EVALUATION OF WAVELENGTH SHIFTERS FOR SPECTRAL SEPARATION OF BARIUM FLUORIDE EMISSIONS

by

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To my parents who taught me the importance of an education and
to my wife who encouraged me to persevere

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CHAPTER I

INTRODUCTION

1.1 Motivation

Within the realms of nuclear robotics and radioactive waste management, there is a need to characterize intense gamma-ray fields. One proposed solution is a gamma-ray imaging camera for mapping the intensity and energy (between 0.5 and 10 MeV [OTT 89]) of a radiation field. In the expected severe conditions under which the gamma-camera must operate, scintillators were chosen as the overall best choice as the gamma radiation detector. The need for a detector that is fast, radiation hard, and has good stopping power for incident gamma rays is apparent. Organic scintillators, for example BC-400, that are typically used by the high energy physics community are fast and radiation hard but fail to have sufficient stopping power for MeV gamma rays. The medical imaging community typically use inorganic scintillators which have good stopping power for gamma rays and can withstand a moderate radiation dose. One of the mainstay scintillators in medical imaging is bismuth germanate (BGO) which has one of the highest stopping powers. Using BGO, a mechanically collimated gamma-ray imaging camera was demonstrated [DEV 90]. Another inorganic scintillator that is the mainstay of the medical imaging community is NaI(Tl). NaI(Tl) has nearly the highest measured luminosity for a scintillator.

The major disadvantage of both NaI(Tl) and BGO is that the signal read out is slow and would ultimately limit the radiation field that the gamma-ray imaging camera could operate in because of pulse pile-up. While barium fluoride (BaF_2) is not ideal it may represent the best compromise between speed, luminosity, stopping power and radiation hardness. In this dissertation, I will discuss briefly the primary disadvantage of BaF_2 and the remainder of the dissertation is devoted to the attempts to circumvent the troublesome feature.

1.2 Basic properties of BaF_2 and comparison to other scintillators

Barium fluoride (BaF_2) scintillation was discovered in the early 1970's [FAR 71]. The light output was measured to be $\approx 10\%$ of NaI(Tl) and to have a single (630 ns) decay time constant. Over a decade later, a fast (0.8 ns) decay time constant [ERS 82, LAV 83] was discovered using a fused silica endwindow photomultiplier tube (PMT). The total luminosity of BaF_2 was determined to be $\approx 20\%$ of NaI(Tl), with 20% of the total BaF_2 emissions having a 0.8 ns decay time constant. Since the discovery of the fast emission there has been an increased interest in discovering other fast, high atomic number scintillators for detection of high energy gamma rays [DER 90, DER 92, LEC 92]. The quest is for a scintillator that is as fast as BaF_2 , has the stopping power of BGO and the luminosity of NaI(Tl). Table 1.1 is a summary of some of the more interesting recent discoveries along with BC-400, NaI(Tl) and BGO. (The list is not exhaustive and includes only scintillators that can be found naturally or can be grown into a crystal of at least 1 cm^3). Although data on all the interesting properties are not available, Table 1.1 indicates that BaF_2 appears to be overall superior to the newer scintillators when comparing radiation hardness,

Table 1.1: Properties of Recently Discovered Scintillators and Comparison to "Traditional" Scintillators

Properties	BaF ₂ [LAV 83]	NaI(Tl)	BGO	BC-400	CeF ₃ [AND 89] [MOS 89]	LaF ₃ :Nd ³⁺ [SCH 88a]	LSO:Ce [MEL 92]
Density (g/cc)	4.87	3.67	7.13	1.03	6.16	5.9	7.4
Radiation length (cm)	2.1	2.6	1.1	11.0	1.7	1.8	1.1
Decay constant* (ns)	0.8 (0.20) 600 (0.80)	230 (1.0)	60 (0.09) 300 (0.91)	2.4 (1.0)	27 (1.0)	6 (?) ≈1000 (?)	40 (1.0)
Peak emission wavelength (nm)	220 310	415	505	423	310	173 354,381,413	420
Total PE Yield	0.20	1.0	0.10	0.28	0.05	0.02 ⁺	0.75
Index of Refraction	1.56	1.85	2.15	1.58	1.68	1.7	1.8
Radiation Hard	Y**	Y	Y	Y	Y	Y	?

* Percent of the total signal is in parenthesis

** See [TZA 69, MAJ 87, WOO 92]

+ Estimate of only the fast component

scintillation decay time and fast scintillation yield.

Figure 1.1 shows the scintillation decay time spectrum of BaF_2 . The fast 0.8 ns and the slow 578 ns decay time constants are apparent. Figure 1.2 shows the emission spectrum of BaF_2 when excited with gamma rays ¹. One of the interesting properties of BaF_2 is that a separation of the emissions in energy (wavelength) is approximately a separation of the emission components with different fluorescence decay times [LAV 83]. The similarity between spectral and temporal separation will be discussed further in chapter IV.

The fast emissions of BaF_2 have peak wavelengths of 220, 195 and 170 nm, listed in decreasing order of intensity. Borosilicate endwindow photomultiplier tubes strongly attenuate light below 300 nm so use with BaF_2 results in detecting only $\approx 38\%$ of the total emissions, and almost none of the fast emissions. A gamma-ray spectrometer utilizing fused silica endwindow PMTs (useful for measuring wavelengths down to ≈ 180 nm) typically yields an energy resolution of 11% full-width at half maximum (FWHM) at 662 keV [KOB 88] resulting from the collection of ≈ 560 photoelectrons (PE) [WEI 91]. Measuring only the fast emissions of BaF_2 , the energy resolution is 30% FWHM [KOB 88] at 662 keV as a result of measuring ≈ 83 PE [WEI 91].

1.3 Wavelength shifting BaF_2 emissions

Wavelength shifters (WLSs) are typically organic compounds that absorb incident energy in the form of UV photons and then release the absorbed energy by emitting visible photons. The emitted photons are at a longer wavelength (lower energy) than the absorbed photons, hence the name “wavelength shifting”. WLSs can be chosen to

¹The details of the measurements shown in figures 1.1 and 1.2 are presented in chapter III. The presentation here is an introductory fashion for the reader.

Figure 1.1: Scintillation decay spectrum of Barium Fluoride measured in 0.556 ns bins and rebinned to 5.56 ns/bin for display. The fitted line is not shown.

Figure 1.2: Barium Fluoride emission spectrum when excited with 662 keV gamma rays.

shift BaF_2 emissions above the cut-off wavelength of borosilicate glass. For some applications the expense of a fused silica PMT may be avoided by using WLSs and conventional borosilicate PMTs. Figure 1.3 shows an arrangement which could be used for shifting BaF_2 emissions (the long-pass filter would not be needed). The WLS absorbs the UV emissions from BaF_2 , $I_{0,\text{BaF}_2}(\lambda, t)$, and with probability Q_f (fluorescence quantum efficiency) releases the absorbed energy by emitting photons, $I_{\text{WLS}}(\lambda, t)$, isotropically at a characteristic wavelength and decay time that is dependent on the WLS. Several researchers have used wavelength shifting techniques in various ways to detect the deep UV emissions of BaF_2 with borosilicate endwindow PMTs. The most common way is to vacuum evaporate a fluor onto the face of the scintillator that is coupled to the PMT [DAF 87, KLA 88, NAM 89, YAN 89]. Vacuum evaporation leaves a whitish translucent film on the scintillator which results in optical trapping, and self-absorption of the shifted light, as well as reflection of the shifted and unshifted light. Fluors dissolved in a polymer matrix [GIE 88, GOR 86, LOR 86] are physically more rigid than vacuum evaporation, and is a medium that is transparent to the solute emissions (but not necessarily to BaF_2 emissions). An interesting idea that has been investigated was to combine BaF_2 powder with the fluor in a polymer matrix [SHI 86] to make large area detectors. Unfortunately the detector had very poor energy resolution. And lastly, liquid wavelength shifter solutions [DEV 92] have been used which allow for better photon yield compared to vacuum evaporation and offer a medium that is more transparent to BaF_2 emissions than typical polymers.

1.4 Separation of the fast and slow emissions of BaF_2

For high count rate applications, it is advantageous to collect the fast photons and eliminate the slow. Several researchers have shown reasonable separation of

the BaF_2 emission components using various techniques. The most straightforward of these techniques uses fast gated integration [LAV 83] to measure only the first ≈ 50 ns of the PMT anode pulse. Gated integration does significantly separate the fast and slow components of the electronic signal, but the slow emissions appear as afterglow in the crystal resulting from scintillation pulse pile-up at high count rates. Because of afterglow, the gated integration technique is not practical for high count rate applications. A more robust technique uses a solar blind (CsTe) photocathode PMT [KOB 88, WEI 91]. The CsTe photocathode has a 4:1 quantum efficiency ratio for the detection of fast and slow BaF_2 photons thus resulting in a fast to slow photoelectron yield ratio, R , of ≈ 1 . Doping BaF_2 with lanthanum [SCH 89c, WOO 89] has been used as a means to quench self-trapped excitons thus decreasing the mechanism for slow photon emission, resulting in $R \approx 1$, with a slight reduction in the fast PE yield. Increasing crystal temperature [BEA 70, SCH 85, WIS 87] results in the same effect as lanthanum doping. Self-trapped excitons are thermally quenched, so by increasing the temperature of the crystal, the slow component is reduced. For both lanthanum doping and elevated crystal temperature, slightly higher values of R are possible, but they come at the expense of decreased fast photoelectron yield. The value of R obtainable with solar blind photocathodes is set by physical limitations of the photocathode material properties.

Another technique that could be employed to spectrally separate BaF_2 emissions is optical band-pass filtering. A band-pass filter can be placed between the crystal and PMT, resulting in the region of the electromagnetic spectrum that is not of interest to be blocked from the PMT. Unfortunately the signal of interest is also attenuated, typically a peak transmission of 30% is obtainable at 220 nm with conventional thin film technology band pass filters. The low efficiency of a band pass

filter results in this technique impractical for our application.

1.5 Spectral separation of BaF_2 emissions using WLS

One of the problems with the techniques described in section 1.4 is the fast emissions are in the UV where they are difficult to detect with a typical PMT. Using wavelength shifting techniques, the absorbed fast emissions are reemitted at a longer wavelength that may be better matched to the spectral response of a conventional PMT.

There are two general techniques available for spectrally separating the BaF_2 emissions: in-line (see figure 1.3) and orthogonal (see figure 1.4). This dissertation determines the properties of the WLS that are needed for these two techniques to be viable for the spectral separation of BaF_2 emissions and to assess if the needed properties are physically possible and acceptable for application to BaF_2 . Aside from the difference in absorption characteristics of the WLS, the other necessary properties are the same for all the techniques: fast decay time, high fluorescence quantum efficiency, and emission in the optimum PMT sensitivity range. There are other additional considerations that may also need to be addressed, but they are secondary to the four presented above and will not be presented in detail. To preserve the inherent speed of the BaF_2 scintillator, the fluorescent decay time of the WLS should be fast, preferably on the order of 1 ns. From the standpoint of energy spectroscopy, the photon yield must be preserved as much as possible, which is determined by the quantum efficiency of the WLS. The energy resolution is also a function of the spectral matching of the WLS fluorescence emission and the PMT sensitivity. In this dissertation, the absorption, fluorescence emission, decay time constant and quantum efficiency of several WLSs will be presented as well as

Figure 1.3: Schematic diagram of the detection geometry for an in-line measurement

Figure 1.4: Schematic diagram of the detection geometry for the perpendicular measurement

the degree of spectral separation that is measured. Discussion on the feasibility of spectral separation using WLS will be discussed along with the limitation to the technique. This dissertation primarily investigates two variations of the in-line technique; the orthogonal technique, which was developed by Lorenz et al. [LOR 92], will be presented for completeness.

CHAPTER II

ORGANIC MOLECULAR PHOTOPHYSICS

2.1 Electronic Structure of Organic Molecules

The structure of organic molecules is largely determined by the electronic structure of the carbon atom. The electronic configuration of the ground state of the carbon atom ($Z=6$) is $1s^2 2s^2 2p^2$. In forming compounds, one of the $2s$ electrons can be excited into a $2p$ state so that the electronic configuration of a carbon atom is $1s^2 2s 2p^3$ [BIR 64]. Covalent bonds are formed by atoms whose outer electron pairs are shared by both atoms. Overlapping atomic orbitals form molecular orbitals of these covalently bound atoms. The four valence orbitals of carbon, one s and three p orbitals (p_x, p_y, p_z), form hybridized molecular orbitals of three different configurations: sp^3 , sp^2 , and sp . The sp^3 hybridization is four equivalent hybrid orbitals that are directed at the corners of a regular tetrahedron. The sp^3 hybridization consists of four σ electrons that form σ bonds. σ bonds are symmetrical about the bond axis and the plane of the molecule and generally do not contribute to luminescence. Because σ electrons are tightly bound, $\sigma \rightarrow \sigma^*$ transitions generally occur only for $\lambda < 200$ nm. The sp^2 hybridization leaves the atomic p_z orbital unchanged and three equivalent hybrid orbitals (sp^2) are formed from the s , p_x , and p_y orbitals. The sp^2 orbitals lie in the same plane and form σ bonds with other atoms. The p_z atomic

orbital is symmetrically located either above or below the plane of the sp^2 orbitals and consist of π -electrons. It is the excited states of π -electrons, typically found in aromatic and conjugated molecules, that are responsible for luminescence and are an essential element of an efficient WLS. Typically $\pi \rightarrow \pi^*$ transitions are highly probable and result from the deposition of less energy than a $\sigma \rightarrow \sigma^*$ transition. The sp hybridization has the p_y and the p_z orbitals unchanged and two equivalent sp hybrid orbitals are formed from the s and p_x molecular orbitals. The sp orbitals form σ -bonds which do not lead to luminescence, but the p_y and p_z orbitals form two carbon-carbon π -bonds which does lead to luminescence.

Unsaturated molecules containing an atom having a lone pair of electrons often give rise to a transition of lower energy than $\pi \rightarrow \pi^*$. The lone pair of electrons occupy a n -orbital having a shape similar to that of an atomic p -orbital. An electron in a n -orbital can undergo a transition to an upper π^* -orbital, i.e. $n \rightarrow \pi^*$. These transitions have a low probability of occurrence and result in an excited state that has a comparatively long decay time constant.

2.2 Absorption

Absorption spectra of condensed hydrocarbons and other aromatic and conjugated molecules contain a sequence of absorption bands in the visible and UV regions of the electromagnetic spectrum. These transitions are attributed to singlet π -electronic excited states. The π -electrons are not localized and are therefore less tightly bound than the localized σ and n -electrons, thus requiring less energy for excitation. Typically, excitation of σ and n -electrons by photons having a wavelength above $\lambda \approx 200$ nm is unlikely but excitation of π -electrons is efficient and highly probable in this region. In this work, the interest is in highly efficient wavelength

shifting of BaF_2 emissions; therefore the focus is on molecules having π -electrons.

The total energy (E_t) of a molecule (excluding translational and internal nuclear energy) is the sum of three components: the electronic energy (E_e), the vibrational energy (E_v) and the rotational energy (E_r).

$$E_t = E_e + E_v + E_r \quad (2.1)$$

A state involving electronic and vibrational energy is referred to as a vibronic state, and a transition between two such states as a vibronic transition. Vibronic transitions occur in the visible and UV region, and transitions to and from rotational energy levels can be neglected at room temperature with liquid solutions. Figure 2.1 is a schematic representation of various vibronic transitions. As represented in the figure the energy levels are discretized. At room temperature molecular rotation, thermal broadening and/or solvent interaction effects blur the vibronic structure of each electronic band system into a sequence of a few relatively broad maxima, as depicted in the absorption spectrum of 9, 10 diphenylanthracene seen in figure 2.2.

A vibronic state is characterized by certain basic properties: excitation energy, multiplicity, symmetry, and parity. The multiplicity selection rule has a major influence on photophysical processes in aromatic molecules. The rule states that electric dipole transitions between electronic states of different multiplicity are spin-forbidden. If a π -electron is excited without a change of spin, the resultant excited electronic state is said to be in a singlet state (the state is denoted, S_{nm} , where n and m signify the electronic and vibrational state, respectively). If a π -electron is excited and its spin reversed, the resultant excited electronic state is called a triplet state. The terms "singlet" and "triplet" refer to the multiplicity of the electronic state. Due to spin-orbit interaction (electron spin and orbital angular momentum), which couples the eigenfunctions of a singlet and triplet state, there is a small but

Figure 2.1: Jablonski diagram illustrating the energy level diagram of a simple organic molecule

Figure 2.2: Absorption spectrum of 9, 10 diphenylanthracene

finite probability of a singlet-triplet transition, which would otherwise not exist. This probability is particularly small with aromatic hydrocarbons because of the low atomic number of the constituent atoms. Inclusion of higher atomic number atoms into a molecule or solvent increases spin-orbit coupling thus increasing the probability of a singlet-triplet transition. The net effect will be discussed in section 2.7.4.

2.2.1 Decadic molar extinction coefficient

For monochromatic light of intensity $I_0(\lambda)$ perpendicularly incident on a sample of thickness x (cm), and molar concentration b (M, molar), the intensity $I(\lambda)$, of the transmitted beam is given by the Beer-Lambert Law:

$$I(\lambda) = I_0(\lambda)10^{-\epsilon(\lambda)bx} \quad (2.2)$$

where $\epsilon(\lambda)$ is called the decadic molar extinction coefficient, or more simply the molar extinction coefficient. $\epsilon(\lambda)$ is a measure of the absorptivity of a molecule and is inherently related to the optical absorption cross-section of the molecule.

The first absorption band is attributed to the transition of the ground state to the first excited state ($S_0 - S_1$) and is normally relatively weak ($\epsilon \approx 10^3$ l/M-cm). Transitions to the second ($S_0 - S_2$) and third ($S_0 - S_3$) excited singlet π -electronic states are stronger ($\epsilon \approx 10^5$ l/M-cm) [BIR 64]. Figure 2.2 depicts the absorption spectrum of 9,10 diphenylanthracene (DPA).

The relationship between $\epsilon(\lambda)$, the fluorescence emission, decay time constant and quantum efficiency is discussed in the following sections.

2.3 Luminescence

Following an absorption, a typical fluor is in an excited vibronic state. To return to equilibrium the molecule must expel the excess energy. The dissipation of

energy can come either radiatively or non-radiatively. Luminescence is defined as the emission of photons at a characteristic wavelength as a result of a radiative transition to return the molecule to equilibrium. In organic fluors, luminescence is an inherent molecular property that is associated with conjugated and aromatic organic molecules and arises from the covalent bonding of these molecules. Luminescence can be subdivided into at least three categories depending on its origin: phosphorescence, delayed fluorescence and fluorescence.

