Molecular dynamics in thin glassy films
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5

Time-Resolved Second-Harmonic Generation

In this Chapter we describe the setup developed for second-harmonic generation measurements as a function of time, extended to short time scale down to 1 μsec. The measurements consist in following the signal generated by polar non-linearly polarisable groups during their reorientational relaxation after poling with a strong external DC field. The main challenges in the realisation of the set-up are the switching of the strong DC field in a short time, the synchronisation of the switching-off with the SH signal collection and the measurement with a good statistic of the intrinsic low SH response from our thin films.

5.1 Introduction

Upon cooling, a viscous liquid changes into a solid glass in a narrow temperature range. The relaxation time increases in a non-Arrhenius way by many orders of magnitude. In terms of relaxation time, the glass transition temperature \( T_g \) is defined as the temperature at which the relaxation time becomes 100 sec (see Sec. 1.1). This characteristic time mainly corresponds to a reasonable duration of a dynamic
experiment with the available techniques. Because of this feature most experiments performed to study the dynamic behaviour of glass formers have to be conducted at temperature above the dynamical glass transition $T_g$.

To probe dynamical processes, two approaches can be used: exciting the system at a certain frequency and measuring its response as a function of frequency (measurements in the frequency domain), or exciting the system at a given time and measuring the subsequent response of a system as a function of time (measurements in the time domain). Most dynamic studies are performed in the frequency domain, with dielectric, rheological and NMR techniques being widely used, among others. In the last few years, the upper limit of the frequency window has been impressively extended, mainly thanks to new technological improvements. Nowadays experimentalists can explore up to 21 orders of magnitude in frequency ($10^{-6} - 10^{15}$ Hz) [123, 124]. In this way it is possible to explore regions far above $T_g$, which can give insight in the origins of the glassy state by detection of fast processes (see for example [125]). On the other hand frequency domain techniques are not applicable for temperatures deep below $T_g$ where dynamics becomes too slow to be studied with sub-second techniques.

Among time domain techniques, we recall steady state probe fluorescence, photobleaching, fluorescence non-radiative energy transfer [126] and second-harmonic generation [127, 128]. Direct time-domain approaches are now becoming very promising especially for studying very fast processes, thanks to the emergence of techniques based on ultrafast optical technology (see for example [129, 130, 131, 132, 133]). Ultrafast measurement systems are often based on relaxation from optically pumped states, but it is not always possible to design a proper experiment that suits any application. As example, we recall the work of Meech [130] who applied a pump and probe method on Malachite green and Rhodamine 6G dye molecules that present isomerisation in the exited states, with a rapid internal conversion and vibrational relaxation to re-populate the ground state. Antoine [129] also used a pump-probe experiment to study the rotational relaxation of an Eosin B interfacial layer after alignment by a pump beam. In Eisenthal's studies using second-harmonic generation, a variety of systems were considered: interfacial solvation dynamics of stearic acid [131], activated photoisomerisation of cyanine dye (3,3'-diethyloxadicarbocyanine iodide) [134], and the solvation dynamics of coumarin 314 [133].

In our experiments we have measured the reorientation relaxation of polar non-linearly polarisable groups. To create the initial state, we first applied a strong DC electric field (so-called poling field) to induce some polar ordering of the polar groups. In this state, the material is able to generate a second-harmonic signal.
At a time \( t=0 \), we switch the electric field off and follow the time evolution of the orientational order towards a non-polar state by measuring the time evolution of the second-harmonic signal generated by the sample. For such a system, with an initial state (for \( t<0 \)) that is not generated by an optical pump beam, the collection of a second-harmonic signal, is very well established for long time scales. The time limit, in the lower bound (\( t \geq 10 \) sec), is mainly due to the fact that the collected SH signal is very small and needs to be averaged over a series of successive intense incident pulses. For measurements in the short time domain, the control of the switching off of the strong external field is also an important limitation, mainly due to the magnitude of the field. A limited time window allows to gather information only deep below \( T_g \). At temperatures approaching and above \( T_g \), however, information at intermediate and fast time scales becomes more relevant.

