For Mum, Dad & Chi
“Công Cha như núi Thái Sơn
Nghĩa Mẹ như nước ốc trong nguồn chảy ra”.

— (ca dao)

“. . . I have the advantage of having found out how hard it is to get to really know something, how careful you have to be about checking the experiments, how easy it is to make mistakes and fool yourself . . .”

— Richard P. Feynman
Declaration

I, My Thi Tra Do, declare that this thesis entitled:

“Femtosecond Nonlinear Coherent Spectroscopy of Carotenoids”

submitted for the degree of Doctor of Philosophy contains no material that has been accepted for the award of any other degree or diploma. To the best of my knowledge, this thesis contains no material previously published or written by another author, except where due reference is made in the text of the thesis. Jeffrey Davis developed the program for analysing the non-interferometric two-dimensional Fourier transform frequency correlation spectra.

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Dated this day, September 8, 2008
Abstract

In this thesis, femtosecond spectrally resolved one- and two-colour four-wave mixing coherent spectroscopy is used to study the population dynamics and coherence dynamics in two carotenoids, lycopene (with eleven conjugated carbon bonds (C=C), \( n = 11 \)) and spheroidene \( (n = 10) \), in \( n \)-hexane solution. This information could play an important role in elucidating the light harvesting function of lycopene and spheroidene in the process of photosynthesis.

The population dynamics of the two carotenoids are studied by measurements of transient grating-like signals. By selecting appropriate wavelengths for the three laser pulses in two-colour measurements, the vibrational relaxation times in the first optically allowed excited state \( 1B_u^+ \) and the ground state \( 1A_g^- \) are determined for lycopene. The results suggest the active role of the conjugated carbon bond \( \text{C}=\text{C} \) in the vibrational relaxation processes of the ground state. The transient grating-like measurements were also successful in detecting the internal conversion process from the \( 1B_u^+ \) state to the dark \( 2A_g^- \) state, from the dark \( 2A_g^- \) state to the ground state \( 1A_g^- \), as well as vibrational relaxation in the \( 2A_g^- \) state, for both lycopene and spheroidene. These results are in agreement with those obtained from other techniques.

The decoherence process of certain transitions in lycopene and spheroidene are studied by one-colour photon echo measurements. The decoherence time of the transition \( 1A_g^-(0) - 1B_u^+(0) \) is determined for lycopene and spheroidene, and that of the transition \( 1A_g^-(0) - 1B_u^+(1) \) is determined for lycopene. The results indicate
a larger scattering rate in the higher vibrational level in the $1B_u^+$ state of lycopene. The results on the population dynamics and the molecular decoherence both indicate a slower dynamical behaviour in spheroidene compared with lycopene, which is consistent with other studies. Investigation of the coherence dynamics were successful in detecting coherent coupling between the levels $1A_g^-(1)$ and $1B_u^+(0)$ in lycopene and the coherence time is found to be less than 100 fs. The spectrally resolved two-colour four-wave mixing signals were able to detect transitions between the dark states $1B_u^-(1)$, $3A_g^-(0)$ and the ground state in spheroidene and indicate the presence of coherent coupling between these dark states and the ground state. The energies of the dark states $1B_u^-(1)$ and $3A_g^-(0)$ are deduced.

A phase retrieval technique that allows one to obtain the phase of the four-wave mixing signal from the spectrally resolved two-colour data without the need for phase stabilised input pulses is reported. The spectrally resolved signal which is processed by a phase retrieval algorithm, yields the time resolved emission signal and Fourier transformed correlation spectra, and hence helps to identify the coherence dynamics of our samples. Preliminary results on the coherent coupling in the laser dye cresyl violet and in lycopene were obtained using this phase retrieval technique. The technique is able to provide additional information about the coherence dynamics and is a very promising tool for future studies.
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My Thi Tra Do
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Chapter 1

Introduction

1.1 Carotenoids

Plants on Earth are alive thanks to the energy they gain from the Sun through the process of photosynthesis. In this process, photosynthetic organisms - plants, algae and photosynthetic bacteria - harvest the sunlight and use its energy to drive their metabolic reaction [1], in which the raw materials carbon dioxide CO$_2$ and water H$_2$O are converted into carbohydrate (such as sucrose, glucose and starch) and oxygen. The molecules that are responsible for the light harvesting and also for inducing colour are called pigments. The popular green colour of plants originates from the pigment chlorophyll [2]. Chlorophyll molecules have different molecular structures such as chlorophyll (Chl) $a$ or $b$ in plants or algae and bacteriochlorophyll (BChl) $a$ or $b$ in photosynthetic bacteria. A second participating pigment, of which the colour is masked by chlorophyll in green leaves but predominates in ripe tomatoes, red grapes, carrots, petals, . . . are the carotenoids [3]. Carotenoids are defined by their chemical structure, which is formally derived from a 35 to 40 carbon polyene chain. This chain, which is considered as the backbone of the molecule, may be terminated by cyclic end-groups (rings) and may be complemented with oxygen-containing functional groups.
The double carbon-carbon bonds (C=C) interact with each other, allowing electrons in the molecule to move freely across these areas of the molecules.

From over 600 different known carotenoids there are two major groups, namely carotenes and xanthophylls [4]. Xanthophylls are carotenoids with molecules containing oxygen, such as lutein and zeaxanthin. The un-oxidized (oxygen-free) carotenoids such as \( \alpha \)-carotene, \( \beta \)-carotene and lycopene are known as carotenes. In non-photosynthetic systems, carotenoids play the role as efficient quenchers of both dangerous singlet oxygen and various reactive radicals by intercepting the chain of the oxidative reaction. This antioxidation function is believed to be a crucial mechanism against various diseases such as cancer, atherosclerosis and macular degeneration in humans [3]. In photosynthetic systems, carotenoids can protect the photosynthetic organism against excessive light by quenching both singlet and triplet states of bacteriochlorophyll [3]. The best known function of carotenoids in such systems, however, is light-harvesting.

In a photosynthetic organism, carotenoids absorb light in the green range of the visible spectrum at around 500 nm into a strongly allowed excited state. The excitation energy is then transferred on a femtosecond time scale and with very high efficiency (nearly 100%) to an energy state of another pigment, for example, to the \( Q_y \) exciton states of the B850 ring in one of the most well-characterized photosynthetic bacteria, purple bacteria. The pathways and mechanism by which this efficient excitation transfer can occur between two pigments remain challenging questions to be answered. According to the theory, the condition for excitation transfer is that the participating excited states are resonant with each other [5]. Since the allowed state of the carotenoids is far away from resonance with the states of (B)Chl (which are at 800 and 850 nm), the excitation energy is transferred to some lower energy states of the carotenoids before being delivered to the (B)Chl. These lower energy states are generally called ‘dark’ states. Where the ‘dark’ states are located in the energy diagram and why the efficiency of the excitation transfer from these ‘dark’ states to (B)Chl is as high as nearly 100% are still not totally clear. Thus, determining the location and
electronic dynamics of the ‘dark’ states as well as the other processes occurring in the carotenoids is an important task in elucidating the role of this pigment in the light-harvesting function.

1.2 Femtosecond Spectrally-Resolved Three-Pulse Two-Colour Nonlinear Coherent Spectroscopy

The study of molecular structure and dynamics is based mostly on spectroscopy through the absorption, emission and scattering of light. The era of modern spectroscopy began with the invention of the laser, which provides intense, coherent and tunable radiation. The intense light fields are able to establish a nonlinear dependence of the absorbed radiation power on the incident power, which is the fundamental process for nonlinear optical spectroscopy [6] and which can help to elucidate many of the nonlinear processes occurring in molecular systems. There are various nonlinear spectroscopy techniques, of which the most common are related to multiwave mixing.

Almost all important processes in a molecular system occur on an extremely short time scale (on the order of a picosecond and less). In order to study these processes experimentally, a sufficiently good time resolution is necessary. Because of this, ultrashort pulse lasers, as well as new detection techniques, have been developed, and the use of laser pulses with duration in the femtosecond range (1 fs = 10^{-15} s) is now possible.

The femtosecond spectrally-resolved three-pulse two-colour spectroscopy that is demonstrated in this thesis is a four-wave mixing (FWM) nonlinear technique. The four-wave mixing technique, in which three laser fields interact with the sample, plays an important role in current studies of nonlinear optical phenomena. Theoretically, the four-wave mixing process involves the third-order polarization $P^{(3)}$. Techniques that involve $P^{(3)}$ include photon echo, transient grating, coherent anti-Stokes Raman
scattering (CARS) and many more. With our experimental set-up, photon echo and transient grating-like signals can be obtained. The transient grating signal [7], which depends on the distribution of molecules in the excited state and ground state, gives information on the population dynamics of the ensemble, whereas the photon echo signal [6], which is the only coherent signal that can eliminate the effect of inhomogeneous broadening in the system, provides information about coherence and decoherence of the molecular system. Moreover, with the ability to employ two colours for the laser pulses, our measurements are able to probe different energy states at the same time, and hence provide a multi-dimensional capability. In order to avoid time gating, the signal is spectrally dispersed with a spectrometer and detected as a function of wavelength.

Femtosecond spectrally resolved three-pulse two-colour nonlinear FWM coherent spectroscopy has proven to be a powerful technique in the study of laser dyes such as cresyl-violet [8], rhodamine B, and rhodamine 101 [9–11], semiconductor systems such as semiconductor quantum dots and quantum wells [12–14], and biological molecules such as carbon monoxy myoglobin (MbCO) [8, 15]. This technique, based on these successes, is a promising tool for elucidating the molecular dynamics of carotenoids.

1.3 Thesis Objectives

In 1943, Duggar et al. confirmed for the first time by experiment the excitation energy transfer process from carotenoids to chlorophylls [16]. From this breakthrough until the late 1980s, experimental work on the dynamics of carotenoids was based mostly on the measurement of fluorescence excitation spectra as ultrafast spectroscopic methods were not yet invented [17]. The most prominent result during this period was the determination of quantum yields for carotenoid–(B)Chl transfer, which was shown to be close to unity in some cases.

In 1972, the demonstration of the so-called ‘dark’ state made a big impact on
further research on carotenoid photophysics. Schulten [18] and Hudson [19] showed that the absorbing state of longer polyenes in solution is not the lowest excited state and that there was another state (a ‘dark’ state) located between the absorbing state and the ground state. A new direction of study to locate this ‘dark’ state and elucidate its role in the light harvesting and photo protection processes started for carotenoid photophysics. The first result came from the theoretical work of Tavan and Schulten [20] who employed the multireference double excitation configuration interaction method (MRD-CI) on polyenes to show the existence of the ‘dark’ states. Experimentally, these dark states were only found very recently [21,22], and researchers have continued to apply new techniques to solve this problem since then.

The availability of ultrafast spectroscopic methods in the late 1980s, which allowed the study of the dynamics of the excited states on a (sub) picosecond time scale, introduced a new era for carotenoids photophysics. There have been numerous experiments performed successively to obtain new information on the dynamics of the carotenoids, such as the lifetime and location of the allowed states and the ‘dark’ states, the internal conversion processes between two states, and the excitation energy transfer to (B)Chl, in both solution and light harvesting complexes. The complicated picture of the carotenoid dynamics has been revealed more and more; however, many questions still remain unanswered and new questions are being raised.

The major motivation for the work presented in this thesis is to apply spectrally resolved three-pulse two-colour nonlinear FWM coherent spectroscopy to study the molecular dynamics of two carotenoids, lycopene and spheroidene. Lycopene and spheroidene are among the most common carotenoids participating in the light-harvesting function of photosynthetic organisms [23–25], the molecular dynamics of which are still not yet finalised. For this reason, different measurements have been performed to obtain valuable information about the state lifetimes, vibrational relaxation, internal conversion processes, molecular coherence and the location of the dark states.
1.4 Thesis Outline

The outline of this thesis is as follows:

Chapter 2 is a literature review on the dynamics of lycopene and spheroidene, in which up-to-date results about the energy and lifetime of the allowed excited states and the dark states, vibrational relaxation processes, and internal conversion processes are summarised.

Chapter 3 gives an introduction to the principles of stimulated three-pulse photon echo and transient grating signals, followed by a detailed description of our technique, which is based on photon echo and transient grating measurements. The nonlinear response function that plays a crucial role in the light-matter interaction of the FWM technique will be discussed. The chapter finishes with a brief review of the theoretical model for interpretation of the nonlinear optical experimental results.

Chapter 4 first describes the ultrafast laser system used to obtain the experimental results presented in this thesis. The detailed experimental set-up for the photon echo and transient grating-like experiments is then presented in Section 4.2. The procedures for preparation and handling the samples, which are important for ensuring reliable experimental results, are also reviewed. The last section of chapter 4 describes in detail the measurements on the samples, lycopene and spheroidene, used in this thesis.

Chapter 5 describes the experimental results obtained from the transient grating-like signals. The results provide information on the population dynamics of the molecular systems lycopene and spheroidene.

Chapter 6 discusses the results on the coherence dynamics of lycopene and spheroidene. The first part of the chapter presents the results on the molecular decoherence deduced from the photon echo signals. The next part discusses the results obtained from the two-colour experiments relating to the coherence dynamics of the samples. The final part of the chapter introduces our phase retrieval technique. This
technique is applied to interpret in detail the coherence dynamics of the laser dye cresyl violet before being applied to the study of the coherence dynamics of lycopene.

Finally, chapter 7 summarises the conclusions drawn from this thesis. Future plans for the project are also discussed.
Chapter 2

Lycopene and Spheroidene Dynamics

2.1 Lycopene and Spheroidene

All-trans-lycopene and all-trans-spheroidene (hereafter, we abbreviate by omitting the ‘all-trans’ in front of each name of the carotenoids) are among the most common carotenoids participating in the light-harvesting function of photosynthetic organisms [23–25]. Figure 2.1 shows the molecular structures of carotenoids having $n = 9 - 13$, in which their central pattern consists of alternating single (C–C) and double (C=C) carbon-carbon bonds and $n$ is the number of C=C bonds. These bonds form a system called a conjugated $\pi$-electron system [17]. The number of double bonds in spheroidene and lycopene is $n = 10$ and $11$, respectively. The approximate $C_{2h}$ symmetry of the conjugated chain of all-trans-carotenoids gives rise to low-lying singlet states with four different symmetries including $k^1A_g^-$, $l^1B_u^-$, $m^1A_g^+$ and $n^1B_u^+$ states, where $k$, $l$, $m$ and $n$ label each type of electronic state from the lowest to the higher energies, and the superscripts $+$ and $-$ are Pariser’s signs showing the symmetry of the electronic configuration [26,27].
Although the scientific objective is to unravel the functions of carotenoids in complex natural and artificial systems, a prerequisite is to study the dynamics of carotenoids in a solution environment. In fact, most of the significant characteristics of the energetics and dynamics of the carotenoids that have proven to be crucial in their functioning have been obtained by experiments performed in solution. In this chapter, the dynamics of spheroidene and lycopene dissolved in a solvent will be reviewed.

In terms of $C_{2h}$ symmetry, the ground state of the carotenoids is of $A_g^-$ symmetry (denoted $1A_g^-$), called the $S_0$ state (see Fig. 2.2). According to selection rules [26,28], the first low-lying excited state that is allowed in a one-photon transition from the ground state is $1B_u^+$, denoted the $S_2$ state.
2.2 $S_2 (1B_u^+)$ State Dynamics

The absorption spectra of lycopene and spheroidene in $n$-hexane are presented in Fig. 2.3. The ability of carotenoids to absorb in the blue–green spectral region originates from the strongly allowed $S_0 - S_2$ transition [29]. For naturally occurring carotenoids having conjugation lengths $n = 7 - 13$, the $0 - 0$ band (in which 0 denotes the first vibrational level of the electronic state) of the $S_0 - S_2$ transition is located between 475 nm and 525 nm and the energy of this transition is shown to decrease with the conjugation length.

The three well separated peaks present in almost all absorption spectra of the
carotenoids constitute the lowest terms of the vibronic progression, built on the backbone stretching vibrations (C–C + C=C). Various techniques have been employed to determine the energy of these levels, such as fluorescence spectroscopy [30, 31], resonant-Raman excitation profiles [21] and electronic absorption spectroscopy [32]. Table 2.1 shows the results derived from those techniques for lycopene and spheroidene in \( n \)-hexane. It is worth pointing out that the energy gap (\( \delta \sim 1350 \text{ cm}^{-1} \)) between vibrational peaks is the result of the combination of two symmetric vibrational modes with energies of \( \sim 1150 \text{ cm}^{-1} \) (C–C stretch) and \( \sim 1600 \text{ cm}^{-1} \) (C=C stretch) [17]. Experimentally, Koyama and co-workers confirmed by means of fluorescence spectroscopy the spacing of the vibrational progression in the \( S_2 \) state to be 1400 cm\(^{-1}\) and in the \( S_0 \) state to be 1100 cm\(^{-1}\) [33].

It is found that for almost all all-trans-carotenoids with \( n = 9 – 13 \) the Stokes shift, which is the shift between the absorption and the emission spectrum, is \( \sim 150– \)
Table 2.1: Energies and width (in parentheses) (in cm$^{-1}$) of the absorptive transitions to the $1B_u^+$, $3A_g^-$, $1B_u^-$ and $2A_g^-$ vibronic states for spheroidene and lycopene in $n$-hexane. Spacings between a pair of neighbouring transitions ($\delta$) are also shown in italics. Table adapted from [32].

<table>
<thead>
<tr>
<th></th>
<th>Spheroidene ($n = 10$)</th>
<th>Lycopene ($n = 11$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$1B_u^+$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>20 660 (850)</td>
<td>19 810 (900)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>1 350</td>
<td>1 340</td>
</tr>
<tr>
<td>(1)</td>
<td>22 010 (1 100)</td>
<td>21 150 (1 100)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>1 370</td>
<td>1 350</td>
</tr>
<tr>
<td>(2)</td>
<td>23 380 (1 180)</td>
<td>22 500 (1 210)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>1 350</td>
<td>1 380</td>
</tr>
<tr>
<td>(3)</td>
<td>24 730 (1 360)</td>
<td>23 880 (1 380)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>1 380</td>
<td>1 360</td>
</tr>
<tr>
<td>(4)</td>
<td>26 110 (1 400)</td>
<td>25 240 (1 350)</td>
</tr>
<tr>
<td>$3A_g^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>19 900 (1 050)</td>
<td>18 100 (1 000)</td>
</tr>
<tr>
<td>$1B_u^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>17 600 (850)</td>
<td>16 200 (1 050)</td>
</tr>
<tr>
<td>$2A_g^-$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(0)</td>
<td>15 330 (1 330)</td>
<td>14 380 (1 380)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>1 570</td>
<td>1 460</td>
</tr>
<tr>
<td>(1)</td>
<td>16 900 (1 330)</td>
<td>15 840 (1 490)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>1 580</td>
<td>1 560</td>
</tr>
<tr>
<td>(2)</td>
<td>18 480 (1 330)</td>
<td>17 400 (1 480)</td>
</tr>
<tr>
<td>$\delta$</td>
<td>1 310</td>
<td>1 380</td>
</tr>
<tr>
<td>(3)</td>
<td>19 790 (1 330)</td>
<td>18 780 (850)</td>
</tr>
</tbody>
</table>

300 cm$^{-1}$ and almost independent of the conjugation length [34, 35]. Furthermore, the emission spectrum constitutes nearly a mirror image of the absorption spectrum. In comparison with the value of a normal Stokes shift for a large molecular system, this value can be considered to be small.

As an allowed excited state, $S_2$ is thought to be the easiest electronic state to study. According to the Strikler equation giving the relationship between absorption intensity and fluorescence lifetime of molecules [36], the radiative lifetimes of $S_2$ were calculated to be in the range of nanoseconds. However, measurement of the quantum yields of the emission from this state results in values in the sub-picosecond range [35, 37]. To
resolve the $S_2$ state dynamics, therefore, one needs to make use of ultrafast time-resolved techniques, of which fluorescence up-conversion and transient absorption are two potential techniques. From [37–40], the lifetime of the $S_2$ state was found to be in the range 100–300 fs and this lifetime is dependent both on the conjugation length and the solvent parameters. Koyama and co-workers determined the lifetime of all-trans-carotenoids having the number of conjugated double bonds $n = 9 – 13$ by means of near-infrared, sub-picosecond time-resolved absorption spectroscopy. The result for the $1B_u^+$ lifetime of spheroidene was 0.10 ps, whereas that of lycopene was only 0.02 ps [41]. These results were supported by the work of Cerullo et al. [42] in which 10–12 fs pulses were employed.

2.3 ‘Dark’ State Dynamics

2.3.1 $S_1$ State ($2A_g^-$)

In terms of $C_{2h}$ symmetry, the $2A_g^-$ state (denoted $S_1$) is the lowest electronic excited state of all-trans-carotenoids. The selection rules [26, 28] indicates that the transition between the ground $S_0$ state and the $S_1$ state is symmetry forbidden. Furthermore, as the conjugation length increases, the $2A_g^-$ and $1B_u^+$ fluorescence signals become less well resolved [43]. For these reasons, more research is necessary to determine the $S_1$ energetics and dynamics.

Since the theoretical prediction of the existence of the $S_1$ dark state as the lowest-excited state in the carotenoids and longer polyenes in 1972 [18], it took more than 20 years for experimentalists to determine the energy of this state for longer carotenoids. As this lowest-excited state emission is very weak, experimental work on the $S_1$ state identification relied on progress in fluorescence techniques to detect the weak emission. In the late 1990s, Koyama and co-workers were successful in determining the energy of the $S_1$ state for spheroidene by measurement of its weak fluorescence spectra [43].
Also, by means of fluorescence spectroscopy, Fujii et al. were able to locate the $S_1$ state in the energy diagram for some longer carotenoids, including lycopene [30], and showed that the energies of $S_1$ for these carotenoids are independent of temperature. These results are consistent with the energy-gap law predictions and show a good fit with the extrapolations made from shorter carotenoids, for which the energies of the dark state $S_1$ were determined by fluorescence spectroscopy [44]. In the early 2000s, the technique of resonance-Raman excitation profiles was developed by Koyama and his group to study the $S_1$ state energy of some carotenoids. The results obtained for lycopene can be found in [21,22] and for spheroidene in [45].

With the development of time-resolved femtosecond spectroscopy, a new and very powerful technique has become available for the location of the $S_1$ state [46]. As the $S_1 - S_2$ transition is symmetry allowed, the molecules are excited to the $S_2$ state first, then relax to the $S_1$ state. The information about the energies of vibrational bands of the $S_1 - S_2$ transition can be obtained by scanning the wavelength of the probe pulse in the time window determined by the lifetime of the $S_1$ state. The location of the $S_1$ state can then be revealed [17]. This technique has been successfully employed to establish the energy of the $S_1$ state for both short and long carotenoids. Some of the results can be found in [47]. Time-resolved spectroscopy has also proven to be a promising technique for research on the dynamics of the $S_1$ and other states.

