

Jessica Berger
advisor: Dr. Iannone
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Senior Research Paper
Chemistry 488

Independent Senior Research Project—
Fluorescence Anisotropy in Dianthracene

-INTRODUCTION-

Objective:

The purpose of this experiment is to measure the fluorescence anisotropy of dianthracene. Anisotropy relates to the probability that emitted radiation will be polarized parallel to the exciting radiation. If the anisotropy value is about .4, then all the emitting and absorbing dipoles are parallel in the molecular frame. If it is about -.2, then they are all perpendicular.ⁱ

Dianthracene :

Dianthracene was first synthesized in the nineteenth century. Its molecular structure was not identified until the late 1950s². This insoluble dimer of anthracene was first synthesized photochemically. It is widely used today to study photodimerization and photodecomposition, as well as molecular dynamics and inertial motions of its excited state. Its unusual butterfly shape, is shown below.

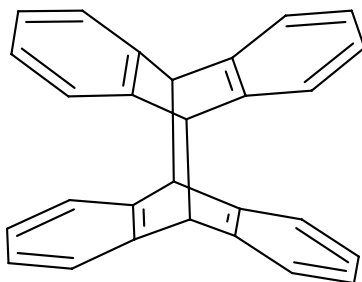


FIGURE 1: DIANTHRACENE, A HIGHLY SYMMETRIC DIMER OF ANTHRACENE

Dianthracene exhibits interesting photochemistry. In order to observe this, the molecule must be frozen into place. This is done by forming a “glass” – a solution of dianthracene in a solvent at liquid nitrogen temperatures. This frozen state will reduce molecular motion and rotation.

Dianthracene can be used to produce “sandwich” dimers of anthracene by photochemical cleavage. These dimers are lined up like the bread of a sandwich. The fluorescence spectra, absorbance spectra, and fluorescence lifetimes of these symmetric dimers have all been studied in great detail.³ If heated, dianthracene will decompose into anthracene. Its emission will give three large peaks⁴, all in the near-ultraviolet region, with the maximum being at 375 nm. These dimers are distinguishable from the fluorescence emission spectrum of dianthracene because its spectrum is a large, broad plateau.

Anisotropy:

Anisotropy is a measurement of the polarization of the light emitted from the molecule. If the excitation light is polarized, emitted light can be resolved into components, parallel and perpendicular to the exciting light, as shown in Figure 2.

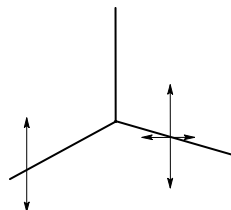


FIGURE 2: PARALLEL AND PERPENDICULAR INTENSITIES

For vertical polarization excitation, the signal has two components, S_{vv} and S_{vh} . The first subscript refers to exciting polarization and the second is the emission polarization. I_{\parallel} is the intensity of the emitted light polarized parallel to the exciting light:

$$I_{\parallel} = I_v = S_{vv}c_1, \quad \text{and similarly,} \quad [1]^5$$

$$I_{\perp} = I_h = S_{vh}c_2. \quad [1']^5$$

The constants of proportionality c_1 and c_2 account for the different sensitivity of optics and detector to horizontal and vertical polarized light.

The ratio $c_1 : c_2$ is wavelength dependent, and is called the G factor:

$$G = \frac{c_1}{c_2} \quad [2]^6$$

The anisotropy is given by:

$$A = \frac{I_{\parallel} - I_{\perp}}{I_{\parallel} + 2I_{\perp}}. \quad [3]^5$$

where A is the anisotropy, I_{\parallel} is the parallel intensity, and I_{\perp} is the perpendicular intensity. This can be equated to the signal of the fluorimeter, through equations 1 and 1'.

$$A = \frac{S_{vv} - GS_{vh}}{S_{vv} + 2GS_{vh}} \quad [4]^5$$

The anisotropy maximum and minimum values have been determined to be 0.4 and -0.2 for randomly oriented molecules.⁵

