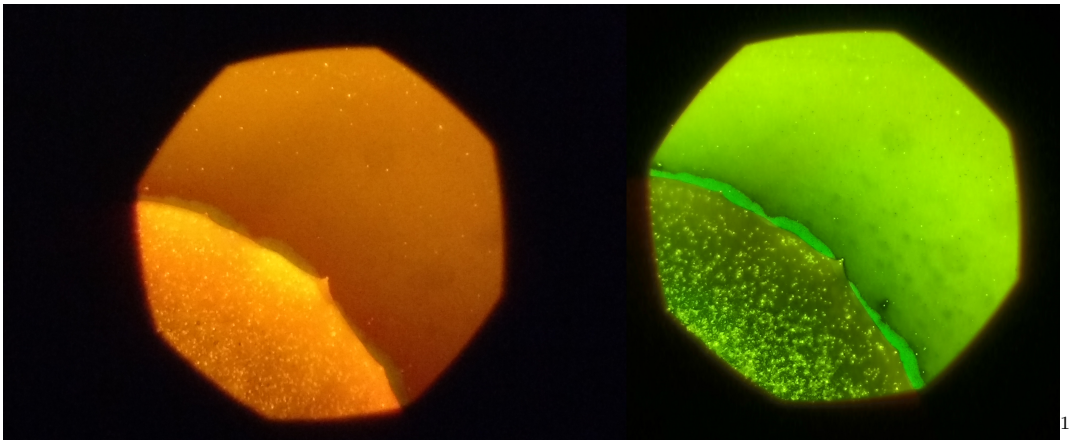
Utrecht University

Physics and Astronomy

Deethylation and Degradation of Dry Rhodamine B Films Under Visible Light Irradiation

Bachelor Thesis

Duncan de Vos

 [1]

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[1] RhB and RhB after five minutes of irradiation

Abstract

Rhodamine B is a commonly used fluorescent dye in many different fields of research. It is a dye that can change colour by losing ethyl groups, deethylation. It is also possible for rhodamine B to degrade under irradiation, making it unable to emit light. Previously it was seen that rhodamine B in solution only undergoes reactions, that lead to the loss of ethyl groups, when a photocatalyst is present under visible light irradiating. However recently it has been seen that these reactions can occur without the presence of a photocatalyst for dry films of rhodamine B. To further understand the reactions that take place, we have studied and modeled the photo induced degradation and deethylation rhodamine B under various conditions. This was done by illuminating dry films of rhodamine B in contact with glass and or air and recording the spectrum the dye emits at several points in time during irradiation. With these spectra we modeled the dynamics of deethylation and degradation using a simple rate-equation model. The dye in contact with glass degrades faster than when not in contact with glass, and changes colour when in contact with both glass and air. This means dry rhodamine B can react without the presence of a photocatalyst under visible light irradiation.

Contents

1 Introduction

Many large industries rely on chemical reactions for production. The efficiency of these reactions are important to both their profit and to the environment. Finding catalytic reactions that can boost this efficiency could therefore be very valuable. One way we try to improve catalytic reactions is by doing fundamental studies on single particles [1]. To model catalytic reactions it can be useful to use fluorescent dyes, they provide a large resolution in both time scale and positional scale. Rhodamine B is one of the dyes that can be used, and it has the added benefit to change colour under certain circumstances giving us insight in the reactions at hand. It is thus of great importance to us to know under what circumstances rhodamine B reacts. Previously, papers have been published looking at the fluorescent emission and luminescent strength of rhodamine B. Watanabe et al. [2] found that aqueous solutions of rhodamine B are considerably stable under visible light excitation, but when powdered Cadmium Sulfide is suspended in the solution, rhodamine B undergoes N-deethylation. Rhodamine B changes colour by deethylation. Wu et al. [3] used multiple methods to show that RhB in an aqueous solution of titania undergoes both N-deethylation and degradation of the molecules (bleaching). Qu et al. [4] also researched solutions of RhB and titania. They too found both N-deethylation and degradation. They attribute the N-deethylation to OOH^* or HO^* radicals. Xeufeng et al. [5] looked at solutions of RhB with vanadate and/or platinum species present. They found the following; RhB undergoes efficient N-deethylation in the presence of VO_2^+ and degradation in the presence of Pt(IV). Zhuang et al. [6] looked at N-deethylation and degradation of aqueous RhB solutions in the presence of thin titania films with varying surfaces. All these studies have in common that for N-deethylation and degradation of RhB in solution a photocatalyst needs to be present. Recently however it has been observed by my supervisor that dry rhodamine B changes colour under visible light irradiation without the presence of a photocatalyst. This raises the question: What are the processes involved in deethylation and degradation of dry rhodamine B films?

Here we study dry films of rhodamine B under visible light irradiation in different environments by measuring spectral shifts. We fabricated a series of samples of rhodamine B spin coated on glass slides. By coating the slides with a polymer film (polymethyl methacrylate; PMMA), before or after spin coating rhodamine B on them, we can control whether rhodamine B is in contact with the glass substrate and/or air. We illuminate these samples and measure their spectra at several points during illumination. Using these spectra we observe whether rhodamine B reacts to glass and whether it reacts with air and what these reactions cause: N-deethylation or degradation. Our findings show that glass allows the rhodamine B to degrade faster than when it is not in contact with glass. When rhodamine B is in contact with both glass and air we see both fast degradation and N-deethylation. When it is not in contact with glass and air, we observed no N-deethylation and a slow degradation.

In the remaining sections we will first provide some background information about the relevant physics at play here. Following this we describe the methods of measuring the processes. Subsequently we present the findings and these will be discussed. Finally we will present our conclusion. In the appendix, spectra of each measurement environment of rhodamine B as well as all the rates of deethylation and degradation corresponding with these spectra can be found. Included will also be the spectra of rhodamine 110 in the different environments.

2 Theory

In this section we will present an overview of prior knowledge used throughout this thesis. Firstly we will give a short explanation on fluorescence by organic dye molecules. This is relevant to us because rhodamine B is a fluorescent molecule and only undergoes deethylation and degradation under light irradiation. Then we give a short overview of fluorescence microscopy, which is what we used to do our measurements. Following this we show what we know about the degradation and deethylation of rhodamine B from previous research and what reaction mechanisms researchers have proposed.

2.1 Fluorescent molecules.

When a photon interacts with a molecule, it can in some cases cause the molecule to emit light. In this case one calls the molecule fluorescent. The way this works is the following: a molecule gets hit by a photon. If the photon has enough energy to promote an electron to a higher orbital, the molecule absorbs this photon. One of its electrons will then be put in a state with a higher energy. This is illustrated in the first two steps of figure 2. The minimum energy of the photon must be the energy needed to bridge the gap from the Highest Occupied Molecular Orbital

(HOMO) and the Lowest Unoccupied Molecular Orbit (LUMO). Some time later this electron can return to the HOMO and doing so emit a photon, because the total energy must be conserved. The energy of the emitted photon is that of the difference in energy between the state the electron was in and the state the electron falls back in. This energy is usually around the same energy as the energy difference of the HOMO and LUMO of the molecule.

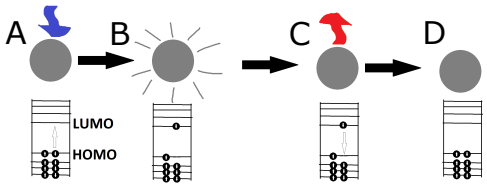


Figure 2: The absorption and emission of a fluorescent molecule: A) a photon hits a molecule, B) the photon is absorbed by the molecule and one electron goes to a higher energy state, C) a photon is emitted and the electron falls back to a lower energy state, D) there is no electron in the LUMO and the molecule is back in its low energy state.

What can also happen is that after getting promoted to a high energy state, the electron transfers to another molecule which has a state for the electron with a lower energy. This is shown in figure 3. When this happens the fluorescent dye will have a charge of plus one. For rhodamine B having this charge allows it to undergo reactions that lead to deethylation and degradation.

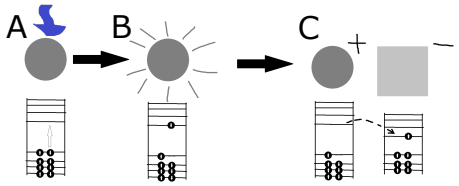


Figure 3: Transfer of an electron from one molecule to another, A) a photon hits a molecule, B) one electron goes into a higher energy orbital, C) the electron transfers to another molecule.

2.2 Fluorescence microscopy.

When looking at fluorescent dyes one can do measurements on the emitted light. This can be done by redirecting the light emitted by the dye to a camera directly or to a camera through a spectrometer. In the latter case the spectrometer will separate light of different wavelengths making it possible to record the spectrum of the dye. To excite the dye however, one needs to irradiate it with light. It is important to ensure this light does not reach the camera and interfere with the emitted light by the sample. To do this one uses three types of filters; longpass filters (LP), shortpass filters(SP) and dichroic mirrors(DC). Longpass filters reflect light of wavelengths shorter than a certain value and allows other light to pass through. Shortpass filters reflect light of wavelengths longer than a certain value. Dichroic mirrors come in the shortpass and the longpass variant. They are made to work under an angle of 45°. What one can do using these filters is excite the dye with light originating from a light source. In the path from the light source to the dye one can place a shortpass filter followed by a dichroic mirror that reflects only light in the transmission range of the shortpass filter and reflective range of the dichroic mirror to the dye. The dye then gets excited by this filtered light and emits its own light. This emitted light and some reflected scource light then hit the dichroic again and most of the source light is reflected away. The wavelengths of light emitted by the dye that the dichroic allows to pass through go through. Behind this dichroic, one places a longpass filter to make sure the light originating from the light source is filtered out. This is schematically depicted in figure 4 with the filters used in our measurements.

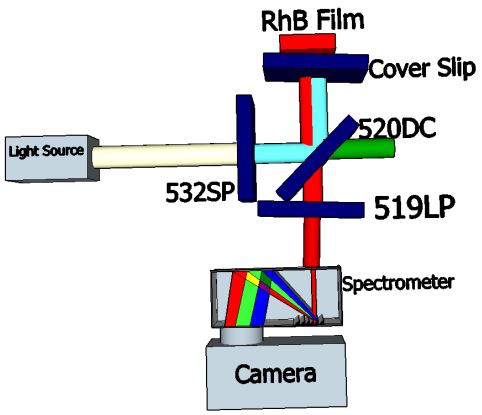


Figure 4: Light from the light scours hits a SP filter with a 532nm cut-off, passes through and hits a DC mirror with a cut-off at 520nm, then hits a sample which emits light that hits the DC mirror and passes through a LP with its cut-off at 519nm after which a spectrometer separates light of different wavelengths and redirects the separated light to a camera.

When using this setup however one needs to make sure that the filtered light that reaches the dye, falls in the absorption range of the dye or the dye will not

be excited. Also one needs to pay attention not to filter out the light emitted by the dye on the way to the camera. For instance: If one wants to look at Rhodamine 110 one might do the following. One places a 590 nm SP filter and 581 nm DC(LP) mirror in between the light source and the dye and a 590 nm LP filter in between the dye and the camera. Indeed the dye does get excited by the light and no light from the light source will reach the camera and interfere. However because Rhodamine 110 mainly emits light in the range of wavelengths below 550nm, it gets filtered out by the LP filter and thus, no light reaches the camera.

2.3 Rhodamine B

Rhodamine B is a fluorescent dye. It can be exited and then emit light. The structure of rhodamine B is shown in figure 5. There are four ethyl groups attached to nitrogen atoms as seen in the the structure. These ethyl groups can under certain circumstances react and form acetaldehyde, leaving the rhodamine B molecule an ethyl group poorer (deethylation). This changes the structure of the rhodamine molecule and in doing so it changes the wavelength of light it emits. For each ethyl group the molecule has less, the spectrum is slightly shifted towards lower wavelengths. To get an idea of how large the shift of the spectrum is we use a solution of rhodamine B in ethanol as an example. For a solution of rhodamine B in ethanol the peak of the spectrum shifts from 571 nm to 525 nm[7]. Once all four ethyl groups have reacted the molecule has become rhodamine 110. There can be zero, one, two, three or four groups attached. In the situation where there are two, there can be two on one side or two on each side. In this Thesis we make no distinction between these. Another process that can happen is that the molecule breaks down, making it unable to emit light (degradation).

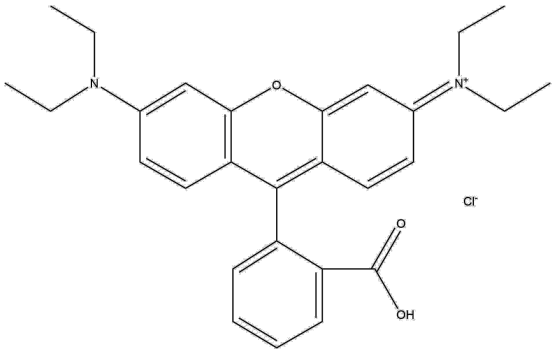


Figure 5: Structure of rhodamine B

To choose different environments in which we can study the dye we need to understand what the dye might react to. To get an idea of what dry rhodamine B films react to we look at the previously proposed reaction mechanisms of rhodamine B in a solution mentioned in the introduction 1. Firstly it has been found that for the initial stage of deethylation rhodamine B must acquire a positive charge. The following mechanism for acquiring this charge using CdS was proposed [2]:

$[>\text{N-C}_2\text{H}_5]_{\text{ads}} + h\nu \rightarrow [>\text{N-C}_2\text{H}_5]_{\text{ads}}{}^*$

$[>\text{N-C}_2\text{H}_5]_{\text{ads}}{}^* \rightarrow [>\text{N-C}_2\text{H}_5]_{\text{ads}}{}^+ + \text{e}^-_{\text{cond}}$.

