

(Jimmy Luper, Report #4, 5/5)

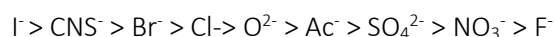
Abstract:

Ostwald ripening is a phenomenon that is observed during the growth of crystalline structures whereby smaller particles tend to form larger particles over time. Zinc oxide exhibits a strong UV absorbance, with the absorbance cutoff wavelength increasing with particle size. This experiment utilizes colloidal zinc oxide nanoparticles in 2-propanol to exemplify this. UV-Vis spectroscopy is used to determine the particle size and therefore the growth kinetics. The results of the experiment show that the particle size starts at 3.9 nm³ and grows to 7.1 nm³ by the end of the 8000 s incubation time. The growth for the first 3000 s does not follow a linear trend however, and suggests an initiation period in the particle growth kinetics.

(Erik Rognerud, Report #4, 19/20)

Introduction:

Fluorescence has had many interesting applications in analytical and physical chemistry. Fluorescence can be used for detection of unknown metals or organics via direct or indirect fluorimetric detections from ion chromatography.¹ Fluorescence has also involved the study of quenching effects. Primarily the effect of quenching quinine with halide ion. Extensive studies have been performed on this general procedure and many variables have been studied.¹⁻⁵ One of these variables is the necessity of sulfuric acid. The solutions must be kept below a pH of 5.80 to ensure that the quinine is protonated; only relevant emission spectra are observed when quinine is protonated.¹ Another variable that has been tested is the effect of the ion in quenching quinine. Work by Dr. Eric Jette and Dr. William West in 1928 found that the strength of the quenching anion follows this order, with iodide as the strongest and fluoride as the weakest.⁵



The following figure, *Figure 1*, generalizes the energy diagram of quinine in UV light. UV light is absorbed by the protonated quinine species. Some energy is lost by non-radiant emission. Finally, the species returns to the ground state by emitting visible light (blue). During quenching, the visible light is absorbed by the respective anion.

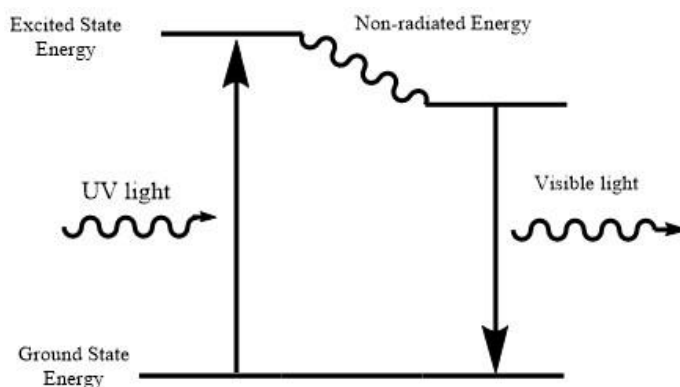
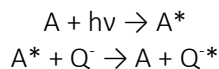


Figure 1: Energy diagram of quinine during excitation. This plot was inspired by Dr. Joseph DiVerdi.

Quenching is an interesting physical chemistry phenomenon. The figure discussed above shows the basics of what happens to quinine on the molecular level. The reaction scheme is well known and is detailed below.³



For this scheme, A is the ground state quinine species and A* is the excited state quinine species. Q⁻ is the quenching agent (chloride in this case) and Q^{-*} is the excited state. The corresponding reaction constant is K_{sv}, a value that is solved for by modeling these reactions. This value contains information about the reaction rate constant, k_q and the fluorescence lifetime, τ₀.³

$$K_{sv} = k_q \tau_0$$

Following the excitation of the quinine, a reaction occurs where the excited quinine 'bumps into' a halide ion and will react in a way that relaxes the quinine and excites the anion. Once the K_{sv} value is solved for, the rate constant can be solved for and compared to rate constants of other reactions with different quenching agents if the fluorescence lifetime is known (usually assumed to be 75 nm).³

Halide quenching of quinine has been known to follow a Stern-Volmer plot.¹⁻⁴ The Stern-Volmer equation follows as such:¹

$$F_0/F - 1 = K_{sv} [Q] \quad (1)$$

F₀ is the fluorescing species' max fluorescence intensity, F is the fluorescing species' fluorescence intensity at a given concentration of quenching agent, [Q]. K_{sv} is the Stern-Volmer constant, described above. This equation is easy to use for analysis and visually pleasing because these plots become linear when the values of (F₀/F - 1) and [Q] are tabulated and graphed; the resulting slope is equivalent to the K_{sv} value. A problem with this plot does exist; the dependence of the F₀ value. Through simple algebraic manipulation, the same values can be plotted to the following curve:

$$f(x) = a/[1+(b*x)] \quad (2)$$

Where f(x) corresponds to the peak intensities (F) as a function of quenching agent concentrations (Q); x. The constant a corresponds to F₀, and the constant b corresponds to the K_{sv} value. This experiment will study the effects of a quenching agent Cl⁻ on aqueous quinine in sulfuric acid. The analysis will be done through comparisons to the Stern-Volmer plot and the plot created by (2).

