Absorption spectroscopy

Laboratory practical

Atomic and Molecular Spectroscopy (FAFF080/FYST14)

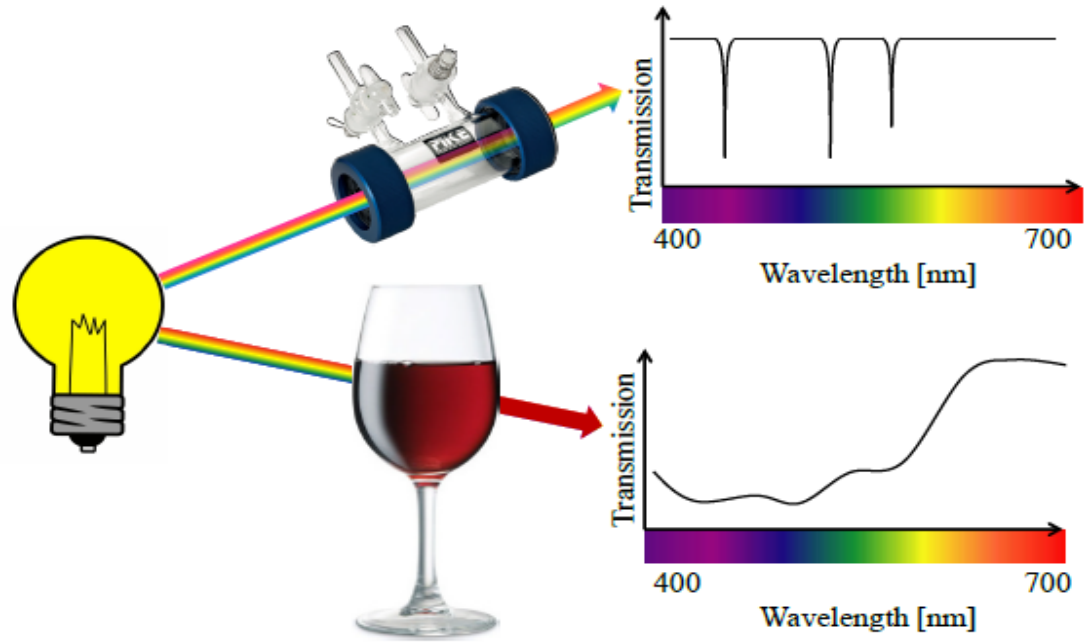

Illustration taken from: P. Lundin, Doctoral Thesis, LRAP-488, Lund University, 2014

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Introduction

The present laboratory practical deals with laser-based absorption spectroscopy, which is a very powerful technique for detection and quantification of species concentrations. While absorption spectroscopy can be used for liquid and solid phase analysis, it is arguably best suited for gas-phase analysis, as free gases are characterized by extremely sharp absorption lines, typically 100 - 10000 times sharper than those encountered in liquids and solids (as schematically illustrated in the figure on the front cover). Pure gas-phase measurements are often easy to quantify as they generally obey the Beer-Lambert law. With a method called Gas in Scattering Media Absorption Spectroscopy (GASMAS) it is possible to probe gases contained in dense, highly scattering, media. By injecting narrowband laser light into a highly scattering and porous material, a gas absorption imprint is generated as the light passes through gas-filled pores. Thus, a spectrum carrying high-resolution gas absorption imprints may be detected at in principle any point. GASMAS is based on tunable diode laser absorption spectroscopy (TDLAS), and the spectrum is thus acquired sequentially by scanning the wavelength of the narrow-band diode laser across an absorption feature.

Purpose

The aim of the laboratory practical is to:

- train the ability to make deductions from absorption spectroscopic measurements and interpretation of data
- get familiarized with experimental equipment commonly used in absorption spectroscopy
- foster critical awareness
- help bridge theory and practice
- illustrate material taught in lectures

Laser safety

A continuous wave diode laser belonging to Class 3B at 760 nm will be used in this lab. This wavelength is not visible to the naked eye but can be seen on an IR sensitive card. The laser light is hazardous if the eye is exposed directly, but diffuse reflection such as those from paper or other matte surfaces are not harmful.
Some general precautions:

- You should always wear laser safety googles made for the wavelength in use to protect against unexpected reflection.
- Do not wear any accessories or clothes that may cause specular reflection, such as jewelry and watches.
- The laser beam should always be below your eye level, which means that you should always stand up in the laser laboratory. If you have to bend down to pick something up, the laser should be turned off or blocked.
- Do not put your hand (or other body part) in the laser beam.
- Make sure that there are no reflections from the optical components directed back into the laser head.
- Food and drink should not be consumed in the laboratory.
- Ask the instructor in case you have any questions or doubts about the equipment or safety precautions.