A number of techniques have been used on all-trans-carotenoids in order to determine their $S_1$ state lifetime. Measurements of the $S_1 - S_N$ excited state absorption were first employed by Wasielewski and Kispert to obtain the lifetime of the first excited state of β-carotene [48]. This technique was then applied to a variety of carotenoids to study not only the $S_1$ lifetime itself but also its dependence on conjugation length, molecular structure and the environment [17]. With the availability of time-resolved spectroscopy techniques, the properties of the $S_1$ state of the carotenoids became much more accessible. By subpicosecond time-resolved absorption spectroscopy, Koyama and co-workers measured the $S_1$ state lifetimes of neurosporene, spheroidene and
lycopene in \( n \)-hexane, which were 21.1 ps, 8.9 ps and 4.1 ps, respectively [41], and both in \( n \)-hexane and bound to the LH2 complexes from different purple bacteria [49]. The lifetime of the \( S_1 \) state of lycopene was also determined by transient absorption spectroscopy and the kinetics were studied in the 475–650 nm region in two solvents with different polarities [50]. Polivka et al. explored the \( S_1 \) lifetime of spheroidene in \( n \)-hexane by means of near-infrared femtosecond absorption spectroscopy at different temperatures [47]. The lifetime of the first lowest excited state of spheroidene and some other all-trans-carotenoids were also determined by steady-state absorption and fast-transient optical spectroscopic techniques in several solvents [51].

In summary, the lifetime of the \( S_1 \) state is found to be in the range of 4–4.7 ps for lycopene and 8–9.5 ps for spheroidene. It is clear that this lifetime decreases as the conjugation length increases, which is well-confirmed by Frank et al. in [52].

### 2.3.2 The Two ‘Dark’ States \( 1B_u^- \) and \( 3A_g^- \)

Since the \( 1B_u^+ \) state and the \( 2A_g^- \) state have different signs of Pariser’s label [26], the selection rules [26, 28] indicate that vibronic coupling (and, therefore, internal conversion) is not allowed between them. This leads to the conclusion that there must be some electronic states located between the \( S_1 \) and \( S_2 \) to facilitate internal conversion that actually takes place between them. In fact, on applying the multireference double excitation configuration interaction (MRD-CI) method on a Pariser-Parr-Pople (PPP) model Hamiltonian, Tavan and Schulten [20] predicted for shorter polyenes the presence of low-lying excited states including the two previously mentioned \( 1B_u^+ \) (\( S_2 \)) and \( 2A_g^- \) (\( S_1 \)) states and the other two, \( 1B_u^- \) and \( 3A_g^- \). Figure 2.4 shows the extrapolation for the case of carotenoids with \( n = 9 – 13 \) from the energy diagram of low-lying singlet excited states of shorter polyenes with \( n = 5 – 8 \), which was calculated by Tavan and Schulten [32]. It is shown that for carotenoids having conjugation length \( n = 9 – 13 \), the \( 1B_u^- \) state lies between \( S_1 \) and \( S_2 \) and that the \( 3A_g^- \) state may also lie between them. Also seen from the figure is that the regression lines of the \( S_1 \) and \( S_2 \) states are
almost parallel to each other whereas the $1B_u^-$ and $3A_g^-$ exhibit much steeper slopes.

![Energy diagram](image)

Fig. 2.4: (a) Energy diagram for the $1B_u^+(\mu = 0 - 4)$, $2A_g^-(\mu = 0 - 3)$, $1B_u^-(0)$ and $3A_g^-(0)$ vibronic transitions in carotenoids with $n = 8 - 13$. (b) Energy diagram for the $1B_u^+$, $2A_g^-$, $1B_u^-$ and $3A_g^-$ states for carotenoids with $n = 8 - 13$ (all for $\mu = 0$ origin) in solution (thicker solid lines), in the crystalline state (broken lines), and in solution determined by fluorescence spectroscopy (dotted broken line). Figure adapted from [32].

The fact that the optical transitions from the ground state to both the $1B_u^-$ and $3A_g^-$ are not allowed [20] makes it a real challenge to locate these states experimentally in the energy diagram and to explore their properties. The situation becomes even more complicated as these two states will relax quickly to the $S_1$ state if populated, limiting their lifetime to be within the hundred femtosecond timescale.

In 1998, Sashima et al. employed resonance-Raman excitation of the C=C and C–C stretching Raman lines to study crystalline all-trans-spheroidene in a KBr disc at 77 K [53]. The result showed the existence of a new singlet state with energy of 17 600 cm$^{-1}$ located between $S_1$ and $S_2$, which was ascribed to the $1B_u^-$ state. A variety of carotenoids such as β-carotene [21], lycopene [21], mini-9-β-carotene [21],
anhydrohodovibrin [22] were then examined by the same technique in the search for this new excited state. With further experimental work performed using resonance-Raman excitation profiles, the other new singlet excited state, which is ascribed to $3A_g^-$ was first identified by Koyama and co-workers [22] for carotenoids having $n = 10 - 13$. The $3A_g^-$ energies of 19,990 cm$^{-1}$, which almost overlaps the $1B_u^+$ state, was obtained for spheroidene and 18,020 cm$^{-1}$, which is well-separated from the $1B_u^+$, for lycopene. These experimental results for the $3A_g^-$ state are in good agreement with the theoretical predictions through the extraction of the energy of this state.

The development of time-resolved spectroscopy techniques has provided us with a promising approach for searching for the two new singlet excited states $1B_u^-$ and $3A_g^-$ as well as identifying their properties. Zhang et al. was successful in performing sub-picosecond time-resolved absorption spectroscopy in the 840–1,040 nm region to locate the $1B_u^-$ state of neurosporene in nonpolar solvents [54]. The analysis of their results was supported by a powerful tool called singular-value decomposition (SVD) and subsequential models. In this work, stepwise internal-conversion processes in the order $1B_u^+ \rightarrow 1B_u^- \rightarrow 2A_g^-$ were demonstrated. This sequential internal conversion was then confirmed by means of sub-picosecond time-resolved Raman spectroscopy using stimulated Raman processes [55]. By studying time-dependent changes of the excited-state absorption in the 850–1,040 nm region, Fujii et al. identified two different pathways of internal conversion in accordance with the energy diagram determined previously for five carotenoids with $n = 9 - 13$ [41]. Distinct spectral shifts of the excited-state absorption on the time scale of 50–300 fs results in the sequential internal conversion $1B_u^+ \rightarrow 1B_u^- \rightarrow 2A_g^-$ for neurosporene ($n = 9$) and spheroidene ($n = 10$), and $1B_u^+ \rightarrow 3A_g^- \rightarrow 1B_u^- \rightarrow 2A_g^-$ for lycopene ($n = 11$), anhydrorhovibrin ($n = 12$) and sprilloxanthin ($n = 13$).
2.4 Vibrational Relaxation

The relaxation processes within the vibrational manifold of particular electronic states of carotenoids has become one of the main tasks for emerging time-resolved spectroscopy techniques. One of the most popular techniques that has been employed to demonstrate the first allowed excited state $S_2$ is up-conversion fluorescence. This technique was successful in setting the upper limit for the time scale of the $S_2$ vibrational relaxation to about sub-100 fs \cite{38,56}. It was also shown that low-frequency modes exhibit a slower $S_2$ relaxation for some carotenoids such as $\beta$-carotene \cite{57}. The fact that vibrational relaxation in the $S_2$ state occurs extremely fast has challenged the limits of time-resolved spectroscopy, and more studies are required to determine these relaxation rates.

Since the ground state to $S_1$ transition is one-photon forbidden it is impossible to rely on measurements based on this excitation to examine the dynamics in general and relaxation processes in particular. Fortunately, there is strongly allowed absorption from $S_1$ to the some upper excited states, denoted $S_N$ (see Fig. 2.2), and this makes it possible to study the vibrational relaxation in $S_1$. By examining the time dependent changes of the spectral profile of the $S_1 - S_N$ transition, the vibrational relaxation in the $S_1$ state of several carotenoids including lycopene is found to take place on a sub-picosecond time scale \cite{47,50,58}. By taking advantage of this type of measurement, information about the lifetime of $S_1$ is also revealed. The detailed analysis of the time dependent spectral profiles of the $S_1 - S_N$ transition shows that the vibrational relaxation in the $S_1$ state is not affected by the structure of carotenoids having the same number of conjugation length $n = 11$ \cite{17}. Siebert et al. \cite{59} used time-resolved transient grating measurements to study the vibrational cooling in the $S_1$ state of $\beta$-carotene and showed that it occurs in 700 fs.

Femtosecond time-resolved Raman spectroscopy was also employed to follow the vibrational relaxation in carotenoids such as $\beta$-carotene \cite{60,61} and showed sub-
picosecond results. Moreover, this technique helps to differentiate separate processes happening in the vibrational relaxation. Applying the femtosecond time-resolved transient grating technique, Siebert et al. suggested that a fraction of the higher vibrational states in $S_1$ of $\beta$-carotene could relax to the ground state directly, creating a new channel competing with vibrational relaxation [59].

To unravel the vibrational relaxation in the ground state, time-resolved anti-Stokes Raman scattering (CARS) has been extensively employed [62]. The good thing about this technique is that it helps to determine the relaxation times for specific vibrational modes [19]. The vibrational relaxation of the C=C stretching mode was shown to be $<1\text{ ps}$, whereas the other modes exhibit longer relaxation times of 5 ps (C–C) and 12 ps (C–CH$_3$).

2.5 The Complete Picture

Knowledge of the properties of the excited states of the carotenoids given in previous sections helps us to create a complete picture about the relaxation pathways within the manifold of excited states after excitation to the first optically allowed $S_2$ state. The model is presented in Fig. 2.5, which includes the two excited dark states $3A_g^−$ (for $n \geq 10$) and $1B_u^-$ in addition to the other well-known states $S_0$, $S_1$ and $S_2$.

In the relaxation picture, the last relaxation step $S_1 - S_0$ is the best understood so far. Knowledge of the energies and lifetimes of $S_1$ indicates that internal conversion between $S_1$ and $S_0$ follows well the energy gap law for radiationless transitions [63]. Since $S_0$ and $S_1$ have the same $A_g^-$ symmetry, the mechanism involving strong vibrational coupling through the totally symmetric $a_g$ stretching modes was proposed for $S_1 - S_0$ internal conversion. It is also shown by means of picosecond time-resolved resonance Raman spectroscopy [64] and femtosecond transient absorption spectroscopy combined with picosecond Raman spectroscopy [65] that vibrational coupling through the C=C stretching mode plays a central role in the $S_1 - S_0$ internal conversion in the
carotenoids.

After excitation to the $S_2$ state, the ensemble will experience the relaxation pathway to the $S_1$ state. However, the mechanisms driving the carotenoids from the $S_2$ state towards the $S_1$ state are only well explained by the existence of additional states between $S_2$ and $S_1$ which have been experimentally confirmed [21, 22, 53]. It was suggested that the location of a $1B_u^-$ state below the $S_2$ state can mediate the $S_2 - S_1$ internal conversion process since $B_u^-$ and $A_g^-$ both have ‘minus’ Pariser’s labels which allows strong vibronic coupling [21, 53], whereas, vibronic coupling between the $S_2$ ($1B_u^+$) and $1B_u^-$ states is allowed, thanks to the small $S_2 - B_u^-$ energy gap ($\sim 2\,100\,\text{cm}^{-1}$), for which the pseudoparity selection rule can be broken [53]. In summary, the $1B_u^-$ state is shown to be crucial for facilitating the $S_2 - S_1$ internal conversion.

However, for longer carotenoids, the $1B_u^-$ state may fall too far below the $S_2$ state
and it is impossible for a relaxation pathway between \( S_2 - 1B_u^- \) to occur. It is suggested that \( S_2 \rightarrow 1B_u^- \rightarrow S_1 \rightarrow S_0 \) is valid only for neurosporene \((n = 9)\) and spheroidene \((n = 10)\). For longer carotenoids such as lycopene \((n = 11)\), anhydrohovibrin \((n = 12)\) and spirilloxanthyn \((n = 13)\), an acceptable relaxation pathway is \( S_2 \rightarrow 3A_g^- \rightarrow S_1 \rightarrow S_0 \), since the \( 3A_g^- \) state is pushed below the \( S_2 \) state for these carotenoids.

### 2.6 Some New Results

In some recent work, Koyama and coworkers have discussed the presence and absence of electronic mixing in shorter-chain and longer-chain carotenoids [67,68].

In neurosporene, knowing the energies of the \( 1B_u^+ (0) \) (21 300 \( \text{cm}^{-1} \)) and the \( 1B_u^- (0) \) (19 800 \( \text{cm}^{-1} \)) as well as the spacing of the vibronic levels in the \( 1B_u^+ \), \( 1B_u^- \) and \( 1A_g^- \) states (1 450, 1 450 and 1 350 \( \text{cm}^{-1} \), respectively), it was shown that \( 1B_u^+ \) and \( 1B_u^- \) are almost in agreement, i.e., \( 1B_u^+(\mu) = 1B_u^-(\mu + 1) \) with \( \mu = 0, 1, 2, ... \). Using sub-picosecond time-resolved spectroscopy after excitation to the \( 1B_u^+(\mu = 0, 1, 2) \) levels and their analysis by means of singular value decomposition (SVD) followed by global fitting, they observed an apparent sum of stimulated emission from the \( 1B_u^+(\mu) \) and \( 1B_u^-(\mu + 1) \) vibronic states. This has been explained by a new theory based on the diabatic approximation.

A similar result was obtained for spheroidene \((n = 10)\), in which stimulated emission was observed from the mixed vibronic levels of \( 1B_u^+(0) + 1B_u^-(2) \) and \( 1B_u^+(1) + 1B_u^-(3) \), and the order of emission is: \( 1B_u^+(1) + 1B_u^-(3) \) stimulated emission \( \rightarrow 1B_u^+(0) + 1B_u^-(2) \) stimulated emission \( \rightarrow 1B_u^-(0) \) transient absorption. However, in lycopene, anhydrohodovibrin and spirilloxanthin \((n = 11 - 13)\), stimulated emission is from the pure vibronic levels of \( 1B_u^+(0) \) and \( 1B_u^+(1) \). It was explained that the \( 1B_u^+ \) state can mix with the \( 1B_u^- \) state but not with the \( 3A_g^- \) state, both being located just below the \( 1B_u^+ \) state. The order for longer chain carotenoids is: slow internal conversion of either \( 1B_u^+(1) \) stimulated emission \( \rightarrow 1B_u^-(0) \) transient absorption or
Chapter 2

$1B_u^+(0)$ stimulated emission $\rightarrow 1B_u^-(0)$ transient absorption.

Importantly, the presence or absence of diabatic mixing has provided strong support that the symmetries of the next low-lying singlet-excited states are indeed $1B_u^-$ and $3A_g^-$. 
Chapter 3

Femtosecond Spectrally Resolved Three-Pulse Two-Colour Nonlinear Coherent Spectroscopy

The advent of femtosecond lasers has enabled coherent spectroscopy to be extended to measurements of a wide range of rapid dynamical processes in molecules. Various ultrafast nonlinear coherent techniques have been developed for application in a range of scientific fields including physics, chemistry and biology. Following the pioneering work in ‘femtochemistry’ by Ahmed Zewail in the 1980s [69], work on multiple-pulse femtosecond techniques in which more than two laser pulses are used have been developed and exploited [70–74]. By employing multiple femtosecond laser pulses, transitions between different states in molecular systems can be manipulated and probed, allowing various dynamical processes that are hidden by macroscopic inhomogeneous broadening to be unraveled. Important information about molecular dynamics such as decoherence times, vibrational relaxation times, population lifetimes and coherence coupling can thus be extracted.

In this project, femtosecond spectrally resolved three-pulse two-colour nonlinear
coherent spectroscopy has been developed and applied to study the dynamics of two important biological light harvesting molecules, lycopene and spheroidene. This chapter will first give an introduction to the principles of stimulated three-pulse photon echoes and transient grating, followed by a detailed review of our technique. The nonlinear response function that plays a crucial role in the light-matter interaction will be recalled with the introduction of Feynman diagrams. A brief review of the theoretical model for interpretation of the nonlinear optical experimental results will also be presented.

3.1 Photon Echo Spectroscopy and Transient Grating Spectroscopy

3.1.1 Photon Echo Spectroscopy

In a three-pulse photon echo experiment, three ultrashort pulses, which are separated in time by two periods, $\tau$ and $T$, are used (see Fig. 3.1). The first pulse excites the molecule coherently into a superposition of the ground and excited states. In the presence of inhomogeneous broadening, the molecular ensemble will experience some “dephasing” (or decoherence) during the period $\tau$. The second pulse converts the superposition into a population in either the ground or excited state. Since the system is no longer in a superposition state, the phase remains unchanged during the period of time $T$ until the arrival of the third pulse. The third pulse then converts the population back into a superposition of states but with all the phases reversed (this reversal occurs because the second superposition is the Hermitian conjugate of the first [6]), resulting in an echo at time $\tau$ after the third pulse when all the oscillators in the inhomogeneous ensemble will be in phase again. [10].

The basic mechanism of the three-pulse stimulated photon echo can be intuitively understood by means of an analogy to ray optics as shown in Fig. 3.2 [75]. Consider a
system with \( n \) molecules involved in the interaction with three laser pulses that have the same frequency and pulse envelope in a three-pulse photon echo experiment. In a ray optics analogy, each molecule is represented by one ray of light. The interaction first occurs at the start point, then at two focusing lenses. The “dephasing” process, due to different molecules in the ensemble having different transition frequencies, during the time period \( \tau \) after the first interaction, is modelled by the fanning out of \( n \) rays from the initial point with different slopes. During the second period of time \( T \), the phases of all the molecules remain fixed and this process is described by the collimation of the rays after the first lens. On interaction with the third pulse, all the phases are reversed. In the third time period, the rays will be refocussed at a time \( t \) equal to the duration of the time period \( \tau \), and this refocussed beam constitutes the stimulated photon echo.

It is worth keeping in mind that the condition for rephasing, and hence the photon echo, is that the transition in the sample is inhomogeneously broadened. In such a molecular system, different molecules absorb at different frequencies because of different local environments or different initial states [6]. This broadening, which reflects the spread in transition frequencies, is static in nature and carries no dynamical information. In contrast, homogeneous broadening, in which the broadening arises from
elastic and inelastic scattering events, provides valuable information on the dynamical interactions of the molecular system with its environment.

In a three-pulse photon echo experiment, the decoherence time $T_2$ is determined by measuring the intensity of the echo signal as a function of the delay time $\tau$, whereas the population relaxation $T_1$ is determined by scanning the population time $T$. The decoherence time $T_2$ and the population relaxation time $T_1$ are two important relaxation times which describe the dynamical interaction processes of the molecular system. The intensity of the photon echo as a function of $\tau$ has been shown to decay as $\exp(-4\tau/T_2)$ [76–80]. In the case of purely homogeneous broadening, a photon echo is not created (there is no rephasing), the polarization of the system will decay freely and the signal is called free induction decay (FID). This signal appears immediately after the third pulse and decays at a rate of $2/T_2$.

The decoherence time $T_2$, in the absence of inhomogeneous broadening, is related to the population time $T_1$ and the “pure” dephasing time $T_2^*$ by $1/T_2 = 1/(2T_1) + 1/T_2^*$ [81].

Fig. 3.2: Ray optics analogy for the three-pulse stimulated photon echo experiment. Figure adapted from [75].
3.1.2 Transient Grating Spectroscopy

Another way to think of the creation of the three-pulse nonlinear signal is based on the transient grating phenomenon [82]. If two time-coincident laser pulses intersect spatially, an interference pattern is formed. When these two pulses overlap in a molecular ensemble, the interference pattern becomes a spatially modulated excitation, and the molecules in the ensemble experience different electric field intensities according to their position. This leads to a spatially modulated refractive index, which can act as a diffraction grating so long as the distribution of molecules in their ground and excited state remains. This is referred to as a transient grating [7] (see Fig. 3.3). The third pulse (probe pulse), on interaction with the sample, will undergo diffraction from the transient grating, forming a diffracted pulse signal at the Bragg angle, which is equivalent to the phase matching angle. According to diffraction theory, the intensity of the diffracted signal depends on the amplitude of the modulation of the transient grating. The modulation depth of the transient grating depends on the relative
population density of the two molecular states. The dynamics of the excited state population of the sample are therefore reflected in the diffracted intensity as the delay between the pump and probe pulses is varied. It is worth noting that, during the experiment, diffusion of the molecules and/or electrons can also destroy the grating. However, in the samples to be studied here, this occurs over a timescale much longer than the lifetime of the excited state population and so can be ignored.

Coming back to the three-pulse photon-echo set-up in Fig. 3.1, the photon echo can be considered as the diffracted signal of pulse 3 from the grating created by pulses 1 and 2 for the condition of $\tau$ being less than the decoherence time, $T_2$. By scanning the second time period $T$, the intensity of the diffracted signal will reveal the dynamics of the molecular population (either in the ground or the excited state) in the transient grating. From these measurements the lifetime of the state being probed can be determined. The rate constant obtained from this decay is twice the inverse lifetime of the probed state [83].

### 3.2 Third-Order Nonlinear Response Function and Feynman Diagrams

A perturbative description is well established for the interaction of pulsed optical radiation with a molecular sample [6, 84]. In this formalism, the polarization induced in an isotropic medium is expanded in a functional series with odd power elements of the electric fields:

$$P(r, t) = P^{(1)}(r, t) + P^{(3)}(r, t) + P^{(5)}(r, t) + ... = P^{(1)}(r, t) + P^{(NL)}(r, t).$$  

(3.1)
In the case when three short optical pulses with electric fields $E_1, E_2, E_3$ and time delays $t_{12}$ and $t_{23}$ are involved, the induced nonlinear optical polarization is the source of the signal electric field [85, 86]:

$$E_s(t) = \left[\frac{4\pi \omega_s}{\Delta kn(\omega_s)c}\right] \times P^{(NL)}(t) \sin(\Delta kl/2) \exp(i\Delta kl/2) \quad (3.2)$$

where $l$ is the length of the sample, $c$ the speed of light, $\Delta k$ the phase-mismatch factor, and $n(\omega)$ the linear refractive index of the sample. Equation 3.2 is derived in the limit of low optical density and with the electric fields assumed to be plane waves with slowly varying envelopes. When perfect phase matching occurs, i.e., $\Delta k = 0$, the radiated signal field will be directly proportional to the nonlinear polarization.

