Title: Fluorescence

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Abstract

In this experiment, it was found that the electron acceptor, $[Ru^{3+}(NH_3)_6]Cl_3^-$, accepted electrons from the electron donor, $Ru^{2+}(bpy)_3$. The quenching rate constant was found to be $8.4*10^8$ $M^{-1}s^{-1}$ and using this constant to find the diffusion rate constant yielded $8.4*10^8$ $M^{-1}s^{-1}$.

Keywords: quenching rate constant, diffusion rate constant, donor, acceptor

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Introduction

The purpose of this experiment was to determine the change in photoluminescence intensity when a quencher is introduced to find the diffusion rate constant. This experiment was done under a bimolecular electron transfer environment with three different rate constants. The relation between the three rate constants is as follows:

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{k_{et}}$$

With k_q being the quenching rate, k_d being the diffusion rate, and k_{et} being the electron transfer rate. In this experiment we're going to assume that the electron transfer rate is way larger than that of the quenching rate. This yields:

$$k_q \approx k_d$$

To find the quenching rate, a modified Stern-Volmer equation must be used where:

$$\frac{F_o}{F_q} = 1 + k_q \tau_0 [Q]$$

F_o is the photoluminescence without the quencher, F_q is the photoluminescence with the quencher, τ_0 is the lifetime of the excited electron donor in zero acceptor concentration, and [Q] is the concentration of the quencher in F_q. The species used in this experiment are $Ru^{2+}(bpy)_3$ with a provided concentration of $1*10^{-4}M$ as the donor and $[Ru^{3+}(NH_3)_6]Cl_3^-$ with a provided concentration of $1.6*10^{-2}M$ as the acceptor.
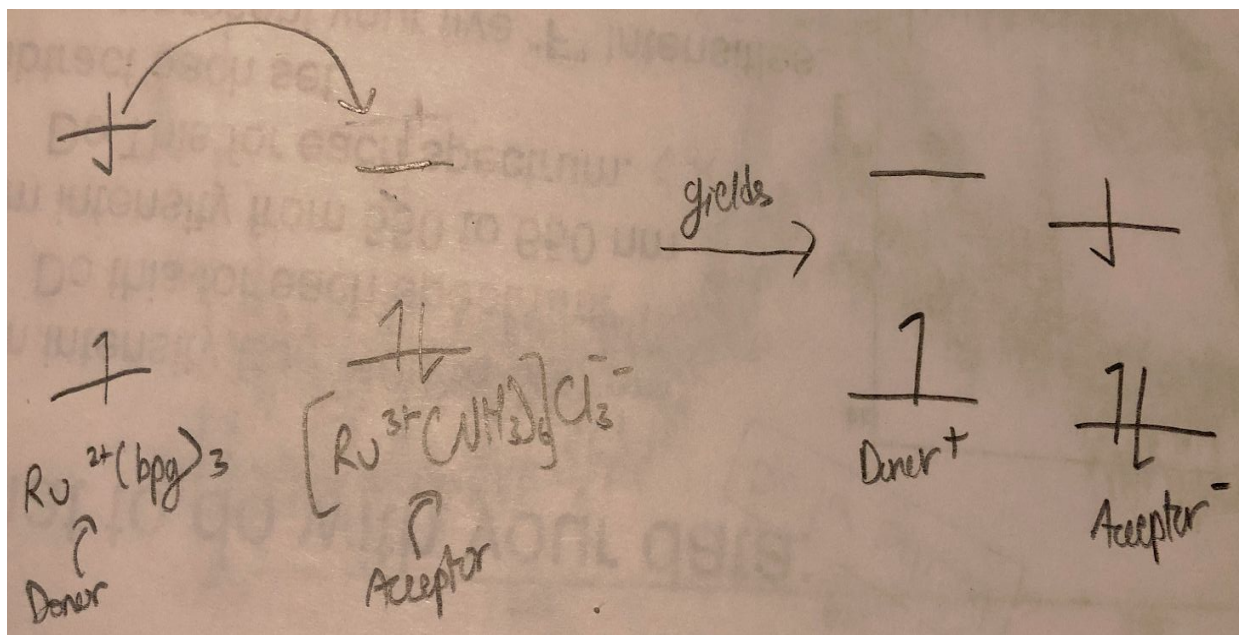

Figure 1. Electron transfer between donor and acceptor atoms.

