Assuming that $A \gg \Delta A$ and $B \gg \Delta B$, similar to the multiplication case, one obtains

$$\begin{aligned} C + \Delta C &\approx \frac{A}{B}\left(1 + \frac{\Delta A}{A}\right)\left(1 - \frac{\Delta B}{B}\right) \simeq \frac{A}{B} + \frac{A}{B}\cdot\frac{\Delta A}{A} - \frac{A}{B}\cdot\frac{\Delta B}{B} \\ &= C + C\Delta a - C\Delta b \end{aligned}$$

where the term with $\Delta A \Delta B$ was neglected. Finally, taking into account that the inaccuracies must be summed independent of the sign

$$\Delta c = \frac{C\Delta a + C\Delta b}{C} = \Delta a + \Delta b \tag{4.32}$$

The result is similar to multiplication, eq. (4.31): the relative error is the sum of the relative errors of the numerator and denominator.

All the previous derivations are true when the error is smaller than the value, i. e. $\Delta A \ll |A|$. Under the same conditions we may derive the error which arises when a function $f()$ is used to calculate value C from A. That is $C = f(A)$, and $C + \Delta C = f(A + \Delta A)$. The function can be approximated by linear dependence around point A

$$C + \Delta C = f(A) + \frac{df(A)}{dA}\Delta A = C + \frac{df(A)}{dA}\Delta A \tag{4.33}$$

Thus,

$$\Delta C = \frac{df(A)}{dA}\Delta A \tag{4.34}$$

In other words, the slope of the function $f()$ at point A determines the accuracy of its result, C.

4.2 Photosensitive devices

4.2.1 Photodetector performance parameters

Photo-detectors convert the light power into electric signal, voltage or current, which can be recorded or measured using standard electronic devices. The photo-detectors characteristics essential for spectroscopy applications are

- sensitivity;
- efficiency;
- spectrum range;
- time resolution.

Lesser critical but still important characteristics for the most of applications are

- area of the photosensitive element;
- dynamic range;
- physical dimensions;
- power consumption and additional electronic devices needed for the operation.

Unfortunately different sets of parameters are used to specify different types of photodetectors. In the following list the parameters, which can be used to compare different classes of detectors, are given with comments on their usage and meanings:

Quantum efficiency: ratio of the photons creating a photo-response, e. g. generating electron, to the total number of the incident photons. This parameter specifies efficiency of the light conversion to the electric signal. It is an important contributor to the sensitivity of the device but not the only one.

Sensitivity: characterizes electric response of the device (current or voltage) created by incident light power. It is measured in A$\cdot$W^{-1} or V$\cdot$W^{-1} depending on the response type, current or voltage, respectively. This parameter tells what to expect of the detector output at a given incident light power. It is wavelength dependent value.[7]

Noise equivalent power (NEP): specifies the minimum light power in frequency band of 1 Hz which could be detected. It is measured in W$\cdot$Hz$^{-\frac{1}{2}}$. For example, if one needs to measure light power in the frequency range of $f = 10$ kHz, i. e. with the time resolution of $\tau = \frac{1}{2\pi f} \approx 16\,\mu$s, and would like to use a photodiode with $NEP = 10^{-12}$ W$\cdot$Hz$^{-\frac{1}{2}}$ (e. g. a Si photodiode), then the minimum detectable light power will be $P = NEP \times \sqrt{f} = 10^{-10}$ W = 0.1 nW. The value of minimum detectable power is higher when the frequency response of the detector is wider (i. e. time resolution is faster), and it is proportional to the square root of the frequency response.[8] This is wavelength dependent value.

Detectivity: many photo-detectors, e. g. photodiodes, exhibit a noise equivalent power that is proportional to the square root of the detector area. For these devices a detectivity is defined as $D = \sqrt{A} \cdot (NEP)^{-1}$, where A is the detector area.

Dark counting rate: for the detectors working in photon counting mode this parameter specifies the average counting rate under no light illumination. Usually it is measured in counts per second, i. e. s^{-1}.

Dark current: for photodiodes and photomultiplier tubes specifies the output current with no incident light. The lower value is better for the same type of detector.

[7] In earlier literature the term responsivity was used as synonym of sensitivity.

[8] From the example of the photon counting problem, one can see that at longer collection time a bigger number of counts is achieved which results in a smaller relative uncertainty of the measurements. The decrease in relative uncertainty is proportional to the square root of the number of counts, thus it is proportional to the square root of the averaging time and inversely proportional to the square root of the detector frequency response. In a sense, this is consequence of the square root law discussed in Section 4.1.2

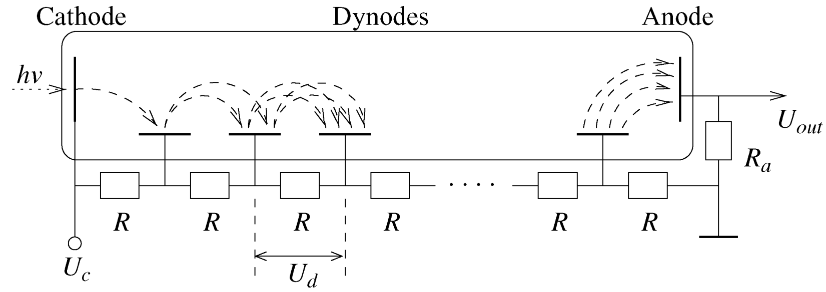

Figure 4.4: Schematic diagram of a photomultiplier.

