

# Kasha's Rule

PY4113 Lab Report

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# Kasha's Rule

## Introduction

This report details one of five experiments completed as part of enrollment in PY4113. The objective of which is to demonstrate/verify Kasha's Rule.

Kasha's Rule is a fundamental principle in the field of photochemistry, offering valuable insights into the behavior of electronically excited molecules. The rule posits that the emission of photons, whether in the form of fluorescence or phosphorescence, primarily occurs from the lowest excited state within a given multiplicity ('singlet' or 'triplet' states) [1].

*"The emitting level of a given multiplicity is the lowest excited level of that multiplicity."*<sup>[1]</sup>

The report begins with a brief discussion of relevant fundamental concepts in photophysics. The remainder of the report is structured typically, with sections for methodology, results (including error analysis where appropriate), discussion, and conclusion.

### 1.1 Fundamentals

#### Lambert-Beer Law

The Beer-Lambert Law establishes a direct relationship between the attenuation of light passing through a substance and the properties of that substance. Consider monochromatic light transmitted through a solution with an incident intensity of  $I_0$ . The Lambert-Beer law states that for a homogeneous medium the Intensity of incident radiation follows an exponential attenuation

$$I = I_0 e^{-\mu x} \quad (1.1)$$

where  $\mu$  is the optical density, and  $x$  is the distance into the body [2].

The transmittance,  $T$ , of the solution is the ratio of transmitted intensity,  $I$ , to incident intensity,  $I_0$ .

$$T = \frac{I}{I_0} \quad (1.2)$$

Considering the Lambert-Beer law, the absorbance of the solution,  $A$ , can therefore be determined as

$$A = \log_{10} \frac{I_0}{I} = -\log_{10} T \quad (1.3)$$

Assuming that the concentration of the sample is uniform, the molar concentration,  $n$  [mol dm<sup>-3</sup>], can be related directly to it's absorbance using a molar attenuation coefficient (or 'molar extinction coefficient'),  $\sigma(\lambda)$  [dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>]

$$A = \sigma(\lambda)nl \quad (1.4)$$

where  $l$  [cm] is the thickness of the propagation material [3].  $\sigma(\lambda)$  can generally be sourced from literature for specific molecules at specified wavelengths  $\lambda$ .

## Kasha's Rule

When a molecule, initially in its electronic ground state (typically denoted as  $S_0$ , assuming a singlet state), absorbs a photon, it undergoes electronic excitation, transitioning to a range of higher electronic states (often designated as  $S_n$ , where  $n > 0$ ). Kasha's Rule dictates that photon emission, particularly in the form of fluorescence in the case of an S state, predominantly originates from the lowest excited state,  $S_1$ .

This principle leads to a significant implication: only one excited state,  $S_1$ , is expected to yield emission. This implies that the wavelength of emitted light is independent of the wavelength of the excitation.

Energy loss can also occur due to translational modes. Energy can be redistributed into various rotational and vibrational modes depending on the orbital an electron is promoted to and distribution of electrons within. Therefore there are more than one state to which the system can transition into (as shown in red in Fig 1.1). This results in a typical Boltzmann distribution of fluorescence about  $h\nu_2$ .

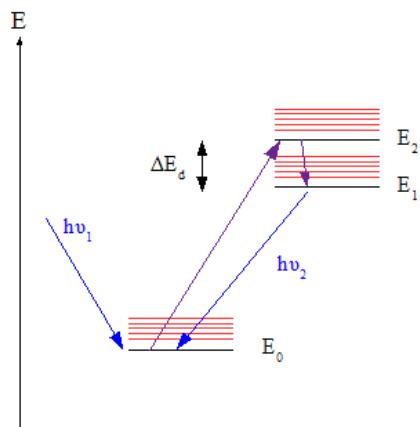
## Stoke's Shift

The Stokes shift is the difference, typically expressed in terms of energy, wavenumber, or frequency units, between the peak positions of absorption and emission spectra (such as those discussed previously) from the same electronic transition [5] in a system.

## 1.2 Motivation

Kasha's Rule and related theory can provide insights into the structure and composition of materials and dilutes. However, it can also be a hindrance. Most of the research publicly available aim to side-step or break Kasha's Rule in a bid to advance various technologies. For example, in [6] a class of materials is presented for organic light-emitting diodes (OLED) emitting from higher-lying triplet states, above the singlet, operational at low temperature. OLEDs are to be seen throughout the modern day, notably in smartphone and tablet screens, offering bright colors and higher contrast than older LED based systems.

Kasha's Rule is predominant in the output wavelength of Dye Lasers. The dye is a crucial consideration when designing a dye laser since the emission of a photon in a molecular system predominantly comes from the lowest excited state as per the discussed.