Methods

Since the labs are cancelled, the data was provided by the professor so there will be no method explanation.

Results

Table I. Standard Table

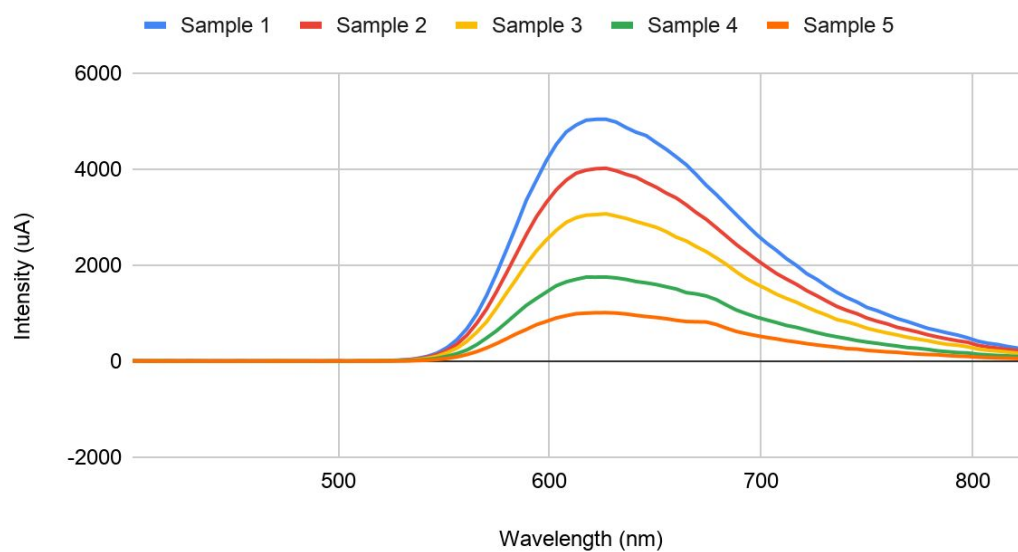|	$Ru^{2+}(bpy)_3$ stock sln	$[Ru^{2+}(NH_3)_6]$ stock sln	DI water	[Q]
Sample 1	1.0 mL	0.0 mL	2.0 mL	0 M
Sample 2	1.0 mL	0.2 mL	1.8 mL	$1.0*10^{-3}$ M
Sample 3	1.0 mL	0.5 mL	1.5 mL	$2.7*10^{-3}$ M
Sample 4	1.0 mL	1.0 mL	1.0 mL	$5.3*10^{-3}$ M
Sample 5	1.0 mL	1.5 mL	0.5 mL	$8.0*10^{-3}$ M

Figure 2. Plot of the steady-state photoluminescence for all five samples.