π -electrons that are excited into one of the vibrational levels of the first excited singlet state lose their energy rapidly ($\approx 10^{-15}$ s) by colliding with surrounding molecules. The loss of kinetic energy drops the π -electron into the lowest vibrational state of the first excited singlet electronic state, S_{10} . π -electrons that are excited into a state higher than S_1 undergo a process known as *internal conversion*, where the molecule passes from a vibrational level of an upper state to a vibrational level of the lower state having the same total energy. This process is depicted in figure 2.1. Because the time scale of these molecular vibrations are on the order of 10^{-12} s, the molecule typically reaches thermal equilibrium before any luminescence occurs. The rapid return to S_1 is the reason for the absence of emission from the higher singlet states. Through internal conversion and loss of kinetic energy by collision with neighboring molecules, the molecule may temporarily reside at the S_{10} state. A fraction of the molecules in the excited state S_{10} may undergo a radiationless transition into a triplet state, T_1 . The *intersystem crossing* transition involves spin reversal through spin-orbit coupling. Phosphorescence is defined as the emission of a photon as an electron makes a transition from the lowest vibrational level of the first excited triplet state, T_{10} , to one of the vibrational levels of the ground singlet state, S_{0m} . Typically molecular energy levels are such that the triplet levels have a

lower energy than the corresponding singlet levels, which results in the wavelength for phosphorescence emission being longer than delayed fluorescence or fluorescence. Also because of the low transition probability, the radiative lifetime for phosphorescence typically is on the order of 10 ms or possibly longer. Due to the long decay time associated with phosphorescence, it is advantageous for the application at hand to employ molecules that do not exhibit much or any phosphorescence.

Once the electron is in the triplet state, the molecule can return to equilibrium either by emission of phosphorescence, or it may remain in T_{10} long enough to acquire sufficient thermal energy to return to the singlet state, S_{10} , depicted as transition β in figure 2.1. Subsequently, the π -electron can make a transition back to the S_{0m} by emission of a photon at the characteristic wavelength for fluorescence. Because of the delay associated with receiving sufficient thermal energy to make the transition from T_{10} to S_{10} , delayed fluorescence has a non-exponential decay time, with a period on the order of 1 ms. As with phosphorescence, delayed fluorescence has time characteristics that are too long to be useful for applications involving BaF_2 . Since the emission is from S_{10} , the emission wavelength of delayed fluorescence is the same as fluorescence.

Fluorescence is defined as the emission of a photon of energy equal to the energy lost by the π -electron undergoing a transition from S_{10} to S_{0m} . Fluorescence emission is typically the quantum mechanically allowed transition (i.e., high efficiency) and has a decay time constant of 1 to 100 ns. The fast decay time constant and high quantum efficiency makes fluorescence the decay mechanism that is studied in this dissertation work.

The absorption and fluorescence processes can also be described with the aid of the Stokes Law and figure 2.3. Figure 2.3 is a 2-D representation of the potential

energy versus the diatomic interatomic distance. The energy levels are actually discrete, the curves are used to represent the ends of the discrete states. The minimum of each state is at a different interatomic distance, corresponding to the electron in the excited state being less tightly bound and therefore somewhat extended in space. The extent of this separation of minima as well as the shape of the potential energy curve determines the amount of self-absorption. The Franck-Condon principle states that the most probable transition is that involving no change in the nuclear position or momentum. The principle is based on the fact that light absorption takes place within $\approx 10^{-15}$ s which is within the vibrational period of the incident light. Thus transitions are represented as vertical lines in figure 2.3. The ground state of the molecule may correspond to the vibrational level labeled CD (S_{00}). The most probable transition is from the midpoint (E) of the vibrational level CD, to the excited state XY. The transition is represented by the solid vertical line EP. Less probable transitions, resulting in weaker absorption cross sections, occur on either side of the EP transition (shown as dashed lines). Once in the excited state, at a vibrational level PQ, the molecule rapidly loses kinetic energy by colliding with neighboring molecules and falls to the lowest vibrational level RS (S_{10}). From the vibronic state represented as RS, the electron can undergo a transition back to the ground state resulting in fluorescence emission. The Franck-Condon principle again states that the most intense emission band corresponds to the solid vertical line drawn from the midpoint of RS to B. Weaker emissions are observed adjacent to AB. Following the transition to the ground state, the electron then loses kinetic energy by colliding with neighboring molecules and dropping back into the lowest vibronic state, CD. The energy difference between the excitation photon and the emission photon represented in wavenumber (inverse wavelength) is termed Stokes shift. The term comes from

Figure 2.3: Simplified potential energy curve of a diatomic molecule [PAR 68].

Stokes Law that states: the wavelength of fluorescence is longer than the excitation wavelength.

2.3.1 The Einstein Coefficient

The absorption and fluorescence spectra usually have "mirror" symmetry. Recall that, absorption is defined as the transition of a π -electron from S_{00} to S_{1m} , whereas, fluorescence is characterized as the transition from S_{10} to S_{0m} . The vibrational levels of the various electronic states are similar, resulting in the symmetry of the absorption and emission spectra. The Einstein A and B coefficients quantifies the relationship between fluorescence and absorption. The following are the results that Albert Einstein used first to describe the steady state of a light absorbing system in equilibrium with its surroundings. The coefficients have also been shown

to be applicable to band spectra where they play an important theoretical role in spectroscopic measurements. An abbreviated derivation of these coefficients can be found in Birks [BIR 70] and will not be reproduced here. The Einstein A coefficient, $A_{u \rightarrow l}$, is the probability per unit time that a molecule will make a transition from an upper electronic state u to a lower electronic state l by spontaneous emission. The Einstein B coefficient, $B_{l \rightarrow u}$, is defined as the probability of stimulated absorption per unit time from l to u and is defined as:

$$B_{l \rightarrow u} \propto \frac{1}{\bar{\nu}_{l \rightarrow u}} \int_{lu} \epsilon(\bar{\nu}) d\bar{\nu} \quad (2.3)$$

The integral is over the vibronic bands $l \rightarrow u$, $\bar{\nu}$ is the wavenumber of radiation, and $\epsilon(\bar{\nu})$ is the molar extinction coefficient of the molecule at wavenumber $\bar{\nu}$ and $\bar{\nu}_{l \rightarrow u}$ is the mean wavenumber of the absorption spectrum.

The relationship between the Einstein A and B coefficients is [BER 71]:

$$A_{u \rightarrow l} \propto \bar{\nu}_{l \rightarrow u}^3 B_{l \rightarrow u} \quad (2.4)$$

therefore,

$$A_{u \rightarrow l} \propto \bar{\nu}_{l \rightarrow u}^2 \int_{lu} \epsilon(\bar{\nu}) d\bar{\nu} \quad (2.5)$$

The relationship between $B_{l \rightarrow u}$ and $A_{u \rightarrow l}$ indicates that the probability of absorption and luminescence is proportional to the area under the absorption spectrum. This relationship is a very powerful theoretical tool when evaluating WLSs, and will be referred to in the following sections.

2.4 Decay Time Constant

The decay time constant of a fluor is determined in the following manner. Let $N(t)$ be the number of excited molecules at time, t , then dN/dt is the number of

molecules that de-excite per unit of time and is proportional to $-kN(t)$, which can be written:

$$N(t) = N_0 e^{-kt} \quad (2.6)$$

or

$$I(t) = I_0 e^{-kt} \quad (2.7)$$

where k is the total rate constant which is determined by the rate a molecule dissipates energy, and $I(t)$ is the photon intensity at time t . The subscript 0 denotes the initial quantity.

Molecules can lose excitation energy by means other than fluorescence, namely, internal conversion, intersystem crossing, dissociation, and energy transfer. The rate of energy dissipation can be written:

$$k = k_f + k_{ic} + k_{isc} + k_d + k_{XY}[Y] \quad (2.8)$$

where k_f , k_{ic} , k_{isc} , and k_d , are the rate constants for a molecule to de-excite by fluorescence, internal conversion, intersystem crossing, and dissociation, respectively. k_{XY} is the rate constant for energy transfer per solute molecule, where X represents the solvent, Y represents the solutes and $[Y]$ is the molar concentration of solute in the solution. If there were additional energy loss mechanisms for a particular system additional rate constants would be added, for example, the rate constant for impurity quenching which will be introduced later. The decay time constant, τ for a molecule is given by:

$$\tau = 1/k = 1/(k_f + k_{ic} + k_{isc} + k_d + k_{XY}[Y]) \quad (2.9)$$

The fluorescence decay time is related to the Einstein A coefficient. A heuristic argument will be presented here, but if the reader is interested in the complete

deviation they are referred to Birks [BIR 70] and the references therein. Recall that the Einstein A coefficient is defined as the probability of luminescence per unit time which is equivalent to the first order rate constant for fluorescence, k_f . If $A_{u \rightarrow l}$ is determined for $u = 1$ and $l = 0$, the following expression can be written:

$$k_f = A_{1 \rightarrow 0} \quad (2.10)$$

where $A_{1 \rightarrow 0}$ denotes a transition rate from S_{10} to S_{0m} . Using the above relationship and equation 2.5 one can derive the expression:

$$k_f = 1/\tau_f \propto \bar{\nu}_{l \rightarrow u}^2 \int_{l_u} \epsilon(\nu) d\nu \quad (2.11)$$

The interpretation of the above equation is that, to a first order approximation, the magnitude of the decay time constant can be estimated from the S_1 absorption spectrum. Making a few more approximations and assumptions about the wavelength of absorption and fluorescence the result is:

$$\tau_f \approx 10^{-4} / \epsilon_{max} \quad (2.12)$$

where ϵ_{max} has units of $1/\text{M}\cdot\text{cm}$ and τ_f is calculated in units of seconds. Equation 2.12 reveals that if a molecule is to have a decay time constant on the order of 1-10 ns then $\epsilon_{max} \approx 10^{4.5} 1/\text{M}\cdot\text{cm}$ for an S_{1m} absorption. Equation 2.12 is a very powerful "rule-of-thumb" for gauging a priori the magnitude of the fluorescence decay time constant from the published absorption spectrum, which typically only includes $S_{00} \rightarrow S_{1m}$ transitions. It should be noted that the above calculation is for the determination of the fluorescence decay time constant, τ_f , which is the decay time constant that would be observed in the absence of all other processes by which the molecule can return to the ground state. The observed decay time constant, τ , will always be less than or equal to the fluorescence decay time, τ_f , i.e., $\tau \leq \tau_f$. As

will be seen in the next section, the difference is related to the fluorescence quantum efficiency.

2.5 Fluorescence Quantum Efficiency

There are many definitions for quantum efficiency or quantum yield. The definition used here for *fluorescence* quantum efficiency, Q_f , is the probability that a molecule *fluoresces* following an absorption. Q_f is less than or equal to the *luminescence* quantum efficiency which is defined as the probability that a molecule *luminesces* following an absorption. In general, because of self-quenching and self-absorption the quantum efficiency values are not the same as the number of fluorescent or luminescent photons emitted divided by the number of incident photons that were absorbed, but can be nearly identical quantities if these loss mechanisms are minimized. Typically dilute solutions are used to measure Q_f in order to minimize the amount of self-quenching and self-absorption. For dilute solutions, Q_f is approximately equal to the number of fluorescence photons divided by the number of absorbed photons.

From the definition of Q_f it seems apparent that there should be a relationship between Q_f and the Einstein A and B coefficients. The previous section showed the relationship between A and τ . In this section the interconnection of the important parameters will come full circle with the quantitative description of Q_f .

Under steady state conditions [BIR 70]¹, the rate of production of excited molecules (in S_1) is balanced by their rate of disappearance via fluorescence, internal conversion, intersystem crossing, dissociation and energy transfer. If $[S_1]$ is the concentration of

¹The analysis of a transient condition is similar with the exception that the fluorescence is integrated over the duration of the pulse, but results in the same conclusion as the steady state condition.

excited singlet molecules when the steady state has been achieved then:

$$I_a = (k_f + k_{ic} + k_{isc} + k_d + k_{XV}[Y'])[S_1] \quad (2.13)$$

where the rate of light absorption is I_a . The total rate of fluorescence emission I_f , can be written several ways, namely:

$$I_f = k_f[S_1] \quad (2.14)$$

$$= I_a Q_f \quad (2.15)$$

$$= (k_f + k_{ic} + k_{isc} + k_d + k_{XV}[Y'])[S_1] Q_f \quad (2.16)$$

hence

$$k_f[S_1] = (k_f + k_{ic} + k_{isc} + k_d + k_{XV}[Y'])[S_1] Q_f \quad (2.17)$$

$$Q_f = \frac{k_f}{(k_f + k_{ic} + k_{isc} + k_d + k_{XV}[Y'])} \quad (2.18)$$

$$= \tau / \tau_f \quad (2.19)$$

Substituting equation 2.10 into equation 2.19 results in

$$A_{1 \rightarrow 0} = Q_f / \tau \quad (2.20)$$

So by experimental determination of the fluorescence quantum efficiency and molecular decay time the Einstein A coefficient can be determined. As it has been defined, $\tau \leq \tau_f$ so $Q_f \leq 1$. The higher that k_f is relative to the other parameters (the higher the probability of fluorescence) the more likely $\tau \approx \tau_f$ and hence $Q_f \approx 1$, which is the desired condition for our application. Based on the molecules that have been studied, it is quite common to have $Q_f > 0.80$ and $\tau < 10$ ns, but when τ is in the sub-nanosecond range, there is a trade-off between τ and Q_f . The trend is that for $\tau < 1$ ns, Q_f is low [FLO 92]. This trend is the result of the excited state decaying by a means other than fluorescence, with a rate constant that is higher than the fluorescence rate constant.

2.6 Energy Transfer

If a solution is composed of an aromatic solvent it is possible to have appreciable energy transfer between the excited solvent molecule and neighboring solute molecules. Initially, theories of the energy transfer mechanism assumed stationary molecules, i.e., polymers [FOR 59], and were later improved upon to describe liquid solutions, which lead to the development of Stern-Volmer kinetics [BIR 68b]. Förster developed a theory to describe energy transfer as a dipole-dipole interaction in which nonradiative energy transfer occurs between the first excited π -singlet state of the solvent and the solute molecules.

The energy transfer mechanism can be described as follows. Energy absorbed by the solvent molecules, X , results in the excitation of π -electronic singlet states of the solvent molecule, X^* . The excited solvent molecule, X^* , transfers the energy to the solute molecule, Y , elevating the solute molecule to its first excited singlet state. The energy transfer kinetics equation is written:

The energy transfer rate parameter is determined by [FOR 60]:

$$k_{XY} = \frac{1}{\tau_X} \left(\frac{R_0}{R} \right)^6 \quad (2.22)$$

where

$$R_0^6 \propto \int_0^\infty I_X(\nu) \epsilon_Y(\nu) \frac{d\nu}{\nu^4} \quad (2.23)$$

τ_X is the decay time constant for a pure solvent molecule, R is the mean separation distance between solvent and solute molecules, R_0 is defined as the critical transfer distance, $I_X(\nu)$ is the relative solvent fluorescence intensity at wavenumber ν , and $\epsilon_Y(\nu)$ is the molecular extinction coefficient of the solute. $I_X(\nu)$ is normalized such

that

$$Q_f = \int_0^{\infty} I_X(\nu) d\nu \quad (2.24)$$

R_0 is a constant for a given solution and is the separation distance at which energy transfer, and re-excitation of X by emission or quenching, are equally probable. Typical values of R_0 are 5-30 Å. Large values of R_0 and high concentrations of solute, c , are needed for efficient energy transfer. High concentrations assure that a short distance between solvent and solute molecules, R , is achieved. Typical concentrations used are $c \approx 0.01$ -10 M.

From the above equations the rate of energy transfer (the probability of energy transfer) can be enhanced by increasing the overlap of the solvent emissions and the solute absorptions, as well as the fluorescence quantum efficiency of the pure solvent and the decay time of the pure solvent. Förster's theory compares well with experimental results in describing the probability of energy transfer in terms that can be measured independently [BRO 91].

The probability of energy transfer, f_{XY} , is determined by a method that compares the relative fluorescence yields of the solute Y when excited in two different spectral regions [BIR 64]. I_X is the intensity of fluorescence when directly exciting the solvent molecules X , $I_X = f_{XY} I_0(\lambda_X) Q_f(\lambda_X)$. I_Y is the intensity of fluorescence when energy is only absorbed by the solute molecules Y , $I_Y = I_0(\lambda_Y) Q_f(\lambda_Y)$. The efficiency is determined by:

$$\frac{I_X}{I_Y} = \frac{f_{XY} I_0(\lambda_X) Q_f(\lambda_X)}{I_0(\lambda_Y) Q_f(\lambda_Y)} \quad (2.25)$$

where $I_0(\lambda)$ is the excitation intensity. The λ subscript denotes the different excitation sources. The probability of energy transfer can also be defined in a manner

similar to Q_f (see equation 2.18):

$$f_{XY} = \frac{k_{XY}[Y]}{k_f + k_{ic} + k_{isc} + k_d + k_{XY}[Y]} \quad (2.26)$$

$$= \frac{k_{XY}[Y]}{k} \quad (2.27)$$

The above equation assumes that the efficiency for a radiative energy transfer is much lower than the non-radiative energy transfer and therefore negligible, which is a good assumption if $[Y]$ is high.

The rate constant for energy transfer, k_{XY} is fixed for a given solvent/solute combination. To increase the efficiency of energy transfer, the solute concentration must be increased. The maximum concentration varies with the choice of solvent for a particular solute and depends on their polarity and electrical properties.

2.7 Other Considerations

Aside from absorption, fluorescence, decay time constant and quantum efficiency of solute molecules there are other processes that influence suitability as a WLS for BaF_2 . Some of these competing processes are collectively known as bimolecular processes, which includes: collisional impurity quenching, self-quenching, self-absorption, heavy atom effects, and solvent effects [PAR 68, BIR 70, BER 71]. In addition, the condensation of the molecule plays an important role in narrowing the scope of fluors that are to be investigated for a particular WLS technique.

2.7.1 Collisional Impurity Quenching

If the WLS solution contains a molar concentration $[q]$ of an impurity molecule q , energy transferred between the excited solute molecule and the impurity molecule may lead to quenching of the excited solute molecule. The impurity quenching is

quantified by an additional rate parameter, k_q to account for this additional loss mode. Substituting this additional term into equation 2.18 results in a reduction in the quantum efficiency, determined by:

$$Q'_f = \frac{k_f}{(k_f + k_{isc} + k_{ic} + k_d + k_{XY}[Y] + k_q[q])} \quad (2.28)$$

$$= \frac{Q_f}{1 + \tau k_q[q]} \quad (2.29)$$

and the decay time constant is reduced from τ , to:

$$\tau' = \frac{\tau}{1 + \tau k_q[q]} \quad (2.30)$$

There are many sources of impurities but oxygen is notorious when working with aliphatic solvents. Oxygen results in a quenching of every excited molecule that comes in contact with it. Oxygen quenching can be reduced by either bubbling oxygen-free nitrogen through the solution, thereby replacing the dissolved oxygen with nitrogen (which is not a quencher), or more effectively by cyclically freezing/thawing/pumping of the solution to remove all dissolved gases.

Oxygen has achieved its notoriety as a fluorescence quenching mechanism because of the ease at which it can dissolve in organic solvents and is always present unless proper precautions are taken. The ground state of molecular oxygen is a triplet state and there are several mechanisms by which oxygen can quench; some of them return the oxygen molecule to its triplet state while others place the molecule in the first excited singlet state. Molecular oxygen in the first excited singlet state is very reactive and may interact with a solute molecule in its ground state [BER 71]. The four mechanisms for oxygen quenching are: [BIR 70]

should be the dominate process for low-viscosity solutions,

should be the dominate process for viscous or rigid solutions,

oxygen quenching of a triplet state can also occur, as well as

which may be energetically possible if the energy difference between the first excited singlet state exceeds the energy of the first excited state of molecular oxygen. In these kinetics equations S and T represents a singlet state, and a triplet state of the fluor, respectively. $O_2(S)$ and $O_2(T)$ represent the singlet and triplet state of molecular oxygen, respectively and * denotes an excited state.