Pre-laboratory activities

Read Section 11.5 in the textbook (Demtröder, Atoms, Molecules and Photons, 2nd edition) and the lecture material on "Molecules". Read this memo and answer all questions (marked in red) incorporated in the text.

Absorption spectroscopy

Direct absorption spectroscopy

The basic principle of direct absorption spectroscopy is simple: light with a frequency close to a transition frequency of the atom or molecule of interest is sent through the sample and the intensity of the light transmitted through the sample is detected (see Fig. 1). In order to determine the absorption, which is related to the concentration of the atom/molecule under investigation, the transmitted intensity is compared to the incident light intensity. It is possible to use either broadband light, for example sun light, in combination with a monochromator or a spectrograph for spectral dispersion of the transmitted light, or a narrowband light source, such as a laser, which does not require spectrally dispersed detection.

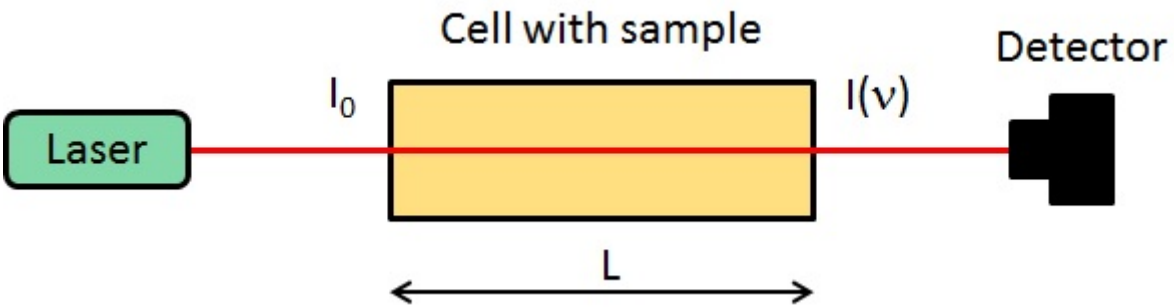

Fig. 1 *Schematic setup for absorption spectroscopy using a narrowband laser*.

Assuming a setup based on a narrowband tunable laser and a gas contained in a cell of length L, as shown in Fig. 1, the transmitted intensity, measured by the detector, is given by the Beer-Lambert law:

$$I(\nu) = I_0 e^{-\alpha(\nu)L} \qquad (1)$$

where $\alpha(\nu)$ is the frequency-dependent absorption coefficient. Since the exponent must be dimensionless, the SI unit of α is m^{-1}, but it is most often given in cm^{-1} in the literature. The number density of absorbing atoms/molecules, N, which has the SI unit molecules/m^3 but most often is given in molecules/cm^3, is contained in the absorption coefficient, which may be expressed:

$$\alpha(\nu) = N\sigma(\nu) \qquad (2)$$

where $\sigma(\nu)$ is the frequency-dependent absorption cross section, whose SI unit is m^2, but it is commonly given in the unit cm^2. Substituting (2) into (1) results in the expression:

$$I(\nu) = I_0 e^{-N\sigma(\nu)L} \qquad (3)$$

The exponent, i.e. Nσ(ν)L, is sometimes referred to as optical depth or optical thickness. A medium is said to be optically thick when Nσ(ν)L > 1 and optically thin when Nσ(ν)L << 1. For an optically thin medium (3) may be simplified (using $e^{-x} \approx 1-x$ for x<<1) into:

$$I(\nu) = I_0(1 - N\sigma(\nu)L) \qquad (4)$$

In the present laboratory practical direct absorption spectroscopy utilizing a tunable diode laser will be carried out for measurement of oxygen (O_2) concentration. The diode laser will be scanned across an absorption line in the so-called A-band of O_2, located near 760 nm, and the oxygen concentration will be determined by analyzing the recorded spectrum using the Beer-Lambert law.

