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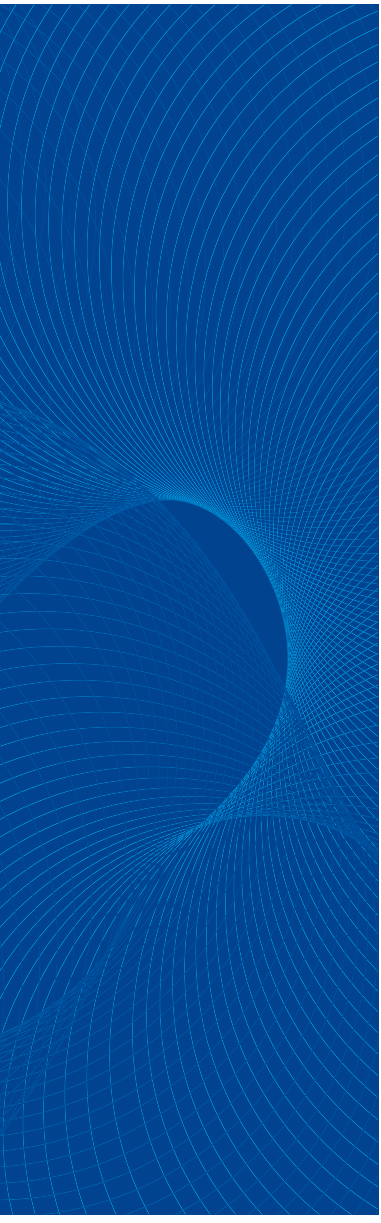
Yuzhu LIU and Bumaliya ABULIMITI

Spectroscopy and Spectral Technique

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Textbooks for Tomorrow's Scientists



Spectroscopy and Spectral Technique

Yuzhu LIU and Bumaliya ABULIMITI

This book provides a comprehensive introduction to spectroscopy, covering its origins and development, as well as the fundamentals of atomic and molecular spectroscopy. It then examines 11 representative spectroscopic techniques, including laser-induced breakdown spectroscopy (LIBS), Raman spectroscopy, and infrared spectroscopy, with detailed coverage of their principles, experimental systems, and advanced applications. The book further explores the integration of multiple spectroscopic techniques in materials science, environmental science, and industrial production, highlighting the advantages of multimodal approaches over individual techniques. It also examines the integration of machine learning and artificial intelligence with spectroscopy and presents a series of spectroscopic simulation projects based on recent research. The book concludes with an outlook on emerging trends and future technological developments in spectroscopy.

The book is a valuable reference for undergraduate and graduate students and university faculty in physics, optics, atmospheric sciences, and related fields. It is also suitable for researchers in optics, remote sensing, atmospheric physics, and astronomy, as well as engineers and technicians working in optoelectronics and related technologies.

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Contents

Chapter 1 Overview of Spectral Techniques 1
1.1 The Origin of Spectral Techniques 1
1.1.1 Spectrum and Spectroscopy 1
1.1.2 The History of Spectral Techniques 1
1.2 The Development of Spectroscopy Instruments 3
1.2.1 The Development of Spectroscopic Theory 3
1.2.2 The Advent of the Laser 4
1.2.3 Development of Spectrometers 5
1.3 Atomic Energy Levels and Atomic Spectrum 5
1.3.1 Atomic Energy Level 5
1.3.2 Atomic Emission Spectroscopy 6
1.3.3 Atomic Absorption Spectrum 8
1.4 Molecular Spectrum 9
1.4.1 Molecular Vibrational Energy Levels and Corresponding Spectral Techniques 10
1.4.2 Molecular Electrons Moving Energy Levels and Corresponding Spectral Techniques 11
References 12
Chapter 2 Laser-induced Breakdown Spectroscopy 15
2.1 Birth and Development of LIBS 15
2.2 Fundamentals of LIBS 17
2.2.1 Laser-induced Plasma 17
2.2.2 Local Thermodynamic Equilibrium 18
2.2.3 Plasma Temperature and Electron Number Density 19
2.2.4 Qualitative and Quantitative Analysis 20
2.3 Instrumentation for LIBS 21
2.3.1 LIBS Experimental Setup 21
2.3.2 Online/In Situ LIBS Instruments 22
2.3.3 Signal Enhancement for LIBS 23
2.4 LIBS Applications 25

2.4.1 Environmental Monitoring ····· 25
2.4.2 Coal Analysis ····· 27
2.4.3 Biomedicine ····· 29
2.4.4 Agriculture and Food Safety ····· 31
2.4.5 Space Exploration ····· 32
2.4.6 Ocean Exploration ····· 34
References ····· 35
Chapter 3 Raman Spectroscopy Technology ····· 41
3.1 Birth and Development of Raman Spectroscopy ····· 41
3.1.1 The Great Founder ····· 41
3.1.2 The Birth of Raman Spectroscopy Technology ····· 41
3.1.3 The Development of Raman Spectroscopy Technology ····· 42
3.2 Principle of Inelastic Scattering ····· 42
3.2.1 Nonconservation of the Kinetic Energy of Particles ····· 42
3.2.2 Elastic and Inelastic Scattering ····· 43
3.2.3 Raman Scattering and Rayleigh Scattering ····· 43
3.2.4 Stokes and Anti-Stokes Lines ····· 46
3.3 Experimental Systems for Raman Spectroscopy ····· 50
3.3.1 The Source and Splitting of the Light ····· 50
3.3.2 Collection and Monitoring ····· 53
3.4 Surface-Enhanced Raman Spectroscopy ····· 54
3.4.1 Defects of Ordinary Raman Spectroscopy ····· 54
3.4.2 Principles of Surface-Enhanced Raman Spectroscopy ····· 55
3.5 Important Applications of Raman Spectroscopy ····· 56
3.5.1 Spectral Fingerprint ····· 56
3.5.2 Real-time Detection of Liquid Phase Raman Spectroscopy Experiment ····· 59
3.5.3 Configuration Analysis of Raman ····· 62
References ····· 64
Chapter 4 Differential Optical Absorption Spectroscopy ····· 68
4.1 Development of DOAS ····· 68
4.1.1 Development of DOAS Abroad ····· 68
4.1.2 Domestic DOAS Development ····· 69
4.1.3 Opportunities and Challenges ····· 70
4.2 Principle of DOAS ····· 71
4.2.1 Lambert-Beer's Law ····· 71

4.2.2 Advantages of DOAS ····72
4.3 Experimental System of DOAS ····73
4.3.1 Active DOAS System ····73
4.3.2 Passive DOAS System (MAX-DOAS) ····74
4.4 DOAS for Multi-platform ····75
4.4.1 DOAS for the Ground Platform ····75
4.4.2 DOAS for Mobile Platforms ····76
4.4.3 Multi-platform Joint Application ····77
4.5 Important Applications of DOAS ····77
4.5.1 The Global Ozone Monitoring Experiment (GOME) ····77
4.5.2 Gaofen-5 Satellite and Atmospheric Pollution Component Inversion Method ····78
4.5.3 Determination of Plume from the Pollution Source ····78
4.5.4 Planar Array Measurements of Volcanic Plumes ····79
4.5.5 Comprehensive Stereoscopic Observation Network ····80
References ····81
Chapter 5 Infrared Spectroscopy ····86
5.1 Background Introduction of Infrared Spectroscopy ····86
5.1.1 Infrared Radiation ····86
5.1.2 IR Region ····87
5.1.3 Development of IR Spectroscopy ····87
5.2 Principle of IR Spectroscopy ····87
5.2.1 Principle and Characteristics of IR Spectroscopy ····87
5.2.2 Infrared Spectrometer ····88
5.3 Fourier Transform Infrared Spectroscopy ····89
5.3.1 Introduction to FTIR ····89
5.3.2 Principle of FTIR Spectroscopy ····89
5.4 Application of IR Spectroscopy ····90
5.4.1 IR Spectroscopy and Environmental Monitoring ····90
5.4.2 IR Spectroscopy and Food Detection ····93
5.4.3 IR Spectroscopy and Microbiological Analyses ····95
5.4.4 IR Spectroscopy and Agriculture ····97
5.4.5 IR Spectroscopy and Forensic Analysis ····100
References ···· 104
Chapter 6 Laser-induced Fluorescence Spectroscopy ···· 107
6.1 Introduction to Fluorescence Spectroscopy ···· 107

