

Contents

1	Mass Spectrometry	1
1.1	Introduction	1
1.1.1	Principles of Mass Spectrometry	1
1.1.2	Techniques for Ionization	2
1.1.3	Overview of the Most Important Mass Analyzers	6
1.2	Molecular Ion M^+ (Molecular Peak) and Isotope Peaks	9
1.2.1	Definition	9
1.2.2	Intensity of the Molecular Peak	9
1.2.3	Protection of the Molecular Peak	9
1.2.4	Check on OE^+ and EE^+ Ions	10
1.2.5	Isotope Peaks	10
1.3	Determination of the Sum Formula as Well as the Number of Double Bond Equivalents (DBE)	11
1.3.1	Calculation of the Number of <i>Carbon</i> Atoms, n_C	13
1.3.2	Recognition of <i>Sulfur</i> and Calculation of the Number of <i>Sulfur</i> Atoms, n_S	14
1.3.3	Recognition of <i>Silicon</i> and Calculation of the Number of <i>Silicon</i> Atoms, n_{Si}	14
1.3.4	Recognition of <i>Chlorine</i> and <i>Bromine</i> and Determination of the Number of <i>Chlorine</i> and <i>Bromine</i> Atoms	15
1.3.5	Recognition of <i>Fluorine</i> and <i>Iodine</i>	15
1.3.6	Recognition of <i>Nitrogen</i>	15
1.3.7	Recognition of <i>Oxygen</i>	16
1.3.8	Recognition of <i>Phosphor</i>	16
1.3.9	Recognition of <i>Metal Ions</i>	17
1.3.10	Recognition of <i>Hydrogen</i>	17
1.3.11	Double Bond Equivalents	17
1.4	Factors That Influence Ion Abundance	22
1.4.1	Stability of the Product ions (Enthalpy Effects)	23
1.4.2	Steric Factors	24

1.5 Important Fragmentation Reactions	26
1.5.1 σ Cleavage	26
1.5.2 α Cleavage	30
1.5.3 McLafferty Rearrangement	39
1.5.4 Loss of Neutral Molecules	44
1.5.5 Charge-induced Cleavage	46
1.5.6 Onium Reactions	48
1.5.7 <i>Retro</i> -Diels-Alder Reaction	49
1.6 Determination of the Molecular Structure	52
1.6.1 Evaluation of the General Pattern of a Mass Spectrum	52
1.6.2 Common Fragment Loss, [M-X] Peaks	54
1.6.3 Common Specific Fragment Ions	54
1.6.4 General Steps for the Interpretation of Mass Spectra	55
Further Reading	61
2 Vibrational Spectroscopy	63
2.1 Introduction	63
2.1.1 Infrared (IR) Spectroscopy	63
2.1.2 Raman Spectroscopy and Some Applications	68
2.1.3 Symmetry, Selection Rules, and Applications	72
2.1.4 Fermi Resonance	77
2.2 Interpretation of Vibrational Spectra of <i>Small</i> Molecules and Ions	78
2.2.1 Determination of the Structure (Symmetry Group) of Molecules and Ions	78
2.2.2 Coordination of Bifunctional Ligands at the Central Atom in Complex Compounds	85
2.2.3 Investigations of the Strength of Chemical Bonds	87
2.3 Interpretation of Vibrational Spectra of <i>Organic</i> Molecules	91
2.3.1 Objectives and Special Features	91
2.3.2 Characteristic Vibrations	92
2.3.3 Structure-Specific Coupled Vibrations	95
2.3.4 The Fingerprint Region	95
2.3.5 Interpretation of Vibrational Spectra of Hydrocarbons	96
2.3.6 Interpretation of Vibrational Spectra of Compounds Containing the Functional Group C-X-R with X=O, N, and S	106
2.3.7 Interpretation of Vibrational Spectra of Carbonyl Compounds Containing the Functional Group -(C=O)-X with X=H, C, OH, OR, O(C=O)R, NR ₂ , and Cl	116
2.3.8 Interpretation of Vibrational Spectra of <i>N</i> -Containing Compounds	125
2.3.9 Interpretation of Vibrational Spectra of S-O-Containing Compounds	127
Further Reading	143

