

# Contents

|          |  |    |
|----------|--|----|
| <b>1</b> | <b>Introduction</b>                                  | 1  |
|          | References   | 4  |
| <b>2</b> | <b>The Helium-3 Spin-Echo Experiment</b>             | 5  |
| 2.1      | Helium Atom Scattering                               | 5  |
| 2.1.1    | Diffraction Measurements                             | 6  |
| 2.1.2    | Adsorption and Desorption Studies                    | 7  |
| 2.1.3    | Measuring Surface Dynamics                           | 8  |
| 2.2      | Helium-3 Spin-Echo Spectroscopy                      | 10 |
| 2.3      | The Cambridge Helium-3 Spin-Echo Spectrometer        | 11 |
| 2.4      | Interpreting Helium-3 Spin-Echo Data                 | 15 |
| 2.4.1    | Jump Diffusion                                       | 17 |
| 2.4.2    | Lateral Interactions: De Gennes Narrowing            | 24 |
| 2.4.3    | Molecular Dynamics Simulations                       | 29 |
|          | References   | 31 |
| <b>3</b> | <b>A New Helium Atom Scattering Apparatus</b>        | 33 |
| 3.1      | Motivation   | 33 |
| 3.2      | Design and Experimental Setup                        | 35 |
| 3.2.1    | Vacuum System  | 35 |
| 3.2.2    | Power Distribution and Computer Control              | 38 |
| 3.2.3    | Beam Source  | 40 |
| 3.2.4    | Scattering Chamber and Sample Preparation Facilities | 40 |
| 3.2.5    | Detector   | 42 |
| 3.2.6    | Two Different Instrument Configurations              | 43 |
| 3.3      | Characterisation                                     | 43 |
| 3.3.1    | Uptake Measurements                                  | 44 |
| 3.3.2    | Diffraction Studies                                  | 45 |
| 3.3.3    | Thermal Desorption Spectroscopy                      | 47 |
| 3.4      | Conclusions  | 48 |
|          | References   | 49 |

|          |  |            |
|----------|--|------------|
| <b>4</b> | <b>An Improved High Intensity Supersonic Helium Beam Source . . .</b>                | <b>51</b>  |
| 4.1      | Introduction . . . . .   | 52         |
| 4.2      | A New Low Temperature Nozzle Assembly . . . . .                                      | 53         |
| 4.2.1    | Design . . . . .   | 54         |
| 4.2.2    | Characterisation . . . . .   | 56         |
| 4.3      | Effects of Size and Shape of the Skimmer and Its Mount. . . . .                      | 61         |
| 4.3.1    | Design . . . . .   | 61         |
| 4.3.2    | Performance . . . . .  | 63         |
| 4.3.3    | Discussion and Future Work . . . . .   | 65         |
| 4.4      | Conclusions . . . . .  | 68         |
|          | References . . . . .   | 68         |
| <b>5</b> | <b>The Dynamics of Cyclopentadienyl on Cu(111) . . . . .</b>                         | <b>71</b>  |
| 5.1      | Literature Background . . . . .  | 72         |
| 5.1.1    | The Structure of Cp . . . . .  | 72         |
| 5.1.2    | Cp Adsorption on Copper Surfaces . . . . .   | 72         |
| 5.1.3    | Cp Adsorption on Other Metal Surfaces . . . . .                                      | 73         |
| 5.1.4    | Metallocene Adsorption . . . . .   | 74         |
| 5.2      | Experimental Methods . . . . .   | 75         |
| 5.3      | Adsorption Behaviour . . . . .   | 76         |
| 5.4      | Measuring the Surface Dynamics . . . . .   | 78         |
| 5.4.1    | Multi-component Lineshapes . . . . .   | 78         |
| 5.4.2    | Jump Diffusion Curves . . . . .  | 81         |
| 5.4.3    | An Activation Energy from Temperature Dependence . . . . .                           | 83         |
| 5.5      | First Principles Density Functional Theory Calculations . . . . .                    | 85         |
| 5.6      | Molecular Dynamics Simulations . . . . .   | 87         |
| 5.6.1    | Creating a Potential Energy Surface . . . . .  | 87         |
| 5.6.2    | Modelling Diffusion on a Lattice of fcc and hcp Sites. . . . .                       | 89         |
| 5.6.3    | Microscopic Aspects of the Friction . . . . .  | 91         |
| 5.7      | Weak Lateral Interactions. . . . .   | 93         |
| 5.8      | Determining the Energy Difference Between fcc and hcp<br>Hollow Sites . . . . .      | 94         |
| 5.9      | Intracell Diffusion as a Handle on Friction<br>and Spring Constant. . . . .          | 98         |
| 5.10     | Conclusions . . . . .  | 101        |
|          | References . . . . .   | 102        |
| <b>6</b> | <b>Quantum Influences in the Diffusive Motion of Pyrrole<br/>on Cu(111). . . . .</b> | <b>105</b> |
| 6.1      | Literature Background . . . . .  | 106        |
| 6.1.1    | The Structure of Pyrrole . . . . .   | 106        |
| 6.1.2    | Pyrrole Adsorption on Copper Surfaces . . . . .                                      | 107        |
| 6.1.3    | Pyrrole Adsorption on Other Transition<br>Metal Surfaces . . . . .                   | 108        |