(Thomas Misek, Report #1, 15/15)

Materials and Methods:

The computer program Gaussian was used to conduct single point ab initio quantum potential energy calculations using Restricted Hartree-Foch method and the 6-113G basis set. An input file (see appendix 1) was created that instructed Gaussian to calculate a diatomic H₂ system energy at varying interatomic radii. The input file was constructed in such a way to calculate the potential energy of the system on both sides of the point where the energy was minimized by running the calculations over a range of interatomic distances which included the equilibrium bond length. This allowed for the determination of the interatomic distance when the potential energy of the system was minimized, i.e. the equilibrium bond length.

The data was then extracted from the end of the Gaussian log file and imported into Matlab for numerical and graphical analysis (see appendices 2 and 3). The energy of the system was then normalized, plotted against the interatomic distance, and fit to a third degree polynomial of the form: $E_p(r) = a_0 + a_1(r-r_0) + a_2(r-r_0)^2 + a_3(r-r_0)^3$ where r_0 is the equilibrium bond length. The system was then modeled as a harmonic oscillator with the a_2 term corresponding the spring constant k in Hooke's Law. From the spring constant, the fundamental vibrational frequency of the diatomic system was then calculated. Diatomic molecules of HF, LiF, and NaF were also analyzed in a similar fashion.

(Noah Knostman, Report #4, 20/20)

Results:

Tabulated results for the experiment are shown in table one. The values for tau and for the intensity were obtained by fitting the following function (5) to a plot of the fluorescent intensity. The function was written into Igor and the guesses for coefficient values were included to obtain a least squares fit for the function.

$$I_f = y_0 + A e^{-(t/\tau)} \quad (5)$$

Where I_f is the intensity of the fluorescence, y_0 is the y offset of the data, A is the intensity maximum or the unquenched intensity and τ is the fluorescence lifetime (see Figure 5 for a plot of the fluorescence intensity and the fit).

Table 1. Results for tau and intensity of the fluorescence signal of quinine hemisulfate monohydrate (40 μ M) in H₂SO₄ (50 mM) over a number of chloride ion concentrations.

entry	[Cl ⁻] (mM)	tau (ns)	A (V)
1	0	21.98	0.293
2	10	8.604	0.274
3	20	5.239	0.291
4	30	3.977	0.303
5	40	3.233	0.301
6	50	2.917	0.305
7	60	2.407	0.307
8	70	2.119	0.344
9	80	1.860	0.369
10	90	1.832	0.333
11	100	1.541	0.424

There was a persistent artifact that can be seen in all fluorescence spectra occurring at approximately 30 ns, this artifact was ignored in the fitting process (all fitted spectra can be seen in the appendix).

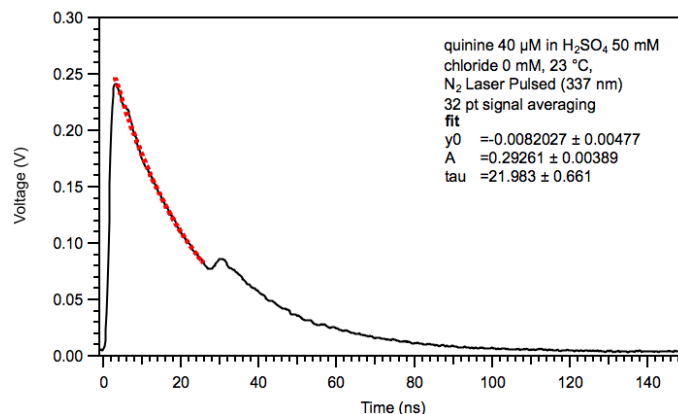


Figure 5. Plot shown the 32-point average of the fluorescence intensity of quinine in the presence of no chloride. Artifact seen to occur at approximately 30 ns.

The change in the time constant and the change in signal intensity can be visualized in several different ways. One being, a plot of all eleven intensity spectra over the range of chloride quencher concentrations (see Figure 6). Two, being plots of both the values for τ , and for A (the fit intensity of the spectra). The fit intensity is here used, due to the oscilloscope convolution causing broadening of smaller signals, and therefore, a predictable decrease in intensity as the solutions are quenched.⁴ In Figure six one can clearly see that the decay of the signal happens quicker as the chloride ion concentration increases. Spectra are shown on a smaller time scale to better display the features of each spectrum. Figure 7 shows a plot of the signal intensities as the chloride ion concentration increases. This plot shows the mean of the data with the points varying randomly above and below to show that there is no Stern-Volmer relationship in the signal intensities.

