7

Contents

Preface	XII	ı
Reference	ces	XVI

1	Plasma as an Object of Spectroscopy 1
	General Notions 1
1.1	The Concept of Low-Temperature Plasma. Diagnostics
	Problems 1
1.2	Equilibrium Plasma 6
1.2.1	Energy Distribution of Particles 6
1.2.2	Law of Mass Action. Neutral and Charged Particle Densities
1.2.3	Heat Emission. Kirchhoff's Law 11
1.3	Models of Equilibrium and the Associated Parameters 14
1.3.1	Local Thermal Equilibrium (LTE) Model 14
1.3.2	Partial Local Thermal Equilibrium (PLTE) Model 16
1.3.3	Model of Coronal Equilibrium (MCE) 20
1.3.4	Collisional-Radiative Model (CRM) 21
1.4	Optical Spectrum and Plasma Parameters 22
	References 25
2	Basic Concepts and Parameters Associated with the Emission,
	Absorption and Scattering of Light by Plasma 27
2.1	Photometric Quantities. Remarks on Terminology 27
2.2	Spectral Line Profile 31
2.2.1	Lorentz Broadening 32
2.2.2	Doppler Broadening 38
2.2.3	Joint Action of Natural, Doppler and Collision Broadening 41
2.3	Absorption in Lines 44
2.4	Emission in Lines. Optical Density Manifestations 46
2.5	Emission and Absorption in Continuous Spectrum 50
2.5.1	ff Bremsstrahlung Emission 52



VIII	Contents
------	----------

2.5.2	ff Bremsstrahlung Absorption 54
2.5.3	fb Recombination Emission 55
2.5.4	Absorption Cross Section in bf Photoionization 57
2.5.5	Emission and Absorption of Radiation in the Case of Joint
	Action of the ff Bremsstrahlung and fb Recombination
	Mechanisms 58
2.6	Scattering of Light 60
2.6.1	Thomson Scattering on a Free Electron 60
2.6.2	Scattering on a Bound Electron 63
	References 63
3	Emission, Absorption and Scattering Techniques for Determining
	the Densities of Particles in Discrete Energy States 67
3.1	Emission Techniques 67
3.1.1	Identification of Spectra 67
3.1.2	Absolute Measurements 68
3.1.3	Emission of Extended Inhomogeneous Sources 71
3.2	Absorption Techniques Using Classical Emitters 75
3.2.1	Absorption Against the Background of Continuous Spectrum 75
3.2.2	Line Absorption 78
3.2.3	Self-Absorption of Multiplet Lines 83
3.3	Absorption Spectroscopy Using Tunable and Broadband
	Lasers 84
3.3.1	On the Advantages of Laser Sources Over Their Classical
	Counterparts in Direct Absorption Measurements 84
3.3.2	On the Noise Limitation of Sensitivity 86
3.3.3	Diode Laser Spectroscopy in the IR Region 88
3.3.4	Nonstationary Coherent Effects in Absorption Measurements 92
3.3.5	Use of the Classical Multipass Absorption Cells 95
3.3.6	Intracavity Absorption 95
3.3.7	Measuring Absorption from the Attenuation of Light with Time 99
3.4	Indirect Methods for Measuring Absorption of Laser Light 103
3.4.1	Induced Fluorescence 104
3.4.1.1	General Characteristic 104
3.4.1.2	Fluorescence Excitation by Continuous-Wave and Pulsed
	Laser Light 107
3.4.1.3	Induced Fluorescence Saturation and Decay 109
3.4.1.4	Induced Fluorescence Quenching and Taking Account
	of this Process 112
3.4.1.5	Restrictions Imposed by the Plasma's Own Glow 118
3.4.2	Optogalvanic Spectroscopy 121

