

Photochemistry and Photophysics Workshop

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Welcome

The notes have been prepared in a package called BookDown for RStudio so that the equations are accessible to screen readers. However, by providing the notes as a .html webpage I can also embed short videos to further describe some of the topics. Further you can download the questions (and later the answers, top left of the screen) in a format that suits you (either pdf or epub) to view offline, or change the way this document appears for ease of reading.

Workshops for Photochemistry & Photophysics

This answerbook for CH30129 workshops will be updated weekly (hopefully the day after workshops) including thoughts and answers from you as a class. I will include video workthroughs of some answers, but others will be text based.

I am using this format as it is an accessible format.

Version history

Week 4 questions started 131020

Updated to correct type on question 3.2.2 121020

Updated to include workshop week 3 questions 091020

Updated to include workshop week 2 questions 021020

Typos on workshop 1 were fixed 280920

The initial commit of this book is dated 25th September 2020.

Chapter 1

Workshop Questions for Week 1

1.1 Short mathematical question - Beer Lambert law

- How far can monochromatic 489 nm light travel through a 0.100 M solution of fluorescein with an extinction coefficient at 489 nm of $92000 \text{ M}^{-1} \text{ cm}^{-1}$ before 90 % of it is absorbed? (*I will use MCQs and UniDoodle to ask this in class*)

1.2 Short conceptual question - molar extinction coefficient

- Modify the molecule in figure 1.1 to increase the molar extinction coefficient (do not worry about what may happen to wavelength).

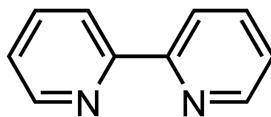


Figure 1.1: The structure of bipyridine (also known as bpy).

(I will use UniDoodle's drawing feature to ask this in class)

1.3 Short conceptual question - intensity of colour

- What factors influence the 'intensity of colour' of the following solutions?

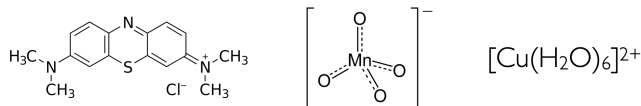


Figure 1.2: The structures of the organic dye methylene blue (left), potassium permanganate (centre) and copper hexa-aqua (right).



Figure 1.3: 1 mM solutions of the organic dye methylene blue (right), potassium permanganate (centre) and copper hexa-aqua (left).

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

1.4 Short conceptual question - line width

- Why are some spectra very broad (figure 1.4), whereas others have sharp peaks (figure 1.5)?

You will need to look at the x-scale to truly note the difference in the width of these emission spectra.

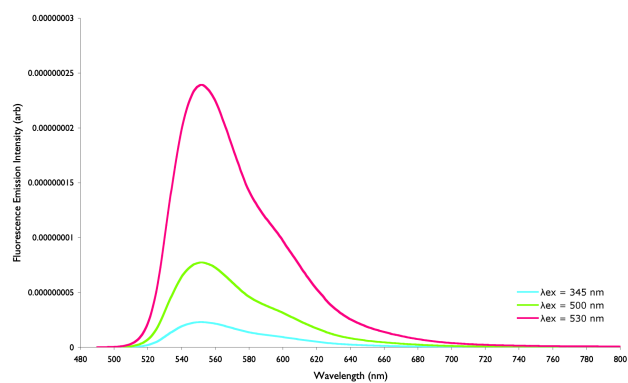


Figure 1.4: The emission spectrum of rhodamine 6G

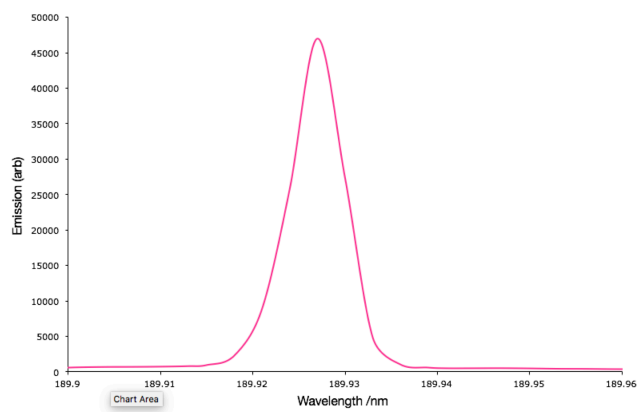


Figure 1.5: The emission spectrum of Sn(II)