6.1.1 The History of Fluorescence Spectroscopy ····· 107
6.1.2 Characteristics of Fluorescence Spectroscopy ····· 108
6.1.3 Traditional Fluorescence Spectroscopy and Laser-induced Fluorescence Spectroscopy ····· 110
6.2 The Technical Basis of Laser-induced Fluorescence ····· 111
6.2.1 The Principle of Laser-induced Fluorescence ····· 111
6.2.2 Affected Factors of Fluorescence ····· 113
6.2.3 The Development of LIF Technology ····· 114
6.3 Experimental System of LIF Spectroscopy ····· 115
6.3.1 Excitation Light Sources ····· 115
6.3.2 Detector ····· 116
6.4 Important Applications of LIF ····· 117
6.4.1 On-line Detection of Carbon Isotopes Based on LIF Spectroscopy of CN Radicals ····· 117
6.4.2 Applications of LIF in Soils and Sediments ····· 122
References ····· 122
Chapter 7 Ultraviolet-visible Absorption Spectroscopy ····· 128
7.1 Introduction of UV-Vis Absorption Spectroscopy ····· 128
7.2 Principles of UV-Vis Absorption Spectroscopy ····· 128
7.2.1 Formation and Characteristics of UV-Vis Absorption Spectrum ····· 128
7.2.2 Main Types of Electronic Transitions ····· 130
7.2.3 Absorption Band ····· 131
7.2.4 Lambert-Beer's Law and Spectrophotometric Analysis ····· 132
7.3 Experimental System for UV-Vis Absorption Spectroscopy ····· 133
7.3.1 Common Laboratory UV-Vis Absorption Spectroscopy Experimental Systems ····· 133
7.3.2 Common Portable UV-Vis Absorption Spectroscopy Instruments ····· 135
7.4 Important Applications of UV-Vis Absorption Spectroscopy ····· 136
7.4.1 Quantitative Analysis by UV-Vis Absorption Spectroscopy ····· 136
7.4.2 Qualitative Analysis by UV-Vis Absorption Spectroscopy ····· 137
7.4.3 The Applications of UV-Vis Absorption Spectroscopy in Some Fields ····· 139
References ····· 140
Chapter 8 Tunable Diode Laser Absorption Spectroscopy ····· 142
8.1 Introduction of TDLAS ····· 142
8.1.1 The Origin and Development of TDLAS ····· 142
8.1.2 Fundamental Principle of TDLAS ····· 143

8.2 Gas Detection Method and System 146
8.2.1 Direct Absorption Spectroscopy 146
8.2.2 Wavelength Modulation Spectroscopy 147
8.2.3 Frequency Modulated Spectroscopy 149
8.2.4 Trace Gas Telemetry System 149
8.3 Important Applications of TDLAS 151
8.3.1 Atmospheric Environment Monitoring 151
8.3.2 Combustion Flow Field Diagnosis 151
8.3.3 Breath Detection in Medicine 152
8.3.4 Application in an Industrial Process 154
References 154
Chapter 9 Photoacoustic Spectroscopy 161
9.1 Introduction to Photoacoustic Spectroscopy 161
9.1.1 History of Photoacoustic Spectroscopy 161
9.1.2 Current Status of Research on Photoacoustic Spectroscopy 161
9.2 Principles of Photoacoustic Spectroscopy and Experimental Systems 162
9.2.1 The Photoacoustic Effect 162
9.2.2 Photoacoustic Signal and Minimum Detectable Concentration 163
9.2.3 Experimental Systems 165
9.3 Applications of PAS 168
9.3.1 Photoacoustic Spectroscopy for Aerosol Characterization 168
9.3.2 Breath Ammonia Levels in a Normal Human Population Study as Determined by Photoacoustic Laser Spectroscopy 171
9.3.3 Non-Invasive Monitoring of Blood Glucose by Photoacoustic Spectroscopy 173
References 175
Chapter 10 Cavity Ring-Down Spectroscopy 178
10.1 The Development of Cavity Ring-Down Spectroscopy 178
10.1.1 Pulsed Cavity Ring-Down Spectroscopy and Its Development 180
10.1.2 Continuous Wave Cavity Ring-Down Spectroscopy and Its Development 181
10.1.3 Optical Fiber Cavity Ring-Down Spectroscopy and Its Development 183
10.2 The Principle and Experimental System of CRDS 184
10.2.1 The Principles of CRDS 184
10.2.2 CRDS Experimental System 187
10.3 Advanced Technology Based on CRDS 188
10.3.1 Optical Cavity-Based Advanced Techniques 188

10.3.2 Optical Cavity-Based Hybrid Techniques ····· 192
10.4 Important Applications of CRDS ····· 198
10.4.1 Environmental Trace Analysis ····· 198
10.4.2 Biomedical Applications ····· 201
10.4.3 Combustion and Plasma Diagnostics ····· 202
References ····· 204
Chapter 11 X-ray Fluorescence Spectrometry ····· 212
11.1 Introduction of X-ray ····· 212
11.1.1 Discovery of X-ray ····· 212
11.1.2 Generation Principle of X-ray ····· 213
11.1.3 Interaction Effects Between X-ray and Matter ····· 214
11.1.4 Representative Detecting Methods Based on X-ray ····· 215
11.2 Principle of XRF and Experimental Setup ····· 216
11.2.1 Characteristics and Advantages of XRF ····· 216
11.2.2 WDXRF and EDXRF ····· 217
11.2.3 Micro X-ray Fluorescence ····· 218
11.2.4 Total Reflection X-ray Fluorescence ····· 219
11.2.5 Qualitative and Quantitative X-ray Fluorescence Analysis ····· 221
11.3 Significant Applications of XRF ····· 222
11.3.1 XRF Applied in Environmental Detection ····· 222
11.3.2 Classification of Species of Plants by XRF ····· 224
11.3.3 Determining the Depth Distribution of Elements Using XRF ····· 225
11.3.4 XRF Applied in Bio-medicine ····· 227
References ····· 229
Chapter 12 Hyperspectral Technology ····· 231
12.1 Introduction to Hyperspectral Technology ····· 231
12.1.1 The Birth of Hyperspectral Technology ····· 231
12.1.2 Present Situation of Hyperspectral Technology ····· 233
12.1.3 Development Prospect of Hyperspectral Technology ····· 235
12.2 Principle and Experimental System of Hyperspectral Technology ····· 236
12.2.1 Experimental Principle of Hyperspectral Technology ····· 236
12.2.2 Introduction to the Experimental System of Hyperspectral Technology ····· 238
12.2.3 Features and Advantages of Hyperspectral Technology ····· 239
12.3 Application of Hyperspectral Technology ····· 240
12.3.1 Application of Hyperspectral Technology in Agricultural Science ····· 240

