

Contents

1	Introduction	1
	References	3
2	Basic Physical Concepts	7
2.1	Nuclear γ -Resonance	7
2.2	Natural Line Width and Spectral Line Shape	9
2.3	Recoil Energy Loss in Free Atoms and Thermal Broadening of Transition Lines	10
2.4	Recoil-Free Emission and Absorption	13
2.5	The Mössbauer Experiment	17
2.6	The Mössbauer Transmission Spectrum	18
2.6.1	The Line Shape for Thin Absorbers	21
2.6.2	Saturation for Thick Absorbers	23
	References	24
3	Experimental	25
3.1	The Mössbauer Spectrometer	25
3.1.1	The Mössbauer Drive System	27
3.1.2	Recording the Mössbauer Spectrum	29
3.1.3	Velocity Calibration	31
3.1.4	The Mössbauer Light Source	34
3.1.5	Pulse Height Analysis: Discrimination of Photons	35
3.1.6	Mössbauer Detectors	37
3.1.7	Accessory Cryostats and Magnets	41
3.1.8	Geometry Effects and Source–Absorber Distance	43
3.2	Preparation of Mössbauer Sources and Absorbers	45
3.2.1	Sample Preparation	46
3.2.2	Absorber Optimization: Mass Absorption and Thickness	49
3.2.3	Absorber Temperature	52

3.3 The Miniaturized Spectrometer MIMOS II	53
3.3.1 Introduction	53
3.3.2 Design Overview	54
3.3.3 Backscatter Measurement Geometry	59
3.3.4 Temperature Dependence and Sampling Depth	62
3.3.5 Data Structure, Temperature Log, and Backup Strategy	65
3.3.6 Velocity and Energy Calibration	66
3.3.7 The Advanced Instrument MIMOS IIa	67
References	69
4 Hyperfine Interactions	73
4.1 Introduction to Electric Hyperfine Interactions	73
4.1.1 Nuclear Moments	75
4.1.2 Electric Monopole Interaction	75
4.1.3 Electric Quadrupole Interaction	76
4.1.4 Quantum Mechanical Formalism for the Quadrupole Interaction	77
4.2 Mössbauer Isomer Shift	79
4.2.1 Relativistic Effects	81
4.2.2 Isomer Shift Reference Scale	81
4.2.3 Second-Order Doppler Shift	81
4.2.4 Chemical Information from Isomer Shifts	83
4.3 Electric Quadrupole Interaction	89
4.3.1 Nuclear Quadrupole Moment	90
4.3.2 Electric Field Gradient	90
4.3.3 Quadrupole Splitting	92
4.3.4 Interpretation and Computation of Electric Field Gradients	95
4.4 Magnetic Dipole Interaction and Magnetic Splitting	102
4.5 Combined Electric and Magnetic Hyperfine Interactions	103
4.5.1 Perturbation Treatment	104
4.5.2 High-Field Condition: $g_N \mu_N B \gg eQV_{zz}/2$	104
4.5.3 Low-Field Condition: $eQV_{zz}/2 \gg g_N \mu_N B$	108
4.5.4 Effective Nuclear g-Factors for $eQV_{zz}/2 \gg g_N \mu_N B$	111
4.5.5 Remarks on Low-Field and High-Field Mössbauer Spectra	112
4.6 Relative Intensities of Resonance Lines	113
4.6.1 Transition Probabilities	113
4.6.2 Effect of Crystal Anisotropy on the Relative Intensities of Hyperfine Splitting Components	118
4.7 ^{57}Fe -Mössbauer Spectroscopy of Paramagnetic Systems	120
4.7.1 The Spin-Hamiltonian Concept	121
4.7.2 The Formalism for Electronic Spins	124
4.7.3 Nuclear Hamiltonian and Hyperfine Coupling	125

4.7.4 Computation of Mössbauer Spectra in Slow and Fast Relaxation Limit	127
4.7.5 Spin Coupling	128
4.7.6 Interpretation, Remarks and Relation with Other Techniques	131
References	132
5 Quantum Chemistry and Mössbauer Spectroscopy	137
5.1 Introduction	137
5.2 Electronic Structure Theory	138
5.2.1 The Molecular Schrödinger Equation	138
5.2.2 Hartree–Fock Theory	139
5.2.3 Spin-Polarization and Total Spin	142
5.2.4 Electron Density and Spin-Density	144
5.2.5 Post-Hartree–Fock Theory	145
5.2.6 Density Functional Theory	146
5.2.7 Relativistic Effects	148
5.2.8 Linear Response and Molecular Properties	149
5.3 Mössbauer Properties from Density Functional Theory	150
5.3.1 Isomer Shifts	150
5.3.2 Quadrupole Splittings	164
5.3.3 Magnetic Hyperfine Interaction	178
5.3.4 Zero-Field Splitting and g -Tensors	185
5.4 Nuclear Inelastic Scattering	186
5.4.1 The NIS Intensity	187
5.4.2 Example 1: NIS Studies of an Fe(III)–azide (Cyclam-acetato) Complex	189
5.4.3 Example 2: Quantitative Vibrational Dynamics of Iron Ferrous Nitrosyl Tetraphenylporphyrin	193
References	196
6 Magnetic Relaxation Phenomena	201
6.1 Introduction	201
6.2 Mössbauer Spectra of Samples with Slow Paramagnetic Relaxation	202
6.3 Mössbauer Relaxation Spectra	205
6.4 Paramagnetic Relaxation Processes	210
6.4.1 Spin–Lattice Relaxation	211
6.4.2 Spin–Spin Relaxation	214
6.5 Relaxation in Magnetic Nanoparticles	220
6.5.1 Superparamagnetic Relaxation	220
6.5.2 Collective Magnetic Excitations	223
6.5.3 Interparticle Interactions	226
6.6 Transverse Relaxation in Canted Spin Structures	229
References	232

