

Contents

Preface to the Fourth Edition xi

Acknowledgments xiii

Glossary and Abbreviations xv

1 / Introduction 1

- 1.1 Appearance of the Mass Spectrum 1
- 1.2 Formation of the Mass Spectrum 4
- 1.3 Mass Analysis of Ions 7
- 1.4 Ion Abundance Measurement 11
- 1.5 Sample Introduction Systems 11
- 1.6 Mixture Analysis 12
- 1.7 Molecular Structure Information 12
- 1.8 Standard Interpretation Procedure 13
- 1.9 General References 15

2 / Elemental Composition 19

- 2.1 Stable Isotopes; Classification According to Natural Abundance 19
- 2.2 "A + 2" Elements: Oxygen, Silicon, Sulfur, Chlorine, and Bromine 20
- 2.3 "A + 1" Elements: Carbon and Nitrogen 23
- 2.4 "A" Elements: Hydrogen, Fluorine, Phosphorus, and Iodine 25
- 2.5 Rings plus Double Bonds 27
- 2.6 Exercises 28
- 2.7 Compositions of All Peaks Where Possible 30
- 2.8 Deducing Elemental Compositions 33

3 / The Molecular Ion 35

- 3.1 Requirements for the Molecular Ion 36
- 3.2 Odd-Electron Ions 36
- 3.3 The Nitrogen Rule 37
- 3.4 Relative Importance of Peaks 38
- 3.5 Logical Neutral Losses 39
- 3.6 Molecular Ion Abundance versus Structure 41
- 3.7 Typical Mass Spectra 41

4 / Basic Mechanisms of Ion Fragmentation 51

- 4.1 Unimolecular Ion Decompositions 52
- 4.2 Basic Factors that Influence Ion Abundance 52
- 4.3 Reaction Initiation at Radical or Charge Sites 54
- 4.4 Reaction Classifications 54
- 4.5 Sigma Bond Dissociation (σ) 56
- 4.6 Radical-Site Initiation (α -Cleavage) 57
- 4.7 Charge-Site Initiation (Inductive Cleavage, i) 64
- 4.8 Decompositions of Cyclic Structures 68
- 4.9 Radical-Site Rearrangements 72
- 4.10 Charge-Site Rearrangements 78
- 4.11 Summary of Types of Reaction Mechanisms 83

5 / Postulation of Molecular Structures 85

- 5.1 General Appearance of the Spectrum 85
- 5.2 Low Mass Ion Series 91
- 5.3 Small Neutral Losses 97
- 5.4 Characteristic Ions 99
- 5.5 Postulating Possible Structures 100
- 5.6 Assignment of the Most Probable Structure 101

6 / Auxiliary Techniques 103

- 6.1 Soft Ionization Methods 103
- 6.2 Ionization of Large Molecules 105
- 6.3 Exact Mass Measurements (High Resolution) 109
- 6.4 Tandem Mass Spectrometry (MS/MS) 109
- 6.5 Combined Techniques 112
- 6.6 The Shift Technique 112
- 6.7 Chemical Derivatives 114
- 6.8 General References 114

7 / Theory of Unimolecular Ion Decompositions 115

- 7.1 Energy Deposition and Rate Functions 115
- 7.2 Thermodynamic vs. Kinetic Effects 117
- 7.3 Quasi-Equilibrium Theory 118
- 7.4 Derivation of $P(E)$ Functions 120
- 7.5 Calculation of $k(E)$ Functions 125
- 7.6 Thermochemical Relationships and Potential Energy Surfaces 127
- 7.7 Examples 132
- 7.8 General References 134

8 / Detailed Mechanisms and Ion Fragmentation 135

- 8.1 Unimolecular Ion Decompositions 135
- 8.2 Product Stability 138
- 8.3 Steric Factors 151

8.4	Reaction Initiation at Radical or Charge Sites	160
8.5	Reaction Classifications	165
8.6	Sigma-Bond Dissociation (σ)	169
8.7	Radical-Site Initiation (α -Cleavage)	171
8.8	Charge-Site Initiation (Inductive Cleavage, i)	173
8.9	Decompositions of Cyclic Structures	179
8.10	Hydrogen Rearrangements	191
8.11	Other Rearrangements	213
8.12	General References	221

9 / Mass Spectra of Common Compound Classes 225

9.1	Hydrocarbons	226
9.2	Alcohols	240
9.3	Aldehydes and Ketones	246
9.4	Esters	251
9.5	Acids, Anhydrides, and Lactones	258
9.6	Ethers	260
9.7	Thiols and Sulfides	265
9.8	Amines	270
9.9	Amides	274
9.10	Nitrile and Nitro Compounds	276
9.11	Aliphatic Halides	278
9.12	Other Types of Compounds	280

10 / Computer Identification of Unknown Mass Spectra 283

10.1	The Database of Reference EI Mass Spectra	284
10.2	Retrieval: The Probability Based Matching System	284
10.3	Interpretation: The Self-Training Interpretive and Retrieval System	287
10.4	Application of PBM and STIRS	290
10.5	General References	291

11 / Solutions to Unknowns 293

Bibliography 321

Appendix 339

Table A.1	Nuclidic Masses and Isotopic Abundances	339
Table A.2	Natural Abundances of Combinations of Chlorine, Bromine, Silicon, and Sulfur	340
Table A.3	Ionization Energy and Proton Affinity Values	343
Table A.4	Molecular Ion Abundances vs. Compound Type	346
Table A.5	Common Neutral Fragments	348
Table A.6	Common Fragment Ions	351
Table A.7	Common Elemental Compositions of Molecular Ions	355

Index 361