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

1.5 Short conceptual question - the effect of solvation on absorbance

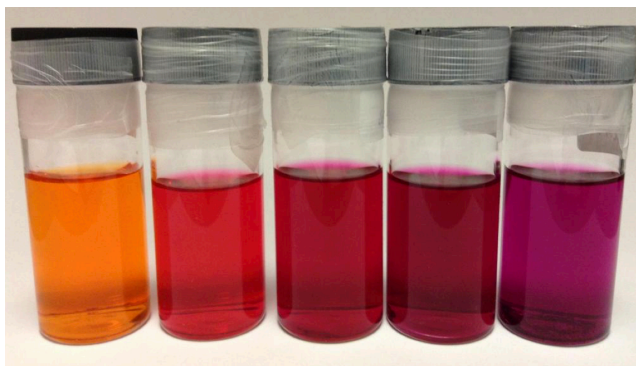


Figure 1.6: Ethidium bromide dissolved in from right; water(orange), methanol, ethanol, propanol and butanol(purple)

- Why does the observed colour of ethidium bromide depend upon the solvent (figure 1.6))?

Think about the effect of solvation on the energy levels and why those energy levels matter! Remember that if light is transmitted through a solution that is the colour we observe...

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

1.6 Extended question - Azobenzene

Azobenzene undergoes the following cis-trans isomerisation, the isomerisation occurs in the ps timescale.

- Why would you expect the absorption spectrum of each isomer to be different?
- Suggest why the trans conformation is more stable than the cis isomer.
- Use the following data to predict the proportion of each isomer under 360 nm excitation.

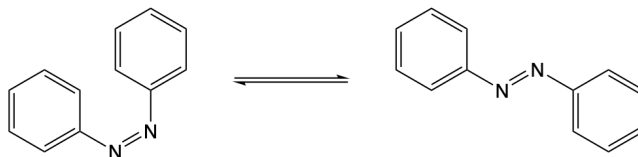


Figure 1.7: The cis-trans isomerisation of azobenzene

Table 1.1: The molar extinction coefficient of the two isomers of azobenzene.

| | $_{360} / \text{M}^{-1} \text{cm}^{-1}$ | $_{460} / \text{M}^{-1} \text{cm}^{-1}$ |
|------------------|---|---|
| trans-azobenzene | 22000 | 4500 |
| cis-azobenzene | 2100 | 5500 |

- Would there be more or less trans azobenzene at 460 nm? Justify your answer.
- It has been suggested the 360 nm absorption is an $S_0 \rightarrow S_2$ absorption, and the 460 nm band is an $S_0 \rightarrow S_1$ absorption. Suggest which energy levels are involved for each of the two transitions and compare it to stilbene which has a similar structure, but the cis and trans absorptions are 280 & 295 nm respectively.

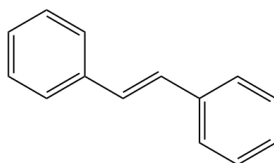


Figure 1.8: The structure of stilbene

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat. I don't expect to finish this question but hope to get far enough through that a good attempt can be made at home after the LOIL)

Chapter 2

Workshop Questions for Week 2

2.1 Short mathematical question - Quantum Yield and lifetime

The quantum yield and lifetime of a dye were measured to be 0.43 & 2.6 ns respectively. What is the natural lifetime?

(I will use MCQs and UniDoodle to ask this in class)

2.2 Short conceptual question - Effect of other processes

For a given value of k_0 what happens to the lifetime and quantum yield as k_{IC} and k_{ISC} increases?

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

2.3 Conceptual question - Effect of structure

Fluorescein (figure 2.1) in basic aqueous solution has a quantum yield of fluorescence, Φ_f , of 0.95, and fluorescence lifetime, τ_f , of 4.1 ns.

