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Surface Raman scattering of alkanethiols at silver and gold

Bryant, Mark Alan, Ph.D.
The University of Arizona, 1991
SURFACE RAMAN SCATTERING OF ALKANETHIOLS
AT SILVER AND GOLD

by
Mark Alan Bryant

A Dissertation Submitted to the Faculty of the
DEPARTMENT OF CHEMISTRY
In Partial Fulfillment of the Requirements
For the Degree of
DOCTOR OF PHILOSOPHY
In the Graduate College
THE UNIVERSITY OF ARIZONA

1991
As members of the Final Examination Committee, we certify that we have read the dissertation prepared by Mark Alan Bryant entitled SURFACE RAMAN SCATTERING OF ALKANETHIOLS AT SILVER AND GOLD and recommend that it be accepted as fulfilling the dissertation requirement for the Degree of Doctor of Philosophy.

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Date 18 Nov 91

Final approval and acceptance of this dissertation is contingent upon the candidate's submission of the final copy of the dissertation to the Graduate College.

I hereby certify that I have read this dissertation prepared under my direction and recommend that it be accepted as fulfilling the dissertation requirement.

Dissertation Director Jeanne E. Pemberton  
Date 21 Nov 91
STATEMENT BY AUTHOR

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Signed: Mark Alan Bryant
DEDICATION

I would like to dedicate this dissertation to my parents, David and Joan, for their loving support through the years. I want to especially dedicate this to Mom, who, one night in a Mexican restaurant in downtown New Haven, Indiana, during a sad time in my sophomore year as a music student, asked me, "Have you thought about changing your major?" I decided immediately that science was the career for me and I haven't looked back since. And I'm certain my parents are glad, too.

I would also like to dedicate this dissertation to my friends of the entering class of 1985: Pam Wexler and Hester Clever for lots of friendship and hiking; Troy Mazely, for all the wine tasting; Scott Pianalto, the department just wasn't as much fun after he left; Jeff Johnson, for all those stories; Sue Mitchell and Dee Pauley, for all the great times watching movies and dancing at Cowboys; Tim "rah" Scott and Mitch Bassi, the jesters; Brian "doom and gloom" Hill; Martha Rahl, hanging out with Comanche; Cathy Gehrig, Kathy Borgelt and Millie Firestone; Chris and Janet Palmer, for their friendship and all those years on the V-Ball teams; Lida Latifzadeh, for the predictions and Persian tea; Stacy Evans and Ed for the parties; Jani and James Ingram, for all those thousands of hours of conversation, who would think Indiana and Arizona are similar?; to my fellow cohorts in crime: Jeff and Elena Koleczynski, for many hours of late-night conversation, and Casey Russell, what's so funny 'bout peace, love, and understanding; Steve McCloskey, for the right grip; last one out turn the lights off.
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# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>LIST OF ILLUSTRATIONS</th>
<th>..................................................</th>
<th>12</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>..................................................</td>
<td>20</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>..................................................</td>
<td>21</td>
</tr>
</tbody>
</table>

## 1. INTRODUCTION: SELF-ASSEMBLED ORGANIC MONOLAYERS AT METAL SURFACES

<table>
<thead>
<tr>
<th>Organic Films at Metal Surfaces</th>
<th>..................................................</th>
<th>23</th>
</tr>
</thead>
<tbody>
<tr>
<td>Self-Assembled Organic Films</td>
<td>..................................................</td>
<td>26</td>
</tr>
<tr>
<td>Self-Assembled Films of S-Containing Adsorbates</td>
<td>..................................................</td>
<td>28</td>
</tr>
<tr>
<td>Alkanethiol Self-Assembled Films</td>
<td>..................................................</td>
<td>30</td>
</tr>
<tr>
<td>Adsorption Mechanism</td>
<td>..................................................</td>
<td>30</td>
</tr>
<tr>
<td>Orientation</td>
<td>..................................................</td>
<td>33</td>
</tr>
<tr>
<td>Film Thickness</td>
<td>..................................................</td>
<td>36</td>
</tr>
<tr>
<td>Kinetics of Film Formation</td>
<td>..................................................</td>
<td>37</td>
</tr>
<tr>
<td>Structural Aspects of Au-S Bond</td>
<td>..................................................</td>
<td>38</td>
</tr>
<tr>
<td>Solvent Interaction</td>
<td>..................................................</td>
<td>38</td>
</tr>
<tr>
<td>Film Overlayer Structure and Long-Range Order</td>
<td>..................................................</td>
<td>40</td>
</tr>
<tr>
<td>Conformational Order</td>
<td>..................................................</td>
<td>42</td>
</tr>
<tr>
<td>Defect Structure in the Electrochemical Environment</td>
<td>..................................................</td>
<td>44</td>
</tr>
<tr>
<td>Summary of Previous Work</td>
<td>..................................................</td>
<td>48</td>
</tr>
<tr>
<td>Raman Spectroscopic Investigation of Alkanethiol Films</td>
<td>..................................................</td>
<td>49</td>
</tr>
<tr>
<td>Research Objectives</td>
<td>..................................................</td>
<td>53</td>
</tr>
</tbody>
</table>

## 2. EXPERIMENTAL

<table>
<thead>
<tr>
<th>Raman Spectroscopic Instrumentation</th>
<th>..................................................</th>
<th>56</th>
</tr>
</thead>
</table>
TABLE OF CONTENTS  --- continued

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Excitation</td>
<td>56</td>
</tr>
<tr>
<td>PMT-Raman System</td>
<td>56</td>
</tr>
<tr>
<td>CCD-Raman System</td>
<td>57</td>
</tr>
<tr>
<td>Electrochemical Instrumentation</td>
<td>62</td>
</tr>
<tr>
<td>Electrochemical Cells</td>
<td>62</td>
</tr>
<tr>
<td>Spectroelectrochemical Cells</td>
<td>62</td>
</tr>
<tr>
<td>Differential Reflectance Instrumentation</td>
<td>66</td>
</tr>
<tr>
<td>SEM Instrumentation</td>
<td>68</td>
</tr>
<tr>
<td>XPS Instrumentation</td>
<td>68</td>
</tr>
<tr>
<td>Materials</td>
<td>69</td>
</tr>
<tr>
<td>Procedures</td>
<td>70</td>
</tr>
<tr>
<td>Electrode Mechanical Polishing Procedures</td>
<td>70</td>
</tr>
<tr>
<td>Electrode Roughening Procedure for Differential Reflectance and Related SERS Experiments</td>
<td>70</td>
</tr>
<tr>
<td>Electrode Roughening Procedure for Alkanethiol Experiments</td>
<td>71</td>
</tr>
<tr>
<td>Chemical Polishing of Single-Crystal Ag Surfaces</td>
<td>71</td>
</tr>
<tr>
<td>Film Formation Procedures</td>
<td>71</td>
</tr>
<tr>
<td>Acquisition of Differential Reflectance Spectra</td>
<td>72</td>
</tr>
<tr>
<td>Raman Spectral Acquisition Procedures for Studies of Pyridine and Cl⁻ Adsorbates</td>
<td>73</td>
</tr>
<tr>
<td>Raman Spectral Acquisition Procedures for Alkanethiol Studies</td>
<td>73</td>
</tr>
<tr>
<td>Curve Fitting Procedures</td>
<td>74</td>
</tr>
<tr>
<td>3. RAMAN VIBRATIONAL ASSIGNMENTS FOR n-ALKANETHIOLS</td>
<td>76</td>
</tr>
<tr>
<td>Introduction</td>
<td>76</td>
</tr>
</tbody>
</table>
# TABLE OF CONTENTS --- continued

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\nu$(C-S) Region</td>
<td>77</td>
</tr>
<tr>
<td>$\nu$(C-C) Region</td>
<td>83</td>
</tr>
<tr>
<td>$\nu$(C-H) Region</td>
<td>92</td>
</tr>
<tr>
<td>Conclusions</td>
<td>99</td>
</tr>
<tr>
<td>4. SURFACE SELECTION RULES IN RAMAN SPECTROSCOPY: DETERMINATION OF ORIENTATION OF ALKANETHIOLS AT Ag AND Au</td>
<td>101</td>
</tr>
<tr>
<td>Introduction</td>
<td>101</td>
</tr>
<tr>
<td>Surface Electric Fields at Metal Surfaces</td>
<td>102</td>
</tr>
<tr>
<td>Surface Selection Rules</td>
<td>106</td>
</tr>
<tr>
<td>Estimation of Alkanethiol Orientation at Rough Ag and Au</td>
<td>108</td>
</tr>
<tr>
<td>Conclusions</td>
<td>126</td>
</tr>
<tr>
<td>5. ORIENTATION AND ORDER OF n-ALKANETHIOLS AT SMOOTH Ag SURFACES IN THE AMBIENT ENVIRONMENT</td>
<td>128</td>
</tr>
<tr>
<td>Introduction</td>
<td>128</td>
</tr>
<tr>
<td>Surface Raman Spectra of Alkanethiol Monolayers at Ag</td>
<td>130</td>
</tr>
<tr>
<td>$\nu$(S-H) Region</td>
<td>130</td>
</tr>
<tr>
<td>$\nu$(C-S) Region</td>
<td>132</td>
</tr>
<tr>
<td>$\nu$(C-C) Region</td>
<td>135</td>
</tr>
<tr>
<td>$\nu$(C-H) Region</td>
<td>138</td>
</tr>
<tr>
<td>Orientation of Alkanethiols at Ag</td>
<td>140</td>
</tr>
<tr>
<td>Conclusions</td>
<td>145</td>
</tr>
<tr>
<td>6. ORIENTATION AND ORDER OF n-ALKANETHIOLS AT SMOOTH Au SURFACES IN THE AMBIENT ENVIRONMENT</td>
<td>146</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS --- continued

<table>
<thead>
<tr>
<th>Page</th>
</tr>
</thead>
</table>

Introduction................................................................. 146
Surface Raman Spectra of Alkanethiol Monolayers at Au........ 147
   $\nu$(S-H) Region..................................................... 147
   $\nu$(C-S) Region...................................................... 149
   $\nu$(C-C) Region..................................................... 152
   $\nu$(C-H) Region..................................................... 154
Orientation of Alkanethiols at Au...................................... 157
Conclusions........................................................................... 163

7. COMPARISON OF SURFACE RAMAN SPECTRA OF PYRIDINE AND n-ALKANETHIOLS AT METAL SURFACES OF DIFFERENT MORPHOLOGY...................................................... 164
   Introduction............................................................. 164
   Enhancement Theories of SERS Active Surfaces............... 165
   Characterization of Ag Surface Roughness Morphology with Differential Reflectance Spectroscopy and SERS......................... 169
     0.1 M KCl System..................................................... 169
       Oxidation-Reduction Cycle and Scanning Electron Microscopy...... 169
       Differential Reflectance Spectroscopy.......................... 174
       Surface Enhanced Raman Scattering............................. 176
     0.1 M KCl/0.05 M Pyridine System................................ 178
       Oxidation-Reduction Cycle and Scanning Electron Microscopy...... 178
       Differential Reflectance Spectroscopy.......................... 183
       Surface Enhanced Raman Scattering............................. 185
   Relation Between Absorption and SERS Behavior of Roughened Ag Electrodes......................................................... 188
10

TABLE OF CONTENTS --- continued

Summary of Differential Reflectivity and SERS Studies............ 194
Comparison of Surface Raman Spectra of n-Alkanethiols at Rough, Smooth, and Single-Crystal Surfaces............................................. 194
  \( \nu(C-S) \) Region................................................................. 196
  \( \nu(C-C) \) Region........................................................................ 201
  \( \nu(C-H) \) Region....................................................................... 205
Conclusions......................................................................................... 213

8. ELECTROCHEMICAL CHARACTERIZATION OF n-ALKANETHIOLS AT Ag AND Au................................................................. 214
  Introduction....................................................................................... 214
  Desorption of Alkanethiol Films at Ag and Au.............................. 215
  Cyclic Voltammetry in 0.1 M KCl..................................................... 215
  Cyclic Voltammetry in 0.5 M KOH.................................................... 220
  Pb Deposition at Alkanethiol Films at Ag in 1 mM Pb\(^{2+}\)/0.1 M KCl........ 226
  Model of Defect Structure of Alkanethiol Films............................... 232
  Conclusions....................................................................................... 236

9. SURFACE RAMAN SPECTROSCOPY OF n-ALKANETHIOLS AT Ag AND Au IN THE ELECTROCHEMICAL ENVIRONMENT .............. 239
  Introduction....................................................................................... 239
  Potential Dependence of Raman Scattering of Alkanethiols at Smooth Ag................................................................. 240
  Potential Dependence of Raman Scattering of Alkanethiols at Rough Ag................................................................. 247
  Potential Dependence of Raman Scattering of Alkanethiols at Rough Au................................................................. 255
### TABLE OF CONTENTS --- continued

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potential Dependent Orientation at Smooth Ag and Rough Au</td>
<td>264</td>
</tr>
<tr>
<td>Potential Dependent Orientation at Rough Ag</td>
<td>270</td>
</tr>
<tr>
<td>Spectroscopic Investigation of Ion Penetration at Alkanethiol Films at Ag</td>
<td>272</td>
</tr>
<tr>
<td>Conclusions</td>
<td>278</td>
</tr>
<tr>
<td><strong>10. SURFACE RAMAN SCATTERING OF THIOPHENOL AT SMOOTH Ag, Au, AND Pt</strong></td>
<td></td>
</tr>
<tr>
<td>Introduction</td>
<td>281</td>
</tr>
<tr>
<td>Normal Surface Raman Spectra of Thiophenol at Pt</td>
<td>283</td>
</tr>
<tr>
<td>Conclusions</td>
<td>292</td>
</tr>
<tr>
<td><strong>11. CONCLUSIONS AND FUTURE DIRECTIONS</strong></td>
<td>295</td>
</tr>
<tr>
<td>Overview of Problem</td>
<td>295</td>
</tr>
<tr>
<td>Objectives of Research</td>
<td>295</td>
</tr>
<tr>
<td>Summary</td>
<td>296</td>
</tr>
<tr>
<td>Future Directions</td>
<td>299</td>
</tr>
<tr>
<td>Raman Vibrational Assignments</td>
<td>300</td>
</tr>
<tr>
<td>Surface Raman Selection Rules for the Determination of Adsorbed Orientation</td>
<td>300</td>
</tr>
<tr>
<td>Film Order</td>
<td>300</td>
</tr>
<tr>
<td>REFERENCES</td>
<td>303</td>
</tr>
</tbody>
</table>
**LIST OF ILLUSTRATIONS**

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.</td>
<td>Schematic diagram for PMT-based Raman spectroelectrochemical system</td>
<td>58</td>
</tr>
<tr>
<td>2.2.</td>
<td>Schematic diagram of the Spex double monochromator</td>
<td>59</td>
</tr>
<tr>
<td>2.3.</td>
<td>Schematic diagram for CCD-based Raman spectroelectrochemical system</td>
<td>60</td>
</tr>
<tr>
<td>2.4.</td>
<td>Schematic diagram of the Spex 1877 Triplemate</td>
<td>61</td>
</tr>
<tr>
<td>2.5.</td>
<td>Electrochemical cell used for cyclic voltammetry and ex-situ roughening</td>
<td>63</td>
</tr>
<tr>
<td>2.6.</td>
<td>Schematic diagram of the spectroelectrochemical cell</td>
<td>65</td>
</tr>
<tr>
<td>2.7.</td>
<td>Schematic diagram of the differential reflectance instrumentation</td>
<td>67</td>
</tr>
<tr>
<td>3.1.</td>
<td>Raman spectra in the $\nu$(C-S) region of liquid alkanethiols</td>
<td>78</td>
</tr>
<tr>
<td>3.2.</td>
<td>Raman spectra in the $\nu$(C-S) region of solid alkanethiols</td>
<td>81</td>
</tr>
<tr>
<td>3.3.</td>
<td>Raman spectra in the $\nu$(C-C) region of liquid alkanethiols</td>
<td>84</td>
</tr>
<tr>
<td>3.4.</td>
<td>Raman spectra in the $\nu$(C-C) region of solid alkanethiols</td>
<td>85</td>
</tr>
<tr>
<td>3.5.</td>
<td>Raman spectra in the $\nu$(C-C) region of nonanethiol: solid to liquid transition</td>
<td>90</td>
</tr>
<tr>
<td>3.6.</td>
<td>Raman spectra in the $\nu$(C-C) region of hexadecanethiol: solid to liquid transition</td>
<td>91</td>
</tr>
<tr>
<td>3.7.</td>
<td>Raman spectra in the $\nu$(C-H) region of liquid alkanethiols</td>
<td>93</td>
</tr>
<tr>
<td>3.8.</td>
<td>Decomposed Raman spectra in the $\nu$(C-H) region of liquid butanethiol, octanethiol, dodecanethiol, and octadecanethiol</td>
<td>96</td>
</tr>
<tr>
<td>3.9.</td>
<td>Raman spectra in the $\nu$(C-H) region of solid alkanethiols</td>
<td>99</td>
</tr>
<tr>
<td>4.1.</td>
<td>Graphic illustration of orientation calculation method</td>
<td>112</td>
</tr>
<tr>
<td>4.2.</td>
<td>Decomposed Raman spectra of 1-butanethiol in bulk and at rough Ag</td>
<td>113</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS --- continued

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.3.</td>
<td>Proposed orientation of 1-butanethiol at Ag.</td>
<td>115</td>
</tr>
<tr>
<td>4.4.</td>
<td>Decomposed Raman spectra of 1-pentanethiol in bulk and at rough Ag.</td>
<td>117</td>
</tr>
<tr>
<td>4.5.</td>
<td>Wavelength excitation dependence of Raman spectra of 1-pentanethiol at rough Ag, 514.5, 600, and 720 nm excitation.</td>
<td>119</td>
</tr>
<tr>
<td>4.6.</td>
<td>Decomposed Raman spectra of 1-butanethiol in bulk and at rough Au.</td>
<td>120</td>
</tr>
<tr>
<td>4.7.</td>
<td>Proposed orientation of 1-butanethiol at Au.</td>
<td>121</td>
</tr>
<tr>
<td>4.8.</td>
<td>Decomposed Raman spectra of 1-pentanethiol in bulk and at rough Au.</td>
<td>122</td>
</tr>
<tr>
<td>4.9.</td>
<td>Decomposed Raman spectra of 2-butanethiol in bulk and at rough Au.</td>
<td>124</td>
</tr>
<tr>
<td>4.10.</td>
<td>Proposed orientation of 2-butanethiol at Ag.</td>
<td>125</td>
</tr>
<tr>
<td>5.1.</td>
<td>Raman spectra in the $\nu$(S-H) region of butanethiol in bulk liquid, at smooth Ag, and rough Ag, and of aqueous butanethiolate.</td>
<td>131</td>
</tr>
<tr>
<td>5.2.</td>
<td>Raman spectra in the $\nu$(C-S) region of alkanethiols at smooth Ag.</td>
<td>133</td>
</tr>
<tr>
<td>5.3.</td>
<td>Raman spectra in the $\nu$(C-C) region of alkanethiols at smooth Ag.</td>
<td>136</td>
</tr>
<tr>
<td>5.4.</td>
<td>Raman spectra in the $\nu$(C-H) region of alkanethiols at smooth Ag.</td>
<td>139</td>
</tr>
<tr>
<td>6.1.</td>
<td>Raman spectra in the $\nu$(S-H) region of butanethiol in bulk liquid, at smooth and rough Au, and of aqueous butanethiolate.</td>
<td>148</td>
</tr>
<tr>
<td>6.2.</td>
<td>Raman spectra in the $\nu$(C-S) region of alkanethiols at smooth Au.</td>
<td>150</td>
</tr>
<tr>
<td>6.3.</td>
<td>Raman spectra in the $\nu$(C-C) region of alkanethiols at smooth Au.</td>
<td>153</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS --- continued

<table>
<thead>
<tr>
<th>Figure</th>
<th>Illustration Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.4.</td>
<td>Raman spectra in the $\nu$(C-H) region of alkanethiols at smooth Au</td>
<td>155</td>
</tr>
<tr>
<td>7.1.</td>
<td>Cyclic voltammogram for ORC of Ag in 0.1 M KCl</td>
<td>170</td>
</tr>
<tr>
<td>7.2.</td>
<td>Chronocoulograms for double-potential step ORCs in 0.1 M KCl</td>
<td>172</td>
</tr>
<tr>
<td>7.3.</td>
<td>Scanning electron micrographs for Ag electrodes roughened in 0.1 M KCl at different current densities</td>
<td>173</td>
</tr>
<tr>
<td>7.4.</td>
<td>Differential reflectance results for electrodes roughened in 0.1 M KCl with double potential step ORCs at different current densities</td>
<td>175</td>
</tr>
<tr>
<td>7.5.</td>
<td>SERS results for $\nu$(Ag-Cl) for Ag electrodes roughened in 0.1 M KCl at different current densities, 514.5 and 600 nm excitation</td>
<td>177</td>
</tr>
<tr>
<td>7.6.</td>
<td>Normalized SERS intensity of $\nu$(Ag-Cl) and $\Delta R/R$ for Ag roughened in 0.1 M KCl</td>
<td>179</td>
</tr>
<tr>
<td>7.7.</td>
<td>Cyclic voltammogram for ORC of Ag in 0.1 M KCl/0.05 M pyridine</td>
<td>181</td>
</tr>
<tr>
<td>7.8.</td>
<td>Scanning electron micrographs for Ag electrodes roughened in 0.1 M KCl/0.05 M pyridine at different current densities</td>
<td>182</td>
</tr>
<tr>
<td>7.9.</td>
<td>Differential reflectance results for electrodes roughened in 0.1 M KCl/0.05 M pyridine with double-potential step ORCs at different current densities</td>
<td>184</td>
</tr>
<tr>
<td>7.10.</td>
<td>SERS results for electrodes roughened in 0.1 M KCl/0.05 M pyridine at different current densities: $\nu$(Ag-Cl) and pyridine ring-breathing modes at 514.5 nm excitation</td>
<td>186</td>
</tr>
<tr>
<td>7.11.</td>
<td>SERS results for electrodes roughened in 0.1 M KCl/0.05 M pyridine at different current densities: $\nu$(Ag-Cl) and pyridine ring-breathing modes at 600 nm excitation</td>
<td>187</td>
</tr>
<tr>
<td>7.12.</td>
<td>Normalized SERS intensity of $\nu$(Ag-Cl) and pyridine ring-breathing modes and $\Delta R/R$ for Ag roughened in 0.1 M KCl/0.05 M pyridine</td>
<td>189</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td></td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td></td>
</tr>
<tr>
<td>7.13</td>
<td>Raman spectra in the $\nu(C-S)$ region of butanethiol, dodecanethiol, and octadecanethiol at smooth and rough Ag.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>197</td>
<td></td>
</tr>
<tr>
<td>7.14</td>
<td>Raman spectra in the $\nu(C-S)$ region of butanethiol, dodecanethiol, and octadecanethiol at smooth and rough Au and the effect of number of ORCs on butanethiol spectra.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>199</td>
<td></td>
</tr>
<tr>
<td>7.15</td>
<td>Raman spectra in the $\nu(C-C)$ region of butanethiol, dodecanethiol, and octadecanethiol at smooth and rough Ag and exposure of octadecanethiol film at rough Ag to ca. 90 °C water.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>202</td>
<td></td>
</tr>
<tr>
<td>7.16</td>
<td>Raman spectra in the $\nu(C-C)$ region of butanethiol, dodecanethiol, and hexadecanethiol at smooth and rough Au and exposure of dodecanethiol and hexadecanethiol films at rough Au to liquid $\text{N}_2$.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>203</td>
<td></td>
</tr>
<tr>
<td>7.17</td>
<td>Raman spectra in the $\nu(C-H)$ region of butanethiol, dodecanethiol, and octadecanethiol at smooth and rough Ag and exposure of octadecanethiol film at rough Ag to liquid $\text{N}_2$.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>206</td>
<td></td>
</tr>
<tr>
<td>7.18</td>
<td>Raman spectra in the $\nu(C-H)$ region of butanethiol, pentanethiol, dodecanethiol, and octadecanethiol at smooth and rough Au.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>207</td>
<td></td>
</tr>
<tr>
<td>7.19</td>
<td>Raman spectra in the $\nu(C-H)$ region of butanethiol at Ag (111) and Ag (100) and octadecanethiol at Ag evaporated onto Cr-coated Si (111).</td>
<td></td>
</tr>
<tr>
<td></td>
<td>211</td>
<td></td>
</tr>
<tr>
<td>7.20</td>
<td>Cyclic voltammograms in 0.75 mM $\text{Ti}_2\text{SO}_4/0.5$ M $\text{Na}_2\text{SO}_4/1$ mM $\text{HClO}_4$ of Ag (111) and Ag (100).</td>
<td></td>
</tr>
<tr>
<td></td>
<td>212</td>
<td></td>
</tr>
<tr>
<td>8.1</td>
<td>Cyclic voltammograms for a) bare Ag, b) butanethiol at smooth Ag, c) butanethiol at rough Ag, d) dodecanethiol at smooth Ag in 0.1 M KCl.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>217</td>
<td></td>
</tr>
<tr>
<td>8.2</td>
<td>Cyclic voltammograms for a) bare Au, b) butanethiol at smooth Au, c) butanethiol at rough Au, d) dodecanethiol at smooth Au in 0.1 M KCl.</td>
<td></td>
</tr>
<tr>
<td></td>
<td>219</td>
<td></td>
</tr>
</tbody>
</table>
## LIST OF ILLUSTRATIONS --- continued

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.3.</td>
<td>Cyclic voltammograms for a) bare rough Au, b) butanethiol at rough Au, c) dodecanethiol at smooth Au in 0.1 M KCl</td>
<td>221</td>
</tr>
<tr>
<td>8.4.</td>
<td>Cyclic voltammograms for a) bare Ag, b) butanethiol at smooth Ag, c) dodecanethiol at smooth Ag in 0.5 M KOH</td>
<td>222</td>
</tr>
<tr>
<td>8.5.</td>
<td>Cyclic voltammograms for a) bare Au, b) butanethiol at smooth Au, c) dodecanethiol at smooth Au in 0.5 M KOH</td>
<td>224</td>
</tr>
<tr>
<td>8.6.</td>
<td>Cyclic voltammograms for a) bare Au, b) butanethiol at smooth Au in 0.5 M KOH</td>
<td>225</td>
</tr>
<tr>
<td>8.7.</td>
<td>Cyclic voltammograms for bare Ag in 0.1 M KCl/0.001 M Pb²⁺</td>
<td>227</td>
</tr>
<tr>
<td>8.8.</td>
<td>Cyclic voltammograms for alkanethiol films formed at smooth Ag for ca. 4 hours; a) and b) butanethiol, c) and d) dodecanethiol, e) and f) octadecanethiol in 0.1 M KCl/0.001 M Pb²⁺</td>
<td>229</td>
</tr>
<tr>
<td>8.9.</td>
<td>Cyclic voltammograms for alkanethiol films formed at smooth Ag for ca. 24 hours; a) butanethiol, b) and c) dodecanethiol, d) and e) octadecanethiol in 0.1 M KCl/0.001 M Pb²⁺</td>
<td>231</td>
</tr>
<tr>
<td>8.10.</td>
<td>Proposed model of chain tilt domain boundary defect</td>
<td>233</td>
</tr>
<tr>
<td>8.11.</td>
<td>Cyclic voltammograms for alkanethiol films formed at rough Ag for ca. 24 hours; a) butanethiol, b) and c) dodecanethiol, d) and e) octadecanethiol in 0.1 M KCl/0.001 M Pb²⁺</td>
<td>235</td>
</tr>
<tr>
<td>8.12.</td>
<td>Cyclic voltammograms for alkanethiol films formed at Ag (100) for ca. 9 hours; a) first scan, b) second scan, c) third scan in 0.1 M KCl/0.001 M Pb²⁺</td>
<td>237</td>
</tr>
<tr>
<td>9.1.</td>
<td>Raman spectra in the (\nu(C-S)) region of butanethiol at a) smooth Ag, -0.4 V, b) smooth Ag, -1.0 V, c) smooth Ag, -1.4 V, d) smooth Ag, in air, e) smooth Au, in air</td>
<td>242</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>9.2.</td>
<td>Raman spectra in the $\nu$(C-C) region of butanethiol at a) smooth Ag, -0.4 V, b) smooth Ag, -1.0 V, c) smooth Ag, -1.4 V, d) smooth Ag, in air, e) smooth Au, in air.</td>
<td>243</td>
</tr>
<tr>
<td>9.3.</td>
<td>Raman spectra in the $\nu$(C-H) region of butanethiol at a) smooth Ag, -0.4 V, b) smooth Ag, -1.0 V, c) smooth Ag, -1.4 V, d) smooth Ag, in air, e) smooth Au, in air.</td>
<td>245</td>
</tr>
<tr>
<td>9.4.</td>
<td>Raman spectra in the $\nu$(C-H) region of pentanethiol at a) smooth Ag, -0.2 V, b) smooth Ag, -1.2 V, c) smooth Ag, in air, d) smooth Au, in air.</td>
<td>246</td>
</tr>
<tr>
<td>9.5.</td>
<td>Raman spectra in the $\nu$(C-S) region of butanethiol at a) rough Ag, -0.4 V, b) rough Ag, -1.4 V, c) rough Ag, in air, d) rough Au, in air.</td>
<td>249</td>
</tr>
<tr>
<td>9.6.</td>
<td>Raman spectra in the $\nu$(C-C) region of butanethiol at a) rough Ag, -0.4 V, b) rough Ag, -1.4 V, c) rough Ag, in air, d) rough Au, in air.</td>
<td>251</td>
</tr>
<tr>
<td>9.7.</td>
<td>Raman spectra in the $\nu$(C-H) region of butanethiol at a) rough Ag, -0.4 V, b) rough Ag, -1.4 V, c) rough Ag, in air, d) rough Au, in air.</td>
<td>252</td>
</tr>
<tr>
<td>9.8.</td>
<td>Raman spectra in the $\nu$(C-H) region of dodecanethiol at a) smooth Ag, -0.2 V, b) smooth Ag, -1.4 V, c) rough Ag, -0.2 V, d) rough Ag, -1.4 V.</td>
<td>254</td>
</tr>
<tr>
<td>9.9.</td>
<td>Raman spectra in the $\nu$(C-S) region of butanethiol at rough Au at a) -0.2 V, b) +0.7 V, c) +0.8 V, d) +0.9 V.</td>
<td>257</td>
</tr>
<tr>
<td>9.10.</td>
<td>Raman spectra in the $\nu$(C-C) region of butanethiol at rough Au at a) -0.2 V, b) +0.7 V, c) +0.8 V, d) +0.9 V.</td>
<td>258</td>
</tr>
<tr>
<td>9.11.</td>
<td>Raman spectra in the $\nu$(C-H) region of butanethiol at rough Au at a) -0.2 V, b) +0.7 V, c) +0.8 V, d) +0.9 V.</td>
<td>260</td>
</tr>
<tr>
<td>9.12.</td>
<td>Raman spectra in the $\nu$(C-H) region of pentanethiol at a) rough Au, -0.2 V, b) rough Au, +0.7 V, c) rough Au, in air, d) rough Ag, in air.</td>
<td>261</td>
</tr>
</tbody>
</table>
LIST OF ILLUSTRATIONS --- continued

<table>
<thead>
<tr>
<th>Figure</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>9.13. Raman spectra in the $\nu(S-S)$ region of butanethiol at rough Au at a) -0.2 V, b) +0.6 V, c) +0.7 V, d) +0.8 V, e) +0.9 V</td>
<td>263</td>
</tr>
<tr>
<td>9.14. Models of orientation of 1-alkanethiols at Ag and Au surfaces. a) and c) chain tilt ($\alpha$) of ca. -15°, and rotation ($\beta$) of ca. 45° about chain axis; c) and d) $\alpha$ of ca. +30° and $\beta$ of ca. 45°. Adsorption of alkanethiols at Ag in 0.1 M KCl at a) -0.2 V, b) -1.0 V. Adsorption of alkanethiols at Au in 0.1 M KCl at c) +0.7 V, and d) -0.2 V</td>
<td>265</td>
</tr>
<tr>
<td>9.15. Model of orientation of methylene agostic interaction with rough Ag surface: a) Positive of the PZC, b) negative of the PZC</td>
<td>271</td>
</tr>
<tr>
<td>9.16. Raman spectra in the $\nu(C-S)$ region of alkanethiol films at smooth Ag subjected to Pb UPD: a) butanethiol, c) dodecanethiol, e) octadecanethiol; alkanethiol films at smooth Ag subjected to bulk Pb deposition: b) butanethiol, d) dodecanethiol, f) octadecanethiol</td>
<td>273</td>
</tr>
<tr>
<td>9.17. Raman spectra in the $\nu(C-C)$ region of alkanethiol films at smooth Ag subjected to Pb UPD: a) butanethiol, c) dodecanethiol, e) octadecanethiol; alkanethiol films at smooth Ag subjected to bulk Pb deposition: b) butanethiol, d) dodecanethiol, f) octadecanethiol</td>
<td>275</td>
</tr>
<tr>
<td>9.18. Raman spectra in the $\nu(C-H)$ region of alkanethiol films at smooth Ag subjected to Pb UPD: a) butanethiol, c) dodecanethiol, e) octadecanethiol; alkanethiol films at smooth Ag subjected to bulk Pb deposition: b) butanethiol, d) dodecanethiol, f) octadecanethiol</td>
<td>277</td>
</tr>
<tr>
<td>9.19. Raman spectra in the $\nu(C-N)$ region of smooth Ag electrodes emersed from 0.75 M NaCN solution: a) bare Ag, b) Ag with dodecanethiol film formed for 60 s</td>
<td>279</td>
</tr>
<tr>
<td>10.1. XPS survey spectra of thiophenol film at smooth, polycrystalline Pt</td>
<td>285</td>
</tr>
<tr>
<td>10.2. Cyclic voltammogram of 2,5-dihydroxythiophenol at smooth, polycrystalline Pt in 0.1 M KCl</td>
<td>288</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>10.3.</td>
<td>Raman spectra in ring-breathing region of bulk thiophenol and aqueous thiophenolate</td>
</tr>
<tr>
<td>10.4.</td>
<td>Raman spectra in ring-breathing region (514.5 nm excitation) of thiophenol at smooth polycrystalline Pt, Ag, and Au</td>
</tr>
<tr>
<td>10.5.</td>
<td>Raman spectra in the $\nu$(C-H) region of butanethiol at smooth polycrystalline Pt</td>
</tr>
</tbody>
</table>
LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1.</td>
<td>Raman Vibrational Assignments and Peak Frequencies in the $\nu$(C-S) Region of $\text{C}<em>n\text{H}</em>{2n+1}\text{SH}$</td>
<td>80</td>
</tr>
<tr>
<td>3.2.</td>
<td>Raman Vibrational Assignments and Peak Frequencies in the $\nu$(C-C) Region of $\text{C}<em>n\text{H}</em>{2n+1}\text{SH}$</td>
<td>87</td>
</tr>
<tr>
<td>3.3.</td>
<td>Raman Vibrational Assignments and Peak Frequencies in the $\nu$(C-H) Region of $\text{C}<em>n\text{H}</em>{2n+1}\text{SH}$</td>
<td>94</td>
</tr>
<tr>
<td>3.4.</td>
<td>Depolarization Ratios of Bands in the $\nu$(C-H) Region of $\text{C}<em>n\text{H}</em>{2n+1}\text{SH}$</td>
<td>97</td>
</tr>
<tr>
<td>4.1.</td>
<td>Peak Area Ratio Data for $\nu$(C-H) Region for Isotropic and Surface Spectra</td>
<td>116</td>
</tr>
<tr>
<td>5.1.</td>
<td>Raman Vibrational Assignments and Peak Frequencies in the $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) Regions of $\text{C}<em>n\text{H}</em>{2n+1}\text{SH}$ at Smooth Ag</td>
<td>134</td>
</tr>
<tr>
<td>5.2.</td>
<td>Peak Area Ratio Data for $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) Region for Isotropic and Surface Spectra at Smooth Ag</td>
<td>144</td>
</tr>
<tr>
<td>6.1.</td>
<td>Raman Vibrational Assignments and Peak Frequencies in the $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) Regions of $\text{C}<em>n\text{H}</em>{2n+1}\text{SH}$ at Smooth Au</td>
<td>151</td>
</tr>
<tr>
<td>6.2.</td>
<td>Peak Area Ratio Data for $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) Region for Isotropic and Surface Spectra at Smooth Au</td>
<td>160</td>
</tr>
<tr>
<td>9.1.</td>
<td>Peak Area Ratios for $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) Region at Ag and Au with Change in Potential</td>
<td>248</td>
</tr>
</tbody>
</table>
The overall goal of this research is a comprehensive characterization of self-assembled alkanethiol monolayer films at Ag and Au surfaces. A combination of surface Raman spectroscopy and electrochemistry is employed to study several important aspects of these films.

Raman vibrational assignments for a series of n-alkanethiols (n = 4, 5, 8, 9, 10, 12, 16, and 18 for C\textsubscript{n}H\textsubscript{2n+1}SH) are determined in the spectral regions from 600 to 1300 cm\textsuperscript{-1} and 2800 to 3000 cm\textsuperscript{-1}. Particular emphasis is given to the trans (T) and gauche (G) ν(C-S) and ν(C-C) bands and the ν(C-H) bands.

Surface Raman spectra of n-alkanethiol films at electrochemically roughened and mechanically polished, polycrystalline Ag and Au surfaces are presented. Strong enhancements of surface Raman scattering are realized at roughened surfaces, while less enhancement is observed at the mechanically polished surfaces. The conformational order of these films at these surfaces is evaluated by the determination of T and G bands present in the spectra.

The orientation of these films at Ag and Au is determined through the use of surface Raman selection rules. A method is developed for the determination of orientation of C-S and C-C bonds and methyl groups. The orientations deduced using the spectral results from each of these regions are found to be self-consistent.

Different orientations are deduced for alkanethiol films at Ag and Au surfaces and are proposed to be influenced by metal-S bonding. The orientations can be altered in the electrochemical environment by control of the applied potential of these metal substrates. The potential-dependent behavior is correlated with the potential of zero-excess charge (PZC) of these metals.
Defect structure of these films at Ag surfaces with various surface morphologies is evaluated with Pb deposition studies. Gross films defects are evaluated with Pb underpotential deposition and ion penetration is studied with bulk Pb deposition.

Finally, surface Raman spectra of monolayer films at non-enhancing surfaces are presented. Spectra for butanethiol at single-crystal Ag surfaces and butanethiol and thiophenol at mechanically polished, polycrystalline Pt surfaces show the utility of Raman spectroscopy for studying films at a variety of surfaces.
Chapter 1

INTRODUCTION:

SELF-ASSEMBLED ORGANIC MONOLAYERS AT METAL SURFACES

Organic films at metal surfaces

Organic thin films at metal substrates create unique interfaces which combine properties of the metal, such as mechanical stability and electrical conductivity, with the specific organic properties of the film, such as non-polar and polar interactions and reactions. This interface can be used in various applications where the wealth of organic molecular interactions available between the thin films and the environment can be exploited.

A panel report for the Materials Sciences Division of the Department of Energy reviewed several areas of technology where the application of organic thin films holds much promise. These include thin-film optics, sensors and transducers, protective layers, patternable materials, surface preparation and modification, chemically modified electrodes, and biomacromolecules. Surface preparation and modification includes topics such as lubrication, adhesion, and wetting.

The technological uses of organic thin films are illustrated with examples in the areas of lubrication and chemical sensors. Lubrication is of interest in the
magnetic tape industry because of the constant contact between the magnetic tape surface and the playback tape head.\textsuperscript{1,2} In this particular application, the organic film must protect the oxide layer and reduce wear of the tape during playback. Additionally, the space between the magnetic layer and the tape head, which limits the thickness of the film, is typically no more than 10 nm.\textsuperscript{1,2} Seto and coworkers investigated the use of Langmuir-Blodgett monolayers on cobalt-based magnetic tape.\textsuperscript{1,3} The deposition of seven monolayers of barium stearate reduced the friction coefficient by a factor of four, compared to the value for a bare cobalt tape surface. The reduced friction coefficient held constant for at least 100 playbacks. Films with the hydrophobic end of the molecule exposed produced a larger effect compared to those terminated with a hydrophilic group. A significant improvement in signal quality during playback was noted with a single monolayer film.

Chemical interactions between organic films and analytes of interest can be exploited to increase the sensitivity of chemical sensors. Surface acoustic wave (SAW) devices show great promise as sensors for various chemical vapors. Adsorption of molecules to SAW devices can be detected by changes in the oscillator frequency of the surface acoustic wave resulting from an increase in mass at the surface of the substrate.\textsuperscript{1,4} Sensitivity to a target vapor is achieved by coating the SAW device with a thin film that will selectively adsorb the vapor. The use of multi-array detectors with different coatings of varying selectivity to target vapors lessens the need for highly selective coatings in the detection of a range of analytes.\textsuperscript{1,5} Grate and coworkers report that partition coefficients of various molecules at fluoropolyol-coated SAW devices agree semi-quantitatively to partition coefficients determined with gas-liquid chromatography under similar conditions.\textsuperscript{1,4} The investigation of a wide range of stationary phases
previously studied in gas chromatography might be readily applicable to SAW devices and similar chemical sensors.

The Materials Science Division panel identified key obstacles to the wide application of organic thin films in science and technology. First, the need for further development of methods and techniques to characterize thin organic films was cited. The possibilities of using organic thin films in novel applications requires the continued expansion of techniques and methods to evaluate the usefulness of organic thin films for various purposes. Spectroscopic techniques are especially capable of providing detailed information on various aspects of these thin films.

The stability and integrity of films must be improved such that they are useful in environments where the fluid-like behavior of organic films is a hindrance. The need for mechanical strength or films of long-range order will prompt the search for new molecules, and therefore, analytical techniques that are versatile and capable of providing a wide range of information. In addition, impurities and defects need to be identified and, if deleterious to their intended function, removed.

The panel also pointed out the need for characterizing the type and degree of order present and desired in films. Macroscopic properties of the films could then be related to the ordering behavior of the molecules. Also, ordering could be correlated with different intermolecular interactions, such as van der Waals interactions, trans/gauche isomerization, and head group/surface bonding.

Langmuir-Blodgett deposition, one method of forming highly-ordered thin films at surfaces, has been developed extensively over several decades. Currently, a wide range of organic molecules have been incorporated into monolayers and multilayers on water and solid substrates. Molecules that have a polar end and
a more non-polar end are used. Commonly, a monolayer film is created with the polar end interacting with a water subphase and the non-polar end oriented in the ambient environment away from the water. These films are then deposited on substrates using mechanical force to compress the molecules into a densely-packed film. This leads to films that are not necessarily thermodynamically stable on metal substrates.1,7,1,8

Self-Assembled Organic Films

Self-assembling monolayer systems are an attractive alternative to Langmuir-Blodgett films, because the mechanical manipulation of aqueous surface films to form thin films is eliminated, which allows ease in preparation. In some cases, monolayers are spontaneously formed by virtue of the strong metal-organic bond created. This bonding creates ordered films, because only one end of the molecule is attached to the metal. The other end can be varied with other functional groups to provide a certain chemical property to the surface. SAMs studied so far have been alkanoic acids, alkyltrichlorosilanes, Zr-phosphate organic films, surfactants, and alkanethiols.

Alkanoic acids in organic solvents have been reported to self-assemble into densely-packed films at Ag1,9-1,12 and oxidized aluminum surfaces.1,13,1,14 These films form complete monolayers after several days.1,9,1,14 IR surface spectra for these films show the acid group deprotonates upon adsorption, and both O atoms interact with the surface.1,9-1,11,1,13 Binding of alkanoic acids to an oxidized Ag surface was suggested.1,12 IR spectroscopy was used to determine the orientation of these films at these substrates. A chain tilt of ca. 12° from the surface normal is calculated for carboxylic acid films at Al oxide,1,14 and an approximately perpendicular orientation was proposed at Ag.1,9 IR spectra of alkanoic acids at
Al oxide suggest that hexadecanoic acid films are disordered, while longer-chain films are more crystalline.\textsuperscript{1,14}

Films of alkyltrichlorosilanes self-assemble at hydroxylated surfaces of glass, aluminum, and silicon.\textsuperscript{1,15-1,17} A strong Si-O bond is formed at the surface, along with a network of Si-O-Si bonds between adjacent Si head groups.\textsuperscript{1,16} These films form within 30 minutes, as measured by ellipsometry and IR spectroscopy.\textsuperscript{1,16,1,17} IR spectra of these films suggest that the alkyl chains are oriented at ca. 10° from the surface normal.\textsuperscript{1,17} Multilayers can be formed by depositing alkyltrichlorosilanes with a terminal vinyl group\textsuperscript{1,18,1,19} or methyl ester group.\textsuperscript{1,17} These terminal groups are then converted to hydroxyl groups, which covalently bond with a second alkyltrichlorosilane layer.\textsuperscript{1,17-1,19} Films with 25 multilayers have been formed.\textsuperscript{1,16}

Self-assembling films containing Zr-phosphate bonds operate on a similar scheme as employed with alkyltrichlorosilanes. Alkane chains with a terminal phosphonic acid group are first attached to a Si surface by adsorbing molecules with silanol head groups.\textsuperscript{1,20,1,21} Zr is then bonded to terminal (-\textit{PO}_3\textsuperscript{2-}) groups by immersion of the film in a ZrOCl\textsubscript{2} solution.\textsuperscript{1,20,1,21} The Zr-terminated surfaces can be further reacted with \(\alpha,\omega\)-alkyl-bisphosphonic acids to add another layer. The bonding of Zr ions and alkyl phosphonic chains has been repeated to produce high-quality films of eight layers.\textsuperscript{1,20,1,21} Immersion times of one hour per solution resulted in films of the same properties as films formed after 24 hours.\textsuperscript{1,21} Asymmetric films can be produced by using hydroxy-terminated alkyl phosphonic acid chains which can be phosphorylated.\textsuperscript{1,22} This results in a -C-O-P-Zr-P-C- asymmetric sequence in the film that might prove useful in non-linear optics studies.\textsuperscript{1,22}

Various surfactants, such as viologen derivatives\textsuperscript{1,23-1,26} and tetraalkyl
ammonium salts\textsuperscript{1.27,1.28}, self-assemble at Au, Pt and Ag electrodes. The viologen groups, which are electroactive, exhibit well-defined surface-confined voltammetric waves.\textsuperscript{1.23-1.26} The packing densities of the films, determined at the Au surface from the cyclic voltammetry and at the air/water interface from surface pressure-area isotherms, are similar to alkane chain packing densities.\textsuperscript{1.26} This suggests that the aromatic groups of the viologen molecules adsorb edge-on to the Au surface with the alkyl chain extending into solution.\textsuperscript{1.26} Nearly ideal cyclic voltammetric behavior for surface-confined species is observed for viologens with long-chain alkyl groups.\textsuperscript{1.24} However, ill-defined or no voltammetric waves were observed for heptylviologen\textsuperscript{1.25} and methylviologen,\textsuperscript{1.24} which suggests that hydrophobic alkyl chain interactions are necessary for self-assembly in this system.