The oxygen A-band is the transition $b^1\Sigma_g^+(v' = 0) \leftarrow X^3\Sigma_g^-(v'' = 0)$, i.e. a transition between the lowest vibrational level, v''= 0, of the electronic ground state, $X^3\Sigma_g^-$, and the lowest vibrational level, v'= 0, of the second excited electronic state, $b^1\Sigma_g^+$.

Question 1: What are the quantum numbers associated with the total electronic spin (S) and the total electronic orbital angular momentum (Λ) of the two states?

Question 2: Is the transition allowed according to quantum mechanical selection rules?

Question 3: Ambient air contains 21.0% O_2. A narrowband diode laser is tuned to the peak of the $R_{15}R_{15}$ transition in the A-band of O_2 (see Table 1) and the absorption path length in ambient air is 100 cm. Calculate how much of the laser light that will be absorbed by the oxygen molecules.

Table 1 *Line positions, peak-absorption cross sections, and assignments for R-branch transitions of the O_2 A-band, i.e. $b^1\Sigma_g^+(v' = 0) \leftarrow X^3\Sigma_g^-(v'' = 0)$.*

Wavenumber (cm^{-1})	Wavelelength (nm)	$\sigma_{peak}\cdot10^{23}$ (cm^2)	Assignment
13128.26932	761.71503	1.3733	R1Q2
13131.49186	761.52810	1.8295	R3R3
13133.44172	761.41504	2.8289	R3Q4
13136.21715	761.25416	3.0199	R5R5
13138.20517	761.13897	3.9024	R5Q6

The signal extracted from tunable diode laser absorption spectroscopy contains a smaller absorption imprint on top of a larger background, as can be seen in Fig. 2. Figure 2 illustrates the major drawback with direct absorption spectroscopy, namely that its sensitivity is limited by strong noise on the detected signal. This noise may originate from laser-intensity fluctuations, laser-frequency fluctuations (if the laser frequency fluctuates when it is within the absorption profile, that frequency fluctuation will be converted into an intensity fluctuation on the transmitted light), detector noise, shot-noise (photon noise), and other technical noise. If the absorption is strong enough, i.e. the concentration of the absorbing species is high enough, providing an adequate signal-to-noise ratio (SNR), it is possible to make accurate measurements with direct absorption spectroscopy. However, for detection of species abundant in low concentrations or species with low absorption cross sections, methods able to reduce noise on the absorption signal are necessary. One such method is wavelength-modulation spectroscopy (WMS).

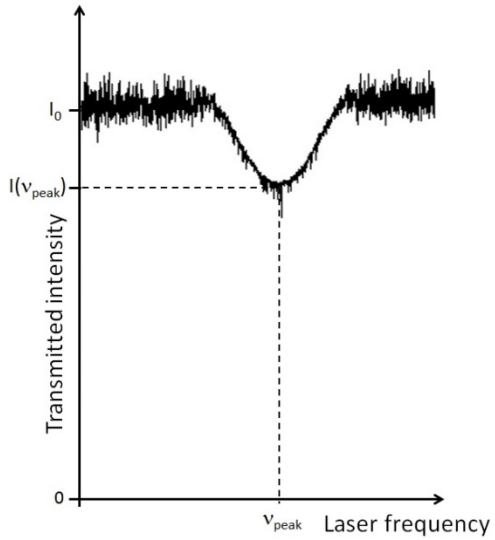

Fig. 2 *Recorded signal using direct absorption spectroscopy.*

Question 4: The sensitivity of direct absorption spectroscopy is dictated by the achievable signal-to-noise ratio (SNR). One way to improve the SNR is to reduce the noise, and this is, as we will see, what WMS does. Could you think of any other possible ways to increase the SNR (except increasing the species concentration or its absorption cross section)?

Wavelength-modulation spectroscopy

Wavelength-modulation spectroscopy is a technique where the wavelength of the laser light is modulated at a relatively high frequency (typically ~10 kHz) and the detected light, after absorption, is evaluated at the modulation frequency or a harmonic of this frequency. Since technical noise primarily resides at low frequencies, often it depends on the frequency as 1/f (hence often termed 1/f noise), WMS allows efficient noise suppression as the detection is shifted to a high frequency where the noise is significantly lower. The detection can be done either with an analog or a digital lock-in amplifier (time domain) or with Fourier analysis (frequency domain).

