

Contents

1	Introduction to Single Molecule Chemistry and Physics	1
2	Basics of Electron Tunneling Processes and Scanning Tunneling Microscopy	5
2.1	Principles of Tunneling Processes	5
2.1.1	Elastic Tunneling Process	5
2.1.2	Inelastic Tunneling Process	8
2.1.3	Two-Step Tunneling Process	14
2.1.4	Resonant Tunneling Effect	14
2.2	Introduction to Scanning Tunneling Microscopy (STM)	15
2.2.1	Introduction to STM	15
2.2.2	STM Contrast Mechanisms	20
2.2.3	Scanning Tunneling Spectroscopy (STS)	22
2.2.4	Measurement of Apparent Tunneling Barrier Height	24
3	Single Molecule Structural Characterization	29
3.1	Molecular Imaging Mechanisms of STM	30
3.1.1	Molecular Orbital Model	31
3.1.2	HOMO-Ionization Potential Model	33
3.1.3	Work Function Model	34
3.2	Single Diatomic Molecules on Metal Surfaces	36
3.2.1	CO	37
3.2.2	O ₂ Molecules	40
3.3	Aromatic Molecules and Macrocyclic Molecules	42
3.3.1	Single Benzene Molecules Observed by STM	42
3.3.2	Phthalocyanines (Pc)	46
3.3.3	Porphyrin	48
3.3.4	Heterocyclic Molecules	51
3.3.5	Fullerene	53
3.3.6	Other Molecules	54
3.4	Single Hydrocarbon Molecules	55
3.5	Single Molecules Immobilized by Molecular Matrix	57
3.5.1	Hydrogen-Bonded Networks and Single Molecule Inclusions	57

VIII Contents

3.5.2	Molecular Networks Stabilized by van der Waals Interaction	59
3.6	Single Molecule Adsorption on Organic Substrates	60
3.6.1	Simple Alkane Lamella	61
3.6.2	Alkylated Amino Acid Molecular Templates	63
3.6.3	Tridodecyl Amine (TDA) Templates	64
3.7	Electron-Spin Resonance Study of Single Molecules	66
4	Single Molecule Diffusion and Chemical Reactions	69
4.1	Molecular Diffusion on Surfaces	69
4.1.1	Thermal-Activated Single Molecule Diffusion	69
4.1.2	Laser-Activated Single Molecule Diffusion	71
4.1.3	Field-Induced Diffusion of Single Atoms	71
4.2	Single Atom and Molecule Manipulations	74
4.2.1	Controlled Manipulation of Single Xe Atoms	74
4.2.2	Si Atoms	75
4.2.3	Gold Atoms	76
4.2.4	CO Molecules	76
4.2.5	C ₆₀ Molecules	77
4.3	Single Molecule Chemical Reactions on Metal Surfaces	78
4.3.1	Single Molecule Oxidative Reaction on Metal Surfaces	79
4.3.2	Dissociative Adsorption of H ₂	82
4.3.3	Dissociative Adsorption of NO	83
4.3.4	Dissociation of NH ₃	84
4.3.5	CO Oxidation	85
4.3.6	Dehydrogenation of Single Molecules	86
4.3.7	Tip-Induced Reactions of Single Iodobenzene on Cu(111)	88
4.3.8	Formation of Metal Ligand Complexes	89
4.3.9	Other Reaction Model Systems	91
4.4	Single Molecules on Semiconductor Surfaces	93
4.4.1	Single H ₂ Molecules on Si(100)	93
4.4.2	Single NH ₃ Molecules on Si Surfaces	94
4.4.3	Single O ₂ on Ge(111), Si(100) and Si(111)	95
4.4.4	Other Molecules on Si Surfaces	96
4.5	Single Molecule Reactions on Metal Oxide Surfaces	97
4.5.1	TiO ₂	98
4.5.2	CO on RuO ₂ (110)	102
4.5.3	Fe Oxide Surfaces	103
4.5.4	Other Oxide Surfaces	105