12.3.2 Application of Hyperspectral Technology in Food Safety ····· 243
12.3.3 Application of Hyperspectral Technology in Biomedicine ····· 246
12.3.4 Application of Hyperspectral Technology in the Military Field ····· 248
References ····· 248
Chapter 13 Spectral Fusion Technology and Application ····· 252
13.1 LIBS and Raman Technologies ····· 252
13.1.1 The Role of LIBS Technology and Raman Technology in the Application ····· 252
13.1.2 Important Application Based on LIBS-Raman Technology ····· 254
13.2 LIBS and LIF Technologies ····· 261
13.2.1 The Role of LIBS Technology and LIF Technology in Application ····· 261
13.2.2 Important Application Based on LIBS-LIF Technology ····· 262
13.3 LIBS, Raman and IR Technologies ····· 263
13.3.1 Advantages of Adding IR Technology to LIBS Raman Technology ····· 263
13.3.2 Important Applications Based on LIBS, IR and Raman Technology ····· 264
References ····· 267
Chapter 14 Intelligent Spectrum Based on Machine Learning ····· 270
14.1 Introduction of Machine Learning and Intelligent Spectrum ····· 270
14.1.1 The Origin and Development of Machine Learning ····· 270
14.1.2 Introduction of Machine Learning Algorithms Commonly Used ····· 270
14.2 Laser-Induced Breakdown Spectroscopy (LIBS) and Machine Learning ····· 271
14.2.1 The Advantages of LIBS Combined with Machine Learning ····· 271
14.2.2 Application of Machine Learning in LIBS ····· 272
14.3 Infrared Spectroscopy (IR) and Machine Learning ····· 279
14.3.1 The Advantages of IR Combined with Machine Learning ····· 279
14.3.2 Application of Machine Learning in IR ····· 280
14.4 Raman Spectroscopy and Machine Learning ····· 285
14.4.1 The Advantages of Raman Spectroscopy Combined with Machine Learning ····· 285
14.4.2 Application of Machine Learning in Raman Spectroscopy ····· 286
14.5 Schematic of Hyperspectral Imaging (HSI) and Machine Learning ····· 295
14.5.1 The Advantages of HSI Combined with Machine Learning ····· 295
14.5.2 Application of Machine Learning in HSI ····· 295
References ····· 310
Chapter 15 Simulation Spectrum Teaching Experiments ····· 312
15.1 Spectral Simulation Software (GaussView & Gaussian) ····· 312

15.1.1 Introduction of GaussView & Gaussian ····· 312
15.1.2 Molecular Structure Modeling by GaussView ····· 314
15.1.3 Molecular Structure Parameter Adjustment ····· 320
15.1.4 Calculation Settings of Gaussian ····· 324
15.2 IR Spectrum Simulation Experiment ····· 330
15.2.1 Introduction to Infrared Spectroscopy (IR Spectrum) ····· 330
15.2.2 The Establishment of Water and Ethanol Molecular Structure ····· 330
15.2.3 Calculation Parameters Setup for IR Spectrum ····· 334
15.2.4 IR Spectral Analysis Simulation ····· 335
15.3 Raman Spectrum Simulation Experiment ····· 338
15.3.1 Introduction to Raman Spectrum ····· 338
15.3.2 The Establishment of Oxygen and Ozone Molecular Structure ····· 339
15.3.3 Calculation Parameters Setup for Raman Spectrum ····· 342
15.3.4 Raman Spectral Analysis Simulation ····· 343
15.4 UV-Vis Spectrum Simulation Experiment ····· 345
15.4.1 Introduction to UV-Vis Spectrum ····· 345
15.4.2 The Establishment of Benzene and Ethylbenzene Molecular Structure ····· 346
15.4.3 Calculation Parameters Setup for UV-Vis Spectrum ····· 347
15.4.4 UV-Vis Spectral Analysis Simulation ····· 348
15.5 Simulation of the External Electric Field of Ethylbenzene ····· 350
15.5.1 Research Significance and Background ····· 351
15.5.2 Theory and Computational Method ····· 351
15.5.3 Method and Basis Set Selection of EB ····· 352
15.5.4 Effect of Electric Field on Bond Length and Energy of the Molecule ····· 353
15.5.5 Effect of Electric Field on Distribution of Molecular Orbital Energy Levels ····· 354
15.5.6 Effect of Electric Field on Infrared Absorption Intensity ····· 356
15.5.7 Extension of Related Research (1) Tunneling Ionization ····· 357
15.5.8 Extension of Related Research (2) Potential Energy Surface Scanning ····· 358
15.5.9 Research Conclusions ····· 360
References ····· 360
Postscript ····· 363

Chapter 1 Overview of Spectral Techniques

1.1 The Origin of Spectral Techniques

1.1.1 Spectrum and Spectroscopy

The spectrum is a pattern of electromagnetic radiation intensity arranged in order of frequency from largest to smallest (or smallest to largest), which reflects the energy level structure of an entire physical system. Usually, we use a one-dimensional curve to represent the spectrum. The abscissa can be frequency, wavenumber, wavelength or energy, and the ordinate can be radiation intensity, absorbance or transmittance.

Spectroscopy is a method of studying the properties of matter through the interaction between matter and electromagnetic waves of different frequencies (or wavelengths) and is an important means of studying the microscopic particles (atoms, molecules, etc.) of matter. The spectra formed by the interaction of light and matter at different frequencies are different, and they can reflect different characteristics of microscopic particles. For example, γ-rays are caused by transitions between atomic nuclei. X-rays are caused by transitions between inner electron energy levels, and ultraviolet and visible light are caused by transitions between outer electron energy levels. Near-infrared and mid-infrared light are caused by molecular vibration energy levels. Far-infrared light and microwaves are caused by transitions between the rotational energy levels of molecules, and radio waves are mainly caused by transitions between electron spin and nuclear magnetic resonance energy levels[1].

1.1.2 The History of Spectral Techniques

The concept of spectroscopy was proposed by the British physicist Newton in the 17th century. In 1666, Newton first discovered the existence of spectra experimentally. In Newton's experiment, sunlight is refracted in a prism through small holes, and it was found that white sunlight can be dispersed into seven colors from red to purple, which is the discovery of the spectrum, and this experiment is the origin of the spectrum.

In 1802, the British chemist William Hyde Wollaston used a set of thin slits instead of the small holes in Newton's experiment to discover that the spectrum of the sun was

not actually a perfect rainbow, but was cut by some black lines. Then, in 1814, the German physicist and optical expert Joseph von Fraunhofer continued to study the solar spectrum and discovered about 574 black lines in the solar spectrum, and selected the relative positions of these black lines. As for black lines in the visible region, Fraunhofer named them A, B, C, and so on in the order of English letters from red to purple. Future generations commemorated him later, naming the black lines of the solar spectrum the Fraunhofer line. In addition, when Fraunhofer put table salt on an alcohol lamp to burn, he accidentally observed the sodium yellow line and found that the line coincided with the position of the D black line in the solar spectrum. In 1853, Ångström and Foucault discovered the connection between the bright line (emission spectrum) and the black line (absorption spectrum), respectively, and experimentally proved that the two yellow lines of the sodium line are consistent with the two D lines of Fraunhofer based on Fraunhofer experiment.

At the same time, due to the rapid development of electromagnetism, the spectra of electric light sources had attracted the attention of many scientists. For example, Wheatstone studied the spectra of different metal electric light sources in 1834. He recorded the number of spectral lines, their positions, and the colors of the bright lines and he finally concluded that the spectra differ between different metals.

In 1859, Kirchhoff and Bunsen first applied spectroscopes to chemical analysis and discovered the new elements cesium (Cs) and rubidium (Rb) by studying the phenomenon that metals emit the same spectrum in evaporation into flames or electrical discharges. This is a major event in the history of spectroscopy, marking the beginning of spectral techniques towards new applications and becoming a new subject. Since then, spectral analysis has begun, and many new elements have been discovered. For example, in 1861, Crookes discovered thallium (Tl) using spectroscopic analysis. In 1863, Reich and Richter discovered indium (In), and in 1875, Boisbaudran discovered gallium (Ga).

Although new elements were constantly discovered through the reflectance spectroscopy techniques of the time, some fundamental problems remained. How is the spectrum of metal generated? Why do different metals have different spectra? These problems have gradually been unraveled with the deepening of the study of atomic structure and quantum mechanics.

1.2 The Development of Spectroscopy Instruments

1.2.1 The Development of Spectroscopic Theory

From the middle of the 19th century, the study of the spectrum of hydrogen atoms became an important topic in spectroscopy. In 1853, Ångström detected the strongest spectral lines of hydrogen atoms. In 1885, Balmer came up with an empirical formula that predicts the spectral line position of hydrogen atoms, known as the Balmer formula:

$$\lambda = \frac{n^2}{n^2 - 2^2}\lambda_0, \quad n = 3,4,5,\cdots \tag{1-1}$$

The wavelength of the spectral line is λ and the unit is Å ($1\ \text{Å} = 1\times10^{-10}\ \text{m}$, λ_0 =3645.7 Å). This is the first theoretical relation of spectral lines in spectroscopy.

