Ultrafast fluorescence studies of excited-state dynamics of a few organic chromophores in solution
van Veldhoven, E.

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Abstract

Ultrafast time-resolved emission spectra of Michler's ketone (MK) in solution are simulated on the assumption that the lowest excited electronic state results from adiabatic coupling between an emissive and a dark state. The simulations are in reasonable agreement with experimental results for MK dissolved in alcoholic solvents. The results are less satisfactory for MK in the non-alcoholic solvent DMF. It is discussed that in alcoholic solvents twisting of two phenyl groups dominates the ultrafast dynamics in the excited state of MK, while in non-alcoholic solvents both solvation and twisting contribute to the ultrafast dynamics.
Chapter 7

7.1 Introduction

Time-resolved spectroscopic studies of intramolecular conformational changes have drawn a lot of interest in recent years [1]. Intramolecular twisting of molecular groups around a single bond is in some cases barrierless. Very high values for the reaction rate (often in excess of THz) can occur for these processes. Tri- and diphenylmethane dyes are examples of molecules for which such ultrafast twisting dynamics has been investigated [2–9].

Steady-state spectroscopy of these molecules shows that the quantum yield of the emission depends on the viscosity of the solvent. In a highly viscous solvent the emission has a relatively high quantum yield, while for a low viscous solvent the emission quantum yield is poor. The results of ultrafast time-resolved spectroscopic experiments show that the lifetime of the emission, and the dynamic Stokes shift also depend on the viscosity of the used solvent [2,3]. The dynamic Stokes shift is accompanied with a drastic reduction of the fluorescence intensity. Both features increase in rate using less viscous solvents.

In Chapter 6 the experimental results for the time-resolved fluorescence upconversion experiments for 4,4′-bis(N,N-dimethylamino)-benzophenone (Michler’s ketone, MK) and 3,6-bis(dimethylamino)-10,10-dimethylanthrone (blocked Michler’s ketone, BMK) in various solvents were described [10]. It was discussed that the time-resolved emission of MK is depending on the twisting of the phenyl groups attached to the central carbon atom (see also Scheme 7.1). By means of ultrashort laser pulses, the probed molecule is prepared in the photoreactive emissive state. The torsional motions of the phenyl groups are hindered in highly viscous solvents, thus radiationless decay is less efficient and the fluorescence is favored. For less viscous solvents the opposite applies.
Several models have been proposed to describe the dynamics on the excited-state surface as a function of the twisting (reaction) coordinate. The first models are one-dimensional and describe the free energy as a function of only the rotational diffusion coordinate. The viscosity controls the dynamics on the potential and hinders the population to move over the potential. Oster and Nishijima [11] presented a model for molecules with a barrierless flat potential independent of the twisting angle. After pulsed excitation, the excited-state population progresses over the excited-state potential performing a Brownian random walk. At a certain twisting angle there is a non-radiative coupling to the ground state. A sink function represents the non-radiative population leakage to the ground state. The model of Oster and Nishijima explains the relation between the fluorescence quantum yield and the viscosity. For time-resolved experiments, it predicts a broadening of the emission band and no dynamic Stokes shift in time. However, a dynamic Stokes shift has been observed in the case for MK dissolved in various solvents.

Förster and Hoffmann [12] considered a parabolic shape for the excited-state potential as a function of the reaction coordinate. A sink function is active at the minimum of the excited-state potential to represent the non-radiative relaxation to the ground state. The parabolic shape of the excited-state potential explains the dynamic Stokes shift as found in the experiments for MK in solution. But it also predicts that the dynamic Stokes shift versus the total integrated emission should follow the $\nu^3$. 

Scheme 7.1: Structure of Michler's ketone (MK)
relation of Einstein for spontaneous emission [13]. As shown in Chapter 6, the emission for MK in different solvents does not follow this relation [10]. Bagchi, Fleming and Oxtoby (BFO) [14] presented a model with a parabolic shape for the excited state potential to explain time-resolved absorption experiments of triphenylmethane dyes. In addition, their model explicitly takes into account that the non-radiative relaxation increases near the minimum of the excited-state potential. This approach predicts a decrease in lifetime for the fluorescence transients to the red-side of the emission band. The fluorescence transients for MK in various solvents show the opposite behavior [10].

