has been used to determine the electrochemistry of gold in thiosulfate systems. The advantages of employing the RDE configuration are that the hydrodynamics of the rotating electrode system are well known and easily controlled. There is a continuous supply of reactants to the surface; therefore a limiting current plateau is seen rather than a current peak if the process is not inhibited. Reaction intermediates are rapidly removed from the electrochemical interface, which simplifies interpretation of the electrochemical data by allowing the reactions of solution species to predominate.

Rough surfaces interfere with RDE operation by inducing turbulent flow at lower rotation speeds and optimal results are obtained by using a polished electrode. SEM studies of the oxidation-reduction cycled surface have shown the formation of a complex microstructure (Watling and Hope 2006). In addition to turbulent flow, this complex structure leads to variability in surface area between preparations; and the formation of a dendritic layer, facilitating entrapment of reaction intermediates and hindering exposure of fresh solution to the entire electrode surface.

Voltammetric studies of sodium and ammonium thiosulfate systems and those with additions of ammonia or thiourea are presented using data from polished rotated fine gold disk electrodes. Comparisons of the RDE voltammetry acquired from oxidation-reduction cycled and polished electrodes have been shown for selected thiosulfate solutions.
5.2. **GOLD IN THIOSULFATE SOLUTIONS**

The voltammetry of smooth and roughened gold surfaces was examined using rotated disk electrodes in sodium and ammonium thiosulfate solutions. Voltammograms were acquired at a rate of 1 mV s⁻¹ from oxidation-reduction cycled and polished gold disk electrodes rotated at 300 RPM in Argon purged solutions.

5.2.1. **Sodium Thiosulfate**

A voltammogram recorded for a rotated smooth gold electrode in a 0.1 mol dm⁻³ Na₂S₂O₃ solution is presented as Figure 5-1.

![Figure 5-1: Voltammogram of 0.1 M Na₂S₂O₃ recorded at 1 mV s⁻¹ with a gold electrode rotated at 300 RPM.](image)

A small prewave can be seen to extend to 500 mV, followed by a rapid increase in current, leading to a peak with maximum current at ~760 mV. The characteristics of the voltammogram are indicative of the inhibition of gold dissolution by a surface species formed during the gold dissolution reaction.
In a rotating electrochemical quartz crystal microbalance study of gold in 0.2 mol dm\(^{-3}\) Na\(_2\)S\(_2\)O\(_3\) solution (Chandra and Jeffrey 2004), mass loss from the electrode was seen to occur from 200 mV, indicating that gold was being oxidized to soluble gold thiosulfate above this potential. By 300 mV, a discrepancy between the observed current and the calculated current from the mass loss was noted, suggesting the commencement of an oxidation process that does not involve gold, such as the oxidation of thiosulfate to tetrathionate (Chandra and Jeffrey 2004).

5.2.1.1. Roughened and Polished RDEs

Figure 5-2 presents linear sweep voltammograms, acquired at a rate of 1 mV s\(^{-1}\), from oxidation-reduction cycled and polished gold disk electrodes rotated at 300 RPM in 0.1 mol dm\(^{-3}\) sodium thiosulfate.

![Comparison of polished and oxidation-reduction cycled gold disk electrodes rotated at 300 RPM in 0.1 M Na\(_2\)S\(_2\)O\(_3\), LSV at 1 mV s\(^{-1}\).](image)

It can be seen that both voltammograms show an oxidation peak at 740 mV, indicating a passivation of the surface. The maximum current density of the oxidation-reduction
The cycled electrode was approximately an order of magnitude higher than the polished electrode, which may be expected due to the increase in surface area from the oxidation-reduction cycling procedure. The oxidation current in both cases may include competitive oxidation reactions to the oxidation of gold to gold(I) dithiosulfate, including oxidation of thiosulfate to tetrathionate.

A pronounced prewave was observed at ~350 mV for the oxidation-reduction cycled electrode. The prewave is shown on a larger scale in Figure 5-3. The prewave commenced in the potential region in which voltammetric current has been seen to deviate from calculated current due to gold dissolution according to REQCM studies (Chandra and Jeffrey 2004).

![Figure 5-3: Comparison of polished and oxidation-reduction cycled gold disk electrodes rotated at 300 RPM in 0.1 M Na₂S₂O₃, LSV at 1 mV s⁻¹. Detail of prewave region.](image)

The nature of the prewave observed in the voltammetry of the oxidation-reduction cycled electrode is unclear. Possible contributions to the current in this region may
include effects due to turbulence and retention of oxidation products. Effects due to the crystalline orientation of the electrodeposited surface required for spectroelectrochemical studies may occur, including an increased reactivity of the tips of the dendritic SERS substrate relative to the branches.

5.2.2. Ammonium Thiosulfate

Figure 5-4 demonstrates the effect of ammonium as a counter ion on the voltammetry of a polished gold RDE in the thiosulfate system. Both sodium and ammonium thiosulfate solutions were 0.1 mol dm$^{-3}$.

![Graph showing comparison between Na$_2$S$_2$O$_3$ and (NH$_4$)$_2$S$_2$O$_3$](image)

Figure 5-4: polished gold rotated disk electrodes in 0.1 M Na$_2$S$_2$O$_3$ and 0.1 M (NH$_4$)$_2$S$_2$O$_3$ at 300 RPM, sweep rate 1 mV s$^{-1}$.

The oxidation current increased in the presence of the ammonium counter ion compared to sodium thiosulfate. The oxidation peak was seen to shift upwards to ~820 mV in the ammonium solution. The peak current in ammonium thiosulfate was ~4.6 times that observed in the sodium thiosulfate solution, demonstrating that surface passivation was greatly reduced when NH$_4^+$ cations were present in the system in place of Na$^+$ cations.
5.3. **ADDITIONS TO SODIUM THIOSULFATE SOLUTIONS**

Additions of ammonia and thiourea were made to sodium thiosulfate solutions in order to observe the effects of these additives upon the RDE voltammetry of polished and ORC roughened gold.

5.3.1. **Addition of Ammonia**

Figure 5-5 presents an RDE voltammogram obtained following in 0.1 mol dm$^{-3}$ sodium thiosulfate, 0.4 mol dm$^{-3}$ ammonia. Two peaks were observed, the first at ~ 450 mV and the second at ~740 mV. The second broader peak occurred at a similar potential and with a similar current maximum to that of the solution containing sodium thiosulfate alone. The peak at higher potential may therefore be a common reaction to both systems, while the peak at the lower potential was specific to a reaction in the system with ammonia addition and would indicate that the complex formed at this potential was more stable than the complex formed at the higher potential.

![Figure 5-5: Comparison of polished gold disk electrodes rotated at 300 RPM in 0.1 M Na$_2$S$_2$O$_3$; and 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$; scan rate 1 mV s$^{-1}$.](image_url)
5.3.2. Addition of Thiourea

Figure 5-6 shows the effect of the addition of thiourea upon the voltammetric current of gold in sodium thiosulfate solution. The current was seen to increase dramatically as compared with thiosulfate alone and with ammonia addition. A prewave was noted at ~300 mV, with a current similar in magnitude to the peak current seen in the sodium thiosulfate solution in the presence of ammonia.

Figure 5-6: polished gold disk electrodes rotated at 300 RPM in 0.1 M Na₂S₂O₃; 0.1 M Na₂S₂O₃, 0.4 M NH₃; and 0.1 M Na₂S₂O₃, 10 mM thiourea, scan rate 1 mV s⁻¹.

Figure 5-7 shows a detail of the thiourea prewave region of Figure 5-6. On comparing data from Figure 5-5 and Figure 5-7, the prewave current in the sodium thiosulfate solution containing thiourea was observed to be similar in magnitude to the current peaks previously seen in sodium thiosulfate solutions with and without ammonia.
Figure 5-7: polished gold disk electrodes rotated at 300 RPM in 0.1 M \( \text{Na}_2\text{S}_2\text{O}_3 \); 0.1 M \( \text{Na}_2\text{S}_2\text{O}_3 \), 0.4 M \( \text{NH}_3 \); and 0.1 M \( \text{Na}_2\text{S}_2\text{O}_3 \), 10 mM thiourea, scan rate 1 mV s\(^{-1}\). Detail of thiourea prewave region.

5.3.2.1. Roughened and Polished RDEs

Figure 5-8 compares oxidation-reduction cycled and polished electrodes in 0.1 mol dm\(^{-3}\) sodium thiosulfate plus 0.01 mol dm\(^{-3}\) thiourea. The prewave region shows a pronounced peak at 280 mV for the oxidation-reduction cycled electrode system.

Figure 5-8: Comparison of polished and oxidation/reduction cycled gold disk electrodes rotated at 300 RPM in 0.1 M \( \text{Na}_2\text{S}_2\text{O}_3 \), 10 mM thiourea, scan rate 1 mV s\(^{-1}\). Detail of prewave region.
5.4. **ADDITIONS TO AMMONIUM THIOSULFATE SOLUTIONS**

Additions of ammonia and thiourea were made to ammonium thiosulfate solutions in order to observe the effects of these additives upon the RDE voltammetry of gold. Peak positions, peak currents and comparative currents at 250 mV for ammonia and thiourea additions to ammonium thiosulfate solutions are listed in Table 4-1.

5.4.1. **Addition of Ammonia**

Figure 5-9 shows the RDE voltammetry of gold in a 0.1 mol dm$^{-3}$ (NH$_4$)$_2$S$_2$O$_3$, 0.4 mol dm$^{-3}$ NH$_3$ solution. The presence of ammonia causes a peak at a lower potential, $\sim$580 mV, while the ammonium thiosulfate shows a broad peak at $\sim$820 mV. The peak current was similar in both systems.

![Graph showing RDE voltammetry of gold](image)

*Figure 5-9: Comparison of polished gold disk electrodes rotated at 300 RPM in 0.1 M (NH$_4$)$_2$S$_2$O$_3$; and 0.1 M (NH$_4$)$_2$S$_2$O$_3$, 0.4 M NH$_3$. Scan rate 1 mV s$^{-1}$.)*
5.4.2. Addition of Thiourea

Linear sweep voltammograms showing the effect of thiourea on gold oxidation half-reactions in 0.2 mol dm\(^{-3}\) ammonium thiosulfate have been previously reported (Chandra and Jeffrey 2004). The authors reported the voltammetric currents specific to the gold oxidation process from calculations based on mass loss from the electrode, measured by a REQCM (Chandra and Jeffrey 2004). The authors noted a rapid rise in current above 125 mV with addition of thiourea, typical of an active dissolution process such as seen in the oxidation of copper (Choo and Jeffrey 2004) or silver (Breuer and Jeffrey 2002). In contrast to the aforementioned REQCM studies (Chandra and Jeffrey 2004), the RDE voltammetric currents in this thesis were not restricted to gold oxidation processes and include contributions from competing oxidation reactions.

Figure 5-10: Comparison of polished gold disk electrodes rotated at 300 RPM in 0.1 M (NH\(_4\))\(_2\)S\(_2\)O\(_3\); 0.1 M (NH\(_4\))\(_2\)S\(_2\)O\(_3\), 0.4 M NH\(_3\); and 0.1 M (NH\(_4\))\(_2\)S\(_2\)O\(_3\), 10 mM thiourea, 1 mV s\(^{-1}\).
Figure 5-10 shows the effect of the addition of thiourea upon the voltammetric current of gold in ammonium thiosulfate solution. As for thiourea addition to the sodium thiosulfate system, the current was seen to increase dramatically as compared with ammonium thiosulfate and ammonium thiosulfate with ammonia addition. As was the case for thiourea addition to the sodium thiosulfate solution, a prewave was also noted in the ammonium system at ~300 mV.

Figure 5-11 shows a detail of the thiourea prewave region of Figure 5-10 for comparison of current at low potentials. The prewave current in the ammonium thiosulfate solution with thiourea was similar in magnitude to that of sodium thiosulfate with thiourea, shown previously in Figure 5-7. In contrast to the sodium case, the prewave current of ammonium thiosulfate with thiourea addition was considerably less than the peak currents seen in ammonium thiosulfate solutions with and without ammonia.
5.4.2.1. Roughened and Polished RDEs

Figure 5-12 compares oxidation-reduction cycled and polished electrodes in 0.1 mol dm$^{-3}$ ammonium thiosulfate plus 0.01 mol dm$^{-3}$ thiourea. The prewave region exhibits a pronounced peak at 280 mV in the oxidation-reduction cycled electrode system, as previously observed for sodium thiosulfate with thiourea.

![Figure 5-12: Comparison of polished and oxidation-reduction cycled gold disk electrodes rotated at 300 RPM in 0.1 M (NH$_4$)$_2$S$_2$O$_3$, 10 mM thiourea, 1 mVs$^{-1}$. Detail of prewave region.](image-url)
5.4.3. Summary of RDE results

Table 5-1 shows a summary of prewave, peak potentials and currents observed during rotating disk electrochemistry of the thiosulfate solutions investigated.

The following points are noted:

- At 250 mV, a potential at which gold leaching is known to occur in thiosulfate solutions, currents in the various systems increased in the following order:

  \[
  \text{Na}_2\text{S}_2\text{O}_3 < (\text{NH}_4)_2\text{S}_2\text{O}_3 = [\text{Na}_2\text{S}_2\text{O}_3 + \text{NH}_3] < [(\text{NH}_4)_2\text{S}_2\text{O}_3 + \text{NH}_3] < [\text{Na}_2\text{S}_2\text{O}_3 + \text{Tu}] < [(\text{NH}_4)_2\text{S}_2\text{O}_3 + \text{Tu}]
  \]

- The oxidation peak potential of 820 mV in the ammonium thiosulfate system was seen to occur at 80 mV higher than the peak found in the sodium system.

- The addition of ammonia to the sodium thiosulfate system resulted in the formation of a second oxidation peak at 450 mV, with the 740 mV peak still evident. This may indicate the formation of a more stable species in the presence of ammonia.

- The addition of ammonia to the ammonium thiosulfate system resulted in the formation of an oxidation peak at 580 mV, which was 150 mV higher than that observed in sodium thiosulfate with ammonia addition.

- Ammonium and sodium thiosulfate behaved similarly with addition of thiourea, both exhibiting a prewave at 300 mV prior to a rapid rise in current representative of an active dissolution process.

- Oxidation-reduction cycled electrodes show a prewave at \(~300\) mV in all systems. This was particularly pronounced in both sodium and ammonium thiosulfate with thiourea addition, in which a well-formed peak was observed.
Table 5-1: Comparison of oxidation peak potentials and maximum currents observed in RDE voltammograms for various thiosulfate systems. First column, shows currents for each system at 250 mV, the potential at which gold is known to oxidised in thiosulfate solutions (Chandra and Jeffrey 2004). Remaining cells represent peak positions and respective current maxima for the various systems.

<table>
<thead>
<tr>
<th></th>
<th>250 mV</th>
<th>Prewave</th>
<th>Peak</th>
<th>Peak</th>
<th>Peak</th>
<th>Peak</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Current density</td>
<td>Potential mV</td>
<td>Current density</td>
<td>Potential mV</td>
<td>Current density</td>
<td>Potential mV</td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>740</td>
<td>3.65</td>
<td></td>
</tr>
<tr>
<td>+ NH$_3$</td>
<td>0.22</td>
<td>450</td>
<td>3.97</td>
<td>740</td>
<td>3.91</td>
<td></td>
</tr>
<tr>
<td>+ Thiourea</td>
<td>2.26</td>
<td>300</td>
<td>4.18</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(NH$_4$)$_2$S$_2$O$_3$</td>
<td>0.20</td>
<td>-</td>
<td>-</td>
<td>820</td>
<td>16.7</td>
<td></td>
</tr>
<tr>
<td>+ NH$_3$</td>
<td>0.74</td>
<td>580</td>
<td>17.52</td>
<td></td>
<td>* no data</td>
<td></td>
</tr>
<tr>
<td>+ Thiourea</td>
<td>3.16</td>
<td>300</td>
<td>5.22</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6. SERS SPECTROELECTROCHEMISTRY
6.1. PREAMBLE

The rotating disk electrochemistry of polished and oxidation-reduction cycled gold electrodes in thiosulfate was considered in Chapter 5. The information acquired from electrochemical data indicated that reactions take place at various potentials, but did not give information as to their specific nature. In this chapter, electrochemical data acquired from oxidation-reduction cycled gold flag SERS electrodes in quiescent or gas-stirred solutions will be augmented by vibrational data acquired concurrently from the electrode surface.

This chapter presents the results of SERS spectroelectrochemical investigations of gold in sodium and ammonium thiosulfate solutions; in thiosulfate solutions with additions of ammonia or thiourea; in cupric tetra-amine ammonium and sodium thiosulfate leaching systems; and in sulfide as a model system for the electro-adsorption of sulfur on gold.
6.2. **LSV UNDER SPECTROELECTROCHEMICAL CONDITIONS**

LSV studies of gold SERS electrodes were undertaken under the conditions that were used to acquire SERS spectroelectrochemical data, in order to compare with the electrochemistry observed under the RDE conditions.

6.2.1. **Sodium Thiosulfate**

Figure 6-1 presents a LSV acquired in a deaerated quiescent 0.1 mol dm\(^{-3}\) Na\(_2\)S\(_2\)O\(_3\) solution. The voltammograms were scanned in the positive direction at 1 mV s\(^{-1}\), starting from –190 mV and ending at 610 mV.

![Graph of current density versus potential for Na\(_2\)S\(_2\)O\(_3\) and Na\(_2\)S\(_2\)O\(_3\) + NH\(_3\) on oxidation-reduction cycled gold flag electrode, scan rate 1 mV s\(^{-1}\) from –190 mV in the positive direction. Inset, RDE voltammetry at same scan rate on polished electrode in same solutions.](image)

Figure 6-1: 0.1 M Na\(_2\)S\(_2\)O\(_3\); and 0.1 M Na\(_2\)S\(_2\)O\(_3\), 0.4 M NH\(_3\) on oxidation-reduction cycled gold flag electrode, scan rate 1 mV s\(^{-1}\) from –190 mV in the positive direction. Inset, RDE voltammetry at same scan rate on polished electrode in same solutions.
A mixed potential of 210 mV was measured in an air-saturated 0.1 mol dm$^{-3}$ \( \text{Na}_2\text{S}_2\text{O}_3 \) quiescent solution. The LSV showed that this potential was concurrent with the onset of a prewave that extended to 410 mV, prior to a rise in current. The voltammetry showed similar behaviour in this potential range to that seen in RDE studies, as observed in the inset of Figure 6-1.