Or when CdS absorbed a photon:

$\text{CdS} + h\nu \rightarrow \text{h}^+_{\text{val}} + \text{e}^-_{\text{cond}}$

$\text{h}^+_{\text{val}} + [>\text{N-C}_2\text{H}_5]_{\text{ads}} \rightarrow [>\text{N-C}_2\text{H}_5]_{\text{ads}}{}^+$.

The function of CdS in these reactions is making the dye positive, either by donating an electron hole or by accepting an electron. Once the dye has a positive charge, the ethyl group can react and form acetaldehyde C_2H_4O [2]. For this to happen oxygen needs to be present. In later research it was found that, when using TiO_2 as the semiconductor and having H_2O_2 present in solution, O_2 becomes O_2^- which then forms OH. This can react with the ethyl groups forming acetaldehyde [3] [4].

For us this means we must find out what rhodamine B donates an electron to or receives a positive electron hole from and how OH forms to make deethylation possible.

3 Experimental Section

3.1 Materials.

Rhodamine B ≥95% (HPLC-grade), Rhodamine 110 chloride ≥99.0%, Ethanol absolute (100%), Poly(methyl methacrylate) PMMA 996000 u and Hexamethyldisilazane HMDS were purchased from Sigma-Aldrich and used without further purification, cover slips #1.5 and microscope slides from Menzel-Gläser were used throughout this research.

3.2 Optical setup.

3.2.1 Setup for measuring spectra.

The microscope setup is as described in the section fluorescence microscopy 2.2. A microscope, Nikon Eclipse Ti-U, and light source the Sola light engine by Lumencore were used. In the path of the light to the sample a 532SP filter and 520DC mirror were placed. In the path from the sample to the spectrometer a 519LP filter was placed. A spectrometer (Andor, the Kymera) and a camera (Andor, iXon Ultra) were used.

3.3 Procedures and Analyses.

3.3.1 Rhodamine films.

Microscopy samples were prepared as follows: The cover slips were prepared by plasmacleaning them for 90 seconds. This ensures there are no impurities on the glass. Then one of three things was done to the cover slips. Some were not treated further. For the others, either 100 µL HMDS was dropcoated on the cover slip, dried at 150 °C then rinsed with EtOH 100%. The Si atoms of HMDS bond to the oxygen atoms on the surface of the glass, making it more hydrophobic. The effect of this changed chemical structure of the glass on the reactions rhodamine B undergoes we can compare to the reactions rhodamine B undergoes on untreated glass. Or 100 µL of 31 nM PMMA in toluene was dropcoated on the cover slip and let dry completely. This creates a layer on which rhodamine can be applied without it being in contact with glass. To create the films, 10 µL of 50 µM rhodamine B in ethanol was spincoated on the cover slips. After spincoating, the sample was left in the dark for an hour to dry. On some of the samples then PMMA was dropcoated to prevent contact with air and they were again allowed to dry in the dark. All films were then stuck on microscope slides with double sided tape.

3.3.2 Spectral measurements.

The samples were then studied using the microscope setup as described in section 3.2. We brought a random part of the film in focus using a low light intensity. Once in focus the light was turned off and the film was moved to a fresh area right outside the area we used to put the film in focus. Then the light was turned on and a measurement of the emission spectra was started, recording at one frame per second, where each frame was the spectrum at that time. This was repeated multiple times for each film.

3.3.3 Data analysis.

From the measured spectra the speed of degradation, speed of N-deethylation and composition change were extracted. To find these properties of the films the following was done. The data corresponding to wavelengths between 519 nm and 700 nm was extracted from the measurements. This was done because of the LP filter of 519 nm and because above 700 nm there is no useful information. Following this a background was subtracted from each frame. This background was determined by averaging over the intensities below 519 nm and above 700 nm. The total intensity of each frame was then calculated by integrating over the intensities of wavelengths between 519 nm and 700 nm. Next, time $t = 0$ was defined as the first frame after turning the light on. Since during each experiment the films slowly degrade in time and thus the intensity decreases, a t_{end} is defined as the frame at which the intensity goes below 5% of the highest recorded intensity for that measurement. This will allow us to compare the duration of degradation in different films. The wavelength associated with the highest intensity for each frame was determined, $\lambda_{\max}$, for each frame between $t = 0$ and $t = t_{\text{end}}$. Through these values a line was fit of the form $\lambda_{\text{maxfit}} = a + bt$ where t gives the time in frames, a gives the estimated value of $\lambda_{\max}$ at $t = 0$ and b gives the speed of change in $\lambda_{\max}$ in units of [nm/frame]. We record one frame per second, thus the parameter b gives us the change in wavelength in units of [nm/s].

We also look at the composition change in time of the films. To do this we fit a combination of the spectra of rhodamine B, 1,2,3-deethylated rhodamine B and rhodamine 110 throught the spectra we measure. The spectra of the intermediates are approximated in the following way: first we take the spectrum at $t = 0$ for each measurement. From this spectrum we subtract the background and normalise it. This will be used as the spectrum of rhodamine B. To estimate the spectra of 1,2,3-deethylated rhodamine B and rhodamine 110 we simply shift this spectrum, in wavelength scale, towards the found value of $\lambda_{\max}$ of rhodamine 110 for that environment in four equally large steps, which could be expected when looking at the absorption spectra of these species as found by Watanabe et al. [2]. One can also analyse the spectra in energy scale, but because the range of wavelengths is so small there is no significant difference when doing so. Then for fifty evenly spread frames between $t = 0$ and $t = t_{\text{end}}$ a fit was made to find the best combination of contributions of each rhodamine molecule to the total emitted spectrum.

To the found contributions of population in time we fit a model for a rate equation where we assume the following reactions can take place; The first reaction is degradation for which we assume the rate constants are the same for all rhodamine species. The second reaction is the deethylation from rhodamine B to 1-deethylated rhodamine B, for which we assume the rate constant is k_1. The last reactions are the deethylation reactions from 1-deethylated rhodamine B to rhodamine 110 for which we assume the rate constant is the same, k_2. We do this to minimise the number of parameters used for the fit. The model we

fit takes the following form:

$$\frac{\mathrm{d}y_{\mathrm{RhB}}}{\mathrm{d}t} = -k_1 y_{\mathrm{RhB}} - k_{\mathrm{deg}} y_{\mathrm{RhB}} \tag{1}$$

$$\frac{\mathrm{d}y_{\mathrm{Rh3}}}{\mathrm{d}t} = k_1 y_{\mathrm{RhB}} - k_2 y_{\mathrm{Rh3}} - k_{deg} y_{Rh3} \tag{2}$$

$$\frac{\mathrm{d}y_{\mathrm{Rh2}}}{\mathrm{d}t} = k_2 y_{\mathrm{Rh3}} - k_2 y_{\mathrm{Rh2}} - k_{\mathrm{deg}} y_{\mathrm{Rh2}} \tag{3}$$

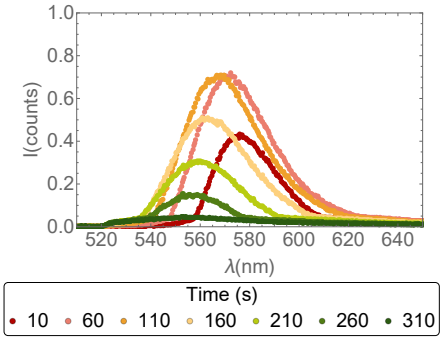
$$\frac{\mathrm{d}y_{\mathrm{Rh1}}}{\mathrm{d}t} = k_2 y_{\mathrm{Rh1}} - k_2 y_{\mathrm{Rh1}} - k_{\mathrm{deg}} y_{\mathrm{Rh1}} \tag{4}$$

$$\frac{\mathrm{d}y_{\mathrm{Rh110}}}{\mathrm{d}t} = k_2 y_{\mathrm{Rh1}} - k_{\mathrm{deg}} y_{\mathrm{Rh110}} \tag{5}$$

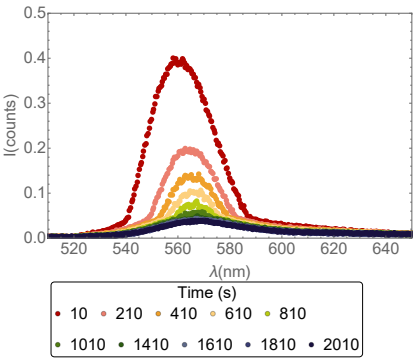
Where y_{RhB}, y_{Rh3}, y_{Rh2}, y_{Rh1}, y_{Rh110} are respectively the amount of rhodamine B, rhodamine with three, two and one ethyl groups, and rhodamine 110. k_1 is the rate constant for rhodamine B losing an ethyl group, k_2 is the rate constant for the other intermediates losing one ethyl group and k_{deg} is the rate constant of degradation. We assume there is only rhodamine B when the reactions start which we use when solving the differential equations. This gives us solutions that depend on $y_{\mathrm{RhB}}(0)$. After fitting this model through the values found for the intermediates, we use k_1 and k_{deg} to compare the rate of degradation and deethylation in different environments.

4 Results and Discussion

Firstly we look at how the emission spectrum of a dry film of rhodamine B on glass in air changes in time. This is shown in figure 6a. The first shown spectrum at $t = 10$ has an intensity peak at 580nm. The total intensity of the following spectra decreases to a small amount and their peak shifts towards the shorter wavelengths. This behaviour was observed before for the absorption spectra of RhB in solution with photocatalysts present[2].



(a)



(b)

Figure 6: Emission spectrum at several points in time under continuous excitation with broadband blue light of (a) a dry rhodamine B film on glass, and (b) a dry rhodamine B film on PMMA.

When we prevent the rhodamine B from being in contact with glass by coating the glass with PMMA we observe the spectra shown in figure 6b. (For all other samples the spectra can be found in the appendix.) Here we see the λ_{max} starts at 570nm and decreases in intensity over time. There are three differences with the previous experiment where rhodamine B is in contact with glass. Firstly the value of λ_{max} does not decrease in value when rhodamine B is not in contact with glass. Secondly it takes substantially more time for rhodamine B to degrade when it is not in contact with glass. Lastly the value of λ_{max} is different for the two samples.

The first difference indicates that for deethylation glass needs to be present. The second difference indicates the glass has some effect on the rate of degradation. The last difference can be explained in the following way: Rhodamine dyes have different emission spectra based on the environment[7], thus allowing rhodamine B to have a different spectrum in these two samples. To make sure these differences in λ_{max} of the spectra of the samples at $t = 10$ are not due to deethylation before the measurement started, we looked at the value of λ_{max} for rhodamine 110 in all

of the environmental conditions in which we do measurements. This is done with rhodamine 110 because it has no ethyl groups left, which means no deethylation is possible for rhodamine 110, and thus we know what dye we are looking at. In figure 7 we see that indeed rhodamine 110 has a different λ_{max} in the different environments. So for the rest of this thesis we will assume that the spectrum corresponding to the start of an experiment originates from RhB and not any deethylated products of rhodamine B. This could be checked in future research by NMR spectroscopy, infrared spectroscopy or measurements on the fluorescent lifetime.

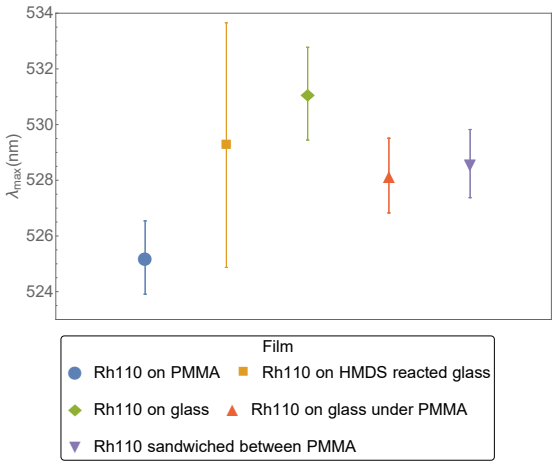
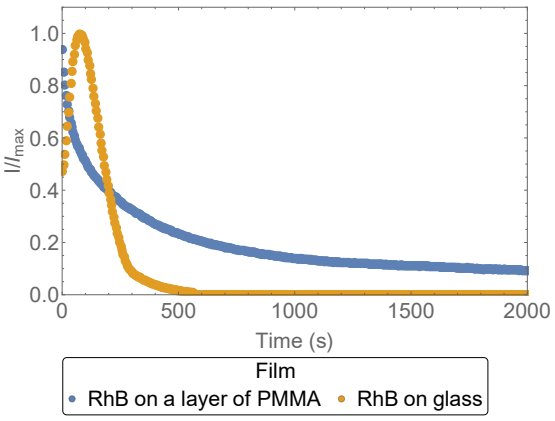
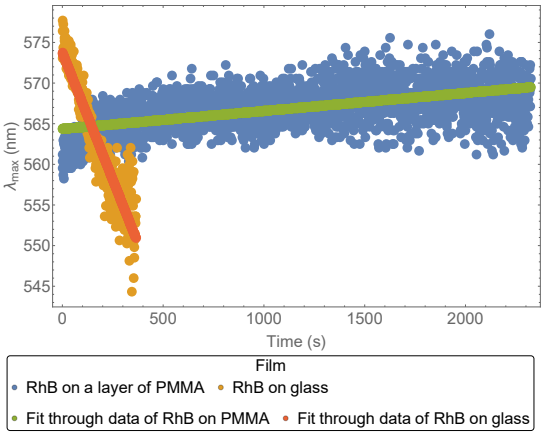


Figure 7: Wavelength with highest intensity for dry rhodamine 110 films in different environments.

