Ultrafast fluorescence studies of excited-state hydrogen transfer reactions in solution

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Chapter 2

Experimental

2.1 Introduction

In this chapter we present the experimental setups used in this thesis. In the first section, section 2.2, we discuss the setups used to perform steady-state absorption and fluorescence measurements. Time-resolved fluorescence measurements were performed on a time scale ranging from the subps to the 25 ns range employing the time-correlated single photon counting apparatus (Section 2.3) and the femtosecond fluorescence upconversion setup (Section 2.4). The principles of fluorescence polarization, which are discussed throughout the thesis, are presented in Section 2.5.

2.2 Steady-state spectroscopy

Steady-state absorption spectra were measured with a Shimadzu UV-visible spectrophotometer (UV-240). The light sources were an iodine-tungsten lamp and deuterium lamp, providing a wavelength scanning range between 190-900 nm. The monochromator was outfitted with holographic grating with a maximum spectral resolution of 0.15 nm.

Steady-state emission was measured with the time-correlated single photon counting setup described below. To reconstruct the steady-state emission spectra, the emission was measured at a representative series of emission wavelengths. At each emission wavelength the photons were counted for a fixed accumulation time. These spectra were corrected for the wavelength sensitivity of the monochromator/photomultiplier detection unit, using an experimentally determined calibration curve. The calibration curve was obtained by measuring the spectral emission from a calibrated EG&G RS-10A lamp system [1].

2.3 Time-correlated single photon counting

Fluorescence measurements in a time window ranging from 15 ps – 25 ns were performed with a time-correlated single-photon-counting (TCSPC) detection system [2, 3]. The setup is shown in Figure 2.1. Single photon counting is based on a statistical detection method. In this method, the exciting pulse acts as a “start” pulse for the counting system. A “stop” pulse is created when the detector detects a photon. In principle, the stop pulse generates a count which is a measure of the time elapsed between the start and stop pulses. After numerous repetitions, the accumulated counts depict the statistical spread of the photons in time and therefore are a measure
of the temporal behavior of the fluorescence kinetics. In our experiments, the setup operated in the reverse mode, i.e. the emission photon served as the “start” pulse and the exciting laser served as the “stop” pulse.

![Experimental setup diagram](image)

**Figure 2.1: Schematic representation of the time-correlated single photon counting (TCSPC) setup**

An Ar⁺-ion laser (Coherent, Innova 200-15) is mode locked by a Coherent 468 mode-locker. The laser produces pulses with a duration of ~ 80 ps at 514.5 nm and a repetition rate of 76 MHz. The Ar⁺-ion laser synchronously pumped a jet dye laser (Coherent, 702-3) nm in which the jets contained a mixture of DQTCI and DTDCI dyes in ethylene glycol. For this dye laser operation is achieved between 610 and 700 nm. A saturable absorber jet was used to shorten the temporal pulse width. The jet-dye laser was outfitted with a cavity dumper (Coherent, 7200) that generated laser pulses with a duration of ~ 1 ps (FWHM autocorrelation trace), an energy of about 25 nJ/pulse and a repetition rate of 3.7 MHz. These pulses were frequency doubled in a 6 mm BBO crystal, yielding pulses at a wavelength between 305 and 350 nm to photoexcite the sample. A dichroic mirror was placed in the laser pathway to exclude the fundamental beam. The fundamental beam was split in two beams; one beam served as the “stop” pulse whilst the other beam was led through an autocorrelator to check the shape of the laser pulse during experiment.
A linear polarizer was inserted in the detection pathway to detect the intensity of the parallel and perpendicular polarized fluorescence and at magic angle conditions. The fluorescence emitted from the sample in a direction perpendicular to the excitation beam was focused onto the entrance slit of a Zeiss M20 monochromator. The spectrally dispersed emission was detected with a Hamamatsu R3809 U (S20) multi-channel plate photodetector.

The signal was subsequently amplified by a Hewlett Packard 8347A amplifier and sent through a Tennelec TC864 time-to-amplitude converter (TAC). The “stop” pulse from the Antel FS1010 photo-detector is led through a Tennelec fraction discriminator, and subsequently into the TAC via a Tennelec TC 412 delay generator. The TAC produces pulses with output intensity proportional to the time delay between “start” and “stop” pulses. These electronic signals are sent into an EG&G Ortec 918 multi-channel buffer (MCB) connected to a personal computer.

The MCB creates the time histograms comprising of 4096 channels. In this manner the selected time window is divided by 4096 channels to detect the fluorescence transients at a resolution of 1.25 ps-6.25 ps per channel for time windows of 5 and 25 ns, respectively. The instrumental response was measured through Raman scattering using a water cell. The instrumental response time of the TCSPC setup was measured as 17 ps (FWHM).