### 6.2.2. Sodium Thiosulfate + Ammonia

Figure 6-1 also shows the voltammetry of a 0.4 mol dm$^{-3}$ \( \text{NH}_3 \), 0.1 mol dm$^{-3}$ \( \text{Na}_2\text{S}_2\text{O}_3 \) solution. In the presence of ammonia, the current was seen to increase more rapidly than in sodium thiosulfate alone, but not as rapidly as seen in the RDE studies presented in the inset of Figure 6-1. The well-resolved peak seen at 450 mV in the RDE study was not observed. These differences may be due to the decreased ability of solution to reach the roughened surface and entrapment of reaction products in the SERS electrode.
6.3. **RAMAN SPECTROSCOPY OF REFERENCE COMPOUNDS**

In order to identify vibrational bands in SERS spectra observed on surfaces, conventional Raman spectra of compounds and solutions relevant to thiosulfate leaching of gold and electro-oxidation of gold in sulfide solutions were recorded.

![Raman Spectra](image)

**Figure 6-2:** Solution Raman from aqueous oxy-sulfur anions 0.1 M Na$_2$S$_4$O$_6$; sat. Na$_3$Au(S$_2$O$_3$)$_2$; 1.0 M Na$_2$S$_2$O$_3$; 0.1 M Na$_2$SO$_4$; and from solid cyclo-octasulfur, α-S$_8$.

Figure 6-2 presents Raman spectra acquired from a 1.0 mol dm$^{-3}$ solution of sodium thiosulfate, Na$_2$S$_2$O$_3$; and a saturated solution of trisodium gold(I) dithiosulfate, Na$_3$Au(S$_2$O$_3$)$_2$, the product of gold dissolution in thiosulfate solutions. Spectra from 0.1 mol dm$^{-3}$ solutions of sodium tetrathionate S$_4$O$_6^{2-}$ and sodium sulfate SO$_4^{2-}$ are also included in Figure 6-2. These are both known oxidation products of sodium thiosulfate. The final spectrum in Figure 6-2 is that of solid α-S$_8$. 
The spectrum of solid sodium thiosulfate has been well characterised (Gabelica 1980; Haigh et al. 1993) and displays bands at 434 cm\(^{-1}\) and 1017 cm\(^{-1}\), assigned to \(\nu_{S-S}\) and \(\nu_{\text{sym}S-O}\), respectively. With the thiosulfate ion in solution, these bands were seen at 445 cm\(^{-1}\) and 999 cm\(^{-1}\), respectively, as shown in Figure 2-16. The solid gold thiosulfate complex, Na\(_3\)Au(S\(_2\)O\(_3\))\(_2\).2H\(_2\)O exhibits \(\nu_{S-S}\) and \(\nu_{\text{sym}S-O}\) modes at 415 cm\(^{-1}\) and 1040 cm\(^{-1}\), respectively; and, from the gold complex ion in solution, at 419 cm\(^{-1}\) and 1019 cm\(^{-1}\) (Woods et al. 2006). The observed values of \(\nu_{S-S}\) and \(\nu_{\text{sym}S-O}\) for the tetrathionate ion in solution were 387 cm\(^{-1}\) and 1040 cm\(^{-1}\), respectively. It must be noted that the \(\nu_{\text{sym}S-O}\) of tetrathionate in solution occurs at the same wavenumber as in the solid Na\(_3\)Au(S\(_2\)O\(_3\))\(_2\).2H\(_2\)O.

The sulfate ion exhibits a sharp \(\nu_{\text{sym}S-O}\) band at 983 cm\(^{-1}\) and elemental sulfur displays a \(\nu_{S-S}\) band at 471 cm\(^{-1}\). Bands corresponding to \(\delta_{S-S-S}\) bending modes of the S\(_8\) molecule occur at 216 cm\(^{-1}\) and 152 cm\(^{-1}\) (Eckert and Steudel 2003); only the former is observable in Figure 6-2.

It can be seen from Figure 6-2 that the \(\nu_{\text{sym}S-O}\) band decreases in wavenumber through the series S\(_4\)O\(_6\)\(^{2-}\) > Au(S\(_2\)O\(_3\))\(_2\)\(^{3-}\) > S\(_2\)O\(_3\)\(^{2-}\) > SO\(_4\)\(^{2-}\). These trends reflect a decrease in bond force constant and increase in bond length along the series, with the sulfate ion having the longest sulfur-oxygen bond length. The opposite trend was seen in the \(\nu_{S-S}\) band, which decreased in wavenumber through the series S\(_8\) > S\(_2\)O\(_3\)\(^{2-}\) > Au(S\(_2\)O\(_3\))\(_2\)\(^{3-}\) > S\(_4\)O\(_6\)\(^{2-}\). In this series, S\(_8\) has the shortest sulfur-sulfur bond and highest force constant. The combination of the two trends in the anions S\(_4\)O\(_6\)\(^{2-}\), Au(S\(_2\)O\(_3\))\(_2\)\(^{3-}\), S\(_2\)O\(_3\)\(^{2-}\) shows an inverse relationship between S-S and S-O bond lengths. In particular, the wavenumber shifts due to coordination of the thiosulfate ion to gold(I) may indicate a relative contraction.
of the S-O bonds and an associated lengthening of the S-S bonds (Eckert and Steudel 2003). Figure 6-3 presents a detailed spectrum of cyclo-octasulfur and a spectrum obtained from an Au$_2$S precipitate, prepared by adding a sodium sulfide solution to gold(I) dissolved in aqueous thiosulfate. Both S-S-S bending modes, $\delta_{S-S-S}$, of cyclo-octasulfur can be seen at 219 cm$^{-1}$ and 155 cm$^{-1}$. The gold sulfide spectrum displays a broad band centred at 340 cm$^{-1}$; analogous spectra have been observed for Cu$_2$O (Ivanda et al. 1997) and Ag$_2$O (Waterhouse et al. 2001), which crystallize in the same cuprite structure as Au$_2$S, with the band for these compounds being centred on 515 cm$^{-1}$ and 490 cm$^{-1}$, respectively.

![Raman spectra from gold sulfide and elemental cyclo-octasulfur](image)

**Figure 6-3: Raman spectra from gold sulfide and elemental cyclo-octasulfur (Irradiation density: 0.0031 kW cm$^{-2}$ and 0.31 kW cm$^{-2}$ respectively; 10 s x 100 accumulations and 0.2 s x 10 accumulations respectively).**

The Raman-active mode of cuprite structures involves the relative motion of the anions about a centre of symmetry of the metal atoms and is a symmetric stretching vibration (Waterhouse et al. 2001). The broad band centred at 340 cm$^{-1}$ observed for Au$_2$S can be assigned to a range of disordered gold-sulfur stretching modes, $\nu_{Au-S}$. 

143
Figure 6-4 presents the Raman spectrum acquired from a polysulfide solution prepared by mixing \( \frac{2}{8} \text{ mol S}_8 \) with 1 mol Na\(_2\)S and boiling for 2 min. No evidence of S\(_8\) was seen in this spectrum, but a band at 194 cm\(^{-1}\) and a shoulder at 240 cm\(^{-1}\) were apparent in the region in which S-S-S bending modes are known to occur. A sharp ν\(_{S-S}\) band was seen at 449 cm\(^{-1}\) with a smaller band at 485 cm\(^{-1}\). Two bending modes were seen, a sharp band at 194 cm\(^{-1}\) and a shoulder at 240 cm\(^{-1}\). These assignments are in close agreement with those reported in the literature (Janz et al. 1976b). A similar experiment, in which the stoichiometry used was \( \frac{1}{8} \text{ mol S}_8 \) to 1 mol Na\(_2\)S, was seen upon Raman examination to retain the presence of S\(_8\) and therefore was not considered characteristic of polysulfide.

![Figure 6-4: Raman spectrum of polysulfide solution prepared by dissolving Na\(_2\)S in deoxygenated water, adding S\(_8\) as flowers of sulfur in the stoichiometric ratio of \( \frac{2}{8} \text{ mol S}_8 \) to 1 mol Na\(_2\)S and boiled for about 2 min until the sulfur had dissolved (Irradiation density: 0.31 kW cm\(^{-2}\) 10 s x 10 accumulations).](image-url)
Figure 6-5 presents Raman spectra of an ammoniacal sodium thiosulfate leach solution that had been oxygen enriched for 10 min then allowed to stagnate for 40 min. The figure also presents 1.0 mol dm\(^{-3}\) solutions of the sodium salts of disulfite, S\(_2\)O\(_5\)\(^{2-}\); thiosulfate, S\(_2\)O\(_3\)\(^{2-}\); and sulfate, SO\(_4\)\(^{2-}\).

The spectrum of disulfite features a strong \(\nu_{\text{symS-O}}\) band at 1053 cm\(^{-1}\). A broader band seen in the spectrum was due to the \(\nu_{\text{symS-O}}\) of hydrogensulfite, HSO\(_3\)\(^-\), into which disulfite dissociates under equilibrium conditions (Meyer et al. 1980). In the spectrum of the artificially aged leach solution, a band due to disulfite was apparent, in addition to bands from sulfate and thiosulfate. The absence of bands due to hydrogensulfite is presumably due to solution pH of 11.4.

Figure 6-5: Solution Raman spectra of 1.0 M solutions of the sodium salts of disulfite, S\(_2\)O\(_5\)\(^{2-}\); thiosulfate, S\(_2\)O\(_3\)\(^{2-}\); sulfate, SO\(_4\)\(^{2-}\); and oxygenated 0.1 M Na\(_2\)S\(_2\)O\(_3\), 0.01 M CuSO\(_4\), 0.4 M NH\(_3\).
6.4. CONCURRENT SERS AND CYCLIC VOLTAMMETRY

Cyclic voltammograms of gold in nitrogen-purged 0.1 \text{ mol dm}^{-3} \text{ Na}_2\text{S}_2\text{O}_3; \text{ and of the same concentration of thiosulfate in the presence of 0.4 mol dm}^{-3} \text{ NH}_3, \text{ are presented in Figure 6-6.} \text{ Scans were initiated from –290 mV and scanned in the positive direction at 10 mV s}^{-1\text{ to an upper potential of }1.21 \text{ V.} \text{ The voltammetric ramp then proceeded in the negative direction to finish at the starting potential.}\

![Figure 6-6:Cyclic voltammograms of 0.1 M Na}_2\text{S}_2\text{O}_3 \text{ and 0.1 M (NH}_4\text{)}_2\text{S}_2\text{O}_3 \text{ on ORC gold flag electrodes, from –290 mV scanned in the positive direction, scan rate 10 mVs}^{-1\text{.}}\]

The voltammograms of both systems showed similar characteristics for oxidation processes. In both cases an anodic peak followed a prewave, with higher current in the case of ammonia addition, as observed in RDE studies. A difference was noted, however, for reduction peaks during scans in the negative direction. The reduction peak observed at ~ –100 mV in the thiosulfate solution was not observed in the presence of ammonia.
6.4.1. Sodium Thiosulfate

Figure 6-7 presents a series of SERS scans acquired at various potentials during the voltammetric excursion for the gold SERS electrode in deaerated 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$. The cyclic voltammogram is shown in Figure 6-6.

![Figure 6-7: SERS spectra acquired during cyclic voltammetry of Au in 0.1 M Na$_2$S$_2$O$_3$. Each scan represents data acquired during a ~70 mV voltammetric excursion, with the marked potential being the centre of the range. The lower scan was acquired at the starting potential.](image)

At the starting potential, ~290 mV, a weak, broad, symmetric $\nu_{S-S}$ band was observed at ~ 450 mV. When the sweep potential had reached 675 mV, the $\nu_{S-S}$ band was asymmetric and had shifted to ~ 460 cm$^{-1}$. The characteristic $\delta_{S_S}$ of S$_8$ at 217 cm$^{-1}$ was also seen at this potential. This band would be expected to be accompanied by the $\nu_{S-S}$ mode of S$_8$, which may be a component of the asymmetric $\nu_{S-S}$ band. At the maximum potential of 1.21 V, the spectrum of S$_8$ was well developed with the $\nu_{S-S}$ mode present at ~ 471 cm$^{-1}$ and, in the reverse scan, loss of the S$_8$ spectrum was coincident with a reduction peak at ~ −100 mV.
In order to observe the behaviour of the SERS bands over the entire voltammetric ramp, SERS data and current density observed during the forward and reverse scans have been plotted against time-based potential in Figure 6-8. The filled circles represent Raman bands characteristic of S₈, while the open circles represent ν₃₃₃₃₃₃ modes of species other than S₈. It can be seen from this figure that S₈ was formed from ~700 mV and observed until the reduction peak at ~100 mV. In the reverse direction, after the vertex potential of 1.21 V, a significant decrease in current was noted concurrent with the reappearance of lower wavenumber ν₃₃₃₃₃₃₃₃ modes. These modes appeared in the presence of S₈ and after its reduction.
6.4.2. Sodium Thiosulfate + Ammonia

Figure 6-9 presents a series of SERS scans acquired at various potentials during the voltammetric excursion of a gold SERS electrode in 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$, 0.4 mol dm$^{-3}$ NH$_3$. The cyclic voltammogram acquired during this experiment was presented in Figure 6-6.

![SERS spectra](image)

Figure 6-9: SERS spectra acquired during cyclic voltammetry of Au in 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$. Each scan represents data acquired during a ~70 mV voltammetric excursion, with the marked potential being the centre of the range. The lowest scan was acquired at the starting potential.

Similarly to the observations for thiosulfate alone, a weak, broad, symmetric $\nu_{S-S}$ band was observed at ~450 cm$^{-1}$ at the starting potential of –290 mV. The $\nu_{S-S}$ band reached a maximum intensity, became asymmetric and shifted to ~455 cm$^{-1}$ as the potential was swept to 390 mV. No evidence of S$_8$ was observed at any potential. The absence of vibrational characteristics of S$_8$ was supported by the lack of a reduction peak as seen in the system with thiosulfate alone.
Figure 6-10: Raman shift positions and current density vs. time-based potential. Dots represent SERS peak positions observed during cyclic voltammetry of Au in 0.1 M Na$_2$S$_2$O$_3$ with 0.4 M NH$_3$. Data on RHS of diagram represents current and SERS data acquired during reverse scan.

Figure 6-10 shows these Au/Na$_2$S$_2$O$_3$/NH$_3$ SERS characteristics over the entire voltammetric sweep. The open circles represent $\nu_{S-S}$ modes of a surface species other than S$_8$ and, at 450 – 455 cm$^{-1}$, of higher wavenumber than the $\nu_{S-S}$ mode of solution thiosulfate. These bands were seen to occur over the entire potential range, with the highest wavenumber band observed during the voltammetric prewave. During the forward scan, bands were observed at $\sim$330 cm$^{-1}$, at the upper limit of the region in which gold-sulfur stretching, $\nu_{Au-S}$, has been observed (Gao et al. 1992a). These bands are presented as filled circles in Figure 6-10. On the reverse scan, bands at $\sim$380 cm$^{-1}$ were observed at potentials below 0 V, occurring in the wavenumber region close to that in which $\nu_{S-S}$ modes of tetrathionate have been seen to occur (Meyer et al. 1980). These bands are represented as grey circles in Figure 5-10.
In summary, SERS spectra acquired during cyclic voltammetric scans of gold in 0.1 mol dm$^{-3}$ sodium thiosulfate at 10 mV s$^{-1}$ provided evidence of the formation of S$_8$ on the surface and its reductive removal at low potentials. When the thiosulfate solution was investigated in the presence of 0.4 mol dm$^{-3}$ NH$_3$, S$_8$ formation was not observed.
6.5. SERS MEASUREMENTS AT STEPPED POTENTIALS

The SERS behaviour of gold in 0.1 mol dm\(^{-3}\) sodium and ammonium thiosulfate solutions was further investigated while holding the gold ORC electrode at a fixed potential. After holding at each potential for 2 min, a spectrum was recorded using a 30 s accumulation. The electrode was then stepped to a higher potential and the procedure repeated.

6.5.1. Sodium Thiosulfate

Figure 6-11 presents SERS spectra from a gold electrode in air-saturated 0.1 mol dm\(^{-3}\) Na\(_2\)S\(_2\)O\(_3\) in equilibrium with air, at the mixed potential of 210 mV and after holding the electrode sequentially at the marked potentials for 2 min.

The SERS spectrum recorded at the mixed potential of 210 mV displays weak, broad bands at 445 cm\(^{-1}\) and 999 cm\(^{-1}\) that are attributed to sulfur-sulfur stretching, \(\nu_{S-S}\), and symmetric sulfur-oxygen stretching, \(\nu_{\text{symS-O}}\), respectively, of thiosulfate at the gold / solution interface. In addition, stronger bands were observed at 378 cm\(^{-1}\) and 1033 cm\(^{-1}\). These bands were in similar positions to those observed from a 0.1 mol dm\(^{-3}\) Na\(_2\)S\(_4\)O\(_6\) solution, but occur 10 cm\(^{-1}\) and 8 cm\(^{-1}\) wavenumbers lower, respectively, than the solution values of 388 cm\(^{-1}\) and 1041 cm\(^{-1}\) (Meyer et al. 1980). The bands observed at mixed potential are thus assigned to \(\nu_{S-S}\) and \(\nu_{\text{symS-O}}\), respectively, of an adsorbed tetrathionate or a tetrathionate-like species on the gold surface. An adsorbate with a c(4x\(\sqrt{3}\)) structure was observed at the OCP in STM studies in 1.0 mol dm\(^{-3}\) Na\(_2\)S\(_2\)O\(_3\) and seen to desorb at higher potentials (Lay et. al., 2003).
On the application of a potential of 350 mV to the electrode for 2 min, weak bands from $\nu_{S-S}$ and $\nu_{\text{sym}S-O}$ of thiosulfate were evident while those arising from the tetrathionate-like species were no longer apparent. At 410 mV, $\nu_{\text{sym}S-O}$ of thiosulfate was still present but barely discernable and the $\nu_{S-S}$ broadened and shifted to higher wavenumbers. The band was lower than the $\nu_{S-S}$ stretching mode at 471 cm$^{-1}$ observed for cyclo-octasulfur, $\alpha$-$S_8$, and the spectrum lacked the $\delta_{S-S}$ bending modes of $\alpha$-$S_8$ reported at 217 and 151 cm$^{-1}$ (Eckert and Steudel 2003). This would indicate that the layer was comprised of a disordered sulfur species that is not $S_8$. 

Figure 6-11: SERS spectra from gold electrode in 0.1 M Na$_2$S$_2$O$_3$ recorded at the mixed potential and after holding at the applied potential for 2 min.
As the potential was increased in 50 mV increments, the intensity of the broad $\nu_{\text{S-S}}$ band increased and shifted to higher wavenumbers, reaching a limiting value of 460 cm$^{-1}$ by 510 mV, as noted by the reference marker in Figure 6-11. Bands due to $\nu_{\text{S-S}}$ at that wavenumber that are either not accompanied by, or are accompanied by very weak bending modes, have been attributed in the literature to stretching modes of polymeric and amorphous sulfur (Eckert and Steudel 2003).

