

5

General Concepts of Laser Spectroscopy

Spectroscopy in general and laser spectroscopy in particular may be defined as the measurement of the outcomes of the interaction of photons, or a light wave, with matter, which, in the context of the topics in this textbook, means atoms and molecules predominantly in the gas phase interacting with laser radiation. Procedures to undertake such measurements can be based on a range of detection methods, including (i) photon detection methods, (ii) charged particle detection methods and (iii) methods exploiting changes of (macroscopic) physical properties of the medium with which the probe light wave interacts.

Photon detection methods are associated with absorption, emission or scattering of electromagnetic radiation by atoms and molecules (or atomic and molecular ions).

Ion detection methods rely on the phenomenon that the interaction of photons with a neutral particle results in its ionization; either the negatively charged electron or the positively charged atomic/molecular ion can be detected.

A range of detection procedures exploit that the absorption of radiative energy changes the physical properties of the absorbing medium; it is the change in the property of the medium that is measured to deduce the interaction process.

Most of the detection methods summarized here, and described in more detail in the following sections,

allow one to study the atoms or molecules themselves (e.g. determination of their energy level structure), or to study physical or chemical processes (e.g. perturbation of thermal equilibrium or the occurrence of a chemical change). Either qualitative or quantitative results, or both, may stand at the end of a measurement evaluation procedure.

It is worth noting that the above-mentioned methods of detection are conducted in a directional or a non-directional manner with respect to the propagation of the incoming laser beam. Absorption measurements are carried out in the forward direction of the laser beam (the loss of photons out of the probing photon flux). In emission and scattering measurements, the fact is exploited that these photons are predominantly leaving the interaction medium off-axis, into any direction of the full solid angle Ω ; in general, the detector is placed at right angles to the propagation direction of the laser beam, for physical reasons (unwanted scattering is often minimal at right angles to the laser beam) and for reasons of convenience (often the geometry of the interaction volume dictates right-angle configurations). The direction for the detection of photoelectrons or photo-ions can be chosen, more or less, at will, since the charged particles can be directed conveniently to a charge-sensitive detector by applying an external electric extraction field. No

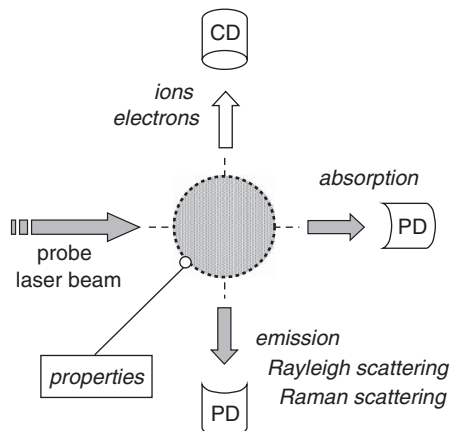


Figure 5.1 Principal detection methods for laser probing of an ensemble of particles

overall directional information is maintained in the methods, which measure the bulk property changes as subsequent to the photon–particle interaction.

The principal detection methods discussed in this chapter are summarized in Figure 5.1.

5.1 Spectroscopy based on photon detection

The interaction of radiation with matter can cause redirection of the radiation and/or induce transitions between the energy levels of the atoms or molecules. A transition from a lower level to a higher level with transfer of energy from the radiation field to the atom or molecule is called *absorption*. A transition from a higher level to a lower level is called *emission* if energy is transferred to the radiation field or *non-radiative decay* if no radiation is emitted. Redirection of light due to its interaction with matter is called *scattering*, and may or may not occur with transfer of energy, i.e. the scattered radiation has a different or the same wavelength.