Time constant and frequency response: The time constant (τ) specifies how fast the signal is formed on the device output when the light is switched on instantly. The frequency response is measured with the sinusoidally modulated light, e. g. light intensity is $I(t) = I_0[1 + \sin(2\pi f t)]$, and specifies the highest frequency f_0 (cut off frequency) at which the photodetector responses without significant signal reduction (usually measured at the level of -3 db relative to the low frequencies response amplitude). The frequency response is inversely proportional to the time constant, $\tau \simeq (2\pi f_0)^{-1}$.[9]

4.2.2 Photomultiplier tubes

Photomultiplier tube (PMT or just photomultiplier) is an electronic device converting the incoming photons to current. It consists of photo-cathode and electron multiplication system. The photo-cathode converts photons to electrons and the multiplication system amplifies the electric signal. A classic scheme of a photomultiplier tube is shown in Fig. 4.4. The photomultipliers require high voltage power supplies to operate properly. The negative high voltage is applied to the photo-cathode, U_c, and divided between the dynodes forming electron multiplication subsystem. When a photon hits the photo-cathode it generates an electron. The electron is accelerated due to the potential between the photo-cathode and the first dynode, so that when it hits the dynode it generates a few secondary electrons (typically 3–4 electrons). The secondary electrons are accelerated by the electric field between the first and the second dynodes and each of them produce another 3–4 electrons. This multiplication process continues until the electrons reach the anode, where the output signal (current) is collected. Typical photomultiplier consists of 9–12 dynodes, and the potential required to obtain multiplication of 3–4 at the dynodes is 100–150 V (the electrons gain energy of 100–150 eV being accelerated between the dynodes). Thus, the power supplier of the the photomultiplier must provide voltage of 800–2000 V, at which the current multiplication factor can be $10^6 - 10^7$.

[9] The proportionality coefficient between the time constant τ and cut off frequency f_0 depends on exact definition of the time constant and on the response order at the detector. Given relation is valid for the first order response and the time constant measured at the level of the signal of $1 - e^{-1} \simeq 0.63$.

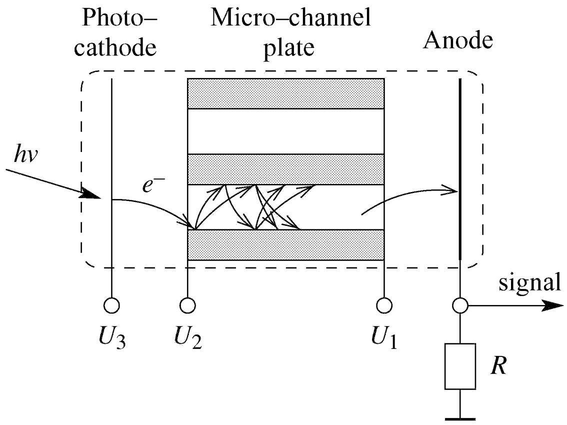

Figure 4.5: Micro-channel plate photomultiplier tube.

The limiting factor of the photomultiplier time resolution is the electron traveling time from the photo-cathode to the anode, which is typically a few nanoseconds. To reduce this time a micro-channel plate amplification system was developed. The micro-channel plates (MCP) are thin plates with great number of microscopic holes, channels, having diameter 6–20 μ. The inner surface of the channels are processed to have proper electric resistance and secondary emissive properties. When a high voltage is applied across the plate the potential is distributed across the plate creating electric field, which can accelerate the electrons.

The micro-channel plates replace the traditional dynode systems of the photomultipliers. A scheme of micro-channel plate photomultiplier tube is shown in Fig. 4.5. The photons are converted to electrons by the photo-cathode, accelerated by potential $U_3 - U_2$ and enter the micro-channels. In the micro-channels the electrons hit the walls and generate secondary electrons. The secondary electrons are accelerated and hit the channel walls thus generating new electrons. Each generation multiplies the number of electrons due to the acceleration similarly to the multiplication process in the dynode system. Therefore, when the electrons are collected by the anode the signal is amplified many times.

The amplification factor of single micro-channel plate is smaller than that of a dynode system of a typical photomultiplier. To achieve amplifications similar to those of traditional PMTs, two or three micro-channel plates are usually assembled one after another inside one photodetector. The electron traveling distance in the micro-channel plate photomultiplier tubes is much shorter than that in the traditional dynode systems, which allows to improve the time resolution by almost one order of magnitude, to less than one nanosecond in real time measurements and to tenth of picoseconds in time correlated single photon counting mode (see Chapter 8).