At 510 mV, concurrent with the limiting $\nu_{\text{S-S}}$ at 460 cm$^{-1}$, the first appearance of $S_8$ sulfur was indicated by a small bending mode at 217 cm$^{-1}$. The disordered sulfur layer began to convert to $S_8$ at 560 mV, as indicated by the appearance of a shoulder at 471 cm$^{-1}$; an increase in the intensity of the 217 cm$^{-1}$ band; and the appearance of a lower wavenumber bending mode at 151 cm$^{-1}$. By 610 mV, the $\nu_{\text{S-S}}$ of $S_8$ was the dominant S-S stretching mode; and above 710 mV the 460 cm$^{-1}$ band was no longer observed. The increased intensity of the 217 and 151 cm$^{-1}$ bending modes as the potential was increased from 610 mV to 810 mV provided further evidence of conversion of the disordered sulfur layer to $S_8$.

6.5.1.1. Laser Restructuring

When the potential was held at $\geq 610$ mV, moving the laser beam to another spot on the gold surface showed a different Raman spectrum. Bending modes characteristic of $S_8$ were no longer seen and a band at 460 cm$^{-1}$, similar to that found at 510 mV, became the dominant $\nu_{\text{S-S}}$. On holding in the same position, the spectrum was seen to rapidly develop the characteristic modes of $S_8$. The SERS spectra can be explained by the oxidation of thiosulfate to form a surface species that decomposes under the laser beam so that elemental sulfur becomes deposited at the illuminated spot.
6.5.1.2. Formation of Polythionates

At potentials $\geq 610$ mV, a cloud of colloid-sized particles was observed in the solution, emanating from the electrode. It is possible that long-chain polythionate species are formed in the anodic process at potentials $\geq 610$ mV; these species are known to rapidly develop into sulfur sols (Steudel 2003a). After holding the potential of the gold electrode at $\geq 610$ mV, the cell solution containing the sulfur sol was collected. No solid particles were evident after storing for a few hours. This could be due to dissolution of the polythionate as a result of dilution on mixing the cell solution.

6.5.1.3. Effect of pH

The effect of pH on the SERS of gold in thiosulfate solution was investigated. The procedure used to acquire the spectra presented in Figure 6-11 was also applied to a gold SERS electrode in 0.1 mol dm$^{-3}$ thiosulfate in borate buffer at pH 9.2 and in hydrogen carbonate / hydroxide buffer at pH 10.5. The spectra recorded were very similar to those in Figure 6-11 indicating that the solution pH did not affect either the potential of formation of the disordered sulfur layer or the potential at which it converted to S$_8$, indicating that the rate-determining step in the deposition of sulfur at this concentration does not involve H$^+$ or OH$^-$ ions.

6.5.1.4. Extended Polarisation at High Potential

Polarisation for an extended time at 710 mV in 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$ at pH 9.2 was carried out in order to identify other species formed when sulfur deposited from thiosulfate. A solution spectrum after polarisation for 70 h showed bands from sulfur and residual thiosulfate and one at 983 cm$^{-1}$ that can be assigned to sulfate.
This indicated that the oxidation of thiosulfate at 710 mV was:

\[ \text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightarrow \text{S}^0 + \text{SO}_4^{2-} + 2\text{H}^+ + 2\text{e}^- \]  \hspace{1cm} (6-1)

### 6.5.2. Sodium Thiosulfate + Ammonia

The SERS behaviour of gold during potential steps in sodium thiosulfate with the addition of ammonia was examined using the same technique as in section 6.5.1 for 0.1 mol dm\(^{-3}\) sodium thiosulfate. The experiments were undertaken to observe the effects of ammonia as an additive to the sodium thiosulfate system. Figure 6-12 presents SERS spectra from a gold electrode in an air-saturated 0.1 mol dm\(^{-3}\) Na\(_2\)S\(_2\)O\(_3\), 0.4 mol dm\(^{-3}\) NH\(_3\) solution. Spectra were acquired at the mixed potential of 80 mV and after holding the electrode sequentially at the marked potentials for 2 min.

![Figure 6-12: SERS spectra from gold electrode in 0.1 M Na\(_2\)S\(_2\)O\(_3\) with 0.4 M NH\(_3\) recorded at the mixed potential and after holding at applied potentials for 2 min.](image-url)
Little detail was seen in the SERS spectrum acquired at the mixed potential scan. The most prominent band was a broad band in the region where thiosulfate bending modes have been observed (Gabelica 1980). A broad, weak $\nu_{\text{symS-O}}$ band was noted between 1000 and 1030 cm$^{-1}$, also a barely discernable broad band in the $\nu_{\text{S-S}}$ region at $\sim$ 460 cm$^{-1}$. No spectral changes were seen with applied potential until 410 mV, when strong bands develop at 1030 and 378 cm$^{-1}$. These bands are assigned to an adsorbed tetrathionate-like species similar to that seen in Figure 6-11 for gold in 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$ solution at the mixed potential. As was observed for sodium thiosulfate at the mixed potential, the $\nu_{\text{symS-O}}$ and $\nu_{\text{S-S}}$ modes were both downshifted by $\sim$10 cm$^{-1}$ from those of solution tetrathionate.

Weaker rounded bands were seen at $\sim$925 cm$^{-1}$ and 460 cm$^{-1}$. The bands at 460 cm$^{-1}$ can be assigned to $\nu_{\text{S-S}}$ region while the band at 925 cm$^{-1}$ was not characteristic of the sulfur anions reviewed in the literature. This band can be tentatively assigned to an antisymmetric N-H bending mode, $\delta_{\text{symN-H}}$, of an adsorbed ammonia molecule. If ammonia were adsorbed on the surface, a gold-nitrogen stretching mode, $\nu_{\text{Au-N}}$, would be expected. This band has been previously observed between 385-365 cm$^{-1}$ for ammonia on gold (de Vooy et al. 2001). It is noted that this wavenumber range is coincident with the $\nu_{\text{S-S}}$ of the tetrathionate and tetrathionate-like species.

A broad band at $\sim$285 cm$^{-1}$ occurred in the region in which $\nu_{\text{Au-S}}$ modes have been noted to occur (Gao et al. 1992a). These modes were retained at 510 mV, with an increase in intensity of the band assigned to $\nu_{\text{Au-S}}$. At higher potentials the spectrum again becomes almost featureless, with a broad band due to gold oxide (Watling et al. 2005) apparent by 810 mV.
It was observed that addition of NH$_3$ to the sodium thiosulfate solution largely prevented the formation of S$_8$ deposits on the gold surface, but lead to the presence of a tetrathionate-like species and the formation of Au-S bonding. It can be argued that some evidence of adsorbed ammonia was also apparent.

### 6.5.3. Ammonium Thiosulfate

The SERS behaviour of gold during potential steps in ammonium thiosulfate was examined using the same technique as in section 6.5.1 for 0.1 mol dm$^{-3}$ sodium thiosulfate. The experiments were undertaken to observe the effects of ammonium as an alternative counter-ion to sodium. Figure 6-13 presents SERS spectra from a gold electrode in air-saturated 0.1 mol dm$^{-3}$ (NH$_4$)$_2$S$_2$O$_3$.

![Figure 6-13: SERS spectra from gold electrode in 0.1 M (NH$_4$)$_2$S$_2$O$_3$ recorded at the mixed potential and after holding at applied potentials for 2 min.](image)
Spectra were acquired at the mixed potential of 77 mV and after holding the electrode sequentially at marked potentials for 2 min. Spectra acquired at the mixed potential showed a barely-discernible weak broad band in the S-S stretching region and slight evidence of the $\nu_{\text{symS-O}}$ modes of thiosulfate. The spectral features observed for the mixed potential were unchanged until the applied potential reached 310 mV. At this potential a very weak broad band in the $\nu_{\text{Au-S}}$ region became apparent.

By 410 mV, well-developed bands were noted at 450, 380 and 320 cm$^{-1}$ and these are assigned to $\nu_{\text{S-S}}$ modes characteristic of a disordered sulfur layer; $\nu_{\text{S-S}}$ of the tetrathionate-like species; and $\nu_{\text{Au-S}}$ modes, respectively. Weak bands were also seen at 1030 cm$^{-1}$ and are assigned to the $\nu_{\text{symS-O}}$ modes of the tetrathionate-like species. The $\nu_{\text{S-S}}$ and $\nu_{\text{Au-S}}$ modes continued to grow as the potential was increased, with bending modes of the $S_8$ ring also visible by 560 mV, indicating the commencement of $S_8$ formation at this potential.

**6.5.4. Ammonium Thiosulfate + Ammonia**

The SERS behaviour of gold during potential steps in ammonium thiosulfate with ammonia was examined using the same technique as in section 6.5.1 for 0.1 mol dm$^{-3}$ sodium thiosulfate. The presence of ammonia in ammonium thiosulfate solutions results in a system similar to that of sodium thiosulfate with ammonia addition, but with a decrease in solution pH from 11.4 to 9.8.

Figure 6-14 presents SERS spectra from a gold electrode in air saturated 0.1 mol dm$^{-3}$ $(\text{NH}_4)_2\text{S}_2\text{O}_3$ solution with 0.4 mol dm$^{-3}$ NH$_3$. Spectra were acquired at the
mixed potential of 58 mV and after holding the electrode sequentially at marked potentials for 2 min.

The spectrum acquired at the mixed potential, 58 mV, exhibited weak $\nu_{\text{symS-O}}$ bands due to thiosulfate and little evidence of $\nu_{\text{S-S}}$ modes on the surface. When the potential was raised to 410 mV, tetrathionate-like bands at 1025 and 380 cm$^{-1}$ were predominant. A broad band in the $\nu_{\text{Au-S}}$ region was also noted at this potential. The tetrathionate-like bands increased in intensity at 510 mV prior to decreasing at 610 mV. At this potential the $\nu_{\text{S-S}}$ modes were seen to increase while the $\nu_{\text{Au-S}}$ bands decreased. Above this potential, the $\nu_{\text{S-S}}$ centred at 450 cm$^{-1}$ was the only significant band.
6.5.5. Summary

Of the four systems examined in this experiment, sodium thiosulfate, ammonium thiosulfate and sodium thiosulfate with ammonia show the most marked difference in surface structures.

The sodium thiosulfate system shows the tetrathionate-like species, present at the mixed potential, to disappear prior to forming S\textsubscript{8} via an intermediate with a \( v_{S-S} \) of 460 cm\(^{-1}\). In ammonium thiosulfate, little spectral detail was seen until the formation of broad \( v_{S-S} \) and \( v_{Au-S} \) bands at 410 cm\(^{-1}\), which were retained as the potential was increased. The bands in the \( v_{Au-S} \) region are similar to those observed in Au\textsubscript{2}S. It was likely therefore that the bands represent a gold-sulfide-like layer, in which bonding also occurs between the sulfur atoms.

In sodium thiosulfate with ammonia, the tetrathionate-like species was not seen until higher potentials and the spectra featured bands that may be assigned to the adsorption of ammonia. The gold-sulfide-like layer was also observed. These spectral features were seen to disappear when the potential was raised to 610 mV, with the appearance of gold oxide at higher potentials. In ammonium thiosulfate with ammonia, the spectral details were similar, but that the oxide formation was not observed. This is likely to be due to the lower pH of the ammonium system (pH 9.8 as compared with pH 11.4 in the sodium system).
6.6. **TIME-DEPENDENT SERS**

SERS spectra were recorded as a function of time from a gold electrode in the potential region in which gold dissolves in practice in thiosulfate leaching. The electrode was held at 210 mV and 310 mV in 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$ and (NH$_4$)$_2$S$_2$O$_3$ solutions and spectra were acquired at various times. Figure 6-15A and Figure 6-15B present the SERS spectra recorded 210 mV and 310 mV, respectively. These represent the potential limits between which dissolution of gold thiosulfate has been observed in REQCM studies (Chandra and Jeffrey 2004).

6.6.1. **Sodium Thiosulfate**

Figure 6-15A shows spectra acquired from 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$ at 210 mV. The spectrum recorded after 2 min shows $\nu_{S-S}$ bands at 446 cm$^{-1}$ due to thiosulfate and at 378 cm$^{-1}$ for the tetrathionate-like species.

The tetrathionate-like band diminished with time, and a band at 282 cm$^{-1}$, assigned to $\nu_{Au-S}$, was seen to develop. At longer times, this band increased in intensity and shifted to 317 cm$^{-1}$. This indicates the formation of a gold sulfide layer on the gold surface. The $\nu_{S-S}$ band was also seen to grow and shift downward in wavenumber, indicating that the formation of Au-S bonds was accompanied by the formation of S-S bonds on the surface.
Similar behaviour to that discussed above was observed at 310 mV in Figure 6-15B, but the gold-sulfide bands developed more rapidly. The $\nu_{\text{Au-S}}$ band ceased to grow after ~45 min, an observation consistent with a limiting coverage of sulfur covalently bonded to gold in the surface layer. As seen at 210 mV, a band in the $\nu_{\text{S-S}}$ region was seen to develop, but at a lower wavenumber consistent with a longer S-S bond.

### 6.6.2. Ammonium Thiosulfate

SERS spectra were also recorded at 210 mV and at 310 mV in 0.1 mol dm$^{-3}$ $(\text{NH}_4)_2\text{S}_2\text{O}_3$ solution. The results at 310 mV are presented in Figure 6-16 and it can be seen that bands indicative of gold sulfide formation occur analogous to those observed in $\text{Na}_2\text{S}_2\text{O}_3$ solution. Spectra recorded at 210 mV were also similar to those at the same potential in $\text{Na}_2\text{S}_2\text{O}_3$ solution (see Figure 6-15A).
6.6.3 Sodium Thiosulfate + Ammonia

The effect of the presence of ammonia on time-dependent SERS spectra was examined using a 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$, 0.4 mol dm$^{-3}$ NH$_3$ solution. The SERS spectrum observed at 310 mV is also presented in Figure 6-16. Again, the spectrum shows that a gold sulfide layer was formed. Similar findings were made at 210 mV. Thus, the formation of gold sulfide occurs on the electrode surface with Na$^+$ and NH$_4^+$ counterions and in the presence of NH$_3$. 

Figure 6-16: SERS spectra recorded at 310 mV for (lower) 0.1 M Na$_2$S$_2$O$_3$ after 135 min, (middle) 0.1 M Na$_2$S$_2$O$_3$ after 202 min, (upper) 0.1 M Na$_2$S$_2$O$_3$ plus 0.4 M NH$_3$ after 160 min.
6.7. **INCREASED THIOSULFATE CONCENTRATION**

The previous studies have used 0.1 mol dm\(^{-3}\) thiosulfate solutions, half the concentration required for the optimal rate of thiosulfate heap leaching (Jeffrey 2001). This section reports the results of SERS examinations of 1.0 mol dm\(^{-3}\) thiosulfate at stepped potentials and at fixed potentials over time.

6.7.1. **Stepped Potentials**

Figure 6-17 presents SERS spectra from a gold electrode in air-saturated 1.0 mol dm\(^{-3}\) Na\(_2\)S\(_2\)O\(_3\), at the mixed potential of 66 mV, and after holding the electrode sequentially at the marked potentials for 2 min. The behaviour in the more concentrated solution differs markedly from that observed in dilute thiosulfate. At the mixed potential, bands at 1003 and 446 cm\(^{-1}\) are assigned to the \(\nu_{\text{symS-O}}\) and \(\nu_{\text{S-S}}\) modes of thiosulfate, respectively.

As the potential was increased to 350 mV, the \(\nu_{\text{S-S}}\) band at 445 cm\(^{-1}\) broadens and another broad band becomes apparent at 320 cm\(^{-1}\). This band was assigned to \(\nu_{\text{Au-S}}\) as bands in this region have previously assigned to gold-sulfur stretching modes in studies of sulfide adsorption and SO\(_2\) reduction on gold (Gao *et al.* 1992a; Quijada *et al.* 2000). The band reaches a maximum at 410 mV, concurrent with the appearance of bands at 1037 and 387 cm\(^{-1}\) assigned to \(\nu_{\text{symS-O}}\) and \(\nu_{\text{S-S}}\), respectively, of an adsorbed tetrathionate.
In contrast to the tetrathionate-like species seen in the 0.1 mol dm$^{-3}$ solution, the $\nu_{S-S}$ modes seen in the more concentrated 1.0 mol dm$^{-3}$ solution were not significantly shifted from the solution tetrathionate values (Meyer et al. 1980). The $\nu_{\text{sym}-S-O}$ modes were downshifted by 4 cm$^{-1}$ from the solution value and were seen to shift even further upwards above the solution value as the potential increased, a phenomenon known as Stark-shifting or Stark-tuning (Gao and Weaver 1986; Lambert 1996). This behaviour is associated with spatially oriented groups within an electric field and is observed during surface adsorption (Gao and Weaver 1986; Lambert 1996).
The intensity of $\nu_{\text{Au-S}}$ was seen to decrease with potential after the appearance of tetrathionate, until it was barely discernible by 560 mV. The first sign of $S_8$ formation was observed at this potential as a shoulder at 471 cm$^{-1}$ in the $\nu_{\text{S-S}}$ and a small band due to a bending mode at 217 cm$^{-1}$. By 610 mV, bands due to tetrathionate have shifted to a maximum value of 450 cm$^{-1}$ and characteristic modes of $S_8$ were seen at 471 and 217 cm$^{-1}$. The $\nu_{\text{symS-O}}$ of tetrathionate was observed to shift by 7 cm$^{-1}$ when the potential was increased from 410 to 610 mV, reaching a maximum value of 1045 cm$^{-1}$. This Stark-shifting behaviour was not observed in the tetrathionate-like species observed in dilute thiosulfate solutions. Remaining bands at 810 mV can be attributed to $S_8$ and solution thiosulfate.

6.7.2. Effect of pH

The procedure used to acquire the spectra presented in Figure 6-17 was applied to the studies of the oxidation of a gold SERS electrode in 1.0 mol dm$^{-3}$ thiosulfate in borate buffer at pH 9.2 and in hydrogen carbonate / hydroxide buffer at pH 10.5. In contrast to the results seen for 0.1 mol dm$^{-3}$ thiosulfate, in which little change was seen, a significant difference in the spectral features was observed with changes in pH in 1.0 mol dm$^{-3}$ Na$_2$S$_2$O$_3$.

Figure 6-18 shows the comparison of spectra acquired from 1.0 mol dm$^{-3}$ neutral, pH 9.2 and pH 10.5 thiosulfate solutions 2 min after the application of 350 mV to the gold surface.
In the neutral solution, $\nu_{S-S}$ and $\nu_{\text{sym S-O}}$ bands of thiosulfate were seen, with a broad band near 325 cm$^{-1}$ assigned to $\nu_{\text{Au-S}}$. A shoulder could be observed in the region in which the $\nu_{\text{sym S-O}}$ of tetrathionate has been seen previously, although no corresponding $\nu_{S-S}$ was observed.