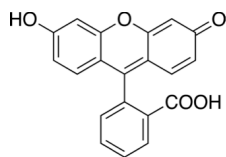


Figure 2.1: The structure of the fluorescent molecule fluorescein

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

2.4 Conceptual question - lack of symmetry in spectra.

The absorption and emission spectrum of fluorescein is shown in figure (2.2)

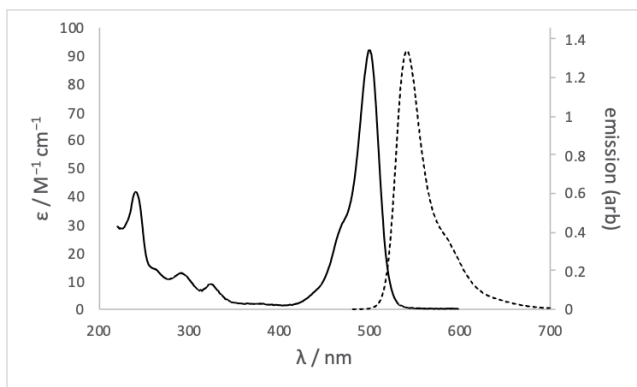


Figure 2.2: The absorption (solid) and emission (dashed) spectrum of fluorescein in basic ethanol.

Why are the absorption bands between 200 – 350 nm not reflected in the emission spectrum?

2.5 Conceptual question - Stokes' shift

The inorganic dye $[\text{Ru}(\text{bpy})_3]^{2+}$ has a measured lifetime in water of 580 ns and a natural lifetime of 13.8 μs . The spectrum is shown in figure 2.3. What is the origin of the large Stokes' shift in this system?

Data from Shi *et al.*, Synthesis and characterization of phosphorescent two coordinate copper(I) complexes bearing diamidocarbene ligands. Dalton Trans.,

2.6. CONCEPTUAL QUESTION - THE EFFECT OF BINDING ON EMISSION15

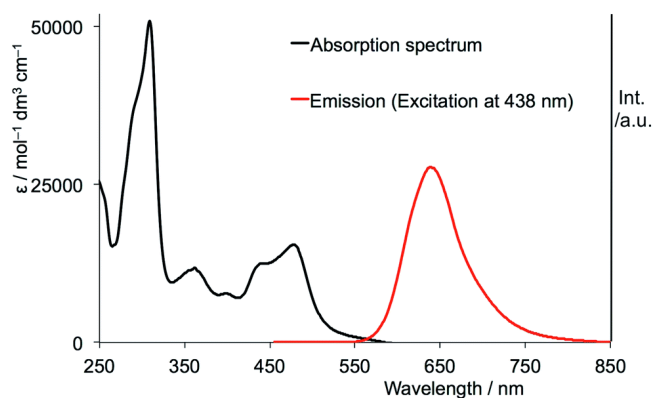


Figure 2.3: The absorption (black) and emission (red) spectrum of ruthenium tris bipyridine in water.

2017,46, 745-752.

2.6 Conceptual question - the effect of binding on emission

The asymmetric cyanine dye YO-Pro-1 is a DNA stain because it has a large increase on fluorescence emission when binding to DNA. The lifetime in free solution is around 2 ps and when bound to DNA is 2.4 ns. What is the structural origin of the large increase of emission upon binding?

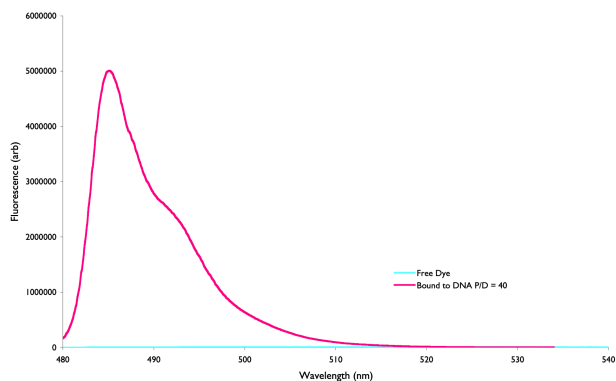


Figure 2.4: The emission spectrum of the chromophore YO-Pro-1 when free in aqueous solution (blue) and when bound to DNA (pink)

(This will be a discussion question - please feel free to raise a hand or write

comments in the zoom chat)

2.7 Extended question - Properties of Ethidium Bromide (Example Exam Question)

Ethidium bromide (EB, figure 2.5) is used as a DNA stain, which is essentially non-fluorescent in aqueous solution, but shows a strong enhancement of emission upon binding to double stranded DNA (which has a negatively charged backbone).

Emission is almost exclusively from the singlet excited state, but a triplet state has been shown to exist, which emits with a low quantum yield ($\Phi_P = 0.00006$).