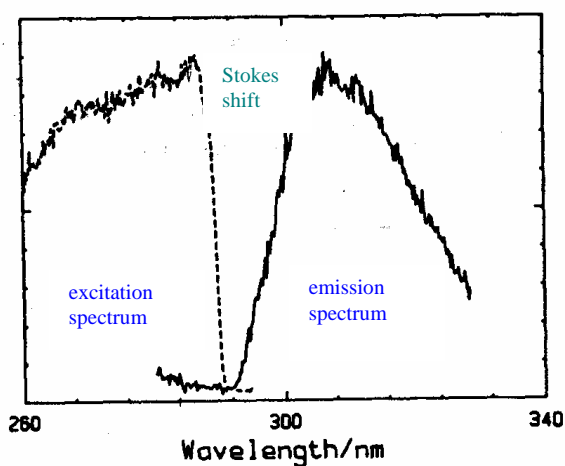
Measurement of the G factor is based on the fact that for horizontally polarized exciting light, if emission is detected at 90° to the excitation, both components of emission are perpendicular and therefore are equal. ⁵

$$I_v = I_h \quad [5]$$

$$c_1 S_{hv} = c_2 S_{hh} \quad [6]$$

$$G = \frac{c_1}{c_2} = \frac{S_{hh}}{S_{hv}} \quad [7]$$

Anisotropy is a tool that can lead to many conclusions about a molecule. It can be used to study the rotational motion of molecules in the excited state. For example, it can validate the Stokes-Einstein relationship- that rotation time is linearly dependent upon solvent viscosity⁷. It also can be used for determine whether fluorescence excitation and emission are caused by the same excited state.



Fluorescence spectra of solid dianthracene at 12K (ref. 3)

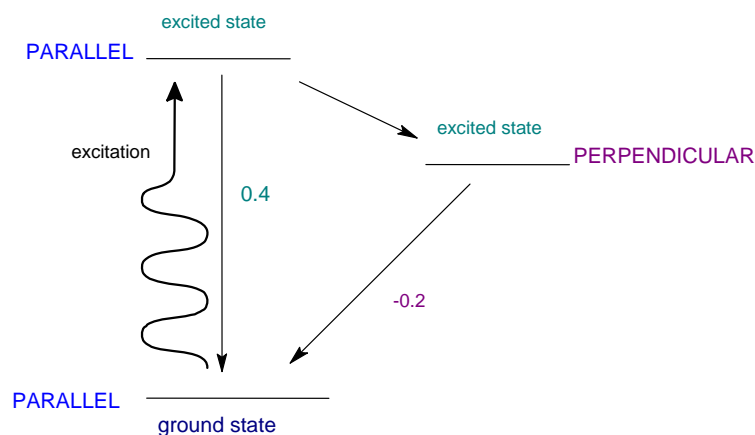


FIGURE 3: THE STOKES SHIFT AND THE PATH OF EMITTED LIGHT

The purpose of this experiment, as stated above, is to determine if the Stokes shift in dianthracene's spectrum is caused by non-radiative relaxation to a second electronic excited state. If the state is polarized parallel to the exciting light, the anisotropy value is 0.4. If the state is polarized perpendicular to the exciting light, the anisotropy value will be -0.2. This is shown in Figure 3.

-PROCEDURE-

To test the spectrophotometer and our techniques, a chemical with a known anisotropy was first tested. This was perylene in propylene glycol. In order to eliminate rotation, the molecule must be frozen into place. This is done by forming a glass at liquid nitrogen temperatures. The emission spectrum was then obtained, the anisotropy was measured and compared to the results reported in Lakowicz, *Principles of Fluorescence Spectroscopy*, reference 5.

For the work on dianthracene, three solvents were considered: methyltetrahydrofuran, methylcyclohexane² (both distilled, then passed through an alumina column), and polymethylmethacrylate. These were all tested for fluorescence in the region being scanned by exciting at 280 and graphing from 290 to 440 nm at liquid nitrogen temperatures. The best solvent was found to be polymethylmethacrylate. The PMMA was purified by precipitation-- dissolving in methylene chloride and then adding methanol. This process was repeated three times. Samples were prepared by casting a film from dianthracene and PMMA dissolved in methylene chloride.