The micro-channel plates can also be used as image intensifiers. In this case a phosphor screen is used in place of the anode (Fig. 4.5). Because of micro-channel structure of the amplifying plate the secondary electrons on its exit keep the positions of the photoelectrons on its input. Therefore, the optical image is converted to electron pattern by the photo-

Table 4.1: Characteristics of photo-cathodes, ϕ_m is the peak quantum efficiency, λ_m is the wavelength of peak efficiency and i_d is a typical dark current (the dark current is very sensitive to the supplied voltage and temperature of the cathode).

cathode	range, nm	ϕ_m, %	λ_m, nm	i_d, nA
bialkali (S-22)	300–630	26	400	0.1
multialkali (S-20)	180–800	20	480	0.2
extended red multialcali (S-25)	300–900	7	600	1
GaAs	300–920	15	700	2
Cs-Te	160–320	14	200	0.01

cathode, which is transmitted to the micro-channel plate, amplified and converted back to an optical image by the phosphor screen.[10]

The main application area of the photomultipliers is detection of low light intensities in visible and ultraviolet (UV) wavelength ranges. Particularly important feature of the photomultipliers is that they can be used in photon counting mode.

At low photon flow the output signal of a photomultiplier consists of electric pulses, with each pulse corresponding to one detected photon. This makes possible to use photomultipliers in photon counting regime. The output of a photomultiplier is connected to the input of a discriminator which rejects low amplitude pulses due to thermal electrons, and forms fixed duration and amplitude pulses for each detected photon. The pulses from the discriminator can be directed to a counter or be used by some other electronic device. The dark counting rate of the photomultipliers is proportional to the dark current. For the ultraviolet–visible sensitive photomultipliers (spectral response 160–600 nm) typical dark counting rate is 10 counts per second, and for specially selected devices it can be just a few counts per second. The dark counts of the photomultipliers sensitive in the near infrared region (spectral response up to 850 nm) is typically higher than 100 s^{-1}, but can be reduced by more than one order of magnitude by cooling down the photo-cathode to $-30\ldots-40\,^{\circ}$C.

The photo-cathodes are the principal parts of the photomultipliers determining their spectrum response and noise characteristics. An example of the photo-cathode characteristics is presented in Table 4.1. Typically the red sensitive photomultipliers have higher value of the dark current, which is due to the fact that for those photomultipliers the work function of the photo-cathode is lower, therefore more thermal electrons can escape the surface.

The most important characteristics of the photomultipliers which can be found in their specifications are:

wavelength range: determined by the type of photo-cathode, typically visible and UV parts of spectrum, a few photo-cathodes can be used in the near infra-red range up to 850 nm (S-20) and even up to 1100 nm (S-1);

peak quantum efficiency: can be up to 20% in visible range;

[10]The micro-channel plate intensifier increases the intensity of the image but all the specific information about the incoming light, such as wavelength, polarization and beam propagation direction, is lost. This makes if different from the laser amplifier, which preserves the wave properties of the amplified light.

size of the sensitive area: can be 2 cm in diameter or even larger;

anode dark current: determines noise level, typically less than nano Ampere for the PMT sensitive in the visible and UV range and somewhat higher than nano Ampere for the near infrared sensitive PMT;

dark counts: dark counting rate, for PMT depends on the type of the photo-cathode. For the cathodes sensitive in the UV and visible part of the spectrum (wavelength shorter than 650 nm) the dark counting rate can be 10 s^{-1} or even smaller. For the photo-cathodes sensitive in the near infrared part of the spectrum the dark counting rate is higher and can be >100 s^{-1}. By cooling the photo-cathode by 30–40 °C the dark counting rate can be reduced by more than one order in magnitude;

amplification factor: typically 10^6;

transient time spread: dispersion of the pulse signal propagation from photo-cathode to anode, typically 0.1-10 ns, important for time correlated single photon counting applications, see Section 8.4.1;

response time: typically a few nanoseconds, but for MCP PMTs can be shorter than nanosecond.

Main advantages of the photomultipliers are:

- high sensitivity, due to the high multiplication factor the sensitivity can be 10^4 $A{\cdot}W^{-1}$;
- can be used in photon counting mode;
- good time resolution (up to 20 ps for micro-channel plate PMT);
- relatively big photo-sensitive area (a centimeter size is typical).

Disadvantages are:

- sensitivity depends on the wavelength;
- relatively big size;
- utilizes high voltage power supply;
- difficult to construct multi-channel devices.

Leading manufactures of photomultipliers, e. g. Hamamatsu Corp., are producing photomultiplier modules which incorporates the photomultiplier and the high voltage power supply, so that the device is supplied with a low voltage only. This simplifies utilization of the photomultipliers. Additionally, there are modules combining togerther photomultiplier pre-amplifier, discriminator, counter and communication port, which can be used as photon counting unit connected directly to a computer or digital controller.

4.2.3 Semiconductor photo-detectors

The most usually used semiconductor photo-detectors are photo-resistors, photodiodes (PD), avalanche photodiodes (APD), photo-transistors, photodiode arrays and charge coupled devices (CCD). Practically important for spectroscopy applications are photodiodes, avalanche photodiodes, photodiode arrays and CCDs.