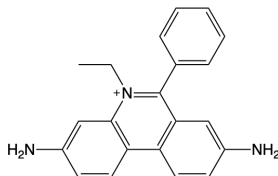


Figure 2.5: The structure of the cationic ethidium bromide chromophore.

- Sketch a Jablonski diagram for the processes you know to occur.
- The molar extinction coefficient, ϵ , of EB has been measured to be $78500 \text{ M}^{-1} \text{ cm}^{-1}$. What factors contribute to EB having such a high extinction coefficient?

The following spectra, lifetimes and quantum yield have been measured for EB in different free solution and DNA systems:

Table 2.1: The lifetimes and quantum yields of ethidium bromide in aqueous solution and when bound to DNA in protiated and deuterated systems.

| | / ns | Φ_f |
|---------------------------|------|----------|
| H ₂ O (no DNA) | 1.6 | 0.012 |
| D ₂ O (no DNA) | 6.3 | |
| DNA | 28.3 | 0.220 |
| DNA (deuterated) | 38.4 | |

- What factors likely lead to an enhancement of fluorescence quantum yield upon binding to DNA?
- Show that the natural lifetime of EB is 129 ns.

2.7. EXTENDED QUESTION - PROPERTIES OF ETHIDIUM BROMIDE (EXAMPLE EXAM QUESTION)17

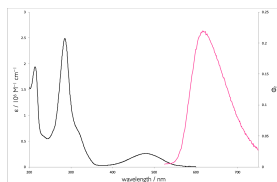


Figure 2.6: The absorption (black) and emission (pink) spectrum of ethidium bromide when bound to DNA.

- What is the origin of the large Stoke's shift ($\lambda_{\text{max ex}} = 520 \text{ nm}$, $\lambda_{\text{max em}} = 608 \text{ nm}$)
- What transitions are responsible for the absorption features in the: * 400-600 nm range * 200-350 nm range
- Why are the features in the 200-350 nm range not replicated in the emission spectrum?
- Why does deuterating the solvent (or DNA) effect the lifetime of the excited state?
- What effect would freezing the samples have on the lifetime, fluorescence quantum yield & phosphorescence quantum yield.

A study of the thermodynamics of the dye DNA system measured the binding constant of EB with DNA to be 1.05×10^6 .

- Why is the measured quantum yield for a system containing $2 \mu\text{M}$ EB and 20 mM DNA only 0.18?
- Why would increasing the ionic strength of the solution, increase the fluorescence intensity of EB in solution with DNA?

Chapter 3

Workshop Questions for Week 3

3.1 Short conceptual question - Electronic-vibrational overlap integrals

On the figure sketch the vibrational energy levels in the ground and the excited state.

How would the following affect this overlap integral? 1. Energy gap. 1. The vibrational energy gaps 1. Reaction coordinate (the difference in structure between ground and excited state)

(I will use drawing in UniDoodle to ask this in class, with the second part being a discussion question)

3.2 Short conceptual question - The effect of structural changes on quantum yield

5,10-dihydroindeno[2,1-a]indene and trans-stilbene (figure 3.2) are similar in structure but have very different fluorescent quantum yields of 1.00 and 0.05 respectively, however for trans-stilbene this increases to 0.75 at 77 K. Suggest a reason for the difference in quantum yield of: - the two molecules - the two temperatures