Lock-in amplifier

A lock-in amplifier is a signal processing instrument that is employed when it is favorable to pick out a certain frequency component of a signal. This is clearly the case in WMS where the laser light is modulated at a specific frequency. The basic principle of a lock-in amplifier is shown in Fig. 3.

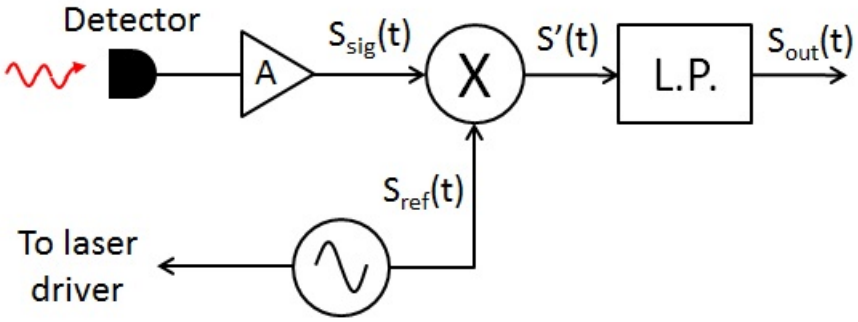

Fig. 3 *Basic schematic of a lock-in amplifier.*

Let us assume a sinusoidal signal at the detector, which after amplification becomes $S_{sig}(t) = A\sin(2\pi ft+\theta)$. A signal generator produces a reference signal that is sent to the laser driver to create the wavelength modulation on the laser radiation. This reference signal is also sent to a mixer where it is multiplied with $S_{sig}(t)$. Assuming a sinusoidal reference signal $S_{ref}(t) = \sin(2\pi f_{ref}t+\phi)$, then the product at the output of the mixer becomes:

$$S'(t) = A\sin(2\pi ft + \theta)\sin\left(2\pi f_{ref}t + \phi\right) \quad (5)$$

The introduction of the phase shift (ϕ) to the reference signal is arbitrary and can be freely set. By using trigonometric identities we can rewrite equation (5):

$$S'(t) = \frac{A}{2}\cos\left(2\pi\left(f - f_{ref}\right)t + (\theta - \phi)\right) - \frac{A}{2}\cos(2\pi\left(f + f_{ref}\right)t + (\theta + \phi)) \quad (6)$$

S'(t) thus contains beats at the sum and difference frequencies. Since we are modulating the laser wavelength with the reference signal, we are only interested in the optical signal generated at the reference frequency. So, with $f = f_{ref}$ equation (6) becomes:

$$S'(t) = \frac{A}{2}\cos(\theta - \phi) - \frac{A}{2}\cos(2\pi\left(2f_{ref}\right)t + (\theta + \phi)) \quad (7)$$

This signal consist of two components; one at zero frequency, i.e. a DC level, and one high-frequency component ($2f_{ref}$). The DC component, which is proportional to the amplitude of the optical signal (A), is extracted by low-pass filtering S'(t), resulting in the output signal:

$$S_{out}(t) = \frac{A}{2}\cos(\theta - \phi) \quad (8)$$

This procedure thus removes all unwanted signals oscillating at frequencies different from f_{ref}. Since the phase of the reference signal (ϕ) is adjustable, we can maximize $S_{out}(t)$ by tuning ϕ until $\phi = \theta$, which means that $S_{out}(t) = A/2$. Equation (8) also shows that a lock-in amplifier allows studies of the phase of the optical signal (θ), and therefore a lock-in amplifier is sometimes referred to as a phase-sensitive detector.

Derivative spectroscopy

The wavelength-modulated laser beam is sent through an absorbing medium and detected with a photodiode connected to a lock-in amplifier. The photodiode measures the intensity of the transmitted light and the lock-in amplifier will output a non-zero signal as soon as there is any signal oscillating at f_{ref}. Figure 4 shows a direct absorption spectrum generated by scanning the laser wavelength over one absorption line (a), and (b) shows the corresponding WMS-signal.