The photodiodes are cheap, compact and easy-to-use devices, therefore they are the most popular photo-detectors. The spectrum range and sensitivity of the photodiodes are determined by semiconductor material. The response time of the diode is mainly determined by the capacitance of the *p-n* junction. In order to improve the response time (decrease the capacitance) *p-i-n* structures were developed. Another characteristic affecting the time resolution is the size of active area – smaller areas have smaller capacitance and provide faster response time. Therefore fast photodiodes have typically small photo-sensitive areas, less than 1 mm for diodes with response time shorter than 1 ns.

Although there are many different types of semiconductors, three of them are the most common in optical spectroscopy applications:

Si photodiodes are sensitive in 300-1100 nm wavelength range and have typically sensitivity up to 0.5 A·W^{-1} at 800 nm.[11] The best *p-i-n* photodiodes have very good time resolution, $\tau < 100$ ps. With a special treatment the sensitivity range can be extended to the ultraviolet part up to 190 nm. The diodes have small dark current (typically less than 1 nA for a millimeter size diode) and good noise equivalent power (NEP), which can be as small as 1.5×10^{-15} W·Hz$^{-\frac{1}{2}}$ (S5973, Hamamatsu, diameter of active area is 0.4 mm).

Ge photodiodes can be used in the wavelength range 800–1700 nm. The devices with small active area have good response time, shorter than nanosecond.

InGaAs photodiodes have typical sensitivity range 900–1700 nm with maximum sensitivity at 1550 nm. The diodes have high quantum efficiency and sensitivity (typically 0.95 A·W^{-1} at peak sensitivity). The dark current can be smaller that nano Ampere, which provides good NEP, e. g. 2×10^{-15} W·Hz$^{-\frac{1}{2}}$ for G8376-1 (Hamamatsu) with active area diameter 0.04 mm.

An advantage of the photomultipliers as compared to the photodiodes is a large amplification of the photoelectrons achieved in dynode system. The amplification can be also achieved in specially designed diodes at certain reverse bias voltages. These devices are called avalanche photodiodes (APD). For Si APDs the gain factor can be as high as 100. Although this amplification is not as high as that of the photomultipliers, it improves sensitivity of the diodes to the level when they can be operated in photon counting regime.[12] An

[11] Ideally, one can expect each photon to be converted to an electron, in which case the sensitivity is $S = \frac{q}{hv} = \frac{q\lambda}{hc}$, where q is the electron charge. At $\lambda = 800$ nm the top possible sensitivity is $S \simeq 0.65$ A·W^{-1}.

[12] To reduce dark current to the level when dark counting rate is reasonably low the area of the APD must be small. For example, for APD PDM 50CT SPAD detector (from Micro Photon Devices) with active area 50 μ, the dark counting rate is 5000 s^{-1} at room temperature.

advantage of the APDs is also a good response time, which can be shorter than nanosecond.[13]

Charge coupled devices (CCDs) are another class of semiconductor photo-detectors which are widely available in the market and actively used in optical spectroscopy. Although general purpose CCDs can be used in non-demanding spectroscopy applications, there specially designed CCD detectors for spectroscopy. These are usually state-of-art devices, which are rather expensive but allow to detect the whole spectrum at once and can reduce significantly the time needed for measurements. The design goals for these detectors (as compared to general purpose CCDs) are better linearity of the response, greater dynamic range (the ratio of the maximum non-distorted signal to the minimum detectable signal) and lower noise level.

Typical characteristics of Si based CCDs are similar to those of the Si photodiodes. The wavelength range is 300–1100 nm. Peak quantum efficiency is 40–90%, which provides sensitivity close to 0.6 $A{\cdot}W^{-1}$. There are also InGaAs linear image sensing arays, which can be used in wavelength rage 900–1700 nm.

The main advantages of the semiconductor photo-detectors are

- small size;
- ease of use and low price;
- high linearity and dynamic range;
- good time response;
- sensitive in near infra-red range.

In addition, the great advantage of CCDs and diode arrays is multi-channel detection, which finds numerous applications in optical spectroscopy.

Disadvantages of the semiconductor detectors are

- sensitivity depends on spectrum;
- relatively low sensitivity as compared to PMT;[14]
- small size of photo-sensitive area for photodiodes with fast time response.

[13] A short comparison of APDs and MCP photomultipliers in time correlated single photon counting applications can be found in Section 8.3.1.

[14] When compared to photomultipliers, the diodes have higher quantum yield but do not provide any amplification of the electric signal, therefore the sensitivity of the diodes is much lower than that of the photomultipliers. Avalanche photodiodes provide an amplification of the electric response and have sensitivity improved by factor of 100 or even greater, but the price of these devices is typically much higher than that of the photomultipliers. The avalanche photodiodes can be used in photon counting mode.