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

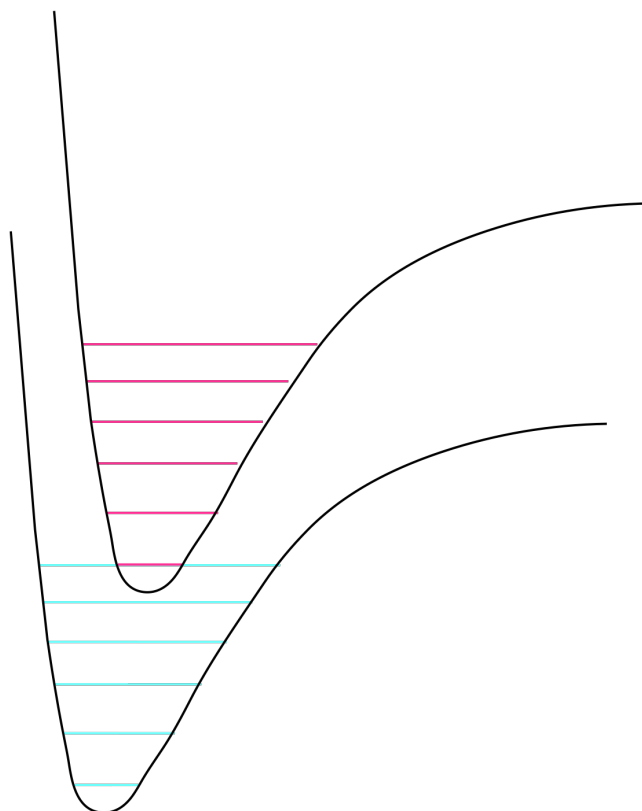


Figure 3.1: The ground and excited state potential wells and the vibrational levels within them.

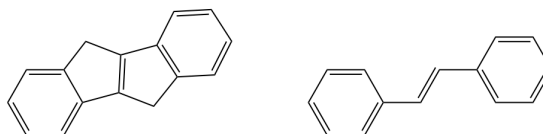


Figure 3.2: 5,10-dihydroindeno[2,1-a]indene (left) and trans-stilbene (right)

3.5. SHORT CONCEPTUAL QUESTION - DEACTIVATION OF EXCITED STATE AROMATIC HYDROCARBS

3.3 Short mathematical question - Effect of the rate of singlet triplet intersystem crossing on the quantum yield of phosphorescence

Why is it likely that the quantum yield of phosphorescence of a sample would increase after the sample is frozen.

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

3.4 Short mathematical question - Determining the quantum yield of phosphorescence

A molecule decays by a combination of internal conversion, intersystem crossing and phosphorescence. What is the quantum yield of phosphorescence?

- $k_{IC} = 2.1 \times 10^{11} \text{ s}^{-1}$
- $k_{ST} = 2.9 \times 10^9 \text{ s}^{-1}$
- $k_{TS} = 7.4 \times 10^6 \text{ s}^{-1}$
- $k_p = 6.2 \times 10^8 \text{ s}^{-1}$

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

3.5 Short conceptual question - Deactivation of excited state aromatic hydrocarbons

Table 3.1: The quantum yields of various deactivation processes in small organic molecules measured at 77 K in a glass matrix.

| | Φ_f | Φ_{ST} | $\Delta E / \text{kJ mol}^{-1}$ |
|------------|----------|-------------|---------------------------------|
| Napthalene | 0.20 | 0.80 | 385 |
| Anthracene | 0.70 | 0.30 | 318 |
| Pyrene | 0.6 | low | 322 |
| Tetracene | 0.1 | 0.65 | 251 |
| Pentacene | 0.10 | 0.15 | 209 |

When examining the data above suggest why it is likely why the quantum yields of both fluorescence and singlet to triplet intersystem crossing decrease with increasing molecule size.

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

3.6 Short conceptual question - Affect of deuteration of solvents.

Singlet oxygen has a phosphorescence wavelength of around 1070 nm and a lifetime of 2 μ s in water, how would you expect this lifetime to change for singlet oxygen in D₂O?

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

3.7 Short conceptual question - Isotope effects on deactivation of an excited state

The fluorescence quantum yield and singlet state lifetime of both protiated and deuterated pyrene are 0.90 and 450 ns respectively. Why does deuteration of the sample have no measureable affect on these values?

Conversely for naphthalene phosphorescence (in glass at 77 K) the quantum yield of phosphorescence increases from 0.05 to ~0.80 on deuteration of the sample. ($\Delta E = 251 \text{ kJ mol}^{-1}$). Explain this observation with respect to the energy gap law.

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

3.8 Short conceptual question - The effect of heavy atoms on the rate of intersystem crossing

Table 3.2: The affect of substitution of different halogens on the rates of phosphorescence and singlet to triplet intersystem crossing.

| | k_p | k_{ST} | Φ_p / Φ_f |
|--------------------|-------|----------|-------------------|
| Napthalene | 0.05 | 0.39 | 0.09 |
| 1-fluoronapthalene | 0.23 | 0.42 | 0.07 |
| 1-chloronapthalene | 1.1 | 2.35 | 5.2 |

3.9. SHORT CONCEPTUAL QUESTION - THE EFFECT OF ABSORBANCE AND EMISSION WAVELENGTHS

| | k_p | k_{ST} | Φ_p / Φ_f |
|--------------------|-------|----------|-------------------|
| 1-bromonaphthalene | 13.5 | 36.5 | 169 |
| 1-iodonaphthalene | 190 | 310 | >760 |

Briefly explain why the rates of these processes increase as we move down the group.