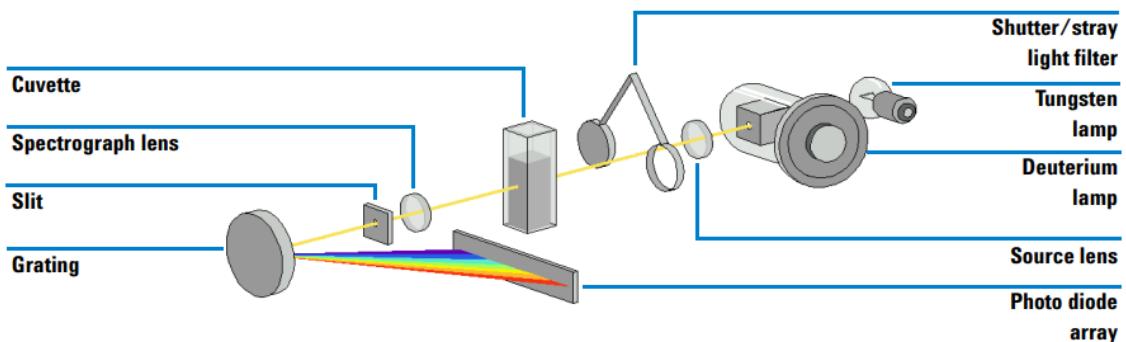
**Figure 1.1:** [4] Scheme of Kasha's rule (Jablonski Diagram). A photon with energy  $h\nu_1$  excites an electron of energy  $E_0$  (ground state) to an excited energy level. Vibrational relaxation takes place and the system transitions to the first excited state  $E_1$ . Remaining energy is dissipated by emission of a photon with energy  $h\nu_2$ , returning the system to its ground state.

# Experimental Methods

This section details experiments carried out to demonstrate the discussed. Cuvettes of Rhodamine B and Coumarin 102 diluted in butanol (concentration initially unknown) were utilised. These are common laser dye, the optical gain material in a dye laser [7]. Coumarin dyes emit in the green region of the optical spectrum, whereas Rhodamine dyes are used for emission in the yellow-red [7].

## Apparatus

Absorption and Fluorescence were measured for both cuvettes using an Agilent 8453 UV-Visible Spectroscopy System. The setup in Kane 102 is capable of measuring Absorption spectra, but without modification is not capable of determining Fluorescence. Solutions to this will be discussed in further detail in respective sections.

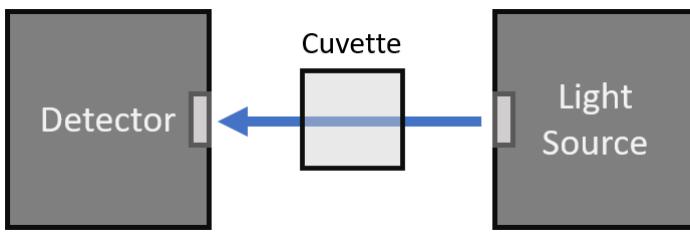


**Figure 2.2:** [8] Optical System of Spectrophotometer used throughout. **Basic description of operation:** The lamps in combination source light from 190nm to 1100nm. The source lens receives the light from lamps and collimates it. The collimated beam passes through the sample. The shutter opens and allows light to pass through the sample for measurements. The spectrograph lens refocuses the collimated light beam after it has passed through the sample. The slit limits the size of the incoming beam and makes sure that each band of wavelengths is projected onto only the appropriate photodiode. The grating disperses the light onto the diode array at an angle linear proportional to the wavelength. The photodiode array then reads intensity at a wavelength range of 190 nm to 1100 nm.

## 2.1 Absorption & Determination of Sample Concentration

### Setup/Procedure

The experiment was setup as shown in Fig 2.3. The absorbance of Rhodamine B and Coumarin 102 samples were measured by following the procedure as described in [8]. First, a blank spectrum was taken of a butanol sample, then the absorption spectra of Rhodamine B and Coumarin 102 were determined using the provided software and saved locally. Integration time for spectrophotometer setup was left at default for absorption measurements.



**Figure 2.3:** Experimental setup for absorption measurement (simplified schematic). There is no change to the apparatus when compared to Fig 2.2. The blue arrow represents the source and direction of incident light on the sample. Detector refers to the spectrograph lens, slit, grating, and photodiode array as shown in Fig 2.2. Light Source refers to the lamps, shutter, filter, and source lens in Fig 2.2.

The concentration can then be found using the Lambert-Beer law (Eq. 1.4), as discussed previously

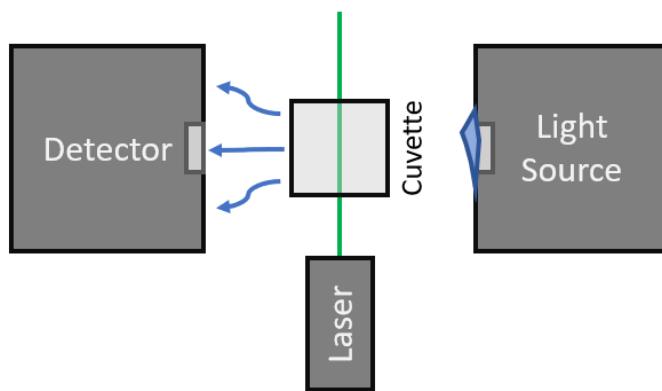
$$A = \sigma(\lambda)nl$$

utilising  $\sigma(\lambda)$ 's sourced from literature.

