

## Chapter 3

### TIME-RESOLVED FLUORESCENCE AND TWO-STATE KINETIC MODELS FOR 1-AZACARBAZOLE

#### 3.1 Introduction

The characteristics of the steady-state fluorescence of 1AC in various neat solvents were described and analyzed in Chapter 2. In this chapter we summarize the observed time-dependence of 1AC emission. In order to facilitate interpretation of the measured excited-state lifetimes to be discussed in later chapters, a number of two-state kinetic schemes are presented. Sections 3.3 and 3.4 contain details of analysis that will be used in Chapters 6 and 7, and the reader may wish to defer reading these sections until later.

In a time-resolved fluorescence experiment, the following fluorescence decay behavior is typically observed. The fluorescence of the normal species of 1AC in neat solvents may be typically characterized by one or two decay components or lifetimes. One short lifetime component may be attributed to the dynamic Stokes shift that results from solvent molecules reorganizing about a different charge distribution of the solute in an excited-state. The second lifetime component is attributed to the time-dependence of the normal species' population. In aprotic solvents that do not catalyze the tautomerization reaction, the normal lifetime is about 10 ns. In protic solvents that

promote the reaction, the emission is quenched and the lifetimes are approximately 10 times shorter. Fluorescence appearing from the tautomer species is typically characterized by three lifetime components: one rising component (attributed to the deactivation of the tautomer) and one or two decaying components attributed to the reaction time and, in some cases, to trace impurities.

### 3.2 Irreversible Proton-Transfer Scheme

A great simplification of a proton-transfer reaction is illustrated in *Figure 3.1*. This irreversible proton-transfer kinetic scheme has proven successful in interpreting photochemistry of 7AI and 1AC in bulk alcohols<sup>1-8</sup> and isolated complexes. The surrounding solvent molecules are neglected temporarily as we focus on the hydrogen-bonded complex presumed to catalyze the reaction. Although acetic acid is paired with 1AC in this example, any of the protic solvents considered in this thesis could be drawn in its place.

Below the molecular cartoon in *Figure 3.1* is a two-state kinetic scheme. The relative energetics of the normal and tautomer species deduced from experiment have also been verified by quantum chemical calculations for 7AI.<sup>9</sup> The normal form of 1AC is lowest in energy and thus the ground-state population of 1AC predominantly consists of this form. If 1AC is promoted to the first excited-state  $S_1$  following absorption of an ultraviolet photon (as discussed in Chapter 2), then one of three processes will depopulate this excited state. (1) The excited normal form may return to the ground state by emitting a photon (the radiative rate,  $k_{\text{rad}}^{\text{N}}$ ). (2) The excited normal form may return to the ground

state by transferring energy to surrounding molecules (the nonradiative rate,  $k_{nr}^N$ ).

(3) The excited normal form will react to form an excited tautomer species (the reaction rate,  $k_{PT}$ ). It is assumed in the irreversible proton-transfer scheme that once the excited tautomer species is formed, only radiative ( $k_{rad}^T$ ) or nonradiative ( $k_{nr}^T$ ) processes will depopulate this product state. Because the ground-state tautomer species is higher in energy than the ground-state normal species, additional proton-transfer reactions occur over a longer time to produce the normal species again (the ground-state reaction rate,  $k_{T \rightarrow N}$ ).

In this model the populations of the excited-state normal ( $N^*(t)$ ) and tautomer ( $T^*(t)$ ) species can be described by the following expressions

$$N^*(t) = N^*(0) \exp(-kt) \quad (3.1)$$

$$T^*(t) = N^*(0) \left( \frac{k_{PT}}{k - k^T} \right) [\exp(-k^T t) - \exp(-kt)] \quad (3.2)$$

$$\text{where } k = k_{PT} + k_{rad}^N + k_{nr}^N, \text{ and} \quad (3.3)$$

$$k^T = k_{rad}^T + k_{nr}^T \quad (3.4)$$

If the proton-transfer reaction is the dominant pathway for depopulating the excited normal species, then the normal species' fluorescence lifetime ( $1/k$ ) will be a measure of the proton-transfer time. The tautomer emission is predicted to be biexponential with one of its two lifetimes corresponding to the proton-transfer time ( $1/k_{PT}$ ), and the other to the deactivation of the tautomer species thus formed time ( $1/k^T$ ). Note that the rising component of the tautomer species does not necessarily correspond to the growth of the product during the reaction. Instead, it is the relative rates of the reaction and of the