The absorption of photons

When atoms or molecules absorb light, the incoming photon excites the particle from its ground state to a

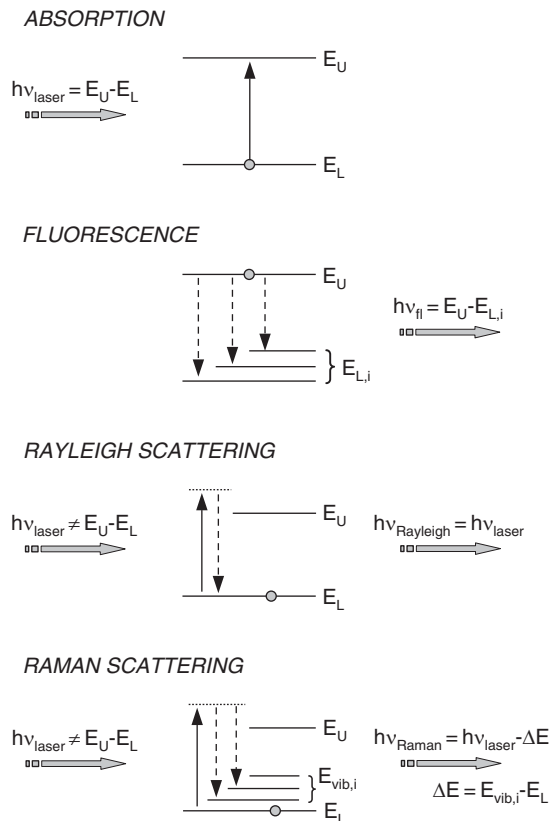


Figure 5.2 Photon detection methods in photon–particle interaction processes

higher (quantized) energy level. In the absorption process the photon energy is equal to the difference between a lower and an upper energy level (see Figure 5.2). The type of excitation depends on the wavelength of the light: electrons are promoted to higher orbitals (in atoms and molecules) by UV or visible light, IR light excites vibrational levels in molecules, and microwaves are normally required to excite rotational levels in molecules.

An absorption spectrum is generated if the light field has a distribution of energies, which simultaneously or sequentially are in resonance with a range of excited levels, i.e. it is the absorption of light as a function of wavelength. The spectrum of an atom or molecule depends on its particular energy level structure, and thus absorption spectra are useful for identifying compounds by exploiting the relationship between spectral lines and energy levels. By

measuring the amplitude of a particular spectral line of an absorbing species in a sample one can derive its concentration by applying the Beer–Lambert law (see Chapter 6).

The emission of photons

Once atoms or molecules have been excited to high-lying energy levels they can decay to lower levels by emitting radiation (emission or luminescence); for the schematic of the process see Figure 5.2. For *atoms* excited by a high-temperature energy source this light emission is commonly called (*atomic*) *optical emission*; for atoms excited by photons it is normally called (*atomic*) *fluorescence*. For *molecules* it is called *fluorescence* if the transition is between states of the same total electron spin, and it is called *phosphorescence* if the transition occurs between states of different total electron spin.

The emission intensity of an emitting species is linearly proportional to the analyte's concentration, at least for low concentrations; in this way, quantification of the emitting species can be realized, provided a number of other parameters are known (see Chapter 7).

The scattering of photons

When a beam of electromagnetic radiation passes through matter, most of the radiation continues in its original direction; however, a small fraction is scattered in other directions.

The process in which light that is scattered in such a way that its wavelength is the same as that of the incoming light is called *Rayleigh scattering*. When light is scattered in such a way that its wavelength is different from the original light wave, due to the interaction with vibrational and rotational levels in molecules, the process is called *Raman scattering*. Raman scattered light is shifted from the incident light by as little as a few wave numbers (for rotational transitions) or by as much as 4000 cm^{-1} (e.g. for H_2 and its vibrational levels) changes. The two processes are shown schematically in the lower half of Figure 5.2. For more details see Chapter 8.

5.2 Spectroscopy based on charged particle detection

Since electrons, or ions, are easier to collect than light, higher efficiency in the optimization of signal detection is often encountered. By avoiding the necessity of detecting photons, resonance ionization spectroscopy (RIS) circumvents one particularly niggling source of background noise, namely scattered light. Thus, charged particle detection can be said to have inherent background-reducing features, in principle producing very 'clean' spectra.

