

Contents

1. Introduction	1
2. Absorption and Emission of Light	5
2.1 Cavity Modes	5
2.2 Thermal Radiation and Planck's Law	8
2.3 Absorption, Induced and Spontaneous Emission	11
2.4 Basic Photometric Quantities	15
2.4.1 Definitions	15
2.4.2 Illumination of Extended Areas.	17
2.5 Discrete and Continuous Absorption and Emission Spectra.	19
2.6 Transition Probabilities	22
2.6.1 Lifetimes. Spontaneous and Radiationless Transitions	24
2.6.2 Semiclassical Description; Basic Equations	26
2.6.3 Weak-Field Approximation	29
2.6.4 Transition Probabilities with Broad-Band Excitation.	31
2.6.5 Phenomenological Inclusion of Decay Phenomena	33
2.6.6 Interaction with Strong Fields.	34
2.7 Coherence Properties of Radiation Fields.	38
2.7.1 Temporal Coherence	39
2.7.2 Spatial Coherence	41
2.7.3 Coherence Volume	42
2.7.4 The Coherence Function and the Degree of Coherence	45
2.8 Coherence of Atomic Systems.	50
2.8.1 Density Matrix	50
2.8.2 Coherent Excitation	51
2.8.3 Relaxation of Coherently Excited Systems	53
Problems.	55
3. Widths and Profiles of Spectral Lines	57
3.1 Natural Linewidth	58
3.1.1 Lorentzian Line Profile of the Emitted Radiation	58
3.1.2 Relation Between Linewidth and Lifetime	61
3.1.3 Natural Linewidth of Absorbing Transitions.	62
3.2 Doppler Width	67
3.3 Collision Broadening of Spectral Lines	71
3.3.1 Phenomenological Description	72
3.3.2 Theoretical Treatment of Elastic Collisions.	74
3.3.3 Relations Between Interaction Potential, Line Broadening and Shifts	80

3.3.4	Collisional Narrowing of Lines	84
3.4	Transit-Time Broadening	85
3.5	Homogeneous and Inhomogeneous Line Broadening	88
3.6	Saturation and Power Broadening	90
3.6.1	Saturation of Level Population by Optical Pumping	90
3.6.2	Saturation Broadening of Homogeneous Line Profiles	92
3.6.3	Power Broadening	93
3.7	Spectral Line Profiles in Liquids and Solids	95
	Problems	98
4.	Spectroscopic Instrumentation	99
4.1	Spectrographs and Monochromators	99
4.1.1	Basic Properties	102
a)	Speed of a Spectrometer	102
b)	Spectral Transmission	104
c)	Spectral Resolving Power	105
d)	Free Spectral Range	111
4.1.2	Prism Spectrometer	111
4.1.3	Grating Spectrometer	114
4.2	Interferometers	122
4.2.1	Basic Concepts	123
4.2.2	Michelson Interferometer	124
4.2.3	Mach-Zehnder Interferometer	129
4.2.4	Multiple-Beam Interference	133
4.2.5	Plane Fabry-Perot Interferometer	140
a)	The Plane FPI as a Transmission Filter	140
b)	Illumination with Divergent Light	142
c)	The Air-Spaced FPI.	145
4.2.6	Confocal Fabry-Perot Interferometer	147
4.2.7	Multilayer Dielectric Coatings	152
4.2.8	Interference Filters	156
4.2.9	Birefringent Interferometer	159
4.2.10	Tunable Interferometers	163
4.3	Comparison Between Spectrometers and Interferometers	164
4.3.1	Spectral Resolving Power	164
4.3.2	Light-Gathering Power	167
4.4	Accurate Wavelength Measurements	168
4.4.1	Precision and Accuracy of Wavelength Measurements	169
4.4.2	Today's Wavemeters	172
a)	The Michelson-Wavemeter	172
b)	Sigmatometer	175
c)	Computer-Controlled Fabry-Perot Wavemeter	177
d)	Fizeau Wavemeter	179
4.5	Detection of Light	181
4.5.1	Thermal Detectors	184
4.5.2	Photodiodes	190