5 Molecular Scale Analysis	
Using Scanning Force Microscopy	107
5.1 Basic Principles of Atomic Force Microscopy (AFM)	107
5.1.1 Introduction of Instrumentation	107
5.1.2 Cantilever	108
5.1.3 Cantilever Deflection Detection	109
5.1.4 Cantilever Calibration	110
5.2 AFM Operating in Contact Mode	112
5.2.1 Contact Mode	112
5.2.2 Friction Force Microscopy	117
5.3 AFM Operating in Oscillatory Modes	118
5.3.1 Tapping Mode	118
5.3.2 Phase Imaging	120
5.3.3 Operations Under Liquids	120
5.3.4 Non-Contact Mode	122
5.4 Magnetic Force Microscopy (MFM)	123
5.4.1 Basic Imaging Mechanism	123
5.4.2 Examples of MFM Studies of Molecular Structures	125
5.4.3 Imaging Single Molecule Magnets	126
5.5 Force Spectrum and Surface Mapping	127
5.5.1 Force Spectrum and Imaging	127
5.5.2 Chemical Force Microscopy	128
6 Intermolecular and Intramolecular Interactions	131
6.1 Techniques for Studying Intermolecular and Intramolecular Interactions	131
6.1.1 Biomembrane Force Probe (BFP)	131
6.1.2 Optical Tweezers	132
6.2 Static Force Measurements of Single Molecules	134
6.2.1 Single Bond Interaction	134
6.2.2 Single Pair Ligand-Receptor Interactions	139
6.2.3 Guest-Host Interactions	141
6.2.4 Desorption of Single Molecules at Interfaces	142
6.3 Intramolecular Interactions of Single Molecules	144
6.3.1 Elasticity of DNA Molecules	144
6.3.2 Folding and Refolding of Single Protein Molecules	148
6.3.3 Stretching Other Biomolecules	149
6.3.4 Polysaccharides	152
6.3.5 Other Polymers	153
6.4 Dynamic Force Measurements of Single Molecules	154
6.4.1 Pulling Rate Effect on Force Spectrum Measurements	154
6.4.2 Pulling Rate Effect on Rupture Force Measurements	155

6.4.3	Force Measurements Relevant to Movements of Biomolecules	158
7	Electrical Conductivity of Single Molecules	159
7.1	Introduction	159
7.1.1	One-Dimensional Molecular Conductance Structures	159
7.1.2	Methods for Measuring Molecular Conductivity	163
7.2	Electrical Conductivity of Molecular Monolayers	165
7.2.1	Linear Alkane Derivatives	165
7.2.2	Conjugated Molecules	166
7.2.3	Rectification Molecular Conductance	167
7.2.4	Switching Behavior of Molecular Conductance	169
7.3	Single Molecule Conductance	170
7.3.1	Molecule-Electrode Contact Effect	170
7.3.2	Conductance of Single Organic Molecules	174
7.3.3	Conductance of Single Nanotubes and Nanowires	176
7.3.4	DNA Molecules	177
7.3.5	Single Molecule Devices	179
8	Single Molecule Fluorescence Imaging and Spectroscopy: Far-Field Studies	183
8.1	Introduction	183
8.1.1	Fluorescence of Molecules	183
8.1.2	General Considerations for Experimental Setup	185
8.1.3	Criteria of Single Molecule Identification	187
8.2	Single Molecule Imaging in Far-Field Configuration	188
8.2.1	Imaging by Confocal Fluorescence Microscopy	188
8.2.2	Wide-Field Imaging: Epi-Illumination Microscopy	188
8.3	Low-Temperature Studies of Single Molecules in Solid Matrices	189
8.3.1	Observation of Single Molecules in Crystalline Matrix	189
8.3.2	Pump-Probe Effects	193
8.3.3	Magnetic Resonance of Single Fluorescence Molecules	195
8.4	Single Fluorescence Molecules in Liquid Conditions	196
8.4.1	Experimental Considerations	196
8.4.2	Examples of Fluorescence of Single Molecules in Solutions	197
8.4.3	Single Molecule Diffusions in Living Cells	200
8.4.4	Single-Pair FRET	202
8.5	Single Molecules in Other Support Media	207
8.5.1	Single Molecules in Polymer Hosts	207
8.5.2	Lateral Diffusion Behavior of Single Molecules	210

8.5.3	Fluorescence from Single Atomic Clusters and Defects	212
8.6	Tip-Induced Single Molecule Fluorescence	212
8.7	Dynamics of Single Polymeric Molecules Studied by Fluorescence Microscopy and Related Techniques	213
8.7.1	Dynamics of Single Macromolecules in Solutions	213
8.7.2	Single Molecules Moving Through Channels	215
8.7.3	Migration of DNA Molecules on Flat Surfaces	217
8.7.4	Single Molecule Condensation of DNA	219
9	Single Molecule Fluorescence Imaging and Spectroscopy: Near-Field Studies	223
9.1	Near-Field Scanning Optical Microscopy	223
9.1.1	Introduction of Near-Field Effect	223
9.1.2	NSOM Probe Designs	226
9.1.3	Approaching Modes	229
9.2	Near-Field Scanning Optical Microscopy and Spectroscopy	230
9.2.1	Near-Field Optical Microscopy	230
9.2.2	Near-Field Optical Spectroscopy	232
9.2.3	Fluorescence Resonance Energy Transfer (FRET) Studied by NSOM	235
9.3	Other Near-Field Optical Microscopy	237
9.3.1	Near-Field Optical Chemical Sensors	237
9.3.2	Scanning Exciton Microscopy	238
10	Surface-Enhanced Raman Scattering (SERS) of Single Molecules	241
10.1	Introduction of SERS Effect	241
10.2	SERS of Single Molecules	244
10.2.1	Single Particle SERS Effect	244
10.2.2	SERS of Nanoparticle Aggregates	245
10.3	Tip-Induced SERS	253
10.4	Near-Field SERS	254
10.5	Raman Spectroscopy of Carbon Nanotubes	256
References		259
Index		299