Four-wave mixing (FWM) spectroscopic signals can be expressed in terms of the third-order nonlinear polarization. According to perturbation theory [6], the third order polarization with wave vector $k_4 = -k_1 + k_2 + k_3$ induced by three laser pulses with electric fields $E_1, E_2$ and $E_3$ can be expressed as [11, 87]:

$$P^{(3)}(t, t_{12}, t_{23}) \approx N(\hbar)^3 \int_0^\infty dt_3 \int_0^\infty dt_2 \int_0^\infty dt_1 [R_A(t_3, t_2, t_1) + R_B(t_3, t_2, t_1)] \quad (3.3)$$

where $N$ is the sample concentration. The optical response functions $R_A$ and $R_B$ are given by:
\[ R_A(t_3, t_2, t_1) = \left[ R_{II}(t_3, t_2, t_1) + R_{III}(t_3, t_2, t_1) \right] \times E_3(t - t_{23} - t_3)E_2(t - t_3 - t_2)E_1^*(t + t_{12} - t_3 - t_2 - t_1) \times exp(-\omega_3(t - t_{23} - t_3)) \times exp(-\omega_2(t - t_3 - t_2)) \times exp(\omega_1(t + t_{12} - t_3 - t_2 - t_1)) \] (3.4)

\[ R_B(t_3, t_2, t_1) = \left[ R_I(t_3, t_2, t_1) + R_{IV}(t_3, t_2, t_1) \right] \times E_3(t - t_{23} - t_3)E_1^*(t - t_{12} - t_3 - t_2)E_2(t - t_3 - t_2 - t_1) \times exp(-\omega_3(t - t_{23} - t_3)) \times exp(-\omega_2(t - t_3 - t_2 + t_1)) \times exp(\omega_1(1 - t_{12} - t_3 - t_2)) \] (3.5)

\( R_I, R_{II}, R_{III}, R_{IV} \) are third-order nonlinear response functions that contain the complete microscopic information for the calculation of the optical response (see Equation 7.11 in [6]). The nonlinear response function has the following physical interpretation in Liouville space: the first interaction with the radiation field sets up an optical coherence in the sample; the second interaction converts this coherence into a population in either the ground or excited state; the system then evolves during the second time separation and the third interaction creates again an optical coherence; finally at time \( t \) the polarization is calculated. The four contributions to the third-order response function represent distinct Liouville space pathways. For an intuitive evaluation of the processes underlying these response functions, double-side Feynman diagrams have proven to be a versatile tool [6, 84]. These diagrams visualize the evolution of the system upon sequential interaction with optical fields and free evolution...
during the time between the interaction. We present here, for example, the Feynman diagrams in the case when the signal is detected in the perfect phase-matching direction $\mathbf{k}_4 = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ for a molecular system with two electronic states, of which the ground state has two vibronic levels, $g$ and $g'$, and the excited state, $e$ and $e'$. According to Equation 7.11 in [6], four-wave mixing signals are generated for any sequence of the three pulses, as long as pulse 1 is not acting as the last pulse. This then gives us four different permutations: $1 - 2 - 3$ (pulse 1 arrives first followed by pulses 2 and 3), $1 - 3 - 2$, $2 - 1 - 3$ and $3 - 1 - 2$ [88]. The Feynman diagrams for these cases are shown in Fig. 3.4 [11].

![Feynman diagrams](image)

Fig. 3.4: Feynman diagrams describing the interaction of three pulses with two electronic levels, each with two vibrational states [11].

When the process is expressed by $R_{II}$ and $R_{III}$, the first and third interactions have opposite phase and a photon echo signal is formed through rephasing of the polarization, provided that the molecular system is inhomogeneously broadened. When the process is expressed by $R_I$ and $R_{IV}$, the first and third interactions have the same phase and the generated signal is a free induction decay (FID). $R_I$ and $R_{II}$ describe the evolution of the excited state population during the population time $t_{23}$ while $R_{III}$ and $R_{IV}$ describe the evolution of the ground state population during time $t_{23}$ [11].
3.3 Spectrally Resolved Femtosecond Three-pulse Two-colour Nonlinear Coherent Spectroscopy

The first photon echo signal was observed by Hartmann et al. when the experiment on a ruby crystal being excited by two short, intense light pulses from a Q-switched ruby laser was performed [76]. Since the pioneering work of Yajima et al. [89], and Weiner and Ippen [90], several forms of photon echo spectroscopy have been demonstrated and applied to study different types of systems [91,92]. In 1985, three-pulse photon echo was first employed by Ippen and co-workers to elucidate the decoherence processes in liquid solutions [90]. In 1996, Fleming and Wiersma [93, 94] suggested measuring the time shift between two photon echo peaks in two phase-matching directions \(-k_1 + k_2 + k_3\) and \(k_1 - k_2 + k_3\) to directly resolve the solvation dynamics. This so-called three-pulse photon echo peak shift (3PEPS) has since become one of the most common three pulse photon echo experiments. With its versatile advantages, three-pulse photon echo peak shift has even been used to study complex biological systems [88, 93, 95–101]. Two other photon echo techniques that should also be noted are time-resolved [102] and heterodyne-detected photon echoes [103,104].

In 1999, Book and Scherer demonstrated that by spectrally resolving the photon echo profile information about molecular dynamics on a very fast time scale (< 100 fs) not apparent from the photon echo peak shift data, could be obtained [105]. It was shown in [105] that contributions from vibrational coupling to the very rapid evolution of the photon echo polarization are apparent ‘at a glance’ in the femtosecond spectrally resolved photon echo (FSRPE) signal . This technique had previously been used to study exciton dynamics in GaAs by Wehner et al. [106]. In 2000, Book and co-workers performed spectrally resolved photon echo experiments to study exciton delocalization and initial dephasing in light-harvesting complex 2 (LH2) of the purple bacterial [107].

Two-colour picosecond stimulated photon echoes were first used by Wiersma and co-workers to elucidate the pathways of vibrational relaxation in pentacene/naphthalene
molecular crystals [108]. Yang and Fleming used two colours for pump and probe pulses in three-pulse photon echo peak shift (3PEPS) to reveal electronic mixing in molecular complexes [109]. They showed in [70] that the most evident type of new information obtained by using two colours instead of only one was the ability to observe dynamics for different regions of the potential surface, perhaps even to map the entire surface, rather than simply describing the disappearance of the initially created population. In the case of photon echo peak shift experiments, the use of two colours provides unique information about the correlation between different initial and final states, since the peak shift method is sensitive to the degree of memory of the transition frequency [88,101,106].

Throughout this thesis, a spectrally resolved three-pulse one- and two-colour femtosecond nonlinear coherent spectroscopy, in which photon echo and transient grating are the main detectable signals, will be employed for the study of two light harvesting biological molecules: lycopene and spheroidene.

3.3.1 Multidimensional Technique

Our spectrally resolved four-wave mixing experiment involves three femtosecond laser pulses illuminating the sample as illustrated in Fig. 3.5. The two pump pulses have the same wavelength $\lambda_1 = \lambda_2$ and wavevectors $\mathbf{k}_1$ and $\mathbf{k}_2$, respectively. The probe pulse has wavevector $\mathbf{k}_3$ and wavelength $\lambda_3$ which can be different to that of the pump pulses. In our experimental set-up, pulse 2 is always fixed in time, whilst the time delay between pulse 1 and pulse 2 and the time delay between pulse 3 and pulse 2 are scanned. The nonlinear signals are detected in two phase-matching directions $\mathbf{k}_4 = -\mathbf{k}_1 + \mathbf{k}_2 + \mathbf{k}_3$ and $\mathbf{k}_6 = -\mathbf{k}_3 + \mathbf{k}_2 + \mathbf{k}_1$ [72]. Two types of experiment are performed: (1) when the delay of pulse 1 is scanned at different fixed delays between pulses 3 and 2; and (2) when the delay of pulse 3 is scanned at different fixed delays between pulses 1 and 2 [9,11].

The use of three-pulse two-colour nonlinear measurements with the above set-up
Fig. 3.5: Schematic set-up of the multidimensional femtosecond three-pulse two-colour nonlinear coherent technique, in which pulse 2 is fixed at zero time delay. Either pulse 1 or pulse 3 can be scanned over a time delay while the other is fixed. The wavelength of the probe pulse $k_3$ can be different from that of the two pump pulses to make a two-colour set-up. The signals can be detected in three phase-matching directions $k_4$, $k_5$ and $k_6$.

provides a technique in which many degrees of freedom in both time and frequency can be controlled, allowing detailed information to be recorded and determined. Firstly, by choosing different wavelengths for the pump and probe pulses, different sets of energy levels in the vibrational manifold can be excited and probed. The redistribution of electrons within the vibrational manifold is dependent on their position in the energy ladder and thus changes in the pump and probe wavelengths can be used to study the photo-induced dynamics and charge transport in the molecules. Secondly, the signals can be detected in three different phase-matching directions at the same time. This availability of multi-channel detection helps to provide supplementary information about the sample being studied when two-colour excitation is employed. When this is the case, i.e. $\lambda_{1,2} \neq \lambda_3$, the FWM signal in the $k_6$ direction will be of a different frequency ($\omega_6 = 2\omega_1 - \omega_3$) to the laser pulses (this does not happen to the signal in the $k_4$ direction), and hence can probe additional information about the vibrational manifold. Thirdly, the ability to scan the delay of two of the pulses, 1 and 3, provides
various possible time-orderings for the three incoming pulses. Depending on the time-ordering of the pulses, the signal can be a stimulated photon echo, a free induction decay, a transient grating, or any combination of these [88].

With all the above possibilities, our three-pulse two-colour nonlinear spectroscopy has become a multidimensional technique. It allows the measurement of the optical decoherence, vibrational relaxation dynamics and vibrational-electronic coupling through the transfer of a coherent ensemble in the vibrational ladder on a femtosecond time scale [9].

### 3.3.2 Time Definition

We define the time axis and delays referred to in this thesis as follows (see Fig. 3.6).

![Diagram](image)

Fig. 3.6: (a) Definition of zero time delay and (b) Time separation between pulse 1 and pulse 2 ($t_{12}$) and time separation between pulse 2 and pulse 3 ($t_{23}$) in a femtosecond three-pulse two-colour coherent nonlinear spectrally resolved experiment.
The zero time point coincides with the arrival time of pulse 2 (Fig. 3.6(a)). \( t_1 \), \( t_2 \) and \( t_3 \) are assigned to be the time at which pulse 1, 2 and 3 arrive, respectively. It is clear that \( t_2 \) is always equal to zero. The time separation between pulse 1 and pulse 2 is called \( t_{12} \) and defined as: \( t_{12} = t_1 - t_2 \). The time separation between pulse 2 and pulse 3 is called \( t_{23} \) and defined as: \( t_{23} = t_3 - t_2 \). Thus, if pulse 1 precedes pulse 2, i.e., \( t_1 < t_2 = 0 \), then \( t_{12} < 0 \); if pulse 2 precedes pulse 1, i.e., \( t_1 > t_2 \), then \( t_{12} > 0 \) (Fig. 3.6(b)). Similarly, \( t_{23} < 0 \) if pulse 3 precedes pulse 2 and \( t_{23} > 0 \) if pulse 2 precedes 3.

In the measurements, when pulse 1 (3) is scanned, the value of \( t_{12} \) (\( t_{23} \)) varies from negative to positive and its absolute value is defined by the position of pulse 1 (3) on the time axis.

### 3.3.3 Photon Echo and Free Induction Decay.

#### Transient Grating

By the interaction of three laser pulses with molecular systems, the signal in a phase-matching direction results from the combination of different nonlinear pathways extracted from the four response functions \( R_I \), \( R_{II} \), \( R_{III} \) and \( R_{IV} \). For an inhomogeneously broadened system, a photon echo is created only for specific pulse orderings that allow rephasing (which can be traced by a Feynman diagram) to occur. Six permutations corresponding to six pulse sequences are possible: 1 – 2 – 3 (pulse 1 comes first, then pulse 2, and pulse 3 comes last), 1 – 3 – 2, 2 – 1 – 3, 2 – 3 – 1, 3 – 1 – 2 and 3 – 2 – 1. The resulting signals based on the six pulse sequences are summarised in Table 3.1 for signals detected in the \( k_4 = -k_1 + k_2 + k_3 \) and \( k_6 = -k_3 + k_1 + k_2 \) directions. Note that the results for \( k_6 \) will be similar to those for \( k_4 \) if the roles of \( k_1 \) and \( k_3 \) are interchanged.

Table 3.1 shows that for the signal in the \( k_4 \) direction, following the time definition described in the previous section for our experiment, a photon echo can occur for
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Table 3.1: Signals resulting from different pulse sequences for the $k_4$ and $k_6$ phase-matching directions. (Note: $^1$ for an inhomogeneously broadened sample; $^2$ for the case of laser pulses with weak field and in the absence of many body interactions only).

<table>
<thead>
<tr>
<th>Pulse sequence</th>
<th>Resulting signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k_4$</td>
<td></td>
</tr>
<tr>
<td>1−2−3 or 1−3−2</td>
<td>3−1−2 or 3−2−1</td>
</tr>
<tr>
<td>2−1−3 or 3−1−2</td>
<td>2−3−1 or 1−3−2</td>
</tr>
<tr>
<td>2−3−1 or 3−2−1</td>
<td>2−1−3 or 1−2−3</td>
</tr>
</tbody>
</table>

negative delays ($t_{12} < 0$) when scanning $t_{12}$, and either positive or negative delays ($t_{23} > 0$ or $t_{23} < 0$) when scanning $t_{23}$ [10]; whereas in the $k_6$ direction, a photon echo can occur for negative delays ($t_{23} < 0$) when scanning $t_{23}$ and either positive or negative delays ($t_{12} > 0$ or $t_{12} < 0$) when scanning $t_{12}$.

From the transient grating point of view, the signal in the $k_4$ direction is a combination of the diffraction of pulse 3 from the transient grating created by pulse 1 and pulse 2, and the diffraction of pulse 2 from the transient grating created by pulse 1 and pulse 3. It should be noted that a grating created by pulse 1 and pulse 3 is difficult to form if $\lambda_{1,2} \neq \lambda_3$, i.e., in a two-colour measurement. When pulse 1 is scanned and pulse 3 is fixed, the two gratings vary with time. And when pulse 1 is scanned far enough from pulse 2 and pulse 3 (i.e., longer than the coherence time), the transient grating will fade away and vanish. When pulse 3 is scanned, the grating created by pulse 1 and pulse 3 still varies with the delay, whereas the grating created by pulse 1 and pulse 2 does not. In the latter case, the grating will evolve as the populations of the molecular states relax to their equilibrium levels, and the intensity of the diffracted signal in the $k_4$ direction will decay as a function of $t_{23}$, giving a long lived transient grating signal. As shown in the previous section, the decay rate of this transient grating signal is twice that of the electric field in the sample, and it can be used to determine the lifetime of the state involved.

Similarly, in the $k_6$ direction, the signal is a combination of the diffraction of pulse
2 from the transient grating created by pulse 1 and pulse 3 and the diffraction of pulse 1 from pulse 2 and pulse 3. Following the same reasoning as with $k_4$, an extended transient grating signal is expected to be seen only when pulse 1 is scanned and is due to diffraction from the grating created by pulses 2 and pulse 3. However, for two-colour experiments, the wavelength of pulse 2 and pulse 3 will be different and since the condition for a perfect grating is that the two pulses have the same wavelength, the transient grating created by pulse 2 and pulse 3 will not be long lived unless there is significant coherent coupling between the two energy levels.

### 3.3.4 Spectrally Resolved Measurements

In photon echo and transient grating measurements, the signal is normally detected as the modulus square of $P^{(3)}$ integrated over all time $t$ for varying values of $t_{12}$ and $t_{23}$:

$$S(t_{12}, t_{23}) \propto \int_0^\infty |P^{(3)}(t, t_{12}, t_{23})|^2 dt$$

(3.6)

In such a time-integrated measurement, information about the temporal evolution of the nonlinear polarization is lost [88,105]. The time resolved emission can be obtained by acquiring time-gated or heterodyne-detected measurements [103,104].

Another way to obtain additional information about the FWM polarization that avoids time gating is to spectrally disperse the signal with a spectrometer and to detect it as a function of wavelength rather than time [72,105]. The frequency dependent nonlinear polarization is related to the time dependent nonlinear polarization by a Fourier transformation with respect to $t$:

$$\tilde{P}^{(3)}(\omega, t_{12}, t_{23}) \propto \int_{-\infty}^{\infty} P^{(3)}(t, t_{12}, t_{23}) exp(\omega t) dt$$

(3.7)
Under conditions of perfect phase matching and neglecting absorption, the (time-integrated) signal field radiated by this polarization is given by:

\[ E_s(\omega, t_{12}, t_{23}) \approx \left[ 2\pi \text{i}\omega / n(\omega)c \right] \tilde{P}^{(3)}(\omega, t_{12}, t_{23}) \]  

(3.8)

and the spectrally resolved photon echo signal is then

\[ S_{WPE}(\lambda_D, t_{12}, t_{23}) \propto |\tilde{P}^{(3)}(\lambda_D, t_{12}, t_{23})|^2 \]  

(3.9)

where \( \lambda_D \) is the wavelength detected by the monochromator.

While the time-resolved and spectrally resolved FWM signals arise from the same nonlinear polarization, they can not be analytically interchanged by Fourier transformation because the intensity measurements lose the phase information in both the time and wavelength domain. Heterodyne-detected FWM methods bridge this gap but are considerably more difficult, especially in the optical regime [105]. However, in order to construct the complex nonlinear response function that completely describes the interaction between the optical radiation and the system under investigation, knowledge of both the amplitude and phase of the nonlinear signal is essential.

3.4 Theoretical Models

It was mentioned in previous sections that the third-order nonlinear response function contains the complete microscopic information for the calculation of the optical response function. In order to quantitatively interpret the nonlinear femtosecond experimental results, one needs to define all interactions and dynamical processes in the
studied system that describe the optical response function. This has become more and more challenging as more and more complex systems are studied by various femtosecond nonlinear techniques.

For sufficiently simple systems with only a few degrees of freedom, an exact fully quantum mechanical treatment is applicable. Multi-level Bloch equations [6] or a driven oscillator model [110] are required to interpret experimental data for more complex systems, such as large molecules or condensed phase systems. However, for elucidating molecular motions in liquids, these models were proven to be inadequate by Shank and co-workers [80]. Using femtosecond photon echo measurements, they showed that optical dephasing in solutions occurs on multiple time scales, and as a result the theoretical description requires a more advanced model than the Bloch one. For example, the basic models fail to predict the Stokes shift in emission, for which the dynamics give a direct indication of the presence of energy relaxation processes involving both the solute and solvent [111]. These particular energy reorganisation processes are especially interesting as they play a vital role in electron transfer systems [112] and (primary) biological functional units [113].

In parallel with the rapid development of femtosecond laser techniques, coherence nonlinear theoretical models have been developed to provide a successful description of the optical dynamics in liquids [6]. Modelling of the system-bath interaction using the spin-boson Hamiltonian and multimode Brownian oscillator model (MBO) was first introduced by Mukamel et al. [114–116] and has quickly been developed and shown to be an advance on previous theoretical models. The key components of the MBO model are the correlation function $M(t)$, the reorganisation energy $\lambda$, the coupling strength, and the line-shape function $g(t)$. The correlation function is often modelled as a sum of Gaussian, exponential, and damped cosine components. These modes represent the inertial and diffusion solvation responses and the intramolecular vibrational modes, respectively. $M(t)$ helps one to derive the line-broadening $g(t)$, from which the third-order response functions are calculated [6].
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Photon echoes and other nonlinear optical spectroscopies have often been interpreted within the MBO model. It has been proven that the relationship between the correlation function $M(t)$ of a system and experimental observables is well-defined. Therefore, the determination of $M(t)$ has been performed for a wide range of systems. One of the most successful results is the work by de Boeij and co-workers for the dye molecule DTTCI (3,3'-diethylthiatricarbocyanine iodide) in several solutions to extract $M(t)$ [88]. De Boeij and co-workers have performed different measurements including three-pulse stimulated photon echo, time-gated photon echo, and transient grating measurements and have used $M(t)$ to fit the experimental data. These correlation functions all featured an initial rapidly decaying component that causes the correlation function to decay to about half of its initial value in about 30 fs. This ultrafast loss of correlation was attributed to ‘a free induction-like’ decay, produced by excitation of vibrational structure across the whole absorption band [88]. To confirm this, more experimental data are necessary. From the results of spectrally resolved stimulated photon echo measurements on DTTCI in methanol, Book and Scherer argued that it would be necessary to model more accurately both the spectrum of high frequency modes coupled to the optical excitation and the mechanism that dephases them in order to account for their experimental measurements [105].

Therefore, the complete analysis of the experimental data for complex systems requires further development of the theoretical models.
Chapter 4

Experimental Section

4.1 Ultrafast Laser System

The laser system in our experiment consists of a diode-pumped frequency doubled $\text{Nd:YVO}_4$, cw laser (Millennia) that provides 5 W of green 532 nm output to pump a mode-locked Ti:Sapphire oscillator (Tsunami). The Tsunami laser has a long cavity able to run at repetition frequencies near 82 MHz and produce 800 nm, 60 fs pulses with an average power of about 1 W (energy 12 nJ). These single pulses are then amplified by a Ti:Sapphire regenerative amplifier (Spitfire) pumped by a 15 W, 1 kHz Q-switched diode-pumped Nd:YLF laser (Evolution) with an overall amplification of about $10^5$. The technique employed here involves stretching the input pulse from the Tsunami, amplifying at reduced peak power, then recompressing the amplified pulse. The result is an 800 nm amplified pulse with an energy of about 1 mJ at a repetition rate of 1 kHz and a pulse width of about 80 fs. This amplified pulse is then split and used to pump two optical parametric amplifiers (OPAs) before being tuned to illuminate the sample (Fig. 4.1).

The OPAs are capable of producing high energy femtosecond pulses (typically 10–100 µJ) at kHz repetition rates which are tunable over a broad wavelength region. An
Fig. 4.1: The ultrafast laser system.

OPA operates on a different principle from that of a laser as it derives its gain from a nonlinear frequency conversion process. This conversion is performed through the process of stimulated down-conversion in a nonlinear optical crystal, where a pump photon ($\lambda_p$) is converted into a lower photon energy signal ($\lambda_s$) and idler ($\lambda_i$), provided that energy and momentum are conserved:

\[ k_p = k_s + k_i. \]  \hspace{1cm} (4.1)

\[ \frac{1}{\lambda_p} = \frac{1}{\lambda_s} + \frac{1}{\lambda_i}. \]  \hspace{1cm} (4.2)

With the use of two optical crystals BBO type I and BBO type II, a broad range of wavelengths (300–2500 nm) can be produced when different frequency conversion processes of the signal or idler pulse and the fundamental beam are applied (second
harmonic generation, fourth-harmonic generation or sum frequency generation). The pulses from these two OPAs have a duration of about 100 fs and bandwidth of about 7–10 nm with a repetition rate of 1 kHz. Since the vibrational energy splitting of lycopene and spheroidene is 1 100–1 400 cm$^{-1}$ (which is much larger than the bandwidth of our femtosecond laser pulse), the femtosecond laser pulses can be used for the elucidation of energies of the specific vibrational levels of these two carotenoids.