tautomer deactivation that determine the correct interpretation of the tautomer rise time. If the tautomer deactivation rate is less than the reaction rate, then the prefactor  $k_{PT}/(k-k^T)$  in Equation 3.2 is greater than zero and the tautomer rise time corresponds to the reaction. On the other hand, if the tautomer deactivation rate is greater than the reaction rate, then this prefactor is negative and the tautomer rise time corresponds to the tautomer deactivation. The importance of the relative magnitudes of the reaction rate and tautomer deactivation rate has also been illustrated in the observation of the excited-state double-proton-transfer in 3-cyano-7-azaindole in water.<sup>10</sup>

The time-resolved emission spectra of 1AC and 7AI in bulk alcohols at room temperature are indeed largely characterized this way (see, for example, *Table 2.3*).<sup>1-5</sup> As already mentioned, it may be necessary to include a rapid decay time in the normal emission to account for a dynamic Stokes shift attributed to solvation dynamics unrelated to the reaction,<sup>1</sup> and a long lifetime with small amplitude (< 5%) to account for impurities.<sup>1-4,11,12</sup> But the underlying kinetics does conform to this scheme in most cases. Additional verification of the model is provided by the consistency of the radiative rates in many bulk protic solvents (*Table 2.3*) determined on the basis of Equations 3.1-3.4.

In cases when the proton-transfer rate is too fast to be resolved, this scheme provides an alternative means for estimating the rate using other quantities which may be more easily measured in experiment. Assuming that an irreversible reaction completely depopulates the normal excited state, the proton-transfer rate is simply:<sup>1-4,6-8</sup>

$$k_{PT} = \frac{k_{rad}^N}{k_{rad}^T} \frac{\phi^T}{\phi^N} k^T \quad ( 3.5 )$$

$\phi^N$  and  $\phi^T$  are the quantum yields of the normal and tautomer species, respectively.

Equation 3.5 will be used both to estimate  $k_{PT}$  when the rate is too fast to measure and to separate  $k_{rad}^N + k_{nr}^N$  from  $k_{PT}$  in the observed rate  $k$  when  $k_{PT}$  becomes slow. To use Equation 3.5, we need  $k_{rad}^N / k_{rad}^T$  which can be obtained in different ways. One way is to assume that the ratio is independent of solvent. The observed rate has been measured in 11 bulk protic solvents at room temperature, and the ratio of radiative rates in this expression falls within the range (Table 2.3):<sup>13</sup>

$$\alpha(1AC) = k_{rad}^N / k_{rad}^T = 8.1 \pm 20\%. \quad ( 3.6 )$$

### 3.3 Prompt Emission and the Irreversible Proton-Transfer Model

As will be discussed in Section 6.5, it is possible that some fraction of the reactants are poised to undergo reaction at a rate greater than can be resolved by our instrumentation (*i.e.*,  $k > (25 \text{ ps})^{-1}$ ). In such cases the emission kinetics we detect will reflect only the slower, remaining portion of the population. Proper interpretation of the kinetics of these reactions depends on being able to assess whether or not an unresolvably rapid reaction has occurred. In this section we discuss how the fraction of a proposed unresolved reaction component can be estimated.

The excited-state tautomerization reaction of 1AC is again examined within the framework of the two-state kinetic model in *Figure 3.1*. The populations of the excited-state normal  $N^*(t)$  and tautomer  $T^*(t)$  species are rewritten below:

$$N^*(t) = N^*(0) \exp(-k t) \quad ( 3.7 )$$

$$T^*(t) = N^*(0) \beta \exp(-k t) - [N^*(0) \beta - T^*(0)] \exp(-k^T t) \quad ( 3.8 )$$

$$\text{where } k = k^N + k^{PT} \quad (3.9)$$

$$\text{and } \beta = k^{PT} / (k^T - k). \quad (3.10)$$

If the entire reaction is observed, then  $T^*(0) = T_0 = 0$ , and Equation 3.8 assumes the form of Equation 3.2. If a subset of the normal population reacts more quickly than may be observed with the experiment's time-resolution, then "prompt fluorescence" of the tautomer species will be measured in addition to the emission recorded during the observed reaction. This fraction undergoing prompt reaction [ $f = T_0 / N_0$ ] may be determined by the following analysis.

