UPCONVERTING LOW POWER PHOTONS THROUGH TRIPLET-TRIPLET ANNIHILATION

Bryn Wilke

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Committee:
Felix Castellano, Advisor
Ksenija Glusac
Peter Lu
ABSTRACT

Felix Castellano

One mechanism to achieve photon upconversion, the frequency conversion of low energy photons to those of higher energy, is sensitized triplet-triplet annihilation, a non-coherent (lasers not required) process. In this scheme, a triplet sensitizer is selectively excited at long wavelengths, eventually transferring its triplet energy to an appropriate acceptor molecule in a bimolecular energy transfer reaction. Finally, a second bimolecular energy transfer reaction occurring between two excited triplet acceptors pools the combined energy onto one molecule, producing the fluorescent excited singlet state of the acceptor molecule. This energized molecule radiatively decays back to its ground state releasing photon energies in excess of that of the excitation source, i.e. upconverted with respect to the incident light. This phenomenon has become realized in various combinations of chromophores resulting in wavelength shifting properties that range from the UV to the near-IR. Recently, the upconversion process has become a viable solution to drive fuel-forming chemistry in photoelectrochemical cells and for display applications in polymer host films. The concepts and experiments related to photon upconversion are facile and readily present an opportunity to educate young chemists in this field. Related to established green-to-blue upconversion systems, [Ru(bpy)3](PF6)2 and 9,10-diphenylanthracene (DPA) in deoxygenated dichloromethane is demonstrated here to be a suitable composition for an undergraduate laboratory experiment in physical and/or inorganic chemistry using a conventional fluorimeter. Quadratic incident light power dependence is displayed from the singlet fluorescence of DPA ($\lambda_{em\,max} = 430$ nm) resulting from selective excitation of [Ru(bpy)3]^{2+} at 500 nm using a conventional single photon counting fluorimeter equipped with a 75 W Xe arc lamp. This is easily justified by the fact that two sensitized triplets must be formed in order to ultimately generate the singlet fluorescence. The nonlinearity of the power dependence establishes that the
photon upconversion was indeed produced from sensitized TTA. Notably, this experiment can be further developed using higher light excitation intensities or sensitizer concentrations or vacuum degassing conditions to gain access to the linear incident power regime. Some of these aspects were also explored in this thesis. In the quadratic incident power regime, the kinetics illustrates a process where the pseudo-first order decay pathways for the triplet state of the acceptor dominate over the bimolecular triplet-triplet annihilation rate whereas a linear power dependence on the upconversion signal is observed when the pseudo-first order decay pathways are rendered slower with respect to the annihilation rate. The efficiency of the triplet sensitization (quenching) reaction can be determined at any quencher concentration and was analyzed and optimized using the Stern-Volmer relation. This thesis builds upon previous research to formulate an experiment in photon upconversion suitable for an undergraduate laboratory and presents new research supporting the weak and strong annihilation limits displayed through incident light power dependence exclusively using non-coherent photons.
This thesis is dedicated to my family for telling me that I am braver than I believe, stronger than I seem, and smarter than I think. I want to thank my parents-Lauren and David, siblings-Caitlyn, Tynan, Kara, and Ian, cats-Sabrina and Ion for both the continued motivation and support in my life endeavors.
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CHAPTER 1: INTRODUCTION

Photon upconversion is the conversion of lower energy photons into higher energy through delayed fluorescence. This upconversion is shown in Figure 1, where the green excitation beam is upconverted into blue fluorescence. When Park er and Hatchard witnessed this phenomenon over 40 years ago in a solution of phenanthrene and anthracene\textsuperscript{1}, they concluded that the upconversion was due to the triplet excited state of the donor transferring energy to the acceptor’s triplet state. Two acceptor triplet states were then annihilated through diffusion, which resulted in one acceptor molecule in the ground state and one in an excited singlet state.\textsuperscript{2} The

Figure 1: $[\text{Ru(bpy)}_3]^{2+} \ (1.4 \times 10^{-4} \text{ M})$ and 9,10-diphenylanthracene $(5\text{ mM})$ in dichloromethane, upconversion is made apparent by a commercial green laser pointer. ($\lambda_{\text{ex}} = 532 \text{ nm, <10 mW peak power}$).
excited singlet acceptor molecule can then fluoresce at a higher energy than the excitation energy.

1.1 Requirements for Donor/Acceptor Molecules for Upconversion

Scheme 1: A generalized Jablonski diagram and upconversion scheme showing the various processes between the acceptor and donor upon low energy absorption to produce high energy emission.

A Jablonski diagram is a great visual aid to show the electronic states of the donor and acceptor molecules and the transitions between them, as shown in Scheme 1. A successful upconversion system has specific requirements for a sensitizer (donor) and annihilator (acceptor) species. Triplet-triplet annihilation (TTA) results from the triplet states of two donor molecules transferring energy to the triplet states of two acceptor molecules which can annihilate to produce a higher energy singlet state of the acceptor. Therefore, the donor is exclusively excited so that the only acceptor fluorescence observed is caused by upconversion. Sensitizers often have
absorption in the visible-to-near-IR region, whereas the acceptors often absorb in the higher energy regions. The anti-Stokes shift is defined as a fluorescence emission band that is displaced to a higher energy with respect to the excitation wavelength. A larger anti-Stokes shift is observed as the distance between the excitation wavelength and the maximum of the acceptor’s singlet emission increases. Prior to TTA, Dexter energy transfer must take place between the sensitizer and acceptor triplet states. The triplet energy of the acceptor must be less than that of the sensitizer to create a downhill triplet-triplet energy transfer process. A larger difference in energy corresponds to a greater driving force for this reaction and a favorable triplet-triplet energy transfer. The sensitizer should have a long lived triplet state lifetime on the order of microseconds, to allow for bimolecular diffusional energy transfer. When the two triplet states of the acceptor combine through triplet-triplet annihilation, one goes to the ground state while the other is excited to a singlet state double the energy of the acceptor triplet state. That state relaxes down to the acceptor’s lowest energy singlet excited state, which must be higher than the singlet state of the donor. This guarantees that low energy excitation can produce a higher energy from the acceptors singlet state. In order to increase the overall upconversion quantum efficiency, annihilators are selected to have a fluorescence quantum yield near unity.