To overcome these problems, Torkelson et al. [135, 136] developed a setup able to collect a SH signal in the short time domain (0.2 msec - 1 msec) for studying the dynamics of a tracer dissolved in a hosting polymer matrix. They concluded that the dynamics of the probe tracer could be coupled to the polymer \( \alpha \)-relaxation. In later studies [62, 127, 137, 138] they extended the collection down to 5 \( \mu \)sec and covered also the intermediate time window 1 msec - 10 sec. They also studied the polymer with the chromophore tracer covalently bound as side-chain.

Following collection protocols similar to the ones used by Torkelson et al., we could cover a time window ranging from 1 \( \mu \)sec till one week (11 orders of magnitude), allowing the monitoring of the reorientation dynamics through the time dependence of a second-harmonic signal both well below and above \( T_g \). By determining the shape of the relaxation dynamics over a wide range in temperature and time, it is possible to identify different relaxation processes. Extended data are also useful for a more precise fitting with non-exponential relaxation functions like the Kohlrausch-Williams-Watts (KWW) equation and the evaluation of the corresponding average relaxation time \( \langle \tau \rangle \) and the stretch exponent \( \beta \) (see Sec. 1.3.2).

We should bear in mind that every technique is related to a particular feature of the studied material. For example dielectric spectroscopy can detect only dynamic processes involving the reorientation of dipolar entities or the displacement of charged entities while rheological measurements are related to the displacement of molecules. In most bulk system, different measurement techniques give consistent results on the dynamic behaviour. Also the results of dynamic second-harmonic generation measurements compare very well with those of dielectric spectroscopy [135, 139].
There is however a notorious exception, namely H-bonded materials as in the case of monohydric alcohols [140]. These materials are known to create H-bonded network clusters. For example dielectric measurements on propanol [85] have shown a second relaxation process with a smaller time constant than the dominant relaxation. The dominant slow relaxation process could be associated to the dynamics of clusters of the associating liquid, while the fast one could be a fingerprint for the reorientation relaxation of free molecules. This indicates that the dominant non-exponential relaxation dynamics is due to more complicated units than simply molecular entities. Moreover the relaxation time for the pure monohydric alcohols was found to be much longer than the structural relaxation time measured with other techniques.

5.2 Fast and intermediate collection method

In this section we explain how data were collected in the short and intermediate time domain (1 μsec ⇒ 3 sec). The aim of the measurements is to obtain the time dependence of the second-harmonic signal $I(t)$ after the poling field has been switched off. To measure a second-harmonic signal (SH), an intense light source is needed, and we therefore made use of a pulsed laser. In the short and intermediate time domain the time separation between pulses is of the same order of magnitude (or slightly bigger) than the explored time scale. This means that the collected second-harmonic signal cannot be averaged over the successive laser pulses, as is done in the standard collection procedure, where only long time scales are considered. To measure a signal at short time scales, we need to collect the SH signal, corresponding to one laser pulse, after a tunable time delay after the poling filed has been switched off. The main challenges of such an experiment are:

- Synchronising the turning off of the external field with the pulse sequence of the incident laser beam.
- Switching off the strong (1.9 \cdot 10^6 V/m) applied DC electric field (HV) in the shortest time possible, which becomes a limitation for the minimum time delay applicable. The upper limit (~3 sec) in the time domain collection, depends mainly on the pulse repetition rate with which the signal is measured.

The other important factor to be considered in these experiments is the low absolute value of the non-linear susceptibility of the sample. This is mainly due to the low degree of polar ordering of the polarisable groups of the macromolecules. Moreover, in the thin films, the amount of polarisable groups is small. As a result, the
collected signal per pulse is at most a few photons. To obtain a reasonable statistic, repeated collections are necessary for each data point, making the measurements time consuming.