Later, in 1889, Rydberg developed Balmer's theory further, culminating in the Rydberg formula:

$$\frac{1}{\lambda} = R\left(\frac{1}{n^2} - \frac{1}{n'^2}\right), n = 1,2,3,\cdots, \quad n' = n+1, n+2, n+3,\cdots \tag{1-2}$$

In the formula, *R* represents the Rydberg constant, which is a very important physical constant used to describe the series of lines in the atomic spectrum.

The Rydberg formula is an epoch-making event for molecular and atomic spectroscopy, and even later modern science, and a milestone in spectroscopy, marking another step towards the microscopic matter.

For truly understanding the mysteries of the spectrum of hydrogen atoms, Balmer and Rydberg's theory is only the beginning, and still does not jump out of the empirical category. It wasn't until 1913 that Bohr gave a definitive explanation of the spectral lines of hydrogen atoms, and the real satisfactory explanation of spectral lines was due to quantum mechanics developed in the 20th century[2]. In 1925, Uhlenbeck and Goudsmit introduced the electron spin hypothesis to explain measurements of the atomic spectra of alkali metals, which provided the theoretical basis for a spin in Dirac quantum mechanics.

It is also worth mentioning the Zeeman effect. In 1895, Zeeman discovered that the spectral lines of atoms split under the influence of magnetic fields, and the following year H. A. Lorentz explained this phenomenon, and the two shared the 1902 Nobel Prize. The Zeeman effect not only has important theoretical value but also has important application value, which can help us effectively understand complex light

harmonics.

In addition, between the 1900s and 1920s, Leonard, de Gramont, and other physical scientists made great progress in spectral quantification. They found a relationship between the number of spectral lines appearing and the number of elements present in the light source, especially de Gramont discovered the Raies Ultimes of the elements in 1907. Beginning in 1920, work in spectroscopy began to focus on the analysis of modern emission spectroscopy. In 1922 the International Union of Pure and Applied Chemistry (IUPAC) appeared, and in 1925 Gerlach proposed the principle of internal standards. This principle was eventually refined by Schweitzer in 1927. At this point, spectroscopic analysis gradually replaced chemical volumetric and gravimetric analysis. Due to the accuracy, precision, sensitivity, and speed of spectral analysis, the spectral analysis method has been widely recognized and applied in the scientific and technological community[3].

1.2.2 The Advent of the Laser

In 1960, Maiman and others manufactured the first ruby laser, which revolutionized spectral techniques and formed a completely new field—laser spectroscopy.

Laser brightness is high. For example, a 1 milliwatt helium-neon light is 100 times brighter than the sun, and the light emitted by Q-switched ruby laser is 10 billion times brighter than the sun. Therefore, lasers can become a special energy source and energy transfer method. In spectroscopy experiments, lasers can be used directly to evaporate samples. In addition, because the spectral brightness of the laser is particularly high, the emitted beam energy is large and the radiation is concentrated in a very narrow bandwidth, which can well enable atoms or molecules to absorb energy from the radiation field, improving the resolution of the spectrum.

Lasers have a high degree of directionality, allowing them to maintain a narrow, focused beam over long distances without diverging quickly like traditional light sources. Because of the excellent performance of directivity and monochromaticity, the spatial coherence is very good and the spatial resolution is high. The light can be concentrated in a small area, so that the energy is highly concentrated, achieving high radiation power density and radiation field strength. At the same time, the resolution of the spectrum is improved. In addition, the spectral line of the laser is very narrow, which can greatly improve the resolution of the spectral line, giving us a chance to study the ultra-fine structure of the spectrum of matter.

With its high brightness, good directivity, and good monochromaticity, the laser

greatly improves the spectral resolution and time resolution, thus further promoting the development of spectroscopy.

1.2.3 Development of Spectrometers

In 1859, Kirchhoff and Bunsen made great contributions to the field of metal spectroscopy by designing a spectroscopic device. This device made the first practical spectroscopic instrument. From the proposal of Newton's concept of spectroscopy to the emergence of Kirchhoff's practical spectroscopic instruments, a total of nearly two hundred years have passed, and the foundation of modern spectroscopic instruments has gradually formed.

In 1882, Rowland invented the Rowland grating, also known as concave grating. The emergence of concave grating makes the structure of spectroscopic instruments more concise.

By the 1950s, the spectroscopic instrument manufacturing industry had formed a relatively complete system. Around the Second World War, with the rapid development of electronic technology, the trend of photoelectric and automation of spectroscopic instruments appeared, which made the spectrometer a huge improvement in speed and accuracy[4].

Since the 1970s, computers and electronic technology have developed rapidly, and electronic computers have begun to tend to be miniaturized. At the same time, the cost is getting lower and lower. With the advantages of fast computer operation speed and high calculation accuracy, the data processing and analysis of spectra have become more accurate, which has greatly promoted the rapid development of spectrometers. From then on, scientists used computers to manipulate spectroscopic instruments. In addition, with the deepening of the field of artificial intelligence and machine learning, spectral techniques are moving toward a bright future.

1.3 Atomic Energy Levels and Atomic Spectrum

1.3.1 Atomic Energy Level

In 1913, Bohr proposed his three hypotheses based on his predecessors and established the hydrogen atom model. The energy assumption is that when an electron transitions from one permissible orbit to another, it emits or absorbs a photon, as the formula

shows:

$$\frac{hc}{\lambda} = E_m - E_n \tag{1-3}$$

Where, E_m and E_n are different energy levels and $E_m > E_n$; h represents the Planck constant, and c stands for the speed of light. This formula reveals the nature of atomic spectra, which means electrons transition between different orbits will emit or absorb spectral lines of different wavelengths, which explains why different elements have different characteristic spectra. Therefore, according to the theory, electrons can only move in certain fixed orbits when moving around the nucleus. Different orbitals correspond to different energies. Orbits farther from the nucleus have higher energy, while orbits closer to the nucleus have lower energy. We call these orbitals atomic energy levels.

1.3.2 Atomic Emission Spectroscopy

Atomic emission spectroscopy analysis is based on measuring the characteristic optical spectrum emitted by gaseous free atoms or particles when they are excited in the wavelength range of ultraviolet, visible, and partially infrared regions. Usually, we use flames, arcs, and sparks as excitation sources as the classical emission spectrum. Due to the very low temperature, the flame generally does not exceed 3000 K, so in addition to being effective for alkali metals and some alkaline earth metals, the excitation ability of most of the other elements is relatively poor, and it has been rarely used. The arc is made of higher arcs with higher electrode temperature and arc flame temperature, so the ability to evaporate the sample is strong, and the spectral lines of many elements can be excited, which means it has a high detection ability. But the fly in the ointment is the poor stability of arc discharge. Spark discharge has a strong excitation ability, but the ability to evaporate the sample is poor, and it is not easy to measure trace elements. Because these light sources have their limitations, classical emission spectroscopy can only be used for qualitative, semi-quantitative, and approximate quantitative analysis.

In the 1960s, Greenfield and Fassel used inductively coupled plasma (ICP) devices for atomic emission spectroscopy analysis, creating the history of the application of inductively coupled plasma in atomic spectroscopy, and inductively coupled plasma atomic emission spectroscopy (ICP-AES) began to gain widespread attention[5]. ICP-AES dominates the entire AES research at present. The plasma excitation light source is very stable, and its discharge temperature which reaches more than 5000 K has

good evaporation, atomization, excitation, and ionization characteristics. So that ICP has truly become a conventional quantitative analysis method for the determination of major and minor components and impurity elements in various samples. In addition, ICP can also become a good method for simultaneous multi-element analysis and trace analysis[6]. The principle of ICP-AES spectroscopy technology is to use an inductively coupled plasma (ICP) to evaporate and vaporize the sample, dissociate or decompose into an atomic state, and the atoms can be further ionized into an ionic state. Then, atoms and ions are excited to emit light in the light source. The spectroscopic system is used to decompose the light emitted by the light source into a spectrum arranged by wavelength. Then the photoelectric device is used to detect the spectrum. In addition, the sample is qualitatively analyzed according to the measured spectral wavelength, and the emission light intensity is quantitatively analyzed. Besides, other plasma light sources such as DC plasma flame (DCP)[7] and microwave-induced plasma (MIP)[8] as well as low-pressure discharge light sources such as Grimm glow discharge[9], have their characteristics and are widely used in emission harmonic analysis.