With all the appropriate qualifications for the donor and acceptor in place for upconversion, the process begins by photo-excitation to populate the sensitizer’s singlet state. Intersystem crossing then proceeds to populate the triplet state to with a quantum yield of near unity due to the heavy atom effect. Direct excitation from the ground state of the sensitizer to
the triplet state is a spin forbidden process. The long-lived lifetime of the sensitizer in the triplet state allows for triplet-triplet energy transfer from the triplet sensitizer to the triplet acceptor. In order for this to occur, there must be Dexter energy transfer. Dexter energy transfer occurs when there is an electron in the excited state of the donor’s lowest unoccupied orbital. This electron transfers to the acceptor, simultaneously while the acceptor transfers an electron from the highest occupied state back to the donor. This kind of energy transfer occurs when the donor-acceptor distances are shorter so there is direct orbital overlap, with a range of about 10 Å. Therefore it helps to have a high quencher concentration with respect to the donor. The collisions of the acceptors’ populated triplet states combine to produce a singlet excited state from the acceptor. The final product shows high energy emission that is achieved by low energy absorption.

In order to maximize the high energy emission produced by upconversion, the quantum yield of the upconversion process must be understood. The overall upconversion quantum yield is based upon three factors: the quenching quantum yield, TTA quantum yield, and fluorescence quantum yield, as seen in Equation 1-1.

$$\Phi_{UC} = \Phi_q \times \Phi_{TTA} \times \Phi_F \quad (1-1)$$

When organic molecules are used as donors, the overall quantum yield of formation of the triplet sensitizer state is very low, as seen by a reduced $\Phi_{UC}$. Intersystem crossing from excited singlet state of the sensitizer is a spin-forbidden process. In order to get more efficient intersystem crossing transition metals are used. The transition metals have a much larger effective nuclear charge than carbon, which results in increased spin-orbit coupling. There is a higher likelihood
of triplet-triplet energy transfer to the acceptor’s triplet state through diffusion when there are more triplet states produced by the donor. Another way to increase the amount triplet states generated by upconversion is to deoxygenate the sample. In order to increase the quenching quantum yield, samples are either deoxygenated with inert gas or by a freeze pump-thaw cell degassing method with a vacuum of 8-10 μm. This process essentially removes all residual dissolved dioxygen in the solutions and decreases the pseudo-first order quenching of the formed acceptor triplets. The deoxygenation removes the competing pathway for $^3A^*$ decay, which facilitates a sample condition that is poised for second-order annihilation chemistry. It has been noted that in a freeze pump-thaw cell all of the unimolecular and pseudo first order decay pathways for $[^3A^*]$, $k_T$, were noticeably reduced.\(^8\)

### 1.2 Development of Upconversion Systems

There has been a lot of activity in the field of photon upconversion in recent years. The review “Photon upconversion based on sensitized triplet–triplet annihilation” has sparked the interest of many scientific groups and set the groundwork for forming successful upconversion systems.\(^2\) When analyzing an upconversion system, the Stern-Volmer constant $K_{sv}$ and quenching constant, $k_q$, are presented to describe the efficiency of photoluminescence quenching. The calculations and determination of these values will be discussed in section 3.3. Another important value of upconversion is the overall upconversion quantum yield of system. This value reports on how efficient the upconversion process is taking place, keeping in mind Equation 1-1, which describes the three factors affecting the overall upconversion yield.
One of the first upconversion systems studied by the Castellano group was \([\text{Ru(dmb)}_3]^{2+}\), where dmb = 4,4’-dimethyl-2,2'-bipyridine, and DPA, where DPA = 9,10-diphenylanthracene. The metal-to-ligand charge transfer absorption band of \([\text{Ru(dmb)}_3]^{2+}\) was excited with an excitation wavelength of 514.5 nm to promote upconversion with DPA. This system yielded a Stern-Volmer constant of \(K_{sv} = 3,465 \text{ M}^{-1}\) and a quenching constant of \(k_q = 4.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}\) from quenching by DPA. Prior to DPA, anthracene was used as an acceptor. Anthracene had an increased quenching constant of \(5.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}\), however, overall upconversion efficiency was lower using anthracene when compared to DPA. This was most likely due to the fact that DPA had a larger fluorescence quantum yield (\(\phi = 0.95\)) than anthracene (\(\phi = 0.27\)). As shown in Equation 1-1, the overall upconversion will increase if the fluorescence quantum yield for the acceptor is larger. The small quantum yield is because an anthracene dimer is produced when the singlet excited anthracene encounters an anthracene molecule in the ground state. This is likely to occur at high concentration of anthracene. The anti-Stokes shift of the \([\text{Ru(dmb)}_3]^{2+}\) and DPA system is 0.38 eV, which in not an incredibly large shift. However, this system can clearly illustrate the energetic limitations and requirements for a photon upconversion experiment.

The many advances of photon upconversion over the years have been made clear by utilization of a variety of heavy metals as sensitizers in tandem with a variety of organic based triplet acceptors in fluid solution. Such examples include Ru(II)\(^9\) and Ir(III)\(^10\), which display metal to ligand charge transfer absorptions, or Pt\(^11\) and Pd\(^12,13\) metalloporphyrins with low energy \(\pi - \pi^*\) transitions. These metals are not abundant and tend to be very expensive. In addition to
lowering costs of donor molecules, the Castellano group has successfully made upconversion possible through soft and hard polymer host matrices. This brings photon upconversion one step closer to cutting edge device integration. Many pivotal applications such as photochemical cells, photocatalysis, photonics, and molecular probes, are being investigated in order to take advantage of using low energy absorption to gain high energy emission. A recent contribution to exploit the upconversion phenomenon is the utilization of sub-bandgap photons in a prototypical photoelectrochemical cell. This was made possible by using palladium (II) octaethylporphyrin (PdOEP) and 9,10-diphenylanthracene in toluene to sensitize nanostructured WO₃ photoanodes, in the future, this process could have major impact for long wavelength light harvesting in next generation solar cells.