2.4 Femtosecond fluorescence upconversion

The principle of fluorescence upconversion is based on frequency mixing of the fluorescence with a laser pulse in a nonlinear crystal to produce a sum-frequency signal [4]. Under proper phase-matching conditions [4] of the propagation wave vectors of the incoming light waves of the fluorescence light (with frequency \( \omega_{\text{fl}} \)) and the gating laser pulse (with frequency \( \omega_{\text{gating}} \)), a sum frequency signal (\( \omega_{\text{sum}} \)) is generated:

\[
\omega_{\text{sum}} = \omega_{\text{gating}} + \omega_{\text{fl}}
\]  

(2.2)

The experimental sum frequency signal is equal to the convolution integral of the fluorescence kinetics and the instrumental response.

\[
I_{\text{sum}}(\tau) = \int_{-\infty}^{\infty} I_{\text{fl}}(t)c(\tau - t)dt
\]  

(2.3)

Here, the time \( \tau \) is the time delay between the fluorescence signal and the instrumental response [5]. The instrumental response is in fact a convoluted signal of the temporal profiles of the exciting laser pulse, the gating pulse and the temporal broadening profile due to Group Velocity Dispersion effects in the optics [5]. The time \( \tau \) is delayed by changing the delay time between the
gating pulse and the fluorescence induced by the excitation pulse. The fluorescence kinetics can
be recovered by employing an iterative convolution routine in which the instrumental response
was fitted iteratively with a multi-exponential function. Optimum fits were judged from
minimization of $\chi^2$, using a simplex algorithm and visual inspection of the fit residuals. The
instrumental response function was experimentally determined through measurement of the cross
correlation signal between excitation and gating beams, and has a full width at half maximum of
\( \sim 300 \text{ fs} \).

Femtosecond fluorescence upconversion experiments were performed using the setup as
shown in Figure 2.2. A mode-locked Tsunami Ti: sapphire laser was optically pumped by a
Spectra-Physics Millennia X Nd:YVO$_4$ CW diode-laser, to produce pulses, at a wavelength of
800 nm, with a duration of about 60 fs and a repetition rate of 82 MHz. A Quantronix
regenerative amplifier system (RGA) was used for amplification of the laser pulse energy to
generate pulses, with an energy of approximately 500 \( \mu \text{J/pulse} \) at a repetition rate of 1 kHz. The
amplified pulses were split into two beams; one beam served as the excitation beam the other as a
gating beam.

The excitation beam was passed through an OPA laser system, to pump an optical
parametric amplifier system (TOPAS Light Conversion Ltd.). In the OPA system non-linear wave
mixing is achieved by means of a BBO crystal. The non-linear wavemixing yields two
components, a signal and an idler beam

$$\omega_{\text{pump}} = \omega_{\text{signal}} + \omega_{\text{idler}} \quad (2.4)$$

The optical frequency of the signal beam could be tuned by changing the alignment of the
BBO crystal. The wavelength-tunable third harmonic of the signal beam was used to optically
excite the sample. Typically, in the upconversion experiments the excitation wavelength could be
varied between 310 nm and 380 nm; in these experiments the duration of the excitation pulses
was about 150 fs, whereas the pulse energy was about 5 \( \mu \text{J} \). Laser fluence was kept low enough to
ensure that the fluorescence intensity was linear dependent on the laser intensity.
The sample solution was contained in a quartz cell of 1 mm thickness. The cell was attached to a sample holder that was driven electrically back and forth perpendicular to the excitation direction to prevent heating of the sample. A 420-nm cut-off filter immediately behind the sample prevented that scattered laser and/or Raman light was included in the detection pathway. The second beam, the gating beam, was led through the optical delay line containing a stepper-motor driven translational stage. The transient fluorescence originating from the sample was focused onto a BBO crystal (1 mm thickness) together with the gating beam (800 nm), to generate the sum-frequency signal (type I phase matching condition). The upconverted fluorescence light was led through an UG 11 band pass filter and focused onto the entrance slit of a Zeiss M4 prism monochromator outfitted with an EMI 9863 QB/350 photomultiplier. It was checked that reliable detection of the upconversion signal intensity was possible for wavelengths
of 410 nm and higher. The spectrally dispersed signal was detected using a photomultiplier tube (EMI 9863 QB/350). The photomultiplier output was connected to a lock-in amplifier that was synchronized with an electronic reference signal of the RGA laser system. The output signal of the lock-in detector was stored and analyzed by means of a personal computer. Time-resolved emission spectra were obtained by applying the spectral reconstruction method. In this method, time zero is well defined and, unlike in the direct measurement of time-resolved emission spectra, additional corrections for group velocity dispersion are not necessary.

An optical polarizer in the excitation pathway was used to control the polarization direction of the excitation pulses relative to the vertically polarized gating-beam pulses. Measurements under magic angle conditions (with the laser-excitation polarization at an angle of 54.7° relative to the vertically polarized gating beam) were also performed. In these experiments, the effects of rotational diffusion motions of the solute molecules in the liquid on the fluorescence depolarization are eliminated [6].