It is worth mentioning that atomic fluorescence spectroscopy also belongs to atomic emission spectroscopy[10]. Atomic fluorescence spectroscopy is based on the measurement and analysis of fluorescence emitted by gaseous free atoms after absorbing characteristic radiation. However, due to the transient nature of fluorescence, the development of fluorescence analysis has taken a long time. The first recorded fluorescence phenomenon was in 1565 by the Spanish botanist N. Monardes. It was not until the 17th century, when Boyle and Newton again observed fluorescence, that a more detailed description was given. In 1852, Stokes discovered that fluorescence is an emitted light when he examined quinine and chlorophyll with a spectrometer, and he was the first to propose the use of fluorescence as a means of analysis. In 1867, the Swiss scientist F. Goppelsröder pioneered fluorescence analysis by using the fluorescence of aluminum-mulberry pigment complexes to determine aluminum[11]. In 1880, Lieberman first proposed the empirical rule of the relationship between fluorescence and compound structure, and systematically studied the theory of fluorescence analysis. By the end of the 19th century, more than 600 fluorescent compounds had been discovered.

Since the 20th century, people have studied the fluorescence phenomenon more deeply and extensively and formed a complete set of fluorescence analysis theories gradually. In 1905, Wood discovered resonant fluorescence[12]. Emil Gabriel Warburg published a series of papers between 1912 and 1921, introducing the concept of "quantum efficiency" and using the Greek letter ϕ to denote it. In 1926, Enrique Gaviola

directly determined the lifetime of fluorescence. In addition, X-ray fluorescence spectroscopy emerged as technology developed. X-ray fluorescence spectroscopy is a technique that uses high-energy X-rays or secondary X-rays excited when a material is bombarded with high-energy X-rays or γ-rays to perform rapid, non-destructive analysis of samples. With its easy use and simple sample preparation, it has a wide range of development prospects[13].

The development of fluorescence analysis theory provides a basis for the development of instruments, and the development of instruments also promotes the continuous progress of fluorescence analysis theory. At present, atomic fluorescence spectroscopy has been widely used, and it is expected to become a good supplementary analysis method for atomic emission and atomic absorption spectroscopy[14].

1.3.3 Atomic Absorption Spectrum

Atomic absorption spectroscopy analysis is based on the absorption of characteristic radiation by gaseous free atoms. Characteristic radiation is emitted by a background light source that produces a sharp line spectrum, and free atoms absorb characteristic radiation to produce spectra[15].

In 1952, Australian scientist A. Walsh conducted the first successful experiment to measure atomic absorption spectra. In 1955, he published a paper exploring the relationship between atomic concentration and absorbance value, proposing that atomic absorption spectroscopy could be used as an effective elemental analysis method, thus pioneering the flame atomic absorption spectrum[16]. In recognition of his contribution to the development of flame atomic absorption spectroscopy, the 27th Colloquium Spectroscopicum Internationale (CSI) in Bergen, Norway, Walsh was awarded the first CSI Prize in 1991.

In 1959, the Soviet scientist B. V. L'vov pioneered electric atomic absorption spectroscopy for graphite furnaces[17]. This method can determine a wide range of elements and is more sensitive than flame atomic absorption spectroscopy. In the following years, the research on electric atomic absorption spectroscopy of graphite furnaces continued, and in 1965, Bowman and Willis used the oxide-acetylene flame to determine refractory elements[18]. This method increased the number of elements that can be determined to more than 70, improving the application range of the atomic absorption spectrum. In 1968, H. Massmann improved the graphite furnace and designed a simpler atomizer for electric graphite furnaces[19].

Atomic absorption spectroscopy is simpler than atomic emission spectroscopy, so

atomic absorption spectroscopy analyzes less spectral interference than emission spectroscopy. However, atomic absorption spectroscopy is not suitable for the simultaneous analysis of multiple elements, and these two spectroscopic techniques have their advantages and disadvantages[20].

1.4 Molecular Spectrum

Molecular spectroscopy refers to the spectrum of light emitted by transitions between molecular energy levels or absorbed by molecules. Compared with atomic spectra, molecular spectra appear much more complex. In the internal movement of molecules, there are rotation, vibration, and electron motion (Fig. 1-1). These three types of motion make up the total energy of the molecule, and this energy is quantization, so all of them may produce spectra. Among these three motions, the difference in rotational energy levels is the smallest, about $10^{-4} - 10^{-2}$ eV, which can be excited by microwaves; the difference in vibration energy levels is centered, about 0.05–1 eV, and infrared light waves can be excited; the energy level difference of valence electron motion is the largest, similar to the difference of each energy level in the atom, about 1–20 eV, which can be excited by ultraviolet-visible light waves; the electrons in the inner layers of the molecule need X-rays to be excited. When molecules absorb electromagnetic radiation energy, the small energy term will change with the large energy term[21]. For example, the absorption of ultraviolet rays by molecules will cause the energy level transition of molecular valence electrons, and at the same time, there will be vibration and transition level transitions. As a result, molecular spectra tend to show a band-like structure rather than a linear structure of an atomic spectrum[22].

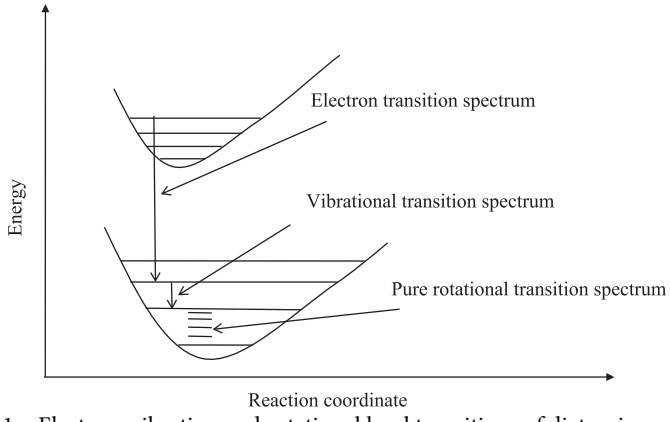


Fig. 1-1 Electron, vibration and rotational level transitions of diatomic molecules

Different movements of molecules generate different energy levels, so the spectral wavelength range of different motions is also different. At present, the main molecular spectra are the infrared spectrum, Raman spectrum, and ultraviolet-visible spectrum.

1.4.1 Molecular Vibrational Energy Levels and Corresponding Spectral Techniques

The functional groups of molecules have their fixed vibration patterns, corresponding to different vibration energy levels according to frequency. Molecular vibration levels contain a lot of information about the composition, structure, and configuration of molecules. When molecules transition between different vibrational energy levels, absorption or emission spectra are produced. Among all molecular spectral techniques, the Raman scattering spectral technique and the Infrared absorption spectral technique are two powerful tools that can quickly detect molecular composition and identify molecular species[23, 24].

In 1800, the British physicist Herschel used a prism to disperse sunlight to study the thermal effect of various parts of light and found that it has the greatest thermal effect on the outside of red light, which indicates that there is radiation outside the red light and he called it "infrared" or "hot wire". Since there was no precision instrument testing at that time, there was not much progress in this regard. It was not until 1892 that Heinrich Gustav Johannes Kayser measured the infrared spectra of more than 20 organic compounds with a rock salt prism and a heat radiometer (resistance thermometer) that attracted widespread attention. In 1905, Coblentz measured the infrared spectra of 128 organic and inorganic compounds, causing a huge sensation in the spectroscopic world[25]. By the 1930s, the establishment and development of quantum mechanics provided an important foundation for infrared spectroscopy theory and technology. Many scientists have calculated the bond force, bond length, energy level, etc. of molecules through vibration theory, so infrared spectroscopy theory has become increasingly mature and perfect, and has been recognized by physicists and chemists[26, 27].