1.3 Annihilation Limits

A completely new way of looking at upconversion exploits the strong annihilation limit of the upconversion process, as opposed to the weak annihilation, which displays quadratic power dependence on a plot of the incident light as a function of integrated emission intensity. This limit occurs when the triplet-triplet annihilation process is so efficient that it is no longer the rate limiting step in the reaction mechanism. A power dependence plot is made from measuring the integrated emission intensities under the upconversion peak from delayed fluorescence at different powers. If triplet-triplet annihilation is the rate determining step, the peak will show a quadratic dependence. This is due to the two-photon process that occurs during photon upconversion. Noncoherent light sources (lamps) have been in the realm of the weak annihilation
limit for many reported upconversion systems, which show a quadratic power dependence plot$^{14,18}$. Increasing the efficiency of triplet excited states within an upconversion system causes the crossover between the weak and strong annihilation limits. This can be done by using a higher power excitation, increasing the concentration of donor molecules in solution, and changing the excitation wavelength to where there is higher absorption. In essence, increasing the concentration of the acceptor triplet states will increase the efficiency of a system pushing it into the strong annihilation kinetic limit. This has been experimentally tested by analyzing documented upconversion systems, but increasing the power of excitation.$^8$

![Graph](image)

**Figure 2:** A double logarithmic plot clearly shows the change from quadratic (slope=2) to linear power dependence (slope=1).$^8$

This shift can be seen in Figure 2, using PdOEP as the donor and DPA as the acceptor.$^8$ Once an upconversion system is in the strong annihilation limit, the triplet-triplet annihilation
process is no longer the rate limiting step. There will be a linear power dependence present, which is generated from the pseudo-first-order decay pathways for $[^3A^*]$. The kinetic equations describing such weak and strong annihilation mechanisms will be discussed in the results section of this paper.

Coherent (lasers) and noncoherent lamp light sources have both produced data that shows the crossover to the strong annihilation limit. Coherent light sources have large light intensities that can be on the order of $\text{MWcm}^{-2}$ and $\text{GWcm}^{-2}$. Noncoherent light sources, such as the sun, can’t reach these high intensities through normal means. It is important to have a low power density for upconversion systems that can reach the strong annihilation limits for application such as solar cells. Upconversion would help to utilize the spectra of the sun so that the longer wavelengths can be unconverted into shorter wavelength to increase efficiency in the solar cells. When creating high overall upconversion efficiency in the low power regime, it serves as a possible way to increase efficiency of various solar cells by using sunlight as a noncoherent excitation source. A goal in future research is to use very low power to get linear results in the power dependence plot.

1.4 Spin-Statistical Factor

Spin-statistical factors explain the likelihood of triplet encounters of the acceptors based on the different spin state possibilities. The interaction of two excited triplet states can produce nine spin states with probability composing three different sublevels--five are quintet, three are
triplet, and one is singlet. These sublevels showing the excited state interactions between acceptor molecules are described in Equation 1-2.

\[ ^3A_1^* + ^3A_1^* \leftrightarrow ^5(AA)_2^* \leftrightarrow ^5A_2^* + ^1A_0 \]  
\[ ^3A_1^* + ^3A_1^* \leftrightarrow ^3(AA)_1^* \leftrightarrow ^3A_2^* + ^1A_0 \]  (1-2) 
\[ ^3A_1^* + ^3A_1^* \leftrightarrow ^1(AA)_0^* \leftrightarrow ^1A_2^* + ^1A_0 \]

Accordingly, the statistical factors predict a quantum yield for upconversion to be a maximum of 11.1% if the quenching efficiency and fluorescence quantum yield of the acceptor is 100%. Although theoretically predicted, it is also noted that the quintet has a 92% chance of decaying into two molecules at the triplet excited state. Therefore, it follows that the upconversion quantum yield can be higher than previously expected. The excited triplets are likely recycled from quintet and triplet dimers. Instead of the predicted 11.1%, the quantum efficiency of triplet triplet annihilation has approached an upper limit exceeding 40%.
1.5 Upconversion as a Basis for an Undergraduate Laboratory Experiment

The nonlinear kinetics that takes place in photon upconversion can be demonstrated using a common spectrofluorometer, which can be found in many university laboratories. This presents the first opportunity to provide a photon upconversion laboratory experiment for undergraduate inorganic chemistry or physical chemistry student. This phenomenon is made apparent with [Ru(bpy)$_3$]$^{2+}$ sensitizer and 9,10-diphenylanthracene (DPA) as the acceptor/annihilator. Clearly, selective excitation of the sensitizer with 500 nm light produces the singlet fluorescence spectrum of DPA anti-Stokes to this excitation exhibiting quadratic incident photon power dependence. It is important to note that photon upconversion using Ru(bpy)$_3^{2+}$/DPA can be visualized using a green laser pointer ($\lambda_{\text{exc}} = 532$ nm, $< 10$ mW peak power), as seen in Figure 3.

**Figure 3:** [Ru(bpy)$_3$]$^{2+}$ ($1.4 \times 10^{-4}$ M) and DPA (5mM) in dichloromethane. An undergraduate student uses a green laser as a visual demonstration of photon upconversion. ($\lambda_{\text{exc}} = 532$ nm, $<10$ mW peak power).
The first part of the experiment contains sample preparation specifications for donor and acceptor solutions in order to provide proper conditions for upconversion. Stern-Volmer quenching is presented as an option portion of the upconversion experiment in part 2. The primary focus of this experiment is to shown in part 3, where students can observe nonlinear kinetics occurring in the upconversion peak by attenuating the incident light with absorptive neutral density filters. Students are able to understand experimentally how triplet-triplet annihilation occurs due to a two-photon process by realizing the quadratic power dependence on incident light for the upconversion region and the visual aid of a green-to-blue energy change. The concepts of upconversion are shown experimentally by showing a two-photon process by the quadratic power dependence displayed in the upconversion fluorescence.
CHAPTER 2: EXPERIMENTAL

2.1 Chemicals and Materials

Spectroscopic grade dichloromethane was purchased from Sigma Aldrich. 9,10-Diphenylanthracene (99%) was purchased from Alfa Aesar. Tris(2,2’-bipyridine)ruthenium dichloride hydrate was purchased from GFS Chemicals and metathesized to the corresponding PF₆ salt in water using excess NH₄PF₆ (Aldrich). Anaerobic glass (fluorescence) optical cells suitable for inert (Ar or N₂) gas purging were obtained from Starna Cells.