The (ideal) tautomer decay is described by a biexponential fit:

$$F_T(\lambda, t) = a_{PT} \exp(-k t) + a_T \exp(-k^T t), \quad (3.11)$$

where one of the normalized amplitudes is negative. The amplitudes of Equation 3.11 are identified with the appropriate coefficients of  $T^*(t)$  in Equation 3.8:

$$1 + a_T/a_{PT} = T_0 / (N_0 \beta). \quad (3.12)$$

If the proton-transfer rate is much greater than the rate of the normal deactivation ( $k^{PT} \gg k^N$ ), the observed tautomer population  $T^*(t)$  is equal to the observed normal population  $N_0$  and the population  $T_0$  formed by the prompt reaction. With this assumption Equation 3.12 simplifies to the following expression for the fraction of species involved in a prompt reaction:

$$1 + \frac{a_T}{a_{PT}} = \frac{f}{1-f} \left( \frac{\tau^{PT}}{\tau^T} - 1 \right), \text{ or } f = \frac{r}{1-r} \text{ with } r = \left( 1 + \frac{a_T}{a_{PT}} \right) / \left( \frac{\tau^{PT}}{\tau^T} - 1 \right). \quad (3.13)$$

In earlier work, it was noted that the emission band of the normal species extended into the region of tautomer fluorescence.<sup>1</sup> To account for this possible spectral contamination

in the tautomer emission, the analysis may be extended. The measured fluorescence is directly related to the species emitting:

$$F(\lambda, t) = f_N(\lambda) \cdot k_{\text{rad}}^N \cdot N^*(t) + f_T(\lambda) \cdot k_{\text{rad}}^T \cdot T^*(t), \quad (3.14)$$

where  $f_X(\lambda)$  is the fraction of species X emitting at a given wavelength and normalized such that  $\int f_X(\lambda) d\lambda = 1$ . Using the constant  $c(\lambda)$  defined in Equation 3.15, Equation 3.16 describes a tautomer pseudopopulation (correcting the population of Equation 3.8) which produces the fluorescence described by Equation 3.17.

$$c(\lambda) = \frac{f_N(\lambda) \cdot k_{\text{rad}}^N}{f_T(\lambda) \cdot k_{\text{rad}}^T} \quad (3.15)$$

$$T'(\lambda, t) = N_0 (c(\lambda) + \beta) \exp(-k t) - (N_0 \beta - T_0) \exp(-k^T t) \quad (3.16)$$

$$F_{T'}(\lambda, t) = a_{PT}' \exp(-k t) + a_T \exp(-k^T t). \quad (3.17)$$

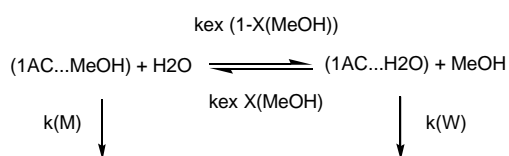
If  $c(\lambda) \ll \beta$ , the correction is not important. Should the correction be significant, the correct amplitude  $a_{PT}$  may be obtained from the measured  $a_{PT}'$  by scaling with the fraction  $\beta/(c(\lambda) + \beta)$ . The fraction of species producing prompt fluorescence is determined by application of Equation 3.13.

### 3.4 Two-State Kinetic Model in Mixed Solvents

Two different mixed solvents will be considered later in this dissertation. In Chapter 6, the reaction of 1AC will be measured in mixtures of methanol and water. In Chapter 8, kinetic isotope effects of 1AC will be studied in mixtures of methanol and

methanol-OD. The following model is useful in understanding the time-dependence of the emission of 1AC in such mixed solvents.