We then compare the change in total intensity and change of maximum wavelength of RhB on glass with the changes of RhB on a layer of PMMA. This is shown in figure 8a. Here you see the the total intensity in time 8a and maximum wavelengths in time 8b. We see that when rhodamine B is in contact with glass there is a strong N-deethylation and faster degradation then for the situation where rhodamine B is not in contact with glass. We also see an increase in intensity during the first 100 s for the situation of rhodamine B on glass. This is likely caused because the light used to excite the dye does not have the same intensity for every wavelength, but has a spectrum that overlaps better with the absorption spectra of the deethylated products.



(a)



(b)

Figure 8: Differences in intensity and emitted wavelength in time under continuous excitation with broadband blue light of rhodamine B on glass versus rhodamine B on PMMA, where (a) shows the change in the integrated emission intensity normalized to the maximum as a function of time, and (b) shows the measured changes in wavelength as a function of time and the fitted line through these measured points for each sample.

We have also looked at samples where rhodamine B is on glass with a layer of PMMA over it preventing it from being in contact with air, samples where rhodamine B is sandwiched between two layers of PMMA preventing it from being in contact with glass and air and samples where rhodamine B is coated on glass that has reacted with HDMS. For all these measurements we show the speed of n-deethylation in [nm/s] in one figure 9. In the same figure we show the time it took the film to reach 5% total intensity in [s].

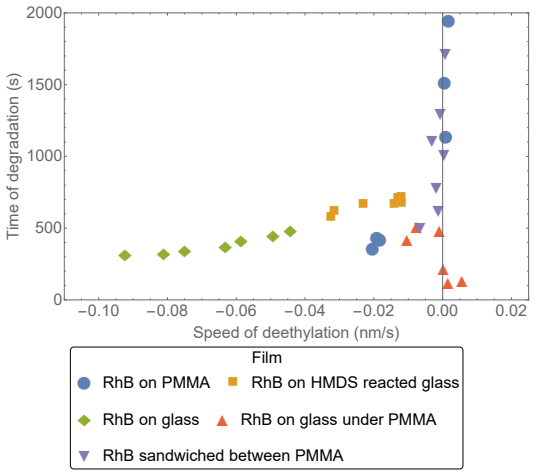


Figure 9: The change in wavelength per time on the x-axis and the time it takes for the total intensity of a spectrum to reach five percent on the y-axis for the different environments.

We see that for the case where rhodamine B is in contact with glass and air there is stronger deethylation and degradation than all other cases, with the exception of rhodamine B on glass with PMMA coated on the rhodamine B which has a faster degradation. We then compare this to rhodamine B on glass reacted with HDMS. In this case we see a slightly slower deethylation and degradation. For the case where rhodamine B is on PMMA or the case where it is sandwiched between two layers of PMMA, there is no deethylation and much slower degradation. The case where rhodamine B is under PMMA there is fast degradation in comparison with the other samples, but no deethylation. In short we see that for all samples where the rhodamine B was in contact with glass there is a fast degradation of the dye but only when the dye is in contact with both air and glass a deethylation occurs.

We can compare this to the parameters found when fitting the analytical model discussed in the data analysis section for a more numeric analysis. As an example of how we do this the results of our fit, that gave the amount of intermediates in time, of one of the samples of rhodamine B on glass is shown in figure 10.

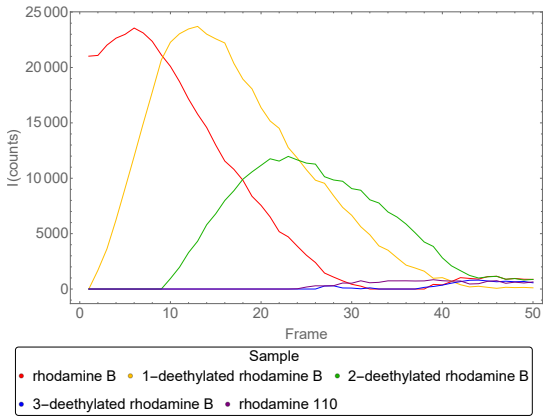


Figure 10: The amount of each of the intermediates shown in time, where each frame is a set time apart, found by fitting a combination of rhodamine species through the total spectra.

Through these amounts of intermediates in time we fit the model found in the section: data analysis.From this fit we get parameters for rate of deethylation and degradation. We plot the amounts of intermediates from analytical model over the amounts seen above in figure 11.

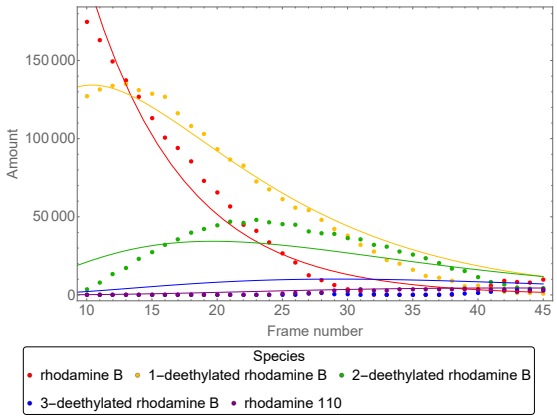


Figure 11: The amount of intermediates found from the fits through measurements as dots and the amount of intermediates found through the model as lines.

We see that the model overlaps reasonably well with the found amounts. We then do this for all samples and compare the parameters that the fits give us. The parameters for rate of degradation and deethylation are shown in figure 12.

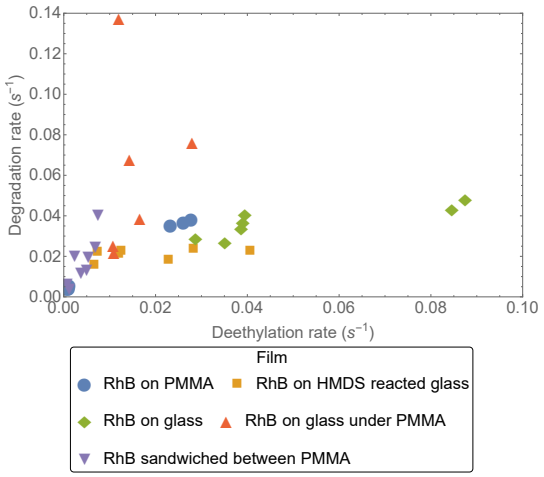


Figure 12: The rate of deethylation on the x-axis and rate of degradation on the y-axis for all the different films of rhodamine B.

We once again observe that the rate of deethylation is fastest for the film on glass and in contact with air. The films on PMMA show slow deethylation and degradation. The film on glass reacted with HDMS has a faster degradation and deethylation than rhodamine on PMMA but slower than rhodamine on glass. The sample of rhodamine on glass under PMMA shows fast degradation and varying rates of deethylation. In short these results agree with the results before where there is fast degradation when rhodamine is in contact with glass and there is also deethylation when it is in contact with both air and glass.

To explain what the reaction mechanisms at work are, we note again that in previous research it has been found that one of the reaction products of deethylation was acetaldehyde[2]. This means an oxygen atom has reacted with an ethyl group during deethylation. However for oxygen to react it first needs to form reactive oxygen species OH. This means hydrogen needs to be present. Using these facts we propose the following for the deethylation of rhodamine B: First rhodamine B gets irradiated by visible light causing an electron to go into an exited state. This electron can be transferred to oxygen forming O_2^-. The point of zero charge of the surface of the glass is at a pH level of approximately 3 [8]. This means that on the surface of the glass there are hydrogen atoms present that are able to react in our situation. These hydrogen atoms react with the O_2^- and form the reactive oxygen species OH^*. These can then react with the dye and form acetaldehyde and 1-deethylated rhodamine. The one hydrogen atom that is left then returns to the surface of the glass. This can be summarised in the following reaction diagrams.

$$\mathrm{RhB} \xrightarrow{h\nu} \mathrm{RhB^*}$$
$$\mathrm{O_2 + RhB^* \longrightarrow {O_2}^{\bullet -} + {RhB}^{+\bullet}}$$
$$\mathrm{Surf-Si-OH + {O_2}^{\bullet -} \longrightarrow OH^{\bullet} + OH^-}$$
$$\mathrm{{RhB}^{+\bullet} + OH^{\bullet} \longrightarrow Rh(C_2H_5)_3 + C_2H_4O + H^+}$$

Where RhB is rhodamine B, Surf-Si-OH is the group on the surface of the glass that contains the hydrogen atoms that react and $Rh(C_2H_5)_3$ is 1-deethylated rhodamine B. This process can also occur from 1-deethylated rhodamine B to 2-deethylated rhodamine B, all the way to rhodamine 110.

This means the requirements for deethylation are that there needs to be air and glass present and that the dye needs to be irradiated by visible light.

5 Conclusions

We have studied dry rhodamine B films under visible light irradiation using fluorescence microscopy and preformed rate equation modeling to analyse the data. We found that dry rhodamine B films in air on glass undergo both deethylation and degradation. A prerequisite for the deethylation is the creation of OH which forms by oxygen reacting with hydrogen on the glass. Degradation is accelerated by the presence hydrogen on the surface of the glass. This means no photocatalyst is needed to deethylate or degrade dry rhodamine B by visible light. In future research one might want to look at whether there are differences in the cis- and tans 2-deethylated rhodamine B. This could reveal what ethyl group is more likely to react. If there is a difference in when cis or trans ethyl groups are more likely to be present depending on environmental factors, this could be useful in identifying products that form during reactions which could be used to get insight in certain catalytic reactions and hopefully allow us to improve them. One can also use the knowledge we now have on the reactions of rhodamine B to study fundamental catalytic reactions with the goal to improve efficiency of many chemical processes.

6 Acknowledgments

I would like to give special thanks to my main supervisor Dr. F.T. Rabouw and daily supervisor S.O.M. Hinterding MSc. for guiding me throughout the project, my student colleagues for the pleasant working environment, my parents for proofreading my work and their support, and the UU SCM group for supplying the needed information and materials.

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A Appendix

In the appending spectra of one sample in each different environment are enclosed with their peak wavelength in time, intensity in time, the concentrations of the intermediates in time found by fitting and the fit of the analytical model through these concentrations. Also the spectrum of one sample in each environment of rhodamine 110 in different environments will be enclosed.

A.1 Rhodamine B.

A.1.1 Rhodamine B on glass.

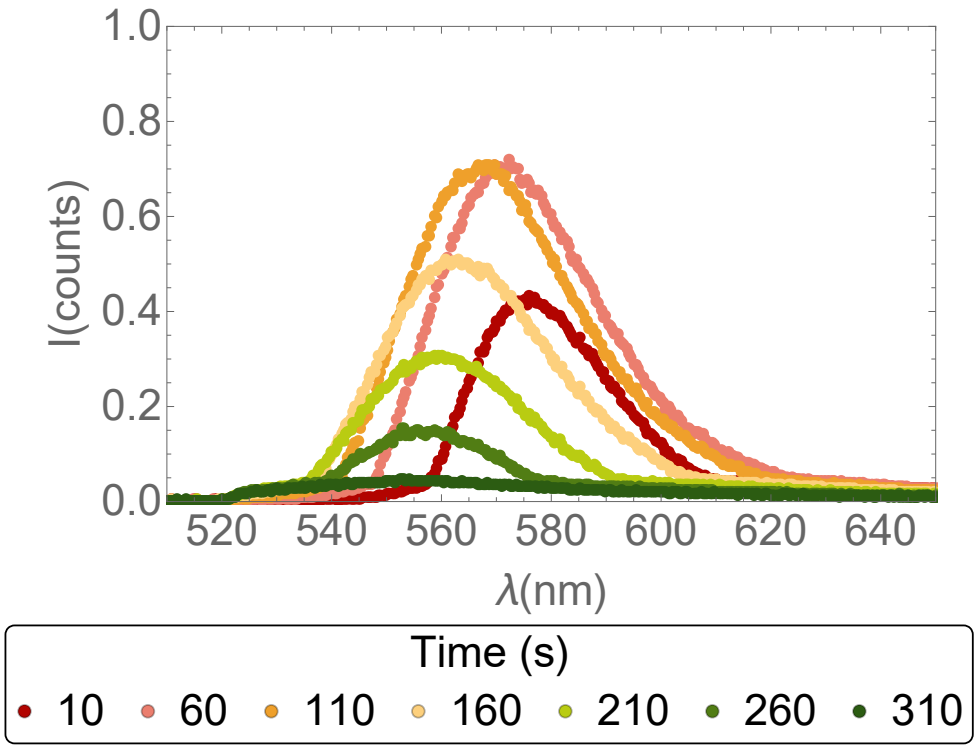

Figure 13: Emission spectrum at several points in time under continuous excitation with broadband blue light of a dry rhodamine B film on glass.

