TWO-DIMENSIONAL SPECTROSCOPY OF MOLECULAR EXCITONS IN A MODEL DIMER SYSTEM

by

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A thesis submitted in conformity with the requirements for the degree of Doctor of Philosophy
Graduate Department of Physics
University of Toronto

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Abstract

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The physics of molecular excitons has been the subject of many recent studies using electronic two-dimensional photon-echo spectroscopy (2DPE), particularly in the context of light harvesting in photosynthesis. Since the spectra for multichromophoric aggregates are congested, particularly so at room temperature, we present a study of a model dimer comprised of identical chromophores with a well defined electronic coupling strength, to provide clear signatures for coherences between vibronic excitons in 2D spectra. We begin by describing the design of a broadband passively phase-stabilized interferometer for collection of 2D spectra, which also allows for the investigation of state preparation in 2D spectroscopy by using shaped excitation pulses. In experiments on the model dimer we observe strong oscillating off-diagonal features in the 2D spectra which are present only before the onset of dephasing, which occurs in less than 100 fs due to strong system-bath coupling. This is in contrast with the parent dye, where low amplitude oscillations associated with Raman active vibrations persist for several ps following excitation. The results of this comparative study indicate that the signals observed earlier in photosynthetic proteins likely reflect vibrational motion in isolated pigments, and not delocalized quantum coherence. While long-lived vibrational coherences are of questionable biological relevance at face value, we conclude with a discussion on initial findings using coherently controlled 2D spectroscopy, where we observe long-lived signatures associated to vibronic coherences at room temperature. These results point to new directions of study using multidimensional spectroscopy to unravel the role of coherence in excitation energy transfer in molecular aggregates in an experimentally direct fashion.
Acknowledgements

I have left this section blank for a very long time, daunted by the task of properly thanking and recognizing all of the individuals who helped out along the way. Now, as the clock ticks down on the official thesis submission deadline, I am forced to be brief and to avoid clichés as best I can!

I am very grateful to have worked in Dwayne Miller’s group for the many years that I did. Dwayne possesses an uncanny ability to come up with ideas for singularly impactful experiments, combined with an unshakeable enthusiasm that keeps his students from getting too discouraged when things inevitably go off-course. He remained supportive of the project even in difficult times, and I especially appreciate his faith in me during the final years of my studies. I also owe many thanks to Valentyn Prokhorenko. Though our professional relationship soured over the years since he was my mentor, he provided me with invaluable benchmarks for experimental quality. Watching Valentyn micromanage every corner of the optical table taught me an important lesson that took years to properly put into practice: running a femtosecond lab requires a level of commitment that borders on obsession.

Next comes Philip Johnson. Besides being an extremely capable colleague, he is actually a pretty swell guy too. I feel very privileged to have worked alongside him for so many years. I have always admired his commitment to design and “clean” solutions, and I strongly value his friendship. Cheers to the great experimental results we obtained, and to the many late nights spent staring at pint glasses and pizza that paved the way for our successes (and maybe some of our failures).
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I thank my Family for their support and encouragement over the years, and look forward to spending a little more time with my beautiful niece and nephew. I could never have finished this thesis without the love and support of Melanie Clarke. Your work ethic is inspirational to me, and I have no words to express how much I appreciate your understanding (since we first met!) in watching me slowly complete this project.

I would have preferred to write a more eloquent and personalized set of remarks, but in closing: while these acknowledgements may be drab, this thesis could never have been completed without the many direct and indirect contributions from my coworkers, friends, and family.

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Acronyms

2DPE Two-dimensional photon-echo.
AOPDF Acousto-optic dispersive filter.
ATP Adenosine triphosphate.
BBO $\beta$ Barium Borate.
BO Born-Oppenheimer.
CARS Coherent Anti-Stokes Raman spectroscopy.
DOE Diffractive-optic element.
EA Excited-state absorption.
EET Excitation energy transfer.
FC Franck-Condon.
FMO Fenna-Matthews Olsen complex.
FWM Four-wave mixing.
GB Ground-state bleach.
HR Huang-Rhys Factor.
LO Local oscillator.
NADPH Reduced form of nicotinamide adenine dinucleotide phosphate
NIR Near-infrared.
NOPA Noncollinear optical parametric amplifier.
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<td>PE</td>
<td>Photon-echo.</td>
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<td>PP</td>
<td>Pump-probe.</td>
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<td>PPC</td>
<td>Pigment-protein complex.</td>
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<td>QB</td>
<td>Quantum beat.</td>
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<td>RF</td>
<td>Radio frequency.</td>
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<tr>
<td>SE</td>
<td>Stimulated emission.</td>
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<td>SHG</td>
<td>Second harmonic generation.</td>
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<td>SPM</td>
<td>Self-phase modulation.</td>
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<td>TA</td>
<td>Transient absorption.</td>
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<td>Transient grating.</td>
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<td>TL</td>
<td>Transform limited.</td>
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<td>TLA</td>
<td>Two-level atom.</td>
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Chapter 1

Introduction

1.1 Coherence in nonlinear spectroscopy

Femtosecond spectroscopy in its many implementations provides a powerful tool for the study of dynamics in atomic and molecular systems. For instance, ultrafast spectroscopic experiments on large molecules have historically provided an indirect visualization of nuclear dynamics [1, 2], and produced subsequent insight into the potential energy surfaces of polyatomic systems [3, 4]. With the increasingly high time-resolution afforded by modern ultrafast light sources, electronic coherences can similarly be studied, even for systems in the liquid phase where strong system-bath coupling leads to dephasing on a femtosecond timescale.

In this aim, two-dimensional electronic spectroscopy has recently been central to a number of studies investigating the decay of coherences between excited states in molecular aggregates [5, 6, 7, 8]. The primary strength of 2DPE spectroscopy lies in its ability to directly measure how excitation at one electronic resonance affects the response at another via interferences in the underlying nonlinear optical polarization [9]. As such, the frequency-frequency maps obtained in 2DPE experiments reveal coupling between electronic transitions directly, which can not be accomplished using conventional third-
order spectroscopic techniques. The associated quantum beats between coupled excited states appear as oscillating peaks and are mapped to specific locations in the 2D spectra, where the decay of these oscillations reflects the loss of coherence between states [10].

Liquids at ambient temperature are unconventional environments for studying fragile quantum coherences, as there the corresponding phase relationships between superpositions of states are short-lived. Despite this fast dephasing, a longtime theme in nonlinear spectroscopy has been the investigation of quantum effects in biological systems [11, 12]. The processes of vision and photosynthesis have garnered the greatest amount of interest in this regard, both due to their efficiencies as well as the subpicosecond timescale along which their primary steps unfold. Though these timescales are at least an order of magnitude slower than typical electronic dephasing times (tens of femtoseconds), wave-like dynamics recorded in recent 2DPE studies on photosynthetic proteins have nevertheless spurred significant efforts in investigating whether photoactive biological systems exploit quantum coherence to accomplish their function [13, 14].

In the aforementioned experiments the signals of interest were assigned to electronic coherences between pigments, and not to the motion of nuclei in impulsively excited molecules. This distinction is critical, and implies that EET may proceed coherently in a spatially delocalized manner due to the nature of the excited states in these systems. The proteins responsible for photosynthesis are by and large composed of aggregates of pigments packed closely together which (via Coulomb interactions) results in the formation of excitons: electronic excitations that are spatially delocalized over multiple pigments.

The exciton model, as pioneered by Davydov and Kasha to explain the optical properties of crystals [15, 16], has been applied to other organic systems such as PPCs for decades. The basic premise underlying the origin of excitons is general, though their specific properties depend on the physical composition of the molecular aggregate. When two (or more) chromophores resonantly interact with one another, the eigenstates of the composite system will consist of linear combinations of the individual chromophore wave-
functions. The excitation or electronic density is thus “shared” or delocalized over each interacting member of the aggregate.

The proteins involved in photosynthesis are typically composed of dozens of these interacting pigments and resulting excitons, and therefore it is far from straightforward to determine the dynamics of energy redistribution in these systems. To do so one must consider a large number of EET steps and photochemical processes, occurring on timescales ranging from sub-picoseconds to milliseconds [17]. The longer timescale processes are unequivocally incoherent in nature, but do the fastest energy transfer steps exploit quantum coherence between excitons to provide directionality to the flow of energy? Robust coherences between excitons at room temperature are intriguing from the point of view of potential applications, but the previous question remains, among others, surrounding the origins and benefits of long-lived quantum mechanical coherences in light-harvesting systems.

1.1.1 Quantum photosynthesis

Photosynthesis is defined as the transduction of energy from the electromagnetic field into chemical energy, stored in the form of ATP and NADPH [17]. Due to the large number of intermediate processes that follow the absorption of a photon by a light-harvesting unit, it is not possible to spectroscopically study this reaction from beginning to end in a single experimental configuration. Experimental 2DPE studies on proteins associated with these intermediate steps have nevertheless revealed coherent oscillatory signals, assigned to inter-pigment energy transfer. These studies have led to the conclusion that quantum coherence could play a role at almost every level of the photosynthetic process, both in plant-based and bacterial systems [5, 18, 19, 8, 20]. A significant issue with this interpretation, however, is that these spectroscopic signals can not be unambiguously assigned to inter-pigment dynamics, nor do they connect directly to established kinetic pathways for EET [21, 22].
The argument concerning the role of quantum coherence highlights a number of experimental and conceptual issues: For one, there is a debate regarding the relation of dynamics observed using femtosecond excitation versus incoherent light found in Nature [23, 24]. In addition, intramolecular vibrational dynamics (unrelated to coherent transport) are universally encountered in organic chromophores [25], and a consensus method for distinguishing signals associated with vibrational wavepacket motion from electronic coherences between delocalized excitons is lacking to this day [26, 27, 28, 29].

Despite the controversy surrounding this debate, the publication of the initial results on biological systems was followed by a surprising absence of control studies on photosynthetic co-factors or mixtures thereof. This has subsequently given rise to much speculation on both the nature and the role of these oscillatory transients. This thesis work seeks to establish the basis for properly assigning electronic coherences within 2D spectra using a well-defined exciton system.

### 1.1.2 Model systems

The work presented here focuses on a rigid, covalently linked dimer of organic cyanine chromophores possessing well-defined geometric parameters and associated inter-pigment coupling strengths [30]. 2DPE spectroscopy is now a mature field from the standpoint of experimental implementation, however methods for analyzing and interpreting the spectra of complicated systems beyond the TLA limit are still under debate, and experimental studies on tractable model systems are in demand.

In the first experimental demonstrations of 2DPE [9, 31], the measured lineshapes closely matched calculations for an inhomogeneously broadened two-level system [32]. There, the authors used narrow laser spectra to excite a single vibronic band in the absorption spectrum of the laser dye in question (IR144). In contrast, the first 2DPE experiments on a PPC (of the FMO complex) at 77°K demonstrated significant complexity, as seen in Fig. 1.1a [33]. This results from the fact that FMO is a trimer, composed of
three identical units themselves comprised of 7 interacting bacteriochlorophyll molecules. Its optical response is thus governed by a large density of overlapping transitions over a narrow spectral range, corresponding to numerous exciton transitions.

Figure 1.1: a) Experimental 2D spectrum of FMO at 77°K (adapted by permission from Macmillan Publishers Ltd: Nature [33], © 2005), where numerous peaks can be resolved. b) Experimental 2D spectrum of FMO taken at ambient temperature (adapted from [7]). The array of sharp spectral features seen at cryogenic temperatures vanishes at ambient temperatures due to fast dephasing.

Subsequent measurements on other PPCs at ambient temperature exhibited similarly congested spectra [18, 7, 8], as shown in Fig. 1.1b, which are broadened by the stronger interaction with the thermal bath and accompanying ultrafast dephasing of the optical polarization. FMO was the first protein where long-lived coherences were observed, yet the broad and featureless character of these experimental spectra masks the spectral features which could be uniquely assigned to interacting quantum states.

The biscyanine system presented here was chosen to contain strongly interacting chromophores to circumvent this issue. The strong coupling results in excitonic transitions that are well resolved despite the broad linewidths encountered at ambient temperature in the liquid phase, leading to more straightforward spectral analysis. In addition, by collecting results for both monomeric and dimeric forms of indocarbocyanine a direct comparison can be made between the signatures of intramolecular wavepacket motion found in the former, and the interpigment dynamics between excitons observed in the
latter. Using a vibronic exciton model to interpret the results allows to isolate contributions to the nonlinear signal associated with inter-exciton dynamics, and helps to clarify ambiguities in the conclusions surrounding 2DPE experiments on more complicated biological systems.

1.2 Two-dimensional photon-echo spectroscopy

Figure 1.2: Conceptual cartoon for the spin-echo measurement. The runners (representing precessing spins) will run at different paces, corresponding to the spins accumulating phase at different rates. In D, when the starter pistol is fired again, the runners turn around and run at the same pace in the opposite direction, and therefore arrive at the starting line at the same time, resulting in the “rephasing” of the magnetization at F (Reproduced by permission from [34]).

Multidimensional spectroscopy has historically been a popular tool in the determination of molecular structure in nuclear magnetic resonance [35]. There, using pulse sequences to measure coupling between nuclear spins, it is possible to determine which nuclei are adjacent to one another. Measurements such as those follow the spin-echo picture of Hahn [36] and the well known illustration in Fig. 1.2, describing how the effect
Chapter 1. Introduction

of dephasing on an ensemble of oscillating dipoles may be reversed, following the application of a sequence of $\frac{\pi}{2}$ and $\pi$ pulses. While some aspects of this pictorial description of the signal generation also apply to optical 2D spectroscopy, the latter experiments are performed in the small pulse area limit, and the photon-echo process is not the singular contribution to the total collected signal. A more complete understanding of the mechanism of signal generation in 2DPE is obtained by turning to the theory of third-order nonlinear spectroscopy and four-wave mixing.

Figure 1.3: Illustrative absorptive 2D spectra for two limiting scenarios. The level diagrams on the top and bottom yield the same linear absorption spectrum, but using 2DPE it is possible to detect whether transitions A and B share a common ground state, as off-diagonal peaks appear for coupled transitions (bottom) but not for independent transitions (top).

Transient absorption is the most commonly used and best understood third-order technique, but suffers from the same spectral congestion which plagues the study of pigment aggregates using linear spectroscopy. Two-dimensional spectroscopy partially overcomes this problem, by projecting the signal onto an additional frequency axis. This is made possible by measuring the full third-order polarization $P^{(3)}(t_1, t_2, t_3)$, which in the case of infinitely short pulses reduces to a direct measurement of the third-order nonlinear susceptibility of the medium [37]. By Fourier transforming the signal along the temporal
dimensions $t_1$ and $t_3$, one can generate correlation maps of the induced absorption of the probe $\omega_3$, as a function of excitation frequency $\omega_1$, as illustrated in Fig. 1.3. This allows to directly monitor how states are coupled, as the resulting interferences in the FWM signal are mapped onto the 2D spectrum at locations corresponding to pumping one resonance and probing the other. Finally, as in transient absorption, population relaxation and the evolution of coupling between states in the system can also be monitored by varying $t_2$.

The sequences of field-matter interactions giving rise to $P^{(3)}$, as well as a complete description of how it is experimentally measured, will be described in greater detail in the following two chapters. However, to provide a more accurate conceptual analogue to 2DPE than spin-echoes, it is helpful to first consider the physical description of three-pulse scattering in a resonant medium.

### 1.2.1 Three-pulse scattering and grating spectroscopy

![Figure 1.4: Geometry of the 3-pulse scattering experiment. Pulses $\vec{k}_1$, $\vec{k}_2$ are separated by $t_1$ and induce a population grating in the sample (pink). The third pulse $\vec{k}_3$ arrives at a time $t_3$ later, and stimulates a nonlinear polarization from this grating, which radiates in directions $\vec{k}_4$, $\vec{k}_5$.](image)

The advancement in femtosecond light sources has led to the development of numerous time domain spectroscopic measurements to probe electronic and vibrational dephasing dynamics in large molecules in the condensed phase. Among these, grating based photon-echo measurements [38, 39] rapidly emerged as a powerful way to probe beneath the
inhomogeneous linewidth of optical transitions, while also reporting on dynamics.

Following the work of Weiner and Ippen [40], we present the physics of laser induced gratings, and how this picture may be extended to 2DPE. To describe grating-based spectroscopy we must consider the action of three noncollinear laser pulses focused into a sample with a resonant frequency $\omega$ close to that of the laser field $\omega_L$, where the detuning between the two is $\Delta \omega = \omega - \omega_L$. We begin by labelling the three laser pulses by their wavevectors $\vec{k}_1, \vec{k}_2, \vec{k}_3$, and as an initial example we consider the sample to be described by a purely homogeneously broadened optical transition possessing a transverse relaxation time of $T_2$.

The first two pulses are separated by a time interval $t_1$ and the second and third pulse by a time $t_2$. The first two laser pulses, which are almost time-coincident and are approximated to be plane waves at the sample position, will interfere to create a standing wave pattern as shown in Fig. 1.4. In regions of constructive interference between the pulses the peak intensity will be high, leading to a spatially periodic variation in the fraction of excited molecules, resulting in the formation of a population grating in the sample. This grating will be generated so long as the pulses are not separated in time by an amount greater than $T_2$. When the third pulse arrives and interacts with this grating, a portion of this beam will diffract in both the $\vec{k}_4 = \vec{k}_3 + (\vec{k}_1 - \vec{k}_2)$ or $\vec{k}_5 = \vec{k}_3 - (\vec{k}_1 - \vec{k}_2)$ directions.

Considering the field at the sample position as

$$E(\vec{r}, t) = a_1 e(t + t_1) \exp \left( -i \vec{k}_1 \cdot \vec{r} \right) + a_2 e(t) \exp \left( -i \vec{k}_2 \cdot \vec{r} \right) + a_3 e(t - t_2) \exp \left( -i \vec{k}_3 \cdot \vec{r} \right),$$

(1.1)

where the electric field amplitudes (real) are written $a_n$ and the complex temporal envelope $e(t)$. This leads to the following expression for the resulting complex grating $\hat{\gamma}$
induced by the first two pulses:

\[
\hat{\gamma}(t_1, \Delta \omega) \sim \int_{-\infty}^{\infty} dt'' \int_{-\infty}^{t''} dt''' \left( e^{*}(t'') e(t''' + t_1) \exp \left[ -\frac{1}{T_2} + i \Delta \omega (t'' - t''') \right] \right) \]
\[
+ e(t'' + t_1) e^{*}(t''') \exp \left[ -\frac{1}{T_2} - i \Delta \omega (t'' - t''') \right].
\]

(1.2)

The previous equation illustrates the dependence of the interference on the temporal overlap between the electric fields, in relation to the dephasing time for the transition. During \(t_1\), the polarization induced by the first pulse is damped by dephasing, requiring that the second pulse arrive at a time that is short with respect to \(T_2\) in order to efficiently excite population. When the third pulse arrives at the sample and interacts with the grating, it generates a third-order polarization which radiates along \(\vec{k}_4\) and \(\vec{k}_5\). Along \(\vec{k}_4\), it can be written

\[
P^{(3)}(\vec{r}, t_1, t_2, t_3) \sim \exp \left( -i \vec{k}_4 \cdot \vec{r} \right) \int_{-\infty}^{t_3} dt' e(t' - t_2) \exp \left( -\frac{t_2}{T_g} \right) \times \]
\[
\hat{\gamma}(t_1, \Delta \omega) \times \exp \left[ (-\frac{1}{T_2} + i \Delta \omega)(t_3 - t') \right].
\]

(1.3)

where we have included a dependence on ground state recovery time \(T_g\), leading to disappearance of the grating for long \(t_2\). The most straightforward method for measuring this polarization is by detecting the intensity of the diffracted signal using a photodetector. By doing so, and assuming that the response time of the detector is slow with respect to the decay of polarization, \(P^{(3)}\) is implicitly integrated along \(t_3\). For pulse durations that are short with respect to the dephasing and ground state recovery timescales, the expression for the measured diffracted energy \(U(t_1, t_2)\) is
\[ U(t_1, t_2) = \int dt_3 |P^{(3)}(\vec{r}, t_1, t_2, t_3)|^2 \]
\[ \propto |\hat{\gamma}(t_1, \Delta\omega)|^2 \times \exp \left( -\frac{2t_2}{T_g} \right) \]
\[ = \exp \left[ -\left( \frac{2t_1}{T_2} + \frac{2t_2}{T_g} \right) \right]. \tag{1.4} \]

Therefore, in this experiment one obtains the longitudinal and transverse relaxation times, respectively, by measuring the decay of the diffracted signal along \( t_1 \) and \( t_2 \). This derivation is not limited to cases of exponential decay for either populations or coherences, and can be modified to account for different relaxation and broadening mechanisms. In particular, when inhomogeneous broadening of the ensemble is included we allow for the possibility of photon-echo generation.