Kim and Hynes [15] proposed a two-dimensional model for molecules undergoing single bond twisting. They explained the experimental results of p-dimethylaminobenzonitrile and derivatives in solution [16] by assuming that twisting and solvation mainly control the excited-state dynamics. In some cases twisting of the phenyl groups is dominant. For example for MK in alcoholic solvents, the excited-state dynamics is faster than solvation. For such a case it suffices to consider the dynamics as a function of the twisting diffusion coordinate only.

A molecule similar to MK is 4,4'-(imidocarbonyl)bis(N,N-dimethylaniline-monohydrochloride) (auramine). For auramine in alcoholic solution an adiabatic coupling model has been proposed [3]. It was assumed that the excited state is an adiabatically coupled state of an emissive state with a non-emissive state. The twisting of the phenyl groups affects the radiative instead of the non-radiative properties of the excited-state. In this Chapter we focus on simulations of the time-dependent fluorescence spectra of MK in protic alcoholic solvents and in aprotic DMF starting from the adiabatic coupling model.
7.2 Adiabatic coupling model

To simulate the fluorescence spectra we consider a three-state system. We first construct the potential energy surface as a function of a generalized twisting coordinate for the ground state (G) and the excited state (Si). The latter is a coupled state of an emissive state (F) and a dark state (D) as a function of the relative twisting coordinate $z$. The twisting coordinate $z$ is defined in terms of the time-dependent twisting angle of the phenyl groups $\varphi(t)$,

\[
z = \frac{\varphi(t) - \varphi(0)}{\varphi(\varphi - \varphi(0))}
\]  

(7.1)

The first excited state (F) has its minimum energy (as a function of $z$) above the ground state minimum ($z=0$) and is emissive. The second excited state (D) has its minimum energy for ($z=1$). The energies of the ground state and the two excited states are taken as harmonic functions with the same harmonicity. This gives,

\[
G(z) = \frac{1}{2} k z^2
\]  

(7.2)

\[
F(z) = F_{eq} + \frac{1}{2} k z^2
\]  

(7.3)

\[
D(z) = D_{eq} + \frac{1}{2} k (1 - z)^2
\]  

(7.4)

$k$ is the rotational force constant, $F_{eq}$ and $D_{eq}$ correspond to the zero-order minimum energies of the emissive state and the non-emissive state, respectively. The functions $F(z)$ and $D(z)$ are given in Figure 7.1a.
We now consider adiabatic coupling of the two excited states \( F \) and \( D \). A new excited state \( S_1 \) is formed. The energy of this new state is given by,

\[
S_1(z) = \frac{1}{2} \left( F(z) + D(z) \right) + \frac{1}{2} \sqrt{(F(z) - D(z))^2 + 4C^2} \tag{7.5}
\]

Figure 7.1: (a) Potential energies of mixed state \( S_1(z) \) (full curve) and the zero order emissive excited state \( F(z) \) (dotted curve) and non-emissive excited state \( D(z) \) (dashed curve). (b) Moment for radiative transition as a function of the normalized twisting coordinate, \( z \).
$C$ is the coupling strength parameter. The energy of the adiabatic coupled state, $S_1(z)$, is also given in Figure 7.1a.

The transition moment for the optical transition from the $S_1$ state to the ground state has become dependent on the relative twisting coordinate $z$ due to the adiabatic coupling of the two diabatic states $F$ (emissive) and $D$ (non-emissive). Normalizing the optical transition moment for $F$ to 1 and that for $D$ to 0, one obtains the dependence of the transition moment ($M(z)$) with the relative twisting coordinate $z$ for the optical transition $G \leftarrow S_1$ to be,

$$M(z) = \cos^2\left(\frac{1}{2} \arctan\left(\frac{2C}{F(z) - D(z)}\right)\right) \quad (7.6)$$

The moment for the radiative transition as a function of $z$ is given in Figure 7.1b.

Initially the ensemble of molecules is in thermal equilibrium with the bath of surrounding solvent molecules. Pulsed excitation lifts the population distributed near $z=0$ to the excited state $S_1$. The excited-state population will be no longer in equilibrium with the bath. In the experiment the laser pulse has a duration of about 150 fs and the excitation energy is above that for the 0-0 transition. Fast relaxation processes prior to twisting are assumed to result in an asymmetric initial population distribution. This asymmetric initial population distribution is represented by a log-normal shaped initial population distribution,
\[ \rho(z, 0) = \begin{cases} 
\exp \left( -\ln(2) \left( \frac{\ln(1 + 2bz/\sqrt{k_B T/k})}{b} \right)^2 \right) 
& \text{if } 2bz/\sqrt{k_B T/k} > 1 \\
0 & \text{else}
\end{cases} \quad (7.7) \]

\( k_B \) is Boltzmann's constant, \( T \) is the temperature and \( b \) is the asymmetry factor.