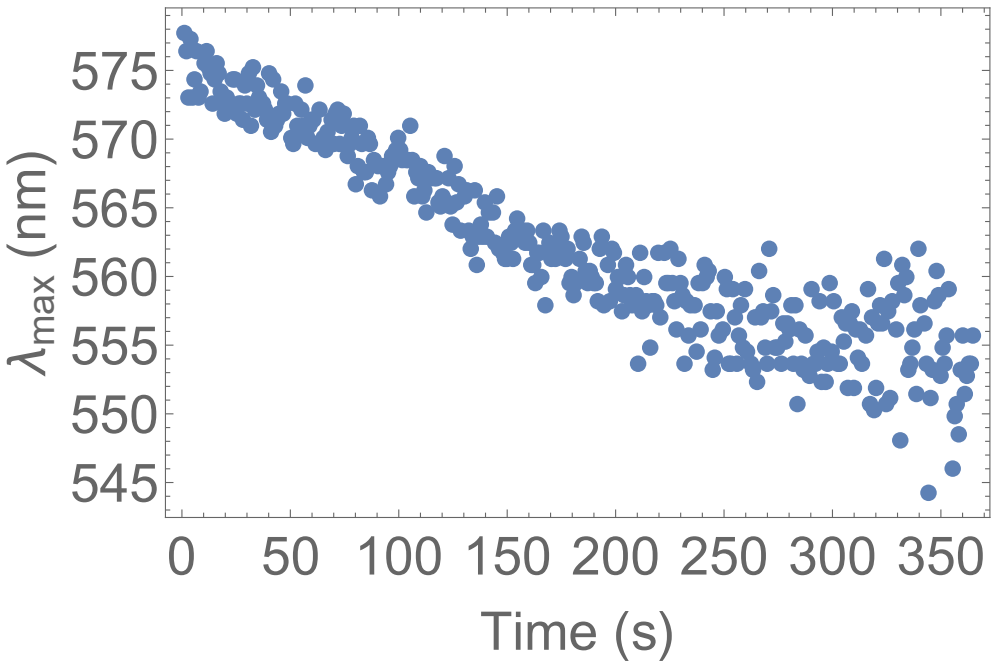

Figure 14: The measured changes in wavelength as a function of time under continuous excitation with broadband blue light of a dry rhodamine B film on glass.

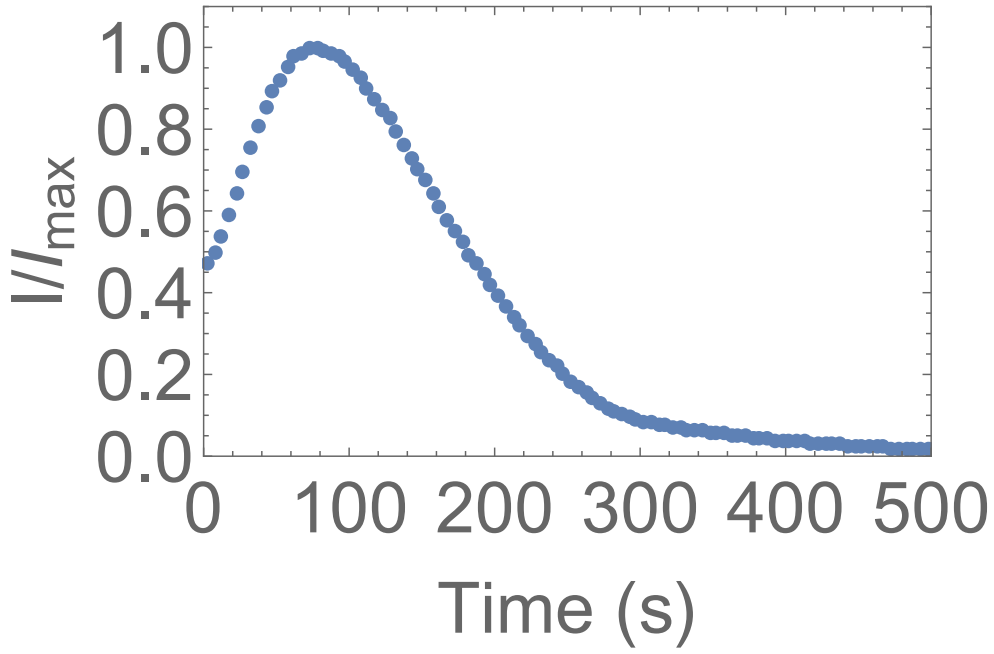

Figure 15: The change in the integrated emission intensity normalized to the maximum as a function of time of a dry film of rhodamine B on glass under continuous excitation with broadband blue light.

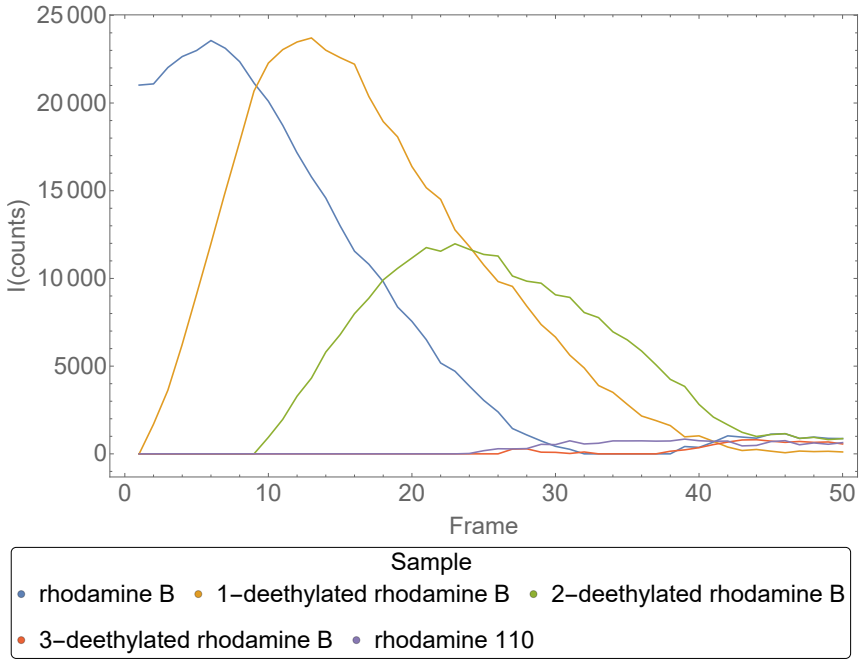

Figure 16: The amount of each of the intermediates shown in time, where each frame is a set time apart, found by fitting a combination of rhodamine species through the total spectra of a dry film of rhodamine B on glass under continuous excitation with broadband blue light.

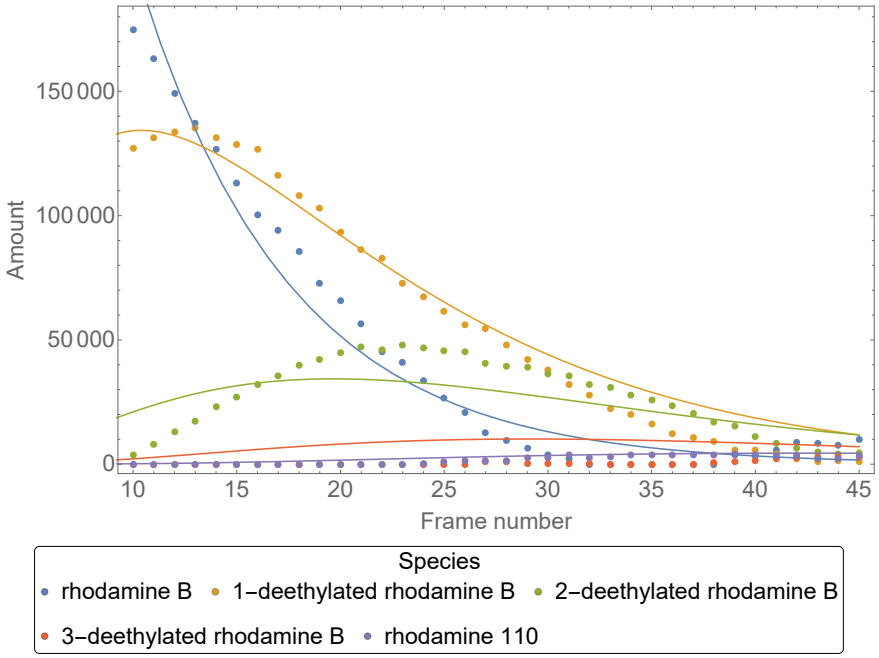

Figure 17: The amount of intermediates found from the fits through measurements as dots and the amount of intermediates found through the model as lines of a dry film of rhodamine B on glass under continuous excitation with broadband blue light.

A.1.2 Rhodamine B on PMMA.

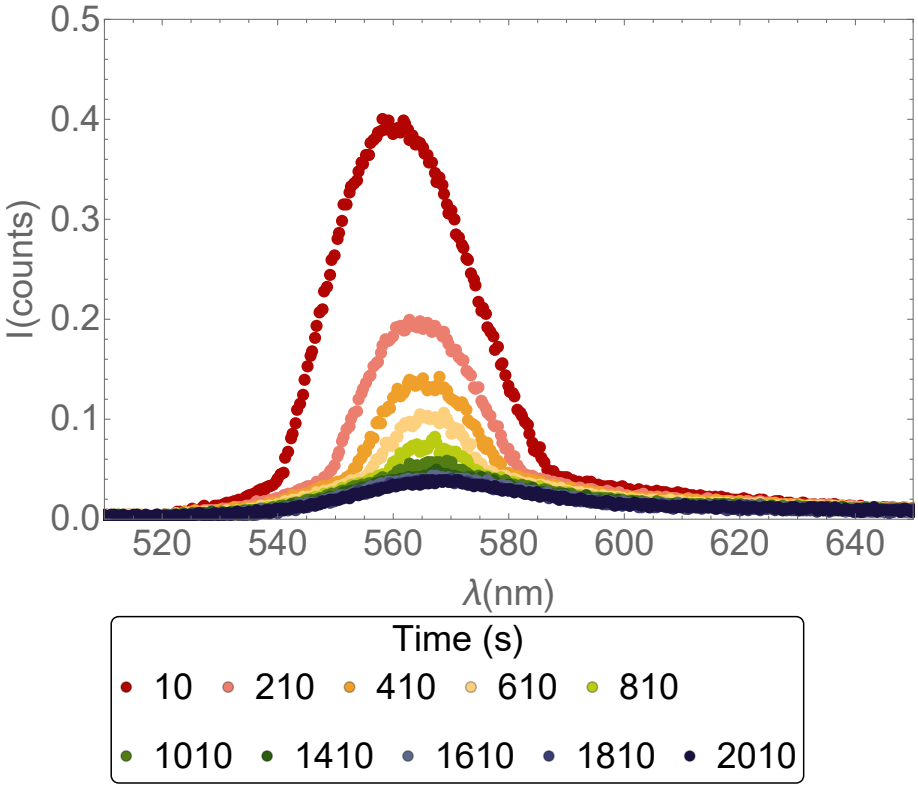

Figure 18: Emission spectrum at several points in time under continuous excitation with broadband blue light of a dry rhodamine B film on glass coated with PMMA.

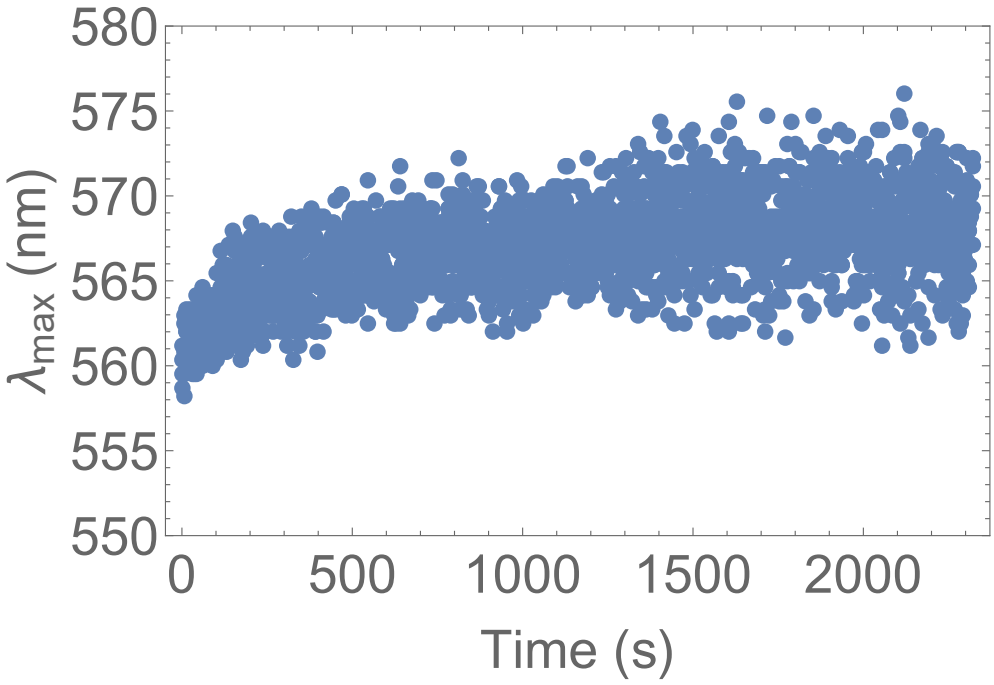

Figure 19: The measured changes in wavelength as a function of time under continuous excitation with broadband blue light of a dry rhodamine B film on PMMA.