A Cary 50 Bio UV-Vis spectrophotometer (Varian) was used to measure the absorption spectra of the samples used in these experiments and a standard PTI spectrofluorimeter equipped with a 75 W Xe lamp source was used in the acquisition of all photoluminescence spectra. The emission spectra are not corrected for detection system response. A 455 nm long pass filter (Newport Optics) was placed in the fluorimeter excitation beam prior to the sample to remove all remnant high-energy photons. A series of neutral density filters (Newport Optics) positioned after the long pass filter was used to systematically attenuate the incident light power striking the sample.
2.2 Sample Preparation and Instrumental Analysis

Dichloromethane or the 4:1 mixture of toluene and acetonitrile was used as a baseline to take UV-vis measurements of a solution containing 2.5 mL of \( \sim 1.0 \times 10^{-4} \) M \([\text{Ru(bpy)}_3]^{2+}\). An optical density of 0.1-0.2 at 488 nm was sufficient for upconversion. Static measurements were obtained using a Cary 50 Bio UV-Vis spectrophotometer (Varian). After collecting the absorbance spectra of \([\text{Ru(bpy)}_3]^{2+}\), the sample is deoxygenated with a slow bubble flow of high purity argon for 30 minutes. The slow bubble flow prevents evaporation of dichloromethane. Meanwhile, a stock solution of 45 mM 9,10-diphenylanthracene was prepared in dichloromethane or the 4:1 mixture of toluene and acetonitrile. After 30 minutes of deoxygenation, the emission spectrum was collected ranging from 500-800 nm. Samples were analyzed in 1 cm\(^2\) quartz fluorescence cells with a septum cap (Starna Cells). A Photon Technology International spectrofluorometer was used in collecting steady-state luminescence data, unless otherwise stated. The specifications of the PTI include a 75 W xenon arc lamp as the excitation source at 488 nm. During steady-state luminescence and lifetime measurements, a 455 nm longpass filter was used to ensure that the sensitizer was exclusively excited at 488 nm. To check for stable and constant emission, the solution was deoxygenated for 5 more minutes and the emission spectrum was compared to the spectral profile of the initial measurements. If these measurements did not overlap, the sample was deoxygenized until spectral profiles match completely and a stable emission is observed.
Once constant emission was observed, the lifetime of the solution was measured. Single wavelength emission intensity decays were acquired with a N₂ pumped dye laser (2-3 nm fwhm) from PTI (GL-3300 N₂ laser, GL-301 dye laser). Coumarin 500 (C500) was used to tune the unfocused pulsed excitation beam to selectively excite \([\text{Ru(bpy)}_3\text{](PF}_6\text{)}_2\). The initial emission and lifetime are recorded as \(I_0\) and \(\tau_0\), respectively. The detector used was a photomultiplier tube (R928-Hamamatsu) that was probed at 595 nm using 650 Volts.

### 2.3 Stern-Volmer Quenching

Once the initial emission spectrum of the phosphorescent peak from \([\text{Ru(bpy)}_3\text{](PF}_6\text{)}_2\) and initial lifetime measurements were collected, acceptor was added. The concentration of DPA stock solution was about 45mM. The first addition was usually about 20 \(\mu\text{L}\), followed by 40 \(\mu\text{L}\), 80 \(\mu\text{L}\), and 160 \(\mu\text{L}\) addition volumes. These values changed for each quenching experiment, but were generally in range of the previously listed acceptor additions. After each addition, the solution was deoxygenated with a slow bubble flow for 5 minutes. Once deoxygenation is completed, the lifetime and emission spectrum was recorded. The nitrogen dye laser recorded the lifetime after each acceptor addition, with a 455 nm longpass filter after the excitation beam. The emission spectra were collected for each addition using the PTI fluorometer. Upon each further addition of acceptor the same steps are followed until the emission was quenched by 80%, which usually occurred when 300 \(\mu\text{L}\) of the 45 mM stock solution was added.
2.4 Power Dependence

A power dependence experiment was performed using the 80% quenched donor-acceptor solution with an acceptor concentration in solution of ~3 mM. A 455 nm longpass filter was used to ensure there was no direct excitation of the DPA and the emission spectra of the upconversion peak were measured in a time-based emission mode at 430nm. The time-based emission measurements were used to ensure that there is stability at the given emission wavelength over a period of 20 seconds. A set of absorptive neutral density filters (Newport Optics) was used to attenuate the power of the lamp. With each consecutive filter, the power was measured at the sample and the emission spectrum is measured. It is important to keep constant slit widths during this portion of the experiment. The spot size was also recorded to measure the density of the power interacting with the sample so that the power density of the excitation beam could be calculated. This was done by holding a ruler where the excitation beam hits the cuvette and measuring the size of the beam. In this experiment, the spot size was determined to be 0.16 cm\(^2\).

2.5 Hazards for the Undergraduate Laboratory Experiment

Students were directed to not look into lasers directly, as they could cause severe eye damage. A well ventilated area, such as a hood, was required for deoxygenation with an inert gas. Gloves were worn at all times during this experiment. Diphenylanthracene should be handled with caution because it may cause skin irritation if absorbed through the skin. Dichloromethane is carcinogenic and should be handled with care. It is not safe to ingest and is an irritant of skin and eyes. Tris(2,2’-bipyridyl)dichlororuthenium(II) hexahydrate may cause
skin and eye irritation. When working with deoxygenating needles, they should be handled carefully because they are sharp. All hazards were discussed prior to the laboratory experiment. Wastes should be disposed in proper labeled containers.
CHAPTER 3: METHODS

3.1 Chemical Structures

The chemical structures of the donor/acceptor in the green-to-blue upconversion are given in Figure 3:

\[ \text{Figure 4: a) } [\text{Ru(bpy)}_3]^{2+} \quad \text{b) 9,10-diphenylanthracene} \]
3.2 Jablonski Diagram

The Jablonski diagram pictured in Scheme 2 explains the process of upconversion in the [Ru(bpy)$_3$]$^{2+}$ and DPA system. The [Ru(bpy)$_3$]$^{2+}$ has a triplet energy of 2.08 eV, which is greater than DPA’s triplet energy of 1.80 eV.$^{19,20}$ The outcome of this upconversion gives rise to an anti-Stokes shift of 0.34 eV.

![Jablonski Diagram](image)

Scheme 2: Jablonski diagram outlining the processes occurring during photon upconversion between [Ru(bpy)$_3$]$^{2+}$ and DPA.