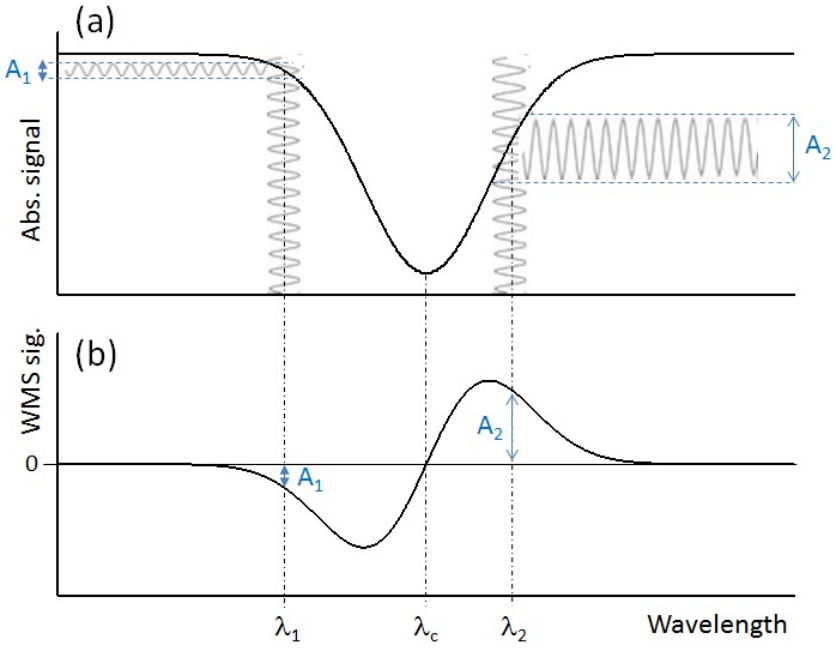

Fig. 4 *(a) Direct absorption signal. (b) Corresponding WMS signal.*

An optical signal with oscillation at f_{ref} appears only when the laser frequency is tuned to an absorption line. An absorption line has a particular spectral profile, whose width and shape is dependent on broadening effects, primarily Doppler and collisional (pressure) broadening. When the laser wavelength resides within the spectral profile of the absorption line, like it does at λ_1, the wavelength modulation, at f_{ref}, on the laser light will be converted into an amplitude modulation, also at f_{ref}, on the transmitted light, which results in an output signal from the lock-in amplifier (see panel b). When the laser wavelength is at λ_2, it is at a point where the absorption profile is very steep, which means that the wavelength modulation generates an amplitude modulation with a large amplitude, and therefore the output signal from the lock-in amplifier will be high, as shown in (b). Figure 4 clearly illustrates that the WMS-signal (b) is essentially the derivative of the direct absorption signal (a). In fact, for low modulation depths, i.e. small wavelength range of the modulation, the WMS signal becomes almost exactly the derivative of the direct absorption signal, and the concept is therefore often referred to as derivative spectroscopy.

The simple derivative description is only valid in the limit of small modulation depth. In general the interaction between the rapidly modulating laser wavelength and a nonlinear absorption feature gives rise to a strong component at f_{ref}, but also harmonic components ($2f_{ref}$, $3f_{ref}$, $4f_{ref}$, …) on the detector signal. Just like the component at f_{ref} can be isolated, any harmonic can also be isolated with a lock-in amplifier. Generally the second harmonic ($2f_{ref}$) is used because like direct absorption, the $2f_{ref}$ signal is strongly dependent on spectral parameters and gas properties and can therefore be compared with spectral simulations to infer gas properties. During the lab we will observe and discuss the shape of the 2*f*-signal and also look at the various harmonics of the signal in the Fourier domain.

Gas in scattering media absorption spectroscopy (GASMAS)

By applying the narrowband laser diode absorption spectroscopic technique to porous material, it is possible to perform spectroscopy on sharp absorption features indicative of gas that is enclosed in the porous material. This concept is called, as mentioned in the introduction, gas in scattering media absorption spectroscopy (GASMAS) and a schematic of an

experimental setup is shown in Fig. 5. Note that the recorded WMS-signal, shown to the right, is a 2f-signal, which is why it does not look like the 1f-signal shown in Fig. 4b. Figure 6a shows, schematically, how GASMAS can be applied for gas detection in a porous medium. The laser light injected into the medium is multiply scattered in the bulk material and at some point it passes through a small volume (pore) containing gas, whereafter the light via multiple scattering finally reaches the detector. Since the light on its way from the laser to the detector passed through a volume containing gas, a sharp imprint will be visible on the recorded spectrum. This is the principle for how GASMAS is applied in porous media, such as wood, paper, snow, baking flour, ceramics, and medical pills. The method can also be used to make measurements inside volumes surrounded by a highly scattering material, as schematically illustrated in Fig. 6b. Examples of this type of application are gas detection in food packages, wood materials, the paranasal sinuses and lungs of premature infants.