4.2 Experimental Set-up

The layout of the set-up used for our experiment is displayed in Fig. 4.2. Three beams of pulses assigned $E_1$, $E_2$ and $E_3$ which are available from the two OPAs are involved in the experiment. The beam from OPA 1 is split by a 50:50 beam-splitter into two beams, which are pulse 1, $E_1$, and pulse 2, $E_2$. OPA 2 gives the third pulse $E_3$. The first pulse then passes through a translation stage to provide a delay relative to the second pulse by a designated time $t_{12}$. The third pulse passes through a second translation stage to provide a delay relative to the second pulse, designated by $t_{23}$. The three pulses are subsequently aligned to be almost parallel to each other before being focussed by a 25 cm convex lens into the sample. On the surface of the lens, the three pulses form a triangle with approximately 1 cm size. Assuming the energy output from the OPAs is about 0.2 $\mu$J and the beam diameter 2 mm, then the beam waist at the focus point (impinging on the sample) is about 150–200 $\mu$m with the peak intensity about $10^{11}$ W/cm$^2$. The energy of the excitation pulses is kept as low as possible to minimise intensity dependent effects. The polarizations of the three beams are made to be parallel.

A quartz cuvette with 1 mm path-length is used to contain the sample solution. To avoid sample bleaching, a stirring system is used, in which a small magnet is rotated in the sample solution by a motor magnet.

The phase-matching geometry of the experiment is shown in the inset of Fig. 4.2.
Fig. 4.2: Experimental set-up for femtosecond spectrally resolved FWM nonlinear spectroscopy (M-mirror; BS-Beamsplitter; L-lens)
The signals are detected in the directions $k_4 = -k_1 + k_2 + k_3$ and $k_6 = -k_3 + k_1 + k_2$ and the third laser pulse is simultaneously detected in the direction $k_3$. They are analysed by two imaging spectrometers: SPEX Model 1681, 0.22 m and ORIEL Model 77480 MS127i, 0.125 m. The spectrometers are calibrated using a mercury lamp. The spectra of the first spectrometer (SPEX) are detected by a Dual-GARRY 3000 series linear CCD with $2 \times 3000$ pixels and pixel size $200 \mu m (H) \times 7 \mu m (W)$. The second spectrometer (ORIEL) is connected to the linear GARRY 3000 series CCD. The intensity of the signals is reduced by neutral density filters before entering the input slits of the spectrometers.

The spectra were measured at different fixed times $t_{12}$ or $t_{23}$ by scanning the other delay time. The scanning is performed by two independent NEWPORT scanned stages Model ESP 300. Time zero for $t_{12}$ is defined as when pulses 1 and 2 overlap and for $t_{23}$ when pulses 2 and 3 overlap. This means that when all three pulses overlap, both $t_{12}$ and $t_{23}$ are equal to zero. These time delays can be scanned over a range as long as 200 ps with step size as short as 6 fs. The wavelength of pulse 3 can be made different from the wavelength of the other two pulses in order to perform the two-colour experiments.

All measurements were taken in dark surroundings to avoid scattering effects. The measuring program allowed us to perform a large sequence of different scans. The data collection was then extracted and made available to be analysed in detail.

### 4.3 Sample Preparation and Handling

All-trans-lycopene and -spheroidene were supplied by the group of Professor Yasushi Koyama, Faculty of Science and Technology, Gakuin University, Sanda, Japan. They were extracted and isolated from different organisms: spheroidene from *Rhodobacter sphaeroides* 2.4.1 [43] and lycopene from tomato [117]. The two samples were stored in three small foil-covered glass tubes when received. They were all at high concentration.
in the solvent \( n \)-hexane.

Since all-trans-carotenoids can easily suffer from unexpected degradation processes, a vital step is the preparation and handling of the carotenoids. Carotenoids can be degraded by a number of factors such as high temperatures, light, oxygen, acids, long processing time,… Due to degradation, all-trans-carotenoids may be converted to cis-isomers as additional energy input results in an unstable more readily oxidizable form of the carotenoids. Figure 3 in [118] shows some different forms of cis-isomers of \( \beta \)-carotene. According to [118], cis-isomerisation of the carotenoids results in a slight loss in colour, a small hypochromic shift (usually 2 to 6 nm for mono-cis) and a hypochromic effect, accompanied by the appearance of a “cis” peak about 142 nm below the longest-wavelength absorption maximum of the all-trans-carotenoids when measured in \( n \)-hexane (see Fig. 6 of [118]). This provides an easy way to roughly examine the trans–cis conversion of our samples by measuring their absorption spectra.

To avoid undesirable degradation, the samples were quickly stored at a temperature of \(-80^\circ\text{C}\) immediately after arriving from Japan. For our experiments, lycopene and spheroidene are dissolved in \( n \)-hexane at a concentration of \( \sim 10^{-6}\text{ M} \). The concentration of these two carotenoids was determined by use of the following molar extinction coefficients: 173 600 M\(^{-1}\) cm\(^{-1}\) at 452 nm for spheroidene and 181 500 M\(^{-1}\) cm\(^{-1}\) at 470 nm for lycopene [49]. The sample preparation and processing were performed as quickly as possible under the conditions of low light, room temperature and minimal exposure to oxygen. Samples when not in use were again stored at \(-80^\circ\text{C}\). Each measurement in our experiment usually lasts about 1 hour. During this time, the sample is kept in a quartz cell that is tightly sealed to avoid oxygen. The samples are circulated by a stirring system as mentioned in section 4.1 and the laser intensity is kept as low as possible to minimise heating.

Some measurements were taken to check the degradation of the sample against the experimental and processing conditions. Figure 4.3 shows the absorption spectra of lycopene in \( n \)-hexane in two cases: (1) pure trans-lycopene and (2) pure trans-lycopene
after a 1 hour experimental measurement. The results show that the degradation rate of the sample is negligible because the “cis” peak is almost the same for both cases and the spectra remain constant. We carried out absorption measurements before and after each experimental measurement to ensure our experimental data was from the pure trans-carotenoids and was reliable.

Fig. 4.3: Absorption spectra of Lycopene in two cases: under normal conditions and after a 1-hour experiment.

4.4 Experimental Measurements

4.4.1 Absorption Measurements

The absorption measurements were taken using a Shimadzu UV-spectrometer that can detect a broad range of wavelengths (190–1 100 nm). Figure 2.3 presents our results of the absorption spectra measurements of lycopene and spheroidene in n-hexane solution. Both spectra show their three-peak features corresponding to the allowed absorption of
three vibrational energy levels of the first allowed excited state $1B_{u}^{+}$. For spheroidene ($n = 10$), the three peaks are 427 nm, 453 nm and 484 nm and for lycopene ($n = 11$), they are 443 nm, 470 nm and 502 nm. The “cis”-peak in the three absorption spectra is negligibly small in comparison with the other peaks, confirming the purity of both samples.

4.4.2 Femtosecond Spectrally Resolved Three-Pulse Two-Colour Nonlinear Measurements

In our experiment, we need to determine the fixed time $t_{12}$ ($t_{23}$) and the scan time $t_{23}$ ($t_{12}$) for each measurement. As a result of the laser system and the time scale properties of the carotenoid samples, two types of measurement were performed:

1. A short-scan measurement: the fixed time was in the range of $-180$ fs to $180$ fs while scanning the other delay time for about $-1000$–$1000$ fs.

   • scan $t_{12}$ with fixed $t_{23}$
   • scan $t_{23}$ with fixed $t_{12}$

2. A long-scan measurement: the fixed time was in the range of $-20$ fs to $20$ fs while scanning the other delay time for about 10 ps.

   The wavelengths of the three laser pulses in our experiment were chosen based on the absorption spectra of the three samples for the purpose of exciting different electronic energy levels and vibrational energy levels, both allowed and forbidden levels. The wavelength of pulse 3 may be chosen to be different from that of the other two pulses, giving a variety of combination wavelengths for the measurement.

   The laser plays an important role in determining the quality of the signal. For each measurement, the laser was checked carefully and was carefully tuned for its pulse width, spectrum and stability.
The experimental measurements were performed for lycopene and spheroidene.

4.5 Convolution of laser pulse with sample response

In our experiments, the duration of the laser pulse ($\sim 100$ fs) may be comparable with the lifetime of the energy levels of the studied molecules. The signal we record, therefore, may be affected by the laser pulse. In this section, this effect is investigated.

For our experiments, there are two cases of interest: (1) dephasing signal with short dephasing time and (2) decay signal with long life time.

4.5.1 Convolution of laser pulse with a dephasing signal

Figure 4.4 shows the results of the convolution of dephasing signals with a Gaussian laser pulse having a full width at half maximum (FWHM) of 100 fs for cases when the dephasing times are: (a) 120 fs, (b) 200 fs and (c) 300 fs. The convolution process is performed in a MATLAB environment. In order to compare quantitatively the original dephasing signals with the convoluted signals, the convoluted signals are fitted with a single exponential decay component function $A_1 \exp((t - A_2)/(T_{\text{convoluted}}/4))$. The region chosen to be fitted is the one in which the intensity is less than or equal half the maximum intensity. This is the region of interest when studying the dephasing time. The fitted results are shown in Tab. 4.1.

Table 4.1: Fitted results for the convoluted signals (green) in Fig. 4.4. The fit function is $A_1 \exp((t - A_2)/(T_{\text{convoluted}}/4))$.

<table>
<thead>
<tr>
<th>$T_{\text{dephase}}$ (fs)</th>
<th>120</th>
<th>200</th>
<th>300</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>0.61</td>
<td>0.57</td>
<td>0.56</td>
</tr>
<tr>
<td>$A_2$</td>
<td>-50</td>
<td>-60</td>
<td>-70</td>
</tr>
<tr>
<td>$T_{\text{convoluted}}$ (fs)</td>
<td>136</td>
<td>204</td>
<td>301</td>
</tr>
</tbody>
</table>
The fitted results show that the convoluted signals decay slower by 16 fs (136 fs compared with 120 fs), 4 fs and 1 fs compared with the original ones for the three cases (a), (b) and (c), respectively. This means that the effect of the laser pulse on the sample decay is about 2% or less if the sample dephasing time is 200 fs or more.

In our real experiments, the laser pulse, however, is not always exactly 100 fs in duration. To study the effect of a laser pulse with different durations on the sample response, another simulation has been made. Figure 4.5 shows the convoluted signals of a signal having a dephasing time of 200 fs with Gaussian laser pulses having FWHM of 80 fs, 100 fs, 120 fs and 150 fs. The fitted results in Tab. 4.2 show that the convoluted signals decay slower by 1 fs, 4 fs, 10 fs and 20 fs compared with the original one for laser pulses having FWHM of 80 fs, 100 fs, 120 fs and 150 fs, respectively. These results indicate that for a dephasing time of 200 fs it is important to have laser pulses that have a short and stable duration of < 120 fs in order for the sample response to be
affected by < 5%.

![Graph showing convolution of Gaussian laser pulse with sample response](image)

**Fig. 4.5**: Convolution of a Gaussian laser pulse having FWHM = 80, 100, 120 and 150 fs with the response of the sample having a dephasing time of 200 fs.

**Table 4.2**: Fitted results for the convoluted signals of laser pulses having FWHM of 80, 100, 120 and 150 fs with the dephasing signal of dephasing time 200 fs. The fit function is $A_1 \exp((t - A_2)/(T_{\text{convoluted}}/4))$.

<table>
<thead>
<tr>
<th>FWHM (fs)</th>
<th>80</th>
<th>100</th>
<th>120</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>0.56</td>
<td>0.57</td>
<td>0.58</td>
<td>0.55</td>
</tr>
<tr>
<td>$A_2$</td>
<td>-60</td>
<td>-60</td>
<td>-70</td>
<td>-70</td>
</tr>
<tr>
<td>$T_{\text{convoluted}}$ (fs)</td>
<td>201</td>
<td>204</td>
<td>210</td>
<td>220</td>
</tr>
</tbody>
</table>
4.5.2 Convolution of laser pulse with a lifetime signal

In our lifetime measurement (transient grating experiment), the signals can show up as a long decay on a ps time scale. Figure 4.6 shows the convoluted signals of a Gaussian laser pulse having FWHM of 100 fs and signals having: (a) $T_{\text{decay}} = 4 \text{ ps}$, (b) $T_{\text{decay}_1} = 400 \text{ fs}$ and $T_{\text{decay}_2} = 4 \text{ ps}$, and (c) $T_{\text{rise}} = 200 \text{ fs}$ and $T_{\text{decay}} = 4 \text{ ps}$.

![Convolution of laser pulse with lifetime signals](image)

Fig. 4.6: Convolved signals (dashed line) of a Gaussian laser pulse having FWHM of 100 fs (solid line) with lifetime signals (dash-dot line) having: (a) $T_{\text{decay}} = 4 \text{ ps}$, (b) $T_{\text{decay}_1} = 400 \text{ fs}$, $T_{\text{decay}_2} = 4 \text{ ps}$, and (c) $T_{\text{rise}} = 200 \text{ fs}$, $T_{\text{decay}} = 4 \text{ ps}$.
Table 4.3 shows the fitted results for the convoluted signals. In all three cases, the laser pulse shows no effect on the long decay components of the signals as the convoluted signal decays with a same rate (4 ps). In case (b), the short decay component increases by 1.5 fs from the original signal (401.5 fs compared with 400 fs). In case (c), the rise component of the convoluted signal is different from the one of the original by 4% (208 fs compared with 200 fs).

Table 4.3: Fitted results for the convoluted signals (green) in Fig. 4.6. The fit functions are: $A \exp(-t/(T_{\text{decay}}/2))$ for (a), $A_1 \exp(-t/(T_{\text{decay1}}/2)) + A_2 \exp(-t/(T_{\text{decay2}}/2))$ for (b) and $-A_1 \exp(-t/(T_{\text{rise}}/2)) + A_2 \exp(-t/(T_{\text{decay}}/2))$ for (c).

<table>
<thead>
<tr>
<th></th>
<th>(a)</th>
<th>(b)</th>
<th>(c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A$</td>
<td>1.0</td>
<td>$A$ 0.20</td>
<td>$A_1$ 0.06</td>
</tr>
<tr>
<td>$T_{\text{decay}}(ps)$</td>
<td>4.0</td>
<td>$T_{\text{decay1}}(fs)$ 401.5</td>
<td>$T_{\text{rise}}(fs)$ 208</td>
</tr>
<tr>
<td>$A_2$</td>
<td>0.77</td>
<td>$A_2$ 1.07</td>
<td></td>
</tr>
<tr>
<td>$T_{\text{decay2}}(ps)$</td>
<td>4.0</td>
<td>$T_{\text{decay}}(ps)$ 4.0</td>
<td></td>
</tr>
</tbody>
</table>

To study the effect of a laser pulse with different durations on the sample response, again another simulation was made. The signal with two decay components in Fig. 4.6 (b) was chosen to be convoluted with laser pulses having FWHM = 80, 100, 120 and 150 fs. The results are shown in Fig. 4.7.

The fitted results for the convoluted signals in Tab. 4.4 show that the long decay components are not affected, whereas the short decay components increase by 1, 1.5, 4 and 9 fs for the case of laser pulses having FWHM = 80, 100, 120 and 150 fs, respectively. The results indicate that for a short decay component of life time 400 fs it is important to have laser pulses having a short and stable duration of $< 150$ fs in order for the sample response to be affected by $\lesssim 2\%$.

The results which are obtained in this section will be taken into account to determine the error of the dephasing time studied in Chapter 6 and of the life time studied in Chapter 5 for lycopene and spheroidene.
Fig. 4.7: Convolution of a Gaussian laser pulse having FWHM = 80, 100, 120 and 150 fs with the response of the sample having two decay components $T_{\text{decay}_1} = 400 \text{ fs}$, $T_{\text{decay}_2} = 4 \text{ ps}$.

Table 4.4: Fitted results for the convoluted signals of a laser pulse having FWHM of 80, 100, 120 and 150 fs with a life time signal having two decay components $T_{\text{decay}_1} = 400 \text{ fs}$, $T_{\text{decay}_2} = 4 \text{ ps}$. The fit function is $A_1 \exp(-t/(T_{\text{decay}_1}/2)) + A_2 \exp(-t/(T_{\text{decay}_2}/2))$.

<table>
<thead>
<tr>
<th>FWHM (fs)</th>
<th>80</th>
<th>100</th>
<th>120</th>
<th>150</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A_1$</td>
<td>0.20</td>
<td>0.20</td>
<td>0.20</td>
<td>0.19</td>
</tr>
<tr>
<td>$T_{\text{decay}_1}$ (fs)</td>
<td>401</td>
<td>401.5</td>
<td>404</td>
<td>409</td>
</tr>
<tr>
<td>$A_2$</td>
<td>0.75</td>
<td>0.77</td>
<td>0.78</td>
<td>0.80</td>
</tr>
<tr>
<td>$T_{\text{decay}_2}$ (ps)</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
</tr>
</tbody>
</table>
Chapter 5

Population Dynamics

In our experimental set-up, the spectrally resolved two-colour three-pulse nonlinear signal is detected in two phase-matching directions \( k_4 = -k_1 + k_2 + k_3 \) and \( k_6 = -k_3 + k_2 + k_1 \). In the \( k_4 \) direction, when pulse 3 is scanned and \( t_{12} \approx 0 \), a transient grating-like signal featuring a long ‘tail’ during the delay time \( t_{23} \) can be detected, whereas when pulse 1 is scanned, the long transient grating-like signal is not generated and a photon echo can show up. In this chapter, the transient grating signal in the \( k_4 \) direction is analysed to study the vibrational relaxation and internal conversion processes occurring within the molecular systems of lycopene and spheroidene as well as the life time of their dark state \( S_1 \).

An important feature of our three pulse nonlinear four-wave mixing technique is the availability of different colours for the pump and the probe pulses. By taking advantage of two colours, information about vibrational relaxation processes among certain vibrational levels of the same electronic state can be deduced.

We consider the interaction of optical pulses with an inhomogeneously broadened ensemble of two-electronic state molecules with a ground state comprising two vibrational levels \( |g\rangle, |g'\rangle \) and an excited state with two vibrational levels \( |e\rangle, |e'\rangle \) [8]. Figure 5.1 shows a schematic illustration of two-colour three-pulse excitation
for this molecular system for the cases: (a) and (b) $\lambda_1 = \lambda_2 < \lambda_3$; and (c) and (d) $\lambda_1 = \lambda_2 > \lambda_3$. The signals are all detected in the $k_4$ direction and have a frequency centred at $\omega_4 = \omega_3 \pm \delta \omega_4$, where $\pm \delta \omega_4$ denotes a frequency shift. It is worth noting that the transitions described in Fig. 5.1 are allowed only if they satisfy the Frank-Condon principle, and that diagrams (c) and (d) are possible only if $\lambda_3$ is at the maximum of the absorption spectrum of the ensemble.

![Diagrams](image)

Fig. 5.1: Schematic illustration of two-colour three-pulse excitation of a two-electronic state molecular system in two cases: (a) and (b) $\lambda_1 = \lambda_2 < \lambda_3$; and (c) and (d) $\lambda_1 = \lambda_2 > \lambda_3$. The signal is detected in the $k_4$ direction. Vibrational relaxation in the ground state and excited state are illustrated in cases (c) and (b), respectively.

When the time ordering of the three pulses is $1 - 2 - 3$ and the first two pulses are tuned to the transition $|g\rangle \rightarrow |e'\rangle$ (Fig. 5.1 (a) and (b)), the first pulse $k_1$ creates optical coherences $\rho_{e'g}$ or $\rho_{ge'}$ and the second pulse $k_2$ generates a population in the ground state $\rho_{gg}$ (a) or the excited state $\rho_{e'e'}$ (b), both of which are coupled to the optical
coherences $\rho_{eg}$ and $\rho_{ge'}$. The third pulse with wavelength longer than the other two pulses can probe the transition between $|g\rangle$ and $|e\rangle$, (a), or $|g'\rangle$ and $|e'\rangle$, (b). This third interaction converts the populations $\rho_{gg}$ (a) or $\rho_{e'e'}$ (b) back into optical coherences $\rho_{ge}$ (a) or $\rho_{e'g'}$ (b), in which the phases of the frequency components are opposite to those of the initial optical coherence contributions. As mentioned previously, for an inhomogenously broadened ensemble, this rephasing of the polarization generates a photon echo signal at a time near $t = t_{12}$ after the third pulse in the phase-matching direction, in this case $k_4 = -k_1 + k_2 + k_3$. The frequency of the signal is $\omega_4 = \omega_3 \pm \delta \omega_4$, where $\delta \omega_4$ allows for a frequency shift associated with the transfer of optical coherence to other transitions. If the third pulse probes the transition $|e'\rangle \rightarrow |g'\rangle$ (b), the population $\rho_{e'e'}$ that was created previously may relax to the lower vibrational level $|e\rangle$ in the excited state vibrational manifold.

If the two pump pulses are resonant with levels $|g'\rangle$ and $|e'\rangle$ (Fig. 5.1 (c) and (d)), the optical coherences $\rho_{g'e'}$ (c) or $\rho_{e'g'}$ (d) can be created and the populations $\rho_{g'g'}$ (c) or $\rho_{e'e'}$ (d) are generated, respectively. The third pulse with shorter wavelength probes the transition $|g\rangle \rightarrow |e'\rangle$ and population relaxation in the ground state level (from $|g'\rangle \rightarrow |g\rangle$ (c)) can occur.

In conclusion, when $\lambda_{1,2} < \lambda_3$, relaxation in the excited state vibrational manifold and transfer of optical coherence to other transitions determine the behaviour of the four-wave mixing signal. When $\lambda_{1,2} > \lambda_3$, it is relaxation in the ground state vibrational manifold and transfer of optical coherence to other transitions that determine the behaviour of the signal.

We note that when the splitting in the ground and excited electronic states (splitting $ee'$ and $gg'$) are similar (to within less than the bandwidth of the laser pulses), the probability to drive the molecule from the second vibrational level of the ground state is rather small (the transition between the first vibrational level of the ground state and the first vibrational level of the excited state may be driven instead). In order to take full advantage of the option in Fig. 5.1 (c) and (d), the wavelength of the pump
pulses should be chosen so that it is resonant with the transition between the second vibrational level of the ground state with the first vibrational level of the excited state. Relaxation of the population in the ground state can then be generated and deduced.

In order for the population in the ground or excited state to be generated properly by the interaction of the second pulse, the time separation between the first pulse and second pulse needs to be less than the relaxation time of the coherence between the relevant levels. The best way to study the population relaxation is when the two pump pulses temporally overlap in the sample. In this case, the signal that is detected in the $k_4$ direction when the delay of pulse 3 is scanned is a long transient population grating signal. By studying the population grating, one can probe the transfer of population as long as the wavelength of the pump and probe are tuned to the proper values.