5.2.1 Collection protocol

For the short time window \((t \leq 5 \text{ msec})\) a protocol similar to that of Torkelson [135] was adopted. A schematic representation of a measurement run is shown in Fig. 5.1. The HV was switched off at a controlled time delay \(\Delta t\) before the laser pulse at which we measure the SH signal. This \textit{time delay} corresponds to the time during which the system is allowed to relax starting from the initial oriented configuration. The laser repetition rate was fixed at 200 Hz, which means that the available time window with this protocol has as upper limit the time interval between two laser pulses \((5 \text{ msec})\). The lower limit is the longest of either the time necessary for the HV to drop to zero, or the length of the laser pulse. With our setup (see Sec. 5.3), the HV fully drops in \(~100\text{ nsec}\) and the laser pulses are \(~200\text{ nsec}\) long. To be on the safe side, we have chosen \(1\mu\text{sec}\) as lower limit in our measurements.

After the HV is switched off, only one data point is measured. Then the HV field is raised again for a sufficiently long time \((7 \text{ pulses} = 35 \text{ msec})\) to recover the signal corresponding to the initial polar oriented configuration, after which the cycle is repeated. In glassy systems this procedure could introduce memory effects as well as dependence on the history of the treatment. This is particularly true at temperatures far below the glass transition temperature. On the other hand it has been seen that dynamics during poling with high DC field is orders of magnitude faster than the relaxation from the oriented configuration. We have also never noticed any shift in behaviour between the sequences measured at the beginning and end of a measurement series. The cycling technique allows to collect replicas of identical switching on/off \textit{sequences}, reducing drastically the collection time necessary to obtain a reasonable statistics. Data points \((i.e.\) the SH intensity \(I(t)\) at a given time \(t)\) were collected in separate measurement runs with the time delay \(\Delta t\) set at different values. This feature allows us to choose the \textit{time delay} properly for equally spaced points either in a logarithmic or linear time scale. To obtain a master plot for all measurements, data were normalised to the intensity prior to switching off of the HV field: \(I_{\text{NO}}(t) = I(t)/I_{\text{HV on}}\). Every single switching on/off \textit{sequence} was first normalised on itself and then averaged with the others in the run. In the fast dynamics time window, the evaluation of the intensity with the field on \(I_{\text{HV on}}\) was done by averaging the intensity measured at the last five laser pulses before the field was switched off.
Figure 5.1: Schematic representation of a measurement run to obtain one data point $I(\Delta t)$ in the plot of the intensity $I$ versus time $t$ with the fast dynamics protocol. The vertical dotted lines represent the laser pulses (=segments), with the small dots giving the incident intensity. The solid line represents the time dependence of the applied poling high voltage. The dashed line gives the expected theoretical variation of the SH intensity, with the circles being the intensity measured at the corresponding laser pulse. Only the gray circles are used to evaluate $I(\Delta t)$.

To extend the accessible time window to longer values (intermediate time regime), we slightly modified the above protocol simply by increasing the time delay (Figure 5.2) to cover more incident pulses (segments). This procedure has the drawback of getting data points only on a linear scale because of the linear distribution of incident laser pulses. Moreover it needs a longer time for reaching the same sampling statistic (a few thousands photons per data point) than in the short time protocol. In each sequence, measurements over three successive segments were averaged, which adds a time error bar on the data.

For the intermediate dynamics time window, we used a 50 Hz repetition rate for the laser pulses to extend the time window explored by each sequence (~4 sec for 193 segments). The HV field was kept on for ~1 sec and the time dependence for the intensity was collected for ~3 sec.

5.2.2 Statistics

Since the second-harmonic intensities measured in one laser pulse are at most a few photons, we need to accumulate enough sequences to obtain a large enough amount
of photons per data point (optimally several thousands) to increase the signal to noise ratio and improve the intrinsic wide scatter of the data. Since the most time consuming step (several seconds) in the experiment is the data transfer between the oscilloscope collecting the data and the computer controlling the equipment, the most time efficient way of accumulating data would be to perform long runs while storing all the necessary sequences in the memory of the oscilloscope. This is however not possible due to the limited available memory space in the oscilloscope. With the fast dynamics protocol, the oscilloscope memory allowed 193 sequences per run and we repeated these runs to accumulate up to 6000 sequences. For the intermediate dynamics protocol, in which sequences are significantly longer, the runs could only contain 8 sequences. To keep the measurements time reasonable, we accumulated only 1500 sequences in this case. As a comparison, measurements performed at long time scale were averaged over approximately 1500 successive laser pulses. This number could be longer at very long time scales. For those cases (high temperatures) where the relaxation dynamics was fast enough (~30 min), the whole relaxation process was repeated, leading to an accumulation over ~5000 pulses per point.