7	Mössbauer-Active Transition Metals Other than Iron	235
7.1	Nickel (^{61}Ni)	237
7.1.1	Some Practical Aspects	237
7.1.2	Hyperfine Interactions in ^{61}Ni	238
7.1.3	Selected ^{61}Ni Mössbauer Effect Studies	246
7.2	Zinc (^{67}Zn)	255
7.2.1	Experimental Aspects	255
7.2.2	Selected ^{67}Zn Mössbauer Effect Studies	262
7.3	Ruthenium (^{99}Ru , ^{101}Ru)	270
7.3.1	Experimental Aspects	270
7.3.2	Chemical Information from ^{99}Ru Mössbauer Parameters	270
7.3.3	Further ^{99}Ru Studies	284
7.4	Hafnium ($^{176,177,178,180}\text{Hf}$)	285
7.4.1	Practical Aspects of Hafnium Mössbauer Spectroscopy	286
7.4.2	Magnetic Dipole and Electric Quadrupole Interaction	288
7.5	Tantalum (^{181}Ta)	289
7.5.1	Experimental Aspects	290
7.5.2	Isomer Shift Studies	292
7.5.3	Hyperfine Splitting in ^{181}Ta (6.2 keV) Spectra	296
7.5.4	Methodological Advances and Selected Applications	300
7.6	Tungsten ($^{180,182,183,184,186}\text{W}$)	301
7.6.1	Practical Aspects of Mössbauer Spectroscopy with Tungsten	303
7.6.2	Chemical Information from Debye–Waller Factor Measurements	305
7.6.3	Chemical Information from Hyperfine Interaction	306
7.6.4	Further ^{183}W Studies	309
7.7	Osmium ($^{186,188,189,190}\text{Os}$)	310
7.7.1	Practical Aspects of Mössbauer Spectroscopy with Osmium	311
7.7.2	Determination of Nuclear Parameters of Osmium Mössbauer Isotopes	313
7.7.3	Inorganic Osmium Compounds	317
7.8	Iridium ($^{191,193}\text{Ir}$)	320
7.8.1	Practical Aspects of ^{193}Ir Mössbauer Spectroscopy	321
7.8.2	Coordination Compounds of Iridium	322
7.8.3	Intermetallic Compounds and Alloys of Iridium	329
7.8.4	Recent ^{193}Ir Mössbauer Studies	337
7.9	Platinum (^{195}Pt)	339
7.9.1	Experimental Aspects	339
7.9.2	Platinum Compounds	341
7.9.3	Metallic Systems	344
7.10	Gold (^{197}Au)	348
7.10.1	Practical Aspects	349

7.10.2 Inorganic and Metal-Organic Compounds of Gold	350
7.10.3 Specific Applications	361
7.11 Mercury ($^{199,201}\text{Hg}$)	373
References	376
8 Some Special Applications	391
8.1 Spin Crossover Phenomena in Fe(II) Complexes	392
8.1.1 Introduction	392
8.1.2 Spin Crossover in $[\text{Fe}(\text{2-pic})_3]\text{Cl}_2\cdot\text{Sol}$	396
8.1.3 Effect of Light Irradiation (LIESST Effect)	399
8.1.4 Spin Crossover in Dinuclear Iron(II) Complexes	403
8.1.5 Spin Crossover in a Trinuclear Iron(II) Complex	408
8.1.6 Spin Crossover in Metallomesogens	411
8.1.7 Effect of Nuclear Decay: Mössbauer Emission Spectroscopy	413
8.2 ^{57}Fe Mössbauer Spectroscopy: Unusual Spin and Valence States	417
8.2.1 Iron(III) with Intermediate Spin, $S = 3/2$	417
8.2.2 Iron(II) with Intermediate Spin, $S = 1$	425
8.2.3 Iron in the High Oxidation States IV–VI	428
8.2.4 Iron in Low Oxidation States	440
8.3 Mobile Mössbauer Spectroscopy with MIMOS in Space and on Earth	447
8.3.1 Introduction	447
8.3.2 The Instrument MIMOS II	448
8.3.3 Examples	451
8.3.4 Conclusions and Outlook	464
References	464
9 Nuclear Resonance Scattering Using Synchrotron Radiation (Mössbauer Spectroscopy in the Time Domain)	477
9.1 Introduction	477
9.2 Instrumentation	478
9.3 Nuclear Forward Scattering (NFS)	479
9.3.1 Quadrupole Splitting: Theoretical Background	480
9.3.2 Effective Thickness, Lamb–Mössbauer Factor	480
9.4 NFS Applications	483
9.4.1 Polycrystalline Material Versus Frozen Solution (Example: “Picket-Fence” Porphyrin and Deoxymyoglobin)	483
9.4.2 Temperature-Dependent Quadrupole Splitting in Paramagnetic ($S = 2$) Iron Compounds (Example: Deoxymyoglobin)	486