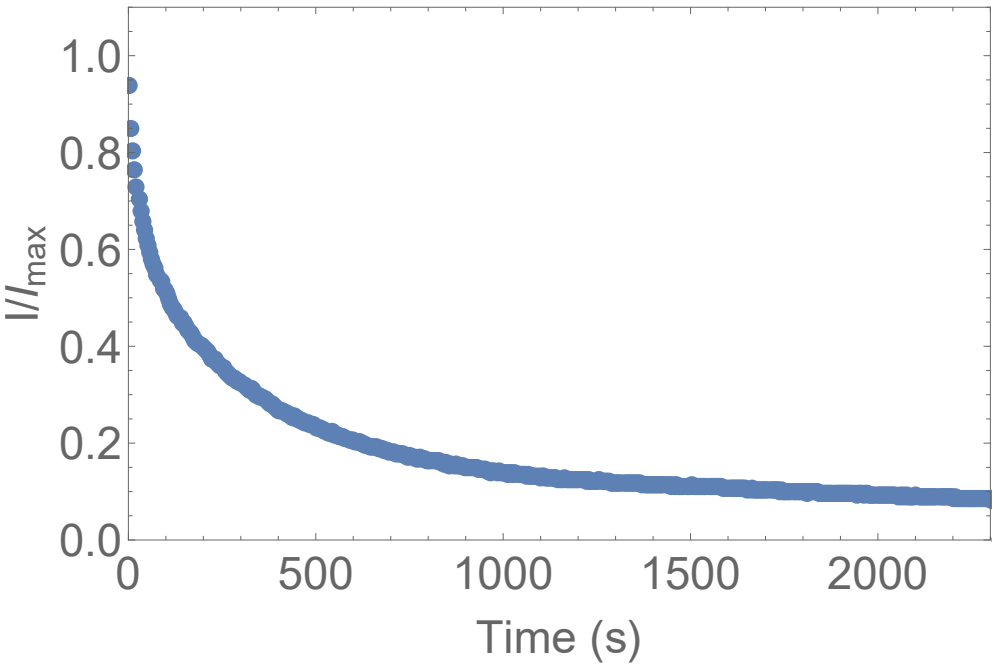

Figure 20: The change in the integrated emission intensity normalized to the maximum as a function of time of a dry film of rhodamine B on PMMA under continuous excitation with broadband blue light.

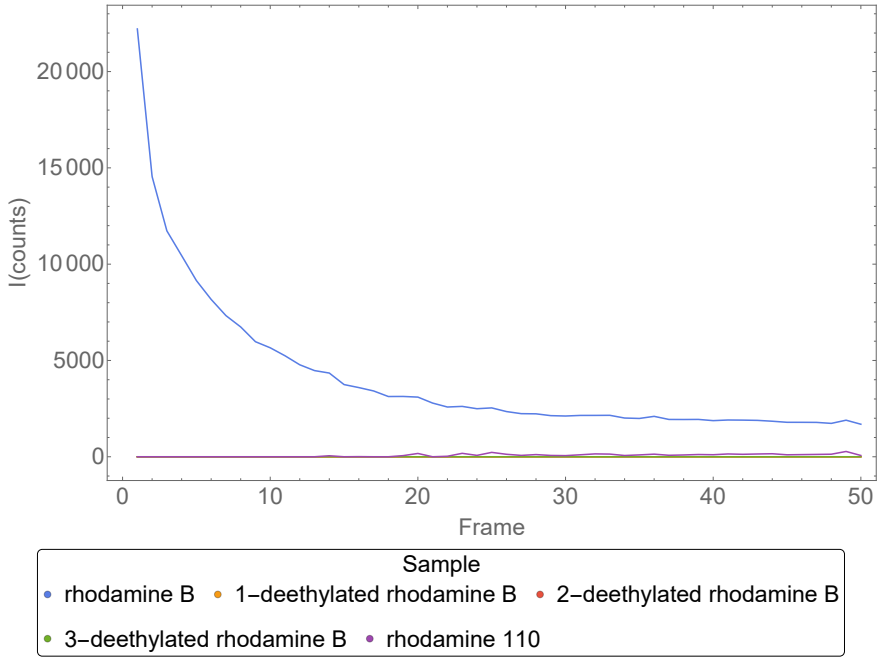

Figure 21: The amount of each of the intermediates shown in time, where each frame is a set time apart, found by fitting a combination of rhodamine species through the total spectra of a dry film of of rhodamine B on PMMA under continuous excitation with broadband blue light.

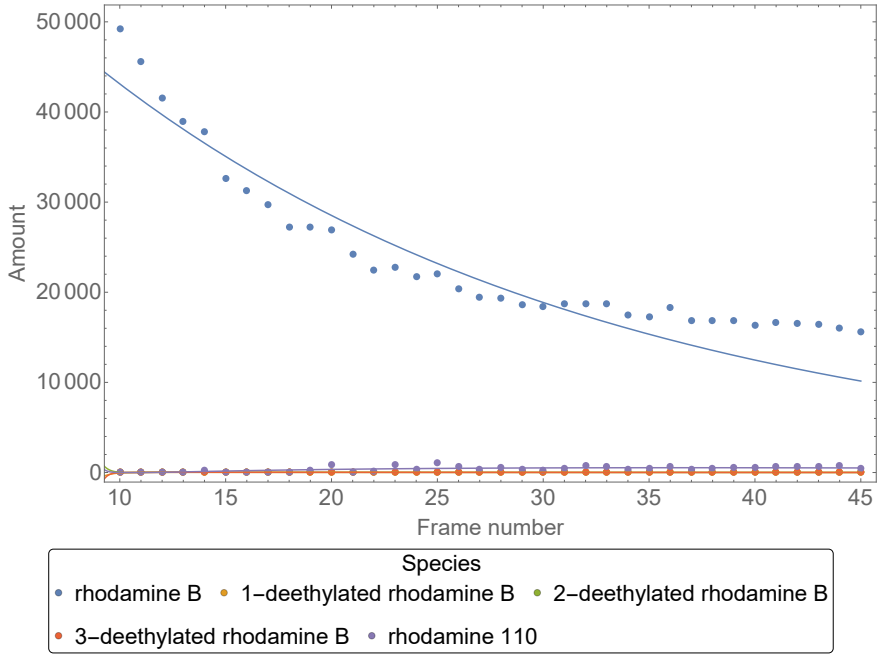

Figure 22: The amount of intermediates found from the fits through measurements as dots and the amount of intermediates found through the model as lines of a dry film of rhodamine B on PMMA under continuous excitation with broadband blue light.

A.1.3 Rhodamine B on glass reacted with HDMS.

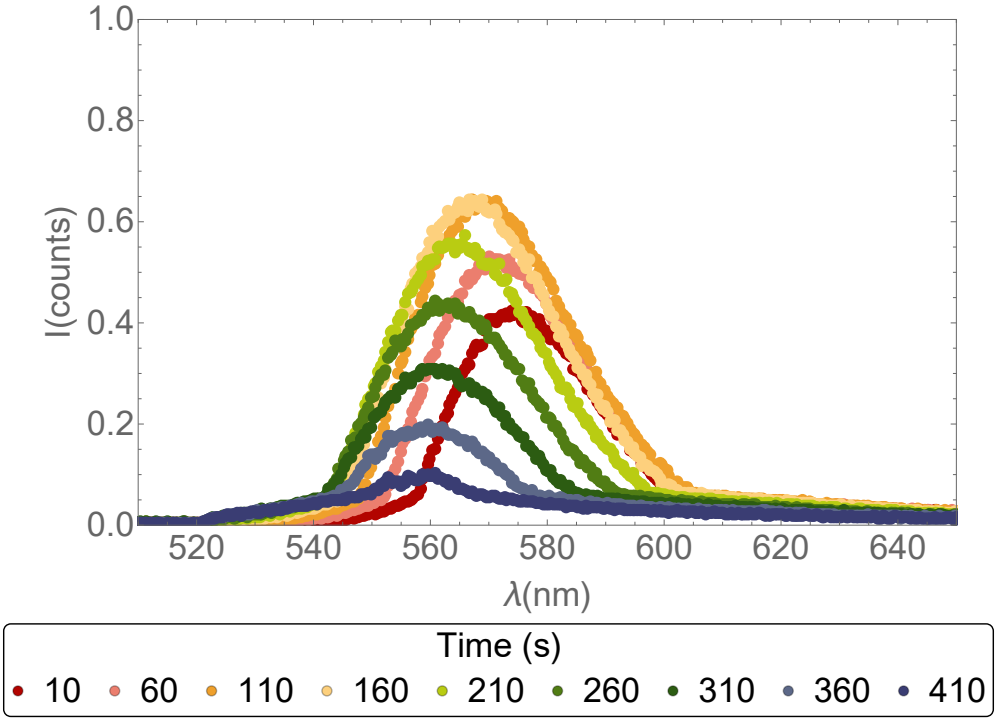

Figure 23: Emission spectrum at several points in time under continuous excitation with broadband blue light of a dry rhodamine B film on glass reacted with HMDS.

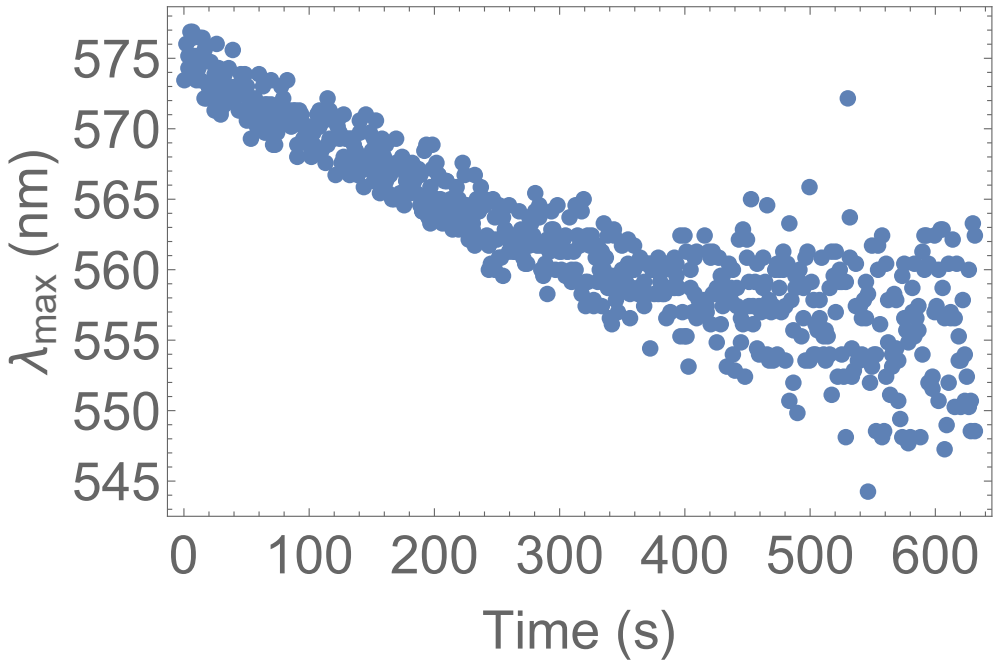

Figure 24: The measured changes in wavelength as a function of time under continuous excitation with broadband blue light of a dry rhodamine B film on glass reacted with HDMS.

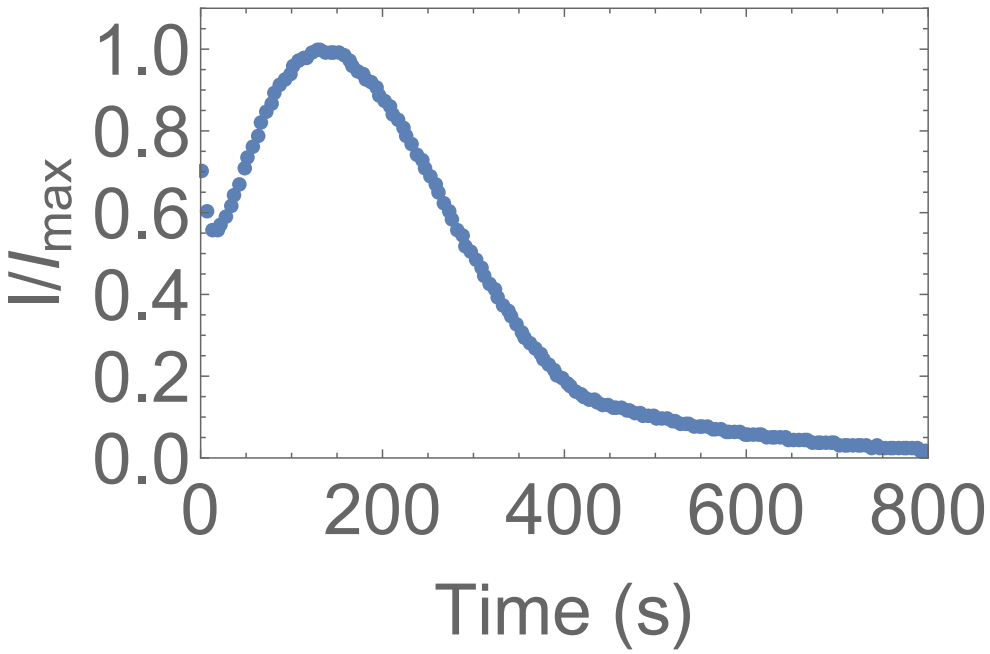

Figure 25: The change in the integrated emission intensity normalized to the maximum as a function of time of a dry film of rhodamine B on glass reacted with HMDS under continuous excitation with broadband blue light.