4.2.4 Other photo-detectors

A disadvantage of PMTs and photodiodes (and similar semiconductor detectors) is dependence of the photo-response on the wavelength, i. e. the sensitivity, S, is rather sharp function of the wavelength, $S = S(\lambda)$. When neither high sensitivity nor high time resolution are required thermal detectors can be used to measure light intensity. The measured parameter is heating produced by the incident light. There are different types of pyroelectric detectors, bolometers and alike. They can operate in wide wavelength range (300–10 000 nm) and are very useful for steady state measurements of the light power higher than 1 mW and the light pulse energy higher than 1 mJ.

4.3 Measurements of the light power

If the light power is rather high, different types of thermal detectors can be used (see above). The main advantage of these devices is the flat spectrum response and a very wide spectrum range (300 nm – 10 μ). Typical detection limit of these detectors is 0.1 mW. Typical measurement error is 10%, however carefully designed devices can provide accuracy better than 1%. To achieve high accuracy the sensitive surface of the device should have equally good absorption (ideally 100%) in a wide spectrum range.

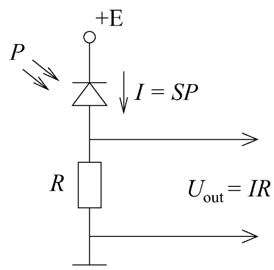

Figure 4.6: Electric circuit for measurements of the light power with photodiode.

If lower light power has to be measured, photodiodes can be used. A typical electric circuit for the measurements consists of the photodiode connected in series with a resistor, R, as shown in Fig. 4.6. The measured value is the potential (voltage), U_{out}, at the resistor R, which is often called load resistor. A bias voltage, E, is supplied to the diode with polarity keeping the diode closed, so that the output voltage is virtually zero ($U_{out} = 0$) without illumination.[15] If the incident light power is P and the photodiode sensitivity is S, then the photocurrent is $I = SP$, and corresponding potential on the resistor is $U_{out} = IR = SRP$. The product, $S_U = SR$, can be called voltage sensitivity. For example, with $S = 0.5$ A/W, and $R = 10$ kOhm, one obtains $S_U = 5000$ V/W, or 0.1 mW of light power will produce 0.5 V response, which is easy to measure with any voltmeter.

As can be seen, the voltage response of the scheme in Fig. 4.6 is higher when the load resistance, R, is higher. The limiting factors for increasing R are (1) the input resistance of the device used to measure potential U_{out}, and (2) the diode dark current. The latter gives some potential on the load even without illumination. For example, a typical dark current for diodes with big sensitive area (which is important for general purpose power measurements) can be as high as $I_{dark} \approx 100$ nA, assuming load resistance to be $R = 1$ MOhm, the output potential is $I_{dark}R = 0.1$ V, which is almost certainly the value one cannot neglect.

Photodiodes (and similar devices) have high sensitivity and wide dynamic range. Obvious disadvantage of the photodiodes is rather sharp dependence of the sensitivity on the

[15] The actual value of the output voltage is determined by the dark current of the photodiode, I_d, so that $U_{out} = RI_d$.

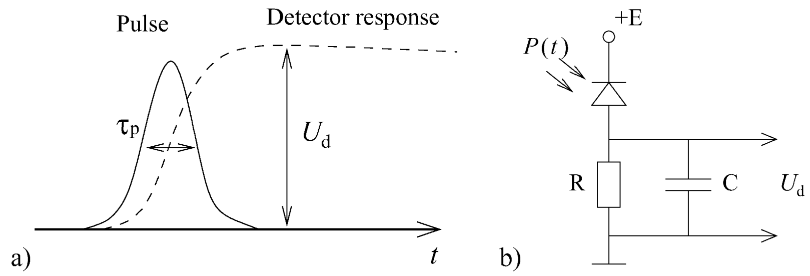

Figure 4.7: Pulse energy measurements: a) integration of the pulse intensity by a slow photo-detector, and b) electric integration circuit for a photodiode.

wavelength. Therefore, the photodiode must be calibrated at the wavelength of light power measurements. Nevertheless, if calibration is done carefully, photodiodes provide very high accuracy of measurements (much better than 1%) in a width range of the incident power from nano to milli Watts. Another advantage of the PD is high time resolution, which allows to reduce measurement time to microseconds or even shorter.

4.4 Measurements of the pulse energy

The same devices as for power measurements can be used for the pulse energy measurements. However, the pulse duration, τ_p, and the time response of the light detector, τ_d, must be $\tau_d \gg \tau_p$ to simplify the procedure, as illustrated in Fig. 4.7 (a). Under this condition the response of the detector is proportional to the integral of the pulse intensity

$$U_d \sim \int I_p(t)dt \tag{4.35}$$

where $I_p(t)$ is the intensity time profile of the pulse. Thus, one has to measure photodetector output right after the pulse. In other words, the detector integrates the pulse intensity profile and output readings of the detector are proportional to the pulse energy. The thermal detectors have relatively slow response time, ranging from milliseconds to seconds. They are usually used to measure pulses shorter than 1 ms and with the energy greater than 0.1 mJ.