3.4.2.1	The Use of the Optogalvanic Effect to Measure Light Absorption
	in Plasma 121
3.4.2.2	High-Resolution Optogalvanic Spectroscopy 124
3.5	Multiphoton Processes. Raman Scattering 129
3.5.1	Two-Photon Absorption 130
3.5.2	Spontaneous Raman Scattering 133
3.5.3	Stimulated Raman Scattering 135
3.5.4	Coherent Anti-Stokes Scattering 137
	References 143
4	Intensities in Spectra and Plasma Energy Distribution in the
	Internal and Translational Degrees of Freedom of Atoms and
4.1	Molecules 147 Donnley Broad arrive Velenity Distribution of Porticles Newtral
4.1	Doppler Broadening, Velocity Distribution of Particles, Neutral
111	Gas Temperature 147 Personal on the Processing of Line Profiles 148
4.1.1	Remarks on the Processing of Line Profiles 148
4.1.1.1	Registered and True Profiles 148
4.1.1.2	Predominantly Doppler Broadening Regions 149
4.1.1.3	Recovery of the Form of the Velocity Distribution of Particles 150
4.1.2	Examples of Abnormal Doppler Broadening and Nonequilibrium
412	Velocity Distributions of Neutral Particles in Plasma 151
4.1.3	Excitation and Relaxation of Atoms and Molecules with
1121	Nonequilibrium Velocity in Interactions with Heavy Particles 154
4.1.3.1	Source Function 154
4.1.3.2	Relaxation of the Average Kinetic Energy of Particles with a
4122	Finite Lifetime 155
4.1.3.3	Relaxation of the Form of the Velocity Distributions of Particles
	in the Case of Large Deviations from Equilibrium and Finite
414	Lifetime 159
4.1.4	On the Determination of the Gas Temperature from the Doppler
	Broadening of the Lines Emitted by Atoms and Molecules
	Excited by Electrons 161
4.1.5	Spectroscopic Manifestations of the Motion of Ions in Plasma 164
4.2	Distribution of Molecules Among Rotational Levels 167
4.2.1	On the Isolation of the Boltzmann Ensembles in the Bound State
	System of Particles 167
4.2.2	Distributions of Molecules Among Rotational Levels in an
	Electronic State with a Long Lifetime 170
4.2.3	Electron Impact Excitation of the Electronic-Vibrational-
	Rotational (EVR) Levels of Molecules 174
4.2.3.1	Observations and General Considerations 174

X	Contents
---	----------

4.2.3.2	Experimental Determination of the Electron-Impact-Induced
	Changes in the Rotational States of Molecules in Plasma 177
4.2.4	Excitation of EVR Levels by Heavy Particles 181
4.2.4.1	OH Radical. Violet Bands 181
4.2.4.2	N ₂ Molecules. Second Positive System 183
4.2.5	On Gas Temperature Measurements in the Presence of Parallel
	Molecular Rotation Excitation Channels 184
4.2.5.1	Extension of the Form of Distribution of the Hot Molecules
	to the Region of Low Rotational Levels 185
4.2.5.2	Spectral Resolution 185
4.2.5.3	Effect of the Conditions Occuring in Plasma on the Rotational
	Temperature of the Hot Group 188
4.3	Line Intensities in the Vibrational Structure of Spectra and
	Distributions of Molecules Among Vibrational Levels 191
4.3.1	Elements of Vibrational Kinetics. Vibrational Energy and
	Temperature 191
4.3.1.1	Harmonic Oscillator Approximation 192
4.3.1.2	Effect of Anharmonicity 194
4.3.1.3	Diatomic Molecular Mixture and Polyatomic Molecules 197
4.3.2	Vibrational Temperature and Distribution Measurements by
	Absorption
	Spectroscopy Techniques 199
4.3.3	Emission Methods in the IR Region of the Spectrum 206
4.3.4	Combinations of Emission and Absorption Techniques.
	Spectrum Inversion 211
4.3.5	Raman Scattering 216
4.3.6	Determination of the Vibrational Temperatures of Molecules in
	the Electronic Ground States from Electronic Transition Spectra 220
4.4	Distribution of Particles Among Electronic Levels 224
	References 227
5	Moscuring Concentrations of Atoms and Malanda age
5.1	Measuring Concentrations of Atoms and Molecules 235 General 235
5.2	Determining Atomic Concentrations by Absorption
J.Z	Techniques 237
5.2.1	Neutral Unexcited Atoms 237
5.2.2	Metastable Atoms 249
5.2.3	Low-Multiplicity Positive Ions 266
5.3	Determination of Molecular Concentration by the Absorption
	Method 268
5.3.1	Probabilities of Optical Transitions in Diatomic Molecules 269

