

Contents

1. Introduction	1
1.1 Why Another Spectroscopy and Another Book?	1
1.2 Development of the NEXAFS Technique	4
2. Theory of Inner Shell Excitation Spectra	8
2.1 Description of the X-Ray Absorption Process.	8
2.1.1 The X-Ray Absorption Cross Section	8
2.1.2 Optical Oscillator Strength and Sum Rules	11
2.2 Time Scales in Inner-Shell Excitations	13
2.2.1 Electron and Hole Lifetimes	13
2.2.2 Separation of Electronic and Nuclear Degrees of Freedom	14
2.3 The Electronic Ground State.	15
2.3.1 The Hartree–Fock Method	15
2.3.2 Roothaan–Hall and Semiempirical Methods	19
2.4 Transition Energies	20
2.4.1 Koopmans’ Theorem	21
2.4.2 The Transition State Method	23
2.4.3 Localized Versus Delocalized Core Hole.	26
2.5 Transition Intensities	26
2.5.1 One-Electron Versus Multi-Electron Transitions	27
2.5.2 Effects of Nuclear Vibrations	27
2.5.3 The Sudden Approximation	28
2.5.4 Adiabatic Versus Sudden Excitation	29
2.6 Bound Versus Continuum Final States.	30
2.6.1 Improved Virtual Orbitals	30
2.6.2 Continuum Final States	31
2.7 The $X\alpha$ Multiple Scattering Method	34
2.7.1 Introduction to the Method	34
2.7.2 Exchange Potential and Latter Tail.	34
2.7.3 Muffin Tin Potential	35
2.7.4 Multiple Scattering Wavefunctions	36
2.7.5 Transition Energies	37
2.7.6 Practical Procedures for Calculation of K-Shell Spectra.	38

2.8	Ab Initio Stieltjes–Tchebycheff Molecular Orbital Method . . .	39
2.8.1	Introduction to the Method	39
2.8.2	Computational Procedure	39
2.8.3	Stieltjes–Tchebycheff Orbitals	41
2.8.4	Feshbach–Fano Method	42
2.9	Shell-by-Shell Multiple Scattering Method	43
2.10	Approximations Leading to the EXAFS Equation	44
3.	Symmetry and Molecular Orbitals	48
3.1	Origin and Labelling of Molecular Orbitals	48
3.2	Some Molecular Orbitals and Irreducible Representations . .	49
3.2.1	Diatomics and Linear Triatomics	49
3.2.2	Hydrogen Fluoride, Water, Ammonia, and Methane .	53
3.3	Molecular Orbitals, Equivalent Orbitals and Hybrid Orbitals	55
3.3.1	Molecular Orbital Versus Valence Bond Theory	55
3.3.2	Ionization Potentials in Methane	58
3.3.3	Bonding in Ethane, Ethylene, and Acetylene	59
3.4	Interactions Between Localized Orbitals: Conjugation	61
3.4.1	First and Second Order Perturbation Treatment	62
3.4.2	Interactions in Chain-Like Hydrocarbons	64
3.5	Splitting of Antibonding Orbitals	
	Due to Bond–Bond Interactions	67
3.5.1	The Linear Combination of Bond Orbitals Method . .	67
3.5.2	Application to σ and π Bonds in Hydrocarbons	67
3.6	Orbital Orientation, Symmetry, and the Dipole Selection Rule	69
3.6.1	Orbital Orientation and Angular Dependence of the Dipole Matrix Element	69
3.6.2	Group Theory and the Dipole Selection Rule	72
3.6.3	Applications of Group Theoretical Selection Rules . .	73
3.7	Spin-Dependent Excitations	75
4.	Experimental and Calculated <i>K</i>-Shell Spectra of Simple Free Molecules	79
4.1	Experimental Methods: The ISEELS Techniques	79
4.2	Characteristic Resonances in <i>K</i> -Shell Spectra	83
4.2.1	Overview	83
4.2.2	π^* Resonances	88
4.2.3	Rydberg and Mixed Valence/Rydberg Resonances . . .	90
4.2.4	σ^* Shape Resonances	93
4.2.5	Multi-Electron Features	95
4.2.6	Correlation of Multiple Scattering and Molecular Orbital Calculations: The N_2 Molecule	97
4.2.7	Molecular Orbitals and Resonances of Simple Hydrocarbons	102
4.2.8	Exchange Splitting in the Oxygen Molecule	104
4.3	Systematics of Resonance Positions	106