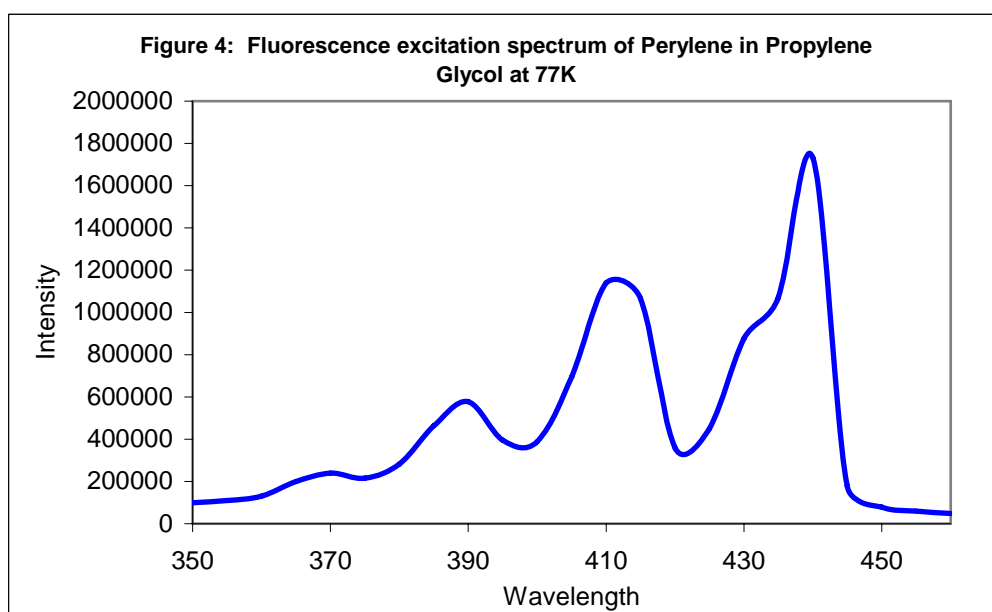
The quartz tube was scanned to determine if any light was emitted. The solvents must be tested for absorbance and fluorescence of light in the regions where dianthracene will emit and absorb. The fluorescence emission spectrum is obtained by exciting at 285 and scanning from 290 to 350 nm. The fluorescence excitation spectrum is found by monitoring emitted light at 320 nm and scanning from 260 to 295 nm.

The fluorescence excitation and emission spectra of dianthracene were obtained to show the Stokes shift. For the fluorescence emission spectrum, the sample was excited at 285 and scanned from 290 to 350. To find the fluorescence excitation spectrum, the sample was excited at 320 and scanned from 260 to 340. The anisotropy of the fluorescence of dianthracene was determined by exciting at 285 and scanning from 295 to 340. This was all done in liquid nitrogen, at 77 K.

-RESULTS-

Background – Perylene in Propylene Glycol:

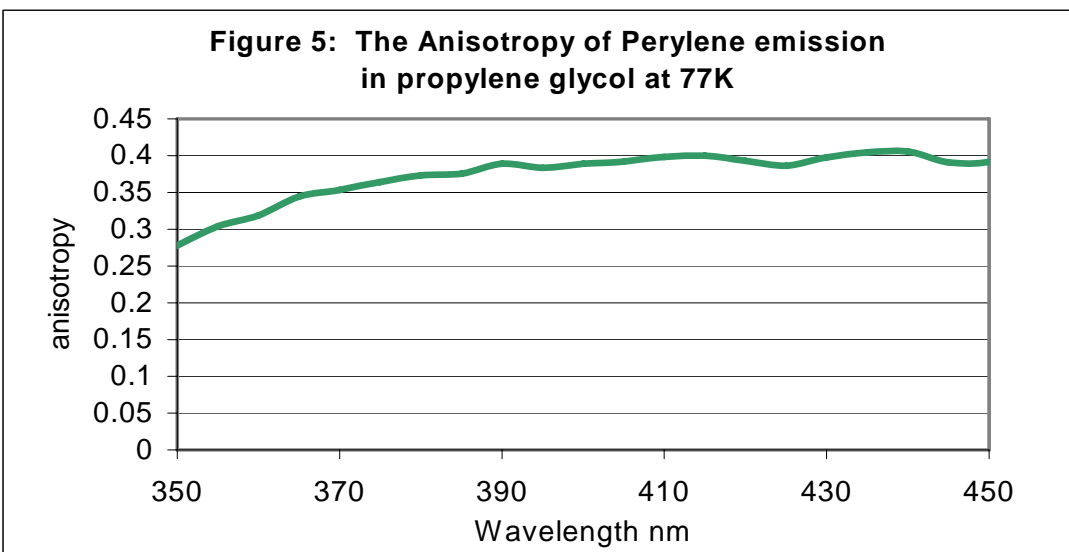
The perylene was dissolved in propylene glycol, degassed, cooled to 77K in liquid nitrogen, and the fluorescence spectrum was obtained. The perylene was excited at 350nm and emission graphed from 360 to 460nm. It was a three-peaked spectrum, with the maxima occurring at 390,



410, and 440 nm. See Figure 4.

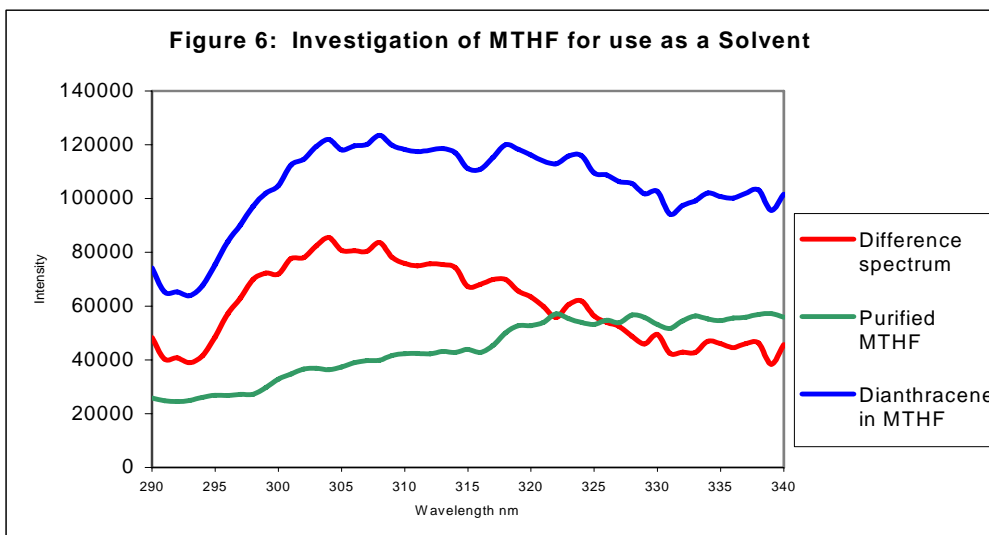
The G constant was determined for emission at 508 nm by measuring the two signals, S_{hh} and the S_{hv} . The value was found to be $.72 \pm .01$.

The anisotropy of the perylene was then obtained. The sample was excited at 345 and graphed from 350-450 nm, to compare to the known data. The value of the anisotropy was close to 0.4, as expected. See Figure 5.



