Analytical Applications of Lasers

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PREFACE

This book is written for a person who has a scientific background and who is interested in learning about the many different ways lasers are used for determining concentrations of a wide variety of chemicals in many types of samples. The person who is familiar with lasers also will find this book helpful in learning more about how lasers are applied in analytical chemistry to solve both unique and common measurement problems.

Lasers make possible the determination of concentrations of chemical species spread over a range of many kilometers, or the counting of individual molecules passing the focal point of a tightly focused beam of light. The chemical species may range from small atoms to very large molecules; from those that are free in a vacuum to those that are bound onto a surface. Samples may be gases, liquids, or solids. Analyte concentrations range from those of major constituents to ultra trace levels.

Lasers allow absorption measurements that are limited only by shot noise over a long period of time, or the observation of transient species on a subpicosecond time scale. High spectral resolution is achieved for species that are otherwise overlapped. Multiphoton transitions populate excited states that would not otherwise be conveniently attainable and thereby improve the selectivity of an analytical determination.

Some laser measurements provide information that is unique and complementary to that obtained by other methods. Some methods take advantage of a special characteristic of a laser and simply substitute the laser as a component in an ordinary type of measurement system. Still other measurements, envisioned decades ago, have now become practical because of the use of lasers.

The book begins with an introductory chapter on the basic principles of lasers, as well as nonlinear optical effects, which are fundamental to some laser methods. The person familiar with lasers and nonlinear effects may skip this chapter or use it as a brief consolidating review. With so many laser methods to cover, the book was further subdivided into several parts, based on prominent characteristics of the methods. This is purely a convenience, and the reader will quickly recognize that the subdivisions are not exclusive; some methods could reside in more than one place.

To preserve the individual styles of the authors, I made few editorial changes in the content of any chapter. Some overlap of material remains in order to help the reader who wishes to concentrate on selected chapters, without having to study preceding chapters (except perhaps for Chapter 1).

It is intended that this book be educational, and that it present some of the most recent advances in the field. Chapters generally include discussions of the principles of the methods, diagrams of instrumental configurations, typical figures of merit, examples of applications to analytical problems, and speculation about the future. I anticipate that this book will find use in graduate level courses for students who are interested in learning more about and using laser methods in analytical chemistry. I also hope that it will attract people to this expanding field, who will bring new ideas to further advance the applications of lasers in analytical chemistry.

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I

INTRODUCTION

CHAPTER

1

BASIC PRINCIPLES OF LASERS AND NONLINEAR OPTICAL EFFECTS

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1. INTRODUCTION

This chapter provides the background for the reader to understand the properties of lasers that are important in the analytical applications discussed in the rest of the book. Lasers emit radiation that has unique properties, which are employed to solve both routine and special problems in analytical chemistry. Because all lasers do not exhibit these properties to the same extent, this chapter will also help in understanding compromises that are often necessary.

We shall start by mentioning important properties and then continue with a brief discussion of the theory of operation of a laser and laser components, which control beam properties. With this background, we shall discuss laser beam properties in sufficient detail to satisfy the requirements for the chapters that follow. Additional details are included in the chapters when appropriate.

Well-known properties of laser beams are high intensity, directionality, and monochromaticity. Coherence is also an important property because it influences the cross-sectional spatial profile, the temporal profile, and the spectral profile of the laser beam. In addition to these properties are characteristics that are important in analytical applications, although one might not immediately think of them when the word *laser* is mentioned. These include polarization and tunability over a wavelength region. And, of course, daily operating costs and serviceability are important in routine applications.

One of the most desirable characteristics of a laser beam for analytical applications is reproducibility. Unfortunately, obtaining a laser beam that has excellent reproducibility in all of the desired characteristics may be expensive, and not always practical. When the unique properties of a particular laser are necessary to help solve a problem, it is important to consider the influence that reproducibility of those properties may have on the final results.

2. STIMULATED EMISSION

The laser is made possible by stimulated emission, an effect which is inherently related to the well-known effects of spontaneous emission and absorption. All three of these effects are related to each other by the Einstein probability coefficients, which occur in the rate constants for the equations that give the rate at which atoms in one energy level make transitions to another energy level. For an atomic system with energy levels E_1 and E_2, the rate of spontaneous decay (per unit volume) to level 1 of the population in the higher energy level 2 is given by

$$\frac{dn_2}{dt} = -A_{21}n_2 \tag{1.1}$$

where n_2 represents the number of atoms per unit volume in level 2 and A_{21} (s^{-1}) is the Einstein probability coefficient for spontaneous emission for that transition. Its reciprocal $\tau_{sp} = 1/A_{12}$ is the radiative lifetime and is a characteristic parameter of that transition. The other two Einstein coefficients apply when the atoms are irradiated by a plane electromagnetic wave, when the radiation beam is polarized and the atoms are randomly oriented, or when the beam is unpolarized. Then the rate of transitions from level i to level j is given by

$$\frac{dn_i}{dt} = -W_{ij}n_i \tag{1.2}$$

where the rate constants W_{ij} (in s^{-1}) are given by

$$W_{ij} = B_{ij}EL(\lambda - \lambda_0) \tag{1.3}$$

In this equation E (W cm^{-2}) is the irradiance of the incident monochromatic radiation, at wavelength λ, and $L(\lambda - \lambda_0)$ is the spectral lineshape function with a central wavelength λ_0 and normalized so that its integral over all wavelengths λ is unity. B_{ij} is the Einstein probability coefficient for stimulated emission when the transition is from the upper level 2 to the lower level 1, and is the Einstein probability coefficient for (stimulated) absorption when the transition is from the lower level 1 to the upper level 2. Equation (1.3) shows that the stimulated transition rates are proportional to the irradiance of the external radiation, and also depend on how far the wavelength λ of the radiation is from the central wavelength λ_0 of the line.

