CHAPTER 3

Spontaneous emission and dephasing in front of a mirror:
Measurement of the ultrafast dynamics of nile blue in a polymer

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References
3.1 Abstract

We show that the spontaneous emission spectrum of a thin sample in front of a mirror exhibits Wiener-type fringes that contain information on the dephasing dynamics of the excited molecules. In order to probe these dynamics, the molecules must be excited with a short optical pulse or with a light field that has a correlation time shorter than the dephasing time constant $T_2$. The technique is used to study the ultrafast dephasing of nile blue in a polymer matrix at room temperature. A homogeneous dephasing time constant $T_2$ of 100±10 fs is obtained.

3.2 Introduction

At the end of the last century Wiener [1] observed that when a photosensitive material in front of a mirror is illuminated with a well-collimated light beam, fringes are formed that run parallel to the flat mirror surface. When lasers became available, several new optical phenomena were discovered, such as the photon echo [2] and transient-grating scattering [3]. The physical basis for these techniques depends on the formation of Wiener-type fringes. The fringe pattern or grating in these experiments is formed by interference of two (non-parallel) pulses in the sample. When the excitation pulses are time-coincident a grating is formed in real space and its decay can be monitored by a third probe pulse. When the excitation pulses are time-delayed with respect to one another, a grating is formed in frequency space. When this frequency grating is excited with a third pulse a stimulated photon echo is generated. It has been shown that a two-pulse photon echo can be described as a self-diffraction effect from a frequency grating [4].

In the last decade transient-grating and photon-echo experiments on the picosecond time scale have been extensively used to study condensed-phase molecular dynamics [5,6]. When femtosecond excitation pulses are used for these
type of experiments, sample damage quite often occurs because of the high electrical fields associated with these short pulses. High intensities, however, are often needed to produce sufficient coherence in the sample to enable detection of the coherent signal, such as a femtosecond photon echo [7]. Therefore it is desirable to have optical probes available having the same information content, but not relying on the formation of a macroscopic polarization.

In this chapter we report a new technique to probe femtosecond dephasing dynamics, requiring only low–excitation intensities. The method is based on the measurement of the spontaneous emission spectrum of a thin sample (about 2 μm) in front of a mirror. The sample is excited by a 40 fs pulse from a colliding-pulse mode–locked (CPM) laser or by a 5 ns pulse of a spectrally broad–band dye laser that has a field correlation time of 55 fs. The presence of a mirror has two effects: Firstly, it leads to the creation of a transient Wiener–fringe pattern; secondly, it leads to an interference effect in spontaneous emission spectrum. The amplitude of this fringe pattern as a function of distance between the sample and the mirror is determined by the optical–dephasing time constant \( T_2 \). Experiments on the dye molecule nile blue doped into a thin film of poly(4–vinyl pyridine) yield a \( T_2 \) of 100±10 fs at room temperature.

### 3.3 Theory

Prior to discussing the experiments in greater detail, we present the theoretical foundation of our new method. Fig. 3.1a shows the simplified level scheme of the dye molecule, and Fig. 3.1b gives the schematics of the experimental arrangement. In our experiments on nile blue, a number of vibronic states \( \{2\} \) are optically excited that relax to the vibrationless excited state \( \{3\} \). From this state \( \{3\} \), emission occurs to the vibrational manifold \( \{1\} \) of the ground state. As low–excitation intensities are used, the pulse angles \( \theta(\mu E/h) \) are small: \( \sin \theta \approx \theta \). Here \( \mu \) is the transition dipole and \( E \) the electric field associated with the pulse and \( h \) Planck's constant divided by \( 2\pi \). The mirror in
Figure 3.1: (A) Relevant level scheme for nile blue. \( \{1\} \) and \( \{2\} \) denote vibrational manifolds in the ground and excited state, while 3 stands for the vibrationless excited singlet state. (B) Schematics of the experimental arrangement. Note that the emission is detected in a direction perpendicular to the mirror.