a) Photoconductive Diodes	192
b) Photovoltaic Detectors	193
c) Fast Photodiodes	195
d) Avalanche Diodes	198
4.5.3 Photodiode Arrays	199
4.5.4 Photoemissive Detectors	202
a) Photocathodes	202
b) Photocells	204
c) Photomultipliers	205
d) Photoelectric Image Intensifiers	209
4.5.5 Detection Techniques and Electronic Equipment	212
a) Photon Counting	212
b) Measurements of Fast Transient Events	214
c) Optical Oscilloscope	217
4.6 Conclusions	218
Problems	220
5. Lasers as Spectroscopic Light Sources	222
5.1 Fundamentals of Lasers	222
5.1.1 Basic Elements of a Laser	222
5.1.2 Threshold Condition	223
5.1.3 Rate Equations	226
5.2 Laser Resonators	228
5.2.1 Open Optical Resonators	229
5.2.2 Spatial Field Distributions in Open Resonators	232
5.2.3 Confocal Resonators	234
5.2.4 General Spherical Resonators	237
5.2.5 Diffraction Losses of Open Resonators	238
5.2.6 Stable and Unstable Resonators	239
5.2.7 Ring Resonators	244
5.2.8 Frequency Spectrum of Passive Resonators	245
5.3 Spectral Characteristics of Laser Emission	248
5.3.1 Active Resonators and Laser Modes	249
5.3.2 Gain Saturation	251
5.3.3 Spatial Hole Burning	253
5.3.4 Multimode Lasers and Gain Competition	255
5.3.5 Mode Pulling	259
5.4 Experimental Realization of Single-Mode Lasers	260
5.4.1 Line Selection	260
5.4.2 Suppression of Transverse Modes	264
5.4.3 Selection of Single Longitudinal Modes	266
5.4.4 Intensity Stabilization	273
5.4.5 Wavelength Stabilization	276
5.5 Controlled Wavelength Tuning of Single-Mode Lasers	287
5.5.1 Continuous Tuning Techniques	287
5.5.2 Wavelength Calibration	292
5.6 Linewidths of Single-Mode Lasers	294
5.7 Tunable Lasers	297

5.7.1	Basic Concepts	298
5.7.2	Semiconductor-Diode Lasers	299
5.7.3	Spin-Flip Raman Lasers	304
5.7.4	Tunable Solid-State Lasers	306
5.7.5	Color-Center Lasers	309
5.7.6	Dye Lasers	312
	a) Flashlamp-Pumped Dye Lasers	316
	b) Pulsed-Laser-Pumped Dye Lasers	318
	c) Continuous-Wave Dye Lasers	324
5.7.7	Excimer Lasers	329
5.7.8	Free-Electron Lasers	331
5.8	Nonlinear Optical-Mixing Techniques	335
5.8.1	Physical Background	335
5.8.2	Second-Harmonic Generation	339
5.8.3	Sum-Frequency and Higher-Harmonic Generation	344
5.8.4	X-Ray Lasers	348
5.8.5	Difference-Frequency Spectrometer	349
5.8.6	Optical Parametric Oscillator	352
5.8.7	Tunable Raman Lasers	356
5.9	Gaussian Beams	358
	Problems	365
6.	Doppler-Limited Absorption	
	and Fluorescence Spectroscopy with Lasers	367
6.1	Advantages of Lasers in Spectroscopy	367
6.2	High-Sensitivity Methods of Absorption Spectroscopy	371
6.2.1	Frequency Modulation	372
6.2.2	Intracavity Absorption	375
6.3	Direct Determination of Absorbed Photons	384
6.3.1	Fluorescence Excitation Spectroscopy	384
6.3.2	Photoacoustic Spectroscopy	389
6.3.3	Optothermal Spectroscopy	394
6.4	Ionization Spectroscopy	396
6.4.1	Basic Techniques	397
	a) Photoionization	397
	b) Collision-Induced Ionization	397
	c) Field Ionization	398
6.4.2	Sensitivity of Ionization Spectroscopy	399
6.4.3	Pulsed vs CW Lasers for Photoionization	400
6.4.4	Resonant Two-Photon Ionization Combined with Mass Spectrometry	402
6.4.5	Thermionic Diode	404
6.5	Optogalvanic Spectroscopy	405
6.6	Velocity-Modulation Spectroscopy	408
6.7	Laser Magnetic Resonance and Stark Spectroscopy	410
6.7.1	Laser Magnetic Resonance	410
6.7.2	Stark Spectroscopy	413
6.8	Laser-Induced Fluorescence	414