It should be noted that in a standard transient grating experiment, the intensity of the third pulse should be low in comparison with that of the two pump pulses. In our experiment, the intensity of three laser pulses are rather comparable. The transient grating signal obtained in our experiments hence should be called “transient grating-like” signal. However, this transient grating-like signal behaves much the same as the transient grating signal that was introduced in Chapter 3.

In the case of lycopene, 472 nm, 503 nm and 530 nm were chosen as the wavelengths of the pump and probe pulses in order to study the vibrational relaxation in the ground state $1A_g^-$ and the first allowed excited state $1B_u^+$. 

5.1 Vibrational Relaxation in the Ground and First Allowed Excited State of Lycopene

5.1.1 Excited State \((1B_u^+)\) Vibrational Relaxation

Figure 5.2 shows the intensity versus scan time \(t_{23}\) of the spectrally resolved signal at the central wavelength when lycopene is excited by three laser pulses having wavelength (1) \(\lambda_{1,2} = \lambda_3 = 472\,\text{nm}\) and (2) \(\lambda_{1,2} = 472\,\text{nm}, \lambda_3 = 503\,\text{nm}\). The signals are detected in the \(k_4\) direction with the fixed time \(t_{12}\) set to zero. The signal in each case has the same wavelength as the third pulse, which is 472 nm and 503 nm, respectively.

In the first case, when the two pump pulses having wavelength 472 nm overlap in time in the sample, a grating of polarized molecules is created because of the intensity modulation. The signal in the \(k_4\) direction is the result of the probe pulse scattering off this grating, and is a transient grating-like signal. Since the pump pulses excite the transition \(1A_g^-(0) - 1B_u^+(1)\), the modulation of the grating is proportional to the population of the molecules either in the \(1A_g^-(0)\) level or the \(1B_u^+(1)\) level. When this population decays, the grating, and hence the transient grating-like signal, will decay during the delay time with a rate given by twice the population decay rate (as analysed in Chapter 3). It is clearly seen that the signal intensity displays a long decay over the scan time (Fig. 5.2 (a)). The same feature occurs for the case when the probe pulse has the wavelength 503 nm, where the transient grating-like signal originates from the transition \(1A_g^-(0) - 1B_u^+(0)\) (Fig. 5.2 (c)).

For long delay times (> 1 ps), the transient grating signals simply reflect the recovery time of the molecules in the ground state. For shorter delay times, however, the signal can have a contribution from other processes depending on which transition the laser probes. The transient grating signal for the case when the probe wavelength is 503 nm (Fig. 5.2 (c)) displays a rising component near zero time delay before it follows a long decay, whereas no rise component is seen in the signal when the probe wavelength
is 472 nm (Fig. 5.2 (a)). Comparing the light-molecule interaction energy schematics for the two cases, the rising component of the signal when probing the transition $1A_g^-(0) - 1B_u^+(0)$ is believed to arise from vibrational relaxation in the excited state. This is precisely what is expected for the case when the pump wavelength is shorter than the probe wavelength ($\lambda_{1,2} < \lambda_3$) as discussed earlier in this chapter (see Fig. 5.1 (b)).

A function which is the summation of an exponential rise component and an exponential decay component, $-A_1 \exp(-t_{23}/(T_{rise}/2)) + A_2 \exp(-t_{23}/(T_{decay}/2))$, is used to fit the transient grating-like signal plotted in Fig. 5.2 (c). (Here we use the
factor \( T_{\text{rise}}/2 \) and \( T_{\text{decay}}/2 \) because the decay rate of the transient grating signal is twice as fast as the actual decay rate of the sample). The fitted results are presented in Table 5.1, which reveals a rise time of \( T_{\text{rise}} = 230 \pm 25 \text{ fs} \) and a decay time of \( T_{\text{decay}} = 4.5 \pm 0.3 \text{ ps} \). From these results it is concluded that vibrational relaxation from the \( 1B_u^+(1) \) to the \( 1B_u^+(0) \) takes place in \( 230 \pm 25 \text{ fs} \).

Table 5.1: Fitted results for the transient grating-like signals presented in Fig. 5.2 with the fit function \( A_1 \exp(-t_{23}/(T_{\text{decay}1}/2)) + A_2 \exp(-t_{23}/(T_{\text{decay}2}/2)) \) for the case \( \lambda_{1,2} = \lambda_3 = 472 \text{ nm} \), and \( -A_1 \exp(-t_{23}/(T_{\text{rise}}/2)) + A_2 \exp(-t_{23}/(T_{\text{decay}}/2)) \) for the case \( \lambda_{1,2} = 472 \text{ nm}, \lambda_3 = 503 \text{ nm} \).

<table>
<thead>
<tr>
<th>( \lambda_{1,2} = \lambda_3 = 472 \text{ nm} )</th>
<th>( \lambda_{1,2} = 472 \text{ nm}, \lambda_3 = 503 \text{ nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A_1 )</td>
<td>0.42 ± 0.04</td>
</tr>
<tr>
<td>( T_{\text{decay}1} ) (fs)</td>
<td>220 ± 25</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>0.63 ± 0.06</td>
</tr>
<tr>
<td>( T_{\text{decay}2} ) (ps)</td>
<td>3.8 ± 0.3</td>
</tr>
</tbody>
</table>

Furthermore, when the sample is pumped and probed at the same wavelength 472 nm (Fig. 5.2 (a)), at a time delay very close to zero, the signal shows a very fast decay before the much longer one. The signal in this case is best fitted by a function containing two exponential decay components \( A_1 \exp(-t_{23}/(T_{\text{decay}1}/2)) + A_2 \exp(-t_{23}/(T_{\text{decay}2}/2)) \). One of the contributions to the signal’s fast decay immediately after the peak intensity is attributed to vibrational relaxation from \( 1B_u^+(1) \) to \( 1B_u^+(0) \). The fitted results show that the signal decays with a time constant \( 220 \pm 25 \text{ fs} \). This value is very close to the result deduced from the rise time for the case \( \lambda_{1,2} = 472 \text{ nm} \) and \( \lambda_3 = 503 \text{ nm} \), which supports our conclusion about the vibrational relaxation rate in the first allowed excited state \( 1B_u^+ \). As discussed in Chapter 2, the time scale for vibrational relaxation in the \( 1B_u^+ \) (\( S_2 \)) state of lycopene was found to be about sub–100 fs from up-conversion measurements [38,56]. It was concluded from other works (for example the work of Ricci et al. in [38]), that vibrational relaxation in the \( S_2 \) state of carotenoids should be faster than 50 fs, and that only the low-frequency modes exhibit a slower rate (220 fs) for \( S_2 \) vibrational relaxation [57]. Our result here
(230 ± 25 fs) is rather far away from that time scale. At the moment we have no explanation for this disagreement.

In the temporal profile of the transient grating signal, there is usually a sharp spike appearing near zero delay time, where the pump and probe pulses overlap [119]. This feature which is called a ‘coherence spike’ gives no information about the dynamics of the ensemble. In our case, the coherence spike is observed in the transient grating-like signal for $\lambda_{1,2} = 472$ nm, $\lambda_3 = 503$ nm, but not for the other case. It is shown in [120] that the amplitude of the coherence spike is not reproducible even for supposedly the same experimental conditions. Thus when analysing the data with a coherence spike, it is acceptable to ignore the spike.

### 5.1.2 Ground State ($1A_g^-$) Vibrational Relaxation

According to the earlier analysis, vibrational relaxation processes in the ground state of the molecular system can be deduced from our experimental set-up if the three laser pulses are tuned to the transitions of the ensemble in which the wavelength of the two pump pulses is longer than that of the probe pulse ($\lambda_{1,2} > \lambda_3$). In the case of lycopene, the two transitions $1A_g^-(0) - 1B_u^+(0)$ and $1A_g^-(1) - 1B_u^+(0)$ have wavelengths 503 nm and 530 nm, respectively. In order to investigate the ground state vibrational relaxation, the wavelength of the two pump pulses are selected to be 530 nm and the wavelength of the probe pulse 503 nm.

The intensity of the central wavelength of the transient grating-like signals for lycopene in the $k_4$ direction versus scan time $t_{23}$ at fixed time $t_{12} = 0$ are shown in Fig. 5.3 for two cases: (1) $\lambda_{1,2} = \lambda_3 = 503$ nm and (2) $\lambda_{1,2} = 530$ nm, $\lambda_3 = 503$ nm. Since the signals are detected in the $k_4$ direction, their central wavelengths will be similar to the wavelength of the probe, which are both 503 nm as shown in the schematic energy level diagrams (b) and (d) in Fig. 5.3. In both cases, the transient grating-like signal exhibits the usual long decay during the scan time. This decay is, again,
attributed to the recovery process of $1A_g^-$ the ground state. Over shorter time scales, when the sample is pumped with the longer wavelength pulse $\lambda_{1,2} = 530$ nm (see Fig. 5.3 (c)), the signal shows a relatively slow rise before its intensity decays slowly to zero, whereas there is no noticeable similar feature for the case $\lambda_{1,2} = \lambda_3 = 503$ nm (Fig. 5.3 (a)). Comparing the two energy schematics (b) and (d) in Fig. 5.3, this rise component is assigned to vibrational relaxation in the ground state $1A_g^-$. This, again, is as expected from the earlier analysis.

The signal plotted in Fig. 5.3 (c) is best fitted by a function that combines an exponential rise and an exponential decay component $y = -A_1 \exp(-t_{23}/(T_{\text{rise}}/2)) + \ldots$
A_2 \exp(-t_{23}/(T_{\text{decay}}/2))$. To fit the signal for the other case plotted in Fig. 5.3(a), a function with only one decay component \( y = A_1 \exp(-t_{23}/(T_{\text{decay}}/2)) \) is necessary. The fitting parameters are presented in Table 5.2. It is found that the population vibrational relaxation time of level \( 1A_g^- (1) \) to \( 1A_g^- (0) \) is 595 ± 25 fs. Previous work has shown that the mode-averaged vibrational relaxation in the ground state occurs on a time scale ranging from less than 1 ps to 5 − 12 ps depending on the stretching mode [61]. While relaxation of the C=C stretching mode is found to be < 1 ps, the other modes such as C–C and C–CH\(_3\) exhibit much longer relaxation times (5 − 12 ps). As in the case of lycopene, only two stretching modes (C–C and C=C) can contribute to the vibrational relaxation. The value of 595 ± 25 fs found for the ground state vibrational relaxation time here is therefore believed to reflect the stretching mode C=C relaxation, rather than the stretching mode C–C. This conclusion is in good agreement with the fact that our sample is trans-lycopene, for which the conjugated bond C=C is much more active.

Table 5.2: Fitted results for the transient grating-like signals presented in Fig. 5.3 with the fit function \( A_1 \exp(-t_{23}/(T_{\text{decay}}/2)) \) for the case \( \lambda_{1,2} = \lambda_3 = 503 \text{ nm} \), and \( -A_1 \exp(-t_{23}/(T_{\text{rise}}/2)) + A_2 \exp(-t_{23}/(T_{\text{decay}}/2)) \) for the case \( \lambda_{1,2} = 530 \text{ nm}, \lambda_3 = 503 \text{ nm} \).

<table>
<thead>
<tr>
<th>( \lambda_{1,2} = \lambda_3 = 503 \text{ nm} )</th>
<th>( \lambda_{1,2} = 530 \text{ nm}, \lambda_3 = 503 \text{ nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( A )</td>
<td>1.3 ± 0.1</td>
</tr>
<tr>
<td>( T_{\text{decay}} ) (ps)</td>
<td>3.2 ± 0.3</td>
</tr>
<tr>
<td>( T_{\text{rise}} ) (fs)</td>
<td>1.0 ± 0.1</td>
</tr>
<tr>
<td>( A_2 )</td>
<td>3.3 ± 0.3</td>
</tr>
</tbody>
</table>

The long decay time deduced from the transient grating-like signal is quite similar for the two cases (3.2 ± 0.3 ps compared with 3.3 ± 0.3 ps). This decay result again represents the restoration of population in the \( 1A_g^- \) and is in agreement with the result derived in the previous section (3.8 ± 0.3 ps), as well as in good agreement with other studies using different techniques [41,50,51].
5.2 Dark State $S_1 (2A_g^-)$ Dynamics

The first excited state of the carotenoids $2A_g^- (S_1)$ is a one-photon optically forbidden state from the ground state $1A_g^- [121]$. However, it is possible for the molecules to be driven from $S_1$ to some upper excited states denoted by $S_N$. This is shown from the work of Frank et al. [51] and Polivka et al. [50] where for lycopene an absorption band around $540 – 550 \text{ nm}$ was shown to be responsible for the excited state absorption between $S_1$ and $S_N$. Because of this excited state absorption, the dynamics of the lowest ‘dark’ state is expected to be deduced. In our work, by selecting the appropriate wavelengths for the pump and probe pulses regarding the excited state absorption for the measurement of the transient grating-like signal in the $k_4$ direction, the dynamics of the ‘dark’ state $S_1$ of lycopene and spheroidene are revealed.

5.2.1 Lycopene

According to the excited state absorption band spectrum of lycopene, the $S_N$ state can be populated by absorption by molecules in the $S_1$ state at wavelengths peaking at $\sim 540 – 550 \text{ nm}$. In order to probe the $S_1 – S_N$ transition, the wavelength of the probe pulse is selected to be $540 \text{ nm}$, whereas the molecular system is pumped to the lowest vibrational level of $S_2$, $1B_u^+ (0)$, (to avoid any contributions from dynamics within the $S_2$ vibrational manifold) by two pulses with wavelength $\lambda_{1,2} = 503 \text{ nm}$ (see Fig. 5.4 (b)).

After being excited to the $1B_u^+ (0)$ by the two pump pulses 1 and 2, the molecular system will follow an internal conversion process to $S_1$ level (as discussed in Chapter 2), generating a grating of $S_1$ state molecules. The probe pulse will be scattered off this grating, giving rise to a transient grating-like signal in the $k_4$ direction, which allows the observation of the population flowing from the $S_2$ state into the $S_1$ state through $S_2 – S_1$ internal conversion, and the subsequent depopulation of the $S_1$ state by means of $S_1 – S_0$ internal conversion. The large amount of excess energy deposited
in the $S_1$ state after $S_2 - S_1$ internal conversion can be a driving force for vibrational relaxation in the $S_1$ state [50], which can be revealed in the transient grating signal as well. In addition, the detection of the intensity of pulse 3 can be considered as a direct measurement of the transmission or absorption process, and can provide supplementary information to signal in the $k_4$ direction.

In Fig. 5.5, contour plots of the transient grating-like signals of lycopene in the $k_4$ direction when pulse 3 is scanned at zero delay time $t_{12}$ are presented for 2 cases: (1) $\lambda_{1,2} = \lambda_3 = 503$ nm (Fig. 5.5 (a)) and (2) $\lambda_{1,2} = 503$ nm, $\lambda_3 = 540$ nm (Fig. 5.5 (e)). The evolution of the probe pulse ($k_3$) versus delay time $t_{23}$ after passing through the sample is also detected and is shown in Fig. 5.5 (c) and (g). The intensity of the central wavelength versus delay time $t_{23}$ of signal in the $k_4$ direction and of pulse 3 in each case are also displayed accordingly.

When the pump and probe pulse have the same wavelength of 503 nm, the transient grating-like signal shows a rapid rise (which is considered to be instantaneous allowing
Fig. 5.5: Spectrally resolved transient grating-like signal in the $k_4$ direction (a) and evolution during delay time $t_{23}$ of the transmission of the probe pulse $k_3$ (c) for the case $\lambda_{1,2} = \lambda_3 = 503\text{ nm}$ for lycopene. The respective intensities of the central wavelength are plotted in (b) and (d). (e), (f), (g) and (h) are the corresponding results for the case when $\lambda_{1,2} = 503\text{ nm}$ and $\lambda_3 = 540\text{ nm}$.

for the duration of the laser pulses), and hence gives no information about the dynamics of the sample at around zero time delay, followed by a long decay over the scan time (Fig. 5.5 (b)). The decay is best fitted by an exponential decay component function $A \exp(-t_{23}/(T_{\text{decay}}/2))$ with $T_{\text{decay}} = 3.3\pm0.2\text{ ps}$ (see Table 5.3). This decay is the result of ground state bleaching and is in good agreement with the results in Section 5.1 and with the results of other researchers [41,50,51,122].
The pulse 3 transmission signal can be considered as a pump probe-like signal and its decay during the scan time gives the population decay of $S_2$, which should also reflect the $S_0$ ground state bleaching. The recovery of the ground state will reflect the dynamics of any intermediate states that influence the rate of repopulation of the ground state. As a pump probe signal, the intensity of pulse 3 versus $t_{23}$ plotted in Fig. 5.5 (d) is fitted with the function $A \exp(-t_{23}/T_{\text{decay}})$, where $T_{\text{decay}}$ indicates the real decay of the sample. (Note that $T_{\text{decay}}$ is used for fitting the pump-probe signal, whereas for the transient grating signal it should be $T_{\text{decay}}/2$). The fitted results indicate that pulse 3 decays with a time constant of $3.4 \pm 0.2$ ps, which is consistent with the value given by the transient grating signal above.

<table>
<thead>
<tr>
<th>$\lambda_1, \lambda_2 = 503$ nm</th>
<th>$\lambda_1, \lambda_2 = 503$ nm, $\lambda_3 = 540$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\lambda_4 = 503$ nm</td>
<td>$\lambda_4 = 540$ nm</td>
</tr>
<tr>
<td>$k_4$</td>
<td>$k_3$</td>
</tr>
<tr>
<td>$A$</td>
<td>$A_{\text{offset}}$</td>
</tr>
<tr>
<td>$T_{\text{decay}}$ (ps)</td>
<td>$T_{\text{rise}}$ (fs)</td>
</tr>
<tr>
<td>3.3 $\pm$ 0.2</td>
<td>$A_2$</td>
</tr>
<tr>
<td></td>
<td>$T_{\text{decay}}$ (ps)</td>
</tr>
<tr>
<td>4.0 $\pm$ 0.1</td>
<td>$A_{\text{offset}}$</td>
</tr>
<tr>
<td>$A$</td>
<td>$T_{\text{rise}}$ (ps)</td>
</tr>
<tr>
<td>$0.72 \pm 0.05$</td>
<td>$T_{\text{decay}}$ (ps)</td>
</tr>
<tr>
<td>$3.4 \pm 0.2$</td>
<td>$A_2$</td>
</tr>
<tr>
<td></td>
<td>$T_{\text{decay}}$ (ps)</td>
</tr>
</tbody>
</table>

When the probe pulse is tuned to 540 nm, unlike the case for 503 nm, the transmitted intensity of pulse 3 shows a rather fast decay feature, and a long rise time, which reflects a transient absorption process in the sample (see Fig. 5.5 (g) and (h)). As the wavelength of the probe is resonant with the excited state absorption of $S_1$, the probe pulse evolution indicates that the population of the $S_N$ state from
the $S_1$ state does indeed occur, as illustrated in the schematic energy level diagram in Fig. 5.4 (b). Therefore the transient grating-like signal in the $k_4$ direction in this case is expected to reveal the dynamics of the dark state $S_1$. In fact, the transient grating signal for a probe wavelength of 540 nm (Fig. 5.5 (f)) shows a long rise time instead of an instantaneous one, as in the case when the probe is resonant with the $1A_g^-(0) - 1B_u^+(0)$ transition (Fig. 5.5 (b)). We attribute this rather slow rise component to internal conversion between the two states $S_1$ and $S_2$. The long decay of the signal in this case results from the lifetime of the dark state $S_1$ as well as its internal conversion to the ground state $S_0$. The signal is fitted with a function with a rise component and a decay component. The fitted results in Table 5.3 show that the rise time of the signal is $490 \pm 20$ fs and the decay $4.0 \pm 0.2$ ps. According to [17,27,123], the internal conversion time of the $S_2 - S_1$ transition of carotenoids is in the range of $100 - 300$ fs. The 490 fs time constant deduced here should result not only from the $S_2 - S_1$ internal conversion but also from vibrational relaxation in the $S_1$ dark state. It is well-known from previous work (for example, see [50] and [59]) that vibrational relaxation time in the $S_1$ state is not dependent on the structure of the carotenoid and that it is of the order of 500 fs in a polar solvent (methanol) and slightly longer in a non-polar solvent ($n$-hexane). These results support our assignment of 490 fs to the vibrational relaxation time in $S_1$. This result also indicates that the ‘dark’ state $S_1$ vibrational relaxation is detectable by selecting the appropriate wavelength for the probe pulse in our two-colour transient grating-like measurement.

The long decay time ($4.0 \pm 0.2$ ps) deduced from the transient grating-like signal when the ensemble is probed by pulse 3 with $\lambda_3 = 540$ nm reveals the lifetime of the $S_1$ state (Fig. 5.5 (f)). The evolution of the transmission of the probe pulse in this case (Fig. 5.5 (h)) gives a very similar decay time $4.1 \pm 0.2$ ps, which supports our result concerning the lifetime of the $S_1$ state. The fitted results for the long decay of the evolution of the transmission of the probe pulse also provide information about the repopulation of the ground state $S_0$. In fact, these results are consistent with those deduced from the transient grating-like signals (see Table 5.3).
It is important to keep in mind that there are two other dark states ($3A_g^-$ and $1B_u^-$) located between $S_2$ and $S_1$ in lycopene. This adds to the complexity of the internal conversion and can, in principle, be responsible for some contributions to the spectral dynamics observed here. However, as reported by the Koyama group, the lifetime of these two dark states is supposed to be very short ($\sim 150$ fs) [30]. The 490 fs component observed here can not be a result of internal conversion between either of these states to $S_1$, supporting our assignment of this component to the internal conversion $S_2 - S_1$ and vibrational relaxation in the $S_1$ state. Nevertheless, these two states can be involved in the initial 200 fs of the $S_2 - S_1$ relaxation component, as suggested in [21].

5.2.2 Spheroidene

In order to study the dynamics of the $S_1$ state of spheroidene, the wavelength of the two pump pulses is selected to be 483 nm, which drives the molecular system from the $1A_g^-(0)$ to the $1B_u^+(0)$, and the wavelength of the probe pulse is chosen to be 517 nm, which is resonant with the $S_1 - S_N$ transition of the sample. Figure 5.6 shows the transient grating-like signal of spheroidene in the two cases: (1) $\lambda_{1,2} = \lambda_3 = 483$ nm, (a), and (2) $\lambda_{1,2} = 483$ nm, $\lambda_3 = 517$ nm, (e). The signal is detected in the $k_4$ direction by scanning the population time $t_{23}$ at a fixed time $t_{12} = 0$. The evolution of the transmission of the probe pulse ($k_3$) during the delay time on probing the sample is also presented in the figure for the above two cases.