### 1.2.2 Grating based echoes

In echo measurements the signal of interest only arises due to the presence of strong energetic disorder in the system, and the associated inhomogeneous distribution in transition energies [36, 34]. Each local transition frequency \( \omega' \) under this distribution will give rise to an associated grating in the sample, which will be a function of the detuning from the true central frequency of the transition. As such, unlike in the homogeneous case, a distribution of population gratings will be induced in the sample at differing positions, reflecting the local environment. Here the complex grating equation will be written

\[ \gamma(\vec{r}, t_1, \Delta\omega) = \exp \left( -\frac{t_1}{T_2} \right) \cos \left( (\vec{k}_1 - \vec{k}_2) \cdot \vec{r} - \Delta\omega t_1 \right). \tag{1.5} \]

Each of these gratings now possesses a phase associated with the detuning \( \Delta\omega \), reflecting the local resonant energy of the material \( \omega_0 \). This is unlike the case of homogeneous broadening, where for a given detuning each induced dipole will acquire phase at the
same rate during $t_1$. Each element of the ensemble is thus labelled according to its local resonant frequency by the second laser pulse. The inhomogeneous broadening will then also attribute a specific phase to each of the polarizations stimulated by the third laser pulse acting at time $t_2$, which we once again take along $\vec{k}_4$ to find

$$P^{(3)}(t_3, t_2, t_1) \propto \exp \left( -\frac{t_3 - t_2 + t_1}{T_2} \right) \int d\omega_0 g(\omega_0) \times \exp \left( -i(\vec{k}_4 \cdot \vec{r}) - \Delta \omega (t_3 - t_2 + t_1) \right), \quad (1.6)$$

where the prefactor $g(\omega_0)$ represents the inhomogeneous distribution of resonant frequencies. Here, constructive interference of the polarizations radiated from each grating $\hat{\gamma}(\Delta \omega)$ in the sample will lead to the formation of a photon-echo signal at a time $t_3 = t_2 - t_1$ following the action of pulse $\vec{k}_3$. This delay in the radiation of the echo is known as the peak-shift, and provides a measure of the degree of heterogeneous disorder in the system. Extensions of this technique have been widely used to investigate the degree of inhomogeneous broadening experienced by chromophores in dynamically changing environments such as proteins undergoing folding [41], and to measure timescales of solvation dynamics and spectral diffusion in electronically excited molecules [42].

Spectral diffusion during $t_2$ removes the system’s ability to radiate an echo after the third interaction with the field, as a result of the local resonant frequencies no longer remaining identical during both $t_1$ and $t_3$. This scrambles the initial phase array prepared by the first two pulses and the polarization no longer rephases, since the members of the ensemble have lost the “memory” of their initial transition energies. It is possible to implement this type of relaxation into the three-pulse scattering calculation, and to extend this model to multilevel systems, however, in this case the straightforward signal dependence on $t_1$ and $t_2$ demonstrated above no longer applies.

The extension to multilevel systems complicates the interpretation due to interferences between the polarizations radiated by neighbouring transitions lying under the
broad absorption bands encountered in solution [40]. This beating between the various transitions would appear superimposed over the decaying envelope associated with each individual underlying resonance. This results in an artificially accelerated dephasing, and leads to great difficulty in assigning kinetics measured in the diffracted energy $U(t_1, t_2)$ directly to specific transitions.

In this respect, the versatility of the technique becomes limited due to its time integrated nature. While it is still possible to perform the measurements at many different wavelengths to disentangle the signals, this requires more sophisticated models than the equations above [43]. This is precisely where 2D spectroscopy is useful, as by detecting the nonlinear polarization in field rather than in intensity, and by spectrally resolving the signal, it is possible to recover the signatures of dephasing and population relaxation for each transition that overlaps with the laser spectrum. In addition, 2DPE provides the information regarding coupling between states via interferences in the polarization which, due to the Fourier transform nature of the measurement, are mapped to corresponding locations on the 2D spectra as is depicted in Fig. 1.3.

In this thesis we will first describe how to determine 2D spectra based on the expression for the third-order polarization. The full characterization of the experimental apparatus is subsequently provided. Following that, we present the 2DPE and transient absorption results obtained on the monomeric and dimeric forms of indocarbocyanine. Finally, we conclude with a discussion of the implications of these results in relation to those on photosynthetic proteins. Future directions of study are highlighted by initial findings on a modified 2DPE using shaped excitation pulses, which could provide significant insight on both the nature of the oscillations observed in biological systems as well as their relevance to EET.
Chapter 2

Nonlinear Spectroscopy

2.1 Introduction

There exist a number of different approaches for the calculation of 2D spectra, reflecting the broad range of problems and systems to which 2D spectroscopy has been applied: studies on single chromophores in a fluctuating environment will demand a different level of computational power than simulations of vibrational energy transfer in bulk liquids [44]. In the visible range one distinction may already be made between non-perturbative [45, 46] and perturbative [32, 47] techniques, with respect to the calculation of the nonlinear polarization. In this section we will focus on an example of the latter, developed in large part by Mukamel and coworkers [48, 37], where the nonlinear signals are broken down into contributions from sequential light-matter interactions, representing pathways allowed by energy and momentum conservation in a given experimental phase-matching configuration.

This method for calculating the nonlinear polarization is widely applied, particularly for the parametric processes probed in third-order spectroscopy. By accounting for phase-matching and time-ordering, one can isolate the complete list of terms from the total third-order nonlinear response function that contribute to each spectroscopic technique.
The number of these so-called Liouville pathways, each representing a sequence of allowed electronic transitions between energy eigenstates, will depend on the system Hamiltonian and are scaled by the transition dipole moment $\mu$ of each underlying interaction between the radiation field and the system.

The starting point for this approach involves the perturbative expansion of the wavefunction (or density matrix). From there, we may introduce the pictorial notation known as ladder diagrams to list the relevant Liouville pathways and describe the time-evolution. In the examples shown here, we restrict ourselves to a phenomenological implementation of dephasing following derivations given in Ref. [49]. The inclusion of the system-bath interaction can be done in a number of ways with varying degrees of rigour, ranging from a Redfield relaxation tensor [50] (a more general extension to the examples below), to models such as the cumulant expansion [37, 51, 52] where a lineshape function is introduced to account for the dynamic fluctuations of energy gaps occurring in solution for each transition during $t_1$, $t_2$ and $t_3$. The interaction of multichromophoric systems with the bath is of significant physical interest, however, the calculations shown here are only for illustrative purposes, which justifies the use of a simple implementation of relaxation.

### 2.2 Perturbative expansion of the wavefunction

We begin by moving to the interaction picture of quantum mechanics. Introducing a Hamiltonian $H(t)$ defined by

$$H(t) = H_0 + H'(t),$$

where $H'(t)$ is taken to be a time-dependent perturbation acting on the system. The unperturbed system Hamiltonian $H_0$ has an associated time-evolution operator

$$U_0(t, t_0) = \exp \left( -\frac{i}{\hbar} H_0(t - t_0) \right).$$
The eigenstates obey the relation

$$|\psi(t)\rangle = U_0(t,t_0)|\psi_I(t)\rangle,$$  \hspace{1cm} (2.3)

where the subscript $I$ denotes the interaction picture. We can then write the Schrödinger equation for the total Hamiltonian, which states:

$$-\frac{i}{\hbar} H(t)|\psi(t)\rangle = \frac{d}{dt}|\psi(t)\rangle \hspace{1cm} -\frac{i}{\hbar} H(t)U_0(t,t_0)|\psi_I(t)\rangle = \frac{d}{dt}U_0(t,t_0)|\psi_I(t)\rangle$$

$$\hspace{4cm} = -\frac{i}{\hbar} H_0U_0(t,t_0)|\psi_I(t)\rangle + U_0(t,t_0)(\frac{d}{dt}|\psi_I\rangle),$$ \hspace{1cm} (2.4)

where now, by subtracting the first term of the RHS of the Eqn. 2.4 from the LHS, and applying $U_0^\dagger(t,t_0)$ from the LHS (recalling that $H'(t) = H(t) - H_0$) we obtain the following expression for the time evolution of $|\psi_I(t)\rangle$:

$$\frac{d}{dt}|\psi_I(t)\rangle = -\frac{i}{\hbar} U_0^\dagger(t,t_0)H'(t)U_0(t,t_0)|\psi_I(t)\rangle,$$

or

$$\frac{d}{dt}|\psi_I(t)\rangle = -\frac{i}{\hbar} H'_I(t)|\psi_I(t)\rangle.$$ \hspace{1cm} (2.5)

From this equation we now possess a starting point for determining the time-evolution of the system when subjected to the weak perturbation provided by the electric field. For the case of several field-matter interactions it is convenient to separate this evolution into multiple segments. This will be especially useful farther along when we consider the induced polarization due to the action of multiple time-ordered laser pulses impinging
on the sample. In this regard the following expansion is useful:

\[
|\psi_I(t)\rangle = |\psi_I(t_0)\rangle - \frac{i}{\hbar} \int_{t_0}^{t} H'_I(t) |\psi_I(t)\rangle \\
= |\psi_I(t_0)\rangle + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \\
\int_{t_0}^{\tau_2} d\tau_1 H'_I(\tau_n) H'_I(\tau_{n-1}) \cdots H'_I(\tau_1) |\psi_I(t_0)\rangle.
\]

(2.6)

After returning to the Schrödinger picture by multiplication of both sides by \(U_0(t, t_0)\), and following some algebraic manipulation, Eqn. 2.6 becomes

\[
|\psi(t)\rangle = |\psi^{(0)}(t)\rangle + \sum_{n=1}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \times \\
U_0(t, \tau_n) H'_I(\tau_n) U_0(\tau_n, \tau_{n-1}) H'_I(\tau_{n-1}) \cdots U_0(\tau_2, \tau_1) H'_I(\tau_1) U_0(\tau_1, t_0) |\psi(t_0)\rangle.
\]

(2.7)

The perturbation acts on the quantum state at particular times, but in between these interactions the evolution of the system is given by the time-evolution operator for the unperturbed Hamiltonian, where the initial state is an unperturbed energy eigenstate of the Hamiltonian \(H_0\) given by \(|\psi^{(0)}(t)\rangle = U_0(t, t_0) |\psi(t_0)\rangle\).

### 2.2.1 Extension to the density operator

When studying ensembles it is common to perform calculations based on the density operator instead of wavefunctions. Relaxation in multilevel systems in particular is straightforward to implement using density operators, as they provide an economical notation describing the populations of quantum states, as well as the coherences between them. By extension of the derivation presented above, a similar expression of the nonlinear polarization can be obtained for the density operator. The density operator \(\rho\) can, like any operator, be transformed into the interaction picture as in the previous section where

\[
\rho(t) = U_0(t, t_0) |\psi_I(t)\rangle \langle\psi_I(t)| U_0^\dagger(t, t_0) = U_0(t, t_0) \rho_I(t) U_0^\dagger(t, t_0).
\]

(2.8)
Using density matrices, the Schrödinger equation reduces to a commutation relation
\[
\frac{d}{dt} \rho_I(t) = -\frac{i}{\hbar} [H'_I(t), \rho_I(t)].
\] (2.9)

Following the same steps as in the previous section for wavefunctions, we obtain an expression for the time evolution of the density operator for a system subject to a perturbation \( H'(t) \):
\[
\rho(t) = \rho^{(0)}(t) + \sum_{n=1}^{\infty} \left( -\frac{i}{\hbar} \right)^n \int_{t_0}^{t} d\tau_n \int_{t_0}^{\tau_n} d\tau_{n-1} \cdots \int_{t_0}^{\tau_2} d\tau_1 \cdot U_0(t_0)[H'_I(\tau_n)[H'_I(\tau_{n-1}) \cdots [H'_I(\tau_1), \rho(t_0)] \cdots ]U_0^\dagger(t_0).
\] (2.10)

Since we now possess an \( n^{th} \) order expansion for the density matrix, it is an appropriate time to introduce the electric field \( E(t) \) as a perturbation to the system via the transition dipole moment operator \( \mu \). With \( H'_I(t) = -E(t)\mu_I(t) = -E(t)U_0^\dagger(t_0)\mu U_0(t_0) \), the density matrix can be written
\[
\rho^{(n)}(t) = \left( -\frac{i}{\hbar} \right)^n \int_{-\infty}^{t} d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \cdots \int_{-\infty}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \cdots E(\tau_1) - \left( -\frac{i}{\hbar} \right)^n \int_{-\infty}^{t} d\tau_n \int_{-\infty}^{\tau_n} d\tau_{n-1} \cdots \int_{-\infty}^{\tau_2} d\tau_1 E(\tau_n) E(\tau_{n-1}) \cdots E(\tau_1) U_0(t_0,-\infty)[\mu_I(\tau_n)[\mu_I(\tau_{n-1}) \cdots [\mu_I(\tau_1), \rho(-\infty)] \cdots ]U_0^\dagger(t_0,-\infty).
\] (2.11)

To see how this expression connects to the nonlinear optical response we must now consider the expression for the electrical displacement field \( D = \epsilon_0 E + P \), where \( P \) is the induced polarization and \( \epsilon_0 \) the permitivity of free space. The macroscopic polarization in the density matrix picture is given by \( P = \langle \mu \rho \rangle = \text{Tr}(\mu \rho) \). We can expand the expression for the polarization in powers of the applied electric field, based on the susceptibility tensor of the medium \( \chi \), such that
\[
P = \epsilon_0 \left( \chi^{(1)} E + \chi^{(2)} E \cdot E + \chi^{(3)} E \cdot E \cdot E + \cdots \right).
\] (2.12)
In this way we see how the expansion of the density matrix in Eqn. 2.11 corresponds to the increasing orders of the nonlinear polarization, such that we may write \( P^{(n)}(t) = \langle \mu \rho^{(n)}(t) \rangle \). Following this line, and changing the absolute time variables \( \tau_n \) into temporal spacings between interactions with the electric field by introducing \( t_n = \tau_{n+1} - \tau_n \), we arrive at the following expression for the nonlinear polarization \( P^{(n)} \):

\[
P^{(n)}(t) = - \left( -\frac{i}{\hbar} \right)^n \int_0^\infty dt_n \int_0^\infty dt_{n-1} \ldots \int_0^\infty dt_1 E(t - t_n) E(t - t_n - t_{n-1}) \ldots E(t - t_n - t_{n-1} - \ldots - t_1) \langle \mu(t_n + t_{n-1} + \ldots + t_1) \rangle \\
\ldots \langle \mu(0), \rho(-\infty) \rangle \ldots \langle \mu(0), \rho(-\infty) \rangle \ldots
\]

or

\[
P^{(n)}(t) = \int_0^\infty dt_n \int_0^\infty dt_{n-1} \ldots \int_0^\infty dt_1 E(t - t_n) E(t - t_n - t_{n-1}) \ldots \]

\[
E(t - t_n - t_{n-1} - \ldots - t_1) S^{(n)}(t_n, t_{n-1}, \ldots, t_1).
\]

Where \( S^{(n)} = - \left( -\frac{i}{\hbar} \right)^n \langle \mu(t_n + t_{n-1} + \ldots + t_1) \rangle \langle \mu(t_{n-1} + \ldots + t_1) \rangle \langle \mu(0), \rho(-\infty) \rangle \ldots \rangle \) is the \( n \)th order nonlinear response function. The nonlinear polarization induced in the sample is then given by the convolution of the various optical fields with this response function. The first instance of \( \mu \) in the expression for \( S^{(n)} \) represents the radiation of this polarization, associated with the non-equilibrium density matrix prepared by the other interactions in the series of commutators. The third-order response function is the lowest accessible nonlinearity to probe in isotropic media such as chromophores dissolved in solution, and from this we may calculate the signals contributing to 2D spectra.
2.3 Response functions

The vast majority of the nonlinear optical phenomena discussed in this dissertation relate to the third-order response function

\[ S^{(3)}(t_1, t_2, t_3) = -\frac{i}{\hbar^3} \langle \mu(t_3 + t_2 + t_1) [\mu(t_2 + t_1) [\mu(t_1) [\mu(0), \rho(-\infty)]] \rangle \]. \quad (2.14) \]

By expanding the commutators in Eqn. 2.14 the full expression for \( S^{(3)} \) can be succinctly written into 8 terms, or 4 pairs of Hermitian conjugates. However, subsequently inserting these terms into the convolution integral in Eqn. 2.13 to obtain the third order polarization is nontrivial in the case of electric fields with arbitrary envelopes. For fields which can be written as \( E(t) = E_1(t) (e^{-i\omega t} + e^{i\omega t}) + E_2(t) (e^{-i\omega t} + e^{i\omega t}) + E_3(t) (e^{-i\omega t} + e^{i\omega t}) \), each convolution of \( E \) for \( t_{1-3} \) requires the inclusion of all 3 pairs of terms corresponding to the three laser fields incident on the system, increasing the elements needed to calculate the polarization to a cumbersome degree.

The experimental conditions allow us to make use of phase-matching to drastically reduce the number of terms, and provide selectivity over which terms of the total response function will contribute to the measured polarization. In addition, the rotating-wave approximation removes all rapidly oscillating contributions to the polarization, further simplifying the expression for the nonlinear signal.

We also invoke the impulsive excitation limit here, where \( E_n(t) = E \delta(t - t_n) \) and \( E \) is now a scalar, to enforce a strict time ordering between the interactions. This once again reduces the number of terms in our calculations, and is a reasonable approximation when the laser pulse is shorter than the electronic dephasing time of the transition. Calculations have shown that the implementation of realistic pulse envelopes mainly acts as a frequency filter in the resulting 2D spectral window [32, 47]. Certain deleterious effects do exist in the region where all excitation pulses temporally overlap, but these reflect the state preparation via induced vibrational wavepackets [32], and are further
discussed in the subsequent Chapters.

### 2.3.1 Example: linear response

Ladder diagrams (or double-sided Feynman diagrams) are a convenient and intuitive method for visualizing the surviving terms of the response function. In these diagrams, based on the time ordering and the phase-matching condition satisfied in the experiment, one can generate a shorthand list of the contributions to the 2D spectra for a given Hamiltonian. The diagrams are double-sided, since they describe how each side (ket and bra) of the density operator evolve following each interaction with the laser field. In these diagrams, time is vertically increasing, and interactions with the laser are depicted as arrows pointing in or away from $\rho$, the direction of which is determined by phase-matching. The simplest example to consider is the linear response for a two-level system, composed of the states $|g\rangle$ and $|e\rangle$:

$$S^{(1)}(t_1) = -\frac{i}{\hbar}(\langle\mu(t_1)\mu(0)\rho(-\infty)\rangle - \langle\mu(t_1)\mu(0)\rho(-\infty)\rangle^*) .$$  \hspace{1cm} (2.15)

![Ladder diagrams](image)

Figure 2.1: Ladder diagrams describing the terms which make up the linear response of a two-level system.

The two diagrams of Fig. 2.1 correspond to the two terms in Eqn. 2.15. In this example the density operator is in a ground-state population until the laser pulse arrives at $t = 0$, when a coherence is created with the excited state. Afterwards, during the time interval $t_1$, that coherence radiates a polarization (corresponding to the dashed arrow) which
decays, reverting the density operator back to a ground state population. This process describes a free induction decay, which could then be measured using an ideal photodiode and Fourier transformed to obtain the absorption lineshape for the $|g\rangle \rightarrow |e\rangle$ transition. Another important note, is that the two diagrams in Fig. 2.1 are complex conjugates, and therefore in the discussion that follows we will only list one set of diagrams letting their conjugates be implicit.

### 2.3.2 Third-order response

![Ladder Diagrams](image)

Figure 2.2: Ladder diagrams describing the third-order response of a three-level system.

The number of terms needed to describe the third-order response is much larger due to the increased number of interactions with the laser field, and can be grouped into the following categories: ground-state bleach, stimulated emission and excited-state absorption. The signal in our measurements is radiated in the direction of $-\vec{k}_1 + \vec{k}_2 + \vec{k}_3$.
set by geometric phase-matching. For this phase-matching condition and time-ordering, the signal is referred to as “rephasing”, and corresponds to a photon-echo. On the other hand, if the second laser pulse in the scheme depicted in Fig. 1.4 precedes the first pulse \( t_1 \leq 0 \text{ fs} \), the phase-matching condition corresponds to \( \vec{k}_1 - \vec{k}_2 + \vec{k}_3 \) or the “non-rephasing” signal.

In Fig. 2.2 we demonstrate the corresponding diagrams, for both rephasing and non-rephasing cases. For a two-level system we would obtain only the two first terms, corresponding to GB and SE, however we are also considering the presence of a second excited state which gives rise to an EA signal. The first two signals will be positive (enhancement of the field corresponding to the \( |g\rangle \langle e| \) coherence) while the last ones while give rise to negative signals due to depletion of the field caused by absorption into state \( |f\rangle \).

In the rephasing phase-matching condition the convention for ladder diagrams states that the first interaction be represented by an arrow pointing to the left (\(-\vec{k}_1\)), followed by two pointing to the right (\(+\vec{k}_2 + \vec{k}_3\)). As such, for the case of GB in Fig. 2.2, the first interaction acts on the RHS of \( \rho \) to couple the system to the field, followed by a second interaction on the RHS to project this coherence onto a ground-state population during \( t_2 \), followed by the generation of a \( |e\rangle \langle g| \) coherence by the third laser pulse that radiates during \( t_3 \).