Our experiments is assumed to be ideal; it has a reflectivity of 1 and imposes a phase shift of \( \pi \) on a reflected light wave. Consider now an ensemble of molecules at a distance \( z \) from the mirror and excited at \( t_0 \). Due to the presence of a mirror these molecules are again excited by a reflected pulse at a time \( t_{21} \).
where \( \nu_p \) is the angle of incidence of the pump beam with respect to the mirror normal, \( c \) the speed of light in vacuum, and \( n \) the refractive index of the sample material. These excitation pulses form a \( \text{Wiener-fringe} \) pattern in both the ground and excited state. When the inhomogeneous broadening of the vibronic and pure electronic transitions are correlated [8], the \( \text{Wiener-fringe} \) pattern in the relaxed excited state \( \rho_{33} \) is proportional to [4]

\[
\rho_{33}(z,\Delta,t) \propto \theta^2 \exp(-\Delta^2/\sigma^2) \exp(-t/T_1)[1-\exp(-\Gamma_{21}t_{21})\cos(\Delta t_{21}+2k_zp^2)],
\]

(3.2)

where \( \theta \) is the excitation pulse angle, \( \Delta \) the detuning from the center of the excitation wavelength, and \( \sigma \) the width of the Gaussian inhomogeneous distribution of optical oscillators. \( T_1 \) is the population relaxation time of state 3 and \( \Gamma_{21} \) the homogeneous linewidth of the vibronic 2\( \leftrightarrow \)1 transition, \( k_zp=\omega_p\cos\nu_p)n/c \) is the projection of the wavevector of the pump beam on the normal to the mirror. In deriving Eq.(3.2) we assumed the excitation pulse duration to be much shorter than the dephasing time constant \( \Gamma_{21} \). The minus sign preceding the damping term in Eq.(3.2) arises from the phase shift of \( \pi \) between the excitation pulses. Note that the population in level 3 as a function of distance to the mirror exhibits an oscillatory behaviour, known as the \( \text{Wiener-fringe} \) pattern [1] or grating.

Eq.(3.2) shows that the amplitude of the transient \( \text{Wiener-fringe} \) pattern is not only damped by a population relaxation \( (T_1) \) process, but also by a homogeneous dephasing \( (\Gamma_{21}) \) process. For two-level systems \( \Gamma_{21}^{-1} \) is known as the optical–dephasing lifetime \( T_2 \).

In order to obtain the emission spectrum of all molecules in the sample we have to convolute \( \rho_{33}(z,\Delta,t) \) with the emission spectrum of a single molecule in the inhomogeneous distribution and then integrate the resulting expression over \( z \) and \( t \). It can be seen from Eq.(3.2) that integration over \( z \), in a sample much longer than the wavelength of light, leads to a severe suppression of the fringe pattern in emission. However, in the presence of a mirror, a single photon
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interference effect in the spontaneous emission should be taken into account. For the subensemble of molecules located at distance \( z \) from the mirror this interference term is \( 1 - \cos(2k_z z) \) [1], where \( k_z = k \cos \nu \), with \( k \) the absolute value of the wave vector, and \( \nu \) the angle of observation with respect to the mirror normal. One thus obtains for the emission spectrum angularly resolved in the direction \( \nu \):

\[
I^\nu(t,\omega) = \int_{L_1}^{L_2} \text{d}z [\rho_{33}(z,\Delta,t) *_{\Delta} I_{\text{hom}}^e(\omega,\Delta)] [1 - \cos(2k_z z)] ,
\]

(3.3)

where \( I_{\text{hom}}(\omega,\Delta) \) is the homogeneous emission spectrum of a single site at position \( \Delta \) in the inhomogeneous line, \( *_{\Delta} \) means a convolution with respect to \( \Delta \), and the integration over \( z \) takes the finite thickness of the sample into account. For \( L_1 = 0 \) the sample is on top of the mirror. Integration over \( z \) gives a number of terms, the dominant one arising from the product

\[
\text{exp}(-\Gamma_{21} t_{21}) \int \text{d}z \cos(\Delta t_{21} + 2k_z z) \cos(2k_z z).
\]

In order to obtain an explicit expression for the emission spectrum, we assume that the spectrum of a single site in the inhomogeneous band is Lorentzian:

\[
I_{\text{hom}}^e(\omega,\Delta) = \frac{\Gamma_{31}}{[\omega - (\Omega_0^e + \Delta)]^2 + \Gamma_{31}^2} .
\]

(3.4)

Here \( \Omega_0^e \) is the center of the inhomogeneously broadened emission line and \( \Gamma_{31} \) is the homogeneous decay rate. Two extreme cases will be considered: In the first case (A), the optical transition is predominantly inhomogeneously broadened, meaning that \( \sigma \gg \Gamma_{31} \). In the second case (B), the transition is predominantly homogeneously broadened, i.e. \( \sigma \ll \Gamma_{31} \).