**Self-Assembled Films of S-Containing Adsorbates**

The chemisorption of organic sulfur compounds at metal surfaces generates versatile self-assembling systems. This is due to the strong metal-S bond created upon adsorption, for such metal surfaces as Au,\textsuperscript{1.28,1.29} Pt,\textsuperscript{1.30} Cu,\textsuperscript{1.31} and Ag.\textsuperscript{1.32} Bain and coworkers surveyed a number of long-chain compounds with different head groups for their ability to spontaneously form monolayers at Au from dilute ethanol or acetonitrile solutions.\textsuperscript{1.33} Monolayers that were stable to ethanol washing and exhibited advancing contact angles $>100^\circ$ for water and $>40^\circ$ for hexadecane were judged to form relatively densely-packed monolayers. Stearamine, heptadecanol, stearic acid, stearamide, stearonitrile, 1-bromodocosane, ethyl hexadecanolate, and didodecynylmercury did not form suitable monolayers, while tricosylisonitrile and trihexadecylphosphine formed films similar to alkanethiol films. Only the phosphine head group showed a
similar preference for adsorption to Au as the thiol head group. Similar conclusions were drawn in a study by Nuzzo and coworkers. Various S head groups have been employed to create self-assembled monolayers. Aromatic thiol monolayers have been studied at Ag and Pt. Low energy electron diffraction (LEED) studies reveal that monolayers were more ordered at Ag (111) surfaces than at Pt (111). Sulfide and disulfide compounds have been studied at Ag and Au surfaces. Sandroff and coworkers and Joo and coworkers observed C-S bond cleavage upon adsorption of disulfide compounds containing aromatic groups to Ag surfaces using surface enhanced Raman spectroscopy (SERS). For example, methyl phenyl sulfide and benzyl phenyl sulfide both form the phenyl mercaptide specie upon adsorption and prolonged laser excitation. Dialkyl sulfides, such as diethyl sulfide, do not cleave. Diaryl and dialkyl disulfide compounds are found to cleave at Ag. Short chain dialkyl disulfides, such as dimethyl disulfide, are observed to cleave at Au as studied by high resolution electron energy loss spectroscopy (HREELS) and x-ray photoelectron spectroscopy (XPS). However, the results of XPS studies for longer chains, though more ambiguous, suggest cleavage of the disulfide bond. Cyclic disulfides, such as substituted 1,2-dithianes were also concluded to adsorb to Au with the S-S bond intact. No C-S bond cleavage was observed by XPS for dialkyl sulfides at Au. Arduengo and coworkers have reported self-assembled films at Au from dialkyl substituted imidazole-2-thiones. Exchange experiments show the binding strength of disulfides to be greater than thiones.
Alkanethiol Self-Assembled Films

Self-assembled films of alkanethiols at Au and Ag have been studied to the greatest extent. Contact angle measurements show that adsorption of alkanethiols to Au is preferred by ca. two orders of magnitude to the adsorption of dialkyl disulfides\(^1\) and dialkyl sulfides.\(^1\) Alkanethiol films are concluded from IR studies to form crystalline-like, densely-packed, ordered monolayers at Au\(^1\) and Ag.\(^1\) On the other hand, monolayers of dialkyl sulfides are concluded to be more disordered.\(^1\) Adsorption of thiols is rapid, with large fractional coverages obtained within minutes from mM concentrations in ethanol.\(^1\) However, nearly complete monolayers, as measured by ellipsometry and contact angle, required up to ca. 16 hours to form.\(^1\) Various methods have shown that adsorption occurs through cleavage of the S-H bond and formation of a Au-S bond.\(^1\)

These aspects of alkanethiol films at Ag, Au and other metals have been characterized by a wide variety of techniques. In addition, many other properties of these versatile films have been investigated by different techniques. The following overview will summarize the results of investigations concerning several important properties of the films. These properties include formation mechanisms and kinetics, orientation, thickness, order, interactions with solvents, defect structure and electron transfer.

Adsorption Mechanism

The SH moiety in alkanethiols is a weak acid and has a pKa of ca. 10.\(^1\) The cleavage of the S-H bond upon adsorption, forming a metal-thiolate species, is proposed to occur.\(^1\) HREELS spectra of a methanethiol monolayer at Au (111) at -150 °C, however, shows the presence of the \(\nu(S-H)\) band.\(^1\) The film is desorbed upon increasing the temperature to 20 °C. On the other hand, S-H
cleavage is observed for methanethiol at Pt (111)\textsuperscript{1,30} and Cu (100)\textsuperscript{1,31} by HREELS. For longer chain alkanethiols at Au, XPS of the sulfur 2p core level yields identical spectra for adsorbed alkanethiols and dialkyl disulfides\textsuperscript{1,28,1,43}.

The evidence for S-H bond cleavage for alkanethiols at Ag is clearly shown in SERS spectra for adsorbed propanethiol\textsuperscript{1,51} and butanethiol\textsuperscript{1,54} The $\nu$(S-H) band is very strong in the Raman spectra of the bulk liquids and completely absent in the surface spectra. In addition, the $\nu$(S-H) band is absent in the HREELS spectrum of propanethiol at Ag (111)\textsuperscript{1,39}.

Widrig and coworkers have studied in further detail the adsorption reaction mechanisms\textsuperscript{1,52} In deaerated aqueous solutions, no decrease in pH was observed upon adsorption of propanethiol to high surface-area Au powder. Hydrogen peroxide, detected spectrophotometrically, was produced upon adsorption of propanethiol at Au powder in an oxygenated water solution. These results suggest that thiol proton is reduced during the adsorption reaction or combines with O$_2$ and is reduced to hydrogen peroxide.

A different reaction scheme is proposed for Ag substrates. The Ag surface, unlike Au, is initially covered in the ambient environment by an oxide, of which a few percent remain upon adsorption of octadecanethiol\textsuperscript{1,50} In addition, the IR spectra for monolayers formed at Ag from alkanethiol and alkanethiolate solutions were found to be similar, while the spectra for monolayers at Au formed from alkanethiolate solutions suggested lower surface coverage than observed with alkanethiol solutions\textsuperscript{1,52} Therefore, alkanethiols are proposed to displace the Ag(I)OH surface species with little redox behavior\textsuperscript{1,52}.

Evans and Ulman have measured the surface potential of alkanethiols films at Au using a Kelvin vibrating electrode arrangement\textsuperscript{1,55} They conclude that the Au-S bond has polar character, but the effective dipole of the C$^+$-S$^-$ bond is
greater than the Au\(^+\)-S\(^-\) dipole.

The purity of these films has been measured with respect to common contaminants such as O and N.\(^{1,34}\) For films formed from organic solutions and handled in the ambient environment, no XPS signals for O and N were detected except when the alkanethiol molecules contained these elements. Surface contaminants are believed to be displaced by the strong adsorption of alkanethiols.\(^{1,43}\) For example, Au surfaces with a propanethiol film, considered an "impurity" in an exchange experiment, are covered with a complete octadecanethiol film after ca. 16 hours, as measured by ellipsometry.\(^{1,43}\)

Temperature programmed desorption (TPD) experiments of the methanethiolate species at Au (111), have been conducted to estimate the heat of adsorption for the methanethiolate group.\(^{1,28}\) The methanethiolate species, formed upon adsorption of dimethyl disulfide at Au, desorbs at ca. 200 °C. Assuming first-order desorption kinetics, the heat of adsorption is estimated to be ca. 28 kcal/mole.

The additional interaction energy available from van der Waals forces between neighboring alkane chains of long-chain alkanethiols has also been estimated from TPD studies.\(^{1,34}\) Desorption of hexadecanethiol from Au (111) occurs at ca. 575 K. Assuming first-order desorption kinetics, the activation energy of desorption is calculated to be ca. 40 kcal/mol. Subtracting the 28 kcal/mole value calculated for the methylthiolate species,\(^{1,28}\) an interaction energy of 0.8 kcal/mole per methylene unit is calculated.\(^{1,34}\) A lower value of 0.2 kcal/mol per methylene unit has been calculated from ellipsometric data for desorption of long-chain alkanethiols at evaporated Au films immersed in hexadecane.\(^{1,43}\)
Orientation

The orientation of the alkanethiol molecules at Au and Ag substrates, specifically chain tilt with respect to the surface normal, has been calculated from IR spectra and diffraction data. More qualitative orientations have been proposed from HREELS studies and sum-frequency generation.

Orientational information is available in surface IR and HREELS spectra due to surface selection rules for these spectroscopies. Molecular vibrations involving transition dipoles perpendicular to the metal surface are enhanced while vibrations with transition dipoles parallel to the surface are greatly attenuated. At grazing angles of incidence and polarization parallel to the plane of incidence, the intensity of vibrations completely parallel to the surface are negligible in IR spectra.

Quantitative angles of orientation, therefore, can be calculated by comparing the intensities of the bands in the surface spectra to intensities of bands calculated from the isotropic, bulk liquid. The relationship is simply \( \cos^2 \theta = \frac{I_{\text{obs}}}{I_{\text{calc}}} \), where \( \theta \) is the angle of the transition dipole, and \( I_{\text{obs}} \) and \( I_{\text{calc}} \) are the observed and calculated band intensities. The angles determined for the transition dipoles of each vibration can be correlated to the geometry of the molecule, and the orientation of the overall molecule can be deduced. The following analyses were made using this method or a similar calculation.

Porter and coworkers calculate the orientation of alkanethiols at Au to be 20-30° from the surface normal. Nuzzo and coworkers estimate the tilt of alkanethiols with various terminal functional groups to be 28-40° with a rotation about the chain axis of 50-55°. Alkanethiols with terminal methyl groups were calculated to tilt ca. 40°, but it was concluded that the range of chain tilts
were within the experimental error of the method.\textsuperscript{1,34} In addition, the absolute tilt of the chain was determined, positioning the C-S bond $>$45° from the surface normal.\textsuperscript{1,34} Chidsey and Loiacono calculate a tilt of ca. 27° for alkanethiols and ca. 15° for flourinated alkanethiols.\textsuperscript{1,57} Walczak and coworkers calculate a tilt of ca. 24° and a rotation of ca. 50°.\textsuperscript{1,49} Laibinis and coworkers calculate a chain tilt of ca. 28° and a rotation of ca. 50°.\textsuperscript{1,50}

Proposed orientations at Ag surfaces are more controversial. For alkanethiols at Ag, Ulman concludes the tilt is much less than observed at Au.\textsuperscript{1,8} Walczak and coworkers estimate the chain tilt at Ag surfaces to be ca. 14° and rotation to be ca. 44°.\textsuperscript{1,49} In addition, the absolute tilt of the alkanethiol positions the C-S bond ca. 27° from the normal, while the C-S bond at Au surfaces is ca. 53°.\textsuperscript{1,49} The C-S bond angles have been taken from their data assuming the C-S bond is parallel to the symmetric methyl transition dipole. Laibinis and coworkers calculate a chain tilt of ca. 12°.\textsuperscript{1,50} However, these researchers conclude that the orientation of the C-S bond with respect to the surface normal alternates with chain length, thus positioning the methyl group at a constant orientation with respect to the surface normal.\textsuperscript{1,50}

The spectral data from these two research groups are actually very similar.\textsuperscript{1,49,1,50} Both observe an odd-even effect in $\nu_{\text{asym}}(\text{CH}_3)$ and $\nu_{\text{sym}}(\text{CH}_3)$ intensities for long-chain alkanethiols (hexadecanethiol and longer) at Au.\textsuperscript{1,49,1,50} In addition, Walczak and coworkers observe the odd-even effect for alkanethiols at Au from butanethiol to octadecanethiol.\textsuperscript{1,49} Both groups observe no odd-even effect in methyl intensity for long-chain alkanethiols.\textsuperscript{1,49,1,50} However, Walczak and coworkers observe an odd-even effect for butanethiol through nonanethiol.\textsuperscript{1,49} Laibinis and coworkers do not present spectra of alkanethiol films at Ag shorter than hexadecanethiol.\textsuperscript{1,50}
Oxidation of the Ag surface with short-chain alkanethiols has been offered as an explanation for the observance of the odd-even effect at Ag. Laibinis report the appearance of broad bands in the IR spectra of octadecanethiol at Ag after several days exposure to the ambient environment. These broad bands, which extend from ca. 1000 to 1200 cm\(^{-1}\), are absent in the spectra of freshly deposited films and are attributed to an oxidized S moiety, possibly sulfonate species. These bands appear after several days of exposure to air. Walczak and coworkers do not observe this band in their IR spectra, nor is this band seen in the SERS spectra of propanethiol or butanethiol at Ag. Laibinis and coworkers contend that nearest neighbor interactions between methyl groups at the chain termini are greater than Ag-S interactions at the metal-alkanethiol interface. However, Laibinis and coworkers report behavior that strongly suggests a strong metal-S bond is created. XPS measurements show that ca. 98% of the Ag surface oxide has been displaced by alkanethiol films. In addition, alkanethiol films with various terminal derivatives exhibit similar orientations at Au, irrespective of the terminal functional groups, ranging from polar to non-polar moieties, incorporated in the films. This suggests that interactions between terminal functional groups are weak compared to Au-S and neighboring alkane chain interactions.

A more plausible explanation is an increase in disorder of films of long-chain alkanethiols at Ag at the end of the alkane chain. This disorder would produce a more random distribution of the orientation of the methyl groups, which would result in the absence of an observed odd-even effect. Diffraction data supporting this proposal is discussed in the section on film overlayer structure and long range order.

Strong and Whitesides calculate an orientation of 25-35° for docosanethiol
at Au (111) using transmission electron diffraction. Samant and coworkers used surface X-ray diffraction to calculate an orientation of ca. 12° for docosanethiol at Au (111) on mica substrates. The angle determined from X-ray diffraction is the lowest chain tilt angle reported in the literature for alkanethiol at Au.

HREELS has been used to study methylthiolate species at Au (111), Pt (111), and Cu (100). Although the orientations deduced from this technique are more qualitative, the C-S bond of the methanethiolate species at all three substrates is concluded to be significantly tilted due to the presence of both ν asym(CH₃) and ν sym(CH₃) bands in the spectra. Gui and coworkers concluded that propanethiol is oriented perpendicular to the surfaces of both Pt (111) and Ag (111). However, the orientational information available in the ν(C-H) region is obscured by the additional presence of methylene stretches for propanethiol. The resolution in these spectra, primarily determined by the energy distribution in the incident electron beam, is 80-120 cm⁻¹, which is insufficient to resolve the methyl bands.

Sum-frequency generation was used by Harris and coworkers to study methylthiolate at Ag (111). The C-S bond is concluded to be directly perpendicular to the Ag surface due to the complete absence of the ν asym(CH₃) band.

Film Thickness

In addition to IR spectroscopy, ellipsometry is a very useful technique for characterizing alkanethiol films. The thickness of the films at Au and Ag are commonly determined with a precision of ca. 3 Å. The thicknesses correspond well to values expected for all-trans extended chains that are nearly...
perpendicular to the surface. However, several factors prevent use of ellipsometry for quantitation of orientation. Taken from measurement of bulk liquid alkanethiols, the refractive index used in the calculations, 1.45 at 632.8 nm, may not be accurate for these surface films.\textsuperscript{1,66} The calculated thickness, however, is only moderately sensitive to changes in the refractive index reference value.\textsuperscript{1,43} Adsorbed contaminants, such as water or organic species present in the ambient environment, are thought to be particularly crucial in ellipsometric measurements. Although contaminants do not appear to adsorb to alkanethiol films,\textsuperscript{1,34} bare metal surfaces, required as a reference in thickness determinations, readily adsorb contaminants.\textsuperscript{1,43}

**Kinetics of Film Formation**

The kinetics of film formation at Au have been studied with ellipsometry and contact angle measurements by Bain and coworkers.\textsuperscript{1,43} Limiting values of thickness and contact angle for octadecanethiol and decanethiol at Au were reached after immersion times of 1000 min in 1 mM solutions. For solution concentrations of $10^{-6}$ M, incomplete monolayers were formed after 1 week, as concluded from the lower ellipsometric and contact angle values achieved.

Thomas and coworkers used SAW devices to monitor the real-time vapor-deposition of heptanethiol and hexadecanethiol at Au.\textsuperscript{1,60} The adsorption kinetics obtained from the frequency shift of the SAW device versus deposition time fit a first-order Langmuir rate law, which suggests no van der Waals interaction between neighboring alkane chains. It was concluded, however, that the kinetic behavior is a consequence of the much stronger metal-S interaction. It was also found that up to four stable multilayers could be formed with hexadecanethiol. Discontinuities in the frequency response corresponding to completion of each
layer suggest that transformation between amorphous and ordered states occurs near monolayer coverages.

Structural Aspects of Au-S Bond

The largely perpendicular orientation of alkanethiols at Au surfaces along with the strong preference for S adsorption at Au has been used as a structural tool to create various films. For example, the adsorption of alkyltrichlorosilane films, which self-assemble at hydroxylated surfaces, is accomplished at Au by first adsorbing a hydroxyl-terminated alkanethiol to Au.1.61 Alkyl silanes then can be attached to the terminal hydroxyl group. In a similar manner, Zr-phosphate multilayers can be created at Au surfaces through the use of phosphonic acid-terminated alkanethiols1.21, and disulfides.1.20 Evans and coworkers formed films at Au from alkanethiols containing polar aromatic groups in the center of the chain.1.62 Whitesides and coworkers coadsorbed alkanethiols and carboxylic acid self-assembled films in defined patterns at substrates containing Au and Al oxide.1.29,1.63 The preference of carboxylic acids for Al oxide and alkanethiols for Au allows lateral film resolution that may be limited by the ability to prepare thin Au and Al oxide substrates.

Solvent Interaction

The chemical nature of the surface of alkanethiol monolayers can be controlled by using molecules with various functional end groups. The largely perpendicular orientation of these films position the terminal groups at the surface. The interactions of these films with solvents can been studied with contact angle measurements. The contact angles of water and hexadecane, chosen for their polar and non-polar character, respectively, can be related to the
terminal surface of the alkanethiol film.\textsuperscript{1,29}

Bain and coworkers measured the wetting behavior of these solvents at films with functional groups of highly-polar and non-polar nature.\textsuperscript{1,43} The contact angles for water and hexadecane at methyl terminated alkanethiols were found to be 112° and 47°, respectively. The high contact angle for water indicates very little wetting of this surface. With a fluorinated end group, -CF₃, the contact angles for water and hexadecane both increase, 118° and 71°, respectively, as expected for a more non-polar film surface. Highly-polar surfaces are extremely wetted by these solvents, as indicated by contact angles below 10° for terminal hydroxyl and carboxylic acid groups. Similar results were reported by Dubois and coworkers.\textsuperscript{1,64}

The depth sensitivity of contact angle measurements was investigated by observing the change in contact angle of solvents at films with an ether group at various positions in the chain, using the alkanethiol series HS(CH₂)₁₈O(CH₂)$_n$CH₃.\textsuperscript{1,29} The contact angle of water at films with $n = 3$ was indistinguishable from that of unsubstituted alkanethiol films. A decrease in contact angle was detected for $n = 2$. Changes in contact angle for glycerol at these films were observed at $n = 1$, while hexadecane exhibited no change in contact angle with the ether linkage between the alkyl chain and a terminal methyl group.

Stole and Porter report in situ IR spectra of octadecanethiol films at Au in various solvents.\textsuperscript{1,65} Spectra in the $\nu$(C-H) region, normally obscured by the intense absorption of solvents in this frequency region, were obtained by using CCl₄, D₂O, and CD₃OD. Thus, interfering $\nu$(C-H) bands from the solvent are not present. Band broadening of the $\nu_{\text{asym}}$(CH₃) mode was observed. They suggest that the broadening is due to partial rotation of the methyl group or increased
disorder at the chain terminus. The use of deuterated solvents holds promise for in situ electrochemical investigations of alkanethiol films using IR spectroscopy.

Several different properties of alkanethiol films, loosely described as "order", have been studied by a wide variety of techniques. These properties range from crystallographic and conformational order to film defects. The following discussion will first focus on orientation of the adsorbate monolayers with respect to single crystal surfaces. Long-range order, as measured by diffraction techniques, will also be discussed. Conformational order, as measured by vibrational techniques, will then be discussed. Finally, film defects, both macroscopic and microscopic, will be discussed in relation to electrochemical experiments.

Film Overlayer Structure and Long-Range Order

Strong and Whitesides studied docosanethiol monolayers at Au (111) and (100) with transmission electron diffraction. The overlayer structure at (100) surfaces is concluded to be c(10 X 10). The data for the (111) system were reinterpreted by Chidsey and Loiacono and the overlayer structure was determined to be (\sqrt{3} X \sqrt{3})R30°. The spacing between S groups was determined to be 4.97 Å, which corresponds to the next-nearest neighbor spacing for Au atoms in the (111) lattice. This S spacing for long-chain alkanethiols has also been determined in helium diffraction studies by Camillone and coworkers, surface X-ray diffraction by Samant and coworkers, and scanning tunneling microscopy (STM) by Widrig and coworkers. The predominant surface lattice for Au substrates is (111), and the number of (100) domains increase with more disordered Au substrates.
The overlayer structure of methanethiolate at Ag (111) has been determined by Harris and coworkers using low energy electron diffraction (LEED). An ordered \((\sqrt{7} \times \sqrt{7})R10.9^\circ\) structure was observed. No LEED patterns were observed for propanethiol at Ag (111) and Pt (111). Fenter and coworkers used He diffraction and grazing incidence X-ray diffraction to study octadecanethiol at Ag (111). They observed an overlayer structure that is incommensurate and rotated ca. 12° with respect to the Ag (111) lattice. While this overlayer structure is similar to that of methanethiolate at Ag (111), a larger nearest-neighbor spacing (ca. 4.7 Å) is observed for octadecanethiol compared to methanethiolate (ca. 4.4 Å).

The long-range order of alkanethiols at predominantly (111) surfaces of Au was also determined by diffraction techniques. Transmission electron diffraction showed film domain sizes of ca. 60 Å and substrate domain sizes of ca. 500 Å. STM studies of ethanethiolate revealed domains that ranged from a few nm² to 600 nm². It was concluded that the STM was imaging the sulfur groups only and not the alkane chains. Surface X-ray diffraction showed film domain sizes of ca. 70 Å and substrate domain sizes of ca. 350 Å. Helium diffraction studies were used to measure the order of the terminal methyl groups. Domain sizes of ca. 35 Å were measured for films at temperatures <100 K. No diffraction patterns were observed above 100 K.

Long-range order was also studied for octadecanethiol films at Ag (111). Grazing angle X-ray diffraction showed film domain sizes of ca. 120 Å, which is indicative of order in the interior of the film. He diffraction, which is sensitive to order at the surface of the film, showed domain sizes of ca. 12 Å. The ratio of domain sizes at the surface of alkanethiol films at Ag (111) compared to the interior of the films is ca. 0.1, while the ratio is ca. 0.5 for alkanethiol films at
Thus, the methyl groups at the end of the alkanethiol films at Ag are considerably more disordered than methyl groups in films at Au. This increased disorder is the probable reason for the absence of an observed odd-even effect in $\nu(\text{CH}_3)$ intensities in the IR spectra for alkanethiol films at Ag, while an odd-even effect is observed for films at Au.

These studies collectively indicate alkanethiol film domain size that is substantially smaller than domain sizes of the metal substrate. These results suggest a significant amount of tilt domain boundaries within single-crystal faces, along with film domain boundaries associated with grain boundaries and other defect sites.

Conformational Order

The diffraction methods discussed above provide information only for films that exhibit a high degree of crystalline order. Vibrational spectroscopies can provide information on the degree of order in alkanethiol films from a different perspective. Vibrations involving both trans (T) and gauche (G) conformations appear in vibrational spectra. Therefore, spectra can be obtained from a variety of films ranging from highly ordered to highly disordered. The degree of order is commonly assessed by comparison with spectra from highly ordered samples, such as solid bulk alkanethiols or other alkanes.

Several vibrations exhibit separate bands for G and T conformers, such as $\nu(\text{C-S})$ bands, methyl rocks and wags, and $\nu(\text{C-C})$ bands. Other bands are indirectly related to G and T conformations, such as the $\nu(\text{C-H})$ region. Complementary information is available with IR and Raman spectroscopies because the intensities of these bands are different in IR and Raman spectra.

In IR spectroscopy, the only alkanethiol bands that are sufficiently intense
for quantitation in surface spectra are the $\nu$(C-H) bands.\textsuperscript{1.34,1.49,1.56} Other bands, such as wagging and twisting/rocking modes, are present but commonly exhibit insufficient signal-to-noise ratios for quantitation.\textsuperscript{1.34,1.49} Of the six $\nu$(C-H) bands present in the surface IR spectra, the $\nu_{\text{asym}}$(CH$_2$) and $\nu_{\text{sym}}$(CH$_2$) are particularly sensitive to crystallinity.\textsuperscript{1.34,1.56} The frequencies of these bands observed in alkanethiol films match closely those observed for bulk solid long-chain alkanethiols.\textsuperscript{1.34,1.56} This similarity suggests all-T conformations in the films.\textsuperscript{1.34}

Further comparisons of surface spectra in the $\nu$(C-H) region to calculated spectra revealed closer fits to spectra containing varying amounts of gauche conformers than spectra with only all-T conformers.\textsuperscript{1.50} Temperature studies suggest that films are more ordered at temperatures below 300 K. Nuzzo and coworkers observed band splitting for the methylene scissors deformation and the $\nu_{\text{asym}}$(CH$_3$) in the IR spectra of docosanethiol at Au at 80 K.\textsuperscript{1.72} This behavior suggests the removal of G conformers in the film at low temperatures.

Raman spectra in the $\nu$(C-H) region are more complex. For example, 14 bands are observed in the spectrum for solid n-octane.\textsuperscript{1.73} These bands are not resolved in the spectra, making intensity and frequency measurements difficult.\textsuperscript{1.70,1.71,1.73} Changes in intensity ratios of several of the bands are observed with upon changes in temperature and crystallinity.\textsuperscript{1.70,1.71}

Analysis of the behavior of G and T conformers of the $\nu$(C-S), which are strong bands in Raman spectra, is more straightforward. These two bands correspond to the conformations about the C-C bond adjacent to the S group.\textsuperscript{1.51,1.54} Using SERS, Joo and coworkers found a significant decrease in the $\nu$(C-S)$_G$ intensity for monolayer coverages of propanethiol and butanethiol at Ag colloids.\textsuperscript{1.51,1.54}
\( \nu(C-C) \) bands are also strong in Raman spectra. The intensity and frequency of these bands are sensitive to conformational order in alkanes and other molecules containing substantial alkyl groups.\(^{1.69,1.70,1.74}\) However, there is some confusion concerning the T and G \( \nu(C-C) \) assignments for alkanethiols and other molecules with long-chain alkyl groups.\(^{1.27,1.75}\) This suggests a need to clarify Raman vibrational assignments for alkanethiols.

Defect Structure in the Electrochemical Environment

Studies of alkanethiol films in the electrochemical environment also provide important information about film order and disorder. In the electrochemical environment, any structural property of the alkanethiol film that allows ions and redox species to approach closer to the electrode surface than the distance of an all-T extended film is considered a defect. These defects can be due to incomplete film coverage of the surface or film disorder, attributed to substrate grain boundaries, film tilt boundaries, or G conformations.

The two current methods of characterizing the order of alkanethiol films at electrode surfaces include capacitance and electron transfer to solution- or surface-confined redox species. Capacitance studies probe the ability of the electrode to store charge. In a simple parallel plate model, the capacitance is directly proportional the area of the plates and to the dielectric constant of the medium between the plates, and indirectly proportional to the distance between the plates. In the electrochemical environment, the electrode can be considered one plate, and ions of closest approach can be the second plate. The dielectric medium is the film. The capacitances are commonly determined by examining the charging current of cyclic voltammograms in non-faradaic potential regions.\(^{1.62,1.56,1.57,1.76,1.77}\)
The capacitances of bare Au electrodes in various electrolytes are greater than 100 $\mu$F/cm$^2$.\textsuperscript{1.76} A dramatic reduction in capacitance is observed with alkanethiol films present on the electrode. Finklea and coworkers report values of 1-5 $\mu$F/cm$^2$ at long-chain alkanethiol films at Au in 0.5 M $\text{H}_2\text{SO}_4$.\textsuperscript{1.76}

Porter and coworkers report similar values for films at Au.\textsuperscript{1.56} In addition, they report that the reciprocal capacitance is directly related to chain length for films ranging from butanethiol to octadecanethiol in 1 M NaF. This relation is expected if the distance between the ions of closest approach and the electrode is defined by the thickness of the films. Linear relations were reported for long-chain films in 1 M KCl and 1 M $\text{HClO}_4$. However, shorter chain films showed markedly increased capacitances in the latter electrolytes, which suggests penetration by $\text{Cl}^-$ and $\text{ClO}_4^-$ ions into the film.\textsuperscript{1.56} It was suggested that ion penetration was related to the specific adsorption behavior of these ions at Au. Miller and coworkers also observed a linear relation between chain length and reciprocal capacitance for hydroxy-terminated alkanethiols at Au electrodes in 0.1 M KCl.\textsuperscript{1.77} Widrig and coworkers report a linear relation for alkanethiols at Au in 0.5 M KOH.\textsuperscript{1.52}

Chidsey and Loiacono measured capacitances of alkanethiols with various terminal functional groups adsorbed at Au in various electrolytes.\textsuperscript{1.57} Capacitance values similar to those of Finklea and coworkers\textsuperscript{1.76} were observed for all systems. However, greater capacitances were measured for nitrile and carboxylic acid terminated alkanethiol films.\textsuperscript{1.57} For the acid specie, greater ion penetration, suggested by the larger capacitance, was correlated with greater disorder in the IR spectra of these films.

Electron transfer studies can provide more detailed information about defect sites in the films. For example, gross defects or pinholes in the film, which
expose regions of the electrode directly to the electrolyte solution, will allow solution-confined redox species to be reduced and oxidized at potentials identical to that observed in the absence of the film.\textsuperscript{1.78} The magnitude of the faradaic current can be related to the area of the exposed electrode surface.

Finklea and coworkers report such behavior for octadecanethiol modified Au electrodes in 1.3 mM Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+/1 M KCl}.\textsuperscript{1.78} Analysis of the magnitude and shape of the current-potential curve determined that ca. 1% of the electrode was exposed for polycrystalline Au electrodes. The average diameter of the pinholes was calculated to be ca. 800 nm. A relatively short film deposition time of 1 hr was employed in these studies, suggesting less than monolayer coverage.

Different current-potential behavior is observed for films with negligible amount of pinholes. For these films, a large overpotential for electron transfer is observed for solution confined species. For example, Chidsey and Loiacono observe no faradaic current for the reduction of Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+} in 0.1 M NaClO\textsubscript{4} at Au electrodes modified with CF\textsubscript{3}(CF\textsubscript{2})\textsubscript{7}(CH\textsubscript{2})\textsubscript{2}SH at the potential of peak reduction for Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+} at bare Au electrodes.\textsuperscript{1.57} On the other hand, redox behavior for the Ru complex at carboxylic acid terminated alkanethiols was almost identical to that observed at bare Au electrodes.\textsuperscript{1.57} As with the capacitance studies, the electron transfer results for the acid terminated alkanethiol films were correlated to the increased disorder inferred from the IR data.\textsuperscript{1.57}

Creager and coworkers studied the blocking behavior of surfactants upon the redox behavior of 1 mM Ru(NH\textsubscript{3})\textsubscript{6}\textsuperscript{3+} in 1 M KCl at octadecanethiol monolayers at Au electrodes.\textsuperscript{1.79} The reductive current for this system was decreased by a factor of four with the addition of dodecyltrimethylammonium bromide to the solution. Addition of this surfactant to solutions with bare Au electrodes resulted
in no inhibition of reduction. It was proposed that the dodecyl chains of the tetraalkyl ammonium molecules penetrated the films at the defect sites, thus blocking diffusion of the Ru complex into the film. Additions of other surfactants, short- and long-chain viologens which are redox active, support the intercalation model.\textsuperscript{1,79}

For defect-free films, electron transfer is expected to occur through a tunneling mechanism, which is exponentially dependent on the distance between the redox species and the electrode.\textsuperscript{1,77} However, an opening in the film, due to a film tilt boundary or G conformer, would allow a redox species to approach much closer to the surface without direct contact. The current for species within these film openings would be vastly greater than the tunneling current of species held at the all-T extended film edge. A large amount of these defects are thought to exist in these films as suggested by electrochemical experiments.

Finklea and coworkers have analyzed the Tafel plot behavior, log(current) versus overpotential, of solution-confined redox species at octadecanethiol films at Au.\textsuperscript{1,76} They conclude that the Tafel plot can be digitally simulated by assuming tunneling current through a perfect monolayer that covers 98% of the surface, together with the current at various "collapsed" sites or film openings that occupy the remaining surface.

Chidsey and coworkers have studied the redox behavior of ferrocene terminated alkanethiols/unsubstituted alkanethiol mixed monolayers at Au in 1 M HClO\textsubscript{4}.\textsuperscript{1,80} These initial mixed monolayers showed surface-confined redox behavior for the ferrocene groups, as shown by the lack of splitting in the reduction and oxidation peak potentials. These mixed monolayer films were also reimmersed in unsubstituted alkanethiol solutions for ca. one week. The cyclic voltammograms revealed a splitting of ca. 70 mV between the reduction and
oxidation peak potentials, indicating slower electron transfer rates.

It is proposed that in the initial mixed monolayer films, a significant fraction of the ferrocene groups are in defect sites, where the terminal ferrocene group can approach much closer to the electrode surface.\textsuperscript{1,80} Thus, the electron transfer rate is dominated by ferrocene groups close to the electrode surface. Upon reimmersion in the alkanethiol solution, the ferrocene molecules at these defect sites are preferentially exchanged with electroinactive molecules. In these exchanged films, the electron transfer rate is dominated by ferrocene groups positioned at a distance further away from the surface, fixed by the length of the alkanethiol chain.

Exchange experiments of Collard and Fox are consistent with this model.\textsuperscript{1,81} A mixed monolayer of 16-(ferrocenylcarbonyloxy) hexadecanethiol and hexadecanethiol at Au was formed initially. A voltammetric wave was observed corresponding to the ferrocene-substituted alkanethiol. This film was then reimmersed for several days in a solution containing 16-ferrocenyl hexadecanethiol. Decrease in the first voltammetric wave was observed, along with the appearance of a second wave, shifted in potential from the first, as expected. After reimmersion for several days in a hexadecanethiol solution containing no electroactive species, decrease in the voltammetric wave of the second ferrocenyl species was observed, while very little decrease in the wave for the first ferrocenecarbonyloxy species was observed. Collard and Fox propose that rapid exchange occurs at defect sites, while very slow exchange occurs within ordered domains.\textsuperscript{1,81}

Summary of Previous Work

In summary, self-assembled monolayers of alkanethiols at various metal
substrates have been well-characterized by a number of techniques. These films form densely-packed monolayers at Au and Ag through strong metal-S bonds and significant neighboring alkane chain interactions. The orientation of the alkane chain of these films has been calculated to be ca. 30° at Au and ca. 15° at Ag. The absolute sign of the chain tilt at Ag remains controversial. The chemical nature of the film surface can be modified by using alkanethiol precursors with various terminal functional groups.

The average domain size of alkanethiol films at Au single-crystal substrates is ca. 50 Å, which is significantly smaller than the average domain size in the Au surface. The films are crystalline-like, but exhibit more ordered behavior at temperatures below 300 K. In the electrolyte solutions, these films are largely insulating and impermeable to ions. However, electron transfer behavior is concluded occur predominately at defect sites, proposed to be grain boundaries and chain tilt domain boundaries.

Raman Spectroscopic Investigation of Alkanethiol Films

Only a few reports of Raman scattering from these films have been published. However, Raman spectroscopy has the capacity to provide complementary and unique information about alkanethiol films at Au and Ag. Various properties, such as order, bonding and orientation, can be characterized with Raman scattering.

Vibrations that are directly related to chain conformations are strong in Raman spectra. The ν(C-S) and ν(C-C) bands, which are too weak for detection in surface IR spectra, include T and G modes which can provide information on disorder in the carbon backbone and adjacent to the S head group. In addition, the ν(C-H) region is sensitive to crystalline order of alkanes.
Relative intensities of various methyl and methylene stretches can be related to liquid and crystalline environments.

Substrate-alkanethiol bonding information can be obtained because $\nu(C-S)$ and $\nu(S-H)$ bands are strong in Raman spectra.\textsuperscript{1.51,1.54} The frequency of the $\nu(C-S)$ band has been found to be sensitive to S-metal bonding.\textsuperscript{1.51,1.54} In addition, disulfide bonds can be detected because the $\nu(S-S)$ is also strong.\textsuperscript{1.82,1.85}

Orientation information can be obtained through the use of surface Raman selection rules.\textsuperscript{1.84,1.85} These rules have been tested for highly symmetric molecules, such as benzene and toluene.\textsuperscript{1.86} These rules have not been applied to molecules of low symmetry, such as alkanethiols. However, it is expected that orientation information is also available with $\nu(C-S)$, $\nu(C-C)$, and $\nu(C-H)$ bands.

Furthermore, the above information is accessible in the electrochemical environment, because water is a weak scatterer. Thus, water is not a spectral interferant as in the case of IR spectroscopy. No in situ spectroscopic investigations of alkanethiols in the electrochemical environment have been reported. However, the spectroscopic characterization of these films under potential control is important to obtain a complete understanding of these films in the electrochemical environment.

The application of Raman spectroscopy to metal surface films has been hampered because of the poor sensitivity inherent in the Raman scattering phenomenon. In 1974, Fleischmann and coworkers reported high quality surface spectra of pyridine at Ag electrodes that were subjected to numerous oxidation-reduction cycles (ORCs).\textsuperscript{1.87} The large signal-to-noise ratio of the spectra was first attributed to multilayers of pyridine and increased electrode surface area created during the roughening pretreatment. Jeanmarie and Van Duyne\textsuperscript{1.88} and Albrecht and Creighton\textsuperscript{1.89} concluded that the ORCs were responsible for surface
enhancements of the adsorbate Raman scattering cross-section on the order of $10^5$ to $10^6$. In addition, the enhancement is realized for species at or in the vicinity of the roughened surface, resulting in a very surface sensitive technique.\textsuperscript{1,84}

Surface enhanced Raman scattering (SERS) has since been widely used to study electrode surfaces in ambient and electrochemical environments.\textsuperscript{1,90} A rough metal surface morphology can produce surface enhancements of up to a factor of $10^7$. Only a few metals have been reported to exhibit large surface enhancements, predominantly Ag, Cu and Au.\textsuperscript{1,90} Other metals, including Rh,\textsuperscript{1,91} Ga,\textsuperscript{1,92} and Pt\textsuperscript{1,93} have also been predicted or claimed to exhibit enhancements under the appropriate conditions of excitation wavelength and surface roughening to produce roughness features of the necessary geometries.\textsuperscript{1,94} The large surface enhancement allows vibrational spectra of high quality to be obtained from adsorbates at these metals with reasonable acquisition times.

However, one problem with the SERS approach is that the surface roughness required for large enhancements is known to affect the Raman spectra for certain adsorbates obtained at these surfaces. Cotton and Furtak have both provided examples of surface adsorbates whose Raman spectra are sensitive to the presence of atomic scale roughness features on electrochemically roughened Ag electrodes. Feng and Cotton reported evidence in the SERS spectra for two types of surface sites for methylviologen adsorbed at roughened Ag electrodes.\textsuperscript{1,95} Byahut and Furtak have reported similar effects for p-nitrosodimethylaniline on roughened Ag electrodes.\textsuperscript{1,96} Different chemical interactions occur at these sites resulting in frequency shifts in the Raman spectra. Additionally, SERS spectra have been shown to be sensitive to the type of roughening pretreatment used to prepare such surfaces.\textsuperscript{1,97}

A second problem with the SERS approach is that the relative contributions
of different enhancement processes are not well-characterized.\textsuperscript{1.90} For example, the magnitude of the charge-transfer enhancement associated with atomic-scale roughness features can change with surface pretreatment, applied potential and excitation wavelength.\textsuperscript{1.96,1.98}

Additionally, a direct comparison between SERS studies and other studies is hindered by the different surface morphologies employed. For example, Joo and coworkers have obtained SERS spectra of butanethiol at Ag colloid surfaces, which support very strong surface enhancement.\textsuperscript{1.54} On the other hand, Walczak and coworkers\textsuperscript{1.49} and Laibinis and coworkers\textsuperscript{1.50} used Ag films evaporated onto polished Si single-crystal wafers in IR spectroscopic investigations. In fact, almost all of the alkanethiol studies cited above involved metal substrates that ranged from mechanically polished, mirrored surfaces to single-crystalline surfaces.

Given these uncertainties about the SERS process, it is clearly desirable to obtain Raman spectra from surfaces of morphology and structure similar to those used in other alkanethiol studies. In addition, spectra obtained from mechanically polished, smooth Au and Ag surfaces can be compared to those obtained at electrochemically roughened electrodes, which exhibit considerably more enhancement. Thus, the general applicability of SERS spectra for the investigation of these self-assembled films can be assessed. These smooth surfaces, however, still exhibit significant enhancement. The ability to obtain surface Raman spectra from metals that do not exhibit this additional surface enhancement, such as Pt, would immensely broaden the range of chemical systems that could be investigated with Raman spectroscopy.

There have been reports of spectra from various surfaces that exhibit less enhancement than observed at electrochemically roughened Ag and Au electrodes.
Surface Raman spectra of pyridine from mechanically polished Ag\textsuperscript{1,99,1,100} and Au\textsuperscript{1,101,1,102} surfaces have been reported. Udagawa and coworkers\textsuperscript{1,103} reported the spectra of pyridine at Ag (100), but significant enhancement was observed at this surface. Campion and coworkers demonstrated the successful use of Raman spectroscopy for the study of benzene and pyridine monolayers on non-enhancing surfaces of single crystal Ag\textsuperscript{1,104,1,105,1,106} pyridine and 4-cyanopyridine at Rh\textsuperscript{1,107,1,108} and nitrobenzene on single crystal Ni\textsuperscript{1,109}. In these cases, spectra have been obtained from aromatic adsorbates that possess strong Raman cross-sections. The acquisition of surface Raman spectra of alkanethiols at mechanically polished Ag and Au and other metal surfaces is more difficult.

Research Objectives

The overall goal of this research project is to more fully characterize self-assembled monolayers of alkanethiols at Ag and Au. Much research has been undertaken in this field, but the combination of Raman spectroscopy and electrochemistry is able to provide unique information that is significant in understanding these monolayers. This research also requires the development of Raman spectroscopy in the investigation of monolayers at non-enhancing surfaces.

Specific goals of this research include:

1.) Assess utility of Raman spectroscopy for investigations of organized molecular assemblies on surfaces.

2.) Determine Raman vibrational assignments for n-alkanethiols in the $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) regions.
3.) Develop methodology for Raman spectroscopy of adsorbates at smooth, mirrored metal surfaces.

4.) Develop methodology for the use of surface Raman selection rules for obtaining orientations of molecules of low symmetry at metal surfaces.

5.) Determine the orientation of alkanethiols at Ag and Au substrates, using information from $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) regions.

6.) Compare Raman spectra from a variety of surface morphologies, including electrochemically roughened, mechanically polished, and single-crystalline surfaces.

7.) Investigate conformational and defect structure of alkanethiol films.

8.) Investigate behavior of alkanethiols in the electrochemical environment.

9.) Investigate factors that influence orientation at different substrates.

10.) Acquire spectra of aromatic thiol monolayers at polycrystalline, mechanically polished Pt metal surfaces.

By studying alkanethiols with a wide-range of chain lengths, the assignments taken from the literature can be evaluated and revised. The determination of orientations of alkanethiols at Ag and Au surfaces involves the development of a method for using surface Raman selection rules. Previously, these rules were applied to highly symmetric molecules. The validity of these rules for highly unsymmetric molecules, such as alkanethiols, is evaluated for $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) regions. Electrochemical methods, such as cyclic voltammetry and under-potential deposition, characterize the desorption behavior and defect structure of these films. The spectroscopic characterization of these films in the electrochemical environment are undertaken to investigate possible potential
dependent reorientation. These in situ results also shed light on the influence of the substrate on orientation. Spectra of aromatic thiols obtained at Pt surfaces are presented in the last chapter.
Chapter 2

EXPERIMENTAL

This chapter provides a detailed description of the instrumentation, materials, and experimental protocol used in the work presented in this dissertation.

Raman Spectroscopic Instrumentation

Laser excitation

Laser excitation at 514.5-nm was provided by a Coherent Radiation Innova 90-5 Ar\(^+\) laser. Excitation at 600 nm was provided by Ar\(^+\) laser pumping of a Coherent CR-599 dye laser containing a Rhodamine 6G/ethylene glycol solution. For excitation at 720 nm, a Pyridin 2/propylene carbonate/ethylene glycol solution was used. A narrow bandpass birefringent filter in the dye laser was used to select the desired excitation wavelength. Plasma and fluorescent lines of the laser excitation beam are removed with bandpass filters from Pomfret Research Optics, Inc. (ca. 3 nm bandpass).

PMT-Raman System

The investigation of the SERS behavior of pyridine and Cl\(^-\) adsorbates at roughened Ag electrodes was performed with a Spex 1403 double monochromator.
The block diagram of this system is shown in Figure 2.1. Scattered radiation is collected using a concave mirror, passed through a planar folding mirror and polarization scrambler onto the entrance slit of the double monochromator.

The configuration of the double monochromator is shown in Figure 2.2. The entrance and exit slits, $S_1$ and $S_4$, were set at 0.8 mm, and the center slits, $S_2$ and $S_3$, were left open at the setting of 10 mm. The double monochromator is equipped with 1800 grooves/mm holographically ruled gratings. Detection is accomplished with a high sensitivity, GaAs photocathode, RCA C31034A photomultiplier tube (PMT), which is thermoelectrically cooled to ca. -25°C. Dark count values typically ranged from 30 to 100 counts/s. The spectrometer is interfaced to a Spex Datamate dedicated microcomputer system.