At pH 9.2, the intensity of $\nu_{\text{Au-S}}$ was increased as compared to that of the neutral solution and the thiosulfate $\nu_{S-S}$ was broader. A band assigned to $\nu_{\text{sym S-O}}$ of tetrathionate was observed at 383 cm$^{-1}$, accompanied by a weak band at 1037 cm$^{-1}$ in the tetrathionate $\nu_{S-S}$ region.
At pH 10.5, the $v_{\text{symS-O}}$ and $v_{S-S}$ of tetrathionate dominate the spectrum, with the characteristic thiosulfate bands also evident. A small shoulder was seen at 415 cm$^{-1}$, the same wavenumber as the $v_{S-S}$ of Na$_3$Au(S$_2$O$_3$)$_2$, with a strong broad band in the region in which the $\delta_{\text{symS-O}}$ of solution Na$_3$Au(S$_2$O$_3$)$_2$ is expected.

These results indicate that, at the higher concentration of 1.0 mol dm$^{-3}$ Na$_2$S$_2$O$_4$, different surface species occur as a function of pH. Thiosulfate and gold sulfide were predominant at neutral pH with gold sulfide reaching its maximum intensity at pH 9.2; and tetrathionate with the possible presence of gold(I) dithiosulfate at pH 10.5.

### 6.7.3. Time-dependent SERS

Figure 6-19 presents the time-dependent behaviour of the gold SERS electrode at the mixed potential in the 1.0 mol dm$^{-3}$ thiosulfate solution at pH 10.5. Spectra were collected at 2, 5 and 10 min at mixed potentials of 61, 65 and 66 mV, respectively. The system behaved similarly to the 1.0 mol dm$^{-3}$ thiosulfate solution at pH 9.2 with applied potential of 350 mV as seen in Figure 6-18, with bands observed due to thiosulfate $v_{\text{symS-O}}$ at 1000 cm$^{-1}$ and $v_{S-S}$ at 446 cm$^{-1}$ and broad bands due to gold-sulfur stretching.

The band at 320 cm$^{-1}$ assigned to $v_{\text{Au-S}}$ increases in intensity with time, indicating bond formation between thiosulfate and the gold during the mixed potential leaching process in alkaline solution.
Figure 6-19: SERS spectra from gold electrode at the mixed potential in 1.0 M Na₂S₂O₃ at pH 10.5 recorded at 2, 5 and 10 min. Reference spectra of solid Au₂S and 0.1 M Na₃Au(S₂O₃)₂ are included for comparison.

A small band is seen at 415 cm⁻¹ on the low wavenumber edge of the thiosulfate νₜₗ bands in the 2, 5 and 10 min scans presented in Figure 6-19. This band appears in a similar position to the νₜₗ observed at 420 cm⁻¹ in a 0.1 mol dm⁻³ solution of Na₃Au(S₂O₃)₂, the spectrum of which is also presented in Figure 6-19. The νₜₗ mode of the solid Na₃Au(S₂O₃)₂ was observed at 417 cm⁻¹. It is noted that νₐₜₗₚₗ modes characteristic of the Au(S₂O₃)₃⁻ anion in solution were absent, making identification of Au(S₂O₃)₃⁻ inconclusive. It is possible that the band at 415 cm⁻¹ may indicate the formation of a gold-thiosulfate or dithiosulfate surface intermediate during dissolution.
6.8. SODIUM TETRATHIONATE

Thiosulfate is oxidised by oxygen in solution to form tetrathionate, a process which is catalysed by Cu$^{2+}$ in ammoniacal copper(II) thiosulfate leach systems. It can be seen from Equation (6-2) that this process is independent of pH.

\[ 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2e^- \]  \hspace{1cm} (6-2)

SERS studies have shown that in both sodium and ammonium thiosulfate with ammonia addition, an adsorbed tetrathionate-like species was observed. This can be seen in Figure 6-12 and Figure 6-14. The same procedure as that used to produce these figures was applied to study the oxidation of tetrathionate on a gold surface.

![Potential-dependent SERS spectra of gold in a 0.1 M sodium tetrathionate solution and solution spectrum.](image)

Bands characteristic of tetrathionate in solution, viz. $\nu_S-S$ and $\nu_{symS-O}$ at 389 cm$^{-1}$ and 1041 cm$^{-1}$, respectively, were observed at all potentials studied. A band at 461 cm$^{-1}$ was
observed when the potential was 560 mV, similarly as seen for the 0.1 mol dm\(^{-3}\) thiosulfate solution in Figure 6-11.

At 610 mV and at higher potentials, the bands characteristic of S\(_8\) became the dominant feature of the spectrum. Thus, tetrathionate behaves in a similar manner to thiosulfate on a gold surface, being oxidized to S\(_8\) via an intermediate disordered sulfur surface layer. The appearance of this disordered sulfur layer occurred, however, at higher potentials than that for thiosulfate oxidation.

SERS of the 0.1 mol dm\(^{-3}\) sodium tetrathionate solution showed that the \(\nu_{\text{symS-O}}\) and \(\nu_{\text{S-S}}\) bands of tetrathionate at all potentials were the same as the solution values. This was in contrast to the tetrathionate-like species observed to form on the surface of the gold electrode during oxidation in thiosulfate solutions, shown in Figure 6-12 and Figure 6-14. In this species, the \(\nu_{\text{S-S}}\) and \(\nu_{\text{symS-O}}\) bands were both downshifted by \(~10\text{ cm}^{-1}\) from the solution value. It is possible that this tetrathionate-like species undergoes a comparative lengthening of both S-S and S-O bonds due to an interaction with the gold surface during its formation.

A different behaviour to both systems was seen in the more concentrated 1.0 mol dm\(^{-3}\) sodium thiosulfate solution, as presented in Figure 6-17. In this experiment, \(\nu_{\text{S-S}}\) and \(\nu_{\text{symS-O}}\) bands were close to the solution tetrathionate value but the \(\nu_{\text{symS-O}}\) band was seen to shift with potential. This behaviour is expected when a surface-adsorbed species is oriented perpendicular to the surface in an electric field (Lambert 1996).
6.9. Ammoniacal Copper(II) Thiosulfate Leaching

SERS spectra were collected from the surface of oxidation-reduction cycled gold electrodes while leaching at the mixed potential in air-saturated cupric tetra-amine sodium and ammonium thiosulfate solutions.

6.9.1. Cupric Tetra-amine Sodium Thiosulfate

Gold electrodes, roughened by oxidation-reduction cycling, were immersed in an air-saturated solution of 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$, 0.4 mol dm$^{-3}$ NH$_3$, 0.01 mol dm$^{-3}$ CuSO$_4$. SERS spectra were collected with 10 exposures of 10 s each. SERS spectra were recorded at the mixed potential as a function of time. The SERS signal was seen to diminish after 20 min leaching, suggesting that the SERS activity was lost as the gold surface dissolved. After 20 min, the electrode was withdrawn from the solution, gently washed, immersed in water, and a SERS spectrum recorded. The electrode was then rinsed in ultrapure water and a spectrum was acquired during the rinsing process. Following rinsing, the electrode was transferred to a deaerated 0.1 mol dm$^{-3}$ H$_2$SO$_4$ solution for determination of surface coverage, the results of which are presented in Chapter 6. A spectrum was acquired in the acid solution prior to the coverage experiment. Figure 6-21 shows in situ SERS spectra after 3 and 15 min leaching, a spectrum recorded in water and a spectrum recorded after transfer to acid.

The in situ spectra shows bands at 383 cm$^{-1}$ and 1017 cm$^{-1}$ that were absent in the two spectra recorded following transfer to water or to sulfuric acid. A tetrathionate-like species was again observed during leaching.
Figure 6-21: SERS spectra recorded in situ after 15 min in a solution of 0.1 M Na$_2$S$_2$O$_3$, 0.4 M NH$_3$, 0.01 M CuSO$_4$ in equilibrium with air and after transfer to water, then 0.1 M H$_2$SO$_4$.

The tetrathionate-like species found in this experiment differed again from those described in Section 6.8. In this case, the $\nu_{S-S}$ band was seen at 383 cm$^{-1}$, which is close to that observed in solution tetrathionate. The $\nu_{\text{symS-O}}$ band however was found to be shifted downward by $\sim$20 cm$^{-1}$ to 1017 cm$^{-1}$. This band was in a similar position to that of the $\nu_{\text{symS-O}}$ in the gold(I) thiosulfate complex in solution. The gold(I) thiosulfate and solution thiosulfate reference spectra are shown in Figure 6-2. A band was apparent at $\sim$265 cm$^{-1}$ after 15 min leaching, and this could be assigned to either a $\nu_{\text{Cu-S}}$ (Brown et al. 1995) or to a $\nu_{\text{Au-S}}$ (Gao et al. 1992a). A band was seen to develop at 635 cm$^{-1}$ in the position in which the symmetric bending modes of the -SO$_3^-$ group, $\delta_{\text{symS-O}}$, are expected.

Broad weak bands were also seen at 450 cm$^{-1}$ in the in situ spectrum, which intensified upon after transfer to water. This band can be assigned to the $\nu_{\text{S-S}}$ modes of a range of S-S bonds on the gold surface. The bands due to the tetrathionate-like species were
absent in water, suggesting that the species is weakly bound and removed during rinsing. On transfer to the acid solution, the $\nu_{\text{S-S}}$ band returned and shifted to 432 cm$^{-1}$ while the $\nu_{\text{Au-S/Cu-S}}$ was maintained at 255 cm$^{-1}$

6.9.2. Stability of SERS Surface During Leaching

In cupric ammonium sodium thiosulfate leaching solutions, diminution of SERS signal was observed on acquisition of spectra at times longer than 20 min. This is attributed to dissolution and removal of the SERS-active nanostructure generated by oxidation-reduction cycling.

![Figure 6-22: Time-evolved SERS spectra from dendritic gold SERS surface leached in ammoniacal copper(II) sodium thiosulfate solution, a) evolution of SERS signal to maximum at 20 min, b) diminution of SERS signal after 20 min.](image)

Figure 6-22: Time-evolved SERS spectra from dendritic gold SERS surface leached in ammoniacal copper(II) sodium thiosulfate solution, a) evolution of SERS signal to maximum at 20 min, b) diminution of SERS signal after 20 min.
Figure 6-22 shows SERS spectra acquired over time during dissolution studies of gold in a cupric tetra-ammine sodium thiosulfate leaching solution. In Figure 6-22A, the bands of the tetrathionate-like species were seen within 5 min of immersion. The intensity increased by 10 min, as had the background of the scan. By 20 min, the bands and SERS background reach a maximum intensity.

Figure 6-22B shows the diminution of both the Raman bands and SERS background by 30 and 50 min, as compared with the 20 min scan. At 50 min a broad weak band was noted at ~ 440 cm⁻¹ attributable to the ammoniacal thiosulfate leach solution. The comparative increase in intensity of this mode compared to those of the surface species may indicate that a similar intensity of Raman scatter is observed from the weakened SERS effect and the conventional Raman scatter of the bulk solution.

6.9.3. Cupric Tetra-ammine Ammonium Thiosulfate

Figure 6-23 presents the results of leaching studies that used an ammonium thiosulfate leach solution composed of 0.1 mol dm⁻³ Na₂S₂O₃, 0.4 mol dm⁻³ NH₃, 0.01 mol dm⁻³ CuSO₄ in equilibrium with air. The same procedure was followed as for the sodium thiosulfate experiment. It can be seen from Figure 6-23 that the SERS characteristics of the ammonium thiosulfate leach solution differ significantly from that of the sodium system. The bands at 1017 and 382 cm⁻¹ that were prominent in the sodium leach solution were evident but very weak.

The thiosulfate anion ν_{sym S-O} mode at 1002 cm⁻¹ was seen as a shoulder of the band at 1017 cm⁻¹ band. A broad band in the ν_{S-S} region has a central position close to that of cyclo-octasulfur, S₈, but the absence of bending modes precludes assignment to the S₈
molecule. Weak broad bands were seen in water and acid media in the Au-S/Cu-S stretching range at ~250 cm\(^{-1}\) and the two \(\nu_{\text{S-S}}\) modes appear to merge as one broad band centred at 450 cm\(^{-1}\) in both media.

Figure 6-23: SERS spectra recorded *in situ* after 15 min in 0.1 M (NH\(_4\))\(_2\)S\(_2\)O\(_3\), 0.4 M NH\(_3\), 0.01 M CuSO\(_4\) in equilibrium with air and after transfer to water, then to 0.1 M H\(_2\)SO\(_4\).

It can be seen from these experiments that SERS examination of surface products formed on gold shows a marked difference between the sodium and ammonium thiosulfate cupric tetra-ammine solutions. The ammonium thiosulfate showed almost featureless spectra both while leaching and when transferred to water and acid.
6.10. Sulfide as a Model System

The study of the electroadsorption of sulfide on gold is useful as a model system for studies involving polysulfur species, oxysulfur anions, alkyl sulfides and the oxidation of sulfide minerals. The interaction of S\textsuperscript{-II} solution species with gold has been studied using surface-enhanced Raman spectroelectrochemical techniques to provide a basis for understanding sulfur layers formed during the leaching of gold in thiosulfate.

Voltammograms and in situ SERS spectra were recorded for gold electrodes in acidic and alkaline sulfide solutions. The nature of the sulfur layer initially formed at low potentials in acidic solutions was closely examined in regard to a rapid potential-dependent shift in band position, particularly with respect to its state of protonation during this transition. The layer was adsorbed on gold from an acidic sulfide solution then removed from solution and subjected to further study in acid without the presence of solution sulfide.

Studies in basic solutions focused upon the identification of the spectral features characteristic of surface species at increasing potentials. The surface coverages of these potential-dependent spectral features were also studied and are presented in the next chapter.
6.10.1. SERS in Acidic Sulfide Media

The spectroelectrochemical behaviour of gold in acidic sulfide solutions was examined in order to clarify the nature of the sulfur surface species present in the region of the voltammetric prewave below the reversible potential of the H$_2$S/$S^0$ system (Alanyalioglu et al. 2001; Briceno and Chander 1990a; Gao et al. 1992a; Hamilton and Woods 1983; Lezna et al. 1990; Vericat et al. 2004). A polished gold electrode was used to characterise the voltammetry prior to SERS studies.

6.10.1.1. Voltammetry on Polished Gold

Voltammetry of a polished gold electrode in 0.1 mol dm$^{-3}$ H$_2$SO$_4$ containing 2x10$^{-3}$ mol dm$^{-3}$ Na$_2$S is presented in Figure 6-24. This gold electrode had not been treated by the oxidation-reduction cycling procedure used to generate a SERS active surface, but had been subjected to potential cycling in 0.1 mol dm$^{-3}$ H$_2$SO$_4$ prior to addition of Na$_2$S to establish a clean surface (Woods 1976).

The underpotential region was characterised by a single anodic peak, which occurred at –80 mV; the corresponding cathodic peak appeared at –170 mV. Hydrogen evolution was observed to commence at –350 mV. Two cathodic peaks in the prewave region have been reported in studies of sulfide in 1.0 mol dm$^{-3}$ NaOH (Hamilton and Woods 1983), while only one cathodic peak was visible under the acid conditions of Figure 6-24. This was because the potential corresponding to reduction of $S^0$ to polysulfide ions is lower than that for reduction to H$_2$S in strong acid media, thus the lowest peak would not be discernible because of significant cathodic currents resulting from hydrogen evolution (Parker et al. in preparation).
On the scan to 310 mV in Figure 6-24, a second wave was apparent, commencing near 350 mV, the $\text{S}^{II}/\text{S}^{0}$ reversible potential in this solution (Van Muylder and Pourbaix 1966). An anodic peak was observed at $\sim$600 mV and reduction of the species produced in that anodic process occurred on the subsequent negative-going scan at potentials that became more negative as the upper limit of the scan was increased.

During scans into the high potential region in Figure 6-24, a cloud of very fine particles was observed to be emanating from the electrode surface. Raman spectra of this
material recorded through the window of the electrochemical cell displayed the characteristic \( \nu_{S-S} \) and \( \delta_{S-S-S} \) modes of elemental sulfur, as shown in Figure 6-3. These particulates were attributed to H\(_2\)S oxidizing to S\(^0\) through polysulfide intermediates in acid solutions. Polysulfides are unstable in acid and decompose to form H\(_2\)S and S\(^0\) (Steudel 2003a).

6.10.1.2. Concurrent SERS and Voltammetry

A voltammogram from an oxidation-reduction cycled gold electrode obtained in 2 x 10\(^{-3}\) mol dm\(^{-3}\) Na\(_2\)S in 0.1 mol dm\(^{-3}\) H\(_2\)SO\(_4\) at 2 mV s\(^{-1}\), starting from –290 mV, is shown in Figure 6-25.

Figure 6-25: Triangular potential sweep voltammogram at starting from –290 mV at 2 mV s\(^{-1}\) in 2 x 10\(^{-3}\) M H\(_2\)S, 0.1 M H\(_2\)SO\(_4\).

Figure 6-25 shows that an anodic current commenced at 150 mV, resulting from the deposition of sulfur on the gold surface. The sulfur layer was reduced to H\(_2\)S on the return scan when the potential was negative of the reversible H\(_2\)S/S\(^0\) value.
Figure 6-26: SERS spectra from a gold electrode in 2 x 10^{-3} M H_2S, 0.1 M H_2SO_4 acquired during the 2 mV s^{-1} voltammogram in Figure 6-25. The lowest scan is first of the series, from the starting potential of -290 mV.

SERS spectra, recorded consecutively during the potential sweep shown in Figure 6-25 are presented in Figure 6-26. A band is evident in Figure 6-26 at ~270 cm^{-1} at low potentials. This band is in the region where ν_{Au-S} appears for Au_2S (Figure 6-3). This is consistent with sulfur being bonded to gold at potentials below those at which elemental sulfur is formed. The 270 cm^{-1} band intensity decreased and then disappeared as the potential was swept more positive. At potentials just negative to 210 mV, very weak, broad ν_{S-S} and ν_{Au-S} bands appear near 450 cm^{-1} and 310 cm^{-1}, respectively. This could be interpreted as the nature of the bonding of sulfur to gold changing with the formation of sulfur-sulfur bonds. The possibility of the formation of a bridged disulfide with
greater that $\frac{1}{3}$ ML coverage has been described in literature (Rodriguez et al., 2003), therefore it is possible that the $\nu_{\text{Au-S}}$ at 310 cm$^{-1}$ could be attributed to a bridged species.