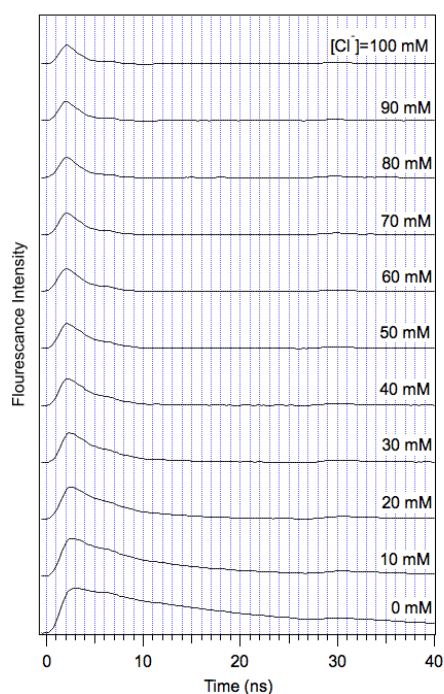


Figure 6. Spectra of all signal intensities from quinine fluorescence, titrated from chloride 0 mM to 100 mM.

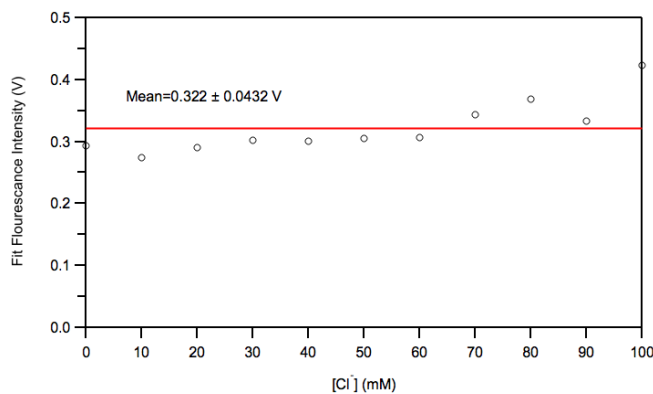


Figure 7. All fit signal intensities and line representing the mean of the data in the intensity dimension. There is a relatively small standard deviation in the intensity dimension suggesting that the peak intensity does not vary greatly and that there is no Stern-Volmer Relationship in the data.

A Stern-Volmer relationship, however, was found in the relationship between tau and the chloride concentration. Therefore, a plot was generated with tau plotted against the concentration of the chloride ion and was fit with a Stern-Volmer equation written thusly:

$$I_f = I_f^0 / (1 + K_{SV}[\text{Cl}^-]) \quad (6)$$

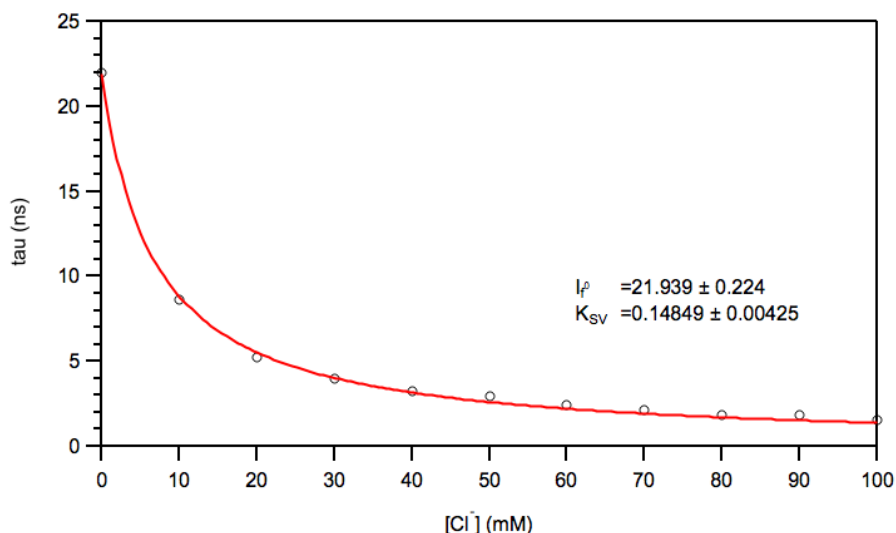


Figure 8. Stern-Volmer relationship between tau and the chloride ion concentration, the fit with the Stern-Volmer function in excellent agreement with the data.

Figure 8 confirms that the time constant of the aqueous quinine hemisulfate monohydrate changes as the chloride ion is introduced, and that the time constant decay follows a Stern-Volmer relationship with $K_{SV} = 0.148 \pm 0.00425 \text{ mM}^{-1}$.