Solvents :

Methyltetrahydrofuran (MTHF)

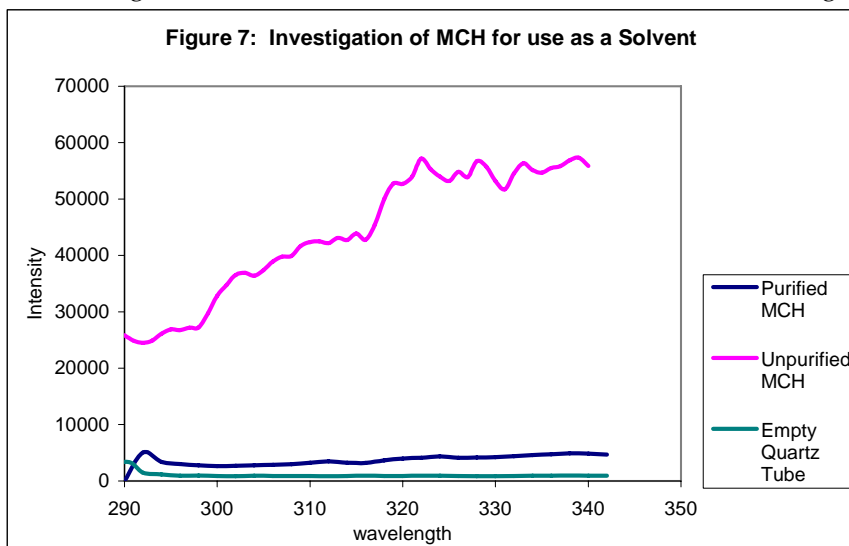


To determine the anisotropy values, various solvents were tried. The first was methyltetrahydrofuran (MTHF). It was seen to fluoresce in the region being studied. It was excited at 280 and scanned from 290 to 340. A glass of dianthracene in MTHF was then formed

and scanned at the same wavelengths. These two spectra were then subtracted from one another. See Figure 6.

Methylcyclohexane (MCH)

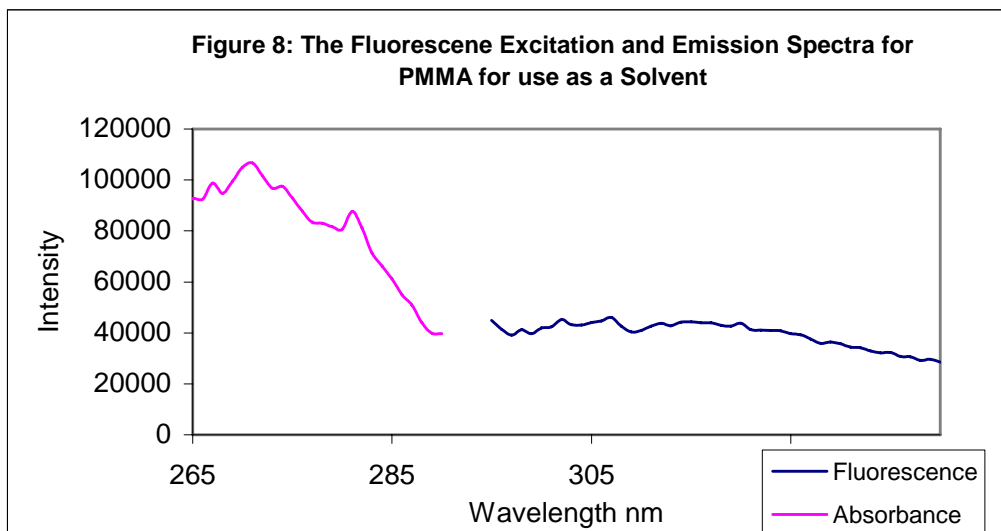
Methylcyclohexane (MCH) was measured next. It was excited at 280 and scanned from 290 to 340. In its unpurified state, it fluoresced strongly. After purification through a column of aluminum oxide, it emitted only slightly more light than the empty quartz tube. This was excited in the same region and did not fluoresce where anthracene would emit light. See Figure 7.



