

Contents

1 Doppler-Limited Absorption and Fluorescence Spectroscopy with Lasers	1
1.1 Advantages of Lasers in Spectroscopy	1
1.2 High-Sensitivity Methods of Absorption Spectroscopy	7
1.2.1 Enhancement of Absorption in External Cavities	7
1.2.2 Frequency Modulation	9
1.2.3 Intracavity Laser Absorption Spectroscopy ICLAS	15
1.2.4 Cavity Ring-Down Spectroscopy (CRDS)	23
1.3 Direct Determination of Absorbed Photons	30
1.3.1 Fluorescence Excitation Spectroscopy	31
1.3.2 Photoacoustic Spectroscopy	35
1.3.3 Optothermal Spectroscopy	41
1.4 Ionization Spectroscopy	46
1.4.1 Basic Techniques	46
1.4.2 Pulsed Versus CW Lasers for Photoionization	49
1.4.3 Sensitivity of the Different Techniques	52
1.4.4 Resonant Two-Photon Ionization (RTPI) Combined with Mass Spectrometry	53
1.4.5 Thermionic Diode	55
1.5 Optogalvanic Spectroscopy	56
1.6 Velocity-Modulation Spectroscopy	59
1.7 Laser Magnetic Resonance and Stark Spectroscopy	60
1.7.1 Laser Magnetic Resonance	61
1.7.2 Stark Spectroscopy	63
1.8 Laser-Induced Fluorescence	64
1.8.1 Molecular Spectroscopy by Laser-Induced Fluorescence	65
1.8.2 Experimental Aspects of LIF	67
1.8.3 LIF of Polyatomic Molecules	70
1.8.4 Photon Bursts	72
1.8.5 Determination of Population Distributions by LIF	72

1.8.6	Laser-Induced Breakdown Spectroscopy LIBS	76
1.9	Comparison Between the Different Methods	76
1.10	Problems	80
2	Nonlinear Spectroscopy	83
2.1	Linear and Nonlinear Absorption	83
2.2	Saturation of Inhomogeneous Line Profiles	91
2.2.1	Hole Burning	92
2.2.2	Lamb Dip	96
2.3	Saturation Spectroscopy	99
2.3.1	Experimental Schemes	100
2.3.2	Cross-Over Signals	104
2.3.3	Intracavity Saturation Spectroscopy	105
2.3.4	Lamb-Dip Frequency Stabilization of Lasers	108
2.4	Polarization Spectroscopy	110
2.4.1	Basic Principle	110
2.4.2	Line Profiles of Polarization Signals	112
2.4.3	Magnitude of Polarization Signals	117
2.4.4	Sensitivity of Polarization Spectroscopy	120
2.4.5	Advantages of Polarization Spectroscopy	123
2.5	Multiphoton Spectroscopy	124
2.5.1	Two-Photon Absorption	124
2.5.2	Doppler-Free Multiphoton Spectroscopy	127
2.5.3	Influence of Focusing on the Magnitude of Two-Photon Signals	131
2.5.4	Examples of Doppler-Free Two-Photon Spectroscopy	132
2.5.5	Multiphoton Spectroscopy	135
2.6	Special Techniques of Nonlinear Spectroscopy	138
2.6.1	Saturated Interference Spectroscopy	138
2.6.2	Doppler-Free Laser-Induced Dichroism and Birefringence	140
2.6.3	Heterodyne Polarization Spectroscopy	142
2.6.4	Combination of Different Nonlinear Techniques	143
2.7	Conclusion	146
2.8	Problems	146
3	Laser Raman Spectroscopy	149
3.1	Basic Considerations	149
3.2	Experimental Techniques of Linear Laser Raman Spectroscopy	155
3.3	Nonlinear Raman Spectroscopy	161
3.3.1	Stimulated Raman Scattering	162
3.3.2	Coherent Anti-Stokes Raman Spectroscopy	168
3.3.3	Resonant CARS and BOX CARS	171
3.3.4	Hyper-Raman Effect	173
3.3.5	Summary of Nonlinear Raman Spectroscopy	175
3.4	Special Techniques	175
3.4.1	Resonance Raman Effect	175