**CCD-Raman Systems**

The remaining Raman spectra were acquired with a Spex 1877 triple monochromator. The block diagram of this system is shown in Figure 2.3. Scattered radiation was collected with a Nikon f/1.4 camera lens or Minolta f/1.2 camera lens (both 50 mm focal length), passed through a depolarization scrambler, and focused onto the entrance slits of the triple monochromator. The configuration of this system is shown in Figure 2.4. The gratings in the filter stage ($G_1$ and $G_2$) were 600 gr/mm, and the grating used in the spectrograph stage ($G_3$) was 1200 gr/mm. Slit widths were varied with the wavelength of excitation. For 514.5 nm excitation, the slit widths for $S_1$, $S_2$, and $S_3$ were typically 0.25 mm, 2.8 mm, and 0.25 mm, respectively. For 600 and 720 nm excitation, the slit widths for $S_1/S_2/S_3$ were either 0.4mm/2.8mm/0.4mm or 0.5mm/2.8mm/0.5mm.

Detection was accomplished with a Photometrics PM512 frontside-illuminated charge coupled device (CCD) cooled with liquid nitrogen between -95 and -125
Figure 2.1. Schematic diagram for PMT-based Raman spectroelectrochemical system. A = analyzer, C = collection lens, M = mirror, S = scrambler.
Figure 2.2. Configuration of Spex double monochromator. M = mirror, G = grating, S = slit.
Figure 2.3. Schematic diagram for CCD-based Raman spectroelectrochemical system.
Figure 2.4. Configuration of Spex 1877 Triplemate.
M = mirror, G = grating, S = slit.
°C. The CCD images were processed with a Photometrics RDS200 system equipped with a custom version of SpectraCalc™.

Electrochemical Instrumentation

Potentials were controlled with an IBM Instruments model EC/225 Voltammetric Analyzer. Total charge passed during oxidation-reduction cycles was monitored with a Princeton Applied Research model 379 digital coulometer. Current-potential curves were recorded on Hewlett-Packard X-Y recorder.

Electrochemical Cells

Cyclic voltammetry and ex-situ roughening were performed in a standard electrochemical cell shown in Figure 2.5. A Pt wire wrapped around the Luggin capillary served as the counter electrode. The working electrodes consisted of Ag and Au disks, 0.7 mm in diameter and ca. 0.2 mm in thickness, Ag-soldered to brass screws of the same diameter. Pt foils were punched to the same diameter. The working electrode was screwed into a threaded brass holder. The working electrode and brass mount were wrapped with parafilm in order to expose only the polished electrode surface to solution. A Ag/AgCl reference electrode was used.

Spectroelectrochemical Cells

The spectroelectrochemical cell used in the SERS and differential reflectivity experiments is shown in Figure 2.6. The body of the cell is made of Kel-F, containing ca. 5 mL of electrolyte. The Pt auxiliary electrode is housed in a separate glass compartment, secured in the Kel-F body with epoxy resin. A medium coarse frit is fitted at the end of the auxiliary compartment and is used
Figure 2.5. Electrochemical cell used for cyclic voltammetry and ex-situ roughening.
Figure 2.6. Spectroelectrochemical Cell.

a = micrometer, b = micrometer shaft, c = set screw, d = Kel-f shroud, e = outer backplate, f = small O-ring, g = inner backplate, h = large O-ring, i = tapered hole for straight bore Hamilton Luer-lok valve, j = cell body, K = right angle Hamilton valve with Luer-lok fitting, l = coiled Pt auxiliary electrode, m = medium porosity glass frit, n = glass housing for auxiliary electrode solution, o = large O-ring, p = pyrex plate, q = front plate, r = L-shaped Lucite bracket, S = hole for micrometer, t = threaded holes for mounting cell body to Lucite bracket, u = threaded holes for mounting cell onto spectrometer sample holder.
Figure 2.6. Schematic diagram of the spectroelectrochemical cell.
for ion conductance. The working electrode is positioned in the cell body by a micrometer shaft. A threaded Kel-F shroud surrounds the end of the shaft and the electrode is screwed in to make electrical contact with the micrometer shaft. The working electrode is wrapped with parafilm in order to expose only the polished surface to solution. A Ag/AgCl reference electrode was used. The window was made of quartz, and the rest of the cell body was made of Lucite. Further details of the cell design and construction are given in reference 2.1.

**Differential Reflectance Instrumentation**

The differential reflectance spectrometer was constructed in-house by Anita Guy\(^2\) and is shown in Figure 2.7. A Harrick model RSS-C 018 rapid scan monochromator is equipped with a General Scanning model G108 galvanometer mounted with a 600 grooves mm\(^{-1}\) grating. The light source is a tungsten halogen lamp. The output of the monochromator is split 50/50 with a bifurcated fused silica fiber optic cable. Half of the output is directed to the spectroelectrochemical sample cell. The other half is detected by a Hamamatsu model 374 photomultiplier tube and used as a reference signal to compensate for fluctuations in the lamp source. The sample beam passes through a Glan-Thompson polarizing prism before being focused onto the sample. The angle of incidence and collection of the sample beam can be varied from 15° to 60° by a rotating arm assembly which holds the optics and the sample spectroelectrochemical cell. The reflected light is focused into another fiber optic cable and detected by a PMT which is matched with the reference beam PMT. The two voltages are then input to an Evans Electronics model 4122 ratiometer where the ratio of the reflected sample voltage to the reference voltage is determined. The ratio is integrated with an Evans Electronics model
Figure 2.7. Schematic diagram of the differential reflectance system. L = lens, P = polarizer.
4130A gated integrator and then digitized and collected by a DEC LSI-11/23 microcomputer equipped with a 12-bit, successive approximations A/D converter. Two scan cycles were run from 400 to 800 nm with increments of 10 nm and an integration time of 1 s under computer control. The angle of incidence and collection of the sample beam was 60° and parallel polarized light was used.

The software routine written for the differential reflectivity instrumentation consisted of a Fortran main routine, REFL.FOR, and a Fortran-callable Assembly language data acquisition routine, SCAN.MAC.² ² Scanning parameters, such as initial and final wavelengths, scan increment, integration time and number of scans, are entered into the main routine. These parameters are transferred to the assembly language subroutine for computer-controlled acquisition and digital conversion of the reflectance signals. The main routine then calculates the differential reflectivity from the collected signals and stores the results to floppy disk. The data were analyzed with software written for LESSA (Laboratory for Electron Spectroscopy and Surface Analysis).² ³

SEM Instrumentation

An ISI-DS130 scanning electron microscope was used to obtain micrographs of electrode surfaces. The electrode surfaces were observed without any coating of the surface. The microscope tilt angle was 0°, and the electron energy was in the range of 15 to 18 KeV. Features that were ca. 50 nm or smaller in size could not be resolved.

XPS Instrumentation

XPS measurements of films at Pt were obtained on a VG ESCALAB MKII electron spectrometer. Monochromatic x-rays from the Al K\textsubscript{α} line were used.
Integrated intensities of the C 1s (286 eV), S 2p (165 eV), and Pt 4f (73 eV) bands were determined by spectral deconvolution using Gaussian profiles. The peak areas so determined were then corrected for scattering cross-sections using accepted values.²⁴

Materials

Ag disks (99.999%), Au disks (99.999%), Ag (111) and Ag (100) single-crystal disks were purchased from Johnson Matthey. Pt foils (99.9%) were purchased from Alfa Products.

1-Butanethiol (99+%), 2-butanethiol (98%), 1-pentanethiol (98%), 1-hexanethiol (95%), 1-octanethiol (97%), 1-nonanethiol (98%), 1-decanethiol (97%), 1-dodecanethiol (98%), 1-hexadecanethiol (92%), 1-octadecanethiol (98%), and thiophenol (99+%) were purchased from Aldrich. The generous donation of 2,5-dihydroxythiophenol by Professor Arthur T. Hubbard (Department of Chemistry, University of Cincinnati) is gratefully acknowledged.

Ethanol (absolute) was purchased from Midwest Grain Products and Quantum Products. Pyridine was purchased from Burdick and Jackson. Sulfuric acid (95%) and NaCl were purchased from Fisher Scientific. Perchloric acid (70%), KOH pellets and NaOH pellets were purchased from Baker. H₂O₂ (30%) was purchased from VWR. KCl was purchased from Fisher Scientific and Mallinckrodt. PbCl₂, Pb(NO₃)₂, and NaCN were purchased from MCB. TINO₃ (99.999%) and NaClO₄ (anhydrous, 99+) were purchased from Aldrich. Inorganic compounds were analytical reagent grade. All were used as received.

Aqueous solutions were made with triply distilled H₂O, the last distillation from basic permanganate, and deaerated with N₂ prior to use in electrochemical studies. Aqueous 1-butanethiolate and thiophenolate solutions were made by
combining one part 1-butanethiol or thiophenol with nine parts 5 M NaOH.

Procedures
Electrode Mechanical Polishing Procedures

Polycrystalline Ag, Au and Pt disks and foils were mechanically polished to a mirror finish using 1.0, 0.3, and 0.05 μm alumina, rinsed with doubly or triply distilled, deionized water (TDI), and then sonicated for 2 min in TDI water to remove any trapped alumina.

Electrode Roughening Procedure for Differential Reflectance and Related SERS Experiments

In these experiments, Ag electrodes were roughened in situ with double-potential step oxidation-reduction cycles (ORCs). Mechanically-polished electrodes were initially held at -0.2 V in 0.1 M KCl or 0.1 M KCl/0.05 M pyridine. The electrode was then subjected to a double-potential step ORC in which 2.6 mC/cm² anodic charge was passed for each trial, and the potential of the electrode was returned to -0.2 V. All ORCs were performed in the absence of laser exposure.

Electrode Roughening Procedure for Alkanethiol Experiments

Rough Ag and Au electrodes used in alkanethiol studies were mechanically polished and roughened ex situ before immersion in alkanethiol/ethanol solutions. Linear potential sweep ORCs were applied to Ag electrodes in the presence of 0.1 M KCl aqueous solution. For Ag, the initial potential was -0.20 V versus a Ag/AgCl reference electrode and the potential sweep was reversed at ca. +0.22 at a scan rate of 10 mV/s, resulting in ca. 40 mC/cm² of anodic charge passed. For
Au electrodes, unless otherwise indicated, 20 linear potential sweep ORCs were performed. The initial potential was -0.20 V and the potential sweep was reversed at ca. +1.20 V at a scan rate of 100 mV/s, resulting in ca. 10 mC/cm² of anodic charge passed per sweep. The electrodes were then removed from solution at open circuit potential, rinsed with TDI water and 100% ethanol and then exposed to the alkanethiol solution.

Chemical Polishing of Single-Crystal Ag Surfaces

Ag (111) and Ag (100) surfaces were mechanically polished to a mirror finish with 1.0, 0.3, and 0.05 μm alumina, rinsed with triply distilled, deionized water (TDI), and then sonicated for 2 min in TDI water to remove any trapped alumina. Two aqueous solutions were then employed for chemical polishing. The first solution contained equal parts 20% H₂O₂ and 0.43 M NaCN and the second contained 0.75 M NaCN. A single-crystal electrode was immersed in the first solution for 1-2 s, during which gas evolution occurred, and then immediately immersed in the second solution, until gas evolution ceased, ca. 5 s. The electrode was stirred a few times in the second solution to aid polishing. The Ag disk was then rinsed with copious amounts of TDI water, and the process was repeated ca. 10 times.

Film Formation Procedures

Alkanethiol films are formed at a variety of surfaces. The designation "smooth" refers to mechanically polished, polycrystalline surfaces. "Rough" refers to electrodes roughened by linear potential sweep ORCs. Smooth, rough, and single-crystal surfaces were immersed in alkanethiol solutions in 100% ethanol for times ranging commonly from 2 hrs to 24 hours to allow the self-assembled
monolayers to form. Alkanethiol solutions were prepared by adding ca. 0.04 mL of alkanethiol with a disposable syringe to ca. 25 mL of ethanol. The resulting concentrations of alkanethiols ranged from ca. 20 mM for butanethiol to ca. 5 mM for long-chain alkanethiols. No differences in behavior were observed with different immersion times, except in the Pb deposition studies, where the immersion times are indicated. These surfaces were then rinsed again with 100% ethanol and allowed to air dry before placement in electrochemical cells or spectral acquisition in air.

1-Octadecanethiol at Ag evaporated onto Si (111) was a gift from Professor Marc Porter (Department of Chemistry, Iowa State University). The Ag substrate was prepared by the initial resistive evaporation of 15-20 nm of Cr onto 2-in. diameter polished p-type Si (111) wafer (Virginia Semiconductors, Inc.), followed by 250-300 nm of Ag (99.9%). The substrate was immersed in ca. 1 mM alkanethiol/ethanol solution for ca. 12-24 hr. 1-Octadecanethiol was purchased from Aldrich.

Acquisition of Differential Reflectance Spectra

Reflectance spectra were obtained on freshly polished Ag electrodes for each trial. An initial scan measured the reflectivity of the smooth Ag surface, which is defined as $R_o$, while the potential of the electrode was held at -0.2 V. The electrode was then subjected to a double-potential step oxidation-reduction cycle in which 2.6 mC/cm² anodic charge was passed for each trial, and the potential of the electrode was returned to -0.2 V. The reflectivity of the roughened surface was then measured and defined as $R_d$. The reflectance spectra are reported as

$$\frac{\Delta R}{R} = \frac{(R_d - R_o)}{R_o}.$$
Raman Spectral Acquisition Procedures for Studies of Pyridine and Cl⁻ Adsorbates

These experiments were performed with the PMT-double monochromator system. The Raman spectra were obtained with 514.5 nm excitation from an Ar⁺ laser or with 600.0 nm excitation from an Ar⁺ laser-pumped tunable dye laser. Laser powers measured at the sample were ca. 150 to 450 mW. An angle of incidence of 60° with respect to surface normal and parallel polarized light were used. Spectra were obtained in single scans with 0.5 cm⁻¹ increments at an integration time of 1 s. All spectra were acquired while the potential of the Ag electrode was poised at -0.2 V.

The background Rayleigh intensity is significant compared to the intensity of the ν(Ag-Cl) band. Therefore, digital subtraction was performed to improve the sensitivity. This was accomplished in the following manner. An initial scan was acquired after an oxidation-reduction cycle (ORC) pretreatment. From this spectral response was subtracted the scan of the surface after the electrode potential had been stepped to -1.2 V for five minutes and then returned to -0.2 V. This negative potential excursion sequence is known to reduce the Raman intensity of the ν(Ag-Cl) significantly. Thus, the Rayleigh background can be adequately removed allowing more accurate quantitation of the peak area of the band.

Raman Spectral Acquisition Procedures for Alkanethiol Studies

Spectra of bulk alkanethiols were acquired with the liquid in a sealed capillary or NMR tube. Solid alkanethiol spectra were acquired by cooling the capillary and sample with liquid nitrogen and obtaining spectra with series of 10 sec integrations to prevent laser warming. Acquisition times were commonly 1-
5 minutes for liquid spectra and 1-2 minutes for solid spectra.

Spectra obtained from alkanethiols films at metal surfaces were obtained in air or within the spectroelectrochemical cell. An angle of incidence of 60° with respect to surface normal and parallel polarized light were used. Commonly, laser powers of 100-200 mW were used for 514.5 and 600 nm excitation and 40 mW for 720 nm excitation. Integration times varied from 1 to 20 min.

Many of the raw surface spectra exhibited a sloping background, which was baseline corrected with a two-point linear correction scheme. Cosmic spikes, commonly 2 pixel units wide, were removed before plotting. Surface spectra exhibiting weak Raman signals were typically collected in a region of the CCD detector with minimal background structure. The background structure was evaluated by collection of the scattered radiation at ca. 2300 cm\(^{-1}\) from bare Au irradiated with 514.5 nm excitation. In this spectral region, no vibrational behavior is observed, but a strong background continuum is detected. This results in a relatively flat spectrum except for background features inherent in the CCD detector. The region of the CCD illuminated with scattered radiation from metal surfaces was commonly 60 pixel units. This image was typically divided into 5 binning groups, and larger number of binning groups were used in some cases to prevent saturation of the analog/digital converter. For bulk spectra, larger portions of the CCD were illuminated and 10 to 20 binning groups were employed. The use of smoothing routines is indicated in the figures.

Curve Fitting Procedures

Spectral decomposition was accomplished with a curve fitting program available in SpectraCalc™. In the \(\nu(\text{C-H})\) region, nine peaks were used to decompose spectra of octanethiol and longer-chain alkanethiols, while eight peaks
were used for butanethiol and pentanethiol. Prior to curve fitting, each spectrum was background subtracted using a two-point linear correction scheme. Peak frequencies were constrained using values observed in bulk liquid and solid spectra. Peak widths were occasionally constrained to obtain consistent curve fits between spectra of similar molecules. Surface peaks were decomposed using a 20% Lorentzian/80% Gaussian peak shape, and bulk liquid peaks were decomposed using 50% Lorentzian/50% Gaussian peak shape. These combinations were found to give the smallest residual for well resolved peaks. Tabulated values involving peak area ratios are calculated from the average of two or more curve fit trials on each spectrum.
Chapter 3

RAMAN VIBRATIONAL ASSIGNMENTS FOR n-ALKANETHIOLS

Introduction

Very few reports appear in the literature on Raman spectroscopic studies with vibrational assignments of n-alkanethiols. The focus of previous work has been on short alkanethiols, such as propanethiol and butanethiol. In addition, spectra in the \( \nu(C-S) \) and \( \nu(C-C) \) regions for liquid and solid hexadecanethiol have been reported.

The \( \nu(C-H) \) region for alkanes and alkanoic acids have been characterized with Raman spectroscopy. This region is very complex, with as many as 14 bands appearing in the solid bulk spectra. The \( \nu(C-C) \) region, which is strong in Raman spectra and weak in IR spectra, has been extensively studied in phospholipid systems. Information concerning the conformations of the acyl segments of phospholipid molecules for membrane modeling studies can be obtained with Raman spectroscopy.

It is expected that Raman spectra for alkanethiols would be similar to spectra for n-alkanes and other molecules with significant alkane segments, such as phospholipids. Indeed, the Raman spectra in the \( \nu(C-H) \) region for alkanethiols and other alkane molecules are similar. However, in the \( \nu(C-C) \) region, there are striking differences in the Raman spectra for several related molecules in the
solid state. In the region from 1050 cm\(^{-1}\) to 1140 cm\(^{-1}\), two bands are observed for long-chain n-alkanes,\(^5\)\(^7\) three bands are observed for phosphatidylcholines,\(^1\)\(^7\)\(^0\)\(^7\)\(^4\) and four bands are observed for hexadecanethiol.\(^1\)\(^7\)\(^5\) Consequently, there has been confusion in the assignments in the \(\nu(C-C)\) region for hexadecanethiol.\(^1\)\(^7\)\(^5\)

This chapter will discuss the assignments for n-alkanethiols in the spectral region from 600 to 1300 cm\(^{-1}\), which includes the \(\nu(C-S)\) and \(\nu(C-C)\) bands, and the \(\nu(C-H)\) region from 2800 to 3000 cm\(^{-1}\). Several approaches have been undertaken to confirm or revise peak assignments. In the \(\nu(C-C)\) and \(\nu(C-S)\) region, gauche (G) and trans (T) assignments have been determined by comparing the frequencies and relative intensities of bands in the Raman spectra for bulk alkanethiols in the liquid and solid state. In the \(\nu(C-H)\) region, assignments for bands are also aided by comparison of bulk liquid and solid spectra. Additionally, the polarization behavior of these bands can be used to assess the symmetric or asymmetric nature of the methyl and methylene bands. Trends in the spectra for all regions will be investigated with respect to chain length. These bands will be compared to previous experimental and theoretical work of various alkyl molecules.

\(\nu(C-S)\) Region

The \(\nu(C-S)\) region between 600 and 750 cm\(^{-1}\) provides conformational information about C-C bonds adjacent to the C-S bond in the alkanethiols, \(C_nH_{2n+1}SH\). Figures 3.1a through i show the liquid spectra for the \(n = 4, 5, 8, 9, 10, 12, 16,\) and 18 alkanethiols and butanethiolate, respectively, in the region from 600 to 950 cm\(^{-1}\). Two \(\nu(C-S)\) bands are assigned in this region. In the liquid alkanethiols, these bands correspond to the gauche (G) \(\nu(C-S)\) at ca. 655 cm\(^{-1}\) and the trans (T)
Figure 3.1. Raman spectra in the $\nu$(C-S) region (514.5 nm excitation) of a) liquid butanethiol, b) liquid pentanethiol, c) liquid octanethiol, d) liquid nonanethiol, e) liquid decanethiol, f) liquid dodecanethiol, g) liquid hexadecanethiol, h) liquid octadecanethiol, i) aqueous butanethiolate. Incident power: 200 mW. Integration times: a-h) 2 min, i) 5 min.
\( \nu(C-S) \) at 730 cm\(^{-1}\).\(^{1,51,54}\) These assignments are based on the work of Joo and coworkers who assigned the \( \nu(C-S)_G \) and \( \nu(C-S)_T \) of butanethiol by comparing the Raman spectra of the bulk liquid, aqueous thiolate solution, and Ag SERS spectra of propanethiol\(^{1,51}\) and butanethiol.\(^{1,54}\) The frequencies of the bands in this region for each molecule are given in Table 3.1.

The spectra for the liquid alkanethiols are almost identical in this region. The \( \nu(C-S)_G \) band is more intense than the \( \nu(C-S)_T \) band in each of the spectra, consistent with the expected disorder in the liquid state. The \( \nu(C-S)_T \) at ca. 730 cm\(^{-1}\) and adjacent bands at slightly lower and higher frequencies overlap in the spectra of alkanethiols longer than pentanethiol.

The \( \nu(C-S) \) region of butanethiolate is somewhat different than that of butanethiol. While the relative heights of the \( \nu(C-S)_G \) and \( \nu(C-S)_T \) bands from the thiolate are similar to those observed in the liquid thiol, the G and T band frequencies have shifted down 4 cm\(^{-1}\). The band observed 708 cm\(^{-1}\) in the bulk liquid has shifted 4 cm\(^{-1}\) higher. Joo and coworkers concluded from this behavior that the 708 cm\(^{-1}\) band is not the \( \nu(C-S)_T \) mode.

Upon cooling the neat alkanethiols to solids with liquid N\(_2\), the bands in this region become better resolved and dramatically different spectra are observed. Spectra for the solids are shown in Figures 3.2a through h for \( n = 4, 5, 8, 9, 10, 12, 16, \) and 18. For pentanethiol through octadecanethiol, the \( \nu(C-S)_G \) band at ca. 655 cm\(^{-1}\) totally disappears from the spectra. This change in relative intensity of the T and G bands is evidence of increased ordering present in the crystalline solid alkanethiols. In butanethiol, there is still significant intensity in the \( \nu(C-S)_G \) band and the bands are generally broad which may be due to incomplete freezing of the material under these conditions.

Definite trends are seen in the bands in the solid spectra. The band at ca.
Table 3.1. Raman Vibrational Assignments and Peak Frequencies in the $\nu$(C-S) Region of $C_nH_{2n+1}SH$.

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Figure 3.2. Raman spectra in the $\nu$(C-S) region (514.5 nm excitation) of a) solid butanethiol, b) solid pentanethiol, c) solid octanethiol, d) solid nonanethiol, e) solid decanethiol, f) solid dodecanethiol, g) solid hexadecanethiol, h) solid octadecanethiol. Incident power: 100 mW. Integration times: ca. 1 min.
82

891 cm\(^{-1}\) in each spectrum has been assigned to the T methyl rocking mode.\(^{3,8}\) The \(\nu(C-S)_T\) band is at ca. 733 cm\(^{-1}\). The rest of the bands in these solid spectra are assumed to be T bands, with the exception of G bands in the butanethiol spectrum.

These other bands follow the trend observed by Snyder and Schachtshneider in the IR spectra of n-alkanes at liquid N\(_2\) temperatures.\(^{3,9}\) They assign these bands to methylene rocking-twisting modes. These bands are described as methylene rocks in Table 3.1 to avoid confusion with a similar series in the 1100-1300 cm\(^{-1}\) region, which will be described as methylene twists. The number of modes increases systematically with chain length. For instance, two bands are observed in this spectral region for solid pentane, and eight bands are observed for solid docosane.\(^{3,9}\) The lower frequency limit of these bands is ca. 720 cm\(^{-1}\), while the upper limit is ca. 1060 cm\(^{-1}\).\(^{3,9}\) These limits were also calculated by Schachtshneider and Snyder using normal coordinate analysis.\(^{3,10}\)

In the solid alkanethiol spectra in Figure 3.2, the bands follow the same trend. The lowest frequency band at ca. 707 cm\(^{-1}\) is lower than the 720 cm\(^{-1}\) limit observed by Snyder and Schachtshneider.\(^{12,13}\) This band has been assigned as a methylene rocking mode by Joo and coworkers.\(^2\) However, it is likely that this band can be attributed to a vibration involving the S group. While the lowest frequency of the methylene rocking modes observed for propane is at a higher frequency of ca. 745 cm\(^{-1}\),\(^{3,9}\) a band at 704 cm\(^{-1}\) is observed for propanethiol.\(^{1,51}\) This band has been designated a T,G band in Table 3.1.

Joo and coworkers have also assigned the band at ca. 856 cm\(^{-1}\) to a CSH deformation.\(^2\) The spectral behaviors in Figure 3.2 suggest, however, that all bands in this region, aside from the \(\nu(C-S)\) and methyl rocking modes, contain significant methylene rocking-twisting character.
As previously noted, the liquid alkanethiol spectra in Figure 3.1 are quite similar. Whereas only the $\nu(C-S)_T$, methyl rock, and 707 cm$^{-1}$ bands are observed at constant frequency in the solid spectra, several more bands have similar frequencies in the liquid spectra. These include the bands at ca. 770, 830, 848, 870, and 925 cm$^{-1}$. Snyder assigns bands in the IR spectra of liquid alkanes at 920 cm$^{-1}$ to T methyl rocks, and bands at 908 and 898 cm$^{-1}$ G methyl rocks. Maissara and Devaure assign the bands at ca. 890 cm$^{-1}$ in the Raman spectra of alkanes to the T CH$_2$ rock, and the bands at ca. 850 and 870 cm$^{-1}$ to G CH$_3$ rocks. The remaining bands in the liquid spectra are assigned to G methylene rocks, except for the few T bands in the butanethiol and pentanethiol spectra, which are included in Table 3.1.

$\nu(C-C)$ Region

The spectra for liquid and solid alkanethiols in the frequency region from 950 to 1325 cm$^{-1}$ are shown in Figures 3.3 and 3.4, respectively. It is instructive to analyze the solid spectra first, where almost all the bands are assumed to be T.

The remaining methylene rocking/twisting bands are observed up to ca. 1055 cm$^{-1}$, which is the limit calculated with normal coordinate analysis by Schachtshneider and Snyder. The number of bands observed between 705 and 1160 cm$^{-1}$ increase approximately linearly with the increase in the number of methylene units.

In the solid alkanethiol Raman spectra in Figure 3.4, only four bands of relatively constant frequency are observed in the region from 1060 to 1135 cm$^{-1}$, unlike the regions at higher and lower frequencies. Schachtshneider and Snyder observe $\nu(C-C)$ bands in this region in the IR spectra of solid alkanes.
Figure 3.3. Raman spectra in the $\nu$(C-C) region (514.5 nm excitation) of a) liquid butanethiol, b) liquid pentanethiol, c) liquid octanethiol, d) liquid nonanethiol, e) liquid decanethiol, f) liquid dodecanethiol, g) liquid hexadecanethiol, h) liquid octadecanethiol, i) aqueous butanethiolate. Incident power: 200 mW. Integration times: a-h) 2 min, i) 5 min.
Figure 3.4. Raman spectra in the $\nu$(C-C) region (514.5 nm excitation) of a) solid butanethiol, b) solid pentanethiol, c) solid octanethiol, d) solid nonanethiol, e) solid decanethiol, f) solid dodecanethiol, g) solid hexadecanethiol, h) solid octadecanethiol. Incident power: a) 200 mW, b-h) 100 mW. Integration times: a) ca. 3 min, b-h) ca. 1 min.
The bands at ca. 1060 cm\(^{-1}\) and 1130 cm\(^{-1}\) have been assigned by Harrand as the \(\nu_a(C-C)_T\) and \(\nu_p(C-C)_T\) modes, respectively.\(^{3,11}\) The results of Rabe and coworkers are consistent with these assignments.\(^{3,12}\) These bands are observed at lower frequencies for pentanethiol and butanethiol.

A third \(\nu(C-C)_T\) band is observed between 1064 and 1104 cm\(^{-1}\) in the spectra of octanethiol through octadecanethiol, Figures 3.4c through h, respectively. This band increases in frequency with increasing chain length. This band is not observed in the Raman spectra of long-chain solid alkanes,\(^{3,7}\) although it is observed in the Raman spectra of phosphatidylcholines.\(^{1,70,1,74,3,3-3,6}\) Frequencies reported for phospholipid molecules with 16 and 18 carbon acyl chains are similar to those for solid hexadecanethiol and octadecanethiol, respectively. The frequencies of the alkanethiol bands in Figures 3.3 and 3.4 are given in Table 3.2. Snyder and Schachtshneider report a similar sequence in the IR spectra for solid alkanes.\(^{3,9}\) The band is observed ca. 1065 cm\(^{-1}\) for pentane and increases to 1125 cm\(^{-1}\) for \(n\text{-C}_{30}H_{62}\).

The fourth band observed at ca. 1110 cm\(^{-1}\) for alkanethiols is not observed in the Raman spectra for solid long-chain alkanes\(^{3,7}\) or phospholipids.\(^{1,70,1,74,3,3-3,6}\) This band is also not observed in the IR spectra for alkanes. The band at 1110 cm\(^{-1}\) is, therefore, likely to involve the S group.

In addition to methylene rocking/twisting bands in the IR spectra of alkanes from 975 to 1060 cm\(^{-1}\), Snyder and Schachtshneider also observe \(\nu(C-C)\) bands in this region exhibiting two different progressions of band frequencies.\(^{3,9}\) In the solid alkanethiol Raman spectra, however, the definite pattern of bands below 1060 cm\(^{-1}\) suggest that these bands are mostly methylene rocks. In addition, the intensity of bands below 1060 cm\(^{-1}\) are weaker than the \(\nu(C-C)\) bands at 1060 cm\(^{-1}\) and above. However, it is possible that several of the bands near 1060 cm\(^{-1}\) may
Table 3.2. Raman Vibrational Assignments and Peak Frequencies in the $\nu$(C-C) Region of C$_n$H$_{2n+1}$SH.

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be \( \nu(C-C) \) bands, especially for longer-chain alkanethiols.

A progression of bands are observed at ca. 1175 cm\(^{-1}\) and higher. As observed in the methylene rocking-twisting region, the number of bands observed increases with chain length. The intense band at ca. 1300 cm\(^{-1}\) has been assigned to a methylene twist.\(^{3,12,170}\) Snyder and Schachtshneider observe two band progressions in this region.\(^{3,9}\) Methylene twisting-rocking bands are observed from ca. 1174 to ca. 1300 cm\(^{-1}\) with a clustering of bands at ca. 1300 cm\(^{-1}\). Also observed in this region is a progression of wagging modes from ca. 1170 to 1415 cm\(^{-1}\).\(^{3,9}\) The bands in the alkanethiol spectra are assigned as methylene twisting-rocking modes, but there is a possibility of methylene wags in this region.

In the liquid alkanethiol Raman spectra, shown in Figure 3.3, the bands have significantly broadened and G bands have been introduced. In the \( \nu(C-C) \) region, the \( \nu_s(C-C)_T \) has shifted slightly higher to ca. 1064 cm\(^{-1}\) for octanethiol and longer chain molecules. The \( \nu_s(C-C)_T \) band has shifted ca. 8 cm\(^{-1}\) lower and is weaker in intensity than the \( \nu_s(C-C)_T \) band. The new band at ca. 1078 cm\(^{-1}\) for longer chain alkanethiols is the \( \nu(C-C)_G \).\(^{1,70,1,74,3,13-3,15}\) This band is seen at slightly lower frequencies for pentanethiol and butanethiol. The G band is broader than the \( \nu(C-C)_T \) bands in the liquid and increases in intensity as the chain length increases. This behavior reflects the greater possibility of G conformers in longer chain lengths.\(^{1,68,3,16}\)

Although the \( \nu(C-C)_T \) band observed at 1084 cm\(^{-1}\) in the spectrum from solid dodecanethiol is at a similar frequency as the \( \nu(C-C)_G \) band in the liquid, the 1084 cm\(^{-1}\) band in the solid spectrum is concluded not to be the \( \nu(C-C)_G \) band. The \( \nu(C-C)_G \) bands for liquid nonanethiol, dodecanethiol, hexadecanethiol, and octadecanethiol all are observed at the same frequency of ca. 1078 cm\(^{-1}\). In addition, spectra obtained for slightly warmed solid nonanethiol,
hexadecanethiol, and octadecanethiol show the fourth band resolved distinctly from the $\nu(C-C)_G$ band. Upon further warming to a liquid, the $\nu(C-C)_G$ band increases in intensity and width, and only the $\nu(C-C)_T$ bands at ca. 1065 cm$^{-1}$ and 1120 cm$^{-1}$ and the $G$ band are observed. Figures 3.5 and 3.6 show this behavior for nonanethiol and hexadecanethiol, respectively. Sandroff and coworkers assigned the Raman band at ca. 1096 cm$^{-1}$ for solid hexadecanethiol as a $\nu(C-C)_G$ mode. However, it is clear from the behavior shown in Figures 3.3 through 3.6 that this is an incorrect assignment.

The bands observed between 950 and 1060 cm$^{-1}$ in the liquid spectra, shown in Figure 3.3, are much broader than observed in the solid spectra, Figure 3.4. The frequencies of these broader bands are shifted from the frequencies of bands observed in the solid spectra. In contrast to that observed in the liquid spectra between 705 and 950 cm$^{-1}$, only the band at ca. 965 cm$^{-1}$ appears at approximately the same frequency in each of the spectra. Therefore, the 965 cm$^{-1}$ is assigned as a $G$ band, but the $G$ and $T$ assignments are more ambiguous for the other bands.

In the region above 1130 cm$^{-1}$ the long-chain alkanethiols exhibit a band at ca. 1144 cm$^{-1}$ in the liquid spectra. This band is lower than that observed in the solid spectra, and therefore, is assigned to $G$ conformers. Additionally the intense methylene twist at ca. 1300 cm$^{-1}$ is significantly broader than observed in the solid alkanethio spectra, indicating significant increase in $G$ conformers.

The spectrum for butanethiolate, shown in Figure 3.3i, is different in the $\nu(C-C)$ region than the spectrum for neat butanethiol, Figure 3.3a. Only three bands are seen for the deprotonated species. The band at 1096 cm$^{-1}$ probably corresponds to the $\nu_s(C-C)_T$ at 1109 cm$^{-1}$ in the neat spectrum, because of the
Figure 3.5. Raman spectra in the $\nu$(C-C) region (514.5 nm excitation) of nonanethiol: a) solid, b) after ca. 10 min laser exposure, c) after ca. 16 min laser exposure, d) liquid. Incident power: 200 mW. Integration times: 1 min.
Figure 3.6. Raman spectra in the $\nu$(C-C) region (514.5 nm excitation) of hexadecanethiol: a) solid, b) after ca. 10 min laser exposure, c) after ca. 12 min laser exposure, d) liquid. Incident power: 200 mW. Integration times: 1 min.
strong intensity. It is not known why this band is sensitive to deprotonation, but it is also noted that this band in the neat spectrum is dramatically lower in frequency than that observed for octanethiol and longer chain alkanethiols.

\( \nu(C-H) \) region

The \( \nu(C-H) \) region is quite complex and contains at least ten bands in the region from 2800 to 3000 cm\(^{-1}\).\(^{1,71,1,73,8,2}\) These bands include \( \nu_{\text{sym}} \) and \( \nu_{\text{asym}} \) modes of methyl and methylene groups and Fermi resonances of these vibrations with \( \delta(C-H) \) overtones. The spectra for liquid alkanethiols and butanethiolate are shown in Figure 3.7, and the bands and their assignments are tabulated in Table 3.3. Two \( \nu_{\text{sym}}(CH_2) \) bands are seen at ca. 2850 and 2860 cm\(^{-1}\). The 2860 cm\(^{-1}\) band corresponds to the \( \nu_{\text{sym}}(CH_2) \) adjacent to the methyl group, while the other band corresponds to the remaining methylene groups. The lower frequency band is more intense in the long chain alkanethiols. Two bands due to the Fermi resonance of the \( \nu_{\text{sym}}(CH_2) \) band with the overtone of the \( \delta(CH_2) \) band appear at ca. 2912 and ca. 2927 cm\(^{-1}\). The \( \nu_{\text{sym}}(CH_2,\text{FR}) \) band at 2912 cm\(^{-1}\) is a shoulder on the broad \( \nu_{\text{asym}}(CH_2) \) band for dodecanethiol and octadecanethiol. The \( \nu_{\text{asym}}(CH_2) \) band appears at ca. 2903 cm\(^{-1}\) for butanethiol and shifts to lower frequencies as the chain length increases, reaching 2886 cm\(^{-1}\) in octadecanethiol. For octanethiol and longer chain alkanethiols, the \( \nu_{\text{asym}}(CH_2) \) band is actually the overlap of two \( \nu_{\text{asym}}(CH_2) \) bands, which are resolved in the spectra for solid alkanethiols. The \( \nu_{\text{asym}}(CH_2) \) has been described as a broad band with asymmetric peak shape.\(^{1,71}\) The frequencies of the bands in the liquid spectra have been determined with the aid of curvefit routines.

The \( \nu_{\text{sym}}(CH_3) \) band appears at ca. 2873 cm\(^{-1}\) and the \( \nu_{\text{sym}}(CH_3,\text{FR}) \) band is observed at 2935 cm\(^{-1}\).\(^{1,71}\) The \( \nu_{\text{asym}}(CH_3) \) band appears at ca. 2960 cm\(^{-1}\) in these
Figure 3.7. Raman spectra in the $\nu$(C-H) region (514.5 nm excitation) of a) liquid butanethiol, b) liquid pentanethiol, c) liquid octanethiol, d) liquid nonanethiol, e) liquid decanethiol, f) liquid dodecanethiol, g) liquid hexadecanethiol, h) liquid octadecanethiol, i) aqueous butanethiolate. Incident power: 200 mW. Integration times: ca. 30 s.
Table 3.3. Raman Vibrational Assignments and Peak Frequencies in the $\nu$(C-H) Region of $C_nH_{2n+1}SH$.

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spectra. Both the $\nu_{\text{sym}}(\text{CH}_2)$ and $\nu_{\text{asym}}(\text{CH}_3)$ bands decrease in intensity relative to the methylene bands as the chain length increases reflecting the increase in number of methylene groups.

The IR spectra of alkanethiols in the $\nu$(C-H) region is relatively simple. Only six bands have been assigned in this region.\textsuperscript{1,49} These include $\nu_{\text{sym}}(\text{CH}_2)$, $\nu_{\text{asym}}(\text{CH}_2)$, two $\nu_{\text{sym}}(\text{CH}_3)$, and two $\nu_{\text{asym}}(\text{CH}_3)$ bands. Of these six bands, only the frequency of the $\nu_{\text{asym}}(\text{CH}_3)$ band, observed at 2919 cm$^{-1}$ in solid octadecanethiol, does not directly correlate with the Raman frequency. Therefore, the polarization behavior of these bands has been used to confirm symmetric/asymmetric assignments.

Polarization studies were performed using excitation with incident radiation polarized perpendicular to the plane determined by the incident beam, sample and spectrometer entrance slits and collection of scattered radiation parallel and perpendicular to the incident beam. The intensity of the Raman scattering perpendicular $(I_I)$ divided by the scattering intensity parallel $(I_P)$ is defined as the depolarization ratio, $\rho$. Non-totally symmetric (depolarized) vibrations have a depolarization ratio, $\rho = 0.75$, while vibrations containing a symmetrical polarizability component have a ratio $0 \leq \rho < 0.75$.\textsuperscript{17,3,18}

Figure 3.8a through d shows the decomposed polarized spectra for liquid butanethiol, octanethiol, dodecanethiol, and hexadecanethiol, respectively. Parallel and perpendicular polarized spectra are indicated in the Figures 3.8a through d. The depolarization ratios for butanethiol, octanethiol, dodecanethiol, and hexadecanethiol are given in Table 3.4. The $\nu_{\text{sym}}(\text{CH}_2)$ bands and the $\nu_{\text{sym}}(\text{CH}_3)$ exhibit $\rho < 0.10$ and are highly symmetric. The $\nu_{\text{asym}}(\text{CH}_3)$ have a large ratio, $\rho \geq 0.5$. The $\nu_{\text{asym}}(\text{CH}_2)$ bands have a lower ratio, ranging from 0.2 to 0.5. The $\nu_{\text{sym}}(\text{CH}_3, \text{FR})$ exhibits $\rho \geq 0.05$, which parallels the behavior of the
Figure 3.8. Decomposed polarized Raman spectra in the ν(C-H) region (514.5 nm excitation) of a) liquid butanethiol, b) liquid octanethiol, c) liquid dodecanethiol, d) liquid hexadecanethiol. The collection polarization is indicated. Incident power: 100 mW. Integration times: 1 min.
Table 3.4. Depolarization Ratios of Vibrations in the $\nu$(C-H) Region of $C_nH_{2n+1}$SH.

<table>
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<th>Depolarization ratios, $p$</th>
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<td>0.3</td>
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<td>0.2</td>
<td>0.3</td>
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<tr>
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<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>$\nu_{\text{sym}}(\text{CH}_3, \text{FR})$</td>
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<td>0.01</td>
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<td>0.02</td>
</tr>
<tr>
<td>$\nu_{\text{asym}}(\text{CH}_3)$</td>
<td>0.5</td>
<td>0.6</td>
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\( \nu_{\text{asym}}(\text{CH}_3) \). On the other hand, the \( \nu_{\text{sym}}(\text{CH}_2,\text{FR}) \) bands at ca. 2815 and 2825 cm\(^{-1}\) are found to have \( \rho \geq 0.1 \). This suggests that there may be other depolarized bands in the spectrum underneath the \( \nu_{\text{sym}}(\text{CH}_2,\text{FR}) \) bands. Nine peaks or less were used in the curvefit routines for these molecules. However, in the Raman spectrum of solid octane, 14 peaks are observed in the \( \nu(\text{C-H}) \) region.\(^1\)\(^7\)\(^3\)

These bands are better resolved in the spectra of the solid alkanethiols as shown in Figure 3.9. The assignments are similar to those in the liquids; however, some notable changes are observed. The \( \nu_{\text{asym}}(\text{CH}_3) \) band is split into two bands at 2952 and 2966 cm\(^{-1}\) in the spectra for butanethiol through decanethiol. The lower frequency band has been assigned to the out-of-plane \( \nu_{\text{asym}}(\text{CH}_3) \) and the higher frequency band to the in-plane \( \nu_{\text{asym}}(\text{CH}_3) \).\(^3\)\(^2\) For octanethiol and dodecanethiol, an additional band at ca. 2950 cm\(^{-1}\) is observed. The \( \nu_{\text{sym}}(\text{CH}_3) \) and \( \nu_{\text{sym}}(\text{CH}_3,\text{FR}) \) bands at ca. 2870 and ca. 2935 cm\(^{-1}\) are weak in intensity for nonanethiol through octadecanethiol.

A dramatic change in the \( \nu(\text{C-H}) \) region upon cooling is the emergence of an intense band at ca. 2882 cm\(^{-1}\). This band is assigned to the \( \nu_{\text{asym}}(\text{CH}_2) \). In fact, the \( \nu_{\text{asym}}(\text{CH}_2) \) is split into a strong band at 2882 cm\(^{-1}\) and a weaker band at ca. 2900 cm\(^{-1}\). A decrease in the intensity of the bands at ca. 2930 cm\(^{-1}\) relative to the bands at ca. 2860 cm\(^{-1}\) is also observed upon cooling.\(^1\)\(^7\)\(^1\)

**Conclusions**

The Raman vibrational bands in the spectral regions 580 to 1320 cm\(^{-1}\) and 2780 to 3020 cm\(^{-1}\) have been assigned. Correct assignments are crucial for the determination of orientation of these films. In contrast to surface IR spectra of alkanethiol films, where only \( \nu(\text{C-H}) \) and methylene wagging modes are present, an abundance of Raman bands are observed in surface spectra.
Figure 3.9. Raman spectra in the $\nu$(C-H) region (514.5 nm excitation) of a) solid butanethiol, b) solid pentanethiol, c) solid octanethiol, d) solid nonanethiol, e) solid decanethiol, f) solid dodecanethiol, g) solid hexadecanethiol, h) solid octadecanethiol. Incident power: 200 mW. Integration times: a) ca. 2 min, b) ca. 30 s, c) ca. 1 min, d-h) ca. 30 s.
Particular attention has been given to T and G assignments for the $\nu$(C-S) and $\nu$(C-C) bands. The Raman spectra for n-alkanethiols in the $\nu$(C-C) region, from 1055 to 1135 cm$^{-1}$, are found to be different than spectra reported for n-alkanes and phospholipids. The spectra observed for alkanethiols in the $\nu$(C-H) region, on the other hand, are very similar to spectra of alkanes and alkanoic acids.

These assignments will be used to assess the conformational order of alkanethiols at Ag and Au surfaces. The surface Raman spectra will be compared to the liquid and solid bulk spectra to determine the presence of G and T modes in the self-assembled films.
Chapter 4

SURFACE SELECTION RULES IN RAMAN SPECTROSCOPY:
DETERMINATION OF ORIENTATION OF ALKANETHIOLS
AT Ag AND Au

Introduction

The orientation of n-alkanethiols at Ag and Au has been calculated by several methods, including vibrational spectroscopies and surface diffraction techniques. Surface selection rules for Raman scattering have been used to determine the orientation of highly symmetric molecules at metal surfaces, but these rules have not been developed for molecules of low symmetry, such as n-alkanethiols.

This chapter will present a method for obtaining methyl orientation with Raman spectroscopy. The origins of surface selection rules for IR and Raman spectroscopy at both atomically smooth and rough surfaces are discussed first. The polarizabilities of \( \nu(CH_3) \) modes and other vibrations are then discussed. The orientations of 1-butanol and 1-pentanol at rough Ag and Au and 2-butanol at rough Ag are deduced from the SERS spectra of these systems in the \( \nu(C-H) \) region. The results are compared to orientations previously proposed for these films. Finally, the excitation dependence of spectra in the \( \nu(C-H) \) region is analyzed in light of SERS theories for rough Ag surfaces.
Surface Radiation Fields at Metal Surfaces

The basis for using IR and Raman spectroscopy in the determination of adsorbate orientation at metal surfaces is the interaction of incident light with the metal. Specifically, the important factors are the wavelength-dependent dielectric properties of the metal and the surrounding medium, the angle and polarization of the incident light, and the vibrational behavior of the adsorbate.