When the ensemble is pumped and probed at the same wavelength $\lambda_{1,2} = \lambda_3 = 483$ nm, the transient grating-like signal shows a coherence spike at around zero delay time, then a fast rise followed by a long decay over the scan time (see Fig. 5.6 (b)). The part of the signal that includes the fast rise and the long decay can be best fitted by a function with a exponential rise component and a exponential decay component $-A_1 \exp(t_{23}/(T_{\text{rise}}/2)) + A_2 \exp(t_{23}/(T_{\text{decay}}/2))$. The fitted results in Table 5.4 indicate that the signal rises with a fast time constant of $150 \pm 30$ fs, which is considered to be instantaneous allowing for the duration of the laser pulses. This rise feature is not
expected to reveal the dynamics of the sample. The decay time of the transient grating is found to be $8.2 \pm 0.2$ ps, which is due to the $S_0$ ground state bleaching as discussed in the case of lycopene.

When the sample is probed by the 517 nm pulse, the transient grating-like signal shows a rather slower rise (see Fig. 5.6 (f)), which is fitted by a time constant of $535 \pm 25$ fs. The evolution of the transmission of the probe pulse $k_3$ in this case (Fig. 5.6 (h)) again confirms the $S_1 - S_N$ absorption process in the sample. It should be noted that there is an initial rise in this evolution before the decrease, where the rise is due
Chapter 5

Table 5.4: Fitted results for transient grating signals (k_4) and the transmission of the probe pulse (k_3). The fitting function for the k_4 signal for the case \( \lambda_{1,2} = \lambda_3 = 483 \text{ nm} \) is \(-A_1 \exp(-t_{23}/T_{\text{rise}}/2)) + A_2 \exp(-t_{23}/(T_{\text{decay}}/2)))\). The fitting functions for the case \( \lambda_{1,2} = 483 \text{ nm}, \lambda_3 = 517 \text{ nm} \) are \(-A_1 \exp(-t_{23}/(T_{\text{rise}}/2)) + A_2 \exp(-t_{23}/(T_{\text{decay}}/2)))\) for the k_4 signal and \( A_{\text{offset}} - (-A_1 \exp(-t_{23}/T_{\text{rise}}) + A_2 \exp(-t_{23}/T_{\text{decay}})) \) for k_3. The k_3 signal for \( \lambda_{1,2} = \lambda_3 = 483 \text{ nm} \) is not fitted.

<table>
<thead>
<tr>
<th></th>
<th>( \lambda_{1,2} = \lambda_3 = 483 \text{ nm} )</th>
<th></th>
<th>( \lambda_{1,2} = 483 \text{nm}, \lambda_3 = 517 \text{ nm} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( \lambda_4 = 483 \text{ nm} )</td>
<td>( \lambda_4 = 517 \text{ nm} )</td>
<td></td>
</tr>
<tr>
<td>( k_4 )</td>
<td>( A_1 ) = 10.3 ( \pm ) 0.5</td>
<td>( A_1 ) = 2.1 ( \pm ) 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( T_{\text{rise}} ) (fs) = 150 ( \pm ) 30</td>
<td>( T_{\text{rise}} ) (fs) = 535 ( \pm ) 25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( A_2 ) = 1.1 ( \pm ) 0.1</td>
<td>( A_2 ) = 1.2 ( \pm ) 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>( T_{\text{decay}} ) (ps) = 8.2 ( \pm ) 0.2</td>
<td>( T_{\text{decay}} ) (ps) = 8.2 ( \pm ) 0.3</td>
<td></td>
</tr>
<tr>
<td>( k_3 )</td>
<td>(not fitted)</td>
<td>( A_{\text{offset}} ) = 0.74 ( \pm ) 0.05</td>
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<tr>
<td></td>
<td></td>
<td>( A_1 ) = 0.64 ( \pm ) 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( T_{\text{rise}} ) (fs) = 495 ( \pm ) 30</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( A_2 ) = 0.46 ( \pm ) 0.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( T_{\text{decay}} ) (ps) = 8.8 ( \pm ) 0.2</td>
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</table>

To \( S_0 \) bleaching and the decrease is due to excited state absorption from \( S_1 \) to \( S_N \). Because of this, the transient grating-like signal probes the population flowing through \( S_1 \) and its rise feature reflects the process occurring between \( S_2 \) and \( S_1 \). Similar to the case of lycopene, we attribute this time constant to internal conversion of \( S_2 - S_1 \) and vibrational relaxation in \( S_1 \). The value of this time constant indicates that vibrational relaxation in \( S_1 \) state of spheroidene is slightly slower than that of lycopene. On the other hand, the decay of the signal provides information about the lifetime of the \( S_1 \), which is deduced to be \( 8.2 \pm 0.3 \text{ ps} \) (see Table 5.4). Fitting the evolution of the transmission of the probe pulse indicates that the probe signal decays as slowly with a time constant of \( 8.8 \pm 0.2 \text{ ps} \). As this can be considered as a pump probe signal, this decay reflects the lifetime of the \( S_1 \) state, which is in good agreement with the result deduced from the transient grating-like signal. The lifetime of the \( S_1 \) state found for spheroidene is consistent with the results of other groups (see, for example, [66]).
5.3 Summary of Results

In this chapter, results from the transient grating-like measurements with the three-pulse one- and two-colour spectrally resolved experimental set-up in the $k_4$ phase matching direction are reported for lycopene and spheroidene.

The transient grating-like signal in the $k_4$ direction is obtained by scanning the pulse 3 when the pulses 1 and 2 overlap in time, i.e., a fixed time $t_{12} = 0$. By selecting the appropriate wavelength for the pump and probe pulses, the evolution of the transient grating has successfully revealed the population vibrational relaxation process, the internal conversion process, as well as the lifetime of the dark state $S_1 (2A_g^-)$. The results for lycopene and spheroidene deduced from these measurements are summarised in Fig. 5.7.

Fig. 5.7: Summary of results from three-pulse two-colour transient grating-like measurements for lycopene and spheroidene. (VR: vibrational relaxation, IC: internal conversion).
Choosing $\lambda_1, \lambda_2 = 472 \text{ nm}$ and $\lambda_3 = 503 \text{ nm}$ for the measurement of lycopene, the vibrational relaxation for the first allowed excited state ($1B_u^+$) is found to be $\sim 230 \pm 25 \text{ fs}$, whereas the vibrational relaxation from $1A_g^-$ (1) to $1A_g^-$ (0) is deduced to be $\sim 595 \pm 25 \text{ fs}$ when $\lambda_1, \lambda_2 = 530 \text{ nm}$ and $\lambda_3 = 503 \text{ nm}$. The value of $230 \pm 25 \text{ fs}$, however, may reflect some other processes occurring between the states $S_2$ and $S_1$. By selecting the appropriate wavelength for the probe pulse to excite the molecules from the dark state $S_1$ ($2A_g^-$) to the upper excited state $S_N$ ($540 \text{ nm}$ for lycopene and $517 \text{ nm}$ for spheroidene), it is shown that the absorption process from $S_1$ to $S_N$ does indeed occur. As a result, the transient grating-like signal in the $k_4$ direction for this probe wavelength can reveal the dynamics of the dark state $S_1$. The lifetimes of the $S_1$ state in lycopene and spheroidene are deduced to be $\sim 4.0 \pm 0.2 \text{ ps}$ and $\sim 8.2 \pm 0.3 \text{ ps}$, respectively, whereas it takes $\sim 490 \pm 20 \text{ fs}$ for lycopene molecules and $\sim 535 \pm 25 \text{ fs}$ for spheroidene molecules to relax from $S_2$ to $S_1$. These time constants are attributed to two processes: (1) internal conversion between $S_2$ and $S_1$; and (2) vibrational relaxation in $S_1$.

The above results have helped to confirm the relaxation pathway for lycopene and spheroidene that was defined by the other techniques: after being excited to the $S_2$ state, the molecular system experiences a relaxation pathway to the dark state $S_1$ before returning to repopulate the ground state $S_0$. During this process, vibrational relaxation in the $S_1$ state is found to occur. The result for the vibrational relaxation in the ground state $S_0$ suggests the active role of the C=C stretching mode. Comparing the results for lycopene and spheroidene helps to reveal the slower dynamics of spheroidene, which could be explained by the difference in the energy levels of these two carotenoids.
Chapter 6

Coherence Dynamics

In the first part of this chapter, one-colour three-pulse spectrally resolved photon echo signals are used to determine the decoherence time of certain transitions in lycopene and spheroidene. In the next part, results for the coherence dynamics in lycopene and spheroidene studied by two-colour spectrally resolved experiments are reported. The last part of the chapter summarises our results on a non-interferometric two-dimensional Fourier transform spectroscopy technique. This technique is applied to the study of coherence dynamics in the laser dye cresyl violet and in our main sample, lycopene.

6.1 One-Colour Spectrally Resolved Photon Echo Study of Molecular Decoherence

According to the analysis in Chapter 3, for a molecular system with inhomogeneous broadening, when the signal is detected in the \( k_4 = -k_1 + k_2 + k_3 \) direction, rephasing is able to occur when the three laser pulses have the time ordering \( 1-2-3 \) or \( 1-3-2 \). When pulse 1 is scanned, a photon echo will therefore be generated when the fixed time
delay $t_{23}$ is either positive or negative, and the delay time $t_{12}$ is negative, i.e., pulse 1 precedes pulse 2. Thus, provided that rephasing takes place and according to our time definition in Chapter 3, the signal in this case will lead to a photon echo in the negative part of delay time $t_{12}$.

6.1.1 Lycopene

Figure 6.1 (a), (b) and (c) presents the spectrally resolved three-pulse FWM signal of lycopene in the $k_4$ direction on scanning $t_{12}$ with the fixed time $t_{23}$ set to be $-80$ fs, $-40$ fs and 0 fs, respectively. The wavelengths of the three laser pulses are $\lambda_{12} = \lambda_3 = 503$ nm, which is resonant with the transition $1A_g^-(0) - 1B_u^+(0)$. The contour plots show a clear development during the fixed time when the signal evolves from an irregular shape with a ‘tail’ feature on the high-frequency side at negative fixed time ($t_{23} = -80$ fs) to a fairly elliptical shape as pulse 2 and pulse 3 overlap in time ($t_{23} = 0$ fs). On the right hand side of each signal, the ordering of the laser pulses is $3 - 2 - 1$, as a result, the signals are simply generated by the overlapping of the laser pulses and give no information about the dynamics of the sample. On the left hand side, all three signals show an asymmetric feature with slightly longer decay, which is due to a photon echo.

Figure 6.1 (d), (e) and (f) shows that the intensity of the spectrally resolved signal depends on the separation time between pulse 2 and pulse 3 ($t_{23}$). The signal has the highest intensity when pulses 2 and 3 overlap in time ($t_{23} = 0$) (Fig. 6.1 (f)), and decreases as the separation between them increases. Moreover, when pulse 3 is moved further away from pulse 2, the peak also moves away from the zero delay time to a negative delay of $t_{12}$. The photon echo part of the signal in each case is fitted by the exponential decay $A \exp((t_{12} - const)/(T_2/4))$, where $T_2$ is the decoherence time for the molecular transition involved and $const$ is equivalent to the value of the fixed time $t_{23}$, which is $-80$ fs, $-40$ fs and 0 fs, respectively. We chose $const$ based on the fact that: when pulse 1 is scanned, the pulse ordering $1 - 3 - 2$, and hence the photon
echo, occurs only during the time pulse 1 precedes pulse 3; when pulse 1 is scanned beyond pulse 3, the pulse ordering will be $3 - 1 - 2$ which results in a free induction decay signal is generated instead (see Table 3.1). The decay time in the fit function is expressed as $T_2/4$ because the photon echo intensity decays four times faster than the molecular decoherence rate, as analysed in Chapter 3. The fitted results in Table 6.1 for the case $\lambda_{1,2} = \lambda_3 = 503$ nm indicate decoherence times of $160 \pm 15$ fs, $175 \pm 15$ fs and $155 \pm 15$ fs at the three fixed times $t_{23} = -80$ fs, $-40$ fs, and $0$ fs, respectively. As $503$ nm is resonant with the transition $1A_g^{-}(0) - 1B_u^{+}(0)$, these time constants represent the decoherence time of this transition. The results show that $T_2$ is slightly different
for different fixed times $t_{23}$.

Table 6.1: Fitted results for the photon echo signals of lycopene in Fig. 6.1 and Fig. 6.2 to deduce the decoherence time $T_2$ for the transition $1A_g^-(0) - 1B_u^+(0)$ ($\lambda_{1,2} = \lambda_3 = 503$ nm) and the transition $1A_g^-(0) - 1B_u^+(1)$ ($\lambda_{1,2} = \lambda_3 = 472$ nm), respectively.

<table>
<thead>
<tr>
<th>$t_{23}$ (fs)</th>
<th>$\lambda_{1,2} = \lambda_3 = 503$ nm</th>
<th>$\lambda_{1,2} = \lambda_3 = 472$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$t_{23} = -80$ fs</td>
<td>$0.64 \pm 0.03$</td>
<td>$160 \pm 15$</td>
</tr>
<tr>
<td>$t_{23} = -40$ fs</td>
<td>$0.73 \pm 0.04$</td>
<td>$175 \pm 15$</td>
</tr>
<tr>
<td>$t_{23} = 0$ fs</td>
<td>$1.6 \pm 0.05$</td>
<td>$155 \pm 15$</td>
</tr>
<tr>
<td>$A$</td>
<td>$T_2$ (fs)</td>
<td>$A$</td>
</tr>
<tr>
<td>$125 \pm 20$</td>
<td>$0.58 \pm 0.04$</td>
<td>$115 \pm 20$</td>
</tr>
</tbody>
</table>

Now if the three laser pulses are chosen to have a wavelength of 472 nm, the molecular system will be excited from the first vibrational level of the ground state, $1A_g^-(0)$, to the second vibrational level of the first allowed excited state, $1B_u^+(1)$. The spectrally resolved signals in the $k_4$ direction when scanning pulse 1 at different fixed times $t_{23} = -80$ fs, $-40$ fs and 0 fs are presented in Fig. 6.2 (a), (b) and (c), respectively. The intensity at the central wavelength at each fixed time is plotted versus the scan time $t_{12}$ in Fig. 6.2 (d), (e) and (f).

The contour plots do not show a clear development of the signal over the fixed time $t_{23}$ as was seen for the case when $\lambda_{1,2} = \lambda_3 = 503$ nm. They all have a fairly elliptical shape with no other remarkable features. However, the intensity plot reveals a slight asymmetry on the left hand side of the spectrally resolved signal for each fixed time, which is believed to result from the photon echo. The photon echo part in this case is again fitted by the exponential function $A \exp((t_{12} - \text{const})/(T_2/4))$. The fitted results (see Table 6.1) show that the decoherence times of the transition $1A_g^-(0) - 1B_u^+(1)$ are $125 \pm 20$ fs, $115 \pm 20$ fs and $125 \pm 20$ fs for the three fixed times $t_{23} = -80$ fs, $-40$ fs and 0 fs, respectively. These values are $\sim 30$–$50$ fs shorter than those of transition $1A_g^-(0) - 1B_u^+(0)$. Since the ensemble is excited from the first vibrational level of the ground state, $1A_g^-(0)$, in both cases $\lambda_{1,2} = \lambda_3 = 503$ nm and
Fig. 6.2: (a), (b) and (c): Spectrally resolved three pulse one-colour photon echo signals of lycopene in the phase-matching direction \( k_4 \) on scanning pulse 1 at fixed times \( t_{23} = -80 \text{ fs} \), \(-40 \text{ fs} \) and \(0 \text{ fs} \) when the sample is pumped and probed by the laser pulses with wavelength \( \lambda_{12} = \lambda_3 = 472 \text{ nm} \). (d), (e) and (f): Intensity of the signal at the central wavelength \( \lambda_4 = 472 \text{ nm} \) for each fixed time versus the scan time. The left hand side of the signal in each case is fitted with the exponential function \( A \exp((t_{12} - \text{const})/(T_2/4)) \), from which the decoherence time of the transition \( 1A_g^-(0) - 1B_u^+(1) \) is deduced.

\( \lambda_{1,2} = \lambda_3 = 472 \text{ nm} \), the difference in their decoherence times should originate from a difference between the dynamics of the molecular system in the two vibrational levels of the first allowed excited state, \( 1B_u^+(0) \) and \( 1B_u^+(1) \). The likely reason for this is that the higher vibrational state is more likely to have a higher rate of collision with other molecules such as solvent molecules or other carotenoid molecules, which is the cause of decoherence. Another reason for the shorter \( T_2 \) is the shorter lifetime of the higher vibrational state. Moreover, the very fast rate of vibrational relaxation between the two vibrational levels of \( S_2 \) (from \( 1B_u^+(1) \) to \( 1B_u^+(0) \)) can explain the faster decoherence rate for the transition \( 1A_g^-(0) - 1B_u^+(1) \).
6.1.2 Spheroidene

To study the decoherence process of the transition $1A_g^-(0) - 1B_u^+(0)$ in spheroidene, three laser pulses with wavelength 483 nm are selected for the experiment. The spectrally resolved signals in the $k_4$ direction when scanning pulse 1 are shown in Fig. 6.3 (a), (b) and (c) for the three fixed times $t_{23} = -80$ fs, $-40$ fs, and 0 fs. The intensity at the central wavelength ($\sim 483$ nm) is plotted versus the delay time $t_{12}$ for each case (Fig. 6.3 (d), (e) and (f)).

$$\lambda_{1,2} = \lambda_3 = 483 \text{ nm}$$

Fig. 6.3: (a), (b) and (c): Spectrally resolved three pulse one-colour photon echo signals of spheroidene in the phase-matching direction $k_4$ on scanning pulse 1 at fixed times $t_{23} = -80$ fs, $-40$ fs and 0 fs when the sample is pumped and probed by laser pulses with wavelength $\lambda_{12} = \lambda_3 = 483$ nm. (d), (e) and (f): Intensity of the signal at the central wavelength $\lambda_4 = 483$ nm for each fixed time during the scan time. The left hand side part of the signal in each case is fitted with the exponential function $A \exp((t_{12} - \text{const})/(T_2/4)$, from which the decoherence time of the transition $1A_g^-(0) - 1B_u^+(0)$ is deduced.

All three contour plots of the spectrally resolved signal are asymmetric, with a ‘tail’
on the left hand side. This asymmetry is again clearly seen in the intensity plots with a rather long decay on the left hand side. The dependence of the peak intensity on the fixed time and the shift of the peak in this case are clearer than in the case of lycopene ($\sim 50 - 60$ fs shift from zero time delay at $t_{23} = -80$ fs) (see Fig. 6.3 (d)). Again the left hand side part of the intensity plot of the signal is fitted with the exponential decay function $A \exp((t_{12} - \text{const})/(T_2/4))$, and the fitted results for each fixed time are presented in Table 6.2.

Table 6.2: Fitted results for the photon echo signal in Fig. 6.3 to deduce the decoherence time ($T_2$) for transition $1A_g^- (0) - 1B_u^+ (0)$ ($\lambda_{1,2} = \lambda_3 = 483$ nm) for spheroidene.

<table>
<thead>
<tr>
<th>$t_{23}$</th>
<th>$A_1$</th>
<th>$T_2$ (fs)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$-80$ fs</td>
<td>$0.55 \pm 0.03$</td>
<td>$345 \pm 15$</td>
</tr>
<tr>
<td>$-40$ fs</td>
<td>$0.80 \pm 0.05$</td>
<td>$285 \pm 15$</td>
</tr>
<tr>
<td>$0$ fs</td>
<td>$1.55 \pm 0.07$</td>
<td>$255 \pm 15$</td>
</tr>
</tbody>
</table>

The fitted results reveal that the decoherence time $T_2$ of spheroidene for the transition $1A_g^- (0) - 1B_u^+ (0)$ is $345 \pm 15$ fs, $285 \pm 15$ fs and $255 \pm 15$ fs for the fixed times $t_{23} = -80$ fs, $-40$ fs and $0$ fs, respectively. These values are two to three times larger than those of lycopene, which indicates that the scattering rate in spheroidene is smaller than that in lycopene in general. Moreover, there is quite a big difference in the value of decoherence time when the time separation between pulses 2 and 3 are different, which is not seen in lycopene. All of the above results indicate a slower dynamical behaviour in spheroidene. This is consistent with the results about the other processes and could be explained by the difference in the energy levels of these two carotenoids.
6.2 Two-Colour Spectrally Resolved Study of Molecular Coherence

6.2.1 Lycopene

In the $k_6 = -k_3 + k_2 + k_1$ direction, the nonlinear four-wave mixing signal can have a different frequency to the frequencies of the laser pulses when two-colour excitation is employed. For this reason, studying the signal in the $k_6$ direction in a two-colour experiment can reveal additional valuable information about the sample as shown in this section.

Again we consider the interaction of optical pulses with an inhomogeneously broadened ensemble of two electronic state molecules with the ground state comprising two vibrational levels $|g⟩, |g'⟩$ and excited state two vibrational levels $|e⟩, |e'⟩$ (see Fig. 6.4) [8]. There are two cases under examination: (1) $\omega_3 > \omega_{1,2}$ (Fig. 6.4 (a)) and (2) $\omega_3 < \omega_{1,2}$ (Fig. 6.4 (b)). The splitting of the two vibrational levels of the ground state ($\Delta_1$) is similar to that of the excited state ($\Delta_2$). In both cases, $\omega_{1,2}$ is resonant with the transition $|g⟩ \rightarrow |e⟩$, whereas $\omega_3$ is resonant with the transition $|g⟩ \rightarrow |e'⟩$ in the case in Fig. 6.4 (a) and with the transition $|g'⟩ \rightarrow |e⟩$ in the case in Fig. 6.4 (b).

When $\omega_3 > \omega_{1,2}$ and the three pulses are in the order $3 - 2 - 1$, the first pulse $k_3$ creates optical coherences $\rho_{ge'}$ and $\rho_{e'g}$ between two vibronic states $|g⟩$ and $|e'⟩$. The second pulse $k_2$ with frequency $\omega_2 < \omega_3$ takes the system down to the second vibrational level of the ground state $|g'⟩$, creating optical coherences $\rho_{e'g'}$ or $\rho_{g'e'}$, and hence the vibrational coherence $\rho_{gg'}$. The third pulse $k_1$ then creates coherences $\rho_{ge}$ and $\rho_{eg}$, and hence $\rho_{eg'}$, allowing the generation of a nonlinear signal for the transition $|e⟩ \rightarrow |g'⟩$ at frequency $2\omega_1 - \omega_3$ in the direction of $k_6 = -k_3 + k_1 + k_2$. This signal results from the interaction of the laser pulses with the transitions of the sample, provided the coherence between $|g'⟩$ and $|e⟩$ is created. The process considered here is similar to
Chapter 6

the process in coherent Stokes Raman spectroscopy. It is noted that since the first two pulses interacting with the sample have different frequencies, there is no population created in the ground or excited state levels.

Fig. 6.4: Four-wave mixing process generates a signal which is resonant with the real transition of the molecule.