To calculate the time evolution of the population density in the excited state, we use Smoluchowski’s equation [14,17].

\[ \frac{\partial \rho(z, t)}{\partial t} = D_r \frac{\partial^2 \rho(z, t)}{\partial z^2} + \frac{D_r}{k_B T} \frac{\partial}{\partial z} \left[ \frac{\partial}{\partial z} S_1(z) \rho(z, t) \right] \quad (7.8) \]

\( D_r \) is the diffusion coefficient representative of the rotational diffusion of the phenyl groups of MK. The first term on the right of expression (7.8) will lead to a spreading out of the population density in the excited state. The second term on the right hand side represents the shift of the population density with \( z \). The rate of the shift is determined by the frictional parameter \( D_r / k_B T \). The differential equation has been numerically solved using the Runge-Kutta method [18].

As a last step, the time-dependent fluorescence spectra are calculated using [19–21].

\[ I_{fl}(\nu, t) \propto \int dz \ g(\nu_0(z), \nu - \nu_0(z)) |M(z)|^2 \rho(z, t) \nu^3 \quad (7.9) \]
\( g(v_0(z), v-v_0(z)) \) is a line shape function characteristic of the Franck-Condon factor. The simulated emission spectrum results from the convolution of the inhomogeneous broadening \( (\rho (z,t)) \) and the homogeneous line shape of the emission. The inhomogeneous broadening is due to the dispersion of the population distribution with \( z \) during relaxation.

### 7.3 Results

Figures 7.2a-d show the simulated spectra together with the experimental spectra for the emission of MK dissolved in various alcohols. The full curves are the experimental emission spectra. The dotted curves are the simulated time-dependent emission spectra. The dynamic Stokes shift, the fast reduction of the emission intensity and the emission band profile of the simulated spectra are in reasonable agreement with the experimental spectra.

The best-fit parameters used in the simulations are presented in Table 7.1. The minimum of the emissive state \( (F_{eq}) \) and the non-emissive state \( (D_{eq}) \) are found to be around 26000 cm\(^{-1}\) and 25000 cm\(^{-1}\), respectively. The potential of the resulting mixed state \( S_i \) is almost barrierless and a coupling strength (\( C \)) of 800 cm\(^{-1}\) is obtained. Figure 7.1a shows the energy dependence of the excited states for MK dissolved in ethanol. The moment for radiative transition as a function of the reaction coordinate for MK in ethanol is shown in Figure 7.1b. Both Figures 7.1a and 7.1b are representative for MK in all alcoholic solvents. The diffusion coefficient \( (D_r) \) varies depending on the viscosity of the solvent. The diffusion coefficient becomes smaller going from methanol to decanol.
Figure 7.2: Comparison of the time-reconstructed emission spectra (solid curves) with the simulated time-resolved emission spectra (dotted curves) for MK dissolved in methanol (a), ethanol (b), n-propanol (c), decanol (d) and DMF (e)
Table 7.1: Best-fit parameters for the simulations of the reconstructed fluorescence spectra with a three state model for MK in different solvents

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Methanol</th>
<th>Ethanol</th>
<th>n-Propanol</th>
<th>Decanol</th>
<th>DMF</th>
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<tr>
<td>0-0 transition (cm⁻¹)</td>
<td>22500</td>
<td>22500</td>
<td>22300</td>
<td>22000</td>
<td>23200</td>
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<td>25900</td>
<td>26000</td>
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<td>26700</td>
</tr>
<tr>
<td>( D_{eq} ) (cm⁻¹)</td>
<td>24600</td>
<td>24800</td>
<td>24900</td>
<td>25300</td>
<td>23500</td>
</tr>
<tr>
<td>( k ) (cm⁻¹)</td>
<td>3900</td>
<td>4000</td>
<td>4000</td>
<td>4000</td>
<td>4000</td>
</tr>
<tr>
<td>( C ) (cm⁻¹)</td>
<td>800</td>
<td>750</td>
<td>800</td>
<td>800</td>
<td>1000</td>
</tr>
<tr>
<td>( D ) (ps⁻¹)</td>
<td>0.072</td>
<td>0.045</td>
<td>0.012</td>
<td>0.004</td>
<td>0.013</td>
</tr>
<tr>
<td>asymmetry ( b )</td>
<td>0.6</td>
<td>0.5</td>
<td>0.65</td>
<td>0.6</td>
<td>0.6</td>
</tr>
<tr>
<td>width (cm⁻¹)</td>
<td>3300</td>
<td>4800</td>
<td>3300</td>
<td>3800</td>
<td>6000</td>
</tr>
</tbody>
</table>