3.4.2	Surface-Enhanced Raman Scattering	176
3.4.3	Raman Microscopy	177
3.4.4	Time-Resolved Raman Spectroscopy	177
3.5	Applications of Laser Raman Spectroscopy	178
3.6	Problems	180
4	Laser Spectroscopy in Molecular Beams	183
4.1	Reduction of Doppler Width	184
4.2	Adiabatic Cooling in Supersonic Beams	192
4.3	Formation and Spectroscopy of Clusters and Van der Waals Molecules in Cold Molecular Beams	200
4.4	Nonlinear Spectroscopy in Molecular Beams	205
4.5	Laser Spectroscopy in Fast Ion Beams	208
4.6	Applications of FIBLAS	211
4.6.1	Spectroscopy of Radioactive Elements	211
4.6.2	Photofragmentation Spectroscopy of Molecular Ions	211
4.6.3	Saturation Spectroscopy in Fast Beams	213
4.7	Spectroscopy in Cold Ion Beams	215
4.8	Laser Photo-Detachment in Molecular Beams	216
4.9	Combination of Molecular Beam Laser Spectroscopy and Mass Spectrometry	218
4.10	Problems	223
5	Optical Pumping and Double-Resonance Techniques	225
5.1	Optical Pumping	226
5.2	Optical-RF Double-Resonance Technique	232
5.2.1	Basic Considerations	232
5.2.2	Laser-RF Double-Resonance Spectroscopy in Molecular Beams	235
5.3	Optical-Microwave Double Resonance	238
5.4	Optical-Optical Double Resonance	242
5.4.1	Simplification of Complex Absorption Spectra	243
5.4.2	Stepwise Excitation and Spectroscopy of Rydberg States	247
5.4.3	Stimulated Emission Pumping	256
5.5	Special Detection Schemes of Double-Resonance Spectroscopy	259
5.5.1	OODR-Polarization Spectroscopy	259
5.5.2	Polarization Labeling	262
5.5.3	Microwave-Optical Double-Resonance Polarization Spectroscopy	263
5.5.4	Hole-Burning and Ion-Dip Double-Resonance Spectroscopy	264
5.5.5	Triple-Resonance Spectroscopy	265
5.5.6	Photoassociation Spectroscopy	266
5.6	Problems	268

6	Time-Resolved Laser Spectroscopy	271
6.1	Generation of Short Laser Pulses	272
6.1.1	Time Profiles of Pulsed Lasers	272
6.1.2	Q-Switched Lasers	274
6.1.3	Cavity Dumping	276
6.1.4	Mode Locking of Lasers	278
6.1.5	Generation of Femtosecond Pulses	287
6.1.6	Optical Pulse Compression	294
6.1.7	Sub 10 fs Pulses with Chirped Laser Mirrors	299
6.1.8	Fiber Lasers	303
6.1.9	Soliton Lasers	304
6.1.10	Wavelength-Tunable Ultrashort Pulses	307
6.1.11	Shaping of Ultrashort Light Pulses	312
6.1.12	Generation of High-Power Ultrashort Pulses	313
6.1.13	Reaching the Attosecond Range	320
6.1.14	Summary of Short Pulse Generation	323
6.2	Measurement of Ultrashort Pulses	324
6.2.1	Streak Camera	325
6.2.2	Optical Correlator for Measuring Ultrashort Pulses	327
6.2.3	FROG Technique	337
6.2.4	SPIDER Technique	340
6.2.5	CRAB- and VAMPIRE-Techniques	344
6.2.6	Comparison of the Different Techniques	345
6.3	Lifetime Measurement with Lasers	346
6.3.1	Phase-Shift Method	348
6.3.2	Single-Pulse Excitation	350
6.3.3	Delayed-Coincidence Technique	351
6.3.4	Lifetime Measurements in Fast Beams	353
6.4	Spectroscopy in the Pico-to-Attosecond Range	356
6.4.1	Pump-and-Probe Spectroscopy of Collisional Relaxation in Liquids	358
6.4.2	Electronic Relaxation in Semiconductors	359
6.4.3	Femtosecond Transition State Dynamics	360
6.4.4	Real-Time Observations of Molecular Vibrations	361
6.4.5	Attosecond Spectroscopy of Atomic Inner Shell Processes	364
6.4.6	Transient Grating Techniques	366
6.5	Problems	367
7	Coherent Spectroscopy	369
7.1	Level-Crossing Spectroscopy	370
7.1.1	Classical Model of the Hanle Effect	371
7.1.2	Quantum-Mechanical Models	375
7.1.3	Experimental Arrangements	377
7.1.4	Examples	379
7.1.5	Stimulated Level-Crossing Spectroscopy	380