9.4.3	Dynamically Induced Temperature-Dependence of Quadrupole Splitting (Example: Oxymyoglobin)	487
9.4.4	Molecular Dynamics of a Sensor Molecule in Various Hosts (Example: Ferrocene (FC))	490
9.4.5	Temperature-Dependent Quadrupole Splitting and Lamb-Mössbauer Factor in Spin-Crossover Compounds (Example: $[\text{Fe}^{\text{II}}(\text{tpa})(\text{NCS})_2]$)	491
9.4.6	Coherent Versus Incoherent Superposition of Forward Scattered Radiation of High-Spin and Low-Spin Domains (Example: $[\text{Fe}^{\text{II}}(\text{tpa})(\text{NCS})_2]$)	493
9.4.7	Orientation-Dependent Line-Intensity Ratio and Lamb-Mössbauer Factor in Single Crystals (Example: $(\text{CN}_3\text{H}_6)_2[\text{Fe}(\text{CN})_5\text{NO}]$)	495
9.5	Isomer Shift Derived from NFS (Including a Reference Scatterer)	497
9.6	Magnetic Interaction Visualized by NFS	498
9.6.1	Magnetic Interaction in a Diamagnetic Iron Complex (Example: $[\text{FeO}_2(\text{SC}_6\text{HF}_4)(\text{TP}_{\text{piv}}\text{P})]$)	498
9.6.2	Magnetic Hyperfine Interaction in Paramagnetic Iron Complexes (Examples: $[\text{Fe}(\text{CH}_3\text{COO})(\text{TP}_{\text{piv}}\text{P})]^-$ with $S = 2$ and $[\text{TPPF}(\text{NH}_2\text{PzH})_2]\text{Cl}$ with $S = 1/2$)	498
9.6.3	Magnetic Hyperfine Interaction and Spin-Lattice Relaxation in Paramagnetic Iron Complexes (Examples: Ferric Low-Spin (Fe^{III} , $S = 1/2$) and Ferrous High-Spin (Fe^{II} , $S = 2$))	503
9.6.4	Superparamagnetic Relaxation (Example: Ferritin)	505
9.6.5	High-Pressure Investigations of Magnetic Properties (Examples: Laves Phases and Iron Oxides)	508
9.7	NFS Visualized by the Nuclear Lighthouse Effect (NLE) (Example: Iron Foil)	511
9.8	Synchrotron Radiation Based Perturbed Angular Correlation, SRPAC (Example: Whole-Molecule Rotation of FC)	512
9.9	Nuclear Inelastic Scattering	516
9.9.1	Phonon Creation and Annihilation	516
9.9.2	Data Analysis and DOS (Example: Hexacyanoferrate)	518
9.9.3	Data Analysis Using Absorption Probability Density (Example: Guanidinium Nitroprusside)	520
9.9.4	Iron-Ligand Vibrations in Spin-Crossover Complexes	523
9.9.5	Boson Peak, a Signature of Delocalized Collective Motions in Glasses (Example: FC as Sensor Molecule)	526
9.9.6	Protein Dynamics Visualized by NIS	528
9.10	Nuclear Resonance Scattering with Isotopes Other Than ^{57}Fe ...	534
	References	536

10 Appendices	541
Appendix A: Optimization of Sample Thickness	541
Appendix B: Mass Absorption Coefficients	543
Appendix C: The Isomer Shift Calibration Constant	544
Appendix D: Relativistic Corrections for the Mössbauer Isomer Shift	546
Appendix E: An Introduction to Second-Order Doppler Shift	547
Appendix F: Formal and Spectroscopic Oxidation States	549
Appendix G: Spin-Hamiltonian Operator with Terms of Higher Order in S	550
Appendix H: Remark on Spin-Lattice Relaxation	551
Appendix I: Physical Constants and Conversion Factors	553
Index	557
Table 7.1 Nuclear data for Mössbauer transitions used in transition metal chemistry	569