## 2.2 Fluorescence of Dye Molecules

### Setup/Procedure

The fluorescence of Rhodamine B and Coumarin 102 samples were measured for various excitation wavelengths using a laser (and additionally a halogen lamp - this will be discussed later). First, a blank measurement was taken of a butanol sample. The spectrophotometer light source aperture was then sealed with blue tack and the experiment was setup as shown in Fig 2.4. With some data transformation, this effectively transforms the setup into a fluorescence spectroscopy setup. The integration time was increased slightly for improved results.



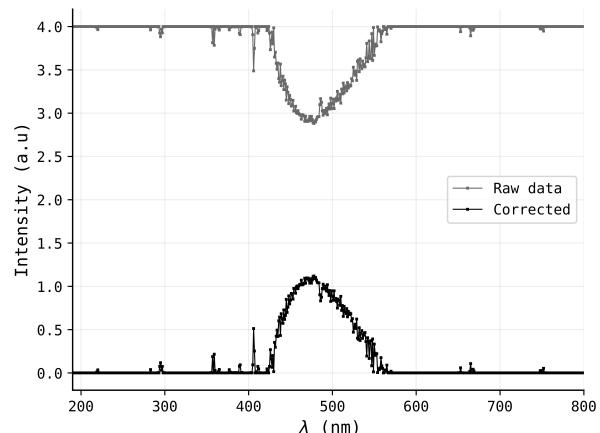
**Figure 2.4:** Experimental setup for fluorescence measurements (simplified schematic). The apparatus has been modified from it's intended setup/use in Fig 2.2 and 2.3. The light source is blocked, during the experiment this was done by using blue tack. A Laser is incident on the cuvette externally such that the detector does not receive incident laser light. The blue arrows represent scattered light from excitation/fluorescence due to the incident laser light. Detector refers to the spectrograph lens, slit, grating, and photodiode array as shown in Fig 2.2. Light Source refers to the lamps, shutter, filter, and source lens in Fig 2.2.

### Analysis

In theory, a 0% transmittance (undetected wavelengths in this setup) should correspond to an infinite absorbance, but practically this is not the case: the raw data from the Agilent 8453 UV-Visible Spectroscopy System (and software) plot 'infinite absorbance' at  $y(\lambda) = 4$ . The resulting data is an inverted and translated representation of fluorescence. Therefore the following transformation (Eq. 2.5) was applied to the data obtained through the outlined procedure, resulting in emission spectra.

$$y(\lambda) = -(y(\lambda) - 4) \quad (2.5)$$

This transformation is demonstrated in Fig 2.5.



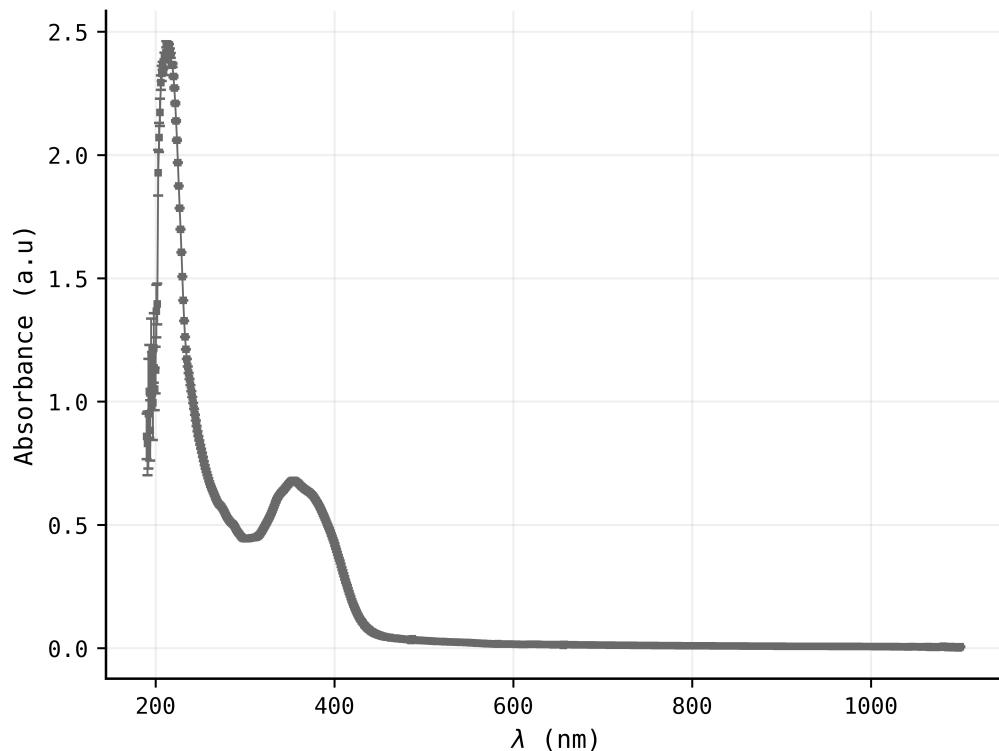
**Figure 2.5:** Example of transformation of raw data using  $y(\lambda) = -(y(\lambda) - 4)$ . The data shown is the excitation of Coumarin 102 using a 405nm laser, which will be discussed at length later.

# Results

The following sub-sections compile and analyse the relevant data obtained by the procedures and methods outlined in the previous section.

