

Contents

| | |
|---|-------------|
| Acknowledgements | i |
| Abstract (English/Rumantsch/Italiano/Deutsch) | iii |
| List of figures | xv |
| List of tables | xvii |
| 1 Introduction | 1 |
| 1.1 Preamble | 1 |
| 1.2 Why exploring adsorbates on insulating films? | 1 |
| 1.3 Why exploring molecular mixtures? | 3 |
| 1.4 Structure and scope of the thesis | 3 |
| 1.5 Author contributions | 4 |
| 2 Experimental and theoretical details | 5 |
| 2.1 Brief historical perspective | 5 |
| 2.2 Principles of Noncontact Atomic Force Microscopy | 6 |
| 2.2.1 Atomic force microscopy | 6 |
| 2.2.2 Different Force contributions | 9 |
| 2.2.3 Kelvin Probe Force Microscopy | 11 |
| 2.3 Instrumental setup | 15 |
| 2.3.1 qPlus sensor | 15 |
| 2.4 Multilayer insulating films | 15 |
| 2.4.1 Film growth | 15 |
| 2.4.2 Thickness determination | 17 |
| 2.4.3 Estimation of voltage drop across insulating film | 18 |
| 3 Controlling and imaging different charge-states of molecules | 21 |
| 3.1 Abstract | 21 |
| 3.2 Introduction | 22 |
| 3.3 Results | 22 |
| 3.3.1 Charge-state control by AFM | 22 |
| 3.3.2 Coulomb repulsion between charged molecules | 25 |

Contents

| | |
|---|-----------|
| 3.3.3 Lateral charge transfer between individual molecules | 27 |
| 3.4 Discussion and Conclusion | 28 |
| 3.5 Methods | 29 |
| 3.5.1 Charge-state manipulation by AFM | 29 |
| 4 Quantifying charge-state properties: the reorganization energy | 31 |
| 4.1 Abstract | 31 |
| 4.2 Introduction | 32 |
| 4.3 Results and discussion | 34 |
| 4.4 Conclusion | 38 |
| 4.5 Methods | 39 |
| 4.5.1 STM and AFM measurements | 39 |
| 4.5.2 Sample preparation | 39 |
| 4.5.3 DFT calculations | 39 |
| 4.5.4 Relation between average residence time fraction r and lifetime τ | 40 |
| 4.5.5 Estimation of the tip-sample distance | 41 |
| 4.5.6 Tip oscillation influence in the tunneling rate and measured voltage broadening of the oxidation and reduction levels | 41 |
| 4.5.7 Fitted frequency shift levels for electron detachment and reattachment | 42 |
| 4.5.8 Measurements uncertainty estimation | 43 |
| 5 Chemical reaction by stably-charged species | 47 |
| 5.1 Abstract | 47 |
| 5.2 Introduction | 47 |
| 5.3 Results and discussion | 48 |
| 5.4 Conclusion | 54 |
| 6 Characterization of dissolved organic carbon with atomic force microscopy | 55 |
| 6.1 Abstract | 55 |
| 6.2 Introduction | 56 |
| 6.3 Materials and Methods | 57 |
| 6.3.1 Sample Collection | 57 |
| 6.3.2 Scanning probe microscopy experiments | 58 |
| 6.4 Results | 59 |
| 6.5 Discussion | 65 |
| 6.6 Implications and Future work | 66 |
| 7 Identifying fuel pyrolysis products and directing the synthesis of standards with atomic force microscopy | 69 |
| 7.1 Abstract | 69 |
| 7.2 Introduction | 70 |
| 7.3 Experimental section | 71 |
| 7.3.1 Pyrolysis experiments and HPLC/UV/MS analysis | 71 |

Contents

| | |
|--------------------------------------|------------|
| 7.3.2 AFM measurements | 72 |
| 7.4 Results and Discussion | 73 |
| 7.5 Conclusion | 78 |
| 8 Conclusion and outlook | 79 |
| References | 81 |
| Curriculum Vitae | 101 |