2.5 Fluorescence anisotropy

When photoexcited with linearly polarized light, only molecules with a transition dipole component oriented parallel to the polarization axis of the laser will become photoexcited. When considering a two level system, Fermi’s Golden rule applies and the rate of the transition, $W_{cr}$, from the ground to the excited state is proportional to the square element of the light-molecule interaction [7].

$$W_{cr} \sim E_0^2 \cdot \hat{E} \cdot f \mu e^2$$

$$\left| E_0^2 \cdot \mu_{ef} \cdot \hat{E} \cdot \mu \right|^2 =$$

$$\left| E_0^2 \cdot \mu_{ef} \cdot \cos^2 \theta \right|^2$$

From this equation it is thus seen that the probability for a molecule to absorb a photon is proportional to the square of the cosine of the projection angle between transition dipole and the laser field polarization axis.

To define anisotropy we introduce two coordinate frames, the molecular and the laboratory frame. The molecular frame is fixed within the molecule. The molecular frame can adopt many orientations relative to the laboratory frame.
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The orientation of the molecular frame relative to the laboratory frame is given by the Euler angles $\theta$, $\varphi$, $\psi$, Figure 2.3. The orientation of the transition dipole in the molecular frame is given by:

$$\hat{\mu} = a \hat{a} + b \hat{b} + c \hat{c}$$  \hspace{1cm} (2.6)

Figure 2.3: The molecular frame ($a, b, c$) and laboratory frame ($x, y, z$) are related through the Euler angles $\theta$, $\varphi$ and $\psi$. Projection of the molecular frame onto the laboratory frame is done through rotation around the rotation angles $-\theta$, $-\varphi$ and $-\psi$

The dipole moment components $(\mu_x, \mu_y, \mu_z)$ in the laboratory frame are obtained by means of a transformation matrix $\lambda$ [8]:

$$(\mu_x, \mu_y, \mu_z) = \lambda(a, b, c) = \begin{pmatrix} \hat{x} \cdot \hat{a} & \hat{x} \cdot \hat{b} & \hat{x} \cdot \hat{c} \\ \hat{y} \cdot \hat{a} & \hat{y} \cdot \hat{b} & \hat{y} \cdot \hat{c} \\ \hat{z} \cdot \hat{a} & \hat{z} \cdot \hat{b} & \hat{z} \cdot \hat{c} \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$  \hspace{1cm} (2.7)

In the transformation matrix (2.7) the products of the unity vectors can now be evaluated to give:

$$\lambda = \begin{pmatrix} \cos \psi \cos \varphi \cos \theta - \sin \psi \sin \varphi \\ \cos \psi \sin \varphi \cos \theta - \sin \psi \cos \varphi \\ -\cos \psi \sin \theta \end{pmatrix} \begin{pmatrix} -\sin \psi \cos \varphi \cos \theta - \cos \psi \sin \varphi \\ -\sin \psi \sin \varphi \cos \theta - \cos \psi \cos \varphi \\ \sin \psi \sin \theta \end{pmatrix}$$  \hspace{1cm} (2.8)
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In the case that a state $n$ is selectively excited with light polarized parallel to $z$ and the fluorescence is detected from state $m$ the anisotropy of the fluorescence is expressed as:

$$r_{nm} = \frac{I_z - I_x}{I_T} = \frac{I_{zz} - I_{xz}}{I_{zz} + 2I_{xz}} = \frac{< (\hat{z} \cdot \mu_{on})^2 \cdot (\hat{z} \cdot \nu_{m0})^2 > - < (\hat{z} \cdot \mu_{on})^2 \cdot (\hat{z} \cdot \nu_{m0})^2 >}{< (\hat{z} \cdot \mu_{on})^2 \cdot (\hat{z} \cdot \nu_{m0})^2 > + 2 < (\hat{z} \cdot \mu_{on})^2 \cdot (\hat{z} \cdot \nu_{m0})^2 >}$$  \hspace{1cm} (2.9)