## 3.1 Coumarin 102

### Absorption Spectra



**Figure 3.6:** Absorption of Coumarin 102 in butanol obtained as per respective procedure outlined. Absorption maximum occurs at 211nm, the next highest absorption occurs at 369nm. These represent electronic transitions from  $S_0$  - See Discussion.

### Determination of Sample Concentration

[9] cites the molar extinction coefficient of Coumarin 102 at  $\lambda = 393\text{nm}$  to be

$$\sigma(393\text{nm}) = 16.5 \times 10^3 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$$

The cuvette thickness  $l$  (according to laboratory demonstrator) was exactly 10mm. Using the Lambert-Beer law and relevant data for  $A$  from Tab 3.1 we can determine the

| $\lambda(\text{nm})$ | $A(\lambda)$ | $\sigma_{DEV}$ |
|----------------------|--------------|----------------|
|                      | ⋮            |                |
| 392                  | 0.503056     | 0.000125349    |
| 393                  | 0.494853     | 0.000172876    |
| 394                  | 0.486102     | 0.000158275    |
|                      | ⋮            |                |

**Table 3.1:** An excerpt of raw data from Absorbance measurement of Couramin 102 as produced by Agilent system and software. A is absorbance for the detected wavelength  $\lambda$ .  $\sigma_{DEV}$  represents the standard deviation in measurement and is equivalent to  $\Delta A$ .

concentration of the solution as follows:

$$A = \sigma(\lambda)nl$$

$$\Rightarrow n = \frac{0.494853}{(16.5 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})(1\text{cm})} = 2.999 \times 10^{-5} \text{ mol dm}^{-3}$$

Assuming an error of  $\Delta l = 0.5\text{mm}$  and  $\Delta\sigma = 0.05$  (This is an assumption as no uncertainty is listed in [9]), a brief error analysis suffices to show

$$\frac{\Delta n}{n} = \frac{\Delta A}{A} + \frac{\Delta\sigma}{\sigma} + \frac{\Delta l}{l}$$

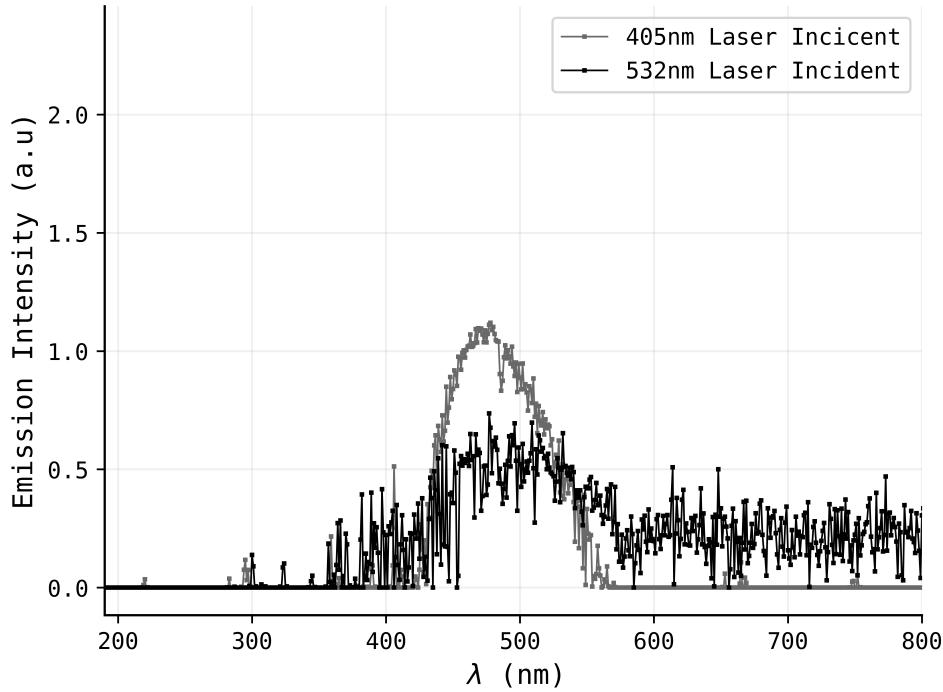
$$\Rightarrow \Delta n = n \left( \frac{0.000172876}{0.494853} + \frac{0.05}{16.5} + \frac{0.5}{10} \right)$$