2.7.2 Self-Quenching

Increasing the molar concentration $[Y]$ of the fluorescence solute commonly causes a decrease in the molecular fluorescence quantum yield through self-quenching. Self-quenching of an excited solute molecule is accomplished by an interaction of an excited solute molecule and a solute molecule in the ground state. Since this is a diffusion-controlled collision process, it can be described by a rate parameter k_D , resulting in additional term appearing in the rate equation 2.18, giving:

$$Q'_f = \frac{k_f}{(k_f + k_{isc} + k_{ic} + k_d + k_{XY}[Y] + k_D[S_1])} \quad (2.35)$$

$$= \frac{Q_f}{1 + \tau k_D[S_1]} \quad (2.36)$$

and

$$\tau' = \frac{\tau}{1 + \tau k_D [S_1]} \quad (2.37)$$

where $[S_1]$ is the molar concentration of solute molecules in S_1 . As in the case of impurity quenching, self-quenching results in a decrease in the expected fluorescence quantum efficiency and decay time constant.

2.7.3 Self-Absorption

Typically an overlap exists between the fluorescence and absorption spectra. Some molecules like p-terphenyl (PTP) show very little overlap (see figure C.33), but others like perylene (see figure C.31) have a significant overlap. The degree of spectral overlap and the concentration of the solution determines the amount of self-absorption that occurs.

Let a be the probability of self-absorption of a fluorescence photon, so $(1 - a)$ is the photon escape probability. The relationship between the observed fluorescence quantum efficiency, Q'_f and the expected fluorescence quantum efficiency, Q_f is given by:

$$Q'_f = Q_f(1 - a) + Q_f(1 - a)aQ_f + Q_f(1 - a)a^2Q_f^2 + \dots \quad (2.38)$$

$$= Q_f(1 - a)[1 + aQ_f + a^2Q_f^2 + \dots] \quad (2.39)$$

$$= Q_f \frac{(1 - a)}{1 - aQ_f} \quad (2.40)$$

The successive terms in the series correspond to photon escapes after 1, 2, 3, ... emissions. The observed decay time constant is increased to

$$\tau' = \frac{1}{(1 - a)k_f + k_{ic} + k_{isc} + k_d + k_{XY}[Y]} \quad (2.41)$$

$$= \frac{\tau}{1 - aQ_f} \quad (2.42)$$

These qualitatively correct expressions used to describe the effect of self-absorption are intended to show the expected trends and do not rigorously describe the process.

To treat the process rigorously, one would have to account for the positional dependence of a because the value at the center of the specimen will be larger than the value of a at the edge of the specimen.

2.7.4 Heavy Atom Effect

Triplet-singlet transitions are quantum mechanically forbidden, but they occur because of spin-orbit coupling between the wavefunctions of the singlet and triplet states (see section 2.3). In aromatic molecules, spin-orbit coupling increases due to increased probability of triplet-singlet transitions that result from the substitution of higher atomic number atoms. This phenomenon is known as the internal heavy-atom effect, and leads to increased phosphorescence.

Another method to increase the spin-orbit coupling is the substitution of higher atomic number atoms into the solvent environment. This phenomenon is known as the external heavy-atom effect. Both internal and external heavy-atom effect results in a decrease of the fluorescence quantum efficiency. Knowledge of the heavy-atom phenomenon results in a rule-of-thumb for evaluating solvents and fluors for use in an efficient WLS.

2.7.5 Solvent Effects

For many aromatic molecules the position and structure of the fluorescence spectrum is strongly dependent on the solvent. In addition to the effects already mentioned, other measurable effects are perturbation of the decay time constant, ϵ_{max} and fluorescence quantum efficiency, as well as loss of vibrational structure. The changes can be attributed to the difference in solvent polarity, index of refraction and dielectric constant. Several mechanisms to describe the interaction of the ex-

cited molecules with the surrounding solvent molecules have been proposed. These are hydrogen bonding [MAT 57], electromagnetic interaction between the dipole moment of the solute with that of the solvent [MAT 64], and reorientation of the solvent molecules [EIS 69]. Depending on the properties of the solvent and solute it is conceivable that more than one of these mechanisms come into play [PAR 68].

2.7.6 Degree of Condensation

There are some general trends that can be used to assist in the selection of the proper solute to be used in a wavelength shifter. Benzene rings have 6 π -electrons which are an essential unit in practically all fluorescent compounds. The fluorescence quantum yield of benzene is ≈ 0.07 and the decay time constant is ≈ 30 ns. The effect of substitutional groups on benzene can be dramatic. In molecules of high symmetry the transition between the ground state and the lowest electronic states are generally forbidden. The addition of substitutes breaks the symmetry and typically results in an increased fluorescence quantum efficiency and decreased fluorescence decay time. For example, substituting a methyl group onto benzene, i.e., toluene, increases Q_f to 0.17 while τ remains about the same.

Biphenyl is a molecule of two phenyl rings (a phenyl ring is a benzene ring less one hydrogen). Biphenyl fluoresces with a decay time from ≈ 1 to ≈ 100 ns, depending on the substituted molecule(s) and the location of those molecule(s) on the biphenyl structure. The fluorescence quantum efficiency of these molecules is still low, $Q_f < 60\%$. p-Oligophenylenes are composed of rings joined together in the para position by single carbon-carbon bonds. The general formula for these molecules is $C_{6n}H_{4n+2}$, where $n \geq 2$ is the number of rings, biphenyl being the first unsubstituted molecule in the series having two rings. The p-oligophenylene series of molecules is

of interest in shifting the emissions of BaF_2 because its fluorescence decay time is short ($\tau < 3 \text{ ns}$) and fluorescence quantum yield is close to unity. The correlations between the physical properties and the scintillation properties of this series are used as an example to describe general trends. As the degree of condensation (the number of phenyl rings) increases, the scintillation efficiency increases and the fluorescence decay time decreases. Another advantage for applications with BaF_2 is as the degree of condensation increases the radiation hardness also increases. Also the absorption to the first excited state becomes stronger and moves to longer wavelengths (see figure 2.4). Interestingly, the absorption into the second excited state does not change with the degree of condensation. The independence of condensation is assumed to be caused by transitions of individual phenyl rings. The last important feature is that there is almost no overlap between the emission and absorption bands, resulting in little loss from self-absorption. There is potentially one drawback to solutions of p-oligophenylene. As the degree of condensation increases, the solubility decreases. Even at low concentrations sufficient absorption of BaF_2 photons may occur, if the molar extinction coefficient is high. Depending on the solute, excitation wavelength and application, this may not be a problem because the molar extinction coefficient is sufficient that the BaF_2 light must transverse several mean free paths before interacting in the photodetector, even at low concentration. Only in the case where the intermolecular energy transfer mechanism is important will solubility be of major concern. Solubility can be increased by substituting alkyl groups on the molecule. The effect of alkyl substitutes on the molecule results in a bathochromic shift (shift to longer wavelengths) of the fluorescence. Figure 2.5 is an example of an exception to that rule, showing the absorption and fluorescence spectra of two members of the terphenyl group (three phenyl rings), namely: p-terphenyl and a two methyl

Figure 2.4: UV absorption spectra of unsubstituted p-Oligophenylenes. Top: biphenyl, Middle: p-terphenyl, Bottom: p-quaterphenyl [WIR 68]

Figure 2.5: Molar Extinction Coefficient (open symbols) and Fluorescence Spectra (closed symbols) for p-Terphenyl and 2,2'' Dimethyl-p-Terphenyl.

substituted p-terphenyl, 2,2" dimethyl-p-terphenyl.

2.8 Summary of General Rules of Thumb

Below are general rules-of-thumb regarding fluorescent molecules. There are many exceptions to these rules so it should be stressed that they should be applied with caution. These rules-of-thumb are a compilation of rules found in Parker [PAR 68], Birks [BIR 70] and Berlman [BER 71] that were formed from observations.

- Hypsochromic shift (shift to a shorter wavelength) of absorption and fluorescence spectra by isotopic substitution of all hydrogen atoms with deuterium.
- Alkyl substitution in an aromatic hydrocarbon usually causes a bathochromic shift (shift to a longer wavelength) of the absorption and fluorescence spectrum.
- Phenyl and vinyl substitution in an aromatic hydrocarbon produces a relatively large bathochromic shift in the spectra, an increase in ϵ_{max} and a decrease in τ .
- Amino, hydroxy or methoxy substitutions in an aromatic hydrocarbon also tends to produce a large bathochromic shift of the spectra associated with a loss of vibrational structure, an increase in ϵ_{max} and a decrease in τ .
- Carbonyl and quinone structure attached directly to the aromatic ring increases the rate of intersystem crossing, k_{isc} .
- Fluorine added to the benzene ring causes a hypsochromic shift in the absorption and fluorescence spectra.
- For excitation of luminescence at wavelengths greater than ≈ 200 nm a π electron system is required.
- High efficiency of fluorescence in fluid solutions usually associated with compounds having $\pi \rightarrow \pi^*$ as the lowest excited singlet state.
- Systems having $n^* \rightarrow \pi$ as the lowest excited singlet state show very low

efficiency for fluorescence in liquid solutions.

- Increased condensation shifts the longest wavelength absorption band to a longer wavelength.

- In the absence of special effects (for example, hydrogen bonding and electrolytic dissociation), the fluorescence emission spectrum is situated immediately to the long-wavelength side of the absorption spectrum.

- The phosphorescence spectrum is situated to the long-wavelength side of the fluorescence spectrum.

- Substitution of ortho-para directing groups does not decrease the probability to fluoresce and may increase it. Most meta-directing groups except carbon and nitrogen reduce the fluorescence quantum efficiency.

- Increased molecular rigidity increases the fluorescence quantum efficiency in liquid solutions.

- Substitution of side groups often shifts the spectra to longer wavelengths and reduces vibrational structure. The effect is least with alkyl groups.

- Substitution of heavy atoms reduces the fluorescence quantum efficiency.

CHAPTER III

EXPERIMENTAL METHODS

The set of criteria that must be evaluated for an organic fluor to determine if it is a likely candidate for the wavelength shifting of BaF_2 emissions, includes: the molar extinction coefficient, fluorescence emission wavelength, quantum efficiency, and decay time constant. Of secondary importance are the solubility, stability, low quenching sensitivity, and large Stokes shift. Because all these properties are important, priorities had to be set. Some of the hierarchy is set by the nature of the problem, e.g., if spectral separation is not physically possible, the stability of the fluor is of no consequence.

Due to the large number of measurements made and the number of different fluors studied, the absorption and fluorescence spectra, fluorescence quantum efficiency and decay time constant are collectively presented in appendix C. Both data measured for this dissertation and published data are presented there. The data presented include both solvents and fluors that were measured or investigated because they had a property that was particularly interesting and/or the lack of published data required further investigation.

In this chapter and the remainder of the dissertation, only a few of the important compounds will be presented formally. The purpose for not presenting all the

acquired data formally is not intended to imply other molecules are not useful, but rather we chose a limited set to clarify the key concepts and avoid detailed comparisons of the particular fluors.

3.1 Sample Preparation

The solvents were obtained from Aldrich Chemical Corporation and Fisher Scientific, and were HPLC (high purity liquid chromatography) or spectrophotometric grade (the purest commercially available grade for each company). The fluors were obtained from Aldrich Chemical Corporation and Lambda Physik, Inc. The fluors from Aldrich were typically 99+% pure, while the purity of the Lambda Physik solutes was unknown. All chemicals were used as delivered, without further purification. However, the solvents were de-oxygenated by bubbling dry nitrogen through them for at least 15 minutes and solutions were stored under dry nitrogen until measurement. In most cases, the cuvettes and optical lenses were made of high purity fused silica because impurities that are typically found in glass products fluoresce at $\lambda_{peak} \approx 390$ nm and have a decay time constant of $\tau \approx 2$ ns [WEB 58]. Also the long pass filter used to demonstrate the various WLS techniques was obtained from Oriel Corporation and was classified as "low-fluorescence".

The BaF₂ crystals were obtained from Optovac, Inc. Both 25 mm x 25 mm and 25 mm dia. x 10 mm right circular cylinders of BaF₂ were used. The crystals were optically polished on all surfaces with 1 μ m alumina.

3.2 Absorption Measurements

Absorption spectrometry is an extremely sensitive non-destructive technique. Despite the great amount of effort that has been put into the prediction of absorp-

Figure 3.1: Experimental schematic used for measuring the molar extinction coefficient.

tion spectra by the calculation of molecular energy levels, most discussions of the structure-spectra correlations are based on empirical rules which are normally limited by provisos and qualifications [KNO 84]. Absorption spectra for solvents and fluors are generally not available below $\approx 250\text{nm}$ [BER 71]. A first step in evaluation of solvent and fluor properties was to determine the absorption characteristics in the shorter wavelength region. Typical spectrophotometers cannot measure the absorption of fluors because the instrument has no means of discrimination between the transmitted spectrophotometer photons and sample fluorescence. For this reason, a technique to measure the absorption of the fluor, with negligible contribution from sample fluorescence, was developed. Figure 3.1 schematically depicts the equipment used¹. An Oriel Spectra-Pro scanning monochromator equipped with a 250 nm

¹When applying this measurement technique, one must be careful since $I_0(\lambda)$ and $I(\lambda)$ are measured at two different times and the conditions of the lamp or monochromator PMT may have changed. Under a more ideal setup measurements of $I_0(\lambda)$ and $I(\lambda)$ would be conducted

blaze, 1200 grooves/mm grating was used for these measurements. A resolution better than 0.1 nm was obtained when the entrance and exit slits of the monochromator were set to a 5 μm width. The Spectra-Pro monochromator is a Czerny-Turner design with five reflection surfaces between the entrance and exit slits. The photon path length was 0.25 m. At the exit slit is a sodium salicylate window. The window is a wavelength shifter which absorbs the deep UV photons that are exiting the monochromator and shifts them to a longer wavelength. As a result, PMT non-linearities at low wavelengths are not a major concern. A Burle 1P28 PMT was used as the photodetector. The Oriel PS-445 was the interface between the monochromator and an IBM XT computer. The PS-445 controlled the data acquisition, PMT bias voltage and digitized the anode current. A maximum anode current of 1 μA resulted in a digitized luminosity of 2.5×10^6 a.u. The PMT anode current was assumed to be linear with luminosity. The digitized anode current was sent to the personal computer for display, storage and preliminary analysis. More extensive analysis was performed on an Apple Macintosh II.

The sample was placed in a fused silica cuvette that was positioned in a cuvette holder. The holder was designed to not allow incident photons to be transmitted through the edges of the cuvette. The sample was illuminated with the broad band emissions of a calibrated deuterium lamp. Both the measured and expected emission spectra are depicted in figure 3.2. The molar extinction coefficient, $\epsilon(\lambda)$ was determined using the Beer-Lambert Law, an empirical relationship between the incident

in coincidence with a system of two monochromators connected in series. The bandwidth and wavelength of both monochromators would be the same, and output from the first monochromator would be split so to provide a monochromatic beam of photons onto the sample and a reference (pure solvent in a optically matched cuvette). The transmitted beam intensity would be measured by the second monochromator at the same wavelength as the incident beam to determine the absorptivity of the sample. The sample absorptivity would then be corrected by the reference absorptivity to determine the absorption of only the fluor. Although such a setup was not available, our data was taken with sufficient care and assumed to be accurate to within 15%.

Figure 3.2: Measured and expected deuterium lamp spectral response. The ratio of the values determines the correction factor.

and transmitted beam of light:

$$I(\lambda) = I_0(\lambda)10^{-\epsilon(\lambda)bx} \quad (3.1)$$

where b is the concentration of solute in M (molar), x is the light path length in cm, and $\epsilon(\lambda)$ has units of $1/M\cdot\text{cm}$. $I_0(\lambda)$ is the intensity of the transmitted beam of normally incident collimated beam of light when the solute concentration is zero and $I(\lambda)$ is the intensity of transmitted light when the concentration is b . Two separate measurements were made to determine $\epsilon(\lambda)$. The transmitted lamp intensity, $I_0(\lambda)$, was first recorded in 1 nm steps with the cuvette filled with pure solvent. Next a measurement of the transmitted light intensity through the fluor dissolved in the solvent, $I(\lambda)$, was made under the same conditions. The ratio, $I_0(\lambda)/I(\lambda)$, measured at each incremental wavelength, determines the molar extinction coefficient averaged over a narrow $\Delta\lambda$ around the wavelength λ . The measured molar extinction coeffi-

cients for p-terphenyl and 2,2'' dimethyl-p-terphenyl are shown using open symbols in figure 2.5. Very dilute samples ($\approx 4.5 \times 10^{-6} M$ in cyclohexane) were used to decrease the contributions from self-absorption and self-quenching [PAR 68].

3.3 Fluorescence

The best light detection efficiency is achieved when the wavelength shifter emissions corresponds to the maximum sensitivity of the photomultiplier tube (typically ≈ 410 nm). Spectral matching can be done either by a one shift system (unitary or binary system) or in a two shift system (ternary system). Examples of unitary waveshifters are molecular crystals and vacuum evaporated solutes. Molecular crystals are difficult to grow and their low quantum efficiency have effectively limited their use. In contrast, vacuum evaporation of high quantum efficiency fluors results in high photon yields, but suffers from the creation of optical traps that are formed during the deposition. Binary wavelength shifters come in two varieties, either with an active or inactive solvent. An active solvent absorbs the incident energy and transfers it to the solute. If the system is designed properly there is only a slight loss in efficiency when employing an active solvent. With an inactive solvent, although energy may be absorbed, it is not transferred to the solute². In this work, for example, the inactive solvents used were cyclohexane and ethanol, and the active solvents included p-dioxane and toluene. Cyclohexane and ethanol were chosen for their low absorptivity of incident photons (see figure 3.3). Both p-dioxane and toluene were chosen for their relatively low absorption of BaF₂ emissions above 240 nm as well as their ability to transfer absorbed energy to the solute (see figure 3.4). The details of these active solvents, as well as other active solvents are presented in chapter IV.

²For absorption measurements of fluors, an inactive solvent must be used.

Figure 3.3: Absorptivity of 10 mm of cyclohexane and ethanol relative to water.

Figure 3.4: Absorptivity of 10 mm of p-dioxane and toluene relative to water.

Figure 3.5: Experimental schematic used for measuring the fluorescence emission spectrum.

Figure 3.6: Transmission of the Oriel Corporation 220 and 310 nm band-pass filters.

The preferred technique for fluorescence measurements employs very dilute solutions and orthogonal illumination [PAR 68]. Figure 3.5 schematically shows the equipment arrangement of the simple fluorometer used to make these measurements. A plano convex fused silica lens imaged the wavelength shifter emissions onto the entrance slit of the monochromator. The monochromator was equipped with a 500 nm blaze, 1200 grooves/mm grating and the entrance and exit slits were set to have a resolution of ≈ 1 nm (500 μ m width). Similar to the absorption measurement, the WLS sample was contained in a fused silica cuvette that was placed in the cuvette holder. The broad-band emissions from the deuterium lamp were filtered with a bandpass filter having peak transmission at 222 nm and a full width at half maximum (FWHM) of 25 nm, or a 310 nm, 8.8 nm FWHM band-pass filter. The band-pass filtered emissions were used in several ways. One way was to measure the response of the fluor when excited with 220 nm photons as compared to 310 nm photons, thus crudely simulating the output of BaF₂. Also the filters offered a means to obtain a "monochromatic" light source from the deuterium lamp. The transmission curves from the Oriel Corporation band-pass filters are presented in figure 3.6 were measured with a Cary 219 spectrophotometer.