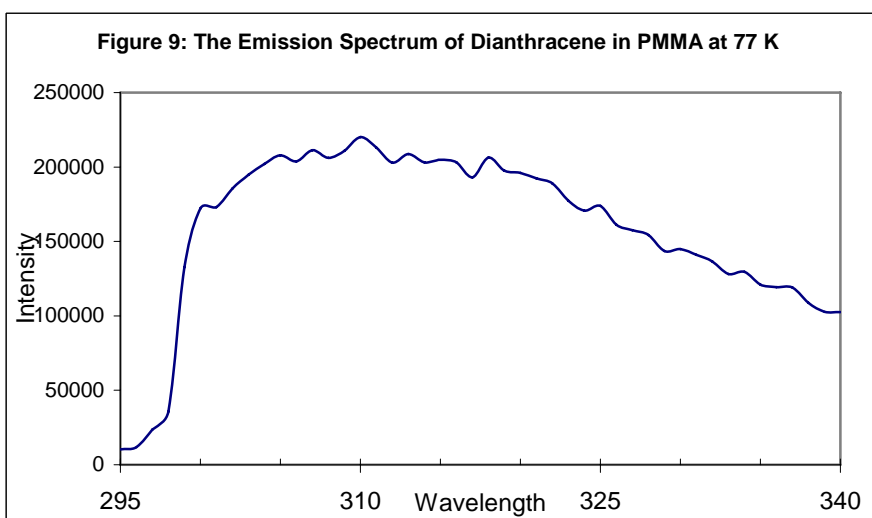
Dianthracene was then dissolved in MCH. The fluorescence due to dianthracene was weak and indistinguishable from background. This is apparently due to low solubility of dianthracene in this solvent.

Polymethylmethacrylate (PMMA)

PMMA was the next solvent that was investigated for use. It was purified and dissolved in methylenechloride and then cast into a thin film. Its fluorescence and excitation spectra after purification were obtained and can be seen in Figure 8. For fluorescence, it was excited at 285 nm and then scanned from 295 to 340 nm. For absorbance, light was emitted at 320 nm, and then scanned from 260 to 290 nm.



A film of dianthracene and PMMA was then made. It was excited at 285 and scanned from 295 to



340 nm at liquid nitrogen temperatures. Results are shown in Figure 9.

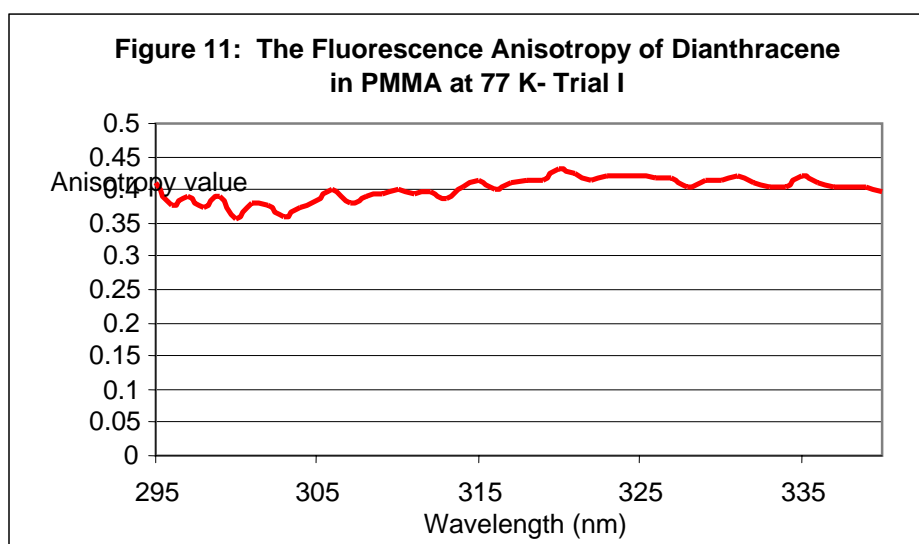
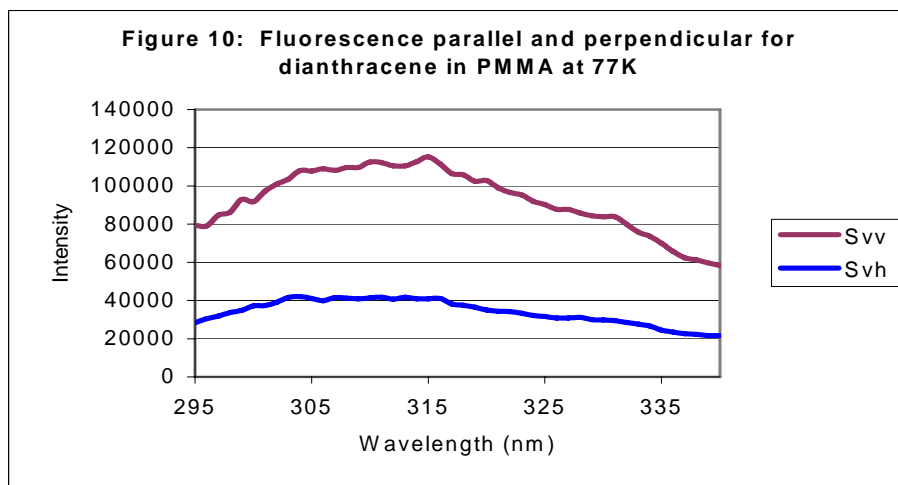
G factor for Dianthracene in PMMA:

The G factor was determined using dianthracene in PMMA, on the same day that spectra were obtained. The average value of G was 1.24 ± 0.02 for trial 1 and $1.98 \pm .08$ for trial 2.

Anisotropy of Dianthracene in PMMA – Trial 1:

The anisotropy of dianthracene was measured in two trials. These trials were performed in the same manner, except the anisotropy for trial 2 corresponds to the 305 through 320 nm wavelengths, and trial 1 had a range of 295 to 340 nm. For unknown reasons, the G factor was not the same for the two trials. However, the emission anisotropies agree within 3%. The anisotropy of trial 1 was found to be $0.401 \pm .02$. The anisotropy of trial 2 was calculated to be $0.389 \pm .02$. The average anisotropy from the two trials is $.39 \pm 0.07$.

The anisotropy was found by measuring the S_{\perp} and the S_{\parallel} and then using equation 4 to calculate the anisotropy. The data from trial 1 are shown in Figures 10 and 11.



DISCUSSION-

Background – Perylene in Propylene Glycol:

Performing this was a large help in becoming familiar with the instrument and being comfortable with the anisotropy value. As shown in the plot from *Principles of Fluorescence Spectroscopy* by Joseph R. Lakowicz, the anisotropy value should peak at a value of 0.4 around 375 nm. This is the value that was observed, and is consistent with the known anisotropy of perylene in propylene glycol.

Solvent:

MethylTHF was discarded as a solvent because of strong fluorescence. Its intensity had counts of around 80,000. Methylcyclohexane was not used as a solvent because the dianthracene did not dissolve very well. The intensity of this was low, as seen in figure 8, but in figure 9, the light being emitted from the sample of dianthracene dissolved in MCH was due mostly to the solvent, but its intensity was low. This proves that dianthracene did not dissolve in methylcyclohexane. Purified polymethylmethacrylate was determined to be the best solvent, because the fluorescence of dianthracene was at least double the fluorescence of PMMA, and this polymer also displayed very weak fluorescence.

Anisotropy:

The anisotropy value was determined to be 0.395 ± 0.07 . This corresponds to the maximum value for anisotropy, which determines that fluorescence does not originate from an electronic state that is perpendicular to the originally excited state.

Conclusion

A Stokes Shift of 10 nm corresponds to an energy difference of about 2.3×10^{-20} J and a Boltzmann factor of about 5×10^{-10} at 77K. If the Stokes shift is the result of relaxation between excited states, thermal population of the upper state is negligible.

The Stokes Shift could be from relaxation within the same state, due to a geometry change, or relaxation to a new state. Our results show that if this second state does exist, it must have the same symmetry as the initially excited state.

-References-

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- 7 G. Porter, P.J. Sadkowski, C.J. Tredwell. *Chemical Physics Letters*.. "Picosecond Rotational Diffusion in Kinetic and Steady State Fluorescence Spectroscopy." 1977.