3.3 Stern-Volmer Analysis

Stern-Volmer analysis looks at the photochemical kinetics that occurs when an excited molecule, *D, is chemically deactivated by a quencher, A at a rate of k$_1$. There is a competition between the unimolecular decay of *D and a bimolecular quenching, k$_q$, of *D by A.$^{21}$ The following reactions describe the processes that occur during quenching$^{21}$:

\[
*\text{R Unimolecular decay: } *D \overset{k_1}{\rightarrow} \text{Product}
\]
\[ *R \text{ and } Q \text{ quenching: } *D + A \stackrel{k_1}{\longrightarrow} \text{Quenching of } *D \]

Quenching Lifetime of \(*D\):
\[
\frac{1}{\tau} = k_1 + k_q[A] = \frac{1}{\tau_0} + k_q[A]
\]

The Stern-Volmer collisional fluorescence quenching is described by the Stern-Volmer equation, as shown in Equation 3-1.\(^{22}\) \(I_o\) and \(\tau_o\) are the integrated intensity of the emission and the lifetime without addition of quencher, respectively. \(I\) is the integrated intensity after additions of quencher and \(\tau\) is the lifetimes after additions of quencher.\(^{21}\)

\[
\frac{I_o}{I} = \frac{\tau_o}{\tau} = 1 + K_{sv} \times [A] \quad (3-1)
\]

This quenching data can be represented in a Stern-Volmer plot. When \((I_o/I)-1\) or \((\tau_o/\tau)-1\) is plotted versus the concentration of quencher the slope is equal to the Stern Volmer constant, \(K_{sv}\). Quenching is a process that will reduce the population of the excited state. Therefore, a decrease in integrated emission intensity and lifetime is expected upon addition of acceptor. Consequently, a linear dependence is expected with both intensity and lifetime as quencher is added.\(^5\)

The quenching rate constant, \(k_q\), is determined by dividing the Stern-Volmer constant by the lifetime of the sensitizer without any addition of acceptor. This value is important because it can be compared between quenching systems to determine the efficiency of quenching. The larger the quenching constant the more efficiently a system is being quenched.\(^5\)
\[ k_q = \frac{K_n}{\tau_o} \quad (3-2) \]

Using Ru(bpy)_3^{2+} as a donor for quenching experiments with the following quenchers produces the results in table 1:

<table>
<thead>
<tr>
<th>Quencher</th>
<th>(K_{sv})</th>
<th>(k_q)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracene</td>
<td>1500</td>
<td>2.2 \times 10^9</td>
</tr>
<tr>
<td>trans-2-</td>
<td>30.9</td>
<td>4.5 \times 10^6</td>
</tr>
<tr>
<td>Styrylpyridine</td>
<td>29.2</td>
<td>4.53 \times 10^6</td>
</tr>
<tr>
<td>trans-stillbene</td>
<td>14.7</td>
<td>2.1 \times 10^6</td>
</tr>
<tr>
<td>cis-1,3-Pentadiene</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*Table 1: Quenching of Ru(bpy)_3^{2+} luminescence in a 2:30 ethanol benzene solvent mixture*

In order to evaluate the limits of the quenching, the diffusion controlled rate constants can be evaluated for solvents in this experiment. These values denote the highest values of diffusional quenching in a given solvent.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>(k_{diff} (25^\circ C) \text{(L mol}^{-1} \text{s}^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dichloromethane</td>
<td>1.6 \times 10^{10}</td>
</tr>
<tr>
<td>Toluene</td>
<td>1.2 \times 10^{10}</td>
</tr>
<tr>
<td>Acetonitrile</td>
<td>1.9 \times 10^{10}</td>
</tr>
</tbody>
</table>

*Table 2: Diffusions controlled limits for various solvents*
3.4 Kinetic Limits

There are two kinetic limits that are related to the $[^3\text{A*}]$ decay, as shown in Equations 3-3 and 3-4. The upconverted fluorescence intensity ($N_f$) is proportional to the square of the $[^3\text{A*}]$. In the following equations, $k_T$ represents all of the unimolecular and pseudo-first-order decay pathways for $[^3\text{A*}]$, $k_{TT}$ is the TTA bimolecular rate constant, and $\Phi_F$ is the fluorescence quantum yield of the acceptor/annihilator.\(^8\)

\[
\frac{d[^3\text{A*}]}{dt} = -k_T[^3\text{A*}] - k_{TT}[^3\text{A*}]^2 \tag{3-3}
\]

\[
N_F = \int_0^\infty I_F(t) dt = \int_0^\infty \Phi_F k_{TT}[^3\text{A*}]^2 \tag{3-4}
\]

Equation 3-5 represents the analytical solution to Equation 3-3, as described by Bachilo and Weisman.\(^{24}\)

\[
[^3\text{A*}] =[^3\text{A*}]_0 \frac{1-\beta}{e^{\beta t} - \beta} \tag{3-5}
\]

\[
\beta = \frac{k_{TT}[^3\text{A*}]_0}{k_T + k_{TT}[^3\text{A*}]_0} \tag{3-6}
\]

When $k_T > k_{TT}$, the weak annihilation dominates the $k_{TT}$ terms become negligible and Equation 3-5 reduces to a single exponential decay of $[^3\text{A*}]_t =[^3\text{A*}]_0 \exp(-k_{TT})$. This is substituted into Equation 3-4 and integrated with respect to time in order to produce Equation 3-7.
This equation explains why the emission intensity will be proportionally related to the $[^3A^*]^2$.

Quadratic dependence is observed with respect to the absorbed optical power. This can be seen in Figure 6a.

The strong annihilation limit occurs when $k_T < k_{TT}$. When this limit takes place, the $k_T$ terms are negligible and Equation 3-5 will simplify to become:

$$\left[^3A^*\right] = \frac{\left[^3A^*\right]_0}{1 + k_{TT} \left[^3A^*\right]_0 t}$$ (3-8)

Once Equation 3-8 is substituted into Equation 3-4 and time-integrated, it simplifies to become Equation 3-9.$^8$

$$N_F = \Phi_F \left[^3A^*\right]_0$$ (3-9)

As shown, the $[^3A^*]$ directly scaled with the absorbed optical power. This exploration into the linear regime does not disprove previous kinetic analysis of delayed fluorescence, but instead shows consistency with kinetic treatments proven over 40 years ago by Birks and Parker.$^{25,26}$
CHAPTER 4: RESULTS

4.1 Absorption and Emission

The normalized emission spectra of the donor, [Ru(bpy)$_3$]$^{2+}$, and the acceptor, DPA, which was measured in a 4:1 toluene acetonitrile mixture, is shown in Figure 4. [Ru(bpy)$_3$]$^{2+}$ has a phosphorescent peak centered around 595 nm and an MLCT absorption maximum at 452 nm. The DPA $\pi$-$\pi^*$ absorption band has a maximum at 432 nm. There are no overlapping features with the chosen excitation wavelength of 488 nm which ensures exclusive excitation of the sensitizer.