Raman spectroscopy, also known as the Raman effect, was discovered in 1928 by Indian physicist C. V. Raman. Raman spectroscopy is derived from the inelastic scattering of light, which is the new radiation line that Raman discovers by irradiating benzene liquid with a mercury lamp. It is a new molecular radiation. Each substance has its own unique Raman spectral line, which can be used as a method to characterize the substance. For this discovery, he won the Nobel Prize in Physics in 1930[28].

At that time, the development of Raman spectroscopy was not all smooth sailing. Due to the 40s and early 60s of the 20th century, the laser light source was too weak, resulting in a low point in the study of Raman scattering. Until the advent of lasers in 1960, Raman spectroscopy research entered a new period of development. In the 1970s, the advent of laser Raman probes made it possible to identify elements and analyze compositions of substances in microregions[29]. In the 1980s, the successful development of probe confocal laser Raman spectroscopy greatly expanded the application range of Raman spectroscopy, and technologies such as confocal microscopic Raman spectroscopy[30] and Fourier transform Raman spectroscopy technology[31] appeared, making Raman spectroscopy widely used in various fields such as medicine[32], industry[33], physics[34], and chemistry[35].

1.4.2 Molecular Electrons Moving Energy Levels and Corresponding Spectral Techniques

The kinetic energy level of molecular electrons is similar to the production of atomic energy levels, that is, the transition of electrons at different energy levels, but more complex than atomic energy levels. Nowadays, the main mature spectral technique using the kinetic energy level of molecular electrons is ultraviolet spectroscopy[36].

The ultraviolet spectrum includes both absorption and emission spectra produced by the interaction of molecules with electromagnetic waves in the wavelength range of 10–400 nm. In 1802, German physicist Johann Wilhelm Ritter discovered ultraviolet light. Beckman introduced the first commercially available UV spectrophotometer in 1940, marking the beginning of the maturation of UV spectroscopy. UV spectroscopy is produced by the absorption of radiation with the appropriate energy by the outer electrons in the ground state of the molecule and thus the transition to the excited state. Molecules with different internal structures have different electron energy levels. So ultraviolet spectroscopy can detect substances with different molecular structures. It is worth mentioning that UV spectroscopy has a unique role in the determination of compounds with cograsping double-bond systems (including aromatic compounds) and double bonds containing unshared electron pairs[37].

Ultraviolet spectroscopy mainly uses the characteristics of electron energy level transitions with groups containing conjugated and double-bonded systems to produce spectra in the ultraviolet or visible light band, which has the advantages of fast, accurate, high sensitivity, simple instrument, and low price[38-40].

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Chapter 2 Laser-induced Breakdown Spectroscopy

2.1 Birth and Development of LIBS

Laser-induced breakdown spectroscopy (LIBS) is a popular spectroscopic analysis method evolving from atomic emission spectroscopy (AES) technology, and more and more scientists are participating in research about LIBS in recent years[1-3]. Compared to other analytical methods, LIBS has many advantages, including rapid analysis, simultaneous determination of multi-element, no sample preparation, non-destructive in nature, and simplicity in operation[4-8]. Furthermore, the LIBS technique can be used for the compositional analysis of solid[9,10], liquid[11,12], gas[13-15], and aerosol samples[16,17]. Owing to its excellent features, the LIBS technique was hailed as the "next superstar" within the group of analytical atomic spectrometry methods[18].

The development of the LIBS technique is directly related to advances in lasers. Since the laser was first successfully operated by Maiman in 1960[19,20], several research groups have experimented with focusing high-power laser beams onto specimens to vaporize small samples[21]. It is believed that LIBS has its origins in the 1960s[22]. After the stimulated emission was predicted by Einstein in 1917, it took more than 40 years to build the first ruby laser. In 1962, LIBS was first reported at the 10th Colloquium Spectroscopicum Internationale by Brech and Cross of Trion Instruments in the same year[23]. They first proposed that laser can be used as the excitation source for atomic emission spectroscopy to determine the elemental compositions in solids, gases, and liquids, and their work received wide attention. The technique was called "Micro-emission Spectroscopy" and marketed as a source unit that could be coupled to any spectrograph, using a ruby laser manufactured by Trion. The invention of the Q-switched laser in 1963, which has extremely high single pulse energy, has significantly promoted the development of LIBS. Shortly thereafter, Runge et al.[24] and Rasberry et al.[25] established a calibration model for quantitative analysis of the Nickel and Chromium elements in the molten steel sample based on the intensity of the characteristic line and the plasma radiation mechanism, proving the feasibility of quantitative detection using LIBS for the first time. In the period from 1964 to 1967, the

first instruments based on this technique were developed by Zeiss (Germany) and Jarrell-Ash (USA)[26, 27]. In 1969, Buzukov et al.[28] firstly studied the plasma generated by ruby laser in water, and clarified the mechanism of this process in the liquid sample from the viewpoint of explosion physics.

Subsequently, in the 1970s, the popularity of LIBS research declined due to the bottleneck of basic theoretical research. By the 1980s, the rapid development of spectral detection technology also indirectly promoted the rapid development of the LIBS field again. In 1983, the researchers at Los Alamos National Laboratory took the lead in using this technology to determine the composition of material elements, and the English abbreviation of laser-induced breakdown spectroscopy was first proposed as LIBS by Radziemski et al.[29], and LIBS thereby has become a brand new spectroscopic technique. In the following decades, with the further development of technology, the basic theory of the LIBS technique has been gradually confirmed, and its application scope has become increasingly extensive[30-34]. Since then, a large number of research groups worldwide have been researching the principle and application of the LIBS technique and gradually pushed it to the detection of steel, coal, and other components.

Nowadays, LIBS has been regarded as a powerful analytical technique for both laboratory and field-going systems due to its unique features[35]. LIBS technique is playing a more and more important role in the field of biomedicine, agricultural products and other food safety testing, industrial control, soil heavy metal pollution, metallurgical analysis, environmental monitoring, cultural relic identification, space exploration, and explosives detection. In the meantime, the related commercial products for practical applications based on LIBS in some fields have also begun to appear. However, the LIBS technique still has some technical shortcomings, such as poor spectral detection sensitivity, and the high limit of detection (LOD) of elemental analysis. What's more, the plasma matrix effect, self-absorption effect, coexisting element effect, the inhomogeneity of sample composition itself, the fluctuations of plasma electron density and temperature, as well as the influence of spectral collection methods, could lead to low accuracy and precision of spectral quantitative analysis, and poor repeatability. Hence, more efforts need to be made to improve the quantitative performance, long-term stability, and sample applicability of LIBS in the future to make LIBS a more competitive analytical technique.

2.2 Fundamentals of LIBS

2.2.1 Laser-induced Plasma

LIBS is a micro-chemical analytical technique employing light emitted by laser-produced plasma (LPP) to produce spectra of the sample for composition analysis of materials. The basic principle of LIBS is shown in Fig. 2-1. It focuses a beam of ultra-high-energy pulse laser light on a small area of the sample surface through a focusing lens. When a high-power laser beam strikes the sample, it produces a plasma plume that has a temperature higher than 10^4 K due to rapid melting and/or vaporization of the sample surface, as shown in Fig. 2-1(a). When the plasma reaches a local thermodynamic balance, the plasma will be at a high temperature of 10^4 K. During this period, the plasma will emit an intense continuous background radiation signal caused by bremsstrahlung which cannot provide any useful information about the composition of the target sample, as shown in Fig. 2-1(b). Whereas, after a short relaxation process, the plasma expands and quickly cools. At this time, the atoms and ions of various elements in the plasma will radiate spectral lines with characteristic wavelengths, as shown in Fig. 2-1(c). The time interval between bremsstrahlung noise and the atomic or ionic transition radiation is about 10 μs. Therefore, the appropriate delay and integral times of the spectrometer are necessary to remove the background noise and maintain the characteristic spectrum signal, and thereby higher signal-noise-ratio (SNR) can be obtained. The atomic and ionic spectral lines emitted from the plasma, which can provide the compositional information of the target sample, are often collected by a spectrometer. By comparing the spectral lines collected from the plasma with the standard database (e.g., National Institute of Standards and Technology[36]), the characteristic lines can be respectively determined, and thus the compositional information of the target sample can be obtained. In addition to the qualitative analysis, the quantitative analysis of each element in the sample can also be realized by establishing the calibration model according to the intensities of characteristic lines. Since LIBS is one kind of emission spectroscopy, the intensity of a spectral line is in direct proportion to the concentration of the corresponding element without consideration of the self-absorption effect. Hence, based on the analysis of characteristic lines, the LIBS technique could simultaneously achieve rapid qualitative analysis and quantitative analysis of the sample.