The difference between rephasing and non-rephasing cases can be seen in the ladder diagrams of Fig. 2.2. In the rephasing case, the coherences during the \( t_1 \) and \( t_3 \) periods are conjugated. Therefore, the phase of the coherences evolve in opposite directions during these two time periods, allowing for the emission of a photon-echo. On the other hand, in the case of non-rephasing signals, there is no such conjugation of the fields, and returning the cartoon of Fig. 1.2, this results in runners who no longer turn around and return to the starting line, but instead continue in the same direction similarly to a free induction decay.
2.4 Building 2D spectra

2.4.1 Three-level system

The way to connect the pathways shown above to 2D spectra can be better understood by considering the evolution of the density matrix during the three time periods:

\[
\begin{pmatrix}
\rho_{gg} & 0 & 0 \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\rightarrow
\begin{pmatrix}
0 & \rho_{ge}^{(1)} & 0 \\
\rho_{eg}^{(1)} & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\rightarrow
\begin{pmatrix}
\rho_{gg}^{(2)} & 0 & 0 \\
0 & \rho_{ee}^{(2)} & 0 \\
0 & 0 & 0
\end{pmatrix}
\rightarrow
\begin{pmatrix}
0 & \rho_{ge}^{(3)} & 0 \\
\rho_{eg}^{(3)} & 0 & \rho_{ef}^{(3)} \\
0 & \rho_{fe}^{(3)} & 0
\end{pmatrix}
\]

Before any laser pulses arrive at the sample position it is in thermal equilibrium. Once the first laser pulse arrives, the \(\rho_{ge}^{(1)}\) coherence is generated during time interval \(t_1\). By introducing a phenomenological homogeneous dephasing time for this transition of \(\Gamma\), we may use the following relation to describe the density matrix element for that coherence:

\[\rho_{ge}^{(1)}(t_1) = \frac{i}{\hbar} \mu_{ge} E e^{-i(\omega_g - \omega_e) t_1} e^{-\Gamma t_1}.\] (2.16)

If \(t_1\) is sufficiently short that the polarization induced by the impulsive excitation of the first laser pulse has not decayed, population will then be excited by the subsequent interaction according to

\[\rho_{ee}^{(2)}(t_1, t_2) = \frac{\mu_{ge}^2 E^2}{\hbar^2} e^{-\Gamma t_1} e^{-\gamma t_2}.\] (2.17)

Here we have introduced \(\gamma\) to reflect the excited state lifetime. In this very simplistic model, we have not introduced any symmetry breaking mechanism (solvation, spectral diffusion) which would differentiate between excited and ground state dynamics along \(t_2\), and as such \(\rho_{gg}^{(2)}\) will be identical to \(\rho_{ee}^{(2)}\). Finally, in the third evolution period we find
that for the rephasing case

\[
\rho_{ge}^{(3)}(t_1, t_2, t_3) = -\frac{2i}{\hbar^3} \mu_{ge}^3 E_3^3 e^{-i(\omega_g - \omega_e)t_1} e^{-\Gamma(t_1 + t_3) - \gamma t_2} e^{-i(\omega_e - \omega_g)t_3} \\
= -\frac{2i}{\hbar^3} \mu_{ge}^3 E_3^3 e^{i(\omega_e - \omega_g)t_1} e^{-\Gamma(t_1 + t_3) - \gamma t_2} e^{-i(\omega_e - \omega_g)t_3},
\]

(2.18)

or, for non-rephasing time ordering

\[
\rho_{ge}^{(3)}(t_1, t_2, t_3) = -\frac{2i}{\hbar^3} \mu_{ge}^3 E_3^3 e^{-i(\omega_g - \omega_e)t_1} e^{-\Gamma(t_1 + t_3) - \gamma t_2} e^{-i(\omega_e - \omega_g)t_3}. 
\]

(2.19)

In these cases, the appearance of the factor of two in the expression arises due to the fact that the ladder diagrams for GB and SE are equivalent. Following the same line for the EA signal, and taking \( P^{(3)}(t) = \langle \mu \rho^{(3)}(t) \rangle = \text{Tr} (\mu \rho^{(3)}(t)) \), we obtain

\[
P^{(3)}(t_3, t_2, t_1) = \text{Tr} (\mu \rho^{(3)}(t_1, t_2, t_3)) \\
= \text{Tr} \left( \begin{pmatrix} 0 & \mu_{ge} & 0 \\
\mu_{eg} & 0 & \mu_{ef} \\
0 & \mu_{fe} & 0 \end{pmatrix} \right) \left( \begin{pmatrix} 0 & \rho_{ge}^{(3)} & 0 \\
\rho_{eg}^{(3)} & 0 & \rho_{ef}^{(3)} \\
0 & \rho_{fe}^{(3)} & 0 \end{pmatrix} \right) \\
= -\frac{i}{\hbar^3} E_3^3 e^{-\Gamma(t_1 + t_3) - \gamma t_2} \left( 2\mu_{ge}^4 e^{\pm i\omega_{eg} t_1} e^{-i\omega_{eg} t_3} - \mu_{ge}^2 \mu_{ef}^2 e^{\pm i\omega_{ef} t_1} e^{-i\omega_{ef} t_3} \right),
\]

where \( \omega_{ab} = \omega_a - \omega_b \), and the \( \pm \) in the terms containing \( t_3 \) correspond to the separate cases of rephasing and non-rephasing phase-matching, respectively. Unlike other third-order spectroscopies such as transient absorption \( (t_1 = 0) \), transient grating \( (t_1 = 0) \) or two pulse photon echo \( (t_2 = 0) \), heterodyne-detected 3 pulse photon-echo spectroscopy theoretically allows the direct measurement the entire third-order response function, as all three time intervals \( t_{1-3} \) are sequentially varied. In this respect, all of the information that can be obtained via third-order spectroscopy regarding coherence, population, and
solvation dynamics, is contained in 2DPE spectra via $P^{(3)}$.

For this model, where we have not included inhomogeneous broadening, the resulting lineshapes for the transitions considered will be Lorentzian with width $\Gamma$. The resulting two-dimensional spectral map $M(\omega_1, t_2, \omega_3)$ will be the sum of the Lorentzian peaks corresponding to the three contributions of GB, SE and EA, such that

$$M(\omega_1, t_2, \omega_3) = e^{-\gamma t_2} \left( 2\mu_{ge}^4 \frac{1}{i(\omega_1 - \omega_{ge}) - \Gamma} \cdot \frac{1}{i(\omega_3 - \omega_{ge}) - \Gamma} + \frac{2\mu_{ge}^4}{i(\omega_1 - \omega_{ge}) - \Gamma} \cdot \frac{1}{i(\omega_3 - \omega_{ge}) - \Gamma} - \mu_{ge}^2 \mu_{fe}^2 \frac{1}{i(\omega_1 - \omega_{ge}) - \Gamma} \cdot \frac{1}{i(\omega_3 - \omega_{ef}) - \Gamma} - \mu_{ge}^2 \mu_{fe}^2 \frac{1}{i(\omega_1 - \omega_{ge}) - \Gamma} \cdot \frac{1}{i(\omega_3 - \omega_{ef}) - \Gamma} \right) \quad (2.21)$$

We see from this expression that the magnitudes of the peaks in the 2D spectra will scale as the fourth power of the transition dipole moment. In addition, since the response function $S^{(3)}(t_1, t_2, t_3)$ is real-valued, the associated $M(\omega_1, t_2, \omega_3)$ is complex. This is seen in Eqn. 2.21, where similarly to the Fourier transform of the linear response, there are absorptive and dispersive components to 2D spectra. In Fig. 2.3 we demonstrate the calculated real 2D spectra (absorptive part) corresponding to Eqn. 2.21. The parameters used for this example are $\Gamma = 250 \text{ cm}^{-1}$, $\mu_{ge} = \mu_{ef} = 1$, $\omega_{ge} = 15000 \text{ cm}^{-1}$, and $\omega_{ef} = 14500 \text{ cm}^{-1}$.

The peaks corresponding to GB and SE of the $|g\rangle$ to $|e\rangle$ transition are located on the diagonal. This is expected, as the frequency of the coherence in $t_1$ is the same during $t_3$ for those terms in the response function. On the other hand, the EA peak associated with the $|e\rangle$ to $|f\rangle$ transition appears away from the diagonal as a cross-peak. This is due to the fact that during $t_1$ the system was evolving in a $\omega_{ge}$ coherence, but during $t_3$ it evolved in a $\omega_{ef}$ coherence. The presence of the cross peak above the diagonal but not below is indicative that the system must first be excited to the state $|e\rangle$ before the $\omega_{ef}$
Figure 2.3: Calculated absorptive 2D spectrum of a 3-level, purely homogeneously broadened system at $t_2 = 0$ fs. Shown are the two separate contributions to the spectra corresponding to the GB and SE contributions (left panel), followed by the EA (middle panel). The total spectrum is the sum of the two, and all plots are normalized by the same scaling factor. Contours given at 4%.

resonance becomes accessible.

This model illustrates how 2D spectra are built up from the different pathways in the response function, and how consideration for relative scalings between transition dipole moments is often a helpful tool in determining the origin of on- and off-diagonal peaks in 2D spectra. The Hamiltonian, however, is more appropriate as a starting point for an anharmonic oscillator [49] rather than an electronic dimer, where the addition of a fourth level significantly increases the complexity of the spectra.

2.4.2 Electronic dimer

The model in Fig. 2.3 is useful to demonstrate how cross-peaks arise in 2D spectra, but does not possess dynamics along $t_2$. In the experimental results that follow we will principally focus on dynamics along the waiting time $t_2$, where coherences between excited states are observed, and the previous level diagram must be modified to introduce these effects.

The following example is an electronic dimer based on the Davydov model is shown...
Figure 2.4: Model level diagram for an electronic dimer. The state $|\epsilon_f\rangle$ corresponds to the doubly-excited state.

in Fig. 2.4 [15]. The first exciton manifold is composed of two states $|\epsilon\rangle$, $|\epsilon'\rangle$ with associated transition dipole moments $\mu_{\epsilon,\epsilon'}$. If either exciton state is populated, there exist transitions to higher energy into the doubly excited state $|\epsilon_f\rangle$. Since that state is a combination band of both single excitons, the transition dipole moment from $|\epsilon\rangle$ to $|\epsilon_f\rangle$ will be $\mu_{\epsilon'}$ and vice-versa.

Following the same protocol as earlier, we begin by writing all of the possible contributions to the third-order response function for both rephasing and non-rephasing phase-matching conditions. The rephasing case is demonstrated in Fig. 2.5, where we immediately note that many more pathways must be considered as compared to the case of even a three-level system (we once again omit the complex conjugate pathways). Most importantly, in this system, there are now diagrams which exist as coherences during the waiting time period $t_2$. These pathways in the response function (labelled $QB$ in Figs. 2.5 and 2.6) give rise to quantum beats between excitons, and they appear in both SE and EA signals.

The quantum beat terms in Fig. 2.5 appear as off-diagonal elements (since the optical coherences during $t_1$ and $t_3$ are not the same), but they are not the only contributing source to the cross-peaks recorded in 2D spectra: the bottom two diagrams in the GB
column will also appear as off-diagonal elements, by virtue of the two excitons $|e\rangle$ and $|e'\rangle$ sharing a common ground state. This is one source of confusion and debate surrounding the interpretation of cross-peaks in 2D spectra, as systems possessing vibronic coupling will demonstrate all of the same GB and SE response function pathways as those shown in Fig. 2.5, and will exhibit identical dynamics to electronic coherences in simple theoretical models \[26, 27\].

![Figure 2.5: Response function pathways for the rephasing phase matching condition $-k_1 + k_2 + k_3$, in the impulsive limit. These are again grouped under GB, SE and EA. In this case however, outlined in red, are quantum beat (QB) terms which will undergo oscillatory dynamics during $t_2$.](image)

Isolating the relevant contributions to the rephasing diagrams, we obtain the following
expression for the QB terms in the response function:

\[
S^{(3)}_{R,QB}(t_1, t_2, t_3) = -\frac{i}{\hbar^3} \mu_e^2 \mu'_e^2 e^{-\Gamma(t_1+t_3)} \left[ (e^{i\omega_e t_1} e^{-i\omega_e' t_3} - e^{i\omega_e' t_1} e^{-i\omega_e t_3}) e^{-i(\omega_e' - \omega_e) t_2} + (e^{i\omega_e' t_1} e^{-i\omega_e t_3} - e^{i\omega_e t_1} e^{-i\omega_e' t_3}) e^{i(\omega_e' - \omega_e) t_2} \right],
\]

(2.22)

where we have once again assumed that all optical coherences decay at a rate \(\Gamma\). Eqn. 2.22 states that the amplitude of the cross-peaks between the two excitons will oscillate at a frequency corresponding to the energy splitting between the two states, due to SE. However, the peaks associated with EA into the doubly excited state overlap with these SE cross-peaks leading to cancellation, which in this model is complete, as by visual inspection Eqn. 2.22 is in fact zero.

For the non-rephasing case, the set of diagrams is listed in Fig. 2.6. Once more, we recover 4 terms that oscillate during \(t_2\). In this phase-matching condition, the SE contribution does not give rise to a cross peak, but rather oscillations along the diagonal. Similarly to the rephasing case, however, the EA peaks also overlap with these SE pathways, and the net sum of the quantum beat terms in Eqn. 2.23 is once more zero:

\[
S^{(3)}_{NR,QB}(t_1, t_2, t_3) = -\frac{i}{\hbar^3} \mu_e^2 \mu'_e^2 e^{-\Gamma(t_1+t_3)} \left[ (e^{-i\omega_e' t_1} e^{-i\omega_e' t_3} - e^{-i\omega_e t_1} e^{-i\omega_e' t_3}) e^{-i(\omega_e' - \omega_e) t_2} + (e^{-i\omega_e t_1} e^{-i\omega_e' t_3} - e^{-i\omega_e' t_1} e^{-i\omega_e t_3}) e^{i(\omega_e' - \omega_e) t_2} \right].
\]

(2.23)

This complete cancellation is a straightforward consequence of the energetic symmetry of the system, and the homogeneous broadening in the relaxation model. In realistic systems there exist a number of symmetry breaking mechanisms which bring the SE and EA pathways out of spectral overlap. For one, typically the doubly-excited state does not possess an energy of exactly \(\epsilon_f = \epsilon_e + \epsilon_e'\), and the EA peak is slightly shifted from the SE and GB cross-peaks. For molecular systems this corresponds to the interaction between the permanent dipoles of the molecules [53, 54], which leads to a lowering of the
Chapter 2. Nonlinear Spectroscopy

Figure 2.6: Response function pathways for the non-rephasing phase-matching condition \( k_1 - k_2 + k_3 \), in the impulsive limit. Once more, outlined in red, are QB terms which will undergo oscillatory dynamics during the waiting time.

doubly-excited state energy by an amount \( \Delta \), referred to as the binding energy.

In Fig. 2.7, we present example calculations where the energy splitting between excitons is 800 cm\(^{-1} \), \( \mu_{e'} = \sqrt{2} \mu_e \), \( \Gamma = 250 \) cm\(^{-1} \), but introducing a binding energy \( \Delta = 100 \) cm\(^{-1} \), resulting in clear dynamics in the off-diagonal peaks arising from the interfering QB pathways in Fig. 2.5. Using these parameters, the spectra consists of 4 peaks arranged in a square, with a dominant diagonal peak at \((\omega_{e'}, \omega_{e'})\), a second much weaker diagonal peak at \((\omega_{e}, \omega_{e})\) and two cross-peaks at \((\omega_{e'}, \omega_{e})\) and \((\omega_{e}, \omega_{e'})\), with amplitudes
on the order of $\mu_\epsilon^2 \mu_{\epsilon'}^2$.

Figure 2.7: Calculated absorptive 2D spectra of a homogeneously broadened electronic dimer at several waiting times ($t_2$). Both diagonal and off-diagonal peaks undergo periodic modulation due to coupling, where $T = \frac{1}{c(\omega' - \omega)}$ (with $\omega$ in units of cm$^{-1}$). Contours given at 4%.

These calculations highlight that the amplitudes of the cross-peaks associated with inter-exciton coherences will be on the order of the diagonal peaks. This simple relationship stands in clear contrast to the experimental observation that nonlinear scalings applied to off-diagonal portions of the 2D spectra were required to observe cross-peaks in a number of studies on PPCs [55, 5, 7, 18]. Barring an additional EA contribution from higher lying singlet electronic states, this single observation warrants explanation as will be discussed further below. We also observe that, as expected, these cross-peaks will be well-resolved from the diagonal peaks if the coupling between states is large enough. The relative amplitudes of the oscillatory components of the cross-peaks, however, will depend on the specific energetics of the system in question, due to the interplay between SE and EA peaks.
Calculations based on minimal models such as those shown here allow to roughly generate the spectra expected from experimental measurements. Caution must be exercised before drawing general conclusions with respect to dynamics when so few energy states are taken into account. A number of protocols have been devised, based on similar analysis, to provide a reliable assignment of the oscillatory beats recorded in $t_2$ to either inter-exciton or vibrational coherences in 2D spectra. These methods rely on the comparison of either the mutual phase of the recorded oscillations of the peak amplitudes [10, 29], or the predominance of the beats in either the rephasing or non-rephasing portions of the 2D spectra [26, 27, 8].

A four-level vibronic system was compared to an electronic dimer in both aforementioned cases, but in the former the dimer was approximated to a four-level system (as in Fig. 2.4) [29] while the latter excluded the doubly-excited state from the model [8]. In this section we demonstrated the increased complexity of the response function moving from a 3-level to a 4-level system, and particularly the importance of the doubly-excited state for dimers with a small binding energy, and as such it is unsurprising that these studies each point to different signatures for electronic coherences.

A more interesting and physically accurate model, which relates directly to both the model systems presented here as well as PPCs, involves the direct inclusion of both electronic and vibronic couplings into the system Hamiltonian [56, 57, 58]. When both vibrational and electronic degrees of freedom are mixed, the rules of thumb determined using few-level systems fail, and the distinction of electronic versus vibrational character for the oscillations in 2D spectra loses much of its meaning. In the context of the biscyanine dimer experiments, we will demonstrate the added nuance to this debate provided by the vibronic exciton model to be discussed below.
Chapter 3

Experimental setup

3.1 Laser system

The laser system is based on a Ti:Sapphire regenerative amplifier (Regen) [59] seeded by a femtosecond Erbium doped fibre laser. The block diagram of the system is illustrated below in Fig. 3.1.

Er doped Fibre Oscillator
\[ \lambda = 778 \text{ nm} \]
52 MHz rep. rate
150 fs pulse duration
70 mW avg. power

Nd:YLF Q-Switched intracavity doubled laser
\[ \lambda = 527 \text{ nm} \]
1 kHz rep. rate
250 ns pulse duration
2.75 W avg. power

Ti:Sapphire multipass regenerative amplifier
\[ \lambda = 778 \text{ nm} \]
1 kHz rep. rate
80 ps pulse duration
500 mW avg. power.

Figure 3.1: Block diagram of the femtosecond laser system. Not shown is the frequency divider/delay generator (Quantum Composers) which converts the 52 MHz clock from the oscillator to 1 kHz, and generates trigger pulses for the subsequent active electronics (Q-switch, Pockels cell driver) and data acquisition cards.
The Buccaneer fibre oscillator (Avesta) produces NIR pulses at 778 nm with a pulse duration of approximately 150 fs. The pump laser for the Regen is a home built Q-Switched intra-cavity doubled Nd:YLF laser, which has an output of 2.75 W at 527 nm. In order to avoid damaging the Ti:Sapphire rod with high peak power, the seed pulses are stretched by several orders of magnitude with a grating stretcher (≃ 80 ps) before injection into the Regen cavity [60]. For the pump power employed, the Regen is in the saturated regime, and so the output power is relatively insensitive to seed power and mirrors the fluctuations in the pump laser. Using a Pockells Cell, the amplified pulse is extracted from the Regen cavity and sent to a grating compressor to restore the pulse duration to ≃ 150 fs, which serves as the fundamental for all downstream sources.

3.1.1 Noncollinear optical parametric amplifier

The NOPA [61] has become the standard tool for nonlinear spectroscopy experiments in the visible. Regenerative amplifiers seeded by a broadband source, such as a Ti:Sapphire oscillator, can also directly achieve broadband operation for high temporal resolution spectroscopy, but are restricted in spectral range (≃ 750 – 850 nm) and are therefore limited in applications. In contrast, even using a narrow-band pump, a properly designed NOPA will generate a broad bandwidth and is tuneable in the range from 500 – 700 nm centre wavelength, supporting pulse durations as short as 10 fs or less [62].

Optical layout

The basic premise of the NOPA involves amplification of a broadband weak seed (in this case supercontinuum generated by filamentation in sapphire), via difference frequency generation with a pump source (here the frequency doubled fundamental) in a BBO crystal.

The fundamental enters the NOPA and is immediately split into two beams by a beamsplitter as shown in Fig. 3.2. The transmitted beam is frequency doubled via type-I
Chapter 3. Experimental setup

Figure 3.2: Optical layout of the NOPA, using the following abbreviations: ID - iris diaphragm, M - plane mirror, BS - beam splitter 95/5 T/R, RR - hollow corner-cube retroreflector, HWP - half-wave plate for 780 nm, BBO1 - doubling crystal, L1 - lens (focal length 5 cm), S - sapphire plate, OAPM - off-axis parabolic mirror (effective focal length 20 mm), SM - spherical mirror (focal length 75 cm), BBO2 - mixing crystal.

phase-matching in a BBO to generate a beam (hereafter referred to as the pump) at a wavelength of 387.5 nm with p-polarization.