5.3 Collection setup

The collection part of the SH setup (see Figure 5.3) consists of a frequency doubled Mode Locked (76 MHz) Q-switched Nd-YAG laser, a photodiode (PD) monitoring the incident laser pulses, whose signal is used as triggering signal, and a photomultiplier (PM) to record the SH signal from the sample. The repetition frequency

Figure 5.2: The same as in Fig. 5.1 for the intermediate time dynamics protocol.
of the Q-switch can be tuned between 3 and 800 Hz, every Q-switched pulse being made of several (≈20) mode-locked pulses. A digital oscilloscope collects the signal.

The HV is controlled by an electro-mechanical switcher. The switching speed is restricted by the speed of the fast transistor used in parallel with a relay inside the HV switcher (the transistor holds the voltage drop and the relay avoids heating of the former) which has a full relaxation time of ≈100 ns.

The setup is completed by a PC that is interfaced to the rest of the equipment by an interface card for the oscilloscope (digital IEEE488) and a high speed counter/timer interface card to connect the computer to a box interface (BI) that handles all the other controls (see Figure 5.3). The high speed counter interface contains two internal clocks of high precision. They are used in the software design to control the Q-switched pulses repetition rate and the time delay between the switching off of the external field and the following incident Q-switched laser pulse. A mechanical shutter (MS) is introduced on the optical path to avoid laser illumination on the sample on the 'dead times', as during the oscilloscope-PC communications or data savings periods. The box interface and the mechanical shutter need low voltage (12V) power supply. The signal from the PD, monitoring the incident pulses through the intensity of a spurious reflection, is meant to:

- Synchronise the external electric field switching with a specific optical incident pulse.
- Trigger the oscilloscope sampling of the PM collecting the SH signal in coincidence with the optical incident pulse.

The electric signal coming from the PD is positive but too small to drive the trigger in the oscilloscope, thus an electronic amplifier was inserted in the BI giving a TTL (5V) output signal. The gating through the amplifier in the BI introduces a systematic retardation time on the amplified triggering signal. On the oscilloscope we explored a time window as wide as a Q-switched pulse of the laser. To center the SH photons in this window, we had to introduce a time delay for taking in consideration the delay of the triggering signal due to the amplifier in the BI. During data analysis, the time delay used in the collection protocol (shown in Figure 5.1), has then to be corrected by such time delay.

The control software was designed making use of LabView (see Appendix A). The graphical interface provided by LabView makes the control and understanding of all parameters straightforward.
5.4 Fast dynamics in liquid crystals

To test our setup and measurement method at for short time scales, we have applied time resolved SHG measurements on a particular system having an unresolved dynamics in the time range accessible by our equipment. Schuildeboom [141, 142] studied the reorientation dynamics of a common liquid crystal molecule: 4-n-ethyl-4-oxycyanobiphenyl (70CB), at a solid interface. In LC display technology these materials function in the liquid crystalline state, and applied fields induce molecular reorientation with a response time of the order of milliseconds. An ultra-thin film made of a few molecular layers was deposited by evaporation on a fused quartz substrate patterned with two gold electrodes as described in Sect. 6.2 (Fig. 6.2). In the 1 mm-gap between the electrodes, the molecules have an isotropic distribution of in-plane orientations. By applying a strong DC field between the two electrodes, molecules in the film were forced to orient away from their equilibrium order. The applied field tends to align the dipoles carried by the molecules along the field direction orientation, inducing a polar anisotropy in the plane of the substrate.
Figure 5.4: Schematic representation of the SH signal with main features. The electric field is switched off at time $t=0$.