The photodiodes and similar devices can be used to detect lower pulse energies. In such case the time response of the photodiode should be slow enough to ensure integration of the light pulse with the accuracy required for the measurements. For example, if the pulse duration is 1 μs and the measurements inaccuracy must be better than 1 %, then the detector integration time must be $\tau_d > 1\mu s/0.01 = 100\mu$s. Most of the photodiodes have time response much shorter then 100 μs. The problem is easily solved by adding simple integration circuit, as shown in Fig. 4.7 (b). In particular case, one may select $R = 100$ kΩ and $C = 10$ nF, which gives $\tau_d = RC = 1$ ms.

Similarly to the light intensity measurements, one has to calibrate the photodiode at the wavelength of measurements in order to obtain absolute power value. However, calibration can be carried out with continuous light, which is easier from the practical point of view. This means that the sensitivity of the photodiode is determined as $S = I/P$, where I is the photocurrent at illumination power P. The pulse energy is the integral of the power

$$E = \int P(t)dt \tag{4.36}$$

The power generates photocurrent $P(t) = I(t)/S$, thus

$$E = \int \frac{I(t)}{S}dt = \frac{1}{S}\int I(t)dt \tag{4.37}$$

The integral of the current gives the total charge generated by the light pulse, $Q = \int I(t)dt$. As far as a short pulse is considered (compared to the time constant of the RC circuit) all the charge will be collected by the capacitor C, creating voltage $U_d = Q/C$. Thus, for the energy one obtains

$$E = \frac{Q}{S} = \frac{C}{S}U_d = \frac{U_d}{S_p} \tag{4.38}$$

where $S_p = \frac{S}{C}$ is the energy sensitivity. In other words, we have obtained pulse energy sensitivity coefficient, $U_d = S_p E$, for the measuring scheme presented in Fig. 4.7 (b) using photocurrent sensitivity, S, and capacitance value, C.

Example 4.2: *Photodiode sensitivity for pulse energy measurements.* Let us consider a pulse energy measurement scheme presented in Fig. 4.7 (b) with capacitor $C =$ 10 nF. A typical silicon photodiode current sensitivity at 800 nm is $S = 0.5$ A/W, which gives sensitivity $S_p = \frac{S}{C} = 5 \cdot 10^7$ V/J. Thus a pulse with energy 1 μJ will create 50 V voltage jump (U_d, as shown in Fig. 4.7 (a)). It is clear, that with this arrangement one can easily measure pulse energies as small as 1 nJ, which will give 50 mV response.

Somewhat limiting parameter for this method of the pulse energy measurements is the pulse repetition rate. The pulses must not arrive faster than the relaxation time of the measuring circuit, τ_d. If this cannot be arranged, then one may determine pulse repetition rate, f, and measure the average power of the pulses, P_{av}, using one of the methods (instruments) available for the power measurements. The pulse energy can be calculated then as $E = \frac{P_{av}}{f}$.

4.5 Measurements of the pulse duration

4.5.1 Direct methods

In direct pulse duration measurements one measures the time profile of the pulse and estimates the pulse duration from this time resolved picture. A duration of the light pulse can be measured using a fast enough photosensitive detector and a device which can record and display the detector electric response. The detector can be a photodiode or photomultiplier. For photomultipliers the time resolution is typically limited by 1 ns and for photodiodes the time resolution can be as short as 100 ps. The general purpose fast oscilloscopes have bandwidth 200–500 MHz. A faster oscilloscopes (e. g. with bandwidth 5 GHz) are available but their prices increase fast with the bandwidth. Therefore a reasonable time resolution for the direct pulse profile measurements is roughly 1 ns. This time resolution is sufficient for flash–photolysis measurements, but in pump–probe experiments the pulse width can be as short as 20 fs. Such short pulse duration cannot be measured directly.

4.5.2 Autocorrelators (indirect methods)

Electronic devices has principal limits in time resolution, one of which is signal propagation delay, which makes direct pulse measurements in time scale approaching picosecond impossible. However there are methods to generate light pulses with duration shorter by a few orders of magnitude, e. g. 6 fs. The time profile of such light pulses cannot be measured using electronic devices. Optical methods were developed to determine duration of the pulses in picosecond and femtosecond time domains.

A short pulse duration means that the peak power of the pulse is extremely high. For example, 1 ps pulse with 1 μJ energy (is 1 μJ a huge energy?) creates power of 1 μJ/1 ps = 1 MW at maximum (how big must be a power station to provide such a power for a time significantly longer than 1 ps?). When such a light pulse propagates in a matter, the response of the matter is not linear any more (see Section 3.7 for discussion of the medium non-linear response). This can be used for pulse duration evaluation. One of the widely used non-linear phenomena is the second harmonic generation (SHG).