6.8.1	Molecular Spectroscopy by Laser-Induced Fluorescence	415
6.8.2	Experimental Aspects of LIF	417
6.8.3	LIF of Polyatomic Molecules	419
6.8.4	Determination of Population Distributions by LIF	421
6.9	Comparison Between the Different Methods	424
	Problems	428
7.	Nonlinear Spectroscopy	430
7.1	Linear and Nonlinear Absorption	430
7.2	Saturation of Inhomogeneous Line Profiles	436
7.2.1	Hole Burning	437
7.2.2	Lamb Dips	441
7.3	Saturation Spectroscopy	444
7.3.1	Experimental Schemes	445
7.3.2	Cross-Over Signals	448
7.3.3	Intracavity Saturation Spectroscopy	450
7.3.4	Lamb-Dip Frequency Stabilization of Lasers	452
7.4	Polarization Spectroscopy	454
7.4.1	Basic Principle	454
7.4.2	Line Profiles of Polarization Signals	456
7.4.3	Magnitude of Polarization Signals	460
7.4.4	Sensitivity of Polarization Spectroscopy	464
7.4.5	Advantages of Polarization Spectroscopy	465
7.5	Multiphoton Spectroscopy	466
7.5.1	Two-Photon Absorption	466
7.5.2	Doppler-Free Multiphoton Spectroscopy	469
7.5.3	Influence of Focussing on the Magnitude of the Two-Photon Signal	473
7.5.4	Examples of Doppler-Free Two-Photon Spectroscopy	475
7.5.5	Multiphoton Spectroscopy	476
7.6	Special Techniques of Nonlinear Spectroscopy	479
7.6.1	Saturated Interference Spectroscopy	480
7.6.2	Doppler-Free Laser-Induced Dichroism and Birefringence	482
7.6.3	Heterodyne Polarization Spectroscopy	484
7.6.4	Combination of Different Nonlinear Techniques	485
7.7	Conclusion	486
	Problems	488
8.	Laser Raman Spectroscopy	489
8.1	Basic Considerations	489
8.2	Experimental Techniques of Linear Laser Raman Spectroscopy	494
8.3	Nonlinear Raman Spectroscopy	499
8.3.1	Stimulated Raman Scattering	499
8.3.2	Coherent Anti-Stokes Raman Spectroscopy	505
8.3.3	Resonant CARS and BOX CARS	508
8.3.4	Hyper-Raman Effect	510

8.3.5 Summary of Nonlinear Raman Spectroscopy	511
8.4 Applications of Laser Raman Spectroscopy	512
Problems	515
9. Laser Spectroscopy in Molecular Beams	516
9.1 Reduction of Doppler Width	516
9.2 Adiabatic Cooling in Supersonic Beams	524
9.3 Formation and Spectroscopy of Clusters and Van der Waals Molecules in Cold Molecular Beams	533
9.4 Nonlinear Spectroscopy in Molecular Beams	536
9.5 Laser Spectroscopy in Fast Ion Beams	538
9.6 Applications of FIBLAS	542
9.6.1 Spectroscopy of Radioactive Elements	542
9.6.2 Photofragmentation Spectroscopy of Molecular Ions	543
9.6.3 Laser Photodetachment Spectroscopy	545
9.6.4 Saturation Spectroscopy in Fast Beams	545
9.7 Spectroscopy in Cold Ion Beams	546
9.8 Combination of Molecular Beam Laser Spectroscopy and Mass Spectrometry	548
Problems	551
10. Optical Pumping and Double-Resonance Techniques	552
10.1 Optical Pumping	553
10.2 Optical-RF Double-Resonance Technique	559
10.2.1 Basic Considerations	559
10.2.2 Laser RF Double-Resonance Spectroscopy in Molecular Beams	562
10.3 Optical-Microwave Double Resonance	565
10.4 Optical-Optical Double Resonance	569
10.4.1 Simplification of Complex Absorption Spectra	570
10.4.2 Stepwise Excitation and Spectroscopy of Rydberg States	574
10.4.3 Stimulated-Emission Pumping	582
10.5 Special Detection Schemes of Double-Resonance Spectroscopy	585
10.5.1 OODR-Polarization Spectroscopy	585
10.5.2 Polarization Labelling	586
10.5.3 Microwave-Optical Double-Resonance Polarization Spectroscopy	589
10.5.4 Hole-Burning and Ion-Dip Double-Resonance Spectroscopy	589
10.5.5 Triple-Resonance Spectroscopy	590
Problems	592
11. Time-Resolved Laser Spectroscopy	594
11.1 Generation of Short Laser Pulses	595
11.1.1 Time Profiles of Pulsed Lasers	595
11.1.2 Q-Switched Lasers	597