The case of atomically smooth metal surfaces has been discussed by Greenler,4.1,4.2 Francis and Ellison,4.3 and Campion.4.4 Consider an incident beam with an electric field $E_i$ that is polarized parallel with respect to the plane of incidence. This beam will produce surface radiation fields according to the Fresnel equations. In the IR, metals are highly reflecting, such as Au and Ag,4.5 and have large negative real components of their complex dielectric constant, $\epsilon_m$, where $\epsilon_m = \text{Re}(\epsilon_m) + \text{Im}(\epsilon_m)$. In the case of an atomically smooth Ag surface in air, the intensity of the normal surface radiation field, $E_n^2$, has been calculated as a function of the angle of incidence of the incident beam.4.4 The ratio of the intensities of the normal field to the incident field, $E_n^2/E_i^2$, increases from zero at 0° to ca. 3.6 at ca. 77° from normal incidence. For Au, the maximum ratio is ca. 3.4.159 At more grazing angles, the normal radiation field intensity rapidly drops. On the other hand, the intensity of the tangential radiation field is zero for any incident angle.4.4,1.59 Therefore, the ratio of $E_n^2$ to $E_t^2$ is infinity.

In the visible region, metals are more poorly reflecting and the Re($\epsilon_m$) is less negative.4.5 This results in a lower $E_n^2$ and a non-zero $E_t^2$. For the case of a 520 nm parallel polarized incident beam at Ag, the maximum $E_n^2/E_i^2$ is ca. 2.2 which occurs at ca. 62°.4.4 At this angle of incidence, $E_t^2/E_i^2$ is ca. 0.3. Thus, $E_n^2/E_t^2$ is ca. 7, indicating a much larger radiation field normal to the surface than
tangential.

For rough surfaces, the situation is surprisingly similar. Greenler and coworkers have calculated the magnitude of surface radiation fields at copper spheres in the IR using various approaches. They conclude that $\frac{E_n^2}{E_t^2}$ is greater than 10 for metal particles 2 nm or greater in radii, where the centers of molecules are 2 Å from the surface.

Moskovits has extended these calculations to rough surfaces in the visible wavelength region. He has calculated the values of the tangential and normal radiation fields at a spherical metal surface, with the electrostatic assumption that the particle size $\ll 0.02$ (wavelength of light).$^{1,84}$

\[
\begin{align*}
E_n^2 & \propto E_i^2 (1 + 2g)^2 \\
E_t^2 & \propto 2E_i^2 (1 - g)^2
\end{align*}
\]

where

\[
g = (\hat{\epsilon}_m - \hat{\epsilon}_o)/(\hat{\epsilon}_m + 2\hat{\epsilon}_o)
\]

$\hat{\epsilon}_m$ and $\hat{\epsilon}_o$ are the complex dielectric constants for the metal and ambient medium, respectively. These equations can be rearranged to the following:

\[
\begin{align*}
E_n^2 & \propto E_i^2 \left[ 3\frac{\hat{\epsilon}_m}{(\hat{\epsilon}_m + 2\hat{\epsilon}_o)} \right]^2 \\
E_t^2 & \propto 2E_i^2 \left[ 3\frac{\hat{\epsilon}_o}{(\hat{\epsilon}_m + 2\hat{\epsilon}_o)} \right]^2
\end{align*}
\]

These equations predict that, for a metal surface with spherical roughness features, the greatest value of $E_n^2$ occurs at the surface plasmon resonance wavelength. At this energy, since $\hat{\epsilon}_o$ is all real, $\text{Re}(\hat{\epsilon}_m) = -2\epsilon_o$. For Ag in air ($\epsilon_o = 1.0$), this wavelength is ca. 370 nm.$^{4,7}$

At this wavelength, the real parts of $\hat{\epsilon}_m$ and $\epsilon_o$ cancel, and the denominators of equations 4.3, 4.4 and 4.5 simplify to $\text{Im}(\hat{\epsilon}_m)$. The maximum enhancement, $G$, is related to $g$ factors for the incident ($g$) and Raman-shifted radiation ($g'$):

\[
G \propto \left| (1 + 2g)(1 + 2g') \right|^2
\]

(4.6)
Therefore, with the incident radiation at the plasmon resonance wavelength and the emitted radiation at a relatively small Raman shift (\(g = g'\)), \(G\) is predicted to be inversely proportional to \(\text{Im}(\varepsilon_m)^4\) at the surface plasmon resonance wavelength.\(^{4.7,4.8}\)

Using equations 4.4 and 4.5, the ratio of the normal and tangential surface radiation fields can be calculated:

\[
\frac{E_n^2}{E_t^2} = \frac{\varepsilon_m^2}{2\varepsilon_o^2} \quad (4.7)
\]

Equation 4.7 predicts a wavelength dependence for the surface field ratios because the dielectric constants are wavelength dependent. For Ag, Equation 4.7 predicts that the intensity of the normal radiation field increases relative to the tangential field when the incident wavelength is shifted from 514.5 nm excitation to 600 nm excitation, due to the wavelength dependence of \(\text{Re}(\varepsilon_m)\). At 514.5 nm and 600 nm, the \(\text{Re}(\varepsilon_m)\) of Ag has been determined to be -10.7 and -16.1, respectively.\(^{4.9}\) \(\frac{E_n^2}{E_t^2}\) increases from 57 at 514.5 nm to 130 at 600 nm.

Direct application of these results to electrochemically roughened Ag electrodes is not appropriate. Scanning electron microscopy (SEM) of electrochemically roughened Ag electrodes reveal a range of roughness particle shapes, in addition to spherical features.\(^{1.99,4.10}\) The effect of non-spherical features upon \(\frac{E_n^2}{E_t^2}\) has also been considered by Moskovits.\(^{4.11}\) Equation 4.3 can be modified for non-spherical roughness features through modification of \(g\) in this manner:

\[
g = (\varepsilon_m - \varepsilon_o) / (\varepsilon_m + \chi\varepsilon_o) \quad (4.8)
\]

where \(\chi\) is an adjustable parameter related to the geometry of the roughness feature. This modification is based on the equations for the electric polarization of metal particles\(^{4.5}\):

\[
E_{\text{surf}} \propto \frac{1}{[1 + A(\varepsilon_m/\varepsilon_o - 1)]} \quad (4.9)
\]
A is a geometric term and is equivalent to

\[ A = \frac{1 - e^2}{e^2} \left[ -1 + \frac{1}{2e} \ln \frac{1 + e}{1 - e} \right] \]  

(4.10)

and

\[ e^2 = 1 - \left( \frac{b^2}{a^2} \right) \]  

(4.11)

where \( a \) and \( b \) are the major and minor axis, respectively, of an ellipsoid.

Equation 4.9 can be rearranged in the following manner:

\[ E_{\text{surf}}^2 \propto (\chi + 1)\epsilon_o/(\hat{\varepsilon}_m + \chi\epsilon_o) \]  

(4.12)

where \( \chi = 1/A - 1 \). For a sphere, \( A = 1/3 \) and \( \chi = 2 \). For a roughness feature with \( a:b \) of 2:1, \( A = 0.17 \) and \( \chi = 4.8 \). For a feature with \( a:b \) of 4:1, \( A = 0.075 \) and \( \chi = 12.3 \). The surface plasmon resonance wavelength, \( \text{Re}(\hat{\varepsilon}_m) = -\chi\epsilon_o \), shifts to longer wavelengths as the \( a/b \) ratio increases.

Combining equations 4.1, 4.2, and 4.8 results in the following:

\[ E_n^2 \propto E_i^2[(3\hat{\varepsilon}_m + (\chi - 2)\epsilon_o/(\hat{\varepsilon}_m + \chi\epsilon_o)]^2 \]  

(4.13)

\[ E_t^2 \propto 2E_i^2[(\chi + 1)\epsilon_o/(\hat{\varepsilon}_m + \chi\epsilon_o)]^2 \]  

(4.14)

Moskovits uses these modifications and calculates the ratio of the surface radiation fields at a Ag surface containing a uniform distribution of particles with \( \chi \) values from 2 to 15. The results are that \( E_n^2/E_t^2 \) ranges from 1.8 at 450 nm excitation to 2.1 at 700 nm excitation. While this ratio changes little with wavelength, the enhancement factor, proportional to \( E_n^4 \), increases approximately an order of magnitude from 450 to 700 nm excitation.

This calculation is only an approximation, for several reasons. SEMs of surfaces that have been electrochemically roughened show an unequal distribution of different-sized roughness features. Also, the sizes of roughness features on these surfaces exceed the limit used in electrostatic calculations, which assumes particle size \( \leq 0.02 \) (wavelength of light). However, the
significance of this calculation is the prediction of a leveling effect upon $E_n^2/E_t^2$, with respect to excitation wavelength, when there is a distribution of particle sizes.

**Surface Selection Rules**

It has been established that with visible excitation, the radiation fields at a Ag surface are greater in the direction normal to the surface than parallel. The surface selection rules for Raman scattering result from coupling of the molecular vibrations of the adsorbate with these surface radiation fields. Simply stated, vibrations with a polarizability tensor component perpendicular to the surface will be enhanced greater than vibrations with little or no perpendicular component.\(^1\textsuperscript{84},\textsuperscript{1.85}\) Vibrations that can couple into the normal surface radiation field, $E_n^2$, will be more enhanced than vibrations that couple into tangential radiation fields, because $E_n^2$ is larger than $E_t^2$.

This surface selection rule can be expanded in the following manner. Consider a molecule on a surface with its molecular z axis perpendicular to the surface and the x and y axes parallel. The polarizability tensor components of the molecular vibrations will be enhanced in the order:\(^1\textsuperscript{84},\textsuperscript{1.85}\)

$$\alpha_{zz} > \alpha_{xx}, \alpha_{yy} > \alpha_{xy}, \alpha_{xx}, \alpha_{yy}$$

To use this information to determine adsorbate orientation, one compares the surface Raman spectra to the bulk spectra. The vibrations that are enhanced to the greatest extent will contain the molecular axis that is most perpendicular to the surface.

The use of these rules to determine orientation of highly symmetric adsorbates has been reviewed by Moskovits\(^1\textsuperscript{84}\) and Creighton\(^1\textsuperscript{.85}\). Molecules that have been investigated include phthalazine,\(^4\textsuperscript{11}\) pyridine,\(^4\textsuperscript{14}\) N-methylpyridinium...
cation, benzene and toluene. Some drawbacks arise in the use of highly symmetric molecules to validate surface selection rules. First, vibrations that are assumed totally symmetric are, for the most part, the strongest bands in the surface and bulk spectra for these molecules. Totally symmetric vibrations contain tensor components of all three axes and, therefore, the intensities of these bands are independent of orientation. Commonly, intensity ratios of the non-totally symmetric bands to the totally symmetric bands are calculated to determine orientation. Comparison of the intensities of bands that are non-totally symmetric to those that are totally symmetric may be difficult, in some cases, due to the weak intensities of some of the Raman-forbidden, non-totally symmetric bands.

Secondly, the relative contributions of the individual tensor components to the total polarizability of a vibration are frequently not accurately known. Different vibrations belonging to the same symmetry class in a point group are frequently found to exhibit different enhancements at a surface relative to bulk. More complete understanding of the tensor components of totally symmetric vibrations would allow determination of orientation using the more intense symmetric vibrations.

Alkanethiols, on the other hand, have very low symmetry and belong, at best, in the $C_\alpha$ point group. In this point group, all vibrations of the adsorbed molecule have a component perpendicular to the surface in all orientations. The relative contributions of the various tensor components to the polarizability of a vibration are generally not completely known. Stretching vibrations, however, are assumed to have a larger contribution from the tensor component along the axis of the vibration. Gao and coworkers have concluded this to be true of the $\nu$(C-H) vibration in benzene and toluene from their SERS spectra at Au
Additionally, Harrand has concluded that the $\nu_{a}(C-C)_T$ of dipalmitoyl phosphatidylcholine has $zz$ polarizability. In his work, the $z$ axis has been defined to be parallel to the alkane chain.

The assumption concerning the polarizability of stretching vibrations is, therefore, considered valid to extend to $\nu(C-S)$ and $\nu(CH_3)$ bands. The polarizability of the $\nu(C-S)_T$ bands is assumed to be along the C-S bond. This band, along with the $\nu(C-C)_T$ band, is assumed to be largely orthogonal to the methylene stretches. The $\nu_{\text{sym}}(CH_3)$ is largely a totally symmetric band\textsuperscript{4,16} while the $\nu_{\text{asym}}(CH_3)$ for the isotropic liquid is expected to have polarizability tensors greatest in the plane orthogonal to the symmetric methyl transition dipole. Therefore, the polarizability of the $\nu_{\text{asym}}(CH_3)$ is orthogonal to the $\nu_{\text{sym}}(CH_3)$ by virtue of one less axis for the $\nu_{\text{asym}}(CH_3)$.

**Estimation of Alkanethiol Orientation at Rough Ag and Au Surfaces**

A method is proposed here to determine adsorbate orientation based on the relative intensity behavior of the $\nu_{\text{sym}}(CH_3)$ and $\nu_{\text{asym}}(CH_3)$ of the adsorbed molecules. This method is predicated on several important assumptions. It is assumed that the polarizability tensors of the molecules do not change upon adsorption to the surface. This allows orientation to be deduced from a direct comparison between the isotropic liquid spectrum and the surface spectrum of the adsorbed molecule. It is assumed that the surface enhancement arises solely from electromagnetic effects and that resonance Raman-like processes do not contribute to the relative intensity measurements reported. This assumption is justified by the use of surfaces on which significant numbers of so-called active sites generally associated with resonance Raman-like (i.e. potential dependent) SERS do not exist. Such surfaces were created in this work by roughening
electrochemically using oxidation-reduction cycle ex-situ before immersing the surfaces in the alkanethiol/ethanol solutions. The active sites described above are too labile to survive the loss of potential control, rinsing and transfer steps associated with this procedure. Moreover, the molecules studied in this investigation are of low symmetry and belong to the \( C_\alpha \) point group. Thus, all vibrations of these adsorbed molecules have a component perpendicular to the surface in all orientations. There are no totally symmetric vibrations, since even the \( A' \) modes have an off-diagonal polarizability tensor component. Therefore, the \( A \)-term, shown to be the most important in resonance Raman-like SERS,\(^{1,85} \) is predicted to be absent for these molecules.

The adsorbed molecules are assumed to feel a total radiation intensity at the surface which is a vector sum of the intensity existing normal and tangential to the surface. Since the radiation intensity is proportional to the square of the electric field strength, this assumption is expressed as

\[
E_{\text{TOT}}^2 = E_n^2 + E_t^2 \tag{15}
\]

For simplicity in demonstrating the predictions of this method, the ratio \( E_n^2/E_t^2 \) is assumed to be 10.

The method is based on a quantitative knowledge of the spatial relation between two vibrations of the same functional group. The methyl group is useful in this regard, because it exhibits \( \nu_{\text{sym}}(\text{CH}_3) \) and \( \nu_{\text{asym}}(\text{CH}_3) \) modes at discrete frequencies.

In using the methyl group modes, it is assumed that the major change in the polarizability ellipsoid is along the direction of the \( \text{C-CH}_3 \) bond for the \( \nu_{\text{sym}}(\text{CH}_3) \) mode and that the major change in the polarizability ellipsoid for the corresponding \( \nu_{\text{asym}}(\text{CH}_3) \) is perpendicular to this direction. These assumptions reduce the three-dimensional polarizability problem of Raman spectroscopy to a
two-dimensional vector problem. This treatment is analogous to treating the vibrations as a transition dipole as in IR spectroscopy.

The vector sum of the normal and tangential components of the surface radiation intensity is used in this method as a multiplier of the isotropic intensity ratio of these vibrations. Thus, it is the surface intensity ratio relative to the intensity ratio measured for the adsorbate in an isotropic environment that is represented by the multiplier value, not the absolute value of the surface intensity ratio. For the methyl group $\nu$(C-H) modes, this can be represented in equation form as follows:

$$\frac{[I(\nu_{\text{asym}}(\text{CH}_3))/I(\nu_{\text{sym}}(\text{CH}_3))]_{\text{SURF}}}{[\frac{E_{\text{TOT}}^2(\nu_{\text{asym}}(\text{CH}_3))}{E_{\text{TOT}}^2(\nu_{\text{sym}}(\text{CH}_3))}]} \times \frac{[I(\nu_{\text{asym}}(\text{CH}_3))/I(\nu_{\text{sym}}(\text{CH}_3))]_{\text{SOLN}}}{(4.16)}$$

$$\frac{[I(\nu_{\text{asym}}(\text{CH}_3))/I(\nu_{\text{sym}}(\text{CH}_3))]_{\text{SURF}}}{[\frac{E_{n}^2(\nu_{\text{asym}}(\text{CH}_3)) + E_{t}^2(\nu_{\text{asym}}(\text{CH}_3))}{E_{n}^2(\nu_{\text{sym}}(\text{CH}_3)) + E_{t}^2(\nu_{\text{sym}}(\text{CH}_3))}]} \times \frac{[I(\nu_{\text{asym}}(\text{CH}_3))/I(\nu_{\text{sym}}(\text{CH}_3))]_{\text{SOLN}}}{(4.17)}$$

$$[I(\nu_{\text{asym}}(\text{CH}_3))/I(\nu_{\text{sym}}(\text{CH}_3))]_{\text{SURF}} = \text{MULTIPLIER VALUE} \times \frac{[I(\nu_{\text{asym}}(\text{CH}_3))/I(\nu_{\text{sym}}(\text{CH}_3))]_{\text{SOLN}}}{(4.18)}$$

This method is graphically shown in Figure 4.1. A C-CH$_3$ moiety is shown at a 0° tilt from the surface normal. The axes denote the magnitude of the surface radiation fields normal and tangential to the surface for the condition
of $E_n^2/E_t^2$ of 10. For this orientation of the methyl group, a quantitative estimate of the multiplier value of the intensity ratio can be calculated as the vector sum of the $E_n^2$ and $E_t^2$ obtained by the projection of the vibrational dipole on the respective axis.

In Figure 4.1, the methyl dipole is oriented at the surface normal and the asymmetric polarizability is parallel to the surface. $E_{TOT}^2$ for the $\nu_{\text{asym}}(\text{CH}_3)$ mode will be the sum of 0 and 1, which are the projections on the $E_n^2$ and $E_t^2$ axis, respectively. For the $\nu_{\text{sym}}(\text{CH}_3)$ mode, the sum will be of 10 and 0. The multiplier value is then 0.1. The absolute magnitude of 0.1 is not significant because $E_n^2/E_t^2$ is not accurately known. However, this method predicts that when the methyl dipole is perpendicular to the surface, the multiplier value will be at a minimum. The multiplier value will be less than 1.0 in the cases where the methyl dipole is oriented from zero to 45° from the surface normal.

For the methyl dipole oriented 45° from the surface normal, the asymmetric polarizability is also 45° from the surface normal. The multiplier value then becomes 1.0. The surface intensity ratio for the methyl bands, in this case, is equal to the ratio in the isotropic bulk solution.

For the methyl dipole oriented greater than 45° from the surface normal, the multiplier value is greater than 1.0. This value reaches the maximum when the methyl dipole is parallel to the surface.

This method is demonstrated for 1-butanethiol at Ag and Au and 2-butanethiol at Ag, all acquired in the ambient environment. The results of this method are compared to the orientations of alkanethiols at Ag and Au that have been previously proposed.

Figure 4.2 shows the decomposed spectra for the neat 1-butanethiol and for a monolayer film of 1-butanethiol at rough Ag. The decomposed peaks have been
Figure 4.1. The model as applied to the terminal methyl group with the methyl dipole oriented perpendicular to the surface.
Figure 4.2. Decomposed Raman spectra in $\nu$(C-H) region (514.5 nm excitation) of 1-butanol a) in bulk liquid and b) at rough Ag. Incident power: a) 200 mW, b) 50 mW. Integration times: a) 5 min, b) 1 min.
calculated using the curvefit procedure outlined in Chapter 2. The $\nu_{\text{sym}}(\text{CH}_3)$ and $\nu_{\text{asym}}(\text{CH}_3)$ bands are observed at ca. 2875 and 2965 cm$^{-1}$, respectively, for 1-butanethiol. Alkanethiols adsorb to metal surfaces by cleavage of the S-H bond with concomitant formation of the surface thiolate molecule. A more detailed discussion of surface Raman spectroscopy on these alkanethiol layers on Ag and Au is presented in the following chapters.

The isotropic value of $[I(\nu_{\text{asym}}(\text{CH}_3))/I(\nu_{\text{sym}}(\text{CH}_3))]$ for 1-butanethiol is ca. 1.7. The corresponding value of this ratio for the Ag surface is ca. 1.9. Thus, the multiplier value is ca. 1.1 which suggests that the 1-butanethiol has the orientation shown in Figure 4.3 with the methyl group at a tilt angle of ca. 45° with respect to the surface normal. The peak area ratios and multiplier values are given in Table 4.1. This orientation of the methyl group is consistent with previously proposed descriptions of the bonding of alkanethiols at Ag surfaces.

Using IR spectroscopy, Walczak and coworkers have proposed that the chain axis of alkanethiols at Ag is tilted ca. 12° from the surface normal with a rotation about the chain axis of ca. 45°. The orientation of the $\nu_{\text{asym}}(\text{CH}_3)$ transition dipole was also calculated to be ca. 45°.

The orientation of the $\nu_{\text{sym}}(\text{CH}_3)$ transition dipole for 1-pentanethiol at Ag is calculated to be ca. 27° from the surface normal, shown in Figure 4.3. The change in methyl group orientation is also reflected in the Raman spectra for 1-pentanethiol. The bulk and surface spectra for 1-pentanethiol at Ag are shown in Figure 4.4a and b, respectively. The isotropic value of $[I(\nu_{\text{asym}}(\text{CH}_3))/I(\nu_{\text{sym}}(\text{CH}_3))]$ for 1-pentanethiol is ca. 1.6. The corresponding value of this ratio for the Ag surface is ca. 1.2. Thus, the multiplier value is ca. 0.75 which corresponds to a methyl group orientation less than 45° from the surface normal.
Figure 4.3. Proposed orientation of 1-butanethiol and 1-pentanethiol at Ag.
Table 4.1. Peak Area Ratio Data for \( \nu(\text{C-H}) \) Region for Isotropic and Surface Spectra.

\[
\frac{I(\nu_{\text{asym}(\text{CH}_2)})}{I(\nu_{\text{sym}(\text{CH}_2)})}
\]

<table>
<thead>
<tr>
<th>Molecule</th>
<th>Bulk Solution</th>
<th>Surface</th>
<th>Multiplier Value</th>
</tr>
</thead>
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<td>1.7</td>
<td>1.9</td>
<td>1.1</td>
</tr>
<tr>
<td>1-Pentanethiol/Ag</td>
<td>1.6</td>
<td>1.2</td>
<td>0.75</td>
</tr>
<tr>
<td>1-Butanethiol/Au</td>
<td>1.7</td>
<td>1.4</td>
<td>0.82</td>
</tr>
<tr>
<td>1-Pentanethiol/Au</td>
<td>1.6</td>
<td>1.5</td>
<td>0.95</td>
</tr>
<tr>
<td>2-Butanethiol/Ag</td>
<td>5.9</td>
<td>5.7</td>
<td>0.97</td>
</tr>
</tbody>
</table>
Figure 4.4. Decomposed Raman spectra in $\nu$(C-H) (514.5 nm excitation) region of 1-pentanethiol a) in bulk liquid and b) at rough Ag. Incident power: 100 mW. Integration times: 1 min.
The spectra for 1-pentanethiol at rough Ag with 514.5 nm and 600 nm excitation, shown in Figure 4.5a and b, respectively, are nearly identical. This result supports the prediction that surfaces with a distribution of roughness features exhibit less change in $E_n^2/E_t^2$ in the visible wavelength region than is predicted for purely spherical particles. However, the spectrum obtained with 720 nm excitation, Figure 4.5c, shows greater methyl intensity relative to the methylene bands. In the orientation model for 1-pentanethiol at Ag, Figure 4.3, the methylene bonds are nearly parallel with the surface and are expected to be less enhanced than the methyl bands. The increase in methyl intensity with 720 nm excitation suggests that $E_n^2/E_t^2$ does increase at longer wavelengths, as expected from equation 4.7.

1-Butanethiol has a different orientation at Au than at Ag. It is generally agreed that the chain axis of alkanethiols at Ag is tilted ca. 30°, in the opposite direction than observed for Ag, with a rotation about the chain axis of ca. 50°. In this case, the $\nu_{\text{sym}}(\text{CH}_3)$ transition dipole is calculated to be 26° from the surface normal. The bulk and surface spectra for 1-butanethiol at rough Au are shown in Figure 4.6a and b, respectively, and the model for orientation is shown in Figure 4.7. The value of $[I(\nu_{\text{asym}}(\text{CH}_3))/I(\nu_{\text{sym}}(\text{CH}_3))]$ for the Au surface is 1.4. The multiplier value, therefore, is 0.8, which is less than the corresponding value for 1-butanethiol at Ag and similar to the corresponding value for 1-pentanethiol at Ag. This is consistent with the model of 1-butanethiol at Au, where the methyl group is more perpendicular to the surface.

For 1-pentanethiol at Au, the $\nu_{\text{sym}}(\text{CH}_3)$ transition dipole is calculated to be 53° from the surface normal. The bulk and surface spectra for 1-pentanethiol at rough Au are shown in Figure 4.8a and b, respectively. The multiplier value for this molecule is 0.95, which corresponds to the more parallel orientation of
Figure 4.5. Raman spectra in $\nu$(C-H) region of 1-pentanethiol at rough Ag: a) 514.5 nm excitation, b) 600 nm excitation, c) 720 nm excitation. Incident power: a) 100 mW, b) 200 mW, c) 30 mW. Integration times: a) 1 min, b) 30 s, c) 5 min.
Figure 4.6. Decomposed Raman spectra in ν(C-H) region of 1-butane thiol a) in bulk liquid and b) at rough Au. Excitation wavelength: a) 514.5 nm, b) 600 nm. Incident power: 200 mw. Integration times: a) 5 min, b) 1 min.
Figure 4.7. Proposed orientation of 1-butethiol and 1-pentanethiol at Au.
Figure 4.8. Raman spectra in ν(C-H) region of 1-pentanethiol a) in bulk liquid and b) at rough Au. Excitation wavelength: a) 514.5 nm, b) 600 nm. Incident power: a) 100 mW, b) 200 mW. Integration times: 1 min.
the methyl group, shown in Figure 4.7.

The multiplier values calculated for these molecules at rough Ag and Au, listed in Table 4.1, are found to be similar in the cases where the methyl group orientation is similar. This suggests that $E_n^2/E_t^2$ is similar for both these substrates, even though the real parts of the dielectric constants are -16.1 and -9.4 for Ag and Au, respectively, at 600 nm.4.9

One final test of the proposed method is the study of 2-butanethiol at Ag. The bulk and surface spectra are shown in Figure 4.9. Two methyl groups exist in this molecule which are in approximately equivalent chemical environments in the neat liquid based on the observation of only one set of methyl vibrational modes. The curvefit of the surface spectra is much broader which suggests multiple environments for the for the methyl groups at the Ag surface. The values of $[I(\nu_{asym}(CH_3))/I(\nu_{sym}(CH_3))]$ are 5.9 and 5.7 for the neat liquid and surface forms, respectively. Thus, the multiplier value is ca. 0.97. The orientation of 2-butanethiol shown in Figure 4.10 is proposed to explain this value. In this model of adsorbed 2-butanethiol, the Ag-S bonding is assumed to be analogous to that observed for 1-butanethiol. One methyl group is proposed to be at a large tilt angle with respect to the surface normal and the other essentially perpendicular to the surface. This leads to the average value of the multiplier observed which is close to an average apparent tilt angle of ca. 45°.

This orientation is consistent with the results of Joo and coworkers in the existence of the molecule in a gauche conformation on the surface.4.17 They observe three conformations for 2-butanethiol at Ag colloids. The T and the two G conformers are indicated in Raman spectra by the frequency of the $\nu(C-S)$ band.4.17-4.19 It was concluded that the G conformation is the most favorable at high surface coverages.4.17 In this study, the frequency of the most intense
Figure 4.9. Decomposed Raman spectra in $\nu$(C-H) region (514.5 nm excitation) of 2-butanethiol a) in bulk liquid and b) at rough Ag. Incident power: 100 mW. Integration times: 30 s.
Figure 4.10. Proposed orientation of 2-butanethiol at Ag.
\( \nu(C-S) \) band for 2-butanethiol at Ag corresponds to the G conformation shown in Figure 4.10.

Additional information is contained in the \( \nu(C-H) \) region for 2-butanethiol at Ag. The frequency of the \( \nu_{\text{asym}}(\text{CH}_3) \) is at 2955, which is lower than the frequency of 2965 observed for 1-butanethiol at Ag. The lower frequency corresponds to the \( \nu_{\text{asym}}(\text{CH}_3, \text{out-of-plane}) \) mode while the higher frequency corresponds to the \( \nu_{\text{asym}}(\text{CH}_3, \text{in-plane}) \) mode.\textsuperscript{1,4,8,2} The transition dipole for the \( \nu_{\text{asym}}(\text{CH}_3,\text{oop}) \) is perpendicular to the methyl dipole and perpendicular to the plane of the carbon backbone.\textsuperscript{1,49} In Figure 4.10, the methyl group orientated parallel to the surface is adjacent to carbon atoms that form a plane parallel to the surface. The \( \nu_{\text{asym}}(\text{CH}_3) \) of this methyl group is expected to be more enhanced than the \( \nu_{\text{asym}}(\text{CH}_3) \) associated with the more perpendicular methyl group. Therefore, the greater intensity of the \( \nu_{\text{asym}}(\text{CH}_3,\text{oop}) \) than the \( \nu_{\text{asym}}(\text{CH}_3,\text{ip}) \) in the surface Raman spectrum strongly suggests that the polarizabilities tensor components are greatest along their transition dipoles.

**Conclusions**

This method has been demonstrated here for the methyl group. The orientation of the \( \nu_{\text{sym}}(\text{CH}_3) \) transition dipole implies orientations for the C-S and C-C bonds in other alkanethiol molecules. Surface selection rules have also been applied to \( \nu(C-S) \) and \( \nu(C-C) \) bands for 1-alkanethiols at Ag and Au and the results are entirely consistent with the models discussed above. A more detailed discussion of these results is presented in Chapters 5 and 6.

The surface selection rules for Raman scattering have been demonstrated to be valid for alkanethiols at rough Ag and Au surfaces. Previous research has concentrated on more symmetric molecules, but the ease of determining
orientation of the methyl dipole for alkane molecules should expand the use of surface selection rules.

The limitations of this method at this point are two-fold. The value of $E_n^2/E_t^2$ needs to be determined to make this method more quantitative. Also, the polarizability components need to be determined for other vibrations. However, these results suggest that if molecular orientation has been previously determined for adsorbates at these metal surfaces, the polarizability components of various bands of these adsorbates may be estimated from SERS spectra.
Chapter 5

ORIENTATION AND ORDER OF n-ALKANETHIOLS AT SMOOTH Ag SURFACES IN THE AMBIENT ENVIRONMENT

Introduction

Several spectroscopic studies of self-assembled n-alkanethiol monolayers at Ag have been reported. These studies have characterized the orientation, adsorption mechanism, and conformational order of these films.

The orientation of alkanethiols at evaporated Ag substrates has been calculated by several groups using IR spectroscopy. Ulman has also concluded that the chain tilt of octadecanethiol is less than $30^\circ$ from the surface normal.\textsuperscript{1.8} Walczak and coworkers, using IR spectroscopy, have calculated a chain tilt of $14^\circ$ from the surface normal with a rotation about the carbon backbone of $44^\circ$.\textsuperscript{1.49} Laibinis and coworkers have also calculated a chain tilt of ca. $13^\circ$ from the surface normal and a chain rotation of ca. $42^\circ$.\textsuperscript{1.50}

Although the chain tilt is generally agreed upon, the absolute direction of the tilt is controversial. Walczak and coworkers propose that the tilt for alkanethiols at Ag is in the opposite direction as that observed at Au substrates.\textsuperscript{1.49} This model positions the C-S bond at a tilt with respect to the Ag surface normal that is less than that observed at Au. Laibinis and coworkers conclude that the C-S bond alternates between largely perpendicular and more parallel orientations.
with incremental change in alkanethiol chain length.\textsuperscript{1.50} Thus, the terminal methyl orientation is constant for odd- and even-numbered alkanethiol films, behavior that is not seen for alkanethiol films at Au.\textsuperscript{1.50,1.49} However, direct information on orientation of the \(\text{C-S}\) bond is not available with IR spectroscopy.

The presence of oxygen on the Ag surface prior to film formation and its removal upon alkanethiol adsorption has been studied.\textsuperscript{1.50,1.52} Ag surface oxide is proposed to affect the adsorption mechanism of alkanethiols at Ag\textsuperscript{1.52} and also the structure of the film.\textsuperscript{1.50} This behavior is significantly different than that observed with Au substrates, which are largely inert to O adsorption.\textsuperscript{1.50}

The order of films at Ag has also been studied by different methods. Harris and coworkers observed an ordered methanethiolate monolayer at Ag (111) using LEED.\textsuperscript{1.32} Joo and coworkers investigated propanethiol and butanethiol films at Ag colloid solutions using SERS.\textsuperscript{1.51,1.54} They observe mostly T conformers adjacent to the \(\text{C-S}\) bond at monolayer coverages. Sandroff and coworkers have reported strong G intensities in the \(\nu(\text{C-C})\) region for hexadecanethiol at Ag using SERS.\textsuperscript{1.75} However, analysis of bulk liquid and solid alkanethiol spectra presented in Chapter 3 argue that the observation of G intensities is based on an incorrect assignment in the \(\nu(\text{C-C})\) region.

Surface Raman investigations of alkanethiols at mechanically polished, polycrystalline Ag surfaces have been undertaken to more fully characterize these films. Orientational information available in the \(\nu(\text{C-H})\), \(\nu(\text{C-S})\), and \(\nu(\text{C-C})\) regions, employing surface Raman selection rules, can provide unique insight into these systems due to the strong intensity of the \(\nu(\text{C-S})\) and \(\nu(\text{C-C})\) bands in Raman spectra, whereas these bands are not observed in surface IR spectra.\textsuperscript{1.49,1.34} Thus, the orientation of the \(\text{C-S}\) bond can be determined along with the chain tilt and methyl group orientations.
Characterization of the conformational structure of these films is also directly available from the spectra in the $\nu$(C-S) and $\nu$(C-C) regions. The conformational order of short- and long-chain alkanethiol films is evaluated in the surface Raman spectra presented in this chapter by comparison to the spectra for liquid and solid bulk alkanethiols, discussed in Chapter 3.

**Surface Raman Spectra of Alkanethiol Monolayers at Ag**

$\nu$(S-H) region

1-Alkanethiols are proposed to form monolayers at Ag by chemisorption of the S head group to the metal substrate. Widrig and coworkers have proposed the adsorption mechanism shown in Scheme 5.1 to explain alkanethiol adsorption at Ag.

![Scheme 5.1](image)

where X may be Cl, I, or OH.

Direct evidence for cleavage of the S-H bond is seen in the Raman spectra in the $\nu$(S-H) region shown in Figure 5.1. The spectrum of neat butanethiol, Figure 5.1a, shows the very intense $\nu$(S-H) band at ca. 2575 cm$^{-1}$. The S-H band is absent in the surface spectra of butanethiol at both smooth and rough Ag surfaces, Figures 5.1b and 1c, respectively. The disappearance of the $\nu$(S-H) band suggests cleavage of the S-H bond upon adsorption.

Butanethiolate can be formed chemically upon addition of butanethiol to basic aqueous solutions. The spectrum from this species is shown in Figure 5.1d. The $\nu$(S-H) band is clearly absent in this spectrum further verifying the thiolate...
Figure 5.1. Raman spectra in the $\nu$(S-H) region (514.5 nm excitation) of butanethiol a) in bulk liquid, b) at smooth Ag, c) at rough Ag, d) aqueous butanethiolate. Incident power: 200 mW. Integration times: a), c), d) 1 min; b) 5 min.
nature of the species adsorbed at Au surfaces. The absence of this band also suggests that no unreacted thiol is present at the Ag surface. No \( \nu(S-H) \) band is observed in surface spectra for any adsorbed alkanethiol studied here. This observation is consistent with the previously reported cleavage of the S-H bond for alkanethiols adsorbed at Ag based on the absence of the \( \nu(S-H) \) band in spectra from these surfaces.\textsuperscript{1,51,54}

The structure of the adsorbed alkanethiol monolayer is, in part, dictated by interactions between neighboring alkane chains. With the polar S atom bonded to the Au and Ag surface, the non-polar alkane chains pack in a dense arrangement to maximize van der Waals forces.\textsuperscript{5,1} This arrangement generates densely packed layers which are believed to be crystalline-like.\textsuperscript{1,34} In the following discussion of the surface Raman spectra for selected alkanethiols ranging from butanethiol to octadecanethiol adsorbed at Ag, the surface Raman spectra are compared with Raman spectra of the corresponding liquid and solid alkanethiols and butanethiolate in order to assess the crystallinity of the films.

\( \nu(C-S) \) Region

The \( \nu(C-S) \) region between 600 and 750 cm\(^{-1}\) provides conformational information about C-C bonds adjacent to the C-S bond in the alkanethiols. Assignments for these bands for liquid and solid alkanethiols are discussed in Chapter 3. The gauche (G) \( \nu(C-S) \) is observed at ca. 655 cm\(^{-1}\) and the trans (T) \( \nu(C-S) \) is observed at ca. 730 cm\(^{-1}\) in the liquid alkanethiols.

Upon adsorption of these alkanethiols at smooth Ag, the frequencies of both \( \nu(C-S) \) bands decrease considerably. These spectra are shown in Figure 5.2 and the frequencies are given in Table 5.1. For butanethiol, the \( \nu(C-S)_G \) band is observed at ca. 630 cm\(^{-1}\) and the \( \nu(C-S)_T \) band at ca. 701 cm\(^{-1}\). It is proposed that
Figure 5.2. Raman spectra in the $\nu$(C-S) region (600 nm excitation) of alkanethiols adsorbed at smooth Ag: a) butanethiol, b) pentanethiol, c) nonanethiol, d) dodecanethiol, e) octadecanethiol. Excitation wavelength: a-c) and e) 600 nm, d) 514.5 nm. Incident power: a) 100 mW, b) 100 mW, c) 200 mW, d) 50 mW, e) 100 mW. Integration times: a-c) 5 min, d) 10 min, e) 2 min.
Table 5.1. Raman Vibrational Assignments and Peak Frequencies in the $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) Regions of $C_nH_{2n+1}S\text{H}$ at Smooth Ag.

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<th>6</th>
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<th>12</th>
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<tr>
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the frequencies of both $\nu(C-S)$ bands are lowered due to the bonding of the S atom to Ag. The frequency of the T band shifts to slightly higher frequency as the alkane chain length increases. Thus, the frequency of this band for adsorbed butanethiol is ca. 7 cm$^{-1}$ lower than for adsorbed octadecanethiol.

A dramatic decrease in $\nu(C-S)_G$ intensity and increase in $\nu(C-S)_T$ intensity are noted upon adsorption of these molecules. This behavior is consistent with an increase in order of these alkanethiols upon adsorption. A similar ratio of T to G intensity is noted for all the alkanethiols studied here suggesting that the environment around the C-S bond, and presumably bonding to the surface, are similar for each alkanethiol. The small amount of G intensity may be due to defects in the film at grain boundaries on the polycrystalline Ag surface.

In general, the CH$_2$ rocking modes are very weak compared to the CH$_3$ rock$_T$ in the surface spectra. This is proposed to be due to orientation effects. Small G intensities of the CH$_3$ rock are observed at ca. 870 cm$^{-1}$ for butanethiol, pentanethiol, and dodecanethiol, suggesting some disorder in these shorter-chain films.

$\nu(C-C)$ Region

The $\nu(C-C)$ region contains additional information about the conformational behavior of the alkane chain. The spectra for adsorbed alkanethiols at smooth Ag are shown in Figure 5.3, and the peak frequencies are given in Table 5.1. The spectra for adsorbed octadecanethiol, hexadecanethiol, decanethiol, and nonanethiol resemble the spectra for the corresponding solid alkanethiols, shown in Figure 3.4. Little G intensity at ca. 1080 cm$^{-1}$ is observed for these adsorbed molecules, strongly suggesting that the adsorbed films are more ordered than the bulk liquid. For nonanethiol, the $\nu_a(C-C)_T$ at ca. 1062 cm$^{-1}$ is buried between the
Figure 5.3. Raman spectra in the $\nu$(C-C) region (600 nm excitation) of alkanethiols adsorbed at smooth Ag: a) butanethiol, b) pentanethiol, c) hexanethiol, d) nonanethiol, e) decanethiol, f) dodecanethiol, g) hexadecanethiol, h) octadecanethiol. Incident power: a-c) 100 mW, f) 50 mW, g) 200 mW, h) 100 mW. Integration times: a-c) 5 min, d and e) 10 min, f) 2 min, g) 5 min, h) 2 min. g) 600 nm excitation.
adjacent bands at 1053 and 1069 cm\(^{-1}\). These latter bands are seen in the spectrum for solid nonanethiol.

The spectrum of adsorbed dodecanethiol in Figure 5.3f appears somewhat anomalous in that it is similar to that of the bulk liquid. However, the band at 1080 cm\(^{-1}\) is not the \(\nu(C-C)_G\) band, but corresponds to the band seen in the solid spectrum at 1084 cm\(^{-1}\). This band is also seen in the other long-chain solid alkanethiol spectra, shown in Figure 3.4. It is observed at 1068, 1073, 1099, and 1104 cm\(^{-1}\) for nonanethiol, decanethiol, hexadecanethiol and octadecanethiol, respectively. This band is also clearly seen in the adsorbed spectra for these molecules. It appears at 1069, 1072, 1097 and 1104 cm\(^{-1}\) for nonanethiol, decanethiol, hexadecanethiol, and octadecanethiol, respectively. This band has been previously reported as the \(\nu(C-C)_G\) in previous SERS reports for hexadecanethiol\(^{1,25}\) and hexadecyltrimethylammonium bromide\(^{1,27}\) at Ag. There is, however, a small amount of \(\nu(C-C)_G\) intensity noted between the 1062 cm\(^{-1}\) \(\nu(C-C)_T\) band and the band at 1080 cm\(^{-1}\). The G component for dodecanethiol and hexadecanethiol is discussed in greater detail in chapter 7, which compares spectra obtained at rough and smooth Ag surfaces.

The spectrum for adsorbed butanethiol in Figure 5.3a is similar to the spectrum of solution butanethiolate in that only three bands are observed. An intense band at 1096 cm\(^{-1}\) is observed in the aqueous butanethiolate and adsorbed butanethiol spectra. The strong intensity of this band in the solution spectrum suggests that it is the \(\nu_s(C-C)_T\) and not the \(\nu(C-C)_T\) band at ca. 1093 cm\(^{-1}\) in the liquid.

The band at ca. 1054 cm\(^{-1}\), assigned to the \(\nu_s(C-C)_T\), exhibits an odd-even behavior in intensity for butanethiol, pentanethiol, and hexanethiol. This behavior is discussed below with respect to orientation.
In the methylene twisting region above 1135 cm\(^{-1}\), C-H twist bands are observed at ca. 1070 cm\(^{-1}\) for butanethiol through dodecanethiol films. These G bands, being very weak compared to the T CH\(_2\) twist at higher frequencies, suggest only a small number of G conformers.

\(\nu(C-H)\) region

The spectra for the adsorbed alkanethiols are shown in Figure 5.4. The spectrum for adsorbed butanethiol, in Figure 5.4a, resembles more closely the spectrum of butanethiolate than that of liquid or solid butanethiol, shown in Figure 3.7b, 3.7a, and 3.9a, respectively. Both adsorbed butanethiol and aqueous butanethiolate exhibit a large decrease in the intensity of the \(\nu_{\text{sym}}(\text{CH}_2,\text{FR})\) at 2925 cm\(^{-1}\). The relative intensity of the \(\nu(\text{CH}_3)\) to \(\nu(\text{CH}_2)\) bands is larger for adsorbed butanethiol than for aqueous butanethiolate. The peak frequencies of these bands are given in Table 5.1.

The longer chain alkanethiols resemble the corresponding liquid spectra more than the solid spectra. The surface spectra also show a large increase in the relative intensity of the \(\nu(\text{CH}_3)\) bands to \(\nu(\text{CH}_2)\) bands as compared to those in the liquid spectra. This is expected from the orientation of these alkanethiols at Ag, shown in Figure 4.3. The methylene groups are almost parallel to the surface, and therefore, the methyl band intensities are more enhanced. The absence of a strong \(\nu_{\text{asym}}(\text{CH}_2)\) band, which is present in the spectra for solid alkanethiols, may be due to orientation effects. Additionally, the Raman spectral data from all three regions suggest that these films are more disordered than solid alkanethiols but more ordered than liquid alkanethiols. This aspect of the data is discussed in more detail in Chapter 7.

The relative intensity of the \(\nu_{\text{asym}}(\text{CH}_3)\) band to the \(\nu_{\text{sym}}(\text{CH}_3)\) band also
Figure 5.4. Raman spectra in the $\nu$(C-H) region (600 nm excitation) of alkanethiols adsorbed at smooth Ag: a) butanethiol, b) pentanethiol, c) hexanethiol, d) nonanethiol, e) dodecanethiol, f) hexadecanethiol, g) octadecanethiol. Incident power: 100 mW. Integration times: 10 min. e) 514.5 nm excitation, 50 mW, 10 min.
contains significant information. The spectra for adsorbed butanethiol, pentanethiol and hexanethiol at smooth Ag, shown in Figures 5.4a through c, respectively, illustrate the significance of the relative intensity behavior of the $\nu(CH_3)$ bands. These spectra have been plotted so that the $\nu_{sym}(CH_3)$ bands of each adsorbed alkanethiol spectrum are of similar intensity. On this intensity scale, a lower $\nu_{asym}(CH_3)$ intensity is observed for the odd-numbered pentanethiol than for the even-numbered butanethiol and hexanethiol. This odd-even effect has been previously noted in Chapter 4 for butanethiol and pentanethiol at rough Ag. This odd-even effect is present, but very small, for nonanethiol and decanethiol. This effect is discussed with respect to surface selection rules below.

**Orientation of Alkanethiols at Ag**

The orientation of alkanethiols at Ag has been discussed in Chapter 4. This section will discuss the use of selection rules to corroborate the orientation model presented in Chapter 4 with the Raman spectral behavior of the C-S and C-C bands.