In each of the aforementioned experiments, the total population of 1AC is measured (Scheme 3.1). Using notation appropriate to the case of water and methanol, we have:



Scheme 3.1

Assuming that proton-transfer is the dominant pathway for deactivation of the normal species with rates characteristic for methanol  $k(\text{M}) = k_{\text{M}}$  and for water  $k(\text{W}) = k_{\text{W}}$ , the total population of 1AC is given by:

$$\frac{N(t)}{N(0)} = \frac{r_+ - r_-}{r_- - r_+} e^{-r_+ t} + \frac{r_- - r_+}{r_+ - r_-} e^{-r_- t} \quad (3.18)$$

$$\text{where } r_{\pm} = 1/2\{(\mathbf{a} + \mathbf{a}') \pm \sqrt{(\mathbf{a} - \mathbf{a}')^2 + 4\mathbf{b}\mathbf{b}'}\}$$

$$\rho = (1-X_{\text{M}}) k_{\text{M}} + X_{\text{M}} k_{\text{W}} + k_{\text{ex}}$$

$$\alpha = k_{\text{M}} + X_{\text{M}} k_{\text{ex}} \quad (3.19)$$

$$\alpha' = k_{\text{W}} + (1-X_{\text{M}}) k_{\text{ex}}$$

$$\beta = X_{\text{M}} k_{\text{ex}}$$

$$\beta' = (1-X_{\text{M}}) k_{\text{ex}}$$

In the limit of rapid exchange of solvent molecules,  $k_{\text{ex}} \gg (k_{\text{M}}, k_{\text{W}})$ , Equation 3.18 becomes a single exponential function whose argument involves the average rate of proton-transfer:

$$N(t)/N(0) \sim \exp\{- (X_{\text{M}} k_{\text{M}} + (1-X_{\text{M}}) k_{\text{W}}) t\} \quad ( 3.20 )$$

In the limit of very slow exchange,  $k_{\text{ex}} \ll (k_{\text{M}}, k_{\text{W}})$ , Equation 3.18 separates into a biexponential function whose rates correspond to the individual proton-transfer rates:

$$N(t)/N(0) \sim X_{\text{M}} \exp\{-k_{\text{M}} t\} + (1-X_{\text{M}}) \exp\{-k_{\text{W}} t\} \quad ( 3.21 )$$

### 3.5 Solvent Dependence of the Observed Reaction Rates

The time-resolved emission and quantum yields of 1AC in a variety of solvents are summarized in *Table 2.3* in the previous chapter. The fluorescent lifetimes observed for the normal and tautomer species of 1AC are consistent with the irreversible proton-transfer scheme (with essentially no prompt tautomer emission) described in this chapter. In this section an overview of the solvent dependence of the observed reaction rates is presented in order to motivate the studies discussed in the following chapters.

An initial study of the proton-transfer reaction of 7AI noted a remarkable correlation between the rate of excited-state tautomerization of 7AI in bulk alcohols and the  $E_{\text{T}}(30)$  solvent polarity scale.<sup>1</sup> A similar correlation was later identified for the reaction involving 1AC.<sup>4</sup> (See *Figure 3.2* for a representative summary of these correlations.) This pair of correlations establishes a linear free-energy relationship<sup>14</sup> between these two structurally similar proton-transfer molecules. The rate of excited-state tautomerization depends on the hydrogen-bond strength between the proton-transfer

molecule and the solvent (hence the correlation with the  $E_T(30)$  solvent scale), and it depends upon some intrinsic feature of the proton-transfer molecules themselves (hence the difference in rates for a given solvent). Nearly temperature-independent kinetic isotope effects<sup>5</sup> for 7AI (IE ~ 3) and 1AC (IE ~ 5) in bulk alcohols further suggested that an intrinsic proton-transfer rate might be conceptually separated from the solvent's role in the reaction.<sup>5</sup> The proposed decomposition of the observed proton-transfer rate,<sup>5,15</sup>

$$k_{\text{obs}} = k_{\text{PT}} \exp(-\Delta G/RT) \quad ( 3.22 )$$

essentially divides the rate into a product of factors consistent with the linear free-energy relationship.