Despite these advantages, RIS is neither the obvious nor the easiest choice for spectroscopic studies. Being a multi-step excitation process (at least two steps are required), more than one laser is often required. In addition, the last step into the ionization continuum normally requires high laser powers. On the other hand, modern laser sources have afforded the implementation of RIS rather efficiently, and it has developed into an extremely useful and versatile tool. The principle is shown schematically in Figure 5.3, for the two possible cases: (i) that the two photons are

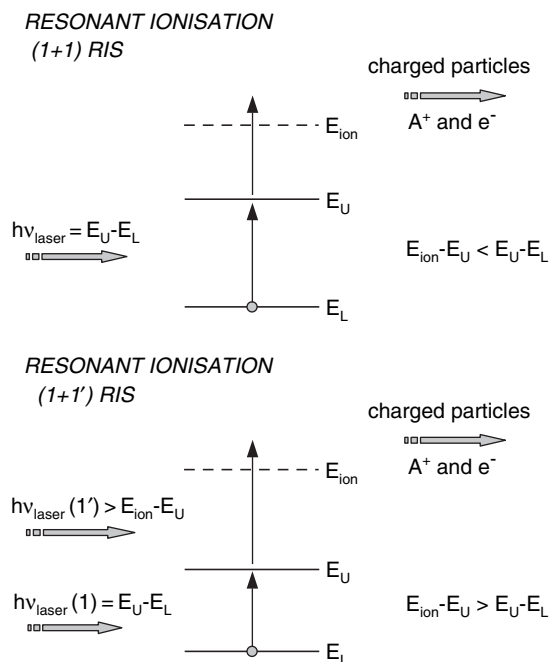


Figure 5.3 Charged particle detection methods: single-photon resonances in photon–particle interaction processes

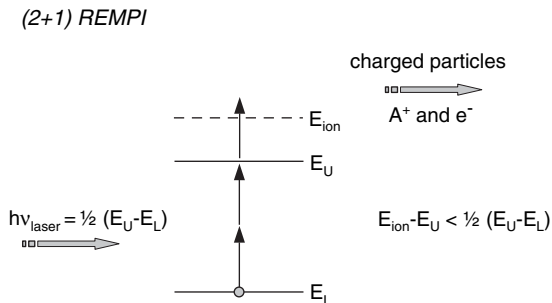


Figure 5.4 Charged particle detection methods: multi-photon resonances in photon–particle interaction processes, here exemplified for a (2 + 1)-REMPI process

equal, i.e. only one laser is required; (ii) that the two photons are different, i.e. two laser sources are required. The two schemes are often addressed as (1 + 1) and (1 + 1') RIS respectively.

Quite often, monochromatic laser light is applied under conditions of high photon flux, to excite the species of interest efficiently. Under such circumstances, a process that utilizes n -photon resonance in the first excitation step and requires additional m photons for final ionization (most frequently $m = 1$ is encountered) occurs with measurable probability and is of analytical relevance. The technique is called REMPI and uses, as noted, stepwise resonant excitation of an atom or molecule via stable intermediate energy levels. It is usually described as $(n + m)$ -REMPI spectroscopy; the most frequently used (2 + 1)-REMPI principle is depicted in Figure 5.4.

Because it is possible to detect single ions, RIS and REMPI are potentially extremely sensitive and a valuable method to investigate many problems in trace analysis and chemical reaction dynamics. For details on ion detection, see Chapter 9.

5.3 Spectroscopy based on measuring changes of macroscopic physical properties of the medium

When laser radiation is absorbed by a medium, broadly speaking this constitutes a deposition of energy and a perturbation of the thermal equilibrium.

In the case that a sufficient number of individual atoms and molecules participate in the photon–matter interaction, the medium undergoes macroscopic changes, which may be global or localized. Such changes can be measured using detectors sensitive to them, and one can deduce properties of the probed species from correlating the system response to the laser wavelength and photon flux density.

Photothermal spectroscopy

One popular technique for the detection of trace gases in standard (room-temperature) gas samples is the method of *photothermal spectroscopy*. Photothermal spectroscopy may be classified as an indirect method, since it does not measure the transmission of light used to excite the sample directly, but rather measures the effects that optical absorption has on the sample, specifically thermal changes; e.g. see Harren *et al.* (2000).

The basic processes responsible for photothermal effects in a medium are summarized in Figure 5.5. Optical radiation, usually from a laser, is absorbed in the sample, which in turn results in an increase of internal energy. This additional internal energy is dispersed by hydrodynamic relaxation, which basically means that a temperature change in the sample is observed.

Three things have to be considered in order to arrive at a quantitative description of the photothermal spectroscopy signal.

