

Contents

ABSTRACT	7
INTRODUCTION.....	13
CHAPTER 1. PTCDA ON AG(111) AS A MODEL SYSTEM	19
1.1. INTRODUCTION	19
1.2. MOLECULAR ORDERING	19
1.3. ELECTRONIC PROPERTIES AND ADSORPTION GEOMETRY.....	21
CHAPTER 2. STRUCTURAL POINT DEFECTS AT THE PTCDA/AG(111) INTERFACE	23
2.1. INTRODUCTION	23
2.2. EXPERIMENTS PREPARATION	23
2.3.PROPERTIES OF STRUCTURAL POINT DEFECTS AT THE PTCDA/AG(111) INTERFACE	24
2.3.I. Appearance at the STM images	24
2.3.II. Electronic properties	25
2.3.III. Conductance peak at the Fermi-level.....	26
2.3.IV. Conductance peaks I, III and IV.....	27
2.3.V. Spectroscopic measurements at different tip heights	29
2.3.VI. Manipulation of the defects	30
2.3.VII. Hydrogen sensitization of the STM tip.....	31
2.3.VIII. Models.	32
2.3.VIII.I. Ag adatom	33
2.3.VIII.II. Reaction with water molecule(s).....	34
2.4. CONCLUSION	34
CHAPTER 3. MOLECULAR MANIPULATION	35
3.1. INTRODUCTION	35
3.2. CONTACTING A SINGLE PTCDA MOLECULE.....	35
3.2.I. Capture and uncontrolled detaching	35
3.2.II. Stretching of a molecular junction.....	37
3.3. CONTROLLED DEPOSITION OF A SINGLE MOLECULE WITH THE STM TIP	38
3.4. PROTOCOL FOR CAPTURE AND CONTROLLED DEPOSITION OF A MOLECULE	38
3.4.I. Capture	38
3.4.II. Deposition	39
3.5. BUILDING OF THE MOLECULAR STRUCTURES	39
3.6. MOLECULAR ORIENTATION ANALYSIS.....	39
3.7. ROLE OF THE MOLECULAR SURROUNDINGS IN THE SUCCESS OF THE CAPTURE PROCEDURE.	41
3.8. THE REASONS FORCING A MOLECULE TO SWITCH: THEORY AND EXPERIMENT.....	42
3.8.I. Jump into the contact (upward to the tip).....	42
3.8.II. Jump out of the contact (downward to the surface)	43
3.8.II.I. Uncontrolled molecular detaching	43
3.8.II.II. Controlled molecular deposition	44
3.9. IMAGING THE OXYGEN SWITCHING	44
3.10. SINGLE SWITCHES AT LOW BIAS	45
3.11. CONCLUSION	46
CHAPTER 4. MOLECULAR SWITCH	48
4.1. INTRODUCTION	48

4.2. PROCESS OF MEASUREMENTS: TECHNICAL DETAILS AND DATA DESCRIPTION.....	49
4.2.I. <i>Technical details</i>	49
4.2.II. <i>Methods</i>	49
4.2.II.I. The first method: fixed tip height, variable bias voltage.....	49
4.2.II.II. The second method: fixed bias voltage, variable tip height.....	50
4.2.III. <i>Measurements with the data acquisition module</i>	52
4.3. DATA PROCESSING.....	52
4.3.I. <i>Employing Mathematica software</i>	52
4.3.II. <i>Tip height calibration</i>	55
4.3.III. <i>Program description</i>	57
4.3.IV. <i>Checking the accuracy of the finished data</i>	59
4.4. CONCLUSION.....	60
CHAPTER 5. SWITCHING PROCESS: ANALYSIS OF THE EXPERIMENTAL RESULTS	61
5.1. INTRODUCTION.....	61
5.2. SWITCHING RATE.....	61
5.3. DEFINING THE PARAMETER WINDOW WHERE THE SWITCHING OCCURS.....	63
5.4. SWITCHING MAPS.....	64
5.5. TWO STATES ANALYSIS.....	65
5.5.I. <i>Residence time analysis</i>	66
5.5.I.I. Oscillations in the residence time spectra.....	67
5.5.I.II. Residence time distribution modeling.....	69
5.5.II. <i>Fractional occupation and time-average conductance as a function of bias voltage and tip height</i>	70
5.5.III. <i>Transfer rates</i>	73
5.6. CONCLUSION.....	76
CHAPTER 6. THEORY OF THE SWITCHING PROCESS.....	77
6.1. INTRODUCTION.....	77
6.2 THEORETICAL MODELS FOR THE ADSORBATE TRANSFER.....	77
6.2.I. <i>Atomic quantum tunneling</i>	78
6.2.II. <i>Thermal activation</i>	79
6.2.III. <i>Coherent phonon process</i>	79
6.2.IV. <i>Electronic excitations</i>	80
6.2.V. <i>Vibrational heating model</i>	80
6.3 INELASTIC TRANSITION RATES.....	82
6.4. APPLYING THE VIBRATIONAL HEATING MODEL TO THE EXPERIMENTAL RESULTS.....	84
6.5. MODIFIED THEORETICAL MODEL.....	85
6.6. APPLYING THE EXTENDED VIBRATIONAL HEATING MODEL TO THE EXPERIMENTAL RESULTS.....	88
6.7. CONCLUSION.....	90
CHAPTER 7. METHODS.....	91
7.1. BASICS OF SCANNING TUNNELING MICROSCOPY.....	91
7.2. LOW TEMPERATURE BEETLE TYPE STM.....	93
7.3. STM TIP PREPARATION.....	94
7.4. SUBSTRATE PREPARATION AND MOLECULAR DEPOSITION.....	95
7.5. NOISE CHARACTERIZATION.....	96
7.6. PREPARATION OF THE ELECTRONICS OF THE STM FOR SPECTROSCOPIC MEASUREMENTS.....	98
7.6.I. <i>Modulation frequency, amplitude, and phase</i>	98
7.6.II. <i>Acquisition time and sensitivity</i>	99
GENERAL CONCLUSION	100

SUMMARY	100
PROSPECTS	103
APPENDIX	105
APPENDIX I. MACHEMATICA PROGRAM. MAIN VERSION	105
APPENDIX II. MATHEMATICA PROGRAM. SECOND VERSION	111
APPENDIX III. PLOTS OF THE TRANSFER RATES	115
III.I. FIRST SERIES	115
III.II. SECOND SERIES	117
III.II. THIRD SERIES	119
III.IV. FOURTH SERIES	123
REFERENCES	125
LIST OF PUBLICATIONS	133
JOURNAL PUBLICATIONS:	133
ORAL PRESENTATIONS:	133
POSTER PRESENTATIONS:	134