

Contents

1	Introduction	1
1.1	Development of the Infrared Technique	1
1.2	Applications of Infrared Spectroscopy	2
1.2.1	Direct Evidence on Constitution	3
1.2.2	Substance Identification by Spectral Comparison	3
1.2.3	Quantitative Analysis	4
1.2.4	Other Uses	6
	References	7
2	Absorption and Molecular Design	9
2.1	Fundamentals	9
2.1.1	Electromagnetic Radiation	9
2.1.1.1	Nature of Electromagnetic Radiation	9
2.1.1.2	Parameters and Units	9
2.1.1.3	Radiation Energy	11
2.1.2	Molecular Design	12
2.1.2.1	The Atom	13
2.1.2.2	The Molecule	14
2.1.3	Infrared Absorption and the Change in Dipole Moment	18
2.2	Absorption of Infrared Radiation	19
2.2.1	Infrared Spectra of Diatomic Molecules	19
2.2.1.1	Rotational Spectra	19
2.2.1.2	Vibrational Spectra	20
2.2.1.3	Rotational-Vibrational Spectra	22
2.2.2	Infrared Spectra of Multiatomic Molecules	24
2.2.2.1	Normal Modes of Vibration	24
2.2.2.2	Vibrational Modes	25
2.2.2.3	Overtone and Combination Vibrations	27
2.2.2.4	Fermi Resonance	28
2.2.2.5	Band Shape	30
2.2.2.6	Symmetry Properties of Molecules	32
	References	36
3	Spectrometers	37
3.1	Design	37
3.2	Radiation Sources	40
3.3	Infrared Detectors	41
3.3.1	Thermal Detectors	43
3.3.2	Photodetectors	45

3.4	Spectral Resolution	47
3.4.1	Dispersive Spectrometers	48
3.4.1.1	Diffraction Grating	48
3.4.1.2	Interference Filters	50
3.4.1.3	Acousto-Optical Tunable Filters (AOTFs)	51
3.4.1.4	Spectral Slit Width, Resolution	51
3.4.1.5	Scattered Radiation	52
3.4.2	Fourier Transform Spectrometers	52
3.4.2.1	Michelson Interferometer	52
3.4.2.2	Important Structural Parts of FT Spectrometers	60
3.4.2.3	Advantages of FT Spectrometers over Dispersive Instruments	62
3.4.3	Acquisition of FT-IR Spectra	63
3.4.3.1	Steps in Spectral Calculation	63
3.4.3.2	Practical Tips for Measuring Spectra	67
3.4.3.3	Photometric Accuracy of FT Spectrometers	69
3.5	Standard Accessories	71
3.5.1	Cells	71
3.5.1.1	Cell Windows	72
3.5.1.2	Handling and Care of Cell Windows	75
3.5.1.3	Dismountable Cells	76
3.5.1.4	Cells with Defined Pathlength	76
3.5.1.5	Cells with Variable Pathlength	77
3.5.1.6	Gas Cells	78
3.5.1.7	Holder for Pellets and Films	78
3.5.1.8	Microcells and Beam Condensers	79
3.5.1.9	Cells for Measurements at Increased and Reduced Temperature	79
3.5.1.10	Cells for Studies under Pressure	80
3.6	Spectral Processing	81
3.6.1	Data Reduction and Spectral Simulation	82
3.6.2	Spectral Smoothing	84
3.6.3	Derivative Spectroscopy	86
3.6.4	Spectral Deconvolution (Resolution Enhancement)	88
3.6.5	Further Practical Methods for Spectral Processing	89
	References	91
4	Sample Preparation	95
4.1	General Remarks	95
4.1.1	Sample Quantity	95
4.1.2	Purity Requirements	96
4.1.2.1	Spectra of Pure Compounds, Reference Spectra	96
4.1.3	Moisture	96
4.1.4	Precautionary Measures	96
4.2	Solids	97