7.2	Quantum-Beat Spectroscopy	383
7.2.1	Basic Principles	384
7.2.2	Experimental Techniques	385
7.2.3	Molecular Quantum-Beat Spectroscopy	389
7.3	STIRAP Technique	391
7.4	Excitation and Detection of Wave Packets in Atoms and Molecules	393
7.5	Coherent Control	395
7.6	Optical Pulse-Train Interference Spectroscopy	396
7.7	Photon Echoes	399
7.8	Optical Nutation and Free-Induction Decay	405
7.9	Self-Induced Transparency	407
7.10	Coherent Dark States and Dark Resonances	409
7.11	Heterodyne Spectroscopy	411
7.12	Correlation Spectroscopy	412
7.12.1	Basic Considerations	413
7.12.2	Homodyne Spectroscopy	417
7.12.3	Heterodyne Correlation Spectroscopy	420
7.12.4	Fluorescence Correlation Spectroscopy and Single Molecule Detection	422
7.13	Optical Coherence Tomography	426
7.14	Problems	427
8	Laser Spectroscopy of Collision Processes	429
8.1	High-Resolution Laser Spectroscopy of Collisional Line Broadening and Line Shifts	430
8.1.1	Sub-Doppler Spectroscopy of Collision Processes	431
8.1.2	Combination of Different Techniques	434
8.2	Measurements of Inelastic Collision Cross Sections of Excited Atoms and Molecules	435
8.2.1	Measurements of Absolute Quenching Cross Sections	436
8.2.2	Collision-Induced Rovibronic Transitions in Excited States	437
8.2.3	Collisional Transfer of Electronic Energy	441
8.2.4	Energy Pooling in Collisions Between Excited Atoms	443
8.2.5	Spectroscopy of Spin-Flip Transitions	444
8.3	Spectroscopic Techniques for Measuring Collision-Induced Transitions in the Electronic Ground State of Molecules	446
8.3.1	Time-Resolved Infrared Fluorescence Detection	447
8.3.2	Time-Resolved Absorption and Double-Resonance Methods	448
8.3.3	Collision Spectroscopy with Continuous-Wave Lasers	452
8.3.4	Collisions Involving Molecules in High Vibrational States	453
8.4	Spectroscopy of Reactive Collisions	455
8.5	Spectroscopic Determination of Differential Collision Cross Sections in Crossed Molecular Beams	460