Typical fluorescence emission spectra are depicted as the solid symbols in figure 2.5 showing p-terphenyl and 2,2' dimethyl-p-terphenyl at concentrations of $\approx 4.5 \times 10^{-5}$ M in cyclohexane. The measured luminescence spectra have been corrected for detection nonlinearities of the monochromator. The deuterium lamp spectral response was calibrated by Optronics Laboratories Inc. The non-linearity correction was performed by comparing the measured deuterium lamp output to the calibrated output. Figure 3.2 shows the comparison of the measurements. The measured value between 200 and 400 nm was made with the 250 nm blazed grating and between

Figure 3.7: Experimental schematic of the measurement of the BaF₂ emission spectrum.

350 and 650 nm with the 500 nm blazed grating. The correction factor that is applied to the emission spectra is simply the ratio of the expected lamp response to the measured lamp response and is depicted on the right vertical axis of figure 3.2. Above ≈ 550 nm, the calibration deviates markedly from the measured deuterium lamp spectral response. The large correction factor was only utilized on a few fluors with emissions in this region and these fluors typically had low luminosity.

3.3.1 BaF₂ Emission Spectrum Measurements

The measurement of the BaF₂ scintillation spectrum was made in a manner similar to the fluorescence emission measurements and is diagrammed in figure 3.7. The entrance and exit slits are set to 500 μm and the PMT was biased at -1000V. A

2.54 cm x 2.54 cm right circular cylinder of BaF_2 ³ was wrapped with two layers of polytetrafluoroethylene (PTFE) and one layer of aluminum foil. The BaF_2 crystal was excited with a 10 mCi Cs-137 gamma-ray emitting source. The scintillation photons were imaged onto the monochromator entrance slits with a fused silica, plano convex lens. Maintaining the same experimental arrangement, the BaF_2 crystal was removed to determine the background spectrum. The background was subtracted from the measured emission spectrum and then corrected for the monochromator non-linearities (see figure 1.2). Because of the low luminosity of the BaF_2 emissions and the low through-put of the monochromator, the signal to noise of this measurement was low. As a result, the emissions below the 220 nm peak emission are not apparent. Under more ideal conditions of higher luminosity and higher monochromator sensitivity, the measured emission spectrum would resemble that shown in figure A.1.

3.4 Luminescence Time Spectra Measurements

The luminescence time spectra measurements were made using the Bollinger and Thomas technique [BOL61] with the modification by Moszyński and Bengtson [MOS 77]. The pulse processing system is shown in figure 3.9. This time-correlated single photon counting technique randomly samples in time the intensity of the luminescence from a sample. Random sampling is achieved by low-efficiency light coupling between the sample and the "stop" PMT. The poor light coupling assures that the probability of detecting one photon, $P_1(t)$, from a given interaction is very much less than one. If $P_1(t) \ll 1$, then it is equally probable

³Two identical crystals were obtained from Optovac, Inc. One of the crystals was cut in half with a diamond saw and the cut surfaces were polished down to a 1 μm particle size. One of these 25 mm x 10 mm crystals was used in the sample assembly presented in figure 3.8. The other 25 mm x 10 mm crystal was used as the "start" detector as depicted in figure 3.9

Figure 3.8: Schematic of sample geometry imposed by the quartz cuvette used to contain the wavelength shifter.

Figure 3.9: Set-up of electronics for the determination of the scintillation decay time.

to detect *any one* of the emission photons generated by a given excitation. The proof is detailed in appendix B. The luminescence time spectra is acquired by measuring the time difference between the excitation of the sample, and the detection of a luminescence photon by the "stop" PMT. The "start" pulse is derived from an external detector that is excited in coincidence with the excitation of the sample. Coincident excitation of the "start" detector and the sample is accomplished with the annihilation photons from the Na-22 source. The output of the start detector is connected to a constant fraction discriminator (CFD) to generate a timing pulse corresponding to the deposition of ≥ 350 keV of energy in the external BaF₂ crystal. The timing accuracy is limited by the time walk of the CFD and the time distribution of the PMT anode pulse. The CFD timing signal is input to the TAC, thus starting the time measurement. The "stop" CFD is set to trigger on a single photoelectron. The timing signal is delayed to assure that the spectrum does not start at the beginning of the TAC range where nonlinearities typically occur. The "stop" signal halts the TAC circuit and outputs an analog signal that is proportional to the time difference between the start and stop signals. The analog signal is input to a 2048 channel analog to digital converter (ADC). The ADC used is an integral part of the hardware and software of the EG&G Ortec Ace card, a multichannel analyzer (MCA) for the IBM personal computer. After many such coincident events, the fluorescent time distribution is formed (see figure 1.1) and is assumed identical to the time spectrum of a single gamma-ray interaction⁴. The digitized raw data is transferred to a DEC Station 3100 for preprocessing then to an IBM RISC 6000 for fitting and analysis.

The following describes TAUFIT [DER 93], a non-linear least squares fitting

⁴Digitizing a single pulse would actually be quite noisy. A better solution is to digitize many pulses and sum them. To be a viable option for BaF₂, one would need to digitize with at least a 10 GHz bandwidth, which is at the leading edge of available technology.

routine specifically written to fit binned luminescent time spectra.

The temporal luminescence intensity of a scintillation event, $I(t)$, can be described by the sum of exponential components:

$$\begin{aligned} I(t) &= \sum_j \frac{a_j}{\tau_j} e^{-t/\tau_j} = \sum_j I_j e^{-t/\tau_j} \quad t \geq 0 \\ &= 0 \quad t < 0, \end{aligned} \quad (3.2)$$

where a_j , τ_j and I_j are the integrated luminescence, characteristic time, and initial intensity of the j^{th} exponential component, respectively. For all luminescent processes, the characteristic time is a decay time constant when the integrated luminescence is a positive value, i.e. $a_{\text{decay}} > 0$. For the case of an exponential population of a luminescent state (as in our case of a WLS being excited with the decay of BaF_2), an additional luminescence component is necessary to describe the process. The additional characteristic time behaves as a negative integrated luminescence, $a_{\text{rise}} < 0$, in this representation, the characteristic time is a rise time constant, and the total integrated luminescence for the process is $a_{\text{rise}} + a_{\text{decay}}$. If a luminescent state is populated by a single exponential process then the absolute value of the initial intensities are equal, $I_{\text{decay}} = -I_{\text{rise}}$.

To determine the true luminescence intensity, $I(t)$, standard nuclear electronics, having an impulse response function, $G(t)$, were used to acquire a timing spectrum. Consequently, the observed luminescence intensity, $H(t)$, corresponds to the convolution of the impulse response function and the true luminescence intensity:

$$H(t) = \int_0^\infty I(t') G(t - t') dt' \quad (3.3)$$

For fitting purposes $I(t)$ was normalized to the total light yield, which is the sum of the a_j terms. With this normalization, a_j represents the fraction of the total light emitted by the j^{th} process.

The measured data, M_k , are the number of counts in the k^{th} bin, corresponding to the time interval t_k to $t_k + \Delta t$, and are analyzed using a non-linear least squares fitting program. The fitted number of counts in the k^{th} bin, F_k , is determined by summing the integral of the observed luminescence intensity and the chance coincidence rate, R_{ch} , contributions to that bin:

$$F_k = R_{ch}\Delta t + \int_{t_k}^{t_k+\Delta t} H(t)dt \quad (3.4)$$

If the condition of $P_1(t) \ll 1$ is met, then the chance rate appears as a flat background on which the luminescence distribution is superimposed. Otherwise the general expression outlined in appendix B must be used. Minimization of χ^2 :

$$\chi^2 = \sum_k \frac{(M_k - F_k)^2}{\sigma_k^2} = \sum_k \frac{(M_k - F_k)^2}{F_k} \quad (3.5)$$

results in the best estimate of a_j and τ_j parameters, where F_k is the best estimate of the variance of the counts in the k^{th} bin. The statistical uncertainties of a_j and τ_j are determined by finding the largest and smallest value of each parameter on the surface defined by $\chi^2 + 1$ when all other parameters are free. Figure 1.1 shows the fitted parameters that resulted in a reduced chi-square value of $\chi^2 = 1.29$.

When the decay time constant is on the same order of magnitude as the PMT response time, deconvolving the impulse response of the system is of utmost importance. The impulse response function, $G(t)$ is determined experimentally using TAUFIT. Assuming the luminescent states of BaF_2 are depopulated by exponential processes and populated instantaneously [DER 92], $G(t)$ was determined by measuring the temporal distribution of BaF_2 and then fitting the data using TAUFIT to:

$$I(t) = \frac{a_1}{\tau_1} e^{-t/\tau_1} + \frac{a_2}{\tau_2} e^{-t/\tau_2} \quad (3.6)$$

Determination of $G(t)$ was an iterative process. As long as $G(t)$ is much faster than a particular characteristic time, the exact determination of $G(t)$ will not effect the fitted characteristic time. Such is the case when determining the slow decay time of BaF_2 . Initially a luminescent spectra was measured with a 1 μs TAC range having 0.556 ns bins to determine $\tau_s=578$ ns. Next another luminescent spectra was acquired with a 100 ns TAC range having 0.055 ns bins. When fitting the second data set τ_f was fixed at 0.8 ns⁵, τ_s was fixed at 578 ns, a_1 , a_2 and $G(t)$ were floating parameters in the fit. $G(t)$ was assumed to be a sum of three exponential terms, one rise and two fall times. The validity of $G(t)$ was checked by acquiring another luminosity spectrum and holding $G(t)$ fixed to determine a_1 , a_2 , τ_f and τ_s , while checking the consistency in the data and the goodness of fit.

Once the validity of $G(t)$ was established it was held fixed while other luminosity data was fit. The sample geometry used to measure the WLS decay time constant is depicted in figure 3.8. The cylindrical BaF_2 crystal had dimensions 25 mm diameter x 10 mm high and all surfaces were optically polished. The cuvette containing the liquid solution was made of synthetic fused silica glass and has good transmissivity down to ≈ 170 nm. The cuvette had an optical path length of 10 mm. After careful cleaning of the BaF_2 crystal and the cuvette with ethanol, glycerol was used to optically couple them. Glycerol was chosen for its good optical transmission properties down to ≈ 200 nm. The assembly was then wrapped with several layers of PTFE followed by a layer of aluminum foil. This arrangement resulted in good optical transmission of the BaF_2 emissions into the WLS solution. A low fluorescence

⁵Laval, et al. [LAV 83] measured the luminescence time spectrum of BaF_2 using the Bollinger and Thomas method as modified by Moszynski and Bengtson, with one exception. A HR400 microchannel plate photomultiplier with very low time jitter was used to resolve two fast components, $\tau=0.6$ ns and $\tau=0.79$ ns. Additionally, data collected with a Phillips XP2020Q PMT and fit to a single fast decay constant resolved $\tau=0.85$ ns.

long-pass filter was placed between the sample assembly and the "stop" PMT. The long-pass filter was chosen to have maximum absorption of the BaF_2 emissions while having maximum transmission of the WLS photons. In this manner, the measured luminescence spectra was composed primarily of WLS photons and are fit to:

$$I(t) = a_1 \left(\frac{1}{\tau_{\text{WLS}}} e^{-t/\tau_{\text{WLS}}} - \frac{1}{\tau_f} e^{-t/\tau_f} \right) + \frac{a_2}{\tau_s} e^{-t/\tau_s} \quad (3.7)$$

It is assumed here that the WLS luminescent states were instantaneously populated. The instantaneous population of the WLS states convolved with the exponential depopulation of the BaF_2 luminescent states results in a temporal distribution that has a rise time component that is associated with the fast BaF_2 decay and a decay time component that is associated with the fluor. Note that the slow component from BaF_2 emissions is indistinguishable from the wavelength shifted slow component in these temporal measurements because the decay time constant of the WLS is over two orders of magnitude faster than the slow BaF_2 emissions. Figure 3.10 illustrates several decay spectra showing the initial 200 ns of the pulse and the variation in the pulse shape with WLS. The values of τ_{WLS} are listed in appendix C for each molecule measured in this study. Decay time constants for the wavelength shifters ranged from 1 ns to 10 ns with a typical uncertainty of a few percent.

Besides τ_{WLS} being determined from the fit, the fraction of the luminescence from the j^{th} component, a_j , was also determined. $R(t)$, the ratio of shifted fast to shifted slow photoelectrons measured from the temporal distribution was calculated as:

$$R^*(t) = R(t) = \frac{a_1}{a_2} \quad (3.8)$$

Note that a $R(t)$ is equal to $R^*(t)$ (the ratio of fast to slow wavelength shifted photons) because both a_1 and a_2 are a measurement at the emission wavelength of the WLS. The measured $R(t)$ for my data indicates a range from 0.03 to 0.35,

Figure 3.10: Luminescence decay spectra for Perylene, DPA and BaF₂ for comparison.

depending, among other things, on the WLS and detection geometry. The details are presented in chapter IV.

A slightly modified geometry was used when evaluating a WLS for the in-line: solvent excitation technique. This technique required very thin samples, which was accomplished by placing the WLS between two fused silica slides. The in-line geometry is depicted in figure 3.11. The spacing between the slides was regulated with a copper foils of various thicknesses, 12.5 μm and 100 μm . Because of the time associated with energy transfer, the data had a rise time constant that was longer than 0.8 ns. The results from these measurements along with the value of $R(t)$ will be presented in chapter IV.

Figure 3.11: Schematic of sample geometry used for the in-line: solvent excitation technique.

3.5 Quantum Efficiency Measurement

Organic fluors with high fluorescence quantum efficiency and large Stokes shift are preferred for use as wavelength shifters because of the high light output and low self-absorption. Determination of the quantum efficiency of a wavelength shifter is necessary to evaluate its usefulness for low photon yield applications. The first reliable method for measuring absolute quantum efficiencies in solution was presented by Vavilov [VAV 24]. Since that time there have been several modifications to the Vavilov technique as well as development of other absolute measurements [DEM 71].

Because of the difficulty associated with making an absolute measurement, most quantum efficiency measurements are made relative to a "known" standard, which typically has an uncertainty of $\pm 10\%$. 9, 10 Diphenylanthracene (DPA) is used as a standard with a $Q_f = 0.86$ and a decay time constant of 7.58 ns when dissolved in cyclohexane [MOR 76]. Both absolute and relative quantum efficiency measurements will be presented in this section.

3.5.1 Absolute Measurement

A new technique to measure the quantum efficiency of an organic solute in solution was used to measure the quantum efficiency of DPA dissolved in cyclohexane. The technique is unique in that it measures variations in the temporal distribution of the luminescence after the fluor is excited by the pulsed broad-band deep UV ($\lambda_{peak} = 220$ nm, $\tau = 0.8$ ns [LAV 83]) emissions of BaF₂. As the solute concentration is increased, the luminescence spectra have a decreased contribution from transmitted UV light and an increased contribution of solute fluorescence. The quantum efficiency of the solute is determined using these data along with a correction for the differences in the detection efficiency of the primary and secondary light. The correction was determined by an optical transport code, DETECT [KNO 88], and the measured photomultiplier tube spectral response. The ratio of the experimental and computer data yields the quantum efficiency of the WLS solute.

3.5.1.1 Experimental Measurement and Results

The same experimental setup used for the luminescence temporal distribution measurements presented in section 3.4 was used here with the exception that the long-pass filter was removed from between the PMT and the WLS sample. The sample geometry is depicted in figure 3.8. The BaF₂ emissions either traverse the WLS and holder or are absorbed. If the BaF₂ emissions are absorbed by the WLS solute, the excited molecule will fluoresce with probability Q_f , emitting photons isotropically. Therefore, the luminescence pulse is composed of three distinct temporal distributions: 1) P , the transmitted fast BaF₂ emissions, 2) S , the wavelength shifted fast BaF₂ emissions, and 3) transmitted slow BaF₂ emissions and wavelength shifted slow BaF₂ emissions. Note that the intensity of the transmitted slow BaF₂

Figure 3.12: Four luminescence time spectra taken at different concentrations of 9,10 diphenylanthracene in cyclohexane. The ordinate of these distributions are each displaced a factor of ten for display.

emissions and wavelength shifted slow emissions are not utilized in the Q_f calculation. Figure 3.12 shows the initial 40 ns of the luminescence time spectra at various concentrations of DPA in cyclohexane. These spectra are fit using TAUFIT to determine $P'(c)$ and $S'(c)$, the contributions (in units of photoelectrons) of $P(c)$ and $S(c)$ at a solute concentration c . As the WLS solute concentration increases, $P'(c)$ will decrease and $S'(c)$ will increase. The light detection efficiencies are different for P and S , so the sum of $P'(c)$ and $S'(c)$ is not a constant.

The luminescence time spectra were taken at different concentrations of DPA in cyclohexane using 52 ps bin widths using an unobstructed fused silica endwindow PMT (C31000M). The measured luminescence pulse was fit to:

$$I(t) = \frac{a_1}{\tau_f} e^{-t/\tau_f} + a_2 \left(\frac{1}{\tau_{WLS}} e^{-t/\tau_{WLS}} - \frac{1}{\tau_f} e^{-t/\tau_f} \right) + \frac{a_3}{\tau_s} e^{-t/\tau_s} \quad (3.9)$$

For a given concentration c , $I(t)$ was integrated to determine the fraction of the

measured luminescence spectra that can be attributed to transmitted fast photons, $P'(c)$, wavelength shifted fast BaF_2 fraction, $S'(c)$, and the fraction of pulse that is transmitted slow BaF_2 and wavelength shifted slow BaF_2 . The total intensity of the measured luminescence was calculated from the area under the luminescence temporal distribution. The total intensity increases monotonically with increased concentration until about 9.08×10^{-5} M, at which point self-absorption becomes significant and results in decreased intensity. Self-absorption sets the maximum concentration that can be used. The minimum concentration is determined experimentally as the point where the difference in the number of transmitted photons becomes small relative to the statistical fluctuations in these data. The lowest concentration used was 1.82×10^{-6} M.

The difference in the spectral response of the PMT to BaF_2 fast emission and the WLS emissions required a correction to $P'(c)$ and $S'(c)$ to evaluate the number of photons of each component that are incident on the PMT. $P'(c)$ and $S'(c)$ are the primary and secondary emissions measured in terms of photoelectrons. The primary and secondary photons that are incident on the PMT, $P(c)$ and $S(c)$, are estimated by correcting for the spectral response of the PMT in the following manner:

$$P(c) = P'(c)/\langle \text{QE} \rangle_{\text{fast}} \quad (3.10)$$

$$S(c) = S'(c)/\langle \text{QE} \rangle_{\text{WLS}} \quad (3.11)$$

where $\langle \text{QE} \rangle_{\text{fast}}$ and $\langle \text{QE} \rangle_{\text{WLS}}$ are the average PMT quantum efficiency weighted over the BaF_2 fast emissions and the DPA emissions, respectively. The spectral response of a Burle C31000M PMT was measured relative to a NIST traceable photodiode by Optronics Laboratories and the results are shown in figure 3.13. $\langle \text{QE} \rangle_{\text{fast}}$ was determined to be 0.112 ± 0.01 , and $\langle \text{QE} \rangle_{\text{WLS}}$ to be 0.140 ± 0.005 . The normalized

values of $P_{\text{exper}}(c)$ and $S_{\text{exper}}(c)$ are plotted against concentration in figure 3.14.

