Photophysics of nanomaterials for opto-electronic applications
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This chapter aims at providing a basic understanding of processes and concepts relevant for optical spectroscopy. The key experimental techniques employed in this thesis will be discussed. Here, a special focus is given to the introduction of Fourier transform infrared spectroscopy, since this technique is rather uncommonly used in the field of non-linear spectroscopy. In the following, the basic principles of photoluminescence- and photoinduced absorption spectroscopy will be discussed and the employed set-ups introduced.

Electromagnetic radiation is classified into different regions according to its energy and its source. This thesis discusses processes covering an energy range from the ultraviolet (UV) to the mid-infrared (MIR) spectral region, i.e. from photons with energy of several eV down to tens of meV. Different units are used to refer to the different spectral regions, depending mostly on the principle with which radiation is measured in these region. In the UV and visible (vis) regime, grating based spectrometers are often applied. These techniques determine the wavelength \( \lambda \) (mostly in nm) of the radiation. In molecular spectroscopy, based on Fourier transform infrared (FTIR) spectrometers, radiation is generally detected as a function of the wavenumber \( \nu \) (in cm\(^{-1}\)), which is the inverse wavelength. Electronic states within a material and transitions between them as well as \( \gamma \)- and X-rays are most commonly described with an energy value \( E \) in eV. For ease of comparability, values in this thesis are predominantly given in eV.

### 3.1 FTIR spectroscopy

Several of the key experiments in this thesis were carried on a set-up based on a Fourier transform infrared spectrometer. The following section is therefore devoted to explaining the measurement principle of such spectrometers, to deriving how this technique is able to provide spectral information and to commenting on details regarding the transformation of the interferogram.

FTIR spectroscopy is based on the principle of interference of two beams. The intensity of the interfering light is monitored as a function of the optical path difference (OPD) between these
Figure 3.1: Scheme of a Michelson interferometer, depicting the light paths as discussed in the main text. The key components are a semitransparent beam splitter and two mirrors, of which one is fixed and the second movable to create an optical path difference.

beams, leading to a so-called interferogram. The two domains of distance and frequency are interconvertible through the Fourier transformation (FT). For a more thorough introduction into FTIR spectroscopy, the reader is referred to the reviews and textbooks included in the bibliography. [1–4]

3.1.1 Measurement Principle and Advantages

The simplest form of an interferometer is the Michelson configuration as depicted in Figure 3.1. The main components include a broadband light source (S) emitting over the spectral range of interest, a semitransparent beamsplitter (BS), two mirrors and a detector. Light emitted by the source is directed onto the BS (1). The incident beam is partially transmitted by the BS and falls onto a fixed mirror $M_1$ (2a). From this fixed mirror, the light runs back to the BS and is partially reflected (3a). The other half of the original beam is reflected by the BS (2b) and is then reflected by the movable mirror $M_2$ (3b). This beam is then also partially transmitted by the BS. The two partial beams created by the BS superimpose when leaving the interferometer (4) and are sent through the sample of interest to be finally detected (D).

The spectral information is acquired by moving the mirror $M_2$. This leads to an optical path difference between the two partial beams and creates an interference at the detector. The measured interferogram, i.e. the intensity $I(x)$ as a function of the OPD, includes all spectral information. In order to access this information, the Fourier transformation between the spatial and spectral domain has to be carried out.

Historically, the main benefits of FTIR spectrometers were the so-called Jaquinot (or throughput) and the Fellget (or multiplex) advantage. The former describes the fact that in FTIR spectrometers, relatively wide circular apertures are employed (as opposed to the narrow slits necessary in
3.1 FTIR SPECTROSCOPY

Grating-based spectrometers, which allow for a higher throughput of radiation. The amount of light is practically only limited by the beam size, thereby giving rise to an increased sensitivity. The acquisition of a spectrum in grating-based spectrometers often has to be carried out sequentially, one wavelength after the other, whereas all wavelengths emitted from the light source are detected simultaneously in an FTIR. With the invention of CCD detectors, however, also grating based spectrometers have become able to use wide apertures and measure several wavelengths simultaneously.

Nonetheless, for a detector that is not shot-noise limited, the FTIR approach leads to large signal to noise ratio. For a spectrum with \( m \) resolution elements, this increase is \( \sqrt{m} \)-fold (Fellget). Moreover, the time needed to measure an entire spectrum in an FTIR spectrometer is equal to the time needed to move the mirror \( M_2 \) over a distance as given by the desired resolution (vide infra) – allowing for spectra acquisition on a ms timescale, which is not accessible for broadband spectra measured with photodetectors.

Since the position of \( M_2 \) is commonly determined using the interference of a HeNe laser emitting at 15802 cm\(^{-1}\) (632.82 nm), also the wavenumber accuracy of the resulting spectrum is much higher than what can be achieved by the mechanically determined values of grating-based spectrometers (\( \approx 0.01 \) cm\(^{-1}\); Connes advantage).