4.2.1	KBr Pellet Technique	97
4.2.1.1	Materials for Producing Pellets	97
4.2.1.2	Handling of Potassium Bromide	98
4.2.1.3	Pressing Tools	99
4.2.1.4	Pellet Production	99
4.2.1.5	Micropellets	100
4.2.1.6	Disturbance by the Christiansen Effect	102
4.2.1.7	Disturbances by Reactions with the Embedding Medium	103
4.2.1.8	Quantitative Analyses	104
4.2.2	Suspensions in Oil	105
4.2.3	Films from the Melt	106
4.2.4	Films	108
4.2.4.1	Pressing of Films	108
4.2.4.2	Cast Films	108
4.2.4.3	Microtomic Sections	109
4.2.4.4	General Tips for Producing Films	109
4.2.5	Films as Sample Substrate	110
4.3	Liquids and Solutions	111
4.3.1	Liquids	111
4.3.2	Solutions	113
4.3.2.1	Solvents	113
4.3.2.2	Purity of the Solvents	114
4.3.2.3	Concentration Ranges	114
4.3.2.4	Production of Solutions	115
4.3.2.5	Solvent Effects	115
4.3.2.6	Microtechnique for Solutions	117
4.4	Gases	118
4.4.1	Filling of Gas Cells	118
4.4.2	Total Pressure Dependency of the Absorptivity in Gas Spectra	119
4.4.3	Micromethods for Gases	120
4.4.4	Trace Gas Studies	121
	References	123
5	Special Sample Techniques	125
5.1	Reflection Methods	125
5.1.1	Measurement of External Reflectance	125
5.1.1.1	Fresnel Reflection	125
5.1.1.2	Reflection-Absorption Spectroscopy	129
5.1.2	Attenuated Total Reflectance	131
5.1.3	Diffuse Reflectance	135
5.2	Fourier Transform Infrared Microspectroscopy	140
5.3	Photoacoustic Detection	142
5.4	Infrared Emission Spectroscopy	143
5.5	Measurements under Extreme Conditions	145
5.5.1	Cryogenics	145
5.5.2	High-Temperature Spectroscopy	149

5.5.3	High-Pressure Measurements	150
5.6	Measurements with Polarized Radiation	151
5.7	Combination of IR Spectroscopy with Chromatographic Methods	153
5.7.1	Gas Chromatography/IR Spectroscopy	153
5.7.2	Thin-Layer Chromatography/IR Spectroscopy . .	158
5.7.3	HPLC- and SFC/IR Spectroscopy	159
5.8	Vibrational Spectroscopic Imaging	161
	References	164
6	Qualitative Spectral Interpretation	171
6.1	Fundamentals	171
6.1.1	IR Spectrum	171
6.2	Initial Inspection of Spectra	172
6.3	General Assignments	176
6.3.1	The Fingerprint Region	176
6.3.2	Group Frequencies	177
6.4	IR Spectra of Individual Compound Classes . . .	178
6.4.1	Alkanes	178
6.4.2	Halogen Compounds	183
6.4.3	Alkenes	185
6.4.4	Molecules with Triple Bonds	191
6.4.5	Aromatic Compounds	193
6.4.6	Ethers	196
6.4.7	Acetals and Ketone Acetals	202
6.4.8	Alcohols	203
6.4.9	Hydrogen Bonding	206
6.4.10	Chelates	208
6.4.11	Carbonyl Compounds	210
6.4.11.1	Ketones	210
6.4.11.2	Aldehydes	214
6.4.11.3	Carboxylic Acids	215
6.4.11.4	Acid Chlorides	219
6.4.11.5	Esters	219
6.4.11.6	Anhydrides	222
6.4.11.7	Amides	223
6.4.11.8	Carboxylic Acid Derivatives	227
6.4.12	Nitrogen Compounds	229
6.4.12.1	Amines	229
6.4.12.2	C=N-Double Bond	233
6.4.12.3	Nitro-Group	233
6.4.12.4	Organic Nitrates, Nitramines, Nitrites, Nitrosamines	236
6.4.12.5	Azo-, Azoxy- and Nitroso-Compounds	236
6.4.13	Compounds with Cumulated Double Bonds . . .	237
6.4.14	Aromatic Compounds: Substituent Effects . . .	238
6.4.14.1	Aromatic Hydrocarbons	239
6.4.14.2	Aromatic Halogen Compounds	240