$$= 0.16 \times 10^{-5} \text{ mol dm}^{-3}$$

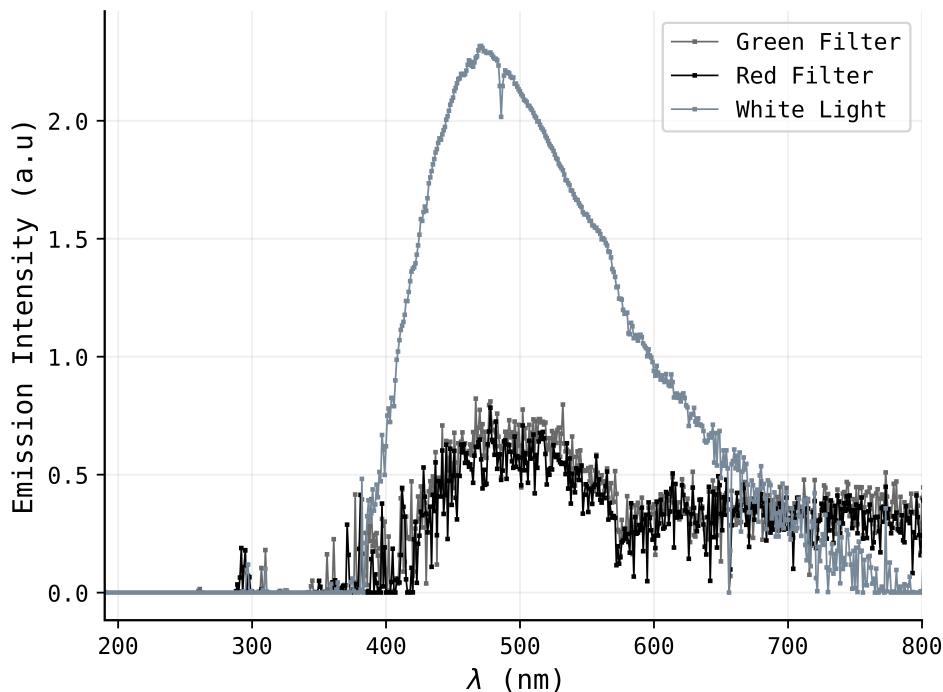
As such the determined concentration is

$$\boxed{n_{C102} = (3.00 \pm 0.16) \times 10^{-5} \text{ mol dm}^{-3}}$$

## Emission Spectra



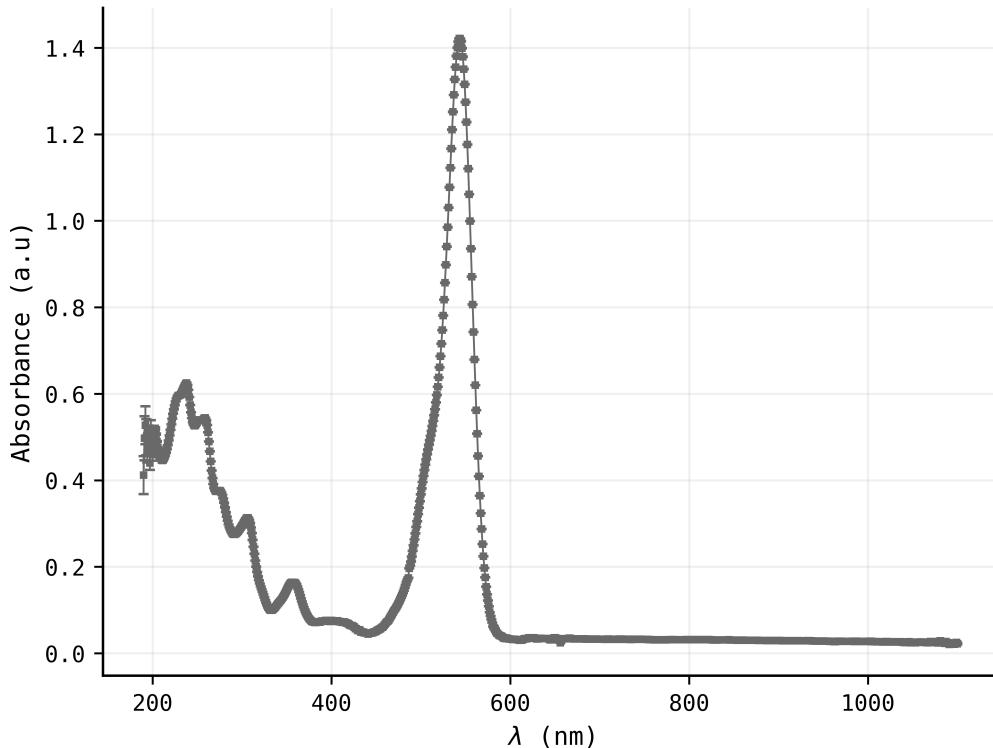
**Figure 3.7:** Emission spectra for Coumarin 102 obtained as per procedure and setup discussed. Kasha's Rule appears to be effective and evident, both lasers cause fluorescence centered about at 480nm.



**Figure 3.8:** Emission spectra obtained for Coumarin 102 by using a halogen lamp (white light and coloured filters) incident on the sample. Kasha's Rule is verified. A strong emission peak occurs at 480nm, the same wavelength as in Fig 3.7.

## 3.2 Rhodamine B

### Absorption Spectra



**Figure 3.9:** Absorption of Rhodamine B in butanol obtained as per respective procedure outlined. Absorption maximum occurs at 543nm.

### Determination of Sample Concentration

| $\lambda(\text{nm})$ | $A(\lambda)$ | $\sigma_{DEV}$ |
|----------------------|--------------|----------------|
| ⋮                    | ⋮            | ⋮              |
| 544                  | 1.42105      | 0.000460861    |
| 545                  | 1.41506      | 0.000611673    |
| 546                  | 1.39912      | 0.000412084    |
| ⋮                    | ⋮            | ⋮              |

**Table 3.2:** An excerpt of raw data from Absorbance measurement of Rhodamine B as produced by Agilent system and software.  $A$  is absorbance for the detected wavelength  $\lambda$ .  $\sigma_{DEV}$  represents the standard deviation in measurement and is equivalent to  $\Delta A$ .