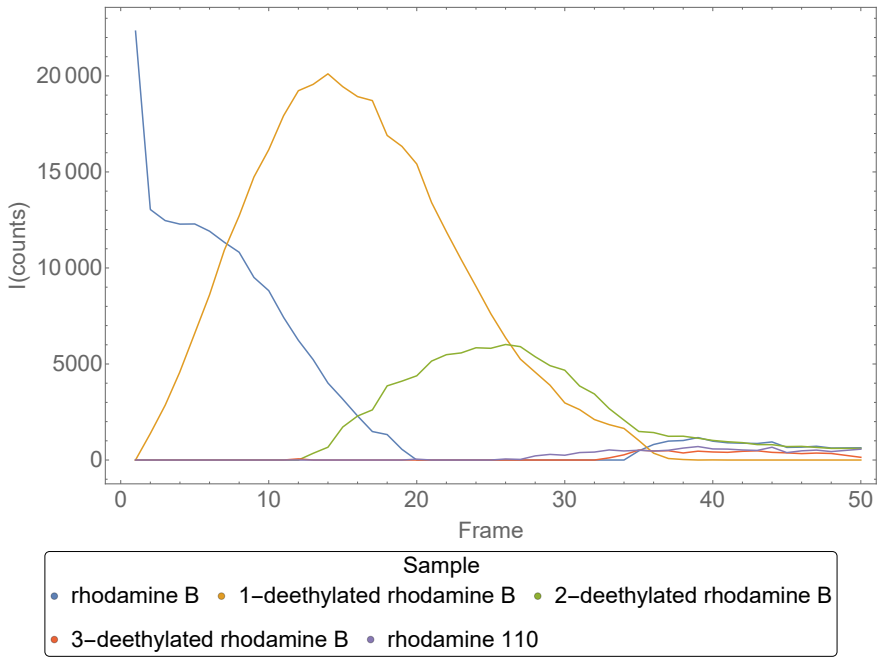

Figure 26: The amount of each of the intermediates shown in time, where each frame is a set time apart, found by fitting a combination of rhodamine species through the total spectra of a dry film of rhodamine B on glass reacted with HMDS under continuous excitation with broadband blue light.

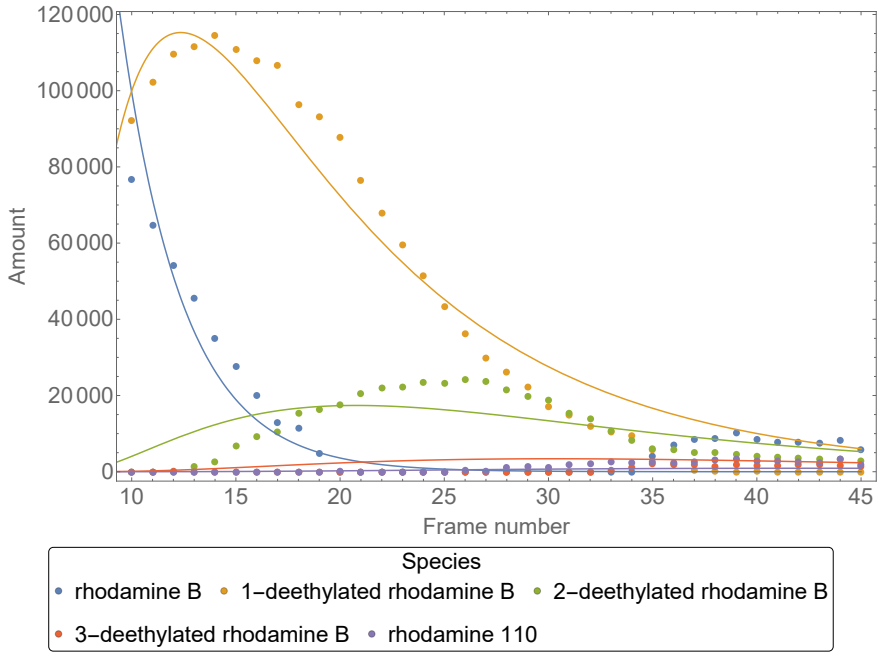

Figure 27: The amount of intermediates found from the fits through measurements as dots and the amount of intermediates found through the model as lines of a dry film of rhodamine B on glass reacted with HMDS under continuous excitation with broadband blue light.

A.1.4 Rhodamine B on glass under PMMA.

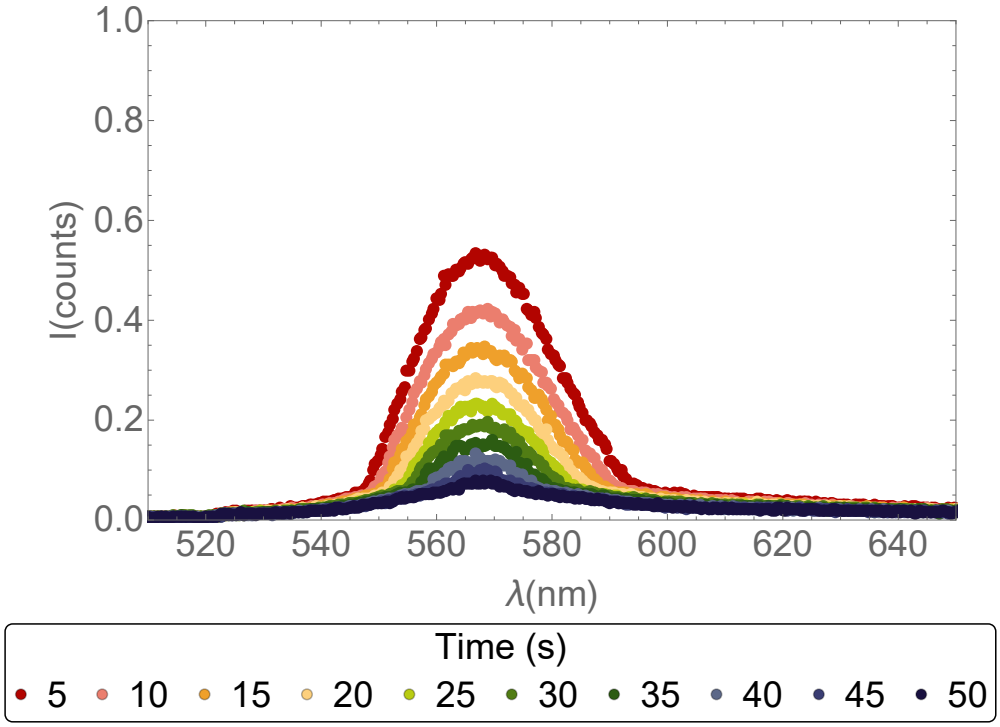

Figure 28: Emission spectrum at several points in time under continuous excitation with broadband blue light of a dry rhodamine B film on glass under a coating of PMMA.

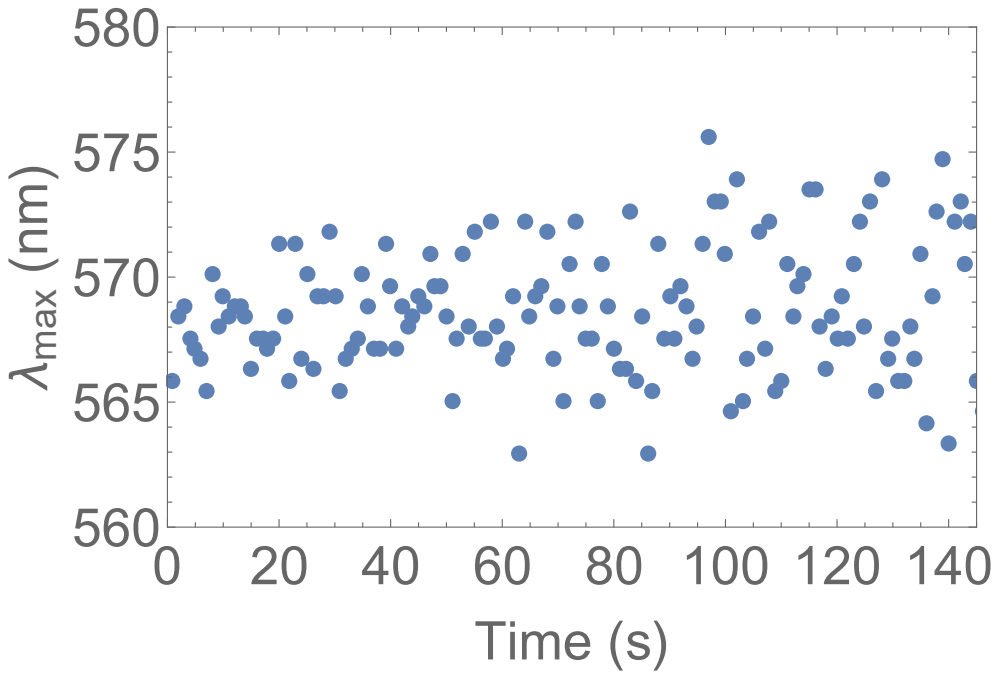

Figure 29: The measured changes in wavelength as a function of time under continuous excitation with broadband blue light of a dry rhodamine B film on glass under a coating of PMMA.

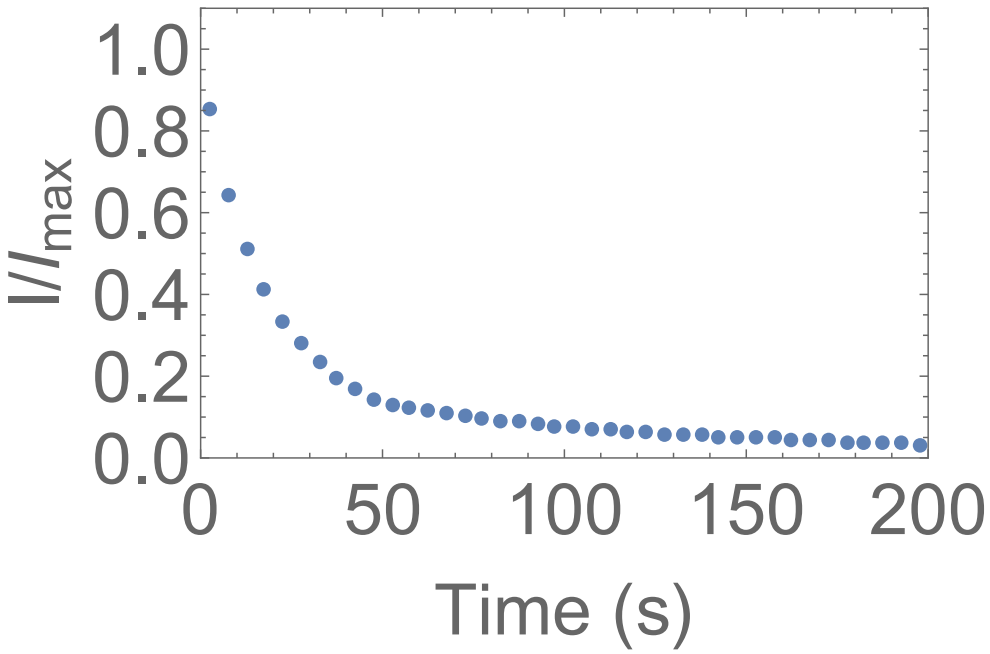

Figure 30: The change in the integrated emission intensity normalized to the maximum as a function of time of a dry film of rhodamine B on glass under a coating of PMMA under continuous excitation with broadband blue light.