### 3.1.2 Fourier Transformation

In general, the Fourier transformation (FT) determines the different (continuous) spectral components \( S(\nu) \) of a continuous function \( I(x) \) as follows:

\[
S(\nu) = \int_{-\infty}^{\infty} I(x) e^{i2\pi \nu x} \, dx. \tag{3.1}
\]

The digitised interferogram \( I(n\Delta x) \), however, consists of a number \( N \) of discrete equidistant points. In order to transform this interferogram into the spectrum \( S(k\Delta \nu) \), the discrete FT needs to be carried out:

\[
S(k\Delta \nu) = \sum_{n=0}^{N-1} I(n\Delta x) \exp \left( i2\pi n k N \right). \tag{3.2}
\]

Here, the continuous variables \( x \) and \( \nu \) were replaced by \( n\Delta x \) and \( k\Delta \nu \). The spacing \( \Delta \nu \) in the spectrum is related to \( \Delta x \) via

\[
\Delta \nu = \frac{1}{N\Delta x}, \tag{3.3}
\]

meaning that the spectral (\( \Delta \nu \)) resolution is proportional to the OPD (\( N\Delta X \)). The discrete FT expresses a given function \( I(n\Delta x) \) as a sum of sine and cosine functions (consider Figure 3.2(a) left), where the resulting spectrum \( S(k\Delta \nu) \) then consists of the corresponding coefficients for this development (right). Apart from a few simple cases, such as a Lorentzian lineshape, the precise shape of a spectrum cannot be determined analytically, but needs to be calculated numerically.
In practice, equation 3.2 is rarely used directly, since it is highly redundant. Instead, a number of so-called fast Fourier transformations (FFTs) can be used, of which the most common is the Cooley-Turkey algorithm. Using such FFTs leads to a considerable reduction of computation time, which comes at the cost, that in practice, FTIR spectrometers only allow for specific sample spacings of $\Delta \nu = \frac{m \nu_{\text{HeNe}}}{2N}$ with $N$ being a power of two.

### 3.2 Photoluminescence Spectroscopy

Photoluminescence spectroscopy is the energy dependent measurement of the light emission of a material upon photoexcitation. This thesis involves both steady-state measurements, in which the intensity is integrated over all times and transient, i.e. time resolved, measurements.

#### 3.2.1 Principle

In PL spectroscopy, a sample is typically exposed to a high photon energy source to assure that excitation above the band gap of the sample material occurs and absorption can take place. The emitted photons are dispersed according to their energy (typically by using a diffraction grating) and finally detected. This might either be carried out sequentially using a photodetector, or for several energies simultaneously, in case a CCD camera is employed. Two measurement modes are distinguished in practice: "emission spectra", where the spectrum of interest is the emission of the sample material upon constant excitation or "excitation spectra" (also known as "action spectra"), where the emission at a certain energy is monitored upon
changing the excitation energy. PL spectra contain a plethora of useful information characterising the excited states of a material. This can include the dynamics of energy migration as well as the character and origin of emitting species.

### 3.2.2 Ultrafast Techniques

Transient photoluminescence can be used to investigate the lifetime $\tau$ of excited states. Radiative decay, with rate $k_r$, generally competes with non-radiative mechanisms – typically summed up in $k_{nr}$. The resulting lifetime of the excited state may then be determined as

$$\tau = k^{-1} = (k_r + k_{nr})^{-1},$$

(3.4)

giving the change in excited state population $N(t)$ as

$$\frac{dN(t)}{dt} = -kN(t)$$

(3.5)

and the number of excited states at a given time as

$$N(t) = N_0 e^{-kt} = N_0 e^{-t/\tau}.$$  

(3.6)

Here, $N_0$ is the initial population of excited states. PL traces are thus proportional to the excited state population and may be used to determine their overall lifetime. It is worth stressing that although this is an investigation of the radiative decay, the radiative lifetime ($\tau_r = k_r^{-1}$) is not directly accessible in a single measurement, given the always competing non-radiative mechanisms. By changing the excitation intensity or the temperature, it is furthermore possible to investigate the recombination mechanisms leading to luminescence or to determine activation and binding energies in case, e.g., of excitons being the emissive species.