When the spectral width of the laser beam is large relative to the atomic linewidth, the rate constants are given by

$$W_{ij} = B_{ij}E_{\lambda_0} \tag{1.4}$$

where E_{λ_0} is the spectral irradiance (irradiance per unit of wavelength interval, W cm^{-2} nm^{-1}) at the atomic line center λ_0.

The Einstein coefficients are directly proportional to each other:

$$A_{21} = \frac{8\pi hc^2}{\lambda_0^5} B_{21} \tag{1.5a}$$

$$B_{12} = B_{21}\frac{g_2}{g_1} \tag{1.5b}$$

where h is Planck's constant, c is the speed of light, and each degeneracy factor, g_1 and g_2 (for energy levels 1 and 2, respectively), is the number of different physical configurations of the atom that happen to have the same energy level in the absence of a magnetic field. It should be emphasized that B_{ij} has been defined in the wavelength rather than the frequency domain, and in terms of irradiance rather than power density or radiant energy density.

2.1. Saturation and Bleaching

Notice in Eq. (1.5) that the probability coefficients for stimulated emission and absorption are equal, except for the factor g_2/g_1, which is unity in the simplest case and is usually not very far from unity in real systems. Consequently, when a population of atoms is strongly irradiated so that the stimulated transitions are much more frequent than spontaneous transitions or transitions caused by collisions (e.g., quenching), the population approaches a condition of saturation, where there is an equal number of atoms in levels 1 and 2. Then it is equally probable that a photon will be absorbed or that a photon will be emitted. Photons that are emitted by stimulated emission have the same wavelength and travel in the same direction as the incident photons. Therefore, when a beam passes through a saturated population of atoms, there is no net gain or loss of photons and the population appears to be transparent or bleached. This effect makes it impossible to invert a two-energy-level population by *optical* pumping, and it has important consequences when exciting an analyte population with a laser beam to obtain a signal.

Because the stimulated transitions (in both directions) in a saturated population are much more frequent than other transitions such as quenching, the fraction of atoms in the excited state in a population in a steady-state condition is not influenced by changes in quenching; a loss by quenching is quickly replaced by an excited state formed by a stimulated transition. Consequently, fluorescence emission, which is proportional to the excited-state population, is independent of irradiance or quenching rates in a saturated population. This contrasts with an unsaturated population in which fluorescence may be dramatically decreased by quenching collisions.

In addition to its advantages, saturation has a disadvantage: it decreases spectral selectivity because it broadens the absorption, or excitation, spectral line profile. Consider the case where a monochromatic excitation beam scans across a spectral transition. At low irradiances the ordinary spectral profile of the transition can be observed by absorption. As the irradiance caused by the excitation beam is increased, the center of the spectral line profile eventually approaches complete transparency, its peak value, while the wings of the profile still absorb. After the center has become transparent, the wings continue to approach transparency (the same peak value) as the irradiance continues to increase. The effect is a profile that becomes broader and broader as the irradiance of the excitation beam is increased. The result is reduced spectral resolution for adjacent spectral lines.

2.2. Beam Amplification

Ordinarily, most atoms in a population are in the lower energy level, and absorption occurs much more frequently than stimulated emission. If the population of atoms were inverted so that most of the atoms were in the upper energy level, then stimulated emission would occur more frequently than absorption. When this happens, the beam gains photons at the same wavelength, all of which travel in the same direction, and the beam is said to be amplified. Beam amplification is basic to the operation of a laser.

3. BASIC LASER COMPONENTS

A laser has three basic components: an optical amplifier, an excited-state pump, and an optical resonator or cavity. The optical amplifier has a population or set of atoms, molecules, or ions with a larger fraction of the population in higher energy levels than in the corresponding lower energy levels. Because an ordinary population has a larger fraction in lower energy levels, the population in the amplifier is said to be inverted. The excited-state pump is the means by which this population inversion is maintained. The resonator is a tuned feedback component that converts the amplifier into an optical oscillator, in much the same way that tuned feedback components are used to convert an electronic amplifier into an oscillator. The characteristics of a particular laser beam depend on the details of the energy levels in the amplifier, the mechanism used to pump the amplifier, and the resonator design. These will be described in more detail.

3.1. Optical Amplifier

An optical amplifier has an active medium containing an inverted population that causes a beam of radiation passing through it to gain photons if the wave-