As the potential continues to increase, the $\nu_{\text{S-S}}$ band intensifies, shifting to a maximum of 460 cm$^{-1}$. The narrowness of the band indicates a relatively constant bond length. As the potential proceeds towards the upper potential limit, the deposited sulfur forms into the stable cyclo-octasulfur structure. On the return sweep, after the $S_8$ had developed, it remained the major phase on the gold surface until the electrode potential dropped below the $H_2S/S^0$ reversible value. The 270 cm$^{-1}$ $\nu_{\text{Au-S}}$ band again appeared when the potential returned to the initial value of $-290$ mV.

6.10.1.3. Protonation of Chemisorbed Sulfide

The band at 270 cm$^{-1}$ has previously been reported in SERS studies of $S^{II}$ electro-oxidation (Gao et al. 1992a). In this study, this mode, and one at 310 cm$^{-1}$, were associated with an anodic and cathodic couple observed on reversing a 20 mVs$^{-1}$ voltammetric sweep prior to $-100$ mV vs. SCE for 2 x 10$^{-3}$ mol dm$^{-3}$ Na$_2$S in acidic solution (0.1 mol dm$^{-3}$ NaClO$_4$ and 0.01 mol dm$^{-3}$ HClO$_4$, pH 2); and prior to $-500$ mV vs. SCE in basic solution (0.1 mol dm$^{-3}$ NaClO$_4$ and 0.01 mol dm$^{-3}$ NaOH, pH 12). Both bands were assigned to a metal-monoatomic sulfur stretch, with the band at 270 cm$^{-1}$ assigned to a protonated form, $\nu_{\text{Au-SH}}$.

The authors (Gao et al. 1992a) proposed a redox couple involving electron loss from an adsorbed (SH)$_{\text{ads}}$ to form an adsorbed deprotonated sulfide. Should this be the case, a band due to a $\nu_{\text{S-H}}$ stretching mode, occurring between 2400 and 2700 cm$^{-1}$, would be observable. The S-H bond is a particularly strong Raman scatterer and absence of a $\nu_{\text{S-H}}$
mode would invalidate such a protonation / deprotonation mechanism. An experiment designed to assess the validity of this mechanism involved holding the electrode at selected potentials and recording a SERS spectrum in both high and low wavenumber regions to observe the presence of any S-H bands.

![SERS spectra of Au electrode in 0.1 M H₂SO₄ and ~20 x 10⁻³ M Na₂S held at various potentials.](image)

**Figure 6-27:** High and low wavenumber regions Raman spectra of Au electrode in 0.1 M H₂SO₄ and ~20 x 10⁻³ M Na₂S held at various potentials.

Figure 6-27 presents the results of such acquisitions. It can be seen in Figure 6-27A that no S-H bands are seen at any of the potentials examined, including that below the reversible potential of the proposed redox deprotonation, at which the 270 cm⁻¹ metal-monoatomic sulfur stretch occurs. This evidence does not support the proposed protonation/deprotonation mechanism reported by Gao and co-workers (Gao et al. 1992a).
6.10.2. Investigation of Chemisorbed Sulfide in Sulfuric Acid

In the previous section, the possibility of protonation being responsible for the change in wavenumber of the Au-S stretch was discounted. The nature of the change in wavenumber was further investigated by removing the electrode from the sulfide solution with the layer intact and placing it into a sulfide-free acid solution in order to undertake SERS and voltammetry of the adsorbed layer.

![Figure 6-28: in situ SERS spectra after immersion of a gold SERS electrode stepped upward in potential in 0.1 M H₂SO₄ following removal from 0.1 M H₂SO₄, 2x10⁻³ M Na₂S. The upper spectrum was acquired after the potential was decreased to -240 mV from 510 mV.](image)

An electrode that had been held at –290 mV in a solution of 0.1 mol dm⁻³ H₂SO₄, 2x10⁻³ mol dm⁻³ H₂S was removed from the electrolyte to examine the adsorbed sulfide layer. The electrode was rinsed with clean 0.1 mol dm⁻³ H₂SO₄ and placed into an
electrochemical cell containing 0.1 mol dm\(^{-3}\) H\(_2\)SO\(_4\). The SERS spectra from the electrode surface are presented in Figure 6-28, with the sulfur coverage on the gold the same as that at -290 mV in the sulfide solution.

The band position at 270 cm\(^{-1}\) at –290 mV was seen to diminish by 110 mV and a second band at 300 cm\(^{-1}\) was seen to appear. This band was retained at higher potentials and conversion to the 270 cm\(^{-1}\) band was seen when the potential returned to –290 mV.

Voltammetry of the adsorbed layer was undertaken at 20 mV s\(^{-1}\) in the 0.1 mol dm\(^{-3}\) H\(_2\)SO\(_4\) solution, from -290 mV to an upper limit of 510 mV before a return to the starting potential. The voltammogram was featureless besides a reduction current due to hydrogen evolution and a small anodic peak observed at ~ –60 mV confidently assigned to oxidation of the dissolved hydrogen evolved at –290 mV. No cathodic peaks were observed on the reverse scan and it can be concluded that a “reduced” sulfur species was not formed from adsorbed sulfur present on the gold surface.

Facile movement from one adsorption site to another has been reported for S on Au (Rodriguez et al. 2003). A possible explanation for the behaviour seen in Figure 6-28 is that at low potentials, sulfur moves from stable three-fold hollow sites, which are favoured at \(1/3\) ML coverage (Rodriguez et al. 2003), to less thermodynamically favoured a-top sites. The possibility of the binding of sulfur to bridged sites as the origin of the higher wavenumber band cannot be excluded.
6.10.3. SERS in Alkaline Sulfide Media

The spectroelectrochemical behaviour of gold in alkaline sulfide solutions was examined to establish the nature of the adsorbates present in the post-prewave region and during the electro-oxidation of sulfide at higher potentials. The voltammetry of the system was examined using polished gold electrodes, with SERS electrodes used to examine the vibrational characteristics of the surface species.

6.10.3.1. Voltammetry on Polished Gold

Figure 6-29 presents voltammograms recorded in 0.05 mol dm\(^{-3}\) Na\(_2\)B\(_4\)O\(_7\) containing 2x10\(^{-3}\) mol dm\(^{-3}\) Na\(_2\)S. The smooth gold electrode had not been subjected to the ORC procedure used to generate a SERS surface, but potential cycles had been applied in 0.05 mol dm\(^{-3}\) Na\(_2\)B\(_4\)O\(_7\) prior to addition of HS\(^-\) to generate a clean gold surface.

It can be seen from Figure 6-29 that the underpotential region was characterised by a single anodic peak that occurred at -500 mV; the corresponding cathodic peak appearing at -570 mV. Above ~ -190 mV an anodic current flowed, peaking at 110 mV. The product of the anodic reaction was reduced to polysulfide ions and to HS\(^-\) in cathodic peaks that appeared at -450 mV and at -560 mV, respectively.
Figure 6-29: Voltammograms at 20 mV s\(^{-1}\) for a gold electrode in 0.05 M Na\(_2\)B\(_4\)O\(_7\) containing 2\(\times\)10\(^{-3}\) M Na\(_2\)S, commenced at -1.09 V and taken to increasing upper potential limits (Parker et al. in preparation).

6.10.3.2. SERS and Voltammetry on Oxidation-Reduction Cycled Gold

A triangular sweep voltammogram of a gold SERS electrode in 1 \(\times\) 10\(^{-3}\) mol dm\(^{-3}\) Na\(_2\)S in 0.05 mol dm\(^{-3}\) Na\(_2\)B\(_4\)O\(_7\) is shown in Figure 6-30. The characteristics of this voltammogram include an anodic prewave due to sulfur adsorption at –490 mV (Hamilton and Woods 1983) and an anodic peak at 60 mV due to the formation of S\(_8\) (Hamilton and Woods 1983).
Figure 6-30: Triangular potential sweep voltammogram at 2 mVs$^{-1}$ in 1 mM Na$_2$S, 0.05 M Na$_2$B$_4$O$_7$ starting from –690 mV.

The potentials marked on the figure are those at which characteristic SERS spectra were collected after holding the gold electrode at the marked potentials for 2 min. Spectra obtained at –240, –140, –40 and 10 mV are shown in Figure 6-31.

Figure 6-31: SERS spectra recorded after holding the potential of a gold electrode in 10$^{-3}$ M Na$_2$S, 0.05 M Na$_2$B$_4$O$_7$ solution, pH 9.2, after holding the potential at the specified value for 2 min.
The potential of -240 mV occurs at the closing stage of the prewave region, while
-140 mV occurs at the onset, and -40 and -10 mV on the rise, of the anodic peak for S\textsubscript{8}
formation.

At -240 mV, a SERS band was apparent at ~280 cm\textsuperscript{-1}, in the region expected for the
monoatomic gold-sulfur stretch, \(\nu_{\text{Au-S}}\) (Gao \textit{et al.} 1992a). This substantiates the
assignment of the underpotential sulfur layer being sulfur atoms bonded to gold. The sudden appearance at -140 mV of a strong, broad and symmetric SERS band centred at ~ 450 cm\textsuperscript{-1} was indicative of the appearance of bonded sulfur with a broad
range of S-S bond lengths. The range was centred in a band position similar to the \(\nu_{\text{Au-S}}\)
polymeric sulfur and can be assigned to polymeric sulfur adsorbed on gold, Au-S\textsubscript{n}. The band attributed to \(\nu_{\text{Au-S}}\) was concurrently seen to disappear prior to its reappearance
at 310 cm\textsuperscript{-1}. This may indicate relaxation into the three-fold hollow sites. Shared bonding of sulfur with three gold atoms would suggest a large number of
possible bonding states and may therefore present a weak Raman spectrum.

As the higher wavenumber band \(\nu_{\text{Au-S}}\) is accompanied by the formation of S-S modes, it
would be reasonable to assign this mode to gold bonded to polyatomic or polymeric
sulfur, \(\nu_{\text{Au-S}_n}\). When the potential was increased to -40 mV, the \(\nu_{\text{S-S}}\) narrowed and
shifted upwards in wavenumber to 460 cm\textsuperscript{-1}. The \(\nu_{\text{Au-S}}\) band decreases in intensity and
the first sign of the S\textsubscript{8} bending mode, \(\delta_{\text{S-S-S}}\), at 217 cm\textsuperscript{-1} was observed, signalling the
formation of bulk cyclic-octasulfur. By 10 mV, the characteristic 471 cm\textsuperscript{-1} band of S\textsubscript{8}
was seen to appear, along with the strong, sharp \(\delta_{\text{S-S-S}}\).
6.10.4. *Ex situ* SERS of Chemisorbed Sulfide

STM studies of an electrode removed from a sulfide solution and examined *ex situ* in air (Gao *et al.* 1992b) revealed a rectangular ‘crown-like’ ring structure of alternately light and dark sulfur atoms. An *ex situ* SERS spectrum, acquired in air, of an electrode withdrawn from the alkaline sulfide solution at the mixed potential and rinsed with ultrapure H₂O, is presented in Figure 6-32. The roughened SERS electrode was hydrophilic *ex situ* although covered by the layer of sulfur.

![Figure 6-32: *Ex situ* SERS spectra from a gold electrode withdrawn from 1 mM Na₂S in 0.05 M Na₂B₄O₇ solution, pH 9.2, upon removal from cell, rinsing and drying in air.](image)

The spectrum exhibited a characteristic sharp $\nu_{S-S}$ band at $\sim 460$ cm$^{-1}$ with a shoulder at 420 cm$^{-1}$. The narrowness of the $\nu_{S-S}$ band indicated an ensemble of S-S bonds of similar length, with the 460 cm$^{-1}$ band, corresponding to a calculated bond length of 205 pm as per the equation (2-32) in section 2.4.1.3. (Eckert and Steudel 2003). Bonding to gold was indicated by the presence of the higher wavenumber $\nu_{Au-S}$ band at 315 cm$^{-1}$ associated with the adsorbed polymeric sulfur. This band was sharper and higher in wavenumber than the $\nu_{Au-Sn}$ bands seen in Figure 6-31, indicating a lower spread of bond lengths and a more contracted Au-S bond. Bending modes of S$_8$ at
217 and 150 cm\(^{-1}\) are absent, as was the characteristic \(\nu_{S-S}\) band of \(S_8\) at 471 cm\(^{-1}\). The absence of bending modes may be due to the \(S_8\) rings being constrained by adsorption in a crown-like structure, i.e. with every second sulfur atom bound to gold.

As well as fitting the characteristics of a surface bonded crown \(S_8\), the spectra were similar to those reported for polymeric sulfur (Eckert and Steudel 2003), in particular, the \(S_\chi\) variant composed of large disordered rings with an average ring size of 25 S atoms. Their spectra of \(S_\chi\) show a strong sharp band at 460 cm\(^{-1}\) accompanied by a weak stretching band at 425 cm\(^{-1}\) and a weak bending mode at 260 – 275 cm\(^{-1}\). The 315 cm\(^{-1}\) band attributed to \(\nu_{(Au-S_n)}\) in spectra of sulfur structures adsorbed on gold \textit{ex situ} is not seen in the spectrum of \(S_\chi\), and the bending mode of \(S_\chi\) was not observed in the \textit{ex situ} scan. The absence of a bending mode in the adsorbed layer may indicate that the sulfur is constrained on the surface and therefore not able to undergo the bending vibration.
6.11. EFFECT OF THIOUREA

REQCM studies have shown thiourea to increase the rate of gold dissolution in thiosulfate solutions (Chandra and Jeffrey 2004). The results of SERS experiments to examine the time-dependent SERS at 210 mV of a thiosulfate solution with thiourea addition are presented. Gold electrodes with surface layers that had been deposited in thiosulfate and sulfide solutions were polarised in thiosulfate solutions containing thiourea in order to observe the effect of thiourea on Au-S and S-S bonding.

6.11.1. Time-dependent SERS of Thiosulfate + Thiourea

Figure 6-33 shows time-dependent SERS spectra acquired at 210 mV from a gold electrode in a 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$, 0.01 mol dm$^{-3}$ thiourea solution.

![Figure 6-33](image)

Figure 6-33: Time-dependent gold SERS spectra of 10 mM thiourea, 0.1 M Na$_2$S$_2$O$_3$ at 210 mV.

The tetrathionate-like species, seen in Figure 6-15 for thiosulfate at this potential in the spectra collected at up to 10 min, was not observed when thiourea was present in the leach solution. The scans showed the presence of thiosulfate at all times during the
experiment due to a $\nu_{S-S}$ band at 446 cm$^{-1}$ and a $\nu_{\text{symS-O}}$ at 1000 cm$^{-1}$. Two broad $\nu_{\text{Au-S}}$ bands at 325 and 270 cm$^{-1}$ were seen to reach a maximum intensity after 10 min. These bands, in the region in which bands due to gold sulfide occur, may also contain a contribution from the gold-sulfur stretching mode, $\nu_{\text{Au-Tu}}$, of a surface bonded gold-thiourea complex. The $\nu_{C-S}$ band of thiourea was seen to be downshifted to 710 cm$^{-1}$ from the value of 732 cm$^{-1}$ found for thiourea in solution (Brown et al. 1995; Liu and Wu 2005), indicating that the thiourea was bonded to the gold surface via the sulfur atom (Holze and Schomaker 1990).

6.11.2. Stripping of Surface Layer after Oxidation in Thiosulfate

A gold SERS electrode was subjected to polarisation for 2 hrs at 210 mV in deaerated 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$. The spectrum acquired from the surface after this treatment is shown in Figure 6-34.

The electrode was allowed to return to the OCP prior to introduction of solid thiourea in order to make the thiosulfate solution 0.01 mol dm$^{-3}$ in thiourea. Deaeration was continued during thiourea addition. Figure 6-34 shows the effect on the SERS from the electrode surface after the addition of thiourea to the thiosulfate solution, while at the OCP and on polarising at 210 mV.

An initial increase in the $\nu_{S-S}$ and $\nu_{\text{Au-S}}$ was observed within 20 min of the addition of thiourea to the thiosulfate solution. With the application of 210 mV in the presence of thiourea, the $\nu_{S-S}$ band was seen to diminish significantly over 10 min, while the $\nu_{\text{Au-S}}$ band was seen to grow. The band due to $\nu_{\text{symS-O}}$ of thiosulfate was also seen as the $\nu_{S-S}$
mode diminishes and a $\nu_{CS}$ at 715 cm$^{-1}$ was assigned to thiourea bonded to gold via the sulfur atom.

Figure 6-34: SERS spectra from gold held in 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$ at 210 mV, followed by returning to the OCP and adding solid thiourea to make the solution 0.1 M $\text{Na}_2\text{S}_2\text{O}_3$, 10 mM Tu. The potential was stepped to 210 mV after 20 min at OCP.

6.11.3. Stripping of Chemisorbed Sulfide

The surface deposit on gold from sulfide solutions was examined \textit{ex situ} and the spectrum is presented in Figure 6-32. The SERS spectrum acquired from the surface deposit was found to conform to a model of an assembly of crown-S$_8$ sulfur molecules with every second sulfur atom bonded to gold. It was seen in the previous section that the addition of thiourea to a thiosulfate solution resulted in the loss of $\nu_{S,S}$ bands on the
surface of a gold SERS electrode. In this experiment a SERS electrode, withdrawn from a sulfide solution and found to have the *ex situ* characteristics seen in Figure 6-32, was immersed in a solution of thiosulfate with the addition of thiourea. The electrode sat at the OCP for 10 min prior to the application of 310 mV. The $\nu_{\text{S-S}}$ bands were seen to disappear after 10 min at this potential, concurrent with an increase in bands due to $\nu_{\text{Au-S}}$.

Figure 6-35: SERS spectra from a gold electrode removed after holding in 1 mM Na$_2$S in 0.05 M Na$_2$B$_4$O$_7$ solution, pH 9.2, for 1 hr at -290 mV then placing in a solution of 0.01 M thiourea in 0.1 M sodium thiosulfate and holding at the marked potentials for the specified times.

Figure 6-35 presents SERS spectra acquired from a gold SERS electrode that had been withdrawn from $10^{-3}$ mol dm$^{-3}$ Na$_2$S in 0.05 mol dm$^{-3}$ Na$_2$B$_4$O$_7$ then rinsed and dried in air prior to immersion in a deaerated solution of 0.01 mol dm$^{-3}$ thiourea in 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$. At the OCP of -160 mV, little change was seen in the spectrum from the electrode, the characteristic *ex situ* spectrum of which was shown in Figure 6-32.
Figure 6-35 shows that a rapid decrease of the $\nu_{S-S}$ mode of the adsorbed sulfide was noted at 310 mV, a potential at which gold dissolution in thiosulfate has been seen to occur (Chandra and Jeffrey 2004). After 2 min at 310 mV, the intensity of the $\nu_{S-S}$ mode was less than that of the $\nu_{\text{Au-S}}$, which has been seen to increase as the $\nu_{S-S}$ mode was diminished. By 10 min at 310 mV, the $\nu_{S-S}$ mode was barely distinguishable and a strong broad $\nu_{\text{Au-S}}$ mode became the dominant spectral feature, indicating the formation of a gold sulfide layer on the surface.