Fluorescence quantum efficiency is defined as the probability of fluorescence given an absorption, which can be approximated by the number of fluorescence photons divided by the number of absorbed photons. The number of absorbed fast BaF₂ photons is $P_0 - P(c)$, where P_0 is the transmitted fast BaF₂ photons when there are no WLS solute molecules present. The number of solute fluorescence photons detected as a result of the absorption is $S(c) - S_0$, where S_0 is the number of wavelength shifted photons when there are no WLS molecules present⁶. The ratio of these two numbers defines R_{exper} , $R_{\text{exper}}(c) = (S(c) - S_0)/(P_0 - P(c))$. Because of the difference in light detection efficiency of the primary and secondary emissions $R_{\text{exper}} \neq Q_f$. R_{exper} is compared to the value of R_{model} that is determined from the computer model to obtain Q_f of the fluor.

3.5.1.2 Computer Model

The calculation of the Q_f depends on the proper optical modeling of the experiment. The complicated geometry makes it difficult to calculate R_{model} theoretically. The approach taken was to use DETECT to calculate the value of R_{model} for the case where the fluor Q_f is 1.0. DETECT is a Monte Carlo computer program developed to study light collection properties in scintillators. DETECT generates individual photons in a specified portion of the scintillating crystal, follows each photon in its passage through the various components and interactions with surfaces, models absorption, scatter, and absorption and re-emission by a wavelength shifting component, and records the fate (absorption, escape, or detection) of each photon. The

⁶ S_0 ideally would be 0, but in order not to bias the fitting, a_2 was left as a floating parameter when pure solvent was measured. The inclusion of a_2 resulted in a slightly better fit and almost negligible contribution to S_0 .

Figure 3.13: Quantum efficiency of Burle C31000M as a function of wavelength.

Figure 3.14: The variation in the number of primary and secondary photons evaluated by both the experiment and computer model as a function of concentration.

mean free path (MFP) to a WLS solute absorption was varied to simulate different concentrations. The output file provides the number of primary, $P_{model}(c)$, and secondary photons, $S_{model}(c)$ ⁷. Figure 3.14 presents how $P_{model}(c)$ and $S_{model}(c)$ vary with concentration. These data were compared with the pure solvent data to determine R_{model} in a manner similar to the calculation of R_{exper} .

The computer model uses the best available data of the modeled parameters. Modeled parameters include: the MFP to absorption of primary and secondary photons in the fused silica of the cuvette, BaF₂ crystal, and WLS solvent; the index of refraction of the cuvette, BaF₂ crystal and WLS solvent at primary and secondary wavelengths; as well as the reflection coefficient of PTFE at primary and secondary wavelengths. Cyclohexane was chosen as a solvent for the experiment because of its low absorptivity down to 200 nm. Although the absorptivity is low, it is not negligible. It would be preferable to conduct the experiment with a more transparent solvent, but other suitable solvents are unknown. The MFP to absorption by the solvent is one of the most critical parameters that determines the value of R_{model} . The absorptivity of cyclohexane was measured on a Cary 219 spectrophotometer. Calculating the average of these data weighted over the fast emission of BaF₂ results in a MFP to absorption of 13.2 mm. The MFP to absorption by DPA was varied between 1 mm (1.82×10^{-4} M) and 100 mm (1.82×10^{-6} M). Because the relative magnitude of the MFP of the solvent and solute are the same, R varied with concentration as seen in figure 3.15. Additional causes for the variation in R result from the difference in the transmissivity and reflectivities of the primary and secondary photons in various sample assembly components.

⁷In the computer model the slow BaF₂ emissions were not simulated.

Figure 3.15: R_{exper} , R_{model} and Q_f as a function of concentration. Error bars indicate the estimated uncertainty in the measurements.

3.5.1.3 Uncertainty Analysis

The analysis of measurement uncertainties can be broken down into two parts by evaluating the uncertainties in R_{exper} and R_{model} . The approach taken was to determine the fluctuation in R as a function of a particular property value, x , while holding all others constant. The property value under investigation was varied between plus and minus two standard deviations from the expected value. The value of R was fit, as a function of the property value, to a second degree polynomial. The polynomial was differentiated to measure the magnitude of the dependence of x on the value of R , i.e., $\partial R / \partial x$. Table 3.1 summarizes x , the uncertainty in each property value, σ_x , $\partial R / \partial x$ and $\partial R / \partial x * \sigma_x$. The ratio $\sigma_{R_{model}} / R_{model}$ is calculated from the square root of the sum of the squares of the values in the last column of Table 3.1 above the horizontal line and is 6.6%.

Table 3.1: Values and Uncertainties of Physical Properties and Fitted Decay Time Constants

Property	Emission	Value (σ)	Uncertainty (σ_z)	$-\partial R/\partial x$	$\partial R/\partial x \approx \sigma_z$
BaF ₂ refractive index	primary	1.538 [HAR 86, MAL64]	0.005	1	5×10^{-3}
	secondary	1.482 [MAL64]	0.005	0.6	3×10^{-3}
BaF ₂ absorptivity	primary	300 mm MFP [WEI 91]	50 mm	9.9×10^{-4}	4.95×10^{-2}
	secondary	400 mm MFP [WEI 91]	50 mm	2.5×10^{-4}	1.25×10^{-2}
WLS refractive index	primary	1.51	0.01	5.75	5.75×10^{-2}
	secondary	1.47	0.01	-4.75	-4.75×10^{-2}
WLS solvent absorptivity	primary	13.2 mm MFP	0.5 mm	-0.11	5.5×10^{-2}
	secondary	400 mm MFP	10 mm	1.9×10^{-4}	1.9×10^{-3}
Fused Silica refractive index	primary	1.53 [ORI 90]	0.005	1.04	5.2×10^{-3}
	secondary	1.465 [ORI 90]	0.005	2.94	1.47×10^{-2}
Fused Silica absorptivity	primary	95 mm MFP [ORI 90]	10 mm	-5.0×10^{-4}	-5.0×10^{-3}
	secondary	195 mm MFP [ORI 90]	20 mm	5.0×10^{-5}	1.0×10^{-4}
PTFE reflectivity	primary	0.96 [WEI 81]	0.02	1.7	3.4×10^{-2}
	secondary	0.98 [WEI 81]	0.02	3.0	6.0×10^{-2}
PMT Cathode QE	primary	0.112	0.01	13.85	1.39×10^{-1}
	secondary	0.140	0.005	10.99	5.5×10^{-2}
τ_f	primary	0.79 ns	0.005 ns	5.0×10^{-3}	2.5×10^{-3}
τ_{WLS}	secondary	7.08 ns	0.08 ns	0.115	9.2×10^{-3}
τ_s	both†	578.8 ns	3.5 ns	4.3×10^{-4}	1.5×10^{-3}

† See text for details

The variation in R_{exper} was calculated relative to the decay times and the uncertainty in the PMT cathode quantum efficiency by using the data below the horizontal line in Table 3.1. $\sigma_{R_{\text{exper}}}/R_{\text{exper}}$ is calculated to have a value of 10.3%. The uncertainty in Q_f is calculated by:

$$(\sigma_{Q_f}/Q_f)^2 = (\sigma_{R_{\text{model}}}/R_{\text{model}})^2 + (\sigma_{R_{\text{exper}}}/R_{\text{exper}})^2 \quad (3.12)$$

and is $\sigma_{Q_f}/Q_f = 12.3\%$. The calculated uncertainties in R_{model} , R_{exper} and Q_f are displayed as error bars in figure 3.15.

3.5.1.4 Quantum Efficiency Calculation

The computer model simulates, among other things, $Q_f = 1$. The Q_f of the organic fluor is thus:

$$Q_f(c) = \frac{R_{\text{exper}}(c)}{R_{\text{model}}(c)} \quad (3.13)$$

$Q_f(c)$ was calculated at several concentrations and these data are presented in figure 3.15. Q_f is an intrinsic property that should not vary with concentration. Several measurements of $Q_f(c)$ were taken to generate some statistics on the experimental fluctuations. Averaging the ten values of $Q_f(c)$ yields a fluorescence quantum efficiency of DPA of $Q_f = 0.76 \pm 0.06$ when excited with the broad-band fast BaF_2 emissions. The quoted uncertainty is the standard deviation in the mean value of Q_f .

3.5.2 Relative Measurement

In contrast to the difficulty associated with the absolute measurement, a relative measurement of the luminescence quantum efficiency is straightforward since a sample is measured relative to a "known" standard. By making a corrections for

index of refraction mismatch, detector response, and the molar extinction coefficient averaged over the excitation source, the relative quantum efficiency of the sample can be determined from [DEM 71]:

$$Q_r = Q_s \left(\frac{A(\lambda_s)}{A(\lambda_r)} \right) \left(\frac{I_0(\lambda_s)}{I_0(\lambda_r)} \right) \left(\frac{n_r^2}{n_s^2} \right) \left(\frac{D_r}{D_s} \right) \quad (3.14)$$

where r denotes the sample and s is the "known" standard solution, $A(\lambda)$ is the fraction of photons that were absorbed by the solute at wavelength λ , $I_0(\lambda)$ is the relative intensity of excitation photons at λ , n is the average index of refraction, and D is the integrated area under the corrected emission spectrum. Because the solvent may also absorb in the wavelength region of the excitation source, $A(\lambda)$ is defined as [GIL 68]:

$$A(\lambda) = \frac{A_{\text{solute}}(\lambda)}{A_{\text{solute}}(\lambda) + A_{\text{solvent}}(\lambda)} \left(1 - 10^{-A_{\text{solute}}(\lambda) - A_{\text{solvent}}(\lambda)} \right) \quad (3.15)$$

$A_{\text{solvent}}(\lambda) = \log[I_0(\lambda)/I(\lambda)]$ is obtained from the data presented in figure 3.3 and $A_{\text{solute}}(\lambda) = \epsilon(\lambda)bx$. $A(\lambda)$ is determined over the 220 nm band-pass filter response. The solutions measured were very dilute and used the same solvent so $n_r^2/n_s^2 \approx 1$. $I(\lambda_s)/I(\lambda_r)$ is set equal to 1 which is a valid approximation because the emission spectra of the unknown and the standard are both measured with the 220 nm band-pass filtered deuterium lamp. Measurements relative to DPA at a concentration of 3.03×10^{-6} M in cyclohexane are presented in chapter IV and appendix C. Also presented in that appendix are comparisons to other Q_f measurements.

Generally, my measurement of Q_f is lower than other reported values shown in Appendix C. One reason for the difference could be that $Q_f(\lambda) \neq \text{constant}$. Except for a few molecules [WEB 58, GIL 68] the assumption that $Q_f(\lambda) = \text{constant}$ has not been tested, nor proven. Because 220 nm photons usually excite to S_2 or S_3 , for $Q_f(\lambda)$ to be a constant implies the probability of making a transition down to S_1

must be 1. If this transition probability is not one, then my measured value of Q_f will be lower than other researchers' values. Quite clearly the constant Q_f assumption also does not take into account dissociation which can become appreciable at higher energies (shorter wavelengths). As an example, DCF dissociated quite rapidly when excited with 220 nm photons. The other possible explanation for our lower values of Q_f is the chemicals were not of sufficient purity and impurity quenching resulted. As indicated in section 2.7.1 quenching not only results in a lower value of Q_f but also a faster decay time constant. The faster decay time constant is consistent with some of the fluors measured here.

3.6 Photoelectron Yield Measurements

Photoelectron (PE) yield is a relative number that depends not only on the photocathode material, but also on the bias voltage, voltage divider circuit, end-window thickness and material, PMT lifetime and manufacturer, the crystal being measured and coupling between the crystal and the PMT. Despite all of these variations, photoelectron yield is still reported to give an estimate of the size of the pulse to be measured. Inherent to determining the PE yield is the determination of the PMT gain. There are several methods available for determining the PMT gain [SAK 87, MIY 84, WRI 81, OCA 84, PEA 91]. The procedure used here to measure PMT gain is outlined in O' Callaghan, et al. [OCA 84], and Peak, et al. [PEA 91]. The technique utilizes a PMT with a well resolved single photoelectron peak to give the best estimate of the gain. An assumption that the PMT has good linearity is reasonable for the Burle C31000M PMT. The C31000M was also chosen for its high gain, negative electron affinity, GaP(Ce) first dynode. The properties of the C31000M with the recommended bias between the cathode and the first

dynode are such that the photocathode signal is well separated from the noise generated in the dynode structure. The resulting single photoelectron distribution had a resolution of 44% FWHM, see figure 3.16.

The relatively narrow distribution allowed for good determination of the mean value of the single photoelectron peak amplitude. The PMT voltage divider was Burle design B and the PMT was biased at -1800V. The PMT anode current was input to a Canberra 2005 charge sensitive pre-amp where the current was converted into voltage. The output of the pre-amp was input to an Ortec 572 linear amplifier with a shaping time of 3 μ s and a gain of 500. A BNC tail pulse generator was used to power the GaP (green) LED while strobing the MCA. Figure 3.17 shows the pulse processing system used to determine the single photoelectron distribution. Figure 3.16 shows a typical single photoelectron distribution when the intensity of the LED is set to ensure that only one photon strikes the photomultiplier tube over the integration time of the shaping amplifier. The current through the LED determines the intensity of the LED, but there is a threshold current that must be overcome before the LED will light. As an aid to measuring only one PE, the PMT was well separated from the LED and the PMT endwindow was masked with aluminum foil except for a pinhole. The LED current was then varied so either no photons were detected or a maximum of one photon per current pulse. Increased current resulted in a greater number of PE being detected. The single PE peak results when a minimum signal is detected.

With the SPE distribution measured, the MCA must be calibrated in units of charge. A charge (q) injected into the Canberra 2005 charge sensitive preamplifier was determined using the shaped square wave method [VAL 92]. The shaped square wave (SSW) method shapes a square wave such that it has the appearance of the

Figure 3.16: Single photoelectron spectrum of a Burle C31000M

Figure 3.17: Schematic of the configuration used to measure the single photoelectron distribution and the photoelectron yield.

differentiated PMT anode current pulse. The output of the SSW circuit was connected to the test input capacitor of the pre-amp. The test capacitor integrates the injected voltage pulse from the SSW circuit resulting in a current pulse that has the same shape as the PMT anode pulse. Using the SSW technique, a correction is made for any ballistic deficit that may result from a finite shaping time. Determining the charge corresponding to the mean value of the single photoelectron peak, the mean photomultiplier tube gain can be calculated by:

$$\langle g \rangle = \frac{Ne}{q} \quad (3.16)$$

where $N(= 1)$ is the number of photoelectrons generated in the photocathode, e is the electron charge and $\langle g \rangle$ is the mean PMT gain. Biasing the C31000M at -1800V gave $\langle g \rangle = 8.0 \pm 0.2 \times 10^6$.

The photoelectron yield from a sample is determined using equation 3.16 but with the only unknown being N . For these measurements the LED and tail pulse generator were replaced with the sample and a 10 μ Ci Cs-137 source. When a BaF₂ crystal was coupled to the C31000M with glycerol the photoelectron (PE) yield was measured to be 1094 PE/MeV for a shaping time of 3 μ s, which agrees well with the results of Wei et al. [WEI 91]. The value of $R(t)$ (ratio of fast to slow PE yield) was determined using the technique discussed in section 3.4 was 0.20 for BaF₂, which calculates to be 186 fast PE/MeV and 909 slow PE/MeV.

When measuring the PE yield of a WLS, the sample assembly illustrated in figure 3.8 or figure 3.11 was utilized. Note the PE yield data for the orthogonal technique was made available from Lorenz [LOR 92] and was not measured here. The long-pass filter was coupled to both the cuvette and the C31000M using glycerol.

CHAPTER IV

DISCUSSION AND RESULTS

In the previous chapter, measurements and measurement techniques of the most important quantities needed for evaluation a wavelength shifters for BaF_2 were presented. Discussion of these measurements and their results will be evaluated for application to the spectral separation of BaF_2 . Also the degree of spectral, and more importantly, temporal separation that was achieved with each of the three techniques is shown. The advantages and disadvantages of each technique, as well as their physical limitations, is also presented.

4.1 General Considerations

The fast 0.8 ns emissions of BaF_2 account for about 1400 photons/MeV [DOR 92]. The disadvantage of BaF_2 is the presence of the dominant (9500 photons/MeV [DOR 92]) ≈ 600 ns decay time constant component. If the slow emissions of BaF_2 can be eliminated, then it can be employed at high count rates with less pulse pile-up than any other inorganic scintillator. Measuring the ratio of the fast and slow emissions, $R_{\text{BaF}_2}(t)$, by a temporal measurement discussed in section 3.4 resulted in $R_{\text{BaF}_2}(t) = a_1/a_2 = 0.20$. $R_{\text{BaF}_2}(t)$ is consistent with other researchers measurements, $R_{\text{BaF}_2}(t) = 0.25$ [LAV 83] and 0.18 [WEI 91]. Note that $R_{\text{BaF}_2}(t)$ is a ratio of the

measured fast and slow photoelectron yield, a quantity that varies with the PMT used in the measurement. A correction for the average PMT photocathode quantum efficiency weighted by the BaF₂ emission, $\langle QE \rangle_{fast}$ and $\langle QE \rangle_{slow}$ (assuming the light collection efficiency for both the fast and slow emissions are the same in the luminosity temporal distribution measurements) reveals $R_{BaF_2}^*(t)$, the ratio of incident fast and slow photons:

$$R_{BaF_2}^*(t) = \frac{a_1 / \langle QE \rangle_{fast}}{a_2 / \langle QE \rangle_{slow}} \quad (4.1)$$

$$= R_{BaF_2}(t) * \frac{\langle QE \rangle_{slow}}{\langle QE \rangle_{fast}} \quad (4.2)$$

$$= 0.24 \quad (4.3)$$

where $\langle QE \rangle_{slow} = 0.132$ and $\langle QE \rangle_{fast} = 0.112$ for the C31000M PMT that was used.

As illustrated in appendix A, the fast and slow emissions are the result of two different scintillation mechanisms having several different peak wavelengths. Separation of the BaF₂ emissions spectrally results in an approximate separation of the emissions temporally, which can be seen using time-resolved emission measurements. Laval, et al. [LAV 83] showed that the fast emissions extend up to ≈ 300 nm (see figure 4.1), and is consistent with the valence-core transitions illustrated in figure A.2. Only the slow emissions are present when exciting a BaF₂ crystal with alpha particles. The slow emission spectrum illustrated in figure 4.2, as presented by Kubota, et al. [KUB 87b], shows that perfect temporal separation is possible only if the emissions below ≈ 200 nm are measured. Detection of only those BaF₂ photons < 200 nm is impractical with conventional PMTs because of the very low intensity and the spectral overlap with the radiant sensitivity of the photocathode is slight. On the other hand, solar blind photocathodes constructed of CsI and CsI/TMAE [AND 92] show very high radiant sensitivities at these wavelengths and may have some practical

Figure 4.1: Time-resolved emission spectrum of barium fluoride [LAV 83].