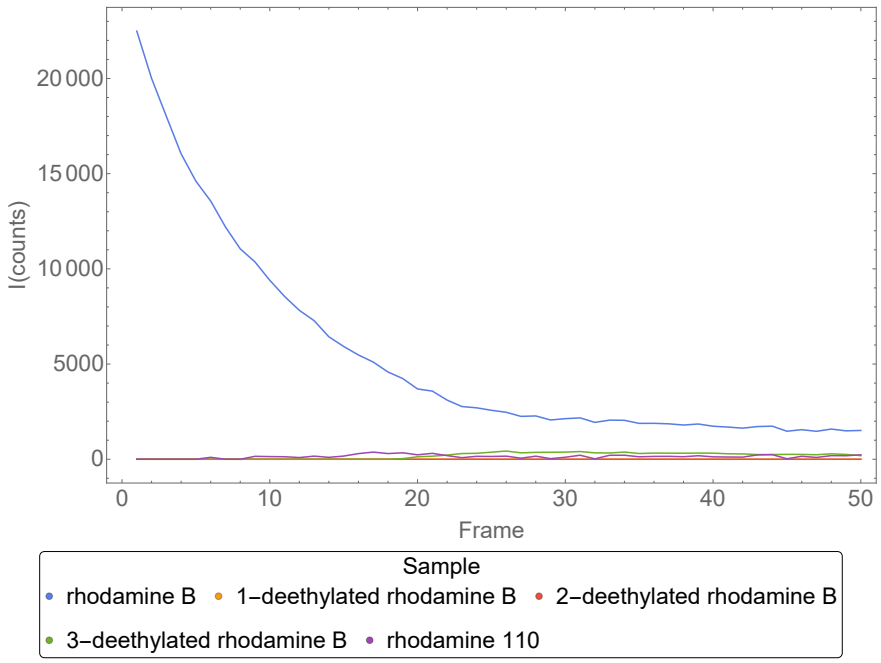

Figure 31: The amount of each of the intermediates shown in time, where each frame is a set time apart, found by fitting a combination of rhodamine species through the total spectra of a dry film of rhodamine B on glass under a coating of PMMA under continuous excitation with broadband blue light.

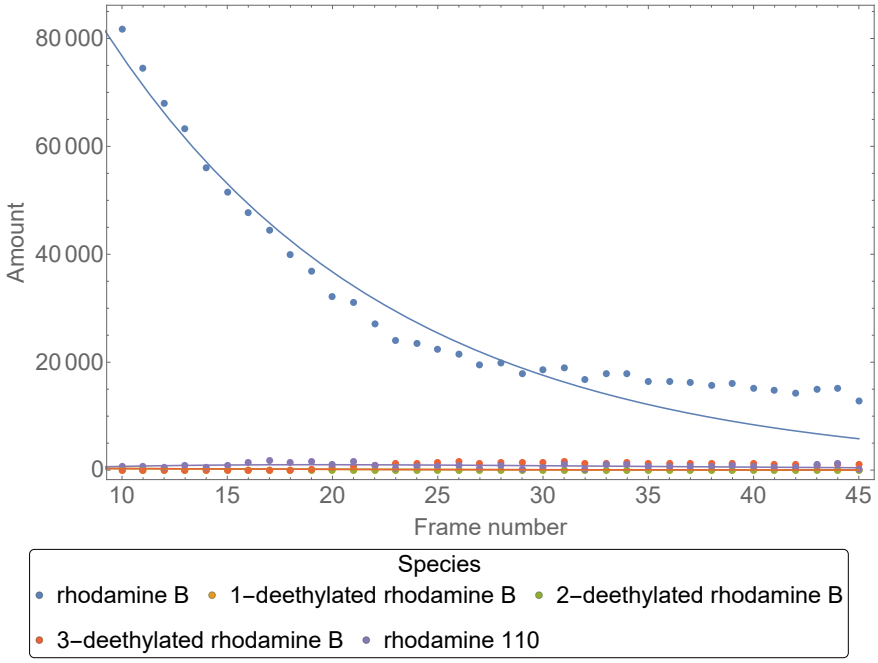

Figure 32: The amount of intermediates found from the fits through measurements as dots and the amount of intermediates found through the model as lines of a dry film of rhodamine B on glass under a coating of PMMA under continuous excitation with broadband blue light.

A.1.5 Rhodamine B in between two layors of PMMA.

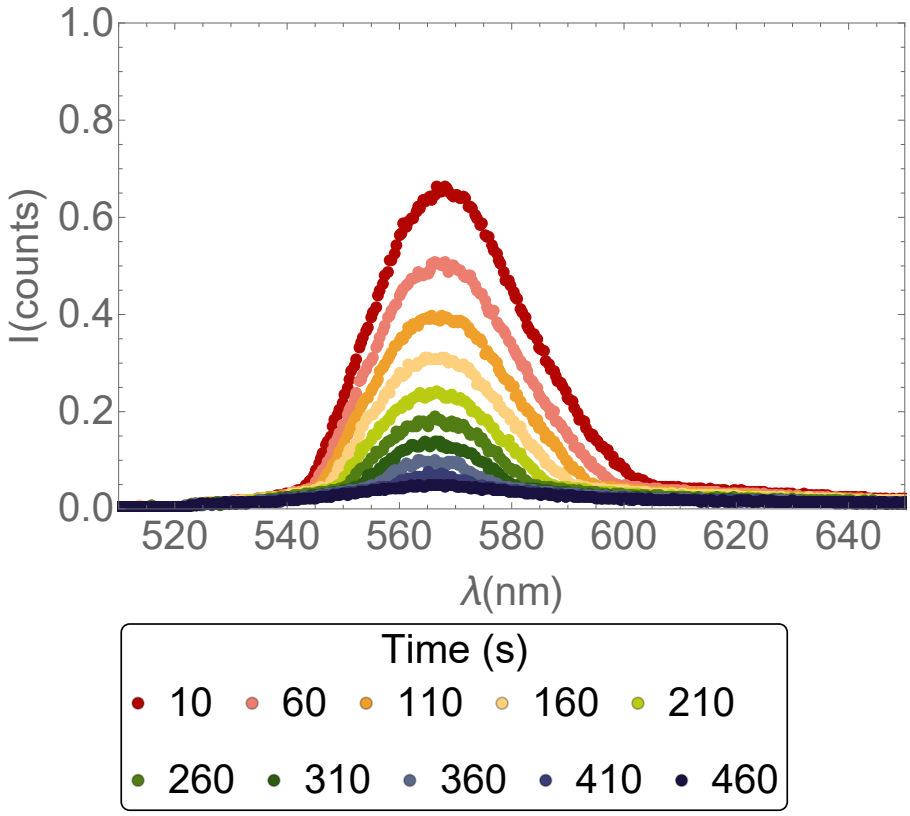

Figure 33: Emission spectrum at several points in time under continuous excitation with broadband blue light of a dry rhodamine B film in between two layers of PMMA.

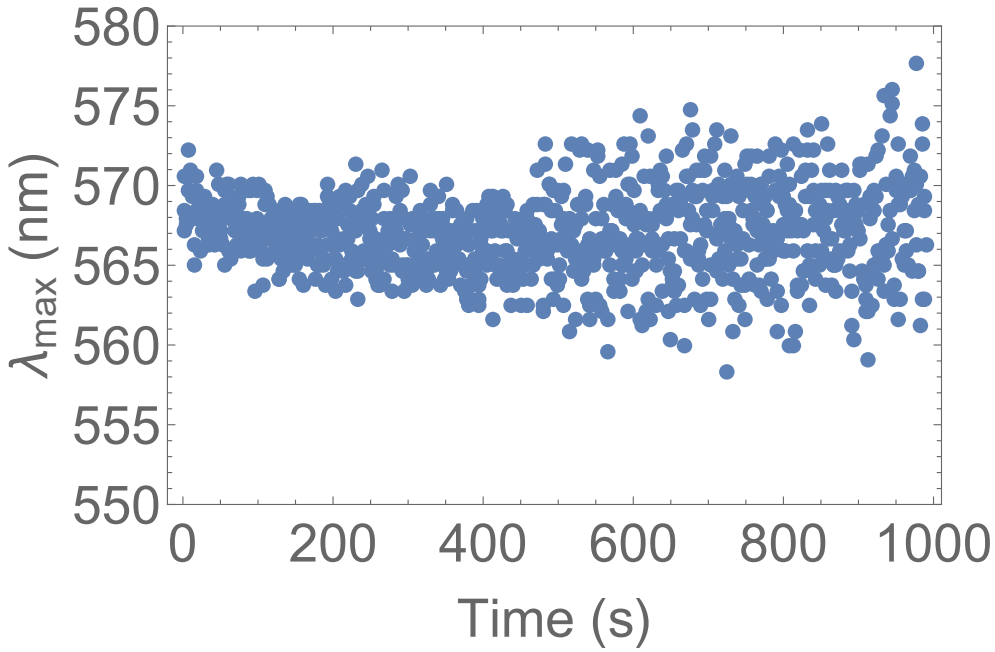

Figure 34: The measured changes in wavelength as a function of time under continuous excitation with broadband blue light of a dry rhodamine B film in between two layers of PMMA.

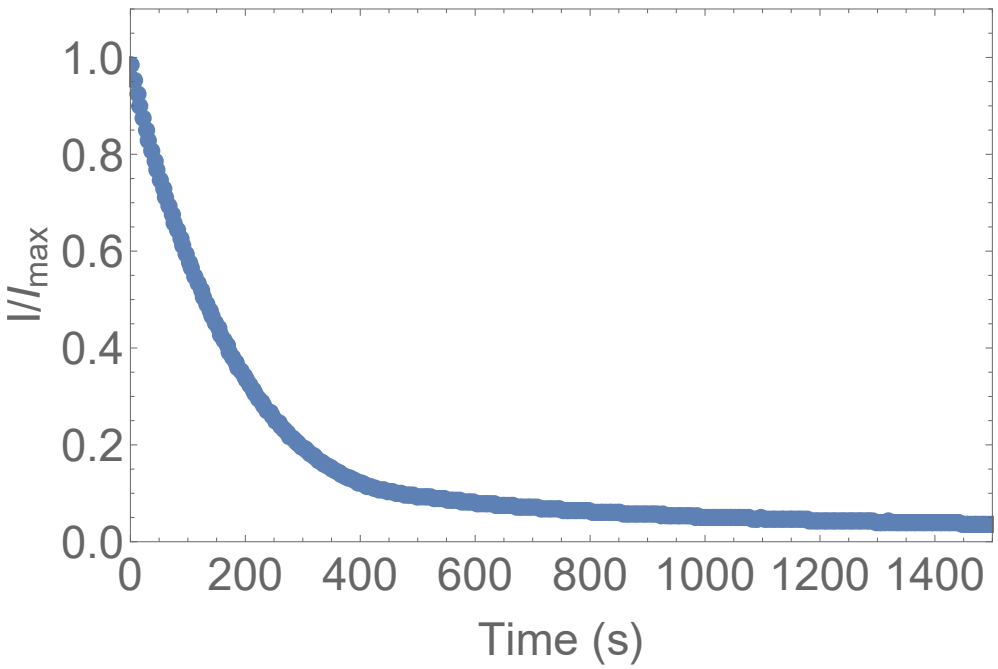

Figure 35: The change in the integrated emission intensity normalized to the maximum as a function of time of a dry film of rhodamine B in between two layers of PMMA under continuous excitation with broadband blue light.

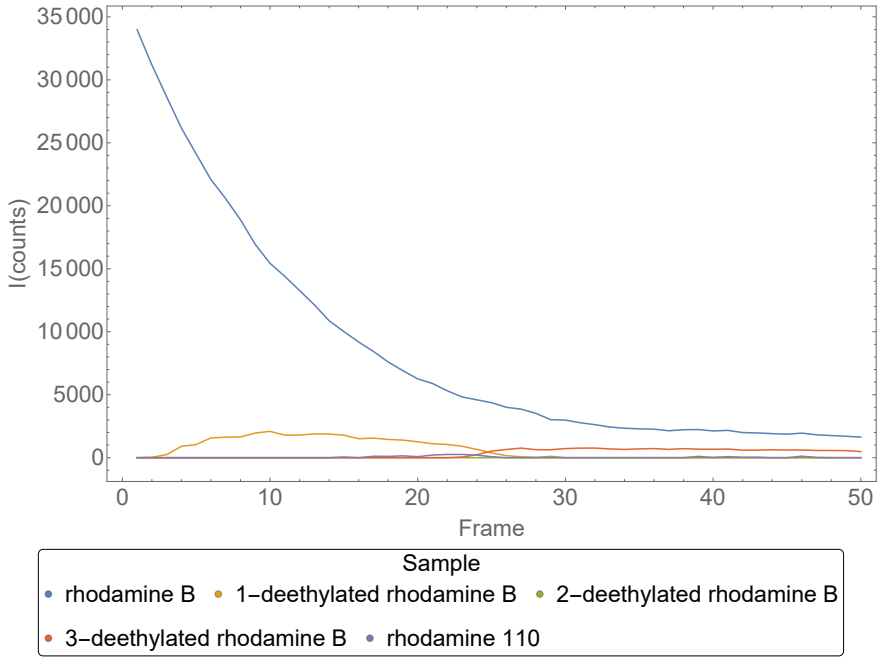

Figure 36: The amount of each of the intermediates shown in time, where each frame is a set time apart, found by fitting a combination of rhodamine species through the total spectra of a dry film of rhodamine B in between two layers of PMMA under continuous excitation with broadband blue light.