Walczak and coworkers have presented results from a study of alkanethiol monolayers at Ag and Au using IR spectroscopy. The tilt angle was calculated to be ca. -14°, opposite in direction to that observed at Au, with a rotation about the chain axis of ca. 45°. The odd-even behavior of the two $\nu(CH_3)$ bands was observed at Ag for short-chain alkanethiols up to nonanethiol. The odd-even effect is a direct consequence of the change in orientation of the methyl groups as the chain length of the alkanethiol film is incrementally increased. However, no odd-even behavior is observed for chain lengths greater than nonanethiol.

Laibinis and coworkers also do not observe this odd-even behavior for alkanethiols of hexadecanethiol and longer. They do not present spectra for
shorter chain alkanethiol films. They concur with the calculation of the chain tilt of ca. 13° and the rotation of ca. 42°. However, they conclude from the absence of odd-even behavior in the \( \nu (C-H) \) region that the methyl group maintains the same orientation with incremental change in the chain length. Consequently, they propose that the C-S bond changes orientation as the chain length is increased.

Laibinis and coworkers\textsuperscript{1.50} propose that the appearance of odd-even behavior in the \( \nu (C-H) \) region for short-chain alkanethiols is due to the existence of Ag oxide in the samples of Walczak and coworkers.\textsuperscript{1.49} Laibinis and coworkers observed ca. 2% of a monolayer of Ag oxide at Ag surfaces with freshly deposited films.\textsuperscript{1.50} After two days exposure to the atmosphere, several broad bands appeared at ca. 1100 to 1200 cm\(^{-1}\) that were initially absent in the surface IR spectra. These bands, were attributed to highly oxidized S groups, possibly sulfonate groups as suggested by the XPS measurements.

However, Walczak and coworkers detected no bands at ca. 1100 cm\(^{-1}\) indicative of S oxidation.\textsuperscript{1.49} Similarly, no bands that can be attributed to oxidized S species are seen the surface Raman spectra presented in this study, shown in Figure 5.3. Likewise, these bands do not appear in the SERS spectra of propanethiol and butanethiol at Ag colloids reported by Joo and coworkers.\textsuperscript{1.51,1.54}

The odd-even behavior is better correlated with film disorder. Fenter and coworkers conclude from diffraction data that the ends of octadecanethiol chains exhibit less long range order than observed in the interior for films at Ag (111).\textsuperscript{1.110} This increased disorder at the alkane chain ends would result in a more random distribution of methyl group orientations, thus resulting in the disappearance of the odd-even effect.

This odd-even behavior of the \( \nu _{\text{asym}}(\text{CH}_3) \) and \( \nu _{\text{sym}}(\text{CH}_3) \) bands is observed
and quantified for butanethiol and pentanethiol at rough Ag, as discussed in Chapter 4. The odd-even behavior of the methyl bands is also observed at smooth Ag surfaces. The ratio of $\nu_{\text{asym}}(\text{CH}_3)$ to $\nu_{\text{sym}}(\text{CH}_3)$ intensity is greater for butanethiol and hexanethiol than for pentanethiol at Ag. It is therefore deduced that the $\nu_{\text{sym}}(\text{CH}_3)$ transition dipole is more parallel to the surface for butanethiol and hexanethiol but is more perpendicular for pentanethiol at Ag. Figure 4.3 shows models for butanethiol and pentanethiol adsorbed at Ag that were determined from the methyl peak area ratio at rough Ag and the results of Walczak and coworkers.\textsuperscript{149} In the spectra of long-chain alkanethiol films, the $\nu_{\text{asym}}(\text{CH}_3)$ band is largely masked by the surrounding methylene bands, making quantitation unreliable.

A similar analysis of the remainder of the surface Raman data was undertaken for butanethiol and pentanethiol at smooth Ag. The use of surface selection rules for the $\nu$(C-S) and $\nu$(C-C) bands, however, is problematic for two reasons. First, the polarizability of the $\nu$(C-S) is assumed to be along the C-S bond and the polarizability of the $\nu_{\text{s}}$(C-C)$_T$ band is reported to be along the carbon backbone.\textsuperscript{3.11} The bands that are orthogonal to the greatest extent to the C-S and the C-C bonds for odd- and even-numbered alkanethiols, are the $\nu$(C-H) bands. Therefore, the ratios of the $\nu$(C-S) and $\nu$(C-C) peak areas are calculated with respect to the entire $\nu$(C-H) region.

Second, the $\nu$(C-S) bands shift significantly in frequency upon adsorption to Ag and Au surfaces. For short chain alkanethiols, the $\nu_{\text{s}}$(C-C)$_T$ shifts significantly in frequency. The polarizability tensor components and cross-sections might change from their bulk values. In addition, there is a significant increase in the T intensities relative to the G intensities for these bands. The decrease in G intensity might not be linear with the increase in T intensity.
Therefore, interpretation of the ratios of the surface bands to the bulk bands must be undertaken with caution. However, comparison of the intensities of these bands at the Ag surface relative to those at the Au surface is straightforward, because similar spectral changes are observed at these two surfaces. The spectral behavior of the $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) bands at Au is presented in Chapter 6.

The ratio of the peak areas of the $\nu$(C-S) bands to the entire $\nu$(C-H) region in the surface spectra was calculated and divided by the $\nu$(C-S)/$\nu$(C-H) ratio in the bulk liquid spectra. These ratios are reported in Table 5.2. Also reported are the corresponding surface and bulk $\nu$(C-C)/$\nu$(C-H) ratios.

The $\nu$(C-S)/$\nu$(C-H) surface/liquid ratios for butanethiol and pentanethiol are ca. 4 and 3, and the $\nu$(C-C)/$\nu$(C-H) surface/liquid ratios are ca. 10 and 8. These ratios suggest that the carbon backbone and the C-S bond are largely perpendicular to the surface. This corresponds to the model of orientation shown in Figure 4.3. The conclusion that the C-S bond is largely perpendicular to the surface for both butanethiol and pentanethiol at Ag is also consistent with the orientation model proposed by Walczak and coworkers.\textsuperscript{1.49} Considering the geometry of the alkanethiol molecule, the C-S bond is parallel to the symmetric methyl transition dipole of odd-numbered alkanethiols, such as pentanethiol. Using the values calculated for the orientation of the symmetric methyl transition dipole, the C-S bond is ca. 27° from the surface normal at Ag.\textsuperscript{1.49} The chain tilt of the carbon backbone is calculated to be ca. 14°.\textsuperscript{1.49}

The absence of the majority of the CH\textsubscript{2} rock and CH\textsubscript{2} twist bands in the surface spectra are explained by orientation of these films at Ag. The methylene bonds are largely parallel to the surface, and, therefore, these bands are weakly enhanced compared to the $\nu$(C-S) and $\nu$(C-C) bands.
Table 5.2. Peak Area Ratio for $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) Regions for Isotropic Bulk and Surface Spectra at Smooth Ag.

\[
\begin{array}{cccc}
\hline
\text{Molecule} & \text{Bulk Solution} & \text{Ag Surface} & \text{Multiplier Value} \\
\hline
\text{Butanethiol} & 0.12 & 0.5 & 4 \\
\text{Pentanethiol} & 0.13 & 0.4 & 3 \\
\hline
\end{array}
\]

\[
\begin{array}{ccc}
\hline
\text{Molecule} & \text{Molecule Bulk Solution} & \text{Ag Surface} & \text{Multiplier Value} \\
\hline
\text{Butanethiol} & 0.03 & 0.3 & 10 \\
\text{Pentanethiol} & 0.02 & 0.16 & 8 \\
\hline
\end{array}
\]
In addition, odd-even behavior is observed for the $\nu_{\alpha}(C-C)_T$ band at 1054 cm$^{-1}$. The band is larger in intensity than the 1093 cm$^{-1} \nu(C-C)_T$ and the 1063 cm$^{-1} \nu(C-C)_G$ bands for pentanethiol at smooth Ag. For butanethiol and hexanethiol, the intensity of the 1054 cm$^{-1}$ band is weaker in intensity. This suggests that the polarizability of this band is along the methyl dipole.

Conclusions

The orientation of alkanethiols at Ag deduced from the spectral behavior of the $\nu(C-S)$ and $\nu_{\alpha}(C-C)_T$ bands is consistent with the orientation deduced from the SERS spectra of the methyl bands, presented in Chapter 4. This orientation is consistent with the orientation models proposed from IR spectral results of the $\nu(C-H)$ region. Thus, it is demonstrated that Raman spectroscopy is capable of providing direct structural information that is suggested by spectral behavior of the $\nu(C-H)$ region. The films are found to be mostly all-T for the long-chain alkanethiols. For shorter films, small G intensities are found in the methylene twisting, methyl rocking, and $\nu(C-C)$ regions.

A similar analysis of the surface Raman spectra of alkanethiols at Au is presented in Chapter 6. At the end of that chapter, the orientation of alkanethiols at Ag is compared to the that observed at Au. The various influences on orientation are discussed in that chapter.
Chapter 6

ORIENTATION AND ORDER OF n-ALKANETHIOLS AT SMOOTH Au SURFACES IN THE AMBIENT ENVIRONMENT

Introduction

Self-assembled films of alkanethiols at Au substrates have been investigated to much greater extent than similar systems at Ag. A wide variety of techniques, such as IR, various surface diffraction methods, temperature programed desorption, and contact angle measurements are currently being used. Raman spectroscopy has not been used to characterize alkanethiols at Au, although as demonstrated in Chapter 5, considerable information is available with this technique.

Previous reports of IR investigations have concluded that long-chain alkanethiols are in the all-T configuration by comparing the frequencies of the $\nu$(C-H) bands with those of solid alkanethiols.\(^{1,2,4}\) With Raman spectroscopy, direct assessment of T and G conformations within the alkane chain and adjacent to the Au surface is possible. The T and G intensities of the $\nu$(C-C) and $\nu$(C-S) bands are strong in surface Raman spectra while these bands are weak in surface IR spectra. The effects of various parameters, such as alkane chain length and surface morphology, can be readily studied.

This chapter will present Raman scattering spectra obtained from a wide
range of alkanethiols at mechanically polished, smooth Au substrates. The behavior in the $\nu$(S-H), $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) regions are discussed with respect to orientation and molecular order. These results will also be compared to those obtained at Ag substrates.

**Surface Raman Spectra of Alkanethiol Monolayers at Au**

**$\nu$(S-H) Region**

1-Alkanethiols are proposed to form monolayers at Au by chemisorption of the S head group to the metal substrate.1,3,4,5 Widrig and coworkers have proposed the following adsorption mechanisms at Au.1,5 The mechanism at Au substrates, shown in Scheme 6.1,

$$2\text{RSH} + 2\text{Au} \rightarrow 2\text{Au-SR} + \text{H}_2$$

$$2\text{RSH} + 2\text{Au} + \text{O}_2 \rightarrow 2\text{Au-SR} + \text{H}_2\text{O}_2$$

**SCHEME 6.1**

involves cleavage of the S-H bond with concomitant oxidation of a Au atom to form a S-Au bond. The lost H may be released as H$_2$ or combine with trace oxidants in solution such as O$_2$ to form H$_2$O$_2$. The proposed mechanism shown in Scheme 6.1 involves the formation of a Au-S bond, which is thought to be largely covalent with some ionic character.1,5

Direct evidence for cleavage of the S-H bond is seen in the Raman spectra in the $\nu$(S-H) region shown in Figure 6.1. The spectrum of neat butanethiol, Figure 6.1a, shows the very intense $\nu$(S-H) band at ca. 2575 cm$^{-1}$. The S-H band is absent in the surface spectra of butanethiol at both smooth and rough Au surfaces, Figures 6.1b and 1c, respectively. The disappearance of the $\nu$(S-H) band
Figure 6.1. Raman spectra in $\nu$(S-H) region (600 nm excitation) of a) bulk liquid butanethiol, b) butanethiol adsorbed at smooth Au, c) butanethiol adsorbed at rough Au, d) aqueous butanethiolate (514.5 nm excitation). Incident power: a) 100 mW, b) 200 mW, c) 100 mW, d) 100 mW. Integration times: a) 1 min, b) 20 min, c) 1 min, d) 1 min.
suggests cleavage of the S-H bond upon adsorption.

Similar behavior is seen for adsorption of alkanethiols at Ag, shown in Figure 5.1. Similarly, the absence of the $\nu$(S-H) band suggests the thiolate nature of the species adsorbed at Au. The spectrum of butanethiolate, shown in Figure 6.1d, shows the absence of the $\nu$(S-H) band. The absence of this band further suggests that no unreacted thiol is present at the Au surface. No $\nu$(S-H) band is observed in surface spectra for any adsorbed alkanethiol studied here.

The spectral behavior of alkanethiols adsorbed at Au in the $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) regions is discussed and compared to liquid and solid alkanethiol spectra, presented in Chapter 3, and to the behavior of alkanethiols at Ag, presented in Chapter 5.

$\nu$(C-S) Region

The $\nu$(C-S) region between 600 and 750 cm$^{-1}$ provides conformational information about C-C bonds adjacent to the C-S bond in the alkanethiols. Upon adsorption of alkanethiols at smooth Au, the frequencies of the two $\nu$(C-S) bands decrease considerably. These spectra are shown in Figure 6.2. The $\nu$(C-S)$_G$ band is observed at ca. 635 cm$^{-1}$ and the $\nu$(C-S)$_T$ band at ca. 710 cm$^{-1}$. It is more difficult to accurately determine the exact position of the G band because of its low intensity. These frequencies are ca. 20 cm$^{-1}$ less than those for neat liquid alkanethiols, shown in Figure 3.1. The frequencies of the bands at smooth Au in the $\nu$(C-S) region, in addition to the $\nu$(C-C) and $\nu$(C-H) regions, are shown in Table 6.1. It is proposed that the frequencies of both $\nu$(C-S) bands are lowered due to the bonding of the S atom to Au. The frequency of the T band shifts to slightly higher frequency as the alkane chain length increases. Thus, the frequency of this band for adsorbed butanethiol is ca. 7 cm$^{-1}$ lower than for
Figure 6.2. Raman spectra in $\nu$(C-S) region (720 nm excitation) of alkanethiols adsorbed at smooth Au: a) butanethiol, b) pentanethiol, c) nonanethiol, d) dodecanethiol, e) octadecanethiol. Incident power: 40 mw. Integration times: a-d) 5 min, e) 10 min.
Table 6.1. Raman Vibrational Assignments and Peak Frequencies in the $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) Regions of C$_n$H$_{2n+1}$SH.

<table>
<thead>
<tr>
<th>n =</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>2</th>
<th>12</th>
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<tr>
<td>Adsorbed Smooth Au</td>
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<tr>
<td>$\nu$(C-S)$_G$</td>
<td>638</td>
<td>641</td>
<td>641</td>
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<tr>
<td>$\nu$(C-S)$_T$</td>
<td>706</td>
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<td>708</td>
<td>710</td>
<td>712</td>
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<tr>
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<td>1053</td>
<td>1066</td>
<td>1064</td>
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<td></td>
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<tr>
<td>$\nu_a$(C-C)$_T$</td>
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<td>1103</td>
<td>1120</td>
<td>1125</td>
<td>1130</td>
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<tr>
<td>$\nu_{sym}$(CH$_2$)</td>
<td>2852</td>
<td>2850</td>
<td>2850</td>
<td>2853</td>
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<td>2852</td>
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<tr>
<td>$\nu_{sym}$(CH$_3$)</td>
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<td>2876</td>
<td>2878</td>
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<tr>
<td>$\nu_{asym}$(CH$_2$)</td>
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<td>2906</td>
<td>2907</td>
<td>2905</td>
<td>2904</td>
<td>2902</td>
<td></td>
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<tr>
<td>$\nu_{sym}$(CH$_3$,FR)</td>
<td>2937</td>
<td>2937</td>
<td>2935</td>
<td>2935</td>
<td>2933</td>
<td>2932</td>
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</tr>
<tr>
<td>$\nu_{sym}$(CH$_3$,FR)</td>
<td>2967</td>
<td>2966</td>
<td>2964</td>
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</table>
adsorbed octadecanethiol.

A dramatic decrease in $\nu(C-S)_G$ intensity and increase in $\nu(C-S)_T$ intensity are noted upon adsorption of these molecules. This behavior is consistent with an increase in order of these alkanethiols upon adsorption. A similar ratio of T to G intensity is noted for all the alkanethiols studied here suggesting that the environment around the C-S bond, and presumably bonding to the surface, are similar for each alkanethiol. The small amount of G intensity may be due to defects in the film at grain boundaries on the polycrystalline Au surface. Similar G and T behavior is observed for alkanethiols at smooth Ag, shown in Figure 5.2.

A significant difference exists between the surface Raman spectra for alkanethiols adsorbed at smooth Ag and smooth Au, shown in Figures 5.2 and 6.2, respectively. The frequencies of the two $\nu(C-S)$ bands are ca. 5 cm$^{-1}$ lower on Ag surfaces than on Au surfaces. This disparity suggests that the M-S bond is stronger for Ag than Au and may be the result of greater ionic bonding at Ag than Au, consistent with the electronegativity differences between S and these two metals. These effects may play an influence in the orientation of the alkanethiol films at Ag and Au as will be discussed below.

$\nu(C-C)$ Region

The $\nu(C-C)$ region contains additional information about the conformational behavior of the alkane chain. The spectra for adsorbed alkanethiols at smooth Au are shown in Figure 6.3. Similar behavior in this region is observed for alkanethiols at smooth Ag, shown in Figure 5.3. The spectrum for adsorbed butanethiol in Figure 6.3a is similar to the spectrum of solution butanethiolate in Figure 3.3i in that only three bands are observed. This behavior further suggests the thiolate nature of adsorbed butanethiol.
Figure 6.3. Raman spectra in $\nu$(C-C) region (720 nm excitation) of alkanethiols adsorbed at smooth Au: a) butanethiol, b) pentanethiol, c) nonanethiol, d) dodecanethiol, e) hexadecanethiol, f) octadecanethiol. Incident power: 40 mW. Integration times: a) 10 min, b-d) 5 min, e,f) 10 min.
For both of these substrates, little G intensity is observed for nonanethiol and longer chain alkanethiols. The spectra for the films resemble the spectra for neat solid alkanethiols more than the neat liquid spectra, shown in Figures 3.4 and 3.3, respectively. This suggests that the molecules are mostly in the all-T configuration and the films are more ordered than the corresponding neat liquids, where considerable G intensity is observed. Further discussion of the G component in dodecanethiol, hexadecanethiol, and octadecanethiol spectra are presented in Chapter 7.

The spectrum of adsorbed dodecanethiol in Figure 6.3d is similar to that observed at smooth Ag, shown in Figure 5.3f. These spectra are similar to that observed for bulk liquid dodecanethiol. However, the band at 1080 cm\(^{-1}\) is not the \(\nu(C-C)_{\text{C}}\) band, but corresponds to the \(\nu(C-C)_{\text{T}}\) band seen in the solid spectrum at 1084 cm\(^{-1}\). This band increases in frequency with increase in chain length in both bulk solid spectra, Figure 3.4, and at smooth Au, Figure 6.3. The band is observed at 1099 and 1103 cm\(^{-1}\) for hexadecanethiol and octadecanethiol at smooth Au, respectively.

An odd-even effect is observed for the \(\nu_{\text{a}}(C-C)_{\text{T}}\) band at ca. 1050 cm\(^{-1}\) for butanethiol and pentanethiol at smooth Au, shown in Figure 6.3a and b. The intensity of this band, relative to the \(\nu_{\text{a}}(C-C)_{\text{T}}\) at ca. 1095 cm\(^{-1}\), is greater for butanethiol and weaker for pentanethiol. This is opposite to the behavior observed for short-chain alkanethiols at smooth Ag, shown in Figure 5.3a,b, and c. This behavior corresponds to the different orientations of the methyl groups of alkanethiols at Au and Ag.

\(\nu(C-H)\) region

The spectra for the adsorbed alkanethiols are shown in Figure 6.4. From the
Figure 6.4. Raman spectra in $\nu$(C-H) region (600 nm excitation) of alkanethiols adsorbed at smooth Au: a) butanethiol, b) pentanethiol, c) nonanethiol, d) dodecanethiol, e) octadecanethiol. Incident power: 100 mW. Integration times: 20 min.
spectrum in Figure 6.4a, it can be seen that adsorbed butanethiol resembles more closely the spectrum of butanethiolate, Figure 3.7i, than that of liquid or solid butanethiol. Both adsorbed butanethiol and aqueous butanethiolate exhibit a large decrease in the intensity of the $\nu_{\text{sym}}(\text{CH}_2,\text{FR})$ at 2925 cm$^{-1}$. The relative intensity of the $\nu(\text{CH}_3)$ to $\nu(\text{CH}_2)$ bands is larger for adsorbed butanethiol than for aqueous butanethiolate. The other adsorbed alkanethiols also show a large increase in the relative intensity of the $\nu(\text{CH}_3)$ bands to $\nu(\text{CH}_2)$ bands as compared to those in the liquid spectra.

The relative intensity of the $\nu_{\text{asym}}(\text{CH}_3)$ band to the $\nu_{\text{sym}}(\text{CH}_3)$ band also contains significant information. Even though the $\nu_{\text{asym}}(\text{CH}_3)$ intensity in the bulk liquid spectra generally decreases with increasing chain length, the relative intensity of the $\nu_{\text{asym}}(\text{CH}_3)$ for adsorbed pentanethiol is stronger than that for adsorbed butanethiol. The spectra for adsorbed butanethiol, pentanethiol and hexanethiol at smooth Au shown in Figures 6.4a through c, respectively, illustrate the significance of the relative intensity behavior of the $\nu(\text{CH}_3)$ bands. These spectra have been plotted so that the $\nu_{\text{sym}}(\text{CH}_3)$ bands of each adsorbed alkanethiol spectrum are of the same intensity. On this intensity scale, a greater $\nu_{\text{asym}}(\text{CH}_3)$ intensity is observed for the odd-numbered pentanethiol than for the even-numbered butanethiol and hexanethiol. In contrast, alkanethiols adsorbed to Ag show the opposite behavior, as shown in Figures 5.4a through c. The spectra at Ag are similar in all respects to those at Au, except that the intensity of the $\nu_{\text{asym}}(\text{CH}_3)$ band is greater for the even-numbered chains (butanethiol and hexanethiol) than for the odd-numbered chains. Although not shown, similar behavior is observed for the relative $\nu(\text{CH}_3)$ intensities for octanethiol and nonanethiol at Au and Ag. The orientation of the terminal methyl group, and hence that of the carbon backbone with respect to the surface normal, can be
deduced from this behavior. The details of this analysis and models for adsorption and orientation of these molecules at Au and Ag based on these data are presented below.

Orientation of Alkanethiols at Au

The orientation of alkanethiols at Au substrates has been investigated by several groups. Ulman and coworkers have used computer modeling to calculate the free energies of various orientations of long-chain alkanethiols. The tilt and rotation angles of adsorbed alkanethiols were predicted from the minima in free energy of the systems based on van der Waals interactions between adjacent molecules at single crystals of Au. The lowest free energy was found for a molecular tilt of the carbon backbone of ca. 30° from normal with a rotation about the chain axis of ca. 55°. Bareman and Klein have also calculated molecular tilt as a function of area per chain using molecular dynamics simulations. An average tilt of ca. 30° was calculated for a nearest-neighbor spacing of 5.0 Å. This spacing corresponds to the spacing of next-nearest atoms for the Au (111) surface.

Nuzzo and coworkers have estimated a tilt angle of ca. 40° from the surface normal for long-chain alkanethiols at Au with a rotation about the chain axis of 50° from IR spectral data interpreted on the basis of surface selection rules. Porter and coworkers proposed the chain tilt to be ca. 20° to 30° using IR spectroscopy and ellipsometry. Chidsey and Loiacono estimate the chain tilt to be ca. 27° using IR spectroscopy. Using electron diffraction, Strong and Whitesides estimated the tilt angle to be 25° to 35°.

The deduction of orientation of alkanethiols at Au using surface selection rules for Raman scattering was presented in Chapter 4. An odd-even effect of
the $\nu_{\text{asym}}(\text{CH}_3)$ and $\nu_{\text{sym}}(\text{CH}_3)$ bands was observed and quantified for butanethiol and pentanethiol at rough Au. The odd-even behavior of the methyl bands is also observed at smooth Au surfaces. As shown in Figure 6.4, the $\nu_{\text{asym}}(\text{CH}_3)$ band is stronger for pentanethiol at Au and weaker for butanethiol and hexanethiol at Au relative to the $\nu_{\text{sym}}(\text{CH}_3)$ band. Thus, based on surface selection rules, the $\nu_{\text{asym}}(\text{CH}_3)$ vibration for pentanethiol at Au is largely perpendicular to the surface. The $\text{C}_4$-$\text{C}_5$ bond, and hence the symmetric methyl transition dipole, is directed largely parallel to the surface, because the $\nu_{\text{asym}}(\text{CH}_3)$ polarizability tensor is presumed to be orthogonal to the $\text{C}_4$-$\text{C}_5$ bond. Based on similar arguments, the methyl dipole must be largely perpendicular to the surface for butanethiol and hexanethiol. Figure 4.7 shows models for butanethiol and pentanethiol adsorbed at Au that were determined from the methyl ratios at rough Au and the results of Walczak and coworkers.\textsuperscript{149}

The behavior of the methyl bands is similar to that observed with IR data by Nuzzo and coworkers. In their previous study, the $\nu_{\text{sym}}(\text{CH}_3)$ and $\nu_{\text{asym}}(\text{CH}_3)$ intensities for heptadecanethiol and octadecanethiol adsorbed at Au were compared.\textsuperscript{134} While the intensities of the two methyl stretches were found to be similar for octadecanethiol, the $\nu_{\text{asym}}(\text{CH}_3)$ was noted to be more intense than the $\nu_{\text{sym}}(\text{CH}_3)$ for heptadecanethiol. Thus, the model proposed for the odd-numbered chain pentanethiol in Figure 4.7 is similar to that proposed by Nuzzo for orientation of heptadecanethiol, and that for butanethiol is similar to Nuzzo's for octadecanethiol.

The model further predicts a significant difference in orientation of the C-S bonds for alkanethiols at Au compared to that observed at Ag. Using the calculations of Walczak and coworkers, the C-S bond at Au is ca. 55° from the surface normal, which is greater than the ca. 25° orientation found at Ag.
substrates. In addition, the tilt of the carbon backbone at Au is ca. 30°, while the tilt is ca. 15° at Ag.

An analysis of the remainder of the surface Raman data was undertaken for butanethiol and pentanethiol at smooth Au and compared to that from smooth Ag surfaces. The ratio of the intensity of the combined \( \nu(C-S) \) bands to the entire \( \nu(C-H) \) region in the surface spectra was calculated and divided by the ratio of the \( \nu(C-S) \) to \( \nu(C-H) \) bands in the bulk liquid spectra. These values are reported in Table 6.2. Also reported are the \( \nu(C-C)/\nu(C-H) \) surface ratios divided by the \( \nu(C-C)/\nu(C-H) \) bulk liquid ratios. For both butanethiol and pentanethiol at Au, the \( \nu(C-S)/\nu(C-H) \) surface/liquid ratio is ca. 1. This result agrees with the model proposed in Figure 4.7, because the decrease in surface \( \nu(C-S) \) intensity strongly implies that the C-S bond is ca. 45° with respect to the surface. This is similar to the value of 55° determined by Walczak and coworkers. On the other hand, the \( \nu(C-C)/\nu(C-H) \) surface/liquid ratio for the adsorbed molecule at Au is greater than one which suggests that the carbon backbone is more perpendicular to the surface than the C-S bond. This picture is also consistent with the model shown in Figure 4.7.

As demonstrated by the data in Tables 5.2 and 6.2, the intensity ratio behavior for alkanethiols adsorbed at Ag is significantly different than that measured from Au substrates. The \( \nu(C-S)/\nu(C-H) \) surface/liquid ratio for butanethiol and pentanethiol is greater than one for Ag suggesting that the C-S bond is largely perpendicular to the Ag surface. In addition, the \( \nu(C-C)/\nu(C-H) \) surface/liquid ratio is also greater than one for these alkanethiols. The enhancement of the surface \( \nu(C-C) \) bands at Ag is greater than at Au which suggests that the tilt angle of the alkanethiols at Ag is less than that at Au. Walczak and coworkers have proposed similar orientations of the C-S bond, based
Table 6.2. Peak Area Ratio for $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) Regions for Isotropic Bulk and Surface Spectra at Smooth Au.

\[
\begin{array}{cccc}
\hline
Molecule & \text{Bulk Solution} & \text{Au Surface} & \text{Multiplier Value} \\
\hline
\text{Butanethiol} & 0.12 & 0.13 & 1.1 \\
\text{Pentanethiol} & 0.13 & 0.09 & 0.9 \\
\hline
\end{array}
\]

\[
\begin{array}{cccc}
\hline
\text{Multiplier Value} & \frac{I_{\nu(C-S)}}{I_{\nu(C-H)}} & \frac{I_{\nu(C-C)}}{I_{\nu(C-H)}} \\
\hline
\text{Butanethiol} & 3 & \text{Not applicable} \\
\text{Pentanethiol} & 4 & \text{Not applicable} \\
\hline
\end{array}
\]
on the orientations of the methyl and methylene groups deduced from IR spectroscopy.\textsuperscript{1.49} Ulman and coworkers have also proposed that the chain tilt angle of octadecanethiol at Ag is less than that at Au, based on IR spectroscopy.\textsuperscript{1.8}

In addition, the odd-even behavior observed for the $\nu_{s}(C-C)_{T}$ band at 1052 cm\textsuperscript{-1} for butanethiol and pentanethiol is opposite to that observed for Ag. The intensity of this band is greatest when the transition symmetric methyl dipole is more perpendicular to the surface, which suggests that the polarizability of this band is along the methyl dipole.

Computer modeling of the orientation of close-packed alkanethiols\textsuperscript{6.1} and alkanes\textsuperscript{6.2} at metal surfaces has been performed. The parameters involved in these models are the spacing between alkane chains, dictated by the spacing of metal atoms at the surface, and the van der Waals interactions between neighboring alkane chains. These models predict that the alkane chains are most stable with a chain tilt of ca. 30°, which is similar to the orientation observed for alkanethiols at Au. Indeed, the spacing between alkanethiol head groups at Au (111) has been observed to correspond to the spacing of the Au atoms, as determined by electron diffraction,\textsuperscript{1.48} helium diffraction,\textsuperscript{1.66} and scanning tunneling microscopy.\textsuperscript{1.67} In addition, a chain tilt of ca. 15° was estimated for CF$_{3}$(CF$_{2}$)$_{7}$(CH$_{2}$)$_{2}$SH at Au by Chidsey and Loiacono using IR spectroscopy.\textsuperscript{1.57} The difference in chain tilt was explained by the larger van der Waal radii of the fluorinated hydrocarbon, thus changing the tilt angle required to maximize van der Waals interaction between neighboring alkane chains.\textsuperscript{1.57}

The surface Raman spectra in the $\nu(C-S)$ support the argument of significant differences in metal-S bonding at the two substrates. The $\nu(C-S)_{T}$ frequencies are ca. 5 cm\textsuperscript{-1} lower for alkanethiols on Ag than on Au. The models shown in Figures 4.3 and 4.7 suggest more $\pi$ interaction of the S lone pairs with Ag than with Au.
The difference $\nu(C-S)$ frequency is accompanied by a significant difference in tilt of the C-S bond. This suggests that the metal-S bonding also has an influence on the orientation of the alkane chain.

Differences in the C-S bond angle have been observed for alkanethiols at Ag and Au. Harris and coworkers, using sum-frequency generation spectroscopy, concluded that the C-S bond of methyl thiolate at Ag (111) is perpendicular to the surface.\textsuperscript{1.32} Nuzzo and coworkers, using HREELS, concluded that the C-S bond of methyl thiolate species at Au (111) is significantly tilted from the surface normal.\textsuperscript{1.28}

Furthermore, the structure of the alkanethiol overlayer are also observed to be different at these substrates. An overlayer structure of (\textsuperscript{\textdegree}3 X \textsuperscript{\textdegree}3)R30° has been determined by several different studies of alkanethiols at Au.\textsuperscript{1.48,1.57,1.66,1.68,1.67} In this overlayer structure, the S atoms are positioned at nearest-neighbor Au atoms, which are 5.0 Å apart. Harris and coworkers observed at (\textsuperscript{\textdegree}7 X \textsuperscript{\textdegree}7)R10.9° overlayer structure for methyl thiolate at Ag (111) using LEED.\textsuperscript{1.32} The spacing of Ag atoms in the (111) lattice is the same as that for Au atoms in the (111) lattice.\textsuperscript{1.49} Thus, the overlayer structure for methyl thiolate at Ag (111) positions the S atoms at distances ca. 4.4 Å apart.\textsuperscript{1.50} Fenter and coworkers report a nearest-neighbor spacing of ca. 4.7 Å for octadecanethiol at Ag (111).\textsuperscript{1.110}

In the molecular dynamic calculations of Bareman and Klein, significantly lower tilt angles are predicted for alkyl chains that are spaced closer than 5.0 Å apart.\textsuperscript{6.2} For a spacing of 4.6 Å, a chain tilt of ca. 6° is predicted. These results strongly suggest that the C-S bond angle and S packing are related to metal-S bonding and that the chain tilt is a consequence of the S packing.

These conclusions further suggest that the orientation of the alkanethiol
films can be controlled by changing the metal-S bonding. Such control is accessible in the electrochemical environment, where the metal surface electronegativities can be systematically varied with potential. Studies concerning the potential dependent orientation of these molecules in electrochemical environments are presented in Chapter 9.

Conclusions

Surface Raman scattering has been used to characterize self-assembled monolayers formed from alkanethiols at mechanically polished, smooth Au surfaces. It is concluded that the alkane chain of adsorbed alkanethiols are mostly in the all-T conformation. The conformations adjacent to the C-S bond are mostly T for all alkanethiols, although a small amount of G is consistently detected.

Surface selection rules are used to develop a clear picture of the orientation of these molecules at Au and Ag. Different metal-S bonding interactions result in different C-S bond orientations and different S spacings at Ag and Au. The chain tilt assumed by alkanethiols is related to maximizing van der Waals interactions between neighboring alkyl chains. Smaller distances between chains result in lower tilt angles.
Chapter 7

COMPARISON OF SURFACE RAMAN SPECTRA OF
PYRIDINE AND n-ALKANETHIOLS AT METAL SURFACES OF
DIFFERENT MORPHOLOGY

Introduction

The vast majority of previous alkanethiol film studies have used Au and Ag substrates that are visually smooth. These surfaces have included evaporated metal films at Si (111), mica, or glass substrates, single-crystal surfaces, and mechanically polished surfaces. In contrast, previous Raman investigations were performed at Ag colloids and evaporated Ag island films which possess a high degree of roughness. These rough surfaces exhibit large enhancements of the surface Raman signals. This enhancement has been necessary for the acquisition of spectra of sufficient quality from PMT-based spectrometer systems. With charge-coupled device (CCD) detection, high quality spectra from less enhancing surfaces can be obtained. The spectra in Chapters 5 and 6 represent the first Raman spectroscopic investigation of alkanethiols at smooth, mechanically polished Ag and Au substrates similar to other reports. The high quality spectra obtained at short acquisition times make SERS an attractive analytical technique for the detection of adsorbed analytes. It is of interest, therefore, to investigate the fundamental effects that the surface roughness have on the spectra obtained.
This chapter discusses two approaches to characterizing the roughened surface. First, the visible absorption behavior of roughened versus smooth Ag electrodes has been studied using differential reflectance spectroscopy. This behavior is correlated with the electrode surface morphology and the SERS intensities for pyridine and Cl⁻ adsorbates. These results are also compared with theoretical predictions from SERS theories.

The second approach is to compare the spectra of alkanethiol films from a variety of substrates. These surfaces include electrochemically roughened Ag and Au, mechanically polished Ag and Au, and single-crystalline Ag. These substrates span a range of enhancement of ca. $10^5$. One should note that the term "smooth" denotes mechanically polished, polycrystalline substrates and the term "rough" corresponds to electrochemically roughened substrates. It is expected that these self-assembled films, which are densely-packed, crystalline-like monolayers, are sensitive to film disruption from rough surface morphologies. The conformational order of these films is assessed by comparing G and T intensities of $\nu$(C-S) and $\nu$(C-C) bands of short- and long-chain alkanethiols at rough and smooth surfaces. Spectra for the $\nu$(C-H) region are presented at all of these substrates for further comparisons between enhanced and unenhanced Raman spectra.

**Enhancement theories for SERS active surfaces**

The electromagnetic enhancement mechanism proposed for SERS involves the amplification of the incident electric field at the surface because of the interaction of the incident radiation with the surface roughness. Adrian¹³ and Moskovits¹¹ present calculations that relate the enhancement to a g factor involving the complex dielectric properties of the metal, $\varepsilon_m$, and surrounding
medium, $\epsilon_o$:

$$g = \frac{(\hat{\epsilon}_m - \epsilon_o)}{(\hat{\epsilon}_m + \chi \epsilon_o)} \quad (4.8)$$

where $\chi$ is an adjustable parameter related to the geometry of the roughness feature. $\chi$ is 2 for a sphere and greater for more prolate metal particles.$^{4,15}$

The surface enhancement factor is related to $g^4$. $^{4,11,4,13}$ The incident radiation intensity and the scattered radiation intensity, each proportional to the square of the electric field, are both a factor in the surface enhancement. The greatest enhancement therefore occurs at the wavelength of the surface plasmon resonance, where $(\hat{\epsilon}_m + \chi \epsilon_o) = 0$. For spherical roughness features in air, $\chi = 2$ and $\epsilon_o = 1$, and the surface plasmon occurs at $\text{Re}(\hat{\epsilon}_m) = -2$, which is ca. 380 nm for Ag.$^{4,5}$ However, for roughness features that are more prolate, $\chi$ is larger and the surface plasmon resonance is shifted to longer wavelengths.$^{4,11,4,13}$

There are several important conclusions that can be drawn from the EM mechanism. It is predicted that the magnitude and wavelength of enhancement can be varied with the morphology of the surface.$^{1,93,1,94}$ Second, the only dependence of the enhancement upon the adsorbate at the surface is the frequency of the Raman scattered radiation.$^{7,1}$ Third, the surface electric fields are preferentially created in the direction normal to the surface.$^{1,84,4,11}$ This gives rise to surface selection rules, previously discussed in Chapter 4.

In addition, Wang and Kerker calculate that SERS intensities are directly related to the absorption of light by 5 nm diameter Ag spheres.$^{7,1}$ The SERS enhancement is calculated to depend upon the surface morphology and not the nature of the adsorbate.

Efforts to correlate absorption properties and SERS have been undertaken for colloidal systems. Creighton and coworkers used Ag and Au colloid solutions of varying size and aggregation to study the relationship between absorption and
SERS intensities for adsorbed citrate. It was found that, in general, the SERS excitation profiles differed significantly from the absorption spectra. These workers did observe, however, that one absorption feature in the spectra appeared to be correlated with SERS intensities for these systems. Siiman and coworkers reported similar SERS and absorption behavior for adsorbed citrate at Ag colloids. Fornasiero and Grieser also observed a linear relationship between absorption and Raman intensities for citrate at Ag colloids. Wang and Lee observed a linear relationship between the surface plasma resonance and SERS intensity for crystal violet adsorbed on Ag island films.

Absorption of light by these surfaces is also important for charge-transfer (CT) enhancement of SERS. Atomic-scale roughness features of Ag are thought to be responsible for this type of enhancement. The size of these atomic-scale features is estimated to be no bigger than five or six Ag atoms by Moskovits. The Ag-adatom complex proposed by Roy and Furtak to be responsible for large enhancements in KCl/pyridine systems is composed of a pyridine molecule bonded to a tetramer of Ag atoms, stabilized by three Cl⁻ ions and three water molecules. Incident light is presumably absorbed by this complex and an electron from the Ag Fermi level of the metal is promoted to an excited state of the pyridine. The electron then relaxes back to the Fermi level of the Ag, and a Raman shifted photon is emitted. Two previous studies show direct evidence for this charge-transfer process. Yamada and coworkers reported an absorption band at ca. 600 nm for pyridine adsorbed onto a vacuum-deposited Ag film that they attribute to this charge-transfer process. Additionally, Demuth and coworkers observed a low energy band at ca. 2 eV in an EELS study of pyridine-dosed vapor deposited Ag films.

Several researchers have studied the optical absorption of coldly deposited
Ag films. In the visible region, a broad absorption band centered at ca. 520 nm is commonly reported for thick Ag films (>60 nm) grown at temperatures <150 K. Whether the origin of this absorbance is related to the EM enhancement model of SERS remains controversial.

This relationship has not been investigated for electrochemically roughened Ag electrodes. In the electrochemical environment, oxidation-reduction cycles (ORCs) are the most common roughening pretreatment of Ag, Cu, and Au electrodes for SERS. Despite enhancements of $10^6$ that are commonly achieved for adsorbates at Ag electrodes, ORC pretreatment is fraught with irreproducibility and is not well understood. Thus, investigations of ORC procedures are necessary for producing SERS-active surfaces that provide optimum, reproducible Raman enhancements for extensive analytical use.

Previous papers from this research group have shown relationships between SERS intensities and various parameters of the ORC, such as oxidation rate, solution pH and adsorbate. Tuschel, Pemberton, and Cook reported that the SERS intensity of the $\nu$(Ag-Cl) band at Ag roughened in 1 M NaCl increases as the anodic current of the ORC increases. SEMs show that the Ag roughness features produced in double-potential step ORCs decrease in size as the rate of oxidation increases. The greatest SERS intensity was observed from a surface prepared with an oxidation rate of 18 mA/cm$^2$. Similarly, Cross and Pemberton reported an optimum SERS intensity for pyridine bands at Ag electrodes roughened in 0.1 M KCl/0.05 M pyridine with an anodic current density of 4 mA/cm$^2$. The Ag roughness feature size was also found to decrease with increasing ORC current density in the 0.1 M KCl/0.05 M pyridine media.

The work here was undertaken with the intent of correlating the surface optical properties of mildly roughened Ag electrodes with the SERS behavior of
these surfaces. Differential reflectance and SERS spectra are reported for Ag electrodes roughened in 0.1 M KCl and 0.1 M KCl/0.05 M pyridine at different anodic current densities. The potential correlation between surface absorption and SERS intensity is investigated for Cl⁻ and pyridine adsorbates. The effect of morphology on the spectra is discussed with respect to EM models of enhancement. The role of charge-transfer absorbance in the reflectance spectra is also discussed.

Characterization of Ag Surface Roughness Morphology with Differential Reflectance Spectroscopy and SERS

0.1 M KCl System
Oxidation-Reduction Cycle and Scanning Electron Microscopy

A representative cyclic voltammogram for the ORC of Ag in 0.1 M KCl is shown in Figure 7.1. The oxidation of Ag to Ag⁺ occurs at potentials more positive than ca. 0.110 V beyond which the anodic current increases linearly with potential. In aqueous Cl⁻ media, the Ag⁺ formed precipitates onto the surface of the electrode as AgCl.⁷,¹⁷ Upon reversal of the potential sweep, the AgCl species are reduced to Ag metal forming Ag nodules of varying shapes and sizes. The size of the nodules formed in a double-potential step ORC has been found to be dictated by the oxidation rate during the ORC.⁴,¹⁰

Double-potential step ORCs were chosen for the roughening pretreatment as opposed to potential sweep ORCs due to the greater uniformity of surface roughening achieved.¹⁹⁹ This method involves stepping the potential of the Ag electrode from an initial potential of ca. -0.200 V, where no electrochemical reactions occur, to a potential where the oxidation occurs at a constant rate
Figure 7.1. Cyclic voltammogram for ORC of Ag in 0.1 M KCl, sweep rate = 10 mV/s.
dictated by the potential. After a sufficient amount of charge has passed, the potential is stepped back to the initial potential, upon which reductive current flows, to generate the roughened Ag surface.

In these experiments, only 2.6 mC/cm² of anodic charge were passed, which corresponds to ca. 17 monolayers of Ag roughened. Even though roughening the Ag surface to a much greater extent would result in greater SERS intensities, the milder ORC conditions chosen for this study minimize the contributions of diffuse light scattering to the reflectance spectroscopy measurements. Visually, these electrodes appear to have a polished surface with a cloudy film resulting from the roughening process.

Figure 7.2 shows typical chronocoulograms for two representative oxidation rates for the double potential step ORCs performed in this study. The constancy of the oxidation rates achieved with this method is demonstrated by the chronocoulograms in Figure 7.2 for 2.0 mA/cm² and 0.08 mA/cm². The generally linear increase in charge with time for the oxidative portion of the ORC indicates a constant rate for the oxidation process. Current densities of 2.0, 0.20, and 0.08 mA/cm² were achieved using oxidation potentials of 0.160 V, 0.120 V, and 0.110 V.

In order to quantitatively characterize the surface morphology of the Ag electrodes used in this study, scanning electron microscopy was performed. Different ORC current densities produce different surface morphologies because of the nature of the oxidation and reduction chemistry occurring at the surface. It has been previously reported that the large scale roughness features measured by SEM decrease in size as anodic current density increases. The electrode surfaces produced in this study, shown in Figures 7.3a-c, exhibit trends similar to those noted in previous investigations. The surfaces created using the
Figure 7.2. Chronocoulogram for double-potential step ORC in 0.1 M KCl. a. 0.160 V, 2.0 mA/cm²; b. 0.110 V, 0.08 mA/cm².
Figure 7.3. Scanning electron micrographs for Ag electrodes roughened in 0.1 M KCl. a. 2.0 mA/cm²; b. 0.20 mA/cm²; c. 0.08 mA/cm².
highest current density of 2.0 mA/cm$^2$ are composed of particles ca. 100 to 300 nm in size. Oxidation at the rate of 0.2 mA/cm$^2$ creates a different surface morphology. Clusters ranging from 500 to 2000 nm in size dominate the surface. Surfaces prepared with a current density of 0.08 mA/cm$^2$ are composed of larger clusters ranging in size from 1000 to 5000 nm. The linear features are due to the mechanical polishing of the surface by the alumina particles.