5. Principles, Techniques, and Instrumentation of NEXAFS	114
5.1 Achieving Adsorbate Sensitivity	114
5.2 Electron Yield Detection	118
5.2.1 Principles	118
5.2.2 Quantitative Description of Electron Yield	122
5.2.3 Adsorbate Versus Substrate Signal	127
5.2.4 Experimental Details and Detectors	130
5.3 Fluorescence Yield Detection	133
5.3.1 Absorption and Scattering of Soft X-Rays	133
5.3.2 X-Ray Reflection and Diffuse Scattering	137
5.3.3 Adsorbate Fluorescent Signal and Substrate Background	139
5.3.4 Practical Scheme for Suppression of Background Signal	141
5.3.5 Experimental Details and Detectors	145
5.4 Comparison of Detection Techniques	149
5.5 Normalization and Background Corrections	154
5.5.1 General Considerations	154
5.5.2 Normalization by a Reference Monitor	156
5.5.3 Division by the Clean Sample Spectrum	158
5.5.4 Subtraction of the Clean Sample Spectrum	160
6. Spectra of Condensed, Chemisorbed, and Polymeric Molecules: An Overview	162
6.1 From Free to Chemisorbed Molecules	162
6.1.1 Influence of Extra-Molecular Interactions on <i>K</i> -Shell Spectra	162
6.1.2 X-Ray Polarization and Molecular Orientation	169
6.2 Chemisorbed Atoms Versus Molecules	172
6.2.1 The NEXAFS Region	172
6.2.2 The SEXAFS Region	176
6.3 The Building Block Approach for Large Molecules	179
6.3.1 Assembly of Pseudodiatomics	179
6.3.2 Experimental Examples: Free, Adsorbed, and Polymeric Molecules	179
6.3.3 Theoretical Foundation of the Building Block Picture	183
6.4 Limitations of the Building Block Picture	185
6.4.1 Effects of Conjugation	185
6.4.2 π^* Bond-Bond Interactions	185
6.4.3 σ^* Bond-Bond Interactions	190
6.4.4 Aromatic Rings: Benzene and Related Molecules	199
6.4.5 Crystalline Solids	202
6.4.6 Effects of Core Hole Localization	205
6.5 Assembly of Functional Groups to Macromolecules	207
7. Analysis of <i>K</i>-Shell Excitation Spectra by Curve Fitting	211
7.1 The Need for a Quantitative Analysis	211
7.1.1 Curve Fitting of Original Spectra	211
7.1.2 Curve Fitting of Difference Spectra	212