11.1.3	Cavity Dumping	599
11.1.4	Mode-Locking of Lasers	601
	a) Active Mode-Locking	602
	b) Passive Mode-Locking	606
	c) Synchronous Pumping with Mode-Locked Lasers	607
11.1.5	Generation of Femtosecond Pulses	610
	a) The Colliding Pulse Mode-Locked Laser	610
	b) Lower Limit of Pulse Width	612
11.1.6	Optical Pulse Compression	614
11.1.7	Soliton Laser	617
11.1.8	Generation of High-Power Ultrashort Pulses	619
11.2	Measurement of Ultrashort Pulses	622
11.2.1	Streak Camera	622
11.2.2	Optical Correlator for Measuring Ultrashort Pulses	624
11.3	Lifetime Measurements with Lasers	630
11.3.1	Phase-Shift Method	632
11.3.2	Single-Pulse Excitation	634
11.3.3	Delayed-Coincidence Technique	635
11.3.4	Lifetime Measurements in Fast Beams	637
11.4	Pump and Probe Technique	640
11.4.1	Pump-and-Probe Spectroscopy of Collisional Relaxation in Liquids	641
11.4.2	Electronic Relaxation in Semiconductors	642
11.4.3	Femtosecond Transition State Dynamics	643
11.4.4	Real-Time Observations of Molecular Vibrations	644
	Problems	647
12.	Coherent Spectroscopy	648
12.1	Level-Crossing Spectroscopy	649
12.1.1	Classical Model for the Hanle Effect	650
12.1.2	Quantum-Mechanical Models	653
12.1.3	Experimental Arrangements	656
12.1.4	Examples	657
12.1.5	Stimulated Level-Crossing Spectroscopy	658
12.2	Quantum-Beat Spectroscopy	661
12.2.1	Basic Principles	661
12.2.2	Experimental Techniques	663
12.2.3	Molecular Quantum-Beat Spectroscopy	667
12.4	Optical Pulse-Train Interference Spectroscopy	671
12.5	Photon Echoes	673
12.6	Optical Nutation and Free Induction Decay	680
12.7	Heterodyne Spectroscopy	682
12.8	Correlation Spectroscopy	683
12.8.1	Basic Considerations	684
12.8.2	Homodyne Spectroscopy	688
12.8.3	Heterodyne Correlation Spectroscopy	690
	Problems	693