Differential Reflectance Spectroscopy

Differential reflectance spectra of Ag electrodes roughened in 0.1 M KCl are shown in Figure 7.4 for electrodes roughened at 2.0 mA/cm$^2$, 0.20 mA/cm$^2$, and 0.08 mA/cm$^2$. Each spectrum shows negative $\Delta R/R$ values corresponding to a decrease in reflectivity upon roughening of the Ag surface. In fact, these spectra are more accurately described as extinction spectra, because the response is due to both absorption and scattering of light by the roughness features.$^{7,1}$

The shapes of the spectra obtained at all current densities appear to be similar. The shoulder of a band is seen starting at ca. 470 nm and becoming more intense at higher energies. A broad band is observed centered at ca. 650 nm for samples prepared with the lowest current density; for the samples prepared with the highest current density, the band is broadened by another band which appears at ca. 750 nm and becomes more intense at lower energies. The spectrum for a current density between these two rates is intermediate in magnitude. The precision of the spectra, ca. ±1.5% at the lowest and highest current densities and ca. ±3% at the intermediate current density, is limited by the ORC procedure.

The spectra presented in Figure 7.4 resemble the spectrum reported by Otto and coworkers for Ag electrochemically roughened to the extent of ca. 35 monolayers in 0.1 M KCl.$^{7,18}$ The maximum decrease in reflectivity reported in
Figure 7.4. Differential reflectance results for electrodes roughened in 0.1 M KCL with double-potential step ORC at different current densities. a. 0.08 mA/cm$^2$; b. 0.20 mA/cm$^2$; c. 2.0 mA/cm$^2$. 
his study was ca. 10%, with a broad absorption maximum at 500 nm. The difference between the magnitude of $\Delta R/R$ reported here (15-20%) and in the work of Otto and coworkers is probably the result of different ORC conditions and different extents of roughening.

**Surface Enhanced Raman Scattering**

The SERS behavior of the electrodes roughened in 0.1 M KCl was also measured to determine whether a correlation with the differential reflectance behavior exists. All spectra were collected with the potential of the electrode held at -0.2 V. The $\nu$(Ag-Cl) vibration at 235 cm$^{-1}$ was observed using 514.5 and 600 nm excitation. The resulting spectra are shown in Figures 7.5a and b, respectively. For 600 nm excitation, the SERS intensities from electrodes roughened at ca. 2.0 mA/cm$^2$ are larger by a factor of 4 than the SERS intensities from electrodes roughened at ca. 0.08 mA/cm$^2$. The large Raman intensity at frequencies less than 235 cm$^{-1}$ in the spectrum for the electrode roughened at 2.0 mA/cm$^2$ is due to incomplete subtraction of the Rayleigh line.

With an excitation of 514.5 nm, the SERS intensities for surfaces prepared at current densities of 0.08, 0.20 and 2.0 mA/cm$^2$ were measured. Again, the SERS intensity increases with increasing current density. This behavior is similar to that reported by Tuschel and coworkers, who reported that, for Ag electrodes roughened to the extent of 20 mC/cm$^2$ in 1 M NaCl over the range of current densities of 1.0 to 18 mA/cm$^2$, the SERS intensity increases as the current density increased. $^{4,10}$ For larger current densities, the SERS intensity decreases slightly.

In the differential reflectivity results, the electrodes roughened at the higher current density exhibit a larger decrease in reflectivity than electrodes roughened at a lower current density. Thus, the decrease in reflectivity correlates with the
Figure 7.5. SERS results for electrodes roughened in 0.1 M KCl. Excitation wavelength of a. 514.5 nm; and b. 600 nm. The spectrum in b. was digitally smoothed.
increased surface enhancement for both 514.5 and 600 nm excitation.

The trends in the differential reflectivity and SERS behavior are not attributable to changes in Cl$^-$ surface concentration. All reflectance and SERS spectra were collected at -0.2 V, thus eliminating potential-dependent adsorption of Cl$^-$. Moreover, it is unlikely that the roughening procedures used here lead to changes in the surface coverage of Cl$^-$. Hupp and coworkers observed little difference in Cl$^-$ surface concentration between a smooth, electropolished Ag electrode and an electrochemically roughened surface, as measured by differential capacitance. These researchers also noted that the adsorption behavior of Cl$^-$ was reversible with respect to cycling between negative potentials, such as -1.2 V, and more positive potentials. Thus, the changes observed in the study reported here must reflect changes in surface properties and not adsorbate coverage.

Figure 7.6 shows plots of $\Delta R/R$ and SERS intensity as a function of current density for 514.5 nm excitation. Although both parameters generally increase as the current density increases, a direct proportionality between $\Delta R/R$ and SERS intensity is not observed. This may be due to contributions to the differential reflectance spectra from multipolar absorbance, which Wang and Kerker estimate arises from Ag roughness features larger than ca. 10 nm. Raman enhancement and extinction spectra are not related linearly when multipolar fields are considered in addition to enhancements due to dipolar fields.

0.1 M KCl/0.05 M Pyridine System

Oxidation-Reduction Cycle and Scanning Electron Microscopy

Oxidation-reduction cycles were also performed in aqueous KCl/ pyridine to further test the correlation between the differential reflectivity and SERS
Figure 7.6. Normalized SERS intensity of $\nu$(Ag-Cl) for 514.5 nm excitation and $\Delta R/R$ at 515 nm versus anodic current density for Ag electrodes roughened in 0.1 M KCl.
behavior. These experiments allow further evaluation of the utility of electromagnetic models to explain the connection between the reflectance and SERS spectra. The EM models predict that, in addition to being dependent upon roughness feature sizes, enhancements are independent of the adsorbate.1.84

The cyclic voltammogram for the system of 0.1 M KCl/0.05 M pyridine at a pH of ca. 8 is shown in Figure 7.7. The electrochemical behavior is different than that observed in 0.1 M KCl. In the presence of pyridine, oxidation still occurs at potentials more positive than ca. 0.110 V, but the reduction trace shows another peak at ca. 0.100 V. This peak is proposed to be due to the reduction of surface pyridine-Ag+ complexes formed during the oxidation.7.21

Double-potential step ORCs were also performed in this system using current densities of 2.0 mA/cm², 0.20 mA/cm², and 0.08 mA/cm². The oxidation potentials corresponding to these rates were 0.170 V, 0.130 V, and 0.120 V. Scanning electron micrographs show that the surface roughness features created in the presence of pyridine are different than those created in 0.1 M KCl. The SEMs for Ag roughened in 0.1 M KCl/0.05 M pyridine at different current densities are shown in Figures 7.8a-c. The trend of decreasing particle size with increasing anodic current density is still observed. However, the particle sizes are smaller for surfaces prepared in the presence of pyridine than those prepared in 0.1 M KCl. In addition to smaller size, the clusters formed in the presence of pyridine are more dispersed on the surface than clusters formed in 0.1 M KCl.

Current densities of 2.0 mA/cm² produce particles ca. 50 to 200 nm in size. Larger particle sizes ranging from ca. 100 nm to 300 nm dominate the surfaces roughened at 0.20 mA/cm². Surfaces roughened at 0.08 mA/cm² are composed of clusters ranging in size from 200 to 500 nm.

Changes in surface morphology at these different anodic current densities
Figure 7.7. Cyclic voltammogram of ORC of Ag in 0.1 M KCl/0.05 M pyridine, sweep rate = 10 mV/sec.
Figure 7.8. Scanning electron micrographs for Ag electrodes roughened in 0.1 M KCl/0.05 M pyridine. a. 2.0 mA/cm$^2$; b. 0.20 mA/cm$^2$; c. 0.08 mA/cm$^2$. 
are again due to the chemistry of the oxidation-reduction cycle. Although the interfacial chemistry is similar to that encountered in 0.1 M KCl, the presence of pyridine increases the complexity slightly. Pemberton and Girand proposed that soluble Ag complexes with both Cl\textsuperscript{-} and pyridine are involved in the ORC chemistry\textsuperscript{7,21}. The increased solubility of Ag\textsuperscript{+} in this medium results in surfaces with different morphologies than are observed in 0.1 M KCl for similar ORC conditions.

Beer and coworkers report that roughening Ag in the presence of pyridine probably leads to "trapping" of pyridine and pyridine-Ag complexes within the roughened Ag surface\textsuperscript{1,97}. The evidence for the trapping is the appearance of several weak bands in the SERS spectra for Ag roughened in 0.1 M KCl/0.05 M pyridine after 15-20 potential sweep ORCs. These bands were not observed when pyridine was introduced into the electrochemical cell after the Ag was roughened in 0.1 M KCl only. The intensity of the 1010 cm\textsuperscript{-1} band was reported to be unaffected by the roughening method.

Differential Reflectance Spectroscopy

The differential reflectance results, shown in Figure 7.9, are markedly different than those observed in 0.1 M KCl. The most striking difference is that the surfaces prepared with the highest current density (2 mA/cm\textsuperscript{2}) are more reflective than those prepared with the lowest current density (0.08 mA/cm\textsuperscript{2}). This behavior is opposite to that observed in 0.1 M KCl. Moreover, samples prepared with intermediate current densities are the least reflective suggesting that an optimum roughening for which the decrease in reflectivity is maximized exists in 0.1 M KCl/0.05 M pyridine.

The shapes of the spectra in this medium are also different than those
Figure 7.9. Differential reflectance results for Ag electrodes roughened in 0.1 M KCl/0.05 M pyridine with double-potential step QRC at different current densities. a. 2.0 mA/cm²; b. 0.08 mA/cm²; c. 0.20 mA/cm².
observed in 0.1 M KCl. Spectra from surfaces prepared with a current density of 0.2 mA/cm² show a broad band centered at ca. 550 nm. Spectra from surfaces prepared with current densities of 0.08 mA/cm² have a band centered at ca. 600 nm. Additionally, the high energy band observed at wavelengths less than 450 nm in 0.1 M KCl appears to be absent in the spectra from surfaces prepared with the two lowest current densities. Spectra from surfaces prepared with the highest current density are flat over most of the visible region, with the start of a band at wavelengths less than 450 nm.

Interestingly, the differential reflectance results are significantly different than those reported by Pettinger and coworkers from electrodes with 8 monolayers of Ag roughened in KCl/pyridine. The spectrum reported by these researchers contains a peak at 775 nm with a shoulder at ca. 630 nm. The maximum decrease in reflectivity was -4.5%. Different ORC conditions and a smaller extent of roughening are the probable reasons for the difference between the results of Pettinger and coworkers and those reported here.

Surface Enhanced Raman Scattering

The SERS intensities of electrodes roughened in 0.1 M KCl/0.05 M pyridine correlate with the reflectance results. All spectra were collected with the Ag electrodes held at a potential of -0.2 V. Figures 7.10a and b show SERS spectra for the Ag-Cl stretching vibration at 235 cm⁻¹ and the pyridine ring breathing modes at 1010 and 1036 cm⁻¹ for an excitation wavelength of 514.5. Figures 7.11a and b show the corresponding results for 600 nm. Surfaces roughened at 0.2 mA/cm² exhibit the largest SERS intensities for the ν(Ag-Cl) and pyridine bands for both 514.5 and 600 nm excitation. The electrodes roughened at 2 mA/cm² exhibit the weakest SERS intensities, while the samples roughened at 0.08
Figure 7.10. SERS at Ag electrodes roughened in 0.1 M KCl/0.05 M pyridine with an excitation wavelength of 514.5 nm. a. $\nu$(AgCl), and b. pyridine ring breathing modes.
SERS at Ag electrodes roughened in 0.1 M KCl/0.05 M pyridine with an excitation wavelength of 600 nm. a. \nu(\text{AgCl}), and b. pyridine ring breathing modes.
mA/cm² exhibit intermediate intensities for both excitation wavelengths.

These data suggest that an optimum SERS intensity is obtained at surfaces roughened at an intermediate current density. This trend is similar to that observed previously by Cross. For Ag surfaces roughened in 0.1 M KCl/0.05 M pyridine over a range of current densities from 1.2 to 14 mA/cm², an optimum SERS intensity was observed at an intermediate current density of ca. 3 mA/cm². Since the electrodes were roughened to the extent of 30 mC/cm², it is not surprising that the optimum current density is larger than that observed in this study (0.20 mA/cm²).

The correlation between SERS intensities and differential reflectivity for the ν(Ag-Cl) and pyridine bands is further illustrated in Figure 7.12. This plot shows the normalized SERS intensities of the ν(Ag-Cl) band and the pyridine band at 1010 cm⁻¹ and ΔR/R as a function of anodic current density for both 514.5 nm and 600 nm excitation. Both plots show that the SERS intensities follow the same trend as ΔR/R. Moreover, the plots for the two adsorbates are very similar, suggesting that changes in enhancement due to ORC pretreatment are adsorbate-independent. This further supports the view that the changes in enhancement are electromagnetic in nature. The mismatch of the SERS intensities from the surfaces prepared at 0.08 mA/cm² may be due to the lower reproducibility of performing an ORC under these low current density conditions.

Relation Between Absorption and SERS Behavior of Roughened Ag Electrodes

The correlation between the reflectance spectra and the SERS intensities for the different ORC pretreatments is proposed to be due to predominantly electromagnetic effects at large-scale surface roughness features. Three reasons
Figure 7.12. Normalized SERS intensities of 1010 cm\(^{-1}\) pyridine band and \(\nu(Ag-Cl)\) and \(\Delta R/R\) versus anodic current density for Ag electrodes roughened in 0.1 M KCl/0.05 M pyridine. a. 514.5 nm; b. 600 nm.
can be cited for invoking the electromagnetic model over the charge-transfer model to explain these experimental results. First, while the number of monolayers of Ag oxidized and reduced was kept constant, significant changes in large scale Ag roughness feature sizes are observed in the surface morphology shown in the SEMs. Secondly, the change in enhancement is adsorbate-independent. Third, an additional experiment was performed in which adatom clusters, proposed to be important in charge-transfer enhancement, are destroyed. The destruction of these species affects the SERS intensities but does not affect the reflectance spectra. This experiment is discussed in greater detail below.

Differential reflectance spectra for these roughened Ag surfaces represent the combination of absorption and scattering of incident light by the surface roughness features. Therefore, these spectra are more accurately called extinction spectra.² It is concluded that the changes in reflectivity and surface enhanced Raman scattering produced by changes in ORC conditions are due to light absorption by the large-scale surface roughness features formed.

Wang and Kerker have calculated the extinction spectra for Ag spheres with radii of 5, 50 and 500 nm.² They conclude that the scattering contribution dominates the extinction spectra for spheres of 50 and 500 nm. However, at an incident wavelength of 600 nm, the scattering contribution to the spectra increases as the Ag sphere radius increases from 50 to 500 nm.

In the results for the 0.1 M KCl system reported here, the reflectivity of the roughened surfaces decreases as the size of the roughness features decreases. This trend is opposite to that predicted by the theoretical results of Wang and Kerker. Similarly, surfaces roughened in 0.1 M KCl/0.05 M pyridine exhibit a decrease in reflectivity as the current density increases from 0.08 to 0.20 mA/cm², resulting in a decrease in roughness feature size. Therefore, it is proposed that
the trends in the reflectance spectra observed here reflect the absorption behavior of these surfaces. This proposal is consistent with ascription of the enhancement of the surface Raman signal to absorption of light by the roughness features. Moreover, it is consistent with other calculations which demonstrate that parameters such as size and shape of Ag roughness features are important in determining the enhancement of the surface Raman signal. For example, Zeman and Schatz calculate that the wavelength of optimum enhancement decreases from 600 nm for a Ag sphere with a radius of 75 nm to a wavelength of 360 nm for a sphere with a radius of 20 nm. Messinger and coworkers calculate that extinction peaks shift to longer wavelengths as the radius of Ag spheres increases from 10 to 150 nm. It is proposed that increased absorption of light by dipolar plasmon resonances in these spheres results in increased enhancement of SERS, although this may not hold for multipolar resonance absorption by larger roughness particles (above 100 nm in diameter). Previous results also suggest that the enhancement is independent of the nature of the adsorbate, except for the wavelength dependence of the emitted Raman scattered light which is also enhanced.

Plots of $\Delta R/R$ and SERS intensity as a function of anodic current density shown in Figures 7.6 and 7.12 for the two systems studied clearly show the correlation between the decrease in reflectivity (increase in absorption) and SERS. Furthermore, the correlation is virtually the same for both adsorbates in the 0.1 M KCl/0.05 M pyridine system suggesting adsorbate-independent behavior. This behavior is expected from the results of EM models discussed above. Due to the complexity of the surface morphology of an electrochemically roughened Ag surface and the broad extinction features in the reflectance spectra, optimum
roughness feature size and shape cannot be determined from these results.

The correlation between surface absorption and SERS intensities is not linear, as seen in Figures 7.6 and 7.12. Siiman and coworkers have also reported a non-linear dependence of enhancement on absorption for colloidal Ag solutions. The absorption spectra for the colloidal solutions showed a strong band centered at ca. 400 nm with a shoulder at 500 nm. The SERS excitation profiles, however, showed a maximum at ca. 550 nm. While the strong absorption feature at 400 nm was not correlated with the SERS behavior, the magnitude of the shoulder feature at 550 nm did correlate with the SERS. Creighton and coworkers, on the other hand, reported a linear relationship between SERS enhancement and the square of the absorbance for Au colloids, and to a lesser extent for Ag colloids. This relationship held for excitation wavelengths centered around the absorption shoulder feature observed at longer wavelengths (575 nm for Ag) and not for the intense feature at 400 nm. Fornasiero and Grieser also observed a linear relationship between absorption and Raman intensities for citrate at Ag colloids. Wang and Lee observed a linear relationship between the surface plasma resonance and SERS intensity for crystal violet adsorbed on Ag island films.

Clear evidence of contributions to the differential reflectance spectra from charge-transfer are not observed. Roughened Ag electrodes subjected to a negative potential excursion show a great loss in SERS intensities. This loss in SERS is proposed to be due to the destruction of atomic-scale roughness features which are involved in the charge-transfer process. These roughness features are proposed to become mobile at negative potentials and be irreversibly incorporated into the metal lattice. In experiments performed to evaluate this effect, the SERS intensities for \( \nu(\text{Ag-Cl}) \) at an electrode subjected a potential
excursion of -1.2 V for several minutes and returned to -0.2 V fell to zero and the bands of pyridine were greatly diminished, giving evidence for charge-transfer contributions to the SERS intensities. However, the differential reflectance spectra from Ag electrodes roughened in either 0.1 M KCl or 0.1 M KCl/0.05 M pyridine show no discernable change upon a similar negative potential excursion to -1.2 V and return to -0.2 V. Thus, charge-transfer absorption by adatom surface cluster species does not contribute significantly to the differential reflectance spectra. Tuschel and coworkers observe no significant change in SEMs of roughened surfaces before and after negative potential excursions.4,10

Although the reflectance spectra are mainly interpreted in terms of an EM model, the spectra do not resemble the theoretical calculations of absorbance and enhancement predicted by EM models. One possible reason for this is that the size of particles found on roughened electrodes is much larger than the limit imposed in electrostatic calculations. In EM calculations, the size of the particle is restricted to less than 2% of the wavelength of light.7,1 The roughness features observed by SEM in this study, which were greater than 100 nm in size, are nearly equal to wavelength of light in the visible region.

Another possible reason for the discrepancy between experimental and theoretical absorption spectra is the relatively large distribution of roughness feature sizes and shapes produced by electrochemical roughening. Buncick and coworkers report absorption spectra for Ag nodules vapor-deposited onto SiO$_2$ posts.7,23 Only two nodule sizes were produced by the procedure. The absorption spectra show a discrete peak for each nodule size, each having a full-width-at-half-maximum of at least 170 nm. An electrochemically roughened Ag surface has a much larger distribution of nodule sizes, and it is expected that the absorption bands would be correspondingly very broad. This expectation is
further supported by the theoretical study of Laor and Schatz of enhancement involving a distribution of Ag nodule sizes and clusters.\textsuperscript{7,24} Their predicted enhancement is basically flat throughout the visible wavelength region.

Summary of Differential Reflectivity and SERS Studies

In summary, the morphology of Ag surfaces can be varied in controlled fashion in the electrochemical roughening pretreatment. These surfaces have been characterized with differential reflectance spectroscopy and with SERS behavior of pyridine and Cl\textsuperscript{-} adsorbates. It has been found that the absorption behavior of electrochemically roughened electrodes, as measured by differential reflectance spectroscopy, correlates well with SERS intensities from Cl\textsuperscript{-} and pyridine adsorbates. Samples exhibiting a greater decrease in reflectivity, and correspondingly greater absorption of light, show a larger SERS response. These results suggest that, with electrochemical roughening of mechanically polished Ag electrodes, much of the enhancement arises from electromagnetic effects at these roughened Ag surfaces.

Charge-transfer enhancement was observed in the SERS investigations. Significant loss of enhancement was observed with negative potential excursions, which are proposed to result in incorporation of atomic-size Ag clusters into the substrate lattice. The loss of the charge-transfer sites are not observed in SEMs of surfaces subjected to negative potential excursions.\textsuperscript{4,10} Charge-transfer behavior is concluded not to contribute to differential reflectance spectra.

Comparison of Surface Raman Spectra of n-Alkanethiols at Rough, Smooth, and Single-Crystal Surfaces

Another class of adsorbates that has been used to characterize
electrochemically roughened electrodes are self-assembled monolayers of alkanethiols. These films are expected to be sensitive probes of the possible effects of surface morphology at Au and Ag surfaces, because they form highly-ordered, densely-packed monolayers. The disruption of film order can be readily assessed by comparing G and T intensities of the $\nu$(C-S) and $\nu$(C-C) bands from various surfaces.

Based on the previous studies with the pyridine and Cl– adsorbates, it is expected the differences in SERS behavior at rough and smooth surfaces will be largely due to the electromagnetic enhancement mechanism. As can be seen by comparing the spectra obtained from rough surfaces presented in Chapter 4 with those from smooth surfaces presented in Chapters 5 and 6, a significant increase in signal-to-noise ratio is realized at rough surfaces. Charge-transfer sites created during the roughening pretreatment are not expected to survive during the alkanethiol film formation step. Laibinis and coworkers report the removal of surface oxide at Ag substrates after alkanethiol adsorption, due to the strong metal-S bonds created.\textsuperscript{150} It is known that these charge-transfer sites are very labile and are not likely to survive the film formation. Further studies of the contributions from charge-transfer sites are more fully evaluated in Chapter 9.

In the following discussion, the surface Raman spectra obtained at electrochemically roughened and mechanically-polished (designated as smooth) Ag and Au are compared in the $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) regions. The roughening procedures used are linear-sweep oxidation-reduction cycles (ORCs). The conformational order can be directly assessed in the $\nu$(C-S) and $\nu$(C-C) regions, and ordering information is also available in the $\nu$(C-H) region. In addition, spectra from samples subjected to liquid N\textsubscript{2} and near-boiling water
temperatures are presented. These studies are useful for assessing the relative order of films at ambient temperatures.

The spectra obtained from butanethiol at single-crystal Ag will also be presented. Campion has concluded that no surface enhancement is realized at this surface beyond the minimum exhibited by a reflecting Ag surface. The spectrum of octadecanethiol at another surface showing very little enhancement, Ag evaporated at Si (111), has also been obtained. The spectra from all these surfaces are used to evaluate the applicability of the surface Raman technique in characterizing alkanethiol self-assembled films.

ν(C-S) Region

It was noted above in Chapters 5 and 6 that a significant difference in frequencies of the ν(C-S)T band is observed for alkanethiols at smooth Ag and Au. These differences are greater for short-chain alkanethiols at rough surfaces. The frequency of the ν(C-S)T band for butanethiol at rough Ag is ca. 698 cm⁻¹, which is 3 cm⁻¹ lower than that observed at smooth Ag. On the other hand, the ν(C-S)T frequency observed for butanethiol at rough Au is observed at ca. 708 cm⁻¹, which is 2 cm⁻¹ than that observed at smooth Au. The frequency difference observed for the longer chain alkanethiols at rough Ag and Au are the same as observed at smooth surfaces.

The effects of surface roughness on film structure can be assessed by comparison of spectra from rough Ag surfaces with spectra from smooth Ag surfaces, shown in Figure 7.13. Only slight differences between the surface spectra in this region for dodecanethiol and octadecanethiol adsorbed at rough and smooth Ag are observed. Butanethiol adsorbed at rough surfaces, Figure 7.13b, exhibits a slightly larger G band intensity compared to smooth surfaces,
Figure 7.13. Raman spectra in the $\nu$(C-S) region (600 nm excitation) for a) butanethiol, smooth Ag, b) butanethiol, rough Ag, c) dodecanethiol, smooth Ag, (514.5 nm exc.) d) dodecanethiol, rough Ag, (514.5 nm exc.) e) octadecanethiol smooth Ag, f) octadecanethiol, rough Ag. Incident power: a, b, c, and f) 100 mW, c and d) 50 mW. Integration times: a) 5 min, b) 2 min, c and d) 10 min, c and f) 2 min.
Figure 7.13a.

ORC pretreatments of Ag in 0.1 M KCl result in roughness features that range in size from several hundred nm to less than 40 nm as determined by scanning electron microscopy. Linear potential sweep ORCs were employed in the roughening procedure in these studies, resulting in a wider range of anodic currents than observed in double-potential step ORCs. The linear sweep method, therefore, produces a wider distribution of particle sizes compared to surfaces roughened as discussed above in the differential reflectance experiments. These roughness features as well as those smaller in size, down to clusters of four Ag atoms, are proposed to exist on the surface and be important in the SERS phenomenon.

The smooth surfaces used here are gently corrugated with features on the order of the size of alumina used in polishing (0.05 μm). These features are the long troughs seen in the SEMs of the mildly roughened electrodes shown in Figures 7.3 and 7.8. Similarity between surface spectra for smooth and rough Ag suggests that the same surface species are probed with surface Raman scattering on mechanically polished surfaces and with SERS on electrochemically roughened surfaces. Similar results have been reported previously for pyridine adsorbed at rough and smooth Ag. Additionally, previous results from this laboratory have shown that similar spectra are obtained for methanol, 1-propanol, and 1-pentanol at rough and smooth Ag surfaces.

Similarly, short-chain alkanethiols at rough Au exhibit larger ν(C-S) intensity than at smooth Au, Figures 7.14, while long-chain alkanethiols show no difference in intensity. A systematic study of the effect of roughening was performed for butanethiol, dodecanethiol, and octadecanethiol at Au. The spectra from smooth Au surfaces and from Au surfaces subjected to 0, 1, 10, and
Figure 7.14. Raman spectra in the $\nu$(C-S) region for a) butanethiol, smooth Au, b) butanethiol, rough Au, 1 ORC, c) butanethiol, rough Au, 10 ORCs, d) butanethiol, rough Au, 20 ORCs, e) dodecanethiol, smooth Au, f) dodecanethiol, rough Au, 20 ORCs g) octadecanethiol smooth Au, h) octadecanethiol, rough Au, 20 ORCs. Excitation wavelength: a, d, e, g, h) 720 nm, b, c, f) 600 nm. Incident power: a, d, e, g, h) 40 mW; b, c, f) 100 mW. Integration times: a, e, f, h) 5 min; b, c, g) 10 min.; d) 1 min.
20 potential cycle ORCs to produce roughness are shown in Figures 7.14a-d, respectively. The intensity of the \( \nu(C-S)_G \) band increases relative to the \( \nu(C-S)_T \) band as the number of ORCs increases. In addition, G methylene rocks at ca. 740 and 795 cm\(^{-1}\) increase in intensity with the number of ORCs. These effects are not observed for octadecanethiol at Au suggesting that the roughness features produced in the ORC disorder only short chain alkanethiol films in the vicinity of the C-S bond. An intermediate increase in G intensity is observed for dodecanethiol films.

The larger G/T \( \nu(C-S) \) intensity ratio observed at rough Au surfaces compared to rough Ag surfaces may be due to orientation. At Ag, the C-S bond is oriented ca. 27° from the surface normal, while at Au the bond is oriented ca. 53°. The film structure adjacent to the S group may be more easily disrupted at Au surfaces because of the closer proximity of the C-S bond to the surface, and therefore, the surface roughness features.

In addition, differences in surface roughness at rough Au and Ag electrodes may be important. SEMs of Au subjected to 10 potential sweep ORCs in 0.1 M KCl show a relatively uniform two-dimensional array of nodules on the surface.\(^7\)\(^27\) Au electrodes subjected to 25 ORCs show a dense three-dimensional network of Au roughness nodules. In contrast, SEMs of Ag electrodes subjected to single ORC pretreatments in 0.1 M KCl show surfaces with mostly dispersed patches of roughness nodules with little three-dimensional growth.\(^4\)\(^,\)\(^10\)\(^,\)\(^7\)\(^,\)\(^14\)\(^,\)\(^7\)\(^21\) Thus, the greater amount of G conformational defects of alkanethiol films at rough Au versus Ag electrodes is also directly related to the greater degree of surface roughness at these Au electrodes.

The similarity in the surface spectra for the \( \nu(C-S) \) region for the longer chain alkanethiols suggests that the roughening pretreatment does not introduce
a significantly greater number of defects in the film near the C-S bond at rough Ag as compared to those that exist in the films formed on smooth polycrystalline Ag.

\( \nu(C-C) \) region

Little difference between spectra obtained at smooth and rough Ag and Au is observed, supporting the generality of the SERS data from ORC-pretreated Ag. The spectra for rough and smooth Ag are shown in Figures 7.15, while the spectra for rough and smooth Au are shown in Figures 7.16. Very few changes in the relative intensities of G and T bands are seen in the \( \nu(C-C) \) region for alkanethiols ranging from butanethiol to octadecanethiol at the two surfaces. Thus, roughening is concluded to strongly influence the conformations of the bonds near the surface as in butanethiol, for example, but not further out along the alkane chains in the molecules.

Further experiments were performed to investigate the extent of order that is present in the long-chain alkanethiol films at rough Ag and Au. The relative amount of G intensity was observed in films subjected to elevated temperatures and liquid N\(_2\) exposure. One experiment consisted of acquisition of the Raman spectrum of an octadecanethiol film on a rough Ag surface warmed above room temperature. The temperature of the sample was raised by periodic immersion in ca. 85 °C water for 10 s and spectral acquisition for 20 s. Figure 7.15f shows the spectrum for octadecanethiol adsorbed to rough Ag before immersion in hot water. Water was chosen as the warming solvent, because it is a weak Raman scatterer in this region. Upon immersion in hot water, the G band at 1082 cm\(^{-1}\) becomes evident, shown in Figure 7.15g, suggesting that the film is disordered by the increased temperature. Figure 7.15h shows the sample after re-immersion of
Figure 7.15. Raman spectra in the $\nu$(C-C) region for a) butanethiol, smooth Ag, b) butanethiol, rough Ag, c) dodecanethiol, smooth Ag, d) dodecanethiol, rough Ag e) octadecanethiol smooth Ag, f) octadecanethiol, rough Ag, g) octadecanethiol, rough Ag, exposed to ca. 90° water, h) sample in g. exposed to ca. 20° water. Excitation wavelength: a-c, e, f) 600 nm; d, g, h) 514.5 nm. Incident power: a-c, e-h) 125 mW; d) 50 mW. Integration times: a, d) 5 min; b, c, e, f) 2 min; g) 3 min, h) 4 min.
Figure 7.16. Raman spectra in the $\nu$(C-C) region (720 nm excitation) for a) butanethiol, smooth Au, b) butanethiol, rough Au, c) dodecanethiol, smooth Au, d) dodecanethiol, rough Au, e) dodecanethiol, rough Au, exposed to liquid N$_2$, f) spectrum d minus spectrum e, g) hexadecanethiol smooth Au, h) hexadecanethiol, rough Au, i) hexadecanethiol, rough Au, exposed to liquid N$_2$, j) spectrum h minus spectrum i, decomposed. Incident power: 40 mW. Integration times: a, g) 10 min; b, d, e, h, i) 1 min; c) 5 min.
this same film into ca. 20 °C water. The G band at 1082 cm\(^{-1}\) has disappeared.

The relative G components of films of dodecanethiol and hexadecanethiol at rough Au were further investigated. The films were subjected to liquid N\(_2\) cooling, and the changes in the \(\nu(C-C)\) region were observed. Figures 7.16d and e show the spectra for dodecanethiol at rough Au at room temperature and exposed to liquid N\(_2\), respectively. The spectra for hexadecanethiol at rough Au at room temperature and exposed to liquid N\(_2\) are shown in Figures 7.16h and i, respectively. The spectra for films of both molecules subjected to liquid N\(_2\) cooling exhibit a decrease in G intensity in the region between the \(\nu_a(C-C)T\) and the \(\nu(C-C)T\) band at ca. 1084 cm\(^{-1}\). Additionally, the T bands are narrower and the \(\nu(C-C)T\) and \(\nu_a(C-C)T\) are shifted to slightly higher frequencies, which are similar to those observed in the solid alkanethiol spectra. Nuzzo and coworkers\(^{1,72}\) have also presented IR spectroscopic evidence for decreased G conformers in long-chain alkanethiols at Au upon cooling to liquid N\(_2\) temperatures.

The spectrum in Figure 7.16f is the difference between Figures 7.16d and e. This difference spectrum, therefore, contains the G intensity present at room temperature for dodecanethiol at rough Au but largely absent after exposure to liquid N\(_2\). The peak at ca. 1078 cm\(^{-1}\) is the G band and the peak at ca. 1030 cm\(^{-1}\) reflects the shift in frequency of the \(\nu_a(C-C)T\) band. The spectrum in Figure 7.16j is the corresponding difference spectrum for hexadecanethiol at rough Au. The peak at ca. 1078 cm\(^{-1}\) is the G band present at room temperature, and the bands at ca. 1090 and 1130 cm\(^{-1}\) reflect shifts in frequencies of the \(\nu(C-C)T\) and \(\nu_a(C-C)T\) bands. The relative G intensity in the room temperature films is estimated by calculating the peak area ratio of the G band in the difference spectra to the \(\nu_a(C-C)T\) band in the room temperature spectra. The difference
spectra for hexadecanethiol at rough Au was curve fit to obtain the peak area of the G band.

For dodecanethiol and hexadecanethiol at room temperature at rough Au, the relative G band intensities are estimated using this procedure to be ca. 25% and 20%, respectively. These numbers should not be taken as absolute indicators of the amount of defect structures in these films. The absolute degree of disordering in the surface films may actually be smaller than estimated, because the changes in $\nu(C-C)_G$ and $\nu_s(C-C)_T$ intensities may not be linear with the number of G conformers in the chain. Additionally, the absolute intensities of these bands may be enhanced to a different extent due to surface selection rules. Finally, in the highly disordered liquid form, the $\nu(C-C)_G$ intensity for the long-chain alkanethiols is greater than that of the $\nu_s(C-C)_T$, shown in Figure 3.1e-h.

The results of these experiments suggest that these surface films are in a liquid-crystalline state, with slightly more disorder than observed in solid neat alkanethiols. Spectral behavior in the $\nu(C-H)$ region also support this conclusion.

$\nu(C-H)$ Region

Comparing the surface spectra for rough and smooth Ag and Au, Figures 7.17 and 7.18, respectively, one notes that in most respects, the spectra are nearly identical. Differences in the relative intensities of the $\nu_s(CH_2)$ bands and the Fermi resonance bands are frequently observed for different samples with adsorbed butanethiol and other short-chain alkanethiols.

The odd-even effect in the $\nu(C-H)$ region, demonstrated in Figures 5.4 and 5.5 for smooth Ag and Au, respectively, is still clearly evident for the $\nu_{asym}(CH_3)$ band at rough surfaces, as demonstrated in Chapter 4. The spectra for
Figure 7.17. Raman spectra in the $\nu$(C-H) region for a) butanethiol, smooth Ag, b) butanethiol, rough Ag, c) dodecanethiol, smooth Ag, d) dodecanethiol, rough Ag, e) octadecanethiol smooth Ag, f) octadecanethiol, rough Ag, g) octadecanethiol, rough Ag, exposed to liquid N$_2$. Excitation wavelength: a, b, e-g) 600 nm; c, d) 514.5 nm. Incident power: a, b, e-g) 100 mW; c, d) 50 mW. Integration times: a, c-e) 10 min; b) 1 min; f, g) 2 min.
Figure 7.18. Raman spectra in the $\nu$(C-H) region (600 nm excitation) for a) butanethiol, smooth Au, b) butanethiol, rough Au, c) pentanethiol, smooth Au, d) pentanethiol, rough Au, e) dodecanethiol, smooth Au, f) dodecanethiol, rough Au, g) octadecanethiol smooth Au, h) octadecanethiol, rough Au. Incident power: a, c, e-g) 100 mW; b, d, h) 200 mW. Integration times: a, c, e, g) 20 min; b, d) 1 min; f) 3 min; h) 5 min.
butanethiol and pentanethiol at rough and smooth Au are shown in Figures 7.18a through d. Therefore, it is concluded that the orientations of these molecules are the same at rough and smooth surfaces.

Greater surface enhancement is realized at rough Ag compared to smooth Ag. The enhancement factor has been estimated by comparing the signal intensities from all three regions from butanethiol and pentanethiol films at rough and smooth polycrystalline surfaces, normalized to incident power and acquisition time. The enhancement factor for rough Ag relative to smooth, polycrystalline Ag for alkanethiol systems is ca. 50.

The \( \nu(CH_3) \) bands are slightly stronger in the surface spectra for alkanethiols at both rough Au and Ag surfaces as compared to smooth surfaces. This is clearly seen for butanethiol at rough Ag and smooth Ag, shown in Figures 7.17a and b, respectively. One explanation is the possibility of an increase in the ratio of the surface electric fields, \( E_n^2/E_t^2 \), at rough surfaces. An increase of the \( \nu(CH_3) \) bands relative to the \( \nu(CH_2) \) bands is observed for pentanethiol at rough Ag as the wavelength of excitation is shifted from 600 nm to 720 nm, shown in Figure 4.5. The increase in \( E_n^2/E_t^2 \) is expected at rough surfaces as the excitation is shifted to longer wavelengths. Moskovits also predicts that \( E_n^2/E_t^2 \) is dependent upon surface morphology. The corrugated roughness features at mechanically polished surfaces are very different than the nearly spherical features at electrochemically roughened surfaces. This difference in surface morphology might result in the differences noted in the rough and smooth spectra.

In wetting studies of octadecanethiol at Au films evaporated on smooth and rough Si wafer surfaces, Bain and coworkers reported no significant differences in advancing contact angles between smooth and rough surfaces. They estimated their roughness features to be on the order of \( \mu m \). However, they did
report an increase in the hysteresis of the measurement at rough samples.

It was previously noted in Chapter 5 that surface spectra in the $\nu$(C-H) region resemble liquid spectra more than solid spectra. This observation is contrary to that observed in the $\nu$(C-S) and $\nu$(C-C) regions. The $\nu_{\text{asym}}$(CH$_2$) band is the most prominent feature in solid long-chain alkanethiol spectra, Figure 3.9, while it is barely seen in the surface spectra, Figures 7.17 and 7.18. The attenuation of the $\nu_{\text{asym}}$(CH$_2$) band is proposed to be mostly due to orientation of the methylene bands parallel to the surface.

An experiment was conducted to determine if a more intense $\nu_{\text{asym}}$(CH$_2$) could be observed by lowering the temperature of octadecanethiol films at rough Ag. The films were subjected to liquid N$_2$ cooling, and changes in the $\nu$(C-H) region were observed. Figures 7.17f and g show the spectra for octadecanethiol at rough Ag at room temperature and exposed to liquid N$_2$, respectively. The spectra for films subjected to liquid N$_2$ cooling exhibit an increase in the $\nu_{\text{asym}}$(CH$_2$) intensity at ca. 2881 cm$^{-1}$. Thus, the spectrum from the liquid N$_2$-cooled sample more closely resembles the solid octadecanethiol spectrum, Figure 3.9h. Additionally, the intensity of the $\nu_{\text{sym}}$(CH$_3$,FR) band at ca. 2935 cm$^{-1}$ is weaker relative to the $\nu_{\text{sym}}$(CH$_2$) band at ca. 2850 cm$^{-1}$. This change has been previously observed for alkanes and lipid molecules that are cooled to temperatures below the melting temperature.$^{7,28}$

Thus, it is concluded that these surface films are more liquid-crystalline than solid alkanethiols. Interestingly, neat octadecanethiol is a solid at room temperature, although small changes can be observed upon cooling with liquid N$_2$, suggesting a metastable solid species at room temperature.

Raman spectra of alkanethiols were also collected at other Ag surfaces. The spectrum for octadecanethiol adsorbed at Ag evaporated onto Cr-coated polished
Si (111) is shown in Figure 7.19c. Walczak and coworkers have used this substrate in IR studies of alkanethiols adsorbed at Ag.\textsuperscript{149} These substrates are visibly defect-free, although SEMs of similarly-prepared Au substrates show subtle variations in thickness, with grain sizes on the order of 50 nm.\textsuperscript{142} The spectrum shown in Figure 7.19c is similar to the spectra of octadecanethiol at Ag, shown in Figures 7.18e through g.

Butanethiol monolayers were also prepared at single-crystal Ag substrates for further comparison. The spectra for butanethiol at Ag (111) and Ag (100) are shown in Figure 7.19a and b, respectively. These spectra have been subjected to a five point Savitsky-Golay smoothing routine. These surfaces were prepared by mechanical polishing followed by chemical polishing, according to the procedure of Bewick and Thomas.\textsuperscript{2.5} These surfaces were then characterized with Ti UPD. The cyclic voltammograms shown in Figure 7.20 are nearly identical to those of Bewick and Thomas,\textsuperscript{2.5} confirming the single-crystalline nature of the surface. The signal-to-noise ratio of the surface Raman spectra before smoothing is ca. 5. However, this ratio is not sufficient for quantitative comparison with spectra at polycrystalline surfaces because of the close overlap of the bands in the $\nu$(C-H) region. These surface films represent the current limits of detection for normal Raman scattering.

The estimate of surface enhancement from mechanically polished polycrystalline Ag surfaces is calculated from the signal intensities of butanethiol from polycrystalline Ag compared to those from Ag single-crystal substrates. The spectra from these substrates were taken under similar conditions and the signal intensities were normalized by dividing by incident power and acquisition time. The enhancement factor of smooth, polycrystalline Ag is ca. 500 relative to single crystal Ag.
Figure 7.19. Raman spectra in the $\nu$(C-H) region (514.5 nm excitation) for a) butanethiol at Ag (111), b) butanethiol at Ag (100), c) octadecanethiol at Ag evaporated onto Cr-coated Si (111). Incident power: a, b) 700 mW; c) 500 mW. Integration times: a, b) 40 min, c) 60 min. Spectra subjected to 9 point Savitsky-Golay smoothing routine.
Figure 7.20. Cyclic voltammograms in 0.75 mM Tl₂SO₄/0.5 M Na₂SO₄/1 mM HClO₄ of a) Ag (111), b) Ag (100). Sweep rate: 300 mV/s.
Conclusions

Differential reflectance spectroscopy and SERS of pyridine and Cl\textsuperscript{-} at mildly roughened Ag electrodes reveal a correlation between enhancement and absorption of visible wavelengths. The surface Raman spectra of alkanethiols films at rough and smooth polycrystalline Ag and Au and single-crystalline Ag are very similar. An increase in the G \( \nu(C-S) \) intensity is observed for short-chain alkanethiols at rough surfaces compared to smooth surfaces, but no differences in G intensity are observed in the \( \nu(C-C) \) region. This suggests that surface morphology can disrupt film order near the metal-film interface, but not in the bulk of the alkane chain. The extent of G conformational defects in the \( \nu(C-C) \) region is estimated for longer-chain alkanethiols. Electrochemical studies of alkanethiol films at various surface morphologies are presented in Chapters 8 and 9.

Stronger \( \nu(CH_3) \) intensity is observed in the \( \nu(C-H) \) region for alkanethiols at rough surfaces compared to smooth surfaces. This suggests a larger \( E_n^2/E_t^2 \) ratio is created at rough surfaces than at mechanically polished, polycrystalline surfaces. The spectra of alkanethiols at Ag single-crystal surfaces have been obtained, but a few minimal improvements in instrumentation and efficiency of light collection are necessary to obtain spectra with sufficient signal-to-noise to quantitate the intensities of the methyl bands. Using surface Raman selection rules as described in Chapter 4, the orientation of alkanethiols at these single-crystal substrates can be determined.
Chapter 8

ELECTROCHEMICAL CHARACTERIZATION OF n-ALKANETHIOLS
AT Ag AND Au

Introduction

Alkanethiol films have been previously characterized by various electrochemical approaches. Several researchers have studied electron transfer through insulating alkanethiol films to solution-confined redox species. Much of the electrochemical behavior in many of these studies was concluded to be associated with defect sites in the film. Studies of surface-confined redox species have further explored the role of defect sites in electrochemical behavior. In addition, Widrig and coworkers have studied the reductive and anodic desorption of alkanethiol films in basic solutions. Spectroscopic investigations have characterized these films as densely packed monolayers. The surface Raman spectra presented in Chapters 5, 6, and 7 show little G intensity in long-chain films. Unlike most spectroscopic approaches used, which are sensitive to presence of alkanethiol films, electrochemical techniques are more sensitive to the absence, or the defect structure, of these insulating layers at the surface.

The goals of this chapter are two-fold. Before the potential-dependent orientation of these films can be studied with Raman spectroscopy, the
The electrochemical behavior of these films must be established. The potential window in which these films can be studied intact is determined for 0.1 M KCl. This electrolyte system is used in the spectroscopic studies presented in Chapter 9. Also, electrochemical results in 0.5 M KOH are presented and compared to the work of Widrig and coworkers.

The second electrochemical study involves the deposition of Pb onto alkanethiol-coated Ag electrodes. This system has features that allow different types of defect structure to be evaluated. The underpotential deposition (UPD) of Pb occurs at potentials positive of bulk reduction and exclusively involves the formation of Pb-Ag bonds. Thus, the amount of gross defects, where bare Ag is exposed to the electrolyte solution, can be assessed. Bulk Pb deposition, on the other hand, is a probe of the permeability, or defect structure, of the intact film. The results of these metal deposition studies are used to construct a model of the defect structure of these films. Deposition at rough, smooth, and single-crystal Ag electrodes are presented to further characterize the effect of surface morphology on alkanethiol films.

Desorption of Alkanethiol Films at Ag and Au

Cyclic Voltammetry in 0.1 M KCl

1-Alkanethiols are proposed to form monolayers at Au by chemisorption of the S head group to the metal substrate.\(^1\) Widrig and coworkers have proposed the following adsorption mechanisms at Au and Ag.\(^1\)\(^2\) The mechanism at Au substrates, shown in Scheme 6.1,

\[
\begin{align*}
2\text{RSH} + 2\text{Au} & \rightarrow 2\text{Au-SR} + \text{H}_2 \\
2\text{RSH} + 2\text{Au} + \text{O}_2 & \rightarrow 2\text{Au-SR} + \text{H}_2\text{O}_2
\end{align*}
\]

SCHEME 6.1
involves cleavage of the S-H bond with concomitant oxidation of a Au atom to form a S-Au bond. The lost H may be released as H$_2$ or combine with trace oxidants in solution such as O$_2$ to form H$_2$O$_2$. A different reaction scheme has been proposed for alkanethiol adsorption at Ag, shown in Scheme 5.1:

$$\text{RSH} + \text{AgX} \rightarrow \text{Ag-SR} + \text{X}^- + \text{H}^+$$

SCHEME 5.1

where X may be Cl, I, or OH.$^{1,52}$ Evidence for the S-H cleavage is reported in Raman studies of these systems. The S-H band, which is strong in the bulk liquid Raman spectra, is completely absent in the surface spectra at Ag and Au, shown in Figures 5.1 and 6.1.