The decomposition of the one observed rate for the excited-state reaction of 7AI or 1AC in any particular bulk protic solvent into two (or more) contributions from different physical effects allows flexibility in interpretation. A two-step model is naturally supported by free-energy relationships that reveal that the observed rates depend on both solute (*e.g.*, intrinsic proton transfer step) and solvent (*e.g.*, polarity) effects. Is one step rate-determining? In Chapter 4 we discuss the ultrafast proton-transfer rate in isolated complexes that adds support to the possibility of a rapid intrinsic rate for a catalytic reaction. Solvent effects are considered in Chapters 5 and 6. In this arena, computer simulations have assisted the interpretation of some experimental observations. For example, the absence of significant prompt tautomer fluorescence (<5%) in all the bulk solvents studied is consistent with recent computer simulations that demonstrate the rarity of cyclically hydrogen-bonded complexes in alcohol solvents.<sup>15</sup> And while the remarkable correlation of the rate with the hydrogen-bond donating ability

of the solvent is consistent with either extreme of a two-step model, recent computer simulations lend support toward the strong influence of the solvent factor through a correlation between the observed rates and “relative reactive fractions.”<sup>15</sup> On the other hand, the reaction of 1AC in solvents such as diols and water appear to be anomalously slow when compared to the rate correlations with other alcohols on the  $E_T(30)$  solvent scale. These “anomalously slow” reactions are considered in detail in Chapters 5 and 6.