3	Electronic Absorption Spectroscopy	145
3.1	Introduction	145
3.1.1	Range Within the Electromagnetic Spectrum	145
3.1.2	Chromophore	146
3.1.3	Term System of Molecules	148
3.1.4	Selection Rules	153
3.1.5	The Structural Pattern of Electron Absorption Bands	158
3.2	Electron Absorption Spectra of Organic Chemical Classes	160
3.2.1	Small Nonconjugated Chromophore	160
3.2.2	Dienes, Enones	162
3.2.3	Aromatic Compounds	168
3.2.4	Polyenes	175
3.2.5	Polymethines	176
3.2.6	Azo Compounds	181
3.2.7	Quinoid Compounds	182
3.3	Stereochemical Influence on the Electron Absorption Spectra of Olefins	184
3.4	Solvent Effects on Electron Absorption Spectra	186
3.5	Some General Remarks About Molecular Structure Determination by Means of UV–Vis Spectroscopy	188
3.6	Electron Absorption Spectra of Inorganic Complex Compounds	199
3.7	Emission Spectroscopy	210
	Further Reading	214
4	Nuclear Magnetic Resonance Spectroscopy (NMR)	215
4.1	Introduction	215
4.2	Spectral Parameters	220
4.2.1	Chemical Shift	220
4.2.2	Intensity of the Resonance Signals	235
4.2.3	Half-Width of NMR Signals	236
4.2.4	Indirect Nuclear Spin Coupling	237
4.2.5	Equivalence in NMR Spectroscopy	247
4.2.6	Nomenclature of Spin Systems	251
4.3	Analysis of ^1H NMR Spectra	257
4.3.1	Simple First-Order Spectra	257
4.3.2	Second-Order Spectra	260
4.4	Experimental Techniques	283
4.4.1	General Remarks	283
4.4.2	Increasing of Magnetic Field Strength	283
4.4.3	Lanthanide Shift Reagents (LSR)	284
4.4.4	Recognition of OH Groups	284
4.4.5	Spin Decoupling	286
4.4.6	Distortionless Enhancement by Polarization Transfer (DEPT)	288

4.4.7 NOE Difference Spectroscopy	288
4.4.8 Correlation Spectroscopy	295
Further Reading	312
5 Molecular Structure Determination by Means of Combined	
Application of Methods	313
5.1 Overview of Determination of Heteroatoms	313
5.1.1 Nitrogen	313
5.1.2 Chlorine, Bromine	314
5.1.3 Iodine	314
5.1.4 Fluorine	314
5.1.5 Sulfur	314
5.1.6 Oxygen	315
5.1.7 Phosphorous	315
5.1.8 Silicium	316
5.2 Determination of the Sum Formula	316
5.3 Geometrical Isomers of the Structural Type $RR'C=CR''R'''$	316
5.4 Molecular Structure Determination	317
5.4.1 Solution to Challenge 5.1	321
Further Reading	437
6 Tables	439
6.1 Mass Spectrometry	439
6.2 Vibrational Spectroscopy	448
6.2.1 Tables of Group Wave Numbers of <i>Inorganic</i> Compounds ..	451
6.2.2 Tables of Group Wave Numbers of <i>Organic</i> Compounds ...	453
6.3 Electronic Absorption Spectroscopy	461
6.4 Nuclear Magnetic Resonance Spectroscopy	465
6.4.1 ^1H NMR Spectroscopy	465
6.4.2 ^{13}C NMR Spectroscopy	472
Further Reading	476
Index	477

Challenges in Molecular Structure Determination

Reichenbächer, M.; Popp, J.

2012, XX, 482 p. 657 illus., Softcover

ISBN: 978-3-642-24389-9