[10] cites the molar extinction coefficient of Rhodamine B at  $\lambda = 545\text{nm}$  to be

$$\sigma(545\text{nm}) = 10.6 \times 10^4 \text{ dm}^3\text{mol}^{-1}\text{cm}^{-1}$$

The cuvette thickness  $l$  (according to lab demonstrator) was exactly 10mm. Using the Lambert-Beer law and relevant data for  $A$  from Tab 3.2 we can determine the concen-

tration of the solution as follows:

$$A = \sigma(\lambda)nl$$

$$\Rightarrow n = \frac{1.41506}{(10.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})(1\text{cm})} = 1.335 \times 10^{-5} \text{ mol dm}^{-3}$$

Assuming an error of  $\Delta l = 0.5\text{mm}$  and  $\Delta\sigma = 0.05$  (This is an assumption as no uncertainty is listed in [10]), a brief error analysis suffices to show

$$\frac{\Delta n}{n} = \frac{\Delta A}{A} + \frac{\Delta\sigma}{\sigma} + \frac{\Delta l}{l}$$

$$\Rightarrow \Delta n = n \left( \frac{0.000611673}{1.41506} + \frac{0.05}{10.6} + \frac{0.5}{10} \right)$$

$$= 0.0074 \times 10^{-5} \text{ mol dm}^{-3}$$

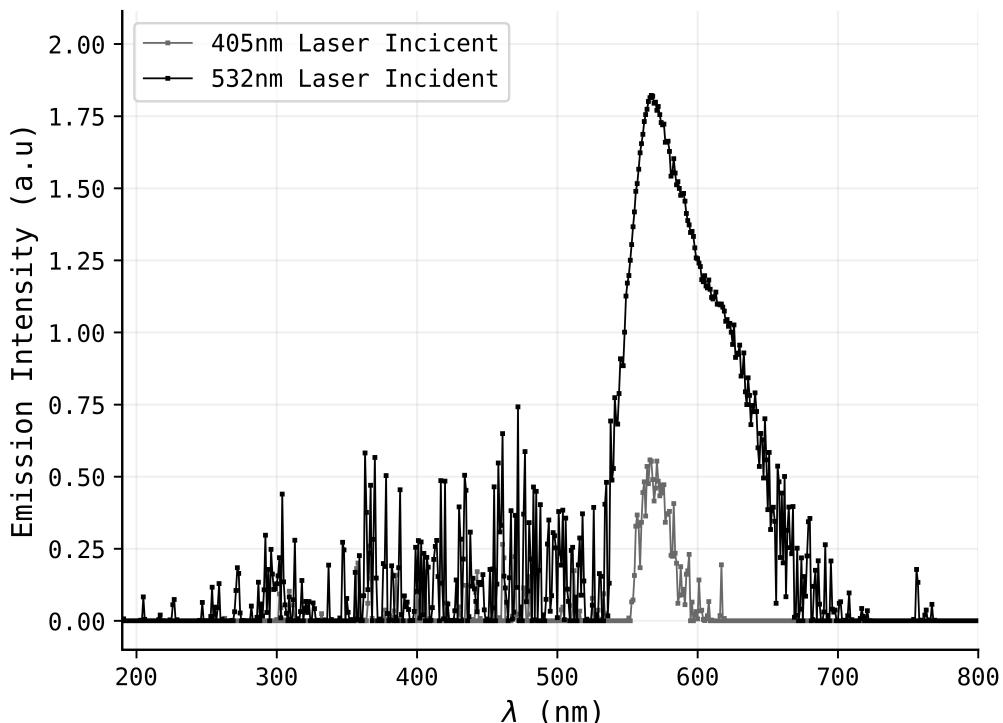