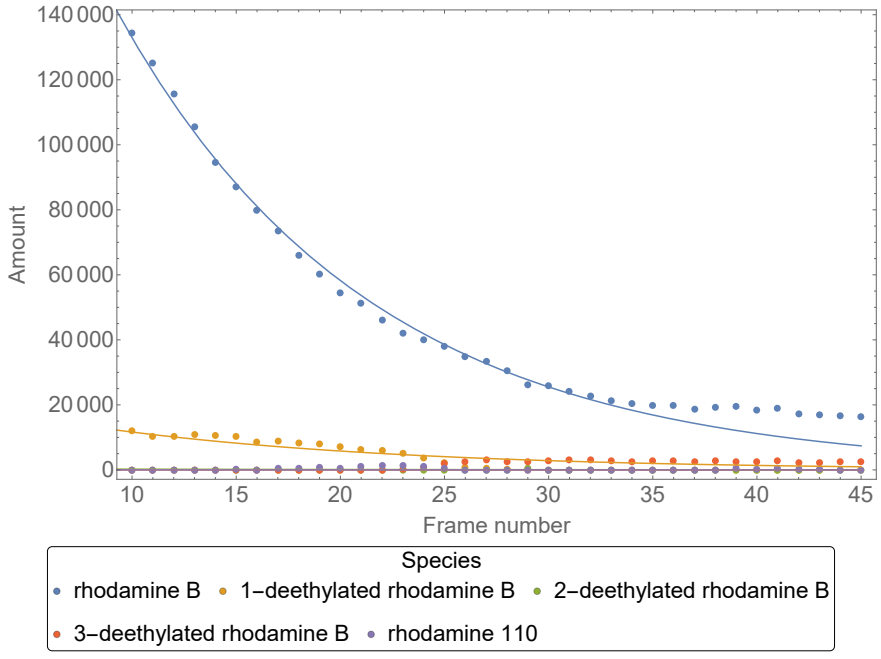

Figure 37: The amount of intermediates found from the fits through measurements as dots and the amount of intermediates found through the model as lines of a dry film of rhodamine B in between two layers of PMMA under continuous excitation with broadband blue light.

A.2 Rhodamine 110.

A.2.1 Rhodamine 110 on glass.

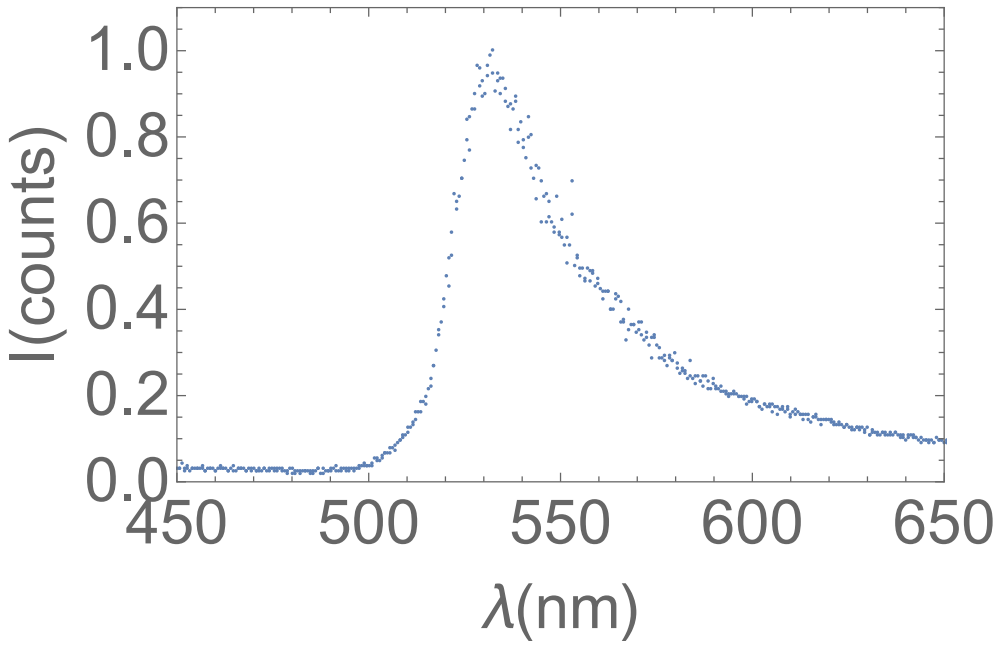

Figure 38: Spectrum of rhodamine 110 spincoated on glass under excitation of a 405 nm laser.

A.2.2 Rhodamine 110 on PMMA.

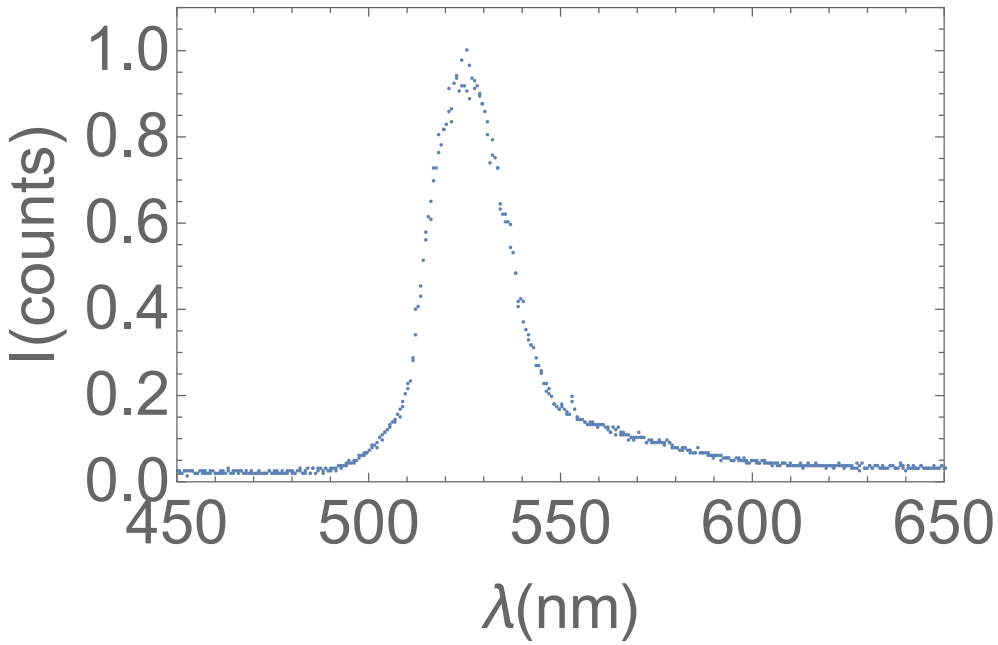

Figure 39: Spectrum of rhodamine 110 spincoated on PMMA under excitation of a 405 nm laser.

A.2.3 Rhodamine 110 on glass reacted with HDMS.

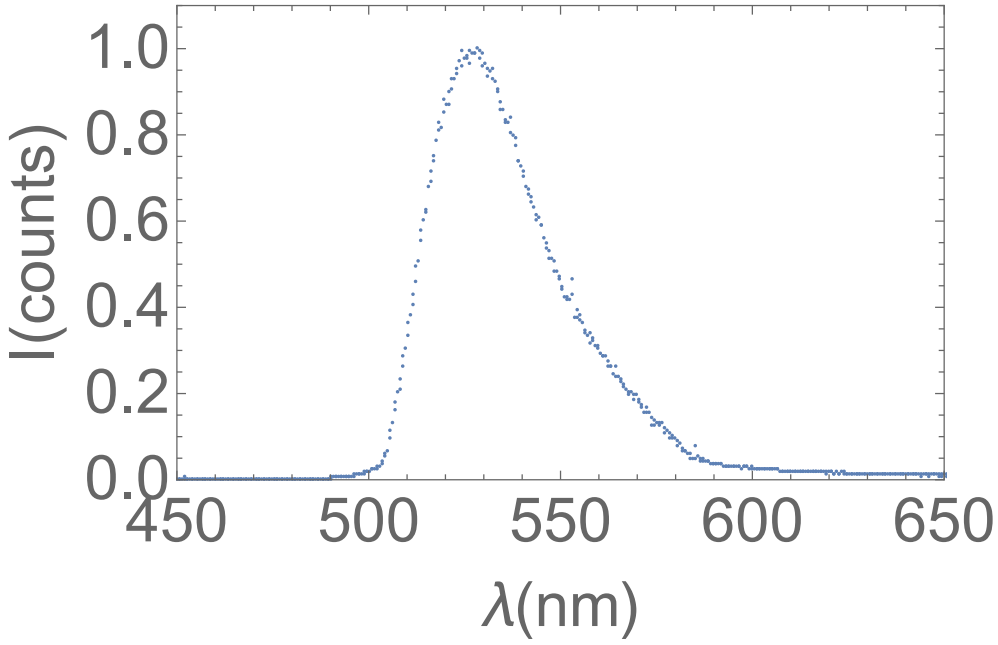

Figure 40: Spectrum of rhodamine 110 spincoated on glass, that has reacted with HMDS, under excitation of a 405 nm laser.

A.2.4 Rhodamine 110 on glass under PMMA.

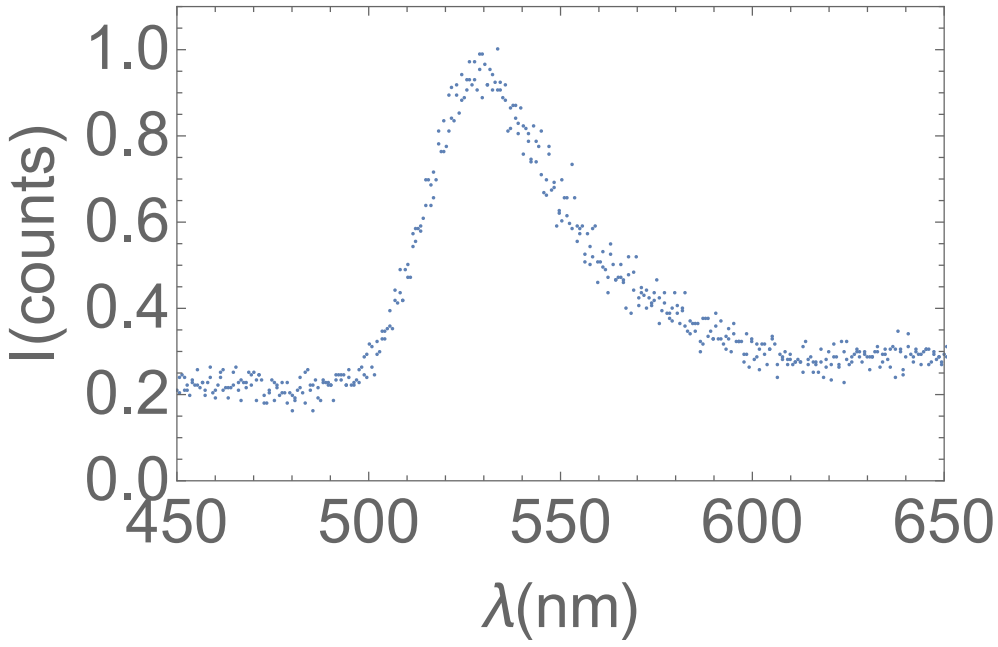

Figure 41: Spectrum of rhodamine 110 spincoated on glass under a coating of PMMA under excitation of a 405 nm laser.

A.2.5 Rhodamine 110 in between two layors of PMMA.

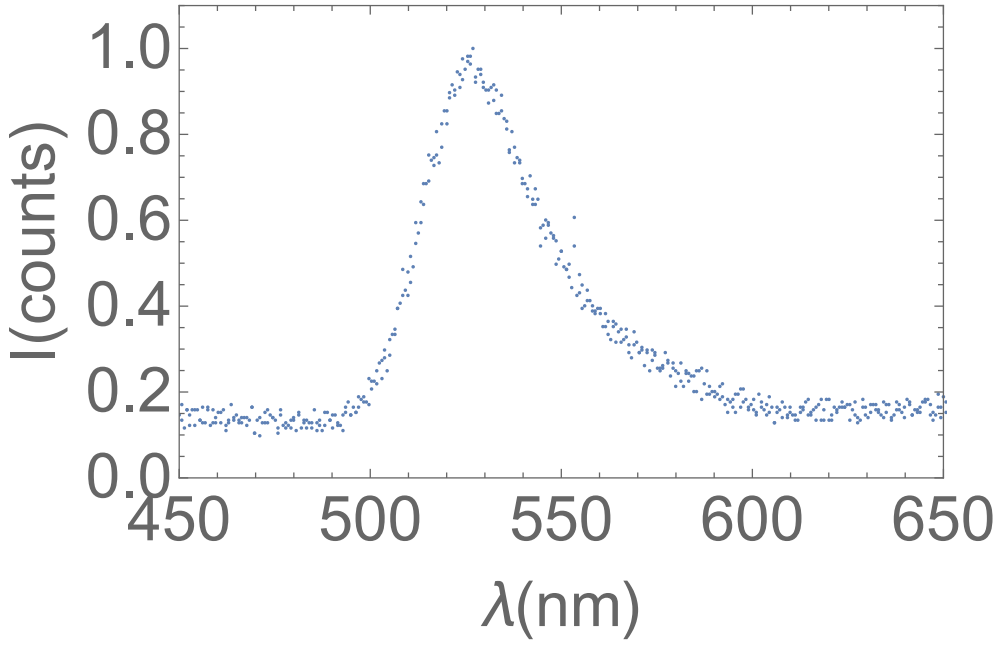

Figure 42: Spectrum of rhodamine 110 in between two layers of PMMA under excitation of a 405 nm laser.