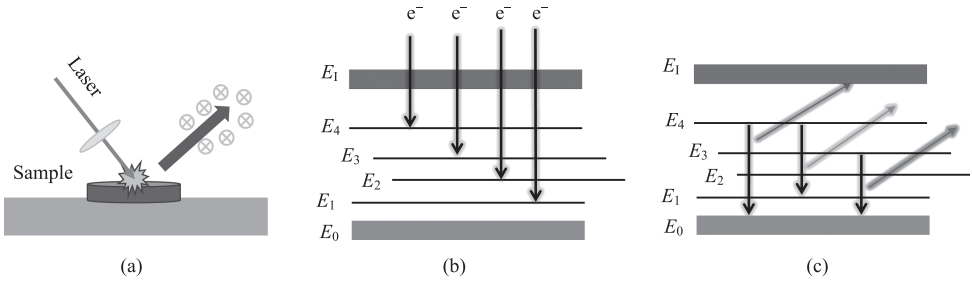


Fig. 2-1 Schematic diagram of LIBS

(a) Laser ablation of the sample, multi-photon ionization to form a plasma; (b) Plasma cooling with continuous light radiation; (c) Atomic and ionic transition radiation. E_0, ground state; E_1, first excited state; E_2, second excited state; E_3, third excited state; E_4, fourth excited state; E_I, ionic state

2.2.2 Local Thermodynamic Equilibrium

Thermodynamic equilibrium is a fundamental concept in thermodynamics, which is a prerequisite for the quantitative analysis of LIBS. It is the internal state of a single thermodynamic system, or the relationship between several thermodynamic systems connected by more or less permeable or impermeable walls. In thermodynamic equilibrium, no net macroscopic flow of matter or energy within or between systems exists. In a system in the internal thermodynamic equilibrium state, macroscopic changes would not occur. Systems in mutual thermodynamic equilibrium are simultaneously in mutual thermal, mechanical, chemical, and radiation equilibrium.

Local thermodynamic equilibrium (LTE) is a special type of thermodynamic equilibrium state that is often used to study the radiation emitted in plasma[37]. In common, the laser-induced plasma can be divided into multiple subsystems, each of which is in thermal equilibrium, and the temperature between the subsystems varies, but the energy flow between the systems is very low. The relaxation time necessary for particles to travel from one subsystem to another to reach equilibrium is very small, and this state is called the local thermal equilibrium state. In local thermodynamic equilibrium, those high-intensity parameters vary in space and time so slowly that at any point one can assume that some neighborhood of that point is in thermodynamic equilibrium. Local thermodynamic equilibrium does not require local or global temperature stationarity, in other words, a constant temperature at every point. However, it requires that each small local change is slow enough to maintain a Maxwell-Boltzmann velocity distribution within the local area.

In the LIBS experiment, the premise of quantitative analysis is that the

laser-induced plasma is in the LTE state[38]. The most popular criterion to evaluate the validity of LTE is the McWhirter criterion, which can be expressed as:

$$N_e \geqslant 1.6\times10^{12}\times T^{\frac{1}{2}}\times(\Delta E)^3 \tag{2-1}$$

Where N_e is the electron number density; T is the plasma temperature (K); and ΔE (eV) is the largest observed transition energy for which the condition holds. It should be noted that, only when the above criterion is satisfied, the collected spectra from the plasma could be effective for the following quantitative analysis.

2.2.3 Plasma Temperature and Electron Number Density

During the LIBS experiments, some important parameters such as plasma temperature and electron density, are crucial to derive reliable quantitative data.

In LIBS measurements, spectral line broadening includes natural broadening, Doppler broadening, Stark broadening, etc., and in general, Stark broadening dominates[39] in the broadening process. The relationship between the number density of electrons and the Stark line width at half maximum width[40] is:

$$\Delta\lambda_{\frac{1}{2}} \approx 2\omega\left(\frac{N_e}{10^{16}}\right)+3.5A\left(\frac{N_e}{10^{16}}\right)^{\frac{1}{4}}\left(1-0.75N_D^{-\frac{1}{3}}\right)\omega\left(\frac{N_e}{10^{16}}\right) \tag{2-2}$$

Where N_e is the electron number density; $\Delta\lambda_{\frac{1}{2}}$ is the full width at half maximum of the spectral line; ω is the electron collision parameter; A is the ion broadening parameter; N_D is the number of particles in the Debye sphere. The first term in the brackets gives the contribution from electron broadening, and the second term stems from ion broadening. Since the contribution of ion broadening to the linewidth is much smaller than that of electrons, Eq.(2-2) can be simplified to:

$$\Delta\lambda_{\frac{1}{2}} \approx 2\omega\left(\frac{N_e}{10^{16}}\right) \tag{2-3}$$

Hence, according to Formula (2-3), the electron number density of plasma in LIBS measurements can be calculated by fitting the characteristic spectral line and then obtaining its full width at half maximum.

In most cases, plasma temperature is calculated according to the Saha-Boltzmann equation, which can be expressed as:

$$\ln\left(\frac{I_{ij}\lambda}{A_{ij}g_k}\right) = -\frac{1}{K_B T}E + \ln\left[\frac{hcN^S}{U^S(T)}\right] \tag{2-4}$$

Where λ and I_{ij} are the wavelength and intensity of the characteristic spectral line, respectively. A_{ij} is the transition probability of the corresponding atom or ion, and g_k is the statistical weight of the energy level on the transition. K_B is the Boltzmann constant; T is the plasma temperature; E is the excitation energy of the upper energy level of electron or ion transition; h and c are the Planck constant and the speed of light in vacuum; N^S is the electron number density; and $U^S(T)$ is the electron or ion partition function. In the NIST atomic standard database, the transition probability A_{ij} of each element, the statistical weight g_k of the energy level on the transition, and the excitation energy E of the energy level on the transition can be found, and the plasma temperature T can be obtained by the linear regression method.

2.2.4 Qualitative and Quantitative Analysis

As an analytical method, the ultimate goal of the LIBS technique is to achieve an accurate determination of elements in the target sample. The quantitative analysis of LIBS measurement is mainly according to the Lomakin-Scheibe equation:

$$I = aC^b \tag{2-5}$$

Where I is the spectral line intensity obtained in LIBS experiments; a is the experimental constant; C is the concentration of the target element; b is the self-absorption coefficient. If the self-absorption effect is ignored, it can be considered that b=1, and the Formula (2-5) can be rewritten as:

$$I = aC \tag{2-6}$$

Hence, select a certain element q as the internal standard element of the quantitative analysis target element P, Eq. (2-6) can be expressed as follows:

$$\frac{I_P}{I_q} = \frac{a_P C_P}{a_q C_q} \tag{2-7}$$

And the equation can be simplified as:

$$I_P^* = AC_P \tag{2-8}$$

Where I_P^* is the relative intensity of the characteristic spectral line of the target element; C_P is the concentration in the target sample. Taking the concentration of the

target element as the abscissa and the relative intensity as the ordinate, the calibration curve can be obtained by fitting. Hence, for the unknown sample, the concentration of target element P can be rapidly calculated according to the LIBS results based on the calibration curve.