Using Eqs.(3.3) and (3.4), we calculate for case (A)

\[
I^\nu(\omega) \propto I_{\text{inhom}}^e(\omega) \{1 + \text{exp}[-(\Gamma_{31} + \Gamma_{21}) t_{21}] \cos[\kappa(L_1 + L_2)] \text{sinc}[K(L_2 - L_1)]\} .\]

(3.5)

Here \( I_{\text{inhom}}^e(\omega) \) is the inhomogeneously broadened emission spectrum.
\( \kappa = (n/c)[(\omega_p + \omega - \Omega_0) \cos \nu_p - \omega \cos \nu], \quad K = k_{zp} - k_z \) and \( \sin x = \sin x/x \). In deriving Eq. (3.5) we have assumed that the sample thickness is such that the transit time \( n(L_2 - L_1)/c \) is short compared to \( (\Gamma_1 + \Gamma_1)^{-1} \). In all our experiments the emission spectrum was detected in the direction perpendicular to the mirror, meaning that \( \cos \nu = 1 \). We then calculate from Eq. (3.5) that the modulation period of the fringe pattern in emission is \( 1/n(1 - \cos \nu_p)(L_2 - L_1) \) (in cm\(^{-1}\)), where \( L_1 \) and \( L_2 \) are expressed in centimeters. For the homogeneous case (B) we obtain an expression of the same form as Eq. (3.5) but with a damping term \( \exp(-\Gamma_2t_2) \) instead of \( \exp[-(\Gamma_1 + \Gamma_1)t_2] \) and with \( \kappa = K = k_{zp} - k_z \). In the homogeneous case we thus find a modulation period in the emission spectrum of \( 1/n(L_1 + L_2) \). Note that exactly the same modulation period is found when the emission spectrum is excited with a cw laser; in this case the fringe amplitude, however, does not depend on dephasing [9].

Eq. (3.5) is the main result of this chapter. It predicts that for short pulse excitation of a thin sample in front of a mirror the emission spectrum exhibits fringes that are damped by the sum of the dephasing constants \( \Gamma_2 \) and \( \Gamma_1 \) (case A) or by the dephasing constant \( \Gamma_2 \) only (case B). Moreover, whether we are dealing with case (A) or case (B) can be ascertained from the modulation period in the emission spectrum.

In closing this section we note that it has been shown [10] that Eq. (3.5) also holds for excitation with a stochastic light source for which the correlation time is much less than the dephasing time.

### 3.4 Experimental

The experiments were performed on thin (about 2\( \mu \)m thick) polymer films, prepared by spincoating a solution of poly(4-vinylpyridine) (P4VP) doped with the fluorescent molecule nile blue. The concentration of nile blue in the dry film was about \( 10^{-3} \)M. The sample was separated from the Al mirror by a transparent poly(styrene) film. A glass plate with index-matching oil was mounted on top of the sample to circumvent etalon effects in the measurement of the emission spectrum. The emission spectra were angularly resolved in a
direction perpendicular to the mirror with a resolution of 25 cm⁻¹.

![Fluorescence intensity (a.u.) vs. Wavenumber (cm⁻¹)](image)

Figure 3.2: Room-temperature emission spectra of nile blue doped in a thin film of poly(4-vinylpyridine). The solid is the spectrum obtained in front of a mirror and excited with a cw HeNe laser operating at 632.8nm. The dashed spectrum is obtained when under the same conditions a 40fs pulse from a CPM laser is used for excitation. The insert shows the spectrum obtained without a mirror.