8.6	Photon-Assisted Collisional Energy Transfer	465
8.7	Problems	470
9	New Developments in Laser Spectroscopy	473
9.1	Optical Cooling and Trapping of Atoms	473
9.1.1	Photon Recoil	474
9.1.2	Measurement of Recoil Shift	476
9.1.3	Optical Cooling by Photon Recoil	478
9.1.4	Experimental Arrangements	481
9.1.5	Three-dimensional Cooling of Atoms; Optical Molasses	487
9.1.6	Cooling of Molecules	489
9.1.7	Optical Trapping of Atoms	491
9.1.8	Optical Micro-traps	498
9.1.9	Optical Cooling Limits	505
9.1.10	Bose–Einstein Condensation	508
9.1.11	Evaporative Cooling	509
9.1.12	Properties of the Bose–Einstein Condensate	513
9.1.13	Atom Lasers	515
9.1.14	Production and Trapping of Cold Fermi-Gases	517
9.1.15	BEC of Molecules	518
9.1.16	Atoms and Molecules in Optical Lattices	520
9.1.17	Applications of Cooled Atoms and Molecules	521
9.2	Spectroscopy of Single Ions	523
9.2.1	Trapping of Ions	523
9.2.2	Optical Sideband Cooling	527
9.2.3	Direct Observations of Quantum Jumps	528
9.2.4	Formation of Wigner Crystals in Ion Traps	531
9.2.5	Laser Spectroscopy of Ions in Storage Rings	533
9.2.6	Quantum Computer with Stored Ions	534
9.3	Optical Ramsey Fringes	535
9.3.1	Basic Considerations	536
9.3.2	Two-Photon Ramsey Resonance	539
9.3.3	Nonlinear Ramsey Fringes Using Three Separated Fields	542
9.3.4	Observation of Recoil Doublets and Suppression of One Recoil Component	545
9.3.5	Optical Ramsey Resonances Obtained Through an Equidistant Train of Laser Pulses	547
9.3.6	Atomic Fountain	548
9.4	Atom Interferometry	550
9.4.1	Mach–Zehnder Atom Interferometer	550
9.5	The One-Atom Maser	553
9.6	Spectral Resolution Within the Natural Linewidth	557
9.6.1	Time-Gated Coherent Spectroscopy	558
9.6.2	Coherence and Transit Narrowing	562
9.6.3	Raman Spectroscopy with Subnatural Linewidth	564

9.7	Absolute Optical Frequency Measurement and Optical Frequency Standards	566
9.7.1	Microwave–Optical Frequency Chains	566
9.7.2	Optical Frequency Combs	569
9.7.3	Spectral Extension of Frequency Combs	573
9.7.4	Applications of Optical Frequency Combs	574
9.7.5	Molecular Spectroscopy with Optical Frequency Combs	575
9.8	Squeezing	576
9.8.1	Amplitude and Phase Fluctuations of a Light Wave	577
9.8.2	Experimental Realization of Squeezing	581
9.8.3	Application of Squeezing to Gravitational Wave Detectors	584
9.9	Problems	586
10	Applications of Laser Spectroscopy	589
10.1	Applications in Chemistry	589
10.1.1	Laser Spectroscopy in Analytical Chemistry	590
10.1.2	Single-Molecule Detection	592
10.1.3	Laser-Induced Chemical Reactions	595
10.1.4	Coherent Control of Chemical Reactions	598
10.1.5	Laser Femtosecond Chemistry	601
10.1.6	Isotope Separation with Lasers	603
10.1.7	Summary of Laser Chemistry	606
10.2	Environmental Research with Lasers	606
10.2.1	Absorption Measurements	607
10.2.2	Atmospheric Measurements with LIDAR	609
10.2.3	Spectroscopic Detection of Water Pollution	616
10.2.4	Earth Science Applications	618
10.3	Applications to Technical Problems	619
10.3.1	Spectroscopy of Combustion Processes	620
10.3.2	Applications of Laser Spectroscopy to Materials Science	622
10.3.3	Laser-Induced Breakdown Spectroscopy (LIBS)	623
10.3.4	Measurements of Flow Velocities in Gases and Liquids	625
10.4	Applications in Biology	626
10.4.1	Energy Transfer in DNA Complexes	626
10.4.2	Time-Resolved Measurements of Biological Processes	627
10.4.3	Correlation Spectroscopy of Microbe Movements	629
10.4.4	Laser Microscope	630
10.4.5	Detection of Single Biological Molecules	635
10.5	Medical Applications of Laser Spectroscopy	636
10.5.1	Infrared and Raman Spectroscopy of Respiratory Gases	638
10.5.2	Lasers for Eye-Diagnostics	640
10.5.3	Detection of Tissue Anomalies and Cancer	642
10.5.4	Heterodyne Measurements of Ear Drums	644
10.5.5	Cancer Diagnostics and Photodynamic Therapy	645
10.5.6	Laser Lithotripsy	647

10.5.7 Laser-Induced Thermotherapy of Brain Cancer	649
10.5.8 Fetal Oxygen Monitoring	649
10.6 Concluding Remarks	650
Solutions	651
References	681
Index	751