5.3.2	Determination of Diatomic Molecular Concentrations from
	Absorption on Electronic Spectrum Lines 272
5.3.3	Determination of Molecular Concentration from Absorption
	in Vibrational–Rotational Spectra 278
5.3.4	Absorption of Radiation by Diatomic Molecules
	in Metastable Electronic States 281
5.3.5	Absorption of IR Radiation by Polyatomic Molecules 281
5.3.6	Absorption of Radiation by Molecular Ions 284
5.4	Actinometric Methods 288
5.5	Negative Ions 297
5.5.1	Concentration Measurements 298
5.5.2	Absorption of Light by the ${ m H^-}$ Ions in Hydrogen LTE Plasma 301 References 303
6	Spectral Methods of Determining Electronic and Magnetic Fields in Plasma 307
6.1	Determination of Electric Fields from the Spontaneous Emission
	of Radiation by Atoms in Plasma 312
6.1.1	Hydrogen-Like Atoms 312
6.1.2	Non-Hydrogen-Like Atoms 318
6.2	Laser Stark Spectroscopy 322
6.2.1	Stark Spectroscopy of Atoms 323
6.2.2	Laser-Induced Fluorescence of Polar Molecules in Electric
	Field 329
6.2.3	Multiphoton Excitation of Atoms 334
6.2.4	Coherent Four-Wave Stark Scattering Spectroscopy 337
6.3	Magnetic Field Investigations 342
6.3.1	Measurements Based on the Faraday Effect 342
6.3.2	Spectral Methods 343
	References 346
7	Determination of the Parameters of the Electronic Component of Plasma 351
7.1	Interferometry 351
7.2	Stark Broadening of Spectral Lines 356
7.2.1	General 356
7.2.2	Plasma Microfields 357
7.2.3	Linear Stark Effect 358
7.2.4	Quadratic Stark Effect 364
7.3	Truncation of Spectral Series of Hydrogen-Like Atoms 367
7.4	Intensities in Continuous Spectrum 371
7.5	Scattering of Light on Electrons 374

7.5.1	Scattering of Light by Randomly Moving Electrons (Thomson Scattering) 375
7.5.2	Manifestation Regions of the Thomson and Collective Scattering Mechanisms 377
7.5.3	Scattered Spectrum and Plasma Parameters (Direct Problem) 379
7.5.4	Determination of Plasma Parameters from Scattered Spectra (Inverse Problem) 381
7.5.5	Limitations of the Method, Sensitivity and Examples 385
7.6	Some Remarks on Measurements from Intensities in Line and
	Band Spectra 391
	References 393
8	Some Information on Spectroscopy Techniques 397
8.1	Characteristics of Optical Materials. Main Relations 398
8.1.1	Reflection at an Interface 398
8.1.2	Dispersion of the Optical Properties of Materials 399
8.1.3	Transmission and Reflection of Thin Films 400
8.1.3.1	Metal Films 400
8.1.3.2	Dielectric Films 402
8.2	Spectral Instruments 406
8.2.1	Slit Instruments 409
8.2.2	Interferometers 414
8.2.3	Spectral Instruments with Interference Modulation 425
8.2.3.1	Fourier(-Transform) Spectrometers 425
8.2.3.2	Interference Spectrometers with Selective Amplitude
	Modulation (ISSAM) 430
8.2.4	Raster Spectrometers 431
8.2.5	Acousto-optic Spectrometers 433
8.3	Gas-Discharge Light Sources 439
8.3.1	Illumination Engineering Quantities 439
8.3.2	Gas Discharges in an Envelope (Lamps) 441
8.3.2.1	Continuous-Discharge Lamps 441
8.3.2.2	Pulsed-Discharge Lamps 448
8.3.3	Open Light Sources 456
8.3.3.1	Continuous-Discharge Sources 456
8.3.3.2	Pulsed-Discharge Sources 456
8.4	Photodetectors 460
8.4.1	Parameters 461
8.4.1.1	Sensitivity 461
8.4.1.2	Noise 462
8.4.1.3	
8.4.1.4	Inertia 464