Similarly, when $\omega_3 < \omega_{1,2}$, in the direction of $k_6$ a nonlinear signal can be generated for the transition $|e'\rangle \rightarrow |g\rangle$, which is similar to a coherent anti-Stokes Raman signal (Fig. 6.4(b)), provided the coherence between $|g\rangle$ and $|e'\rangle$ is created.

In the case of the lycopene molecular system, the vibrational separations $\Delta_1$ and $\Delta_2$ are of similar magnitude ($1200 \text{ cm}^{-1}$ and $1340 \text{ cm}^{-1}$, respectively [30, 32]). We made use of the above theory by applying the wavelengths 503 nm (which is equivalent to $19880 \text{ cm}^{-1}$) and 472 nm ($21186 \text{ cm}^{-1}$) as the three input laser pulses, where 503 nm is resonant with the $1A_g^-(0) - 1B_u^+(0)$ transition and 472 nm is resonant with $1A_g^-(0) - 1B_u^+(1)$. For the case in Fig. 6.4 (a), i.e., $\omega_{1,2} < \omega_3$, we chose $\lambda_{1,2} = 503 \text{ nm}$ and $\lambda_3 = 472 \text{ nm}$ (see Fig. 6.5 (c)). When $\lambda_{1,2} = 472 \text{ nm}$ and $\lambda_3 = 503 \text{ nm}$, the corresponding energy scheme is shown in Fig. 6.5 (f). This is similar to the case shown in Fig. 6.4 (b), where the two levels $1B_u^+(1)$ and $1B_u^+(2)$ are considered as the vibrational levels $|e\rangle$ and $|e'\rangle$, respectively. When the molecular system is excited by $\lambda_{1,2} = 503 \text{ nm}$ and $\lambda_3 = 472 \text{ nm}$ (Fig. 6.5 (c)), the FWM signal from the laser pulses in the $k_6$ direction should have wavelength $\sim 538 \text{ nm}$ ($\sim 18574 \text{ cm}^{-1}$), whereas in the case shown in Fig. 6.5
Fig. 6.5: Spectrally resolved two-colour FWM signals for lycopene for two combinations of laser wavelength: $\lambda_{1,2} = 503$ nm, $\lambda_3 = 472$ nm ((a) and (b)) and $\lambda_{1,2} = 472$ nm, $\lambda_3 = 503$ nm ((d) and (e)). The signals are detected in the $k_6$ direction when scanning $t_{12}$ with two fixed times $t_{23} = -80$ fs and 0 fs. (c) and (f) are schematic diagrams of the three pulse interaction for the molecular system of lycopene for the cases $\lambda_{1,2} = 503$ nm, $\lambda_3 = 472$ nm and $\lambda_{1,2} = 472$ nm, $\lambda_3 = 503$ nm, respectively.

(f), when $\lambda_{1,2} = 472$ nm and $\lambda_3 = 503$ nm, the FWM signal should have wavelength $\sim 445$ nm ($\sim 22492$ cm$^{-1}$).

In Fig. 6.5, contour plots showing the spectrally resolved signal from lycopene in the $k_6$ direction when scanning $t_{12}$ at two fixed delays $t_{23} = -80$ fs and 0 fs are shown for the two cases: (1) $\lambda_{1,2} = 503$ nm, $\lambda_3 = 472$ nm ((a) and (b)), and (2) $\lambda_{1,2} = 472$ nm, $\lambda_3 = 503$ nm ((d) and (e)). In each plot (a) and (b), the signal can be separated into two parts: one part peaking at $\sim 537$ nm with high intensity and the other peaking at $\sim 544$ nm with lower intensity. The part with central wavelength $\sim 537$ nm occurs when
the temporal overlap of the three laser pulses is greatest. This occurs at $t_{12} \sim -100 \text{ fs}$ in Fig. 6.5 (a) ($t_{23} = -80 \text{ fs}$) and at $t_{12} \sim 0$ in Fig. 6.5 (b) ($t_{23} = 0$). This part of the signal starts when the scanned pulse 1 begins to overlap pulse 3 and lasts until pulse 1 is scanned beyond pulses 3 and 2. As the central wavelength of this part of the signal is very similar to the expected wavelength of the pure FWM signal from the mixing of the three laser pulses $\lambda_{1,2} = 503 \text{ nm}$, $\lambda_3 = 472 \text{ nm}$, we attribute this part of the signal to the FWM signal, which exists as long as the three laser pulses overlap in time. As analysed in Fig. 6.5 (c), the second part of the signal, which peaks at $\sim 544 \text{ nm}$ ($\sim 18380 \text{ cm}^{-1}$), is considered to be due to the transition $1B_u^+(0) - 1A_g^- (1)$ in the molecular system. Using fluorescence spectroscopy, Watanabe et al. found that the fluorescence from the vibronic level $1B_u^+(0)$ to level $1A_g^- (1)$ for lycopene in n-hexane solution at 295 K is $18400 \text{ cm}^{-1}$ [30], which is consistent with our conclusion about the detection of emission from this molecular transition.

The ability to detect FWM emission from a molecular transition in the $k_6$ direction shows that our two-colour measurement reveals the coherence of the molecular system and is able to detect it. As can be seen from the energy schematic in Fig. 6.5 (c), emission from the transition $1B_u^+(0) - 1A_g^- (1)$ is created because there is coherence between these two vibronic levels. In this case, the first pulse $k_3$ creates coherence between $1B_u^+(1)$ and $1A_g^- (0)$, the second pulse $k_2$ brings the ensemble back to the $1A_g^-$ state, creating coherence between the $1B_u^+(1)$ and $1A_g^- (1)$, the third pulse $k_1$ excites the molecular system to $1B_u^+(0)$ and the coherence between the $1B_u^+(0)$ and $1A_g^- (0)$ is generated. Because of the coherences established by each of the pulses, coherence between $1B_u^+(0)$ and $1A_g^- (1)$ is created and radiates to give the detected signal at 544 nm. The fact that the part of the signal that originates from the transition $1B_u^+(0) - 1A_g^- (1)$ occurs only at $t_{12} = \pm 100 \text{ fs}$, i.e., when pulse 1 is separated by less than $\sim 100 \text{ fs}$ from pulse 2, indicates that the coherence between the vibronic levels $1B_u^+(0)$ and $1A_g^- (1)$ lasts for a time less than 100 fs.

In the second case when $\lambda_{1,2} = 472 \text{ nm}$, $\lambda_3 = 503 \text{ nm}$, the spectrally resolved signal
only peaks at one central wavelength $\sim 445 \text{ nm}$ for both fixed delays $t_{23} = -80 \text{ fs}$ and $t_{23} = 0 \text{ fs}$ (Fig. 6.5 (d) and (f)). When pulse 3 precedes pulse 2 by 80 fs (i.e. $t_{23} = -80 \text{ fs}$), the signal starts when pulse 1 is about to temporally overlap with pulse 3 and lasts until pulse 1 is scanned away from pulse 2 (when $t_{12} \sim 100 \text{ fs}$) (see Fig. 6.5 (d)). Similarly, when the separation between pulse 3 and pulse 2 is zero (i.e., $t_{23} = 0$) (Fig. 6.5 (e)), the signal is centred at $t_{12} \sim 0 \text{ fs}$ where the three pulses overlap. As the pure FWM signal for $\lambda_{1,2} = 472 \text{ nm}$, $\lambda_3 = 503$ will have wavelength $\sim 445 \text{ nm}$ ($\sim 22,492 \text{ cm}^{-1}$), and because of the analysis above, the spectrally resolved signals shown in Fig. 6.5 (d) and (e) are attributed to the pure FWM signal of the three input laser pulses. However, according to the absorption spectrum of lycopene in Fig. 2.3, the separation between $1A_g^-(0)$ and $1B_u^+(2)$ corresponds to a wavelength of $\sim 444 \text{ nm}$, which is very similar to the wavelength of the pure FWM signal. It is possible that part of the signal is due to the molecular transition $1B_u^+(2) - 1A_g^-(0)$ as shown in the energy schematic in Fig. 6.5 (f), but it is difficult to differentiate this from the pure FWM signal in the spectrally resolved plots.

6.2.2 Spheroidene

6.2.2.1 $k_6$ Study: Coherent Coupling and Location of $1B_u^-(1)$

As a shorter chain carotenoid, the energy gap between the dark states ($3A_g^-, 1B_u^-$ and $2A_g^-$) and the first allowed excited state $1B_u^+(0)$ of spheroidene is smaller than that of lycopene. This fact makes it easier to identify these dark states of spheroidene. Locating these dark states has been an important task in understanding the electron dynamics in carotenoids.

In the first two-colour experiment, two pump pulses $k_1$ and $k_2$ with wavelength $483 \text{ nm}$ ($20,704 \text{ cm}^{-1}$), which is resonant with the transition $1A_g^-(0) - 1B_u^+(0)$, are chosen. The wavelength of pulse $k_3$ is selected to be $530 \text{ nm}$ ($18,868 \text{ cm}^{-1}$). The wavelength of the pure FWM signal that results from the mixing of the three laser
Fig. 6.6: Spectrally resolved two-colour three pulse four-wave mixing signal of spheroidene. The signals are detected in the $k_6$ direction when scanning $t_{23}$ at two fixed times $t_{12} = 0$ and $-80$ fs, for the two cases: $\lambda_{1,2} = 483$ nm, $\lambda_3 = 530$ nm ((a) and (b)), and $\lambda_{1,2} = 483$ nm, $\lambda_3 = 517$ nm ((c) and (d)). (e) is the energy schematic of three laser pulses interacting with the molecular system of spheroidene when the wavelength of the probe pulse is 530 nm or 517 nm.

Figure 6.6 (a) and (b) show the spectrally resolved two-colour signals in the $k_6$ direction as a function of $t_{23}$ for $t_{12} = 0$ fs and $-80$ fs, respectively, for the case $\lambda_{1,2} = 483$ nm and $\lambda_3 = 530$ nm. It is clearly seen that the signals in both cases consist of two separate parts: one with strong intensity and broad shape centred at wavelength $\sim 445$ nm, which is assigned to the FWM signal from the laser pulses, and another with lower intensity and narrower shape centred at wavelength $\sim 453$ nm. When pulse 3 is scanned, the FWM part starts (at $t_{23} \sim -100$ fs) as pulse 3 begins to overlap in time with pulse 1 and lasts until pulse 3 is scanned away from pulse 2 (at $t_{23} \sim 150$ fs when pulses in the $k_6$ direction in this case is $\sim 444$ nm.
$t_{12} = 0$ and $t_{23} \sim 100\, \text{fs}$ when $t_{12} = -80\, \text{fs}$). This strong signal spans a time range of $\sim 200 - 300\, \text{fs}$ along the scan time axes, whereas the signal centred at $\sim 453\, \text{nm}$ lasts for less than 100 fs on scanning $t_{23}$. Furthermore, the signal at $\sim 453\, \text{nm}$ occurs when pulse 3 arrives at the sample well before the other pulses, and its intensity decreases dramatically when pulse 1 is fixed further away from pulse 2.

To investigate the origin of the second part of the spectrally resolved signal in the above case ($\lambda_1, \lambda_2 = 483\, \text{nm}$, $\lambda_3 = 530\, \text{nm}$), an additional experiment was performed. This time, the wavelength of the pump pulses 1 and 2 is still 483 nm, but the wavelength of pulse 3 is set to 517 nm. The spectrally resolved signal in the $k_6$ direction as a function of $t_{23}$ for fixed delays $t_{12} = 0$ and $-80\, \text{fs}$ are shown in Fig. 6.6 (c) and (d). In both cases, the signal is centred at only one wavelength, $\sim 453\, \text{nm}$, which is close to the wavelength of the expected FWM signal of the laser pulses in this case. This signal has a peak intensity when the three laser pulses overlap the most in time (at $t_{23} \sim 0$ for fixed time $t_{12} = 0$ and at $t_{23} \sim -50\, \text{fs}$ for fixed time $t_{12} = -80\, \text{fs}$).

If we compare the two experiments described above (when the wavelength of pulse 3 is 530 and 517 nm, respectively), it is seen that a signal is present with a central wavelength $\sim 453\, \text{nm}$ in both cases. In the first case when $\lambda_3 = 530\, \text{nm}$, this signal is separated from the pure FWM signal of the laser pulses, whereas in the case of $\lambda_3 = 517\, \text{nm}$ it corresponds to the expected pure FWM signal. Since the signal with wavelength $\sim 453\, \text{nm}$ in Fig. 6.6 (a) and (b) is not the pure FWM signal from the three laser pulses, it must come from the interaction of the laser pulses with a real transition of the molecular system. We therefore conclude that the probe pulse with wavelength $\lambda_3 = 517\, \text{nm}$ is resonant with a real transition in the molecular system of spheroidene, and the probe pulse with wavelength $\lambda_3 = 530\, \text{nm}$ is not resonant with a real transition. Accordingly, in the case when $\lambda_3 = 530\, \text{nm}$, the creation of the resonant signal at 453 nm can be interpreted as follows: pulse 3 arrives at the sample first, driving the unknown transition non-resonantly, so that when $t_{23} \sim 0$ (and $t_{12} \sim 0$), the pure FWM signal appears at 445 nm. When $t_{23} < 0$, there is a finite time after the arrival
of pulse 3 in which the polarization of the unknown transition can begin to oscillate at its natural frequency, creating a coherence between the ground state $1A_g^-(0)$ and an excited energy state (let us call it state X) which is lower than the $1B_u^+(0)$ state. The second pulse, which is resonant with the $1A_g^-(0) - 1B_u^+(0)$ transition, then arrives at the sample and generates a coherence between the $1A_g^-(0)$ and $1B_u^+(0)$ states. As a result of these two interactions, a coherent coupling between energy state X and $1B_u^+(0)$ is created, and after the interaction of pulse 1 with the sample, a signal which results from the mixing of this coherence with pulse 1 is then created (see Fig. 6.6 (e)), with wavelength $\sim 453$ nm. In the case when $\lambda_3 = 517$ nm, the existence of a signal at 453 nm can be interpreted similarly, except for the fact that pulse 3 will drive the real transition resonantly and the signal at 453 nm in this case also results from the FWM of the three laser pulses.

The energy state $X$ that participates in the interaction with the laser pulses in these two experiments lies below level $1B_u^+(0)$ in the energy diagram and is separated from the ground state $1A_g^-(0)$ by $\sim 19\,340\,\text{cm}^{-1}$ (i.e., $\sim 517\,\text{nm}$). This energy can be assigned to either one of the two dark states $3A_g^-(0)$ or $1B_u^-(1)$. Koyama et al., using resonance-Raman excitation profiles, reported the detection of the dark state $3A_g^-$ and found that it was located $\sim 19\,900\,\text{cm}^{-1}$ from the ground state [22]. In other work, Koyama and co-workers found that the energy of the $1B_u^-(1)$ dark state is $\sim 19\,130\,\text{cm}^{-1}$. From a symmetry point of view, the probability of coherent coupling between $1B_u^-$ and $1B_u^+$ is greater than that between $1B_u^+$ and $3A_g^-$, as the $1B_u^+$ and $1B_u^-$ states have the same $B_u$-type symmetry. For this reason, we assign the state involved in our experiments here to be $1B_u^-(1)$. Furthermore, in a very recent paper, which assigned the symmetries of the $1B_u^-$ and $3A_g^-$ states for shorter-chain and longer-chain carotenoids [68], Koyama stated that, in spheroidene, diabatic electronic mixing takes place between $1B_u^+$ and $1B_u^-$ due to the same $B_u$-type symmetry, and that the mixing occurs as follows: $1B_u^+(1)+1B_u^-(3)$, $1B_u^+(0)+1B_u^-(2)$, $\ldots$ These results strongly support the above conclusion.
6.2.2.2 \( k_4 \) Study: Location of \( 3A_g^- (0) \)

Continuing the work of the previous section, this section reports our results obtained for the dark states of spheroidene, but from the spectrally resolved FWM signal in the \( k_4 = -k_1 + k_2 + k_3 \) direction.

Figure 6.7 (a) and (c) shows the spectrally resolved signals in the \( k_4 \) direction when scanning \( t_{12} \), for fixed time \( t_{23} = 40 \) fs, for two cases: (1) \( \lambda_{1,2} = 483 \) nm, \( \lambda_3 = 502 \) nm, and (2) \( \lambda_{1,2} = 483 \) nm, \( \lambda_3 = 510 \) nm. When pulse 3 has wavelength 502 nm, the contour plot of the signal in Fig. 6.7 (a) shows a strong peak centred at \( \sim 505 \) nm and a weaker peak at shorter wavelength (500 – 502 nm). In this case, the FWM signal from the three laser pulses 483 nm, 483 nm and 502 nm in the \( k_4 \) direction is expected to have wavelength 502 nm. The stronger peak centred at 505 nm may reflect the non-resonant interaction of the laser pulses with a real transition of the molecular system. Because the separation between the two peaks in the signal in Fig. 6.7 is rather small (less than 5 nm), it is possible that the peak at 505 nm may be the result of splitting in the incident spectrum of pulse 3. In order to check this, the spectrum of pulse 3 is compared to that of the signal at \( t_{12} \sim -60 \) fs with a peak at 502 nm (\( S_1 \)) and at \( t_{12} = 0 \) fs with a peak at 505 nm (\( S_2 \)) as shown in Fig. 6.7 (b). It is shown that the laser pulse 3 has a good profile without any splitting and/or enhancement at 505 nm where the strong peak \( S_2 \) is centred.

In the second case, when pulse 3 has wavelength 510 nm, the contour plot of the spectrally resolved signal in the \( k_4 \) direction in Fig. 6.7 (c) shows a strong peak at wavelength 510 nm, which is similar to the wavelength expected for the pure FWM signal from the laser pulses. Also present in the contour plot is a weaker peak centred at \( \sim 505 \) nm. Figure 6.7 (d) shows that the intensity of this latter peak is comparable with that of the peak at 510 nm, and that it is not the result of splitting and/or enhancement of the laser pulse 3.

From these two results, the peak at 505 nm (19 800 cm\(^{-1}\)) is attributed to a real
transition in the molecular system of spheroidene and we assign this transition to the $1A^-(0) - 3A^g(0)$ transition, as shown in Fig. 6.7 (e). This result (19 800 cm$^{-1}$) for the location of the dark state $3A^g_-$ in the energy diagram is consistent with results reported by Koyama et al. (19 900 cm$^{-1}$) [32]. In conclusion, by selecting the appropriate wavelength for the probe pulse $k_3$, our two-colour spectrally resolved experiment has been able to locate the dark state $3A^g_-$ of spheroidene.
6.3 Non-Interferometric Two-Dimensional Fourier Transform Spectroscopy

So far in the chapter, our spectrally resolved three-pulse one- and two-colour nonlinear four-wave mixing technique has proven to be a powerful tool for elucidating the molecular coherence dynamics of the light harvesting molecules lycopene and spheroidene. However, the polarization of our experimental signal which is integrated over the detection time carries no phase information, which makes it difficult to study the coherence dynamics of the molecular system in detail. For this reason, the necessity of restoring the complete signal (with both phase and amplitude) has become important. In order to obtain the phase of the electric field of the measured signal, one may use a heterodyne-detected technique, in which the signal is interfered with a local oscillator (see [124], for example). The difficulty of this set-up is that phase stability is required for all three input pulses as well as for the local oscillator. This can be achieved provided that the pulses have the same frequency [125]. With a multi-level molecular system such as the carotenoids, the use of heterodyne detection to directly measure the phase is not possible as a two-colour experiment is needed.

We have developed a phase retrieval technique that allows us to obtain the phase of the three-pulse two-colour four-wave mixing signal from spectrally resolved intensity data, without the need for phase stabilized input pulses [126].

The spectrally resolved signal is processed by a phase retrieval algorithm [127] which yields the time-resolved emission signal and the Fourier transformed correlation spectrum, and hence helps to resolve the coherence dynamics of our sample. In this chapter, the phase retrieval method is described. The technique is first applied to study the photon echo signal of the well understood dye molecule cresyl violet. It is then applied to one of our main carotenoid samples, lycopene.
6.3.1 Phase Retrieval from One- and Two-Colour Photon Echo Experiments

Phase retrieval techniques have been employed in imaging applications such as crystallography, radio-astronomy and electron microscopy. In general, this technique can be used if two intensity measurements, or one intensity measurement plus a priori knowledge in the conjugate Fourier plane, are provided. In our case, one intensity measurement is taken in the frequency domain and we will use a priori knowledge of the dynamics of the sample in the time domain. A detailed description of the phase retrieval technique used here is presented in our paper [126]. The main points are summarised as follows.

![Flow chart of the phase retrieval algorithm](image)

**Fig. 6.8:** Flow chart of the phase retrieval algorithm, which constrains the electric field $E_{\text{sig}}(\tau, \omega_t)$ with respect to the temporal support of $s_T(\tau, t)$ and the spectral support of $S_T(\omega_\tau, \omega_t)$. $\omega_t$ is the detected frequency of the signal at time $t$ and $\omega_\tau$ is the frequency during the time between the first two pulses.
Referring to the familiar photon echo experiment, there are three time intervals of interest: the time between the interaction of the first and second pulses with the system, $\tau$, the time between the interaction of the second and the third pulses with the system, $T$, and the time over which the signal field is generated following the third pulse, $t$ (see Fig. 3.1). In our experiment, the signal is averaged over all the phase differences between the pulses, and the magnitude of $E_{\text{sig}}(\tau, \omega_t)$ is measured for a fixed value of $T$. $E_{\text{sig}}(\tau, \omega_t)$ is related to the time-dependent signal, $s_T(\tau, t)$, by an inverse Fourier transform with respect to $\omega_t$ and to the frequency correlation spectrum $S_T(\omega_T, \omega_t)$ by a Fourier transform with respect to $\tau$. The process by which the phase information is retrieved is illustrated in Fig. 6.8. At first, random complex values of $s_T(\tau, t)$ for $(\tau, t) \in \mathcal{T}$ are chosen, and $s_T(\tau, t) = 0$ otherwise. $\mathcal{T}$ is the effective two-dimensional domain over which $s_T(\tau, t) \neq 0$, which we base on these facts: (1) $s_T(\tau, t) = 0$ for $\tau \ll 0$ and $t < 0$; (2) $|E_{\text{sig}}(\tau, \omega_t)|$ falls to negligible values for values of $\tau$ greater than some cutoff, $\tau_{\text{max}}$; and (3) significant signal is not expected for $t > \tau_{\text{max}}$ since dephasing occurs within $t < \tau_{\text{max}}$ and rephasing occurs at $t = \tau$ for a photon echo. Consequently, the signal is defined by a support function, $\mathcal{T}_S$, defined by:

$$\mathcal{T}_S(\tau, t) = \begin{cases} 
1 & \text{for } 0 < \tau < \tau_{\text{max}}, 0 < t < \tau_{\text{max}} \\
0 & \text{otherwise}
\end{cases} \quad (6.1)$$

In the $(\omega_T, \omega_t)$ domain, further constraints may be imposed by the transition frequencies and broadenings, and the laser frequencies. In the simplest implementation of the scheme, the iteration is continued until the rms deviation between the measured amplitudes of $E_{\text{sig}}(\tau, t)$ and those obtained by propagation fall below a specified tolerance.