Second-harmonic generation measurements were used to measure the degree of polar ordering and its time evolution upon release of the field. The decay of the SH signal presented three main features as schematically represented in Fig. 5.4. After switching off the poling field, a first jump corresponding to $\sim 20\%$ of the overall SH signal was completed in less than 1 msec after the switching off of the field [142]. In their experiment 1 msec was the lowest time accessible in the measurements of the SH signal. At longer time scales two distinct relaxation regimes could be seen (see Fig. 5.5). The experimental data were fitted using a double exponential function:

$$\sqrt{S(t)} = \exp[b] + \exp\left[\frac{-t}{\tau_f} + l_f\right] + \exp\left[\frac{-t}{\tau_s} + l_s\right]$$

(5.1)

with characteristic decay times of $\tau_f \sim 10$ sec and $\tau_s \sim 300$ sec. $\exp[b]$ is a very slowly decaying component that can be treated as constant on the considered time scale, and $l_f$ and $l_s$ are weighting factors respectively for the fast and slow processes. The slow and fast relaxations were associated respectively to molecules in the first layer in contact with the substrate (surface layer) and to molecules in the rest of the film (covering film). The dynamics in the surface layer was slowed down with respect to that in the covering film by the interaction of the surface molecules with the substrate. This was confirmed by the absence of the fast relaxation in films made only of a surface layer. Note that in contrast to our findings in the glass-
Figure 5.5: Decay of the square root of the SH intensity $I_{ss}$ determined by Schuddeboom [141, 142] after switching off the poling field for a thin film of 7OCB. Plotted data at time larger than 100 sec were averaged over five successive raw data points. The lines represent the fittings for the slow (dashed) and overall relaxation process (solid) (Eq. 5.1).

forming materials described in Chap. 3, the effect of the substrate on the dynamics is significant on this ordinary (not glass forming) system. This is because in the present case, the effect of the interaction with the surrounding molecules is much weaker than in a glass-former.

The fact that the fast relaxation time $\tau_f$ was so long with respect to the value expected in a liquid, was tentatively explained by correlations between the dipoles carried by the molecules. Evidence for such correlations was also found in the static behaviour of the molecules under the application of the poling field [143].

For the interpretation of the first jump, effects of the applied poling field could be rejected. The DC field can in principle modify the intra-molecular potential of the electrons, changing the molecular non-linear polarisability $\alpha_{\xi\xi\xi}$. Nevertheless to induce this effect much higher fields than the one employed are needed.

Another possible effect caused by the electric poling field is electric-field-induced second-harmonic (EFISH) generation. A high DC field $E(0)$ can mix with the inci-
dent electromagnetic wave at frequency $\omega$ to give a non-vanishing third-order nonlinear term $\chi^{(3)}$ in the susceptibility. The second-order susceptibility component arising from this process is:

$$\chi^{\text{EFISH}}_{ijk} = \chi_{ijk}^{(3)} E_i(0)$$

(5.2)

For the case of intense applied poling fields and with the third-order susceptibility not particularly smaller than the second-order susceptibility, the electric-field induced second-harmonic generation becomes not negligible. In this case, the expression of the polarisation induced in the material (Eq. 4.1) becomes:

$$P = \chi^{(2)} : E(\omega)E(\omega) + \chi^{(3)}(2\omega = \omega + \omega + 0) : E(\omega)E(\omega)E_i(0)$$

(5.3)

The EFISH term was estimated as being at least 2 orders of magnitude smaller than the second-order term for the considered system. Finally it was concluded that the jump was not an artifact but associated to a very fast relaxation of a part of the molecules. These molecules would not be involved in correlated reorientation but would be "free" to rotate individually [144]. However no other information could be obtained about this unresolved relaxation process.

The widening of the explored time scale is expected to give insight on fast processes having characteristic times below 1 msec. Typical characteristic times for molecular dynamics in the liquid phase are below 1 msec and, for a complex system as a liquid crystal, we can expect to find typical behaviour precisely in the time interval from 1 $\mu$s to 1 msec. We wanted to investigate the nature of this fast jump using the experimental setup described in this Chapter.