7.2	Lineshapes of NEXAFS Resonances	213
7.2.1	Gaussian, Lorentzian and Voigt Functions	213
7.2.2	Asymmetric Gaussian and Lorentzian Lineshapes	214
7.2.3	Giant Resonance Lineshape	219
7.2.4	Giant Resonance Versus Asymmetric Gaussian Lineshapes	221
7.3	Lineshapes of NEXAFS Steps	222
7.3.1	Origin of Steps	222
7.3.2	Gaussian and Lorentzian Shaped Steps	223
7.4	Examples of Steps	225
7.4.1	Continuum Steps for Free Molecules	225
7.4.2	Continuum Steps for Condensed Molecules, Polymers, and Solids	228
7.4.3	Steps for Physisorbed and Chemisorbed Molecules	231
8.	σ^* Resonance Position and Bond Length	239
8.1	Theoretical Predictions and the Search for a Correlation	239
8.2	Predictions by Scattering Theory	242
8.3	Predictions by Molecular Orbital Theory	245
8.4	Empirical Correlation for Simple Free Molecules	249
8.4.1	The Energy Reference Question	250
8.4.2	Bonds Involving High-Z Atoms	252
8.5	Correlation for Large Molecules	255
8.5.1	Chain-Like Hydrocarbons with Alternating Bonds	255
8.5.2	Non-aromatic Hydrocarbon Rings	258
8.5.3	σ -Conjugated and Aromatic Molecules	260
8.6	Extension to Condensed, Physisorbed, and Chemisorbed Molecules	264
8.6.1	Chemical Shifts and Resonance Positions	265
8.6.2	Weakly Adsorbed Molecules	267
8.6.3	Strongly Adsorbed Molecules Without Bonding Shifts	269
8.6.4	Strongly Adsorbed Molecules with Bonding Shifts	271
8.6.5	General Rules, Comments and the Use of Standards	272
9.	The Angular Dependence of Resonance Intensities	276
9.1	Classification of Molecules	276
9.2	Resonance Intensities for Elliptically Polarized X-Rays	277
9.3	Angular Dependence of the Transition Matrix Elements	279
9.4	Effect of Substrate Symmetry	283
9.4.1	General Considerations	283
9.4.2	Twofold or Higher Substrate Symmetry	283
9.4.3	Threefold or Higher Substrate Symmetry	284
9.5	Intensity Plots for π^* and σ^* Vector Orbitals	285
9.6	Intensity Plots for π^* and σ^* Orbitals in a Plane	287
9.7	An Example: The π^* Resonance Intensity in Graphite	288
9.8	Angular Dependence of Intensities in Difference Spectra	290

10. Selected Applications of NEXAFS	292
10.1 What Can We Hope to Learn?	292
10.2 CO on Pt(111) and the Effects of Na and H ₂	295
10.2.1 CO/Pt(111) and CO/Na/Pt(111)	295
10.2.2 CO/Pt(111) in the Presence of H ₂ Gas	299
10.3 Molecular Oxygen on Pt(111) and Ag(110)	301
10.3.1 Physisorbed Versus Chemisorbed O ₂ on Pt(111)	302
10.3.2 Chemisorbed O ₂ on Ag(110)	306
10.3.3 Hybridization and Bond Length	307
10.4 The Bonding of Simple Hydrocarbons on Metals	309
10.4.1 Bonding and Orientation of C ₂ on Ag(110)	310
10.4.2 Di-sigma Bonded C ₂ H ₄ on Pt(111)	315
10.5 The Bonding of Phenyl-Ring-Based Molecules to Metal Surfaces	317
10.5.1 General Comments	317
10.5.2 Benzene	319
10.5.3 Phenyl Thiolate and Phenoxide	322
10.5.4 Pyridine	325
10.5.5 Reaction Intermediates: Benzyne	327
10.6 Thiophene on Pt(111) and Polythiophene on Pt	329
10.7 Langmuir–Blodgett Chains on Si(111)	333
10.7.1 Experimental Results	334
10.7.2 Chain Tilt, Intra-Chain Bonding, and Origin of Resonances	337
10.7.3 Analysis of Difference Spectra	337
10.7.4 Curve Fits of Original Spectra	338
10.7.5 Structural Results	340
11. A Look into the Future	342
11.1 Micro-NEXAFS	342
11.2 Liquid Surfaces	343
11.3 Time-Resolved Studies	344
11.4 Monosized Cluster Ions	345
11.5 Molecular Subgroups in Complex Environments	347
Appendices	349
A. Derivation of the EXAFS Equation	349
B. Chemisorbed Molecules Studied by NEXAFS	359
References	363
Subject Index	393
Listing of Illustrated K-Shell Spectra	401