Figure 4.2: Emission spectra from a BaF_2 when excited by (a) electrons and (b) alpha particles [KUB 87].

applications to BaF₂ emissions. To achieve good spectral separation while maintaining high detection efficiency of the fast photons, detection of the photons <240 nm appears to be optimum. The central theme of wavelength shifting techniques to spectrally separate BaF₂ emissions has been to minimize detection of the emissions between $240 < \lambda \leq 400$ nm and maximize detection for $\lambda \leq 240$ nm.

As a comparison to $R_{BaF_2}(t)$, $R_{BaF_2}(\lambda)$ is calculated in the following manner:

$$R_{BaF_2}(\lambda) = \frac{\sum_{\lambda \leq 240} I_{BaF_2}(\lambda)}{\sum_{\substack{\lambda < 180 \\ \lambda \leq 400}} I_{BaF_2}(\lambda)} \quad (4.4)$$

$$= 0.134 \quad (4.5)$$

where $I_{BaF_2}(\lambda)$ is the background-subtracted, nonlinearity corrected emission spectrum presented in figure 1.2. Noting the overlap shown in figures 4.1 and 4.2, the assertion that spectral separation also results in a temporal separation is not strictly correct¹. To make an accurate quantitative comparison of $R_{BaF_2}(t)$ and $R_{BaF_2}(\lambda)$, time resolved emissions measurements need to be made. While these measurements were not taken, knowing the fast and slow photon distributions would have assisted in the comparison of $R(t)$ and $R(\lambda)$, the ratio of fast to slow wavelength shifted emissions as measured temporally and spectrally, respectively. Note that knowing the fast and slow distributions is not essential for this work. The goal is to minimize the contribution of the slow component coming from the BaF₂ while shifting the fast component to a wavelength in the peak spectral range of the PMT. The figure of merit, R , for how well a WLS accomplishes spectral separation can be derived using λ or t . Because of the spectral overlap of the fast and slow emissions of BaF₂,

¹In some instances the difference between $R(\lambda)$ and $R(t)$ may be attributed to the inefficiency of an electron making a transition from S_{nm} to S_{10} . It is generally accepted that these higher order transitions occur with unity probability, but compounds should be evaluated on an individual basis to determine whether the assumptions has validity.

$R(t) \neq R(\lambda)$. However, because the overlap is relatively minor, either $R(t)$ or $R(\lambda)$ is sufficient to make quantitative comparisons of the relative effectiveness of various WLS. In most cases it is easier and/or faster to evaluate $R(\lambda)$ than $R(t)$. $R(\lambda)$ was used merely as a tool to evaluate a compound for spectral separation, whereas $R(t)$ is our final quantity of interest.

4.2 Properties of WLSs Needed for Spectral Separation

There are four primary properties of the WLS needed for applications involving BaF_2 emissions: fluorescence at or near the peak spectral response of the photodetector, high fluorescence quantum efficiency, fast decay time constant, and absorption characteristics tailored to the BaF_2 emission spectrum. In this section, each of these properties is addressed.

The quantum efficiency of a PMT photocathode is defined as the probability that an incident photon generates a photoelectron which is collected. A typical PMT has a peak quantum efficiency of 10-30% at ≈ 410 nm, and falls off markedly at 300 nm and 575 nm. The spectral response range of the PMT can be extended by use of special endwindow material that is transparent down to ≈ 160 nm, or by using an extended red photocathode, a spectral response up to ≈ 650 nm is possible². The spectral response of a PMT is limited; therefore, it is advantageous that the solute fluoresce at ≈ 350 – 450 nm to maximize spectral matching between the PMT sensitivity and the solute fluorescence emission.

Fluorescence quantum efficiency is as important as the fluorescence emission

²Photodiodes (PD) typically have a higher quantum efficiency and a wider range of spectral response compared to conventional PMTs. The quantum efficiency of a PD is defined as the probability of creating an electron-hole pair in the semiconductor for an incident photon. Current technology PIN photodiodes and associated electronics typically have noise levels on the order of 300 electrons FWHM. Because of the low luminosity of the fast component of BaF_2 (≈ 1400 photons/MeV) the signal to noise for a 1 MeV gamma ray is low; therefore PIN photodiodes were not considered for our application.

wavelength because it also dictates the number of photons that will eventually be detected. The fluorescence quantum efficiency of the WLS is an indication of the amount of BaF_2 emissions that are shifted to longer wavelengths. The quantum efficiency of a photocathode at 220 nm is typically lower than at 410 nm. So when wavelength shifting, if the losses imposed by the WLS with $Q_f < 1$ are outweighed by the gain associated with the increased spectral matching, the signal-to-noise of the WLS/PMT system will increase. To assure negligible degradation in the signal the fluorescence quantum efficiency should be as high as possible. Molecules with $Q_f > 0.5$ were considered in this work.

The property that makes BaF_2 of so much interest is the decay time of its luminescence when excited with gamma rays and beta particles. BaF_2 is one of the fastest known inorganic scintillating crystals. For an application that includes high count rates, signal speed is of utmost importance. When wavelength shifting, the speed at which the signal can be acquired is dictated by the WLS decay time constant. It is therefore advantageous to utilize a fluor that is as fast as possible. The maximum solute decay time constant that was investigated was 10 ns. Although 10 ns is considerably slower than the 0.8 ns decay time constant of BaF_2 , it is still faster than other scintillators that could be used for many applications (cf. table 1.1).

Optical absorption was also studied in detail. The fluorescence spectra, fluorescence quantum efficiency and decay time constant are not sensitive to the particular wavelength shifting technique used. However, the overall efficiency of the WLS in separating the BaF_2 emissions depends strongly on the absorption characteristics. To best describe these absorption characteristics, each detection technique will be presented separately.

4.2.1 Orthogonal Geometry

As shown in figure 1.4, the orthogonal geometry technique is named for the geometrical arrangement of the scintillator/WLS and the PMT. Using this detection geometry, the photon intensity emitted from the BaF₂ crystal $I_0(\lambda, t)$ is incident on the WLS. The transmitted photon intensity, $I(\lambda, t)$, is a measure of the photons that pass through the WLS without absorption. The intensity of the absorbed photons, $I_0(\lambda, t) - I(\lambda, t)$, is proportional to the probability of absorption by the solute, $A_{\text{solute}}(\lambda)$, and the solvent, $A_{\text{solvent}}(\lambda)$. The fraction of the absorbed photon intensity that is absorbed by the solute is $A_{\text{solute}}(\lambda)/(A_{\text{solute}}(\lambda) + A_{\text{solvent}}(\lambda))$. If absorbed at wavelength λ by the solute, the probability that the solute will fluoresce at wavelength λ' is defined as $Q_f(\lambda)$. Hence the intensity of the wavelength shifted component is:

$$I_{WLS}(\lambda', t) = Q_f(\lambda) \frac{A_{\text{solute}}(\lambda)}{A_{\text{solute}}(\lambda) + A_{\text{solvent}}(\lambda)} [I_0(\lambda, t) - I(\lambda, t)] \quad (4.6)$$

In the orthogonal technique a solute is chosen such that λ_{max} (the wavelength above which $\epsilon = 0$) is as low as practical. As discussed earlier in section 2.7.6, as the degree of condensation of the fluor increases, the maximum wavelength of absorption increases, the decay time constant decreases, and fluorescence quantum efficiency increases. Therefore, trade-offs have to be made between optimizing $R(\lambda)$, and τ and Q_f , simultaneously.

The maximum value of $R(\lambda)$ is achieved with the molecules having the fewest number of phenyl rings possible i.e. benzene (one ring) and its derivatives where $\lambda_{\text{max}} \geq 265$ nm. The disadvantage to the one ring system is that Q_f is low (≤ 0.15) and τ is long (≈ 100 ns). Going to a two ring system, i.e., biphenyl or naphthalene ($\lambda_{\text{max}} \geq 285$ nm), results in a lower value of $R(\lambda)$ because of increased absorption at

longer wavelengths, but has the advantage of Q_f being higher (typically $\leq 50\%$) and τ shorter (typically $\approx 10\text{--}30$ ns). The optimum balance between $R(\lambda)$, and Q_f and τ seems to exist for the orthogonal geometry technique in a three ring compound, i.e., terphenyl group of the p-oligophenylene series (cf. figure 2.4). Typical values of $Q_f > 0.70$ and $\tau \leq 3$ ns exist for three ring compounds. Unfortunately, $\lambda_{max} \geq 300$ nm, so that at best only about half of the slow component can be separated.

As discussed in section 2.3, the absorption leading to excitation into S_1 determines the approximate emission wavelength. For the terphenyl group, the fluorescence occurs in the emission band of BaF_2 (cf. figure 2.5), so geometrical discrimination rather than wavelength discrimination must be used to separate the various components of the emissions. By placing the PMT orthogonal to the axis of the BaF_2 crystal and WLS, minimum transmitted BaF_2 photons will be detected. For maximum spectral separation using the orthogonal technique, the BaF_2 emissions that were not absorbed by the solute on a single pass through the WLS must not be detected. As a result, photon reflectors around the WLS should not be used, particularly on the face of the WLS that is parallel to the crystal/WLS interface. The lack of reflectors results in a low light collection efficiency.

A small signal will be detected in the orthogonal technique because of the low light collection efficiency for the wavelength shifted photons. Lorenz [LOR 92] reported measuring a total of 50 PE/MeV using the orthogonal technique with BMT. $R(t)$ was calculated using the technique outlined in section 3.4 and was determined to be 0.27 and 0.33 for PTP and BMT, respectively. The product of these two numbers determines a typical fast PE yield of 17 PE/MeV. The temporal measurement can be compared to the product of the BaF_2 emission spectrum and the measured absorption

Table 4.1: Properties and Results of Orthogonal Technique

Molecule	$R_{08\%}(\lambda)$	$R(\lambda)$	$R(t)$	Q_f	τ (ns)	Fast PE Yield [†]
PTP ¹	0.21	0.19	0.27	0.69	1.14	16
BMT ²	0.42	0.24	0.33	0.58	1.09	17

¹ p-Terphenyl (2.17×10^{-3} M) cyclohexane

² 2, 2" Dimethyl-p-terphenyl (3.87×10^{-3} M) cyclohexane

[†] Based on $R_{WLS}(t)$ and data obtained from Lorenz [LOR 92]

spectrum to determine $R(\lambda)$, which is calculated in the following manner:

$$R(\lambda) \approx \frac{\sum_{\lambda \leq 240} Q_f(\lambda) I_{BaF_2}(\lambda) (1 - 10^{-\epsilon(\lambda)bx})}{\sum_{\substack{\lambda > 180 \\ \lambda \leq 400 \\ \lambda > 240}} Q_f(\lambda) I_{BaF_2}(\lambda) (1 - 10^{-\epsilon(\lambda)bx})} \quad (4.7)$$

where $(1 - 10^{-\epsilon(\lambda)bx})$ is an approximation to the absorption probability. $R(\lambda)$ was calculated to be 0.20 and 0.24 for PTP and BMT, respectively. Table 4.1 summarizes the pertinent values of the molecules that were studied for the orthogonal technique. The value of $R_{08\%}(\lambda)$ will be discussed in detail in the next section.

The orthogonal method of spectral separation has the most constraining property requirements and is the least efficient method to spectrally separate the BaF_2 emissions because of its low light collection efficiency of the wavelength shifted photons. The fast photoelectron yield of BaF_2 coupled directly to the PMT was 186 PE/MeV and the measured value of fast wavelength shifted photoelectron yield is typically 17 PE/MeV. Higher light collection efficiency and hence a greater signal can come only at the expense of decreased spectral separation when using photon reflectors.

Figure 4.3: Transmission of Oriel Corporation 395 nm long-pass filter used for the in-line techniques.

4.2.2 In-line Geometry

The idea of maximum detection of the emissions below 240 nm combined with minimum detection of the emissions above 240 nm is the same for the in-line measurements as in the orthogonal measurement, but the method to discriminate between the BaF_2 and WLS photons is different. Figure 1.3 illustrates the detection geometry used. The long-pass filter is chosen for maximum absorption of the incident BaF_2 emissions and minimum absorption of the WLS emissions. Figure 4.3 depicts a typical absorption spectrum of a 395 nm long-pass filter.

The advantage of the in-line geometry over the orthogonal geometry is that there is higher light collection efficiency in the former as a result of photon reflectors being used. The choice between emphasizing solute and solvent excitation is an inherent difference in the wavelength shifting system that is used.

4.2.2.1 Solute Excitation

The in-line: solute excitation technique places a strong emphasis not only on the magnitude of the fluor molar extinction coefficient but also the shape of $\epsilon(\lambda)$. The principle behind the technique involves choosing a fluor that has minimum absorption corresponding to the maximum BaF₂ emission (300 nm) and the width of the "valley" of the absorption spectrum that is as wide as the FWHM of the BaF₂ slow emissions (≈ 75 nm). Figure 4.4 depicts an example of an absorption spectrum of a fluor that could be used for in-line: solute excitation. To assure that the decay time of the WLS is "fast" the absorption into S₁ has to be strong, $\epsilon \approx 10^4$ /M-cm, and for good spectral separation, absorption into S₂ and S₃ must be stronger, $\epsilon \geq 10^5$ /M-cm. As shown in section 2.7.6, the more phenyl rings composing a fluor, the larger is λ_{max} and consequently, the fluorescence emissions move to longer wavelengths. Fluors used for in-line: solute excitation were confined to 4 or 5 phenyl ringed molecules to assure that the fluorescence emissions are in the peak spectral response range of the PMT. For the solute excitation technique, the "fast" BaF₂ photons are to be absorbed into singlet states S₂ or S₃ and the transitions S₂ $\rightarrow$ S₁ and S₃ $\rightarrow$ S₁ must be fast and efficient for the technique to be viable. The speed of these intramolecular transitions are usually on the order of picoseconds, and the efficiency of these transitions is traditionally considered to be unity. High transition efficiencies are of utmost importance and therefore should be evaluated for the particular molecule before being considered³.

As with the orthogonal technique, the value of $R(\lambda)$ using the in-line: solute

³Some of my recent preliminary data indicates that the transition efficiency is less than one for PTP and DPA. The concept of S₂ $\rightarrow$ S₁ and S₃ $\rightarrow$ S₁ transition efficiencies not being unity is unconventional and warrants further precision spectroscopy to verify and confirm these initial results.

Figure 4.4: Molar extinction coefficient of perylene, determined at a concentration of $\approx 10^{-6}$ M in cyclohexane.

Figure 4.5: $R(\lambda)$ and absorption efficiency of the BaF₂ fast emissions for perylene dissolved in cyclohexane as a function of concentration.

excitation technique can also be predicted using equation 4.7. Analysis of $R(\lambda)$ gives additional insight if calculated as a function of solute number density (bx) and figure 4.5 illustrates the results for perylene dissolved in cyclohexane. The figure shows that as the number density decreases the fraction of incident fast photons that are absorbed decreases. For in-line: solute excitation technique to yield optimum results there must be great disparity between $\langle \epsilon \rangle_{fast}$ and $\langle \epsilon \rangle_{slow}$, where $\langle \epsilon \rangle_{fast}$ and $\langle \epsilon \rangle_{slow}$ represent the average molar extinction coefficient weighted over the fast and slow BaF_2 emission regions, respectively. For $\langle \epsilon \rangle_{fast} > \langle \epsilon \rangle_{slow}$ the probability that a fast photon is absorbed is always greater than the corresponding probability for a slow photon. The highest fast absorption efficiency and the largest value of $R(\lambda)$ result when $\langle \epsilon \rangle_{fast} \gg \langle \epsilon \rangle_{slow}$ which is accomplished when the fluor absorption spectrum has an absorption "valley" that is deep and wide. Characterizing a fluor for in-line: solute excitation facilitated the need to measure the absorption spectrum. For the compounds examined here, the order of magnitude of the absorption valley, $\epsilon_{min}(\lambda)$, is typically no more than one order of magnitude below ϵ_{max} . Because of this "property", $R(\lambda)$ obtainable with this technique is limited.

Because large values of $R(\lambda)$ and high absorption efficiency of the fast emissions are in competition with each other, a metric, $R_{98\%}(\lambda)$, is defined to evaluate the possible potential of a fluor. $R_{98\%}(\lambda)$ is the ratio of the wavelength shifted fast to slow signal that would be expected if 98% of the fast photons that are incident on the WLS are absorbed. To calculate $R_{98\%}(\lambda)$, the number density needed for 98% absorption of the fast emissions is used to calculate the amount of absorption of the

Table 4.2: Properties and Results of In-line: Solute Excitation Technique

Molecule	$R_{99\%}(\lambda)$	$R(\lambda)$	$R(t)$	Q_f	τ (ns)	Fast PE Yield [†]
DPA ¹	0.15	0.32	0.23	0.76*	7.08	60
Perylene ²	0.29	0.50	0.32	0.53	5.94	52
DOCI ³	0.26	0.34	0.055	0.017	2.37	0.3
DASBTI ⁴	0.27	0.29		0.088		
DCF ⁵	0.26	0.29	0.083	0.51	7.75	13

*Temporal absolute measurement, others measured relative to DPA $Q_f = 0.86$

¹9,10 diphenylanthracene (3.03×10^{-5} M) cyclohexane

²perylene (3.96×10^{-5} M) cyclohexane

³3,3'-diethylthiopyranine (4.35×10^{-5} M) ethanol

⁴2(p-dimethylaminostyryl)-benzothiazolylethyl iodide (4.58×10^{-5} M) ethanol

⁵9-(o-carboxyphenyl)-2,7-dichloro-6-hydroxy-3H-xanthen-3-one (4.99×10^{-5} M) ethanol

[†] Perylene PE yield was measured, the other values were scaled relative to the measured values of Q_f

slow component:

$$R_{99\%}(\lambda) \equiv \frac{\sum_{\lambda \geq 180}^{\lambda \leq 240} 0.98 I_{B_0 F_2}(\lambda) Q_f(\lambda)}{\sum_{\lambda > 240}^{\lambda \leq 400} I_{B_0 F_2}(\lambda) Q_f(\lambda) (1 - 10^{-\epsilon(\lambda) \delta x})} \quad (4.8)$$

Table 4.2 summarizes a few of the fluors that were investigated for the in-line: solute excitation technique. Additional fluor data are presented in Appendix C. From the fluors listed in table 4.2 it is clear that, with the exception of perylene, the highest value of $R_{99\%}(\lambda)$ exists for those compounds having the lowest quantum

efficiencies. The conclusion is that fluors may exist with larger values of $R_{98\%}(\lambda)$, but data needed to calculate $R_{98\%}(\lambda)$ is not always available and would need to be measured. As discussed earlier, the physical limitations on $\epsilon(\lambda)$ make large values of $R_{98\%}(\lambda)$, with the in-line: solute excitation technique, unlikely.