For an absorption dipole moment along the molecular c-axis we have $\mu_{on} = (0,0,1)$ and for an emissive dipolemoment $\nu_{m0} = (a,b,c)$. The terms in the nominator of equation (2.9) can be evaluated as,

$$< (\hat{z} \cdot \mu_{on})^2 \cdot (\hat{z} \cdot \nu_{m0})^2 > = \int_0^{2\pi} \int_0^{\pi} \int_0^{\pi} (\cos \theta)^2 ((\cos \theta)^2 - a \cos \psi \sin \theta + b \sin \psi \sin \theta + c \cos \theta)^2 d\psi d\theta =$$

$$\frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} (\cos \theta)^2 ((\cos \theta)^2 - a \cos \psi \sin \theta + b \sin \psi \sin \theta + c \cos \theta)^2 \sin \psi d\psi d\theta =$$

$$\frac{1}{4} \left( (1 - c^2)(\sin \theta)^2 (\cos \theta)^2 + 2c^2(\cos \theta)^4 \right) d(\cos \theta) \hspace{1cm} (2.10)$$

and

$$< (\hat{z} \cdot \mu_{on})^2 \cdot (\hat{z} \cdot \nu_{m0})^2 > =$$

$$\frac{1}{4} \int_0^{2\pi} \int_0^{2\pi} (\sin \theta)^2 (\cos \theta)^2 + (\cos \theta)^4 + 2c^2(\cos \theta)^2(\cos \theta)^2 d(\cos \theta) \hspace{1cm} (2.11)$$

In evaluating (2.10) and (2.11), all cross-product terms have been omitted, since they will become zero when spherical integration is performed. For the terms in the nominator of (2.9) one now obtains:

$$< (\hat{z} \cdot \mu_{on})^2 \cdot (\hat{z} \cdot \nu_{m0})^2 > - < (\hat{z} \cdot \mu_{on})^2 \cdot (\hat{z} \cdot \nu_{m0})^2 > = \frac{3c^2 - 1}{15} \hspace{1cm} (2.12)$$

The terms in the denominator of equation (2.9) are evaluated as,

$$< (\hat{z} \cdot \mu_{on})^2 \cdot (\hat{z} \cdot \nu_{m0})^2 > + 2 < (\hat{z} \cdot \mu_{on})^2 \cdot (\hat{z} \cdot \nu_{m0})^2 > =$$

$$< (\hat{z} \cdot \mu_{on})^2 > + < (\hat{z} \cdot \nu_{m0})^2 > + < (\hat{z} \cdot \nu_{m0})^2 > + < (\hat{z} \cdot \nu_{m0})^2 > \hspace{1cm} (2.13)$$

$$\frac{1}{8\pi^2} \int_0^{2\pi} \int_0^{2\pi} \int_0^{\pi} \cos^2 \theta \sin \psi d\psi d\theta = \frac{1}{3}$$
The denominator is thus independent on the orientation distribution of the emissive dipole and represents the isotropic fluorescence intensity. For the anisotropy we finally obtain,

\[
r_{nm} = \frac{\left(\hat{z} \cdot \hat{\mu}_{a} \right)^2 \cdot \left(\hat{z} \cdot \hat{\nu}_{a} \right)^2 - \left(\hat{z} \cdot \hat{\mu}_{a} \right)^2 \cdot \left(\hat{x} \cdot \hat{\nu}_{a} \right)^2}{\left(\hat{z} \cdot \hat{\mu}_{a} \right)^2 \cdot \left(\hat{z} \cdot \hat{\nu}_{a} \right)^2 + 2 \left(\hat{z} \cdot \hat{\mu}_{a} \right)^2 \cdot \left(\hat{x} \cdot \hat{\nu}_{a} \right)^2} = \frac{3c^2 - 1}{5}
\]  

(2.14)

Using the normalization condition, \(a^2 + b^2 + c^2 = 1\), equation (2.14) becomes,

\[
r = \frac{3\cos^2 \theta - 1}{5}
\]  

(2.15)

For a non-degenerate electronic state, and colinear transition dipoles for absorption and emission, the theoretical upper limit for the anisotropy is 0.4 [6, 8]. When the emission is probed from a different electronic state than initially photoexcited, a limiting anisotropy value of -0.2 is expected when the orientation of the emissive dipole is perpendicular to the absorption transition dipole.

Relaxation processes that influence the nature of the excited electronic states or the orientation of the molecules in space cause a time dependence of the fluorescence anisotropy. The time dependence of the anisotropy, \(r(t)\), is expressed as,

\[
r(t) = \frac{\sum \frac{I_n(t)}{I_{nm} r_n}}{\sum \frac{I_n(t)}{I_{nm}}}
\]  

(2.16)

where the summation is over the anisotropy contributions of states \(n\), with emissive intensities \(I_n(t)\). Thus by performing time dependent measurements of the anisotropy, changes of the character of the excited state wavefunction during excited state relaxation can be monitored in time [9, 10].

In liquid solution, anisotropy decay may also be caused by orientational diffusion motions of the molecules. These motions will eventually randomize the orientations of the transition dipoles in time, giving an isotropic distribution of emissive dipoles and a zero value for the anisotropy.

To eliminate the effects of depolarization in the “normal” fluorescence experiments due to reorientational motions, the pump beam is polarized at 54.7° (“magic angle” conditions) relative to the gating beam. Under these conditions, depolarization effects are averaged out and the measured fluorescence intensity decay is determined only by population dynamics in the emissive state.
2.6 References