![Normalized Absorbance vs Wavelength](image)

**Figure 5:** Absorption and emission spectral profiles are shown for [Ru(bpy)$_3$]$^{2+}$ and DPA in dichloromethane. Intensities have been normalized to arbitrary maxima of 1. The arrow indicated the 488 nm excitation wavelength. [Ru(bpy)$_3$]$^{2+}$ has a phosphorescent maxima at 595 nm and absorbance maxima at 480 nm. DPA has a $\pi$-$\pi^*$ absorption band has a maximum at 432 nm.
4.2 Solubility of Donor/Acceptor

The solubility of [Ru(bpy)\textsubscript{3}](PF\textsubscript{6})\textsubscript{2} and DPA were tested in order to find a suitable solvent for upconversion experiments. Results are summarized in Table 3.

<table>
<thead>
<tr>
<th>Solvent</th>
<th><a href="PF%5Ctextsubscript%7B6%7D">Ru(bpy)\textsubscript{3}</a>\textsubscript{2}</th>
<th>DPA</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>slightly soluble</td>
<td>insoluble</td>
</tr>
<tr>
<td>methanol</td>
<td>soluble</td>
<td>insoluble</td>
</tr>
<tr>
<td>acetonitrile</td>
<td>soluble</td>
<td>insoluble</td>
</tr>
<tr>
<td>toluene</td>
<td>insoluble</td>
<td>soluble</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>insoluble</td>
<td>soluble</td>
</tr>
<tr>
<td>dichloromethane</td>
<td>soluble</td>
<td>soluble</td>
</tr>
<tr>
<td>benzonitrile</td>
<td>soluble</td>
<td>slightly soluble</td>
</tr>
<tr>
<td>dimethylformamide</td>
<td>soluble</td>
<td>Insoluble</td>
</tr>
</tbody>
</table>

Table 3: Solubility of [Ru(bpy)\textsubscript{3}](PF\textsubscript{6})\textsubscript{2} and DPA
4.3 Stern-Volmer Plots

Two solvent systems were studied to analyze the bimolecular quenching constant and Stern-Volmer constant of the [Ru(bpy)₃]²⁺ and DPA system. The first solvent condition was a 4:1 toluene-acetonitrile mixture. The second solvent used was dichloromethane. This was utilized as the solvent in preparation for the undergraduate experiment.

Using a 4:1 toluene-acetonitrile mixture, the bimolecular quenching constant was determined to be $1.19 \pm 0.16 \times 10^9$ M⁻¹ s⁻¹ using Equation 3-2. A Stern-Volmer plot generated from integrated emission intensity is shown in Figure 6, and a Stern-Volmer plot using lifetimes is shown in Figure 7.
Figure 6: Stern-Volmer plots are generated from emission measurements with a $\lambda_{ex}=488$ nm using a 4:1 toluene acetonitrile solvent system for [Ru(bpy)$_3$]$^{2+}$ and DPA. A PTI fluorometer with a 75 W Xe Arc lamp was used as the excitation source.
Figure 7: Stern-Volmer plots are generated from lifetime measurements in a 4:1 toluene acetonitrile solvent system for [Ru(bpy)$_3$]$^{2+}$ and DPA. A nitrogen-dye laser was used to tune the wavelength to approximately ~488 nm.

\[ K_{sv} = 1269 \text{ M}^{-1} \]

\[ k_q = 1.41 \times 10^9 \text{ M}^{-1} \text{ s}^{-1} \]
Reproducibility of data was also tested for the 4:1 solvent mixture, as shown in Table 4.

<table>
<thead>
<tr>
<th>OD at 488</th>
<th>Conc. DPA Stock Solution (mM)</th>
<th>Lifetime (μs)</th>
<th>$K_{sv}$ (M$^{-1}$) (intensity)</th>
<th>$k_q$ (M$^{-1}$ s$^{-1}$) (intensity × 10$^9$)</th>
<th>$K_{sv}$ (M$^{-1}$) (lifetime)</th>
<th>$k_q$ (M$^{-1}$ s$^{-1}$) (lifetime × 10$^9$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.33</td>
<td>44.27</td>
<td>0.88</td>
<td>1061</td>
<td>1.21</td>
<td>806</td>
<td>0.916</td>
</tr>
<tr>
<td>0.23</td>
<td>44.27</td>
<td>0.88</td>
<td>1062</td>
<td>1.21</td>
<td>1155</td>
<td>1.31</td>
</tr>
<tr>
<td>0.15</td>
<td>44.27</td>
<td>0.9</td>
<td>1197</td>
<td>1.33</td>
<td>1270</td>
<td>1.41</td>
</tr>
<tr>
<td>0.14</td>
<td>37.68</td>
<td>0.89</td>
<td>1046</td>
<td>1.18</td>
<td>1066</td>
<td>1.2</td>
</tr>
<tr>
<td>0.24</td>
<td>60</td>
<td>0.87</td>
<td>840</td>
<td>9.66</td>
<td>931</td>
<td>1.07</td>
</tr>
</tbody>
</table>

**Table 4:** Reproducibility of data for Ru(bpy)$_3$$^{2+}$/DPA in the 4:1 toluene acetonitrile solvent mixture

The average bimolecular rate constant was $k_q = 1.19 \pm 0.16 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

Dichloromethane was also used as a solvent. The bimolecular quenching constant was determined to be $2.47 \pm 0.18 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ using Equation 3-2. Stern-Volmer plots from both integrated emission and lifetime measurements are shown in Figure 8 and 9.
Figure 8: Stern-Volmer plots are generated from emission measurements with a $\lambda_{ex}=488$ nm using dichloromethane solvent system for $[\text{Ru(bpy)}_3]^{2+}$ and DPA. A PTI fluorometer with a 75 W Xe Arc lamp was used as the excitation source.
Figure 9: Stern-Volmer plots are generated from lifetime measurements in a 4:1 toluene acetonitrile solvent system for [Ru(bpy)$_3$]$^{2+}$ and DPA. A nitrogen-dye laser was used to tune the wavelength to approximately ~488 nm.
The reproducibility of the \( \text{Ru(bpy)}_3\text{]^{2+}} \) and DPA was tested using dichloromethane, as shown in Table 5.