By measuring in scattering media, additional challenges are introduced. Since the light has undergone multiple scattering, the length in Beer-Lambert's law is no longer a known quantity and therefore the gas concentration is no longer easily obtained. A common approach is to express the concentration in an entity called *equivalent mean absorption path length*, which is the length that the light has to travel at atmospheric conditions (21 % oxygen) in order to experience the same absorption as in the scattering sample. This also means that if we know that our sample is measured under atmospheric conditions, then the equivalent mean absorption path length is the actual mean absorption path length through the sample.

Question 5: Are there any technical advantages by using scattering media to measure gas concentrations? (Should be discussed in the report)

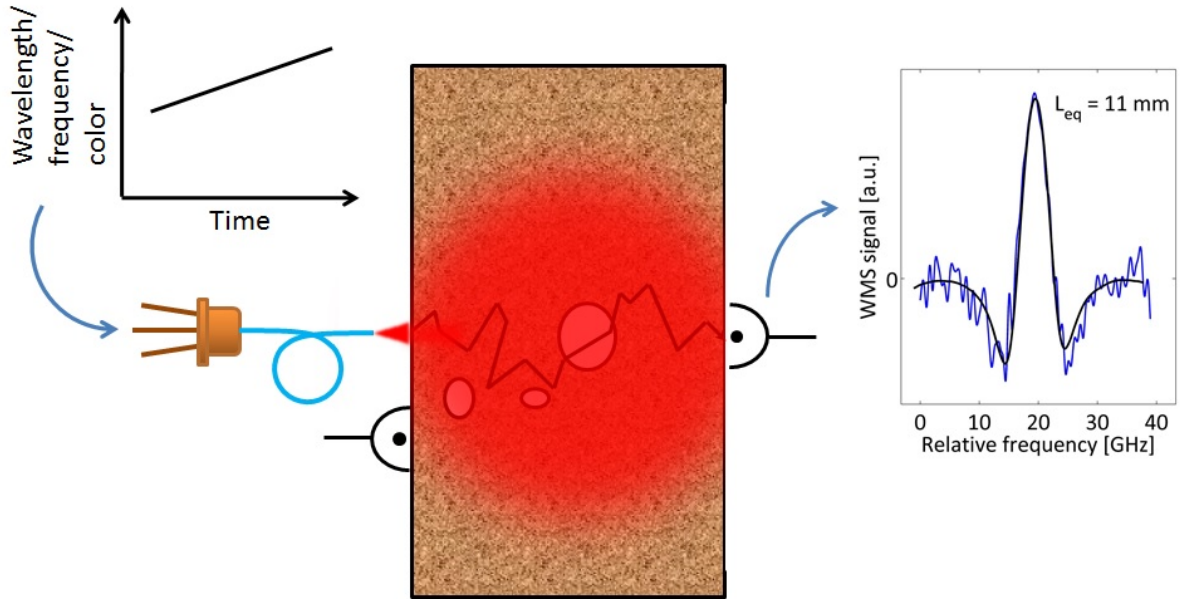

Fig. 5 *Basic principle of GASMAS.*

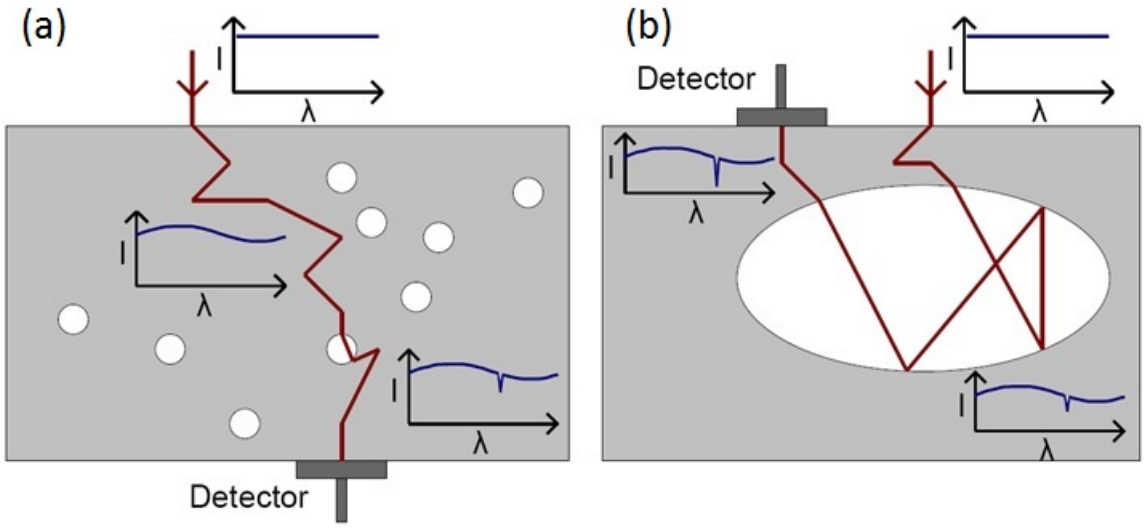

Fig. 6 *(a) GASMAS in a porous material, e.g. wood, paper, snow, baking flour, ceramics, and medical pills. (b) GASMAS in a medium characterized by a larger cavity filled with gas surrounded by a scattering medium, e.g. ping-pong ball, food package with gas head space, Sinus cavity, and lung.*

Laboratory tasks