6.4.14.3	Aromatic Ethers	240
6.4.14.4	Phenols	240
6.4.14.5	Aromatic Amino Compounds	240
6.4.14.6	Aromatic Nitro Compounds	241
6.4.14.7	Aromatic Carbonyl Compounds	241
6.4.14.8	Aromatic Conjugated Triple Bonds and Cumulated Double Bonds	243
6.4.14.9	Aromatic Oximes, Azomethines and Azo Compounds	243
6.4.15	Heterocycles	244
6.4.16	Boron, Silicon, Sulfur and Phosphorus Compounds	245
6.4.16.1	Boron Compounds	245
6.4.16.2	Silicon Compounds	246
6.4.16.3	Sulfur Compounds	246
6.4.16.4	Phosphorus Compounds	247
6.4.17	Inorganic Compounds	248
6.5	Causes of Band Shifts, Effects on the Spectrum	248
6.5.1	Mass Effect	248
6.5.2	Steric Interactions	251
6.5.3	Resonance Effects	252
6.5.4	Inductive Effects	252
6.5.5	Dipole-Dipole Interactions (Field Effect)	254
6.5.6	Intermolecular Interactions	255
6.6	Spectral Interpretation as a Multidimensional Task	258
6.6.1	Band-Structure Correlations	259
6.6.2	Spectral Comparison	260
6.6.3	Examples for Spectral Interpretation	260
6.7	Particularities and Artifacts	266
6.8	Spectral Calculation	268
	References	274
7	Quantitative Spectral Assertions	279
7.1	Fundamentals	279
7.1.1	Beer's Law	279
7.1.2	Determination of Pathlength	281
7.1.3	Determination of Absorbance	283
7.1.4	Absorptivity	284
7.2	Calibration	285
7.2.1	Baseline Correction for Absorbance Determination	285
7.2.2	Determination of Calibration Data	286
7.2.3	Multi-Component Analysis with Separated Analytical Bands	288
7.2.4	Evaluation via Relative Absorbance Values	289
7.2.4.1	Quantitative Measurement of Liquids	289

7.2.4.2	Quantitative Measurement with Pellets	290
7.2.5	Quantitative Gas Analysis	290
7.3	Interpretation of Quantitative Results	292
7.3.1	Mean Value and Standard Deviation	293
7.3.2	Scattering Range of Individual Measurements and Confidence Interval of Mean Values	294
7.3.3	Random and Systematic Errors	295
7.4	Calibration Functions and Confidence Intervals .	297
7.4.1	Linear Regression	297
7.4.2	Special Method Parameters	298
7.5	Multi-Component Analysis with Multivariate Evaluation	301
7.5.1	Classical Model Formation	301
7.5.2	Statistical Model Formation	303
	References	306
8	Spectroscopy in Near- and Far-Infrared, as well as Related Methods	309
8.1	Spectral Regions Beyond Mid-Infrared	309
8.1.1	Near-Infrared Spectroscopy	309
8.1.1.1	Comparison of Mid-Infrared and Near-Infrared Spectroscopy	309
8.1.1.2	Applications of Near-Infrared Spectroscopy . . .	310
8.1.2	Far-Infrared Spectroscopy	312
8.2	Infrared Laser Spectroscopy	313
8.3	Raman Spectroscopy	315
8.3.1	Physical Foundations	315
8.3.2	Instrument Design	322
8.3.2.1	Conventional Grating Spectrometer	322
8.3.2.2	FT-Raman Spectrometer	324
8.3.3	Applications	325
8.3.3.1	Assignment of Vibrational Bands	325
8.3.3.2	Aqueous Samples	325
8.3.3.3	Quantitative Analysis	326
8.3.3.4	Investigation of Solids	326
	References	327
9	Reference Spectra and Expert Systems	329
9.1	Spectral Collections	329
9.1.1	Reference Collections	329
9.1.2	Digital Spectral Libraries	331
9.2	Computer-Supported Research	332
9.2.1	Library Search	332
9.2.2	Incorporation of Various Types of Spectroscopy	336
9.3	Interpretative Systems	336
9.3.1	Computer-Interpretation According to Empirical Rules	337

9.3.2	Multivariate Methods for Spectral Interpretation	338
9.3.3	Pattern Recognition Methods	339
9.4	Qualitative Mixture Analysis	340
	References	342
10	Appendix	347
10.1	Positions of the Most Frequent Disturbing Bands in the IR Spectrum	347
10.2	Spectra of Frequently Used Solvents	347
Index		355