(Adam Wilson, Report #1, 23/25)

Discussion:

When determining a molecule's wavenumber with the method used in this experiment an accurate a_2 value with a small uncertainty is necessary. This is achieved when the uncertainty of the measurement is less than one percent of the measurement value. This is achieved for all measured molecules as there is not an error that rises above one percent. The largest error of an a_2 occurred with LiH where the percent uncertainty of the a_2 value was found to be 0.254% of the measured a_2 . With an accurate a_2 value this will allow for accurate force constant value for the molecules. The same percent uncertainty carries over to the force constant values as there was only a simple unit conversion where all values were integers without uncertainty attached to them. Since there is a low uncertainty with our molecular force constants it would be expected that the calculated wavenumbers would correspond closely to the actual literature values for the specific molecules.

This appears to be that case, as the calculated wavenumbers end up being very close to the literature values. For H_2 the calculated wavenumber is only 0.02858 times greater than the literature value. For LiH, and NaH, the calculated wavenumbers are 0.03956, 0.6057 times larger than the literature values respectively. For KH the calculated wavenumber actually ends up being 94.133% of the literature value, 985 cm^{-1} . This may be due to the literature value being from a different source than the other molecules' values, or just due to uncertainty due to the variations in measurement by the Gaussian09

program. This could also be a reason for the difference in wavenumber values for the other molecules as well.

This uncertainty in wavenumber could potentially be reduced by changing the .inp file values to have larger number of data points collected with a smaller change in bond length between each reading. This change would also increase the certainty of where the ideal bond length for each molecule resides which experimentally have large uncertainties. Below, in **Table 4**, are the experimentally found bond lengths for LiH, NaH, and KH from this experiment compared to the bond lengths determined by T. Noro, M. Sekiya, and T. Koga.⁴ The H₂ bond length was found on Joseph DiVerdi's website.⁵

Table 4. Measured Ideal Bond Length and Literature Values

	H ₂	LiH	NaH	KH
x ₀ (pm)	74	160	192	237
x _{lit} (Å)	0.74	1.60	1.88	2.24

The same story seems to apply to the ideal bond lengths of the molecules as it did for their respective wavenumbers. There is a small discrepancy between the experimental values and the found literature values. The calculated bond lengths correspond almost exactly to those of the literature values with just a few picometers of discrepancy between the values.

When looking at the experimental values of wavenumber and ideal bond length there is little discrepancy when compared to the literature values. This shows that Gaussian09 as a predicting tool is useful as it gives relatively accurate measurements. This points to the harmonic oscillator model as being a good way to determine these values numerically. Additionally, these values make sense when compared between molecules. H₂ has the largest force constant, as well as the smallest ideal bond length. This makes sense as there is less shielding around a hydrogen molecule than compared to a sodium or potassium molecule. This allows for a stronger bond, reflected in the larger force constant, and leads to a smaller ideal bond length due to a larger restoring force acting upon the molecule's bond. Since KH has a smaller force constant we know that it will have a less strong bond between the molecules.

Since the force constant is small leading to a weaker bond, this also means that the overall average bond length will be longer as there will not be as large of a force acting to restore the bond length back to equilibrium which causes the average bond length to elongate. This can also be explained in terms of atomic shielding of the molecule as potassium has more electrons when compared to the other alkali earth metals and hydrogen. With more shielding there is a decrease in attractive force between the hydrogen and potassium molecules due to the presence of a greater number of electrons around the nucleus. This increased electron density decreases the attraction between the two molecules' nuclei which leads to the overall weaker bond between the molecules, and also the longer bond length as there is less force to hold them more closely together.

(Noah Knostman, Report #4, 5/5)

Conclusion:

Quinine has historically been used as a fluorescence-lifetime standard and the fluorescence-lifetime can be determined via laser technology.^{1,4} An in-lab apparatus to measure the fluorescence-lifetime of aqueous quinine over a range of chloride quencher concentrations was used. It was found that the fluorescence lifetime was 1.541 to 21.543 ns, however, these values are high compared to literature

values and this may be due to a malfunction in the laser. The Stern-Volmer constant determined from the values of the lifetime plotted against chloride quencher concentration was $K_{SV} = 0.148 \pm 0.00425 \text{ mM}^{-1}$. The mechanism by which the quinine hemisulfate monohydrate was quenched was likely a collisional mechanism because little change was seen in signal peak intensity, however tau changed drastically as chloride quenching agent was added to the solution.

(Thomas Misek, Report #4, 5/5)

References:

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- [2] Misek, Thomas M. Colorado State University, Fort Collins, Colorado. CHEM 475 Lab Report 3: Steady State Fluorescence of Aqueous Quinine with Determination of the Stern-Volmer Constant and Sensitivity Analysis. 2017
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