The reflected beam sends a small portion of the initial fundamental energy to a delay stage, after which it is focused into a sapphire plate to generate supercontinuum white-light by SPM, hereafter referred to as the seed. Along the way to the sapphire, the fundamental beam traverses a variable neutral density filter for fine adjustment of its intensity. While the intensity fluctuations of the white-light typically follow that of the fundamental, if the incident power at 778 nm is too high multi-filamentation occurs, leading to instability in the supercontinuum. Using the neutral density filter we adjust the power of the incident fundamental such that we are only slightly above the threshold for stable white light generation in the sapphire plate.
The supercontinuum is then collimated by a short focal length off-axis parabolic mirror, which offers the advantage of not introducing group-delay dispersion (as would a lens). The beam then strikes a 75 cm focal length spherical mirror, and is reflected at a small angle towards a plane mirror, which is then used to steer the seed towards the second BBO crystal where amplification takes place. The pump beam is focused by a 100 cm focal length lens after SHG, and sent to the same BBO crystal at the appropriate external angle via dielectric routing mirrors. The power of the pump (typically $\sim 15$ mW) is set using a half-wave plate before the doubling crystal, and the temporal overlap between the pump and the seed in the mixing crystal can be adjusted using the seed delay stage (RR in Fig. 3.2).

**Optical parametric amplification**

![Diagram of phase-matching condition for optical parametric amplification in BBO](image)

Figure 3.3: Schematic of the phase-matching condition for optical parametric amplification in BBO. The seed beam is normal to the crystal face. OA: Optical axis of the crystal. $\alpha_{\text{cut}}$ is the angle between the optical axis of the crystal and the crystal normal.

In the NOPA, a weak seed beam is amplified by a much more intense pump at a different wavelength [63]. The process is schematically illustrated in Fig. 3.3. In order to conserve both momentum and energy, is accompanied by the generation of an idler field,
at a lower energy than both the signal and the pump. The phase matching condition for
this process corresponds to $\Delta \vec{k} = \vec{k}_s - \vec{k}_p + \vec{k}_i$, where $\vec{k}_s$ corresponds to the wave-vector
of the signal field, $\vec{k}_p$ the pump field, and $\vec{k}_i$ the idler. To achieve maximal amplification
of the seed, the wave-vector mismatch must be minimized, such that $\Delta \vec{k} = 0$. Following
this line we introduce the phase-matching angle $\theta_{PM}$ [64, 65], which can be calculated
based on the Sellmeier coefficients for BBO [66]. From $\theta_{PM}$, an optimal crystal cut may
be determined for a given noncollinear angle $\alpha_{int}$ between the pump and the seed, where
the wave-vector mismatch is minimal over a broad spectral range.

![Figure 3.4: Calculated phase-matching curve (red) for optical parametric amplification
in BBO for an internal angle of $\alpha_{int} = 3.8^\circ$ and a pump wavelength of $\lambda_p = 387$ nm.
The curve is relatively flat over a large spectral range, resulting in a broad amplification
bandwidth of the supercontinuum seed (overlaid in light blue, a.u.).](image)

Typically in our experiments, the absolute gain for a given signal wavelength is not
prioritized. Rather, due to the broad bandwidth of the seed, we choose a crystal cut
such that the total amplification bandwidth is maximized, so that the pulse duration in
an experiment may then be minimized. For a given noncollinear angle $\alpha_{int}$, the phase
matching angle $\theta_{PM}$ corresponding to the pump wavelength of 387 nm is shown in Fig. 3.4.
We observe that $\theta_{PM}$ is relatively flat over a very broad range, which in turn signifies
a small wave-vector mismatch over that spectral range. Based on the calculated values
of $\theta_{PM}$ for the correct $\alpha_{int}$ corresponding to the desired phase-matching bandwidth, the
BBO must be cut at an angle $\theta_{\text{cut}} = \theta_{PM} - \alpha_{\text{int}}$ with respect to the crystal’s optical axis.

Using the Sellmeier coefficients for BBO for p-polarization, we may determine the appropriate external angle $\alpha_{\text{ext}}$ corresponding to the noncollinear angle plotted in Fig. 3.4 using $\alpha_{\text{ext}} = \arcsin (n_{\text{BBO}}(387 \text{ nm}) \sin \alpha_{\text{int}})$. The precise value of $\alpha_{\text{ext}}$ is only used as a guideline, since due to its intrinsic size and divergence the laser beam will actually possess a range of $\alpha_{\text{int}}$ angles in the crystal [65].

### 3.1.2 Pulse compression

Due to the intrinsic chirp of the supercontinuum seed, the beam leaving the NOPA possesses a pulse duration of over 100 fs despite its broad bandwidth. Moreover, en route to the sample, the NOPA beam traverses a number of dispersive optics, which will introduce additional group velocity dispersion to the pulse. It is possible to correct for this dispersion using the appropriate combination of optics, however, the spectral phase of the laser pulse must first be measured and the pulse characterized.

The different orders of spectral phase can be better understood by expressing the laser pulse as a complex function of frequency $E(\omega) = A(\omega) \exp (-i\omega_0t + \phi(\omega))$. The spectral phase $\phi(\omega)$ can then be expanded about the central laser frequency $\omega_0$ and written

$$
\phi(\omega) = \phi_0 + \frac{d\phi}{d\omega}(\omega - \omega_0) + \frac{d^2\phi}{d\omega^2}(\omega - \omega_0)^2 + \frac{d^3\phi}{d\omega^3}(\omega - \omega_0)^3 + \frac{d^4\phi}{d\omega^4}(\omega - \omega_0)^4 + O(\omega^5). 
$$

Linear chirp in the time domain is caused by the quadratic term in Eqn. 3.1 [67]. Typically, prism compressors are used to eliminate this chirp by introducing a path length difference between the red and blue spectral components of a given laser pulse, as is seen in the ray-tracing of Fig. 3.7. Due to refraction, the blue and red rays are deflected by different angles and therefore experience a difference in optical path length in P2. Prism compressors are very useful, as they are relatively simple to align and possess a very high
throughput (the only losses are due to Fresnel reflections). Nevertheless, for sufficiently large bandwidths, the higher order terms in spectral phase cannot be ignored.

**Pulse characterization - Frequency Resolved Optical Gating (FROG)**

![Diagram of FROG setup](image)

Figure 3.5: Optical layout of the FROG setup, using following abbreviations: ID - iris diaphragm, BS1: 70/30 (R/T) beamsplitter, BS2: 50/50 beamsplitter, M: plane mirrors, RR: hollow corner cube retroreflectors, CP: compensating plate, OAPM: off-axis parabolic mirror (2" effective focal length), FS: fused silica plate (150 µm thickness), L: 75 mm focal length lens. Not shown here is a removable plane mirror which can direct the FROG signal towards a photodiode instead of the spectrometer.

Frequency resolved optical gating (or FROG) possesses a number of implementations [68, 69]. The premise relies on the measurement of the intensity autocorrelation of the pulse, followed by the application of iterative retrieval algorithms. These serve to invert the FROG signal to an corresponding electric field, characterized by its spectral amplitude and phase. The experimental setup is shown in Fig. 3.5: two of the beams arrive simultaneously ($\vec{k}_1, \vec{k}_2$), and their interference in the glass slide leads to an grating in the index of refraction from which the third pulse ($\vec{k}_3$) diffracts to give the signal in the $-\vec{k}_1 + \vec{k}_2 + \vec{k}_3$ direction. This process is also well described by the example presented in §1.2.1 and Ref. [40], only in the limit of the material dephasing being much shorter.
than the laser pulse. The resulting signal has the form

\[
I_{\text{sig}}(\omega, t_2) = \left| \int_{-\infty}^{\infty} E_1(t) E_2^*(t) E_3(t - t_2) \exp(-i\omega t) dt \right|^2 \\
= \left| \int_{-\infty}^{\infty} |E(t)|^2 E(t - t_2) \exp(-i\omega t) dt \right|^2 ,
\]

(3.2)

where the second expression is obtained by considering that all beams are identical in this setup. The measurement produces a time-frequency map, which reflects the temporal distribution of the instantaneous frequencies of the laser pulse. The retrieval algorithm (Femtosoft) then inverts the measured FROG trace, allowing for the unique determination of the electric field.

Figure 3.6: a) Experimental FROG trace for compressed NOPA pulse. b) Retrieved temporal envelope of the laser pulse. c) Retrieved spectral phase.

Fig. 3.6 demonstrates an experimental trace from the FROG setup along with the retrieved electric field. The gravity centre of the spectrum of the FROG trace remains the same as a function of the scanning time \( t_2 \). Linear chirp would manifest itself as a gravity centre sweeping across the spectrum in a linear fashion over \( t_2 \), while additional structure in the trace would be indicative of higher order chirp. Here the phase has been rendered as flat as the compression system will permit. In order to properly compress our laser pulses, we employ two pulse shapers: one programmable commercial unit, as well as a home-built device based on a two-state compressor using conventional optics.
Two-stage compression

By complementing a traditional prism compressor with a deformable mirror based pulse shaper, it is possible to obtain sub-15 fs pulses at any central wavelength produced by the NOPA. The general approach of this compression setup, is to sequentially compensate for the increasing orders of the nonlinearity in phase. The optical layout for this pulse compression setup is illustrated in Fig. 3.7.

The shaper consists of a grating, a spherical mirror (SM) and a membrane-based deformable mirror (DM, OKO Technology), and is a basic implementation of a 4\(f\) shaper [70]. The DM is coated with protected aluminum, and the shape of the membrane is varied by deflections induced via a 19x3 array of electrodes. The grating (600 l/mm) horizontally disperses the spectrum onto the SM, which then focuses the spectrum onto the DM. Modifying the potentials of the electrodes varies the shape of the membrane, inducing an optical path length difference between the spectral components of the pulse.
The DM is tilted slightly away from normal incidence, so that the outgoing beam is not collinear with the incoming beam and can be picked off with ease, before being sent to the prism compressor.

This implementation behaves similarly to a grating compressor when the distance between the SM and the grating in the DM shaper is changed, and this may be used to correct for the linear chirp before applying any potentials to the DM itself [62]. While both grating and prism based compressors are shown to remove linear chirp, ray tracing has shown that it is more efficiently removed using a grating compressor due to stronger dispersion [71]. Moreover, while a grating compressor also induces normal third-order dispersion (addition of positive third order chirp to the spectral phase), it can be compensated by a prism compressor. As such, by combining the two, it is possible to eliminate the majority of phase distortions to a pulse.

In order to monitor the pulse compression, we use the integrated FROG signal collected using a photodiode. To compensate for linear chirp, we vary the position of the grating in the DM shaper to maximize the FROG signal. Once this has been accomplished, a relatively short pulse can be obtained, but it will be distorted by third-order chirp. Consequently, following the work in Ref. [71], we then set a prism-spacing between P1 and P2 such that the third-order chirp may also be cancelled. The process is iterative, as the prism compressor will also introduces linear chirp of its own. Following this approach, it is possible to use the DM to correct for all remaining higher order phase distortions, by using a genetic search algorithm (MATLAB) to find the DM profile which leads to the largest integrated FROG signal. This approach is very robust, and allows for rapid and efficient compression down to pulse durations of $\sim 10$ fs.

### 3.1.3 Acousto-optic pulse shaper

For certain experiments we also made use of a commercial AOPDF (FastLite Dazzler) to compress or shape our laser pulses. The AOPDF is a useful device for performing
arbitrary pulse shaping of femtosecond pulses as it is a standalone unit, which requires only a collimated laser beam as its input [72, 73]. Its principle of operation is based upon the acousto-optic effect in a uniaxial birefringent crystal.

Figure 3.8: Principle of operation for the AOPDF. The pulse enters the crystal aligned along its ordinary axis, and a portion of the intensity is diffracted by an acoustic wave onto the extraordinary axis. The resulting temporal profile of the diffracted field will be a convolution of the original temporal profile of the pulse and that of the acoustic wave, and as such phase corrections may be programmed via the generation of the appropriate acoustic field. Reprinted with permission from [73]. © 2000 Optical Society of America.

A schematic of the Dazzler pulse shaper is shown in Fig. 3.8, illustrating the incident light field being diffracted onto the slow axis of the crystal via an acoustic wave. In this diagram, the transducer which generates the acoustic wave is not shown. This transducer takes the output of an arbitrary RF signal generator, and produces an acoustic wave which reflects the RF field which is input by the user in software. The relation between the input and output can be written

\[
E_{\text{out}}(t) = E_{\text{in}}(t) \otimes S(\frac{t}{\alpha}),
\]

or

\[
E_{\text{out}}(\omega) = E_{\text{in}}(t) \otimes S(\alpha \omega),
\]

where \( \alpha = \Delta n \left( \frac{V}{c} \right) \). Here \( \Delta n \) is the difference in index of refraction seen by the o- and e-rays at a given optical frequency, and \( V \) is the speed of the acoustic wave in the medium [72]. As such, by generating the appropriate RF waveform, the various coefficients of
Eqn. 3.1 may be directly modified, leading to a high degree of control over the dispersion compensation.

Unlike the previous compression scheme, in this case there is no spectral dispersion of the laser beam followed by application of appropriate path length compensations for the different spectral components in the Fourier domain. In this design the pulses are shaped in the time-domain, which leads to a conveniently small footprint for the pulse shaper. The drawbacks, however, arise due to the geometric properties of the device. The shaping window is dictated by the difference in optical path length in the crystal (here TeO$_2$) between given spectral components in the laser pulse, which in turn depends entirely on the index of refraction of the crystal at this wavelength as well as the length of the crystal (25 mm in our model), without even taking into consideration the restriction in bandwidth for RF waveform generators. The device also suffers from nonlinearities at high RF power as well as amplitude-phase shaping cross-talk, however for compression and shaping of pulses with modest bandwidths ($\sim 1500$ cm$^{-1}$) it performs very well.

3.2 2D Setup

In order to generate electronic 2D spectra, it is necessary to construct a broadband spectrometer capable of collecting the underlying FWM signals. This problem was initially solved using a four-beam interferometer based on conventional optics and delay lines, operating at Ti:Sapphire wavelengths in a noncollinear geometry [9], much like the FROG device shown in Fig. 3.5. Extending 2DPE deeper into the visible with broad bandwidths requires significant dispersion management and phase-stability, in order to interferometrically extract the full signal field with high temporal resolution.

The spectrometer presented below achieves both of these ends, by using very few transmissive optics to limit the amount of dispersion, and a diffractive optic element to provide passive phase stability between the laser pulses [74]. In addition, the setup
is designed to allow the use of shaped pulses, without a significant decrease in phase
stability, opening the door for 2D coherent control measurements to investigate the effects
of state-preparation on 2D spectra [75].

Since the first reported 2DPE results, a number of approaches have been implemented,
which can be categorized either as partially collinear, and noncollinear solutions. In the
partially collinear case the experiment is performed in the pump-probe geometry, where
two pump pulses separated by $t_1$ are produced using a pulse shaper, and the probe
pulse (which also acts as a local oscillator for heterodyne detection) is delayed using
a conventional delay stage to set $t_2$ [76]. In this case, in order to properly isolate the
photon-echo signal, which is used to generate the 2D spectra it is necessary to perform
phase-cycling using the pulse-shaper [77].

In the noncollinear instruments, all of the beams possess a different wave vector, so
to fulfill geometric phase matching of $\vec{k}_{sig} = -\vec{k}_1 + \vec{k}_2 + \vec{k}_3$, the signal is radiated in a new
direction. The directionality of the signal presents an immediate advantage by reducing
potential sources of contamination to the photon-echo signal, as there is no background
other than spurious scatter, which makes the method significantly more sensitive that
the two beam pump-probe geometry. This allows the use of lower excitation energies
to avoid saturation effects, preventing higher order nonlinear signals from obscuring the
response function of interest. However, this approach presents a technical challenge,
requiring the construction of an interferometer with four phase-locked beams, which can
be independently delayed. A setup accomplishing this using typical commercial optics
has been demonstrated, however it required stabilization of the interferometer via active
feedback to maintain phase stability [78].

It is possible to avoid using active feedback or other potential complications to the
experiment, by exploiting correlated path length fluctuations between pairs of beams.
Using a diffractive optic to generate the four beams in the experiment, it was demon-
strated that it is possible to passively phase lock the pulses to within $\lambda/60$ at optical
frequencies [74]. The key is that the four beams in the measurement possess a common phase reference, as they are all generated by the DOE. So long as the pairs of pulses strike common optics downstream, phase fluctuations between pulse pairs cancel out, and the interferometer maintains high phase stability, even over large propagation distances.

3.2.1 Overview

The optical layout of the setup is presented in Figure 3.9. For conventional 2DPE measurements (with identical TL pulses) the beamsplitter at the RBS position is in place, and the beam from the AOPDF does not enter the setup. The original beam is split into two arms, one corresponding to the excitation pulse pair and the other to the probe/LO pulses. Delay stage 1 (DL1) varies the $t_1$ variable whereas DL2 varies $t_2$. The delay stages used possessed a minimum step size of 50 nm (VP-25X, Newport Corporation), allowing for a temporal resolution of less than 1 fs in $t_1$ and $t_2$. The pulse diagram in relation to the delays is shown in Fig. 3.10. The setup is designed such that the local oscillator delay is always fixed with respect to the beam which is scanned in the experiment.
Figure 3.10: Schematic of pulse ordering in the 2D setup. The dashed line represents the local oscillator (LO) pulse, which is attenuated. The echo (shown schematically in red) is emitted at a time $t_1$ after the third interaction with the laser field after the relaxation time $t_2$.

The LO pulse traverses a thin fused silica cover slip, coated with a layer of chromium to provide attenuation, which delays the pulse by approximately 420 fs with respect to the other pulses in the interferometer. The sample cell is a home-built flow cell, with 0.15 mm thickness windows and a path length of 0.25-0.4 mm, depending on the sample concentration. The camera used in this work is a 512 pixel Tec5 OEM preamplifier and interface, combined with a Hamamatsu S3902 CMOS sensor, which can be externally triggered and read out at the repetition rate of the laser (1 kHz). A series of home-built shutters, controllable using the digital output of a National Instruments data acquisition card, allows to conveniently toggle between homodyne (intensity detected), heterodyne, and pump-probe measurements, by blocking the appropriate beams in the setup.

For experiments with shaped excitation pulses, the BS in Fig. 3.9 is removed, an appropriate compensating plate is placed in the path of the beam arriving from the DM shaper, and no further adjustments to the interferometer are necessary. In that configuration the probe and LO beams remain broadband TL pulses, but the pulses coming from the AOPDF are shaped, providing control on the state preparation in the sample. Using flip-mirror mounts it is possible to direct the beams in either arm of the interferometer to an independent home built spectrometer (Hamamatsu C7884 camera,
S3902 CMOS sensor) and FROG setup, to fully characterize each pulse.

### 3.2.2 Passive phase stability

To explain the origin of the phase stability in this design, it is useful to compare the optical path length change induced by an unstable optical element on each of the four beams in the system. Writing $\Delta \phi_i = \sum_n \delta_{m_i}$ as the phase fluctuation of beam $i$ caused by fluctuations each optical element $m$ (where $\delta \phi_m = \frac{x}{n} \delta l_i$), we find

\[
\begin{align*}
\Delta \phi_1 &= \Delta_{\text{pump}} + \delta_{OAPM1} + \delta_{M1} + \delta_{RR1} + \delta_{OAPM2}, \\
\Delta \phi_2 &= \Delta_{\text{pump}} + \delta_{OAPM1} + \delta_{RR2} + \delta_{M2} + \delta_{OAPM2}, \\
\Delta \phi_3 &= \Delta_{\text{probe}} + \delta_{OAPM1} + \delta_{M1} + \delta_{RR1} + \delta_{OAPM2}, \\
\Delta \phi_4 &= \Delta_{\text{probe}} + \delta_{OAPM1} + \delta_{RR2} + \delta_{M2} + \delta_{OAPM2},
\end{align*}
\]

where $\Delta_{\text{pump}}$ and $\Delta_{\text{probe}}$ denote the phase fluctuations experienced by the beams reflected and transmitted by RBS in Fig. 3.9, respectively. Given that $\phi_{\text{sig}} = \phi_2 - \phi_1 + \phi_3 - \phi_4 + \phi_{\text{echo}}$, we can rewrite

\[
\begin{align*}
\Delta \phi &= \Delta \phi_2 - \Delta \phi_1 + \Delta \phi_3 - \Delta \phi_4 \\
&= (\Delta \phi_3 - \Delta \phi_1) + (\Delta \phi_2 - \Delta \phi_4) \\
&= (\Delta_{\text{probe}} - \Delta_{\text{pump}}) + (\Delta_{\text{pump}} - \Delta_{\text{probe}}) \\
&= 0. \quad (3.4)
\end{align*}
\]

By having the four excitation beams interact with the optics following the DOE in pairs, we achieve very robust cancellation of phase instabilities caused by mechanical vibrations of the optical elements. Another significant advantage of using DOEs, is that the tilted phase fronts they produce subsequently lead to better overlap between the 4 beams at the sample position, resulting in more efficient generation of the nonlinear signal [79, 80].
In order to measure the inherent phase stability of the setup in both single- and dual-beam operations, a plate of SF11 was placed at the sample position, and the spectrogram corresponding to the heterodyne detected FWM signal was recorded. By performing a Fourier transform, it is possible to isolate the heterodyne signal \( A(\omega_3) \) from the DC homodyne component. From there, the phase of the signal at a given optical frequency \( \omega \) is determined by the relation

\[
\phi = \Im(\ln A(\omega)) = \phi_0 + \delta \phi,
\]

where \( \phi_0 \) is the sum of the phases of the incoming laser beams and that of the photon-echo signal, while \( \delta \phi \) represents phase fluctuations. In Fig. 3.11, we show the phase stability as a function of time. For the conventional configuration with a single input beam it is greater than \( \lambda/100 \) on the timescale of a single scan and \( \lambda/80 \) on the timescale of a full measuring run. For the dual beam configuration, a decrease of phase stability of approximately 10% was observed, despite the fact that the two beam lines are split approximately three meters before the entrance to the 2D setup. Even though the two beams strike a number of different, independent optics en route to the setup, the pairwise cancellation of phase fluctuations described above maintains excellent phase stability.