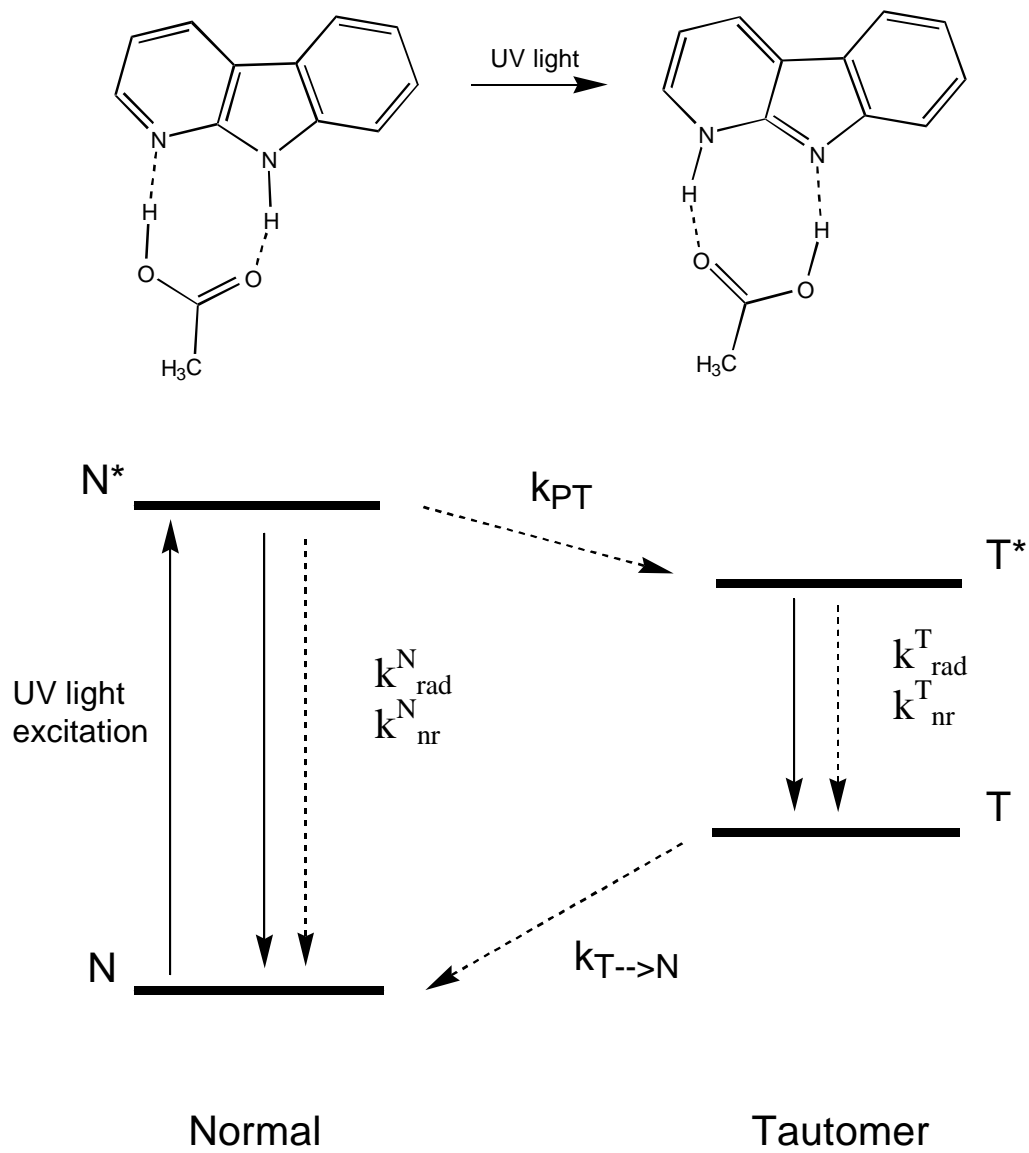


Figure 3.1: Irreversible Proton-Transfer Scheme

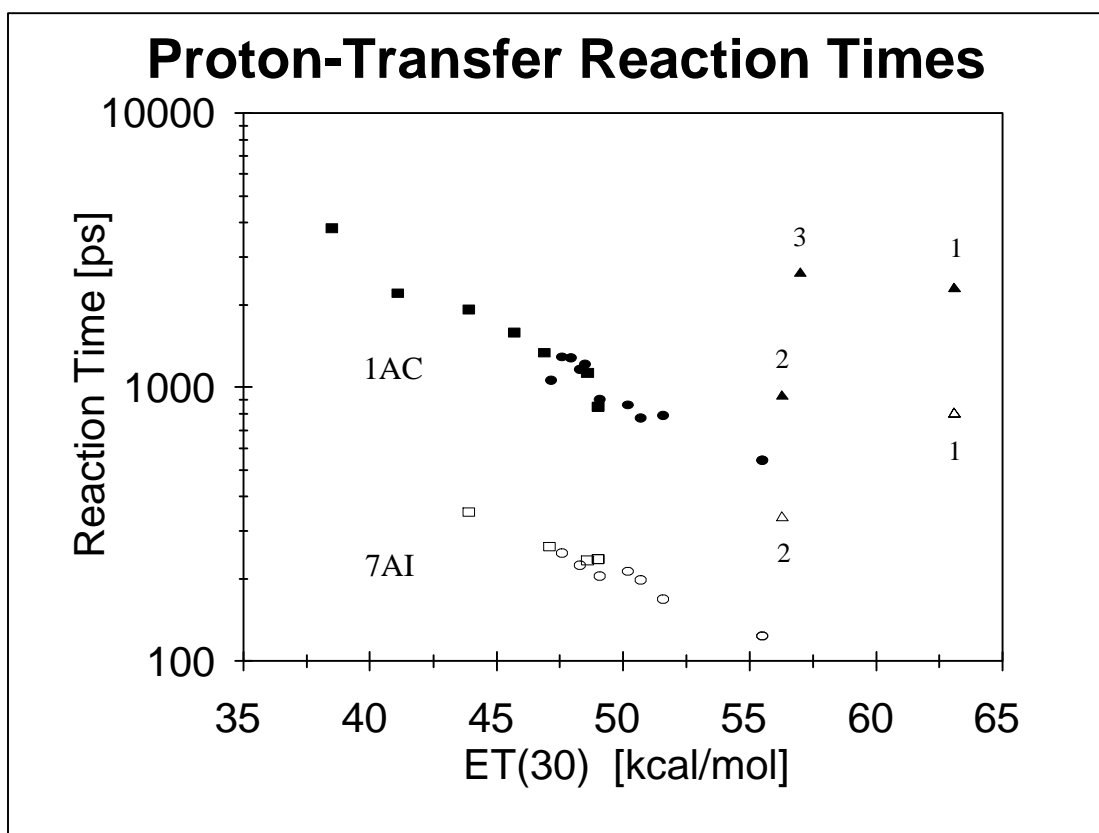


Figure 3.2: 1AC and 7AI Reaction Rate Correlations with  $E_T(30)$  Solvent Scale