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

3.9 Short conceptual question - The effect of absorbance and emission wavelengths on the quantum yield of emission

Table 3.3: The spectroscopic details of a family of osmium complexes.

| | abs / nm | em / nm | ΔE / eV | / ns | Φ_{em} |
|--|----------|---------|-----------------|------|-------------|
| $[\text{Os}(\text{phen})_3]^{2+}$ | 650 | 720 | 0.186 | 260 | 0.016 |
| $[\text{Os}(\text{phen})_2(\text{dppene})]^{2+}$ | 455 | 609 | 0.69 | 1830 | 0.138 |
| $[\text{Os}(\text{phen})(\text{dppene})_2]^{2+}$ | 400 | 530 | 0.761 | 3600 | 0.518 |

Why does the fluorescence lifetime increase as the phenanthroline ligands are replaced with dppene ligands?

(This will be a discussion question - please feel free to raise a hand or write comments in the zoom chat)

Chapter 4

Workshop Questions for Week 4

4.1 Short mathematical question - Determining rates of diffusion controlled quenching

The rate of diffusion (k_d) in solution is given by equation (4.1), where η is the viscosity of the solution.

$$k_d = \frac{8RT}{3\eta} \quad (4.1)$$

Determine the maximum possible rate of diffusion controlled quenching at 20 °C in:

- a. water ($\eta = 1.0016 \text{ mPa s}$)
- b. methanol ($\eta = 0.594 \text{ mPa s}$)

(I will use UniDoodle to ask this in class - please attempt before the LOIL)

4.2 Short mathematical question - Determining the effect of diffusion controlled quenching on emission intensity

What emission intensity would you expect if 50 mM of a quencher quenches the emission of a chromophore dissolved in basic ethanol at 10 °C, with natural

lifetime of 13.2 ns and emission quantum yield, Φ_f , of 0.32, if the unquenched intensity is 35240.

η -EtOH, 10 °C \sim 1.394 mPa s

(This will be a discussion question - please attempt before the LOIL and be ready to contribute to the maths process)

4.3 Short conceptual question - static quenching

Something something something something - effect of counter ions or something something

4.4 Long mathematical question - Quenching of emission of acridone

Acridone (figure 4.1) is found to be quenched in the presence of potassium iodide in aqueous solution at 26 °C. Solutions were maintained at constant ionic strength by use of KNO₂, the KNO₂ does not affect the emission intensity of the solution.

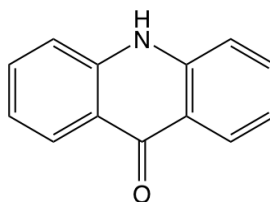


Figure 4.1: The structure of acridone.

The following data were collected for the emission of acridone.

Table 4.1: The effect of potassium iodide concentration on emission intensity and fluorescence lifetime of acridone in aqueous solution.

| [KI] / M | [KNO ₂] / M | Emission intensity / arb | / ns |
|----------|-------------------------|--------------------------|-------|
| 0 | 1.100 | 16580 | 17.60 |
| 0.040 | 1.060 | 3753 | 3.90 |
| 0.100 | 1.000 | 1566 | 1.80 |
| 0.200 | 0.900 | 721 | 0.95 |
| 0.300 | 0.800 | 446 | 0.64 |
| 0.500 | 0.600 | 242 | 0.39 |

4.4. LONG MATHEMATICAL QUESTION - QUENCHING OF EMISSION OF ACRIDONE27

| [KI] / M | [KNO ₂] / M | Emission intensity / arb | / ns |
|----------|-------------------------|--------------------------|------|
| 0.800 | 0.300 | 121 | 0.25 |

1. Using an appropriate plot (or plots) determine if the quenching is static, dynamic or a combination of both mechanisms.
2. Determine any relevant quenching constants (k_d and/or K_S)

(This will be a discussion question - please be ready to contribute to the maths process)