8.4.2	Main Types of Single-Element Detectors 464
8.4.2.1	Thermal Detectors 464
8.4.2.2	Photoelectric (Quantum, Photonic) Detectors with
	Extrinsic Photoeffect 466
8.4.2.3	Photoelectric Detectors with Intrinsic Photoeffect 470
8.4.2.4	Photoemulsion 471
8.4.2.5	Comparative Characteristics of Single-Element Detectors 473
8.4.3	Multielement and Distributed Photodetectors 477
8.4.3.1	Spatial Resolution 477
8.4.3.2	Photographic Detectors 478
8.4.3.3	Image Converter and Intensifier Tubes 479
8.4.3.4	Charge-Coupled Detectors 480
	References 484
Append	lix A
	Statistical Weights and Statistical Sums 487
A.1	Statistical Weight of Energy Levels in Atoms and Ions 487
A.2	Statistical Weight of Electronic States in Molecules 488
A.3	Statistical Weight of Vibrational Levels of Molecules 488
A.4	Statistical Weight of Rotational Levels of Molecules 489
A.4.1	Statistical Sum of Atoms and Ions 492
A.4.2	Statistical Sum of Molecules 492
	References 495
Append	lix B
	Conversion of Quantities Used to Describe Optical
	Transition Probabilities in Line Spectra 497
	References 497
Append	
	Two-Photon Absorption Cross Sections for Some Atoms and
	Molecules in the Ground State 499
	References 503
Append	
	Information on Some Diatomic Molecules for the Identification
D 1	and Processing of Low-Temperature Plasma Spectra 505
D.1	Brief Information from Molecular Spectroscopy – Designations
	of States and Transitions, Coupling Types, Selection Rules,
D11	General Spectrum Structure 505
D.1.1	General Rules 508
D.1.2	More Particular Rules 509
D.2	Nitrogen N_2 , N_2^+ 513

D.2.1	Electronic States, Electronic Transition Systems (Bands) 513	į
D.2.2	Molecular Constants of the Ground and Combining States	513
D.2.3	Second Positive (2 ⁺) System 513	
D.2.3.1	Vibrational Structure of the $C^3\Pi(v')$ – $B^3\Pi(v'')$ Transition 5:	17
D.2.3.2	Rotational Structure 517	
D.2.4	First Positive (1 ⁺) System 519	
D.2.4.1	Vibrational Structure of the $B^3\Pi_g(v')$ – $A^3\Sigma_u^+(v'')$ Transition	519
D.2.4.2	Rotational Structure 519	
D.2.5	First Negative (1 ⁻) System 522	
D.2.6	Vibrational Structure of the $B^2\Sigma_u^+(v')$ – $X^2\Sigma_g^+(v'')$ Transition	522
D.2.6.1	Rotational Structure 522	
D.3	Carbon Oxide CO 526	
D.3.1	Electronic States, Electronic Transitions 526	
D.3.2	Molecular Constants of the Ground and Combining States	526
D.3.3	Ångström Bands System $B^1\Sigma^+$ – $A^1\Pi$ 526	
D.3.3.1	Vibrational Structure 526	
D.3.3.2	Rotational Structure of the $B^1\Sigma^+$ – $A^1\Pi$ Bands 526	
D.4	Hydrogen H ₂ and Deuterium D ₂ 528	
D.4.1	Electronic States, Electronic Transitions 528	
D.4.2	Molecular Constants of the Ground and Combining States	528
D.4.3	Ortho- and Para-Modifications 529	
D.4.4	Fulcher- α Bands System $d^3\Pi_u$ - $a^3\Sigma_g^+$ 530	
D.4.4.1	Vibrational Structure 531	
D.4.4.2	Rotational Structure 531	
D.4.5	$I^{1}\Pi_{g}-B^{1}\Sigma_{u}^{+}$ Transition 533	
D.4.5.1	Vibrational Structure 533	
D.4.5.2	Rotational Structure 535	
D.4.6	$G^{1}\Sigma_{g}^{+}$ – $B^{1}\Sigma_{u}^{+}$ Transition 537	
D.4.6.1	Vibrational Structure 537	
D.4.6.2	Rotational Structure 537	
D.5	Nitrogen Oxide NO 541	
D.5.1	Electronic States, Electronic Transitions 541	
D.5.2	Molecular Constants of the Ground and Combining States	541
D.5.3	γ System (195–340 nm) 541	
D.5.3.1		
D.5.3.2	Rotational Structure 542	
D.6	Cyanogen CN 543	
D.6.1	Electronic States, Electronic Transitions 543	
D.6.2	Molecular Constants of the Ground and Combining States	545
D.6.3	Violet System 546	
D.6.3.1	Vibrational Structure 546	

