

Contents

INTRODUCTION	1
CHAPTER 1. INSTRUMENTATION	5
The ionization chamber	5
The ion accelerator	9
The magnetic analyzer	9
The energy analyzer	13
Double-focusing instruments	16
Modified instrumentation for studies of metastable ions	18
CHAPTER 2. TYPES OF IONS FORMED IN A MASS SPECTROMETER	19
Positively charged ions	19
Negatively charged ions	19
Molecular ions	20
Multiply charged ions	22
Fragment ions	22
Rearrangement ions	25
Stable ions	27
Unstable ions	28
Metastable ions	28
Ion—molecule reactions	30
Collision-induced fragmentation	31
Charge-exchange collisions	32
Ionization by the collision gas	33
Ion—molecule reactions within the ionization chamber	34
CHAPTER 3. FOCUSING AND KINETIC ENERGY MEASUREMENT OF ION BEAMS	37
Metastable peaks in normal mass spectra	38
Ion kinetic energy spectra	40
Spectra obtained by accelerating voltage scanning	41
Energy spectra obtained with prior mass analysis	42
Calibration of the mass scale for various methods of scanning	44
Advantages and disadvantages of the various scanning methods	48
Fragmentation in non-field-free regions	50
The effect of energy release on peak shape	57
Requirements for observing metastable peaks at high sensitivity or high resolution	70
Collision-induced dissociation	78
Equipment for IKES and MIKES work	82
Metastable peaks in other instruments	85
CHAPTER 4. THE PROPERTIES OF METASTABLE IONS	89
Appearance potential measurements	89

Kinetics of the fragmentation of metastable ions	97
Effects of internal energy	97
Isotope effects	101
Release of kinetic energy	104
Effects of reverse activation energy and of excess internal energy	104
Energy release as an ion structure characteristic	118
Isotope effects	120
Reactions of small metastable ions	122
Collision-induced charge transfer reactions	128
Symbolism used in describing these reactions	130
Quantitative aspects of energy transfer	130
Measurement techniques employed	134
Production of multiply charged ions	135
Charge-exchange processes	146
Collision-induced fragmentation	153
 CHAPTER 5. ANALYTICAL APPLICATIONS	 159
Elucidation of fragmentation pathways	159
Analysis of mixtures	165
Rearrangement processes	168
Isotope measurements	172
Identification of isomers	174
Exact mass measurements	180
 CHAPTER 6. APPROACHES TO THE STRUCTURES OF GASEOUS IONS	 181
Introduction	181
Abundances of metastable ions	183
Isotopic labeling	187
Ion kinetic energy spectrometry	189
Isotope effects	201
Thermochemistry	203
Stereochemistry	206
Ion cyclotron resonance and ion—molecule reactions	210
A specific example of an ion structure determination	214
 APPENDIX I. THEORY OF MASS SPECTRA	 217
Introduction	217
The statistical hypothesis	219
Rate constant dependence upon internal energy	225
Simplified applications of the quasi-equilibrium theory to complex organic compounds	232
Equipartition effects in homologous series	235
Tunnel effects	236
Rates of crossing of energy surfaces and similarities to tunneling aspects	240
Potential energy surfaces and correlation rules	242
Mathematical section	245
The RRKM evaluation of internal energy distributions	245
Some formal properties of the quasi-equilibrium theory	247
Generalized wave functions and effects of energy barriers	251
The energy levels of large polyatomic ions	254

APPENDIX II. RANDOMIZATION OF ISOTOPIC LABELS	255
APPENDIX III. PRESSURE AND ENERGY UNITS	256
APPENDIX IV. COMMONLY USED METASTABLE ION FORMULAE	267
References	269
Subject index	279
Compound and formula index	293