Detecting the PL transients is here carried out by using a so-called streak camera. These systems are able to monitor the PL with up to a ps time resolution. In order to achieve such a high resolution, the sample excitation is carried out with a highly stable light source (typically a Ti:sapphire laser) with ultrashort light pulses (width below 150 fs) and at a repetition rate of approximately 76 MHz. While the output of this laser commonly lies around 800 nm an optical parametric amplifier (OPA) can be used to to allow for excitation with a higher harmonic (typically the second harmonic at 400 nm). The sample excitation leads to photoluminescence, which is collected and dispersed (e.g. horizontally in x-direction) in a so-called spectrograph (consider Figure 3.3 for an illustration of the used set-up). The spectrally dispersed light is then directed onto a photocathode, which emits photoelectrons. These electrons are successively subjected to and deflected by an electric field, which is triggered by the original excitation source. Finally,
the so_redirected electrons are detected on a screen. As the result, for a certain energy, \textit{i.e.} at a certain x-position, a streak of electrons arrives on the display. The number of electrons (or intensity) detected at a certain point is thus proportional to the number of photons emitted by the material for a specific energy and with a specific delay after the excitation. The result is hence a two-dimensional map, with the temporal information in z-direction and the spectral information in x-direction.

Besides the streak camera, the most important component in this set-up is the Ti:sapphire laser. The high intensity and high repetition rate laser pulses emitted by this device are created through the so-called mode-locking technique. The active medium in the Ti:sapphire laser (red in Figure 3.3) is pumped continuously by a Nd:vanadate laser (green) emitting at 532 nm. Inside the laser, only light of a wavelength corresponding to the cavity modes can be supported (\textit{i.e.} wavelengths for which the optical path inside the cavity generates constructive interference) and emission can in principle be achieved for all these modes falling into the region of the medium’s emission. While initially the laser output of the different modes will occur randomly, the key is to introduce a fixed relationship between them (mode-locking), \textit{for which the output occurs as a train of short and high intensity pulses.}

3.3 Photoinduced Absorption Spectroscopy

3.3.1 Basic Principle

Photoinduced absorption or pump-probe spectroscopy is a powerful technique to characterise excited states and their dynamics in different materials. The measurement generally includes a sample, which is excited by an ideally monochromatic light beam (pump). A second beam
(a)

(b)

Figure 3.4: Measurement principle of pump-probe spectroscopy (a) and illustration of the contributions to the PIA spectrum (b). PA denotes a photoabsorption, GSB is the ground state bleach and SE stimulated emission. Adapted from Ref. [7].

(probe), which may be either monochromatic or broad band, is then used to investigate the changes evoked by the pump light (consider Figure 3.4(a)). Depending on the technique, continuous wave light sources may be employed (steady-state) or again pulsed lasers, to allow for transient investigations.

The pump beam is absorbed by the material and excites it from its equilibrium ground state into a higher lying state. The probe beam maps the absorption of the sample in its excited state and the differential spectrum is typically analysed. In these differential spectra, signals are categorised as photobleach (PB) or photoabsorption (PA), depending on their sign. There are different conventions, regarding what to plot with respect to the ordinate, but throughout this thesis, data will be plotted as $-\Delta T/T$, i.e. everything negative is a PB and everything positive is a PA (Figure 3.4(b)).

Photobleaches are generally evoked by the depopulation of the ground state. As a consequence, the oscillator strength of ground state transitions becomes lower and the PIA spectrum shows less absorption than in the unperturbed case. The ground state bleach (GSB) thus coincides with the band gap energy. Photoabsorptions can generally be due to two different effects. The first is the excitation of the formed singlet to a higher state $S_1 \rightarrow S_n$ and the second is due to the absorption of species formed by the pump light. In practice, these might be triplet states, which are excited by the probe beam ($T_1 \rightarrow T_n$) or formed charge carriers. Additionally, as known from Einstein’s discussion on two level systems,6 a photon directed onto an excited state can also induce stimulated emission, in which case, two photons reach the detector for each photon expected. This effect appears as an increased transmission, thus as a PB, in the differential spectrum and typically occurs around the energy of the material’s photoluminescence peak.

The probe beam in these experiments is commonly set to a significantly lower power to only act as perturbation to the population created by the pump. In the so-called small signal limit, the
change in transmission is then equal to

\[ \frac{-\Delta T}{T}(E, t) = \sum_{i, j} \sigma_{i, j}(E) \Delta N_j(t) d \approx \Delta \alpha(E, t) d, \]  

(3.7)

where \( i \) and \( j \) denote the involved levels in the transitions, \( \Delta N_j \) is the change in final-state population, \( \sigma_{i, j} \) is the cross section of the transition, \( \Delta \alpha \) is the change in extinction coefficient and \( d \) is the thickness of the sample.