First, a description of the optical absorption and excited-state relaxation processes is required. Optical excitation followed by excited-state relaxation results in sample heating if the non-radiative transfer mechanisms dominate over radiative decay back to the ground state. The rates and amounts of excited-state excitation and relaxation determine the actual rate and magnitude of heat production. The energy transfer steps that need be accounted for are also shown in Figure 5.5. Note that energy may also be transferred to the sample by optical absorption and inelastic scattering processes, such as Raman scattering; however, scattering is normally very inefficient and the amount of energy deposited in a sample is usually too small to be detectable.

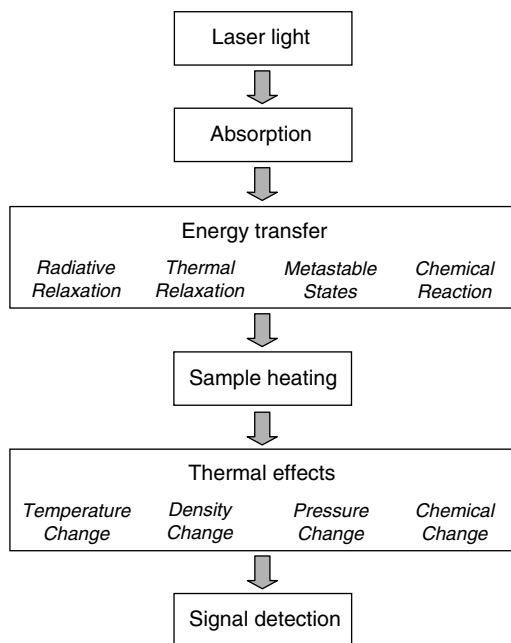


Figure 5.5 Processes involved in photothermal spectroscopy. Absorption of laser radiation is followed by non-radiative energy transfer, which affects the sample temperature, pressure and particle density. The effects of these sample changes are detected

Second, hydrodynamic (macroscopic) relaxation of the deposited energy and the related heat needs to be considered. After optical heating, the sample is not at thermal equilibrium with itself or with the surrounding environment during a measurement. Thus, heat generated by the optical excitation and relaxation processes will result in thermal gradients within the sample and with its surroundings; because of these thermal gradients, heat transport ensues to move the sample toward thermal equilibrium again. The hydrodynamic relaxation addressed here basically generates changes in the temperature, pressure, and density of the (gaseous) sample.

Third, the processes responsible for signal generation need to be contemplated. In essence, photothermal spectroscopy signals are based on changes in sample temperature or related thermodynamic properties of the sample, as just outlined. These are usually monitored through density or refractive index changes of the sample; the most sensitive

methods probe the spatial or temporal gradients of these properties.

It should be noted that the laser excitation of a sample with a given absorption coefficient will generate a temperature change directly proportional to the optical power (in the case of continuous excitation) or energy (in the case of pulsed excitation). The subsequent photothermal spectroscopy signal is, in general, proportional to the temperature change. This means that the greater the power or energy of the excitation source, the larger the resulting signal. It should be noted that the temperature change is not only proportional to the optical power or energy, but also is inversely proportional to the volume over which the light is absorbed, since heat capacity scales with the amount of interacting sample particles.

The principle configurations of how to realize a photothermal spectroscopy experiment are summarized in Figure 5.6. In general, the analyte is confined within a small, fixed-volume enclosure V ; the absorption of photon energy generates a (local) thermal disturbance ΔT . For the signal generation one exploits, for example, the particle density or the refractive index gradient caused by this thermal disturbance. As a result, a second probe laser beam (at a wavelength not being absorbed by the sample) experiences a sample volume whose properties vary