The top spectrum in Figure 6-35 also shows the presence of thiosulfate $\nu_{\text{symS-O}}$ modes at 1002 cm$^{-1}$ and a band at 715 cm$^{-1}$ that can be assigned to the $\nu_{\text{C-S}}$ mode of thiourea. The $\nu_{S-S}$ mode was found to have shifted downward in wavenumber to 715 cm$^{-1}$, as compared with 732 cm$^{-1}$ found for thiourea in solution (Brown et al. 1995; Liu and Wu 2005). This has been interpreted in previous studies to indicate adsorption of thiourea on gold via the sulfur atom (Holze and Schomaker 1990). From this evidence it would appear that thiourea is capable of disrupting networked sulfur-sulfur bonds on the gold surface.
7. **EX SITU TECHNIQUES**
7.1. **PREAMBLE**

Various *ex situ* techniques were employed to gain further insight into the nature and degree of coverage of surface species present on gold electrodes after polarisation in sulfide or thiosulfate solutions and after leaching in ammoniacal copper(II) thiosulfate solutions. XPS was used to determine the composition and chemical state of sulfur, copper and nitrogen surface species; ATR-FTIR to observe the presence of Raman-insensitive surface species such as ammonia; and electrochemical methods to quantify the copper and sulfur coverage. Polished electrodes were used for all *ex situ* techniques with the exception of those for which SERS investigations were also undertaken to compare with the outcome of the *ex situ* experiment. Quantitative AAS solution analyses were performed to monitor the dissolution rate of gold in ammoniacal copper(II) thiosulfate leaching solutions.
7.2. **VOLTAMMETRIC COVERAGE DETERMINATION**

It has been shown that the initial adsorption of oxygen on gold electrodes from an acid solution is restricted to a monolayer and that this observation provides the basis for measuring the exposed surface area of a gold electrode (Hamilton and Woods 1983; Woods 1976). The procedure recommended by the authors is to hold the gold electrode at 1.8 V for 100 s in 0.1 mol dm$^{-3}$ H$_2$SO$_4$ and then apply a negative-going scan at 40 mV s$^{-1}$ (Hamilton and Woods 1983). Figure 7-1 presents a voltammogram for the reduction of a monolayer of oxygen adsorbed on a polished gold electrode held at +1.81 V for 100s. The integrated cathodic charge corresponds to the two-electron reduction of the oxygen monolayer to water.

![Figure 7-1: Reference oxide monolayer stripping peak for polished gold flag electrode used for sulfide electro-oxidation studies. Negative-going linear sweep from 1.81 to 0.21 V at 40 mVs$^{-1}$ after holding at 1.81 V for 100 s.](file://)
In the study described in this chapter, the coverage of oxidisable species such as sulfur and copper sulfide was determined by a bolometric method. Polished electrodes were used in sulfide solutions to minimise entrapment of oxidised species and SERS electrodes were used in thiosulfate solutions to concurrently examine the surface. The species quantifiable by this method are sulfur and copper.

7.2.1. Sulfide

Sulfur deposited on gold from sulfide solution has been shown to oxidise quantitatively to sulfate on a positive-going scan to high potentials (Hamilton and Woods 1983). In order to determine the sulfur coverages after deposition of surface sulfide in borate for 100 s, the gold electrodes was withdrawn from the cell, washed thoroughly with ultrapure water and transferred to a cell containing de-aerated 0.1 mol dm$^{-3}$ H$_2$SO$_4$. A triangular potential scan at 40 mV s$^{-1}$ was applied from the OCP of ~ 410 mV to an upper limit of 1.81 V. The formation and stripping of an oxide monolayer was applied immediately following each sulfur and copper coverage experiment.

The voltammograms used for determination of surface coverage of sulfur at various sulfide deposition potentials are shown in Figure 7-2. Each was normalised to the charge passed by the reduction of the gold-oxide layer for each system.
Figure 7-2: Triangular sweep voltammograms in 0.1 M H$_2$SO$_4$ from a gold electrode after holding at the specified potential for 100 s in 1 mM Na$_2$S, 0.05 M Na$_2$B$_4$O$_7$ solution, pH 9.2.

Integration of the anodic charge on the positive going scan gives a measure of the 6e$^-$ oxidation of sulfur on the gold surface to sulfate ions, combined with that of oxygen adsorption on the gold surface. On the return sweep, the oxide layer on the gold electrode is reduced and the charge passed in this step can be subtracted from the anodic charge to give the charge due to sulfur oxidation alone. The sulfur coverage of the surface was then determined by comparing this charge to that for reduction of the oxygen monolayer. The sulfur coverages determined for the electrodes held at set potentials in 10$^{-3}$ mol dm$^{-3}$ Na$_2$S in 0.05 mol dm$^{-3}$ Na$_2$B$_4$O$_7$, pH 9.2, are presented in Table 7-1.
Table 7-1: Sulfur coverage on a smooth gold electrode held at the marked potential for 100 s in 1 mM Na₂S in 0.05 M Na₂B₄O₇, pH 9.2 as determined by voltammetry in 0.1 M H₂SO₄.

<table>
<thead>
<tr>
<th>Potential / V</th>
<th>−240 mV</th>
<th>−140 mV</th>
<th>−40 mV</th>
<th>10 mV</th>
<th>10 mV †</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coverage / ML</td>
<td>0.35</td>
<td>0.42</td>
<td>0.72</td>
<td>0.94</td>
<td>1.89</td>
</tr>
</tbody>
</table>

† Acquired from a roughened (oxidation-reduction cycled) gold electrode held at 10 mV for 20 min.

The coverages range from \( \frac{1}{3} \) ML at −240 mV, in agreement with values for the \((\sqrt{3} \times \sqrt{3})R30^\circ\) monolayer observed in STM studies (Gao et al. 1992b; Lay et al. 2003; Vericat et al. 2004), to ~1 ML in the potential region in which bulk S₈ is actively formed. The increase in surface coverage at −140 mV with the onset of the oxidative current was coincident with the formation of S–S bonds as observed by SERS. A coverage of \( \approx \frac{2}{3} \) ML was seen at −40 mV, at which potential the characteristic adsorbed polymeric sulfur band at 460 cm⁻¹ became apparent. This is in agreement with the coverage value reported for arrays of rectangular sulfur rings at potentials close to the reversible potential for S₈ formation (Vericat et al. 2001). The near-monolayer value at 10 mV represents the coverage of the surface after having undergone significant bulk S₈ formation as evidenced by SERS. A coverage value of 1.89 ML acquired on a roughened SERS electrode after 20 min at the same potential may indicate that sulfur species, such as polysulfide ions, which are intermediates in the oxidation of S⁻² to S⁰ (Hamilton and Woods 1983), were trapped in the roughened SERS surface.
7.2.2. Thiosulfate Solutions

Sulfur coverages were determined after various treatments in thiosulfate media on a gold SERS electrode held at various potentials of interest. SERS scans were acquired prior to removal of the electrode for coverage determination. The experiment involved holding an electrode in sodium or ammonium thiosulfate solutions, with and without ammonia additions, for 18 min at lower potentials or 5 min for higher potentials before removal. Upon removal from the cell, the electrode was rinsed thoroughly with ultrapure water and transferred to a cell containing 0.1 mol dm$^{-3}$ H$_2$SO$_4$. A triangular potential scan was then applied from the rest potential to an upper limit of 1.81 V. SERS spectra were collected in real time during the scan. The oxide monolayer coverage was then measured to determine the effective electrode area.

A typical voltammogram after holding the potential at 510 mV for 15 min in 0.1 mol dm$^{-3}$ (NH$_4$)$_2$S$_2$O$_3$, is presented as Figure 7-3A. Integration of the anodic charge on the positive going scan gave a measure of the 6e$^-$ oxidation of sulfur on the gold surface to sulfate ions together with that of oxygen adsorption on the gold surface. The latter charge was obtained by integration of the cathodic peak from the return scan arising from reduction of the oxide layer. Figure 7-3A also presents the oxide monolayer stripping voltammogram recorded for that particular electrode, applied immediately following the scans to determine the charge due to oxidation of sulfur to sulfate.
Figure 7-3. (A) A cyclic voltammogram from 0.21 V, initially in the positive-going direction, with potential limits of 0.21 V and 1.81 V, recorded after a gold electrode was held at 0.51 V for 15 min in 0.1 mol dm$^{-3}$ (NH$_4$)$_2$S$_2$O$_8$; negative-going linear potential sweep voltammogram after the electrode was then held at 1.81 V for 100 s in 0.1 mol dm$^{-3}$ H$_2$SO$_4$ (dashed line). Scans at 40 mV s$^{-1}$. (B) SERS spectra recorded in real time at each of the potentials marked on the voltammogram; these potentials are: initial positive-going scan, A 0.41 V, B 1.14 V, C 1.48 V; return scan, D 1.34V, E 1.21 V, F 0.81 V; second positive-going scan G 0.41 V.
Figure 7-3B presents SERS spectra recorded in real time during the potential scan shown in Figure 7-3A. At the start of the positive-going potential scan, point [A], a SERS band was observed at 432 cm⁻¹ that was assigned to νₜₛₛ. The band remains up to the commencement of an anodic current at [B]. The νₐₜₛ band disappears when the anodic current flows and a band at 490 cm⁻¹ appears attributed to νₐₜₒ from adsorption of oxygen on the gold surface ([C]). The νₐₜₒ band remains on the return scan ([D] and [E]) until the cathodic peak arising from oxygen desorption has passed. At lower potentials on the negative-going scan, no discernible Raman bands were observed in the relevant wavenumber region ([F] and [G]).

For each of the systems studied, i.e., 0.1 mol dm⁻³ Na₂S₂O₃; 0.1 mol dm⁻³ (NH₄)₂S₂O₃; 0.1 mol dm⁻³ Na₂S₂O₃, 0.4 mol dm⁻³ NH₃; 0.1 mol dm⁻³ (NH₄)₂S₂O₃, 0.4 mol dm⁻³ NH₃; the sulfur coverage at 310 mV was close to ⅓ ML. That is, one sulfur atom was adsorbed for three surface gold atoms.

### Table 7-2: Sulfur coverage on gold electrode determined by voltammetry

<table>
<thead>
<tr>
<th>Monolayer Sulfur Coverage</th>
<th>18 min at 310 mV</th>
<th>18 min at 510 mV</th>
<th>5 min at 710 mV</th>
<th>5 min at 810 mV</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1 M Na₂S₂O₃</td>
<td>0.35 / 0.43*</td>
<td>0.51</td>
<td></td>
<td>0.90</td>
</tr>
<tr>
<td>0.1 M (NH₄)₂S₂O₃</td>
<td>0.35</td>
<td>0.42</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>0.1 M Na₂S₂O₃, 0.4 M NH₃</td>
<td>0.38</td>
<td>0.32, 0.38</td>
<td>†</td>
<td>†</td>
</tr>
<tr>
<td>0.1 M (NH₄)₂S₂O₃, 0.4 M NH₃</td>
<td>0.36</td>
<td>0.37</td>
<td>0.34</td>
<td></td>
</tr>
</tbody>
</table>

* held at 310 mV for 140 min  † passivates with gold oxide formation

The SERS spectra for gold in the various thiosulfate solutions at 310 mV are shown in Figure 7-4. Scans acquired in water following removal from the sulfide solution and on transfer to the acid solution are also shown. All systems show evidence of
gold-sulfur and sulfur-sulfur bonding, with the exception of the ammonium thiosulfate, which shows only a weak, broad \( \nu_{\text{S-S}} \). The tetrathionate-like species was observed with ammonia addition to both sodium and ammonium thiosulfate solutions.

Figure 7-4: SERS spectra acquired for gold in various thiosulfate solutions at 310 mV prior to coverage determination in acid.

At 510 mV in the absence of ammonia, the sulfur coverage increases to \( \sim 1/2 \) ML, whilst in the presence of ammonia it remains at \( \sim 1/3 \) ML. At this potential the SERS scans show the formation of surface-bonded \( S_n \), and some bulk \( S_8 \) in the sodium solution; predominantly bulk \( S_8 \) in ammonium thiosulfate; and the tetrathionate-like species. The thiosulfate solution in the presence of ammonia shows bands at 925 cm\(^{-1}\), which may tentatively be assigned to the \( \delta_{\text{symN-H}} \) mode of adsorbed ammonia (Handy et al. 1999).
At 810 mV, the sulfur coverage observed for 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$ was close to a 1:1 S/Au ratio. The anodic current could not be controlled at 810 mV in 0.1 mol dm$^{-3}$ (NH$_4$)$_2$S$_2$O$_3$ by the potentiostat available; hence the coverage value of 0.62 ML was determined at 710 mV. The 0.1 mol dm$^{-3}$ (NH$_4$)$_2$S$_2$O$_3$, 0.4 mol dm$^{-3}$ NH$_3$ solution was also examined at 710 mV and the coverage remained ~$\frac{1}{3}$ ML. At higher potentials in this solution, SERS spectra displayed a broad band centred at 490 cm$^{-1}$ due to gold oxide formation. The oxide layer passivated the gold surface and prevented the adsorption of sulfide.
Figure 7-6: SERS spectra acquired for gold in various thiosulfate solutions at (A) 710 mV, (B) 810 mV & (C) 710 mV prior to coverage determination in acid.
The atomic radius of elemental sulfur is 0.104 nm and the ionic radius of sulfur(-II) is 0.184 nm (Atkins 1978). The atomic radius for Au\(^0\) is 0.144 nm hence a much higher S/Au ratio becomes possible when sulfur converts from the S\(^{-II}\) to the S\(^0\) state. The radius of sulfur covalently bonded to gold is significantly larger than the atomic radius of gold metal and hence the S/Au ratio must be much less than unity. If the S-S distance in the ad-layer is similar to that of 0.502 nm in the Au\(_2\)S crystal (Ishikawa et al. 1995), then the S/Au ratio would be \(\frac{1}{3}\), which is close to the ratio found in this investigation.

There was some correspondence between the sulfur coverages reported in Table 7-2 and the voltammetric currents for gold dissolution shown in Figure 5-5 in that the presence of ammonia results in lower sulfur coverages in the potential region of thiosulfate oxidation (> 310 mV) and correspondingly higher thiosulfate oxidation rates. Other factors must also be operative however in determining the rate of gold dissolution at 310 mV. The role of ammonia in enhancing gold oxidation is clearly more complex than that of simply reducing the sulfur surface coverage.

**7.2.3. Ammoniacal Copper(II) Thiosulfate**

Copper sulfide is known to oxidize to Cu\(^{2+}\) by a two electron process, irrespective of the formal valence of copper in the sulfide layer (Woods et al. 1987). In order to determine copper and sulfur coverages after leaching in tetra-ammine copper(II) ammonium and sodium thiosulfate media, the gold electrode was withdrawn from the cell, washed thoroughly with ultrapure water and transferred to a cell containing deaerated 0.1 mol dm\(^{-3}\) H\(_2\)SO\(_4\). For copper determination, a linear sweep at 1 mV s\(^{-1}\) was applied from the OCP to 710 mV, then a triangular potential scan at 40 mV s\(^{-1}\) applied between
710 mV and an upper limit of 1.81 V. Typical voltammograms used for determination of surface coverage of copper and sulfur after leaching gold in a tetra-ammine copper(II) sodium thiosulfate solution are shown in Figure 7-7.

An anodic peak can be seen on the linear sweep voltammogram with current commencing at ~ 410 mV, which is in the region expected for oxidation of copper sulfides to elemental sulfur (Woods et al. 1987). Further corroboration of this peak being due to removal of copper was obtained by running analogous experiments in the absence of copper. As expected, no anodic peaks were observed in this potential region when copper ions were not present in the leach solution. Copper coverages were calculated by integration to determine the charge passed, then comparing this charge to that passed on reduction of an oxygen monolayer.

Figure 7-7: A linear potential sweep voltammogram at 1 mV s\(^{-1}\) after immersion for 15 min in 0.1 M Na\(_2\)S\(_2\)O\(_3\), 0.4 M NH\(_3\), 0.01 M CuSO\(_4\); and transfer to 0.1 M H\(_2\)SO\(_4\) (---); a subsequent cyclic voltammogram at 40 mV s\(^{-1}\) commenced at 710 mV in the positive-going direction, with potential limits of 1.81 V and 210 mV (-----); a following negative-going linear potential sweep voltammogram after the electrode was then held at 1.81 V for 100 s (----).
Table 7-3 presents sulfur and copper coverages obtained for a gold electrode at various times during a sodium thiosulfate leach and Table 7-4 for an ammonium thiosulfate leach. The sulfur coverages of both the sodium and ammonium leach systems show a similar trend over time, with \( \frac{1}{2} \) monolayer (ML) coverage at 20 min increasing to \( \frac{2}{3} \) ML coverage when held overnight. The copper coverage of both systems was close to \( \frac{1}{3} \) ML overnight. The determined S/Cu ratio of 2:1 would support the proposal that sulfur was bound to both copper and gold on the electrode surface.

**Table 7-3: Sulfur and copper coverage on gold electrode in cupric tetra-ammine sodium thiosulfate leach solution as determined by voltammetry.**

<table>
<thead>
<tr>
<th>Leaching time</th>
<th>Fractional coverage / ML</th>
<th>Cu²⁺/NH₃/Na₂S₂O₃</th>
<th>Cu²⁺/NH₃/(NH₄)₂S₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min</td>
<td></td>
<td>S 0.47</td>
<td>Cu 0.33</td>
</tr>
<tr>
<td>1 hr</td>
<td></td>
<td>S 0.56</td>
<td>Cu 0.21</td>
</tr>
<tr>
<td>2 hr</td>
<td></td>
<td>S 0.66</td>
<td>Cu 0.25</td>
</tr>
<tr>
<td>5 hr</td>
<td></td>
<td>S 0.62</td>
<td>Cu 0.19</td>
</tr>
<tr>
<td>16 hr</td>
<td></td>
<td>S 0.65</td>
<td>Cu 0.26</td>
</tr>
</tbody>
</table>

**Table 7-4: Sulfur and copper coverage on gold electrode in cupric tetra-ammine ammonium thiosulfate leach solution as determined by voltammetry**

<table>
<thead>
<tr>
<th>Leaching time</th>
<th>Fractional coverage / ML</th>
<th>Cu²⁺/NH₃/(NH₄)₂S₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>20 min</td>
<td></td>
<td>Cu²⁺/NH₃/Na₂S₂O₃</td>
</tr>
<tr>
<td>1 hr</td>
<td></td>
<td>S 0.50</td>
</tr>
<tr>
<td>2 hr</td>
<td></td>
<td>S 0.55</td>
</tr>
<tr>
<td>5 hr</td>
<td></td>
<td>S 0.52</td>
</tr>
<tr>
<td>16 hr</td>
<td></td>
<td>S 0.68</td>
</tr>
</tbody>
</table>
7.3. **Leaching Rate in Ammoniacal Copper(II) Thiosulfate**

In the previous chapter, the diminution of SERS signal on oxidation-reduction cycled gold electrodes was reported after 20 min immersion in ammoniacal copper(II) thiosulfate leaching solutions. A leaching experiment was performed in order to verify that gold leaching continued after the loss of SERS signal and that the loss of signal was not due to a passivation of the leaching process. This experiment demonstrated that, for both cupric tetra-ammine sodium or ammonium thiosulfate solutions, leaching continued at a constant rate over a 5-hour period.