Fo/F - 1 vs [Q] (M) for samples 2-5
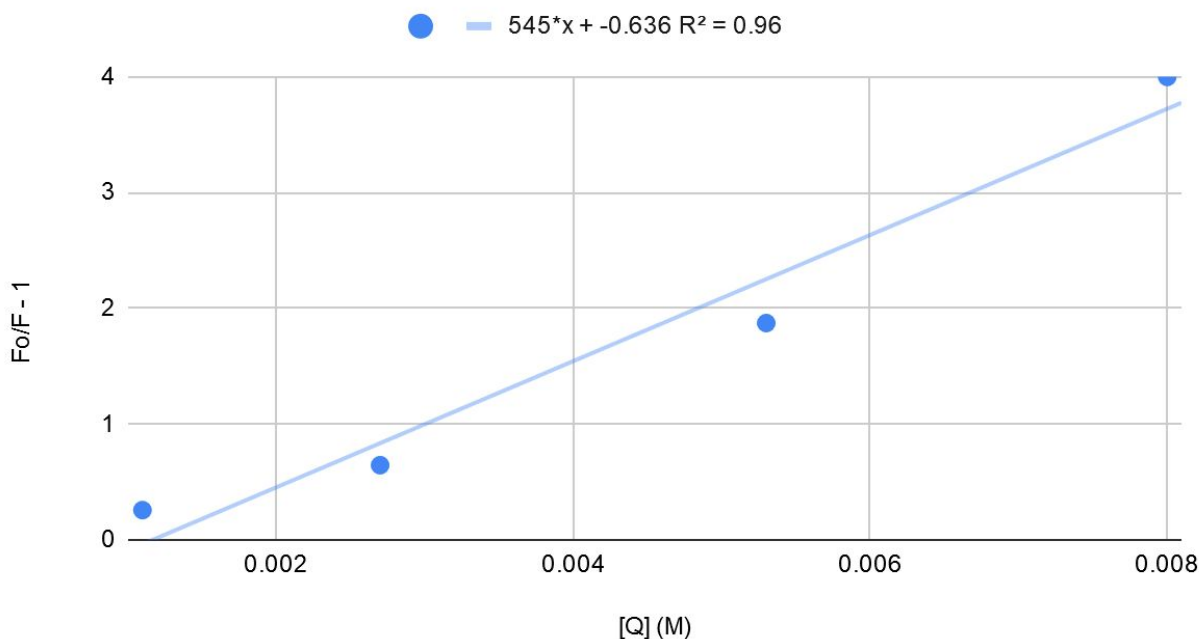

Figure 3. Plot of steady-state Stern-Volmer to obtain quenching rate.

Sample Calculations:

Concentration of quencher:

0.2mL * $1.6*10^{-2}$M = 0.0032ml*M / 3mL = 0.001M

Finding F_o: Sum of values from 550nm to 650nm - Sum of Background from 400nm to 500nm both from Sample 1

75163.07 - 155.93 = 75007.14 = F_o

Finding F_{qn}: Sum of values from 550nm to 650nm - Sum of Background from 400nm to 500nm both from Sample n

Ex: Sample 2; 59739.94 - 85.00 = 59654.94 = F_{2q}

Finding k_q:

Using the slope of Figure 3, which is equal to: $k_q \tau_0 [Q]$

$k_q = 1 / \tau_0 [Q] = 545 / 650*10^{-9}$s = $8.4*10^8$ $M^{-1}s^{-1}$

Since $k_q = k_d$, $k_d \approx 8.4*10^8$ $M^{-1}s^{-1}$.

Conclusion

        The value that was acquired was $8.4*10^8$ $M^{-1}s^{-1}$. Comparing this value to the literature value from Navon and Sutin[1] being $2.1*10^9$ $M^{-1}s^{-1}$, there is a seen difference. This difference of value could be different from the published value because of the instrumentation that has evolved through the 50 years from when it was first published. This means that the instrumentation has evolved to be more sensitive and acquire better backgrounds if the samples were prepared correctly. Another possible difference from the value could be due to the fact that our samples were made using DI water as solvent while Navon and Sutin used 0.5M Sulfuric Acid. Since the two solvents are different, there can be electron interactions between the solvent and the acceptor of the system that causes this change in the diffusion constant.

Acknowledgements

        I used the lab manual, the document on Sakai provided by the professor, the lecture slides, and the lecture video.

Discussion Questions

        None in the Lab Manual.

References

1. Navon, G.; Sutin, N. Mechanism of the Quenching of the Phosphorescence of Tris(2,2-Bipyridine)Ruthenium(II) by Some Cobalt(III) and Ruthenium(III) Complexes. *Inorganic Chemistry* **1974**, *13* (9), 2159–2164.