As such the determined concentration is

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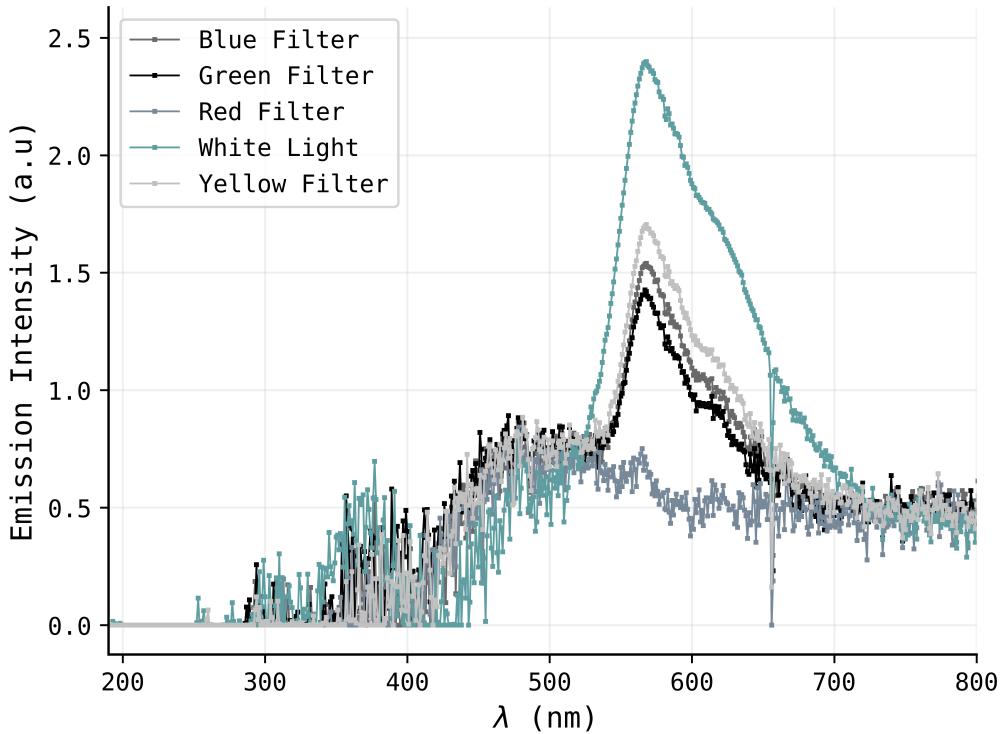

$$n_{RhB} = (1.335 \pm 0.007) \times 10^{-5} \text{ mol dm}^{-3}$$


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## Emission Spectra



**Figure 3.10:** Emission spectra for Coumarin 102 obtained as per procedure and setup discussed. Kasha's Rule appears to be effective and evident, both lasers cause fluorescence centered about at 572nm.



**Figure 3.11:** Emission spectra obtained for Rhodamine B by using a halogen lamp (white light and coloured filters) incident on the sample. Kasha's Rule is further verified. A strong emission peak occurs at 572nm, the same wavelength as in Fig 3.10, for every filter/colour of light except red.

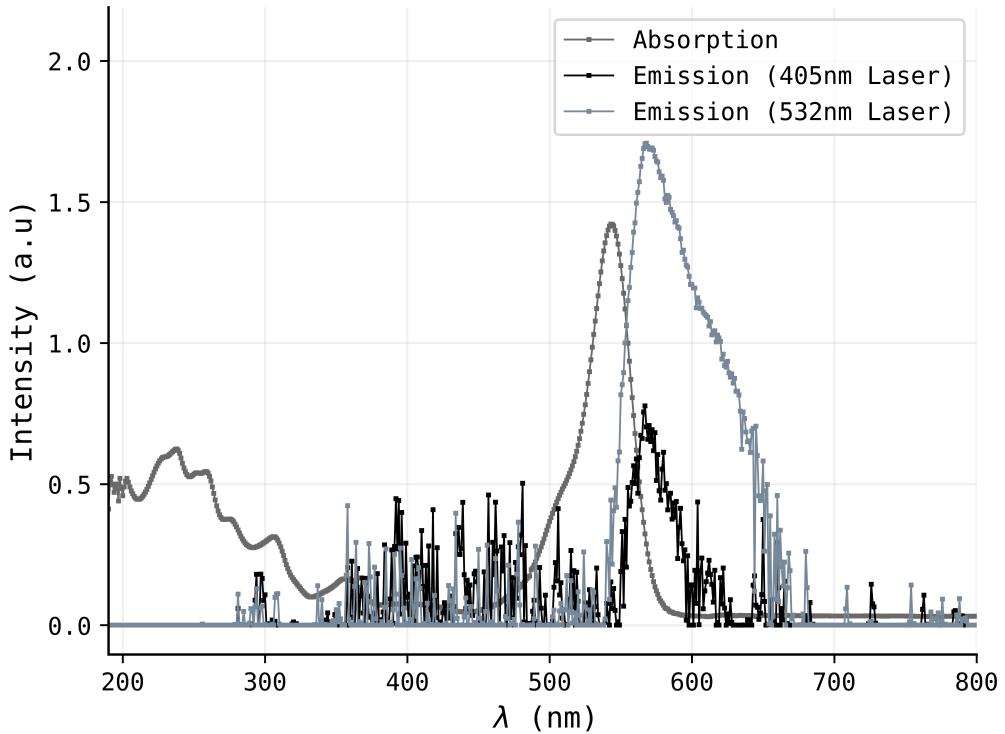
## Discussion

From the results as shown in Fig 3.8, 3.7, 3.11, 3.10, Kasha's Rule is evident and effective. Regardless of excitation wavelength, emission peaks occur at identical wavelengths as per Kasha's Rule in almost all recorded cases.