<table>
<thead>
<tr>
<th>OD at 488</th>
<th>Conc. DPA Stock Solution (mM)</th>
<th>Lifetime (μs)</th>
<th>( K_\text{sv} ) (M(^{-1})) (intensity)</th>
<th>( k_\text{q} ) (M(^{-1}) s(^{-1})) (intensity × 10(^9))</th>
<th>( K_\text{sv} ) (M(^{-1})) (lifetime)</th>
<th>( k_\text{q} ) (M(^{-1}) s(^{-1})) (lifetime × 10(^9))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.18</td>
<td>46.96</td>
<td>0.67</td>
<td>1717</td>
<td>2.65</td>
<td>1788.00</td>
<td>2.68</td>
</tr>
<tr>
<td>0.10</td>
<td>45.75</td>
<td>0.59</td>
<td>1511</td>
<td>2.56</td>
<td>1369.00</td>
<td>2.30</td>
</tr>
<tr>
<td>0.23</td>
<td>53.22</td>
<td>0.70</td>
<td>1578</td>
<td>2.26</td>
<td>1666.00</td>
<td>2.39</td>
</tr>
</tbody>
</table>

**Table 5**: Reproducibility of data for \( \text{Ru(bpy)}_3\text{]^{2+}} \) and DPA in dichloromethane

The average bimolecular rate constant was \( k_\text{q}=2.47 \pm 0.18 \times 10^9 \) M\(^{-1}\) s\(^{-1}\).

### 4.4 Power Dependence

The analysis of the incident light intensity dependence on the sensitized upconversion emission signal was measured with a quenched \( \text{Ru(bpy)}_3\text{]^{2+}} \) and DPA (3.31 mM) solution in dichloromethane, shown in Figures 7 and 8. The emission intensity data points were plotted against the incident power density and were normalized. Time-based measurements in Figure 8 show how stable emission is over a period of time in addition to gathering the intensities at different incident power densities. The trend line represents the slope generated from fitting the data points on a double log plot.
Figure 10: (a) Upconverted emission intensity profile of a Ru(bpy)$_2^{2+}$ and DPA solution in dichloromethane as a function of 488 ± 18 nm incident power density (b) Normalized integrated emission intensity data from part (a) as a function of incident power. The line is fitted to data in a double log plot, normalized to the highest incident intensity 3.228 mW/cm$^2$. Spot size: 0.16 cm$^2$. 

y=2.03x
Figure 11: (a) Upconverted emission intensity monitored at the emission maximum 430 nm of a Ru(bpy)$_3$$^{2+}$ and DPA solution as a function of 488 ± 1 nm incident power density for 20 seconds (b) Normalized integrated emission intensity data from part (a) as a function of incident power. The line is fitted to data in a double log plot, normalized to the highest incident intensity 3.228 mW/cm$^2$. Spot size: 0.16 cm$^2$. 
4.5 Crossover between Linear and Quadratic Dependence

Figure 12: Quadratic power dependence is seen with power ranging from 3 mW/cm$^2$ to 0.9 mW/cm$^2$. Acceptor concentration $= 38 \mu$M $\cdot \lambda_{\text{exc}} = 488$ nm. PTI fluorometer, lamp excitation. Argon degassed for 30 minutes. Linear power dependence is seen with power ranging from 28.6 mW/cm$^2$ to 5.7 mW/cm$^2$. Acceptor concentration $= 26.5 \mu$M $\cdot \lambda_{\text{exc}} = 500$ nm. Edinburgh fluorometer, lamp excitation. This analysis was degassed using a Freeze-pump thaw cell.

In the strong annihilation limit the intensity is linearly dependent with respect to absorbed optical power. This is observed in Figure 6 b). It is noted that at higher power regimes, the linear strong annihilation limit dominates. This can be contrasted with the quadratic power dependences observed for low power excitation.
4.6 Control Experiment

Figure 13: Control experiment was done with a) (Red line) $8.05 \times 10^{-5}$ M [Ru(bpy)$_3$]$^{2+}$ concentration and a 46.54 μM acceptor concentration in a 4:1 toluene and acetonitrile mixture. b) No [Ru(bpy)$_3$]$^{2+}$ and a 46.54 μM acceptor concentration in a 4:1 toluene and acetonitrile mixture

A control experiment was done to prove that the [Ru(bpy)$_3$]$^{2+}$ was being exclusively excited. This was achieved by combining stock solution of DPA with a 4:1 toluene and acetonitrile mixture without adding any [Ru(bpy)$_3$]$^{2+}$. As seen in Figure 7, there is no emission generated from an excitation wavelength of 488 nm without [Ru(bpy)$_3$]$^{2+}$, however there is emission from triplet-triplet annihilation when [Ru(bpy)$_3$]$^{2+}$ is present.
CHAPTER 5: DISCUSSION

There are many goals that the phenomenon of photon upconversion has inspired. One such goal is to get upconversion to work in a common fluorometer, which many universities have access to. [Ru(bpy)$_3$]$^{2+}$ and DPA was utilized as the upconversion system because it is well known and requires relatively inexpensive commercially available reagents. The outcome of this upconversion gives rise to an anti-Stokes shift of 0.34 eV. In order to make this upconversion system possible in a fluorometer, the DPA acceptor stock solution was raised to 45 mM in order to efficiently quenching of the phosphorescence of [Ru(bpy)$_3$]$^{2+}$ using a 75 W Xe Arc lamp. Since 300 μL was added to get a fully quenched solution, the final concentration of acceptor in solution was 3 mM, which was about 20 times more concentrated than the [Ru(bpy)$_3$]$^{2+}$ starting concentration (~1x10$^{-4}$ M). At this accelerated concentration of DPA, it was important to run a control experiment to ensure that the DPA was not being exclusively excited. As seen in Figure 7, there was no emission generated from an excitation wavelength of 488 nm in conjunction with a 455 nm longpass filter without [Ru(bpy)$_3$]$^{2+}$, however there was emission from triplet-triplet annihilation when [Ru(bpy)$_3$]$^{2+}$ was present. Once this experiment was verified to work in a common fluorometer, the next step was a formulation of a laboratory experiment that would be suitable for undergraduates.