4.2.2.2 Solvent Excitation

Of the three techniques to spectrally separate BaF_2 emissions using wavelength shifting techniques, in-line: solvent excitation technique has the greatest potential of achieving the largest value of R while delivering high efficiency and fast characteristic times. The solvent excitation technique is a combination of the best features of the orthogonal and in-line: solute excitation techniques. In the previous techniques, the solute was directly excited by the UV emissions of BaF_2 , the solvent was present merely as a "holder" of the solute molecules, any energy absorbed by the solvent was dissipated intramolecularly. In the in-line: solvent excitation technique, the solvent plays an active role in the absorption of the incident energy. If the solvent molecule absorbs the incident UV energy, it is elevated to an excited π -electronic state. If the solvent is pure, the excited solvent molecule can decay by emission of fluorescence with a very low probability ($Q_f \leq 0.15$) and a long decay time ($\tau < 100$ ns). If the solvent is in solution with an aromatic molecule, the excited π -electronic state of the solvent may instead transfer the excitation energy to the solute. An example of a system that has appreciable energy transfer, under the proper conditions, is 9,10 diphenylanthracene dissolved in toluene. Intermolecular energy transfer is dependent on having a sufficient concentration of solute, and if the conditions outlined in section 2.6 are met, then the energy absorbed by the solvent can be very efficiently transferred to the solute. The transfer results in the excitation

of π -electrons of the solute. The excited solute molecule can then fluoresce with its high quantum efficiency and fast characteristic times. The largest value of $R(\lambda)$ is achieved by selecting a good aromatic solvent with minimal absorption of the slow BaF_2 emissions. The BaF_2 emissions that are not absorbed by the solvent are absorbed by the long pass filter that is positioned between the WLS and PMT as illustrated in figure 1.4. As with the in-line: solute excitation technique the filter is set to have maximum absorption of the BaF_2 emissions and minimum absorption of WLS emissions.

There are many good aromatic solvents to choose from: benzene, toluene, phenylcyclohexane and p-xylene, just to name a few⁴. Under optimum conditions the rate constant for intermolecular energy transfer, $k_{XY}[Y]$, will be the dominant rate constant. If the total rate constant, k , is dominated by $k_{XY}[Y]$, energy is transferred to the solute on the order of nanoseconds or less and has a high probability of occurrence $f_{XY} \approx 0.90-1.0$.

The difficulty with the in-line: solvent excitation technique is finding a good aromatic solvent that does not absorb above 240 nm. The needed solvent could be attained from a hypsochromic shifted benzene absorption spectrum. Although benzene is a reasonably good aromatic solvent, it begins to absorb at ≈ 265 nm. By exchanging all the hydrogen atoms in benzene with deuterium the absorption spectrum undergoes a hypsochromic shift of ≈ 5 nm. Fluorinated benzene also results in a hypsochromic shift of the absorption spectrum, but fluorine is a hetero atom which quenches fluorescence. Other solvents that have n -orbitals (e.g., p-dioxane) rather than π -orbitals absorb at lower energies, but result in lower energy transfer

⁴Birks [BIR 64] presents a fairly extensive review of possible solvents and the relative efficiencies of various solutions. The general consensus is that alkyl benzenes typically yield the highest efficiency.

efficiency. *p*-Dioxane depicted in figure 4.6 only begins to absorb at $\lambda \leq 210$ nm. Because *p*-dioxane does not transfer the absorbed energy efficiently, higher than normal concentrations of solute are needed. Also *p*-dioxane is a weak absorber, so thick samples are needed to have a high probability of absorption up to 240 nm. These two effects result in the solute number density that is too high for negligible direct solute absorption, resulting in a lower than ideal $R(\lambda)$.

Toluene, a well established efficient aromatic solvent, was chosen to demonstrate the idea of intermolecular energy transfer. Although toluene will ultimately result in a lower value of $R(\lambda)$ than benzene, it is a more efficient solvent because of the higher Q_f and shorter τ . As seen in figure 4.6, toluene begins to have appreciable absorption at ≈ 277 nm, which is a slightly longer wavelength than benzene. *p*-Xylene is a more efficient solvent than toluene, but the additional methyl group causes a bathochromic shift in the absorption spectrum, as compared to toluene, resulting in a still lower value of $R(\lambda)$. Very thin samples depicted in figure 3.11 were made to assure minimum direct absorption by the solute. Figure 4.7 shows the absorptivity and fluorescence of DPA dissolved at a concentration of 3.03×10^{-3} M in toluene. Note the apparent large Stokes shift that results from the solvent excitation technique. Some direct absorption by the solute exists and can be seen by the structure at 350-400 nm, but the primary absorption is by the toluene. The fluorescence from the sample is quite clearly attributed to the DPA. The calculated value of $R(\lambda)$, using equation 4.7 is 0.53 for DPA (3.03×10^{-3} M) in toluene. As the sample thickness is decreased, there is less absorption of the fast emissions thus decreasing the WLS overall efficiency, but the value of $R(\lambda)$ increases because the absorption cut-off has a hypsochromic shift. These trends are presented in figures 4.8 and 4.9.

Although this technique does offer the greatest potential for "large" R and high

Figure 4.6: Molar extinction coefficient of toluene and p-dioxane.

Figure 4.7: Absorptivity and fluorescence of DPA dissolved in toluene at a concentration of 3.03×10^{-3} M.

Figure 4.8: Absorptivity of DPA dissolved at a concentration of 3.03×10^{-3} M at various sample thicknesses.

Figure 4.9: $R(\lambda)$ and absorption efficiency of BaF_2 fast emissions for DPA/toluene as a function of sample thickness.

Table 4.3: Properties and Results of In-line Solvent Excitation Technique

Sample	$R_{98\%}(\lambda)$	$R(\lambda)$	$R(t)$	τ_r (ns)	τ (ns)	Fast PE Yield
DPA / Toluene ¹	0.53	0.53	0.30	3.22	6.63	41

¹ DPA (3.03×10^{-3} M) Toluene

efficiency wavelength shifting, $R(\lambda)$ is not as large as initially hoped. Because of the physical limitations on efficient solvents, it seems highly unlikely that the target value of $R = 10$ can be obtained. As was demonstrated with DPA dissolved in toluene at a $12.5 \mu\text{m}$ thickness, if the thickness is decreased or if toluene is substituted with benzene, then it may be possible to hypsochromically shift the absorption by 10 nm, resulting in a calculated value of $R_{98\%}(\lambda)$ of 0.8.

The value of $R(t) = 0.29$, measured using the technique outlined in section 3.4, for DPA/toluene ($12.5 \mu\text{m}$) sample is lower than expected based on $R(\lambda)$. The difference may be attributed to the fact that $R(\lambda)$ is only an approximation to $R(t)$ as well as the possibility that $f_{XY}(\lambda)$ may not be constant. The reasons for the latter statement are similar to the arguments for $Q_f(\lambda) \neq \text{constant}$. The possibility of $f_{XY}(\lambda)$ and $Q_f(\lambda)$ not being constant are important questions that should be addressed, but are beyond the scope of this dissertation.

Other researchers [GRA 83, VIE 79] have shown that wavelength shifting efficiency of a thin film WLS can be greater than 90%. Such a high efficiency combined with the high light detection efficiency would result in a fast photoelectron yield that is higher than that presented here.

CHAPTER V

CONCLUSIONS AND FUTURE WORK

The goal of this dissertation was to determine if spectral separation of BaF_2 emissions using wavelength shifting techniques is an efficient and viable technique for the temporal separation of the emissions. Some enhancement of fast to slow signal was achieved, but not to the degree that was desired. $R(\lambda)$ and $R_{98\%}(\lambda)$ were used as a metric to assess the ability of a WLS to perform spectral separation. Both $R(\lambda)$ and $R_{98\%}(\lambda)$ are only approximations to $R(t)$, the important quantity, and the source of differences in these values have been discussed. Table 5.1 summarizes $R_{98\%}(\lambda)$, $R(t)$ and the fast PE yield of the best data obtained for each technique. The greatest potential for high efficiency spectral separation comes from the in-line geometry techniques. More work with the solvent excitation technique may be the best place to concentrate further efforts, particularly in trying different solvents. Benzene, deuterated benzene and phenylcyclohexane, seem the most likely candidates. If one of these solvents offers sufficient solubility and a thin sample is used, it may be possible to move the absorption cut-off as low as 260 nm and obtain a $R_{98\%}(\lambda)$ of ≈ 0.8 . Unfortunately, as with the other techniques used to spectrally separate BaF_2 emissions, wavelength shifting is limited by physical properties imposed by the particular technique.

Table 5.1: Summary of wavelength shifting techniques for spectral separation of BaF₂ emissions

Technique	$R_{98\%}(\lambda)$	$R(t)$	Fast PE Yield (PE/MeV)
Orthogonal Technique	0.42	0.33	17
In-line: solute excitation	0.29	0.32	50
In-line: solvent excitation	0.53	0.30	41

The photoelectron yield results are presented in chapter IV represent typical values. Light collection efficiency imposed by the geometry arrangement reduced the PE yield. The measurements made with liquid WLS could be repeated under similar conditions using a polymer solvent. Use of polymers would alleviate the need for cuvettes and slides. In addition a thin film of a non-fluorescent doped polymer could be used as a long-pass filter. The idea is to reduce the spacing between the PMT and the BaF₂ hence increasing the light collection efficiency and thus increasing the PE yield. It is theoretically possible for the fast PE yield from a WLS to approach or exceed the fast PE yield of BaF₂ coupled directly to a fused silica endwindow PMT. The wavelength shifter fluoresces at a longer wavelength (lower energy) than the absorbed photons resulting in better spectral matching between the fluor emissions and the spectral response of the PMT results. If the losses imposed by the quantum efficiency of the solute and the WLS geometry are on the same order as the gains in photoelectron yield resulting from better matching of the solute emission and photomultiplier tube spectral response, then the photoelectron yield remains the same or possibly increases.

In addition to the idea of spectral separation of BaF₂ emissions using WLS, the

other unique aspect of this dissertation is the temporal quantum efficiency measurement of a fluor in solution. The measurement technique assesses both the absorption and fluorescence on a given sample at the same time and yields a direct measure of the fluorescence quantum efficiency without having to correct for delayed fluorescence and phosphorescence. Another advantage to the measurement is a less stringent requirement for a "reference" since the sample is measured against itself. One of the limitations is its dependence on the computer model for the geometrical corrections used to calculate Q_f . The dependence on the model could be reduced or possibly eliminated with the use of a less absorbing solvent and/or a different sample assembly geometry. Another disadvantage is the finite decay time of the BaF_2 fast emissions, thus limiting the choice of solutes to those that have a decay time constant that is appreciably longer than 0.8 ns. The longer solute decay time allows for better discrimination of the transmitted fast BaF_2 emission. Measurement of the absolute quantum efficiency with the temporal technique allows for an independent measurement of important "standard" molecules. The technique was demonstrated using DPA dissolved in cyclohexane and yielded $Q_f = 0.76 \pm 0.09$ when excited with the broad-band fast emissions of BaF_2 , which is lower than the value that was previously reported $Q_f = 0.86$ [MOR 76]. The technique should be further investigated with other fluors to determine its general applicability.

One possible explanation for the difference in my values of Q_f and the published values is the difference in the excitation wavelength¹. My data was acquired with a "monochromatic" 220 nm pump source, which is more energetic than typically used, thus exciting into S_2 and S_3 rather than into S_1 which is more typical. Another

¹It should be pointed out that it is not unusual for two different research groups to come to opposite conclusions about the wavelength independence of Q_f for a particular solution (see, for example, [DAW 68, GIL 68]). Weber, et al. [WEB 58], states that quantum efficiency is wavelength independent and presents data on 26 organic fluors to "prove" the point.

possible explanation for the lower calculated values of quantum efficiency is impurity quenching, as the result of impure fluors and/or solvents. Impurity quenching also results in decreased decay times, which is consistent with some of my measured values of τ_f . Decay time constants that are shorter than expected is typically used as an indication of impurity quenching. The idea that $Q_f(\lambda)$ is not constant with wavelength needs further investigation to determine if they are contributing to the difference between $R(\lambda)$ and $R(t)$.

Many absorption spectra of aromatic compounds [BER 71, FRI 51, KOD 87, BRA 86] were examined to determine their usefulness as a potential WLS component. In some cases, available data on fluor properties was either incomplete or unavailable, thus requiring further measurements of the needed data. In the end, only a handful of promising fluors and solvents for each of the techniques were identified. Enough insight was gained into the underlying physical properties and theories to argue that spectral separation using WLS is possible, but not to the extent that was initially hoped for. Rather WLS techniques for the spectral separation of BaF_2 emissions should be used in conjunction with a crystal of elevated temperature or with a lanthanum doped crystal to enhance the degree of separation that these two techniques offer separately. The maximum R obtainable by either temperature elevation or lanthanum doping without any reduction in the fast signal has been shown experimentally to be 1.0. Because these two other techniques reduce the slow component by suppressing the same scintillation mechanism, using them both simultaneously does not further increase R . It is possible however to combine either elevated crystal temperature or lanthanum doping with a solar blind PMT or with the wavelength shifting techniques presented here to increase the value of R . Wei, et al. [WEI 91], measured the emissions from $\text{BaF}_2(\text{La})$ with a Cs-Te solar blind photocathode and

calculated a value of $R(t)=4.2$ with 76 PE/MeV. Woody et al. [WOO 89] performed a similar experiment without such dramatic results. In his work, a 1 mole-% lanthanum doping of BaF_2 measured with a CsTe photocathode yielded a value of $R(t)=1.2$ and 102 fast PE/MeV. The difference is possibly attributed to the photocathode spectral response and crystal quality. Similar results should be obtained by combining the in-line: solvent excitation technique to a lanthanum doped BaF_2 crystal.

Recent advances in solar-blind PMTs currently seem to be the best technique for high efficiency, fast timing and good spectral separation. Work by two different research groups using different photocathode materials have made great advancements. CsI and CsI/TMAE photocathodes [AND 92] have the advantage of good timing, high quantum efficiency at low wavelengths (<200 nm) and good spectral separation possibilities. The disadvantage of these photocathodes is that they have a very weak response to photons with wavelengths longer than ≈ 200 nm. The photocathodes have excellent spectral separation because they do not detect any slow BaF_2 signal, but fail to utilize all (or even most) the fast BaF_2 emissions. It is estimated that the CsI and the CsI/TMAE photocathodes only collect a few percent of the fast emissions. In addition, work being conducted for the development of a BaF_2 calorimeter for the Superconducting Super-Collider involves the development of a PMT with either a CsTeK or a RbTe photocathode [WIS 92]. The sensitivity cut-off of these solar blind photocathodes is ≈ 280 nm. With the CsTeK and RbTe photocathodes, the degree of spectral separation is not superior to the CsI and the CsI/TMAE photocathodes, but the fast photon efficiency is significantly higher.

As an alternative to spectral separation of BaF_2 emissions, additional research and development of "new" scintillators should be pursued. Cerium fluoride (CeF_3) is relatively fast, relatively luminous, and radiation hard detector. The unfortunate

property of CeF_3 is that the scintillation emissions are self-absorbing. The fast emissions of the trivalent cerium ion are attractive and has resulted in research to find a suitable host crystal for this activator [MOS 90b, SUZ 92, TAI 86, VIS 91]. The recent discovery of LSO:Ce [MEL 92] uses the LSO (lutetium oxyorthosilicate) crystal lattice as sites for the Ce^{3+} ions and is transparent to the emissions of the ion. The result is a luminosity that is 75% of NaI(Tl) and a decay time of 40 ns. The radiation hardness of LSO:Ce still needs to be evaluated before it would be considered for intense radiation fields. Further development in other host crystals to the Ce^{3+} ion can be explored as well as other compounds that scintillate by a cross-over transition. The "forbidden" cross-over transitions, demonstrated in BaF_2 , is a signature for a fast scintillation decay time constant and could be studied further to understand and predict its occurrence in other scintillator materials. Another area that appears fruitful is the fast 5d-4f rare earth transitions, which are present in $\text{LaF}_3\text{:Nd}^{3+}$ [SCH 88a, DOR 90]. Again suitable host crystals need to be found to increase the luminosity of these transitions.

APPENDICES

APPENDIX A

BaF₂ SCINTILLATION MECHANISM

The earliest reported discovery of the scintillation of BaF₂ was by Farukhi and Swinehart [FAR 71] in 1971. The scintillation emission with peak emission wavelength at 310 nm and decay time constant of 600 ns was attributed to self-trapped excitons (STE). An STE consists of a self-trapped hole¹ bound to an electron. The STE exists in a metastable state resulting in the relatively long decay time constant. Independent confirmation of the existence of STE decay was reported by Ershov, et al., [ERS 82] and later studied experimentally by Aleksandrov, et al. [ALE 84], using synchrotron radiation. The energy of the synchrotron radiation was varied revealing that the STE emissions existed only when the incident energy was greater than 10.5 eV, which corresponds to the bandgap energy.

One of the more interesting discoveries is that the metastable STE state can either decay radiatively, which yields the luminescence at 310 nm, or decays by thermally activated dissociation of the electron from the self-trapped hole center. Thermally quenching of STE states was first studied by Beaumont, et al. [BEA 70], and later demonstrated with BaF₂ by Schotanus, et al. [SCH 85], showing decreased slow emissions with elevated crystal temperatures. It is speculated that quenching

¹A self-trapped hole or V_k center comprises a hole localized to two adjacent halide ions thereby bound to each other in an X_2^- molecular configuration [WIL 76]

caused by dissociation can also be caused by lanthanum ions in the crystal [SCH 89c]. Schotanus, et al. [SCH 89c], and Wei, et al. [WEI 91], show that negligible fast emissions are quenched up to a La^{3+} doping of 1 mole-%. Woody, et al. [WOO 89], shows a slight decrease in fast emissions over the same region. With no loss of fast signal, $R(t) = 0.8$ was obtained [SCH 89c]. Schotanus, et al., demonstrated that higher values of $R(t)$ were possible, but only at the expense of decreased fast signal.

The most intriguing property of BaF_2 is the sub-nanosecond luminescence that was discovered by several Soviet scientists in 1982 [ERS 82]. The first theoretical explanation for the fast luminescence component came from another group of Soviet scientists headed by Aleksandrov [ALE 84]. Aleksandrov, et al., using pulsed synchrotron photons with energies between 9 and 30 eV, probed the BaF_2 crystal in order to determine its band structure. The presence of the 220 nm emission only occurred when the excitation photon energy was >18.1 eV. The explanation for the fast luminescence component was proposed by Valbis et al. [VAL 85]. The threshold excitation energy corresponds to the ionization of cations, i.e., formation of holes in the $5p\text{Ba}^{2+}$ (core) band. Electrons are lifted into the conduction band, crossing over the $2p\text{F}^-$ (valence) band. Such a transition is called a crossover transition. The observed luminescence is the result of electrons making a transition from the valence band to the core band. Because of the energy difference between the conduction and valence band ($E_g = 10.5$ eV) is greater than the energy difference between the valence and core bands ($E_{vc} = 7.8$ eV) the crossover transition luminescence is seen as an intense component of the intrinsic luminescence because Auger electron² emission is energetically impossible. "Auger-free" luminescence has been the subject of intense

²An Auger electron is an electron of energy equal to the difference between the original atomic excitation energy and the binding energy of the outer atomic shell from which the electron was ejected.

development [ITO 88], not only in conjunction with understanding BaF_2 scintillation mechanism, but also other scintillation materials because of the connection between "Auger-free" luminescence and fast emissions [KUB 90].

The structure in the fast luminescence band with peaks at 220, 195 and a very weak 178 nm [VAL 85, SHI 88] (see figure A.1) is not caused by spin orbit splitting of the Ba^{2+} core levels since these emission bands have the same excitation threshold of 18.1 eV [VAL 85, ITO 88]. Rather the structure can be attributed to the density-of-states of the valence band [STA 81, KUB 87b]. All of the "Auger-free" luminescence emissions of BaF_2 have the same decay time constant and temperature dependence.