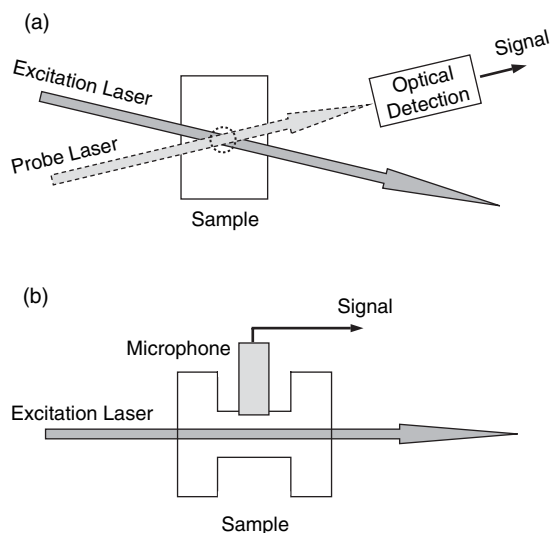


Figure 5.6 Generic measurement set-ups for (a) photothermal and (b) photoacoustic detection

locally, and hence its passage through the medium is affected (see Figure 5.6a). Most commonly, three methods of photothermal spectroscopy exploiting refractive index changes and gradients in the medium are used.

In *interferometry* the refractive index change of the medium is measured directly (for this the excitation and probe beams are collinear); the sample is placed within an interferometer cavity, and the changed refractive index affects the interference fringes measured for the probe beam.

The excitation volume generated by a Gaussian profile laser beam constitutes a *thermal lens*, and hence a probe beam focuses or defocuses on passage through the thermal lens volume. Therefore, a different spot size of the probe laser beam is observed at the location of a photodetector; the diameter change can be measured directly with a position-sensitive detector.

Similar to the thermal lens effect is exploitation of the fact that a narrow probe laser beam exhibits *deflection* as a consequence of a refractive index gradient; again, the amount of deflection can be measured using a position-sensitive photodetector.

Further details on photothermal spectroscopy methods, particularly their applications in chemical

analysis, may be found, for example, in Bialkowski (1996).

A particular variant of the photothermal response of a medium to laser excitation is *photoacoustic spectroscopy*. In this detection technique one exploits the thermally induced pressure change. A change in temperature ΔT translates into a pressure change Δp , according to the gas kinetic equation $\Delta pV = R\Delta T$, where R is the gas constant. It is the pressure change that is then detected. For the method to work efficiently, the excitation by laser light should be periodic (the light intensity is modulated). The principle of the technique is shown in Figure 5.6b. The intensity-modulated laser beam originates either from a continuous laser whose beam is periodically interrupted by a chopper, or from a pulsed laser source. For signal detection, sensitive pressure transducers or microphones are used, depending on the frequency range of the laser beam modulation. It should be noted that the term photoacoustic spectroscopy indicates that the modulation is in the range of acoustic frequencies, i.e. about 20–20 000 Hz. An example for photoacoustic detection of trace particles in a gas volume, namely soot particles in diesel exhaust gases, is shown in Figure 5.7.

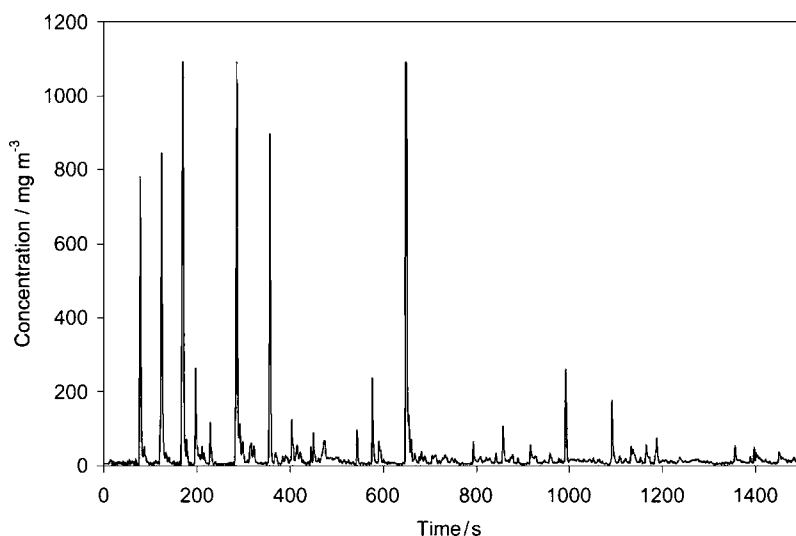


Figure 5.7 Photoacoustic signal of a driving cycle during diesel engine testing, simulating in sequence a vehicle driving through a city, on a highway and on a motorway. Data adapted from Haisch and Niessner; *Spectroscopy Europe*, 2002, **14/5**: 10, with permission of John Wiley & Sons Ltd

Optogalvanic spectroscopy

The interaction of resonant radiation with atoms or molecules present in a discharge can induce variations in the electrical properties (impedance) of the discharge. This effect, known as the optogalvanic (OG) effect, has been shown to be a powerful and inexpensive technique for the spectroscopic investigation of atomic and molecular species.