In order to create a simple upconversion experiment, it was first necessary to test the solubility of [Ru(bpy)$_3$]$^{2+}$ and DPA in different solvents, as shown in Table 3. The first
experiments were done using a 4:1 mixture of acetonitrile and toluene. This solvent mixture produced a quenching constant of $k_q = 1.19 \pm 0.16 \times 10^9 \text{M}^{-1}\text{s}^{-1}$, which was able to be reproduced in a variety of quenching experiments, as shown in Table 4. The diffusion controlled limits of toluene and acetonitrile are $1.2 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$ and $1.9 \times 10^{10} \text{M}^{-1}\text{s}^{-1}$. The quenching constant calculated for the quenching of $[\text{Ru(bpy)}_3]^{2+}$ was lower than the diffusion controlled limit by an order of magnitude, so this process was not diffusion limited. This solvent mixture was utilized because the volatility of dichloromethane was causing a change in concentrations due to evaporation from high bubble flow or argon gas. However, this was remedied by having a slower bubble flow which would not evaporate the dichloromethane. In later experiments the dichloromethane was chosen as the solvent for the undergraduate experiment because it was simpler to use one solvent instead of a solvent mixture. The quenching constant from these experiments was determined to be $k_q = 2.47 \pm 0.18 \times 10^9 \text{M}^{-1}\text{s}^{-1}$. Table 5 shows the reproducibility of this quenching constant with different optical densities and acceptor concentrations. In dichloromethane the energy transfer was not limited by diffusion because the diffusion controlled limit is $1.6 \times 10^{10}$. These values show that the quenching constant not quite approaching the diffusion controlled limit for dichloromethane.
Once the system was deemed reproducible with dichloromethane as the solvent, it was necessary to alter the experiment to be simplified so that it could be done in a 3-hour lab period. Many of the experimental parameters that are used in reported upconversion systems can be substituted for simpler calculations. Instead of using the integrated emission intensity for Stern-Volmer plots and power dependences, students can use the maxima of emission to simplify calculations. The power dependences provide a valuable source of concepts to show the two-photon process occurring during upconversion. The low power excitation from the 75 W Xe Arc lamp is in the regime where quadratic dependence is achieved from the weak annihilation limit of \( k_{TT} > k_T \). Students can plot double log plots using the percent transmittance acquired from neutral density filters on the x-axis versus the emission maxima at different percent transmittance of incident light. Such a plot can be generated using excel, as shown in Figure 14.

**Figure 14:** Double logarithm Plot of typical student data using normalized transmission and normalized maxima at 430 nm. Logarithmic values of a quenched [Ru(bpy)_3]^{2+}/DPA upconversion system. \( \lambda_{exc}=488 \text{ nm} \pm 2 \text{ nm}, 75 \text{ W Xe Arc Lamp.} < 4 \text{ mW/cm}^2 \text{ power density at 100% transmission.} \)
The incident light intensity dependence on the sensitized upconversion was also measured using standard calculations with integrated emission peaks, instead of emission maxima. These power dependence plots generated the equations $y = 2.03x$ and $y = 2.22$, as shown in Figures 10 and 11. The expected slope from a double-log plot at low powers for the integrated emission or emission intensity at 430 nm is $y = 2x$. It is clear that these slopes are in range for what is expected from a power density plot of the phosphorescent regions. This clearly demonstrates that the intensity of this singlet fluorescence displays quadratic ($x^2$) incident light power dependence. The nonlinearity of the power dependences establishes that the photon upconversion was produced from sensitized TTA, which was why the emission signal was proportional to the square of the incident power, and accordingly to the square of DPA concentration. This coincides with the conclusion that second order annihilation chemistry was the predominant rate-limiting step that occurs at low powers.

Power dependences have also given insight to the efficiency of the photon upconversion process. The normal second order quadratic power dependence in the upconversion peak caused by triplet triplet annihilation has a rate of $k_{TT}$. This is understood as a conceptual basis to prove that the upconversion is a two-photon process. When linear results are achieved, the upconversion rate of $k_{TT}$ has become so efficient that it is no longer the rate limiting step. The power dependence crosses over into the linear regime where the pseudo first-order rate constant of $k_T$ governs the kinetics of the upconversion peak. By raising the power of excitation, it is possible to achieve this crossover into efficient upconversion, as witnessed in Figure 12. This
realization has pushed groups studying photon upconversion into thinking about steps to get this linear strong annihilation limit by using higher powers or larger concentrations of acceptors and donors.

CHAPTER 6: CONCLUSION

Photon upconversion can be simplified into an undergraduate chemistry experiment that can take place in 3-hours using common laboratory equipment. Using [Ru(bpy)$_3$](PF$_6$)$_2$ and DPA as an upconversion system gives reproducible results using relatively cheap commercially available reagents. The power dependence plots generated from this experiment teaches valuable information about the nonlinear kinetics that take place during photon upconversion. The quadratic dependence displayed shows the predominance of second-order annihilation chemistry occurring in the delayed fluorescence of the DPA. Due to the low excitation from the coherent 75 W Xe Arc lamp, the upconversion was in the weak annihilation limit where $k_{TT}$ is the rate limiting step. The annihilation limits of photon upconversion were investigated using this system and show both linear and quadratic power dependence under different experimental conditions, such as when the excitation power is raised. In the strong annihilation there is pseudo-first order linear kinetics which can be determined from plot of integrated emission intensity of the singlet delayed fluorescence as a function of incident light power. In addition, the quenching process can be analyzed by Stern-Volmer plots and quenching kinetics. The [Ru(bpy)$_3$]$^{2+}$/DPA upconversion system provides a simplified glance into the concepts of photon upconversion.
However, the formulation of an undergraduate laboratory has the potential to inspire future young chemists to push the limits of photon upconversion innovations in years to come.
REFERENCES