The hole in the $2p\text{F}^-$ band, resulting from the transition to the $5p\text{Ba}^{2+}$ band, may subsequently recombine with an electron from the conduction band under the formation of a STE. Thus, the production of a hole in the core band results in two kinds of luminescent states: "Auger-free" and self-trapped exciton [SCH 89a]. The band diagram of BaF_2 (figure A.2 [SCH 88]) illustrates the various emissions and their relation to the energy difference of the bands.

Figure A.1: Emission Spectrum of Barium Fluoride, Highlighting Slow Emission Spectrum [SCH 87]

Figure A.2: Band Diagram for Barium Fluoride

APPENDIX B

STATISTICAL DERIVATION OF THE BOLLINGER AND THOMAS TECHNIQUE

B.1 Probability of Intervals

The underlying concept of the Bollinger and Thomas method is that for a given excitation of the scintillator the probability that the photomultiplier tube detects a photon is very much less than 1. The scintillation light intensity is thus randomly sampled in time, and after the detection of many pulses the scintillation luminescence time distribution is formed. The following is a mathematical derivation of the technique for a single exponentially decaying source.

The probability of detecting a photon from a given energy deposition in a scintillator decreases exponentially with time because the mean number of excited states decreases exponentially with time. Since the mean is time dependent, the generalized Poisson distribution must be used to solve the problem. Consider the following definitions for an exponentially decaying source:

$i \equiv$ photon detection rate at $t = 0$

$i * e^{-t/\tau} =$ photon detection rate at time t

Using these definitions the following definitions follow:

$$\begin{aligned}
 p_1(t)dt &\equiv \text{differential probability of detecting one photon in } (t, t + dt) \\
 &\quad \text{for a given excited state} \\
 &= i * e^{-t/\tau} dt
 \end{aligned} \tag{B.1}$$

$$\begin{aligned}
 \mu(t) &\equiv \text{average number of photons detected in } (0, t) \\
 &= \int_0^t p_1(t') dt'
 \end{aligned} \tag{B.2}$$

$$= \int_0^t i * e^{t'/\tau} dt' \tag{B.3}$$

$$= i\tau (1 - e^{-t/\tau}) \tag{B.4}$$

Note that $\mu(\infty) = i\tau$ is the mean number of photons detected for a given excitation.

$$\begin{aligned}
 p_0(t)dt &\equiv \text{differential probability of detecting no photons in } (t, t + dt) \\
 &= 1 - p_1(t)dt
 \end{aligned} \tag{B.5}$$

$$= 1 - i * e^{-t/\tau} dt \tag{B.6}$$

$$P_0(t) \equiv \text{probability of detecting no photons in } (0, t)$$

The probability of detecting no events in $(0, t)$ is the probability of not detecting a photon in the interval $(0, t_1)$ multiplied by the probability of not detecting a photon in the interval $(t_1, t_2) \dots$ multiplied by the probability of not detecting a photon in the interval (t_{n-1}, t_n) , where the interval $(0, t)$ is split into n intervals. Writing this mathematically:

$$P_0(t) = p_0(0) dt * p_0(t_1) dt * \dots * p_0(t_{n-1}) dt \tag{B.7}$$

$$= (1 - i * e^{-0/\tau} dt) * (1 - i * e^{-t_1/\tau} dt) * \dots * (1 - i * e^{-t_{n-1}/\tau} dt) \tag{B.8}$$

If the intervals are evenly distributed such that the value t/n is substituted for dt and the limit is taken as $n \rightarrow \infty$

$$\begin{aligned}
P_0(t) &= \left(1 - i * e^{-0/(n\tau)} \frac{t}{n}\right) * \left(1 - i * e^{-t/(n\tau)} \frac{t}{n}\right) * \dots \\
&\quad \dots * \left(1 - i * e^{-(n-1)t/(n\tau)} \frac{t}{n}\right) \quad n \rightarrow \infty \\
&= \prod_{j=0}^{n-1} \left[1 - i * e^{-jt/(n\tau)} \frac{t}{n}\right] \quad n \rightarrow \infty \quad (B.9)
\end{aligned}$$

By taking the natural logarithm of both sides equation B.9 can be written:

$$\ln(P_0(t)) = \sum_{j=0}^{n-1} \ln \left[1 - ie^{-jt/(n\tau)} \left(\frac{t}{n}\right)\right] \quad n \rightarrow \infty \quad (B.10)$$

Noting:

$$\ln(1 - x) = -(x + x^2/2 + x^3/3 + x^4/4 + \dots),$$

then:

$$\ln(1 - x) = -x \quad \text{as } x \rightarrow 0.$$

Making the above substitutions:

$$\ln(P_0(t)) = \sum_{j=0}^{n-1} -i * e^{-jt/(n\tau)} \left(\frac{t}{n}\right) \quad n \rightarrow \infty \quad (B.11)$$

$$= -\left(\frac{it}{n}\right) \sum_{j=0}^{n-1} e^{-jt/(n\tau)} \quad n \rightarrow \infty \quad (B.12)$$

The above sum is a geometric series, hence it has a closed form solution:

$$\sum_{j=0}^{n-1} aq^j = \frac{a(1 - q^n)}{1 - q} \quad (B.13)$$

Also note another simplification: $e^{-x} = 1 - x$ as $x \rightarrow 0$

$$\ln(P_0(t)) = \left(-\frac{it}{n}\right) \frac{1 - e^{-t/\tau}}{1 - e^{-t/(n\tau)}} \quad (B.14)$$

$$= \left(-\frac{it}{n}\right) \frac{1 - e^{-t/\tau}}{1 - [1 - t/(n\tau)]} \quad (B.15)$$

$$= \left(-\frac{it}{n}\right) \frac{1 - e^{-t/\tau}}{t/(n\tau)} \quad (B.16)$$

$$= (-i\tau)(1 - e^{-t/\tau}) \quad (\text{B.17})$$

Hence :

$$P_0(t) = e^{-i\tau(1 - e^{-t/\tau})} \quad (\text{B.18})$$

$$= e^{-\mu(t)} \quad (\text{B.19})$$

$$\text{where : } \mu(t) = i\tau(1 - e^{-t/\tau})$$

Defining a few more terms:

$f(t) \equiv$ probability density function for detecting at least one photon

$f(t)\Delta t \equiv$ probability of detecting at least one photon in $(t, t + \Delta t)$

$F(t) \equiv$ probability of detecting at least one photon in the interval $(0, t)$

$$= 1 - P_0(t) \quad (\text{B.20})$$

$$= \int_0^t f(t') dt' \quad (\text{B.21})$$

Remember that $P_0(t)$ is the probability of detecting no photons in $(0, t)$, so $(1 - P_0(t))$ is the probability of detecting at least one photon in $(0, t)$.

$$\frac{dF(t)}{dt} = f(t) = \frac{-dP_0(t)}{dt} \quad (\text{B.22})$$

Solving for $f(t)$

$$f(t) = \frac{-d}{dt} [e^{-\mu(t)}] \quad (\text{B.23})$$

$$= e^{-\mu(t)} \frac{-d}{dt} [\mu(t)] \quad (\text{B.24})$$

$$= i * e^{-t/\tau} e^{-\mu(t)} \quad (\text{B.25})$$

The term, $e^{-\mu(t)}$, is a correction factor that needs to be applied if the probability of detecting a single photon is *not* much less than 1. Stating this differently, the mean number of photons detected for a given excitation is very much less than one, i.e.,

$\mu(\infty) = i\tau \ll 1$, or the correction factor must be applied.

For $\mu(\infty) = i\tau \ll 1$

$$e^{-\mu(t)} \approx 1 - \mu(t)$$

$$f(t) \approx i * e^{-t/\tau} * (1 - \mu(t)) \quad (\text{B.26})$$

$$\approx i * e^{-t/\tau} * [1 - i\tau(1 - e^{-t/\tau})] \quad (\text{B.27})$$

$$\approx i * e^{-t/\tau} \quad (\text{B.28})$$

The result is that if the probability of detecting a photon from a given excitation is much less than one, then the probability of detecting at least one photon is equivalent to the probability of detecting one photon, and is directly proportional to the intensity of photons that are emitted at a given time, for a given excitation, $I(t) = i * e^{-t/\tau}$. This proves the Bollinger and Thomas method is valid for determining the scintillation decay spectrum if the above assumptions are met.

The above derivation was for a single excitation on the scintillation crystal. When extending the problem to many excitations, the distribution now becomes:

$$I(t) = \sum_{j=1}^n i(j) * e^{-t/\tau} \quad (\text{B.29})$$

$$= I_0 * e^{-t/\tau} \quad (\text{B.30})$$

where n is the total number of detected excitations and $i(j)$ is the photon intensity at time $t = 0$ for the j^{th} detected excitation. I_0 is just a constant and the distribution in a does not have to be known as long as one is only interested in the decay time constant. In the case of two or more exponential, the individual I_0 's carry no meaning, but relative comparisons of the I_0 's are consistent. If data are collected in a manner such that $\mu(\infty) \ll 1$ then the general relationship must be used:

$$I(t) = i * e^{-t/\tau} e^{-i\tau(1 - e^{-t/\tau})} \quad (\text{B.31})$$

For a sequences of these measurements:

$$I(t) = \sum_{j=1}^n i(j) * e^{-t/\tau} e^{-i(j)\tau(1-e^{-t/\tau})} \quad (\text{B.32})$$

In the more general case, the distribution of i 's must be known. The distribution of i is simply the pulse height distribution of the sample when excited with a Na-22 source. Although the correction is straight forward, it is an added degree of complexity that isn't necessary. Therefore, it is always better to collect data in a manner such a manner that $i\tau \ll 1$ for all i or implement the technique suggested by Moses [MOS 92]. Harris and Selinger [HAR 79] showed the validity of using equation B.32. In their system, a flash lamp excited an organic molecule. In this arrangement the values of i are all approximately the same. Therefore, the correction is a bit easier to apply than when having to infer the distribution in i .

B.1.1 Generalized Poisson Distribution

The following is a rederivation of the work that was initially presented by Ruark, et al. [RAU 36].

The Poisson Distribution is typically used for cases having a constant mean, μ . This section develops the ground work for the generalized Poisson Distribution which includes the case of the mean varying exponentially with time. First, a few definitions:

$P_n(t + \Delta t) \equiv$ probability of detecting n photons in the interval $(0, t + \Delta t)$

$P_{n-1}(t) \equiv$ probability of detecting $n - 1$ photons in $(0, t)$

$P_n(t) \equiv$ probability of detecting n photons in $(0, t)$

$p_0(t)\Delta t \equiv$ probability of detecting 0 photons in $(t, t + \Delta t)$

$p_1(t)\Delta t \equiv$ probability of detecting 1 photon in $(t, t + \Delta t)$

The probability of detecting n photons in $(0, t + \Delta t)$ is equal to the probability of detecting $n - 1$ photons in the interval $(0, t)$ multiplied by the probability of detecting 1 photon in $(t, t + \Delta t)$ combined with the probability of detecting n photons in $(0, t)$ times the probability of detecting no photons in $(t, t + \Delta t)$. This assumes that the probability of more than 1 photon in the interval $(t, t + \Delta t)$ is negligible, i.e., $p_0(t)\Delta t = 1 - p_1(t)\Delta t$ (in the limit that Δt becomes a differential time this becomes an exact expression). Mathematically, this is written as:

$$P_n(t + \Delta t) = P_{n-1}(t)p_1(t)\Delta t + P_n(t)p_0(t)\Delta t \quad (\text{B.33})$$

$$= P_{n-1}(t)p_1(t)\Delta t + P_n(t)[1 - p_1(t)\Delta t] \quad (\text{B.34})$$

$$= p_1(t)[P_{n-1}(t) - P_n(t)]\Delta t + P_n(t) \quad (\text{B.35})$$

$$P_n(t + \Delta t) - P_n(t) = p_1(t)[P_{n-1}(t) - P_n(t)]\Delta t \quad (\text{B.36})$$

$$\frac{P_n(t + \Delta t) - P_n(t)}{\Delta t} = p_1(t)[P_{n-1}(t) - P_n(t)] \quad (\text{B.37})$$

In the limit that Δt is a differential time step, the following is true

$$\frac{dP_n(t)}{dt} = p_1(t)[P_{n-1}(t) - P_n(t)] \quad (\text{B.38})$$

The above differential equation can be solved with the appropriate boundary conditions:

$$P_0(0) = 1 \quad (\text{B.39})$$

$$P_n(0) = 0 \quad (\text{B.40})$$

Solving for $n = 1, 2$ and 3 , the general form of the solution to the differential equation can be defined.

$$n = 0 : \frac{dP_0(t)}{dt} = -p_1(t)P_0(t) \quad (\text{B.41})$$

$$P_0(t) = e^{-\int_0^t p_1(t')dt'} \quad (\text{B.42})$$

$$n = 1 : \frac{dP_1(t)}{dt} + p_1(t)P_1(t) = p_1(t) * e^{-\int_0^t p_1(t')dt'} \quad (\text{B.43})$$

$$P_1(t) = \left(-\int_0^t p_1(t')dt'\right) * e^{-\int_0^t p_1(t')dt'} \quad (\text{B.44})$$

$$n = 2 : \frac{dP_2(t)}{dt} + p_1(t)P_2(t) = p_1(t) \left[\left(\int_0^t p_1(t')dt'\right) * e^{-\int_0^t p_1(t')dt'} \right] \quad (\text{B.45})$$

$$P_2(t) = \frac{1}{2} \left(-\int_0^t p_1(t')dt'\right)^2 * e^{-\int_0^t p_1(t')dt'} \quad (\text{B.46})$$

$$\text{In general : } P_n(\mu(t)) = \frac{[\mu(t)]^n e^{-\mu(t)}}{n!} \quad (\text{B.47})$$

$$\text{where : } \mu(t) = \int_0^t p_1(t')dt' \quad (\text{B.48})$$

Equations B.47 and B.48 represent the generalized Poisson Distribution, where $\mu(t)$ is the time varying mean. With these equations, the validity of the Bollinger and Thomas method can again be shown. For an exponentially decaying source such as luminescence, $p_1(t) = i * e^{-t/\tau}$. Making these substitutions into equation B.47 and B.48 and setting $n = 0$, we get the same results as seen in equation B.19.

B.2 Conclusion

Two different methods for determining the validity of the Bollinger and Thomas method of measuring the scintillation decay curve have been shown. Under the appropriate assumptions both methods give the same result. That is, if the mean number of photons detected for a given excitation is very much less than one then the probability of detecting at least one photon for a given excitation is directly proportional to the emission intensity in $(t, t + \Delta t)$. In addition, if the condition that the probability of detecting a single photon for a given excitation cannot be

met then a correction factor can be applied to the fitting function.

When fitting decay curves to a light pulse that originates at two different wavelengths, the assumption is normally made that the probability of detection by the photodetector is independent of wavelength. That may not be the case if there are two different emission wavelengths. In that case, the probability of generating a signal is dependent on the quantum efficiency of the photodetector and this difference in probability of detection is a correction factor for the amplitude terms of the fitting equation. The methods shown here can be easily extended to luminescence pulses that have two or more exponentials.

APPENDIX C

EXPERIMENTAL AND PUBLISHED DATA

Table C.1: Solvents and fluors that were investigated

Compound	Measured τ (ns)	Measured Q_f	Published τ (ns)	Published Q_f
Benzene			29 ^a	0.07 ^a
Biphenyl			16 ^a	0.18 ^a
Phenylcyclohexane			26.4 ^a	0.15 ^a
p-Xylene			30 ^a	0.40 ^a
Toluene			34 ^a	0.17 ^a
BBOT ¹	1.5	0.97	1.1 ^a	0.61 ^b
BMT ²	1.09	0.58		
Coumarin 2 ³	3.7			
Coumarin 4 ⁴	3.55			
Coumarin 120 ⁵	3.52			
DASBTI ⁶		0.089		
DCF ⁷	7.75	0.51		
DMA ⁸	9.33			
DM-POPOP ⁹	1.52	0.76	1.5 ^a	0.77 ^b
DPS ¹⁰	3.49		1.1 ^a	
DOCI ¹¹	2.37	0.017		
DPA ¹²	7.08	0.76	7.58 ^c	0.86 ^c
Perylene	6.01	0.53	6.4 ^a	0.78 ^b
PTP ¹³	1.14	0.69	0.95 ^a	0.77 ^b

¹2,5-Bis(5-tert-butyl-2-benzoxazolyl)thiophene²2,2" Dimethyl-p-terphenyl³4,6-Dimethyl-7-ethylamino-coumarin⁴7-Hydroxy-4-methylcoumarin⁵7-Amino-4-methylcoumarin⁶2(p-Dimethylaminostyryl)-benzothiazolylethyl iodine⁷2,7-Dichlorofluorescein⁸Dimethyl anthracene⁹1,4-Bis(4-methyl-5-phenyloxazol-2-yl) benzene¹⁰Diphenyl stilbene¹¹3,3'-Diethyloxacarbocyanine iodide¹²Diphenyl anthracene¹³p-Terphenyl^a Data from [BER 71]^b Data from [BIR 70]^c Data from [MOR 76]

Figure C.1: Benzene absorption and emission spectrum [BER 71].

Figure C.2: Biphenyl absorption and emission spectrum [BER 71].

Figure C.3: Phenylcyclohexane absorption and emission spectrum [BER 71].

Figure C.4: p-Xylene absorption and emission spectrum [BER 71].

Figure C.5: Toluene absorption and emission spectrum [BER 71].

Figure C.8: Published BMT absorption spectrum [BRA 86].

Figure C.9: Measured BMT absorption and emission spectrum.

Figure C.10: Published coumarin 2 absorption spectrum [BRA 86].

Figure C.11: Measured coumarin 2 emission spectrum.

Figure C.12: Published coumarin 4 absorption spectrum [BRA 86].

Figure C.13: Measured coumarin 4 emission spectrum.

Figure C.14: Published coumarin 120 absorption spectrum [BRA 86].

Figure C.15: Measured coumarin 120 emission spectrum.

Figure C.16: Published DASBTI absorption spectrum [BRA 86].

Figure C.17: Measured DASBTI absorption and emission spectrum.

Figure C.18: Published DCF absorption spectrum [BRA 86].

Figure C.19: Measured DCF absorption and emission spectrum.

Figure C.20: Published DMA absorption spectrum [LAN 61].

Figure C.21: Measured DMA emission spectrum.

Figure C.22: Published DM-POPOP absorption and emission spectrum [BER 71].

Figure C.23: Measured DM-POPOP absorption and emission spectrum.

Figure C.24: Published DPS absorption and emission spectrum [BER 71].

Figure C.25: Measured DPS emission spectrum.

Figure C.26: Published DOCI absorption spectrum [BRA 86].

Figure C.27: Measured DOCI absorption and emission spectrum.

Figure C.28: Published DPA absorption spectrum [FRI 51].

Figure C.29: Measured DPA absorption and emission spectrum.

Figure C.30: Published perylene absorption and emission spectrum [BER 71].

Figure C.31: Measured perylene absorption and emission spectrum.

Figure C.32: Published PTP absorption and emission spectrum [BER 71].

Figure C.33: Measured PTP absorption and emission spectrum.

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