The cyclic voltammograms for butanethiol films at mechanically polished and electrochemically roughened Ag in 0.1 M KCl are shown in Figures 8.1b and c, respectively. A broad reduction wave is observed at ca. -1.4 V for butanethiol at smooth and rough Ag. The only difference observed in these voltammograms between the smooth and rough substrates is one of current magnitude. Variations in peak potential or wave shape are not noted suggesting that the reductive process is similar on both types of surface.

The products of this reduction are proposed to be Ag$^0$ and thiolate species, RS$^-$. These species are similar to those proposed for the electrochemical reduction of alkanethiols at Ag in 0.5 M KOH electrolyte solution.$^{1,52}$

The reduction wave is irreversible as no oxidation wave is observed on the return scan. In subsequent scans, the reduction wave is still observed but it is smaller in magnitude. Reductive desorption of the butanethiol film occurs at potentials negative of -1.0 V. An electrode that is held at -1.0 V for one minute
Figure 8.1. Cyclic voltammograms for a) bare Ag, b) butanethiol at smooth Ag, c) butanethiol at rough Ag, d) dodecanethiol at smooth Ag. Sweep rate = 100 mV/s in 0.1 M KCl.
shows little decrease in the magnitude of the reduction current in a subsequent potential sweep to negative potentials. Electrodes held at increasingly negative potentials show increasing loss of the reduction current in the subsequent sweeps. However, a reduction wave at ca. -1.4 V can still be observed in scans performed after holding the potential at -2.0 for several minutes. Furthermore, strong Raman scattering is still observed for butanethiol at Ag subjected to a potential of -2.5 V for 10 minutes. These results suggest that the reduction wave does not represent complete desorption of the monolayer in this medium. These effects may be due to slow kinetics involved in the solvation of the thiolate species. These results are contrary to the conclusion by Widrig and coworkers that desorption is complete after a potential sweep in 0.5 M KOH to -1.4 V.1.52

For longer chain length alkanethiols such as dodecanethiol and octadecanethiol, no reduction peak is observed, as shown in Figure 8.1d. However, the onset of reduction current is observed at potentials slightly positive of that observed at bare Ag. Reductive desorption of the film along with solvent breakdown is probably occurring to some extent at potentials negative of ca. -1.4 V in these systems, because a shift in the onset of reduction current to more negative potentials is observed upon subsequent scans. Similar to that observed for butanethiol, however, Raman scattering is still observed from these molecules after subjecting the Ag surface to potentials negative of -2.0 V.

The cyclic voltammograms for Au in the potential region between -0.2 V and -1.6 V are shown in Figure 8.2. For butanethiol at rough and smooth Au, Figures 8.2b and c, respectively, a reduction peak is observed at ca. -1.1 V, 0.30 V more positive than measured at Ag for the same molecule. The shift in reductive desorption potential to more positive potentials was also observed by Widrig and coworkers in 0.5 M KOH.1.52 As for Ag, strong surface Raman signals are
Figure 8.2. Cyclic voltammograms for a) bare Au, b) butanethiol at smooth Au, c) butanethiol at rough Au, d) dodecanethiol at smooth Au. Sweep rate = 100 mV/s in 0.1 M KCl.
observed from these films at Au electrodes subjected to -2.0 V. No definite reduction wave is observed for dodecanethiol, Figure 8.2d, or longer chain alkanethiols at Au in 0.1 M KCl. However, the onset of reduction current is slightly more positive than that observed at bare Au.

Cyclic voltammograms were also performed with Au electrodes in the positive potential region from -0.2 V to +1.4 V. These results are shown in Figure 8.3. On bare Au, Figure 8.3a, oxidation of the Au surface to soluble complexes with Cl⁻ occurs at potentials greater than ca. +1.00 V. For butanethiol at Au, Figure 8.3b and c, a small shoulder can be seen at ca. +0.9 V on this Au oxidation process. This shoulder may correspond to oxidation of the surface thiolate to a surface disulfide species. Spectroscopic evidence for such disulfide formation is given in the surface Raman spectral results discussed in Chapter 9.

The oxidative behavior of the longer chain alkanethiols in 0.1 M KCl is slightly different than that of butanethiol. The onset of the oxidation current due to disulfide formation is shifted to more positive potentials. Thus, it cannot be seen in the voltammograms due to oxidation of the Au surface.

Cyclic Voltammetry in 0.5 M KOH

Cyclic voltammograms were also performed on these films in 0.5 M KOH solutions. The results for negative potential sweeps at Ag are shown in Figure 8.4. A reduction peak for butanethiol at smooth Ag is observed at ca. -1.2 V in Figure 8.4b. The reduction waves are at more positive potentials than observed in 0.1 M KCl. This is probably due to the increased solubility of alkanethiolate species in basic solutions. In addition, a reduction wave is observed for dodecanethiol at ca. -1.4 V in Figure 8.4c. Widrig and coworkers reported the reduction wave peak potential for butanethiol at Ag to be at ca. -1.2 V; the wave
Figure 8.3. Cyclic voltammograms for a) bare rough Au, b) butanethiol at rough Au, c) dodecanethiol at smooth Au. Sweep rate = 100 mV/s in 0.1 M KCl.
Figure 8.4. Cyclic voltammograms for a) bare Ag, b) butanethiol at smooth Ag, C) dodecanethiol at smooth Ag. Sweep rate = 100 mV/s in 0.5 M KOH.
Figure 8.5 shows the voltammetry behavior for butanethiol and dodecanethiol at Au in 0.5 M KOH in the potential region from -0.2 V to -1.4 V. A reduction wave is observed at ca. -1.2 V for butanethiol in Figure 8.5b, while no wave is observed for dodecanethiol, Figure 8.5c. Dodecanethiol reduction occurs negative of solvent reduction, which is observed here at ca. -1.3 V. Widrig and coworkers report reduction potentials of ca. 250 mV more positive for butanethiol at Au and a peak at ca. -1.3 for octadecanethiol at Au in 0.5 M KOH. In that case, Au electrodes were prepared by evaporation of Au onto mica. The voltammetry at electrodes of Au evaporated onto Si (111) wafers and glass microscope slides was reported to be ill-defined and not reproducible. The Au polycrystalline electrodes in this study probably resemble these latter substrates more closely than Au films at mica.

As noted for butanethiol at Ag and Au in 0.1 M KCl, a reduced, but still significant, Raman signal from butanethiol is still detected at these electrodes in 0.1 M KOH at ca. -1.7 V. Thus, complete reductive desorption is not occurring for these films, as concluded by Widrig and coworkers.

In the potential region from -0.5 V to +1.2 V, an oxidation wave for butanethiol at Au is seen at ca. +0.6 V, shown in Figure 8.6b. A similar oxidation wave has been reported for propanethiol at Au in 0.5 M KOH. However, in contrast to the disulfide production proposed for 0.1 M KCl electrolytes, the sulfenic acid species, RSO₂⁻ was proposed to be formed under those conditions. The oxidative electrochemistry of organic sulfur compounds is complex. Dryhurst has reported that the disulfide species is the favored anodic oxidation product of 6-thiopurine at pH 2.3, while the sulfonamide and sulfenic acid product is favored at pH 9 in an ammonia buffer solution, and the sulfonic acid
Figure 8.5. Cyclic voltammograms for a) bare Au, b) butanethiol at smooth Au, c) dodecanethiol at smooth Au. Sweep rate = 100 mV/s in 0.5 M KOH.
Figure 8.6. Cyclic voltammograms for a) bare smooth Au, b) butanethiol at smooth Au. Sweep rate = 100 mV/s in 0.5 M KOH.
product is favored at pH 9 in a carbonate buffer solution.8.1 Products formed from these oxidations depend on the nature of the electrode material as well as the medium.1.53 Thus, differences in products observed between KCl and KOH electrolyte solutions are not surprising.

**Pb Deposition in Alkanethiol Films at Ag in 1 mM Pb\(^{2+}\)/0.1 M KCl**

The previous electrochemical studies characterize the potential windows for these alkanethiols at Ag and Au. Studies involving electrochemical reactions that occur within the potential windows established in the previous voltammetry can be used to characterize the behavior of intact films. Pb deposition onto alkanethiol films at Ag can provide significant information on defect structure and ion penetration into these films. Bulk and underpotential deposition of Pb occurs at potentials sufficiently positive of alkanethiol reductive desorption and negative of Ag oxidation to provide detailed information about several aspects of these films.

A cyclic voltammogram for the deposition of Pb onto bare Ag from 0.1 M KCl/1 x 10\(^{-5}\) M Pb\(^{2+}\) is shown in Figure 8.7. The cathodic wave beginning at ca. -0.31 V and peaking at ca. -0.37 V is the underpotential deposition (UPD) of Pb. The peak current for bulk deposition occurs at ca. -0.49 V. The underpotential deposition occurs at more positive potentials because a Pb-Ag bond is formed that is more thermodynamically stable than Pb-Pb bonds in the bulk deposition.8.2 Thus, only a monolayer of Pb is deposited positive of bulk deposition. The extent of Pb UPD that occurs at Ag electrodes modified with alkanethiol films can be a measure of the bare Ag exposed through gross defects in the alkanethiol monolayer.

While UPD is a probe of ion penetration to the Ag surface, bulk Pb
Figure 8.7. Cyclic voltammograms for bare Ag. Sweep rate = 15 mV/s in 0.1 M KCl/0.001 M Pb^{2+}. 
deposition is a probe of electrolyte penetration into the alkanethiol film. The peak potential for Ag deposition has been found to be correlated to the extent of cross-linking in poly(4-vinylpyridine) films at glassy carbon. The barrier properties of the polymer film with respect to ion penetration were concluded to increase with cross-linking. As the amount of cross-linking increased in these polymer films, the Ag deposition peak potential shifted more negative. In a similar manner, the peak potential of the bulk Pb reduction wave is used to probe the barrier properties of these films.

The CVs for smooth Ag immersed in butanethiol, dodecanethiol, and octadecanethiol solutions for ca. 4 hours are shown in Figure 8.8. In Figures 8.8a, c, and e, the scans were restricted to potentials positive of bulk deposition. In Figures 8.8b, d, and f, the scans were reversed negative of the bulk deposition peak.

Substantial UPD is observed for butanethiol-modified Ag. The peak potential for the Pb UPD, however, has been shifted to ca. -0.45 V. The UPD wave is not resolved from the bulk deposition wave for this film. The Pb stripping waves are also shifted negative. This suggests that gross defects, or bare Ag, are present to a very small extent. However, Pb ions are capable of penetrating through the film to the Ag surface. The negative shift in potential suggests that less stable Pb-Ag bonds are formed in the presence of adsorbed S atoms.

In the anodic sweep, waves are observed at ca. -0.45, -0.42, and -0.38 V. The most negative wave corresponds to bulk stripping, while the other two correspond to underpotential stripping. In Figure 8.8b, in which the scan has been reversed at -0.53 V, the bulk deposition wave is observed at ca. -0.50 V. The slight negative shift in bulk deposition, ca. 10 mV, indicates a small resistance to
Figure 8.8. Cyclic voltammograms for alkanethiol films formed at smooth Ag for ca. 4 hours. a) and b) butanethiol, c) and d) dodecanethiol, e) and f) octadecanethiol. Sweep rate = 15 mV/s in 0.1 M KCl/0.001 M Pb^{2+}. 
electrolyte penetration into the butanethiol film. Saiki and coworkers observed a ca. 110 mV negative shift in Ag deposition at poly(4-vinylpyridine) films. The thickness of these films was estimated to be on the order of μm. Upon cross-linking of the polymer film, additional negative shifts up to ca. 250 mV were observed.

In the anodic sweep, large waves are seen at -0.45 V and -0.38 V, along with a wave at -0.42 V. The increase of the anodic wave at -0.38 V suggests that Pb bulk deposition has also resulted in Pb deposition at the Ag surface. Bulk Pb deposition may be damaging the butanethiol film.

Different behavior is seen with dodecanethiol and octadecanethiol films at smooth Ag. As seen in Figures 8.8c and e, a substantial amount of Pb UPD is observed at potentials that are shifted little from those at bare Ag. This suggests that gross defects are contained in films that have been formed at polycrystalline Ag for several hours. Less UPD is observed for dodecanethiol and octadecanethiol films formed for ca. 18 hours, suggesting a decrease in gross defects with longer film deposition times.

Bulk Pb deposition is observed at ca. -0.51 V, which is a shift of 20 mV from the potential of bulk deposition at bare Ag. This small shift suggests significant ion penetration in these longer chain alkanethiol films. In the anodic sweep, an increase in the underpotential stripping wave is observed, compared to dodecanethiol films subjected only to UPD and not bulk deposition. The small increase in underpotential stripping suggests an increase in gross defect structure resulting from film damage during bulk metal deposition.

The cyclic voltammograms for Pb deposition at films formed for ca. 24 hours are shown in Figure 8.9. The voltammogram for butanethiol films, shown in Figure 8.9a, is nearly identical to that observed for butanethiol films formed at
Figure 8.9. Cyclic voltammograms for alkanethiol films formed at smooth Ag for ca. 24 hours. a) butanethiol, b) and c) dodecanethiol, d) and e) octadecanethiol. Sweep rate = 15 mV/s in 0.1 M KCl/0.001 M Pb^{2+}. 
ca. 4 hours. The increase in bulk current is due to a slightly greater concentration of Pb$^{2+}$ in the electrolyte.

For dodecanethiol and octadecanethiol films, a dramatic decrease in UPD is observed compared to Ag exposed for less time to alkanethiol solutions. Thus, longer times are necessary to form complete defect-free monolayers for longer-chain alkanethiols in ethanol solution. This may be due to the lower alkanethiol concentrations in the ethanol solutions, due to the decrease in solubility of the long-chain alkanethiols. Also, formation of densely packed long-chain alkanethiol monolayers may be more difficult due to increased possibilities of G conformations in dodecanethiol and octadecanethiol solutions.

Insufficient film formation time is most likely the reason for the existence of large pinholes in these films, ca. 800 nm as estimated by Finklea and coworkers in one of their studies.$^{1,78}$ They immersed polycrystalline Au electrodes for ca. one hour in 10-50 mM alkanethiol solutions. The deposition results presented here suggest that times of at least ca. 24 hours are required for minimal gross defects. Bain and coworkers, using ellipsometric and contact angle measurements, conclude that ca. 16 hours are necessary for complete monolayer formation.$^{1,43}$

Model of Defect Structure of Alkanethiol Films

A model of the packing in these long-chain alkanethiol films is shown in Figure 8.10. The molecules are shown in the all-trans configuration, although some G conformers are observed at Ag electrodes, as discussed in Chapter 7. No exposed bare Ag is present when the electrodes have been immersed in the alkanethiols/alcohols for a sufficient amount of time. However, a significant number of grain boundaries are present because of the polycrystalline nature of
Figure 8.10. Model of alkanethiol tilt domain boundary.
the surface and the mechanical polishing pretreatment. The pretreatment leaves macroscopic features, such as grooves with dimensions on the order of the alumina particle sizes used during polishing.

The defects in the substrate are envisioned to result in defects in the alkanethiol monolayers at these surfaces. Most of the alkanethiol molecules can be in the all-trans configuration and oriented $15^\circ$ with respect to the surface normal, but domains of alkanethiol molecules can oriented at different angles with respect to each other. This may result in an opening in the film at a chain tilt domain boundary, pictured in Figure 8.10. This model has also been proposed by Chidsey and coworkers.\textsuperscript{1,80} Chain tilt domains may exist even on a large single-crystal substrate. Strong and Whitesides observed domain sizes of ca. 60 Å for octadecanethiol monolayers at Au (111) surfaces which had domain sizes of ca. 500 Å.\textsuperscript{1,48} This opening would allow ions to penetrate the film and approach the electrode surface but not adsorb to the metal substrate.

This model was further tested using Pb deposition at films on Ag surfaces with different morphologies. These include electrochemically roughened and single-crystalline Ag surfaces.

The cyclic voltammograms for butanethiol, dodecanethiol, and octadecanethiol at rough Ag are shown in Figure 8.11. These films were formed for ca. 24 hours. The results in the UPD region are similar to those for films at mechanically polished, polycrystalline Ag substrates. However, the bulk deposition wave for dodecanethiol is shifted to slightly more positive potentials. For octadecanethiol, a bulk reduction wave is observed at practically the same potential for deposition at bare Ag, along with a more negative potential wave.

These results strongly suggest greater ion penetration occurs at films at more disordered electrode surfaces. There is no increase in gross defect structure in
Figure 8.11. Cyclic voltammograms for alkanethiol films formed at rough Ag for ca. 24 hours. a) butanethiol, b) and c) dodecanethiol, d) and e) octadecanethiol. Sweep rate = 15 mV/s in 0.1 M KCl/0.001 M Pb^{2+}. 
the film that would expose bare Ag, as seen by the negligible amount of UPD for dodecanethiol and octadecanethiol films. However, the surface roughness features are expected to increase the number of grain boundaries in the film, thus increasing the number of sites at which ions can approach close to the electrode surface and decreasing the overpotential for bulk Pb deposition.

This model was further tested by Pb deposition at Ag single-crystal surfaces immersed in dodecanethiol solutions for 9 hours. The CVs for Ag (100) are shown in Figure 8.12. As shown in Figure 8.12a, no UPD is detected at this surface, in contrast to the small, but detectable, amount observed at films formed for 24 hours at polycrystalline and rough Ag. Note that current scale in Figure 8.12a is a factor of ca. 10 greater in sensitivity than that shown in Figures 8.11 and 8.9.

In addition, a larger negative shift in the bulk Pb deposition peak potential is observed, as shown in Figure 8.12b. The peak potential is ca. 60 mV more negative than bulk deposition at bare polycrystalline Ag and ca. 45 mV more negative than observed for dodecanethiol at polycrystalline Ag. This behavior is consistent with the expectation that films formed at these atomically smooth substrates have fewer domain boundary defects and are more resistant to electrolyte penetration. However, bulk Pb deposition is a destructive probe. The second potential sweep into the bulk deposition region also reveals a more positive bulk deposition wave at the same potentials as observed for alkanethiol monolayers at polycrystalline surfaces.

Conclusions

In summary, reductive desorption waves are observed for butanethiol films at Ag and Au. These waves appear to correspond to less than monolayer desorption. The waves are affected to a small extent by electrolyte composition.
Figure 8.12. Cyclic voltammograms for dodecanethiol films formed at Ag (100) for ca. 24 hours. a) first scan, b) second scan, c) third scan. Sweep rate = 15 mV/s in 0.1 M KCl/0.001 M Pb\textsuperscript{2+}. 
On the other hand, the oxidation desorption of butanethiol at Au is shifted significantly more positive in 0.5 M KOH compared to 0.1 M KCl.

Pb deposition studies suggest that there is significant Pb$^{2+}$ ion penetration of short-chain alkanethiol films. For long-chain films formed for ca. 24 hours, little bare Ag is exposed to solution. However, there is significant ion penetration into long-chain films at smooth polycrystalline Ag, and, to a greater extent, at rough Ag surfaces. On the other, ion penetration is significantly inhibited at Ag single-crystal surfaces. A model is presented proposing that openings in the film are present at film domain boundaries, allowing ion penetration into the film but not to the surface.
Chapter 9

SURFACE RAMAN SPECTROSCOPY OF n-ALKANETHIOLS AT Ag AND Au IN THE ELECTROCHEMICAL ENVIRONMENT

Introduction

The Raman spectral data presented in Chapters 5 and 6 suggest that the metal-S bond strongly influences orientation of alkanethiols at Ag and Au. The C-S bond and alkane chain are observed to be more perpendicular at Ag substrates than at Au substrates. The orientation of the C-S bond implies greater π interaction of the S lone pairs with the Ag surface than with the Au surface. Smaller S nearest-neighbor distances are observed for methyl thiolate at Ag (111)\(^{1,22}\) compared to alkanethiols at Au (111).\(^{1,48,1,57,1,66,1,58,1,67,1,110}\) The closer spacing of the S head group, and therefore, the alkane chains, is proposed to be a possible explanation for the smaller chain tilt for alkanethiols at Ag than at Au.

Investigations into the factors dictating the orientation, therefore, need to consider the influence of the metal-S bond on orientation. Electrochemistry is a powerful tool for systematic alteration of surface charge, and potentially, the metal-S interaction. This hypothesis is tantamount to control of the orientation by the surface electronegativity, and hence, surface charge. Thus, if the surface charge of a metal could be systematically varied, control of orientation of these self-assembled monolayers might be realized.
No in situ spectroscopic investigation has been undertaken to determine the orientation of these films in the electrochemical environment. As detailed in Chapters 3 through 6, Raman spectroscopy is capable of providing detailed orientation information. Vibrational information can be obtained on the C-S, C-C, and C-H bonds. From this information, orientation can be deduced for the molecule and also for the various bonds in the molecule. Additionally, metal-S interactions can be probed with the various vibrations that involve the S atom. This information is accessible with Raman scattering because the weak Raman signal from water is not a spectral interference, as in the case of IR spectroscopy.

This chapter demonstrates that the orientation of alkanethiols at Ag and Au can be controlled and, in fact, interconverted, through systematic variation of electrode surface charge by changing the applied electrode potential. The Raman spectroscopic verification of the interconversion of the two orientations at both smooth and rough Ag and rough Au electrodes is detailed here. In addition, the effects of surface roughness on the interconversion of orientations are described.

In addition, the studies of Pb\(^{2+}\) penetration in alkanethiol films at Ag have been continued with Raman spectroscopy. The electrochemical studies strongly suggest that Pb ions penetrate the alkanethiol films at polycrystalline, smooth Ag. The surface Raman spectra for films subjected to monolayer and bulk Pb deposition are presented. In addition, CN\(^{-}\) has been used as a spectroscopic probe for ion penetration to the Ag surface. The spectral behavior for this ion at dodecanethiol films at Ag is presented.

**Potential Dependence of the Raman Scattering of Alkanethiols at Smooth Ag**

The potential dependence of the surface Raman scattering of butanethiol at smooth Ag electrodes was obtained in 0.1 M KCl in the potential region negative
of 0.0 V to prevent oxidation of the Ag surface. Spectra obtained at potentials between 0.0 V and -0.40 V were essentially identical to those obtained at -0.40 V. Thus, only spectra at -0.40 V are shown in the Figures.

In the $\nu$(C-S) region, two bands are observed. In bulk liquid butanethiol, the $\nu$(C-S)$_G$ is observed at 653 cm$^{-1}$ and the $\nu$(C-S)$_T$ at 730 cm$^{-1}$. Assignments for Raman bands in neat alkanethiol spectra are discussed in Chapter 3. Figures 9.1a,b and c show the $\nu$(C-S) region for butanethiol at Ag in 0.1 M KCl at potentials of -0.40, -1.00 and -1.40 V, respectively. At -0.40 V, the $\nu$(C-S)$_G$ vibration is observed at ca. 630 cm$^{-1}$ and the $\nu$(C-S)$_T$ band occurs at 701 cm$^{-1}$. These frequencies are considerably lower than those observed for bulk butanethiol suggesting substantial withdrawal of electron density from the C-S bond due to the formation of the Ag-S bond.

The frequencies of these bands at -0.40 V are the same as observed for butanethiol at Ag in air, shown in Figure 9.1d. However, as the potential is made negative of -0.40 V, the frequencies of the bands increase. At -1.40, the frequency of the $\nu$(C-S)$_T$ band has shifted to 704 cm$^{-1}$. This value is similar to the frequency of 706 cm$^{-1}$ observed for butanethiol at Au in air, shown in Figure 9.1e. Thus, the bonding behavior of butanethiol at Ag at these negative potentials mimics the bonding behavior at Au based on the frequency of the $\nu$(C-S)$_T$ band.

In the $\nu$(C-C) region, small changes in relative intensity of the bands for butanethiol at smooth Ag in 0.1 M KCl are noted as a function of potential. Figures 9.2a,b and c show the data for this system at -0.40, -1.00 and -1.40 V, respectively. The $\nu$(C-C)$_T$ at 1096 cm$^{-1}$ decreases slightly in intensity relative to the $\nu$(C-C)$_G$ at 1065 cm$^{-1}$ and the $\nu_a$(C-C)$_T$ at 1055 cm$^{-1}$, as the potential is made negative of -0.60 V. The spectrum at -0.40 V is similar to the spectrum of butanethiol at Ag in air, shown in Figure 9.2d. However, the spectrum obtained
Figure 9.1. Raman spectra in the $\nu$(C-S) region of butanethiol at a) smooth Ag, -0.4 V, b) smooth Ag, -1.0 V, c) smooth Ag, -1.4 V, d) smooth Ag, in air, e) smooth Au, in air. Excitation wavelength: a-d) 600 nm, e) 720 nm. Incident power: a-c) 200 mW, d) 100 mW, e) 40 mW. Integration times: a-c) 1 min, d and e) 5 min.
Figure 9.2. Raman spectra in the $\nu$(C-C) region of butanethiol at a) smooth Ag, -0.4 V, b) smooth Ag, -1.0 V, c) smooth Ag, -1.4 V, d) smooth Ag, in air, e) smooth Au, in air. Excitation wavelength: a-d) 600 nm, e) 720 nm. Incident power: a-c) 200 mW, d) 100 mW, e) 40 mW. Integration times: a-c) 2 min, d) 5 min, e) 10 min.
at -1.40 V resembles that for butanethiol at Au in air, shown in Figure 9.2c.

In the ν(C-H) region, changes in relative intensity of the ν_{asym}(CH₃) and ν_{sym}(CH₃) bands of adsorbed butanethiol are observed as a function of potential. The spectra for butanethiol at smooth Ag at -0.40, -1.00, and -1.4 V are shown in Figures 9.3a,b and c, respectively. Interestingly, the overall intensity of the ν(C-H) region increases in going from -0.40 V to -0.70 V, and then decreases at potentials negative of -1.00 V.

The ratio of the intensities of the ν_{asym}(CH₃) to ν_{sym}(CH₃) bands has been shown in Chapters 4, 6, and 7 to be a sensitive indicator of orientation of these alkanethiols. The value of this ratio for butanethiol is smaller at -1.40 V than at -0.40 V suggesting different orientations at these two potentials. This conclusion is consistent with the observations that the spectrum at -0.40 V resembles butanethiol at Ag in air, shown in Figure 9.3d, while the spectrum at -1.40 V resembles butanethiol at Au in air, shown in Figure 9.3e. These data suggest that the orientation of butanethiol on Ag becomes more Au-like at these negative potentials.

Based on the previously documented odd-even effect of the methyl end group orientation as a function of chain length, the opposite behavior of this intensity ratio is predicted and observed for pentanethiol at Ag electrodes. Thus, the value of the ν_{asym}(CH₃)/ν_{sym}(CH₃) intensity ratio of pentanethiol at Ag electrodes at -1.20 V, shown in the spectrum in Figure 9.4b, is greater than that observed at -0.20 V, shown in the spectrum in Figure 9.4a. This behavior is opposite to that noted above for butanethiol. Spectra for butanethiol at smooth Ag and smooth Au in air are shown in Figure 9.4c and d, respectively. As for butanethiol, the spectrum for pentanethiol at Ag at -0.20 V is essentially identical to that for pentanethiol on Ag in air, while the spectrum at -1.20 V is essentially identical
Figure 9.3. Raman spectra in the \( \nu(\text{C-H}) \) region (600 nm excitation) of butanethiol at a) smooth Ag, -0.4 V, b) smooth Ag, -1.0 V, c) smooth Ag, -1.4 V, d) smooth Ag, in air, e) smooth Au, in air. Incident power: a-c) 200 mW, d and e) 100 mW. Integration times: a-c) 1 min, d) 10 min, e) 20 min.
Figure 9.4. Raman spectra in the $\nu$(C-H) region (600 nm excitation) of pentanethiol at a) smooth Ag, -0.2 V, b) smooth Ag, -1.2 V, c) smooth Ag, in air, d) smooth Au, in air. Incident power: a and b) 200 mW, c and d) 100 mW. Integration times: a and b) 2 min, c) 10 min, d) 20
Similar changes in the surface Raman spectra are observed for other systems including alkanethiols of different chain lengths. Thus, the increase in frequency of the $\nu(C-S)_T$ at negative potentials is observed for butanethiol at Ag in 0.1 M NaClO$_4$ and dodecanethiol at Ag in 0.1 M KCl. On the other hand, this band for octadecanethiol shows only a small increase in frequency at negative potentials. The spectroscopic behavior described above is, for the most part, reversible upon alternating between positive and negative potentials.

The intensities of the $\nu(C-S)_T$ and $\nu(C-C)_T$ bands, and the total integrated intensity of the $\nu(C-H)$ region change with potential. The ratios of their peak areas at -1.00 V relative to -0.40 V are listed in Table 9.1. The potential of -1.00 V was chosen, because it is positive of the reductive process observed for butanethiol in the cyclic voltammetry. Therefore, changes in intensity of the bands are less likely to be due to desorption of the film. For both butanethiol and octadecanethiol, the $\nu(C-S)_T$ and $\nu(C-C)_T$ ratios is less than one while the $\nu(C-H)$ ratios are greater than one. These ratios, along with the changes in frequency and relative intensities described above, are discussed below in terms of reorientation of alkanethiols at the surface of the Ag.

**Potential Dependence of the Raman Scattering of Alkanethiols at Rough Ag**

Ag electrodes subjected to an ex-situ ORC as described above were modified with alkanethiols and placed in the electrochemical environment. Spectra for the $\nu(C-S)$ region of butanethiol at rough Ag are shown in Figure 9.5. Butanethiol at rough Ag at potentials of -0.40 V and -1.40 V are shown in Figures 9.5a and b. The frequencies for the $\nu(C-S)_T$ band show the same trend with potential as was observed at smooth Ag. The spectrum at -0.40 V resembles the spectrum from
Table 9.1. Peak Area Ratios for $\nu$(C-S), $\nu$(C-C), and $\nu$(C-H) Bands at Ag and Au with Change in Potential.

<table>
<thead>
<tr>
<th></th>
<th>Area at -1.00 V</th>
<th>Area at -0.40 V</th>
<th>Area at +0.70 V</th>
<th>Area at -0.20 V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\nu$(C-S)$_T$</td>
<td>$\nu$(C-C)$_T$</td>
<td>$\nu$(C-H)</td>
<td></td>
</tr>
<tr>
<td>Butanethiol at smooth Ag</td>
<td>0.8</td>
<td>0.6</td>
<td>1.7</td>
<td></td>
</tr>
<tr>
<td>Octadecanethiol at smooth Ag</td>
<td>0.5</td>
<td>0.8</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>Butanethiol at rough Au</td>
<td></td>
<td></td>
<td>1.7</td>
<td>1.1</td>
</tr>
<tr>
<td>Octadecanethiol at rough Au</td>
<td>1.0</td>
<td>1.0</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>
Figure 9.5. Raman spectra in the $\nu$(C-S) region of butanethiol at a) rough Ag, -0.4 V, b) rough Ag, -1.4 V, c) rough Ag, in air, d) rough Au, in air. Excitation wavelength: a-c) 600 nm, d) 720 nm. Incident power: a and b) 200 mW, c) 100 mW, d) 40 mW. Integration times: a and b) 10 s, c) 2 min, d) 1 min.
rough Ag in air, Figure 9.5c, while the spectrum at -1.40 V resembles the spectrum from rough Au in air, Figure 9.5d. The frequency observed for butanethiol at rough Ag in air is 2 cm\(^{-1}\) less than observed at smooth Ag in air. The frequency observed at rough Au is 2 cm\(^{-1}\) higher than observed for smooth Au.

Changes in relative intensity are also noted in the \(\nu(C-C)\) region as a function of potential. Butanethiol at rough Ag at -0.40 V and -1.40 V are shown in Figures 9.6a and b, respectively, and butanethiol at rough Ag and Au in air are shown in Figures 9.6c and d, respectively. At -0.40 V, the \(\nu_a(C-C)\) band at 1050 cm\(^{-1}\) is weaker than the \(\nu(C-C)_G\) band at 1070 cm\(^{-1}\), similar to the behavior observed at Ag in air. At -1.40 V, the \(\nu_a(C-C)\) band at 1050 cm\(^{-1}\) becomes greater in intensity than the \(\nu(C-C)_G\) band at 1065 cm\(^{-1}\). Thus, the spectrum at rough Ag at -1.40 V is similar to the spectrum at rough Au in air.

Potential dependence of the Raman scattering behavior in the \(\nu(C-H)\) region for butanethiol at rough Ag is considerably different than observed at smooth Ag. Butanethiol at rough Ag at -0.40 V and -1.40 V are shown in Figures 9.7a and b, respectively. The spectrum at -0.40 V is similar to that obtained at Ag in air, Figure 9.7c, but the spectrum at -1.40 V does not resemble butanethiol at rough Au in air, Figure 9.7d, as did the spectrum at smooth Ag. Instead, the band at 2836 cm\(^{-1}\) in the spectrum at -0.40 V increases in intensity and shifts lower in frequency to 2830 cm\(^{-1}\) in the spectrum at -1.40 V. The 2836 cm\(^{-1}\) band appears to correspond to the \(\nu_{sym}(CH_2)\) band observed at 2842 cm\(^{-1}\) in the bulk liquid. This band has been assigned to the \(\nu_{sym}(CH_2)\) for all of the methylene groups except the one immediately adjacent to the terminal methyl group which is assigned to the band at 2857 cm\(^{-1}\)\(^{1.73}\).

This behavior was further investigated for a longer-chain alkanethiol. Spectra in the \(\nu(C-H)\) region for dodecanethiol adsorbed at rough and smooth Ag
Figure 9.6. Raman spectra in the $\nu$(C-C) region of butanethiol at a) rough Ag, -0.4 V, b) rough Ag, -1.4 V, c) rough Ag, in air, d) rough Au, in air. Excitation wavelength: a-c) 600 nm, d) 720 nm. Incident power: a and b) 200 mW, c) 100 mW, d) 40 mW. Integration times: a and b) 10 s, c) 2 min, d) 1 min.
Figure 9.7. Raman spectra in the \( \nu(\text{C-H}) \) region (600 nm excitation) of butanethiol at a) rough Ag, -0.4 V, b) rough Ag, -1.4 V, c) rough Ag, in air, d) rough Au, in air. Incident power: a and b) 200 mW, c) 100 mW, d) 200 mW. Integration times: a and b) 10 s, c and d) 1 min.
are shown in Figure 9.8. No band at 2830 cm\(^{-1}\) is observed in the spectrum for dodecanethiol at smooth Ag at -0.20 V and -1.40 V, shown in Figures 9.8a and b, respectively. However, the band at 2830 cm\(^{-1}\) is observed in the spectrum for dodecanethiol at rough Ag at -1.40 V, shown in Figure 9.8d, but not at -0.20 V, shown in Figure 9.8c.

For bulk liquid dodecanethiol, the frequencies of the \(\nu(CH_2)\) bands are slightly higher in frequency than those observed for bulk butanethiol.\(^1\)\(^,\)\(^7\) The \(\nu_{\text{sym}}(CH_2)\) band for the methylene adjacent to the methylene group is at 2861 cm\(^{-1}\), and the 2852 cm\(^{-1}\) band is assigned to the \(\nu_{\text{sym}}(CH_2)\) of the remaining methylene groups. In the spectrum for dodecanethiol at -1.40 V, the 2830 cm\(^{-1}\) band is present in addition to the two \(\nu_{\text{sym}}(CH_2)\) bands just noted, which appear similar in intensity to those in the spectrum at -0.20 V. These observations suggest that if the 2830 cm\(^{-1}\) surface band is related to the 2850 cm\(^{-1}\) bulk liquid band, few of the methylene groups are involved.

One possible explanation for this behavior is that it is due to small-scale roughness features formed during the ORC procedure. These features have been proposed to be associated with charge-transfer enhancement of the Raman scattering.\(^9\)\(^,\)\(^1\) They are proposed to be small clusters of Ag atoms\(^1\)\(^,\)\(^9\) which become labile on the surface at negative potentials and are incorporated irreversibly into the metal lattice.\(^1\)\(^,\)\(^8\)\(^,\)\(^4\)\(^,\)\(^9\)\(^,\)\(^1\)

To investigate possible adatom participation in the spectra acquired at rough surfaces, Ag electrodes were first roughened with an ORC and then subjected to a negative potential excursion before immersion into butanethiol/ethanol solutions. After a linear potential sweep ORC in 0.1 M KCl, Ag electrodes were held at -1.20 V or -2.00 V for 10 minutes, and then returned to -0.20 V. After the negative potential application, the electrodes were modified with butanethiol and
Figure 9.8. Raman spectra in the $\nu$(C-H) (514.5 nm) region of dodecanethiol at a) smooth Ag, -0.2 V, b) smooth Ag, -1.4 V, c) rough Ag, -0.2 V, d) rough Ag, -1.4 V. Incident power: 100 mW. Integration times: 1 min.
spectra in the \( \nu(C-H) \) region were obtained. Similar potential behavior was obtained for these electrodes as obtained for rough Ag electrodes discussed above. Thus, the unique behavior observed at the rough Ag electrodes does not appear to be associated with atomic scale roughness features important in the chemical enhancement mechanism of SERS. This behavior must therefore be due to the disruption of the film structure resulting from the gross surface roughness produced by the ORC.

Interestingly, a similar band at 2830 cm\(^{-1} \) was observed in SERS studies of short-chain normal alcohols at rough Ag at negative potentials.\(^9\) This band was assigned to agostic interactions between the H atoms of the methylene unit adjacent to the O atom and the surface. If this previous assignment is correct, a similar scenario can be envisioned for alkanethiols at domain edges on rough Ag at negative potentials. A greater number of domains would be predicted on the rough surface due to the smaller domain size. Thus, the extent to which this agostic bonding is possible would be increased. The propensity for reorientation which would allow agostic bonding at negative potentials would be expected to be greater for the shorter-chain alkanethiols.

**Potential Dependence of the Raman Scattering of Alkanethiols at Rough Au**

Au has a much wider accessible potential window than Ag. Thus, spectra for alkanethiols at rough Au could be obtained in the potential region between +0.9 V and -1.5 V. The spectra obtained in the \( \nu(C-S) \), \( \nu(C-C) \) and \( \nu(C-H) \) regions for butanethiol at rough Au in 0.1 M KCl at -1.40 V are essentially identical to those obtained at -0.20 V, except that the overall intensity of all the bands decreased, corresponding to reductive desorption at -1.1 V, as discussed above. No significant changes in relative intensities of the bands were observed. The only
other noticeable change is a slight shift in the frequency of the $\nu(C-S)_T$ band from 708 cm$^{-1}$ at -0.20 V to 706 cm$^{-1}$ at -1.40 V. This behavior is in marked contrast to the behavior noted at Ag. Thus, negative surface charge appears incapable of altering the orientation of butanethiol at rough Au.

In contrast, at potentials positive of -0.20 V at rough Au, interesting behavior is observed in the $\nu(C-S)$, $\nu(C-C)$, and $\nu(C-H)$ regions for butanethiol in 0.1 M KCl. The frequency of the $\nu(C-S)_T$ band is 708 cm$^{-1}$ at -0.20 V as shown in the spectrum in Figure 9.9a. As the potential is made positive of +0.20 V, a shift of this band to lower frequency is observed. At +0.70 V, the frequency is 694 cm$^{-1}$ as shown in Figure 9.9b. The frequency of the $\nu(C-S)_T$ observed at -0.20 V is the same as is observed for butanethiol at rough Au in air, Figure 9.5d. On the other hand, the frequency observed for butanethiol at +0.7 V is similar to that observed at rough Ag in air, shown in Figure 9.5c.

At +0.80 V, the frequency is 5 cm$^{-1}$ lower and the $\nu(C-S)_G$ intensity is greater as shown in Figure 9.9c. At +0.90 V, both $\nu(C-S)$ bands are very broad and another band at 662 cm$^{-1}$ is observed as shown in Figure 9.9d. The band at 662 cm$^{-1}$ is assigned to the $\nu(C-S)_T$ band of surface dibutyl disulfide species. The $\nu(C-S)_T$ and $\nu(C-S)_G$ bands are observed at 704 and 636 cm$^{-1}$, respectively, for bulk dibutyl disulfide.$^{0.3}$ A decrease of 42 cm$^{-1}$ in the $\nu(C-S)_T$ of the disulfide species at the surface is comparable to the decrease of 29 cm$^{-1}$ of the $\nu(C-S)_T$ band for butanethiol upon adsorption. More evidence for disulfide formation is presented below.

A similar trend is noted in the $\nu(C-C)$ region. The spectrum for butanethiol at rough Au at -0.20 V shown in Figure 9.10a is identical to the spectrum for butanethiol at rough Au in air, shown in Figure 9.6c. Upon changing the potential to +0.70 V, the spectrum for butanethiol at rough Au, Figure 9.10b,
Figure 9.9. Raman spectra in the $\nu$(C-S) region (720 nm excitation) of butanethiol at rough Au at a) -0.2 V, b) +0.7 V, c) +0.8 V, d) +0.9 V. Incident power: 40 mW. Integration times: 1 min.
Figure 9.10. Raman spectra in the $\nu$(C-C) region (720 nm excitation) of butanethiol at rough Au at a) -0.2 V, b) +0.7 V, c) +0.8 V, d) +0.9 V. Incident power: 40 mW. Integration times: 1 min.
appears similar, although not identical to, that observed for rough Ag in air, Figure 9.6d. The difference between these spectra is the presence of a strong $\nu(C-C)$ band at 1070 cm$^{-1}$ in the spectrum at rough Au at +0.70 V that is not in the spectrum at rough Ag. The presence of this band may be related to formation of the disulfide species. The spectra at +0.80 and +0.90 V, Figures 9.10c and d, respectively, show a slight decrease in overall $\nu(C-C)_T$ intensity compared to the spectrum at +0.70 V. All of these changes begin to appear in the spectra at +0.20 V and become more pronounced as the potential is made more positive.

In the $\nu(C-H)$ region, changes in the relative intensities of the $\nu_{ asym}(CH_3)$ and $\nu_{ sym}(CH_3)$ bands are observed. The spectrum at -0.20 V, shown in Figure 9.11a, is the same as seen from rough Au in air, Figure 9.7d. At potentials positive of +0.50 V, the relative intensity ratio of methyl bands changes. Although the overall intensity of the methyl bands decreases relative to the other $\nu(C-H)$ bands, the $\nu_{ sym}(CH_3)$ band intensity decreases to a greater extent than the $\nu_{ asym}(CH_3)$ at +0.70 V. Thus, the spectrum at +0.70 V resembles that for butanethiol at rough Ag in air, shown in Figure 9.7c. At +0.80 V, Figure 9.11c, the trend continues, and at +0.90 V, Figure 9.11d, the methyl intensities are barely visible above methylene intensities.

For pentanethiol at rough Au, the opposite behavior is observed for the methyl intensities. The relative intensity of the $\nu_{ asym}(CH_3)$ to the $\nu_{ sym}(CH_3)$ band is greater at -0.20 V, Figure 9.12a, compared to that at +0.70 V, Figure 9.12b. The spectrum at +0.70 V resembles that of pentanethiol at rough Ag, shown in Figure 9.12d, while the spectrum at -0.20 V resembles that at rough Au in air, Figure 9.12c.

The $\nu(C-S)_T$ and 1090 cm$^{-1}$ $\nu(C-C)_T$ bands increase in intensity relative to the $\nu(C-H)$ region for butanethiol at Au as the potential becomes more positive.
Figure 9.11. Raman spectra in the $\nu$(C-H) region (720 nm excitation) of butanethiol at rough Au at a) -0.2 V, b) +0.7 V, c) +0.8 V, d) +0.9 V. Incident power: 40 mW. Integration times: 1 min.
Raman spectra in the $\nu$(C-H) region (720 nm excitation) of pentanethiol at a) rough Au, -0.2 V, b) rough Au, +0.7 V, c) rough Au, in air, d) rough Ag, in air. Incident power: 40 mW. Integration times: 5 min.
suggesting a more vertical orientation of the molecule. The ratio of the peak areas of the bands at +0.70 V to those at -0.20 V are shown in Table 9.1. In contrast to the behavior of butanethiol, the spectra for octadecanethiol show no changes in intensity except for a decrease in all of the $\nu$(C-H) bands as the potential is made positive. The ratios reported for octadecanethiol have more uncertainty than the analogous ratios obtained at smooth Ag, because the S/N is poorer in the spectra for octadecanethiol at rough Au. However, for octadecanethiol at rough Au, the $\nu$(C-S)$_T$ frequency is 5 cm$^{-1}$ lower at +0.80 V compared to that at -0.20 V suggesting that similar reorientation is occurring for the longer chain alkanethiols as well.

At the positive potentials accessible on Au electrodes, oxidation of the butanethiolate to the corresponding to disulfide is observed. The $\nu$(S-S) band for neat dibutyl disulfide is observed at 511 cm$^{-1}$.\textsuperscript{11,82,93} For butanethiol at rough Au beginning at +0.60 V, this disulfide band at 511 cm$^{-1}$ can be observed as shown in Figure 9.13b. The intensity of this band increases and the frequency decreases as the potential becomes more positive. The frequency of the band reaches 499 cm$^{-1}$ at +0.90 V as shown in Figure 9.13e. The disulfide band appears at the same potential as the change in the methyl group intensity noted above, but at ca. 0.3 V more positive than the changes observed in the $\nu$(C-S) and $\nu$(C-C) regions. The disulfide band was observed for octanethiol at ca. +0.70 V and more positive potentials, but with less intensity than observed for butanethiol. No disulfide band is observed for octadecanethiol suggesting that oxidation of the longer chain alkanethiols is increasingly difficult as the chain lengthens.