3.5 Results and Discussion

Fig.3.2 displays two emission spectra of nile blue in front of a mirror: one excited with a HeNe laser, the other with 40fs pulses from a CPM laser. The first thing to note is that the fringe period in both spectra are identical, consistent only with the case of a homogeneously broadened emission spectrum. If the emission spectra was predominantly inhomogeneously broadened the modulation
period would have been 10 times larger \((\cos \nu_p \approx 0.9)\) than in the present experiment. The reduced intensity of the fringes in the emission spectrum when the CPM laser is used for excitation, is attributed to homogeneous dephasing between the excitation pulses. To measure the homogeneous dephasing time constant \(T_{21}\), a number of samples were made with varying thickness of the spacer layer and their emission spectra recorded using the CPM and a HeNe laser as excitation source. Identical conditions regarding excitation spot size, detection angle and detection aperture were used.

![Relative fringe visibility in emission](image)

**Figure 3.3:** Relative fringe visibility in emission of nile blue doped in poly(4-vinylpyridine) as a function of delay between the incident and reflected pulse from the mirror. The delay times were calculated from the modulation period in emission and use of Eq.(3.1). The open circles are data points obtained using the CPM laser; the closed triangles are data points obtained by stochastic excitation with a spectrally broad-band dye laser.

Fig. 3.3 shows a plot (open circles) of the relative fringe visibility in
emission as a function of distance between the emitting layer and the mirror for CPM versus HeNe excitation. The fringe visibility is defined as \((I_{\text{max}}-I_{\text{min}})/(I_{\text{max}}+I_{\text{min}})\), where \(I_{\text{max}}\) is a maximum and \(I_{\text{min}}\) a minimum of the modulation in the emission spectrum. For short pulse delays (dashed line in Fig.3.3) the fringe intensity follows closely the excitation pulse correlation function. For pulse-delay times greater than 40 fs, the decay of the fringe intensity is fitted to an exponential with a time constant of 100 ± 10 fs (solid line in Fig.3.3). The closed triangles in Fig.3.3 are data points obtained by stochastic excitation using a dye–laser pulse with a field–correlation time nearly identical to that of the CPM–laser pulse. As can be seen the results obtained with a stochastic and coherent light source are identical. We therefore conclude that the homogeneous dephasing time for the lowest singlet transition of nile blue in P4VP is 100 ± 10 fs at room temperature. For nile blue in solution at room temperature, Becker et al. [7] measured an optical \(T_2\) of 65 fs, using the photon–echo technique. It is surprising to find that in a polymer the bath fluctuations occur on a comparable time scale as in a solution. This raises the following question: To what extent, in a polymer at room temperature, can one separate the time scales for homogeneous and inhomogeneous broadening?

De Silvestri et al. [11] concluded from femtosecond three–pulse scattering experiments that dye–doped polymer systems are homogeneously broadened at room temperature. This conclusion is supported by excitation–wavelength–dependent emission spectra of nile blue in P4VP. Only a small spectral shift (≤ 25 cm\(^{-1}\)) of the emission band is observed upon varying the wavelength of an exciting light source (bandwidth 6 cm\(^{-1}\)) over the spectral range of the 40 fs CPM–laser pulse. From consideration of these facts, the question arises of what the relationship is between the measured optical–dephasing time of 100 ± 10 fs and a "relaxation time" of 7 fs (calculated from the 1450 cm\(^{-1}\) "homogeneous" width in the emission spectrum. We propose that the apparent "homogeneity" of the emission spectrum is caused by overlap of spectra from many different initial vibronic states. As our method relies on the interference effect of a single photon emitted from a particular vibronic state, it measures the vibration–averaged dynamics of a wavepacket on the excited–state potential–energy surface.

In conclusion: a new technique to measure ultrafast dephasing processes has
been demonstrated and discussed. In this method a mirror aids in the formation and detection of a frequency and spatial grating excited by a light field with a short correlation time. A major advantage of the method is that only low-excitation powers are needed; it suffices to detect the spontaneous emission of the sample. An interesting aspect of the method is that it also provides information on the homogeneous and inhomogeneous contributions to the spectrum. Since the detected emission arises from an incoherently populated state, the measured decay is not complicated by quantum beats as in femtosecond photon–echo–decay experiments.

References