Let us consider an optical device similar to one shown in Fig. 4.8. In both cases the incoming beam is split into two equal parts which are then combined back to form beams propagating in one and the same direction but delayed in respect to each other. In the upper scheme (a) this is achieved by utilizing Michelson interferometer with mirror M_3 placed on mechanical translation line to provide variable delay time between the beams on the interferometer output. In the lower scheme (b) the incoming pulse, $I(t)$, is divided into two equal parts by mirror M_1. One part is reflected by mirrors M_2 and M_3 and arrives to mirror M_4 with delay t_1. Another part is reflected (twice) by two right angle reflectors, M_5 and M_6, and arrives to mirror M_4 with delay t_2. The reflector M_6 is placed on mechanical translation line and can be moved along its axis, so that direction of the beam does not change but delay, t_2, depends on the displacement of the translation line. This arrangement is called optical delay line. After the mirror M_4 the beams are propagating together and they are directed to a non-linear optical crystal, which operates as a second harmonic generator (SHG).

The measured parameter for both schemes is the light intensity at the second harmonic, 2ω, as function of the delay time. The intensity of the second harmonic is proportional to the square of the light intensity at the entrance of the SHG

$$I_{2\omega}(t) = \alpha I_{in}^2(t) \tag{4.39}$$

where $I_{in}(t)$ is the intensity at fundamental harmonic before the SHG, which is the sum of

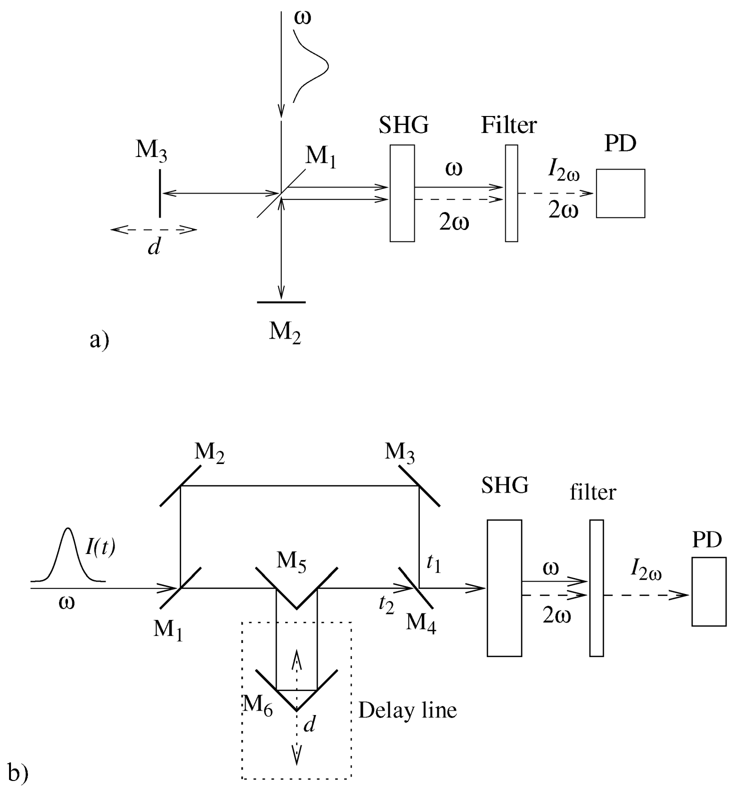

Figure 4.8: Optical autocorrelators: a) Michelson interferometer scheme and b) right angle reflector delay line scheme.

intensities of two beams, I_1 and I_2,

$$I_{in}(t) = I_1(t + t_1) + I_2(t + t_2) \tag{4.40}$$

Since we may choose zero time arbitrary, eq. (4.40) can be rewritten as

$$I_{in}(t) = I_1(t) + I_2(t + t_2 - t_1) = I_1(t) + I_2(t + \triangle t)$$

where $\triangle t$ is the delay between the pulses 1 and 2 and we can change it by moving the delay line (positions of the reflectors M_6 or M_3 for schemes b) and a), respectively), so that

$$\Delta t = \frac{2d}{c} \tag{4.41}$$

where d is the position of the delay line. For the beams of equal intensities $I_{in}(t) = I(t) + I(t + \triangle t)$, thus

$$\begin{aligned} I_2\omega(t) &= \alpha\left(I(t) + I(t + \triangle t)\right)^2 \\ &= \alpha I^2(t) + \alpha I^2(t + \triangle t) + 2\alpha I(t) I(t + \triangle t) \end{aligned} \tag{4.42}$$

where α is the efficiency of the second harmonic generation.

The measured value is the total pulse energy at the second harmonic (at 2ω)

$$\begin{aligned} P_{2\omega} &= \int\limits_{-\infty}^{+\infty} I_{2\omega}(t)dt \\ &= \alpha \int\limits_{-\infty}^{+\infty} I^2(t)dt + \alpha \int\limits_{-\infty}^{+\infty} I^2(t+\triangle t)dt + 2\alpha \int\limits_{-\infty}^{+\infty} I(t)I(t+\triangle t)dt \end{aligned} \tag{4.43}$$

The first and the second integrals give the same results since integration is performed in infinite limits, $\int I^2(t)dt = P_o$. The last integral in eq. (4.43) is autocorrelation integral of the function $I(t)$. It depends on parameter $\triangle t$, i. e. on delay line position,

$$P_c(\triangle t) = 2\alpha \int\limits_{-\infty}^{+\infty} I(t)I(t+\triangle t)dt \tag{4.44}$$

and it is the function of our interest. The value of $P_c(\triangle t)$ shows how much the pulses $I(t)$ and $I(t+\triangle t)$ overlap each other. When the delay between pulses is zero ($\Delta t = 0$) the result of integration is $P_c(0) = 2P_o$ and when the delay between the pulses is much longer than the pulse duration, the integration gives $P_c(\infty) = P_c(-\infty) = 0$, since at time when the first pulse has non-zero intensity the second pulse has zero intensity and vise versa.