### 5.4.1 Experimental

Using the same approach as Schuddeboom [142], we deposited a multilayer of 7OCB ($T_m = 55^\circ\text{C}, T_{NI} = 75^\circ\text{C}$, chemical structure in Fig. 5.6), purchased from Merk Ltd.
5.4 Fast dynamics in liquid crystals

(Darmstadt, Germany), on a fused quartz substrate. The substrate was previously patterned with two gold electrodes with a gap of 1 mm in between. The deposition was realised by condensing a vapor of the LC generated by a hot stage placed above the surface. After deposition the cell was sealed and dry nitrogen was flushed during the course of the experiment to preserve the sample from contamination. All measurements were conducted on the supercooled liquid crystalline state at 30 °C. The optical setup is the one described in Fig. 4.4, while for the poling field and data collection, we used the scheme showed in Fig. 5.3. The electric poling field between the two electrodes was $1.9 \cdot 10^6$ V/m. The SH signal was measured in the time interval 1 μsec - 2000 sec.

5.4.2 Results

The full SH decay profile ($\chi_{NO}^{(2)}(t)$) collected in the s-in-s-out polarisation configuration is shown in Fig. 5.7. The square root of the SH signal ($\chi^{(2)}(t)$) is normalised to the square root of the signal before switching off the field ($\chi^{(2)}(0)$).
Effect of the poling electric field

In the evaluation of the normalised second order susceptibility $\chi^{(2)}_{NO}$, we neglected the existence of the EFISH effect. The validity of this assumption is confirmed by the value of $\chi^{(2)}_{NO}$, remaining approximately constant (unity) for 1 $\mu$sec, while the poling field drops to zero within 100 ns. This confirms the hypothesis of the absence of any artificial jump due to the switching off of the electric field. If the second harmonic signal would contain the third order effect EFISH, a first decrease of the signal should be visible already within 100 ns after switching off the external field.

Multiple relaxation dynamics

Our experimental results (Fig. 5.7) clearly show two separate decays at time lower than $10^{-1}$ sec. For larger times the data are scattered and for the interpretation we used the results of Schuddeboom [142]. We fitted our results for the normalised second-order susceptibility using a sum of four distinct exponential relaxations:

$$\chi^{(2)}_{NO} = \sum_{i=1}^{4} a_i(\tau) e^{-\tau/\tau_i}$$

(5.4)

where $a_i$ are weighting prefactors. For the long time domain we adopted the value of $\tau_3 = \tau_f = 13$ sec and $\tau_4 = \tau_s = 320$ sec previously obtained [142] for the fast and slow relaxations. For the other two processes we obtained $\tau_1 = 7.7$ $\mu$sec and $\tau_2 = 5.7$ msec. Using the microscopic picture depicted above with both collectively rearranging dipoles and free molecules, the two relaxations $\tau_1$ and $\tau_2$, at short time scales, can be associated to the reorientation of free molecules in the covering film and at in the surface layer, respectively.

From the different characteristic relaxation times $\tau_i$ (see Tab. 5.1) we can evaluate the ratios $r_{cov} = \tau_3/\tau_1$ and $r_{surf} = \tau_4/\tau_2$ as the retardation effect caused by the dipolar correlations for molecules laying in the film ($r_{cov}$) or in the surface layer ($r_{surf}$). We find that $r_{cov}/r_{surf} \approx 54$, which would mean that the effect of the correlations is 54 times larger in the covering film than in the surface layer. A possible explanation for this is that the dynamics of the molecules in the surface layer is dominated by the interaction with the substrate. Our measurements show that the reorientation dynamics of liquid crystal molecules in the vicinity of a surface is very complex. A deeper understanding of the system would require to study the whole dynamics as a function of film thickness and to evaluate the variation of the ratios between the weights of the different processes.
5.4.3 Conclusion

The above measurements on liquid crystal films show that our measurement setup and protocol are able to distinctly resolve dynamic features in the time window 1 μsec - $10^3$ sec. This is essential for studying systems with a complex dynamic behaviour such as systems with distinct exponential relaxations, as observed in this Chapter, or with a continuous distribution of relaxation times, as observed in glassy systems and presented in next Chapter.