The second panel of Fig. 3.11 illustrates how the main limiting factor to phase stability is beam pointing. Slow drift is not uncommon over such long beam lines, and therefore we implement a beam pointing stabilizer at the input of the setup. The first mirror shown in Fig. 3.9 transmits \( \sim 5\% \) of the incoming laser light, which is focused onto a CCD camera (Point Grey) using a 75 cm focal length lens. In this way, once the alignment has been optimized, a reference position for beam pointing can be recorded, and any drift is corrected every minute using feedback on a computer controlled mirror mount.
Chapter 3. Experimental setup

Figure 3.11: a) Phase stability of 2D setup in both single (red) and dual (blue) beam configurations. b) Stability when beam pointing was systematically varied, single arrowheads denote vertical changes of approximately 300 mrad, double arrowheads horizontal.

3.2.3 Data collection and treatment

The spectrograms collected in the experiment (at a particular value for $t_2$) are given by

$$I_S(t_1, \omega_3) = I_{LO}(\omega_3) + I_{PE}(t_1, \omega_3) + E_{LO}^*(t_1, \omega_3)e^{i\omega_3(\Delta T_{LO}+t_1)} + c.c. \quad (3.6)$$

While the intensity of the PE can be recorded without using a local oscillator (delayed by $\Delta T_{LO}$), the final two terms of Eqn. 3.6 allow the determination of the PE field. The interferometric nature of the detection highlights the importance of phase stability between the four beams, as stressed earlier. By chopping one of the excitation beams, it is possible to subtract $I_{LO}$, as well as any optical scattering of three of the four beams. This leads to

$$I'_S(t_1, \omega_3) = I_{PE}(t_1, \omega_3) + \tilde{A}(t_1, \omega_3)e^{i\omega_3(\Delta T_{LO}+t_1)} + \tilde{A}^*(t_1, \omega_3)e^{-i\omega_3(\Delta T_{LO}+t_1)}$$

$$+ I_{PP}(t_1 + \Delta T_{LO}). \quad (3.7)$$

We are left with 4 terms, consisting of the interferogram containing the desired electric field of the photon-echo, the homodyne or modulus squared of that signal field, as well
as an additional PP signal associated with the chopped beam, which is a consequence of our local-oscillator pulse arriving later than the other pulses in the measurement. In Fig. 3.12, we outline the procedure used to extract $E_{PE}$ and generate 2D spectra.

Figure 3.12: Sequence of steps used to generate 2D spectra from the heterodyne detected PE data collected along $t_1$. a) Raw data for a typical experimental PE scan. b) Cross-section of $I'_S(t_1, \omega_3)$ through $t_1 = 0$ fs. c) Inverse Fourier transform of b, showing corresponding time-domain signal and filter. d) Real (blue trace) and imaginary (brown, displaced by 200 counts) parts of the signal field.

First, the signals described in Eqn. 3.7 must be collected over a $t_1$ range covering the full dephasing time, and with appropriate sampling. The resulting array is shown in Fig. 3.12a, where the rapidly oscillating terms in $\omega_3$ corresponding to the heterodyne detected echo are evident over a range of $t_1 = \pm 50$ fs. The two bands which are present at all time points correspond to the $I_{PP}$ term in Eqn. 3.7. In Fig. 3.12b, we show the interferogram corresponding to $t_1 = 0$ fs for this particular experiment. By performing an inverse Fourier transform along $\omega_3$ we obtain Fig. 3.12c, which represents

$$I'_S(t_1, t_3) = \tilde{I}_{PE}(t_1, t_3) + A(t_3 - \Delta T - t_1) + A^*(t_3 + \Delta T + t_1).$$  

(3.8)

The signal corresponding to the rapidly oscillating trace in Fig. 3.12b is shifted in the time
domain, and can be isolated from the homodyne (DC) component of the signal by using an appropriate filter, shown as the shaded area in Fig. 3.12c. By Fourier transforming the positive and negative time signals back to the frequency domain, we obtain

\[ I'_+(t_1, \omega_3) = \tilde{A}(t_1, \omega_3)e^{i\omega_3(\Delta T_{LO} + t_1)}, \]  
\[ I'_-(t_1, \omega_3) = \tilde{A}^*(t_1, \omega_3)e^{-i\omega_3(\Delta T_{LO} + t_1)}. \]  

Multiplication by a factor of \( e^{\pm i\omega_3 \Delta T_{LO}} \) allows to remove the fringes along \( \omega_3 \) and obtain the signal

\[ S_+(t_1, \omega_3) = E_{PE}(t_1, \omega_3)E_{LO}^*(t_1, \omega_3)e^{i\omega_3 t_1}, \]  
\[ S_-(t_1, \omega_3) = E_{PE}^*(t_1, \omega_3)E_{LO}(t_1, \omega_3)e^{-i\omega_3 t_1}. \]  

From there, since \( E_{PE} \) is complex, we can define a modulus and a phase for the spectra such that

\[ |E_{PE}(t_1, \omega_3)| = \sqrt{\frac{S_+(t_1, \omega_3)S_-(t_1, \omega_3)}{I_{LO}(t_1, \omega_3)}}, \]  
\[ \phi_{PE}(t_1, \omega_3) = \arg(S_+) - \omega_3 t_1. \]  

Since \( I_{LO}(t_1, \omega_3) \) is measured for each \( t_1 \) due to the chopper, the spectra are normalized along \( \omega_3 \) for each time point. From here, the real and imaginary parts of the PE field may be recovered, and used to plot the absorptive and dispersive parts of the third-order signal, as shown in Fig. 3.12d. We then perform a final inverse Fourier Transform along \( \omega_3 \) to obtain \( E_{PE}(t_1, t_3) \), from which we generate the 2D spectrum by built-in two-dimensional Fourier transform algorithms from MATLAB. The procedure above emphasizes how the correct determination of \( \Delta T_{LO} \), also known as phasing of the data, is a crucial step of the experiment.
3.2.4 Phasing

There exist a number of methods to phase 2D spectra, and new protocols continue to appear in the literature in an effort to achieve the most straightforward and reliable solution [81]. Some approaches require modifications to the experimental setup [82], for instance by interfering the LO pulse with additional light scattered by an object placed in the focal plane [83]. Other methods include the projection slice theorem [32, 31], which states that the integrated real part of the 2D spectrum must match the differential transmission signal for all $t_2$ times. This method is quite commonly employed, as it is theoretically very reliable and requires no modifications to the experimental setup, however it does require the iterative generation of a large number of 2D spectra based on the experimental data, which are then integrated and fit to the corresponding differential transmission spectrum.

In order to phase the data collected in our setup, we adopt a similar approach to the latter example, but we make use of an additional property of the design, in that the LO pulse tracks the scanning beam. As such, the determination of $\Delta T_{LO}$ is only necessary to perform once for a given experiment, as while $t_1$ is scanned, $\Delta T_{LO}$ remains unchanged. To determine this delay, we make use of a property of the third-order polarization, which states that for identical pulses, at $t_1 = t_2 = t_3 = 0$ fs, the signal fields corresponding to pump-probe, transient grating and photon-echo phase matching geometries are identical. In this respect, it should be possible to directly compare the photon-echo signal $S_{PE}(0, 0, \omega_3)$ to a complementary pump-probe measurement $S_{PP}(0, 0, \omega_3)$. The latter measurement is achieved by blocking pulses 1 and 3 in our setup, and removing the LO filter from the beam path, leaving the now temporally overlapping pulses 2,4 at the sample position.
Similarly to above, we can write these signals in the following way:

\[
S_{PP}(\omega_3) = \tilde{A}_{PP}(\omega_3) + \tilde{A}_{PP}^*(\omega_3) + |A_{PP}(\omega)|^2, \tag{3.15}
\]

\[
S_{PE}(\omega_3) = \tilde{A}_{PE}(\omega_3)e^{i\omega_3 \Delta T_{LO}} + \tilde{A}_{PE}^*(\omega_3)e^{-i\omega_3 \Delta T_{LO}} + |A_{PE}(\omega_3)|^2. \tag{3.16}
\]

In the case of temporal overlap, the underlying third-order polarization \( P^{(3)} \) is the same for each factor of \( \tilde{A}_{PP/PE} \), and the above quantities should be identical after removal of the rapidly oscillating contributions to the PE signal caused by spectral interference with the LO. Based on a pump-probe scan with the LO filter still in place, it is possible to obtain a fairly accurate (±10 fs) estimation of \( \Delta T_{LO} \), and so by multiplying the expression for \( I_{PE} \) by the appropriate factors of \( e^{\pm i\omega_3 \Delta T} \), we may then perform a search over a smaller range of values \( \delta T \), to find the exact value such that

\[
\tilde{A}_{PE}(\omega_3)e^{i\omega_3 \delta T} + \tilde{A}_{PE}^*(\omega_3)e^{-i\omega_3 \delta T} + |A_{PE}(\omega_3)|^2 = S_{PP}(\omega_3). \tag{3.17}
\]

An example of this approach towards phasing is shown in Fig. 3.13, for experiments on indocarbocyanine. For the particular value of \( \Delta T_{LO} = 421.25 \text{ fs} \), the agreement between
the PP (blue dashed) and PE (red solid) traces is maximized. This phasing technique only suffers in cases where either the transient absorption signal is small in the vicinity of pulse overlap, or alternatively for experiments where the fluence is high enough to lead to significant non-resonant response generated by the solvent and sample cell windows. In such cases, it is also possible to perform an analogous procedure, by comparing differential absorption spectra at later times to heterodyne detected TG signals where $t_2$ is scanned at $t_1 = 0$ fs.

By separating the 2D spectra into real and imaginary parts, dispersive effects will not be mistaken for dynamics between populations. Foregoing the phasing and studying amplitude 2D spectra is possible, however not recommended for systems possessing many different transitions which are resonant with the laser field. Positive and negative features become mixed, and interferences between the absorptive and dispersive responses distort the dynamics. By designing the interferometer such that the LO pulse moves synchronously with the scanned beam, the requirement of independent phasing for each spectrum is relaxed. This reduces the time needed to perform full experimental runs, and by exploiting passive phase stabilization the determined value for $\Delta T_{LO}$ remains accurate for a long duration in time, ensuring reliable phasing of the data.
Chapter 4

2D spectroscopy of a molecular dimer system

4.1 Introduction

Photosynthetic excitons involve multiple cofactors or pigments, interacting with one another via dipole-dipole interactions that are well-defined and set by the interchromophore distances and orientations. FMO for instance, is composed of a trimer of identical subunits each containing seven pigments, leading to a spectrally congested optical response due to overlapping transitions [84]. This system is, however, relatively straightforward compared to the other commonly studied photosynthetic proteins. For example, in the bacterial systems where it is found, the FMO complex assists in redirecting the energy collected by the light-harvesting chlorosomes, consisting of thousands of strongly interacting pigments, towards the reaction center [17].

To study these cofactors directly in small aggregates is possible by dissolving the pigments in appropriate solvents, leading to spontaneous aggregation, but controlling the level of aggregation is difficult. This leads to heterogeneous samples, in particular with respect to interpigment coupling. Another approach is to instead synthesize a dimeric
system out of other small chromophores to mimic the optical properties of light-harvesting units. Organic dyes are attractive building blocks, as they possess large transition dipole moments leading to strong resonant nonlinear optical signals.

Cyanine dyes form one category of such pigments, and have been studied at length [85], and consist of cyclic end groups linked by a polymethine chain. They possess strong absorptivity concentrated over a narrow range in the visible, due to $\pi$-conjugation of the electrons in the polymethine skeleton [86]. A number of dimeric biscyanine compounds have also been synthesized [87], with tuneable spectral properties based on molecular geometry. These biscyanine systems present a situation which is physically similar to that which is found in the binding pockets of PPCs, where the distance and angle between chromophores is fixed.

Before presenting the experimental data on indocarbocyanine and its dimer, we will first outline the elementary physics of molecular excitons. We will also introduce the Franck-Condon model for intramolecular vibrations, and discuss its extension to molecular aggregates and the optical properties of excitons. Cyanines, much like other organic pigments, exhibit vibronic coupling leading to vibrational wavepacket motion, which can be mistaken for quantum beats between excitons in 2DPE experiments.

To conclude our theoretical introduction of the physics underlying the optical response of these molecular systems, we will additionally discuss the vibronic exciton model. This model, incorporating both intramolecular vibrations and dipole-dipole coupling in the system Hamiltonian, has recently provided insight on the dynamics observed in PPCs [57, 88], and is well suited to interpret the biscyanine results. We will then proceed with an account of the experimental studies comparing the monomer and the dimer, demonstrating the differences between monomeric and excitonic systems, and how these results shed new light on the observations made previously on more complex biological aggregates.
4.2 Molecular excitons

4.2.1 Electronic dimer

Variations of this basic model describing the interaction between two interacting dipoles has led to a greater understanding of many of the optical properties of systems ranging from the small aggregates discussed here, to proteins, organic crystals, and polymers [15, 53]. Initially, we consider two independent two-level systems as shown in Fig. 4.1, interacting via a coupling term $J$.

![Figure 4.1: Schematic of the interaction between two chromophores in a homodimer, and the associated splitting observed in the absorption spectrum. The selection rules for the transitions to exciton states $|e^+\rangle$ and $|e^-\rangle$ depend on the interchromophore angle $\alpha$. The monomeric transition energy is denoted by $E_m$.](image)

The Hamiltonian describing dipole-dipole coupling between these systems can be written

$$H = H_1 + H_2 + V_{12},$$

where the subscripts represent molecule number. The ground state energy of the composite molecule becomes

$$E_g = E_{1g} + E_{2g} + \langle g_1 | V_{12} | g_2 \rangle g_1,$$

where the Van der Waals interaction between the molecules' permanent dipoles given by the last term of Eqn. 4.2 leads to a raising or lowering of the dimer ground state energy.
relative to the monomer. The dimer system studied in this work is based on identical chromophores, and therefore for sake of clarity we will neglect the molecule label wherever possible, and so \(E_{1g} = E_{2g} = E_g\) will represent the monomeric ground state energy and likewise \(E_e\) the energy of the first singlet excited state. The new excited state wave functions can be written as a linear combination of the excited states of the constituent monomers, with appropriate coefficients \(r\) and \(s\) such that
\[
|\tilde{e}\rangle = r|e_1\rangle|g_2\rangle + s|g_1\rangle|e_2\rangle.
\]

The Schrödinger equation for the dimer Hamiltonian is given by
\[
\begin{pmatrix}
H_{11} & H_{12} \\
H_{21} & H_{22}
\end{pmatrix}
|\tilde{e}\rangle = \tilde{E}|\tilde{e}\rangle, \tag{4.3}
\]
where the subscripts in \(H\) represent the matrix elements of the total Hamiltonian in the site basis. The solution of the corresponding linear system for a homodimer yields the following eigenvectors for the new molecular system:
\[
|e^+\rangle = \frac{1}{\sqrt{2}}(|e_1\rangle|g_2\rangle + |g_1\rangle|e_2\rangle), \tag{4.4}
\]
\[
|e^-\rangle = \frac{1}{\sqrt{2}}(|e_1\rangle|g_2\rangle - |g_1\rangle|e_2\rangle), \tag{4.5}
\]
where the exciton wave functions are now symmetrically delocalized over both chromophores composing the dimer. The corresponding eigenenergies are given by
\[
E^\pm = E_e + E_g + (e_1|\langle g_2|V_{12}|g_2\rangle|e_1\rangle \pm (e_1|\langle g_2|V_{12}|e_2\rangle|g_1\rangle.
\]

Using the point-dipole approximation, the expression describing the interaction \(V_{12}\) can be written
\[
V_{12}(\vec{d}) = \frac{\vec{\mu}_1 \cdot \vec{\mu}_2}{d^3} - \frac{3}{d^5} \left( \vec{\mu}_1 \cdot \vec{d} \right) \left( \vec{\mu}_2 \cdot \vec{d} \right), \tag{4.7}
\]
where \(\vec{d}\) is the position vector of \(\vec{\mu}_2\) (taking \(\vec{\mu}_1\) as a reference), and \(d\) is the centre to centre distance between dipoles. The point-dipole approximation is only truly appropriate in
cases where the wave functions of the two chromophores overlap minimally. In more
general cases, the exchange interaction between electrons on either chromophore must
be taken into account \[89\]. Taking \(\alpha\) as the angle between molecular planes (or “twist”
as shown in Fig. 4.1), and \(\theta\) as the angle made by chromophores with respect to the line
joining molecular centres (the “tilt”), we obtain the following expression for the splitting
between exciton states resulting from a given molecular geometry \[53\]:

\[
\Delta E = E^+ - E^- = \frac{2|\vec{\mu}|^2}{d^3} \left( \cos \alpha - 3 \cos^2 \theta \right). \tag{4.8}
\]

We will restrict our discussion to the case of \(\theta = 90^\circ\). There, by varying the twist angle \(\alpha\)
between transition moments, the interaction between the dipoles will be weakened, and
then change sign as the chromophores go from a parallel to antiparallel alignment.

The interaction of the exciton states with the electromagnetic field will also depend on
these geometric parameters, and the transition dipole moments for each exciton resonance
can be determined by projecting the new eigenvectors \(|e^\pm\rangle\) onto the transition moments
of the constituent chromophores. This can be done by generating a matrix \(M\) consisting
of the transition moments of the aggregate (in the site-basis):

\[
\vec{\mu}^\pm = M|e^\pm\rangle = \frac{\mu}{\sqrt{2}} \begin{pmatrix}
0 & \sin \alpha \\
1 & \cos \alpha
\end{pmatrix} \begin{pmatrix}
1 \\
\pm 1
\end{pmatrix} = \begin{pmatrix}
\pm \sin \alpha \\
1 \pm \cos \alpha
\end{pmatrix}. \tag{4.9}
\]

Physically this reflects how depending on the angle between the chromophores, the in-
terference between the polarizations caused by in-phase (\(|e^+\rangle\)) or out of phase (\(|e^-\rangle\))
oscillating dipoles on each site either be constructive or destructive. In the limiting case
where the chromophores are parallel (\(\alpha = 0^\circ\)), the oscillator strengths of both transitions
add constructively for \(|e^+\rangle\), maximizing \(\mu^+\) (or \(\mu^-\) if the chromophores are antiparallel).
For intermediate angles the oscillator strengths carried by the exciton states will vary
according to the relation \(\frac{|\mu^-|^2}{|\mu^+|^2} = \tan^2 \left( \frac{\alpha}{2} \right)\).
This model is appropriate to illustrate the effect of electronic coupling on the energetics and absorptive properties of dimers, and the basic mechanism by which molecular excitons are formed. The above derivation for a homodimer demonstrates how the resonant interaction between the coupled pigments leads to delocalization of the exciton wavefunctions over both chromophores in the composite system. For large molecules at room temperature, however, a model of interacting TLAs does not entirely capture the physics needed to explain the absorption lineshapes of pigment aggregates, as molecules intrinsically possess an elaborate spectrum of intramolecular vibrational modes.

4.2.2 Vibronic coupling: the Franck-Condon model

The Franck-Condon model for vibronic coupling describes how, within the framework of the Born-Oppenheimer approximation, the electronic transition from $S_0$ to $S_1$ in a given molecule is perturbed by the harmonic motion of intramolecular vibrations [1, 2, 90]. The BO approximation assumes separability of the electronic and nuclear contributions to the total wavefunction, but also requires that the transition dipole moment be independent of the internuclear distance.

![Diagram of vibronic coupling due to a Franck-Condon active intramolecular vibration.](image)

Figure 4.2: Schematic of vibronic coupling due to a Franck-Condon active intramolecular vibration. The upper potential energy surface $S_1$ is displaced from $S_0$ along the vibrational coordinate by an amount $\Delta$, giving rise to a vibronic progression in the absorption spectrum (right).
In Fig. 4.2, we schematically demonstrate the Franck-Condon model for two potential energy curves. The two harmonic potentials corresponding to $S_0$ and $S_1$ are displaced by a dimensionless coordinate $\Delta$, and the Huang-Rhys factor of $\frac{\Delta^2}{2}$ is typically used to describe the degree of vibronic coupling [91, 37]. Physically speaking, this displacement reflects the difference in equilibrium positions of the nuclei, corresponding to the lowest energy configuration for the molecule on the $S_0$ and $S_1$ potential energy surfaces.