### 3.3.2 Steady State Photoinduced Absorption Spectroscopy

Long-lived changes in the sample can be observed in steady-state measurements. Since the expected changes in sample absorption are commonly of the order of \( \leq 10^{-3} \), a simple detection of the probe with and without pump light is generally not sensitive enough to detect the changes. A common way to increase the sensitivity is to employ lock-in amplifiers. A standard experiment, as depicted in Figure 3.5 (a), involves a chopped pump beam, leading to a modulated excitation (i.e. a repetition of "pump on"/"pump off" states). The difference between the two cases is detected through the phase sensitive lock-in amplifier. Often, only the acquired in-phase signals are discussed for this measurement. Strictly speaking, this is not a steady-state technique anymore, but as long as the modulation occurs slowly (typically 10-1000 Hz) compared to the lifetime of the photogenerated charges, the difference is negligible. In this technique, species with a lifetime in the region of \( \mu s - ms \) are typically observed. This commonly includes triplet excitons and free charge carriers.

Additional to the steady-state spectral information obtained with this technique, it is also possible to study the recombination mechanism and lifetime of the signals by varying the chopper frequency and the pump intensity whilst mapping the probe at a defined energy. A thorough discussion of such investigations can be found elsewhere.

Photoinduced absorption can also be measured with an FTIR spectrometer. In the set-up employed in this thesis (illustrated in Figure 3.5(b)), the measurement is carried out in a simpler way than for the grating based investigations. The broadband light from the spectrometer is used as a probe, which is already modulated, because it passes the interferometer (consider section 3.1). The pump light, which is responsible for the population in the sample, is continuous in this case, making it a real steady-state experiment. Since the detector is only sensitive to the modulated probe beam, noise and background artefacts are strongly suppressed in this set-up. Accordingly, as discussed in section 3.1 the measurement principle allows for a high dynamic range – a lock-in amplifier is thus not necessary in this experiment.

An important aspect, though, is that all involved components through which the probe beam passes, need to be transparent in the mid infrared spectral region. For this reason, a special cryostat with two ZnSe windows on opposing sides is used. The pump light, in contrast, is di-
3.3 PHOTOINDUCED ABSORPTION SPECTROSCOPY

Figure 3.5: Depiction of the employed steady-state set-ups to measure photoinduced absorption in the vis/NIR (a) and NIR/MIR (b) spectral region. For the vis/NIR, the pump beam is chopped and the probe beam is phase-sensitively detected using a lock-in amplifier. The modulation in the MIR set-up occurs through the interferometer.

rected onto the sample through one of two additional quartz windows, as indicated in Figure 3.5. Furthermore, measuring in a cryostat not only allows for investigations at low temperatures, but evacuating the beam path also reduces the impact of strongly absorbing gases (mainly H₂O and CO₂) in the spectral region of interest.

3.3.3 Transient Absorption Spectroscopy

If, instead of continuous light sources, pulsed laser light is used, it is possible to track spectral changes over time. This technique is commonly referred to as transient absorption (TA) and has the big advantage to also allow for short-lived phenomena to be observable. The onset dynamics and possible spectral shifts of features over time can additionally be tracked, giving way for a much deeper insight into the excited state behaviour of the sample material.\textsuperscript{9,10} The resolution for such an experiment is physically governed by the pulse width and might be as high as a few fs (obviously, also attosecond time resolution can be achieved in certain experiments, but this is not relevant for the discussions in this work). For measurements with a ps-resolution spanning windows of several ns, it is generally sufficient to use a mechanical delay line to change the optical path length of one of the pulses an thereby change the time-separation of the pump and probe pulse on the sample.

In most cases, amplified systems operating at kHz repetition rate, e.g. Ti:sapphire lasers are used as pump, given their high output power and pulse stability, as well as the aforementioned short pulse duration. The light of the Ti:sapphire laser is also often used as a source for white light generation as a probe, thus allowing for a broadband mapping of the spectrum over time.

In contrast, the TA experiments in this thesis are carried out with a simpler set-up (Figure 3.6). In order to reduce the pulse intensity and thereby suppress higher order excitation phenomena...
3.3 PHOTOINDUCED ABSORPTION SPECTROSCOPY

**Figure 3.6:** Transient absorption set-up. Both pump and probe beam are emitted from a supercontinuum laser. The former traverses a mechanical delay line and a chopper wheel before exciting the sample. The probe is split into a reference and the measurement part and both are detected with a balanced photoreceiver.

whilst retaining a high sensitivity, a laser system operating with a tunable repetition rate in the MHz range is used instead. This way the sample is subjected to a peak energy of $nJ/cm^{-2}$ instead of $\mu J/cm^{-2}$. The employed supercontinuum laser source is used to emit two monochromatic light beams as pump and probe respectively (two-colour set-up). The pump beam is subjected to a mechanical delay line and sent through a chopper wheel, before arriving at the sample. Meanwhile, the probe beam is partially reflected and transmitted at a beamsplitter. The latter light is sent to traverse the sample in the area exited by the pump and the former is used as a reference. The balanced detector corrects the changes in probe beam intensity by calibrating the measured beam with the reference and is only sensitive to the pump-induced differences.
Bibliography