D.6.3.2	Rotational Structure 546		
D.7	Carbon Radical C ₂ 548		
D.7.1	Electronic States, Electronic Transitions 548		
D.7.2	Molecular Constants of States 548		
D.7.3	Swan Bands System 548		
D.7.3.1	Vibrational Structure 548		
D.7.3.2	Rotational Structure 550		
D.8	CH Radical 551		
D.8.1	Electronic States, Electronic Transitions 551		
D.8.2	8	553	
D.8.3	$B^2\Sigma^-$ – $X^2\Pi$ Transition 555		
D.8.3.1	Rotational Structure 556		
D.8.4	$C^2\Sigma^+$ – $X^2\Pi$ Transition 556		
D.9	Hydroxyl Radical OH 558		
D.9.1	Electronic States, Electronic Transitions 558		
D.9.2	Molecular Constants of the Ground and Combining States	560	
D.9.2.1	Rotational Structure 560		
	References 566		
Append	liv F		
Append	Rotational Line Intensity Factors in the Electronic–Vibrational		
	Transition Spectra of Diatomic Molecules 569		
E.1	Singlet Transitions 570		
E.1.1	${}^{1}X_{-}{}^{1}X_{+}\Delta\Lambda = 0$ Transitions 570		
E.1.2	1 X $^{-1}$ Y, $\Delta \Lambda = \pm 1$ Transitions 570		
E.2	Doublet Transitions 570		
E.2.1	$^{2}X-^{2}X$, $\Delta\Lambda = 0$ Transitions 571		
E.2.2	$^{2}X-^{2}Y$, $\Delta\Lambda = \pm 1$ Transitions 572		
E.3	Triplet Transitions 573		
E.3.1	${}^{3}X - {}^{3}X$, $\Delta \Lambda = 0$ Transitions 574		
E.3.1.1	Dipole-Forbidden Branches 576		
E.3.2	$^{3}X-^{3}Y$, $\Delta\Lambda = \pm 1$ Transitions 577		
E.3.3	$^{3}\Sigma^{-3}\Delta$, $\Delta\Lambda = \pm 2$ Transitions 579		
E.4	Remarks on the Normalization of Rotational Line Intensity		
	Factors 580		
E 5	On Symbolic Notation 581		

References 582

Ap	pen	dix	F
----	-----	-----	---

Measurement of the Absolute Populations of Excited Atoms by Classical Spectroscopy Techniques 583

Yu. B. Golubovskii References 595

Appendix G

	General Information for Plasma Spectroscopy Problems 597
G.1	Physical Constants 597
G.2	Atomic Values 598
G.3	Correspondence between Spectral and Traditional Energy
	Measurement Units 598
G.4	Electrical Units 599
G.5	Units from Molecular Kinetics 599
G.6	Quantities from Gas-Discharge Physics 600
	References 600

Index 603

Appendix H

Optical Constants of Materials* 611

H.1 Transmission 611 H.2 Refractive Indices 635 H.3 Reflection 638 References 651