A polished rotating gold electrode of the same purity as the electrode used for SERS studies was leached in thiosulfate solutions over a 16 hr period. Samples of cupric tetra-ammine sodium and ammonium leach solutions were extracted hourly for the first five hours and analysed for gold using AAS analysis to determine the rate of gold dissolution. The results of the analyses are presented in Figure 7-8.

![Figure 7-8: Leaching kinetics of gold in cupric tetra-ammine sodium (Na⁺) and ammonium (NH₄⁺) thiosulfate solutions as determined by AAS.](image)
The gold concentration was seen to increase linearly for the leaching period from one to five hours. The leaching rates were calculated to be 8.3 and 4.0 mol m$^{-2}$ s$^{-1}$ for the sodium and ammonium thiosulfate systems, respectively. Similar rates were observed in REQCM studies, in which initial rates prior to 13 min were found to be non-linear and consistent with transient passivation (Jeffrey 2001). The sodium thiosulfate leaching system was seen to proceed at twice the rate of the ammonium system, with the difference in rate attributable to the higher pH of 11.4 in the sodium system, as compared with pH 9.8 in the ammonium system. The copper(II) tetra-ammine complex was stabilised in the more alkaline sodium solution by coordination of OH$^-$, allowing the solution to maintain an increased concentration of copper(II) as compared with the ammonium system (Breuer and Jeffrey 2000).

As the gold was seen to continue dissolving after 1 hr, the diminution of SERS signal seen after 20 min leaching would appear to be due to the loss of SERS surface and not to a cessation of the leaching process.
7.4. **X-ray Photoelectron Spectroscopy**

XPS was employed in order to determine the presence and chemical state of surface species on gold electrochemically polarised in sodium thiosulfate solutions and leached in ammoniacal copper(II) thiosulfate solutions. The studies showed the presence of various types of sulfur on polarised electrodes and of sulfur, nitrogen and copper on leached electrodes. Both oxidation-reduction cycled and polished electrodes were used in polarisation studies of gold in thiosulfate solutions, the former in order to relate the XPS characteristics to the species observed in the SERS spectra.

7.4.1. **Oxidation-Reduction Cycled Gold in Thiosulfate**

Oxidation-reduction cycled gold electrodes were exposed to thiosulfate solutions in order to compare XPS results with SERS spectra acquired from the electrodes while still in solution and *ex situ* prior to use as an XPS sample. The XPS spectra acquired from the roughened electrode would be expected to differ from that acquired from an optimally prepared sample on a smooth electrode due to surface roughness and potential for entrapment of solution species within the dendritic structure. The results of this experiment were primarily intended to allow the observation of relationships between SERS and XPS spectra.

7.4.1.1. **Sodium Thiosulfate at 310 mV for 1 hr**

Oxidation-reduction cycled gold electrodes were polarised in 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$ at 310 mV, a potential at which gold dissolution is known to occur. SERS spectra were collected for up to one hour *in situ*. The electrode was then removed from the thiosulfate solution and placed in ultrapure water to remove soluble species from the surface. The electrode was then withdrawn and allowed to dry in air.
Figure 7-9: SERS spectra from a gold electrode prior to XPS examination: *in situ* at 310 mV in 0.1 M Na₂S₂O₃ solution and *ex situ* immersed in water and after drying in air.

Figure 7-9 shows SERS spectra taken from the electrode prior to XPS examination. *In situ*, a broad band at 325 cm⁻¹ assigned to $\nu_{\text{Au-S}}$ in gold sulfide and a $\nu_{\text{S-S}}$ mode at 447 cm⁻¹ were seen to develop with time. The intensity of these bands decreased when the electrode was removed from solution under potential control and immersed in ultrapure water. A dramatic change was seen upon removal of the electrode from water and drying in air, with the formation of a sharp $\nu_{\text{S-S}}$ band at 413 cm⁻¹ and a broad $\nu_{\text{symS-O}}$ centred at 1018 cm⁻¹. Raman bands of solid gold dithiosulfate presented in Figure 2-16 are seen to occur at 415 cm⁻¹ and 1039 cm⁻¹ for $\nu_{\text{S-S}}$ and $\nu_{\text{symS-O}}$, respectively, therefore it is possible that gold dithiosulfate had formed on the surface after *ex situ* exposure (Woods *et al.* 2006). A strong, sharp $\nu_{\text{Au-S}}$ band at 266 cm⁻¹ was seen in the region in which monoatomic gold sulfide stretches have been observed.
(Gao et al. 1992b), with a shoulder at 325 cm\(^{-1}\), the peak maximum for Au\(_2\)S, as shown in Figure 6-3.

An XPS survey scan of the oxidation-reduction cycled electrode is shown in Figure 7-10. The scan shows the presence of carbon, oxygen and approximately 4 atom\% of sulfur on the underlying gold substrate. The relative atomic and mass percentages of the atoms are presented in Table 7-5. Quantification of the oxygen and sulfur peaks gives an approximate value due to poor signal to noise ratio, approaching the limit of detection of the instrument.

Figure 7-10: Al K\(_\alpha\) XPS survey scan of gold SERS electrode after polarising at 310 mV in 0.1 M Na\(_2\)S\(_2\)O\(_3\) for 1 hr.
Table 7-5: Quantification of XPS survey scan for a gold SERS electrode polarised for 1 hr at 310 mV in 0.1 M Na$_2$S$_2$O$_3$.

<table>
<thead>
<tr>
<th></th>
<th>BE (eV)</th>
<th>FWHM (eV)</th>
<th>Raw Area (CPS)</th>
<th>RSF</th>
<th>Atom%</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>532</td>
<td>3.296</td>
<td>31932.5</td>
<td>0.780</td>
<td>9.7</td>
<td>1.7</td>
</tr>
<tr>
<td>C 1s</td>
<td>285</td>
<td>3.294</td>
<td>46890.0</td>
<td>0.278</td>
<td>44.9</td>
<td>6.0</td>
</tr>
<tr>
<td>S 2p$_{3/2}$</td>
<td>162</td>
<td>4.401</td>
<td>8625.0</td>
<td>0.668</td>
<td>4.0</td>
<td>1.4</td>
</tr>
<tr>
<td>Au 4f$_{7/2}$</td>
<td>84</td>
<td>2.937</td>
<td>752552.6</td>
<td>6.250</td>
<td>41.4</td>
<td>90.9</td>
</tr>
</tbody>
</table>

The level of contamination of the surface by carbon and oxygen was greater than that seen in an oxidation-reduction cycled electrode without thiosulfate treatment (34.7 and 6.8 atom%, respectively, from section 4.4.2); but less than that seen on a polished gold electrode (16.8 and 65.3 atom%, respectively, from section 4.4.1).

The sulfur region was investigated in a detailed scan, which is presented in Figure 7-11. Sulfur doublets were fitted using a Gaussian-Lorentzian lineshape and a linear background, assuming a splitting of 1.18 eV and intensity ratio 2:1.

Figure 7-11: Detail of sulfur 2p region of Al K$_{\alpha}$ XPS scan from gold SERS electrode after polarising at 310 mV in 0.1 M Na$_2$S$_2$O$_3$ for 1 hr.
The peak fitting indicated the presence of S 2p$_{3/2}$ peaks at 162.0 and 163.3 eV, quantified as 75 and 25 %, respectively, of the total sulfur. The lower-energy S 2p$_{3/2}$ peak at 162.0 eV lies between 161.2 eV, as reported for sulfur bound to metal (Buckley et al. 1987; Moulder et al. 1995), and 162.3 eV, as reported for pyritic sulfur, S$_2^{2-}$ (Buckley et al. 1987). The value of the higher binding energy S 2p$_{3/2}$ peak at 163.3 eV lay between that of pyritic sulfur and the S$_0^{0}$ 2p$_{3/2}$ binding energy of 164.0 eV (Moulder et al. 1995).

The S/Au ratio for this sample was found to be ~0.10, close to the value of 0.084 reported for a self-assembled monolayer (SAM) of butanethiol on a Au(111) surface (Hutt and Leggett 1997). That SAM had a ($\sqrt{3}$x$\sqrt{3}$)R30° structure with the sulfur atom in each thiol molecule sited between three gold atoms, i.e., the ratio of sulfur to gold atoms in the surface layer is 1:3. This value is in reasonable agreement with the electrochemical surface coverage of sulfur reported in Table 7-2 for 0.1 mol dm$^{-1}$ thiosulfate held at 310 mV.

### 7.4.1.2. Sodium Thiosulfate at the mixed potential for 72 hrs

An oxidation-reduction cycled gold electrode was leached at the mixed potential in a 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$ solution over a 72 hr period. The initial mixed potential of this system was 150 mV, which increased to 180 mV over 16 hrs. The electrode was removed from the thiosulfate solution and placed in ultrapure water to extract water-soluble species from the surface. Figure 7-12 shows SERS spectra taken from the *in situ* surface and from the *ex situ* surface after rinsing in ultrapure water and drying in air.
The SERS spectra show similar characteristics to that observed \textit{ex situ} on a gold electrode withdrawn from 1 mM Na$_2$S in 0.05 M Na$_2$B$_4$O$_7$ solution as seen in Figure 6-32 and may indicate the development of a layer of adsorbed S$_8$. Characteristic vibrational modes of thiosulfate and gold sulfide are absent from the spectrum.

An XPS survey spectrum collected from this surface is presented in Figure 7-13. Similarly to that for the electrode held at 210 mV, the scan shows the presence of carbon, oxygen and sulfur on the underlying gold substrate.
Figure 7-13: Al Kα XPS survey scan of gold SERS electrode leaching in 0.1 M Na₂S₂O₃ at the mixed potential in air for 72 hrs.

The relative atomic and mass percentages of the atoms are presented in Table 7-6. The level of contamination of the surface by carbon and oxygen was seen to increase relative to that of the electrode held in solution for an hour.

Table 7-6: Quantification of XPS survey scan for a gold SERS electrode after leaching in 0.1 M Na₂S₂O₃ at the mixed potential in air for 72 hrs.

<table>
<thead>
<tr>
<th></th>
<th>BE (eV)</th>
<th>FWHM (eV)</th>
<th>Raw Area (CPS)</th>
<th>RSF</th>
<th>Atom%</th>
<th>Weight%</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1s</td>
<td>532</td>
<td>3.281</td>
<td>45207.5</td>
<td>0.780</td>
<td>11.3</td>
<td>2.4</td>
</tr>
<tr>
<td>C 1s</td>
<td>285</td>
<td>4.110</td>
<td>65317.5</td>
<td>0.278</td>
<td>51.8</td>
<td>8.2</td>
</tr>
<tr>
<td>S 2p₃/₂</td>
<td>163</td>
<td>3.845</td>
<td>7220.0</td>
<td>0.668</td>
<td>2.8</td>
<td>1.2</td>
</tr>
<tr>
<td>Au 4f₇/₂</td>
<td>85</td>
<td>6.391</td>
<td>751507.6</td>
<td>6.250</td>
<td>34.1</td>
<td>88.2</td>
</tr>
</tbody>
</table>
The sulfur region was investigated in a detailed scan, which is presented in Figure 7-14. Sulfur doublets were fitted using a Gaussian-Lorenzian lineshape and a linear background, assuming a splitting of 1.18 eV and intensity ratio 2:1. The weak sulfur peak was fitted to three doublets, with S 2p\textsubscript{3/2} peaks of 161.7, 162.5 and 163.4 eV.

Figure 7-14: Detail of sulfur 2p region of Al K\textsubscript{α} XPS scan from a gold SERS electrode after leaching in 0.1 M Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} at the mixed potential in air for 72 hrs.
The binding energy of the peak at 161.7 eV, close to that of 161.2 eV reported for metal sulfides (Buckley et al. 1987; Moulder et al. 1995), comprised 47 % of the total sulfur on the surface. The peak at 162.5 eV was closer to the value of 162.3 eV found for pyritic sulfur, \( \text{S}_2^{2-} \) (Buckley et al. 1987) and represented 30 % of the sulfur coverage. The peak with the highest binding energy at 163.4 eV approaches the \( \text{S}^0 \) 2p\(_{3/2}\) binding energy of 164.0 eV (Moulder et al. 1995) and comprised 23 % of the sulfur coverage. The S/Au ratio for this sample was found to be ~0.08.

### 7.4.2. Polished Gold in Thiosulfate

Experiments were performed using polished electrodes in order to improve the sensitivity of XPS studies of sulfur environments on gold polarised in thiosulfate solution by eliminating sulfur species trapped in the dendritic structure of the ORC surface. The electrodes were abraded on P1200 SiC paper, sonicated in ultrapure water then subjected to 1 hr in an oven at 450 ºC prior to immersion in 0.1 mol dm\(^{-3}\) sodium thiosulfate solutions. The electrodes were polarised at 210 and 310 mV, potentials between which gold dissolution is known to occur in REQCM studies (Chandra and Jeffrey 2004).

XPS regional sulfur scans from polished electrodes polarised at 210 and 310 mV in 0.1 mol dm\(^{-3}\) sodium thiosulfate solutions are presented in Figure 7-15. The spectra both show doublets at 161.6 eV in the region expected for metal sulfides (Buckley et al. 1987; Moulder et al. 1995). The intensity of the doublets is close to 2:1, with splitting close to the expected value of 1.18 eV. The S 2p\(_{3/2}\) peak in the 310 mV sample may also contain a higher energy sulfur component at 163 eV, but this
in within the order of the spectral noise. The S/Au ratios were found to be 0.05 for the sample polarised at 210 mV and 0.07 for that polarised at 310 mV.

Figure 7-15: S 2p$_{3/2}$ region of XPS spectrum of gold polarised in 0.1 M Na$_2$S$_2$O$_3$ at (A) 210 mV and (B) 310 mV.

7.4.3. Ammoniacal Copper(II) Sodium Thiosulfate

A gold electrode abraded with P 1200 SiC was used for XPS studies of ammoniacal copper(II) sodium thiosulfate leaching. Following abrasion, the electrode was sonicated in ultrapure water then subjected to 1 hr in an oven at 450 ºC. The electrode was then oxidised by peroxide in an ammonia solution to minimise copper impurities prior to immersion in cupric-ammonium sodium thiosulfate solution. Identical samples were placed in the vacuum simultaneously and examined within an hour of each other. These samples were designated A & B, with sample A spending approximately 15 min under vacuum prior to examination. In order to maximise the signal from the surface species,
a pass energy of 40 eV and X-ray power of 225 W were used and this was considered an upper limit for use with samples containing volatile species such as sulfur and ammonia.

XPS examination of the gold electrode after immersion for 1 hr in a solution containing 0.1 mol dm$^{-3}$ sodium thiosulfate, 0.4 mol dm$^{-3}$ ammonia and 0.01 mol dm$^{-3}$ copper(II) sulfate showed the presence of copper, nitrogen and sulfur on the gold surface. Figure 7-16 presents XPS spectra of the Cu 2p and N 1s regions from sample A. The copper binding energies of both samples were found to be typical of copper(I) compounds, as tabled in Table 2-5, with the Cu 2p$_{3/2}$ peak appearing at 932.0 eV for both samples A and B. The N 1s spectra displayed peaks at 399 eV in both samples, may arise from the presence of ammonia in the surface layer.

It is not possible to distinguish unequivocally between sulfur bonded to gold and to copper from the S 2p binding energy as that for sulfur bonded to copper and to gold are similar. The S 2p$_{3/2}$ binding energy for sulfur in Cu$_2$S is 161.5 eV (Gebhardt et al. 1986) and a value of 161.2 eV has been observed for sulfur bonded to gold (Buckley et al. 1987). Evidence of copper(I) on the gold surface would confirm the presence of copper as a sulfide. Due to the inability to determine the presence of an oxidised gold(I) species on the surface due to the massive background substrate signal of gold(0), the bonding of sulfur to gold can be neither demonstrated nor excluded by this technique.
7.4.3.1. Sulfur 2p Region

The predominant S 2p\textsubscript{3/2} peaks had binding energies at \(~161.3\) eV, in the region expected for a metal sulfide. The ratio of the intensities of the S 2p\textsubscript{3/2} spectrum to that of the S 2p\textsubscript{1/2} from the surface was slightly less than two, which indicated that there was more than one sulfur environment. A minor intensity was observed near 168 eV in the S 2p spectrum, which indicates that there was a small amount of sulfate on the gold surface. Region sulfur scans were fitted using a Gaussian-Lorentzian lineshape for doubles of spacing 1.18 eV, FWHM 0.9 eV and a ratio of 1:2. Three coupled doublets were required in each case to fit these criteria. The fitted spectra are shown in Figure 7-17. A difference is noted between both samples, with the results of the quantifications tabled in Table 7-7.

Figure 7-16: Al K\textsubscript{a} XPS detail spectra of: a) Cu 2p; b) N 1s regions for gold leached for 1 hr in a solution of 0.1 mol dm\textsuperscript{-3} Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3}, 0.4 mol dm\textsuperscript{-3} NH\textsubscript{3}, 0.01 mol dm\textsuperscript{-3} CuSO\textsubscript{4}. Pass energy 40 eV, X-ray power 225 W. This sample (A) had spent minimum time under vacuum.
Figure 7-17: Al Kα XPS detail spectra of S 2p regions for gold leached for 1 hr in a solution of 0.1 mol dm⁻³ Na₂S₂O₃, 0.4 mol dm⁻³ NH₃, 0.01 mol dm⁻³ CuSO₄. Sample A had spent minimum time under vacuum, with sample B having spent a further hour under vacuum. Pass energy 40 eV, X-ray power 225 W.

Table 7-7: Binding energies and percentages of S 2p types on gold leached for 1 hr in a solution of 0.1 mol dm⁻³ Na₂S₂O₃, 0.4 mol dm⁻³ NH₃, 0.01 mol dm⁻³ CuSO₄. Sample (A) had spent minimum time under vacuum, with sample B having spent a further hour under vacuum.