No disulfide band is observed at Ag in these experiments due to the limited potential window accessible on this electrode. Only one case of the observation of the $\nu$(S-S) band at Ag has been reported. Cystine was reported to oxidize at
Figure 9.13. Raman spectra in the $\nu$(S-S) region (720 nm excitation) of butanethiol at rough Au at a) -0.2 V, b) +0.6 V, c) +0.7 V, d) +0.8 V, d) +0.9 V. Incident power: 40 mW. Integration times: 5 min.
potentials positive of -0.05 V at rough Ag generating an observable \( \nu(S-S) \) band.\(^{0.4}\)

Oxidation of alkanethiolate species to the corresponding disulfide is thermodynamically possible at potentials of ca. -1.5 V,\(^{1.53}\) but these dialkyl disulfides are unstable and cleavage of the S-S bond upon adsorption to Ag and Au surfaces has been reported.\(^{1.42,9.5}\)

**Potential Dependent Orientation at Smooth Ag and Rough Au**

The orientation of alkanethiols at Au substrates in air has been studied by several researchers using several methods. With the exception of work by Samant and coworkers,\(^{1.58}\) the tilt angle of these species on Au surfaces is generally accepted to be ca. 25 to 30°.\(^{1.34,1.48,1.49,1.56,1.57}\)

Studies at Ag substrates in air reveal a different orientation. In general, results from these studies suggest a tilt angle of ca. 12° with respect to the surface normal.\(^{1.8,1.49,1.50}\) These orientations are represented by the illustrations in Figures 9.14a and d for butanethiol at Ag and Au, respectively. The tilt of 30° of the alkane chain on Au is approximately an average of angles reported. The rotation about the chain axis is shown to be ca. 45°. In this orientation, the C-S bond is more than 45° from the surface normal and the symmetric methyl dipole is almost perpendicular to the surface. For pentanethiol at Au, which has one more methylene group, this orientation places the methyl dipole more parallel to the surface due to the tetrahedral nature of carbon bonding.

The orientation proposed for Ag shows the tilt of the alkane chain at 15° in the opposite direction from that at Au. This results in the C-S bond being more perpendicular to the surface than for Au. In addition, this orientation places the butanethiol methyl dipole more parallel to the surface than that on Au.

The surface Raman spectra presented in this paper strongly suggest that the
Models of orientation of 1-alkanethiols at Ag and Au surfaces. 
a) and c) chain tilt ($\alpha$) of ca. $-15^\circ$, and rotation ($\beta$) of ca. $45^\circ$
about chain axis; c) and d) $\alpha$ of ca. $+30^\circ$ and $\beta$ of ca. $45^\circ$.
Adsorption of alkanethiols at Ag in 0.1 M KCl at a) -0.2 V, b) -1.0 V. Adsorption of alkanethiols at Au in 0.1 M KCl at c) +0.7 V, and d) -0.2 V.
orientation of alkanethiols at both Ag and Au can be changed with applied potential in an electrochemical environment. These changes lend important insight into the driving forces behind the existence of different orientations on these two metals in ambient gas environments.

As shown in orientational models in Figure 9.14, the butanethiol methyl dipole has different angles of tilt at Ag and Au. These differences in tilt angles can be deduced from the spectra for butanethiol at Ag and Au in air, shown in Figures 9.3d and e, respectively, using surface selection rules, which have been discussed in detail in Chapter 4. The $\nu_{\text{asym}}(\text{CH}_3)$ intensity is greater relative to the $\nu_{\text{sym}}(\text{CH}_3)$ intensity for butanethiol at Ag than at Au, indicating a more parallel orientation of the methyl dipole for this molecule at Ag.

Under potential control, the intensity ratio of the $\nu_{\text{asym}}(\text{CH}_3)$ to $\nu_{\text{sym}}(\text{CH}_3)$ bands is greater for butanethiol at Ag at -1.00 V than at -0.40 V suggesting that the methyl dipole has reoriented to be more perpendicular to the surface. This orientation resembles the orientation observed for this molecule at Au in air. A similar reorientation is also observed for pentanethiol at Ag.

The polarizability components of the $\nu(\text{C-S})$ vibrations are assumed to be primarily along the C-S bond. For butanethiol and pentanethiol, the ratio of the intensity of the $\nu(\text{C-S})$ bands to the $\nu(\text{C-H})$ bands is greater at Ag surfaces than Au suggesting that the C-S bonds are more perpendicular to the Ag surface than Au. The different orientations of the C-S bonds are shown in the models proposed in Figure 9.14.

Changes in the $\nu(\text{C-S})$ region also support reorientation with a change in electrode potential. For butanethiol at Ag, the intensity ratio of the $\nu(\text{C-S})$ bands to the $\nu(\text{C-H})$ bands is greater than at Au suggesting that the C-S bonds are more perpendicular to the Ag surface than to the Au surface. As the potential of the
Ag surface is made negative, however, the $\nu(C-S)_T$ band decreases in intensity relative to the $\nu(C-H)$ bands suggesting that the C-S bond becomes more parallel to the surface as the potential becomes more negative.

Concurrent with this decrease in intensity is the increase in frequency of the $\nu(C-S)_T$ band at more negative potentials, becoming similar to that observed for butanethiol at smooth Au in air. These two observations strongly support reorientation of butanethiol at smooth Ag at negative potentials to resemble the orientation observed at Au.

Further observations in the $\nu(C-C)$ and $\nu(C-H)$ region support this claim. In the $\nu(C-C)$ region, the polarizability of the $\nu_a(C-C)_T$ band at ca. 1060 cm$^{-1}$ is found to be along the symmetric methyl transition dipole, as discussed in Chapters 5 and 6. The $\nu(C-C)_T$ band at 1090 cm$^{-1}$ for butanethiol is assumed to have similar polarizability as the $\nu_e(C-C)_T$. Harrand reported the polarizability of the $\nu_e(C-C)_T$ band to be along the carbon backbone. The intensity ratio of the 1090 cm$^{-1}$ $\nu(C-C)_T$ band for butanethiol at Ag at -1.00 V to that at -0.40 V is 0.6, consistent with reorientation to a more parallel configuration at negative potentials.

Although not shown, the spectra for dodecanethiol and octadecanethiol show similar changes in these regions with potential. Due to the greater complexity of these molecules, the spectral changes are somewhat more subtle, however. These changes suggest that long chain alkanethiols also reorient at Ag at negative potentials to become similar to the orientation at Au. Similar analysis of the spectral data obtained for alkanethiols at rough Au suggests that at potentials positive of +0.60 V, the alkanethiols reorient to the orientation observed at Ag.

The differences in orientation are proposed to be due to the changes in metal-S bonding as the metal surface charge varies with electrode potential. In
fact, in the electrochemical environment, the orientation of the alkanethiols is correlated with the potential of zero charge (PZC) of the substrate. The PZC for Au$^{9.6}$ and Ag$^{9.7}$ in non-adsorbing electrolyte solutions are ca. 0.0 V and -0.9 V versus the Ag/AgCl reference electrode, respectively. The orientation of the alkanethiol films at potentials positive of the PZC at both metals is the same as observed at Ag in air. The surface has a positive excess charge allowing more interaction between the S lone pair electrons and the surface. This bonding is reflected in a perpendicular C-S bond at the surface, shown in Figures 9.14a and c. At potentials negative of the PZC, the S lone pairs are further away from the surface, resulting in the C-S bond being more parallel to the surface, shown in Figures 9.14b and d. The reorientation of alkanethiols at Ag occurs at potentials positive of the reduction wave at -1.4 V. The onset of the reduction wave is just negative of -1.0 V, while reorientation has largely taken place by -1.0 V. On the other hand, the reduction wave at Au is observed ca. 0.3 V more positive than seen at Ag. These observations suggest that bonding of the film in an orientation that is similar to Au in air is a necessary precursor state for reductive desorption from the surface.

The spectral data obtained at rough Au suggest that, at potentials positive of the PZC, the alkanethiols change to an orientation resembling that proposed for Ag in air. At very positive potentials, the S atoms are oxidized to disulfide groups. The onset of disulfide formation occurs at the same potential as the changes in the $\nu$(C-H) region are observed and at potentials ca. 0.3 V positive of observable changes in the $\nu$(C-S) and $\nu$(C-C) region. The $\nu$(C-S)$_T$ associated with disulfide is seen at 662 cm$^{-1}$. The $\nu$(C-C)$_G$ increases in intensity at more positive potentials which suggests that disulfide formation results in a disruption of the film order.
The frequency of the disulfide band also suggests that the orientation of the alkanethiols at Au changes to the orientation proposed for Ag positive of the PZC. The frequency of the $\nu$(S-S) is 511 cm$^{-1}$ at +0.60 V, which corresponds to that observed for bulk aliphatic disulfides. As the potential becomes more positive, the $\nu$(S-S) intensity increases while the frequency decreases to 499 cm$^{-1}$ at +0.90 V. This change in frequency corresponds to a change in the CS-SC dihedral angle. For a frequency of 511 cm$^{-1}$, the dihedral angle is ca. 60°, while for a frequency of 499 cm$^{-1}$, the dihedral angle is ca. 30°. The decrease in CS-SC dihedral angle is consistent with a more perpendicular C-S bond at Au at these positive potentials, similar to the orientation proposed for these molecules at Ag. Furthermore, the decrease of the $\nu$(S-S) frequency suggests that the metal-S lone pair interaction is sufficiently strong to position the CS-SC bond in a more strained conformation.

It is concluded that potential dependent orientation of alkanethiols at Ag and Au is the same when the electrode potential is related to the PZC of the metal. The different orientation observed for alkanethiols at Ag and Au in air, then, is a result of the open circuit potential established in the ambient environment. This ambient open circuit potential is negative of the PZC for Au and positive of the PZC for Ag. This potential is probably established by the electroactive species of O$_2$ and H$_2$O in the air. Comparing the spectra obtained for alkanethiols at Ag and Au in situ and ex situ, this ambient open circuit potential is estimated to be in the range between 0.0 and -0.4 V.

Therefore, it might be possible to predict the orientations of alkanethiols at other metals in the ambient environment. For both Cu and Pt, the PZCs are estimated to be ca. -0.1 V and ca. 0.0 V vs. Ag/AgCl reference, respectively, in non-adsorbing medium. However, these potentials fall in the range estimated
for the ambient open circuit potential. Thus, a prediction is somewhat difficult for these molecules. In addition, Laibinis and coworkers report that ordered films could not be formed at Cu substrates due to substantial oxidation of the surface.\textsuperscript{1.50} Using HREELS, Gui and coworkers that propanethiol has the same orientation at Pt (111) as Ag (111).\textsuperscript{1.39} However, the inherent lack of resolution of this vibrational spectroscopy makes the determination or orientation difficult.

**Potential Dependent Orientation at Rough Ag**

The spectral behavior in the $\nu$(C-S) and $\nu$(C-C) regions for butanethiol at rough Ag is similar to that observed at smooth Ag. However, in the $\nu$(C-H) region, the appearance of the intense band at 2830 cm$^{-1}$ in the spectra at rough Ag markedly changes the spectra compared to smooth Ag. This band may result from reorientation of the alkanethiol at the rough Ag surface at negative potentials. Sobocinski and Pemberton report a band at 2827 cm$^{-1}$ for propanol and 2830 cm$^{-1}$ for pentanol at rough Ag at negative potentials.\textsuperscript{9.2} These bands were proposed to be due to agostic bonding between the surface and the hydrogens of the methylene group next to the oxygen.

For alkanethiols at rough surfaces, reorientation at negative potentials might position the methylene hydrogens adjacent to the S head group closer to the surface. This is shown schematically in Figure 9.15. In this configuration at potentials negative of the PZC, the methylene hydrogens adjacent to the S atom would be closer to the surface than at potentials positive of the PZC. The 2830 cm$^{-1}$ band may be more intense at rough Ag, because the surface morphology may increase the likelihood of surface-methylene interaction. This postulate is further supported by the observation that the $\nu$(C-S)$_G$ intensity is greater for butanethiol at rough Ag, shown in Figure 9.5c, than at smooth Ag, shown in
Figure 9.15. Model of orientation of methylene agostic interaction with rough Ag surface. a) Positive of the PZC, b) negative of the PZC.
Figure 9.1c suggesting that surface roughness has induced disorder in the part of the molecule close to the surface. The greater intensity of the $\nu$(C-H) due to agostic interaction for alkanethiols relative to alcohols may be due to the strong metal-S bond that leads to densely-packed monolayers. The weaker metal-O bond may allow the alcohol molecules to shift their position with respect to surface roughness features to minimize methylene-metal interaction. The cross-section of this band appears to be large, resulting in a large distortion of spectra in the $\nu$(C-H) region for short-chain alkanethiols.

**Spectroscopic Investigation of Ion Penetration at Alkanethiol Films at Ag**

In addition to the potential-dependent orientation of these films, the penetration behavior of Pb$^{2+}$ and CN$^-$ ions has been studied. In these studies, alkanethiol films at smooth Ag are subjected to underpotential deposition (UPD) and bulk deposition of Pb. These films are then emersed and studied in air to investigate the effect of Pb deposition on the various regions of the surface Raman spectra. In the CN$^-$ penetration study, the presence of CN$^-$ is determined after emersing electrodes with and without alkanethiol films from NaCN electrolyte solutions.

Figure 9.16 shows the surface Raman spectra in the $\nu$(C-S) region obtained from alkanethiol films at smooth Ag subjected to Pb deposition. The films were formed for ca. 4 hours and then placed in an electrolyte solution of 0.1 M KCl and 0.001 M Pb$^{2+}$. Monolayer deposition was accomplished by sweeping the potential to ca. -0.48 V, disconnecting the applied potential and emersing the electrode. The final potential for bulk deposition was ca. -0.54 V. Significant UPD was observed for these films.

In Figures 9.16a,c, and e, the spectra for butanethiol, dodecanethiol, and
Figure 9.16. Raman spectra in the \( \nu(\text{C-S}) \) region (600 nm excitation) of alkanethiol films at smooth Ag subjected to Pb UPD: a) butanethiol, c) dodecanethiol, e) octadecanethiol; alkanethiol films at smooth Ag subjected to bulk Pb deposition: b) butanethiol, d) dodecanethiol, f) octadecanethiol. Incident power: 100 mW. Integration times: a and c-f) 1 min, b) 4 min.
octadecanethiol films, respectively, subjected to Pb UPD are shown. Surprisingly, these spectra are similar to the spectra for obtained at films with no Pb, shown in Figure 5.2. On the other hand, spectra obtained for films subjected to bulk Pb deposition show slightly different behavior. In Figure 9.16b, an increase in \( \nu(C-S)_G \) is observed for butanethiol films. No increase in G intensity is observed for dodecanethiol and octadecanethiol films, 9.16d and f, respectively. However, a shoulder appears on the \( \nu(C-S)_T \) band for all three films at ca. 680 cm\(^{-1}\).

The appearance of the 680 cm\(^{-1}\) band is possibly due to a perturbation of the metal-S bonding for a fraction of the alkanethiol film, resulting in a slight change in frequency of the \( \nu(C-S)_T \) band. The perturbation would presumably be due to the presence of Pb atoms near the S head groups, because the band is not observed in spectra for films subjected to Pb UPD only, in which Pb atoms are deposited directly at the bare Ag surface. Pb-S interaction, in addition to Ag-S bonding, might possibly account for the decrease in frequency of the \( \nu(C-S)_T \) band.

The surface Raman spectra in the \( \nu(C-C) \) region for these films are shown in Figure 9.17. In Figures 9.17a,c, and e, films of butanethiol, dodecanethiol, and octadecanethiol, respectively, have been subjected to Pb UPD, while the corresponding films subjected to bulk Pb deposition are shown in Figure 9.17b,d, and f. The spectra obtained after UPD deposition are similar to those observed for films with no Pb present, shown in Figure 5.3. However, in the spectra obtained after bulk Pb deposition, a strong band at ca. 1050 cm\(^{-1}\) is observed for each of the films. The similarity in frequency of this band in the three spectra suggests that the frequency is independent of chain length. This band does not appear in other surface spectra for dodecanethiol or octadecanethiol films. However, a weak band is seen in solid octadecanethiol at ca. 1050 cm\(^{-1}\) while no
Figure 9.17. Raman spectra in the \( \nu(C-C) \) region (600 nm excitation) of alkanethiol films at smooth Ag subjected to Pb UPD: a) butanethiol, c) dodecanethiol, e) octadecanethiol; alkanethiol films at smooth Ag subjected to bulk Pb deposition: b) butanethiol, d) dodecanethiol, f) octadecanethiol. Incident power: 100 mW. Integration times: a-d) 4 min, e and f) 1 min.
band is present at this frequency for solid dodecanethiol.

The 1050 cm\(^{-1}\) might be a G \(\nu(C-C)\) band or a G methylene rock, which are observed in this region.\textsuperscript{3,9,3,10} These assignments would suggest that Pb bulk deposition occurs along the alkane chains of the film, in addition to deposition near the S head group.

The surface Raman spectra in the \(\nu(C-H)\) region for films subjected to Pb deposition are shown in Figure 9.18. The spectra for films subjected to Pb UPD only, shown in Figures 9.18a, c, and e, are similar to spectra for films without Pb deposition, shown in Figure 5.4. After bulk Pb deposition, the intensity of the \(\nu_{\text{sym}}(\text{CH}, \text{FR})\) band at ca. 2935 cm\(^{-1}\) is greater relative to the \(\nu_{\text{sym}}(\text{CH}_2)\) bands at ca. 2850 and 2860 cm\(^{-1}\), as shown in Figures 9.18b, d, and f. The spectrum for octadecanethiol, shown in Figure 9.18f, shows the least change upon bulk Pb deposition.

The increase in intensity of the \(\nu_{\text{sym}}(\text{CH}_3, \text{FR})\) band is concluded to be due to increased disorder with bulk Pb deposition. This spectral behavior in the \(\nu(C-H)\) region was previously discussed in Chapter 7. The increase in disorder is possibly due to Pb deposition that is proposed to occur near the S head group and along the alkane chain. The greater disorder in the \(\nu(C-H)\) region after bulk Pb deposition supports the possible G assignment of the 1050 cm\(^{-1}\) band.

The appearance of the significant spectral changes for films subjected to bulk Pb deposition suggests that Pb is present within the alkanethiol film domains near the S head group and along the alkane chain. In addition, the presence of Pb in the butanethiol films is sufficient to disorder the film in the region adjacent to the surface, although this is not observed for the other films. As discussed in Chapter 7, butanethiol films are observed to be more susceptible to disordering than longer chain alkanethiol films. The similarity between films
Figure 9.18. Raman spectra in the $\nu$(C-H) region (600 nm excitation) of alkanethiol films at smooth Ag subjected to Pb UPD: a) butanethiol, c) dodecanethiol, e) octadecanethiol; alkanethiol films at smooth Ag subjected to bulk Pb deposition: b) butanethiol, d) dodecanethiol, f) octadecanethiol. Incident power: 100 mW. Integration times: a, c) 1 min; b, d-f) 4 min.
subjected to Pb UPD and no Pb deposition suggests that Pb that adsorbs directly to the Ag surface at gross defects may not significantly affect alkanethiol domains.

Ion penetration was further studied with CN⁻ as a spectroscopic probe. Figure 9.19a shows the surface Raman spectra of CN⁻ adsorbed at a smooth Ag electrode at open circuit potential in 0.75 M NaCN and then emersed from the solution and rinsed with TDI water. The observed surface CN⁻ band is significantly shifted from the frequency of 2080 cm⁻¹ of this band in 0.75 M NaCN. Figure 9.19b shows a smooth Ag electrode that has been previously modified with a dodecanethiol film formed for one minute. The electrode was then subjected to the NaCN solution as previously described. The CN⁻ band is observed at a frequency slightly higher than that observed at bare Ag surfaces. No CN⁻ is observed at samples with dodecanethiol films formed for one hour or greater.

Based on the bulk Pb deposition studies, the CN⁻ ion is expected to penetrate films formed for ca. one hour to a significant extent. The inability to detect significant intensity in the CN⁻ band in the surface Raman spectra suggests that electrochemistry is a more sensitive technique for studying ion penetration in the films.

Conclusion

Surface Raman spectroscopy is a powerful for the characterization of self-assembled alkanethiols at Ag and Au substrates. This method can provide unique information on metal-S bonding and its influence on the orientation of alkanethiols at these two metal surfaces. This information is also available in the electrochemical environment, where the surface charge of the metal electrodes
Figure 9.19. Raman spectra in the $\nu$(C-N) region (600 nm excitation) of smooth Ag electrodes emersed from 0.75 M NaCN solution: a) bare Ag, b) Ag with dodecanethiol film formed for 60 s. Incident power: 100 mW. Integration times: 1 min. Spectrum in b) subjected to 7 point Savitsky-Golay smoothing routine.
can be systematically varied over a wide potential range.

It has been demonstrated that the orientation of alkanethiols at Au and Ag is directly correlated with the surface charge of the metal. Although two distinct orientations are observed for alkanethiols at these two metals in the ambient environment, the orientations, in fact, can be reversibly interconverted between the two by changing the electrode potential. These observations suggest that orientations of alkanethiols at other metal surfaces may be predicted by considering their surface electronegativities.
Chapter 10

SURFACE RAMAN SCATTERING OF
THIOPHENOL AT SMOOTH Ag, Au, AND Pt

Introduction

Raman spectroscopy has the potential to become a powerful tool for characterizing organic thin films at a variety of metal surfaces. The spectral results presented in the preceding chapters have shown the capacity of Raman scattering to provide vibrational information on adsorbate-metal bonding, orientation, conformational order and defects within films. However, the application of Raman spectroscopy to metal surface films has been hampered because of the poor sensitivity inherent in the Raman scattering phenomenon.

SERS, on the other hand, is an extremely surface sensitive technique, due to the surface enhancements of up to a factor of $10^7$ at metals with the appropriate rough surface morphology. Large surface enhancements have been predominantly reported for Ag, Cu and Au.\textsuperscript{1,90} Smaller, but still significant, enhancements have been predicted or claimed of other metals, including Rh,\textsuperscript{1,91} Ga,\textsuperscript{1,92} and Pt,\textsuperscript{10,1} under the appropriate conditions of excitation wavelength and surface roughening to produce roughness features of the necessary geometry.\textsuperscript{1,94}

As concluded in Chapter 7, Raman spectra from alkanethiols at rough Ag and
Au are nearly identical to spectra at mechanically-polished, polycrystalline surfaces. A disruption of film conformational order at rough substrates was noted for short-chain alkanethiols. In Chapter 8, a significant increase in ion permeability is realized at rough Ag surfaces compared to smooth surfaces. In addition, a further substantial increase in film barrier behavior is observed for alkanethiol films at single-crystal Ag. It is concluded that surface substrate defects are manifested as defects in the alkanethiol monolayers. Although, in some cases, only the minimal enhancement available at reflecting metal surfaces will be available, it is clearly desirable to obtain Raman spectra of self-assembled films from metal surfaces without a roughening pretreatment.

As shown in Chapter 7, the acquisition of Raman spectra from monolayers at single-crystal Ag presents a distinct challenge for Raman spectroscopy. Surface Raman spectroscopy at mechanically-polished Pt is a similar challenge, because Pt is generally accepted to be a non-enhancing metal under conditions of visible wavelength excitation.\textsuperscript{1,94,10,2} Based on the extensive utility of Pt as an electrode and electrocatalyst in many technologically important processes, considerable interest in surface phenomena at Pt exists. Pettinger and Tiedemann reported surface resonance Raman spectra for crystal violet at smooth Pt electrodes.\textsuperscript{10,3} Pettinger, Friedrich and Tiedemann also reported in-situ surface Raman spectra of perchlorate ions at smooth Pt electrodes.\textsuperscript{10,2} Fleischmann and coworkers reported the FT Raman spectrum for surface pyridine at smooth Pt electrodes in 0.1 M KCl.\textsuperscript{10,4} Interestingly, however, Campion noted potential problems associated with surface luminescence processes at Pt that might make observation of Raman signals from monolayers of surface-confined organics extremely difficult.\textsuperscript{1,108}

Hubbard and coworkers have reported studies of monolayers of various thiol-
containing adsorbates at Pt (111). These include thiophenol, 2,5-
dihydroxythiophenol, benzyl mercaptan, 1-propanethiol, 2-mercaptoethanol, and
2-aminoethanethiol. Densely-packed films are observed with Auger spectroscopy
and cyclic voltammetry, although no LEED patterns are observed, indicating lack
of long-range order. Methanethiol has also been studied at Pt (111) by
HREELS.  

This chapter presents the normal Raman spectra for a monolayer of
thiophenol at mechanically polished, polycrystalline Pt electrodes. Thiophenol
has been chosen because it is known to form a single monolayer at Pt and
possesses a larger Raman cross-section relative to alkanethiols. XPS, REELS, and
cyclic voltammetry studies of thiophenol and 2,5-dihydroxythiophenol at Pt are
also presented.

Normal Surface Raman Spectra of Thiophenol at Pt

Adsorption of thiophenol and related molecules at single crystalline Pt has
been studied by Hubbard and coworkers using EELS, Auger spectroscopy, and
electrochemistry. It was concluded that thiophenol forms one monolayer
at Pt surfaces, with the S-H bond cleaving upon adsorption to form a Pt-S bond.
This behavior is consistent with the behavior generally accepted for both
aliphatic and aromatic thiol compounds on commonly employed transition metal
surfaces such as Au and Ag. Previous studies by Hubbard on the influence of
surface structure and morphology of Pt surfaces on the extent of adsorption of
aromatic compounds similar to thiophenol have resulted in the general finding
that very few differences in coverage are observed when comparing single
crystalline and polycrystalline surfaces. In the few cases where differences
have been observed, the surface coverage on the polycrystalline or rough Pt
surface is less than that on the single crystalline surface. This behavior was attributed to disruption of intermolecular cooperativity in the film by the presence of surface roughness.

Adsorption of thiophenol at rough Ag has been studied using SERS by Joo and coworkers and at rough Au by Garrell and coworkers both of whom propose a similar adsorption mechanism resulting in monolayer formation. All of these previous studies lend support to the postulate that the surface coverage of thiophenol on Pt surfaces is limited to, at most, a single monolayer.

Verification that a monolayer of thiophenol is formed on the Pt surfaces used in this study came from two types of measurements. XPS measurements of the decrease in intensity of the signal from the underlying Pt substrate in the presence of a thiophenol film were performed. In addition, coulometric experiments involving the oxidation of a film of 2,5-dihydroxythiophenol on Pt were performed.

XPS measurements were performed on thiophenol films formed for ca. 1 hour at polycrystalline Pt foil. The XPS spectra, shown in Figure 10.1, indicates the presence of C and S at the surface, along with O. Integrated intensities of the C 1s (286 eV), S 2p (165 eV), and Pt 4f (73 eV) bands were determined by spectral deconvolution using Gaussian profiles. The peak areas so determined were then corrected for scattering cross-section using accepted values. Film thicknesses were estimated from the Pt 4f band intensities using the conventional expression:

\[ I_{Pt} = I_{Pt}^0 \exp \left(-\frac{d}{\lambda \cos \theta}\right) \]

where \( I_{Pt} \) is the intensity of the Pt 4f bands in the presence of the film, \( I_{Pt}^0 \) is the intensity of the Pt 4f bands in the absence of the film, d is the film thickness, \( \lambda \) is the attenuation length of the Pt 4f electrons through the film and \( \theta \) is the
Figure 10.1. XPS survey spectra of thiophenol at smooth polycrystalline Pt.
angle at which the Pt 4f electrons are collected with respect to the surface normal. Measurements of the intensity of the Pt 4f bands were made at \( \theta \) values of 0°, 30°, and 60°. The ratio of the C 1s to S 2p bands was also determined from the XPS data to be 5.5:1. This value is consistent with the 6:1 C:S ratio in this molecule and suggests that the layer is stable and not significantly contaminated.

A value for \( d/\lambda \) was determined from a plot of \( \ln [\text{I}_{\text{Pt}}] \) versus \( 1/\cos \theta \). Using a value of \( \lambda \) of ca. 40 Å,\(^{10,8,10.9} \) \( d \) is estimated to be 9.2 Å. Calculations of the thickness of one monolayer of thiophenol using standard bond lengths\(^{10,10} \) and assuming a vertical orientation as previously proposed by Hubbard\(^{1,40} \) yield a value of ca. 8.6 Å. This value is in very close agreement with the value of film thickness estimated from the XPS measurements.

The value of \( \lambda \) used here has been taken from the XPS studies of alkanethiol monolayers at Au, Ag, and Cu.\(^{10,8,10.9} \) Organic alkyl films of known thickness were formed at the metal surfaces by adsorption of alkanethiols of various chain lengths. The thicknesses were calculated from the orientations of the alkanethiol films, determined from IR spectroscopy,\(^{1,50} \) and the bond lengths within the adsorbate molecules. The attenuation length is observed to be a function of the energy of the photoelectrons and Auger electrons. However, \( \lambda \) is found to be independent of the metal substrate. Therefore, it is assumed the attenuation lengths calculated in those studies are applicable for Pt substrates.

The assumption that attenuation lengths calculated from alkanethiol monolayers can be used for aromatic thiol monolayers was tested. Pentanethiol and thiophenol films at Pt foils were studied with XPS to determine thickness of the films as described above. The thicknesses of pentanethiol films at Ag\(^{1,49} \) and Au,\(^{1,42} \) calculated from ellipsometric data, are estimated to be ca. 10 and 6 Å, respectively. The \( d/\lambda \) values calculated from the XPS results for thiophenol
and pentanethiol films at Pt are -1.3 and -0.9, respectively. These values are within ca. 40% of each other. These results are only qualitative because the orientation of pentanethiol and thiophenol at Pt are not completely known. Larger thicknesses are calculated from these numbers (ca. 40 Å), possibly due to less number of gross defects in the film. Further work is necessary to determine the value of λ for these systems.

Further verification that only one monolayer of thiophenol is formed on the polycrystalline Pt surfaces used in these experiments comes from coulometric experiments. Thiophenol could not be used for these measurements, because it is not redox-active in the potential window accessible on Pt. Thus, the structurally-related molecule 2,5-dihydroxythiophenol which can be oxidized by two electrons in the surface-confined state was used. Cyclic voltammetry was performed in 0.1 M KCl on a film of 2,5-dihydroxythiophenol formed by immersion of polycrystalline Pt into a saturated aqueous solution of this molecule for 12 hours. The cyclic voltammogram is shown in Figure 10.2. Integrating the charge under the oxidation wave for the surface-confined 2,5-dihydroxythiophenol and using the surface area determined on the same Pt electrode from H adsorption measurements in H₂SO₄ yielded a surface coverage of 2.3 x 10⁻¹⁰ moles/cm², a value in close agreement with the value of 2.6 x 10⁻¹⁰ moles/cm² previously reported by Hubbard and coworkers for this molecule on Pt(111) electrodes. Cyclic voltammetric measurements at 200 mV/s on Pt electrodes in 1 M H₂SO₄ in the H adsorption region were used to determine surface area using the value of 254 μC/cm² for monolayer H coverage reported previously. Thus, the results of both measurements are consistent with formation of a single monolayer of thiophenol on the polycrystalline Pt surfaces used for the surface Raman spectroscopy measurements.
Figure 10.2. Cyclic voltammogram of 2,5-dihydroxythiophenol at smooth, polycrystalline Pt in 0.1 M KCl. Sweep rate = 5 mV/s. Area of electrode is 0.64 cm².
The Raman spectrum for neat liquid thiophenol is shown in Figure 10.3a. Figure 10.3b shows the spectrum for aqueous thiophenolate, formed by adding one part thiophenol to nine parts 0.5 M NaOH. The bands at 1000, 1024, and 1092 cm\(^{-1}\) are assigned to in-plane ring-breathing mode, in-plane (C-H) bend, and in-plane ring-breathing mode in conjunction with \(\nu(C-S)\), respectively.\(^{1,36}\) Upon deprotonation in basic solution, the 1092 cm\(^{-1}\) shifts 6 cm\(^{-1}\) lower, due to the \(\nu(C-S)\) component. A similar shift in frequency of the \(\nu(C-S)\) modes for butanethiol is noted upon deprotonation, as discussed in Chapter 3.

Figure 10.4a shows the surface Raman spectrum of thiophenol at smooth Pt. Laser powers and integration times are listed in the figure caption. The spectrum is similar to deprotonated thiophenol spectrum in Figure 10.3b, indicating Raman scattering from an adsorbed species and not from bulk liquid. The band at 1086 cm\(^{-1}\) in the bulk deprotonated spectra has shifted to a lower frequency of 1073 cm\(^{-1}\) upon adsorption, suggesting substantial electron withdrawal from the S group. This effect is also noted for alkanethiols at Ag and Au, as discussed in Chapters 5 and 6. For comparison, the Raman spectra for thiophenol at smooth Ag and at smooth Au are also shown in Figures 10.4b and c, respectively. Very little surface enhancement is realized for smooth Au with 514.5 nm excitation. However, the spectrum from smooth Au is of lower signal-to-noise-ratio than that from smooth Pt because of the higher background intensity observed from Au. The background intensity from smooth Pt is surprisingly small under the conditions used here.

The enhancement factor (EF) of 2000 for smooth Ag relative to smooth Pt has been calculated by comparing the respective surface Raman signals normalized to incident power and acquisition time. This is a larger than the EF calculated for smooth Ag relative to single-crystal Ag, as discussed in Chapter 7. The higher
Figure 10.3. Raman spectra in ring-breathing region (514.5 nm excitation) of a) bulk thiophenol and b) aqueous thiophenolate. Incident power: 100 mW. Integration times: 1 min.
Figure 10.4. Raman spectra in ring-breathing region (514.5 nm excitation) of thiophenol at smooth polycrystalline a) Pt, b) Ag, c) Au. Incident powers and integration times: a) 400 mW, 30 min, b) 200 mW, 1 min, c) 40 min, 100 mW. Slit widths: 0.4mm/2.8mm/0.4mm for a) and b), 0.25mm/2.8mm/0.25mm for c). The scale bar represents the following intensity ADUs: a) 160, b) 5300, c) 85.
EF factor for smooth Ag relative to smooth Pt is probably due to the decreased reflectivity of the Pt surface.

Changes in relative intensities of the bands for the different metal substrates are probably due to differences in orientation of thiophenol at the surface. Particularly noteworthy is the difference in relative intensity of the 998 and 1025 cm\(^{-1}\) bands at these substrates. All three vibrational bands observed in this spectral region are of the same symmetry \((a_1)^{1.36}\) making deduction of orientation difficult.

The normal surface Raman spectrum for butanethiol at smooth Pt is shown in Figure 10.5. The signal-to-noise is ca. 7 in this figure; however, due to the complexity of spectra in this region, the bands are not well resolved. The peaks in the region from 2860 to 2970 cm\(^{-1}\) correspond reasonably well to peaks observed for butanethiol at smooth Ag, Figure 5.4a, but an unknown peak at ca. 2810 cm\(^{-1}\) is also present in the Pt spectrum. This is possibly due to the background features resulting from the CCD detector. Spectra for butanethiol and pentanethiol at smooth Pt with increased signal-to-noise and resolution would permit a qualitative determination of orientation of alkanethiols at Pt. This spectrum, therefore, represents the current challenge in surface Raman spectroscopy of alkanethiols at metal surfaces.

**Conclusions**

In summary, the normal Raman spectrum of reasonable quality from a monolayer of thiophenol at smooth Pt surfaces is presented. Further improvements in the quality of spectral data acquired in such studies may it possible to determine the orientation of alkanethiols at Pt by considering the \(\nu(CH_3)\) bands. The use of surface Raman spectroscopy for Pt and other catalytic
Figure 10.5. Raman spectra in the $\nu$(C-H) region (514.5 nm excitation) for butanethiol at smooth polycrystalline Pt. Incident power: 100 mW. Integration time 30 min.
metal surfaces may lead to an increased understanding of surface chemistry important in areas such as electrochemistry and catalysis.
Overview of Problem

Self-assembled films of n-alkanethiols at Ag and Au are well-characterized systems. The orientation and adsorption mechanism of these adsorbates have been studied by a variety of techniques. The behavior of these films in the electrochemical environment is currently being studied with great interest for their insulating properties. Several aspects that are not as well understood are the factors that influence the orientation of these films at different substrates and the effect of surface morphology on the films. Specifically, structural characterization of these films in the electrochemical environment with spectroscopic techniques has not been previously undertaken.

Objectives of Research

The objective of this research, therefore, is a comprehensive characterization of alkanethiol monolayers at Ag and Au within and without the electrochemical environment. This research has provided some unique information about these systems, in addition to confirming conclusions from other research endeavors. The characterization of these organic films has also resulted in the further development of surface Raman spectroscopy as an attractive method for
analyzing organic thin films at a variety of metal surfaces.

Summary

A greater number of vibrational bands are present in surface Raman spectra compared to surface IR spectra for alkanethiol thin films. In order to take advantage of this greater wealth of vibrational information, it was necessary to determine peak assignments for n-alkanethiols in the spectral regions for 600 to 1300 cm$^{-1}$ and 2800 to 3000 cm$^{-1}$. Particular emphasis was given to trans and gauche assignments in the $\nu$(C-S) and $\nu$(C-C) regions in order to assess film order of alkanethiols at metal surfaces. In the spectral region from 600 to 1300 cm$^{-1}$, the Raman vibrational behavior of alkanethiols was found to be similar to that observed for alkanes with IR spectroscopy. A few bands in the solid spectra are still not identified; these are proposed to be directly related to S group. The behavior in the $\nu$(C-H) region for alkanethiols was found to be similar to previous Raman studies of alkanes. Thin films composed of alkanethiol derivatives will be investigated with Raman spectroscopy in the future, thus making these vibrational assignments necessary in the characterization of new monolayer films.

A method for determination of the orientations of alkanethiols at metal surfaces was developed and tested. Whereas previous research efforts have focused on the use of surface Raman selection rules for highly-symmetric molecules, this method involves the $\nu$(CH$_3$) modes for low symmetry molecules such as alkanethiols and alcohols. The orientations determined for alkanethiols at rough Ag and Au using solely the ratio of $\nu_{\text{asym}}$(CH$_3$) and $\nu_{\text{sym}}$(CH$_3$) peak area ratios are consistent with orientation models based on previous IR and Raman spectral data. In addition, the use of this method to the $\nu$(C-S) and $\nu$(C-C) regions
produced results consistent with those observed in the $\nu(C-H)$ region.

The application of surface Raman selection rules to determine orientation has stalled in recent years when considering adsorption of molecules with low symmetry. Although the method presented here is semi-quantitative at this point, the high degree of correspondence with quantitative IR data suggests that absolute angles of orientation may be directly calculated with Raman spectroscopy. It is hoped that these results would stimulate Raman spectroscopic investigations of other molecular films. A more quantitative understanding of the polarizability components of various vibrations and the magnitude of surface radiation fields is necessary for increased accuracy in orientation calculations.

Different orientations of the C-S bond and carbon backbone are observed for alkanethiols at Ag and Au. It is proposed that metal-S bonding is an important factor in the C-S bond orientation, and the tilt of the alkane chain is related to the spacing between nearest-neighbor molecules. This model is supported by Raman spectral results for alkanethiols in the electrochemical environment. Alkanethiols at Ag and Au are observed to reorient with change in applied potential, and this behavior is correlated with the PZCs of these metals. The C-S bond is concluded to be more perpendicular at Ag and Au positive of their respective PZCs, while the bond becomes more parallel at potentials negative of the PZC. The metal-S interaction is proposed to be directly affected by the applied potential, and thus the surface charge density, and the orientation of the C-S bond at both Ag and Au can be changed. Spectral results in the $\nu(C-C)$, $\nu(C-H)$, and $\nu(S-S)$ regions are also consistent with potential-dependent reorientation. These studies suggest that the orientation of alkanethiols at Ag and Au in air is a consequence of the open-circuit potential in air for these substrates.

These studies are the first to spectroscopically characterize the structure of
alkanethiol films in the electrochemical environment. These results suggest that metal-S bonding is an important factor in determining orientation. Future models of alkanethiols in the electrochemical environment will need to account for a more dynamic structure. Orientations of alkanethiols at other metal substrates may be predicted by considering substrate lattice spacings and PZCs.

Surface Raman spectra obtained at electrochemically roughened and mechanically polished surfaces are nearly identical, for the most part, in the $\nu$(C-C) and $\nu$(C-H) regions. Long-chain alkanethiol films at smooth and rough surfaces exhibit mostly all-T behavior in the $\nu$(C-C) region, with a small amount of $\nu$(C-C)$_G$ intensity. However, significant increases are seen in the G $\nu$(C-S) band for short-chain alkanethiols at rough Ag and Au surfaces. Longer chain alkanethiols show little or no difference in the $\nu$(C-S) region. It is concluded that alkanethiol films are disrupted near the surface of a highly roughened electrode, but the order of the rest of the film is not adversely affected. Thus, spectra obtained from self-assembled monolayers at highly-roughened, SERS-active metal surfaces will reflect greater disorder than spectra at much smoother surfaces.

Pb under-potential deposition was used to characterize the defect structure of these films. Pb UPD, which is a result of Pb-Ag bonding, is observed at a significant fraction of the smooth Ag surface for long-chain films formed for 4 hours or less. A large decrease in UPD is observed after film formation for ca. 24 hours. This suggests that sufficient deposition time is necessary for forming self-assembled films free of gross defects. Butanethiol films exhibit a large amount of UPD for films formed for ca. 24 hours, suggesting that Pb ions can easily penetrate short-chain alkanethiol films. No detectable amount of UPD was observed for dodecanthiol at Ag single-crystal surfaces.

The peak potential for bulk Pb deposition was used as a probe of ion
penetration at these films. Compared to deposition at bare Ag, a shift in potential of ca. 15 mV is observed for alkanethiol films at smooth Ag, and little or no shift is observed at rough Ag. A larger potential shift, ca. 60 mV, is observed for films at single-crystal Ag. It is concluded that significant ion penetration occurs within films at rough surface and, to a lesser extent, mechanically polished surfaces. Substrates with virtually no surface defects, such as single-crystal substrates, are necessary for good ion-barrier properties.

A model is presented that proposes ion penetration largely occurs at defect sites in the film. These defects do not expose the metal substrate to solution, but are probably related to chain tilt domain boundaries within the film. Although these domain boundaries are probably present within single-crystal domains of the substrate, their number increase with the number of substrate defects. Thus, surface pretreatments beyond mechanical polishing need to be considered in future investigations.

Normal surface Raman spectra have been obtained for self-assembled butanethiol and thiophenol monolayers at mechanically polished, smooth Pt. The high-quality spectra presented for thiophenol films at Pt show the feasibility of obtaining vibrational information for a wider variety of organic thin films at other metal surfaces.

**Future Directions**

The studies presented here suggest a wide range of further Raman spectroscopic investigations of alkanethiol self-assembled systems. In addition, experimental approaches discussed in this chapter and previous chapters are applicable to other organic thin film systems. The experiments outlined here will concentrate on band assignments, surface selection rules, and film order.
Raman Vibrational Assignments

In the region from 600 to 1300 cm\(^{-1}\), the assignments for two bands, at ca. 707 and 1110 cm\(^{-1}\), are still not known. These bands do not appear in spectra of alkanes or alcohols, which suggests that these bands involve the S group. The Raman spectra for similar alkyl molecules might prove useful in determining the identity of these bands and confirming other band assignments. Similar compounds include n-alcohols, n-haloalkanes, and Se-alkanes. Normal coordinate analysis of alkanethiols may be worth pursuing.

The confirmation of methyl and methylene band assignments could be achieved with selectively deuterated alkanethiols. The most useful position to deuterate is the methyl group. The bands affected by this deuteration could be directly attributed to methyl modes. This would also simplify the C-H region. Another position of importance is the methylene group adjacent to the methyl group. Deuteration of this site would confirm CH\(_2\)-Ag agostic interactions.

Surface Raman Selection Rules for the Determination of Adsorbate Orientation

The high degree of correspondence between the SERS and IR spectral calculations of alkanethiol orientation strongly suggest that an even higher level of quantitation is available with Raman spectroscopy. The limitations to increased quantitation appear to be the necessity for curve fitting the \(\nu\)(C-H) region, the lack of quantitation of polarizabilities of bands, and the uncertainty in the surface electric field ratio, \(E_n^2/E_t^2\).

These films offer an experimental method for determining polarizabilities of bands. Assuming an all-T extended model for alkanethiols at Ag and Au with the appropriate orientations, the polarizability components of various bands, such
as rocking, twisting, wagging, and scissoring methyl and methylene modes, can be estimated by comparison of the surface Raman spectra of these films to bulk spectra. Bands that are greatly enhanced must have a large component of the vibration that is oriented perpendicular to the surface upon adsorption.

It might be possible to produce films with drastically different orientations for comparison by judicious placement of the S group. For example, 4-decanethiol or 6-octadecanethiol might adsorb flat on the surface if they maintain all-T extended conformations. Ellipsometry might be used to confirm these orientations. Odd- and even-numbered alkanedithiols and dimethyl sulfide might prove interesting in a similar manner.

The polarizability components of the intense bands of highly-symmetric molecules could also be explored. These bands commonly share the totally-symmetric class. For example, in the thiophenol spectra at Ag and Pt, the bands at ca. 1000 and ca. 1070 cm\(^{-1}\) are both totally-symmetric (\(a_1\)) but the 1070 cm\(^{-1}\) band is enhanced to a greater extent. Both bands are ring-breathing modes, but the 1070 cm\(^{-1}\) band involves the \(\nu(C-S)\) mode. If it is assumed that the major polarizability component of this band is along the C-S bond, the spectra suggest that the C-S bond is largely perpendicular at Ag and Pt.

Film Order

More information on G and T conformers is available from bands besides the \(\nu(C-S)\) and \(\nu(C-C)\) modes. The methyl rocking modes at ca. 900 cm\(^{-1}\) and the wagging modes at ca. 1350 cm\(^{-1}\) contain conformational information such as end-gauche, kink, and double-gauche conformations. Band assignments in these regions need to be more fully characterized and applied to thin films.

A method of creating conformational disorder in a controlled fashion might
be the coadsorption of alkanethiols of different length. A series of experiments could involve formation of mixed monolayers of ca. 95% pentanethiol and 5% of a second alkanethiol. The second alkanethiol could be varied from sample to sample. It is envisioned that as the length of the second alkanethiol is increased, the amount of G conformers will increase. In addition, as the chain length of the second alkanethiol increases, the amount of kink and double-gauche conformers should increase. The second alkanethiol could be tagged for quantitation by XPS or other surface analytical technique.

Using alkanethiols containing a double bond at various positions as the second alkanethiol also might increase disorder in the mixed monolayers in a controlled fashion. Placement of the double-bond near the S group might have a different effect than a double-bond near the methyl group.

Defects in monolayer films can be created by immersion of the metal surfaces in ethanol solutions containing μM concentrations of alkanethiols. Adsorption of a second alkanethiol species would presumably occur at the defect sites in the original film.

On the other hand, films of increased order than observed with mechanically-polished, polycrystalline surfaces could be deposited and studied. Chemically polished, polycrystalline surfaces would probably have a fewer defects while still exhibiting sufficient enhancement for the acquisition of spectra with reasonable signal-to-noise. In addition, an annealing method might be developed to remove defects in monolayers.
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Chapter 1


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Chapter 2


Chapter 3


Chapter 4

Chapter 6.

Chapter 7.
Chapter 8


Chapter 9.


Chapter 10