In order to understand the OG effect, it is useful to recall briefly the basics of low-pressure gaseous discharges. When the DC potential V applied across the two electrodes in series with a current-limiting resistor R_L surpasses the so-called breakdown voltage, a self-sustained (luminous) discharge is produced, sustained by charge carriers (electrons and ions). The nature of the buffer gas, its pressure, the geometry of the cell, the separation of the electrodes, their size and their material are parameters that can change the appearance and the properties of the discharge.

When laser radiation is tuned to a resonant transition of an atomic or molecular species present in the discharge, the discharge is perturbed by the deposition of energy, essentially via (i) variations of electron-ion pair production and (ii) variation of the electron and gas temperatures. As a consequence, the electrical properties of the discharge are changed. If one considers the gas discharge volume as being equivalent to a variable resistor R_D in series to the load resistor R_L , then any changes in R_D imply a current change in the circuit (associated with a change in voltage drop across the resistors). Thus, the OG signal can be measured using a sensitive current meter or

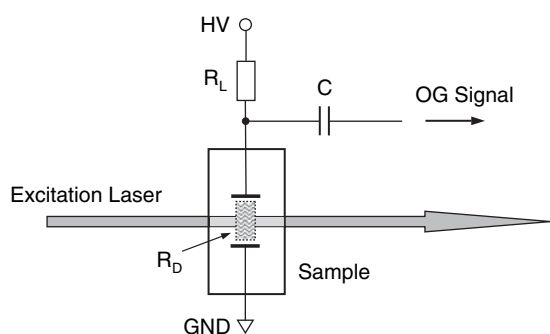


Figure 5.8 Generic measurement set-up for OG detection

voltmeter; no photodetector is required. The principle of OG signal generation and detection is shown in Figure 5.8.

It should be noted that, in general, the changes in discharge properties are extremely small, and hence direct DC measurements, relative to the high voltage driving the discharge, are normally very difficult. If one exploits transient excitation by modulated or pulsed laser radiation, the related AC changes in the discharge can be decoupled from the DC component via a capacitor. A typical example for an OG signal measured in this way, for excitation of a transition in an argon discharge, is shown in Figure 5.9. One of the most common applications of OG spectroscopy is in the absolute wavelength calibration of laser sources.

Finally, we would like to mention a derivative of OG spectroscopy, which is conducted not in a discharge cell but in a (hot) flame; the technique is often referred to as *laser-enhanced ionization* (LEI). The technique is used for sensitive detection of trace atoms and molecules. The excitation of the species under investigation populates high-lying energy levels; the thermal heat of the hot flame is sufficient to ionize the species out of their excited levels. Electrodes placed around the flame detect the charge carriers generated in this way. Further details on the principles and applications of OG spectroscopy and LEI can be found, for example, in Stewart *et al.* (1989).

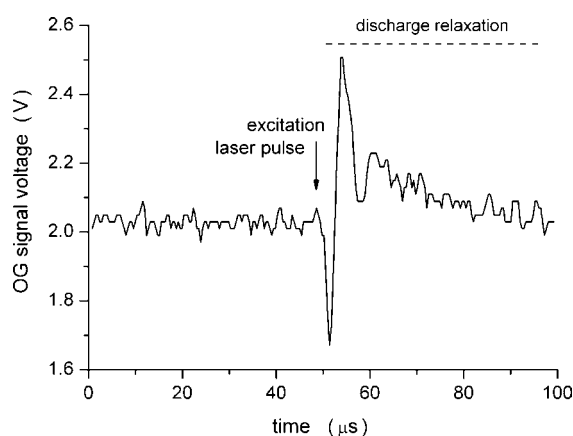


Figure 5.9 Time evolution of an OG signal in a hollow-cathode discharge lamp, associated with an atomic transition (Ar line at 811.369 nm), after excitation with a 10 ns pulse from a Ti:sapphire laser