<table>
<thead>
<tr>
<th>Sample A</th>
<th>Sample B</th>
</tr>
</thead>
<tbody>
<tr>
<td>S 2p₃/₂ type</td>
<td>Binding energy, eV</td>
</tr>
<tr>
<td>S1</td>
<td>161.1</td>
</tr>
<tr>
<td>S2</td>
<td>161.5</td>
</tr>
<tr>
<td>S3</td>
<td>162.7</td>
</tr>
</tbody>
</table>
The lower binding energies of the S1 designated sulfur type at 161.1 eV found in both samples were lower than the 161.5 eV expected for copper sulfide (Gebhardt et al. 1986) and closer to 161.2 eV reported for sulfur on gold (Buckley et al. 1987). The S2 sulfurs vary in binding energy between the samples, with 161.5 eV in sample A the same as expected for copper sulfide and 162.0 eV for samples B closer to the 162.3 eV found for pyritic sulfur, S$_2^{2-}$ (Buckley et al. 1987). Both samples show similar S3 binding energies at 162.7 and 162.9 eV, respectively. These energies are very close to the 162.9 eV attributed as being due to monolayer sulfur on gold (Buckley et al. 1987).

7.4.3.2. Volatility of Adsorbates

The quantification of the Cu, S and N peaks intensities are listed as atom% in Table 7-8. The values were calculated relative to gold values of 79.9 and 82.2 atom% for samples A and B, respectively. The table shows results the two leaching specimens designated A and B, both treated identically, but with sample B having spent up to an hour longer under the spectrometer vacuum. The lower nitrogen value found in specimen B could be due to loss of the nitrogen-containing species to the vacuum. Coincident with the decrease in signal of nitrogen, a higher copper content was observed. This may indicate that the ammonia was bound to copper atoms in the surface layer and sited above them, thus causing some attenuation of the copper signal. Thus, the nitrogen content of the surface while still in equilibrium with the solution and prior to rinsing may have been similar to, or greater than, the value of 12% found for copper in specimen B. It would not be possible to preserve such a volatile layer for examination by XPS due to the immediate loss of ammonia from the surface after removal of the electrode from solution.
Table 7-8: Nitrogen, sulfur and copper intensities on gold electrode in cupric tetra-ammine sodium thiosulfate leach solution as determined by XPS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Atom%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>N</td>
</tr>
<tr>
<td>A</td>
<td>7.7</td>
</tr>
<tr>
<td>B</td>
<td>2.2</td>
</tr>
</tbody>
</table>

The S/Au ratios for the samples A and B were 0.07 and 0.04, respectively. The ratio for sample A was similar to the value obtained after treatment for 1 h at 310 mV in 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$, with the lesser value obtained for sample B perhaps indicating the loss of sulfur under vacuum. The decrease in sulfur observed in sample B may indicate volatility of various sulfur compounds, which has been reported for bulk S$_8$ (Grano et al. 1977) and adsorbed surface species with binding energies of 162.9 eV, approaching that of S$_8$ (Buckley et al. 1987). The sulfurs with the higher binding energies decreased under vacuum, while those with the lower binding energies, characteristic of sulfides adsorbed on gold, underwent relative increase.

Factors such as volatility of surface compounds; attenuation of signal due to adsorbates; and sub-monolayer concentrations of elements being close to the instrumental limit; the determination of surface coverage by this method would appear to be less reliable than by the voltammetric method.

7.5. ATR-FTIR IN CUPRIC TETRA-AMMINE SODIUM THIOSULFATE

Ammonia is a weak Raman scatterer, particularly under the lower frequency lasers, such as HeNe, required for SERS examination of gold. Also, electrochemical methods are unable to provide evidence of the presence of ammonia on the gold surface. ATR-FTIR has therefore been used as a complementary technique to confirm the presence of
coordinated ammonia on the surface of a leached gold electrode. A smooth surface was required for ATR-FTIR due to the need for contact between the reflecting prism and the sample surface. A smooth gold electrode was prepared using P1200 SiC paper followed by oven treatment at 450 °C for 1 hr prior to leaching.

Figure 7-18 shows the ATR spectrum observed after immersion of a smooth gold electrode in 0.1 mol dm$^{-3}$ Na$_2$S$_2$O$_3$, 0.4 mol dm$^{-3}$ NH$_3$, 0.01 mol dm$^{-3}$ CuSO$_4$ for 1 hr, followed by rinsing in ultrapure water and drying in an ultrapure nitrogen stream. The spectrum displayed bands characteristic of an ammine complex. A broad peak centred at 3333 cm$^{-1}$ was observed in the frequency region expected for stretching vibrations, $\nu_{\text{N-H}}$ of N-H bonds in NH$_3$. Peaks observed at 1597 and 1376 cm$^{-1}$ can be assigned to $\delta_{\text{asymH-N-H}}$ and $\delta_{\text{symH-N-H}}$, and at 719 cm$^{-1}$ to $\rho(\text{NH}_3)$ (Nakamoto 1997b). A strong peak at 425 cm$^{-1}$ can be assigned to $\nu_{\text{Cu-N}}$ of ammonia complexed to copper.
(Nakamoto 1997b) and may include contributions from $\nu_{S-S}$ of the sulfur species present on the surface. Weaker peaks at 1118, 1052 and 998 cm$^{-1}$ may be due to the $\nu_{S-O}$ modes of sulfate and other surface species, including polythionates and thiosulfate.

It can be concluded therefore from the ATR-FTIR results that ammonia was present on the surface of gold leached in ammoniacal copper(II) sodium thiosulfate solution and that it was likely to be bound to copper.
8. CONCLUSIONS
8.1. SUMMARY OF RESULTS

The aim of this work has been to characterise the surface species found on gold during electrochemical experiments in thiosulfate and sulfide solutions in order to elucidate the surface processes which passivate the leaching of gold in ammoniacal copper(II) thiosulfate systems. The electro-oxidation of gold in sulfide solutions was studied as a model system. Techniques employed including in situ electrochemistry and concurrent SERS; and ex situ techniques such as XPS and ATR-FTIR. RDE studies were undertaken in order to clarify the electrochemistry of various thiosulfate systems and kinetic studies were undertaken to determine dissolution rates using AAS to measure gold in solution. The following sections summarise the results of experiments using the various experimental techniques.

8.1.1. Rotating Disk Electrochemistry

In RDE investigations of the thiosulfate systems, sodium thiosulfate was found to have the lowest current at gold leaching potentials. The use of ammonium as a counter ion was found to cause an increase the current. Further increase in current occurred with addition of ammonia to both ammonium and sodium thiosulfate solutions. This may indicate disruption of a passive surface coating or the formation of a more stable compound than found in the absence of ammonia. Extremely high currents characteristic of unhindered dissolution resulted from addition of thiourea to both thiosulfate systems.

8.1.2. SERS Substrate

The morphology of the substrate was characterised to determine the nature of the gold SERS surface. The surface was found to show a complex dendritic structure with
nanoscale features in the spatial range associated with the activation of SERS in the more traditional nanoparticulate and grating systems (Kneipp et al. 1999; Moskovits 1985; Tian 2002). This work resulted in the first literature publication of a robust dendritic gold SERS substrate suited to SERS of gold dissolution (Watling and Hope 2006). The substrate was seen to maintain its SERS activity for up to 20 min during dissolution in ammoniacal copper(II) thiosulfate solutions.

8.1.3. Sulfide as a Model System

Studies of the model system of sulfur on gold in acidic conditions showed that a voltammetric prewave occurred below the reversible potential of $S^{2-}/S^0$. This layer was found to have sulfur coverage of $\frac{1}{3}$ ML (Lay et al. 2003; Rodriguez et al. 2003; Vericat et al. 2001; Vericat et al. 2004). There is agreement in the literature that this represents a $(\sqrt{3} \times \sqrt{3})R30^\circ$ structure with sulfur atoms occupying hollow sites between three gold atoms (Gao et al. 1992b; Rodriguez et al. 2003). Spectroscopic evidence showed that the layer was retained in the hydrogen evolution region in acid and borate solutions and only desorbed in 1.0 mol dm$^{-3}$ NaOH.

SERS studies showed the layer to be characterised by the appearance of a $\nu_{Au-S}$ band at 270 cm$^{-1}$ at potentials in the hydrogen evolution region. It is proposed that this may be due to a shift from thermodynamically favoured three-fold sites to the less stable a-top orientation at low potentials with the possibility of interference due to intermediates in hydrogen evolution reactions. This band was seen to diminish with increased potential, concurrent with the appearance of a higher wavenumber $\nu_{Au-S}$ band at $\sim$310 cm$^{-1}$ in sulfide solutions prior to the appearance of $\nu_{S-S}$ bands assigned to a polysulfide species. The possibility of the higher wavenumber $\nu_{Au-S}$ being attributed to bridging sites cannot
be discounted. A literature assignment of this shift as being due to a protonation/deprotonation mechanism of the adsorbed sulfide (Gao et al. 1992b) was shown to be incorrect as ν\text{S-H} bands that would have indicated adsorption of SH\textsuperscript{-} species were found to be absent. When the chemisorbed layer was examined in a sulfide-free acid solution, the band was retained and also displayed a facile change to higher wavenumber with potential. The shifting of ν\text{Au-S} in the absence of sulfide may indicate involvement of both α-top and bridging sites. Due to the high number of possible vibrational states of S atoms shared between three gold atoms in the hollow sites, it is likely that only a weak, broad band in the Raman spectrum would be observed.

At potentials above the S\textsuperscript{III}/S\textsuperscript{0} reversible value, the surface coverage increased. SERS spectra at a sulfur coverage of 0.42 ML show a broad symmetric band centred at 450 cm\textsuperscript{-1} in the ν\text{S-S} region, accompanied by a strong ν\text{Au-S} band at the higher wavenumber of 310 cm\textsuperscript{-1}. These bands can be confidently assigned to the formation of an adsorbed polysulfide species, Au-S\textsubscript{n}.

With increased potential and coverage of 2/3 ML, SERS spectra show the ν\text{S-S} to shift upward to a 460 cm\textsuperscript{-1}, with an associated narrowing of the band and concurrent decrease in intensity of the ν\text{Au-S} band. This can be confidently assigned to the commencement of formation an array of S-S bonds in the adsorbed S\textsubscript{n}. The concurrent decrease in intensity of the ν\text{Au-S} band may indicate a lessening degree of Au-S bonding as the value of \(n\) increases. STM studies at relevant potentials show a close-packed S adlayer composed of arrays of square or rectangular ‘rings’ described as an adsorbed polymeric S\textsubscript{8}, with an estimated sulfur coverage of 2/3 ML (Gao et al. 1992b; Lay et al. 2003; Vericat et al. 2001). It is likely therefore that, above 1/3 ML coverage, the value of \(n\) in
the $S_n$ ranges from 2 and 8 with potential and that the limiting $\nu_{S-S}$ at 460 cm$^{-1}$ is characteristic of $n$ reaching a maximum value of 8. As the potential is further increased, the coverage increases further to 0.9 ML and both $\nu_{S-S}$ and $\delta_{S-S-S}$ bands appear that are characteristic of the formation of bulk $S_8$.

On removal from sulfide solutions at the OCP, a characteristic spectrum was seen to have a sharp $\nu_{S-S}$ band at 460 cm$^{-1}$ and a weak $\nu_{Au-S}$ band at 325 cm$^{-1}$. STM images of a highly regular array of $S_8$ rings in a crown configuration, bound to gold by every second atom, were reported to occur ex situ after withdrawal of a gold electrode from sulfide solution (Gao et al. 1992b). The characteristic SERS bands seen ex situ can be confidently assigned to an adlayer of $S_8$ adsorbed in a crown configuration, Au-$S_8$.

### 8.1.4. Thiosulfate with Additives

The application of increasing potentials to thiosulfate showed varied SERS characteristics in different thiosulfate systems. The sodium thiosulfate system showed a tetrathionate-like species present at the mixed potential, which disappeared prior to the formation of bulk $S_8$ via an Au-$S_8$ intermediate. At potentials greater than the mixed potential in the presence of the ammonium cation, bands appeared that are similar to Au-$S_n$ in the model sulfide system, but with more intense and broader bands in the $\nu_{Au-S}$ region. These bands were similar to that seen in gold sulfide, suggesting that the product formed was a surface gold sulfide with a component of polymeric sulfur, $S_n$.

In the presence of ammonia, a tetrathionate-like species was observed at potentials higher than the mixed potential, on a background of bands due to the presence of a mixed gold sulfide/polysulfide, designated Au$_2$S/$S_n$. Bands occurred at 925 cm$^{-1}$ in
sodium thiosulfate solutions with ammonia addition. These bands appeared to be unrelated to sulfur or sulfoxy species have been tentatively assigned to deformation modes of adsorbed ammonia. Little spectral detail was seen at the mixed potential in thiosulfate systems in the presence of ammonia or ammonium.

Surface species formed over time at leaching potentials showed the formation of $\text{Au}_2\text{S}/S_n$ regardless of cation or presence of ammonia. As this layer was observable experimentally for over 3 hrs, it would indicate the formation of a passive coating as compared with the loss of SERS signal attributed to dissolution of the active surface seen after 20 min in the cupric tetra-amine sodium thiosulfate leach solution.

8.1.5. Thiourea

Thiourea as an additive to thiosulfate solutions was seen to disrupt the S-S bonding of $\text{Au-S}_8$ and $\text{Au}_2\text{S}/S_n$ surface species. The $\text{Au-S}_8$ layer had been formed by chemisorbed sulfide at the OCP, and the $\text{Au}_2\text{S}/S_n$ by holding in sodium thiosulfate solution for 2 hrs at 210 mV. With the disappearance of the bands due to $\nu_{S-S}$, the $\nu_{\text{symS-O}}$ modes of thiosulfate and $\nu_{C-S}$ of thiourea became evident. This indicated bonding of the sulfur atom of thiourea to gold and exposure of thiosulfate to the surface.

8.1.6. Ammoniacal Copper(II) Thiosulfate Leach Solutions

The dominant feature of SERS spectra of the cupric ammonium sodium thiosulfate system were bands due to a tetrathionate-like species with the $\nu_{\text{symS-O}}$ downshifted by ~20 cm$^{-1}$. Bands assigned to $\nu_{\text{Cu-S/Au-S}}$ (Brown et al. 1995; Gao et al. 1992a) and $\delta_{\text{symS-O}}$ were also present. No significant bands were observed in any SERS study of gold in cupric tetra-amine ammonium thiosulfate, despite showing similar coverages of
copper and sulfur in voltammetric studies. The leaching rate in the more alkaline sodium thiosulfate leach solution was seen to be twice that of the ammonium thiosulfate solution and this is attributed to the stabilisation of the cupric tetra-ammine complex with hydroxide at the higher pH of the sodium system.

It has been noted that the SERS activity of the surface was seen to diminish after 20 min and it has been reported that leaching rates in the first 13 min were found to be non-linear and consistent with transient passivation (Jeffrey 2001). It is likely therefore that the species revealed during the 20 min window of opportunity for SERS activity of gold in the ammoniacal copper(II) sodium thiosulfate system may include these transient passivating species. Species that passivate the gold surface are more likely retain SERS activity of the underlying substrate, making the technique more appropriate to the study of passive coatings than to actively dissolving systems.

The presence of ammonia coordinated to copper on the surface of gold leaching in cupric tetra-ammine sodium thiosulfate was observed *ex situ* using ATR FTIR spectroscopy. The presence of copper on the surface of gold leached in cupric tetra-ammine sodium thiosulfate was confirmed using XPS, which showed it to be present in the form of a copper sulfide. XPS studies showed nitrogen intensity to decrease with time under vacuum, accompanied by an increase in the intensity of copper. This may indicate co-adsorption of ammonia is to copper sites at the copper sulfide/solution interface.

Voltammetric coverage experiments indicated that both the ammonium and sodium thiosulfate leach solutions had a S/Cu ratio of 2:1 after leaching for 16 h, indicating that
the sulfur was associated with both gold and copper on the surface. A return of S-S stretching bands observed by SERS after introduction of the rinsed leached surface to an acid solution may indicate the ability of the metal sulfide bonds to weaken and for sulfur-sulfur bonds to form under acid conditions.
8.2. **FUTURE WORK**

Many fundamental questions have been raised during the process of this work. The nature of surface adsorbed tetrathionate-like species seen on the surface of gold in thiosulfate systems warrants further investigation due to its practical significance. It is possible that the different band positions observed in the surface-bound species in the various thiosulfate solutions may be due to adsorption and templating of the S-S bonds by the gold surface during formation and that this may be influenced by factors such as the concentration of thiosulfate and presence of additions.

Observation of the solution chemistry of the ageing leach solutions by conventional Raman spectroscopy was only lightly undertaken and is an area of interest. Thiourea was examined only as an additive to thiosulfate and deserves further investigation as a system in its own right. Research into thiosulfate systems based upon alternative oxidant systems to ammoniacal copper(II) would be of considerable significance.

Studies of gold-sulfide bonding in the hydrogen evolution region have raised questions regarding the specific nature of sulfur adsorption sites and will be the subject of further investigation by our research group.
8.3. CONCLUDING REMARKS

This study has identified the presence of various forms of sulfur on the surface of gold electooxidised in sulfide solutions and leached in thiosulfate solutions. Passivation of the gold surface in sulfide solutions appears to be coincident with the formation of a range of polymeric sulfur surface structures, $\text{Au-S}_n$, where $n = 2$ to 8. When the gold surface was removed from solution and exposed to air, evidence of a highly-ordered layer of adsorbed $\text{S}_8$ was observed. In thiosulfate solutions, an adsorbed tetrathionate $\text{Au-S}_4\text{O}_6$ was formed, which converted to $\text{Au-S}_n$ species with time and increased potential. The addition of ammonia, known to enhance gold dissolution in thiosulfate solutions, caused the appearance of bands in the $\text{Au}_2\text{S}$ region in addition to $\text{Au-S}_n$. The addition of thiourea as an additive disrupted the S-S bonding and favoured the formation $\text{Au}_2\text{S}$, indicating that, during active dissolution, strong $\text{Au}_2\text{S}$ bands are predominant.

The relevance of this work to industrial processes of thiosulfate leaching is that an additive appears to be required to prevent the formation of passivating S-S bonds on the gold surface during thiosulfate leaching. Also, of significance is the formation of the $\text{Au-S}_8$ layer on gold when removed from both thiosulfate and sulfide solutions and exposed to air. This would suggest that admission of air into the leaching system could favour passivation of the gold surface by the formation of a tightly adsorbed layer of $\text{S}_8$. 
8.4. References


249


256