The results of the measurements using devices presented in Fig. 4.8 is the autocorrelation function of the input signal, therefore these devices are called autocorrelators.

If the function $I(t)$ is a pulse, then its autocorrelation function is a pulse too. For example, for a Gaussian pulse $I(t) = e^{-t^2}$ the autocorrelation function is

$$\begin{aligned} P_c(\triangle t) &= \int\limits_{-\infty}^{+\infty} e^{-t^2-(t+\triangle t)^2} dt = \int\limits_{-\infty}^{+\infty} e^{-\left(\left(\sqrt{2}t+\frac{\triangle t}{\sqrt{2}}\right)^2 - \left(\frac{\triangle t}{\sqrt{2}}\right)^2\right)} dt \\ &= e^{-\frac{\triangle t^2}{2}} \int\limits_{-\infty}^{+\infty} e^{-\frac{(2t+\triangle t)^2}{2}} dt = Ce^{-\frac{\triangle t^2}{2}} \end{aligned} \tag{4.45}$$

which is the Gaussian pulse, but it is $\sqrt{2}$ times broader than the original pulse. This is shown in Fig. 4.9, where autocorrelation function was normalized to fit the scale.

The pulse autocorrelation function is obtained by measuring dependence of the second harmonic intensity as function of the delay, i. e. relative position of the reflectors M_3 or M_6 in schemes a) and b), respectively. An estimation of the pulse width is done by assuming a certain pulse shape. For example, for Gaussian pulse the autocorrelation function is roughly 1.4 times wider than the original pulse width.

A series of two Gaussian pulses has autocorrelation function shown in Fig. 4.10. The autocorrelation function consists of three "pulses". The integral, eq. (4.44), has maximum at $\triangle t = 0$ when both pulses are overlapping with each other. Two other peaks appear

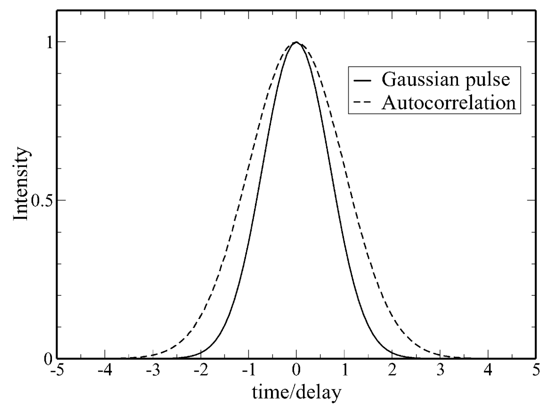

Figure 4.9: Autocorrelation function (dashed line) of a Gaussian pulse, $I = e^{-t^2}$ (solid line)

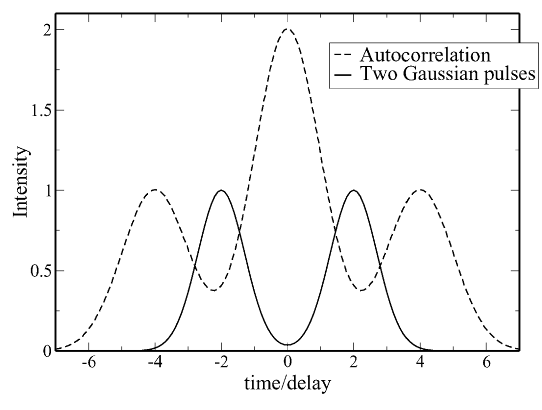

Figure 4.10: Autocorrelation function (dashed line) of two Gaussian pulses, $I = e^{-(t-2)^2} + e^{-(t+2)^2}$ (solid line)

when one pulse of $f(t)$ overlaps one pulse of $f(t + \triangle t)$, but two another pulses are not overlapping each other, which takes place at $\triangle t = 4$ and $\triangle t = -4$ for the example shown in Fig. 4.10.

The example in Fig. 4.10 shows that the autocorrelation function and actual pulse may have very different shape. In particular, the autocorrelation function is always symmetrical, whereas the actual pulse can be unsymmetrical. Therefore, the autocorrelators can be used to estimate the pulse width, but they cannot provide exact information on the pulse shape.

The time limiting factors for the pulse duration measurements using autocorrelators are pulse broadening in optical components of the autocorrelator and mechanical accuracy of the delay line. For thoroughly designed devices a few femtosecond pulses have been measured, which is sufficient time resolution for optical spectroscopy applications.