The validity of the method was tested by applying it to a set of test data which was obtained for a V-type three-level system. The test results show that our retrieval
method is able to accurately reproduce the complete complex phase of the photon echo emission signals from spectrally resolved intensity data, given appropriate constraints and starting guesses [126].

The phase retrieval technique thus allows us to obtain the same information as two-dimensional Fourier transform spectroscopy (2DFTS) experiments without the requirement of phase stability between the four pulses. 2DFTS is the most common implementation of optical multi-dimensional Fourier transform spectroscopy which originated from nuclear magnetic resonance (NMR) in the 1970s [128]. 2DFTS measures the full nonlinear polarization of a quantum system and correlates the oscillation frequencies of the signal during two different time periods [129,130]. 2DFTS is well-known for its power in elucidating intermolecular interactions (couplings), which play a very important role in molecular microscopic dynamical processes. To intuitively understand the results obtained from 2DFTS, as well as from our phase retrieval technique, we will analyse the 2DFTS spectra of a molecular system.

After being processed by the phase retrieval method, our spectrally resolved signal will be in the form of a 2D-spectrum \( S(\omega_\tau, T, \omega_t) \), where \( \tau \) is scanned with a fixed time \( T \), \( \omega_t \) is the detected frequency of the signal integrate over all time \( t \), and \( \omega_\tau \) is the frequency during the time between the first two pulses (see Fig. 4. in [124]). In a simple photon echo experiment, each molecule will have the same frequency during the first time interval \( \tau \) and the third detected time interval \( t \) (i.e., \( \omega_\tau = \omega_t \)). However, because of the effect of inhomogeneous broadening, there will be a broad distribution of transition frequencies. Thus, the 2D-spectrum will feature an elongation along the diagonal, which reveals the inhomogeneous broadening as well as the homogeneous broadening, whilst the homogeneous linewidth can still be determined from the cross-section of the diagonal [126].

The more informative contribution of a 2D-spectrum, however, is the off-diagonal (cross) peaks as shown in Fig. 6 of [124]. The appearance of off-diagonal peaks indicates that there has been some transfer of carriers and/or energy between states. This can
be in the form of population relaxation processes, coherent energy transfer, or as a result of state mixing effects. Specifically, what the off-diagonal peaks show is that the system absorbs (and oscillates) at one frequency during the interval $\tau$, but the signal emission is at a different frequency as a result of some coupling between states. Thus, the off-diagonal peaks contain valuable information about the molecular couplings as well as coherence dynamics.

As mentioned above, our phase retrieval technique can be applied to obtain phase information and correlation spectra from two-colour experimental data, whereas traditional 2DFTS experiments that rely on heterodyne detection can provide results for one-colour excitation only. Since two-colour photon echo experiments provide much important information about the molecular dynamics, for example, the coherent transfer of electrons between excited states as identified in [126], our phase retrieval technique has a distinct advantage. It should be noted that the diagonal of a 2D-spectrum from a two-colour experiment is different from that for a one-colour experiment. For example, if the photon echo is detected in the $k_6$ direction, for which the signal frequency is $\omega_6 = -\omega_3 + \omega_1 + \omega_2$, the diagonal is the line along which $\omega_t = -\omega_\tau + \omega_1 + \omega_2$ provided pulse $k_3$ arrives first, instead of $\omega_t = -\omega_\tau$ as is the case for one-colour experiments.

### 6.3.2 Non-interferometric 2DFTS Study of Cresyl Violet

Cresyl violet, for which the chemical structure and the absorption spectrum are shown in Fig. 6.9, is an oxazine laser dye that binds strongly to DNA and RNA-rich cell compounds, e.g., in nerve tissues. The detection of DNA at very low concentration is made possible by labelling the DNA with cresyl violet. In an earlier paper [8], we used the two-colour spectrally resolved photon echo technique to investigate the vibrational and electronic dynamics in cresyl violet. We found that there is strong coherence coupling in the ground and excited state of the molecule. Based on this result, we now apply the non-interferometric 2DFTS to this data to study the coupling dynamics in
detail, as an introduction to the application of non-interferometric 2DFTS to our main samples, the carotenoids. In the first part of this section, results that reveal the strong coherent coupling in cresyl violet from our spectrally resolved two-colour experiment are presented.

![Absorption spectrum of cresyl violet](a) and its molecular structure (b).

6.3.2.1 Spectrally Resolved Two-Colour Results

In Fig. 6.10, the spectrally resolved signals of cresyl violet in the $k_6$ direction are shown for the case $\lambda_{1,2} = 600\text{nm}$, which is at the maximum of the absorption (see Fig. 6.9), and $\lambda_3 = 615\text{nm}$. The signal is detected at fixed time $t_{12} = -80\text{fs}$ when scanning $t_{23}$, (a), and at fixed time $t_{23} = -80\text{fs}$ when scanning $t_{12}$, (b).

When $\lambda_{1,2} = 600\text{nm}$, $\lambda_3 = 615\text{nm}$, the FWM signal from the lasers in the $k_6$ direction is expected at $\sim 586\text{nm}$. The contour plot in Fig. 6.10 (a) shows that when $t_{23}$ is scanned at fixed $t_{12} = -80\text{fs}$ the signal consists of two parts. The first part with high intensity is centred at $\sim 585\text{nm}$ and occurs at $t_{23} \sim -150\text{fs}$ to $50\text{fs}$, i.e., when the three pulses overlap; thus this is attributed to the FWM signal of the laser pulses. The second part with slightly lower intensity which is centred at $\sim 600\text{nm}$ occurs at
Fig. 6.10: Spectrally resolved two-colour three-pulse four-wave mixing signal of cresyl violet. The signals are detected in the $k_6$ direction for the case $\lambda_{1,2} = 600\text{ nm}$, $\lambda_3 = 615\text{ nm}$ when scanning $t_{23}$ at fixed time $t_{12} = 80\text{ fs}$, (a), and when scanning $t_{12}$ at fixed time $t_{23} = -80\text{ fs}$, (c). (b) and (d) are the energy schematics for three laser pulses interacting with the molecular system of cresyl violet for the two corresponding cases (a) and (c), respectively. Gr.C: Ground state coupling.

$t_{23} \sim -170\text{ fs}$. This signal is created when the three pulses have the ordering 3-1-2 (see Fig. 6.10 (b)). Since pulses 1 and 2 with wavelength 600 nm are resonant with the transition $|g\rangle \rightarrow |e\rangle$ and pulse 3 with wavelength 615 nm is resonant with $|g'\rangle \rightarrow |e\rangle$, the second part which has the same wavelength as pulses 1 and 2 is attributed to the diffraction of pulse 2 from the population grating created by pulses 3 and 1 following coherent transfer from $|g'\rangle$ to $|g\rangle$ as long as the pulse ordering 3-1-2 remains, (see Fig. 6.10 (b)). This signal then vanishes as pulse 3 is scanned further away. When $t_{12}$ is scanned at fixed time $t_{23} = -80\text{ fs}$ (Fig. 6.10 (c)), the signal starts at $t_{12} \sim -100\text{ fs}$, where pulse 1 is about to overlap with pulse 3, with a small blue shift and persists until pulse 1 is scanned $\gg 300\text{ fs}$ from pulse 2. This long-lived signal which can be
considered as a transient grating-like signal created by the diffraction of pulse 1 from the grating formed by pulses 2 and 3 confirms that pulses 2 and 3 create a modulated population in state $|g\rangle$, and thus indicates a transfer of coherence from $|g'\rangle$ to $|g\rangle$ (see Fig. 6.10 (d)). Furthermore, the long-lived signal shows a clear splitting of $\sim 12$ nm ($\sim 340$ cm$^{-1}$), which is close to the lowest vibrational mode (335–343 cm$^{-1}$ [131]) of cresyl violet.

### 6.3.2.2 Non-Interferometric 2DFTS Results

In this section, non-interferometric 2DFTS will be applied to the spectrally resolved data of cresyl violet. The set of data which was selected is the signal in the $k_6$ direction when scanning $t_{23}$ shown in Fig. 6.10 (a).

![Frequency correlation spectrum](image)

**Fig. 6.11:** Frequency correlation spectrum calculated from the raw data for cresyl violet using the phase retrieval algorithm. The spectrally resolved signal (see Fig. 6.10 (a)) is detected in the $k_6$ direction for fixed time $t_{12} = -80$ fs, when scanning $t_{23}$ for the case $\lambda_{1,2} = 600$ nm, $\lambda_3 = 615$ nm.

When $\lambda_{1,2} = 600$ nm (i.e, $\omega_{1,2} \sim 2.07$ eV), $\lambda_3 = 615$ nm ($\omega_3 \sim 2.02$ eV), the FWM signal from the lasers in the $k_6$ direction will be at $\sim 2.12$ eV. This FWM signal is shown as a strong peak at the excitation energy $\omega_\tau = \omega_3 \sim 2.02$ eV and the detection energy
\( \omega_t \sim 2.12 \text{ eV} \) (see Fig. 6.11). There are two other peaks in the correlation spectrum, one of which, the peak at \( \omega_t = 2.07 \text{ eV} \) and \( \omega_r = 2.08 \text{ eV} \), is a diagonal peak. This peak is attributed to the transient grating-type signal described above and/or non-resonant excitation of the \( |g\rangle \rightarrow |e\rangle \) transition \((600 \text{ nm} / 2.07 \text{ eV})\) by pulse 3 \((615 \text{ nm} / 2.02 \text{ eV})\). The off-diagonal peak which is at the excitation energy \( \omega_r = 2.07 \text{ eV} \) and the detection energy \( \omega_t = 2.10 \text{ eV} \) provides evidence of coherent coupling between the vibrational levels in the ground state.

### 6.3.3 Non-interferometric 2DFTS Study of Lycopene

The previous section has shown the ability of the non-interferometric 2DFTS technique to study the strong coherent coupling in the molecular system of the laser dye cresyl violet. The technique is now applied to our main molecule, lycopene, for which the coherent coupling and coherence transfer are not sufficiently revealed by the raw spectrally resolved data. We selected the set of data of lycopene when it was excited by laser pulses with \( \lambda_{1,2} = 503 \text{ nm} \) \((\omega_{1,2} \sim 2.47 \text{ eV})\), which are resonant with the transition \( 1A_g^-(0) - 1B_u^+(0) \), and \( \lambda_3 = 472 \text{ nm} \) \((\omega_3 \sim 2.63 \text{ eV})\), which is resonant with the transition \( 1A_g^-(0) - 1B_u^+(1) \). The signal was detected in the \( \mathbf{k}_6 \) direction on scanning \( t_{12} \). This set of data was analysed earlier in Section 6.2.1 of this chapter.

Figure 6.12 shows the spectrally resolved signal for lycopene for fixed delays \( t_{23} = 0 \text{ fs} \) (a), \(-80 \text{ fs} \) (b) and \(-160 \text{ fs} \) (c). The detection energy \( \omega_t \) in eV is presented along the vertical axis instead of the detected wavelength. The FWM signal of the three laser pulses in the direction \( \mathbf{k}_6 = -\mathbf{k}_3 + \mathbf{k}_1 + \mathbf{k}_2 \) will be at \(-\omega_3 + \omega_1 + \omega_2 = 2.31 \text{ eV} \).

From the spectrally resolved signal, it can be clearly seen that there are signals at \( \sim 2.31 \text{ eV} \), which is the FWM signal of the laser pulses, and \( \sim 2.28 \text{ eV} \). As analysed in section 6.2.1, the signal at \( \sim 2.28 \text{ eV} \) is attributed to the real molecular transition \( 1B_u^+(0) - 1A_g^-(1) \) (we call the corresponding energy of this transition \( \omega^* \)), which results from the coherent coupling of the two states \( 1B_u^+(0) \) and \( 1A_g^-(1) \). This coherence is
Fig. 6.12: Spectral intensity data from two-colour spectrally resolved experiments on lycopene as a function of delay $\tau$ (i.e., $t_{12}$) for fixed delay $T$ (i.e., $t_{23}$) of (a) 0 fs, (b) $-80$ fs and (c) $-160$ fs. The corresponding frequency correlation spectra calculated from the raw data using the phase retrieval algorithm are shown in (d-f).

created through the interaction of the laser pulses with the ensemble.

The correlation spectra show a similar trend, but also reveal more information. At $t_{23} = 0$ (i.e., $T = 0$) (see 6.12 (d)), there is a diagonal peak at the excitation energy $\omega_3 = 2.63$ eV and the detection energy $\omega_t = 2.31$ eV. This peak is attributed to the FWM signal from the lasers. There is a weaker off-diagonal peak at the detection energy $\omega_t = 2.28$ eV and the excitation energy $\omega_3 = 2.63$ eV. The fact that this off-diagonal peak occurs at lower $\omega_t$ energy when excited by pulse 3 indicates that there is a transfer of the laser frequency to the transition frequency and that a coherence created between two vibronic states $1A_g^{-}(0)$ and $1A_g^{-}(1)$. When $t_{23} = -80$ fs (i.e., $T = -80$ fs),
the diagonal peak at $\omega_\tau = \omega_1$ is still strong, but the off-diagonal peak is stronger than at $t_{23} = 0$, and there is a second diagonal peak appearing at $\omega_\tau = 2.67 \text{ eV}, \omega_2 = 2.27 \text{ eV}$. This indicates that the polarization is oscillating partially at the transition frequencies and partially at the laser frequency over the period $\tau$, which can now be up to 80 fs, and there is further coupling to the transition after the second pulse. At $t_{23} = -160 \text{ fs}$ (i.e., $T = -160 \text{ fs}$), the diagonal peak at $\omega_\tau = \omega^* \ (= 2.67 \text{ eV})$ is increased relative to the other two peaks, indicating that in this case, over the period $\tau$, the polarization is predominantly oscillating at the transition frequency, and a coherent superposition between the two excited state vibrational levels is generated.

While we have been able to use the phase retrieval algorithm to obtain additional information from both cresyl violet and lycopene, the technique is still not fully refined. It is expected that with further development of the phase retrieval algorithm we will be able to produce correlation spectra even more reliably and with greater detail. This will allow further details of the coupling and mechanisms in complex molecular samples to be revealed.
Chapter 6

6.4 Summary of Results

In the first part of this chapter, spectrally resolved three-pulse one-colour photon echo measurements in the $k_4$ direction when pulse $k_1$ is scanned were employed to study the decoherence process of certain transitions in lycopene and spheroidene. The results reveal that the decoherence depends slightly on the time separation of pulses 2 and 3. In lycopene, the decoherence time of the transition $1A_g^-(0) - 1B_u^+(0)$ is in the range of $155 - 175\text{ fs}$ and is about $30 - 50\text{ fs}$ longer than the decoherence time of the transition $1A_g^-(0) - 1B_u^+(1)$. These results indicate that the scattering rate of the higher vibronic level ($1B_u^+(1)$) is larger than that of the lower vibronic level ($1B_u^+(0)$) in the $S_2$ state of lycopene. The decoherence time of the transition $1A_g^-(0) - 1B_u^+(0)$ is found to be $\sim 255 - 345\text{ fs}$ in spheroidene. This result indicates the slower dynamical behaviour in spheroidene compared with lycopene, which could be explained by the difference in the energy levels of these two carotenoids.

In the next part of the chapter, spectrally resolved three-pulse two-colour coherent FWM measurements were used to study the molecular coherence dynamics in lycopene and spheroidene. Following excitation using the transitions $1A_g^-(0) - 1B_u^+(1)$, $1B_u^+(1) - 1A_g^-(1)$ and $1A_g^-(0) - 1B_u^-(0)$, coherence between the levels $1A_g^-(1)$ and $1B_u^+(0)$ was detected for lycopene. The coherence time was found to be less than $100\text{ fs}$. In spheroidene, transitions between the dark states $1B_u^-(1)$ and $3A_g^-(0)$ and the ground state $1A_g^-(0)$ were detected. These results indicate coherent coupling between these two dark states and other states of the spheroidene molecule. They also provide information on the location of the energy levels $1B_u^-(1)$ (which is $\sim 19\text{ 340 cm}^{-1}$ from the ground state $1A_g^-(0)$) and $3A_g^-(0)$ (which is $19\text{ 800 cm}^{-1}$ above the ground state $1A_g^-(0)$) for spheroidene.

In the final part of the chapter, we presented a phase retrieval technique which allows us to obtain the phase of the three-pulse two-colour FWM signal from spectrally resolved intensity data, without the need for phase stabilized input pulses. The
spectrally resolved signal which is processed by a phase retrieval algorithm yields the time resolved emission signal and Fourier transformed correlation spectra, and hence helps to resolve the coherence dynamics in our sample. The technique was applied to study the coherent coupling first in the laser dye cresyl violet, and then in our main sample, lycopene. The results indicate that our phase retrieval technique was successful in providing additional information about the coherence dynamics in cresyl violet and lycopene.
Chapter 7

Conclusions and Future Prospects

In this thesis, results using femtosecond spectrally resolved one- and two-colour four-wave mixing nonlinear coherent spectroscopy on the population dynamics and coherence dynamics of two carotenoids, lycopene and spheroidene, in \( n \)-hexane are reported. The main conclusions of this work are summarised as follows:

By setting the time separation between pulses 1 and 2 to zero (\( t_{12} = 0 \) fs), the signal detected in the \( k_4 = -k_1 + k_2 + k_3 \) direction when scanning pulse \( k_3 \) is a transient grating-like signal which provides information on the population dynamics of the molecular system. By selecting appropriate wavelengths for pulses \( k_1, k_2, \) and \( k_3 \), measurements were made of the vibrational relaxation time in the first optically allowed excited state \( 1B_u^+ \) (230 ± 25 fs) and the ground state \( 1A_g^- \) (595 ± 25 fs) in lycopene. The results suggest the active role of the carbon double bond C=C in the vibrational relaxation process in the ground state. The transient grating-like measurements were also successful in detecting the internal conversion process from the state \( 1B_u^+ \) to the dark state \( 2A_g^- \), from the dark state \( 2A_g^- \) to the ground state \( 1A_g^- \) as well as vibrational relaxation in the \( 2A_g^- \) state, for both lycopene and spheroidene. The results show that internal conversion between the two states \( 2A_g^- \) and \( 1A_g^- \) occurs in 4.0 ± 0.2 ps and 8.2 ± 0.3 ps in lycopene and spheroidene, respectively. The time constants, which are
attributed to both internal conversion and vibrational relaxation between $1B_u^+$ and $2A_y^-$ are $490 \pm 20$ fs and $535 \pm 25$ fs for lycopene and spheroidene, respectively. All of these results are in agreement with those obtained by other techniques.

The spectrally resolved one-colour four-wave mixing measurements in the $k_4$ direction when scanning the delay time $t_{12}$ were able to detect the photon echo signals from lycopene and spheroidene, from which decoherence times of certain transitions in these two carotenoids could be deduced. Depending on the separation between pulses $k_2$ and $k_3$, the decoherence time of the transition $1A_y^-(0) - 1B_u^+(0)$ is in the range $155 - 175$ fs for lycopene and $255 - 345$ fs for spheroidene, whereas the decoherence time of the transition $1A_y^-(0) - 1B_u^+(1)$ is $115 - 125$ fs for lycopene. The results indicate that the scattering rate for the higher vibronic level is larger than that of the lower vibronic level in the $1B_u^+$ state of lycopene.

The results on the population dynamics and molecular decoherence both indicate a slower dynamical behaviour in spheroidene compared with lycopene, which could be explained by the difference in the energy levels of these two carotenoids. Furthermore, the fast vibrational relaxation from $1B_u^+(1)$ to $1B_u^+(0)$ explains the faster decoherence, and hence the larger scattering rate, of the vibronic energy level $1B_u^+(1)$.

The spectrally resolved two-colour four-wave mixing signal enabled the study of the coherence dynamics of lycopene and spheroidene. In lycopene, following excitation using the transitions $1A_y^-(0) - 1B_u^+(1)$, $1B_u^+(1) - 1A_y^-(1)$ and $1A_y^-(0) - 1B_u^-(0)$, coherence between the levels $1A_y^-(1)$ and $1B_u^+(0)$ was detected and the coherence time was deduced to be less than 100 fs. In spheroidene, by selecting appropriate wavelengths for the three laser pulses, the signals allowed the successful detection of transitions between the dark state levels $1B_u^-(1)$, $3A_y^-(0)$ and the ground state for spheroidene and demonstrated the ability of the technique to detect coherent coupling between these dark states and the ground state. From these results, the energies of the $1B_u^-(1)$ and $3A_y^-(0)$ were found to be $19340$ cm$^{-1}$ and $19800$ cm$^{-1}$ above the ground state level $1A_y^-(0)$, respectively. These results strongly support the work of the Koyama...
group using electronic absorption spectroscopy [32].

The results on the population dynamics and coherence dynamics in lycopene and spheroidene demonstrate that spectrally resolved three-pulse one- and two-colour four-wave mixing coherent nonlinear spectroscopy is a powerful multidimensional technique. However, the experimental signals which are integrated over the detection time carry no phase information. This makes it difficult to study the coherence dynamics of the molecular system in detail. In Section 6.3 of Chapter 6, we reported the development of a phase retrieval technique, which allows us to obtain the phase of the four-wave mixing signal from the spectrally resolved data without the need for stabilized input pulses. Preliminary results on coherent coupling in the laser dye cresyl violet and lycopene were obtained using this phase retrieval technique. The technique was able to provide additional information about the coherence dynamics and is a very promising tool for future studies.

The subject of this thesis could be expanded in a number of directions. Firstly, as the carotenoids are systematically related to each other in theory, it would be interesting to apply our technique to investigate other carotenoids such as neurosporene \((n = 9)\), anhydrohodovibrin \((n = 12)\) and spirilloxanthin \((n = 13)\), in addition to the two carotenoids studied in this thesis, spheroidene \((n = 10)\) and lycopene \((n = 11)\), in order to test the theory and to obtain a complete picture on the state energies and molecular dynamics of the carotenoids. Secondly, the dynamics of the carotenoids in the light-harvesting complexes where the singlet-energy is transferred between two carotenoids and between one carotenoid and (B)chlorophyll would be of considerable interest. Knowledge of the dynamics and energies of the carotenoids in solution will be a good reference for the study of carotenoids in these light-harvesting complexes. Finally, the phase retrieval technique which was presented in Section 6.3 of Chapter 6 is worth refining and developing further to produce correlation spectra more reliably and with greater detail. This would be especially useful for studying coherent coupling and mechanisms of the carotenoids in light-harvesting complexes.
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Publications of the Author