Earlier studies noted a remarkable correlation between the excited-state proton-transfer reaction time and the  $E_T(30)$  polarity scale for alcohol solvents. 7AI data are from: (a) R. S. Moog and M. Maroncelli, *J. Phys. Chem.*, **95**, 10359 (1991). (b) C. F. Chapman and M. Maroncelli, *J. Phys. Chem.*, **96**, 8430 (1992). 1AC data are from: S. J. Boryschuk, M.S. Thesis, The Pennsylvania State University, 1993. The solvents that appear to be anomalous on this correlation are considered in Chapters 5 and 6. The numbered points correspond to the solvents: (1) Water. (2) Ethylene Glycol. (3) Glycerol.

## ENDNOTES

- <sup>1</sup> R. S. Moog and M. Maroncelli, *J. Phys. Chem.*, **95**, 10359-10369 (1991).
- <sup>2</sup> C. F. Chapman and M. Maroncelli, *J. Phys. Chem.*, **96**, 8430-8441 (1992).
- <sup>3</sup> C. F. Chapman, Ph.D. Thesis, The Pennsylvania State University, 1993.
- <sup>4</sup> S. J. Boryschuk, M.S. Thesis, The Pennsylvania State University, 1993.
- <sup>5</sup> See pp. 2761-2762 of A. V. Smirnov, D. S. English, R. L. Rich, J. Lane, L. Teyton, A. W. Schwabacher, S. Luo, R. W. Thornburg, and J. W. Petrich, *J. Phys. Chem. B.*, **101**, 2758-2769 (1997).
- <sup>6</sup> J. Herbich, J. Sepiol, and J. Waluk, *J. Mol. Struct.*, **114**, 329-332 (1984).
- <sup>7</sup> M. A. El-Bayoumi, P. Avouris, and W. R. Ware, *J. Chem. Phys.*, **62**, 2499 (1975).
- <sup>8</sup> Quantitative discussions are also available in standard texts. See, for example, J. I. Steinfeld, J. S. Francisco, and W. L. Hase, *Chemical Kinetics and Dynamics*, (Englewood Cliffs, N.J., Prentice Hall, 1989).
- <sup>9</sup> See, for example, G. M. Chaban and M. S. Gordon, *J. Phys. Chem. A.*, **103**, 185-189 (1999).
- <sup>10</sup> P.-T. Chou, W.-S. Yu, C.-Y. Wei, Y.-M. Cheng, and C.-Y. Yang, *J. Am. Chem. Soc.*, **123**, 3599-3600 (2001).
- <sup>11</sup> In the case of 7AI, at least two groups have noted the presence of additional fluorescent impurities that are difficult to remove by recrystallization or vacuum sublimation. See: (1) S. K. Kim and E. R. Bernstein, *J. Phys. Chem.*, **94**, 3531 (1990). (2) Y. Chen, F. Gai, and J. W. Petrich, *Chem. Phys. Lett.*, **222**, 329 (1994).
- <sup>12</sup> An alternative state of solvation ["blocked species"] has been advocated to account for this long lifetime by Y. Chen, F. Gai, and J. W. Petrich, *Chem. Phys. Lett.*, **222**, 329 (1994). Their model is addressed in Chapter 6.
- <sup>13</sup> Although the relative tautomer radiative rate is slightly longer (smaller  $\alpha$  values) in the very polar solvents like formamide, N-methylformamide, and ethylene glycol, the average of  $\alpha$  values for the wide variety of protic solvents will be the best determination of the relative radiative rates for 1AC isolated complexes. (If one chooses to be more

selective about the choice of solvents used in the determination of the ratio of radiative rates, a different value will be obtained; for example,  $\alpha(1AC) = 9.0 \pm 10\%$  (Table 2.3.)

<sup>14</sup> T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry, Third Edition*. (New York, HarperCollins Publishers, 1987). p. 143.

<sup>15</sup> S. Mente and M. Maroncelli, *J. Phys. Chem. A*, **102**, 3860-3876 (1998).