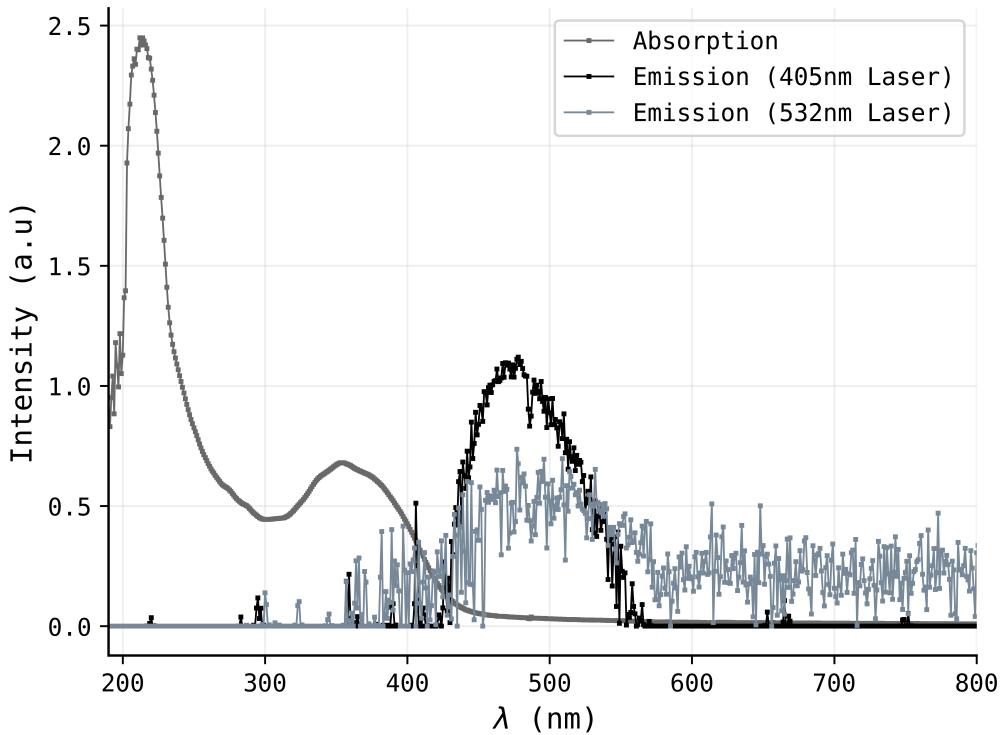
An observation in the case of the mentioned figures is that filtered measurements trend toward reducing in magnitude with higher wavelengths (lower energy). This could simply be due to the halogen lamp having stronger spectral components at certain frequencies over others. [11] states "*the intensity of fluorescence emission is directly proportional to the intensity of the incident radiation*"[11], supporting the claim.

However a more plausible explanation is down to absorbance. For example, in Fig 3.7 the 405nm laser causes a higher intensity of fluorescence compared to 532nm. In Fig 3.6, Coumarin 102 is shown to have a significantly higher absorbance at 405nm than at 532nm; in fact at 532nm the absorbance is almost null. By this observation the intensity of emission appears to be characterised by the absorbance curve. Intuitively this makes sense as without absorbance there cannot be emission as discussed in the 'Fundamentals' section. This is further demonstrated in Fig 3.9, 3.10 where the 532nm incidence corresponds to a point high on the absorbance curve, while the 405nm incidence does not, analogous to the measured absorbance curve.

Stokes shift (briefly discussed) can be observed for both Rhodamine B and Coumarin 102. This is visualised in Fig 4.12, 4.13.



**Figure 4.12:** Compiled measurements from Rhodamine B data. Stokes shift is observed in Rhodamine B measurements. The observed Stokes shift is  $\lambda_s \approx 29\text{nm}$ . Plots are not to a normalised scale and are for indication only.



**Figure 4.13:** Compiled measurements from Coumarin 102 data. Stokes shift is observed in Coumarin 102 measurements. The observed Stokes shift is  $\lambda_s \approx 111\text{nm}$ . Plots are not to a normalised scale and are for indication only.

An interesting observation to be made is that the emission peaks resemble a flipped or "mirror image"<sup>[12]</sup> of absorption peaks. This is because the same transitions are most favorable for both absorption and emission [12] [13]; "*the probability of an electron returning to a particular vibrational energy level in the ground state is similar to the probability of that electron's position in the ground state before excitation*"<sup>[12]</sup>. Note that Fig 4.12, 4.13 do not compare halogen lamp measurements, this is intentional because the mirror image observation may break down due to scattered light from the lamp.

A number of peaks in the absorbance measurements in Fig 3.6, 3.9 can be from 200nm to 400nm (before emission - demonstrated in Fig 4.13, 4.12). These represent electronic transition energies of singlet states, where by an electron may transition from  $S_0 \rightarrow S_n$ . Since we are dealing with absorbance these transitions only occur from  $S_0$ . The corresponding energy  $E_n$  of a given  $S_n$  increases with  $n$ , as such the peaks are ordered in reverse (The emission peak represents  $S_0 \rightarrow S_1$ ) due to the inverse wavelength dependence of energy  $E = \frac{hc}{\lambda}$ .

## Conclusion

A spectrophotometry setup is utilised to determine the absorbance of dye samples Rhodamine B and Couramin 102 diluted in butanol. Subsequent data and analysis allowed for the calculation of molar concentration of given samples using the Lambert-Beer law. The previously utilised setup is successfully modified to determine fluorescence of a given sample. Kasha's Rule is demonstrated and verified. A relationship can be observed between the absorbance of a given wavelength and the intensity of fluorescence due to excitation at that wavelength. Stoke's shift due to vibrational relaxation is observed and the mirror image rule identified and discussed.

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