The results of the simulated time-dependent fluorescence spectra of MK in an aprotic solvent DMF are presented in Figure 7.2e. The simulated (dotted curves) and experimental spectra (solid curves) are found to be in less good agreement than for MK dissolved in alcohols. The fitting parameters are included in Table 7.1. The energies of the two excited states are somewhat shifted and the coupling strength between the two states is found to be 1000 cm⁻¹, i.e., about 200 cm⁻¹ larger than for MK dissolved in alcohols. The diffusive coefficient obtained in the simulation is in the same order as for the simulations for MK in n-propanol.
Chapter 7

7.4 Discussion

First we focus on the time-resolved emission spectra of MK dissolved in various alcohols. As discussed in Chapter 6, the emission of MK in these solvents shows a fast dynamic Stokes shift accompanied by a reduction of the emission intensity depending on the viscosity of the used solvent. The temporal behavior of the emission intensity can be explained assuming diffusive twisting of the phenyl groups attached to the central carbon atom. The simulations for the time-resolved emission spectra are in reasonable agreement with the experimental spectra. It is noted that on account of the quasi-barrierless shape of the excited-state potential, the population dynamics is on the (sub)picosecond times, in agreement with the experimental results. The parameters in the model are almost constant for the various solvents and adjustment of only the rotational diffusion coefficient is sufficient to obtain a good fit.

Naturally, the model has its limitations. For instance, only twisting is considered to determine the excited-state dynamics, twisting is controlled by a single normalized coordinate, the diabatic potentials are assumed to have the same harmonic properties, etc. These assumptions all affect the line shape of the emission band. Even with the mentioned limitations the model reasonably reproduces the experimental dynamic Stokes shift and the reduction of the emission, although on the blue side of the emission the agreement is less. The model does not include loss of excited-state population and time-dependent changes in the Franck-Condon factor. This could be the reason for the disparity of the simulated spectra compared with the experimental results at the longer times.
Figure 7.3: Diffusion coefficient ($D_r$) as numerically evaluated from the simulations as a function of $T/\eta$. The dotted line represents the best linear fit.

According to the Debye-Einstein-Stokes relation [22], one has

$$D_r = \frac{k_B T}{12V\eta}$$  \hspace{1cm} (7.10)

where $V$ is the volume of the diffusive sphere, $\eta$ is the viscosity and it is taken into account that the MK has two phenyl groups. We find from the slope of the best linear fit to the points of Figure 7.3 that the effective radius of the sphere involved in the twisting diffusional motion is 1.6 Å. The value of the van der Waals radius for a phenyl group is approximately 1.2 Å. Thus the extrapolated radius of the twisting
group found from Figure 7.3 is found to be of the right order of magnitude and this is taken as further support for the applied model. It is seen from Figure 7.3 that the data point obtained for MK in DMF deviates appreciatively from the trend as found for the diffusion coefficient of phenyl-MK in alcoholic solution. A value of $D_r = 0.013 \text{ ps}^{-1}$ is obtained from the simulation, which is about the same result as for MK in n-propanol. According to the applied model, DMF and n-propanol would have about the same viscosity, whereas in reality the viscosity for n-propanol is 1.945 mPas and for DMF the value is 0.794 mPas [23].

One explanation for the apparent slowing down of the twisting process in DMF is that not all of the excited-state dynamics is determined by twisting but that in fact an additional relaxation process should be taken into account. As already noted, a dynamic Stokes shift for the emission of MK in DMF of 2 ps is found [10]. This time constant is in the same order as the solvation dynamics for DMF found for other probe molecules [24,25]. Thus solvation might be a competitive candidate for the excited-state relaxation. This would reduce the effective rate for the diffusional twisting motion and thus lead to a lower effective value for the diffusion constant $D_r$.

In conclusion, simulations with a simple one-dimensional model give reasonable results for the emission spectra of MK in alcoholic solvents. It suffices to consider only the diffusion coefficient as the only variable parameter. For MK in DMF, the one-dimensional model is not as satisfactory and inclusion of the effects of solvation is proposed.
Simulations of the Excited-State Twisting Dynamics of Michler's Ketone in Solution

References