Quantum mechanically, the FC approximation can be understood by separating the expression for the molecular dipole $\vec{\mu}$ into electronic and nuclear parts, such that

$$
\vec{\mu} = -e \sum_i \vec{r}_i + e \sum_j Z_j \vec{R}_j = \vec{\mu}_e + \vec{\mu}_N,
$$

(4.10)

where $\vec{r}_i$, $\vec{R}_i$ are the positions of the electrons and nuclei respectively, and $Z_j$ is the atomic number of a given atom. The BO approximation states that the nuclear degrees of freedom affect the electronic ones only parametrically, under the assumption that the motion of the electrons is much faster than that of the nuclei, and that the electronic wave functions will therefore instantaneously reflect the nuclear positions. Due to this separability, we can consider the vibronic basis set $|e, \nu\rangle$, where $e$ corresponds to an electronic excitation and $\nu$ to the vibrational quantum number for the FC active mode. As per BO, the corresponding wavefunctions take the form of a product $\psi_e(r; \vec{R}) \chi_\nu(\vec{R})$, and using these wavefunctions we may compute the transition dipole moment connecting different vibronic states $\vec{\mu}_{e', e, \nu', \nu}$:

$$
\langle e', \nu' | \vec{\mu} | e, \nu \rangle = \int \int \psi^*_e(r; \vec{R}) \chi^*_\nu(\vec{R}) (\vec{\mu}_e + \vec{\mu}_N) \psi_e(r; \vec{R}) \chi_\nu(\vec{R}) d\tau_N d\tau_e \\
= \int \int \psi^*_e(r; \vec{R}) \chi^*_\nu(\vec{R}) \vec{\mu}_e \psi_e(r; \vec{R}) \chi_\nu(\vec{R}) d\tau_N d\tau_e + \\
\int \chi^*_\nu(\vec{R}) \vec{\mu}_N \left( \int \psi^*_e(r; \vec{R}) \psi_e(r; \vec{R}) d\tau_e \right) \chi_\nu(\vec{R}) d\tau_N \\
= \vec{\mu}_{e', e} \int d\tau_N \chi^*_{\nu'}(\vec{R}) \chi_{\nu}(\vec{R}).
$$

(4.11)
The transitions between vibronic states will be proportional to $\mu_{\nu', \epsilon}$, but weighted by the overlap integral $f_{\nu', \nu} = \int d\tau N_{\nu'}(\vec{R}) \chi_{\nu}(\vec{R})$ between vibrational wavefunctions, also known as Franck-Condon factors. Vibronic coupling results in the progression of transitions observed in the absorption and emission spectra of large molecules, but also allows for borrowing of oscillator strength by weak or even forbidden transitions [90]. The latter phenomenon of vibronic borrowing can play an important role in the optical properties of dimeric systems [92, 93], necessitating the inclusion of vibrational degrees of freedom into the system Hamiltonian, even for systems where the Huang-Rhys factors are small.

### 4.2.3 Holstein model

A diagram of the chemical structure of the biscyanine dye study in this thesis is shown in Fig. 4.3 in blue. The butyl chains which link the parent chromophores at two locations make for a nearly parallel orientation of transition dipole moments, which are roughly oriented along the central polymethine chain of the dyes.

![Molecular structure of indocarbocyanine (red) and its dimer (blue), accompanied by an illustration of the Holstein model, where both electronic and vibronic coupling are taken into account in the system Hamiltonian.](image)

Figure 4.3: Molecular structure of indocarbocyanine (red) and its dimer (blue), accompanied by an illustration of the Holstein model, where both electronic and vibronic coupling are taken into account in the system Hamiltonian.

Calculations of the molecular structure (using Hyperchem) indicate an approximate interchromophore angle of $\alpha = 15^\circ$ and a distance of $d = 10$ Å. The transition dipole mo-
ment into the first singlet excited state of indocarbocyanine is similarly calculated to be $\mu \sim 13 \, D$. This corresponds to an electronic coupling strength $|J| = 5040 \mu^2 \cos(\alpha)/d^3 \sim 850 \, \text{cm}^{-1}$ [17]. As is shown in Fig. 4.4, the indocarbocyanine parent molecule demonstrates a vibronic progression typical of cyanine dyes, with a frequency of approximately 1200 cm$^{-1}$ in its absorption spectrum, resulting from displaced C–C stretches in its polymethine skeleton [94].

![Absorption Spectrum](image)

Figure 4.4: Absorption spectrum of indocarbocyanine monomer (dashed), displaying characteristic vibronic progression of $\sim 1200 \, \text{cm}^{-1}$. The biscyanine absorption spectrum (solid), however, demonstrates a complex lineshape consisting of a multitude of peaks.

Theoretically, the determination of the absorption spectrum of an electronic dimer coupled to intramolecular vibrations was solved a number of years ago [95, 96, 97]. As can be seen in the work of Ref. [95], reproduced in Fig. 4.5, keeping the vibronic coupling parameter fixed and varying the electronic coupling strength leads to very different limiting behaviours. In these calculations, the electronic coupling strength increases from top panel to bottom. The positive bands depict transitions to exciton states with symmetric combinations of electronic excited state wavefunctions ($|e^+\rangle$ in Eqn. 4.5), and the negative bands antisymmetric ($|e^-\rangle$). The total absorption spectra will be the sum of the absolute values of each contribution.

For the case of very weak electronic coupling (weaker than the linewidth of individual vibronic peaks), little splitting is observed besides a slight broadening of the monomeric peaks. In the bottom panel on the other hand, where the electronic coupling is strongest,
the spectrum resembles two vibronic progressions, clearly resolved from one another. In
the middle panels we observe the “intermediate” coupling regime, which has recently
been the subject of renewed interest. There, it has been shown that the composition
of the exciton eigenstates is extremely sensitive to this interplay to the electronic and
vibronic coupling strength [92, 93]. This point is of central importance in the discussion
surrounding photosynthetic proteins, where the electronic coupling strengths are typically
weak (≤ 500 cm$^{-1}$) and on the order of numerous low-frequency modes [98].

In the vibronic exciton model, the Holstein Hamiltonian [56] is used to account for
the vibronic coupling intrinsic to the chromophores in the dimer:

\[
H = \epsilon_1 c_1^\dagger c_1 + \epsilon_2 c_2^\dagger c_2 + J \left( c_1^\dagger c_2 + c_2^\dagger c_1 \right) + \hbar \omega_{\text{vib}} b_1^\dagger b_1 + \hbar \omega_{\text{vib}} b_2^\dagger b_2 + \\
\hbar \omega_{\text{vib}} \sum_{n=1,2} c_n^\dagger c_n \left[ \lambda (b_n^\dagger + b_n) + \lambda^2 \right].
\] (4.12)
In the terms of this Hamiltonian the subscripts once again refer to particle number (site-basis). Ladder operators for the electronic and vibrational states are denoted \( c \) and \( b \), respectively. The electronic transition possesses an energy of \( \epsilon \) and couples to a single vibrational mode with frequency \( \omega_{\text{vib}} \). The electronic coupling between molecules is once more denoted by \( J \) while the electron-phonon coupling is \( \lambda \omega_{\text{vib}} \). The Huang-Rhys factor for that vibrational mode is given by \( \lambda^2 \), and the final term in the Hamiltonian describes the vibrational reorganization energy in the electronic excited state.

The new total eigenstates of the vibronic dimer system will be built up of the basis of

\[
|e_1, \tilde{\nu}_1; g_2, \nu_2 \rangle \quad \text{and} \quad |g_1, \nu_1; e_2, \tilde{\nu}_2 \rangle
\]

for the one-exciton wavefunctions, with a manifold of doubly-excited states

\[
|e_1, \tilde{\nu}_1; e_2, \tilde{\nu}_2 \rangle
\]

Here \( \tilde{\nu}_n \) denote excited-state vibrational wavefunctions, which are related to their ground-state counterparts by the Franck-Condon factors such that

\[
f_{\tilde{\nu}_n, \nu_n'} = \langle \tilde{\nu}_n | \nu_n' \rangle.
\]

Figure 4.6: Calculated linear absorption spectra of a series of homodimers with parallel chromophores using a vibronic exciton model. In each panel the Huang-Rhys factor \( S \) is listed, the solid (dashed) lines correspond to strong (weak) electronic coupling. Reprinted from [93], © 2012, with permission from Elsevier.

Example calculations of absorption spectra determined using the vibronic exciton model are shown in Fig. 4.6, for the case of homodimers \((\epsilon_1 = \epsilon_2 \text{ in Eqn. 4.12})\) in a limiting geometry \( \alpha = 0^\circ \), where only the transition to the high energy exciton state
is allowed in the electronic dimer model. The dashed lines represent strong electronic coupling, and the solid lines weak, with $S = \lambda^2$ denoting the Huang-Rhys factor for a $\omega_{vib} = 1500 \text{ cm}^{-1}$ vibrational mode. Contrary to predictions based on the electronic dimer model for this molecular geometry, multiple peaks appear in the absorption spectrum for all nontrivial combinations of parameters [93].

To obtain the total wavefunction of each exciton, the coefficients describing the contributions both from vibrationally excited states and zero-phonon states representing “pure” electronic mixing can be determined for each case shown in Fig. 4.6. This helps in quantifying the relative importance of each effect, however, in all cases the two are invariably mixed and vibronic in character. The implications of this model on the interpretation of dynamic signals measured in ultrafast spectroscopy is significant, prompting the question: is it in fact even possible to distinguish “electronic” from “vibrational” coherences in these systems, as has been attempted in a number of models where vibronic and electronic couplings were treated separately [8, 28, 29]?

Since both vibrational and electronic wavefunctions are necessary to accurately describe the eigenstates of dimers in this model, there is no system-independent protocol to a priori isolate the vibrational contribution to interexciton coherences in experimental third-order spectroscopic signals. This highlights the importance in collecting complementary experimental data to support 2DPE measurements on excitonic systems, prior to assigning the measured dynamics to quantum coherences.

4.3 Monomer

The monomeric dye provides an excellent control for the subsequent studies on the dimer, to establish which of the observed dynamics are unique to the excitonic system.
Chapter 4. 2D spectroscopy of a molecular dimer system

4.3.1 Linear spectroscopy

The linear spectroscopic properties of the monomer follow the typical profile for a cyanine dye and are shown in Fig. 4.7. The absorption maximum in a methanol solution is located at 18400 cm$^{-1}$, and besides the main peak there are secondary peaks corresponding to a vibronic progression dominated by a $\sim 1200$ cm$^{-1}$ mode, assigned to C–C modes in the polymethine chain that are displaced in the electronic excited state [94]. The fluorescence emission spectrum appears qualitatively similar, possessing a maximum at 17 800 cm$^{-1}$ corresponding to a Stokes shift of approximately 500 cm$^{-1}$. The quantum yield of fluorescence is relatively low for this dye ($\sim 5\%$), as the molecule isomerizes upon photoexcitation, leading to deactivation of the excited state [30, 99].

4.3.2 Kinetics

Using a femtosecond supercontinuum probe transient absorption set up [100], we are able to measure the population dynamics occurring up to 1 ns following excitation over a broad spectral range (probe spectrum shown in Fig. 3.4). The temporal resolution, or instrument response, is approximately 40 fs and is limited by dispersion compensation in the supercontinuum probe. The TL pump pulse is approximately 25 fs in duration, and

Figure 4.7: Normalized absorption (light red) and emission (dark red) spectra of indocarbocyanine in methanol.
is primarily limited by the output bandwidth of the AOPDF in this spectral range. The signal in this measurement is given by

\[ S_{PP}(\omega_3, t_2) = -\log \frac{I(\omega_3, t_2)}{I_0(\omega_3, t_2)}, \]  

(4.13)

where \( I \) is the transmitted probe spectrum when the pump is present, and \( I_0 \) is the reference transmitted probe spectrum in the absence of the pump.

Figure 4.8: Indocarbocyanine kinetics monitored via transient absorption. The decay traces demonstrate the short excited state lifetime, and highlight the vibronic transitions seen in the linear response. Excitation energy of 18500 cm\(^{-1}\) (contours at 4% intervals).

In the data shown in Fig. 4.8, we observe the main bleach band situated at \( \omega_3 = 18300 \) cm\(^{-1}\), as well as a secondary bleach feature at \( \omega_3 = 19500 \) cm\(^{-1}\), corresponding to the vibronic shoulder seen in Fig. 4.7. At early times, an induced absorption appears for probe energies greater than 20000 cm\(^{-1}\), assigned in previous studies to excitation from \( S_1 \) into a higher lying singlet electronic state [101]. Finally, to the red we observe additional bleach signals corresponding to stimulated emission from \( S_1 \), at energies corresponding to those measured in the steady state fluorescence emission spectrum in Fig. 4.7. By fitting the single wavelength trace taken through the main bleach band to an exponential decay, we determine that the excited state lifetime in indocarbocyanine is approximately...
40 ps. At delays greater than 100 ps, we recover the emergence of an induced absorption at an $\omega_3 = 17750 \text{ cm}^{-1}$, corresponding to $S_0$-$S_1$ absorption by molecules in the isomerized conformation.

Transient absorption data over such a wide range helps determine overall population kinetics, but masks much of the initial coherent dynamics in the molecule. The data shown in Fig. 4.8 verify the excited state lifetime and possible pathways for population decay, which here is shown to be primarily due to internal conversion.

### 4.3.3 Vibrational dynamics

![Figure 4.9: Short timescale transient absorption of indocarbocyanine](image)

Figure 4.9: Short timescale transient absorption of indocarbocyanine, using short (12 fs) pulses as pump and probe pulses, centred on the main absorption band. The modulations observed in the signal are associated with vibrational wave packet motion.

In both 2DPE and PP, impulsive excitation of the molecule leads to the observation of wavepacket motion due to FC active vibrational modes, until the onset of vibrational relaxation [25]. In Fig. 4.9 we observe the signatures of these vibrational modes on the transient bleach signal, which persist for picoseconds following excitation. These coherent modulations can be isolated by subtracting the exponential kinetics associated with slow population relaxation from the decay trace. Fourier transformation of the obtained residuals provides a power spectrum of the beat frequencies as shown in Fig. 4.10. It should be noted that we are not sensitive to frequencies higher than 1500 cm$^{-1}$ in the
presented data due to temporal sampling of the data points.

Figure 4.10: Pump-probe trace and power spectrum of oscillatory transients in indocarbocyanine probed at 18300 cm$^{-1}$.

We observe that the two dominant modes present in the transient absorption at the bleach maximum are at approximately 610 cm$^{-1}$ and 380 cm$^{-1}$. These modes were both recorded in published resonant Raman spectra [102], where the 610 cm$^{-1}$ mode was assigned to a C=C–C stretch in the polymethine chain, and the 380 cm$^{-1}$ to out of plane torsions of the indole ring terminal groups [103, 104]. The 1200 cm$^{-1}$ mode is seen to modulate the response for the first 80 fs in Fig. 4.10a, before subsequently being replaced by lower frequency oscillations for the following 5 ps, resulting in the absence of this peak in Fig. 4.10b. This points to relaxation on S$_1$ of the mostly localized high frequency stretches in the 1000-1500 cm$^{-1}$ range, to more delocalized motions of the chromophore skeleton.

The supercontinuum probe data in Fig. 4.8 shows evidence of EA to higher lying states and isomerization, but these occur at higher energies and on longer timescales, respectively, than those which are probed in the forthcoming 2DPE measurements. The particular vibrational modes which appear in $t_2$ following femtosecond excitation depend on the overlap of the excitation spectrum with the absorption spectrum of the compound in question [105]. Therefore, approximately the same laser spectrum used in 2DPE is used in the TA measurements shown in Fig. 4.9, providing a glimpse of the expected dynamics in the 2D spectra. These data indicate that the monomer 2D spectra will be
dominated by the bleach band corresponding to the absorption maximum, and that the recorded dynamics are expected to be restricted to a few key vibrational modes following 100 fs of relaxation time.

### 4.3.4 2D spectroscopy

A similar monomeric dye has been previously studied using 2DPE, to compare the dynamics of high frequency intramolecular vibrations and electronic coherences at the spectral locations of cross-peaks linking transitions in 2D spectra [26]. In that study, it was shown that the electronic dimer model (as shown in Fig. 2.4) and a four-level vibronic system only possess two distinct nonlinear response function pathways, related to biexciton EA, and resonant Raman GB, respectively. These unique pathways do not hold, however, in the more general vibronic exciton model, as well be further discussed in the context of the biscyanine experiments.

![Absorption Spectrum](image)

**Figure 4.11:** Absorption spectrum of indocarbocyanine monomer in methanol, with laser spectrum overlaid in green.

Regarding the signatures of ground-state wavepacket motion, this point highlights the importance of studies on simple systems using broadband 2DPE. Prior to that work,
the experimental results on pigment aggregates were interpreted in the framework of models where resonant Raman processes were not explicitly considered, and where only couplings between excited states will give rise to oscillating cross-peaks in 2D spectra.

**Early dynamics**

The excitation laser spectrum used in the experiments is shown in Fig. 4.11, and only minimally overlaps with the vibronic shoulder. We therefore do not expect to observe significant cross-peaks, though the pulses are sufficiently short (14 fs) to resolve 1200 cm$^{-1}$ oscillations. The correlation spectrum is shown in Fig. 4.12, where we observe a line shape that is slightly inhomogeneously broadened. The peak skews above the diagonal, due to GB signal corresponding to probing at the absorption maximum following excitation at the vibronic shoulder (red square). The corresponding cross-peak below the diagonal (blue square) is not prominent, due to low spectral overlap with the laser.

![Figure 4.12](image)

Figure 4.12: a) Correlation spectrum ($t_2 = 0$ fs) of indocarbocyanine with markers indicating anticipated cross-peak locations corresponding to vibronic shoulder. b) Dynamics of off-diagonal signal at marker locations. The dashed line denoted the time corresponding to half a period of oscillation at 1200 cm$^{-1}$.

In the right panel of Fig. 4.12, we show the time series for the dynamics at the locations in the 2D spectrum where off-diagonal beats associated with vibronic shoulder would appear. Below the diagonal we do not record any significant high frequency os-
cillations corresponding to this vibration. A period of oscillation at 1200 cm$^{-1}$ may be present, however it is difficult to assign this unequivocally to a quantum beat, due to potential distortions from nonresonant signals during pulse overlap. Likewise, the above diagonal cross-peak possesses only very small amplitude fluctuations with no clear dominant periodic component, likely due to interferences between the numerous vibrations observed the PP traces of Fig. 4.10 immediately following excitation.

**Long term dynamics: persistent oscillations.**

Moving to longer waiting times, as shown in Fig. 4.13, we observe a more homogeneous line shape than at $t_2 = 0$ fs, which is redshifted away from the diagonal due to spectral diffusion and solvation of the excited state. At this point, the dynamics exhibit more obvious periodicity. The modulation of the signals matches the 600 cm$^{-1}$ mode observed in the transient absorption. This is expected, as weakly-displaced low frequency modes have been shown to lead to periodic modulations of the entire peak shape [106, 107], caused by interferences between the rephasing and non-rephasing contributions to the line-shape.

![Figure 4.13](image_url)

**Figure 4.13:** a) Absorptive 2D spectrum ($t_2 = 2$ ps) of indocarbocyanine. b) Dynamics of off-diagonal signal at marker locations. A fit to a sinusoid shows that the signal is strongly modulated by the 600 cm$^{-1}$ vibrational mode.
This observation illustrates the danger in placing of probes directly onto broad 2D lineshapes for more complicated molecular systems during analysis. The peak shown in Fig. 4.13 has undergone spectral diffusion and is featureless, yet at practically any location in the 2D spectrum shown in Fig. 4.13 it is possible to recover a significant 600 cm\(^{-1}\) oscillatory component, particularly far from the diagonal or on the slope of the peak, where small spectral shifts will translate to large amplitude changes in integrated spectral density.

### 4.3.5 Discussion

The measurements on the monomer illustrate how similar information is obtained from transient absorption and 2DPE with respect to the study of oscillatory dynamics in the third-order response. The two techniques are shown to be very complementary for these excitation conditions, where the unique information provided by 2DPE relates to spectral relaxation and diffusion timescales, and the homogenous lineshape. Regarding the high frequency signals associated with vibronic quantum beats, spectral overlap inhibits a quantitative comparison of this particular experiment to predictions for vibronic monomers. However, since the above data were taken using the same approximate excitation spectra as in the biscyanine experiments below, they are more suitable for the main objective of these controls: the comparison of monomers and dimers.

In separate measurements (unshown), where both the main vibronic bands in Fig. 4.11 overlap with the laser spectrum, the results and conclusions differ little from previously published accounts on vibronic monomers [26, 27], except that the interference between many FC active modes in indocarbocyanine lends itself poorly to comparisons to calculations invoking a single vibrational mode [29]. In the previously discussed measurements on pinacyanol chloride [26], where both its ultrafast and Raman responses are dominated almost entirely by a single 1360 cm\(^{-1}\) mode, due to more complete \(\pi\)-conjugation and symmetry in that system.
At lower vibrational frequencies, the observation of long-lived oscillations in the TA data is reproduced in the 2D spectra, where the 600 cm$^{-1}$ mode is manifest as a modulation of the shape of the broad and featureless main transition in the 2D spectrum for over 1 ps following excitation. This underlines a serious issue surrounding the a priori experimental assignment of oscillatory signals in 2DPE of spectrally congested systems, without cross-referencing the signals to pump-probe data. Though it is possible to collect supporting TA data in virtually all experimental 2DPE setups, these measurements seldom accompany the 2DPE results presented in the literature, where it has been commonplace to present standalone spectra of aggregated systems, placing markers at the expected locations of excitonic cross-peaks.