|          |  |            |
|----------|--|------------|
| 6.2      | Experimental Methods . . . . .   | 110        |
| 6.3      | Adsorption Behaviour . . . . .   | 111        |
| 6.4      | Measuring the Surface Dynamics . . . . .   | 116        |
| 6.4.1    | Experimental Lineshapes . . . . .  | 116        |
| 6.4.2    | Hopping over an Energy Barrier . . . . .   | 119        |
| 6.4.3    | Momentum Transfer and Coverage Dependence<br>of the Dynamics . . . . .                     | 119        |
| 6.5      | First Principles Density Functional Theory Calculations. . . . .                           | 124        |
| 6.6      | Molecular Dynamics Simulations Investigate the Effect<br>of Lateral Interactions . . . . . | 126        |
| 6.6.1    | Creating a Potential Energy Surface . . . . .  | 127        |
| 6.6.2    | Modelling the Diffusion of Pyrrole/Cu(111). . . . .  | 128        |
| 6.6.3    | Interaction Potential . . . . .  | 133        |
| 6.6.4    | Influences of Lateral Interactions on the Lineshapes . . . .                               | 135        |
| 6.7      | Lateral Changes in the Zero Point Energies<br>of Vibrational Modes . . . . .               | 138        |
| 6.8      | Conclusions and Outlook . . . . .  | 139        |
|          | References . . . . .   | 140        |
| <b>7</b> | <b>The Atomic-Scale Motion of Thiophene on Cu(111). . . . .</b>                            | <b>143</b> |
| 7.1      | Literature Background . . . . .  | 144        |
| 7.1.1    | The Structure of Thiophene . . . . .   | 144        |
| 7.1.2    | Thiophene Adsorption on Cu(111) . . . . .  | 145        |
| 7.2      | Experimental Methods . . . . .   | 148        |
| 7.3      | Adsorption Behaviour . . . . .   | 148        |
| 7.4      | Measuring the Surface Dynamics . . . . .   | 152        |
| 7.4.1    | Complex Lineshapes . . . . .   | 152        |
| 7.4.2    | Two Competing Activated Processes. . . . .   | 155        |
| 7.4.3    | Jump Diffusion. . . . .  | 156        |
| 7.4.4    | Activated Rotation . . . . .   | 158        |
| 7.4.5    | Flapping of the Molecular Ring . . . . .   | 159        |
| 7.5      | First Principles Density Functional Theory Calculations. . . . .                           | 162        |
| 7.6      | Molecular Dynamics Simulations Reveal an Exceptionally<br>High Friction . . . . .          | 162        |
| 7.7      | Conclusions . . . . .  | 166        |
|          | References . . . . .   | 167        |
| <b>8</b> | <b>Conclusions . . . . .</b>   | <b>169</b> |
| 8.1      | Equipment Development . . . . .  | 169        |
| 8.2      | Dynamics Experiments. . . . .  | 170        |
|          | References . . . . .   | 172        |

Studying Complex Surface Dynamical Systems Using  
Helium-3 Spin-Echo Spectroscopy

Lechner, B.A.J.

2014, XV, 172 p. 98 illus., 39 illus. in color., Hardcover

ISBN: 978-3-319-01179-0