2.3 Instrumentation for LIBS

2.3.1 LIBS Experimental Setup

A typical LIBS experimental setup is shown in Fig. 2-2[41]. It normally consists of a pulsed laser, focusing optics, light collection optics, and a spectrometer. In LIBS, a high-power laser pulse is utilized to generate plasma by excitation and ionization of atoms of the sample. The Q-switched Nd:YAG (neodymium doped yttrium aluminum garnet) lasers are the most commonly employed light source for the generation of plasma in a LIBS setup. Laser pulse firstly interacts with the sample, ablating a minute amount of material of the sample. The luminous plasma is subsequently generated and each specie in the plasma cloud become excited and then de-excited, expansion and condensation of the plasma plume occur which causes to produce electromagnetic radiations containing information about each specie present in the sample. Fiber optics then transmits the emitted light to the spectrometer. Finally, the spectral fingerprint is developed by system software. The collimating lens bends these radiations towards diffraction grating placed 0°–45° field of view and orthogonal to plasma expansion. Radiations emitted by plasma are collected as pixels which develop intensity data.

In LIBS experiments, the integral time was controlled by the AvaSoft software, and the collection time delay was controlled by a digital delay generator. Fig. 2-3[42] presents the LIBS spectra of air captured by the spectrometer with the growth of time delay. The integral time and time delay are the key parameters of LIBS measurements, which have a great effect on the LIBS signal quality recorded by the spectrometer. As shown, in the early stage of plasma generation, there exists a strong continuous background radiation signal, which will seriously interfere with the results of LIBS detection experiments, especially on element calibration. The intensity of the background radiation decays quickly with the growth of time, while the atomic spectral lines can be maintained for a long time. Therefore, to obtain a high SNR, it is necessary to set an appropriate time delay for the LIBS experiment.

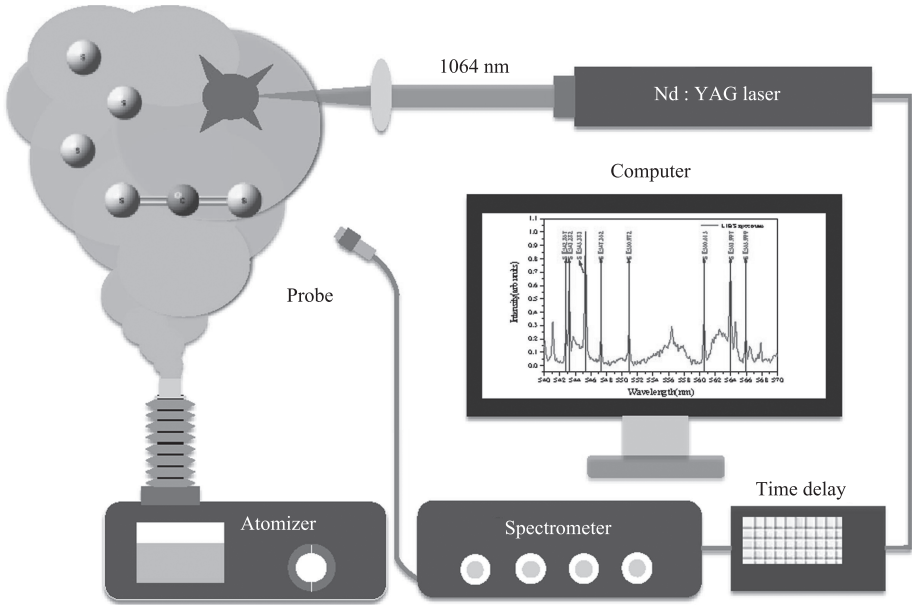


Fig. 2-2 Schematic diagram of typical LIBS setup[41]

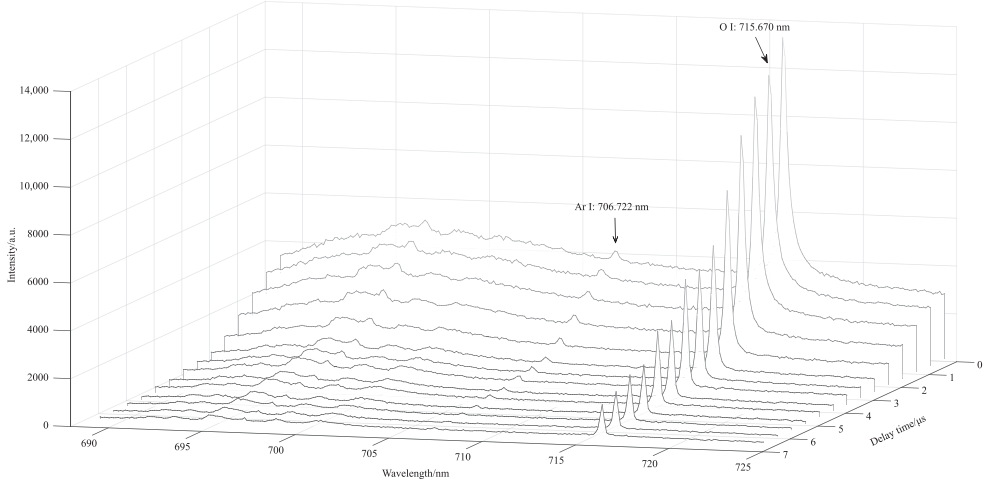


Fig. 2-3 The variations of the LIBS spectra with different time delays of measurements[42]

2.3.2 Online/In Situ LIBS Instruments

Because of the unique advantages of in-situ, real-time, fast, and no need for complex sample pretreatment, the LIBS technique can quickly realize the online measurements

of a large number of samples in situ. Under special situations where the target sample is hard to collect or process, LIBS can be an excellent analytical method to obtain the compositional information in a short time. Zhang et al.[43] proposed an online LIBS setup and applied it to the in situ detection of smoking in a public area. As shown in Fig. 2-4, to realize the in situ detection, the laser pulse generated by a high-intensity Q-switched Nd:YAG laser is directly focused on the smoke, and the emission spectrum is obtained by the monitor. The plasma radiation emission was directly collected by an optical fiber coupled to a high-resolution spectrometer.

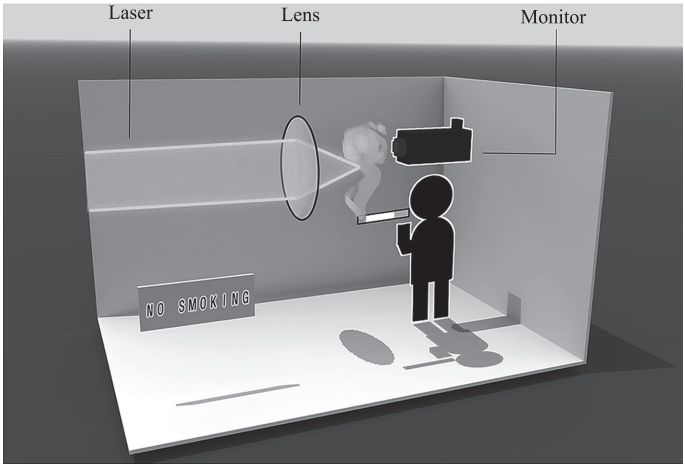


Fig. 2-4 The schematic diagram of the online LIBS experimental setup for smoking detection[43]

2.3.3 Signal Enhancement for LIBS

For decades, the LIBS setup has undergone a dramatic transformation in terms of hardware and software. Since the lack of detection sensitivity has severely limited, LIBS for widespread applications, some advancements like double-pulse LIBS, magnetic and/or spatial confinement, have been proposed by researchers to enhance the LIBS signals.

Double-pulse LIBS is the most common transformation of conventional LIBS setup. Double-pulse LIBS was first proposed by Piepmeier and Malmstadt in 1969[44]. The principle of the double-pulse LIBS is that the first laser pulse interacts with the material after focusing and is then excited and melted. At a suitable time, the second laser pulse will re-excite the generated plasma and the secondary melting of the sample. This enhances the characteristic spectral signal. Double-pulse LIBS is mainly divided