The corresponding oscillations have been directly associated with beats between photosynthetic excitons [6, 18, 7], however, none of these studies discuss the potential contamination by vibrational wavepacket effects [106, 107]. In those systems the problem is further exacerbated by the low frequencies of the oscillations of interest ($\leq 500$ cm$^{-1}$), where Fourier analysis must be done carefully to not be influenced by slow decays and growths in the signal due to population relaxation or spectral shifts.

In this respect, we stress that the comparison of measured dynamics in 2DPE spectra to TA data provides a useful and essential benchmark. Recent theoretical efforts have even gone so far as to suggest that, in the limit of very broad excitation bandwidths, transient absorption rather than 2DPE is better suited to fully isolate coherences between excitons [108]. Though the requirements on laser bandwidth in those calculations is somewhat unrealistic, the fact remains that pump-probe can be used to determine the spectrum of vibrational modes impulsively excited by a given laser spectrum in an experiment [109, 110], which can then complement the analysis of oscillatory transients in associated 2D spectra.
4.4 Dimer

4.4.1 Linear spectroscopy

The absorption line shape of the dimer differs significantly from that of the monomer, as is observed in Fig. 4.4. Instead of the FC progression observed in the parent dye, the spectrum is characterized by a sharp narrow peak at higher energy than the absorption maximum of the monomer (19700 cm$^{-1}$) surrounded by several lower intensity sub-bands, both to the blue and the red. The emission spectrum, shown alongside the absorption in Fig. 4.14, also possesses a number of peaks, most notably at 17100 cm$^{-1}$ and 15900 cm$^{-1}$, and does not resemble the mirror image of the absorption spectrum, indicative of non-radiative relaxation pathways in the coupled system [90].

Figure 4.14: Absorption (blue) and emission (red) spectra of biscyanine in methanol. The three peaks resonant with our laser pulse are labelled A, B, C.

Peak Assignment

The main peak is labelled A, with the next most prominent peaks in the absorption spectrum occurring at 20800 cm$^{-1}$, 18300 cm$^{-1}$ (B), and at 17500 cm$^{-1}$ (C). As alluded to earlier, the assignment of the peaks in the linear spectrum of this compound to either exciton band is not straightforward, since it is in the intermediate coupling regime.
Based on earlier work [111, 92, 93, 58], it follows that peaks \(A\) and \(B\) correspond to transitions to excitons composed of symmetric combinations of monomeric wavefunctions, with state \(A\) lying at higher energy due to an additional strong contribution of excited vibrational wavefunctions. The weakly absorbing \(C\) peak, on the other hand, represents absorption from the exciton state composed of antisymmetric combinations of monomeric wavefunctions.

As mentioned earlier in the description of the vibronic exciton model, the vibrational contribution does not detract from the delocalized character of these states, unless there is an additional source of symmetry breaking caused by disorder in the site energies, which would localize the excitons on particular pigments [53, 88, 112].

### 4.4.2 Kinetics

Following the approach for characterizing the monomer, using a supercontinuum probe it is possible to observe the relaxation dynamics of biscyanine over long timescales. In Fig. 4.15, we once more observe very different behaviour compared to the parent dye. The recovery time for the bleach is significantly longer (now on the order of 200 ps) and there is no appearance of an absorptive signal due to isomerized molecules as was the case before. This results from the butyl chains linking the two chromophores, as the increased rigidity of the molecular structure inhibits the isomerization process, which is the primary deactivation channel for S1 in the parent dye [30, 99].

Peaks \(A\), \(B\) and \(C\) from the linear absorption spectrum are recovered, but the shoulder to the blue of peak \(A\) can not be resolved due to weak spectral brightness of the probe at that energy. There is a weak emissive feature at 15800 cm\(^{-1}\), which we attribute to stimulated emission, as the energy is consistent with the fluorescence emission spectrum in Fig. 4.14.

Turning our attention to the early time dynamics shown in Fig. 4.16, we present TA measurements using short pump and probe pulses generated by the NOPA (\(\tau_{\text{pulse}} \sim 12\)
Figure 4.15: Transient absorption data of biscyanine over a long timescale. Excitation with a 25 fs pulse at 18500 cm$^{-1}$.

fs). In Fig. 4.16a we observe that the bleach traces in the dimer also demonstrate different behaviour from the monomeric dye. The response is dominated by the dimer’s $A$ band and the differential absorption spectrum shown in Fig. 4.16b illustrates how the bleach at peak $A$ is roughly ten times larger than $B$.

In Fig. 4.16c we show the time series corresponding to probing at peaks $A$ and $B$ (enlarged by a factor of 5), where we find that both curves exhibit a very flat decay. Taking the power spectrum corresponding to the transients of both decay curves suggests that any apparent oscillatory behaviour is not significant with respect to the noise floor, and the two dominant modes observed in the monomer transient absorption are conspicuously absent as seen in Fig. 4.16d.

On these timescales it is possible to directly monitor ultrafast interexciton energy transfer using TA, provided the time-resolution of the instrument is adequate. In the case of photosynthetic proteins, TA combined with global analysis [113] has uncovered many of the pathways for energy transfer between excitons for a number of PPCs [114, 21]. We do not observe any clear signatures of energy transfer in the biscyanine dimer, even with an instrument response of $\sim 15$ fs, although this is not entirely surprising: For one,
Figure 4.16: Short timescale, high time-resolution transient absorption of biscyanine in methanol. a) Spectrally resolved data, contours at 4%. b) $\Delta A$ spectrum at $t_2 = 100$ fs. c) Time series corresponding to probe energies of peak A (blue) and peak B (red, magnified by factor of five). d) Power spectrum of pump-probe transients for peak A (blue) and peak B (red).

the lowest energy excitons are practically dark, making it difficult to measure increases in populations of those states. Secondly, in the measurements on PPCs the interpigment couplings are significantly lower, and the timescales for EET are relatively slow with respect to laser pulse durations ($\geq 100$ fs). The only feature of the biscyanine signal which could be interpreted as EET is shown in Fig. 4.16c: After the initial rise of the signal, the bleach at peak A drops by 8 mOD (15% of the maximum) on a timescale of approximately 40 fs. This is somewhat speculative though, without complementary observations, as such a fast timescale is very close to our the instrument response.

More importantly, the transient absorption demonstrates that vibrational wave-packet motion does not modulate the decay dynamics in biscyanine as was the case for its monomer. In these data and for these excitation conditions it is difficult to pinpoint clear signatures of inter-exciton dynamics, in the form of either coherences or EET. Using the additional dimension provided by 2DPE, however, we are able to separate overlapping transitions in the PP to uncover the coherent beats between excitons.
4.4.3 2D spectroscopy

In the monomer, the dynamics observed in the 2D spectra were reminiscent of a number of earlier studies on small organic molecules exhibiting vibronic coupling [107, 26, 27]. In this vibronic dimer system, strong coupling between chromophores leads to well resolved exciton transitions, which can be used to isolate signals due to excitonic coherences. The large transition dipole moment of peak $\mathbf{A}$ relative to the other transitions complicates the 2DPE experiment slightly, however. As can already be seen in the TA data of Fig. 4.16, the signal associated with peak $\mathbf{A}$ towers over the other contributions. Secondly, peak $\mathbf{A}$’s location in the visible spectrum is in a region where NOPAs begin to experience difficulty achieving broadband phase-matching, limiting the ability to cover the entirety of the $\mathbf{A}$ band while remaining resonant with peaks $\mathbf{B}$ and $\mathbf{C}$. As such, we present sets of measurements over two spectral ranges.

Homogeneous linewidth of peak $\mathbf{A}$

By first focusing our attention on peak $\mathbf{A}$, we can measure the homogeneous linewidth of that transition, which reports on the timescale for loss of coherence between the ground state and exciton $\mathbf{A}$, caused primarily by interactions with the solvent.

Figure 4.17: 2D spectroscopy of exciton $\mathbf{A}$ in bscyanine. a) Absorption spectrum (blue solid) and laser spectrum (black dashed). b) Correlation spectrum ($t_2 = 0$ fs) with anti-diagonal cross section overlaid. c) Anti-diagonal width, with fit to Lorentzian with a width of 230 cm$^{-1}$. 
In Fig. 4.17a, the laser spectrum overlaid on the linear absorption profile is sufficiently broad to cover the entire width of the A peak, allowing the separation of inhomogeneous broadening from the broadening associated with pure dephasing [32]. Fig. 4.17b depicts the correlation spectrum \((t_2 = 0 \, \text{fs})\), corresponding to the stimulation of the photon-echo prior to any evolution of the excited quantum states. The diagonal peak \(A\) is elongated along the diagonal, due to inhomogeneous broadening, and is quite symmetric. Taking an anti-diagonal cut through this peak in the 2D spectrum, a fit to a Lorentzian function is performed, such that

\[
S(\omega) = \frac{\alpha}{\pi} \frac{\Delta \omega}{\frac{\Delta \omega^2}{2} + (\omega - \omega_0)^2},
\]

where \(\omega_0\) is the central frequency, \(\Delta \omega\) is the FWHM, and \(\alpha\) is a scaling factor. From the fit, we determine that the homogeneous line width for peak \(A\) of the dimer to be on the order of 250 cm\(^{-1}\) (FWHM) as shown in Fig. 4.17c. The corresponding electronic dephasing time for this transition is determined to be \(\frac{1}{\pi c \Delta \omega} = 45 \, \text{fs}\) [115]. Due to the presence of negative features in the vicinity of the diagonal peak, the peak may be slightly narrowed due to interference and the linewidth is likely a lower bound. These negative signals flanking the diagonal peak primarily arise from excited state absorption into doubly excited states, but also potentially from Raman pathways which exist during pulse overlap that do not appear in impulsive treatments of the response. In either case they are associated with violation of time-ordering, occurring for realistic pulse durations [32, 47].

The laser spectrum used here leads to 2D spectra that are dominated by the diagonal peak \(A\). For this reason, measuring the dynamics of off-diagonal couplings between \(A\) and the other transitions is better achieved by shifting the excitation spectrum towards the red.
Balanced excitation

Figure 4.18: Absorption spectrum of biscyanine (blue) with laser spectrum overlaid (green)

The relative amplitudes of features in the 2D spectra can be drastically modified by taking advantage of spectral weighting, since each product of the electric field strength $E(\omega)$ with a transition dipole moment $\mu_i$ in the frequency domain analogue of Eqn. 2.13 will act to scale the peaks. Unlike the calculations shown in the impulsive limit for a model dimer in Fig. 2.7, in experiments the spectral weighting of the Liouville pathways such as those shown in Fig. 2.5 is considerable, particularly in this case where one transition is significantly stronger than all others.

The laser spectrum used to mitigate the amplitude of peak $A$ is shown in Fig. 4.18 alongside the absorption line shape. In the following experiments the laser is centred on peak $B$, but possesses sufficient bandwidth to also cover peaks $A$ and $C$. Unfortunately, due to the seed spectrum in the NOPA it is not possible to simply move the entire spectrum towards the red, and a minor loss of bandwidth occurs with respect to the previous results leading to an increase in the pulse duration to $\tau_p = 16$ fs, but this is still sufficiently short to resolve the relevant oscillations. In the 2D spectra shown in Fig. 4.19 we observe a number of dynamically evolving on- and off-diagonal peaks at early times.
Figure 4.19: Absorptive 2D spectra of biscyanine at selected waiting times following excitation. The diagonal peaks and well resolved cross peaks between the main transition and lower energy peaks are evident. Additionally, we observe dramatic modulations to the spectra persisting until approximately 50 fs following excitation, upon which point they become relatively static.

The above-diagonal half of the spectrum in particular oscillates with large amplitude for the first 50 fs of waiting time, after which point the spectra no longer exhibit large amplitude dynamics, but rather relax to the static shapes observed at $t_2 = 100$ and 150 fs. Due to the large number of overlapping transitions underlying these spectral shapes, rather than integrating over small spectral boxes, we produce spectral slices of the dynamics over restricted ranges in $\omega_1$ and $\omega_3$. This presents the advantage of visualizing whether there are substantial frequency shifts of the off-diagonal peaks along either dimension, due to fast decay of any of the underlying signals. These slices are
shown in Fig. 4.20, where the signals in the top and bottom panels are given by

\[ S_{\text{top}}(\omega_3, t_2) = \int_{\omega_1'}^{\omega_1''} d\omega_1 S_{2D}(\omega_1, t_2, \omega_3), \]  

\[ S_{\text{bot}}(\omega_1, t_2) = \int_{\omega_3'}^{\omega_3''} d\omega_3 S_{2D}(\omega_1, t_2, \omega_3). \]  

The domain of integration in each case is indicated by the shaded regions in the \( t_2 = 0 \) fs spectrum shown in Fig. 4.20c. The above-diagonal signals oscillate with a period of 23 fs and an amplitude of \( \pm 10\% \) of the signal maximum. Below the diagonal we also observe two cycles of the same oscillation as well but at much smaller amplitude. The drawback of this spectral weighting is that it is difficult to comment on the behaviour of the bleach at \( \omega_3 = \omega_A \), as it lies at the edge of the spectral window provided by our laser pulse, and on the red falling edge of the line shape of peak A (seen in Fig. 4.18). For both slices, the coherent signatures in the evolution of the system vanish by \( t_2 = 100 \) fs. This is consistent with the transient absorption data, where the dynamics are very flat beyond \( t_2 = 100 \) fs, and unlike the monomeric dye, where small but robust signatures of vibrational wavepacket motion persist both in the TA and 2DPE.

Shifting attention to the above diagonal cross peak, it is helpful to turn to the response functions and the nonlinear pathways that contribute to the measured signals. In the electronic dimer example shown in Chapter 2, we demonstrated how in this portion of the 2D spectrum there are both static and dynamic contributions from GB, SE, and EA terms, as summarized in Figs. 2.5, 2.6. For that model, in the limit of a vanishing biexciton binding energy, the EA contributions to the signal are predicted to cancel with the SE pathways, complicating the extraction of inter-exciton coherences at cross-peak locations \( (\omega_A, \omega_B) \) and \( (\omega_B, \omega_A) \).

In the vibronic exciton model, however, even for vanishing binding energy this perfect cancellation is no longer valid, largely due to the increased number of transitions made possible by vibronic coupling. As shown previously in Fig. 4.14, we observe that there
Figure 4.20: Spectral slices of off-diagonal dynamics of biscyanine along selected regions of \( \omega_1 \) (a) and \( \omega_3 \) (b) as shown in shaded areas on the correlation spectrum (c). d) Line profiles through the slices corresponding to \( \omega_3 = 17800 \text{ cm}^{-1} \).

exist many absorptive peaks that link the ground state to the single exciton manifold. Likewise, a number of new pathways in the third-order response function appear upon introduction of vibronic coupling. For the populations and coherences evolving in the single exciton manifold during \( t_2 \), this translates to new resonances which couple to the third laser field which stimulates radiation of the nonlinear polarization during \( t_3 \), leading to corresponding peaks in the 2D spectra.

One such Liouville pathway is of notable interest under the present experimental conditions, and relates to EA into the doubly-excited manifold. Calculations to determine the exciton level diagram for this compound using the Holstein Hamiltonian [58], determined that there is a strong transition into a doubly-excited state with a peak occurring at \( \omega_1 = \omega_A \) and \( \omega_3 \sim 17000 \text{ cm}^{-1} \), corresponding to the Liouville diagram shown in Fig. 4.21. The peak energy of this transition is to the red of our excitation bandwidth, however due to the broad linewidths of the transitions, and the strength of \( \mu_A \) in the first
Figure 4.21: Response function pathway leading to EA peak in the vicinity of A/B cross-peak. The system is in a $|A\rangle\langle B|$ coherence during $t_2$, so the dynamics of this peak reflect the inter-exciton coherence between states $A$ and $B$. The subscript in $d_0$, denotes that this doubly-excited state possesses no excited phonons ($\tilde{\nu}_1 = \tilde{\nu}_2 = 0$). Adapted from [58].

field-matter interaction, this EA is nevertheless apparent in the 2D spectral dynamics shown in Fig. 4.21.

The presence of this transition is important, as an additional complication arises in the direct assignment of the dynamics at $(\omega_A, \omega_B)$ to the coherence between the states $A$ and $B$. Due to the similar values of the energy split between excitons (1400 cm$^{-1}$) and the vibrational energy (1200 cm$^{-1}$), oscillations due to vibrational motion in the ground state will theoretically strongly overlap with the $(\omega_A, \omega_B)$ cross-peak [29]. In this respect, probing the inter-exciton coherence via an EA pathway, displaced from other GB/SE contributions to the signals, provides a strong basis to attribute the decay timescale of the oscillations in Fig. 4.20 to the rapidly vanishing $AB$ coherence.

4.4.4 Discussion

The above measurements demonstrate that even in a homodimer, possessing one dominant periodic component in its ultrafast dynamics, the attribution of coherent off-diagonal signals to inter-exciton beats must be done carefully. It is intuitive, based on the model outlined in Chapter 2, to focus attention on the cross-peaks between transitions to reveal the coherent dynamics between excitons. However, dynamics due to intramolecular ground state vibrational motion will also appear at cross-peak locations, and making the
distinction between the two is difficult in practice.

In this regard, 2DPE results should be complemented by transient absorption data to verify self-consistency of the measured dynamics. In this case, performing spectrally weighted 2D allows us to isolate the coherences of interest by separating peaks which overlap in the PP and mapping them onto off-diagonal sections of the 2D spectra. In neither experiment do we observe long-lived coherences, even relating to underdamped ground state wavepacket motion.

The comparison study of the monomer is helpful to demonstrate that in the absence of well resolved cross-peaks, the analysis of off-diagonal peaks in 2D spectra demands caution due to FC active modes. In the vast majority of the photosynthetic studies the various cross-peaks associated with coupling between states could not be effectively isolated, particularly at room temperature where the linewidths are very broad, and effects associated with vibrational wavepackets on each pigment were overlooked. Based on the similarity of the spectra shown in Fig. 1.1b (FMO) and Fig 4.13a (monomeric indocarbocyanine), and the presented dynamics in the latter, the danger in doing so is obvious. The 2D spectra of biscyanine also demonstrate an important point, that even in the limit of fast dephasing the cross-peaks should possess amplitudes on the order of the diagonal peaks, and should not require nonlinear scalings to amplify their sizes [5, 55, 7, 18].

Based on the spectral slices, it is not immediately obvious whether the observed oscillations are contaminated by ground state wave packet motion. However, if there is a significant contribution from ground-state oscillatory dynamics, it should be very apparent at $\omega_3 = \omega_A$, and the below diagonal peak does not oscillate with regularity. The transient absorption data also display little evidence for ground-state vibrational wavepacket motion, despite the presence of two modes strongly modulating the response of the parent dye under similar experimental conditions. The 600 cm$^{-1}$ mode which oscillates for several ps following excitation in the monomer does not appear at all in
the transient absorption of the dimer, nor in Raman scattering measurements. Such a disappearance of Raman modes has already been observed in another similar dimer but was not explained [116]. Here, we speculate that the butyl chains lead to an increased rigidity of the polymethine chains in the pigments.

Figure 4.22: Wavefunction coefficients for the vibrational contributions to exciton states at each pigment in biscyanine for homogeneous ($\epsilon_1 = \epsilon_2$) and detuned ($\epsilon_1 = \epsilon_2 + 500$ cm$^{-1}$) site energies. Red denotes positive and blue negative values for the coefficients. We limit ourselves to $\nu' \leq 1$ for clarity. Adapted from [58].

The role of vibrations is nevertheless significant: applications of the vibronic exciton model to systems such as biscyanine and other more complicated aggregates [88, 57, 58] has provided a wealth of insight with respect to the interpretation of signals measured in 2DPE. Beyond the significant modifications to the linear and 2D spectra of dimers caused by vibronic transitions, this model also predicts that excitons may become localized and see their coherences prolonged by vibronic coupling.

In a perfect homodimer the excitonic states are symmetrically delocalized over both pigments. An example of this is shown in Fig. 4.22, where the relative contributions of vibrationally excited wavefunctions at each site for the exciton states $A$ and $B$ of biscyanine are shown for two different energetic regimes [58]. The first row demonstrates the case of equal site energies, where the wavefunction coefficients for each pigment are identical for each exciton. States $A$ and $B$ are made up of symmetric combinations of monomeric wavefunctions, with state $A$ possessing a larger contribution from $\nu' = 1$
vibrational wavefunctions. Exciton $C$ on the other hand, is shown to be composed of antisymmetric combinations of wavefunctions, with only a weak involvement of $\nu' \geq 1$ wavefunctions.