13. Laser Spectroscopy of Collision Processes	694
13.1 High-Resolution Laser Spectroscopy of Collisional Line Broadening and Line Shifts.	695
13.1.1 Sub-Doppler Spectroscopy of Collision Processes . .	696
13.1.2 Combination of Different Techniques.	699
13.2 Measurements of Inelastic Collision Cross Sections of Excited Atoms and Molecules	701
13.2.1 Measurements of Absolute Quenching Cross Sections	701
13.2.2 Collision-Induced Rovibronic Transitions in Excited States	702
13.2.3 Collisional Transfer of Electronic Energy	707
13.2.4 Energy Pooling in Collisions Between Excited Atoms	709
13.2.5 Spectroscopy of Spin-Flip Transitions.	711
13.3 Spectroscopic Techniques for Measuring Collision-Induced Transitions in the Electronic Ground State of Molecules . .	713
13.3.1 Time-Resolved Infrared Fluorescence Detection . .	714
13.3.2 Time-Resolved Absorption and Double-Resonance Methods	715
13.3.3 Collision Spectroscopy with CW Lasers	718
13.3.4 Collisions Involving Molecules in High Vibrational States	720
13.4 Spectroscopy of Reactive Collisions	721
13.5 Spectroscopic Determination of Differential Collision Cross Sections in Crossed Molecular Beams	726
13.6 Photon-Assisted Collisional Energy Transfer	731
Problems	735
14. New Developments in Laser Spectroscopy	736
14.1 Optical Cooling and Trapping of Atoms	736
14.1.1 Photon Recoil.	737
14.1.2 Measurements of the Recoil Shift	739
14.1.3 Optical Cooling by Photon Recoil	741
14.1.4 Experimental Arrangements	744
14.1.5 Induced Dipole Forces in a Radiation Field	749
14.1.6 Optical Trapping of Atoms	751
14.1.7 Cooling Limits	753
14.1.8 Applications of Cooled Atoms	755
14.2 Spectroscopy of Single Ions	757
14.2.1 Trapping of Ions	757
14.2.2 Optical Sideband Cooling	759
14.2.3 Direct Observations of Quantum Jumps	761
14.2.4 Formation of Wigner Crystals in Ion Traps.	764
14.2.5 Laser Spectroscopy in Storage Rings.	766
14.3 Optical Ramsey Fringes	767
14.3.1 Basic Considerations.	767
14.3.2 Two-Photon Ramsey Resonances	771
14.3.3 Nonlinear Ramsey Fringes Using Three Separated Fields	775

14.3.4	Observation of Recoil Doublets and Suppression of One Recoil Component	778
14.4	Atom Interferometry	779
14.5	The One-Atom Maser	781
14.6	Spectral Resolution Within the Natural Linewidth	785
14.6.1	Time-Gated Coherent Spectroscopy	785
14.6.2	Coherence and Transit Narrowing	790
14.6.3	Raman Spectroscopy with Sub-Natural Linewidth	791
14.7	Absolute Optical-Frequency Measurement and Optical-Frequency Standards	794
14.8	Squeezing	797
14.8.1	Amplitude and Phase Fluctuations of a Light Wave	798
14.8.2	Experimental Realization of Squeezing	802
14.8.3	Application of Squeezing to Gravitational Wave Detectors	804
15.	Applications of Laser Spectroscopy	806
15.1	Applications in Chemistry	806
15.1.1	Laser Spectroscopy in Analytical Chemistry	806
15.1.2	Laser-Induced Chemical Reactions	809
15.1.3	Laser Femtosecond-Chemistry	813
15.1.4	Isotope Separation with Lasers	815
15.1.5	Summary of Laser Chemistry	817
15.2	Environmental Research with Lasers	818
15.2.1	Absorption Measurements	818
15.2.2	Atmospheric Measurements with LIDAR	820
15.2.3	Spectroscopic Detection of Water Pollution	824
15.3	Applications to Technical Problems	825
15.3.1	Spectroscopy of Combustion Processes	825
15.3.2	Applications of Laser Spectroscopy to Materials Science	827
15.3.3	Measurements of Flow Velocities in Gases and Liquids	829
15.4	Applications in Biology	830
15.4.1	Energy Transfer in DNA Complexes	830
15.4.2	Time-Resolved Measurements of Biological Processes	831
15.4.3	Correlation Spectroscopy of Microbe Movements	833
15.4.4	Laser Microscope	834
15.5	Medical Applications of Laser Spectroscopy	835
15.5.1	Applications of Raman Spectroscopy in Medicine	836
15.5.2	Heterodyne Measurements of Ear Drums	837
15.5.3	Cancer Diagnostics and Therapy with the HPD Technique	838
15.5.4	Laser Lithotripsy	840
15.6	Concluding Remarks	841
	References	843
	Subject Index	917