5.A Collection Software

Figure 5.8 shows a screen shot of the LabView graphical interface we have developed to control the signal collection at the short and intermediate time scale$^1$. This interface shows the two signals collected by the oscilloscope over the time window in which the intensity of the second-harmonic signal is measured. This time window is defined by two parameters set using the interface: the time base of the oscilloscope (right bottom corner, generally 200 ns/div) and the number of samples in the window (samples, generally 88). The delay between the trigger signal from the photodiode (see Fig. 5.3) and the beginning of the time window is set on the oscilloscope. These setting ensure that the time window coincide with the laser pulses. Channel 1 records the signal driving the switching of the high voltage to verify the synchronisation of the voltage switching with the laser pulses. Channel 2 records the signal from the PM. The offset of channel 2 (set on the right of the trace) is chosen such that the signal of the PM is just outside the displayed range if no photon is detected. For the computer treating the signal, there is then no signal. The presence of a detected photon gives a negative peak in the signal of the PM, which makes a peak appearing in the displayed range.

\[ \begin{array}{|c|c|c|}
\hline
 & \text{Free} & \text{Correlated} \\
\hline
\text{Cover film} & \tau_1 = 7.7 \, \mu\text{sec} & \tau_3 = 13 \, \text{sec} \\
\text{Interface} & \tau_2 = 5.7 \, \text{msec} & \tau_4 = 320 \, \text{sec} \\
\hline
\end{array} \]

Table 5.1: Values of the relaxation times $\tau_i$ determined with Eq. 5.4.

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$^1$in collaboration with Paul Collignon of the electronic workshop of the Chemical Engineering Department
Due to low speed of LabView as data processor, the raw data from the oscilloscope are converted in ASCII by binning the vertical axis of the oscilloscope in 128 bins. Thus the intensities of the PM signal are written as numbers between 0-127 in a matrix in the output file. To detect the presence of a peak (=1 SH photon) in a trace we have chosen the value of 125 as minimum threshold: when the trace value changes from 126 to 125, it means that a photon was detected by the PM. The number of these events, inside the measurement time window corresponding to one laser pulse, gives the number of photons detected during this pulse.

As explained in Sec. 5.3 and shown schematically in Fig. 5.1 and Fig. 5.2, the measurements are performed by repeating a sequence of the type: switching field on, measuring, switching field off, waiting. The duration of this sequence is fixed by the time delay between the switching off of the field and the last laser pulse (segment) during which the signal is measured ($HV$ switch off $x$ msec before segments $y$). In the short time protocol, the signal is measured only during 1 segment ($y=1$), while in the intermediate time protocol, the signal is measured during $y$ (>1) segments following the switching off. After the last segment used in the signal measurement,
the HV is switched on after half a repetition period of the laser pulses and kept on during 7 pulses, after which the following sequence starts. A number of sequences are repeated till the memory of the oscilloscope is full. This makes a run.

The information is then transferred to the PC, the memory emptied and the collection repeated in the following run. The number of runs in a given measurement is set in such a way that the data file containing all the raw data collected during the measurement keeps a reasonable size. If necessary, a certain number of measurements were repeated.

One major problem was the long exposure of the sample to the incident laser beam, which could eventually induce local heating. To avoid this, we introduced 'dark' times between runs (after run delay x sec) and/or measurements (shutter closed for x sec after measurement), during which the shutter was closed.

A simple routine has been written to process data files corresponding to one measurement. These are big matrixes of size \((88 \text{ samples} + 1) \times [(\text{segments} \cdot \text{sequences})+1] \cdot \text{runs}\). The program scans all the binned traces of the oscilloscope for every single segment and checks for the presence of photons. Then the numbers of photons are averaged over all sequences and runs in parallel for every single segment at a certain time often the field is switched off.