On the other hand, in the lower row where the energy of site 2 is lowered by 500 cm$^{-1}$, we observe that the coefficients for both $A$ and $B$ are biased towards the lower energy site, leading to localization of the exciton. In such a case, the coherence between states $A$ and $B$ will theoretically be less susceptible to dephasing, as the energy fluctuations between $A$ and $B$ will be correlated by virtue of being localized on the same site. By extension, for FMO [88], this model predicts long lived inter-exciton beats without invoking any a priori correlations in the system-bath interaction, only these are primarily intra-pigment in character, and are ultimately mediated by an associated vibrational mode.

We do not observe enhancement of the inter-exciton dephasing times in biscyanine, though modelling predicts a prolongation of the $AB$ coherence to nearly 100 fs [58]. Moreover, the lifetime of the oscillations measured in the dimer system appear to be entirely dictated by the homogeneous line width for the excitonic transition. This point is quite contentious in the discussion of coherences between excitons, as the homogeneous linewidth measured in our experiments reports on the decay of the induced polarization, which evolves during both the first evolution period $t_1$ and the final one $t_3$, and thus reflects the timescale of ground-excited state energy gap fluctuations.

The inter-exciton coherences, which evolve during $t_2$, are indeed of much lower frequency than the optical transitions. They are also not physically required to decay at the same rate. The exciton states are more similar to one another than to the ground state, leading to some correlations in energy gap fluctuations between these states, due to localization as shown in the two limiting cases of Fig. 4.22. These, however, only represent two extremes. For the case of a molecule in solution the site energies will fluctuate dynamically, and the coupled system will sample the continuum bridging the homogeneous case (top row of Fig. 4.22) to the detuned case where the exciton is more
localized (bottom row of Fig. 4.22) as a function of time.

Experimental 2DPE on FMO led to the hypothesis that the protein backbone introduces additional correlated fluctuations in site energies [7], however molecular dynamics simulations suggest that this is not the case [117], lending further support to the conclusion that the long-lived coherences are vibronic in nature. More importantly, the prolongation of inter-exciton coherence due to localization of the wavefunction is conceptually difficult to reconcile with the picture of coherent inter-pigment energy transfer. The application of the vibronic exciton model has redirected discussion away from a debate over the electronic or vibrational assignment of the oscillations observed in 2DPE, towards the more biologically relevant questions surrounding the localized or delocalized nature of the excitons probed in 2DPE.
Chapter 5

Conclusion

5.1 Summary: Implications for PPCs

The results for the synthetic system studied here lead us to conclude that the spectral signatures that have been previously associated with long-lived coherences between spatially delocalized excitons are more readily explained by vibrational wave packet motion. This questions their prospective role in directing EET in PPCs, particularly at room temperature. In the bicineanine system, sample properties limit our ability to further investigate this issue. The inherent symmetry of the molecule, and strong coupling between chromophores, complicates the in-depth exploration of energy transfer dynamics.

Nevertheless, we have demonstrated that the amplitudes of quantum beats between excitons in 2D spectra are not small, as was observed in many protein studies. In this vibronic exciton system, the signals associated with inter-exciton coherences can be reliably extracted, and are shown to possess similar amplitudes to the main features in the FWM signal. This is a key observation, as the signals associated with quantum beats are scaled by the transition dipole moments for the underlying optical transitions, in the same way as the other peaks in the 2D spectra. The nonlinear scalings of the off-diagonal data, implemented in previous works, to visualize the oscillations of interest casts doubt
on their assignment to inter-exciton dynamics without further justification.

Vibronic enhancement of inter-exciton coherence has been predicted for similar systems via localization of the exciton by disorder, but we find that the decay timescale for the biscyanine coherences is nevertheless on the order of tens of fs. The similarity between this timescale and the homogeneous dephasing time for the optical transition, directly measured in 2DPE, indicates that strong uncorrelated dynamic disorder plays an important role in the disrupting coherences between excitons at room temperature.

Appreciable enhancement of inter-exciton coherence due to vibronic coupling only occurs for strongly localized excitons. The selected homodimer possesses a fixed orientation between dipoles, mimicking the cases found in proteins where the interaction between chromophores is well-defined. However, unlike in that environment, here it is not possible to set a static distribution of site energies to break the symmetry of the system. As such, the degree of localization of the excitonic wave functions will vary as a function of the fluctuations experienced by each pigment during $t_2$, which would prevent the predicted temporal enhancement of the coherence through vibronic coupling [88, 58]. Vibrational relaxation also contributes to the short-lived nature of the coherent signals between vibronic excitons in biscyanine: in control measurements on the monomeric parent dye, the high frequency vibrational modes do not give rise to modulations to the signal long after excitation, unlike the case for a similar pinacyanol dye [26].

Taking these numerous complementary observations into consideration, this work points to a revised interpretation of the signals observed in proteins, as originating from strongly localized excitons undergoing weakly damped vibrational motion on the excited state. This paints a decidedly different picture of the nature of these oscillations, and how they contribute to the function of the PPCs where they have been observed.

Vibronic coupling has previously been shown to affect energy transfer rates in theoretical models for pigment aggregates [57, 93]. Using a different approach, non-adiabatic
vibronic coupling has additionally been proposed to explain how such coherences contribute to the redistribution of energy in FMO [118]. In comparison to other biological systems which utilize vibronic coupling, however, such effects are not an obvious design principle. For example, in the rhodopsin protein responsible for low-light vision, the necessity of strong vibronic coupling is an obvious requirement since the pigment (retinal) undergoes isomerization during the photochemical reaction [119]. In photosynthetic proteins on the other hand, the biological function is not accompanied by analogous conformational changes in the underlying pigments that would strongly implicate intramolecular vibrations.

In light of the conclusions from theoretical modeling, we argue that a crucial challenge facing researchers is to provide a quantitative experimental demonstration that the oscillations measured in 2DPE are directly related to irreversible EET. Recent work on fluorescence in single molecules of LH2 from Rhodopseudomonas acidophila does support this hypothesis [120], for instance, only without turning to vibronic coupling at all to interpret the measured energy transfer dynamics.

Similar model systems to bisscyanine would provide ideal starting points in this aim, only with more appropriately selected parameters. Barring a sudden substantial increase in the bandwidth of laser sources in the visible, it would be helpful to explore regimes of lower coupling, and differing symmetry. Relatively large control over the degree of vibronic coupling can then be achieved, by the appropriate selection of dyes [103, 25]. Recent experiments along these lines on other synthetic heterodimeric systems have lent further support to the claim of long-lived room temperature coherences enhancing energy transport [121]. Those measurements, however, were performed in a homodyne configuration, where the signatures of EET will be strongly masked by the mixing of absorptive and dispersive contributions to the nonlinear response. This, combined with the absence of a theoretical description of the compounds, casts uncertainty on the assignment of the coherent dynamics observed in the corresponding 2D spectra.
As an extension to existing 2DPE measurements, we propose that techniques from quantum control may in fact assist in unraveling the significance of quantum coherence in multidimensional spectroscopy, by studying the effect of state preparation on energy transfer dynamics.

5.2 2D coherent control

In the 2DPE results shown earlier all excitation beams were identical, due to the high time resolution needed to capture both the fast oscillations and rapid decay timescales associated with the interexciton coherences. However, the interferometer used to collect data may also be operated using two independent input beams, where the probe and LO pulses remain transform limited and short, but the first two pulses which create the population (in the limit of well-separated pulses) are shaped using a programmable pulse shaper [72, 73].

This allows a measurement of the frequency correlations in 2D spectra induced by non-transform limited pulses, while retaining a broad probe spectral window. This pulse sequence was originally conceptualized in an effort to shed light on earlier coherent control experimental results conducted in a TA configuration, with shaped pump pulses. There, it has been shown that the optimal pulses for photoexcitation of many molecules in solution are not pulses with the highest peak power [122, 100], and that the promotion of population from $S_0$ to $S_1$ is instead quite sensitive to the phase profile of the electric field used for excitation [123, 124, 125, 126].

Detractors of coherent control studies have correctly noted that the excitation fields obtained in optimal control measurements, where a given spectral observable is maximized using search algorithms to arbitrarily vary the excitation pulse shapes, are typically impossible to invert back onto the system Hamiltonian. Furthermore we have demonstrated that even in relatively simple exciton systems, peak assignments in 2D
spectra must be rigorously justified. Nevertheless, 2DPE offers a unique possibility to spectrally resolve the interferences generated via the third-order response using shaped excitation pulses. By observing the correlations induced by these pulses in the 2D spectra, this technique potentially provides a starting point to interpret the mechanisms by which shaped excitation fields enhance population transfer, or control branching ratios in photochemical reactions, in the weak-field limit at room temperature [126, 127].

Theoretically it was predicted many years ago that, using shaped pulses and genetic search algorithms, cross-peaks in 2D spectra of excitonic systems such as those investigated here could be enhanced by an iterative process [128, 129]. Those simulations, however, appeared much earlier than the first 2DPE experiments using pulse shaping [75], and the experimental feasibility of closed loop control to optimize fine features in 2D spectra is not practically achievable, due to data acquisition timescales.

While closed-loop optimal control experiments invariably yield complicated pulse shapes, which cloud the subsequent interpretation of the underlying control mechanism, they typically consist of pulse trains with overlying linear chirp. Efforts to theoretically extract the effect of either chirp or pulse trains are ongoing [130, 131, 132, 133], as are open-loop measurements where, in lieu of a genetic search, the pulse shaping window is parametrized to better understand the control mechanism [127, 134]. In 2DPE, by generating the appropriate pump pulses, the relaxation of the wavepacket and its associated spectral signatures for both linear chirp and pulse trains may be directly monitored.

5.2.1 Linear chirp

For these measurements, the laser dye rhodamine 101 (Rh101) was selected as a sample. It possesses a quantum yield of $\sim 1$ in methanol, indicating that there are effectively no nonradiative pathways for internal conversion in $S_1$. This molecule was also chosen for historical reasons, as previous optimal control experiments on this compound demonstrated that the population transfer efficiency from $S_0$ to $S_1$ could be varied by $\pm 10\%$.
Figure 5.1: Absorption spectrum of rhodamine 101 dissolved in methanol (red trace), with spectrum of excitation pulses overlaid in shaded yellow.

[125]. Shown in Fig. 5.1 is the absorption spectrum of Rh101 with laser spectrum overlaid. Using the Dazzler it is possible to select a 45 nm width pulse from the output of the NOPA, corresponding to a TL pulse of approximately 25 fs. The optimal pulses for population transfer in rhodamine, corresponding to the same spectral bandwidth, consist of a comb of sub-pulses spaced approximately 150 fs apart, with overlying positive linear spectral chirp.

By applying linear chirp to the excitation pulses, we observe dramatic variations to the 2D correlation spectra at $t_2 = 0$ fs. These results, along with the corresponding $t_2 = 40$ ps spectra are shown side by side in Fig. 5.2. For comparison, the spectra generated using transform-limited excitation pulses are also shown. Based on the spectral bandwidth of the excitation, which does not overlap whatsoever with the vibronic transitions in rhodamine seen in Fig. 5.1, the spectra for TL pulses resemble the limiting case of a single inhomogeneously broadened transition. At $t_2 = 40$ ps, spectral diffusion and thermalization have taken place, and the spectral shape assumed is round, homogeneous, and slightly displaced off-diagonal, reflecting vibrational cooling on $S_1$.

The effect of linear chirp, here $\phi'' = \pm 400$ fs$^2$ (or enough to stretch the pump pulses to
a duration of $\sim 80$ fs), induces the appearance of off-diagonal elements in the correlation spectrum of rhodamine. These do not relate to coupling between states, but instead occur due to the time-ordering of pulses being affected by the chirped excitation during pulse overlap, leading to mixing of absorptive and dispersive signal contributions. In these data, however, the effect of the chirp vanishes on the timescale corresponding to pulse overlap. Furthermore, at waiting times long with respect to electronic and vibrational dephasing, we observe no difference (within experimental error) between the 2D spectral lineshapes generated using chirped and TL pulses. Similar experiments were also independently
performed by a separate group, for the case of chirp applied to any of the excitation pulses, with equivalent outcomes [135].

We do, however, observe that the amplitude of the 2DPE signal is approximately 15% lower for negative chirp than it is for positive at identical excitation energies. This observation is consistent with the previously measured chirp dependence of population transfer from ground to excited states [125]. Previously, a pump-dump scheme has been used to interpret the decreased population transfer observed using negative chirp, though this effect is more pronounced at high intensities [136]. There, over the course of the laser-molecule interaction, the later arrival of the lower frequency components of the laser spectrum, which possess more overlap with the emission spectrum of the molecule, leads to “dumping” of excited population back to \( S_0 \).

Deeper insight into this mechanism in terms of dynamics in the 2D spectra is precluded by the rapid disappearance of the manifestations of chirp caused by dephasing, leading to difficulty in distinguishing the signatures of state preparation from effects due to optical distortion via the phase-matching. These experiments do however highlight that pulse compression must be performed very carefully for 2DPE measurements where the dynamics shortly following \( t_2 \) are of primary interest, due to the possibility of induced off-diagonal spectral peaks caused by phase distortions in the excitation fields.

### 5.2.2 Pulse trains

A significantly more unexpected result arises in the case when pulse trains are used to excite the sample. In this case, a spectral phase is applied to the laser pulse of the form

\[
\phi(\omega) = a \sin \left( 2\pi \frac{\omega}{\omega_m} \right),
\]

where \( a \) reflects the relative amplitude of the sub-pulses, and \( \omega_m \) is the modulation frequency which sets the spacing between the sub-pulses in the time domain [137]. The
temporal profile of the resulting pulses are shown in Fig. 5.3 for the case of \( \omega_m = 220 \text{ cm}^{-1} \), where the FROG trace shows a series of 5 sub-pulses spaced apart by approximately 150 fs.

![Figure 5.3: Retrieved temporal profile (via FROG) of a laser pulse possessing the spectrum shown in Fig. 5.1, and an applied phase modulation corresponding to Eqn. 5.1, with \( \omega_m = 220 \text{ cm}^{-1} \) and \( a = 1.23 \). a) Intensity of the laser field. b) Real (blue, solid) and imaginary (black, dashed) parts of the corresponding electric field. The imaginary part is shifted downwards by 0.5 for clarity.]

In rhodamine 101, a series of sub-pulses spaced apart by approximately the same temporal delay was demonstrated to optimally transfer population transfer to \( S_1 \) [125]. This period correlates well with that of the most prominent vibrational mode present in the transient absorption of rhodamine 101 following impulsive excitation, as shown in Fig. 5.4a, where the differential absorption through the linear absorption maximum exhibits an oscillatory component in the decay of the bleach peaking at roughly 220 cm\(^{-1}\).

To investigate this effect in the 2D spectra, the sample was excited by pulse trains corresponding to a range of \( \omega_m \) values in the vicinity of this frequency. For these experiments, due in part to the limited pulse shaping bandwidth for the Dazzler, we set \( a = 1.23 \) leading to a first pair of satellite pulses possessing approximately half the amplitude of the central pulse. Following excitation with these pulses, a dramatic change is observed both in the 2D spectra on short and long timescales in \( t_2 \) [138]. The results for \( \omega_m = 220 \text{ cm}^{-1} \) are shown in Fig. 5.5.

At \( t_2 = 0 \) fs the 2D lineshapes are no longer broad and smoothly varying as in the
Figure 5.4: a) Transient absorption of rhodamine through its absorption maximum in methanol ($\omega_3 = 17700\ \text{cm}^{-1}$). b) Power spectrum of oscillatory transients in the residuals, following a fit to a decaying exponential function.

In the case of TL or chirped excitation pulses, instead, we observe a grid-like distribution of very narrow peaks. At first glance, these peaks resemble the lineshapes corresponding to 2D spectra of systems with very weak optical dephasing [32], but the frequency spacing between these peaks in the vicinity of $t_2 = 0\ \text{fs}$ depends on the choice of $\omega_m$. This indicates that the sharp grid is due to interferences between resonant and nonresonant signals, and not caused by suppression of optical dephasing. This notwithstanding, an additional consequence of pulse train excitation shown in Fig. 5.5b can not be so easily explained, as at $t_2 = 40\ \text{ps}$ a significant modulation persists along $\omega_1$ in the 2D spectrum.

We specifically show the absolute value spectra, to stress that these results can not be due to a possible error in the phasing of the data. Also, this spectral signature would not be observed in transient absorption, since in that measurement one implicitly integrates over $\omega_1$. This observation is surprising for a number of reasons: firstly, the expression for the homodyne FWM signal for $t_2$ times longer than all vibrational and electronic dephasing timescales is independent of the phase profile of the excitation pulses, and depends only on the intensity spectra of the fields [37]. This is plainly borne out in the previous results, where the spectra at $t_2 = 40\ \text{ps}$ are identical for chirped and TL excitation. A second important characteristic of this signal is that, unlike the grid of
peaks observed at $t_2 = 0$ fs, at long waiting times the frequency of these ripples in $\omega_1$ is consistently $190$ cm$^{-1}$ irrespective of $\omega_m$, confirming that this signal originates from the response of the solute and is not an optical artifact.

Moreover, the relative amplitude of this effect displays a resonant character as a function of $\omega_m$: in Fig. 5.6 we show a plot of the integrated difference between the $t_2 = 40$ ps absolute value spectra for shaped and unshaped pulses

$$\Delta S(\omega_1) = \int d\omega_3 (|S_{\text{shaped}}(\omega_1, \omega_3)| - |S_{\text{unshaped}}(\omega_1, \omega_3)|).$$  

(5.2)

$\Delta S$ is shown to be strongest when $\omega_m$ is tuned to the 220 cm$^{-1}$ mode observed in the PP experiments, and drops off rapidly as one moves away from this resonance. The origin of this effect, however, remains unclear. Based on Fig. 5.6, the amplitude of $\Delta S$ is strongest for higher $\omega_1$, pointing to a ground state origin, as the stimulated emission contribution to the total 2D lineshape at long $t_2$ is redshifted due to thermalization. It is not possible to determine the origin with absolute certainty here, however, without investigating a broader spectral range, as earlier work has concluded that pulse train excitation enhances
vibrational wavepackets on both $S_1$ and $S_0$ [139, 140].

From an experimental standpoint, it would be of interest to examine systems with higher energy phonons than in rhodamine, to investigate the resonance effect. The isomerization of retinal in bacteriorhodopsin would be an additional problem to revisit using this technique. In that system (for which the photochemistry also demonstrates sensitivity to phase [126, 100]) it would be more straightforward to determine if the above effect originates from the ground state. There, as demonstrated in Fig. 5.7, the contributions of ground and excited state dynamics are separated in the 2D spectra for short $t_2$ as a result of ultrafast isomerization of the chromophore. 2D coherent control measurements could be used to investigate whether the effect of phase shaping traverses conical intersection between excited state potential energy surfaces, as vibrational coherence has previously been shown to be conserved in other isomerization reactions [119, 141].

5.3 Future directions

The long-lived “memory” of the excitation shown for measurements using pulse train excitation, using the instrumentation described in this thesis, provides one particular
example of how coherent control can be applied to better understand the role of both quantum coherence or vibronically assisted energy transfer in photosynthesis. At present, this subsection of the field is heavily biased towards the measurement of oscillations along \( t_2 \), as described in the previous Chapter, though the unique information contained in 2DPE versus other ultrafast spectroscopic techniques is in fact found along \( t_1 \) or \( \omega_1 \).

As we have shown here via the resonances presented in Fig. 5.6, using excitation pulses with sinusoidal phase modulation it is possible to observe signatures of FC active vibrational modes at very long waiting times, despite the effects of spectral diffusion. In a light-harvesting molecular aggregate, by probing the location on the 2D spectrum corresponding to SE from a low energy “acceptor” state using similar excitation pulses, it is in principle possible to directly measure whether the excitation of particular excited-state vibrational mode results in enhanced energy transfer in the system.

Further to this, linear chirp has also previously been demonstrated to enhance or suppress vibrational wavepacket motion in the excited state [142, 143]. On the one hand, we demonstrated that the signatures of chirped excitation rapidly disappear in the 2D
spectra of monomeric systems. On the other hand, however, if long-lived vibronic coherences significantly contribute to the energy relaxation network in PPCs, the effect of an enhancement of the relevant vibrational modes using chirped pulses should nevertheless be measurable to high accuracy in this experimental configuration, long after vibrational dephasing.

As was demonstrated in the work on the model exciton system, even in systems where the response is dominated by a handful of levels, the overlapping contribution of peaks in the 2D spectra of excitons corresponding to GB, SE and EA contributions to the spectra must be rigorously taken into account. Furthermore, based on the decay times and magnitudes of the previously reported inter-exciton coherences observed in more complex aggregates, it seems evident that the attribution of oscillations in those 2D spectra to coherent electronic beatings between excitons must be corrected. It is important to bear in mind, that the additional information potentially provided by 2DPE is enticing but limited, as the relevant dephasing times for the electronic transitions at room temperature are so fast that the dynamics along $t_1$ decay extremely rapidly.

Additional extensions to 2DPE have been proposed, to overcome some of the limitations encountered in the visible range. For instance, the extension to new spectral windows could serve to complement the previously collected data [144, 145] by investigating different electronic transitions in the aggregates of interest. Even in these new spectral windows, the importance of performing control measurements on tractable systems can not be overstated. Control studies such as these allow to more accurately interpret existing results, but also help design future experiments to better verify hypotheses on the physics of more complicated systems, making use of the full information offered by broadband 2D spectroscopy.
Bibliography