The major equipment and arrangement used in this laboratory practical are shown in Fig. 7. There are three main tasks to be carried out. The first task is to measure the oxygen concentration in air using a direct absorption spectroscopy setup. The same measurement will then be performed with WMS and the results will be analyzed and discussed. Finally, GASMAS will be used to measure on some everyday items.

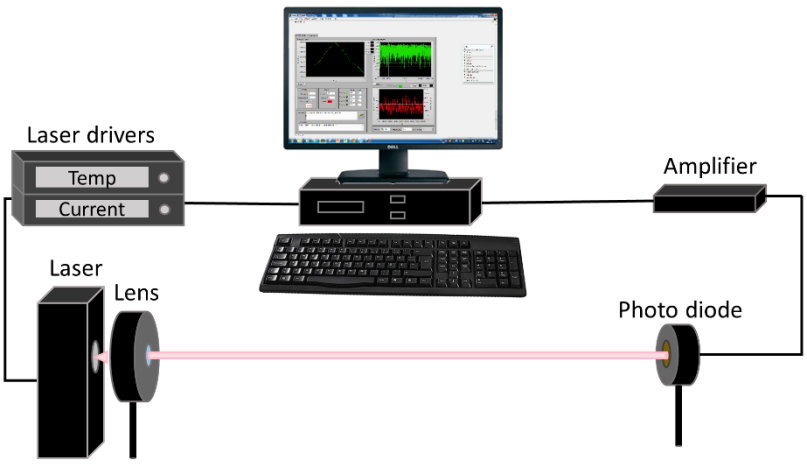

Fig. 7 *Absorption spectroscopy setup.*

Part 1: Direct absorption spectroscopy

1. Build a direct absorption spectroscopy setup.
2. Perform measurement.
3. Analyze the recorded absorption line (spectrum). Estimate the signal-to-noise ratio?
4. Use Beer-Lambert's law to calculate the oxygen concentration. Peak absorption cross-sections are given in Table 1 (on page 4).
5. Move the detector closer to the laser. What happens to the signal? When does the signal disappear?

Part 2: WMS

1. Turn on the wavelength modulation.
2. Perform the same measurement as in task 1.5. What does the signal look like and why?
3. Look at the signal in the frequency domain and try to explain its appearance.

Part 3: GASMAS

1. Perform some measurements on some everyday items. Remember to place the object right next to the detector.
2. Estimate the mean equivalent path length in polystyrene foam by measuring the absorption signal at different air absorption offsets, then extrapolate to find the mean equivalent absorption path length.

Post-laboratory activities

Write a laboratory report following the guidelines that can be found on the course home page under "Laboratory exercises".